Structured Systems in Gas Separation

I  Silicalite-1 Zeolite Membranes

II  Manganese Based Sorbents for High-Temperature H₂S removal

Wridzer J.W. Bakker
Structured Systems in Gas Separation

I Silicalite-1 Zeolite Membranes
II Manganese Based Sorbents for High-Temperature H₂S Removal

Proefschrift

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ter nagedachtenis aan mijn vader
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voor mijn moeder
Preface

Structured Systems

This thesis describes the development of two structured systems for gas separation. Structuring of systems is considered as a breakthrough methodology for precision process technology.

The approach has been to develop, conceptually, separation equipment, including development of the functional materials. The emphasis has been on the structured materials, but also the perspective towards the engineering of these materials in the proper large-scale equipment is dealt with.

The two systems are designed for operation at high temperatures and in a chemically aggressive gas environment. System one is a zeolite membrane with the accompanying membrane module. System two is a monolith shaped sorbent with the accompanying rotating reactor. In these systems several scales of structuring are distinguished: nm: zeolite pores, µm: membrane thickness and crystal size of the active components in the sorbent, mm: channel size and structure of the monoliths, m: rotating reactor and membrane module.

Separation principles

The separation principles of the equipment described in this thesis, a membrane module and a rotating reactor, are schematically shown in the Figures 1 and 2. In the membrane module the components A and B are separated by a permselective layer. B diffuses preferentially through this layer and a continuous separation between component A and B is obtained.

Figure 1. Simplified separation principle of a membrane module.
Figure 2. Simplified separation principle of a rotating reactor.
In the rotating reactor a continuous separation between component A and B is obtained by simultaneous operation of an uptake and regeneration process. The reactor contains two main sections: one for uptake and one for the release of component B. In the uptake section component B preferentially reacts with the sorbent and component C is released. In the regeneration section component C reacts with the sorbent and component B is released.

Outline of thesis

A subdivision into two parts has been made for this thesis. Each part can be read separately.

Part I

Part one (Chapters 1-6) of the thesis reports on the preparation and the mass transport characteristics of a metal-supported silicalite-1 zeolite membrane.

In Chapter 1 a short introduction is given on membranes and membrane reactors. Chapter 2 deals with synthesis and characterization of the membrane. Also an introduction is given on zeolites and some membrane preparation methods are reviewed. Furthermore, a model for the crystal growth is proposed which describes the in-situ hydrothermal synthesis of a MFI layer in an all-metal module. A qualitative description of mass transfer through porous media is given in Chapter 3. Hereby the focus is on diffusion in micropores such as present in zeolites. Chapter 4 is devoted to one-component mass transport through a silicalite-1 membrane over a broad temperature range. Besides the experimental data and a literature review on zeolite diffusion, a general model is presented for mass transport in micropores. In Chapter 5 binary mass transport through the silicalite-1 membrane is presented. Hereby, not only the steady state data are reported, but also transient permeation data. An evaluation is given in Chapter 6.

Part 2

Part two (Chapters 7-12) focuses on the development of a manganese based sorbent for coal gas cleaning at very high temperatures, above 873 K, and the development of a reactive rotating reactor for continuous operation of cyclic processes like regenerative H₂S removal from coal gas.

In Chapter 7 an introduction is given on coal gasification processes and coal gas cleaning. Also metal oxides for high temperature desulfurization are reviewed. Chapter 8 deals with the preparation of manganese sorbents using both particles and monoliths as support. In Chapter 9 typical sulfiding reactions with metal oxides,
including manganese oxides are reported. Chapter 10 is devoted to a thermodynamical analysis of manganese oxides for application in high temperature coal gas cleaning. Chapter 11 deals with the performance and characterization of the developed sorbent. Also a sulfiding and regeneration mechanism is proposed. In Chapter 12 the development of the rotating reactor is described. The applicability of the developed sorbent in the rotating reactor is reported as well. Furthermore, new process configurations for coal gas cleaning and sorbent regeneration are proposed.

Objectives

The objectives for the zeolite membrane and high temperature desulfurization project were as follows:

- Development of a silicalite-1 zeolite membrane and an accompanying high temperature membrane module;
- Testing of this membrane module with the emphasis on the mass transport through the zeolite layer;
- Modeling of this mass transport: qualitative for one-component and binary transport and also quantitative for one-component transport;
- Sorbent development and design of a rotating reactor for regenerative desulfurization of coal gas at very high temperature (above 873 K). The sorbent should be applicable in the rotating reactor and the regeneration product should preferably be elemental sulfur.
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Part 1

Silicalite-1 Zeolite Membranes
Membranes and Membrane Reactors

1 Introduction

Inorganic membranes hold great promise for various separation and catalytic processes due to their good mechanical properties and their stability at high temperatures and in severe environments. To achieve for most small molecules of industrial interest a size-selective separation of reactants and products, the need exists for inorganic membranes with pores $< 0.6$ nm. In this regard, the unique combination of properties of zeolites, such as microporosity with uniform pore dimensions of molecular size, ion-exchange capacity, and high thermal stability makes them attractive for application in inorganic membranes. Below, an general introduction is given on membranes and membrane reactors.

2 Application of Membranes

Separation of liquid- and gas mixtures are essential steps in many (petro-) chemical processes. Membranes are everywhere. Not only are they a key part of many industrial processes, but they have an impact on many compounds and materials of our daily life such as the medicines we rely upon, the food we eat. Figure 1 shows an overview of the membrane spectrum and their typical applications. Membranes for gas separation are highlighted in the left part of the figure. The pore size of an MFI type zeolite is also indicated.

Membranes for gas or liquid separation, standing alone or in combination with an existing technique, can offer significant economic, environmental, and product quality advantages compared to the older and more widely used processes in the separation technology, such as distillation, extraction, crystallization and adsorption.

Membranes can be solid or liquid can and be made of organic or inorganic materials. Their structure may be homogeneous or heterogeneous, symmetric or
asymmetric. Membranes can act as a barrier which restricts the transport of different chemical components in a specific way. But they may also act as a reactor combining the transport of mass with a chemical reaction resulting in new products. Important parameters for a membrane are its selectivity, permeability and its chemical, mechanical and thermal stability.

<table>
<thead>
<tr>
<th>Micrometer</th>
<th>Atomic Force Microscope</th>
<th>Scanning Electron Microscope</th>
<th>Optical Microscope</th>
<th>Visible to Naked Eye</th>
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<tr>
<td>Angstrom</td>
<td>10</td>
<td>100</td>
<td>1,000</td>
<td>10^7</td>
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<tr>
<td>Molecular Weight</td>
<td>100</td>
<td>200</td>
<td>1,000</td>
<td>100,000</td>
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Relative Size of Common Material

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Radius</th>
<th>MFI</th>
<th>Metal Ion</th>
<th>Aqueous Salt</th>
<th>Carbon Black</th>
<th>Paint Pigment</th>
<th>Human Hair</th>
<th>Beach Sand</th>
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<td>Endotoxin</td>
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<tr>
<td>Membrane Separation Process</td>
<td>Reverse Osmosis</td>
<td>Ultrafiltration</td>
<td>Particle Filtration</td>
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<td>Gas Separation</td>
<td>Nanofiltration</td>
<td>Microfiltration</td>
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<td>Pervaporation</td>
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Figure 1. "The membrane spectrum." Gas separation is highlighted in the left part of the figure. The pore size of an MFI type zeolite is also indicated, ~0.55 nm. This zeolite is used for the membrane described in this thesis. For literature on membranes and membrane processes the reader is referred to the book of Mulder¹ and references therein.

The potential of membranes and membrane processes for the controlled mass transfer and thus for the separation of molecular mixtures was already recognized more than 150 years ago when Pfeifer² studied the osmotic phenomena and Graham³ discovered that rubber exhibits different permeabilities to different gases. The large scale industrial exploitation of membrane processes began in the seventies with the development of the artificial kidney and the desalination of sea and brackish water by reverse osmosis. Today synthetic membranes are used on an industrial scale in three main applications:

- the separation of molecular mixtures
- the controlled release of active agents
- the immobilization of catalysts, micro-organisms, and living cells

The separation of molecular mixtures is by far the most relevant application of synthetic membranes. E.g. hollow fiber, polymer membranes are used on a large scale for hydrogen separation and separation of nitrogen from air⁴. The world-wide
sales of membranes and membrane modules in 1996 were in excess of 3.500 million US$ and the market for membrane products is growing by about 15% per year.

*Polymer membranes* have some intrinsic drawbacks⁴, viz. a low thermal, chemical stability, a low mechanical strength, causing *e.g.* compression of the membrane at high pressures, and polymeric membranes cannot be cleaned by thermal treatment. Furthermore, the application of membranes in a multi-functional reactor in which reaction and separation are combined needs in most cases temperatures above 473 K, which is too high for polymeric membranes. Therefore, in the last decade much research has been focused on the development of *inorganic membranes* which in principle lacks these drawbacks. Disadvantages of most of the current inorganic membranes are, however, the high production costs and their brittleness. Moreover, for separation on a molecular level almost no commercial membranes are available with a pore-size below 0.6 nm, and effective sealing in a module is still difficult, see Chapter 6.

For the separation of hydrogen and oxygen, respectively, non porous metal and metal oxide inorganic membranes can be used. Well documented are palladium/(ruthenium, silver)⁵ membranes for hydrogen purification and perovskite membranes⁶ for the separation of oxygen from gas mixtures. The selectivity of these membranes is very high and rely on selective solution of a component in the membrane. The flux through these dense membranes is, however, rather low and no large systems are available yet.

Vycor Glass⁷,⁸, carbon molecular sieves⁹,¹⁰ and multi-layer dip coated membranes¹¹-¹³ are examples of microporous inorganic membranes. Generally, the gas-transport in such membranes is controlled by Knudsen diffusion or, in the case of condensable gases, a combination of Knudsen diffusion and surface diffusion, see Chapter 3. The maximum separation selectivities which can be obtained with these separation mechanisms are limited, see Chapter 3. Reduction of the number of defects in these membranes can lead to membranes in which mass transport is controlled by the molecular sieving mechanism and high separation selectivities come into reach.¹⁴

A breakthrough in the application of highly selective inorganic membranes is expected from inorganic zeolite membranes¹⁵-¹⁷ because of their uniform pore size of molecular dimensions. For more references see Chapters 2-6. The development and mass transport characteristics of silicalite-1 (MFI type) zeolite membranes will be discussed in the next chapters.
Chapter 1

3 Membrane reactors

In the process- and chemical industry, in the area of catalytic conversions, one is faced with several aspects in the design and control of catalytic reactor systems. Many industrial processes are limited by thermodynamics, like ammonia and methanol synthesis, water gas shift, dehydrogenation and isomerization. In spite of superior catalysts with superior activities one cannot beat the thermodynamic limits per single pass through the reactor. Other processes, like oxidation and hydrogenation, are highly exothermal, and low feed concentrations and good heat transfer measures have to be used to avoid hot spots in the catalyst bed and runaways. Many processes suffer from low selectivities due to the occurrence of consecutive or parallel reactions, like in selective oxidation and hydrogenation reactions.

Since in general chemical transformations are accompanied by heat effects, good measures have to be taken to transfer heat to or from the catalyst bed. Sometimes in plants chemical products are formed by endothermic reactions, while they are subsequently used in exothermic conversions, which mean that large amounts of sensible heat are pumped around.

The application of an emerging new type of catalytic reactor, the catalytic membrane reactor, offers in principle a way out of these dilemmas. Figure 2 indicates schematically some configurations that can be applied to the above mentioned cases.

![Diagram of catalytic membrane reactors](image)

*Figure 2. Configurations of catalytic membrane reactors.*
Introduction on membranes and membrane reactors

In reactor I products are selectively removed from the reaction mixture, thus allowing higher single pass conversions by 'shifting' the equilibrium and higher selectivities by the removal of the desired, valuable intermediate products. Reactor II can handle reactions in which for reasons of exothermicity or reaction selectivity the reactants should not be fed to the catalyst bed completely mixed. Here, a selective membrane controls the feed rate of one of the components to the reaction mixture over the whole length of the reactor. Configuration III allows the direct separation of the reaction mixture in the reactor environment, without the need of heat exchange and coupled unit operations, lowering the size of the equipment. Reactor IV is an example of reaction coupling. In the inner catalyst an endothermal reaction takes place, e.g. the production of hydrogen, which permeates selectively through the membrane to the outer catalyst where it reacts exothermally with the reactant fed through the annular space, e.g. an oxidation reaction. The heat produced by this reaction is transferred through the membrane by conduction and provides the endothermal reaction with heat. This idea might be applied in fuel cells where steam reforming can be combined with the oxidation of hydrogen to produce electricity. In all these cases it can be envisaged that the membrane itself is the catalytic medium, is coated with catalytic material or the catalytic material is present near the membrane.

Characteristic features of these membranes is that they need to be permselective and thermostable and allow fluxes that are compatible with the catalytic conversion rates. The application of zeolites as membrane material in a catalytic reactor looks quite promising, because the uniform pore size of molecular dimensions enables highly selective separations. Moreover, zeolites can be made catalytically active themselves.

4 Literature

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24
Synthesis and Characterization of a Silicalite-1 Zeolite Membrane

Abstract
An introduction is given on zeolites and the preparation of zeolite membranes. Also the in-situ crystallization of silicalite-1 zeolite layers on (porous) stainless steel is discussed.

A continuous silicalite-1 layer has been obtained during hydrothermal synthesis in an all stainless steel membrane module. The thickness of this layer and the synthesis temperature is around 50μm and 458 K, respectively. Crystal growth occurs from a gel layer which is formed on the metal, but also direct growth from the synthesis solution occurs. No separate sealing is needed in this membrane module, because the membrane layer itself seals the transition from porous to non-porous steel. It has been shown that several formulations lead to continuous zeolite layers. These layers are gastight before calcination and only opens up above 623 K after decomposition of the template molecule TPA (tetrapropylammonium). Besides zeolite pores the membrane also contains a small amount of somewhat larger pores. The membrane is remarkably stable upon thermal cycling between 200 and 700 K.

* The subject of this Chapter has been investigated in close cooperation with the group of organic chemistry and catalysis of the Delft University of Technology. The results have been reported in a joint publication.
1 Introduction

It is not surprising that molecular sieve membranes have received a lot of attention from scientists both in industry and academia. Fascinating multi-component mass transport phenomena has been observed. The potential in separation applications is high\(^1,2\). Components differing in adsorption behavior can be separated with high selectivity. Moreover, selective separations by molecular sieving, the high intrinsic thermal and chemical stability, and the possibility to construct multi-functional reactors in which reaction and separation are combined might make zeolite membranes very suitable for use in industrial applications.

In this chapter an introduction is given on zeolites and zeolite membranes. Furthermore, the synthesis of a metal-supported silicalite-1 zeolite membrane in an all metal membrane module is discussed.

1.1 Zeolites

The word zeolite is derived from the Greek word “zeo” and “lithos”, meaning “I boil” and “stone”. The first discovered zeolite Stilbite in 1756 by Cronstedt was found to exhibit a rather peculiar phenomenon for a stone upon heating: it fizzed and gave off steam. This phenomenon has been explained as water, incorporated inside the mineral, which desorbs upon heating. Nowadays, many natural zeolites are known and numerous new structures and modifications have been prepared in the laboratory.

<table>
<thead>
<tr>
<th>Process</th>
<th>Zeolite</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic cracking</td>
<td>Faujasite</td>
<td>gasoline, fuel oil</td>
</tr>
<tr>
<td>Hydro-cracking</td>
<td>Faujasite</td>
<td>kerosene, jet fuel</td>
</tr>
<tr>
<td>Hydro-isomerization</td>
<td>Mordenite</td>
<td>iso-paraffins</td>
</tr>
<tr>
<td>iso-/n-paraffin separation</td>
<td>Ca-A</td>
<td>pure n-paraffins</td>
</tr>
<tr>
<td>Dewaxing</td>
<td>ZSM-5, Mordenite</td>
<td>low pour point lubes</td>
</tr>
<tr>
<td>Olefin drying</td>
<td>K-A</td>
<td>polyolefin feed</td>
</tr>
<tr>
<td>Benzene alkylation</td>
<td>ZSM-5</td>
<td>ethyl benzene</td>
</tr>
<tr>
<td>Xylene isomerization/separation</td>
<td>ZSM-5/Faujasite</td>
<td>p-xylene</td>
</tr>
<tr>
<td>Removal Mg, Ca ions from</td>
<td>Na-A, Na-P</td>
<td>“soft” water</td>
</tr>
<tr>
<td>washing water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zeolites are commercially applied on a large scale in detergents as alternative for phosphates. Further they are widely used as catalyst in petro-chemistry and oil processing (e.g. distillate dewaxing and fluid catalytic cracking) and to a lesser
Synthesis and characterization of a silicalite-1 zeolite membrane

extent, in separation processes. In Table 1 an overview is given of some major commercial zeolite processes.

*Figure 1a. The 3-dimensional drawing of MFI structure (silicalite-1, ZSM-5; 10 ring, 2D pores). Adapted from Meyer and Olson.*

Zeolites are defined as crystalline alumina-silicates with an "infinitely" extended open three-dimensional anion network. The framework consists of four-connected silicate, SiO$_4$\(^{4-}\), or aluminate AlO$_4$\(^{5-}\) tetrahedra, linked to each other by sharing all four oxygens. Each silicon atom in the framework with formal charge 4\(^+\) balances the negative 2\(^-\) oxygen charges. The substitution of Si\(^{4+}\) by Al\(^{3+}\) creates an excess negative charge. Charge neutralization is achieved by an equivalent number of cations enclosed in the open framework. These cations are mostly metal cations (e.g. K\(^+\), Na\(^+\)), but also protons, organic cations or transition metal ion complexes, which can be incorporated by ion exchange or synthesis.

The silica and alumina tetrahedra are geometrically arranged, with Al-O-Al bonds excluded. The unit cell formula is generally written as:

$$\text{M}^{n+}_{x/n} \text{Al}_x\text{Si}_{(1-x)}\text{O}_2.y\text{H}_2\text{O}$$ (1)

where Mn\(^{n+}\) is the cation which balances the negative charge, associated with the aluminum ions in the structure. The three dimensional structure of some zeolites is given in Figure 1 and some properties of MFI in Table 2.

The properties of a zeolite are dependent on the topology of its framework, the size, shape and accessibility of its free channels, the location, charge and size of the cations within the framework, and the presence of faults and occluded material.
Chapter 2

Figure 1b. The 3-dimensional drawing of MOR (Mordenite, 12 ring 1D pores). Adapted from Meyer and Olson⁴.

Figure 1c. The 3-dimensional drawing of FAU (Faujasite X,Y; 12 ring, 3D pores)⁴.

Figure 1d. The 3-dimensional drawing of LTA (zeolite A; 8 ring, 3D pores)⁴.
Therefore, structural information is very important to understand the adsorptive and catalytic properties of zeolites.

The main properties which have led to the application of molecular sieves in catalysis are the incorporation of the catalytic activity of various metals, the introduction of strong acid sites and the size and shape selectivity of zeolites.

Table 2. Some characteristics of the as-synthesized and calcined MFI zeolite framework. Phase transition from orthorhombic to monoclinic of calcined H-ZSM-5 crystals occurs around 343 K.

<table>
<thead>
<tr>
<th></th>
<th>TPA-ZSM-5⁵</th>
<th>H-ZSM-5⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice parameters (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>2.0022</td>
<td>1.9879 (-0.70%)</td>
</tr>
<tr>
<td>b</td>
<td>1.9889</td>
<td>2.0107 (+1.05%)</td>
</tr>
<tr>
<td>c</td>
<td>1.3383</td>
<td>1.3369 (-0.105%)</td>
</tr>
<tr>
<td>β (°)</td>
<td></td>
<td>90.67</td>
</tr>
<tr>
<td>Overall thermal expansion coeff. (K⁻¹)</td>
<td>8.5e-6 [7]</td>
<td>unknown</td>
</tr>
<tr>
<td>Channel size, min.-max (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sinusoidal, a-direction</td>
<td>0.529-0.555</td>
<td>0.501-0.589</td>
</tr>
<tr>
<td>straight, b-direction</td>
<td>0.522-0.575</td>
<td>0.527-0.583</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.06</td>
<td>1.80</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
<td></td>
<td>1.84</td>
</tr>
<tr>
<td>(N₂-adsorption at 77 K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.2 The preparation of zeolite layers

The selectivity of zeolites for molecular sorption has inspired the creation of highly selective membranes, chemical sensors, and catalytically active coating in structured reactor systems. Even the release of active agents such as antifungal compounds from zeolite films has been proposed.

Three different methods for the preparation of zeolitic layers can be distinguished see Figure 2. Hereby the preparation of zeolite filled polymeric membranes⁸⁹ is not considered because this type of membrane is basically a polymeric membrane. Method I involves the deposition or embedding of preformed crystals on a support. Spaces between crystallites are filled up with a gastight matrix. The matrix is introduced by a sol-gel technique¹⁰, e.g. silica, by CVD¹⁰, e.g. zirconia, electrochemically¹¹, e.g. Ag, or by deposition of an epoxy resin¹²,¹³ or low-melting glaze¹⁰. Method II uses the transport of colloidal or polymeric, material to a support. Hereby, favorable supersaturated conditions for nucleation and growth under hydrothermal conditions in the vicinity of the surface are provided via e.g. dipcoating ¹⁴,¹⁵. Additionally, rubbing of the support with small zeolite crystals is in some cases applied to promote the crystallization process. Method III involves the
direct nucleation on the surface from a gel film or solution, followed by growth\textsuperscript{16} (in situ hydrothermal synthesis). This method is applied for synthesis of the zeolite layers described in this thesis. In practice, the synthesis mechanism is often unknown, a distinction between method II and III is sometimes difficult to make.

![Diagram](image)

**Figure 2. Methods for the design of zeolite layers. After Bein et al.\textsuperscript{17}**

The synthesis of both free standing and supported zeolite layers has been reported. Free standing layers zeolites were grown on materials\textsuperscript{22} from which zeolite layer could be (mechanically) removed\textsuperscript{18-22}. Because free standing zeolite film are very brittle, most research is focused on supported layers. Supported layers have been prepared on all kind\textsuperscript{3} of metals\textsuperscript{21,23-27}, ceramics\textsuperscript{4} and carbon\textsuperscript{28}. Alumina\textsuperscript{15,29-38} is the most popular porous support but also the synthesis on other porous materials\textsuperscript{39-47} have been reported\textsuperscript{5}.

Although the variety of zeolites is very large, only a few are suitable for membrane synthesis\textsuperscript{47}. For example, zeolites can be unsuitable because of thermo-instability above 473 K, a pore structure which collapses upon dehydration, or needle shaped

\textsuperscript{2} PTFE (Teflon), PE, silver, cellulose mouldings.

\textsuperscript{3} Al, Ni, Cu, Pt, Ti, Mo, Fe, Sn, Au.

\textsuperscript{4} Silicon, Vycor glass, quartz, mica, sapphire, clay, metal oxides (mainly alumina), mixed metal oxides (e.g. cordierite, mullite).

\textsuperscript{5} Porous stainless steel\textsuperscript{39-42}, clay\textsuperscript{43,44}, fused silica glass\textsuperscript{45}, porous sintered glass\textsuperscript{44}, nickel\textsuperscript{46}, and silicon/silicon nitride\textsuperscript{47}.

30
crystals which makes the formation of a continuous gastight layer difficult. Most articles on zeolite layers deal with MFI type zeolites (silicalite-1, ZSM-5) membranes. This type of zeolite is known to grow relatively easy on various surfaces. But also layers of other zeolites\textsuperscript{21,22,24-26,28,33,48} have been reported\textsuperscript{67}. Only a few of these layers are, however, proven membranes, see Chapter 4.

1.3 Model for the growth of a silicalite-1 zeolite layer via in situ hydrothermal synthesis

1.3.1 Growth from a gel layer

The formation of a zeolite layer by in situ hydrothermal synthesis (method III) can be described with the following model\textsuperscript{16,24,47}. Under aging, the silicon-source is hydrolyzed and small sol particles are formed. These silicon oxide sol-particles try to lower surface energy by precipitation on the support surface and form, at certain concentration ranges and temperatures, a gel layer on the support, see Fig 3a. Vroom\textsuperscript{14} calls this the incubation period. This tendency increases due to a pH drop resulting from Hofmann degradation reaction (Eq. 2) of the template used, in this case tetr-propylammonium ions (TPA), which are converted into tri-propylamine and propene. The decrease in pH causes a decrease in solubility of the silicon species.

\[
\text{Pr}_4\text{N}^+ + \text{OH}^- \rightarrow \text{CH}_2=\text{CH-CH}_3 + \text{Pr}_3\text{N} + \text{H}_2\text{O}
\]  

(2)

*Figure 3. Evolution of the crystal growth on a smooth silicon wafer of silicalite-1. a) incubation b) crystal growth, and c) stationary phase. Adapted from Jansen et al.\textsuperscript{16}.*

Infrared and elemental analysis indicate that no TPA is present in the interior of the gel phase\textsuperscript{24}. Therefore, it can be concluded that the crystallization starts at the

\textsuperscript{67} Na\textsubscript{X}, Na\textsubscript{Y}, Na\textsubscript{X}\textsubscript{25,56}, Fer\textsuperscript{33}, Gmelite\textsuperscript{24}, SAPO-\textsubscript{n}\textsuperscript{22}, Mordenite\textsuperscript{28}, ZSM-11\textsuperscript{22}, ZSM-35\textsuperscript{32}, and (Na\textsuperscript{21,24},K,Ca)-A
interface of gel and liquid phase and proceeds into the gel sphere. This is the crystal growth period, see Figure 3b. Presumably, the crystal growth is relatively fast for those nuclei oriented with the fastest growth directions parallel to the interface of both nutrient pools, being TPA in the liquid phase and SiO₂ in the gel phase. From the start crystallites are already more or less oriented parallel to the gel layer which orientation is determined by the support surface. The crystals consume the gel until they reach the support surface, see Figure 4. As soon as the crystal touches the support surface it may be attracted with the a-c-plane, the largest plane of the crystal, by electrical and surface tension forces. Subsequently, the crystal may be chemically bonded to the support by condensation reactions of the terminal OH-groups with an oxidic layer on the support. The binding to the support depends on the local chemistry. In the case of metals usually the surface is oxidized under ambient conditions, enabling chemical bonding. Mutual attachment of the crystals can result in a continuous phase without grain boundaries as concluded from HREM observations²⁴. When supersaturation of silica does not exist anymore, the crystal growth is strongly reduced, see Figure 3c.

![Figure 4. Schematic principle of gel formation and crystal growth on a surface. After Jansen et al.²⁴.](image)

Depending on the composition of the mother liquid, sol-particles can form larger units by coagulation in the liquid phase, and move to lower parts in the autoclave due to gravitational forces, forming a thicker gel on the bottom than on other parts of the synthesis module. In the mother liquid crystals can nucleate as well, especially because the solution is often contaminated, e.g. with dust particles. Loose crystals on top of a zeolite layer after the synthesis indicate the occurrence of crystal formation.
in the liquid phase. In order to form a uniform gel layer, the concentration of impurities should be kept as low as possible. For that reason, the use of sodium-free synthesis is favorable together with an initially relatively high pH (>13) and a high TPA-concentration.

The controlling factor for the formation of a zeolite layer is the nucleation/crystallization in the gel, and not so much the chemical nature of the support. As mentioned above the support can, however, stimulate the formation of a gel layer. Also, in some cases, the support partially dissolves and provide nutrients which are incorporated in the zeolites layer. For example Al³⁺ leaching from an alumina support will lead to the incorporation of Al³⁺ in particular at the support/crystal interface.

Also important is the morphology of the support. Inevitably, the growth on a rough surface will lead to a more randomly grown crystalline layer, because the crystal growth proceeds from nuclei with a variation in orientation.

The rate of transport of TPA plays an important role. When crystals grow together, diffusion of TPA to the support surface is hindered and the gel layer may not be completely converted into crystalline material.

1.3.1 Growth from the liquid phase
The presence or absence of a continuous gel layer determines if the zeolite crystals are either laterally or axially oriented with respect to the support. Axial orientation is obtained when no gel layer is present, see Figure 5. In this case nucleation occurs directly on the support and the crystal grows in the direction of the highest nutrient concentration, leading to axial orientation. Sometimes a second layer is grown, probably epitaxial, on a zeolite layer formed from a gel, see Discussion. The crystals in this second layer are not well interconnected. Such a layer is, of course, not desired for a membrane.

*Figure 5. Axially oriented silicalite-1 zeolite crystals on a metal support. Adapted from Jansen et al.¹⁶*
1.3.2 Growth parameters
The relevant growth parameters of MFI zeolite layers are a matter of debate and still not fully understood. The growth is dependent on many parameters which are often not independent from each other. For a Lermert type synthesis with relatively high TPA and silicon concentrations, silica, OH−, TPA and metal ion concentrations are important parameters which influence the process of gel formation and crystal growth. Also the synthesis time and temperature are significant parameters. Metal ions stimulate gel formation but strongly inhibit the attachment of TPA on the gel sphere, and thus the crystallization process. TPA on the other hand stimulates the crystallization. If we divide the crystal growth process in an incubation, a layer growth, and a stationary period, the incubation and layer growth time increase with decreasing synthesis temperature and the particle size increases with increasing synthesis temperature14. For a mathematical description of the crystallization the reader is referred to Jansen et al.24.

2 The Synthesis of a Metal-Supported Silicalite-1 Zeolite Membrane in an all Metal Membrane Module

2.1 Experimental

2.1.1 Membrane preparation
Porous, sintered stainless steel (316) supports with a thickness of 3 mm were obtained from Krebsoege (Radevormwald, Germany). The high-porosity supports were provided with a thin (50−150 μm) top layer of metal wool, see Figure 9 b and c. The 10 μm thick wires of this top layer are 0-50 μm apart. The overall porosity of the support was 0.52 and the "particles" of the second layer are 0-250 μm apart.

To perform permeation measurements at high temperatures and to demonstrate a simple module concept an all stainless steel module was developed. It was constructed by placing the sintered metal support, at liquid nitrogen temperature, with a diameter of 20.07 mm (@ 293K) into a solid stainless steel disk, at 673 K, with a hole of 20.00 mm (@ 293K). The solid disk was connected, with a gold alloy, between two cylinders provided with flange connections. In Figure 6 a photograph of the module is shown.

Prior to the formation of MFI layers within the modules, several hydrothermal syntheses were performed on separate porous supports within Teflon-lined (50 ml) autoclaves. In these experiments, the chemical composition of the synthesis mixture was optimized for the formation of a continuous MFI layer, fully covering the
porous metal support. The metal disks were installed into tight-fitting Teflon holders, thus only exposing the smooth top face of the disks to the synthesis mixture.

![Figure 6. Stainless steel high temperature membrane module and Teflon cylinder and sealing rings.](image)

The synthesis mixtures contained in principle only silica, tetrapropylammonium (TPA) as a template, and water. In the first experiments, gel compositions were based on the synthesis procedure according to Lermer\textsuperscript{49}: Ludox AS-40 (Du Pont), ammonia (25\%, Baker), and TPAOH (40\%, CFZ, Zaltbommel, Netherlands). For other synthesis mixtures we focused on more diluted synthesis mixtures at high pH (13.5-14) and higher template concentrations. In these experiments Aerosil 200 (Degussa) was used as the silicon source, and TPA was added from two sources: TPABr (CFZ), and TPAOH. Low concentrations of potassium and sodium were introduced in the synthesis mixture by the TPAOH source (1.2 wt\% K; 0.04 wt\% Na). For comparison, the in Geus et al.\textsuperscript{7,44} applied synthesis mixture for the preparation of continuous MFI layers on ceramic supports has been tried as well.

In Figure 7 a flow sheet of the preparation and testing procedure of a silicalite-I layer is depicted. The synthesis mixture was aged while shaking the mixture under ambient conditions. Before synthesis the support or membrane module was thoroughly cleaned to assure a good wetting. After the synthesis, the metal disk or the membrane module was washed with water and ethanol, and dried in air. The MFI layers were characterized by light and electron microscopy (SEM), and by X-ray diffraction. Chemical analysis by ICP and AAS was carried out on both the initial synthesis mixtures and the solution after hydrothermal treatment (supernatants) and in some cases after dissolving the membrane from the membrane module with a 0.5 KOH solution. EDAX elemental analysis was performed on an MFI/metal composite, as prepared according to the optimized synthesis procedure.
The optimized synthesis mixture was applied to prepare continuous MFI layers within the module, see Figure 6. The module section with the smooth top layer of the support was filled with the synthesis mixture while the other section was closed with a Teflon plug. During synthesis both sides of the module were closed with flange connections using Teflon sealing rings. After syntheses these flange connections were removed and replaced by two flanges with tubing for gas supply and removal. During calcination and permeation experiments copper sealing rings were used. The membrane module was used several times. The MFI layer can be removed from the membrane module by treatment with an 0.5 M KOH solution. Subsequently, the membrane module could be used for another membrane synthesis.

To be able to characterize the membrane layer in the membrane module, small pieces of the stainless steel support (diameter 9 mm) were placed on the bottom of the non porous part of the membrane module. Characterization of these pieces was performed by SEM and by measuring the weight increase.
Table 3. Preparation results of the in situ crystallization of MFI on porous, stainless steel supports. The reaction temperature was 453 K unless stated otherwise in column 3.

<table>
<thead>
<tr>
<th>Exp. a)</th>
<th>Gel composition</th>
<th>Time (h)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1 b)</td>
<td>100 SiO₂ : 54 NH₃ : 6 TPAOH : 6330 H₂O (molar ratio's)</td>
<td>58</td>
<td>Thick layer containing mesopores</td>
</tr>
<tr>
<td>SS-1</td>
<td>100 100 50 10000</td>
<td>48</td>
<td>Continuous, polycrystalline layer (thickness 75 μm)</td>
</tr>
<tr>
<td>SS-2</td>
<td>100 150 50 100000</td>
<td>26</td>
<td>Many, small (60 μm length) crystals</td>
</tr>
<tr>
<td>SS-3</td>
<td>100 400 50 100000</td>
<td>45</td>
<td>Near to continuous layer</td>
</tr>
<tr>
<td>SS-4</td>
<td>100 230 230 25000</td>
<td>102</td>
<td>Intergrown crystals, partly covering the support</td>
</tr>
<tr>
<td>SS-5 c)</td>
<td>100 300 300 16670</td>
<td>174</td>
<td>Separate large crystals (up to 400 μm length)</td>
</tr>
<tr>
<td>HTSS-1</td>
<td>100 100 50 11000</td>
<td>49</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
<tr>
<td>HTSS-2</td>
<td>100 230 75 14000</td>
<td>45</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
<tr>
<td>HTSS-1a</td>
<td>100 100 50 9000</td>
<td>36</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
<tr>
<td>WTSS-1c</td>
<td>100 195 65 14000</td>
<td>12 (465 K)</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
<tr>
<td>WTSS-2b</td>
<td>100 230 75 14000</td>
<td>40</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
<tr>
<td>WTSS-1d</td>
<td>100 195 65 14000</td>
<td>15 (463 K)</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
<tr>
<td>WTSS-1e</td>
<td>100 195 65 14000</td>
<td>13 (462 K)</td>
<td>Continuous intergrown polycrystalline layer (55-60 μm)</td>
</tr>
<tr>
<td>WTSS-2c</td>
<td>100 230 75 14000</td>
<td>35</td>
<td>Continuous intergrown polycrystalline layer (52-57 μm)</td>
</tr>
<tr>
<td>WTSS-2e</td>
<td>100 230 75 14000</td>
<td>37</td>
<td>Continuous intergrown polycrystalline layer</td>
</tr>
</tbody>
</table>

a) M and SS denote stainless steel support in Teflon holder; HTSS and WTSS denote high temperature membrane module.
b) With Ludox AS-40 and ammonia.
c) TPABr and NaOH instead of TPAOH.
2.1.2 Membrane testing and calcination

After synthesis, the template molecule tetrapropylammonium is present in the zeolite pores and no mass transport can occur through the pores. In order to test if the membrane is gastight after synthesis first a droplet of water was put on the membrane. If no visible absorption of the droplet occurred, the small molecule neon (@100 kPa, 295 K, 100 ml min^{-1} (NTP)) was introduced on the feed side for 45 minutes, prior to calcination. Helium was flushed (@100 kPa, 100 ml min^{-1} (NTP)) over the other site and the permeate was analyzed using a mass spectrometer.

It is standard procedure to remove the template molecules by calcination. During calcination a 80/20 mixture of nitrogen and oxygen was flushed over both sides of the membrane. 20 kPa krypton was added to this mixture at one side of the membrane to observe the development of the permeance of the silicalite-1 zeolite layer during calcination. The heating rate was 1 K/min to 673 K, the calcination lasted 16 hours at 673 K and the total pressure at both sides of the membrane was 100 kPa.

3 Results

An overview of the resulting MFI products obtained from different synthesis mixtures is presented in Table 3. This table includes the experiments within the membrane modules, WTSS and HTSS. For convenience the nomenclature used earlier^{40,50} is applied throughout the thesis. Exclusively MFI material is formed, which was confirmed by XRD and light and electron microscopy. However, the morphology of the MFI phase on the metal disks strongly depends on the synthesis mixture composition, and varies from separate crystals for SS-5 and SS-2 to continuous layers for SS-1 and the syntheses in the membrane modules. In Figure 8-12 some photographs of the resulting layers are shown.

A seemingly continuous MFI layer, but in fact still containing mesopores, is obtained from the synthesis mixture according to M-1. This has been established by applying some water on top of the dried, as-synthesized layer. In all cases, the water is readily adsorbed through the deposited MFI layer into the porous metal support. In Figure 8 a cross-sectional view of the MFI layer is shown. The layer consists of small aggregated crystals, in which some mesopores are visible. Apparently this synthesis mixture, which is very much alike the mixture used in Tsikoyiannis^{51} for the growth of unsupported MFI layers on Teflon slabs, is not satisfactory. Therefore, this approach has been abandoned at an early stage.

In contrast to the M-1 layer, the synthesis mixtures which are used for the synthesis of SS-1 and the syntheses in the membrane module yields continuous MFI layers. In Figure 9 a to c, SEM photographs of the continuous silicalite-1 membrane
and the two layer metal support are shown. Figure 9d and e represents the cross-sectional overview of a silicalite-1 membrane on a two layer metal support by SEM and EDAX elemental image, respectively. A pure silica MFI layer (red) is supported by the stainless steel support (blue), consisting of mainly iron, chromium, and nickel. The red dots within the blue support are small MFI crystals.

Figure 8. SEM-picture of a cross section of the MFI layer on stainless steel, prepared according to M-1, containing mesopores.

Table 4. Chemical analyses of the liquid phase before and after the synthesis of a silicalite-1 membrane.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Si (g/kg)</th>
<th>SiO₂ dep. (mg)</th>
<th>Thickness (μm)</th>
<th>Na (mg/kg)</th>
<th>K (g/kg)</th>
<th>pHb</th>
<th>Leached materials (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
<td>after</td>
<td>in</td>
<td>out</td>
<td>in</td>
<td>out</td>
<td></td>
</tr>
<tr>
<td>SS-3</td>
<td>4.8</td>
<td>1.0</td>
<td>0.29</td>
<td>-</td>
<td>50</td>
<td>60</td>
<td>1.6</td>
</tr>
<tr>
<td>SS-4</td>
<td>5.5</td>
<td>3.5</td>
<td>0.14</td>
<td>-</td>
<td>90</td>
<td>110</td>
<td>2.8</td>
</tr>
<tr>
<td>SS-5</td>
<td>7.0</td>
<td>3.0</td>
<td>0.33</td>
<td>-</td>
<td>1700</td>
<td>1900</td>
<td>0.00</td>
</tr>
<tr>
<td>HTSS-2</td>
<td>9.1</td>
<td>0.6</td>
<td>0.45</td>
<td>69</td>
<td>50</td>
<td>53</td>
<td>5</td>
</tr>
<tr>
<td>HTSS-1a</td>
<td>14.4</td>
<td>2.7</td>
<td>0.40</td>
<td>95</td>
<td>53</td>
<td>54</td>
<td>1.5</td>
</tr>
<tr>
<td>WTSS-1c</td>
<td>9.7</td>
<td>1.85</td>
<td>0.42</td>
<td>64</td>
<td>53</td>
<td>51</td>
<td>1.6</td>
</tr>
<tr>
<td>WTSS-2b</td>
<td>8.8</td>
<td>1.20</td>
<td>0.41</td>
<td>62</td>
<td>54</td>
<td>49</td>
<td>1.7</td>
</tr>
</tbody>
</table>

a Layer thickness calculated from the liquid composition before and after synthesis.
b Initial pH calculated from the initial liquid composition.

In Figure 10 the resulting MFI phase on top of the stainless steel support is shown (SS-2) prepared from a tenfold diluted mixture, as compared with SS-1. In this case, the support is only partly covered by thin crystals of 60 μm length. Increasing the TPA concentration with about a factor 3, as compared to SS-2, yields a nearly continuous layer for SS-3, see Figure 11.
Figure 9. SEM photographs of the silicalite-1 membrane. (a) Top view of silicalite-1 membrane WTSS-2d. The length of the crystals is 10-60 μm. (b) Top view of the two layer metal support (c) Cross section of the membrane WTSS-2D. The thickness of the silicalite-1 layer is 50-60 μm. Cross-sectional overview of the silicalite-1 membrane SS-1 by SEM (d) and by EDAX (e). The color photographs of the EDAX picture e is printed at the end of the thesis in Appendix I; blue refers to metals, red to silicon.
During the synthesis of membranes SS-4 and SS-5 the availability of nutrients for crystallization is limited by lowering silica-to-hydroxide (SiO$_2$/OH$^-$) ratio. For SS-4 this results in intergrown crystals partly covering the support, see Figure 12. For SS-5 only large separate crystals were observed. For decreasing SiO$_2$/OH$^-$ ratios, the solubility of silica is enhanced, and a substantial amount of the nutrients for crystallization remains in solution. In Table 4 the ICP and AAS chemical analyses before and after (supernatants) hydrothermal synthesis are presented for some experiments. After a long synthesis time, 174 h, the consumed silica for SS-5 with a SiO$_2$/OH$^-$ ratio of 0.3 is 57%. For higher SiO$_2$/OH$^-$ ratios, 0.7 to 2.0, which were applied for SS-4, SS-3 and de synthesis in the membrane modules, the yield is at least 80%, after only 12 h.

Figure 10. (above left) SEM-picture of small silicalite-1 crystals on top of a two-layer stainless steel support, prepared according to SS-2.

Figure 11. (above) SEM-picture of a near to continuous layer of intergrown MFI crystals on a two-layer stainless steel support, prepared according to SS-3

Figure 12. (left) SEM-picture of a partly covered two-layer stainless steel support, prepared according to SS-4.
From the amount of silica consumed during synthesis, see Table 4, an overall layer thickness in the whole module can be estimated. Hereby an uniform layer thickness is assumed. This value is compared with the, via SEM, measured membrane thickness. It appears that both values are in close agreement. The observed layer thickness in the module ranged from to 52-60 μm depending on the synthesis procedure.

The data in Table 4 show that high silica MFI (silicalite-1) is formed. Generally, no T atoms or trivalent other cations (Fe, Cr), originating from the metal support and/or silica source, are detected in either the synthesis gels or the supernatants (< 0.2 ppm). A minor amount molybdenum (maximal concentration of 10 ppm) is detected in the analyzed supernatants, especially under more extreme conditions, such as has been used for SS-5 (pH = 14, 174 h). Under the assumption that the chemical compositions of the synthesis mixture and the MFI phase are equal (except for TPA), all Si/T ratio’s are higher than 5000. The concentration of alkali (Na, K) ions within the framework is also low. The Si/Na ratio is at least 3000. The same holds for the potassium concentration, the minimal Si/K ratio amounts to 300. The liquid phase for SS-5 gave large separately grown crystals (not depicted). The same result was obtained with an inert zirconia support.

3.1 Membrane testing and calcination

Before calcination, the silicalite-1 layers appeared to be gas-tight and no water adsorption has been observed. The uncalcined membrane was tested with neon and the permeation flux of neon was < 2×10⁻⁸ mmol.m⁻².s⁻¹ at 295 K. In Figure 13 the krypton permeation during calcination of several membranes in the membrane module is shown. Membrane WTSS-1c remains gas-tight up to 623 K. The other membranes show some permeation between 473-543 K. For membrane 1e and 1b this permeation is 1-2 % of the maximum permeation after calcination while for membrane 2b this permeation is higher and amounts to about 6 %. Above a temperature of 623 K the permeation flux increases strongly with temperature, while at 673 K the profile levels off and a constant level is reached within 1 hour. After calcination no cracks were visually (SEM, visible light) observed in the silicalite-1 layer.

4 Discussion

The results demonstrate that continuous, polycrystalline intergrown MFI layers can be prepared on inert stainless steel supports, but the chemical composition of the synthesis mixture is restricted. In the first place, relatively thick layers are required
to achieve a complete coverage of the porous parts within the membrane module. Secondly, a rapid but homogeneous nucleation and crystal growth should proceed on all (externally) exposed surfaces. A high TPA concentration within the synthesis gel is expected to enhance nucleation (compare SS-2 to SS-3). A relatively low SiO₂/OH⁻ ratio also gives rise to a high nucleation rate (high super saturation), and moreover leads to an efficient use of the silica within the synthesis mixture for the formation of a continuous MFI layer. As shown in Table 3 several formulations and synthesis temperatures lead to a continuous intergrown polycrystalline layer. The MFI membrane preparation with a relatively high TPA concentration, is favorable to obtain these layers. Further optimization of the membrane preparation, however, seems possible, for instance by more variation in the synthesis time and/or temperature. This may also lead to another composition of the synthesis mixture. Also the synthesis procedure could be optimized by using continuous processes or semi-batch procedures.

![Figure 13. Permeation of Krypton during temperature programmed oxidation (heating rate 1 K/min.) of membrane HTSS-1b, WTSS-2b, WTSS-1c, WTSS-1e. To the feed, O₂/N₂ (20/80), 20% Krypton was added to monitor the calcination process. Only the curve of WTSS-1c is on the correct x coordinate. For reasons of clarity the others are moved somewhat to the left or to the right in the x-direction.](image)

EDAX and SEM show that continuous silicalite-1 layers are deposited mainly on top of the two-layer metal support. In the metal top layer also some growth occurs. Especially at the interface between support and zeolite layer the open space between the metal wires is completely filled up⁷. The support has retained, however, the greater part of its porosity. This is rationalized by the low silica concentration applied, compared to method II, in connection with the limited amount of the synthesis mixture within the macropores of the support. During the crystallization process, the pores within the metal support become isolated from the bulk solution by the developing MFI layer. On the outer surface, on the other hand, the crystal growth can continue from nutrients in the bulk solution.

⁷ After removal of the layer on top of support the membrane may, therefore, be still suitable for separations. This has not been checked.
Unless the crystallization is favored in a specific direction as on the extremely smooth and non-porous Si-wafers\textsuperscript{16}, total coverage of the porous support requires a relatively large layer thickness. Inevitably, the growth on a macroporous support will lead to a more randomly grown crystalline layer, because the crystal growth proceeds from nuclei with a variation in orientation. Hence, the minimal layer thickness is expected to be more or less correlated to the maximal pore size of the porous support, and also to depend on the smoothness of the support top face. For this reason the two-layer stainless steel supports have been used, thus combining a high porosity support and a smooth top layer with a smaller pore size. On one layer stainless steel supports without the metal wool layer the nucleation has been found\textsuperscript{40} to proceed on each metal particle separately, and no continuous layers are obtained.

The crystallization process, however, is not limited to the porous stainless steel support, and also proceeds on the non-porous parts in the stainless steel membrane module which have been in contact with the synthesis mixture. The silicalite-1 layer itself covers the connection between the porous part to the non porous part of the module\textsuperscript{52}. An attractive feature is that no additional sealing is needed. So only two materials are used for the membrane module; stainless steel and zeolite, see Figure 14.

The calculated and the measured membrane thickness on the bottom (vertical in Figure 13) of the membrane module are about the same. From this it is concluded that an equally thick layer is formed in the whole membrane module. Settling of coagulated particles due to gravitational force would cause a thicker layer on the bottom of the membrane cell. Apparently, no or little coagulation of the sol particles in the liquid phase occurs. This implies that a uniform zeolite layer is present everywhere on the metal surfaces of the module. This allows some optimism with respect to scale-up. Other authors\textsuperscript{14,16,47} report differences in the zeolite layer thickness depending on the place of a support in Teflon lined autoclave. Hereby, gel formation occurs in the solution and large gel spheres settle, due to gravitational

\textbf{Figure 14. Schematic cross-section of the silicalite-1 membrane in the all-metal membrane module. With this construction no additional sealing between the non-porous and porous part is needed.\textsuperscript{52} The zeolite layer itself acts as a sealing.}
force, to the bottom of the, Teflon lined, autoclaves. This leads to thicker layers if the membrane is placed horizontally on the bottom of the autoclave than if it is vertically placed or in the middle or top of the autoclave.

The successful results, presented here, may be explained by the presence of a relatively large metal surface in the membrane module compared to a Teflon lined autoclave which is most often used. The leaching of a small amount of metal ions during the synthesis in an all metal module may stimulate a quick gel formation on the whole surface of the module. The transport of silica to a gel layer results in a relatively low amount of silicon in the remaining solution. Together with the low metal concentration in the solution itself this possibly avoids coagulation of gel particles in the liquid. After gel formation the crystal growth starts.

The non-interconnected crystals on top of the zeolite layer, see Figure 10a, are likely grown directly from the liquid phase on top of the first layer. In Figure 15 a schematic principle of layer growth in the module is given.

**Figure 15.** Schematic principle of gel formation and crystal growth in the all-stainless steel membrane module. 1 = formation of gel layer followed by crystallization. 2 = crystal growth from the solution on zeolites formed from the gel layer.

From the low iron, nickel, and chromium concentrations in the solution after synthesis the applied stainless steel can be considered almost inert under the required hydrothermal synthesis conditions. The minor amount of ions which are released stimulate gel formation at the metal surface. These ions may be incorporated in the zeolite layer but not as T-atoms. This in contrast with a clay support. Thereby, part of the support is dissolved and alumina and silica act as nutrients for the crystals growth.

From the above considerations it may be argued that the present silicalite-1 layer consists of almost randomly oriented intergrown MFI crystals. On top of this layer a
second zeolite layer is present which is likely formed by direct growth from the liquid phases on a first layer which is grown from a gel layer. The crystals in this second layer are more axially oriented and not interconnected. The effective thickness of the zeolite layer for permeation will therefore be less than the calculated average thickness.

The relative inertness of the stainless steel material under the required hydrothermal conditions at high pH allows for recycling of the module. This compensates for the fact that rather complex modules have to be constructed, in order to achieve a high specific surface area.

4.1 Calcination and thermostability
Up to 600 K the decomposition of the template molecule tetrapropylammonium (TPA) has resulted in the formation of tripropylammonium, which is expected to block the zeolite pores effectively. At 623 K the template molecule degrades further and the zeolite pores are emptied. This is in accordance with the observed strong increase of krypton permeation at this temperature. With the applied heating rate of 1 K/min the zeolite pores are completely opened up once the temperature reaches 673 K.

From the TPA degradation behavior it might be expected that krypton permeation occurs only above 623 K but this was only observed for membrane WTSS-1c. The small krypton permeation below 623 K may, therefore, be attributed to imperfections in the zeolite layer (e.g. 90° intergrowths with plane boundaries in the crystals, grain boundaries, etc.). This important question is treated in detail by Van de Graaf.

Membranes which were not calcined after synthesis and kept in a humid environment for some months were not strongly bonded to the support anymore and could be mechanically removed. Calcined membranes were, however, stable over the period they were tested. Some membranes have been used for more than two years without seeing any change in the permeation properties. Water can hydrolyse the chemical bonding between the metal oxide and zeolite layer to some extent. If after synthesis the membrane layer is only partly bonded to the support, the layer will be less stable than in case of full bonding. Probably part of the bonding occurs during calcination. This has also been suggested by Den Exter.

Jansen reported on thin (< 1 μm) MFI coatings which can be used at temperatures up to 873 K. Heating as well as cooling does not affect the stability of the crystals on the support. According to van der Puij oriented crystals in a thin coating also do not follow the orthorombic/monoclinic phase transition upon cooling after calcination. Our relatively thick silicalite-1 layers were tested up to 700 K and also remained stable during subsequent heating and cooling. The observed stability of the silicalite-1 layer is remarkable as the expansion coefficients of silicalite-1 and stainless steel are quite different during calcination; 8.5*10⁻⁵ versus 19.3*10⁻⁶. After
calcination it is expected that still a significant difference in expansion coefficients exists. Possibly, the silicalite-1 layer is, despite its thickness, rather flexible and follows, at least partly, the support. Presumably, the thermostability is also due to the synthesis conditions; it is produced at a elevated temperature, 453-465 K, so that the difference with the highest temperature is limited to 240 K. The quality of the membrane is discussed further in Chapter 6.

5 Conclusions

Continuous polycrystalline membranes of MFI have been grown on a two layer porous sintered stainless steel support and in a all-stainless steel membrane module. High temperature sealing in the membrane module is avoided by the formation of the zeolite layer on both porous and non-porous stainless steel parts of an all metal high temperature membrane module. During calcination most zeolite pores opened up above 623 K which is in accordance with the degradation mechanism of TPA and indicate that mainly zeolite pores are present. The membrane appears to be remarkably stable upon thermal cycling, probably because of a high flexibility of the silicalite-1 layer.

6 Literature

30. Suzuki, H., Composite having a zeolite, a layered compound or a crystalline-lattice material in the pores of a porous support and processed for production thereof, European Patent Application (180 200) (1985)
Theory of Mass Transport in Zeolites, Experimental Set-Up, and System Characteristics

Abstract
A qualitative description is given of mass transport through porous media, focusing on micropore/zeolite diffusion. Also the experimental set-up for permeation and adsorption measurements and some system characteristics are discussed. Mass transport through porous media are strongly dependent on pore size, pressure (difference) and temperature. The smaller the pore size the more important the interaction with the pore walls. For micropores also the size and the shape of the molecules is important and the mass transport is activated. At low temperatures, strong adsorption dominates and permeation is described by a combination of adsorption and surface diffusion. At high temperatures the mass transport is described by an activated type of gaseous diffusion. The flux through the membrane is dependent on the experimental method and should be corrected to obtain the real membrane characteristics. In this work the Wicke-Kallenbach method has been used to measure the mass transport of single components and binary mixtures. Helium has been used as carrier gas and the temperature and pressure have been varied between 190 and 700 K and 0.05 and 10 bar, respectively. Components under investigation were the noble gases, linear and branched alkanes (C$_1$-C$_8$) and several inorganic gases like H$_2$, CO$_2$, CO, N$_2$ and SF$_6$. 
Chapter 3

1 Theory of mass transport through porous media

1.1 Introduction

With the development of zeolite membranes a new way of studying diffusion in zeolites has become available. A good understanding of sorption processes in molecular sieve materials is not only relevant for gas separation by zeolite membranes but also in adsorption and catalytic processes in which zeolites are applied.

One of the main characteristics of gas diffusion in micropores, i.e. pores with a diameter of less than 2 nm, is the fact that molecules are always in the force field of the porous structure. This gives rise to an activated diffusion process\(^1\). So far, most experimental techniques to study diffusion in zeolites are limited to either fast or slow systems, and can only be applied in the temperature range where adsorption occurs. Furthermore, results for diffusion in zeolites and other microporous materials are not conclusive; different techniques give different results. Diffusivities obtained, for the same gas-zeolite system, with different techniques can differ orders of magnitude\(^2\). Sometimes, a different trend for the diffusion coefficient as function of temperature or pressure is found. For the self-diffusivity of propane, as function of the amount adsorbed, both an increasing and a decreasing behavior is observed, depending on the technique used\(^3\).

The silicalite-1 membrane in a Wicke-Kallenbach cell provides a unique opportunity to study mass transport in zeolites; both steady-state as well as transient, for a wide range of conditions. An interesting aspect is that species with different adsorption properties can be investigated. In principle, the diffusion of all species which can enter the zeolite pores can be studied in this way.

In this chapter a description of mass transport through porous media is given. In particular, zeolite micropore diffusion is discussed. The experimental set-up used for permeation and adsorption experiments will be explained and some system characteristics such as support resistance will be discussed.

1.2 Mass transport in porous media

Gas separation can be achieved by imposing a pressure, a concentration or more formally a chemical potential gradient over porous or dense media. The actual mass transport in porous inorganic membranes can be through various mechanisms depending on pore size, conditions and the actual components.
Transport Regimes in Porous Media

- **Molecular Diffusion**: > 50 nm, ΔP = 0
- **Convective Flow**: > 50 nm, ΔP > 0
- **Knudsen Diffusion**: < 50 nm
- **Molecular sieving, Configurational Diff.**: < 1nm

Increasing Pressure/Decreasing Temperature

- **Gaseous**
- **Gaseous and Surface Diffusion**
- **Capillary Condensation Liquid diffusion**

Transport in Dense Polymers

- **Solution Diffusion**

**Figure 1.** Transport regimes in porous materials. For comparison the transport mechanism through a dense polymer is also shown.
A number of these mechanisms can contribute to the permeation selectivity of a membrane: Knudsen diffusion, surface diffusion, capillary condensation, configurational diffusion and molecular sieving. Hereby, configurational diffusion is diffusion in micropores and molecular sieving the exclusion of molecules which are too large to enter the pores.

Often a distinction is made between mass transport in macro (d > 50 nm), meso- (2 nm < d < 50 nm) and micropores (d < 2 nm). In Figure 1 an overview of different mass transport mechanisms is given and in Figure 2 the effect of the pore diameter on the molecular diffusivity and the activation energy of diffusion are depicted.

Figure 2a. Effect of the pore diameter on the molecular diffusivity, after Post4.

Figure 2b. Effect of the pore diameter on the energy of activation for diffusion, after Post4.

1.2.1 Macro- and mesopores
Molecular diffusion is characterized by elastic collisions between the molecules and can only occur in macro and meso pores. Molecule-molecule collisions prevail over molecule-wall collisions, as the mean free path for the molecules is much smaller than the dimensions of the gas phase. In case of a significant pressure gradient over the membrane, convective flow becomes important and much larger than the mass transport by molecular diffusion. Therefore, in the non-isobaric cases only the convective flow is considered.

Knudsen diffusion occurs if the mean free path of the molecules is much larger than the pore radius of the porous medium. Molecules collide with the pore wall much more than they collide with each other. If mass transport proceeds via Knudsen diffusion, the permeation flux is independent of pressure. The selectivity arises from the difference in diffusivity and the separation factor is proportional to the square root of the molecular masses. As most molecule masses, of the molecules
considered in this thesis, are in between 2 and 100 the separation selectivity obtained by Knudsen diffusion is never very high. Moreover, only lighter components can be preferentially removed.

In the transition region, neither the requirements for Knudsen flow, nor for molecular diffusion are met. Two situations are distinguished: isobaric and non-isobaric. In the isobaric case, Knudsen and molecular diffusion are the extremes on either side of the transition regime. In the non-isobaric system the convective flux contribution is much larger than the molecular diffusion and usually molecular diffusion is assumed to be negligible. Knudsen diffusion and convective flow will not take place simultaneously within a system with a uniform pore size at a given temperature and pressure. Cocurrent surface diffusion, however, can occur with Knudsen, molecular diffusion or convective flow. In practice, most systems contain a pore size distribution, in which different transport regimes may occur depending on the actual conditions such as temperature and pressure. In Figure 3 the flux, of the diffusing species within a porous membrane with a pore size distribution, is envisaged in a scheme analogous to an electric circuit.

Figure 3. Electric analogue circuit picturing the flux of the diffusing species within a porous medium with different pores sizes, after Van den Broeke.

Surface diffusion is described as molecules adsorbed on the pore walls and migrating along the surface. This migrating can be envisaged as jumps between minima in a potential energy field, see Figure 4. As surface diffusion and gas phase diffusion occur in parallel, surface diffusion increases the permeability of the more strongly adsorbed components in a diffusing mixture. Simultaneously, the permeability of the components in the gas phase is decreased by decreasing the effective space for gas phase diffusion. This diffusion mechanism is more important for membranes with small pores. For example, the number of molecules in a monolayer on the wall of a 5-nm diameter pore can be over 200 times larger than the number of molecules in the gas phase of that pore at 1 bar. The effectiveness of
surface diffusion depends on the product of adsorption and mobility. Too strong adsorption will lead to a high surface coverage of relatively immobile sorbate molecules, for which low fluxes are expected (low mobility versus high concentration).

Figure 4. Model for mass transfer through a MFI zeolite membrane and schematic representation of the potential energy in the horizontal pores. The model represents qualitatively the permeation process through a MFI zeolite pore. Steps 1, 2, 3, 4, and 5 are respectively: adsorption from the gas phase to the external surface, mass transport from the external surface into the zeolite pores, intracrystalline zeolite diffusion, mass transport out of the zeolite pores to the external surface, and desorption from the external surface to the gas phase. $E_D$ is the activation energy for intracrystalline diffusion, $\Delta H_0$ is the energy difference between molecules adsorbed in the micropores and molecules in the gas phase $\chi$ is the diffusional free length.

Multi-layer adsorption is an extension of monolayer adsorption. Especially for multi-layer surface diffusion the permeabilities of condensable gases may exceed the permeability for pure gas phase diffusion. As soon as capillary condensation coexists with multi-layer diffusion, the transport behavior changes. This capillary condensation blocks the gas phase diffusion of other gaseous components through
the pores. This may result in extremely high separation factors in favor of the condensable component.

If the kinetic diameter of a molecule is larger than the pore diameter while the diameter of other components in a mixture is smaller, "absolute" molecular sieving occurs. This leads to absolute separation by permitting small molecules to diffuse while excluding the larger molecules.

1.2.2 Micropores/zeolite diffusion
The characteristics of diffusion in micropores, which includes zeolite diffusion, are very much related to the above described surface and Knudsen diffusion mechanisms. Zeolite adsorption (physically) combines the aspect of surface diffusion and the pore blocking due to capillary condensation. An important advantage of zeolites, while describing diffusion, is that the sorption is very well defined, due to the well-defined lattice structure throughout the separating film. The diffusive process largely depends on type and composition of the zeolite. In the zeolite pores a migrating molecule will never escape from the force field in the zeolite lattice.

The mechanisms of one and multi-component mass transport through or in zeolites is still a matter of debate. The mass transport through a zeolite layer is qualitatively envisaged in Figure 4 by a five step model\textsuperscript{7,8}:

1) Adsorption from the gas phase to the external surface
2) Mass transport from the external surface into the zeolite pores
3) Intracrystalline zeolite diffusion
4) Mass transport out of the zeolite pores to the external surface
5) Desorption from the external surface to the gas phase

Steps 1 and 5 depend on the conditions on either side of the membrane. For weakly adsorbing species, adsorption on the external surface, which includes the pore mouths, will hardly occur; step 1+2 and 4+5 can be conveniently lumped. If entering occurs directly from the gas phase, molecules have to move under the right angle otherwise they will be scattered back. In general, bulky molecules will have more difficulty to enter the pores than small molecules. Entering of the zeolite pores is therefore a more or less activated process.

Intracrystalline zeolite diffusion (step 3) is often described as configurational diffusion. If strong interaction exists between the zeolite frame work and the molecules, and the molecules have a low kinetic energy, they lose their gaseous characteristics. The molecules vibrate at a fixed position before accumulating enough energy to jump to neighboring sites. This type of diffusion can be related to the above described surface diffusion. With increasing temperature the kinetic energy of the
molecules increases and above a given temperature the interaction with the lattice is negligible compared to the kinetic energy of the molecule and no adsorption will take place. The molecules in the lattice retain their gaseous character. Consequently, going from low temperature to high temperatures transition from a surface diffusion regime toward an activated gaseous (Knudsen-like) diffusion regime will take place. This transport in the gaseous regime is activated, mainly due to the structural constraints of the lattice upon passage\textsuperscript{2}. In which regime mass transport takes place, depends on the operating conditions and the components studied. In reality, in most cases the activation energy for the diffusion is a combination of these two types of activation energy. The total flux is than the sum of the surface diffusion and the gaseous diffusion. Figure 5 shows the general permeation behavior of single component as function of the temperature. In the thesis diffusion in the adsorbed phase will be indicated as surface diffusion and diffusion in the gaseous phase as gas translation diffusion.

In the region of strong adsorption and high occupancies, molecules will have strong interactions with each other unlike in the region of weak adsorption (Henry region). Interactions among molecules will affect the diffusional behavior.

In case of MFI type zeolites it is assumed that molecules can only pass each other via the intersection of two pores. In general, if the kinetic diameter of a molecule is greater than the diameter of the zeolite pore, the molecule will not be able to enter the zeolite pore and the membrane behaves as a true molecular sieve. A certain degree of flexibility of molecules and the zeolite pores have to be taken into account\textsuperscript{9,9a}.

![Figure 5](image.png)

Figure 5. General permeation behavior as function of temperature. The maximum can be explained by the combined temperature dependency of diffusion and adsorption\textsuperscript{8,11}. The minimum is explained by occurrence of activated gaseous diffusion\textsuperscript{12}. For details on the diffusion mechanisms, see Chapter 4.

Step 1 and 5 are generally assumed to be fast processes. Step 2, 3, and 4 are usually activated processes, see Figure 4\textsuperscript{7}. Depending on the activation energy, in principle each step or combination of these steps may be rate determining. However, the
contribution of the surface processes (step 2 and 4) to the total activation energy decreases with increasing membrane thickness and in most cases the intracrystalline diffusion is considered to be rate determining step\textsuperscript{10}. A mathematical description of one and two component mass transport through zeolite micropores is given in Chapters 4 and 5.

2 Experimental Method for Permeation and Adsorption Experiments

2.1 Permeation experiments

Transient and steady-state permeation measurements were performed with the membrane module according to the Wicke-Kallenbach method\textsuperscript{13}. The Wicke-Kallenbach method is schematically depicted in Figure 7. In Figure 6 a scheme of the experimental set-up is given and Figure 9 shows photographs of the experimental set-up and the membrane module. The feed was supplied with thermal mass flow controllers or with an HPLC pump connected with an evaporation unit. The component or mixture under investigation was introduced as a step to the feed side of the membrane while helium was used as sweep gas at the permeate side. During most isothermal experiments the total pressure and the feed and the sweep gas (helium) flow rate amounted to 100 kPa and 100 ml/min (NTP), respectively. For most temperature programmed experiments the sweep gas flow rate amounted 200 ml/min (NPT). If other flows or pressures or flow rates were applied, this is mentioned in the text or the captions of the Figures.

Feed, retentate, and permeate were monitored with a quadrupole mass spectrometer (Leybold/Inficon) and in some cases, e.g. for n-butane/i-butane mixtures, the analysis was also done with a gas chromatograph. With this method both transient and steady-state data were obtained. The transient experiments were corrected for the equipment response. The equipment response was obtained by operating the system with a module containing only the sintered metal support. In Figure 8 a typical example is given.

Due to the preparation method the membrane side of the reactor was also covered with a layer of zeolite crystals. To avoid re-adsorption by this zeolite layer the membrane surface was always facing the feed gas (see system characteristics). Prior to the experiments the membrane was flushed with helium until no other components could be detected. After experiments with strongly adsorbing components the membrane reactor was heated to 473 K while flushing with helium.
Figure 7. Schematic picture of the membrane module and the Wicke-Kallenbach method. During most experiments the total pressure at both sides of the membrane amounted to 100 kPa. The sweep gas (helium) flow rate and the feed gas flow rate was in most cases 100 ml/min (NPT), but for most temperature programmed one component permeation experiments the sweep gas flow rate amounted to 200 ml/min (NPT). Furthermore, the membrane was usually facing the feed flow.

Figure 8. Transient concentration profile after a feed step of methane on: a) the porous metal support and b) the silicalite-1 membrane. The time before the first vertical dashed line is the response time of the equipment. The double ended arrow denote the time needed to reach 95% of the steady-state permeation flux.
Figure 9a. Photograph of the experimental set-up. Left side: feed supply section and oven with membrane module; right side: mass spectrometer.
Theory of mass transport in zeolites, experimental set-up, and system characteristics

Figure 9b and c. Photographs of the all metal high temperature membrane module with two flanges with tubing for gas supply and removal. b) (upper) module mounted in experimental set-up. c) in detail. During membrane synthesis the membrane module is closed at both sides with solid disks (see Chapter 2).
2.2 Adsorption experiments

Adsorption data are essential to understand the permeation behavior and to model the permeation fluxes. Therefore, both isothermal and temperature programmed adsorption measurements were carried out. Isothermal adsorption, at 295 K and from 0-1 bar was carried out in a conventional volumetric equipment and in a thermobalance using 15 mg of silicalite-1. The sample of silicalite-1 crystals was prepared under similar conditions as used for the zeolite membrane synthesis. Before the adsorption measurements the samples were outgassed in air at 673 K to remove adsorbed impurities.

The total pressure in the thermobalance was fixed at 100 kPa, while the partial pressure was varied by adding helium to the flow. A total flow rate of 100 ml/min (NTP) was maintained.

Adsorption data as function of the temperature were obtained by operating the thermobalance in a temperature programmed manner (1-2 K min⁻¹). The raw data were corrected for flow and buoyancy effects by the data of a run without the silicalite-1 sample, carried out under identical conditions.

2.3 Conversion of raw permeation data

In this thesis both the experimental permeation flux \( J \) (mmol.m⁻².s⁻¹) and the permeance \( \Pi \) (mmol.m⁻².s⁻¹.bar⁻¹) are used to indicate the observed mass transport through the silicalite-1 membrane. The flux, \( J_f \), and the counter flux, \( J_s \) of the sweep gas were calculated from a mass balance over the membrane, at the steady-state. Hereby, the mol fraction of the feed in the permeate (\( x_f \)) and the sweep gas in the retentate (\( x_s \)), and the retentate, \( F_r \), and permeate gas, \( F_p \), flow rate are taken into account, see Eqs. 1, 2 and Figure 7. The numerical procedure is demonstrated in Figure 10 for the permeation of methane and helium as function of the temperature.

\[
J_f = \frac{x_f F_p}{A} \quad (1)
\]

\[
J_s = \frac{x_s F_r}{A} \quad (2)
\]

With \( A \) the surface area of the membrane. Hereby the permeate and the retentate flow rate are calculated according to Eqs. 3 and 4.

\[
F_p = \frac{F_r - x_s (F_f + F_r)}{1 - x_s - x_f} \quad (3)
\]
Theory of mass transport in zeolites, experimental set-up, and system characteristics

\[ F_r = \frac{F_f - x_f (F_f + F_i)}{1 - x_i - x_f} \]  

\[ \text{Figure 10.} \]
Conversion of raw permeation data of methane (upper figure) and the sweep gas helium (100 kPa feed pressure) to fluxes and permeances.

As will be shown below and in Chapter 4 upon heating the flux through the membrane changes with temperature. Therefore, the partial pressure difference over the membrane is not constant. The permeance \( \Pi \) is used to compensate for the change in partial pressure difference over the membrane. The permeance is related the fluxes and the partial pressure difference over the membrane, \( \Delta p_i \), in the following way:

\[ \Pi_f = \frac{J_f}{\Delta p_f} \]  

where \( \Delta p_i \) is the partial pressure difference of component \( i \) over the membrane. The feed permeate and the sweep gas retentate partial pressure are calculated according:

\[ \Delta p_f = p_f - (x_f p_f) - (x_i p_i) \]
\[ \Delta p_s = p_s - (x_s p_f) - (x_p p_f) \]

In Figure 10 methane and helium are given as an example of three different ways to represent permeation data: the partial pressure of methane at the permeate side and of helium at the retentate side (raw data), the methane and helium flux and the permeance of methane and helium. The results show the same trend but a constant conversion factor from raw data to the results can not be applied. A constant conversion factor results in a deviation of up to 20\%, especially at low and high temperatures.

2.4 Separation selectivity

In the case of mixtures separation selectivities become important. In this thesis the separation selectivity, \( \alpha \), is defined as the enrichment factor of one component in the permeate as compared to the feed composition ratio.

\[ \alpha_{1,2} = \frac{(y_{f1}/y_{f2})_p}{(y_{f1}/y_{f2})_f} \]  

With: \( y_1, y_2 \) = the molar fractions of component 1 and 2 in the feed, \( f \), or permeate \( p \). Often the selectivity is based on the ratio of one-component permeabilities obtained from pure gas permeation experiments. This so called "ideal selectivity" does only reflect the separation selectivity of binary mixtures if both components are in the gas translation regime\(^8\), where competitive adsorption takes place.

2.5 Boundary conditions

Below the equations are given which were used to correct the permeation results for the support resistance\(^7\). In the experimental set-up the silicalite membrane is facing the feed flow, and the metal support the helium purge flow. In Figure 11 a schematic representation of the concentration profiles in the zeolite layer and the support is given. This gives for the feed side the following condition, assuming Langmuir equilibrium adsorption between the gas phase and the adsorbed phase:

\[ \theta (x = 0) = \theta' = \frac{bP}{1 + bP} \]

At the permeate side also equilibrium adsorption between the gas phase and the adsorbed phase exists. As shown in Chapter 2 the metal support has a very open structure with large pores. Therefore, the mass transport coefficient in the support layer is several orders higher than in silicalite-1. This difference is, however, partly annulled because the metal support of 3 mm is about 60 times thicker than the
silicalite-1 layer. This leads to a significant concentration difference over the support. To calculate the equilibrium amount adsorbed, $\theta$, at the permeate side of the silicalite-1 layer the measured permeate concentration should be corrected for the concentration difference over the support. The concentration difference over the support can be described by:

$$N = D_{12} \frac{dC}{dx} \bigg|_{\text{support}} + \bar{v} \frac{dC}{dx} \bigg|_{\text{support}} = \frac{N - \bar{v}C}{D_{12}}$$  \hspace{1cm} (10)$$

with $D_{12}$ the molecular diffusion, which is also a function of the temperature and $vC$ the convective flow in the support. The molecular diffusion coefficient is calculated from the relation given by Fuller$^{14}$.

$$D_{1,\text{le}} = \alpha \frac{T^{1.75}}{P} \left( \frac{M_1^{-1} + M_{\text{le}}^{-1}}{V_1^{\text{le}} + V_{\text{le}}^{\text{le}}} \right)^{\frac{3}{2}}$$  \hspace{1cm} (11)$$

with $\alpha = 1.0 \times 10^{-5}$ g$^{1/2}$ m$^2$ s$^{-1}$ N K$^{-7/4}$ mol$^{-1/6}$

---

**Figure 11.**

Schematic representation of concentration profiles in the zeolite layer and the metal support. 1 = concentration profile for strongly adsorbing component, 2 = concentration profile for a weakly adsorbing component. For calculations the film resistance at the membrane side is neglected. In reality the support is about 60 times thicker than the zeolite layer.

---

$^{1}$ For the calculation of the diffusion coefficient as presented in Chapter 4 the corrected permeation results are used.
For example, for methane the molecular diffusion $D_{CH4,He} = 5\times10^{-5} \text{ m}^2\text{s}^{-1}$ at 300 K. This gives rise to a pressure difference of about 10 kPa, over the metal support of 3-mm thickness. The ideal gas law is used to calculate the pressure, at the interface of the silicalite-1 layer and the metal support, from the concentration. This pressure is used to calculate the driving force for permeation, which is given by the difference in occupancy and the difference in the partial pressure over the silicalite-1 layer. Section 3.1 shows the influence of the support on the permeation experimentally. In Chapter 4 the permeation through the silicalite layer is described in detail.

3 System characteristics

3.1 Positioning of the silicalite-1 layer (feed or permeate side)

The silicalite-1 layer is grown on a porous stainless steel disk, see Chapter 2. In this way an asymmetric membrane is formed. The effect of the orientation of the membrane has been studied by performing two series of experiments. In the first series of experiments the silicalite-1 layer was facing the feed gas. In the second series this was the other way around, and the silicalite-1 layer was facing the helium sweep gas.

![Figure 12a. Flux of carbon dioxide, methane, and, nitrogen as function of the pressure at 300 K for the silicalite-1 layer facing the feed and the sweep. Open symbols: Silicalite-1 facing feed. Closed symbols: Silicalite-1 facing sweep gas. Dashed lines are to guide the eye.](image1)

![Figure 12b. Flux of hydrogen and n-butane, as function of the pressure at a temperature of 303 K, through the silicalite-1 layer, with the silicalite-1 layer facing the feed and sweep. Open symbols: Silicalite-1 facing feed. Closed symbols facing sweep. Dashed lines are to guide the eye. Dashed lines are to guide the eye.](image2)

If the support layer is put at the side of the sweep gas the molecular diffusion in the metal support introduces an extra diffusional resistance. This results in a partial pressure difference over the metal support. Because of the thickness of the support,
about 3 mm, the partial pressure at the interface of the silicalite-1 and the metal support is typically about 10 kPa higher than the partial pressure at the edge of the support, where the sweep gas enters the metal support layer. This means that at the interface of the silicalite-1 and the metal support a considerably higher amount is adsorbed, as would have been obtained if the partial pressure in the sweep gas is used.

3.1.1 Steady-state results

In Figure 12a a comparison is made between results for the moderately adsorbed carbon dioxide and the weakly adsorbed methane and nitrogen, obtained with the silicalite-1 layer at the feed side and with the silicalite-1 layer at the sweep side. The results for the fluxes are for a temperature of 303 K and for a feed pressure between 10 and 101 kPa. Clearly, the situation with the silicalite-1 layer facing the sweep gas gives the highest steady-state flux. It is expected that for a higher amount adsorbed, or for strongly adsorbed gases, purging at the side with the silicalite-1 layer becomes more important. This is confirmed by the two following experiments; the steady-state flux of n-butane at 303 kPa and the temperature dependence of the permeance of methane.

The effect of the equilibrium adsorption on the permeation follows from Figure 12b. At a temperature of 303 K the lowest amount adsorbed in silicalite-1 is obtained for hydrogen and neon. At this temperature the strongest adsorbed gases in silicalite-1 are n-butane and i-butane. Therefore, as expected, a considerable difference between the permeation of hydrogen and of n-butane is recorded for the two cases.

For a temperature of 303 K a difference of about 50% is obtained between the n-butane fluxes. At this temperature n-butane is strongly adsorbed and has an almost rectangular isotherm, see for example Abdul-Rehman et al.\textsuperscript{15} and Bakker et al.\textsuperscript{11} Hydrogen is very weakly adsorbed at 303 K, and the flux is almost independent of the orientation of the silicalite-1 layer. In Figure 13 the permeance of methane is presented for the two cases, but now as function of the temperature. At low temperatures, say below 250 K, the permeance with the silicalite-1 layer facing the sweep gas is about twice as high as compared to the situation where the support layer faces the sweep gas. The solid line is a prediction using the diffusion and adsorption parameters from Table 4 in Chapter 4. Only the boundary conditions have been adjusted. Because the membrane is reversed, there is almost no effect of the support on the permeation. In the prediction, for the situation with the support at the feed side, the equilibrium at the feed side is taken equal to the adsorption equilibrium for the reversed situation where the silicalite-1 crystals are in direct contact with the feed. At the permeate side the amount adsorbed is now directly related to the partial pressure of the permeating methane.
3.1.2 Transients results

Also, a number of transient experiments have been performed. The results for the transient profiles for n-butane for the two cases, are shown in Figure 14. The approach to equilibrium is faster for the situation with the silicalite-1 layer facing the feed, although the final steady-state flux is lower, as compared to reversed situation. By putting the silicalite-1 layer at the feed side the adsorption in the crystals of the membrane is better defined.

![Temperature vs. Permeance](image1)

*Figure 13. Permeance of pure methane at 101 kPa as function of the temperature, for the case with, respectively, the silicalite-1 layer facing the feed and the sweep. The dashed line is a fit, the solid line a prediction. Sweep gas flow 100 ml.min⁻¹. Open symbols: Silicalite-1 facing feed. Closed symbols: Silicalite-1 facing sweep.*

![Time vs. Flux](image2)

*Figure 14. Effect of the membrane orientation on the transient and steady permeation of n-butane at 101 kPa and 295 K.*

The slower approach to equilibrium is due to the re-adsorption in the silicalite-1 crystals which are not really part of the membrane, but which are part of the sealing and cover part of the module, see Figure 14 in Chapter 2. During steady-state operation there is equilibrium between the gas in the crystals on the porous part of the flange and the gas phase and re-adsorption does not contribute to the mass transport.

The fact that the support layer has such a pronounced effect on the flux makes it difficult to compare the diffusivities obtained from transient and steady-state measurements.

3.2 Counter diffusion

3.2.1 Influence of helium on the permeation of a non-absorbing component

In Bakker et al.⁸,¹¹ and in Figure 7 of Chapter 4 it is shown that at conditions when weak or no adsorption of the feed at silicalite-1 occurs the sweep gas helium permeates from the permeate to the feed side of the membrane. To be able to calculate the mass balance
over the membrane, see Eqs. (1) and (2), the helium counter-diffusion was measured during most experiments.

It is assumed that helium does not hinder the permeation of the components under investigation significantly because it does not show any (measurable) adsorption in the zeolite pores. It is easily understood that this is true when strong adsorption of the feed gas occurs but it is questionable with weakly adsorbing feed gases because, in that case, some helium moves in the opposite direction and thus hinders the feed molecules to some extent. To validate the influence of helium on the permeation of weakly adsorbing molecules, this has been investigated. Therefore, helium was supplied at the permeate side and hydrogen, which is essentially non-adsorbing at room temperature, at the feed side of the membrane. The permeance at 295 K of both components was determined while increasing the absolute pressure at the permeate side (helium) from 100 to 500 kPa and keeping the pressure at the feed side (hydrogen) constant at 100 kPa.

![Figure 15. Influence of increasing the pressure at permeate (helium) side, from 1 to 5 bar, on the permeance of hydrogen. Hereby, 100 ml/min NPT helium was dosed at the permeate and 100 ml/min NPT hydrogen at the feed side of the membrane. The pressure at the feed side was kept constant at 100 kPa. The extrapolated value at zero permeate pressure is 14% higher than the permeance of hydrogen at 100 kPa permeate pressure.](image)

The result of this experiment can be seen in Figure 15. With increasing the pressure at the permeate (helium) side of the membrane, from 1 to 5 bar, the hydrogen permeance decreases. Based on extrapolation of this trend a 14% higher hydrogen permeance is predicted if a vacuum would be applied at the permeate side of the membrane, instead of the sweep gas helium. From this it can be concluded that the counter-diffusion of helium hindered the permeation of hydrogen significantly. Because the helium counter-diffusion increases strongly with increasing temperature, it is expected that the sweep gas helium may also affect the permeation of larger and heavier molecules at higher temperatures. This point is subject to further investigation. Nevertheless, it is clear that the Wicke-Kallenbach method is a practical and accurate method for membrane permeation measurements. This was confirmed by Vroon\textsuperscript{16}, who found that the Wicke-Kallenbach method was consistent, within 20%, with the Dead-End method which used a vacuum.
3.2.2 Argon versus helium as a sweep gas
To minimize the influence of the sweep gas on the permeating gas their concentration in the zeolite pores should be as low as possible to minimize collisions with molecules in the opposite direction. Moreover, if the sweep gas is adsorbing, its presence also affects the permeance of the pure component, through the binary absorption isotherm. To demonstrate this, the permeation of N₂, CH₄, and CO₂ was studied by using argon, which is weakly adsorbing, and helium as a sweep gas. The results are shown in Table 1. Also the equilibrium amount adsorbed in silicalite-1 is indicated.

Obviously, the hindrance by argon on the permeating molecules is much higher than with helium. As expected the stronger the component is adsorbed the smaller the reduction in the flux. This also holds for the sweep gas argon, because both argon and nitrogen are weakly adsorbed in silicalite-1 a relative high amount of argon is permeating through the silicalite-1 membrane. For carbon dioxide as the feed, which is much stronger adsorbed than argon in silicalite-1, the lowest flux for argon is observed.

<table>
<thead>
<tr>
<th>Feed gas</th>
<th>θ (°) [-]</th>
<th>He sweep</th>
<th>Ar sweep</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeate Jₜ</td>
<td>Retentate Jₜ&lt;sub&gt;He&lt;/sub&gt;</td>
<td>Permeate Jₜ</td>
</tr>
<tr>
<td>argon</td>
<td>0.08</td>
<td>16</td>
<td>2.4</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.08</td>
<td>15.2</td>
<td>2.6</td>
</tr>
<tr>
<td>methane</td>
<td>0.18</td>
<td>25.8</td>
<td>1.3</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.45</td>
<td>32.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 1. Effect of the sweep gas on the permeation flux through the silicalite-1 membrane. Results for a feed and sweep gas pressure of 101 kPa and a temperature of 303 K. Flux J<sub>t</sub> (nmol m<sup>-2</sup> s<sup>-1</sup>) refers to the flux of the feed component at the permeate side for the two different sweep gases.

<sup>a</sup> Equilibrium fractional occupancy in silicalite-1 at 101 kPa and 303 K

3.3 Sweep gas flow rate and partial pressure difference over the membrane
The pressure difference over the membrane changes with a variation of the sweep gas flow rate. Under ideal conditions the sweep gas flow rate is infinite, so the permeate concentration approaches zero and the partial pressure difference over the membrane is equal to the imposed feed pressure. In our experimental set-up the permeate partial pressure of the component under investigation was usually kept below 10 kPa. The counter diffusion of helium dilutes the feed to some extend. This also reduces the partial pressure difference over the membrane. This may lead, for the conditions applied, to a difference between 0-15% between the observed flux and the calculated permeance at a feed pressure of 100 kPa, see Figure 10. From this it was concluded that the observed
fluxes are a very reasonable indication for the permeance through the membrane. In general, the flux is a more convenient property to estimate the mass transport in practical applications while the permeance can be better used for a more fundamental approach.

It is assumed that the flux through the membrane is dependent on the occupancy gradient over the membrane, see Chapter 4. This occupancy gradient is related to the concentration gradient via the adsorption isotherm. E.g. for weakly adsorbing molecules the flux will be linearly dependent on the concentration gradient over the membrane as the absorption is linear dependent on the concentration difference over the membrane\textsuperscript{11}. More strongly adsorbing components show a non-linear relationship with the pressure difference due to the non-linearity of the adsorption isotherms for these components\textsuperscript{11}. With increasing sweep gas flow rate, the concentration difference over the membrane increases, so the flux should increase. However, a higher sweep gas flow rate may partly change the transport mechanism in the support from molecular diffusion to convective flow. The latter would lower the concentration gradient over the support and thus increases the concentration gradient over the zeolite layer. This would lead to an extra increase in the permeation flux which should be accounted for during modeling of a membrane process.

![Figure 16. Effect of sweep gas flow variation (25-500 ml/min) on the permeation flux of neon, argon and krypton. The permeance is constant for all components. Results for a feed and sweep gas (He) pressure of 101 kPa and a temperature of 295 K.](image)

To check the influence of sweep gas flow variation on the permeation, the permeation of neon, argon, and krypton flux at room temperature through the membrane was measured with a sweep gas flow rate varying from 25 to 500 ml/min at room temperature. The feed pressure was 100 kPa and the feed flow rate 100 ml (NPT) min\textsuperscript{-1}. In Figure 16 the resulting flux and the permeance is shown. As expected the flux decreases with decreasing sweep gas flow rate but the permeance remained constant. So it was concluded that support resistance remained virtually unchanged in the flow regime applied.
4 Conclusions

A qualitative description has been given of mass transport through porous media. Hereby the focus is on diffusion through zeolite micropores. Two diffusion regimes exist in micropores. Surface diffusion and activated gas translational diffusion. The type of diffusion which is dominating depends on the interaction with the micropores and the kinetic energy of the molecules (read temperature).

The effect of various process conditions on the one-component gas permeation through an asymmetric supported silicalite-1 membrane has been studied. The relative importance of a number of operating modes has been presented. In this way it is possible, depending on the mode of operation, to choose the optimal operating conditions.

The counter diffusion of the sweep gas helium hinders the permeation of hydrogen, which is practically non adsorbing at room temperature. It was estimated that compared to the dead end method (vacuum) the permeance of hydrogen was 14% lower. It is concluded that the applied Wicke-Kallenbach method is suitable for permeation measurements.

If an adsorbing sweep gas is used, argon, the flux through the silicalite-1 membrane is reduced, as compared to the situation where helium is used as the sweep gas. The stronger the feed component is adsorbed the smaller the effect of the argon sweep on the permeation.

The positioning of the silicalite-1 layer, feed or permeate side, has a large effect on the permeation flux. Considerable differences exist depending on the adsorption properties of the gases studied. For a strongly adsorbed gas, like n-butane, a difference of about 50% in the flux for the two situations has been obtained. For weakly adsorbed gases, like nitrogen and hydrogen, a difference of about 10% in the flux is obtained at 300 K. For steady-state permeation the highest flux is obtained when the silicalite-1 layer is facing the sweep gas.

5 Literature

One-Component Permeation

Abstract
The one-component steady-state permeation of gases through a silicalite-1 zeolite membrane is studied over a broad temperature range, 190-680 K. Alkanes, noble gases and some inorganic molecules are used as probe molecules and helium is used as sweep gas. Also the adsorption characteristics of most components under investigation have been measured.

Large differences have been found between the different one-component permeation fluxes. The permeance for various gases, for a feed pressure of 101 kPa, span four orders of magnitude. The lowest permeation is for i-butane at 300 K: a permeance of $0.07 \times 10^{-8}$ mol.m$^{-2}$.s$^{-1}$.Pa$^{-1}$. The highest value is observed for methane: a permeance of $70 \times 10^{-9}$ mol.m$^{-2}$.s$^{-1}$.Pa$^{-1}$ at about 240 K. Generally, the permeation and diffusion coefficient decrease with increasing molecular size.

A remarkable temperature dependency has been observed. In general, with increasing temperature the permeance shows a maximum followed by a minimum. For gases which are weakly adsorbed at 300 K, such as hydrogen, the permeance has only a minimum, for gases which are strongly adsorbed at 300 K, such as n-butane, only a maximum is observed in the permeance. For i-butane the permeance only increases steadily with temperature. A comparison between the adsorption isobars and the temperature dependence of the steady-state permeance shows that at the temperature where the amount adsorbed decreases strongly a maximum in permeation occurs and that where the amount adsorbed vanishes the permeance starts to increase. The temperature dependence of the steady-state fluxes through the silicalite-1 membrane can only be described if two diffusion mechanisms are taken into account. For high occupancies the mass transport can be described by equilibrium adsorption and surface diffusion and for low occupancies the mass transport can be described by activated gaseous diffusion. With increasing temperature the mass transport mechanism shifts from the surface diffusion regime to the activated gaseous diffusion regime. Also referred to as activated gas translation diffusion.

Using these two diffusivities good agreement is obtained between the modeling and the experimental results for the one-component flux through the silicalite-1 zeolite membrane. Confirmed by the one-component permeation results for the silicalite-1 membrane, as presented in this work, a general model for mass transport in micropores is available.
Chapter 4

1 Introduction

One-component permeation and adsorption data are essential in studying the mass transport mechanisms in a zeolite membrane. In this chapter an overview is given of one-component permeation and adsorption data for a number of hydrocarbons, noble gases and inorganic molecules over a large temperature range, 190-680 K. The experimental results are described by a combined surface and activated gaseous diffusion model which is derived in the first part of this Chapter. Also a literature review is given on microporous membranes.

1.1 Microporous membranes, literature review

1.1.1 Theory

Diffusion in microporous media is described in terms of adsorption and surface diffusion; mass transport takes place in an adsorbed phase and can be pictured as molecules hopping between fixed sites. For the mass transport an activation energy of diffusion has to overcome. Diffusion in zeolites is described as an activated process and different situations are discussed in terms of different diffusional paths. In this way the hopping model is derived, called the solid vibration model, as well as an activated gas phase (Knudsen-like) diffusion model, called the gas translation model, is obtained. Different derivations of an activated gaseous diffusion coefficient, for micropore diffusion, have been given by Petropoulos and Hadvredaki and by Shindo et al.

It is generally accepted that the concentration dependence of the Fick micropore or surface diffusivity is given by the Darken equation, \( D_F = D_S(0) \frac{d\ln P}{d\ln q} \). This relation relates the Fick diffusivity to an intrinsic diffusivity \( D(0) \). The thermodynamic factor, \( \Gamma = \frac{d\ln P}{d\ln q} \), relates the gas phase pressure to the amount adsorbed and is obtained when the gradient in the chemical potential is used as the driving force for diffusion. Using the concept of transition state theory Chen and Yang derived a modified form of the Darken relation which takes into account the effect of the constriction of the zeolite structure on the mass transport. With this model different behaviors for the one-component Fick diffusivity in different zeolites, as function of the amount adsorbed, are described. It has been found that one-component diffusion in MFI zeolites (silicalite-1 and ZSM-5) is a strong function of the amount adsorbed. The diffusion of hydrocarbons, including 2-methylbutane and benzene, in ZSM-5 is studied by Xiao and Wei. For a loading higher than four molecules per unit cell, the Fick diffusivity increases with an increase in the amount adsorbed. This behavior is confirmed by Molecular Dynamics simulations for one-component diffusion of methane in silicalite-1.

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1.2 Microporous membranes

1.1.2 Zeolite membranes

The results reported in this Chapter have been obtained with the same experimental set-up and membrane synthesis procedure as described by Bakker et al.\textsuperscript{12} and by Geus et al.\textsuperscript{13}, see Chapters 2 and 3. The permeation of one- and two-component gaseous system through a silicalite-1 zeolite layer on a metal support, using a Wicke-Kallenbach diffusion cell, have been described by Bakker et al.\textsuperscript{12,14,15}. Typical permeation behavior is demonstrated by the system composed of hydrogen, n-butane, and the silicalite-1 membrane. The selectivity for a 1:1 mixture of hydrogen and n-butane, for 101 kPa feed pressure, depends on the temperature. At room temperature the n-butane is adsorbed much stronger than the hydrogen, resulting in a separation factor of about 50, towards butane. With increasing temperature the amount adsorbed will decrease and the difference in mobility, through the gas phase in the micropores, will be the governing mechanism for separation. For this mechanism the membrane selectivity is in favor of the hydrogen. At 600 Kelvin a separation factor of about 4, towards hydrogen, is found. For the permeation as function of the time, the faster moving but weakly adsorbed, hydrogen shows a maximum in the permeation flux. The hydrogen enters the silicalite crystal first, because of its higher mobility, and is then replaced by the slower moving but stronger adsorbed butane\textsuperscript{15}.

Vroon et al.\textsuperscript{16} studied the synthesis of a silicalite-1 membrane on a ceramic support. Results are presented for the one-component permeation of methane, ethane, propane, n-butane, i-butane, and the permeation of some binary mixtures, as function of the partial pressure and temperature. The permeation of 50 kPa methane and 50 kPa n-butane mixture, as function of temperature clearly shows the effect of the stronger adsorbed n-butane on the weaker adsorbed methane. At a temperature of 373 K the flux of methane, in the mixture, has dropped by an order of magnitude as compared to the one-component situation.

Yan et al.\textsuperscript{17} presented results for a ZSM-5 membrane on an alumina support. Several synthesis experiments are described, which have been performed to find the optimal conditions to form a continuous zeolite layer. It was found that the one-component n-butane permeation was between 18 and 31 times higher than the i-butane permeation, over the temperature range of 303 to 458 K.

The group of Falconer and Noble\textsuperscript{18,19} use a tube covered with ZSM-5 zeolite to study one- and two-component diffusion. Results are reported for the one-component permeation of five gases, hydrogen, argon, n-butane, i-butane, and sulfurhexafluoride, over the temperature range of 300 to 600 Kelvin. For hydrogen and argon a small minimum is observed in the permeance, as function of the
temperature. For the other three gases, \( n \)-butane, \( i \)-butane, and sulfurhexafluoride, the permeance increases monotonously with increasing temperature. At a temperature of 298 K the permeance of \( n \)-butane is higher than the permeance of \( i \)-butane, above this temperature \( i \)-butane permeates faster than \( n \)-butane\(^{18} \). Also, results are reported for aromatic hydrocarbon vapors permeating through the ZSM-5 membrane. Over the temperature range of 380 to 480 Kelvin it was found that the one-component permeance of the three xylene isomers, benzene, ethylbenzene, and toluene all increase with an increase in temperature. The sequence of the permeance did not follow the sequence of the kinetic diameter. For various binary mixtures of the aromatic hydrocarbons it was observed that the faster permeating species were slowed down to the rate of the slower permeating molecules, and as a consequence no separation is possible\(^{19} \).

Nishiyama et al.\(^{20} \) reported results of one-component permeation through a Ferrierite zeolite membrane over the temperature range of 295 to 385 Kelvin. For a number of gases, including hydrogen, methane, oxygen, and carbon dioxide a minimum is observed in the one-component permeation as function of the temperature.

1.1.3 Carbon molecular sieve membranes
Membranes of microporous activated carbon have been used by Barrer and co-workers to study the diffusion in porous materials. Koresh and Soffer\(^{22} \) used fibrous carbon molecular sieve (CMS) and carbon molecular sieve membranes\(^{23,24} \) to study the effect of pore structure and pore opening on the mass transport. By gradually enlarging the pore openings of the carbon from 0.31 to 0.56 nm the cross section related to adsorption and diffusion of various molecules was established. Recently, with the development of carbon molecular sieves the interest for this type of microporous membrane has been renewed.

Chen and Yang\(^{25} \) developed a carbon molecular sieve membrane on a macroporous graphite support by controlled pyrolysis. A carbon molecular sieve layer of 15 \( \mu \)m thickness was obtained, the support thickness is 0.457 cm. Steady-state permeation experiments were performed for methane, ethane, and binary mixtures of these gases. From the concentration dependence of the single-component diffusivities the binary fluxes could be predicted using a loading ratio correlation for the isotherms.

Rao and Sircar\(^{26} \) developed a CMS membrane for the separation of hydrogen from small hydrocarbons. Results are reported for permeation of a mixture of hydrogen, methane, ethane, and propane, at a temperature of 295 K. The mass transport through the micropores, with a diameter of about 1 nm, is by adsorption and surface diffusion. Separation was achieved by a difference in the amount
adsorbed. Although the mobility of the hydrogen, in the CMS membrane is higher than the mobility of the hydrocarbons, the membrane selectivity is in favor of the more strongly adsorbed hydrocarbons, rather than for the hydrogen which is relatively poorly adsorbed. This behavior is completely analogous to the behavior of a mixture of hydrogen and \( n \)-butane through the silicalite-1 membrane.

1.1.4 Glass membranes
Kamermeyer and co-workers\textsuperscript{27,29} and Inoue and co-workers\textsuperscript{7,30} studied the one-component diffusion in Vycor glass membranes with a pore diameter of about 40 nm. Okubo and Inoue\textsuperscript{30} also studied a modified Vycor glass, with a pore diameter of about 4 nm. The permeation results for this modified membrane show the same trend as observed for the membrane with the larger pore diameter. In the modified glass membrane the permeation was one order of magnitude smaller as compared to the original glass membrane.

The various results for the adjusted permeability, \( IT^{1/2} \), of noble gases, nitrogen, and carbon dioxide as function of the temperature (200 - 600 K) through Vycor glass membranes all show the same behavior. As the temperature is increased, starting at about 200 K, the adjusted permeability decreases, but for most of the gases it reaches a minimum around 300 Kelvin, and by further increasing the temperature the adjusted permeability starts to increase.

Ma and co-workers\textsuperscript{31,32}, studied the permeation through a bidisperse Vycor glass over the temperature range of 300 to 700 Kelvin. The result for the permeability of helium, methane, and carbon dioxide all increase with increasing temperature. The pore diameter of the Vycor glass membrane ranges from 0.5 to 1.5 nm.

2 Mathematical description of one-component permeation through zeolite micropores

Below a model to describe zeolite adsorption and the permeation flux through the metal supported zeolite membrane is given. This model is used for simulations of the experimental results. In this model the following assumptions are made: (i) Mass transport occurs only through silicalite-1 zeolite pores. (ii) Equilibrium adsorption occurs at both sides of the membrane. (iii) Intracrystalline diffusion is the rate determining step (step 3).
2.1 Equilibrium adsorption

Often the Langmuir isotherm is used to describe the relation between the amount adsorbed, \( q \), and the gas phase pressure, \( p \).

\[
\theta = \frac{q}{q_{\text{sat}}} = \frac{bP}{1 + bP}
\]  

(1)

The fractional occupancy \( \theta \) is also a function of the temperature. The temperature dependence is given by the Langmuir parameter:

\[
b = b^0 \exp \left( \frac{-\Delta H}{RT} \right)
\]

\[= \exp \left( \frac{\Delta S}{R} \frac{\Delta H}{RT} \right)\]  

(2)

In this work we assume that the entropy of adsorption, \( \Delta S \), and the heat of adsorption, \(-\Delta H\), are constant. For Langmuir adsorption the so-called thermodynamic correction factor, see Eq. (1) and (8), is given by:

\[
\Gamma = \theta \frac{\partial \ln p}{\partial \theta} = \frac{1}{1 - \theta}
\]  

(3)

2.2 One-component diffusion

Following Xiao and Wei\(^5\) we start with the most general expression for the Fick diffusion coefficient.

\[
D_F = \frac{u \lambda}{z} \exp \left( \frac{-E_D}{RT} \right)
\]  

(4)

with \( u \) the velocity of the diffusing molecules, \( \lambda \) the diffusional free length, \( z \) a constriction or probability factor, and \( E_D \) the activation energy for diffusion.

For the silicalite-1 zeolite it will be shown that two different diffusion regimes are possible, depending on the temperature. Generally, for low temperatures mass transport diffusion takes place by diffusion in an adsorbed phase. If the temperature is increased, the kinetic energy of the molecules increases while the interaction with the zeolite pores remains constant. This results in a decrease of the adsorption and above a given temperature no adsorbed phase will be present in the zeolite channels.
and the mass transport is by activated gaseous diffusion. The former will be denoted as surface (S) diffusion, the latter as gas translation (GT) diffusion.

The total flux, $J_{\text{tot}}$, through a zeolite membrane can be envisaged as the sum of the surface diffusion, $J_S$, and the gas translation diffusion $J_{\text{GT}}$.

$$J_{\text{tot}} = J_S + J_{\text{GT}}$$ (5)

### 2.2.1 Surface diffusion

Surface diffusion in the zeolite pores can be described based on a sorption diffusion model. Hereby the molecules are “hopping” from adsorption to adsorption site. Assuming a random walk mechanism for mass transport, Eq. (4) gives the following relation for the surface diffusion coefficient.

$$D_S(q) = \frac{\lambda^2}{z} \nu(q) \exp\left(\frac{-E_{D,S}}{RT}\right)$$

$$= D_S^0(q) \exp\left(\frac{-E_{D,S}}{RT}\right)$$ (6)

With $\lambda$ the distance between two adjacent sites, which is equal to the diffusional length. The velocity of the diffusing molecules, $u$, is related to the jump frequency, $\nu$, of the adsorbed molecules by $u = \lambda \nu$. The flux through the silicalite-1 membrane for this situation is given by:

$$J_S = \varepsilon \rho D_S(q) \frac{dq}{dx}$$ (7)

with $\varepsilon$ the porosity of the support and $\rho$ the density of silicalite-1. In general the surface diffusivity is a function of the amount adsorbed $q^8$.

In the Fickian approach, see Eq. (7), the concentration gradient in the zeolite is used as driving force while in the Maxwell-Stefan (MS) approach the gradient of the thermodynamic potential is the driving force. The driving force for the diffusion of the adsorbed species, $\nu_{\mu}$, is balanced by the friction that moving species experience from each other and their surroundings. Hereby the vacancies are treated as participating species. See for an extensive treatment the work of Van de Broeke and Krishna$^{4,53}$ and references therein.

With the driving force for diffusion given by the gradient in the chemical potential one can derive a relation between the Fick diffusivity and intrinsic (MS) diffusivity. The concentration dependence of the (Fick) surface diffusion, in Eq. (6), is then given by:
Chapter 4

\[ D_S(q) = D_0^s(q) \exp \left( -\frac{E_{D,S}}{RT} \right) \]
\[ = D_s(0) \frac{d \ln p}{d \ln q} \]
\[ = D_s(0) \Gamma \] (8)

This equation is also known as the Darken equation and used to introduce some quantities. The diffusivity \( D_0^s \) is generally referred to as a limiting diffusivity, which is independent of the temperature. The diffusivity \( D_s(0) \) is referred to as intrinsic diffusivity, which is independent of the amount adsorbed. The results to be presented below will be given in terms of \( D_0^s(0) \). The thermodynamic correction factor \( \Gamma \) can be calculated from the adsorption isotherm.

2.4 Gas translation diffusion

For high enough temperatures no adsorbed phase will exist in the zeolite pore. Following Xiao and Wei\(^5\), we say that the molecules inside the silicalite-1 pores retain their gaseous character, but for diffusion, form site-to-site, the molecules have to overcome an energy barrier imposed by the pore structure. Again, the diffusivity can be derived from Eq. (4). The velocity of the diffusing molecules is obtained from the kinetic gas theory, the diffusional length is denoted by \( \lambda \).

\[ D_{GT} = \frac{\lambda}{z} \left[ \frac{8RT}{\pi M} \right] \exp \left( -\frac{E_{D,GT}}{RT} \right) \] (9)

For this situation the flux is given by

\[ J_{GT} = \varepsilon D_{GT} \frac{1}{RT} \frac{dp}{dx} \] (10)

In the preceding theory, with the separate contributions is demonstrated in Figure 1 for the permeation of krypton. Also, plotted is the modified permeance, \( \Pi T^{0.5} \), from which the temperature dependence is better observed. In this way the total temperature dependence of the activated gaseous flux is taken into account; see Eqs. 9 and 10.
Simulations

Taking Eqs. 1 to 10 together the total flux through the membrane is given by:

\[ J_{tot}(T) = \varepsilon \rho q_{sat} D_S^0(0) \frac{1}{1 - \theta} \exp \left( -\frac{E_{D,S}}{RT} \right) \frac{d\theta}{dx} + \frac{\lambda}{z} \sqrt{\frac{8}{\pi M RT}} \exp \left( -\frac{E_{D,GT}}{RT} \right) \frac{dp}{dx} \]  
(11)

It is noted that in this equation the occupancy \( \theta \) is a function of the temperature, given by Eqs. (1) and (2).

In the paper of Xiao and Wei\textsuperscript{5} a general picture is given of diffusion in MFI zeolite crystals; the activated gas translation diffusion was discussed in detail. For the zeolite structure studied in this work the activation energy for the gas translation diffusion can be interpreted as the difference in the potential energy, \( U \), between a molecule in the intersections and in the channels. This can be written as:

\[ E_D = | U_{max} - U_{min} | \]  
(12)

The potential energy can be calculated from, for example, the 6-12 Lennard-Jones potential. The distance between the sites also determines the diffusional path, \( \lambda \), for surface and gas translation diffusion; in silicalite-1 the distance between two adjacent sites is about 1 nm. An interesting behavior is seen for the intrinsic diffusivity as a function of the ratio of the kinetic diameter to the channel diameter (cf. figure 10 of the paper of Xiao and Wei\textsuperscript{5}). If the ratio of the kinetic diameter to the channel diameter is smaller than 0.6, the diffusivity is more or less independent of this ratio. On can say that diffusion takes place in the Knudsen regime, On the other hand, if the kinetic diameter approaches the channel diameter, the diffusivity decreases sharply. This diffusion regime is referred to as configurational diffusion.

In this work the relative contributions of surface diffusion and gaseous diffusion will be investigated. In the simulation to be presented we have four unknown parameters. We have used from Eq. (6) the limiting diffusivity, \( D_S^0(0) \), and the activation energy, \( E_{D,S} \), and from Eq. (9) the diffusional length, \( \lambda \), and the activation energy, \( E_{GT} \), as fitting parameter. The diffusional length \( \lambda \) for gas translation diffusion has been fitted because its interpretation is not completely clear. The equilibrium parameters are obtained from independent measurements of the amount adsorbed as function of the temperature; isobars at 101 kPa over the range of 200 to 600 K. The boundary conditions as described in Chapter 3 are taken into account.
In Figure 1 is illustrated for the permeation data of krypton in which way the surface diffusion and gas translation diffusion contribute to the total permeation flux through the silicalite-1 membrane. The effect of variation of the activation energy for surface diffusion, $E_{D,S}$, and heat of adsorption, $\Delta H$, on the permeation are shown in Figure 2a and 2b, respectively. An increase in the enthalpy of adsorption has as effect that the amount adsorbed will increase, and therefore the maximum in the flux occurs at a higher temperature. The activation energy for diffusion has only an effect on the height of the maximum.
3 Experimental

In Chapter 3 a detailed description of the experimental method and the equipment is given.

4 Results

4.1 One-component adsorption on silicalite-1 crystals

4.1.1 Isobars

To establish the diffusion regime where adsorption is important the equilibrium amount adsorbed has been obtained as function of the temperature, for most of the gases studied in this work. The results for a number of isobars over the temperature range of 200 to 500 K, at a pressure of 101 kPa, are given in Figure 3.

![Figure 3. Isobars on silicalite-1 crystals at 101 kPa over the temperature range of 200 to 500 K.](image)

The isobars for the first four n-alkanes have been reported previously by Bakker et al.\textsuperscript{15}. The following sequence in the amount adsorbed is observed: \(n\text{-}C_4\text{H}_{10} > C_3\text{H}_8 > C_2\text{H}_6 > CH_4\). From Figure 3 it follows that by increasing the temperature the amount adsorbed decreases, and above a given temperature no measurable adsorption takes place. For the strongest adsorbed components, xenon, \(i\)-butane, and \(n\)-butane, this temperature is about 600 K. From the isobar at low temperatures it is clear that different components have a different saturation capacity, \(q_{sat}\). From the noble gases, neon and helium are essentially non-adsorbing; at a temperature of 200 K less than 0.1 mmol g\(^{-1}\) of these gases is adsorbed.

The isobars are described with the Langmuir isotherm with the \(b\) parameter as function of the temperature. The fits are obtained using, in Eq. (2), a constant enthalpy of adsorption and a constant entropy of adsorption. The results of these fits
are given in Table 2. From the isobars also the saturation capacity for the different components has been derived. These results obtained from the isobars are used in the description of the temperature dependence of the one-component permeance.

Table 1. Equilibrium adsorption of simple gases in silicalite-1, obtained from independent isobaric data.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$M_{g/mol}$</th>
<th>$\Delta S_{J/mol K^{-1}}$</th>
<th>$-\Delta H_{kJ/mol}$</th>
<th>$q_{sat}_{mmol/g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ne*</td>
<td>20</td>
<td>-37</td>
<td>5.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>-49</td>
<td>13.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Kr</td>
<td>84</td>
<td>-57</td>
<td>19.3</td>
<td>4.9</td>
</tr>
<tr>
<td>Xe</td>
<td>131</td>
<td>-69</td>
<td>29.9</td>
<td>3.1</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2</td>
<td>-43</td>
<td>5.9</td>
<td>5.4</td>
</tr>
<tr>
<td>N$_2$</td>
<td>28</td>
<td>-50</td>
<td>13.8</td>
<td>5.4</td>
</tr>
<tr>
<td>CO*</td>
<td>28</td>
<td>-55</td>
<td>17.9</td>
<td>5.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>44</td>
<td>-58</td>
<td>24.1</td>
<td>5.0</td>
</tr>
<tr>
<td>SF$_6$*</td>
<td>146</td>
<td>-74</td>
<td>37.9</td>
<td>2.1</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>16</td>
<td>-70</td>
<td>22.6</td>
<td>4.5</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>30</td>
<td>-74</td>
<td>30.4</td>
<td>3.0</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>44</td>
<td>-80</td>
<td>38.2</td>
<td>2.4</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>58</td>
<td>-85</td>
<td>45.9</td>
<td>2.2</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>58</td>
<td>-82</td>
<td>34.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

4.2 One-component permeation

4.2.1 Concentration dependent diffusion

We discuss the results for steady-state experiments as function of the feed pressure to confirm the concentration dependence of the one-component Fick diffusivity. In Figure 4 results are presented for propane as function of the (partial) feed pressure, for three different temperatures. At a temperature of 303 K the flux of propane shows a non-linear dependence on the (partial) feed pressure. At a higher temperature the amount adsorbed in the silicalite-1 crystals of the membrane is lower, and the flux shows a linear dependence on the feed side pressure. An interesting aspect is the fact that the flux of propane for a temperature of 373 K is higher than the flux at a temperature of 423 K. This aspect of the flux, showing a maximum, will be described below. The results presented for propane, in Figure 4, indicate that the temperature dependence of the permeance will not follow an Arrhenius relation. It is, therefore, important to cover a large temperature range.
One-component permeation

![Graph](image)

**Figure 4.** One-component flux of propane through membrane WTSS-1e. Results are for three different temperatures, 303, 373 and 423, over the pressure range of 0 to 101 kPa. The dashed lines are a guide to the eye.

![Graph](image)

**Figure 5.** Normalized one-component surface diffusivity for ethane (o) and propane (□) as function of the dimensionless amount adsorbed. Results obtained from the flux at a temperature of 303 K. The solid line is the thermodynamic factor obtained from the Langmuir isotherm, Eq. (2).

In Figure 5 the normalized surface diffusivity, at 303 K, is plotted as function of the amount adsorbed. For the permeation of propane at 300 K main contribution is by surface diffusion and we can neglect the contribution from the gas translation diffusion. The surface diffusivity is calculated from the total flux, by using Eq.(7). As we will see below for the permeation of propane at 303 K the gas translation contribution to the overall permeance is in the order of 1%. For ethane this is about 8%, at the same temperature. Clearly, the surface diffusivity varies with the amount adsorbed, and follows closely the thermodynamic factor, \( \Gamma = 1 / (1 - \theta) \). In the following the concentration dependent surface diffusion will be used in the description of the temperature dependence of the one-component permeance.

4.2.2 Permeance as function of the temperature

In Figs. 6 and 7 the various results for the one-component permeation as function of the temperature are presented. Three different groups of gases are considered; noble gases, light hydrocarbons, and inorganic gases.

For the four linear alkanes, carbon monoxide, carbon dioxide, sulfurhexafluoride, krypton, and xenon a clear maximum and minimum is observed in the permeance through the silicalite-1 membrane. For helium (against neon), nitrogen, hydrogen, neon, and argon only a minimum in the permeance is seen. For \( i \)-butane the permeance increases monotonously with increasing temperature.

All the results for the permeance are described with a concentration dependent diffusion coefficient and taking the two different diffusion coefficients into account,
see Eq. (11). The permeance is fitted with Eq. (5) of Chapter 3 and Eq. (11), and the results of the fits are given in Table 4. In Figure 7 the permeance of helium, from the purge to the feed side, is compared for three different feed gases.

**Figure 6.** One-component permeance at a pressure of 101 kPa as a function of the temperature (190 to 680 K). (a) Permeance of the hydrocarbons: CH₄ and C₂H₆ through membrane WTSS-1c, C₃H₈, n-C₄H₁₀, and i-C₄H₁₀ through membrane WTSS-1e. (b) Permeance of the inorganic gases: N₂, CO, and CO₂ through membrane WTSS-1e. (c) Permeance of the inorganic gases: H₂ and SF₆ through membrane WTSS-1e. (d) Permeance of the noble gases: He, Ne, Ar, Kr, and Xe through membrane WTSS-1c.

### 4.3 One-component diffusion

For the gases studied the corrected surface diffusion at a temperature of 303 Kelvin is depicted in Figure 8 as function of the kinetic diameter. This is based on Eq. (6) with the data given in Table 2, and taking a vanishing amount adsorbed in Eq. (3). We see that there are essential two regions. In the first region the diffusivity is almost independent of the kinetic diameter. In the second region the diffusivity
One-component permeation decreases rapidly with an increase in kinetic diameter. By going from argon to sulfurhexafluoride the diffusivity drops by a factor of 500.

![Figure 7: Helium permeance through membrane WTSS-1e, from the purge to the feed side, as a function of the temperature for three different gases at the feed side.](image)

![Figure 8: One-component diffusion coefficient as a function of the kinetic diameter, at a temperature of 303 K. The dashed lines are a guide to the eye.](image)

A series of experiments have been performed with all the 15 different gases at 673 K, with the same membrane (WTSS-1e). The results for the permeance are plotted in Figures 9a and 9b. In Figure 9a we have plotted the one-component permeance at a temperature of 673 K, as function of the square root of the mass and in Figure 9b as function of the kinetic diameter. In both plots the same trend is seen, the permeance through the silicalite-I layer decreases rapidly if the mass or the size of the permeating molecules increases. In Figure 9a we have also plotted the permeance, as function of the square root of the mass, calculated with a constant activation energy of 10 kJ mol\(^{-1}\) for the activated gaseous diffusion. This is the dashed line.

5 Discussion

5.1 Steady-state permeance as function of the temperature

The following general behavior is observed for the permeance as function of the temperature. Initially, the permeance goes through a maximum if the temperature is increased. If the temperature is further increased a minimum is observed in the permeance.

The maximum in the flux can be described by equilibrium adsorption and activated surface diffusion. For this case mass transport takes place by molecules hopping between sites. This is an activated process and the diffusivity increases with
temperature. The amount adsorbed is based on equilibrium and decreases with temperature. The sequence in the maxima of the permeance follows the sequence of the equilibrium amount adsorbed in silicalite-1. For the linear hydrocarbons this sequence is methane < ethane < propane < n-butane.

The amount adsorbed is taking into account by the enthalpy of adsorption, see Table 1. An increase in the enthalpy of adsorption has as effect that the amount adsorbed will increase, and therefore the maximum in the flux occurs at a higher temperature. The activation energy for diffusion has only an effect on the height of the maximum. One of the most interesting effects is the increase in the permeance if the temperature is further increased. This is clearly seen for methane and the noble gases.

Table 2. Intrinsic diffusion coefficients and activation energies for diffusion*.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Membrane</th>
<th>d_{st}^{14} nm</th>
<th>E_{D,S}</th>
<th>D_{0}^{6}(0) 10^{-4} m^{2}.s^{-1}</th>
<th>E_{D,GT}</th>
<th>λ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (/Ne)</td>
<td>WTSS-1c</td>
<td>0.260</td>
<td>1.0</td>
<td>2.0</td>
<td>8.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Ne</td>
<td>WTSS-1c</td>
<td>0.275</td>
<td>1.9</td>
<td>2.4</td>
<td>8.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Ar</td>
<td>WTSS-1c</td>
<td>0.340</td>
<td>4.9</td>
<td>1.9</td>
<td>7.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Kr</td>
<td>WTSS-1c</td>
<td>0.360</td>
<td>7.4</td>
<td>1.7</td>
<td>7.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Xe</td>
<td>WTSS-1c</td>
<td>0.396</td>
<td>10.3</td>
<td>1.4</td>
<td>5.8</td>
<td>1.2</td>
</tr>
<tr>
<td>H_{2}</td>
<td>WTSS-1e</td>
<td>0.289</td>
<td>2.1</td>
<td>1.5</td>
<td>8.3</td>
<td>0.9</td>
</tr>
<tr>
<td>N_{2}</td>
<td>WTSS-1e</td>
<td>0.364</td>
<td>5.5</td>
<td>1.3</td>
<td>8.4</td>
<td>0.8</td>
</tr>
<tr>
<td>CO</td>
<td>WTSS-1e</td>
<td>0.376</td>
<td>7.1</td>
<td>0.9</td>
<td>9.9</td>
<td>0.8</td>
</tr>
<tr>
<td>CO_{2}</td>
<td>WTSS-1e</td>
<td>0.330</td>
<td>9.6</td>
<td>0.7</td>
<td>10.3</td>
<td>0.9</td>
</tr>
<tr>
<td>SF_{6}</td>
<td>WTSS-1e</td>
<td>0.550</td>
<td>17.4</td>
<td>0.8</td>
<td>12.4</td>
<td>0.8</td>
</tr>
<tr>
<td>CH_{4}</td>
<td>WTSS-1c</td>
<td>0.380</td>
<td>8.8</td>
<td>3.9</td>
<td>7.9</td>
<td>1.0</td>
</tr>
<tr>
<td>C_{2}H_{6}</td>
<td>WTSS-1c</td>
<td>0.390</td>
<td>10.5</td>
<td>1.7</td>
<td>7.2</td>
<td>1.0</td>
</tr>
<tr>
<td>C_{3}H_{8}</td>
<td>WTSS-1e</td>
<td>0.430</td>
<td>12.2</td>
<td>0.75</td>
<td>11.4</td>
<td>0.9</td>
</tr>
<tr>
<td>n-C_{4}H_{10}</td>
<td>WTSS-1e</td>
<td>0.430</td>
<td>13.7</td>
<td>0.40</td>
<td>13.1</td>
<td>0.8</td>
</tr>
<tr>
<td>i-C_{4}H_{10}</td>
<td>WTSS-1e</td>
<td>0.500</td>
<td>15.1</td>
<td>0.15</td>
<td>13.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* For all gases the permeability was measured with helium as purge flow. The permeability for helium, from the purge to the feed side, was obtained the permeation experiment with neon.

For most of the gases studied the permeance increases, with increasing temperature, for a temperature above 650 Kelvin. For xenon and n-butane the permeance reaches a plateau between 650 and 673 Kelvin. The minimum in the flux occurs because, above a given temperature, the equilibrium amount adsorbed in the silicalite-1 pore vanishes. This increase in the permeance can only be described with
a second diffusion mechanism. For the explanation of the increasing trend an activated process must exists. This behavior is described with Eq. (9) for the gas translation diffusion coefficient. Without an additional term for the activation energy, Knudsen diffusion can not describe the observed increase. It is noted that with an increasing adsorption the minimum takes place at higher temperatures. From a comparison between the permeance and the isobars it is seen that the temperature of the minimum corresponds within 50 Kelvin with the temperature where the amount adsorbed vanishes.

Figure 9. One-component permeance for the different gases at 673 K.
(a) As a function of the square root of the mass.
(b) As a function of the kinetic diameter.

5.1.1 Permeation of i-butane
It seems that i-butane shows a slightly different behavior as function of the temperature as compared to the other gases; no maximum and no minimum is observed. This is a consequence of the fact that for the permeation of i-butane the contribution from surface diffusion is much smaller than the contribution from the gaseous diffusion. This becomes clear if the properties for n-butane and i-butane, as presented in Table 1 and 2, are compared. From simulations it follows that if for i-butane, for example, the activation energy, $E_{DS}$, would be decreased to about 12 kJ mol$^{-1}$ also a maximum and a minimum in the temperature dependence of the overall permeance would be observed. So, the experimental and simulated results for i-butane confirm that a general theory for micropore diffusion is available.

5.1.2 Counter-diffusion of helium
During the temperature programmed experiments the helium flow from the purge to the feed side is recorded at fixed interval, about every 30 Kelvin. The permeation of helium through the membrane depends on the amount adsorbed of the feed gas,
see Figure 7. Helium is more hindered by stronger adsorbed molecules; for helium to move through the gas phase sufficient space is required inside the zeolite pores. This confirms that the activated gas diffusion takes place in the zeolite pores.

At a temperature of 673 K, it is found that the helium permeates essentially independent of the kind of feed gas. For all the gases considered the permeance of the counter-diffusing helium lies around $50 \times 10^{-8} \text{ mol m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$, at 673 K.

5.2 One-component diffusivities

5.2.1 Surface diffusion
From Figure 8 it follows that for a kinetic diameter up to about 0.3 nm the surface diffusivity is almost constant. This corresponds with a kinetic diameter to pore diameter ratio of 0.55. Above this ratio the corrected diffusivities decrease strongly, on half logarithmic scale, with the kinetic diameter. A relatively large difference is observed for carbon dioxide; the corrected diffusivity is about an order of magnitude lower than expected from an extrapolation based on the diffusivity of the other gases. We can say that, at 300 K, for helium, neon, and hydrogen the diffusion is in the Knudsen regime, for the other gas the diffusion is in the configurational regime.

5.2.2 High temperature limit: Gas translation diffusion
For a temperature above 650 Kelvin almost no gas adsorption takes place in the silicalite-1 crystals. For this situation the mass transport will be solely determined by activated gaseous diffusion. From Figure 9 it follows that all the results for the permeance lie in a small band around an average activation energy for gas translation diffusion of about 10 kJ mol$^{-1}$. From the plot of the permeance as function of the kinetic diameter it follows, as expected, that the permeance strongly decreases with increasing size of the molecules.

From Table 2 it is clear that the diffusional length $\lambda$ is the same for all the gases. The distance of about 1 nm is clearly of intracrystalline dimensions, and is about the distance between two intersections.

6 Conclusions

Results for the one-component steady-state gas permeation through a silicalite-1 zeolite membrane have been presented and modeled. Good agreement is obtained for a wide range of properties, including the heat of adsorption, the activation energy for diffusion, and the size and the mass, of 15 different gases.

From the permeation through the silicalite-1 membrane a new diffusion regime is established. This regime is difficult to study with the existing experimental
techniques. It has been demonstrated that the temperature dependence of the steady-state fluxes, over the range of 190 to 680 K, can only be described if two diffusion mechanisms are taken into account. At conditions where a considerable amount is adsorbed, the diffusion takes place by mass transport through an adsorbed layer. This can be pictured as molecules jumping between adsorption sites. This is referred to as surface diffusion. For high temperatures, where no adsorption takes place, the diffusion is by transport in the gas phase in the zeolite pores. This is referred to as gas translation diffusion. The existence of two different diffusion regimes is in agreement with the mass transport of gases in other microporous inorganic membranes, like, for example, Vycor glass.

Comparing the isobars, for the equilibrium amount adsorbed on silicalite-1 at 101 kPa, with the fluxes as function of the temperature we see that the minimum in the fluxes occurs at the temperature where the amount adsorbed vanishes. At this temperature the one-component flux through the silicalite-1 membrane starts to increase. It was found for the helium purge that the permeability, from the retentate to the permeate side depends on the feed gas. The helium starts to permeate at a higher temperature if the feed gas is adsorbed stronger. The diffusional path in the high temperature range of about 1 nm. This is clearly an intracrystalline property and corresponds to the distance between two pore intersections. It is, therefore, concluded that essentially all transport through the membrane takes place through the pores of the silicalite-1 zeolite.

7 Literature

1. Barrer, R.M., Migration in crystal lattices, Trans. Faraday Soc. 37 (1941) 590
Binary Permeation

Abstract
Permeation data are presented of several mixtures, which gives an overview of the separation characteristics of the metal supported silicalite-1 membrane over a broad temperature and pressure range.

In many cases the separation selectivity of a mixture does not reflect the one-component permeation ratio. Besides molecular sieving and difference in diffusivity, difference in adsorption appears to be a key factor in separation selectivity. The permeation of weakly adsorbing molecules, e.g. hydrogen at 295 K, can drop over two orders of magnitude in the presence of strongly adsorbing molecules, e.g. n-butane at 295 K. This results in high separation selectivities favoring the strongest adsorbing component. Typical separation selectivities for n-butane/hydrogen (295 K, 95 kPa/5 kPa), n-butane/i-butane (295 K, 50 kPa/50 kPa), and methane/iso-octane (423 K, 25 kPa/5 kPa) mixtures, are 125, 27 and > 300, respectively. An inversion in separation selectivity is observed during a temperature programmed permeation which is explained from the temperature dependence of adsorption and diffusivity. The separation factor is also a function of the composition and the feed pressure. It is concluded that the binary equilibrium adsorption can not be described with the extended Langmuir model.
Chapter 5

1 Introduction

To explore the separation potential and mechanisms of the metal-supported silicalite-1 membrane, permeation experiments were performed with a number of representative binary mixtures. Permeation fluxes and separation factors are reported as a function of the temperature, pressure, and feed composition. The interpretation of the reported results is qualitative. For a detailed description and modeling of the binary permeation results is the reader referred to a separate publication\(^1\). A short literature review on binary permeation and adsorption is given below. Also an theoretical introduction is given on the mathematical description of binary diffusion and adsorption in microporous materials.

1.1 Literature review

Multi-component diffusion in microporous materials, adsorbents with a pore diameter smaller than 2 nm, is characterized by a strong interaction between the adsorbed species. Coupling between the species can be of kinetic and of equilibrium origin. One of the first results demonstrating the interaction between species adsorbed in microporous materials was presented by Habgood\(^2\). For the transient uptake of methane and nitrogen in zeolite 4A an overshoot is seen in the faster moving-weakly adsorbed nitrogen. Similar results have been reported for a number of other systems. Karger and Bulow\(^3\) studied, as a function of the time, the amount adsorbed of a mixture of benzene and n-heptane in zeolite NaX. A maximum is observed in the uptake curve of n-heptane. Karge and Niessen\(^4\) reported results for the uptake of benzene and ethylbenzene in H-ZSM-5. During co-diffusion the faster moving benzene has an overshoot in the uptake profile. For the transient permeation of a mixture of methane and n-butane and a mixture of butane and hydrogen through a silicalite-1 membrane an overshoot is observed in the permeation of the faster diffusing methane and hydrogen (Bakker et al.\(^5,6\)).

The results can be well described with the Maxwell-Stefan theory for micropore diffusion (Krishna\(^7\); Van den Broeke\(^8\)). In the description of multi-component sorption kinetics it would be ideal to predict the mass transport of mixtures based on one-component equilibrium adsorption and diffusion data. With the Maxwell-Stefan formulation the kinetic and equilibrium contributions are considered separately, providing clues about the various interactions between the adsorbed species. If no interaction exists between the adsorbed components of a mixture the uptake profiles of the individual species increase monotonously.

Other descriptions of multi-component diffusion in microporous materials are available. Do and et al.\(^9,10\) used the Fick and Onsager description to model the diffusion of hydrocarbons in activated carbon. Yang et al.\(^11\) used the Onsager
formulation to describe binary diffusion of carbon dioxide and ethane in zeolite 4A. It has been demonstrated by Krishna\textsuperscript{7} that the Maxwell-Stefan formulation can be derived from the Fick and the Onsager equations. Chen and Yang\textsuperscript{12,13} presented a description for surface diffusion and zeolitic diffusion based on transition theory. In this approach the diffusion process is described by a random walk and the mass transport takes place by molecules hopping between sites. The elements of the matrix of Fick diffusion coefficients are expressed in terms of a sticking parameter.

In the description of multi-component sorption kinetics the equilibrium adsorption of mixtures gives rise to some fundamental problems. A proper description of the equilibrium adsorption of mixtures requires a thermodynamic consistent model. Such a model must be capable of dealing with the fact that often the saturation capacities of the adsorbed species are different, and the model must be capable of taking the heterogeneous character of the sorbent into account, if necessary (Mauer\textsuperscript{14}). Gu et al.\textsuperscript{15} extended the Langmuir model for mixtures to the situation where for adsorbed species the saturation capacity is different. Some examples were given, for breakthrough curves, to indicate the consequence of uneven saturation capacities.

In this work silicalite-1 is the adsorbent. For the description of the equilibrium adsorption of mixtures in silicalite-1 several studies have been reported.

Abdul-Rehman et al.\textsuperscript{16} studied the one-component adsorption of the first four n-alkanes and some binary and ternary mixtures of these gases in silicalite-1. Several adsorption models were compared. It was found that the best description of the single component and the multi-component equilibrium adsorption processes was obtained with the Toth model.

Buss and Heuchel\textsuperscript{17} obtained, as a function of the composition, a variable separation factor for binary mixtures of methane and tetrafluoromethane in silicalite-1. The separation factor, towards the stronger adsorbed CF\textsubscript{4}, decreases with an increase in the mole fraction of tetrafluoromethane.

A reasonable description of the binary adsorption was given with both the Ideal Adsorption Solution theory (Meyers and Prausnitz\textsuperscript{18}) and the (binary) multi-site Langmuir model (Nitta et al.\textsuperscript{19}). It is noted that the two models describe the binary isotherms better than the binary separation factor. In the IAS theory the Toth model was used to describe the one-component isotherms.

Rees and co-workers studied\textsuperscript{20,22} the equilibrium adsorption of various binary mixtures in silicalite-1 using an isosteric method. The Henry's law constant for binary mixtures, including CO\textsubscript{2}-N\textsubscript{2} and C\textsubscript{2}H\textsubscript{6}-C\textsubscript{3}H\textsubscript{8}, was found to be linearly proportional to the gas phase composition.
1.2 Theory

1.2.1 Diffusion in mixtures

In general, the flux in microporous materials is described with the Fick formulation. The flux is divided by the concentration gradient to give the diffusivity. For a binary mixture we have a matrix of Fick diffusivities, $D_{ij}$, and two concentration differences, $dq_{i}/dx$. For a two component mixture it is to be determined whether to include adsorbate-adsorbate momentum exchange. The pores of silicalite-1 are that small that it is assumed that this exchange is negligible and the permeation is described by single file diffusion. The single-component permeation data that determine $D_{ij}$ and the adsorption data are in that case sufficient to predict the binary fluxes.

The fluxes are given by the set:

$$J_1 = D_{11} \frac{dq_1}{dx} + D_{12} \frac{dq_2}{dx}$$  \hspace{1cm} (1)

$$J_2 = D_{21} \frac{dq_1}{dx} + D_{22} \frac{dq_2}{dx}$$  \hspace{1cm} (2)

1.2.2 Binary equilibrium adsorption

For the description of the adsorption isotherms of mixtures in micropores essentially two approaches can be followed. One can extend the one-component models to multi-component isotherm models or one can use a thermodynamic approach. For the first case, the isotherm models describing the adsorption of a mixture can be written in a general way as the Langmuir-Freundlich isotherm.

$$\theta_i = \frac{q_i}{q_{i,sat}} = \frac{b_i p_i}{1 + (b_i p_i)^{n_i} + (b_j p_j)^{n_j}}$$  \hspace{1cm} (3)

The well-know Extended Langmuir model is obtained for $n_i = 1 = n_j$. Equation (3) gives for $n_i = n_j$ the multi-component Toth isotherm. This line of approach has been used by Abdul-Rehman et al.\textsuperscript{16} to study one- and multi-component gas adsorption in silicalite-1. For the adsorption of methane and ethane in silicalite-1 Abdul-Rehman et al.\textsuperscript{16} reported values of $n$ or equal or close to unity. This means that for the system CH$_4$-C$_2$H$_6$-silicalite-1 the adsorption can be described by the (Extended) Langmuir model. It was found that the saturation capacities decrease with an increase in temperature. This has as a consequence that for a given temperature the isotherm must be available to determine the adsorption parameters by fitting an isotherm model to
the experimental results. It is also noted that Abdul-Rehman et al.\textsuperscript{16} did not report separation factors.

The second approach is based on the Ideal Adsorption Solution (IAS) theory (Myers and Prausnitz\textsuperscript{18}; Ruthven\textsuperscript{24}). Buss and Heuchel\textsuperscript{17} used the IAS theory to predict the binary adsorption of CH\textsubscript{4} and CF\textsubscript{3} in silicalite-1, from single component adsorption data. Good agreement is obtained, and the one-component isotherms were described with the Toth model. Especially, the variation of the separation factor with the gas phase composition could be well described.

2 Experimental

Permeation experiments with several mixtures and under varying operation conditions were performed to study the relevant separation mechanisms in the silicalite-1 membrane. Fluxes and separation factors were measured as a function of the temperature, pressure and feed composition. Both steady-state and transient permeation were measured. For most experiments membrane WTSS-2B has been used.

It was expected that besides the shape and size\textsuperscript{11} of the molecules, adsorption is important for the separation selectivity. Therefore, binary mixtures were studied with various combinations of weakly (w), moderately (m) or strongly (s) adsorbing components, see Table 1. The investigated mixtures at 295-300 K were: n-butane/hydrogen, n-butane/methane, i-butane/methane (s/w adsorption), propane/propane (s/s), ethane/ethene (m/m), carbon dioxide/hydrogen (m/w), methane/neon (w/w). The w/w adsorption combination occurs for methane/n-butane and i-butane/hydrogen at high temperature, 623 K. i-butane/methane at 300 K was measured to study the combination of a slowly moving strongly adsorbing component with a weakly adsorbing component. The transient permeation behavior for different feed ratios of the methane/n-butane mixture was studied at 300 K.

Also the temperature and pressure dependence of several mixtures was measured. The permeation of a n-butane/hydrogen and a carbon dioxide/hydrogen mixture as a function of the temperature, from 295 to 623 K, were examined.

To study the influence of the feed pressure, the permeation of a methane/ethane mixture at pressures, from 100-500 kPa, was researched. The effect of the feed composition was studied for a carbon dioxide/nitrogen mixture.

\textsuperscript{11} these properties are directly related to the diffusion coefficient
Finally, the permeation of a \( n \)-butane/\( i \)-butane mixture, at 295 K and 403 K, and methane/\( iso \)-octane/\( n \)-butane mixture, at 323 K, were measured to investigate the shape selectivity and molecular sieving of the silicalite-1 membrane.

3 Results

Figure 1a shows the transient permeation curves for a 95 kPa/5 kPa hydrogen/\( n \)-butane mixture, while the one-component data are presented in Figure 1b. The difference between the binary mixture and the one-component systems is remarkable. For the mixture, a maximum in the hydrogen permeation is observed prior to attaining the steady-state. The steady-state permeation flux of hydrogen in the mixture is much lower compared to its one-component permeation flux and drops from 19 mmol.m\(^{-2}\).s\(^{-1}\) in the one-component case (Figure 1b) to about 0.15 mmol.m\(^{-2}\).s\(^{-1}\) for the binary system. The \( n \)-butane permeation remains, however, nearly unaffected. This results in a high separation selectivity of about 125 in favor of \( n \)-butane.

![Graph a](image1.png) ![Graph b](image2.png)

**Figure 1a.** Breakthrough curves of a hydrogen/\( n \)-butane (95 kPa/5 kPa) mixture at 295 K. The separation selectivity towards \( n \)-butane amounts to about 125.

**Figure 1b.** One-component breakthrough curves of \( n \)-butane (5 kPa) and of hydrogen (95 kPa) at 295 K. The total pressure was 100 kPa, obtained by adding helium to the feed.

For a 50 kPa/50 kPa hydrogen/carbon dioxide mixture, which is depicted in Figure 2, only a small maximum in the hydrogen permeation is observed. The steady-state hydrogen permeation flux is much lower compared to the one-component permeation flux, which results in a high separation selectivity of 12 towards carbon dioxide.

In Figure 3 the transient profiles for a 50 kPa/50 kPa ethane/ethene mixture are given. The ethene permeation shows a weak maximum. As the ethene permeation flux in the mixture is 55% lower than the one-component permeation flux and the ethane
permeation flux about equal, a small separation selectivity of 1.9 towards ethane is observed.

**Figure 2.** Breakthrough curve of a hydrogen/carbon dioxide (50 kPa/50 kPa) mixture at 295 K. The one-component steady-state permeation fluxes at 50 kPa feed pressure are indicated at the right side of the Figure. The separation selectivity towards carbon dioxide equals 12.

**Figure 3.** Breakthrough curve of a ethane/ethene (50 kPa/50 kPa) mixture at 295 K. The one-component steady-state permeation fluxes at 50 kPa feed pressure are indicated at the right side of the Figure. The separation selectivity towards ethane equals 1.9.

**Figure 4.** Breakthrough curve of a propane/propene (50 kPa/50 kPa) mixture at 295 K. The one-component steady-state permeation fluxes at 50 kPa feed pressure are indicated at the right side of the Figure. The separation selectivity towards propane equals 1.3.

**Figure 5.** Breakthrough curves of a methane/neon mixture (50 kPa/50 kPa) at 300 K. The separation selectivity towards methane equals 7.

In the propane/propene (50 kPa/50 kPa) permeation, depicted in Figure 4, no maximum occurs upon reaching the steady-state permeation flux. In the mixture, for both propane and propene the permeation is lower than the one-component
permeation; 40 % and 60%, respectively. The separation selectivity is in favor of propane and equals 1.3.

Neon/methane (50/50 kPa) resemble the one-component separation ratio and no maximum is observed, see Figure 5. The separation selectivity equals 7.

Figure 6. Breakthrough curves of a i-butane/methane mixture (50 kPa/50 kPa) at 300 K. The separation selectivity equals 1.3. towards i-butane.

Figure 6b. Breakthrough curves of a methane/i-butane mixture (50 kPa/50 kPa) at 623 K. The separation selectivity towards methane equals 2.3.

In Figure 6 the transient profile of methane/i-butane is depicted. This profile is very similar to the hydrogen/n-butane profile. Although the methane permeation is strongly reduced the separation selectivity is only 1.3 in favor of i-butane. In Figure 6b the transient behavior at 623 K is depicted. No maximum is observed and the separation selectivity equals the one-component ratio which is 2.3 in favor of methane.

In Figure 7a, b, and c transient permeation of methane/n-butane mixtures of different composition is presented. Similar to the hydrogen/n-butane mixture a maximum is observed in the methane permeation prior to the steady-state. The height of this maximum depends on the n-butane concentration in the feed. The steady-state flux of methane is at least two orders lower as compared to the one-component flux. This results in high selectivities in favor of n-butane which flux is hardly affected by the presence of methane. For comparison also the transient one-component permeation at 295 K is given in Figure 7d.
The temperature dependency of a 50 kPa/50 kPa hydrogen/n-butane and a 50 kPa/50 kPa hydrogen/carbon dioxide mixture is shown in Figures 8 and 9. The steady-state permeance and the separation selectivity is plotted as a function of the temperature. For the hydrogen/n-butane mixture, the permeance of hydrogen is low at 303 K but increases strongly after 410 K. At 623 K the hydrogen permeance amounts to 60 mmol.m².s⁻¹.bar⁻¹. The observed temperature dependency of n-butane is close to its one-component dependency, see Figure 1b. Consequently, the separation selectively inverses; from 55 in favor of n-butane at 303 K to 3.4 in favor of hydrogen at 623 K.

The hydrogen permeance steadily increases with temperature for the carbon dioxide/hydrogen mixture, and amounts to 60 mmol.m².s⁻¹.bar⁻¹ at 623 K. The
selectivity also inverts; it changes from 12 in favor of carbon dioxide at 295 K to 2.4 in favor of hydrogen at 623 K.

Figure 8. Temperature programmed permeation and separation selectivity towards n-butane of a n-butane/hydrogen mixture (50 kPa/50 kPa).

![Graph showing temperature programmed permeation and separation selectivity towards n-butane.](image)

Figure 9. Temperature programmed permeation and separation selectivity towards carbon dioxide of a carbon dioxide/hydrogen mixture (50 kPa/50 kPa).

![Graph showing temperature programmed permeation and separation selectivity towards carbon dioxide.](image)

The effect of a pressure increase, from 100 to 500 kPa, with steps of 100 kPa, on the permeation of a 50/50 ethane/methane mixture at 295 K is shown in Figure 10. The separation selectivity towards ethane is considerably high, but not constant with pressure. Upon increasing the absolute feed pressure, the separation selectivity towards ethane decreases from 7 to 5. At higher temperatures (not depicted) the separation selectivity remains about constant with changing absolute pressure\(^1\).

Figure 11 shows the results for the permeation of binary mixtures of carbon dioxide and nitrogen as function of the feed composition. The binary flux of carbon dioxide is hardly effected by the presence of nitrogen. On the other hand the permeation of nitrogen is reduced considerably compared to the one component permeation. The separation selectivity increases with increasing carbon dioxide concentration from 3 with 10% CO\(_2\) to 5 with 90% CO\(_2\).
Figure 10. Permeation and separation selectivity towards ethane of a methane/ethane mixture (50/50) as a function of the absolute pressure at feed side at 295 K. The pressure at the permeate (helium) side was kept constant at 100 kPa.

Figure 11. Permeation and separation selectivity towards carbon dioxide of a carbon dioxide/nitrogen mixture as function of the feed composition at a pressure of 100 kPa and a temperature of 303 K.

In Figure 12 the breakthrough curve of a 50 kPa/50 kPa n-butane/i-butane mixture shows a maximum in permeation, before reaching the steady-state. The steady-state values of n-butane and i-butane were measured separately (with a GC; data are not shown). For this situation the n-butane permeation is, compared to its one-component permeation, 60 % lower in the presence of the i-butane, while the i-butane permeation flux remains low. The separation selectivity is 27 at 295 K and 23 at 403 K towards n-butane.

Figure 13 shows the permeation at 323 K of iso-octane (5 kPa), iso-octane/methane (5 kPa /25 kPa) and iso-octane/methane/n-butane (5 kPa/25 kPa/25 kPa, at 425 K). The iso-octane permeation is very small and does not change after subsequent addition of methane and n-butane. The methane permeation flux amounts to 8 mmol.m⁻².s⁻¹ which is near the one-component permeation but drops over two orders of magnitude after addition of n-butane. The n-butane signal was not measured during this experiment.
4 Discussion

4.1 Separation mechanism

In many cases separation selectivities do not reflect the one-component permeance ratio. From the presented results, see Table 1, it becomes clear that besides molecular sieving and difference in diffusivity, difference in adsorption strength is a key factor in determining the separation selectivity.

The picture arises that the permeation behavior of a component can be influenced if a moderately or strongly adsorbing component is present. Due to competitive adsorption the stronger adsorbing component may lower considerably the occupancy of the other component. The strongest adsorbing molecule is only significantly hindered if other strongly adsorbing molecules are present, which is the case for propane in the presence of propene (Figure 4). From the adsorption data and the observed separation selectivities, see Table in Chapter 4, it can be concluded that the
larger the difference in adsorption strength between two components the larger the separation selectivity.

As illustrated in Figure 1a, 5 kPa of the strongly adsorbing \( n \)-butane suppresses the permeation of 95 kPa hydrogen, leading to a separation selectivity in favor of \( n \)-butane of about 125. So \( n \)-butane dominates the adsorption and suppresses the permeation flux of hydrogen. In Figure 7c it was illustrated that at 295 K even 0.05 kPa \( n \)-butane effectively blocks the permeation of 50 kPa methane.

For the mixtures carbon dioxide/hydrogen, ethane/ethene, and propane/propene, in which the difference in adsorption is much smaller, separation selectivities at 295 K decrease with decreasing difference in adsorption strength, and amount to 10, 1.9, and 1.3, respectively (Figures 2, 3, and 4).

**Table 1. Separation selectivities and mechanisms of some binary mixtures through membrane WTSS-2B. The results between brackets are measured with membrane WTSS-1e. s = strong, m = moderately, w = weak**

<table>
<thead>
<tr>
<th>Separation Mechanism</th>
<th>Mixture</th>
<th>Feed ratio (kPa/kPa)</th>
<th>Temp. (K)</th>
<th>Figure</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>adsorption (s,s)</td>
<td>propane/propane</td>
<td>50/50</td>
<td>295</td>
<td>4</td>
<td>1.3</td>
</tr>
<tr>
<td>adsorption (s,w)</td>
<td>( n )-butane/hydrogen</td>
<td>5/95</td>
<td>295</td>
<td>1a</td>
<td>&gt;100</td>
</tr>
<tr>
<td>adsorption (s,w)</td>
<td>( n )-butane/methane</td>
<td>5/95</td>
<td>300</td>
<td>7b</td>
<td>380</td>
</tr>
<tr>
<td>adsorption (s,w)</td>
<td>( i )-butane/methane</td>
<td>50/50</td>
<td>300</td>
<td>6</td>
<td>1.5</td>
</tr>
<tr>
<td>adsorption (m,m)</td>
<td>ethane/ethene</td>
<td>50/50</td>
<td>295</td>
<td>3</td>
<td>1.9</td>
</tr>
<tr>
<td>adsorption (m,m)</td>
<td>CO(_2)/hydrogen</td>
<td>50/50</td>
<td>295</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>adsorption (m,w)</td>
<td>CO(_2)/nitrogen</td>
<td>50/50</td>
<td>303</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>diffusivity (size)</td>
<td>hydrogen/( n )-butane</td>
<td>50/50</td>
<td>623</td>
<td>8</td>
<td>3.4 (12)</td>
</tr>
<tr>
<td>diffusivity (size)</td>
<td>hydrogen/CO(_2)</td>
<td>50/50</td>
<td>623</td>
<td>9</td>
<td>2.4 (5)</td>
</tr>
<tr>
<td>diffusivity (shape)</td>
<td>( n )-butane/( i )-butane</td>
<td>50/50</td>
<td>295</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td>diffusivity (shape)</td>
<td>( n )-butane/( i )-butane</td>
<td>50/50</td>
<td>403</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>molecular sieving</td>
<td>methane/iso-octane</td>
<td>25/5</td>
<td>323</td>
<td>13</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

If a mixture contains only weakly adsorbing components, like methane/neon, and methane/\( i \)-butane methane/\( n \)-butane at 623 K, the difference in one-component diffusivity determines the separation selectivity and thus the mixture resembles the one-component permeation ratio.

Shape selectivity is demonstrated in the case of the \( i \)-butane/\( n \)-butane mixture. The \( n \)-butane separation selectivity over \( i \)-butane amounts to 27 at 295 K and 23 at 403 K. The difference in permeation flux cannot be explained by a relatively small difference in adsorption strength (factor 1.3 at 295 K). Moreover, at 403 K where the adsorption of both components (Figure 3 Chapter 4) is much weaker, still a high separation selectivity towards \( n \)-butane is observed. Although \( n \)-butane is hindered by the "slow" \( i \)-butane molecules, it is concluded that they can pass each other in the crossings of the
zeolite pore structure. Otherwise, for the mixture a much lower \( n \)-butane permeation flux would have been observed. This demonstrates the good transparency properties of this membrane which possesses a three dimensional pore structure (see also transient permeation, section 4.4, and Figure 1 of Chapter 2).

The high separation selectivity, \( >300 \), in favor of methane for the permeation of a methane/iso-octane mixture can be explained by the molecular sieving mechanism (Figure 12). The iso-octane can not enter the zeolite pores while methane can. No absolute separation was obtained, probably due to the presence of some imperfections in the zeolite membrane (e.g. 90° intergrowths with plain boundaries in the crystals), which allows iso-octane to permeate. At the conditions applied the methane permeation is not significantly hindered by the presence of iso-octane although it was expected that iso-octane adsorbed at the outer surface of zeolite lattice could hinder methane. The introduction of \( n \)-butane to the methane/iso-octane mixture leads to a drop in permeation of methane and confirms that the mass transport of methane and \( n \)-butane via the zeolite pores is dominating. See also the discussion on the quality of the membrane in Chapters 2 and 6.

4.2 Temperature dependency

During the temperature programmed permeation of a \( n \)-butane/hydrogen (Figure 8) and a carbon dioxide/hydrogen mixture (Figure 9), the separation selectivity shifts drastically. At low temperature adsorption dominates and hydrogen hardly permeates. At high temperatures only weak adsorption occurs and the separation selectivity reflects the one-component permeation ratio. For the carbon dioxide/hydrogen mixture up to 423 K carbon dioxide permeates preferentially. At 623 K, a separation selectivity of 2.4 in favor of hydrogen is found. For the \( n \)-butane/hydrogen mixture a similar trend is observed. As \( n \)-butane adsorbs much stronger than carbon dioxide, adsorption of \( n \)-butane hinders hydrogen permeation up to higher temperatures.

Based on extrapolation of the observed trends, higher separation selectivities are expected at low temperatures \( < 295 \text{ K} \) in favor of carbon dioxide and \( n \)-butane and at high temperatures \( > 623 \text{ K} \) for hydrogen. The single component data as presented in Chapter 4 show a ideal separation selectivity at 673 K of 12 towards hydrogen\(^2\).

4.3 Pressure and feed composition

The observed decrease in separation selectivity with increasing feed pressure, as depicted in Figure 11 for a 50/50 methane/ethane mixture, shows that a constant feed

\(^2\) the quality of the membrane was better in comparison with the membranes used in this chapter

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ratio, at 295 K, does not result in a constant separation selectivity. For higher
temperatures it does. First we like to state that diffusion of binary mixtures in zeolites
is not yet completely understood, especially at high occupancies. Secondly, the
following point can be made for this case; at 295 K methane adsorbs in the linear
Henry region while ethane adsorbs in the non-linear Langmuir region, under the
applied conditions. At higher temperatures both components are in the linear region.
The non-linear adsorption of ethane can be responsible for some of the deviation from
a constant separation factor at room temperature. No difference is, however, predicted
with the Extended Langmuir theory. In Van den Broeke et al.\textsuperscript{1} it will be shown that the
observed behavior decrease in separation factor can be predicted by using the IAS
theory. The same reasoning as above hold for the observed variation in separation
selectivity as function of the feed composition for the nitrogen/carbon dioxide
separation.

4.4 Transient permeation

A peculiar phenomenon in the hydrogen/\textit{n}-butane permeation is the maximum
observed in the permeation flux of hydrogen (Figure 1). This phenomena is generally
observed for combinations of weak and strong adsorbates, see also Figure 6 and 7\textsuperscript{6,25}.
This behavior can be explained by the adsorption process of the strongest adsorbing
molecule. Just after the feed step little \textit{n}-butane is adsorbed and only a few zeolite
pores will be blocked, which allows hydrogen to permeate relatively easily. As the
adsorption process proceeds, more pores will be blocked which results in the observed
decrease in hydrogen permeation. The steady-state permeation is likely to occur as the
equilibrium adsorption of \textit{n}-butane is reached.

It was shown in Figure 7 that the height of the permeation maximum is dependent
on the concentration ratio of the components in a mixture. From this and from the
transient permeation experiments presented in Figures 1 to 9 it is concluded that: The
larger the difference in adsorption strength and the lower the concentration of the
stronger adsorbing component, the higher the permeation maximum of the weakest
adsorbing component. Consequently for propane/propene (Figure 4) no maximum
was observed as these molecules adsorb nearly equally strongly. Weakly adsorbing
molecules do not hinder each other significantly which explains the absence of a
maximum.

An exception is the transient permeation of a \textit{n}-butane/\textit{i}-butane mixture (Figure
11). The difference in adsorption strength between \textit{n}-butane and \textit{i}-butane is much
smaller than the difference in one-component diffusivity (Table 2 and 4 in Chapter 4).
At 295 K both components adsorb strongly; \textit{n}-butane about 1.5 times as strong as
\textit{i}-butane. The maximum is observed in the \textit{n}-butane permeation, in contrast with the
\textit{n}-butane permeation of a \textit{n}-butane/hydrogen mixture at 295 K (Figure 1a).
Chapter 5

It is concluded that, in this case, the large difference in diffusivity between i-butane and n-butane is more important than the difference in adsorption. This leads to a permeation decrease of n-butane as the concentration of the slowly moving i-butane in the zeolite pores increases. On the other hand the permeation of i-butane may be accelerated somewhat by the fast moving n-butane.

4.5 Simulation

The simulation of the transient permeation of n-butane/hydrogen with the Maxwell-Stefan equations is qualitatively in accordance with the experimental data\textsuperscript{5,26}. The model predicts the maximum in the permeation of hydrogen and at steady-state condition a separation selectivity in favor of n-butane. Simulation with Fick formulation in \textsuperscript{25,26} fails even at the qualitative level to explain the observed behavior.

5 Conclusions

An overview is given of important mechanisms for separation selectivity. In many cases the separation selectivity does not reflect the one-component permeation ratio. Besides molecular sieving and difference in one-component diffusivity, difference in adsorption strength is a key factor in separation selectivity. Hereby the strongest adsorbing component suppresses the permeation of the other component leading to high separation selectivities. An inversion in separation selectivity could be observed during a temperature programmed permeation of a mixture when the separation mechanism shifts from adsorption (at low temperatures) towards diffusivity (at high temperatures). The separation factor is also a function of the composition and the feed pressure. It is concluded that the binary equilibrium adsorption cannot be described with the Extended Langmuir model.

6 Literature


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Evaluation

Abstract
The application potential and the quality of the metal supported silicalite-1 zeolite membrane are discussed in this chapter. Also the commercial states of zeolite membranes and the results of zeolite pore modification via silanation with trimethylchlorosilane are given. It appears that the membrane is thermally stable upon thermal cycling over a broad temperature range, from 200 to 700 K. It can withstand a pressure difference of at least 10 bar and a heating rate of over 15 K.min⁻¹. Regeneration of the membrane after deliberate coking results in the recovery of the original properties. Individual membranes have been tested during a long period, up to 2 year, and their permeation characteristics did not change significantly over this period. Permeation results are reported for two different silicalite-1 membranes. Only a small difference is observed, indicating a high reproducibility of the zeolite membrane synthesis. It has been demonstrated that silanation is a way to influence, selectively the permeation behavior. Larger and more strongly adsorbed molecules are more affected by the modification than smaller and more weakly adsorbed molecules. The first commercial zeolite membrane modules are available. They are used for pervaporation applications.
Chapter 6

1 Introduction

In chapter 1 it is stated that inorganic membranes hold a great promise for various separation and catalytic processes due to their good mechanical properties and stability at high temperatures. Zeolite membranes would be excellent candidates for size selective separations due to their well defined pore structure of molecular dimensions. In 1992 The Delft University of Technology (Geus, E.R. and the present author) were the first to prepare a high temperature module for zeolite membranes and to show that the synthesis of a continuous zeolite layer in this module was successful. At present, the first commercial zeolite membrane modules, on m² scale, are available (Mitsui Shipbuilding Co., Smart Company). Zeolite A, Y and MFI are grown on tubular stainless steel- and ceramic supports. The modules are simple and not yet suited for application at high temperatures, > 323 K. The zeolite layers are not perfect and their pH stability is limited. Nevertheless, they have a high application potential for a number of liquid separations (pervaporation) in which polymer membranes cannot be used and distillation is difficult (azeotropes). Typical examples are: Dewatering of an azeotropic mixture of polymer unfriendly organics with zeolite A or Y membranes; Removal of water during equilibrium limited esterification reactions with a zeolite A or Y membrane; Removal of methanol from water with an MFI membrane.

In pervaporation the main separation mechanism is adsorption difference, often in combination with molecular sieving or difference in diffusivity. This may lead to very high selectivities. For example, in many esterifications, water is the only small molecule in the reaction mixture, and it is selectively adsorbed in the zeolite pores.

Selective adsorption of water takes also place in the imperfections of the zeolite layer. Therefore, a “non-perfect” membrane still may have a high separation performance.

Below the quality and the application potential of our metal supported silicalite-1 zeolite membrane is discussed. Also a comparison with some permeation and adsorption data from literature has been made. Finally the membrane performance is reported after modification of the silicalite-1 membrane by silanation with trimethylchlorosilane (TMCS).

1.1 Application potential of silicalite-1 membranes

High temperature resistance, catalytic activity and high separation selectivities triggered the interest in zeolite membranes. Especially, membranes which are selective for hydrogen or oxygen (from air) would have a high application potential in gas phase membrane reactors. Also isomer separations like xylenes separation would be interesting.
Evaluation

From the permeation measurements it appeared that besides molecular sieving other separation mechanism can have a very important contribution to the separation performance of a zeolite membrane: difference in diffusivity and difference in adsorption. Figure 1 shows a simplified representation of these separation mechanisms.

For hydrogen removal at high temperatures a high separation selectivity, \( e.g. > 100\), is desired to avoid an extra cooling\(^1\), separation and recompression step. Silicalite-1 has a pore size of about 0.55 nm, see Chapter 2. Many molecules used in the petrochemical industries have a pore size below 0.55 nm. Thus for the typical dehydrogenation reactions with C\(_1\)-C\(_4\) compounds no hydrogen separation is possible via molecular sieving. The best separation obtained in this work at a high temperature, 673 K, is about 15 for \( \text{H}_2/\text{i-C}_4 \) and 25 for \( \text{H}_2/\text{SF}_6 \), see Chapter 4. This separation, which is based on difference in diffusivity, is too low compared to the performance of commercially available polymeric membranes. Also \( \text{O}_2/\text{N}_2 \) separation is not possible with a silicalite-1 membrane\(^3\).

At low temperatures, high separation selectivities were obtained via the adsorption mechanism, for example hydrogen/\( n \)-butane and methane/\( n \)-butane. However, polymeric membrane-condensation systems, \( e.g. \) of MTR membrane technology research) in San Francisco, effectively remove hydrocarbons and are commercially available. Probably, isomer separation is still attractive; high separation selectivities were obtained for \( n \)-butane/\( i \)-butane\(^4\) and xylenes separations. More research is this field is recommended.

![Figure 1. Separation mechanisms observed during permeation measurements with the silicalite-1 zeolite membrane: A = molecular sieving, B = difference in diffusivity, and C = difference in adsorption. Depending on the feed and the operation conditions (temperature, pressure) different mechanisms play a role in the separation selectivity. High application potential for silicalite-1 membranes have the removal of small organic molecules from liquids and isomer separation, \( e.g. \) xylene separation.](image)

As mentioned above, the first commercial zeolite membranes are used in pervaporation applications. Especially the removal of methanol from water with a

\(^1\) No compressors are available which can operate at temperatures above 573 K.
silicalite-1 membrane seems attractive. Good separation selectivities in favor of methanol, 25, have been measured and no polymeric membrane for this separation is available. Moreover, the separation of a small amount of methanol from water via distillation is energy-intensive. Also organic/organic separations can be attractive with silicalite-1 membranes. For example, the removal of the relatively small acetic acid molecule from an other organic compound

Pore size modification as discussed in Section 4 can be attractive to enhance the separation selectivities provided that the fluxes remain sufficiently high.

2 Quality of the membrane

2.1 Robustness

One of the most important characteristics of the membrane(module) is its stability over a long period of time and under varying process conditions.

To study the performance of the silicalite-1 membranes over a period of time, undergoing a number of temperature and pressure cycles in the mean time, we have repeated a number of permeation experiments with carbon dioxide. The permeance of carbon dioxide for different pressures over the temperature range of 300 to 400 K is given in Figure 1.

![Figure 2. Reproducibility of the flux for carbon dioxide for a number of temperatures in the range of 300 - 400 K, for four different pressures. Time span between the two runs is about one year. Dashed lines are to guide the eye.](image)

The time span between the two series of experiments is about one year. The membrane has been used permanently during the year, undergoing about 50 temperature cycles. A typical temperature cycle is from 200 to 700 K and back to 303 K, at a rate of 1-2 K min⁻¹. The pressure was varied between 5 and 500 kPa, but also a small number of experiments have been performed up to 1000 kPa. We see in Figure 2 that virtually no change in the flux has occurred, over this period of about
one year of operation. An other membrane showed that regeneration with air at 773 K of the membrane after deliberate coking results in the recovery of the original properties. Even after a test with a heating rate of about 15 K/min., up to 623 K, the permeation performance remained unchanged. This membrane was tested for a period of two years.

The observed thermostability of the membrane, which is a composite of stainless steel and a ceramic layer, is remarkable; in particular as the thermal expansion coefficients of the silicalite-1 and stainless steel are quite different. Apparently, the silicalite-1 layer is rather flexible. Presumably, the thermostability is partly due to the synthesis conditions; it is produced at a elevated temperature, 453 K, so that the difference with the highest temperature is limited to 240 K. In Chapter 2 this matter is discussed in more detail.

The permeation experiment with iso-octane (2,2,4-trimethylpentane), see Chapter 5, and the fact that the performance is constant over a long period shows that the zeolite layer comprises a stable two pore system in which the mass transport via the zeolite pores is dominating. The ratio between zeolite pores and the secondary pores is about constant. It is, therefore, unlikely that secondary pores are cracks in the zeolite layer; they would proceed in time and change the membrane performance. The amount of secondary pores can vary depending on e.g. the synthesis procedure and the quality of the support. This has been shown by the variation of krypton permeation, before 623 K, during calcination, see Figure 13 in Chapter 2. The effect of imperfections in the zeolite layer on the permeation is discussed in detail by van de Graaf et al.

The use of stainless steel for the membrane module has a number of advantages over ceramics; high mechanical strength, relatively good heat conductivity, and easy scaling up and construction (heat exchanger with porous tubes concept). Furthermore, the metal support itself has, compared to ceramic supports, a low mass transfer resistance. The latter is due to the relatively large pores in the metal support and little adsorption on the metal support.

2.2 Comparison of different silicalite-1 membranes

To study the reproducibility of the synthesis of the silicalite-1 membrane the temperature dependence of the permeance of methane through two different membranes has been compared. For the first membrane, WTSS-1e, the synthesis temperature was 363 K, the second membrane, WTSS-2d, was synthesized at a temperature of 353 K. The results for the permeance of methane over the temperature range of 200 to 700 K are given in Figure 3.

For both membranes the same temperature dependence is observed for the permeance of methane. At low temperatures a maximum is observed in the permeance and at high temperatures the permeance has a minimum. The largest
difference is observed for low temperatures; the values of the maxima differ by about 20 %. For higher temperatures the difference is smaller, indicating a high reproducibility of the synthesis of the continuous silicalite-1 layer. Apparently, the mass transport through the zeolite layer is somewhat affected by the synthesis temperature.

Figure 3. Permeance as function of the temperature for methane through two different membranes, WTSS-1e and WTSS-2d. The feed and sweep gas pressure are equal to 101 kPa. The dashed lines are fits with Eq. 12 of Chapter 4. Applied flow rate at the permeate side 100 ml (NPT) He min⁻¹.

In Figure 3 the results of a fit using Eq. 12, in Chapter 4 are also given. The equilibrium properties used in the fits were obtained form separate isobaric experiments, see Table 4 in Chapter 4. In the fits of the two runs the equilibrium properties were kept fixed. Only three diffusion parameters where varied; the intrinsic diffusivity $D^0_S(0)$ and the two activation energies, $E_{D,S}$ and $E_{D,GT}$. The difference between the parameters for permeation through the two membranes is about 5 %. For membrane WTSS-1e the intrinsic diffusivity $D^0_S(0)$ is lower and the activation energies $E_{D,S}$ and $E_{D,GT}$ are higher than the ones obtained from the results with membrane WTSS-2d. The values of the diffusion parameters of methane in the silicalite-1 membrane WTSS-1e are given in Table 2 of Chapter 4.

3 Comparison with Literature

3.1 Permeation data

For a number of different zeolite membranes permeation data have been reported in literature. In Table 1 a comparison is made between different MFI membranes and a Ferrierite membrane. Ferrierite has pore dimensions similar to those of the MFI zeolites. Results are compared for the weakly adsorbed hydrogen, the moderately adsorbed methane, and the strongly adsorbed $n$-butane. From the permeation results
through the various membranes some differences are found. A number of explanations can be put forward. First of all, the membrane thickness has a distinct influence. Compared to the results presented in this work for a membrane with a thickness of $\delta=50 \, \mu m$, the difference with Bai et al.\textsuperscript{7} for the permeation of hydrogen is in the order of a factor 2, after a correction for the membrane thickness. The difference with Nishiyama et al.\textsuperscript{8} and Yan et al.\textsuperscript{9} becomes larger after taking the membrane thickness into account. This may be caused by the fact that they also have a different type of zeolite layer and support.

**Table 1. Comparison of reported one-component permeation data through different zeolite membranes**

<table>
<thead>
<tr>
<th>Zeolite/Support</th>
<th>$\delta$ ((\mu m))</th>
<th>$H_2$</th>
<th>$CH_4$</th>
<th>n-C\textsubscript{4}H\textsubscript{10}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrierite/alumina</td>
<td>-</td>
<td>0.8</td>
<td>0.3</td>
<td>-</td>
<td>Nishiyama et al.\textsuperscript{8}</td>
</tr>
<tr>
<td>ZSM-5/(\alpha)-Al\textsubscript{2}O\textsubscript{3}</td>
<td>10</td>
<td>1.0</td>
<td>-</td>
<td>1.11**</td>
<td>Bai et al.\textsuperscript{7}</td>
</tr>
<tr>
<td>Silicalite-1/(\gamma)-Al\textsubscript{2}O\textsubscript{3}</td>
<td>5</td>
<td>340</td>
<td>-</td>
<td>5.9</td>
<td>Yan et al.\textsuperscript{9}</td>
</tr>
<tr>
<td>Silicalite-1/(\alpha)Al\textsubscript{2}O\textsubscript{3}</td>
<td>&lt; 5</td>
<td>-</td>
<td>10*</td>
<td>3*</td>
<td>Vroon et al.\textsuperscript{10}</td>
</tr>
<tr>
<td>Silicalite-1/stainless steel</td>
<td>50</td>
<td>15</td>
<td>30</td>
<td>5</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Results are for pure component with a pressure of 101 kPa and a temperature of about 300 K; $\delta$ is the thickness of the zeolite membrane.
** At 381 K
+ Results obtained from flux $J, P = J/\Delta p$, With $\Delta p = 1*10^5$ Pa.

More interesting to compare is the observed trend for the permeation of, in particular, the hydrocarbons, as function of the temperature through the different MFI supported membrane. For these gases a comparison is possible with results presented by Vroon et al.\textsuperscript{10} and by Bai et al.\textsuperscript{7}. The results presented by Vroon et al.\textsuperscript{10} for the flux of the first four alkanes and i-butane, see Figures 7 and 8 in Chapter 4, through a silicalite-1 layer on $\alpha$-Al\textsubscript{2}O\textsubscript{3} support, show a similar behavior as reported in this work. A maximum is observed in the flux of ethane, propane, and n-butane over the temperature range studied. For i-butane an increasing behavior is observed. It is noted that they also find that, over the temperature range of 300 to 575 K, the flux of n-butane is always higher than the one obtained for i-butane. Yan et al.\textsuperscript{11} reported results, for a ZSM-5 layer on $\alpha$-Al\textsubscript{2}O\textsubscript{3} support, where n-butane permeates 18 to 31 times faster than i-butane, over the temperature range of 303 to 458 K. On the other hand, Bai et al. reported results for the permeation of n-butane and i-butane, through a silicalite-1 layer on a $\gamma$-alumina support, which differ from the other results for MFI membranes. First of all no maximum is observed in the permeance of n-butane. Secondly, above 350 K i-butane has always a higher permeance than n-butane, see Figure 6a in Chapter 4. As all other groups find that
the permeance of \( n \)-butane is higher than the \( i \)-butane permeance, through MFI membranes, the result of Bai et al.\(^{11} \) is questionable.

Further, the influence of a ceramic support on the permeation is higher compared to our stainless steel supports, as ceramic supports have a higher mass transfer resistance. Additionally, most reported experiments were performed over a limited temperature and pressure range and no transient or counter-diffusion experiments were reported. Nevertheless, similar trends, although less pronounced as reported in this thesis, were observed in separation selectivity and permeation. It can be concluded that, for most results, agreement exists.

3.2 Diffusivities

Most results reported in literature for the one-component diffusion in silicalite-1 are for linear and aromatic hydrocarbons. Unfortunately, most results presented are, in general, Fick diffusivities and should be corrected by the thermodynamic factor \( \Gamma \). For the other gases studied there is almost no data, to our knowledge, available.

The one-component diffusion of the linear alkanes in silicalite-1 has been studied by Hufton and Danner\(^{12} \) using gas chromatography. Results are obtained for very diluted systems, which makes a comparison with the results reported in Chapter 4 possible. Also, an overview is given of the various values of the diffusivity of the first four linear alkanes, in silicalite-1, measured with different techniques.

Comparing the results from Hufton and Danner\(^{12} \) with the results for the first four linear alkanes, as presented in this work, it is found that the results differ by less than a factor four. The largest differences are found for methane and \( n \)-butane. The difference for methane can be a consequence of the two different diffusion regimes discussed in this work. Considering the strong adsorption of \( n \)-butane a difference of a factor four is not considered to be a large difference. At 1 kPa about 1.5 mmol g\(^{-1} \) is adsorbed on silicalite-1, this correspondence to a fractional occupancy of about 0.7. This also indicates that, in general, macroscopic diffusion results should be discussed by taking the amount adsorbed into account.

3.3 Equilibrium adsorption

Various results for the one-component adsorption isotherms on silicalite-1 are available in literature\(^{12-15} \). For the linear alkanes Abdul-Rehman et al.\(^{13} \) reported a linear dependence for the heat of adsorption as function of the carbon number. Up to \( C_{10} \) the heat of adsorption increases with about 10.1 kJ mol\(^{-1} \) for adding a CH\(_2\) group. From Table 4 in Chapter 4 it can be seen that the heat of adsorption increases by about 8 kJ mol\(^{-1} \) with increasing carbon number. From the description of the isobars,
Figure 3 in Chapter 4, we see that for a large amount adsorbed some deviation occurs between the experimental results and the fits with the Langmuir model.

Our results for the saturation capacity and the heat of adsorption are in reasonable agreement with the results of Golden and Sircar. However, these authors concluded that the Langmuir models did not provide a good description of the equilibrium isotherm on silicalite-1. A good description of the one-component isotherms was obtained with the multi-site Langmuir model. Another explanation for the difference between the Langmuir model and the results for isobars is the fact that both the heat of desorption and the entropy of adsorption can be a function of the amount adsorbed. Rees et al. presented results for the heat of adsorption and the entropy of adsorption, for the adsorption of carbon dioxide on silicalite-1, showing that both quantities are a function of the amount adsorbed.

4 Modification of the Zeolite Pores by Silanation

Silanation is a technique to modify the adsorption and diffusion properties of zeolites by adjusting the pore size or the pore entrance. A reduction in the pore aperture is achieved by the reaction of a silane, e.g. SiH₄, (CH₃)₃SiCl (TMCS) or (C₃H₇)₃ClSi, or, with accessible zeolitic OH-groups. To demonstrate the effect of silanation on the diffusion through a silicalite-1 layer one of the membranes was treated for two hours with TMCS under a nitrogen gas flow, to give

≡Si-OH + Si(CH₃)₃Cl → ≡Si-O-Si(CH₃)₃ + HCl

A comparison was made between the steady-state flux of a number of pure components, at 293 K and 101 kPa, before and after silanation. The results for the permeation through membrane WTSS-1c before and after modification are summarized in Table 3.

<table>
<thead>
<tr>
<th>Component</th>
<th>dₜₜ (nm)</th>
<th>Flux Before (mol.m⁻².s⁻¹)</th>
<th>Flux After (mol.m⁻².s⁻¹)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>0.43</td>
<td>5</td>
<td>0.3</td>
<td>16.7</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.33</td>
<td>36.8</td>
<td>4.1</td>
<td>9.0</td>
</tr>
<tr>
<td>methane</td>
<td>0.38</td>
<td>29.6</td>
<td>5.2</td>
<td>5.7</td>
</tr>
<tr>
<td>hydrogen</td>
<td>0.29</td>
<td>15.9</td>
<td>2.5</td>
<td>6.4</td>
</tr>
<tr>
<td>neon</td>
<td>0.28</td>
<td>4.9</td>
<td>0.81</td>
<td>6.1</td>
</tr>
<tr>
<td>krypton</td>
<td>0.36</td>
<td>33</td>
<td>3.3</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Chapter 6

After the silanation the flux of all the gases through the silicalite-1 membrane have decreased. The relative decrease of the flux is: \textit{n}-butane > krypton > carbon dioxide > hydrogen ~ neon ~ methane.

Silicalite-1 has a pore diameter of about 0.55 nm\textsuperscript{18}, after the modification the pore aperture will be smaller. A clear impression of the relation between the pore size of the silicalite-1 structure and the size of the adsorbed molecules follows from the results for \textit{n}-butane. For \textit{n}-butane, with a kinetic diameter of 0.43 nm\textsuperscript{17} there is a reduction in the flux by about a factor 17 after the modification. From the results for methane and carbon dioxide it follows that both the adsorption and the diffusion properties are affect by the modification. Methane has a larger kinetic diameter than carbon dioxide, however, the reduction in the methane flux after the modification is smaller than the reduction in the flux of carbon dioxide. On the other hand, carbon dioxide is stronger adsorbed than methane in silicalite-1. If the reduction in the flux would have been of a kinetic origin only, one would have expected that the flux of methane is reduced more than the flux of carbon dioxide.

It is noted that the flux includes a contribution from both the diffusivity and the equilibrium amount adsorbed. From the results in Table 3 it follows that silanation of the silicalite-1 crystals can be used to improve the separation performance, but at the cost of a lower flux.

5 Conclusions

The developed metal supported silicalite-1 membrane is very robust. It is thermally stable over a large temperature range, 200 - 700 K, and can withstand a heating rate of over 15 K min\textsuperscript{-1} and a pressure difference over the membrane of at least 10 bar. Moreover, the performance is about constant over a period of two years and the permeation through two different membranes is comparable which indicates a good reproducibility of the membrane, even if the synthesis procedure is somewhat different.

Good separation selectivities and fluxes were obtained for many mixtures, but often existing polymeric membranes or other techniques have a better or comparable performance. A high application potential of silicalite-1 membranes have the removal of small organic molecules from liquids and isomer separation, \textit{e.g.} xylene separation. Silanation of the silicalite-1 crystals can be used to improve the separation performance, but at the cost of a lower flux. The first commercial zeolite membrane modules are available. They are used for pervaporation applications. For many of the presented results agreement exists with literature data, although in some cases only qualitatively.
6 Literature


Part 2

Manganese Based Sorbents for High-Temperature H$_2$S Removal
General Aspects of Coal Gasification and Hot Gas Cleaning

Abstract
A short introduction is given on coal gasification processes and gas cleaning. Special attention is given to sorbents for high temperature desulfurization and the selection aspects of these sorbents. An overview is presented of regenerable metal oxide acceptors which are currently under investigation or being applied.

Different gasification processes and coal types result in different coal gas compositions and temperatures of the gas leaving the gasifier. Sorbent development or selection depends on the type of coal gas and the desired regeneration product. Zinc ferrite and zinc titanate have received much attention over the last 15 years and it has become clear that besides advantages they also exhibit some limitations. Other sorbents are promising at temperatures at which the often commercially used zinc based sorbents cannot be applied, $T > 873$ K, and if direct sulfur production during regeneration is desired. It is discussed that a hot gas cleaning above 873 K can be attractive. For example, if the cleaned fuel gas is directly applied as in a solid oxide fuel cell or in other applications for which a very hot fuel gas is beneficial. Manganese based sorbents can be applied up to very high temperatures. Moreover, direct sulfur production during regeneration is possible. The Mn-sorbents have a high potential to be applied for relatively dry coal gases such as produced in the Shell gasification process.
1 Introduction

1.1 Coal gasification in electric power generation

About one-third of the world’s energy fuels consumption is in generating electricity of which almost 60% is produced from fossil fuels. The role of coal in electricity production and the production of chemicals is expected to become more and more important, as the world supply of oil and gas is diminishing. It is foreseen that the world demand for electricity will increase by a factor 2.5 in the first half of the next century to 7-12 EJ/year or 4.5-6.3 TW. Should 40% be regenerated by coal, then 1.7-2.5 TW coal based capacity must be installed, which is the equivalent of 3000-4000 units of 600 MW each. So, there is a huge potential market for clean and more efficient coal technologies to emerge.

![Diagram of coal gasification process](image)

*Figure 1. Simplified schematic block diagram for Integrated Gasification Combined Cycle (IGCC) Power generation with low temperature gas cleaning. Gas cooling and heating are necessary before and after the gas cleaning, respectively. The dust removal*

In conventional coal fired plants the coal is directly combusted. Hereby, about two-third of the fuels heating value is lost during the generation of electricity, hence there is an important opportunity to improve energy efficiency. The overall efficiency of conventional coal combustion systems is limited by the relatively low inlet temperature of the combustion gases. Promising technologies to improve the usage of chemical coal energy more efficiently (up to over 50% electric eff.) are, amongst others, Integrated Coal Combined Cycle power generation (IGCC), and the

\[ E = \text{exa} = 10^{18}, \ T = \text{tera} = 10^{12}, \ M = \text{mega} = 10^6 \]
so called "Topping cycle" or hybrid cycles, which have been developed in particular by British Coal\(^\text{P}\). Also direct fired plants with an ultra super critical steam cycle (USC) have a much higher efficiency. The latter will not be discussed in this chapter.

In an IGCC unit, as schematically depicted in Figure 1, both a gas and steam turbine are used. Fuel gas is generated in the gasifier, then cooled, and purified in the gas clean-up system. Gas is sent to the gas turbine where it is burned with compressed air to provide a stream of hot gas which drives the turbine to generate electricity. The exhaust gases from the turbine pass to a waste heat boiler where steam is raised at high temperature and pressure. The steam passes to the steam turbine which generates electricity. Integration with chemical process technology, adapted from other applications, opens a number of possible routes for coal utilization, which are capable to meet very stringent environmental standards. A good example of an advanced coal gasification plant is the 250 MW\(_{e}\) IGCC demonstration in Buggenum (The Netherlands).

![Diagram of the gasification and gas cleaning process](image)

**Figure 2.** Schematic block diagram for the British Coal Topping Cycle. Dust removal is not separately indicated.

In one of the possible topping cycle configurations pressurized fluidized bed combustion (PFBC) and coal gasification are coupled. This is schematically shown in Figure 2. In this system of gasifier and combustion, 60-80 % of the coal is gasified by air. The resulting char is added to the rest of the coal and passed to the combustor. The fuel gas is cleaned and then burned in the combustor to raise the inlet temperature of the turbine to 1535 K. In early proposals, fuel gas from the gasifier
was used to “top up” the gas temperature at the inlet to the gas turbine, thus enhancing the temperature of gases leaving a PFBC combustor. More recent proposals use a topping combustor to convert non-gasified char. In this case, high carbon conversion in the gasifier becomes less critical and the efficiency is somewhat higher than in the early proposals.

The IGCC and the topping cycle process provide a significantly higher energy efficiency than conventional, pulverized coal-fired, combustion plants. In Table 1 and Figure 3 this is quantitatively illustrated. Several studies on the performance of design options have been conducted. Apart from the influence of the system configuration, other aspects of coal utilization technology have a large influence on the efficiency and capital cost, as well.

The most important aspects are:
- Gasification technology (Fluid bed, fixed/moving bed, entrained flow)
- Gasification oxidant (air/oxygen)
- The extent of integration of different parts of the process (e.g. air separation plant)
- Gas turbine technology and steam cycle configuration/operation
- Coal type and type of feed system
- Scale of the process

Table 1. Plant size, efficiency, capital cost and environmental impact data based on UK installation, 1994.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Unit</th>
<th>Conventional plants</th>
<th>PFBC</th>
<th>IGCC</th>
<th>Topping Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal size</td>
<td>MWe</td>
<td>200</td>
<td>200</td>
<td>250 (400)</td>
<td>330</td>
</tr>
<tr>
<td>Net efficiency</td>
<td>%</td>
<td>38.8</td>
<td>41.4</td>
<td>43 (47)</td>
<td>46.9</td>
</tr>
<tr>
<td>Specific capital cost</td>
<td>$/kWe</td>
<td>1780</td>
<td>1460</td>
<td>1520</td>
<td>1355</td>
</tr>
<tr>
<td>CO₂</td>
<td>kg/kWh</td>
<td>87</td>
<td>82</td>
<td>78</td>
<td>72</td>
</tr>
<tr>
<td>Sulfur retention</td>
<td>%</td>
<td>90</td>
<td>90</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>NOₓ, @ 6 % O₂</td>
<td>mgNOₓ/m³</td>
<td>500-650</td>
<td>150-300</td>
<td>120-300</td>
<td>200-300</td>
</tr>
<tr>
<td>Particulates, @ 6 % O₂</td>
<td>mg/m³</td>
<td>40</td>
<td>10</td>
<td>-</td>
<td>30</td>
</tr>
</tbody>
</table>

- not reported

It should be noted that the somewhat higher efficiency and lower specific capital cost in Table 1 of the Topping cycle, as compared to the IGCC technique, is mainly due to the higher nominal size of the installation and, as a consequence, its potential might be overestimated.
1.2 Coal gasification

Gasification uses 20-30% of the oxygen theoretically required for complete combustion to carbon dioxide and water. Carbon monoxide and hydrogen are the principal products, in particular at high temperature. The basic reactions involved are given below.

**Heterogeneous reactions**

\[
\begin{align*}
C + H_2O & \rightarrow CO + H_2 \quad \Delta H^\circ = 136 \text{ (kJ/mol)}^a \\
C + CO_2 & \rightarrow 2 \text{ CO} \quad \Delta H^\circ = 173 \\
2C + O_2 & \rightarrow 2 \text{ CO} \quad \Delta H^\circ = -222 \\
C + O_2 & \rightarrow \text{ CO}_2 \quad \Delta H^\circ = -394 \\
C + 2H_2 & \rightarrow \text{ CH}_4 \quad \Delta H^\circ = -87
\end{align*}
\]

\( ^a \Delta H^\circ \) of all equation at 800 K (kJ/mol), \( \Delta G^\circ \) has a different value.

**Homogeneous reactions**

\[
\begin{align*}
2 \text{ CO} + O_2 & \rightarrow 2 \text{ CO}_2 \quad \Delta H^\circ = -172 \\
\text{ CO} + H_2O & \rightleftharpoons \text{ CO}_2 + H_2^3 \quad \Delta H^\circ = -37 \\
\text{ CO} + 3 \text{ H}_2 & \rightleftharpoons \text{ CH}_4 + \text{ H}_2O \quad \Delta H^\circ = < 0 \\
2 \text{ CO} + 2 \text{ H}_2 & \rightleftharpoons \text{ CH}_4 + \text{ CO}_2 \quad \Delta H^\circ = < 0
\end{align*}
\]

Both endothermic as well as exothermic reactions occur, where the heat needed for the endothermic reactions is released by partial combustion, methanation and shift reactions. The complex mixture of organic and mineral compounds is pyrolysed into porous carbonaceous material (char), primarily on hot char surfaces. For a detailed description of the heterogeneous and homogeneous reactions and the

\(^3\) Water-gas-shift reaction
thermodynamics of coal gasification the reader is referred to Van Diepen and Mouljijn.

Table 2. Operating conditions and gas composition of four typical gasification processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Air blown, various processes</th>
<th>British Gas/ Lurgi slagging</th>
<th>Shell</th>
<th>Texaco</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidant</td>
<td>Air</td>
<td>Oxygen</td>
<td>Oxygen</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Feed type</td>
<td>Mainly Dry</td>
<td>Dry</td>
<td>Dry</td>
<td>Slurry</td>
</tr>
<tr>
<td>Bed type</td>
<td>Mainly fluidized</td>
<td>Moving</td>
<td>Entrained flow</td>
<td>Entrained flow</td>
</tr>
<tr>
<td>Typical outlet temperature* (K)</td>
<td>1073-1273</td>
<td>723</td>
<td>1173</td>
<td>973</td>
</tr>
<tr>
<td>Typical press. (MPa)</td>
<td>1-3</td>
<td>2.5</td>
<td>3</td>
<td>4-4.5</td>
</tr>
<tr>
<td><strong>Components</strong> (mol%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>15-30</td>
<td>54-57</td>
<td>62-65</td>
<td>45</td>
</tr>
<tr>
<td>H₂</td>
<td>18-25</td>
<td>29</td>
<td>28-30</td>
<td>30</td>
</tr>
<tr>
<td>CO₂</td>
<td>2-15</td>
<td>4.5</td>
<td>1.6-2</td>
<td>5-8</td>
</tr>
<tr>
<td>H₂O</td>
<td>3-11</td>
<td>-</td>
<td>0.4-2</td>
<td>18</td>
</tr>
<tr>
<td>N₂</td>
<td>45-55</td>
<td>3</td>
<td>0.7-3.1</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Typical impurities</strong> (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>750-7000</td>
<td>6000-7000</td>
<td>1260-4000</td>
<td>1100-3500</td>
</tr>
<tr>
<td>COS</td>
<td>25-500</td>
<td>-</td>
<td>75-240</td>
<td>30-100</td>
</tr>
<tr>
<td>NH₃</td>
<td>50-500</td>
<td>-</td>
<td>300</td>
<td>800</td>
</tr>
<tr>
<td>HCN</td>
<td>0.2-50</td>
<td>-</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>HCl/HF</td>
<td>&lt;50</td>
<td>-</td>
<td>200-830</td>
<td>170-690</td>
</tr>
<tr>
<td>Dust (mg/m³)</td>
<td>-</td>
<td>-</td>
<td>17000</td>
<td>8300</td>
</tr>
</tbody>
</table>

* temperature after gas quench
** typical values, strongly dependent on type of coal
- not reported

The composition of the coal gas is variable and dependent on the type of coal, feed system, gasifier, the oxidant and the gasification temperature. The hydrogen to carbon monoxide ratio can range from 0.4 to 1, see Table 2.

Generally, two feed systems can be distinguished. The main difference between the two systems is the amount of water present in the feed mixture.

Either air or oxygen is used as gasification oxidant. Air blown gasifiers have, in their specific application, a somewhat higher net efficiency and are mostly used in
lower temperature processes such as the moving bed and fluidized bed gasifier. High temperature processes, such as the entrained flow gasifier, generally use oxygen. In these processes the equipment is somewhat smaller and the carbon conversion somewhat higher. The typical gas compositions of the gas leaving the gasifier of four different processes are summarized in Table 2.

In the present study the most important parameter is the $\text{H}_2\text{O}$ content. When this is below 2% it will be referred to as dry coal gas, between 2-10% as humid coal gas and above 10% as wet coal gas.

**Table 3. The maximum allowable concentration of impurities in the coal gas.**

<table>
<thead>
<tr>
<th>Impurities</th>
<th>Max. conc. in coal gas</th>
<th>Unit</th>
<th>Determined by:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{S} + \text{CO}_2$</td>
<td>20-100</td>
<td>ppm</td>
<td>Boiler kettle corrosion</td>
</tr>
<tr>
<td>$\text{NH}_3/\text{HCN}$</td>
<td>&lt; 90</td>
<td>g NO$<em>x$/GJ$</em>{th}$</td>
<td>Emission standards</td>
</tr>
<tr>
<td>HCl/HF</td>
<td>60</td>
<td>ppm</td>
<td>Emission standards</td>
</tr>
<tr>
<td>dust</td>
<td>4.5</td>
<td>mg/m$^3$</td>
<td>Protection gas turbine</td>
</tr>
<tr>
<td>Alkali</td>
<td>0.5</td>
<td>mg/m$^3$</td>
<td>Protection gas turbine</td>
</tr>
</tbody>
</table>

1.3 Gas cleaning

As shown in Table 2, coal gas contains several impurities, of which dust, the sulfur compounds hydrogen sulfide and carbonyl sulfide, ammonia, and hydrogen halides are the most important ones. Downstream requirements, for example protection of the gas turbine, and environmental regulations dictate that the raw fuel gas produced by a coal gasifier must be cleaned before further use, see Table 3. A wide variety of existing commercial and well developed processing systems is available for the removal of sulfur, ammonia and other undesirables from the fuel gas.

The removal of the various components is mainly achieved by wet scrubbing at temperatures generally below 350 K, whereas sulfur is often removed using liquid absorbents based on chemical or physical absorption of hydrogen sulfide at low temperatures. Most liquid absorbents are solutions of amines or mixtures of amines. During regeneration of the H$_2$S loaded sorbent the temperature is increased while the pressure is kept low. By stripping with steam the complexes are decomposed and the acid gas components are set free.

After the acid gas mixture is removed, the concentrated acid gas mixture is usually sent to a Claus unit, where H$_2$S is converted towards elemental sulfur. Other processes use direct conversion of H$_2$S to elemental sulfur, thus eliminating the use of a Claus unit. Several commercial low temperature H$_2$S removal processes are given in Table 4. A major drawback of gas cleaning at low temperatures is an
efficiency loss because of the cooling of the coal gas, from 1000-1600 K to typically below 350 K, and after the gas cleaning the heating up of the gas to 673 K. Systems studies, show that the efficiency of an IGCC-plant can be raised (2-4 %, absolute) and the capital cost can be reduced (6 %) by applying high-temperature gas cleaning. Therefore, attention has been given to the development of hot cleaning techniques that can be applied in the “gasification bed” or directly at the gasifier outlet.

Table 4. Commercial low temperature processes for the removal of \(H_2S\)\textsuperscript{1,10,11}.

<table>
<thead>
<tr>
<th>Name</th>
<th>Class\textsuperscript{1)</th>
<th>Sorbent</th>
<th>(T) (K)</th>
<th>Prod.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanol amines</td>
<td>CS</td>
<td>methyl diethanolamine (MDEA)</td>
<td>300</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Girbotol</td>
<td>CS</td>
<td>monoethanolamine (MEA)</td>
<td>295-315</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>SNPA-DEA</td>
<td>CS</td>
<td>diethanolamine (DEA)</td>
<td>295-315</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Econamine</td>
<td>CS</td>
<td>diglycolamine (DGA)</td>
<td>315-355</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>ADIP</td>
<td>CS</td>
<td>di-isopropanolamine (DIPA)</td>
<td>305-315</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Benfield,</td>
<td>ICS</td>
<td>hot K-carbonate ((K_2CO_3 + \text{water}))</td>
<td>355-395</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Catacarb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum carbonate</td>
<td>ICS</td>
<td>sodium carbonate &amp; catalyst</td>
<td>293-313</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Sulfinol</td>
<td>PS/CS</td>
<td>mixture of diisopropanolamine</td>
<td>295-335</td>
<td>(H_2S)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(DIPA) or MDEA, sulfolane and (H_2O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amisol</td>
<td>PS/CS</td>
<td>mixture of methanol &amp; MEA, DEA,</td>
<td>278/313</td>
<td>(H_2S)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>diisopropylamine or diethylamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selexol</td>
<td>PS</td>
<td>dimethyl ether of polyethylene glycol</td>
<td>295</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Rectisol</td>
<td>PS</td>
<td>methanol</td>
<td>245-355</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Purisol</td>
<td>PS</td>
<td>N-methyl-2-pyrolidone</td>
<td>310-355</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>CNG</td>
<td>PS</td>
<td>carbon dioxide</td>
<td>220</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Sepasolv</td>
<td>PS</td>
<td>oligoethylene glycol &amp; methyl isopropyl</td>
<td>310-355</td>
<td>(H_2S)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ethers therof</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluor Solvent</td>
<td>PS</td>
<td>propylene carbonate</td>
<td>&lt; 293</td>
<td>(H_2S)</td>
</tr>
<tr>
<td>Stretford (Localt,</td>
<td>O/DC</td>
<td>solution of Na-salts of (H_2CO_3)</td>
<td>295-315</td>
<td>S</td>
</tr>
<tr>
<td>Sulforex, Sulfint</td>
<td></td>
<td>anthraquinone-2-sulfonic acid, and</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>vanadic acid (iron based chelate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>replacing sodium metavanadate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Takahax</td>
<td>O/DC</td>
<td>solution of Na-salts of (H_2CO_3) and</td>
<td>295-315</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,4-naphthoquinone-2-sulfonic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Townsend</td>
<td>O/DC</td>
<td>aqueous solution of triethylene glycol</td>
<td>340-395</td>
<td>S</td>
</tr>
</tbody>
</table>

\textsuperscript{1) CS = chemical solvent, PS = physical solvent, ICS = inorganic chemical solvent, PS/CS = both chemical/physical solvent, O/DC = oxidation/direct conversion.
1.4 Objective with respect to the cleaning temperature

The optimal temperature for hot gas cleaning is subject to debate. It appears that the benefit of hot gas cleaning compared to low temperature scrubbing is most clearly present up to say 575-675 K. The reason is that phase transitions are omitted. Materials that can withstand high temperatures are more costly. As a consequence, 675 K is often considered as the optimal cleaning temperature. On the other hand, a dedicated hot gas cleaning process operating at temperatures above 675 K might lead to additional large savings because heat exchange equipment is omitted. A good example is the radiation gas cooler present in high temperature gasifiers - gas turbine set-ups. A operation temperature of 1200 K might well be optimal.

It could be argued that the potential material problems in the turbine make a temperature above say 700 K very unattractive. However, research is being performed on the development of high temperature resistant turbine blades and valves. This results in a steady increase of the temperature resistance of these parts, enabling higher gas inlet temperatures. Moreover, other new technologies emerge, such as the solid oxide fuel cell (SOFC), which might operate with fuel gas at much higher temperatures. We decided to focus our work on application of new high temperature technology. The incentive is to remove impurities between 1000 - 1200 K. We restrict ourselves to the cleaning of a dry coal gas. It is anticipated that it can also be applied to other applications, for example, the desulfurization of fuel gas obtained from the gasification of heavy residues from oil industry.

2 High Temperature Desulfurization

For desulfurization the removal of sulfurous gases (H₂S and COS) at high temperatures practically all studies use gas-solid absorption processes. Sulfurous compounds can either be removed by sorbents mixed with the coal, so called in-bed removal, or after the gasification in an external sorbent bed. A combination of both is of course also a possibility. In most cases the desulfurization efficiency should be above 98.5 %, in order to remove sulfur containing compounds to an acceptable level, see Table 2. The most important factors to be considered in process design and, associated herewith, sorbent selection are schematically given in Figure 4. Below, we will discuss some points which are important for sorbent selection.
2.1 Sorbent selection (see Figure 4)

2.1.1 Thermodynamics

The main requirements for (external) sorbents are that they are stable and that they selectively react with H₂S and COS in a reducing coal-gas environment at 1 to 4 MPa and 675-1175 K. In general, the following reactions should be carried out at conditions favorable for adsorption:

\[
\begin{align*}
\text{Me}_x\text{O}_y + x\ H_2\text{S} + (y-x)\ H_2 & \rightarrow x\ \text{MeS} + y\ \text{H}_2\text{O} \quad (9) \\
\text{Me}_x\text{O}_y + x\ \text{COS} + (y-x)\ \text{CO} & \rightarrow x\ \text{MeS} + y\ \text{CO}_2 \quad (10)
\end{align*}
\]

where Me refers to any metal.

For regenerable sorbents the desired regeneration reactions can be presented as:

\[
\begin{align*}
x\ \text{MeS} + (x+y/2)\ \text{O}_2 & \rightarrow \text{Me}_x\text{O}_y + x\ \text{SO}_2 \quad (11) \\
x\ \text{MeS} + \text{H}_2\text{O} & \rightarrow \text{Me}_x\text{O}_y + \text{H}_2\text{S} + (y-x)\ H_2 \quad (12) \\
x\ \text{MeS} + (y/2)\text{SO}_2 & \rightarrow \text{Me}_x\text{O}_y + (y/2)\text{S} \quad (13)
\end{align*}
\]

Evaluations to determine the metal oxides to be used in high temperature removal of H₂S have been carried out by several investigators. Westmoreland et al.\textsuperscript{13,14} showed that the oxides of Ba, Ca, Co, Cu, Fe, Mn, Mo, Sr, W, V, and Zn are from a thermodynamical point of view feasible candidates. In principle, Ce and Sn are feasible, too. In this respect the type of coal gas is also important. Desulfurization of dry and thus strongly reducing coal gas leads to different demands on the sorbent than wet coal gas which is less strongly reducing. Under practical conditions, even if the coal gas is strongly reducing, manganese oxide can not be reduced to the metal form. This is a favorable property because the metal is expected to be subject to sintering and evaporation. This is in contrast with tin oxide which can relatively easily be reduced to Sn and evaporation is a point of concern. Tin oxide should, therefore, not be used in a strongly reducing environment\textsuperscript{15} at very high temperatures.

Mixed metal oxides

Mixed metal oxides have high potential because they can be designed from information on the stability and performance of existing sorbents\textsuperscript{16}. The thermodynamics of most mixed oxides are unknown and strongly depend on the concentration of the metal in the sorbent. Moreover, besides bulk properties also the characteristics of the surface phase are important. Up to now the thermodynamical data are lacking for most metal oxides. This makes a selection based on
thermodynamics very time consuming, if not impossible. In Chapter 9, we will discuss the thermodynamics of manganese based sorbents in more detail.

![Diagram showing factors for high temperature desulfurization with solid sorbents.](image)

**Figure 4.** Important factors for high temperature desulfurization with solid sorbents.

### 2.1.2 Supported versus unsupported Sorbent

In general, supported metal oxide acceptors have advantages over unsupported metal oxides for high temperature desulfurization because of higher reaction rates. The amount of active metal in the reactor and, as a consequence, the adsorption capacity is in most cases somewhat less than for bulk sorbents. The support has a relatively large surface area and the metal oxide is spread out on this surface. If desired, stabilization of the support is possible in many cases. When the reaction takes place exclusively at the surface, stabilization is essential for stable operation. At higher temperatures it is generally observed that sintering occurs which might slow down the reaction. However, we discovered for Mn-based sorbents that the performance at high temperature is quite satisfactory, see Chapter 11. The explanation is as follows. Solid state diffusion is an activated process and, as a
consequence, with increasing temperature diffusion in the solid phase is accelerated and, therefore, (partly) compensates the decrease in reactivity by the loss of surface area. This is discussed in detail in Chapters 8 and 11.

2.1.3 Reactivity
Some elements which were rejected because their oxides (or carbonates) are stable, relative to the sulfided element, or because they are not reactive throughout the temperature range from 600-1200 K. This includes Al, Cr, K, Li, Mg, Na, Ti, Zr. Some elements were rejected because of their inadequate desulfurization potential. These are Ag, La, Ni, and Sb.

2.1.4 Reduction to a low melting metal
The melting point of a metal is relatively low compared to its metal oxide. Melting of the sorbent results in most cases in a deactivation of the sorbent. Therefore, the thermodynamics and/or kinetics of the following reduction reactions should be unfavorable:

\[
\text{MeO (s) + H}_2(\text{g}) \quad \Rightarrow \quad \text{Me (s) + H}_2\text{O (g)} \quad (18)
\]

and

\[
\text{MeO (s) + CO (g)} \quad \Rightarrow \quad \text{Me (s) + CO}_2(\text{g}) \quad (19)
\]

Addition of stabilizers to the (bulk) sorbent by reduce the ease of reduction. Bi, Cd, Pb and Sn are elements which can be rejected because their metal oxide can be reduced to a low melting metal. Sn is a border line case and deserves a special treatment because it can be applied in wet fuel gas. In that case Sn is not present as the metal and the problem of melting does not occur. Moreover, stabilizers for Sn-based have been developed\textsuperscript{15}.

2.1.5 Coke and sulfate formation
An important aspect is the possibility of coke and sulfate formation, which should be minimized. Some metals catalyze the formation of coke, for example Fe. Especially at temperatures below 1050 K coke formation can occur. Small amounts of coke may be acceptable because they may be removed during H\textsubscript{2}O regeneration. Sulfate formation generally leads to volume expansion and swelling of the sorbent causing them to spall and crack. Moreover, H\textsubscript{2}S or SO\textsubscript{2} formation can occur during the sulfiding step which is undesirable. Mn bases sorbents do not catalyze coke formation and sulfate formation does not occur above 723 K, see Chapter 9.
2.1.6 Volatile metal chlorides and carbonyls
The possibility of extensive volatilization of the sorbent at too high operating
temperatures might be easily overlooked. The presence of HCl and HF in the fuel
gas causes the formation of metal chlorides or fluorides which are much more
volatile than the corresponding metal oxides. Loss of metal by volatilization of metal
chlorides or fluorides causes deactivation of the sorbent. Large differences exist in
melting and boiling points between different metal chlorides. ZnCl₂ has a boiling
point of 1005 K whereas MnCl₂ has a boiling point of 1504 K. Carbonyl Me(CO)₆
formation can have the same effect and can lead to efficient evaporation of the metal.
The possibility of carbonyl formation should always be checked.

2.1.7 Stability and mechanical strength and reactor type
Regenerable sorbents should properly perform during many cycles (1000-100000) to
make them economically competitive with disposable sorbents. They should possess
a good mechanical strength and should be resistant towards attrition. Especially
when the sorbent is applied in a fluidized bed reactor this is an important factor. For
example, Zn-ferrite¹⁷ suffers from this problem. The aspects of the different types of
reactors is discussed in detail in Chapter 12.

2.1.8 Regeneration products
Regeneration of the sorbent requires an oxidation step in which a sulfur ion is
exchanged with an oxygen ion. From a process point of view the production of
elemental sulfur during regeneration is most effective. However, such processes are
still in the development stage. When no elemental sulfur can be made, the
production of H₂S is preferred over SO₂, unless SO₂ can be directly used for the
production of H₂SO₄. At present, regeneration with oxygen is most common. The
reaction with oxygen is, however, very exothermic. To avoid local overheating the
oxygen or air has to be diluted, resulting in very diluted SO₂ as a product of the
regeneration. Reducing gases are needed to convert SO₂ in H₂S and in general the
H₂S stream should be concentrated to > 15 mol %, before entering a Claus unit. It
should be noted that catalytic processes are feasible for more diluted streams.

For some sorbents regeneration is possible with H₂O leading to the formation of
H₂S. However, a good regenerability with H₂O also means a high sensitivity for H₂O
during the sulfidation. These sorbents can only be applied for the desulfurization of
dry coal gas or in combination with a sorbent which is not sensitive for H₂O. For the
direct production of elemental sulfur regeneration with SO₂ is an option. Sulfate
formation is, however, in many cases a problem.
### Table 5. Overview of novel alternative regenerable metal oxide and mixed metal oxide sorbents for high temperature desulfurization.

<table>
<thead>
<tr>
<th>Sorbent type (developer)</th>
<th>Absorption T, P, desulfurization depth, capacity</th>
<th>Regeneration T, regenerant, product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide on SiO₂ and Al₂O₃,²⁸  (Utrecht University, VEG-Gas-instituut/Gastec, Kema, Netherlands)</td>
<td>473-773 K, 0.1 MPa, H₂S lower than 1 ppm in off-gas. Capacity 3-6 wt.% S.</td>
<td>773 K with 1 vol% O₂, with SiO₂ mainly elemental sulfur produced. With Al₂O₃ also 0.1 vol% SO₂.</td>
</tr>
<tr>
<td>Iron oxide on TiO₂, Honeycomb structured support (IHI/CREPLI, Japan)</td>
<td>573-773 K, Typically 673 K, 1.6 MPa. H₂S outlet concentrations &lt; 100 ppm at 1000 ppm inlet. Capacity 10-15 wt.% S</td>
<td>673 K (inlet temp.), 1.5 vol% O₂, diluted SO₂ is formed.</td>
</tr>
<tr>
<td>Iron oxide or manganese oxide on γ-Al₂O₃ support¹⁰,¹¹ (Delft University of Technology)</td>
<td>648-873 K, &lt; 20 ppm Low capacity &lt; 1.5 wt.% S</td>
<td>638-873 K, steam (up to 70 mol%), [H₂S] &gt; 15 mol%</td>
</tr>
<tr>
<td>Iron oxide and molybdenum oxide on silica or amorphous aluminium sulfate³⁰, ⁴⁸-⁵⁰ (Utrecht University, Kema, Netherlands)</td>
<td>673-873 K, 0.1 Mpa, &lt; 20 ppm. Capacity 3-5 wt.% S.</td>
<td>Iron oxide: &gt;923 K, oxygen-iron-molybdenum oxide: 753-850 K, SO₂. Molybdenum oxide prevents sulfate formation and direct production of S is possible.</td>
</tr>
<tr>
<td>Iron oxide or zinc oxide on zeolite³¹ (Faujasite Y) (Recycle Metals, USA)</td>
<td>723-923 K, 0.1-0.2 MPa. H₂S 0-200 ppm at outlet for inlet concentration of up to 8000 ppm.</td>
<td>723-923 K. Regeneration in 11% O₂ gas and nitrogen purge (reduces residual sulfates).</td>
</tr>
<tr>
<td>Iron ore or iron oxide particles³² (fluid bed) (IHI/NEDO, Japan)</td>
<td>733 (-823) K, Efficiency 90-96%</td>
<td>1023 K, Air. Elemental sulfur is obtained by reaction with anthracite in SO₂ reductor.</td>
</tr>
<tr>
<td>Copper and manganese oxides³³ (CuMnO₂ and CuMn₂O₄ in 1:1 and 1:2 Cu to Mn atomic ratios (Electrochem Inc., USA)</td>
<td>773-873 K: CuMnO₂ 973-1023 K: CuMn₂O₄. 30 and 50 ppm H₂S. H₂S absorption decreases rapidly with 20 vol% H₂O at 923 K</td>
<td>CuMnO₂: 923-973 K. Air. Diluted SO₂ is obtained. Higher temperatures destroys stability of mixed oxide spinels. No evidence of sulfate forming.</td>
</tr>
</tbody>
</table>
General aspects of hot gas cleaning and coal gasification

Copper and manganese oxides on zeolites\textsuperscript{34} (99% pure SiO\textsubscript{2})
(Morganstern Energy Technology Center, USDOE)

811-1033 K, 0.14 MPa, 0-200 ppm H\textsubscript{2}S at outlet for inlet up to 2000 ppm. Zeolite catalyses COS formation.

Copper-Iron-Alumina oxides\textsuperscript{35}
(C3FA with atomic ratio 3:2:1)
(MIT, USA)

923-1023 K (C3FA), < 60 ppm H\textsubscript{2}S


Copper-alumina oxides (CA with atomic ratio 1:1)
(MIT, USA)

823-1073 K (CA), < 120 ppm H\textsubscript{2}S both with inlet of 10,000 ppm.

CA: 823-1073 K, 10 % O\textsubscript{2}. Sulfate not formed >1023 K. Principally SO\textsubscript{2}.

Zinc oxide on zinc aluminate and cobalt titanate on titania\textsuperscript{36}
(IGT, USA)

923 K, 1.7 MPa. Reduces 5000 ppm inlet H\textsubscript{2}S to 20 ppm in a two stage fixed bed.

1143 K, 0.1 MPa. Oxygen. Zn sorbent stage: SO\textsubscript{2} produced. Cobalt bed: direct reduction to sulfur.

Zinc titanate\textsuperscript{16,24-27} (0.8-2 \(\text{ZnO:TiO}_2\)) (several developers)

<1033 K, typically 823 K. 6-10 wt. % capacity. Less sensitivity to reducing gases compared to zinc ferrite. 1.5 \(\text{ZnO:TiO}_2\) shows best performance. Capacity 9-15 wt. % S.

1000-1040 K, 1-3% O\textsubscript{2}. Product: diluted SO\textsubscript{2}

Zinc oxide with nickel oxide matrix\textsuperscript{37,38} (several developers)

813 K, < 50 ppm
Capacity 10 wt. % S (after 50 cycles)

923-1000 K, 2.5% O\textsubscript{2}
Product: 1.8% SO\textsubscript{2}

Cerium Oxide\textsuperscript{39}
(Gas desulfurization Corp., USA)

973-1273 K, 3-10 ppm H\textsubscript{2}S for inlet up to 1.1 vol%.
Higher adsorption rate with increasing temperature and CO/CO\textsubscript{2} ratio.

1200 K Air, 30% O\textsubscript{2} or pure oxygen. Product SO\textsubscript{2}. Low residual sulfates.

Manganese oxide \textsuperscript{40,41}

1123 K, 0.1 MPa, < 200 ppm.
10 wt. % S.

1173 K, 3% O\textsubscript{2}
Product: diluted SO\textsubscript{2}

Manganese oxide on manganese aluminate\textsuperscript{42-44}
Honeycomb structured support.
(Delft University of Technology, The Netherlands)

673-1273 K, typical 1123 K < 40 ppm, for dry coal gas (2.1 % H\textsubscript{2}O), Capacity 10-20 wt. % S.

673-1273 K, typically 1123-1173 K. SO\textsubscript{2}: product pure S, H\textsubscript{2}O: product H\textsubscript{2}S. During 110 cycles < 20% deactivation

Limestone or dolomite\textsuperscript{45} (Twente University, Netherlands)

823-1023 K. 3-step process with half calcined dolomite (bulk, 1023 K), and half-calcined limestone 823 K, capacity 2 wt. % S.

723-1023 K, Mixtures of CO\textsubscript{2}/H\textsubscript{2}O. Product: H\textsubscript{2}S. Only dolomite completely regenerable.

Natural Based Calcium oxide\textsuperscript{46}
(Twente University, Netherlands)

573-1123 K, optimum 1100 K, small particles (0.18 mm), capacity 15-20 wt. % S.

873-1133K and > 1273 K, 10% SO\textsubscript{2} in N\textsubscript{2}. Product = S\textsubscript{2} + O\textsubscript{2}

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2.2 Examples of Sorbents

In-bed sorbents often form an essential part of the gasification process. Relatively, cheap and abundantly available materials like limestone (calcium carbonate) and dolomite (a mixture of calcium and magnesium carbonates) are often used\textsuperscript{18-22}. The sorbent is initially calcined in the gasifier to form calcium and magnesium oxides.

Sorbents for external use are usually based on regenerable metal oxides. Zinc ferrite and zinc titanate have received much attention\textsuperscript{16,23-27} as external sorbents over the past 15 years. From a theoretical point of view, they have desirable properties, like high sulfur capacity (~ 10 wt.\% S), the ability to remove H\textsubscript{2}S from coal derived fuel gas to levels of a few ppm, and the feasibility of regeneration with air.

Several other regenerable mixed oxide sorbents are currently under development, the most important ones are listed in Table 5. Some of these sorbents are based on iron and zinc oxides, but are stabilized on inert carriers such as alumina or zeolites. In other applications, oxides of cerium, copper, cobalt, manganese and tin are used in the sorbent formulations. Most of these sorbents are currently being evaluated in laboratory or bench-scale tests, to establish the optimum chemical formulation, or to develop improved physical properties and stability for repeated use in multiple absorption/regeneration cycles. The use of these sorbents will depend on their improved performance relative to zinc ferrites or titanates and/or their ability to use simple and cost-effective schemes for treating regenerator off-gas.

In general it is, of course, not possible to decide on the best adsorbent independently of the specific application. The major parameters are the sulfidation temperature, water content in the feed and the desired sulfur product formed during regeneration, i.e. elemental sulfur, H\textsubscript{2}S, SO\textsubscript{2} or another compound. Of course the price is also important.

In the present study, Mn based sorbents have been chosen because it is felt that:

- they have sufficient desulfurization potential for dry coal gas at high temperatures (873-1173 K)
- direct production of elemental sulfur during regeneration is thermodynamically feasible
- they are robust and stable and because Mn-oxides and sulfides are not reduced to the elemental metal and its metal chlorides, fluorides are not very volatile compared to many other metals. Moreover, carbonyl formation and coke formation are expected not to occur
- knowledge and experience is present on manganese based materials because of previous research at the Delft University of Technology\textsuperscript{10,46,47}.
3 Conclusions

In sorbent development and selection attention should be given to the type of coal gas, desired reaction conditions and the intended desulfurization/regeneration process. New sorbents are promising at temperatures where zinc based sorbents cannot be applied, $T > 873 \, \text{K}$, or if direct sulfur production during regeneration is possible. For application of regenerable sorbents at very high temperatures, $T > 873 \, \text{K}$, and in relatively dry and thus strongly reducing coal gas a manganese based sorbents seems a good option. In the next chapters manganese based sorbents will be discussed in more detail.

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The Preparation of Manganese based Sorbents

Abstract
The preparation is described of manganese based sorbents for desulfurization of coal gas at very high temperatures (> 873 K). Both wet impregnation and deposition precipitation have been used to deposit manganese oxides on γ-Al₂O₃ particles and monoliths. Wet impregnation with manganese acetate appears to be a good method to prepare high loading samples with a relatively good manganese distribution. A typical manganese loading is 36 wt% and the type of γ-Al₂O₃ support seems of minor importance. Deposition precipitation resulted in samples with a poor manganese distribution. Mn₃O₄ and, at high manganese loading, also Mn₂O₃ is formed after impregnation and calcination at 873 K. For the samples prepared via deposition precipitation only Mn₃O₅ was observed. The applied multi-step impregnation method is relatively expensive. For the production of a commercial sorbent, the development of a one step method is recommended.
1 Introduction

The research on high-temperature regenerative sulfur removal at the Delft University of Technology was started by van der Linde\(^1\). He explored among other things the removal of hydrogen sulfide with metal oxides. One of the promising candidates was supported manganese oxide. Regeneration appeared to be possible with steam under the formation of concentrated H\(_2\)S. This acceptor material was tested between 748 and 823 K.

Soerawidjaja\(^2\) used both manganese acetate and manganese nitrate for the preparation of a sorbent. The preparation with manganese acetate resulted in a highly dispersed manganese phase, while the dispersion obtained via manganese nitrate was poor. The good dispersion of MnAc\(_2\) can be explained in several ways: a good interaction of with the support, see Eqs. (2) and (3), transport properties during drying (high viscosity), good crystallization behavior of the acetate solution on a microscopic level, and decomposition behavior of the precursor NO\(_2\) prevents interaction with support\(^3,4\). The sorbent was investigated at 873 K and a rather detailed reaction model was proposed. It was suggested that the active phase was a surface manganese aluminate spinel. Soerawidjaja described the adsorption process in analogy with an ion exchange column\(^5,6\).

Wakker et al.\(^7,8\) besides dry impregnation also studied sol gel precipitation, co-precipitation, pore volume impregnation and wet impregnation. The influence of the composition of coal gas and the regeneration gas on the sulfidation and regeneration behavior was extensively studied between 673 K and 873 K. Also a test of 50 cycles behind a pilot gasifier was performed. Although the level to which the H\(_2\)S was removed was satisfactory and the H\(_2\)S concentration in the regeneration gas was sufficiently high, the sorbent capacity was too low for a practical process, typically 1 wt.% S.

Ben-Slimane et al.\(^9,10\) studied the H\(_2\)S removal with unsupported manganese oxide particles at temperatures up to 1273 K. The regeneration was carried out with diluted oxygen, under the formation of SO\(_2\). Although the H\(_2\)S removal was rather efficient, < 200 ppm, and the capacity was high, the SO\(_2\) produced will be for most applications an undesirable regeneration product.

Wakker\(^7\) concluded that manganese based acceptors with a high surface area only were effective for high temperature coal gas desulfurization. Operation at a temperature of 873 K with a maximum loading of 8 wt.% manganese was concluded to give the highest possible acceptor capacity. Hereby, about a mono-layer Mn-oxide on the support was obtained and little sintering occurred. It was assumed, but not
proven, that the active phase was MnAl₂O₄ spinel. So, in his view, part of the γ-Al₂O₃ support was converted to form a manganese-alumina metal oxide.

To obtain a higher uptake capacity a higher metal loading is necessary. The preparation of a "multi-layer" sorbent is then inevitable. However, Wakker showed that at 873 K sintering occurs and at that temperature bulk diffusion is too slow to contribute to the acceptor capacity. Consequently, sintering results in a decrease in acceptor capacity at that temperature. However, a solution presented itself. Solid state diffusion is an activated process and, as a consequence, with increasing temperature, diffusion in the solid phase, at least partly, compensates the decrease in reactivity by the loss in surface area. So, operation at higher temperatures might be advantageous.

From thermodynamic calculations, see Figure 9 and 11 in Chapter 10, it appears that above 700 K MnS supported by Al₂O₃ can be regenerated with SO₂ leading to the direct formation of elemental sulfur and MnAl₂O₄. This might well be attractive in practice, in particular as at these high temperatures sulfate formation is unlikely.

Regeneration of unsupported MnS (MnS without interaction with alumina) is only feasible with oxygen. Regeneration with either steam (to H₂S) or with SO₂ (to S) is very difficult. Therefore, optimal Mn-sorbents should exhibit a good interaction with alumina and, as a consequence, the specific surface area of the system should be kept as high as possible to avoid rapid decline in capacity.

The stoichiometric amount of Mn in MnAl₂O₄ is 31.8 wt.%. The maximum capacity of bulk manganese aluminate is for that reason limited to about 20 wt.% S, corresponding with Mn : S = 1 : 1. Further increase in Mn loading is possible but, it is expected, that in that case a mixture of MnO and MnAl₂O₄ will be formed. As indicated above, for the regeneration of MnS to MnO either oxygen or a large excess of SO₂ or H₂O are needed. Therefore, for very high Mn loadings, a small amount of oxygen must be added to the regeneration gas to regenerate "super"-stoichiometric MnS. This will be discussed in more detail in Chapter 11 and 12. Another important aspect is the role of surface sites as they can provide a better desulfurization depth than the bulk sites. This will be shown in Chapter 11.

Summarizing: Bulk manganese aluminate can be a good option for a high capacity, for high temperature desulfurization sorbent. The specific surface area of the system should be kept as high as possible to minimize bulk diffusion limitation. This limitation can, however, be at least compensated by higher reaction temperatures.
1.1 Objectives with respect to sorbent research

It appeared that bulk MnAl₂O₄ could be an attractive material for high temperature desulfurization of dry coal gas, see Chapters 7 and 10. Therefore, the sorbent research at the Delft University of Technology was revisited and focused on manganese based sorbents. The following objectives were defined:

- increase the capacity of the existing “Delft sorbent”
- investigate the feasibility to produce elemental sulfur during regeneration
- get a better understanding of the sulfiding and regeneration mechanisms
- prepare a monolith shaped acceptor which can be applied in a rotating reactor (for details on the desulfurization process the reader is referred to Chapter 12).
- investigate (theoretically) the influence of dust and other impurities on the sorbent

Furthermore, the starting points were the following:

- desulfurization at very high temperatures (1000-1200 K)
- dry coal gas (< 2% H₂O), such as produced in a Shell type gasifier
- application of the cleaned coal gas for combustion in, for example, new generation gas turbines or other non-conventional devices such as a solid oxide fuel cell (SOFC).

1.2 Impregnation versus deposition precipitation

For low loading sorbents (< 10 wt.%), impregnation with manganese acetate is a proven method to apply manganese oxide in a dispersed form on an alumina carrier. Therefore, this method was chosen to prepare high loading manganese sorbents. For comparison some samples were prepared via deposition precipitation. Below a theoretical introduction is given on the deposition of metal oxides on γ-Al₂O₃ by impregnation and deposition precipitation.

1.2.1 (Wet) Impregnation

During impregnation the solution containing the metal precursor is contacted with the porous support which absorbs the solution. After absorption the solvent is evaporated. Subsequently, the precursor is treated at elevated temperatures in a chosen gas atmosphere, which leads to the desired phase. Manganese-acetate is decomposed by reaction with O₂:

\[ \text{Mn(Ac)}_2 + \text{O}_2 \rightarrow \text{Mn}_3\text{O}_x + \text{H}_2\text{O} + \text{CO}_2 \]  

(1)
The success of the method depends to a large extent on the nature and properties of both the support and the precursor. Especially during the drying process of the impregnated support the macroscopic distribution of the active phase is established. The distribution after drying will mainly be determined by the interaction between the precursor and the support level and the crystallization behavior of the solution on a molecular level.

Selective adsorption of the metal precursor can occur because of interaction with the hydroxyl groups on the amphoteric support. The (wet) impregnation process is envisaged as follows:

1. The solution penetrates into the pores of the acceptor.
2. A certain part of the metal ion adsorbs on the surface of the pores.
3. Ions diffuse into the pores from the bulk solution due to concentration gradients which are caused by adsorption of manganese on the pore wall (wet impregnation).

The pore volume impregnation, also referred to as "dry" impregnation, is described by steps (1) and (2) only.

Metal ions remain on the pore surface by direct adsorption and because precipitation of the manganese occurs, during evaporation of the liquid out of the pores. The penetration of the solution into the pores is a relatively fast process compared to ion diffusion. If during wet impregnation a significant amount of ion adsorption occurs the concentration in the pores will decrease and metal ions will start to diffuse from the solution into the pores. This diffusion process is relatively slow. For a diffusion coefficient for divalent ions of about $1.2 \times 10^{-9}$ m$^2$s$^{-1}$, it takes several hours to reach equilibrium for a particle with a diameter of 3-5 mm. If the total amount of metal ions adsorbed at the pore-wall is small compared to the total amount present in the liquid of the pore, a long impregnation time may be not required, because in that case the characteristic diffusion length is the pore diameter rather than the particle diameter.

Ion exchange can occur with terminal OH groups on the surface of the alumina support according to the following reaction.

$$\text{Al-O-H} + \text{Ac}^- \rightleftharpoons \text{Al-O}^- + \text{HAc}$$  \hspace{1cm} (2)

$$2 \text{Al-O}^- + \text{Mn}^{2+} \rightleftharpoons (\text{Al-O})_2\text{Mn}^{2+}$$  \hspace{1cm} (3)

If the interaction with the surface is only weak, during drying a part of the solution is transported out of the pores, due to the capillary forces. This results in a so-called eggshell distribution. Other than via interaction with the support, the transport of the
metal precursor can be suppressed by using very high drying rates, e.g. by using microwave heating, or by increasing the viscosity of the impregnation solution.

1.2.2 Deposition Precipitation
The concept of deposition precipitation is based on a chemical reaction of the active precursor at the surface of the support, resulting in a uniform distribution of small active particles over the support. Essential for this method is that the support facilitates the nucleation of the active precursor.

For the preparation of a manganese based sorbent, Mn(NO₃)₂·4H₂O is dissolved in de-ionized water. After heating the mixture to about 363 K, urea is added which slowly hydrolyses according to:

\[
\text{CO(NH₂)₂ + 3 H₂O} \rightarrow 2 \text{NH}_4^+ + \text{CO}_2 + 2 \text{OH}^- \quad (4)
\]

Upon addition of urea, the pH increases and manganese hydroxide species are generated according to:

\[
\text{Mn}^{2+} + 2 \text{OH}^- \rightarrow \text{Mn(OH)}_2 \quad (5)
\]

The hydroxyl ions are produced homogeneously throughout the solution. Strong mixing is necessary to minimize concentration polarization at the support surface. When the hydroxyl concentration exceeds the solubility limit, metal hydroxide particles can nucleate and grow. Precipitation exclusively on the support surface can be achieved because of the presence of an active precursor-support interaction. Nucleation of the catalyst precursor (manganese hydroxide) at the surface of the support proceeds at lower concentrations than those needed for precipitation in the bulk of the solution. The reaction is continued for the desired period of time, after which the solution is withdrawn, and the sample is washed with de-ionized water.

For a good metal distribution in the pores the hydroxyl ions have to be present everywhere in the pores. As diffusion into the support is rather slow, compared to the decomposition of urea, deposition precipitation becomes increasingly effective with decreasing particle diameter.

2 Experimental

Most of the acceptor material was prepared by wet impregnation of the carrier material but also some acceptor material was prepared via deposition precipitation. Three types of acceptor material were used: γ-Al₂O₃ monoliths (62 cells/cm²), cordierite monoliths
(62 cells/cm²) with about 25 wt.% γ-Al₂O₃ washcoat layer, and particles in different sizes ranging from 60 μm to 7 mm. The largest particles were extrudates with a length of 7 mm an a diameter of 2 mm. For the acceptor preparation via deposition precipitation in all cases washcoated monoliths were used. The specific surface area of the fresh support was, based on the amount of alumina in the sample, around 160-210 m²/g γ-Al₂O₃.

2.1 Wet impregnation

The wet impregnation method an excess amount of the impregnation solution is added to the carrier material. In Figure 1 a simplified flow scheme of the acceptor preparation is given. The material was contacted with a 0.5-2 mol/l aqueous solution of MnAc₂·4H₂O, which was continuously circulated through the monolith channels or around the particles during impregnation. The impregnation time varied between 6-12 hours and the temperature between 300 and 325 K. After impregnation the excess solution was removed from the channels with pressurized air (monoliths) or by centrifugation (particles). The samples were dried in a microwave oven (115-230 W). The drying time was dependent on the sample weight and was 3-6 minutes for 25 g
sample. After drying in the microwave most samples were kept for 12 hours in a conventional oven at 353 K. Calcination was performed in static air at 873-973 K for at least 6 hours. The \( \gamma \)-\( \text{Al}_2\text{O}_3 \) monoliths/particles and the washcoated monoliths had about a 6-8 wt.% and 3 wt.% manganese loading, respectively, after a single impregnation with a 2 mol/l solution. To obtain higher manganese loadings the procedure was repeated.

Acceptor preparation via wet impregnation on a kilogram scale (10 kg/batch) was also performed but is described elsewhere\textsuperscript{16}.

2.2 Deposition precipitation

Five small monolithic blocks (diameter 1 cm, length 2 cm) were added to 200 ml 0.04 M solution of Mn(NO\textsubscript{3})\textsubscript{2}. The reactor vessel was equipped with a stirrer and a condenser. After heating the mixture to 361 K, urea was added. The pH-value was continuously monitored. After a certain reaction time, which varied from 2 to 22 hours, the solution was withdrawn and the samples were washed with de-ionized water. The samples were dried in a conventional oven for 12 hours and calcined at 973 K.

2.3 Manganese content in \( \gamma \)-\( \text{Al}_2\text{O}_3 \) and washcoated monoliths

The samples are labeled by their manganese content in wt.% Mn based on the total amount (including cordierite, if applicable). Both pure \( \gamma \)-\( \text{Al}_2\text{O}_3 \) alumina support and cordierite monolith samples with a 25 wt.% \( \gamma \)-\( \text{Al}_2\text{O}_3 \) washcoat layer were used. In the latter case, the numbers should not be misinterpreted. Compared to the alumina supported samples the amount of manganese relative to the alumina present is much higher for the same reported manganese content. For convenience, the manganese loading of washcoated cordierite samples, normalized to the relative amount of washcoat, is given between brackets in Table 1.

It should be noted that at 31.8 wt.% Mn on alumina, the stoichiometric Mn/Al ratio for MnAl\textsubscript{2}O\textsubscript{4} is reached. Above this percentage also the presence of a MnO phase is expected, even if all the alumina is transformed into MnAl\textsubscript{2}O\textsubscript{4}.

2.4 Characterization

The acceptors were characterized with a number of techniques: XRD to determine the type and the dispersion of the component on the sorbent, BET to determine the surface area of the sorbent, AAS and ICP-AES to determine the amount of manganese on the sorbent. Analysis were performed after impregnation and calcination.

For X-ray diffraction (XRD) analysis of the washcoated monolith, the washcoat layer was mechanically removed from the washcoated monoliths and carefully ground. The \( \gamma \)-\( \text{Al}_2\text{O}_3 \) based samples were ground as such. A Siemens d500 diffractometer with
diffracted beam monochromator and CuKα-radiation was used during all XRD experiments.

BET surface analyses, by adsorption of N₂ at 77 K, were performed with a Micromeretics Digisorp 2600 and a Quantachrome Autosorp 6B.

To determine the metal loading of the samples the manganese was dissolved with a concentrated HCl solution. ICP-AES or flame atomic absorption spectrometry (AAS) was performed to determine the metal loading of the samples.

3 Results

3.1 Characterization after impregnation and calcination

A series of acceptor materials was prepared with manganese loadings ranging from 1.4 to 36 wt.%. Table 1 gives an overview of the samples prepared. Figure 2 shows that the manganese loading increases with the number of impregnations. For particles and alumina monoliths the increase is almost linear, but with increasing manganese loading a saturation behavior is visible. For washcoated monoliths an almost linear increase over the whole concentration range is observed.

![Figure 2](image)

The color of the samples after impregnation and calcination ranged from light brown to very dark brown or black going from low to high loadings. In Figure 3 a cross section of a washcoated impregnated and calcined monolith sample is shown. The washcoat layer (dark brown) can be clearly seen on the white cordierite support. The color of the samples, which were prepared via deposition precipitation, was black.
Table 1. Samples used for sulfiding and regeneration experiments (see Chapters 10, 11, and 12). The absolute wt.% Mn is given. If applicable the values relative to the active phase (washcoat + manganese phase) are given between brackets. The most frequently used samples are given in bold. I = impregnated, D = deposition precipitation, M = monolith, P = particle, W = washcoated, S = small (50-70 μm), L = large (3-7 mm), 1-12 is the sample number which indicates the number of impregnations (except for the washcoated samples). Low = low loading sample (Mn < 8wt.%), medium = medium loading sample (8 < Mn < 32 wt.%), high = high loading sample (32 < Mn < 40 wt.%), vhigh = very high loading (Mn > 40 wt.%) sample. Standard procedure is wet impregnation with 2 M MnAc2 solution and calcination in air at 873-973 K. The procedure is indicated in the column “procedure”.

<table>
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<th>Sample code</th>
<th>Mn Loading</th>
<th>Procedure</th>
<th>Wt.% Mn (1)</th>
<th>$S_{BET}$ m$^2$/g</th>
<th>Pore vol ml/g</th>
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<td>γ-Al2O3, Mn3O4, Mn2O3</td>
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<td>standard</td>
<td>12</td>
<td>167</td>
<td>0.36</td>
<td>γ-Al2O3</td>
</tr>
</tbody>
</table>
The preparation of manganese based sorbents

| IPS3 | medium | standard | 16 | 146 | 0.32 | γ-Al₂O₃, Mn₃O₄ |
| IPS4 | medium | standard | 20 | 130 | 0.29 | γ-Al₂O₃, Mn₃O₄ |
| IPS5 | medium | standard | 23 | 114 | 0.26 | γ-Al₂O₃, Mn₃O₄ |
| IPS8 | high  | standard | 33 | 83  | 0.18 | γ-Al₂O₃, Mn₃O₄, Mn₂O₃ |
| IPS10| high  | standard | 35 | 76  | -    | -               |

MnO₂  | n.p.   | 63    | -  | -   | -    |
Mn₂O₃ | see Ch.10 | 69 | 0.4 | -    | Mn₂O₃ |
Mn₃O₄ | n.p.   | 72    | -  | -    | -    |
MnO   | see Ch.10 | 77  | -  | -    | MnO  |
MnAl₂O₄| see Ch.10 | 31.8 | 14-75 | -    | MnAl₂O₄ |

n.p.: not produced.
- not measured.
1) number of impregnations with a xM solution MnAc₂.
2) reaction time.
3) value between brackets is the wt.% Mn or surface area per gram active phase (Mn₃O₄ + γ-Al₂O₃). For the calculation it is assumed that Mn is present as Mn₃O₄ and that 25 wt.% washcoat is present on a non-impregnated sample.
4) from XRD analysis.

In Figure 4 XRD spectra for impregnated samples (IPS) are shown as function of the manganese loading. If available the results for the other samples are given in Table 1. XRD reveals crystalline Mn₃O₄ and Mn₂O₃ (joint committee for powder diffraction data (JC-PDS) 10-69 and 16-154;) for samples with high loadings, see IPS5 and IPS10. For impregnated samples with low loadings (IPS1, IPL1, IM1), however, only γ-Al₂O₃ (JC-PDS 10-425) can be seen. For samples with an intermediate loading, see for example IPS3, Mn₃O₄ is observed. The same picture is observed for impregnated large particles and (washcoated) monoliths, see Table 1. In samples prepared via deposition precipitation only Mn₂O₃ is observed, also at very low metal loadings. For comparison, XRD spectra of samples prepared via impregnation and via deposition precipitation are shown in Figure 5. It can be clearly seen that the impregnated sample contains both Mn₂O₃ and Mn₃O₄ and that the sample prepared via deposition precipitation contains exclusively Mn₂O₃. Furthermore, it can be deduced that the manganese dispersion of the impregnated sample is much higher than of the sample prepared via deposition precipitation.

In Figure 6 the specific surface area, in m².g⁻¹cat⁻¹, as function of the manganese loading is depicted for impregnated samples. With increasing manganese loading it decreases. This decrease seems only dependent on the amount Mn₃O₄ deposited and not on the type of support used. For the IPS sample the theoretical line is also indicated. Up to about 20 wt.% Mn, the Mn uptake during an impregnation step is linear with the available surface area. At higher Mn loadings the decrease in surface area is significantly lower than expected. Remarkably, for samples prepared via deposition precipitation no decrease in surface area was observed (see DMC samples in Table 1).
Figure 3. Photograph of the cross-section of an impregnated and calcined washcoated monolith. Dark brown part is washcoat, white part is cordierite support. The full color photograph is shown in Appendix 2.

Figure 4. X-ray diffraction patterns for IPS samples with increasing Mn loading. Estimated crystal size for high sample IPS10 < 10 nm. \( + = \text{Mn}_2\text{O}_3 \), \( o = \text{Mn}_3\text{O}_4 \)

Figure 5. X-ray diagram of a medium loading sample prepared via deposition precipitation (DMW) and a sample prepared via wet impregnation (IPS). With Mn relative to active phase is for both sample about equal. \( + = \text{Mn}_2\text{O}_3 \), \( o = \text{Mn}_3\text{O}_4 \)
For impregnated samples also the pore-volume should decrease with increasing number of impregnations, see Table 1. In Figure 7 the pore-volume, ml/g$_{\text{sorbent}}$, of the sorbent is correlated to the increase in manganese loading after each impregnation. Also the theoretical line is depicted which is calculated for a pore volume impregnation with a 2 M manganese acetate solution, assuming complete deposition of the Mn-ions present in the liquid in the pores at the start of the impregnation. The experimental points approach the theoretical line, though after the first impregnations the amount Mn deposited is somewhat (up to 20\%) higher than the theoretical value.

**Figure 6.** Specific surface area vs. the wt.\% Mn on several samples. The surface area of the washcoated samples is related to the active material. The theoretical Mn loading at a given surface area is also given\(^1\). + = IPL samples, * = IPS samples, ■ = IM samples.

**Figure 7.** Relationship between available pore volume and increase in manganese loading after wet impregnation. The theoretical increase is also indicated. It is assumed that the increase of the amount of manganese is equal to the amount which would be obtained with pore volume impregnation.

### 4 Discussion

It is shown by XRD that repeated wet impregnation followed by calcination at 873-973 K can result in samples with a large amount of homogeneously distributed manganese oxides (Mn$_3$O$_4$ and Mn$_2$O$_3$; Figure 3)\(^2\). Hereby the type of support used is unimportant. Even at high loadings, up to 33 wt.\% Mn, the crystal size remains small, see Figure 4. At low manganese loadings (< 8 wt.\% Mn; IPS1, IPL1, IMW1) the

\(^1\) It is assumed that the Mn uptake during each impregnation is linearly dependent on the available surface area: 0.038 g Mn/m$^2$ sorbent. Furthermore, Mn:O = 1:1.4 is assumed.

\(^2\) XRD showed Mn$_3$O$_4$ and Mn$_2$O$_3$ on the impregnated samples after calcination (Figure 4). From thermodynamics, see Figure 1 in Chapter 10, only Mn$_3$O$_4$ is expected. Probably, at a lower Mn loading a better interaction with the support results in a reduction of the manganese oxide phase to Mn$_3$O$_4$. With the same reasoning it can be explained that samples prepared via deposition precipitation and samples with a very high loading contain mainly Mn$_3$O$_4$. 

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manganese oxide is likely present as a mono-layer because these phases can not be detected by XRD. Theoretically, a mono layer can contain about 0.4-0.5 mg Mn/m², which is close to the amount of Mn deposited on these samples. Other authors\textsuperscript{11,12,17} showed that for relatively low loading, < 0.5 mg Mn/m², the preparation of alumina-supported manganese oxide catalysts by using manganese acetate as precursor results in a highly dispersed oxide phase. For low loading the good dispersion can be explained by the ionic interactions with acidic, up to 2 wt.% manganese, and basic, above 2 wt.% manganese, surface -OH groups of the alumina\textsuperscript{11}. For high loading other factors may play an important role because only a limited number of -OH groups is available at the surface of the support. As already mentioned in the Introduction the Mn-acetate solution might have a favorable crystallization behavior on a microscopic level leading to a high dispersion. The high drying rate by microwave heating will positively contribute to this behavior\textsuperscript{14}.

The deposition precipitation method results in relatively large Mn₂O₃ crystals, see Figure 5. Due to the release of OH⁻ ions, see Introduction, the manganese precursor crystallizes somewhere on the support. The fact that, with increasing Mn loading, no decrease in surface area is observed indicates that precipitation occurs mainly at the outside, instead of the inside of the pores of the support. As indicated in the Introduction diffusion into the pores is a rather slow process, so crystallization at the outside of the pores may be explained by diffusion limitation. Another factor may be insufficient interaction with the alumina and drying phenomena, or crystallization occurring preferably on existing crystals. In Figure 8 a schematic representation is given of the presumed manganese distribution after deposition precipitation and after wet impregnation.

With increasing loading the size of the manganese crystals, of course, increases as has been shown in Figure 4. Also the amount of manganese which can be deposited on the support during each impregnation step decreases with increasing Mn loading.

It is not clear whether the increase in manganese loading should be correlated to the available surface area or to the available pore volume. Obviously, a correlation with both these properties exists. From Figures 6 and 7 it follows that up to about 20 wt.% Mn a good correlation is obtained with the available surface area, and at higher Mn loadings to the available pore volume. This suggests that homogeneous deposition occurs throughout the particle. The fact that during the first impregnations the amount of Mn deposited in the pores is somewhat higher than the theoretical amount indicates that some Mn²⁺ diffuses from the bulk solution to the support surface during the first steps. However, its contribution to the total amount Mn deposited on the support (typically 35 wt.% Mn) is not very large. Therefore, it is concluded that the long impregnation times used in this thesis are not necessary to obtain a high manganese loading and it is expected that dry impregnation can also be used to obtain high Mn
loadings. Probably the dispersion will be somewhat better using wet impregnation. Furthermore, it is expected that the drying at 363 K (12 hours) and the calcination time (6 hours) can be reduced towards 1-2 hours, in total.

For the preparation of a high loading sorbent on an industrial scale a one step method would be more attractive than the, currently, applied multi-step method. In the ideal case manganese acetate powder is mixed with an alumina precursor after which it is extruded and calcined, e.g. by microwave heating. A typical price per kilogram for extruded particles and monoliths would be 3-4 ECU and 9-13 ECU, respectively. This should be a subject to future research.

Figure 8. Schematic representation of the distribution of manganese oxide in/near the pore of the support as function of the manganese loading after:
A. (multiple) impregnation with manganese acetate and calcination.
B. deposition precipitation with manganese nitrate and urea.

5 Conclusions

The impregnation of γ-Al₂O₃ via wet impregnation with a manganese acetate solution appeared to be a good method to deposit a large amount of manganese oxide (Mn₃O₄ and Mn₂O₃) homogeneously onto an alumina or alumina washcoated support. Hereby, the type of γ-Al₂O₃ support is of minor importance. For low Mn loadings the
high dispersion obtained can be explained by a good interaction of Mn$^{2+}$ ions with the alumina support. For high Mn loadings it is presumed that also a favorable crystallization behavior of manganese acetate plays a role.

The applied deposition precipitation method results in the formation of relatively large manganese oxide (Mn$_2$O$_3$) crystals outside the pores of the support and is therefore not suitable as preparation method in this case.

It is expected that the production time of a sorbent can be strongly decreased by reducing the impregnation, drying, and calcination time. The preparation of a high loading sample remains, however, rather time-consuming. For production on an industrial scale the development of a one step process is recommended.

6 Literature

Sulfiding Reactions

Abstract
Sulfiding reactions have been elucidated using temperature programmed sulfiding profiles of MoO$_3$, WO$_3$, Ni, NiO and several manganese oxides on $\gamma$-Al$_2$O$_3$, and manganese aluminate (MnAl$_2$O$_4$). Also the temperature programmed steam regeneration profiles of MnS and MnS on $\gamma$-Al$_2$O$_3$ are discussed in relation to their sulfiding behavior.

Metal oxides sulfide mainly via O-S exchange and metals via oxidation. In the reduction of oxides the temperature is the most important factor, but the concentration of H$_2$S and H$_2$ is also important. During sulfiding the dispersion (crystal size) plays a major role. Solid state diffusion is slow, although strongly activated. Therefore, only at very high temperatures, typically 1200 K, the samples are completely sulfided. It is concluded that temperature programmed steam regeneration is a useful additional tool to clarify sulfiding reactions.

Furthermore, the experimental set-up for TPS, and isothermal sulfiding and regeneration experiments is discussed.
1 Introduction

Regarding sulfiding reactions an extensive amount of literature\textsuperscript{1-15} has been published. The most extensive amount of literature is on Temperature Programmed Sulfiding (TPS) studies. This chapter focuses on TPS to illustrate sulfiding reactions. Typical examples from literature are given for metal oxides which are important building blocks of commercial hydrotreating catalysts, CoMo-, NiMo-, NiW/Al\textsubscript{2}O\textsubscript{3}. Also examples are given from own experimental work on manganese based materials: manganese oxides (MnO\textsubscript{x}) and manganese aluminate (MnAl\textsubscript{2}O\textsubscript{4}). Furthermore, temperature programmed regeneration with steam of sulfided manganese samples is studied.

Depending on the temperature the following types of reactions might be expected for metal oxides or metal oxysulfides during TPS:

\textit{Sulfiding}\textsuperscript{*} of metal oxides by O-S exchange:

\[
\text{MeO}_x + \text{H}_2\text{S} \quad \Rightarrow \quad \text{MeO}_{x-1}\text{S} + \text{H}_2\text{O}
\] (1)

\textit{Sulfiding of metal oxysulfides} by O-S exchange:

\[
\text{MeO}_x\text{S}_y + \text{H}_2\text{S} \quad \Rightarrow \quad \text{MeO}_{x-1}\text{S}_{y+1} + \text{H}_2\text{O}
\] (2)

\textit{Reduction of metal oxides}\textsuperscript{2*}:

\[
\text{MeO}_x + \text{H}_2 \quad \Rightarrow \quad \text{MeO}_{x-1} + \text{H}_2\text{O}
\] (3)

\textit{Reduction of metal oxysulfides}\textsuperscript{4*}:

\[
\text{MeO}_x\text{S}_y + \text{H}_2 \quad \Rightarrow \quad \text{MeO}_{x-1}\text{S}_{y+1} + \text{H}_2\text{S}
\] (4)

\textit{Reduction of metal sulfides}\textsuperscript{1*}:

\[
\Delta T
\]

\[
\text{MeS}_x + \text{H}_2\text{S} \quad \Rightarrow \quad \text{MeS}_{x-1} + 0.5 \text{S}_2 + \text{H}_2\text{S}
\] (5a)

\[
\text{MeS}_x + \text{H}_2 \quad \Rightarrow \quad \text{MeS}_{x-1} + \text{H}_2\text{S}
\] (5b)

\textsuperscript{*} Besides sulfiding with H\textsubscript{2}S, sulfiding with other sulfur containing components like COS, CS\textsubscript{2} and S\textsubscript{2} is, in many cases, also possible.

\textsuperscript{2*} In most cases reduction without hydrogen is also possible at certain temperatures. In that case oxygen is formed in stead of H\textsubscript{2}O, or S\textsubscript{x} in stead of H\textsubscript{2}S. See respectively, Figure 1 and Figure 3 in Chapter 10.
Sulfiding reactions

Sulfiding of metals:

\[
\text{Me} + \text{H}_2\text{S} \quad \Rightarrow \quad \text{MS} + \text{H}_2
\]  

(6)

2 Experimental

In order to study the sulfiding reactions and mechanisms of bulk or supported metal oxides Temperature Programmed Sulfiding (TPS) proved to be an excellent technique\(^2,\,5,\,8,\,16\)

![Diagram of experimental setup](image)

**Figure 1a.** Simplified scheme of the experimental set-up for TPS and isothermal sulfiding and regeneration experiments. A detailed scheme see is given in Appendix 1.

A simplified scheme of the TPS apparatus is shown in Figure 1a. In Figure 1b a photograph of the equipment is shown. The samples are held in a quartz tube between two quartz-wool plugs. The composition of the sulfiding gas mixture is 2-4 mol\% H\(_2\text{S}\), 25-50 mol\% H\(_2\) and 46-72 mol\% Ar. A UV (ultra-violet) spectrophotometer is used to determine H\(_2\text{S}\) consumption or production and a TCD (thermal conductivity detector) to determine the H\(_2\) consumption or production. In some cases a mass spectrometer has been used to monitor the H\(_2\text{O}\) concentration in
the effluent gas. The sulfiding is divided in an isothermal sulfiding stage at room
temperature, followed by the temperature programmed sulfiding stage and an
isothermal stage at the end of the temperature program. The equipment was also
used for temperature programmed regeneration with steam. In that case a mixture
of argon and steam (70/30) was led over a sulfided sample. In some cases the TPS
was used for TPR (temperature programmed reduction) experiments to determine
the O/Mn ratio of a sample. During these experiments the feed contained H₂ and
Argon (70/30).

The metal oxides discussed here were made in house. For the preparation of Mo,
W, and Ni systems the reader is referred to the literature. To obtain supported
manganese oxides, a γ-Al₂O₃ support was impregnated with a manganese acetate
solution and calcined at 875 K. Details about the preparation are given in Chapter 8.

TPS profiles were recorded from supported and unsupported manganese oxide
samples. Also temperature programmed regeneration with steam with supported
and unsupported manganese sulfide samples have been performed. Below an
overview of the samples studied is given.

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<th>Sample code, Mn loading</th>
<th>Treatment after calcination, analysis technique</th>
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<td>-, TPS</td>
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<td>-, TPS</td>
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<td>MnO</td>
<td>-</td>
<td>2 sulf. and reg. with steam at 1223 K, TPR</td>
</tr>
<tr>
<td>MnS</td>
<td>-</td>
<td>2 sulf. and 1 reg. with steam at 1123 K, TPR</td>
</tr>
</tbody>
</table>

a) The crystalline structure could not be determined with XRD because of the high
dispersion. TPR revealed a O/Mn ratio of 1.7. This component is a mixture of MnO₂ and
Mn₄O₇.
b) The composition of these samples was determined with XRD. The O/Mn ratio measured
with TPR was in accordance with XRD.
c) This sample is calcined at 575 K.
**Figure 1b.** Photograph of the experimental set-up for TPS and isothermal sulfiding and regeneration measurements.
3 TPS Profiles of Transition Metal Oxides

The results are treated by discussing the three classes of transition metal oxides in some detail:

- oxidic and reduced Ni/γ-Al$_2$O$_3$
- manganese oxides (see Table 1)
  - supported (MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$ on γ-Al$_2$O$_3$)
  - unsupported (Mn$_2$O$_3$, MnO and MnAl$_2$O$_4$)

The results of the manganese oxides are supported by temperature programmed regeneration of the corresponding manganese sulfides.

3.1 Sulfiding of MoO$_3$/γ-Al$_2$O$_3$ and WO$_3$/γ-Al$_2$O$_3$ catalysts

Figure 2 shows a typical TPS pattern of a MoO$_3$/γ-Al$_2$O$_3$ catalyst. Already at room temperature H$_2$S consumption takes place due to adsorption on, or sulfiding of specific sites, probably electron deficient Mo sites; this uptake is not depicted. In the low-temperature region, below 500 K, a major H$_2$S consumption is observed which correlates to a H$_2$O production. No H$_2$ consumption is observed in this region. This shows that sulfiding takes place by O-S exchange on Mo(VI), Eq. (1) and (2). At approximately 500 K, H$_2$S is produced in a sharp peak, coupled with H$_2$ consumption. This peak can be explained by the breaking of Mo(VI)-S bonds, resulting in the reduction of Mo(VI) to Mo(IV) and the formation of H$_2$S, Eq. (4). This should not be taken too literally. H$_2$ might well assist the Mo-S bond breaking. At high temperatures, above 500 K, sulfiding is completed to form MoS$_2$, again via O-S exchange, Eq. (2).

A typical TPS pattern of a WO$_3$/γ-Al$_2$O$_3$ catalyst is shown in Figure 3. Again an H$_2$S consumption is observed at room temperature, indicating that sulfiding already takes place at very mild conditions. In the temperature programmed stage two regions can be distinguished. Sulfiding takes place at a steady rate below 600 K with a broad maximum in the rate of H$_2$O production. H$_2$ uptake is only seen in the high-temperature region. Sulfiding below 600 K is not coupled to reduction (H$_2$ consumption). Therefore, it can be concluded that it proceeds through the formation of W(VI) oxysulfides via O-S exchange, Eqs. (1) and (2). Above 600 K the sulfiding is accelerated (onset of H$_2$ consumption). This suggests that H$_2$ removes oxygen from the oxysulfide, and, thereby, creates sites where sulfiding can continue, Eqs. (1) and (2).
From the TPS patterns, the following sulfiding mechanism for MeO₃/Al₂O₃ (Me is Mo or W) catalysts can be deduced, see Figure 4. In comparison with MoO₃/Al₂O₃ catalysts, WO₃/Al₂O₃ catalysts are more difficult to sulfide. This lower sulfidability is ascribed to the difference in the binding energy of the metal-oxygen bond. W and O are more strongly bonded than Mo and O leading to a relatively high stability of WO₃/Al₂O₃.

In summary: Tungsten and Molybdenum 6+ transition metal oxides sulfide into 4+ sulfides. The ease of sulfiding and the temperature the metal is reduced at is, however, dependent on the specific metal which, in turn, determines the specific bonding strength between the metal and oxygen.
Figure 4. Schematic representation of the sulfiding mechanism for MeO$_2$/Al$_2$O$_3$ catalysts. Me is W or Mo. After Arnoldy$^1$.

Figure 5. TPS patterns ($H_2S$, $H_2$) for NiO/$\gamma$-Al$_2$O$_3$ catalyst. Adapted from Janssens et al.$^3$.

Figure 6. TPS patterns ($H_2S$, $H_2$) for reduced Ni/$\gamma$-Al$_2$O$_3$ catalyst. Adapted from Magnus$^4$. 
3.2 Sulfiding of oxidic and reduced Ni/γ-Al₂O₃ catalysts

The TPS patterns of an oxidic and reduced Ni catalyst are shown in Figure 5 and 6. The oxidic Ni catalyst shows an isothermal H₂S uptake at room temperature followed by a small desorption of H₂S upon temperature increase. The major H₂S consumption peak is found between 350 and 550 K, which demonstrates sulfiding by O-S exchange. Between 500 and 600 K an H₂S production coupled with an H₂ consumption is found indicating reduction of the nickel sulfide, Eq. (5). From the profiles it can be calculated that formally sulfiding takes place from NiO in NiS to Ni₃S₂. Therefore, sulfiding of the oxidic Ni takes place according to:

\[
\begin{align*}
+H₂S & \quad +H₂ \\
NiO & \rightarrow NiS & \rightarrow Ni₃S₂ \\
-H₂O & \quad -H₂S
\end{align*}
\] (8)

Reduced Ni/γ-Al₂O₃ catalysts, which consist of alumina supported Ni⁰-crystallites, show a different sulfiding behavior than NiO/γ-Al₂O₃ catalysts. The reduced catalysts show besides the isothermal sulfiding at 210 K and a small H₂S desorption slightly above 210 K, a large H₂S consumption peaks at 270, 300 and 380 K coupled with a H₂ production, Eq. (6). At 750 K a small H₂S production coupled with H₂ consumption takes place. This indicates that the sulfiding reaction takes place according to:

\[
\begin{align*}
+H₂S & \quad +H₂ \\
Ni^0 & \rightarrow NiS & \rightarrow Ni₃S₂ \\
-H₂ & \quad -H₂S
\end{align*}
\] (9)

Obviously the reduction to Ni₃S₂ is only partially.

An interesting difference between the sulfiding of oxidic and reduced Ni catalysts is that the reduced catalysts sulfide at a significantly lower temperature. This is explained by a higher dissociation rate of H₂S on the nickel metal surface and a higher solid state diffusion rate in the reduced nickel core.

**In summary:** both oxidic and metallic Ni sulfide to NiS, followed by reduction to Ni₃S₂. Ni⁰, however, sulfides more easily than Ni²⁺ because Ni⁰ is more active towards H₂S dissociation and the solid state diffusion rate is higher in the reduced nickel core.
4 Sulfiding of Manganese Oxides and Regeneration of Manganese Sulfide

4.1 Temperature Programmed Sulfiding

A typical TPS profile of $\gamma$-Al$_2$O$_3$ supported Mn$_2$O$_3$ and MnO$_2$ (MnO$_{1.7}$) is given in Figure 7. Analog to the previous cases, already at room temperature H$_2$S consumption takes place. Physically adsorbed H$_2$S is released at the beginning of the temperature program. A broad H$_2$S absorption band is observed from 375 to 575 K, Eqs. (1) and (2). At 675 K H$_2$S is produced, corresponding with H$_2$ consumption. Obviously, at this temperature MnS$_2$ is reduced to MnS, Eq. (5).

At higher temperatures, 700-1200 K, a broad band of H$_2$S absorption can be seen and H$_2$ consumption is observed again at 780 and 970 K. This H$_2$ consumption coincides with a somewhat reduced H$_2$S absorption. Apparently, at these temperatures simultaneous reduction of manganese(IV) sulfide (H$_2$S production) and H$_2$S adsorption by manganese oxide occurs.

In Chapter 10 the thermodynamics of manganese oxides and manganese sulfides are discussed. From a thermodynamical point of view, all manganese oxides and manganese aluminate can be sulfided at room temperature, see Figure 6 in Chapter 10. In practice, only a small part of the manganese oxide is sulfided at room temperature. Furthermore, theoretically the reduction of Mn$^{4+}$ to Mn$^{2+}$ takes place around 675 K, see Figure 3 in Chapter 10. Indeed, a large part of the reduction is observed around this temperature but also two reduction peaks are observed at higher temperatures. The deviation of the absorption and reduction temperatures from the theoretical temperatures can be explained by the occurrence of diffusion limitation in the solid phase of the materials used. In the core of the material the diffusion limitation is most severe, and decreases towards the surface. As solid state diffusion is strongly activated, material at the surface will be sulfided at a lower temperature than material in the core. Only at very high temperatures (> 1200 K) the thermodynamical equilibrium for the whole material is reached and the actual phases can be used as a reference point.

It was estimated from Figure 7 that the total amount of H$_2$ consumed was 0.76 times the net amount$^3$ of absorbed H$_2$S (adsorbed-released). If all MnO$_{1.7}$ is converted to MnS this value should be 0.70, so it is concluded that the experimental value is close to the theoretical value. The reactions which take place during the TPS of MnO$_{1.7}$ are:

---

3$^*$ net amount = H$_2$S absorbed minus H$_2$S produced

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Sulfiding reactions

\[
\begin{align*}
\text{MnO}_{1.7} + \text{H}_2\text{S} & \rightarrow \text{MnS}_{1.7} + \text{H}_2 \\
-\text{H}_2\text{O} & \rightarrow & -\text{H}_2\text{S} \\
& \Rightarrow & \text{MnS}
\end{align*}
\]

\[\text{H}_2\text{S} \quad \text{H}_2 \quad \text{isotherm} \]

\[\text{Temperature (K)} \]

\[\text{Figure 7. TPS pattern and hydrogen consumption of } \gamma\text{-Al}_2\text{O}_3 \text{ supported MnO}_{1.7}. \text{ The } \text{H}_2 \text{ and } \text{H}_2\text{S signals may be compared quantitatively.}\]

\[\text{Figure 8. TPS patterns of different supported and unsupported manganese oxides: a) Mn}_3\text{O}_4 \text{ on } \gamma\text{-Al}_2\text{O}_3, \text{ b) unsupported Mn}_3\text{O}_3, \text{ c) unsupported MnAl}_2\text{O}_4, \text{ d) unsupported MnO. Only the H}_2\text{S profile is shown.}\]

It should be mentioned that MnO\(_{1.7}\) is not a stable crystalline manganese oxide phase but as the crystals on the support are too small the actual crystalline structure could not be determined. Probably several phases exists: MnO\(_2\), Mn\(_2\)O\(_3\) and amorphous phases, see also Chapter 11. In the next section the MnS phases are discussed in more detail.

In Figure 8 TPS patterns of supported and unsupported manganese oxides are compared. In this figure the H\(_2\) signals are not depicted but, if required, they will be included in the discussion.

In Figure 8a the TPS curve of \(\gamma\)-alumina supported Mn\(_3\)O\(_4\) is depicted. Absorption occurs between 375 and 650 K. A minor H\(_2\)S absorption peak is observed around 425 K, and a major absorption peak around 600 K. At 675 K a H\(_2\)S production peak is
observed. This H$_2$S production is clearly smaller than the H$_2$S production depicted in Figure 7.

Approximately, the same sulfding pattern as described above is observed for the unsupported Mn$_2$O$_3$ sample, which is shown in Figure 8b. The onset and the end of the H$_2$S absorption shifts, however, to higher temperatures; 450 and 850 K, respectively. Remarkably, no H$_2$S production peak is observed and the H$_2$ consumption occurs around 725 K.

MnS and MnS$_2$ are the only stable manganese sulfides, see Figure 3 in Chapter 10. From thermodynamic calculations in Chapter 10, it follows that during sulfding of Mn$_2$O$_3$ and Mn$_3$O$_4$ below 625 K both MnS$_2$ and MnS are formed. At higher temperatures Mn$^{4+}$ is reduced to Mn$^{2+}$ and MnS and H$_2$S or S formed, depending on whether hydrogen is present. The amount of H$_2$S production and H$_2$ consumption is, of course, dependent on the O/Mn ratio of the initial manganese oxide. The higher this ratio the higher the H$_2$S production and H$_2$ consumption. This difference is clearly illustrated with the sulfding of MnO$_{1.7}$ and Mn$_2$O$_4$.

If the absorption rate is higher than the reduction rate no H$_2$S production will be detected. This explains why in Figure 8b no H$_2$S production can be observed, although reduction of the manganese takes place. Around 675 K, where H$_2$S production takes place, the net H$_2$S absorption is, however, clearly reduced.

The shift towards higher sulfding temperatures of the unsupported manganese oxide material, as compared to the supported material, can be explained by diffusion limitation in the relative large crystals of the unsupported material.

From above it can be concluded that during the sulfdation of Mn$_3$O$_4$ and Mn$_2$O$_3$ the following reactions take place.

\[
\begin{align*}
\text{Mn}_3\text{O}_4 + &H_2 \text{S} &\rightarrow &2 \text{MnS} + \text{MnS}_2 \rightarrow 3 \text{MnS} \quad (11) \\
- &H_2\text{O} &\rightarrow & - &H_2\text{S} \\
\text{Mn}_2\text{O}_3 + &H_2 \text{S} &\rightarrow & \text{MnS}_2 + \text{MnS} \rightarrow 2 \text{MnS} \quad (12) \\
- &H_2\text{O} &\rightarrow & - &H_2\text{S}
\end{align*}
\]

MnAl$_2$O$_4$, depicted in Figure 8c, shows two major absorption peaks around 1000 K. XRD revealed the formation of MnS and $\gamma$-Al$_2$O$_3$, see Figure 3 in Chapter 11. No H$_2$ consumption or H$_2$S production was observed. Unsupported manganese oxide, depicted in Figure 8d, shows its major absorption peak at 500 K, Eq. (1). From
800-1200 K a broad adsorption band can be seen. Also no H₂ consumption or H₂S production was observed.

Comparing MnO and MnAl₂O₄ a remarkable difference is observed: MnAl₂O₄ is more stable towards sulfiding although the dispersion of the sample is much higher. This can be explained by the thermodynamics for sulfiding, which are more favorable for MnO, see Figure 6 in Chapter 10. The diffusion limitation in MnO is expected to be more severe because of its rocksalt structure (see section 2.1 of Chapter 10). Therefore, at least part of the sulfidation takes place at a higher temperature. In the core of MnO the diffusion is so severe that sulfidation temperature is comparable or even higher than the sulfiding temperature of MnAl₂O₄. Generally, a metal aluminate is more stable towards sulfiding than its corresponding metal oxide. This seems unfavorable during sulfiding, but during regeneration the opposite holds.

Under the conditions applied Mn²⁺ can not be reduced to Mn⁰, see Chapter 10. It is therefore self-evident that during the TPS of MnO and MnAl₂O₄ no H₂S production or H₂ consumption is observed. This leads to the following reactions for MnAl₂O₄ and MnO:

\[
\begin{align*}
\text{MnAl}_2\text{O}_4 + \text{H}_2\text{S} & \rightarrow \text{MnS} + \gamma-\text{Al}_2\text{O}_3 & (13) \\
\text{MnO} + \text{H}_2\text{S} & \rightarrow \text{MnS} + \text{H}_2\text{O} & (14)
\end{align*}
\]

4.2 Temperature programmed regeneration with steam of γ-Al₂O₃ supported and unsupported MnS

In principle, the structure of sulfides can also be studied by temperature programmed regeneration of a metal sulfide17,18. Temperature programmed regeneration of MnS with steam was carried out for supported samples with respectively 16 and 35 wt% Mn (IPS3 and 10, see Chapter 8), and unsupported MnS. The results are given in Figure 9. During regeneration of IPS3 three main H₂S production peaks are seen at 475, 730 and 1050 K.

The high loading sample, IPS10, has its main H₂S production between 1020 K and 1220 K, with a maximum at 1175 K. Around 500 K also some small H₂S production is observed and from 800-1020 K a small but increasing amount of H₂S is detected.
Unsupported MnS is clearly more difficult to regenerate. The regeneration starts around 800 K and increases up to 1273 K, the highest temperature applied. After one hour at 1273 K the sample is still not completely regenerated.

The most interesting observation during regeneration with steam is the fact that supported MnS is easier to regenerate than the unsupported MnS, while, as has been shown above, the opposite holds during sulfidation. This can be explained by thermodynamics (Figure 6 in Chapter 10). The metal-oxygen bonding in a metal aluminate is stronger than in a normal metal oxide. During sulfiding the metal-oxygen bond has to be broken, whereas during regeneration a metal-oxygen bond is formed. Sulfiding of metal aluminates is, therefore, relatively difficult. As a consequence the formation of such a stable bond during regeneration is relatively easy.

![Graph](image)

*Figure 9. Temperature programmed regeneration with steam of MnS. The profiles of a medium (IPS3) and high loading γ-Al₂O₃ supported sample (IPS10), and of unsupported MnS are depicted.*

On the other hand the occurrence of solid state diffusion limitation in the core of the bulk material also plays an important role because, theoretically, regeneration is possible at lower temperatures. This is also shown by the difference between IPS3 (16 wt% Mn) and IPS10 (35 wt% Mn). The shift to a higher regeneration temperature for IPS 10 compared to IPS3 can be explained by the occurrence of less diffusion limitation in IPS3.

The regeneration peak observed for IPS3 at 450 K represent surface sites which regenerate relatively easy. For IPS10 only small H₂S peaks are observed at low
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temperatures because the relative contribution of surface sites is small. Moreover, the surface sites of IPS10 partly consist of MnS which during regeneration has to be transformed into MnO which is, relatively difficult. The role of surface sites is important for the desulfurization depth in a desulfurization process and will be discussed in more detail in Chapter 11.

In contrast with the sulfiding reactions no re-oxidation occurs during TP-regeneration with steam because this is thermodynamically not possible with H₂O.

From the discussion given above the following reactions for the regeneration with steam of unsupported and γ-Al₂O₃ supported MnS are deduced:

\[
\begin{align*}
\text{MnS} & \quad + \quad \text{H}_2\text{O} \\
& \rightarrow \\
\text{MnO} & \quad \text{- H}_2\text{S}
\end{align*}
\]

(15)

\[
\begin{align*}
\text{MnS/γ-Al}_2\text{O}_3 & \quad + \quad \text{H}_2\text{O} \\
& \rightarrow \\
\text{MnAl}_2\text{O}_4 & \quad \text{- H}_2\text{S}
\end{align*}
\]

(16)

In summary: During TPS all manganese oxides and manganese aluminate can be sulfided. Besides thermodynamics, diffusion limitation at low temperatures plays a role as, thermodynamically, all components can be sulfided at room temperature. Analogously to the previous cases physisorbed H₂S is released at the beginning of the temperature program. Supported manganese oxides, sulfide relatively easy at low temperatures compared to bulk manganese oxides. This can be explained by relatively severe solid state diffusion limitation in the core of the unsupported bulk materials. The driving force for sulfidation of MnAl₂O₄ is less than for MnO, which causes sulfidation of MnAl₂O₄ to occur at higher temperatures. It is apparent that solid state diffusion is strongly activated. Therefore, only at very high temperatures, for example 1200 K, the thermodynamic equilibrium can be used as a reference point. Between 600-700 K manganese is reduced to Mn²⁺ which results in the simultaneous production of H₂S and consumption of H₂. This is in accordance with thermodynamic calculations. It is self-evident that no reduction was observed

---

4 IPS10 has a relatively low surface area compared to that of IPS3. This is due to the more severe pretreatment of IPS10 and the higher Mn loading. See also Chapters 8 and 11.

5 MnAl₂O₄ contains 31.8 wt% Mn. Samples with a higher Mn loading such as IPS10 can, therefore, not be completely regenerated towards MnAl₂O₄.
during the sulfidation of MnO and MnAl₂O₄ as Mn²⁺ is the most reduced state under the conditions applied.

Comparing the temperature programmed regeneration profiles of supported MnS and unsupported MnS with the corresponding TPS profiles, of MnAl₂O₄ and MnO it can be concluded that MnO is sulfided easily and difficult to regenerate and that MnAl₂O₄ is relatively difficult to sulfide but easy to regenerate. During regeneration no re-oxidation of manganese occurs.

5 Conclusions

Temperature programmed sulfiding is a very useful tool to clarify sulfiding reactions. Metal oxides sulfide mainly via O-S exchange and metals via oxidation. In the reduction of oxides the temperature is very important, H₂S and H₂ also is important. During sulfiding the dispersion (crystal size) plays a major role. Solid state diffusion is slow, although strongly activated. Therefore, only at very high temperatures, typically 1200 K, the samples are completely sulfided. It is concluded that temperature programmed regeneration is a useful additional tool to clarify sulfiding mechanisms.

6 Literature

1. Arnoldy, P., Temperature-programmed reduction (TPR) and sulfiding (TPS) of hydrodesulfurization catalysts, Ph.D. Thesis, University of Amsterdam (1985)
A Thermodynamic Analysis of Manganese based Sorbents for High Temperature Coal Gas Desulfurization

Abstract
The thermodynamical properties and structure of manganese oxides, manganese sulfides and manganese aluminate (\(\text{MnAl}_2\text{O}_4\)) have been reviewed. Also the thermodynamics of sulfidation and regeneration with different reactants, viz. \(\text{O}_2\), \(\text{H}_2\text{O}\), \(\text{SO}_2\), \(\text{CO}_2\), and \(\text{H}_2\) are summarized. Furthermore, the reactions with other components, such as \(\text{HCl}\), \(\text{HF}\), \(\text{CO}\), \(\text{H}_2\), \(\text{HCN}\) and \(\text{NH}_3\), present in coal gas are dealt with.

Manganese oxides and manganese-aluminate both absorb \(\text{H}_2\text{S}\) over the temperature range studied. Compared with \(\text{MnAl}_2\text{O}_4\), manganese oxides absorb \(\text{H}_2\text{S}\) and \(\text{COS}\) more strongly. Consequently, regeneration of sulfided manganese oxides is relatively difficult and oxygen is needed for regeneration. The resulting regeneration product, \(\text{SO}_2\), is in most cases not desired. Sulfided \(\text{MnAl}_2\text{O}_4\) can be regenerated with \(\text{SO}_2\) and \(\text{H}_2\text{O}\) leading to elemental sulfur and \(\text{H}_2\text{S}\), respectively. Especially, elemental sulfur is an attractive regeneration product. It is concluded that desulfurization of dry coal gas with \(\text{MnAl}_2\text{O}_4\) is attractive, eventually in combination with another sorbent, because elemental sulfur can be produced during regeneration.

\(\text{HCl}\) and \(\text{HF}\) are also absorbed by \(\text{MnO}\) and \(\text{MnAl}_2\text{O}_4\) but at high temperatures \(\text{H}_2\text{S}\) and \(\text{COS}\) absorb preferentially. An advantage from a process point of view is that \(\text{MnCl}_2\) on \(\text{Al}_2\text{O}_3\), in principle, does not react with \(\text{SO}_2\) but relatively easy with steam. This enables a component specific regeneration.
1 Introduction

Thermodynamic calculations can be a powerful tool to investigate the properties and potential of materials for regenerative high temperature desulfurization. In Chapter 7 a comparison has been made between oxides of several metals. In this chapter a detailed thermodynamical analysis will be presented for sulfiding and regeneration of different oxides of manganese and manganese aluminate. Also the crystalline structures will be discussed.

Compared to gases and liquids accurate calculations of thermodynamical properties of solid materials is time consuming as, up till now, experimental data are needed. Only for 8000 solid compounds these data are available. For reactions carried out at low temperatures one should not overestimate the value of these calculation as bulk diffusion limitation and the kinetics can be so slow that the calculated equilibrium is never reached. At high temperatures this does apply to a much lower extent.

In this chapter equilibrium constants and specific concentrations for the reactions of interest are calculated as a function of the temperature at atmospheric pressure (the absolute pressure has very little influence on the solid-gas equilibria). In most cases also the heat of reaction is calculated. The thermodynamic data are not specified for each crystallographic structure separately and may, therefore, not be complete.

Analogous to sulfiding the regenerative desulfurization process is a gas-solid reaction where the gas is contacted with the solid acceptor material. In the calculations, the solid material and the gases are supposed to be in a closed box. The equilibrium compositions of the reactions are calculated by minimizing the Gibbs Energy, using the program “Chemsage 3.0” with “Microterm” database. This program calculates the thermodynamics of the bulk material. Hereby it is assumed that the solid phase have a constant “activity”. Below this is discussed further.

When the solid phase is in excess one can assume that the activity of the solid is constant and, as a consequence, the equilibrium $K^{eq}$ constant can be expressed as the ratio of the gas phase concentrations. So for the sulfiding of a metal oxide:

$$\text{MeO (bulk) + H}_2\text{S} \rightleftharpoons \text{MeS (bulk) + H}_2\text{O}$$

(1)

$$K^{eq} = \left( \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{S}]} \right)^{eq}$$

(2)

If the $[\text{H}_2\text{O}]/[\text{H}_2\text{S}]$ ratio is larger than $K^{eq}$, the sulfided phase is unstable and will
disappear, and if the ratio is higher than $K^b_{\text{eq}}$, H$_2$S uptake takes place and a sulfided phase is formed.

In previous work$^{1,2}$ it was assumed that mainly surface sites act as acceptor sites during the sulfidation. In analogy to heterogeneous catalysis one can argue that surface sites concentrations are not constant. When this separate surface phase consisting of sulfidable sites is taken into account they should also be included in the equilibrium expression.

$$\text{MeO (surface)} + \text{H}_2\text{S} \quad \Rightarrow \quad \text{MeS (surface)} + \text{H}_2\text{O}$$  \hspace{1cm} (3)

In a thermodynamic sense the surface is considered to be a separate phase. The equilibrium constant $K^s_{\text{eq}}$ can be defined as:

$$K^s_{\text{eq}} = \frac{[\text{H}_2\text{O}] [\text{MeS (surface)}]}{[\text{H}_2\text{S}] [\text{MeO (surface)}]}_{\text{eq}}$$  \hspace{1cm} (4)

The role of surface sites will be discussed further in Chapter 11. To obtain good desulfurization, thermodynamics requires that either, $K^b_{\text{eq}}$ should be sufficiently high (Eq. 2) or the sorbent should have a high surface area (Eq. 4), resulting in a good surface capacity, even if bulk sulfide would be non-existing according to thermodynamics.

2 Thermodynamic Stability and Structure of Manganese Oxides, Aluminates and Sulfides

Many different types of manganese oxides exist. The majority of literature$^{3-17}$ on manganese oxides applies to oxides with manganese in the oxidation states 2, 3, 4, and 7. Most manganese oxides can be formed out of another manganese oxide, depending on the temperature and atmosphere.

In Figure 1 the stability of manganese oxides as function of temperature is shown. MnO$_2$ is the most stable form up to about 770 K. Above this temperature it decomposes towards Mn$_2$O$_3$ which is stable up to about 1250 K. Hereafter it is further reduced towards Mn$_3$O$_4$. Above 1900 K MnO is the only stable phase.$^*$

Further reduction to metallic manganese is neither possible with hydrogen nor with carbon monoxide as reducing agents in the temperature range studied (300-3000 K).

---

$^*$ At room temperature MnO is oxidized in air to an extent depending on the particle size. Usually only the surface of MnO particles will be oxidized.
From Figure 2 it is clear that, if Al₂O₃ is present, MnAl₂O₄ (manganese aluminate) is the most stable phase between 1100 and 2450 K. At lower temperature Mn₂O₃, between 800 and 1100 K, or MnO₂, below 800 K, is stable. These data agree with the literature cited above.

Figure 1. Stability diagram for the Mn-O system. Equilibrium amounts for reaction of 1 mol O₂ and 1 mol Mn as a function of the temperature. Calculated with "Chemsage 3.0" and "Microterm" database.

Figure 2. Stability diagram for the Mn-O-Al system. Equilibrium amounts for reaction of 1 mol O₂, 1 mol Mn and 1 mol Al₂O₃ as a function of the temperature. Calculated with "Chemsage 3.0" and "Microterm" database.

The stability diagram for manganese sulfides is given in Figure 3. Up to about 625 K MnS₂ is the most stable phase. At higher temperatures manganese is reduced from Mn⁴⁺ to Mn²⁺ under the formation of sulfur and MnS. These data agree with literature, where manganese sulfides are mainly in the oxidation state 2 or 4⁺. The reduction of Mn⁴⁺ to Mn²⁺ has also been measured and is depicted in Chapter 9, Figures 7 and 8.

Figure 3. Stability diagram for the Mn-S system. Equilibrium amounts for reaction of 1 mol S₂ and 1 mol Mn as a function of the temperature. Calculated with "Chemsage 3.0" and "Microterm" Database. L and G means liquid and gas, respectively.
2.1 Lattice structures and colors\textsuperscript{21-23}

The unit cell of a spinel MnAl\textsubscript{2}O\textsubscript{4} contains 32 oxygen ions in cubic closest packing and corresponds to the formula Mn\textsubscript{8}Al\textsubscript{16}O\textsubscript{32}, see Figure 4. The unit cell contains 32 octahedral holes and 64 tetrahedral holes, in which 8 Mn\textsuperscript{2+} ions and 16 Al\textsuperscript{3+} ions are arranged. Eight out of the 64 tetrahedral holes are occupied by Mn\textsuperscript{2+} ions and 16 out of the 32 octahedral holes are occupied by Al\textsuperscript{3+} ions, which is normally the case for spinel structures. The number of unoccupied sites is large and therefore metal ions are relatively mobile in this lattice. In Chapter 11 it is shown that this mobility is important in a sulfiding-regeneration process.

![Figure 4](image_url) \hspace{1cm} ![Figure 5](image_url)

*Figure 4. The lattice structure of spinel. The large circles represent oxygen ions. Small circles represent octahedral cations (black, Al\textsuperscript{3+} in MnAl\textsubscript{2}O\textsubscript{4}) and tetrahedral cations (white, Mn\textsuperscript{2+} in MnAl\textsubscript{2}O\textsubscript{4}), respectively.*

*Figure 5. The rock salt crystal structure. Small circles represent cations (Mn\textsuperscript{2+} in MnO or MnS), large circles anions (S\textsuperscript{2-} or O\textsuperscript{2-} in MnS and MnO, respectively).*

The position of the Mn\textsuperscript{2+} ion in the aluminate spinel is different from the position in its simple oxide form. MnO and MnS have a rock salt structure shown in Figure 5; all the Mn\textsuperscript{2+} ions occupy octahedral holes.

\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} is an important alumina support, with a high specific surface area. This material is relatively stable up to 1073 K. The structure of \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} is very similar to the spinel structure discussed above. Compared to a spinel however, one-ninth of the positions normally occupied by cations is unoccupied. These cation vacancies may be distributed in different ways among the tetrahedral and octahedral holes. An increased stability and mechanical strength can be obtained in several ways, \textit{e.g.} by addition of a small amount of divalent metal ions, or surface stabilization by La, Si\textsuperscript{24}. 

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The color of manganese oxides, aluminates and sulfides is given in Table 1.

**Table 1. Colors of manganese oxides, aluminates and sulfides.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>black-brown</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>black</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>brown-black</td>
</tr>
<tr>
<td>MnO</td>
<td>green</td>
</tr>
<tr>
<td>MnAl₂O₄</td>
<td>beige</td>
</tr>
<tr>
<td>MnS (crystalline)</td>
<td>green</td>
</tr>
<tr>
<td>MnS (amorphous)</td>
<td>pink</td>
</tr>
</tbody>
</table>

3 Thermodynamics of Reactions During Sulfiding of MnₙOₙ and MnAl₂O₄

In this paragraph the thermodynamics of the reactions during sulfiding of manganese based sorbents in a coal gas environment are considered.

3.1 Sulfiding of MnO and MnAl₂O₄

The sulfidation of a bulk metal (Me) oxide can be represented as:

\[ \text{Me}_x\text{O}_y \text{(bulk)} + x \text{H}_2\text{S} + (y-x) \text{H}_2 \Leftrightarrow x \text{MeS} \text{(bulk)} + y \text{H}_2\text{O} \]  

Hereby the oxygen is exchanged with sulfur and, if the metal is reduced, hydrogen consumption takes place, see also Chapter 9.

The equilibrium constant \( K_{eq}^{b} \) can be expressed as the ratio of the gas phase concentrations under equilibrium conditions. In Eq. 6 \( K_{eq}^{b} \) is given for \( x = y \).

\[ K_{eq}^{b} = \frac{[\text{H}_2\text{O}]/[\text{H}_2\text{S}]}{[\text{H}_2\text{S}]_{eq}} \]  

The reaction for the sulfiding of MnO with H₂S is:

\[ \text{MnO} + \text{H}_2\text{S} \Leftrightarrow \text{MnS} + \text{H}_2\text{O} \]  

For MnAl₂O₄ the reaction is given by:

\[ \text{MnAl}_2\text{O}_4 + \text{H}_2\text{S} \Leftrightarrow \text{MnS} + \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O} \]
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From a thermodynamical analysis it appears that reaction with H₂S is favorable for all manganese based metal oxides. The equilibrium constants for the reaction with H₂S of MnAl₂O₄, MnO and some other manganese oxides are presented in Figure 6 and Table 2. Sulfiding is thermodynamically possible over the whole temperature range indicated: 600 to 1400 K. For MnAl₂O₄ it is less favorable than for MnO. At 600 K the equilibrium constant for sulfiding of MnO is 30000 while for MnAl₂O₄ it is 25. The difference with the other manganese oxides is even larger. The relatively low equilibrium constant for MnAl₂O₄ makes it relatively sensitive for water. With increasing temperature the equilibrium constant decreases. So, with increasing temperature the water sensitivity increases.

The enthalpies of reaction for sulfiding, which are given in Table 2, are almost constant with increasing temperature and amount to -10 kJ/mol for MnAl₂O₄ and -50 kJ/mol for MnO. The reaction enthalpies for the other manganese oxides is rather high and amounts to about -150 kJ/mol.

![Figure 6. Equilibrium constants of different manganese oxides and MnAl₂O₄ for reaction with H₂S (Eqs. 7 a-d and 8).](image1)

![Figure 7. Equilibrium constants for reaction of MnO (solid lines) and MnAl₂O₄ (dotted lines) with HF and HCl (Eqs. 11-14).](image2)

In coal gas a part of the sulfur is present as COS; typically 10% of the H₂S concentration. It is calculated that both MnO and MnAl₂O₄ can effectively remove COS from the coal gas, although MnO to a lower level than MnAl₂O₄; see Table 2. The reaction for the sulfiding of MnO with COS is:
\[
\begin{align*}
\text{MnO} + \text{COS} & \rightleftharpoons \text{MnS} + \text{CO}_2 \\
\text{For MnAl}_2\text{O}_4 \text{ the reaction is given by:} \\
\text{MnAl}_2\text{O}_4 + \text{COS} & \rightleftharpoons \text{MnS} + \text{Al}_2\text{O}_3 + \text{CO}_2 
\end{align*}
\]

(9)

(10)

Table 2. Equilibrium constants and reaction enthalpies of several reactions with manganese based solids during sulfiding. The most important reactions are written in bold.

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Reaction</th>
<th>Temperature (K)</th>
<th>}</th>
<th>10^5\log K_{\text{eq}}</th>
<th>\Delta H_r(T)_{\text{kJ/mol}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>MnO + H$_2$S $\rightleftharpoons$ MnS + H$_2$O</td>
<td>600</td>
<td>4.5</td>
<td>2.6</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>MnAl$_2$O$_4$ + H$_2$S $\rightleftharpoons$ MnS + Al$_2$O$_3$</td>
<td>1000</td>
<td>1.4</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>7b</td>
<td>MnO$_2$ + 2 H$_2$S $\rightleftharpoons$ MnS$_2$ + 2 H$_2$O</td>
<td>1400</td>
<td>13.5</td>
<td>7.8</td>
<td>6.3</td>
</tr>
<tr>
<td>7c</td>
<td>MnO$_3$ + 3 H$_2$S $\rightleftharpoons$ MnS$_2$ + MnS + 3 H$_2$O</td>
<td>600</td>
<td>13.7</td>
<td>8.1</td>
<td>6.6</td>
</tr>
<tr>
<td>7d</td>
<td>MnO$_4$ + 4 H$_2$S $\rightleftharpoons$ MnS$_2$ + 2 MnS + 4 H$_2$O</td>
<td>1400</td>
<td>15.1</td>
<td>9.3</td>
<td>7.8</td>
</tr>
<tr>
<td>9</td>
<td>MnO + COS $\rightleftharpoons$ MnS + CO$_2$</td>
<td>600</td>
<td>7.1</td>
<td>-3.9</td>
<td>3.1</td>
</tr>
<tr>
<td>10</td>
<td>MnAl$_2$O$_4$ + COS $\rightleftharpoons$ MnS + Al$_2$O$_3$ + CO$_2$</td>
<td>600</td>
<td>4.0</td>
<td>-2.4</td>
<td>2.0</td>
</tr>
<tr>
<td>11</td>
<td>MnO + 2 HCl $\rightleftharpoons$ MnCl$_2$ + H$_2$O</td>
<td>600</td>
<td>6.9</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>12</td>
<td>MnO + 2 HF $\rightleftharpoons$ MnF$_2$ + H$_2$O</td>
<td>600</td>
<td>7.8</td>
<td>1.4</td>
<td>0.001</td>
</tr>
<tr>
<td>13</td>
<td>MnAl$_2$O$_4$ + HCl $\rightleftharpoons$ MnCl$_2$ + Al$_2$O$_3$</td>
<td>600</td>
<td>3.8</td>
<td>-0.21</td>
<td>-0.86</td>
</tr>
<tr>
<td>14</td>
<td>MnAl$_2$O$_4$ + 8 HF $\rightleftharpoons$ MnF$_2$ + 2 AlF$_3$ + 4 H$_2$O</td>
<td>600</td>
<td>21.7</td>
<td>0.04</td>
<td>-5</td>
</tr>
</tbody>
</table>

Summarizing: From a thermodynamical analysis it follows that for all manganese based metal oxides reaction with H$_2$S and COS is favorable. The best desulfurization depth towards H$_2$S and COS is obtained with Mn$_3$O$_7$. MnAl$_2$O$_4$ is, however, also suitable for desulfurization unless the feed contains a large amount of water, for example 15 vol.%.²

3.2 Influence of HCl, HF and other impurities on the sulfidation performance

As already mentioned in Chapter 7 the influence of other impurities than H$_2$S and COS on the performance of the acceptor is a point of major concern. If these impurities would react with the acceptor and this reaction would be irreversible, the acceptor capacity might be reduced during prolonged operation. It is well

² Surface sites on MnAl$_2$O$_4$ have a relatively good desulfurization depth. This will be discussed in Chapter 11.
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conceivable that during reaction/regeneration cycles corrosion occurs due to reaction with impurities. Also coke and carbonyl formation may decrease the acceptor performance.

Thermodynamic calculations showed that HCl and HF can also be absorbed by manganese oxides and manganese aluminate, see Figure 7. NH₃ and HCN do not react with the system, not depicted in a Figure. The reaction of MnO and MnAl₂O₄ with HCl and HF are given below.

\[
\begin{align*}
\text{MnO} + 2 \text{HCl} & \rightleftharpoons \text{MnCl}_2 + \text{H}_2\text{O} & (11) \\
\text{MnO} + 2 \text{HF} & \rightleftharpoons \text{MnF}_2 + \text{H}_2\text{O} & (12) \\
\text{MnAl}_2\text{O}_4 + 2 \text{HCl} & \rightleftharpoons \text{MnCl}_2 + \text{Al}_2\text{O}_3 & (13) \\
\text{MnAl}_2\text{O}_4 + 8 \text{HF} & \rightleftharpoons \text{MnF}_2 + 2 \text{AlF}_3 + 4 \text{H}_2\text{O} & (14)
\end{align*}
\]

Table 2 shows that HF and HCl are absorbed less strongly at high temperatures, say 1100 K, than H₂S and COS. This means that H₂S and COS are preferably absorbed at the preferred operation temperature of 1123 K. However, during sulfiding the acceptor capacity will not be fully used by H₂S and COS, but also some HCl and HF will absorb. The reaction of HCl and HF with the sorbent is reversible; thus regeneration with steam is possible. HCl and HF can however not be removed by SO₂. This enables a design for a component specific regeneration, see the discussion in section 4 and Chapter 12.

Metal chlorides are relatively volatile and therefore some loss of manganese might occur in case the sorbent is applied at very high temperatures, \( T_{\text{boil}} \text{MnCl}_2 = 1503 \text{ K} \). The boiling point for most other metal chlorides is lower, e.g. \( T_{\text{boil}} \text{ZnCl}_2 = 1005 \text{ K} \), and application at very high temperatures will lead to a steady sorbent deactivation in time if the coal gas contains a considerable amount of HCl. Compared to other sorbents MnCl₂ is relatively stable.

In summary: Both HCl and HF can be absorbed by both MnO and MnAl₂O₄. At 1100 K they are less strongly absorbed than H₂S and COS. HCN and NH₃ are not absorbed.

3.3 Other Possible Reactions during Sulfidation

Coal gas contains several components and many reactions can occur between them. Some of these reactions take place in the gas phase but are accelerated by the presence of a sorbent. The most important reactions for the manganese based sorbents are summarized below. In Table 3 the equilibrium constants and heats of reaction are given.
3.3.1 Water Gas Shift Reaction

\[
\text{CO} + \text{H}_2\text{O} \quad \Rightarrow \quad \text{H}_2 + \text{CO}_2 \quad (15)
\]

From Table 3 it is concluded that the water gas shift reaction can be an important exothermic reaction in coal gas; in particular at low relatively temperatures. The reaction reduces the amount of water in coal gas. A decrease in water percentage in coal gas improves the desulfurization depth of a sorbent which is, of course, favorable (see Eq. 6)

3.3.2 "Sour-gas Shift Reactions"

\[
\begin{align*}
\text{COS} + \text{H}_2\text{O} & \quad \Rightarrow \quad \text{CO}_2 + \text{H}_2\text{S} \\
\text{CO} + \text{H}_2\text{S} & \quad \Rightarrow \quad \text{COS} + \text{H}_2
\end{align*}
\]

(16) \hspace{1cm} (17)

Table 3 shows that the conversion of COS to H$_2$S via the reaction shown in Eq. (16) is favorable and, therefore, much of COS in coal gas can be transformed into H$_2$S. On the other hand, always some COS will be formed via the reaction shown in Eq. (17) if no COS is present in the coal gas.

3.3.3 "Other reactions"

\[
\begin{align*}
\text{H}_2\text{S} & \quad \Rightarrow \quad 0.5 \text{S}_2 + \text{H}_2 \\
\text{H}_2\text{S} + 2 \text{H}_2\text{O} & \quad \Rightarrow \quad 3 \text{H}_2 + \text{SO}_2
\end{align*}
\]

(18) \hspace{1cm} (19)

Table 3. Equilibrium constants and reaction enthalpies for the most important reactions in the gas phase.

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Reaction</th>
<th>Temperature (K)</th>
<th>$10^2 \log K_{eq}$</th>
<th>$\Delta H_f(T)$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>CO + H$_2$O $\Rightarrow$ H$_2$ + CO$_2$</td>
<td>600 1100 1400</td>
<td>-1.5 0 -0.34</td>
<td>-39 -31</td>
</tr>
<tr>
<td>16</td>
<td>COS + H$_2$O $\Rightarrow$ CO$_2$ + H$_2$S</td>
<td>600 1100 1400</td>
<td>-1.1 -1.4 -1.4</td>
<td>-7.5 -2.9</td>
</tr>
<tr>
<td>17</td>
<td>CO + H$_2$S $\Rightarrow$ COS + H$_2$</td>
<td>600 1100 1400</td>
<td>2.5 1.3 1.0</td>
<td>-31 -30</td>
</tr>
<tr>
<td>18</td>
<td>H$_2$S $\Rightarrow$ 0.5 S$_2$ + H$_2$</td>
<td>600 1100 1400</td>
<td>-5.2 -1.7 -0.8</td>
<td>87 91</td>
</tr>
<tr>
<td>19</td>
<td>H$_2$S + 2 H$_2$O $\Rightarrow$ 3 H$_2$ + SO$_2$</td>
<td>600 1100 1400</td>
<td>-14.8 -6.1 -3.8</td>
<td>210 228</td>
</tr>
</tbody>
</table>
Eqs. (18) and (19) show the formation of \( S_2 \) and \( SO_2 \) from \( H_2S \). The data in Table 3 show that at low temperatures and if hydrogen is present this will practically not occur. However, at high temperatures and without hydrogen or CO present a considerable amount of \( S_2 \) and some \( SO_2 \) can be formed. Of course, in coal gas this is not realistic but during steam regeneration a considerable amount of the \( H_2S \) formed can be converted into these components, see Chapter 11.

3.3.4 Coke formation
The formation of coke is not expected because manganese is not a catalyst for coke formation, contrary to e.g. metallic iron. Also the preferred very high operation temperature suppresses coke formation. In case a minor amount of coke is formed on the sorbent it can, however, easily be removed by steam, for example during the regeneration.

In summary: The water gas shift reaction can be a very important reaction during high temperature desulfurization as it indirectly increases the desulfurization depth of the sorbent. Furthermore, COS is easily converted to \( H_2S \). Other reactions are of minor importance in the coal gas environment.

4 Regeneration of Manganese Sulfides with Different Reactants
In this paragraph the sorbent regeneration with different reactants, viz. \( O_2 \), \( H_2O \), \( SO_2 \), \( CO_2 \), and \( H_2 \), is discussed.

Sorbent regeneration is the exchange of a sulfur ion for an oxygen ion. Generally, oxygen is applied for regeneration, although this has distinct disadvantages. The regeneration process is very difficult to control because of its highly exothermal nature and, as a consequence, the oxygen flow has to be diluted strongly and a highly diluted \( SO_2 \) containing gas is the result. Moreover, \( SO_2 \) is not a very attractive product. Alternative regeneration methods may be based on the use of \( H_2O \), \( SO_2 \), \( CO_2 \), and \( H_2 \) to remove sulfur from the acceptor bed. Even exchange of a sulfur ion for another ion than oxygen is a possibility although this is not (yet) a realistic option. We investigated several possibilities: for example, regeneration with \( OF_2 \) might lead to the direct production of the commercially attractive \( SF_6 \). A number of regeneration reactions are summarized below and in Table 4. Reaction equilibrium constants as function of the temperature for MnS and MnS on \( Al_2O_3 \) are depicted in Figures 8 and 9 and an overview of reaction enthalpies is given in Table 4.

Steam-regeneration is simply the reverse of the original sulfiding and \( H_2S \) is the product formed. The regeneration product which is formed with \( SO_2 \) is mainly \( S \).
while regeneration with CO₂ produces S₄ and SO₂, see Eqs. 24, 25, 29, 30. Of course the production of S₄ is in most cases desirable. To clarify the meaning of S₄ its phase equilibria are shown in Figure 10. It shows that at temperatures just above the boiling point of sulfur mainly S₂-8 are formed. With increasing temperatures S₂ becomes the most stable phase.

4.1 Regeneration of manganese sulfide

\[
\begin{align*}
\text{MnS} + 1.5 \text{O}_2 & \rightleftharpoons \text{MnO} + \text{SO}_2 & (20) \\
\text{MnS} + \text{H}_2\text{O} & \rightleftharpoons \text{MnO} + \text{H}_2\text{S} & (21) \\
\text{MnS} + 0.5 \text{SO}_2 & \rightleftharpoons \text{MnO} + 0.75 \text{S}_2 & (22) \\
\text{MnS} + \text{CO}_2 & \rightleftharpoons \text{MnO} + \text{CO} + 0.5 \text{S}_2 & (23) \\
\text{MnS} + 3 \text{CO}_2 & \rightleftharpoons \text{MnO} + \text{SO}_2 + 3 \text{CO} & (24) \\
\text{MnS} + \text{H}_2 & \rightleftharpoons \text{Mn} + \text{H}_2\text{S} & (25)
\end{align*}
\]

4.2 Regeneration of Manganese Sulfide on Alumina

\[
\begin{align*}
\text{MnS} + \text{Al}_2\text{O}_3 + \text{O}_2 & \rightleftharpoons \text{MnAl}_2\text{O}_4 + \text{SO}_2 & (26) \\
\text{MnS} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{MnAl}_2\text{O}_4 + \text{H}_2\text{S} & (27) \\
\text{MnS} + \text{Al}_2\text{O}_3 + 0.5 \text{SO}_2 & \rightleftharpoons \text{MnAl}_2\text{O}_4 + 0.75 \text{S}_2 & (28) \\
\text{MnS} + \text{Al}_2\text{O}_3 + \text{CO}_2 & \rightleftharpoons \text{MnAl}_2\text{O}_4 + \text{CO} + 0.5 \text{S}_2 & (29) \\
\text{MnS} + \text{Al}_2\text{O}_3 + 3 \text{CO}_2 & \rightleftharpoons \text{MnAl}_2\text{O}_4 + \text{SO}_2 + 3 \text{CO} & (30)
\end{align*}
\]

As follows from Figures 8 and 9, the regeneration of MnS with H₂O is thermodynamically difficult. The same holds for regeneration with SO₂. Also regeneration with CO₂ and H₂, see Table 4, is practically impossible.

The regeneration of MnS on alumina is much easier with all regenerants, provided that during regeneration MnAl₂O₄ is formed instead of MnO. SO₂ is a better regenerant than H₂O above 800 K. Although the regeneration with CO₂ is thermodynamically more favorable than for unsupported MnS it is expected that it is practically impossible.
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Figure 8. Thermodynamic equilibrium constants of MnS with different regenerants (Eqs. 20-25)\textsuperscript{3}. Figure 9. Thermodynamic equilibrium constant of MnS/Al\textsubscript{2}O\textsubscript{3} with different regenerants (Eq. 26-30)\textsuperscript{3}.

Table 4. Equilibrium constants and reaction enthalpies for regeneration of MnS with several reactants. The most important reactions are written in bold.

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Reaction</th>
<th>Temperature (K)</th>
<th>(10^3 \log K_{eq} )</th>
<th>( \Delta H_r^o(T) ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>MnS + 1.5 O\textsubscript{2} \rightleftharpoons SO\textsubscript{2} + MnO</td>
<td>600</td>
<td>36</td>
<td>-469</td>
</tr>
<tr>
<td>20</td>
<td>MnS + 1.5 O\textsubscript{2} \rightleftharpoons SO\textsubscript{2} + MnO</td>
<td>1100</td>
<td>18</td>
<td>-469</td>
</tr>
<tr>
<td>20</td>
<td>MnS + 1.5 O\textsubscript{2} \rightleftharpoons SO\textsubscript{2} + MnO</td>
<td>1400</td>
<td>13.2</td>
<td>-469</td>
</tr>
<tr>
<td>21</td>
<td>MnS + H\textsubscript{2}O \rightleftharpoons MnO + H\textsubscript{2}S</td>
<td>600</td>
<td>-4.5</td>
<td>49</td>
</tr>
<tr>
<td>21</td>
<td>MnS + H\textsubscript{2}O \rightleftharpoons MnO + H\textsubscript{2}S</td>
<td>1100</td>
<td>-2.6</td>
<td>52</td>
</tr>
<tr>
<td>22</td>
<td>MnS + 0.5 SO\textsubscript{2} \rightleftharpoons MnO + 0.75 S\textsubscript{2}</td>
<td>600</td>
<td>-5</td>
<td>73</td>
</tr>
<tr>
<td>22</td>
<td>MnS + 0.5 SO\textsubscript{2} \rightleftharpoons MnO + 0.75 S\textsubscript{2}</td>
<td>1100</td>
<td>-2.1</td>
<td>73</td>
</tr>
<tr>
<td>22</td>
<td>MnS + 0.5 SO\textsubscript{2} \rightleftharpoons MnO + 0.75 S\textsubscript{2}</td>
<td>1400</td>
<td>-1.3</td>
<td>73</td>
</tr>
<tr>
<td>23</td>
<td>MnS + CO\textsubscript{2} \rightleftharpoons MnO + 0.5 S\textsubscript{2} + CO</td>
<td>600</td>
<td>-11.2</td>
<td>176</td>
</tr>
<tr>
<td>23</td>
<td>MnS + CO\textsubscript{2} \rightleftharpoons MnO + 0.5 S\textsubscript{2} + CO</td>
<td>1100</td>
<td>-4.3</td>
<td>174</td>
</tr>
<tr>
<td>23</td>
<td>MnS + CO\textsubscript{2} \rightleftharpoons MnO + 0.5 S\textsubscript{2} + CO</td>
<td>1400</td>
<td>-2.5</td>
<td>174</td>
</tr>
<tr>
<td>24</td>
<td>MnS + H\textsubscript{2} \rightleftharpoons H\textsubscript{2}S + Mn</td>
<td>600</td>
<td>-15.8</td>
<td>188</td>
</tr>
<tr>
<td>24</td>
<td>MnS + H\textsubscript{2} \rightleftharpoons H\textsubscript{2}S + Mn</td>
<td>1100</td>
<td>-8.7</td>
<td>190</td>
</tr>
<tr>
<td>24</td>
<td>MnS + H\textsubscript{2} \rightleftharpoons H\textsubscript{2}S + Mn</td>
<td>1400</td>
<td>-6.2</td>
<td>190</td>
</tr>
<tr>
<td>25</td>
<td>MnS + 3 CO\textsubscript{2} \rightleftharpoons MnO + SO\textsubscript{2} + 3 CO</td>
<td>600</td>
<td>-34</td>
<td>381</td>
</tr>
<tr>
<td>25</td>
<td>MnS + 3 CO\textsubscript{2} \rightleftharpoons MnO + SO\textsubscript{2} + 3 CO</td>
<td>1100</td>
<td>-8.7</td>
<td>374</td>
</tr>
<tr>
<td>25</td>
<td>MnS + 3 CO\textsubscript{2} \rightleftharpoons MnO + SO\textsubscript{2} + 3 CO</td>
<td>1400</td>
<td>-4.8</td>
<td>374</td>
</tr>
<tr>
<td>26</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 1.5 O\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + SO\textsubscript{2}</td>
<td>600</td>
<td>40</td>
<td>-509</td>
</tr>
<tr>
<td>26</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 1.5 O\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + SO\textsubscript{2}</td>
<td>1100</td>
<td>19</td>
<td>-511</td>
</tr>
<tr>
<td>26</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 1.5 O\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + SO\textsubscript{2}</td>
<td>1400</td>
<td>14</td>
<td>-511</td>
</tr>
<tr>
<td>27</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + H\textsubscript{2}O \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + H\textsubscript{2}S</td>
<td>600</td>
<td>-1.4</td>
<td>9.2</td>
</tr>
<tr>
<td>27</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + H\textsubscript{2}O \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + H\textsubscript{2}S</td>
<td>1100</td>
<td>-1.1</td>
<td>9.5</td>
</tr>
<tr>
<td>27</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + H\textsubscript{2}O \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + H\textsubscript{2}S</td>
<td>1400</td>
<td>-0.99</td>
<td>9.5</td>
</tr>
<tr>
<td>28</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 0.5 SO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + 0.75 S\textsubscript{2}</td>
<td>600</td>
<td>-1.9</td>
<td>33.4</td>
</tr>
<tr>
<td>28</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 0.5 SO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + 0.75 S\textsubscript{2}</td>
<td>1100</td>
<td>-0.6</td>
<td>31.1</td>
</tr>
<tr>
<td>28</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 0.5 SO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + 0.75 S\textsubscript{2}</td>
<td>1400</td>
<td>-0.29</td>
<td>31.1</td>
</tr>
<tr>
<td>29</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + CO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + 0.5 S\textsubscript{2} + CO</td>
<td>600</td>
<td>-8.1</td>
<td>135</td>
</tr>
<tr>
<td>29</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + CO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + 0.5 S\textsubscript{2} + CO</td>
<td>1100</td>
<td>-4.9</td>
<td>131</td>
</tr>
<tr>
<td>29</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + CO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + 0.5 S\textsubscript{2} + CO</td>
<td>1400</td>
<td>-1.5</td>
<td>131</td>
</tr>
<tr>
<td>30</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 3 CO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + SO\textsubscript{2} + 3 CO</td>
<td>600</td>
<td>-20.6</td>
<td>341</td>
</tr>
<tr>
<td>30</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 3 CO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + SO\textsubscript{2} + 3 CO</td>
<td>1100</td>
<td>-6.5</td>
<td>331</td>
</tr>
<tr>
<td>30</td>
<td>MnS + Al\textsubscript{2}O\textsubscript{3} + 3 CO\textsubscript{2} \rightleftharpoons MnAl\textsubscript{2}O\textsubscript{4} + SO\textsubscript{2} + 3 CO</td>
<td>1400</td>
<td>-3.8</td>
<td>331</td>
</tr>
</tbody>
</table>

\textsuperscript{3} The lines for CO\textsubscript{2} in Figures 8 and 9 refers to the sum of Eqs. 23, 25, and 29, 30, respectively.
Application of SO₂ for the regeneration is for most metal oxides associated with undesirable sulfate formation. For MnS on alumina, however, above 700 K direct production with SO₂ is possible without sulfate formation. This is clearly shown in Figure 11. Beside the formation of sulfur it is predicted that also a small amount of S₂O is formed. In practice the SO₂ needed for regeneration can be obtained by burning part of the produced sulfur. Possible process options will be discussed in more detail in Chapter 12.

In summary: Regeneration with oxygen is always highly exothermic and (diluted) SO₂ is in most cases not the desired regeneration product. Therefore, alternative regeneration methods have been investigated from a thermodynamic point of view. Regeneration of unsupported MnS with other reactants than oxygen is very difficult. Alumina supported MnS can be regenerated with both SO₂ and H₂O because of the formation of the thermodynamically stable MnAl₂O₄ (compared to MnO). Especially regeneration with SO₂ seems promising as elemental sulfur can be formed as regeneration product. Regeneration with H₂ or CO₂ will be practically impossible. Removal of Cl and F from the sorbent is thermodynamically feasible by treatment with steam but not with SO₂. This enables a component specific regeneration.

5 Conclusions

The thermodynamic properties of manganese oxides, sulfides and manganese aluminate have been studied with respect to high temperature coal gas desulfurization.

Manganese oxides and manganese-aluminate both absorb H₂S over the temperature range studied. Compared with MnAl₂O₄ manganese oxides absorb H₂S
and COS more strongly than. Consequently, regeneration of sulfided manganese oxides is relatively difficult and oxygen is needed for regeneration. The resulting regeneration product, SO₂, is in most cases not desired. Sulfided MnAl₂O₄ can be regenerated with SO₂ and H₂O leading to elemental sulfur and H₂S, respectively. Especially, elemental sulfur is an attractive regeneration product. It is concluded that for desulfurization of dry coal gas with MnAl₂O₄ is attractive, eventually in combination with a other sorbent, because elemental sulfur can be produced during regeneration. HCl and HF are also absorbed by MnO and MnAl₂O₄ but at high temperatures H₂S and COS absorb preferentially. An advantage from a process point of view is that MnCl₂ on Al₂O₃, in principle, does not react with SO₂ but relatively easy with steam. This enables a component specific regeneration.

6 Literature

Performance and Characterization of Manganese Based Sorbents in High Temperature Desulfurization

Abstract
The applicability of a manganese based sorbent for high temperature desulfurization of dry coal gas has been studied. It appears that a “dual” sorbent consisting of crystalline MnAl$_2$O$_4$ and a small amount of disperse MnO performs best in the desulfurization of a dry type coal gas (desulfurization depth lower than 50 ppm H$_2$S). Beside these phases also an amorphous Mn-Al-O phase is present at the surface of the sorbent.

Elemental sulfur, is the only observed regeneration product during regeneration with SO$_2$, H$_2$S, and above 1000 K also some sulfur and SO$_2$ are formed with steam regeneration. The sorbent can be used in the temperature range between 673 to 1273 K but the optimum capacity is obtained between 1100 and 1200 K. For regeneration with SO$_2$ the regeneration temperature should be > 873 K to avoid sulfate formation. The acceptor capacity is high, up to 20 wt.% sulfur, and the sample appears to be stable during at least 110 sulfiding and regeneration cycles at 1123 K. The practical capacity, with a desulfurization depth of 100 ppm H$_2$S is up to 14 wt..% The surface area is relatively high after stabilization. It amounts to 13-24 m$^2$g$^{-1}$ after more than 50 cycles at 1123 K.

At high temperatures, > 1100 K, the thermodynamic calculations in Chapter 10 are in accordance with the observed (solid) phases after sulfiding and regeneration and it is concluded that thermodynamic calculations are a helpful tool to predict the actual gas and solid phase compositions at high temperatures. The performance of the surface sites can, however, not be predicted with the applied method. These surface sites play an important role during desulfurization. At “low” temperatures, below 700 K, absorption occurs mainly on these sites.

Furthermore, a sulfiding and regeneration mechanism within the sorbent material is proposed. It is discussed that during sulfiding the Mn$^{2+}$ diffuses out of the spinel structure, while Al$^{3+}$ diffuses into the spinel structure to fill the created vacancies. The resulting oxygen is exchanged with sulfur, and MnS with a rock salt crystal structure is formed. During regeneration most of the Mn$^{2+}$ diffuses back into, and Al$^{3+}$ out of, the spinel structure. After some rearrangements the O$^{2-}$ is included and one MnAl$_2$O$_4$ phase is formed. The amorphous phase present on the sorbent seems favorable for the mass transport during sulfiding and regeneration.
1 Introduction

In Chapter 7 it has been shown that the performance of a sorbent for high temperature desulfurization depends on many factors such as: the type of coal gas, the operating conditions and the reactor type in which the sorbent is used. Also the desired regeneration product is important. For these reasons, development of a tailored sorbent is in most cases coupled to its application. For example, it has been shown in Chapter 7 that the composition and temperature of coal gas vary, depending on the type of gasifier and coal. A material which is an attractive acceptor for a dry and thus strongly reducing coal gas, such as produced in a Shell type gasifier, is likely not the optimal sorbent for a wet coal gas, such as produced in a Texaco type gasifier. This is especially the case if the desired regeneration product is elemental sulfur. Also a fixed bed reactor requires a different sorbent than a fluidized bed reactor¹.

In this thesis we focus on the high temperature desulfurization of a dry type of coal gas at gasifier outlet conditions in a rotating reactor. Furthermore, the production of elemental sulfur is desired during regeneration. According to the thermodynamic calculations described in Chapter 10, MnAl₂O₄ is one of the most promising materials for this application. Not only direct production of elemental sulfur during regeneration seems possible, but the material is also relatively stable towards high temperatures, even in the presence of HCl and HF.

Chapter 8 describes the deposition of manganese oxides on γ-Al₂O₃ particles and (coated) monoliths. It is expected that these materials are, at least partly, converted into MnAl₂O₄ during regeneration. In this chapter the overall performance of the samples described in Chapter 8 is investigated. Also much attention is given to the sample characterization after sulfiding and regeneration. The list below shows the most important research items reported in this chapter. These items were chosen as they are the key items for successful development of a sorbent for high temperature coal gas desulfurization.

- characterization of the sorbent material
- sulfur uptake capacity of different samples
- desulfurization depth of different samples
- optimal absorption and regeneration temperature
- aspects of manganese loading and feed composition variation
- regeneration with H₂O and SO₂
- mechanical and thermal stability of the sorbent
- sulfiding and regeneration mechanisms
2 Experimental

2.1 Characterization of the acceptors after sulfiding and regeneration

After sulfiding and regeneration the acceptors\(^7\) were characterized with a number of techniques: XRD, BET, TEM, AAS and EDAX. These analyses were performed to correlate (a change in) the composition and morphology of the sorbent, to the sulfiding and regeneration performance at specific operation conditions. For example, if after regeneration, of an initially disperse acceptor, large MnS crystals are present and the surface area is low, it is likely that sintering occurred and that the sorbent is deactivated. In this case one could e.g. check if the operation conditions should be changed.

XRD and BET are described in Chapter 9. Transmission electron microscopy (TEM) was performed using a Philips CM 30 ST electron microscope with field emission gun as the source of electrons operated at 300 kV. Samples were mounted on a micro grid of a carbon polymer, supported by a copper grid, by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions. Also energy dispersive analysis of X-rays (EDX) was performed on the samples which were studied with TEM.

2.2 Absorption and regeneration experiments

Absorption and regeneration tests were carried out using monoliths and particles with different manganese loadings. The most important points of investigation during these tests are given in the introduction of this chapter. Table 1 shows an overview of the conditions applied. The "standard" conditions and feed composition given in Table 1 were used if no conditions are given for a specific experiment.

2.2.1 Experimental set-up

A simplified scheme of the experimental set-up is depicted in Figure 1 of Chapter 9\(^2\). It is equipped with an UV-Vis spectro photometer (Cary-1, Varian), a thermal conductivity detector (TCD, VICI) and a quadrupole mass spectrometer (MS; Leybold/Inficon). Water and H\(_2\)S were removed after passing the UV spectrophotometer with a tubular membrane dryer of Nafion\(^\circledR\) (Perma Pure) and zinc oxide bed at 723 K, respectively. In case the MS was used the zinc oxide bed and the TCD were bypassed. Gases were supplied with thermal mass flow controllers and led

\(^7\) In Table 1 in Chapter 8 an overview is given of the prepared samples and their codes. For convenience they are divided into four classes: low loading; [Mn] < 8 wt%, medium loading; 8 wt% < [Mn] < 32 wt%, high loading; 32 wt% < [Mn] < 40 wt%, very high loading; [Mn] > 40 wt%.
to a quartz reactor tube. The inner diameter of this tube was 6 mm for particles and 10 mm for monolith samples⁴. If desired, water was added to the regeneration or sulfiding gas by passing argon through a saturator.

Table 1. Overview of the applied experimental conditions.

<table>
<thead>
<tr>
<th>Sulfiding, regeneration and flushing</th>
<th>Units</th>
<th>Range</th>
<th>Standard ¹</th>
<th>Simulated coal gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>(K)</td>
<td>673-1273</td>
<td>1123</td>
<td>1123</td>
</tr>
<tr>
<td>Pressure</td>
<td>(MPa)</td>
<td>0.1-0.2</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Flow rate</td>
<td>(μmol/s)</td>
<td>7.5-75</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>Velocity</td>
<td>(m/s)</td>
<td>0.2-2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sample weight</td>
<td>(g)</td>
<td>0.1-4</td>
<td>0.25</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Sulfiding**

H₂  mol %  0-50  50  17
CO  mol %  0-70  0   35
H₂S mol %  0-5  1   0.64
COS mol %  2)  0   2) 2)
H₂O mol %  0-8  0   2.1
CO₂ mol %  2)  0   2) 2)
Ar  mol %  balance  balance  balance

**Regeneration**

H₂O  mol%  0-60  30  0
SO₂  mol%  0-100 0    50
O₂  mol%  0-8   0   0
H₂  mol%  0-70  0   0
Ar  mol%  balance  balance  balance

**Flushing**

Argon  mol%  100  100
duration  minutes  5-15  10

¹ If no experimental conditions are given in the figures or tables the "standard" conditions are used and the sample is regenerated with standard steam regeneration.
² These components are not added to the feed but are formed from the other components in the feed.

In general, the experiments involved a number of cycles. Most cycles consisted of four steps: sulfiding, flushing, regeneration, and flushing, see Figure 1. Before and after every step the composition of the feed gas, and during a step the composition of

² Appendix 1 shows the complete flow scheme of the equipment.
³ In some cases the monoliths were crushed to fit in a reactor tube with an inner diameter of 6 mm.
the gas leaving the reactor was measured. Figure 2 shows a typical profile of the UV signal at 230 nm during one cycle with steam regeneration at 1123 and 723 K. This signal is proportional to the H₂S concentration in the gas phase. During sulfiding the sample initially adsorbs all H₂S and essentially no H₂S is detected at the exit of the reactor. After a certain time, breakthrough occurs and the signal stabilizes at the feed level. The regeneration starts with a sharp and high H₂S production peak, after which the production tails off slowly. When almost all sulfur is removed the H₂S production quickly drops to zero. Elemental sulfur was produced during regeneration with SO₂ at 1123 K but could not be measured with the UV spectrometer.

During experiments two wavelengths were selected for UV absorption measurements in the range between 205 and 280 nm. Which wavelengths were selected depended on the components, H₂S or SO₂, and their concentrations. 205 nm was used to measure low H₂S concentrations. High H₂S concentrations were measured at 230 nm because the absorption is relatively low at this wavelength; if the UV absorption is very strong, the absorption is not linear to the concentration of the absorbing component.

SO₂ practically does not absorb at 230 nm. Above 260 nm only SO₂ adsorbs. The contribution of SO₂ to the absorption at 205 can be calculated if the SO₂ absorbance at, for example, 280 nm is also measured.

**Figure 1.** Schematic representation of a cycle during sulfiding and regeneration experiments. A cycle consists of 4 steps. Before and after every step the composition of the feed, and during a step the composition of the gas leaving the reactor was measured. See for experimental details Table 1.

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4° H₂O was released during sulfiding. H₂O could be condensed from the gas leaving the reactor by cooling of this gas in a cold trap.

5° CO and COS also absorb at 205 nm. If simulated coal gas was used as feed this wavelength could not be used for quantitative analyses. In that case 230 nm was used.
Automation of the equipment

The equipment was fully computerized. An OPTO 22 controller was used to control temperatures, pressures, flows, valves, and the sequence of the steps during the experiments. A complete set of experiments could be easily programmed in the Cyrano® software package and also the data recording and processing was automated. Not only the UV signal, but also the actual pressures, temperatures and flows were recorded. This made it possible to check experiments performed for a couple of days.

After each cycle a variable could be changed, for example, the composition of the sulfiding gas or the temperature. Within one step the variables were kept constant.*

![Graph](image)

**Figure 2a.** Typical curves for isothermal sulfiding at 1123 K of a high loading sample (IMW6). Co-current regeneration with steam in a fixed bed reactor**. 1) sulfiding, 2) flushing, 3) regeneration, and 4) flushing. 1a/b and 3a/b are feed signals before and after sulfiding and regeneration.

**Figure 2b.** Typical curves for isothermal sulfiding at 723 K of a high loading sample (IMW6). Co-current regeneration with steam at 723 K in a fixed bed reactor.

3 Results

3.1 Characterization**

3.1.1 Colors

The sample colors observed were green after sulfiding and beige to gray after regeneration. For some washcoated high loading samples green or pink spots after

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* In Chapter 9 the temperature was varied within the sulfiding or regeneration step.

** Time needed to sulfide all the manganese present with the chosen feed composition. Hereby an S/Mn equilibrium ration of 1 is taken.

* The fresh and calcined samples are discussed in detail in Chapter 8.
regeneration were observed. Some representative photographs of a fresh unloaded
γ-Al₂O₃ monolith, a fresh impregnated and calcined high loading monolith, a
regenerated high loading monolith, and a sulfided high loading monolith are shown
in Figure 3. The colors are white, dark brown, beige, and green, respectively.

Figure 3. Colors of different high loading monolith samples.
1) fresh unloaded (IM0), 2) fresh impregnated and calcined at
973K, 3) regenerated with steam
at 1123K after sulfiding at
1123 K., 4) sulfided after two
cycles at 1123 K. Crystalline
MnS is green and manganese
aluminate is beigt. The full color
photograph is given in
Appendix 2.

3.1.2 XRD
Figure 4 shows XRD patterns of a fresh unloaded γ-Al₂O₃ monolith, a fresh
impregnated and calcined high loading monolith, a steam regenerated high loading
monolith, and a sulfided high loading monolith. The XRD of the fresh unloaded
sample shows the diffraction pattern of γ-Al₂O₃ (10-425)². The XRD of the fresh
impregnated and calcined monolith shows the diffraction patterns of Mn₃O₄ (16-154)²
only superimposed on the pattern of γ-Al₂O₃. The XRD of the (sulfided and)
regenerated⁹ sample shows mainly MnAl₂O₄ (29-880)², but also some MnS (6-518)².
The XRD of the sample which is sulfided¹⁰ shows MnS (6-518)² and γ-Al₂O₃. The

⁹ After two sulfiding/regeneration cycles at 1123 K
¹⁰ After three sulfidings and two regenerations at 1123 K
particle size of the manganese species in pattern 2-4 is estimated with the Scherrer formula\(^3\) to be in between 10 and 20 nm. Table 2 gives an overview of the XRD results.

Regeneration with SO\(_2\) at 1123 K resulted in comparable XRD profiles as depicted in Figure 4 (not shown). However, after regeneration with SO\(_2\) below 873 K, XRD reveals also sulfate, and after regeneration at 1123 K with oxygen or SO\(_2\)/O\(_2\) XRD shows some MnO.

![Figure 4. XRD patterns for a fresh unloaded γ-Al\(_2\)O\(_3\) monolith (1, IM0), fresh impregnated and calcined (at 973 K) monolith (2), a regenerated monolith (3), and a sulfided monolith (4). a = γ-Al\(_2\)O\(_3\); b = Mn\(_3\)O\(_4\); c = MnAl\(_2\)O\(_4\); d = MnS. 2, 3, and 4 are a high loading sample (IM8).](image)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Loading of sample</th>
<th>wt% Mn (g_{\text{Mn}}/g_{\text{total}})</th>
<th>XRD regenerated with steam(^1)</th>
<th>XRD sulfided</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM8</td>
<td>high</td>
<td>32</td>
<td>MnAl(_2)O(_4) (+ minor MnS)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
<td>IM3</td>
<td>medium</td>
<td>16</td>
<td>MnAl(_2)O(_4)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
<td>IMW1</td>
<td>low</td>
<td>5.4</td>
<td>γ-Al(_2)O(_3)</td>
<td>γ-Al(_2)O(_3)</td>
</tr>
<tr>
<td>IMW6</td>
<td>high</td>
<td>36</td>
<td>MnAl(_2)O(_4)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
<td>IMW7</td>
<td>high</td>
<td>46</td>
<td>MnAl(_2)O(_4), MnO</td>
<td>γ-Al(_2)O(_3), MnS</td>
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<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
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<td>γ-Al(_2)O(_3), MnS</td>
</tr>
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<td>γ-Al(_2)O(_3), MnS</td>
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<td>MnAl(_2)O(_4)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
<td>IPS1</td>
<td>low</td>
<td>6.4</td>
<td>γ-Al(_2)O(_3)</td>
<td>γ-Al(_2)O(_3)</td>
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<tr>
<td>IPS3</td>
<td>medium</td>
<td>16</td>
<td>MnAl(_2)O(_4)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
<td>IPS5</td>
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<td>MnAl(_2)O(_4)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
<tr>
<td>IPS10</td>
<td>high</td>
<td>35</td>
<td>MnAl(_2)O(_4)</td>
<td>γ-Al(_2)O(_3), MnS</td>
</tr>
</tbody>
</table>

\(^1\) regeneration at 1123 K with SO\(_2\) gave similar results
Samples with a lower Mn loading showed the same manganese phases as described above, but the peaks broaden with decreasing manganese loading. For three sulfided samples\textsuperscript{11} with a different manganese loading this is shown in Figure 5. Also, the peak position shifts to a larger diffraction angle, while going from high loading to a low Mn loading. The unidentified peaks originate from SiC, which was used as diluent in the reactor bed.

\textbf{Figure 5.} XRD profiles after 4 sulfiding and steam regeneration cycles of samples with a different manganese loading. The manganese loading increases from bottom to top. + is MnAl\textsubscript{2}O\textsubscript{4}. Peaks not indicated originate from SiC which was used as a diluent in the reactor bed.

\textbf{Figure 6.} XRD of a medium loading sample (IPL4) after 1, 2, 3, and 5 sulfiding and steam regeneration cycles, respectively.

For samples with a low manganese loading XRD did not reveal any crystalline manganese aluminate or sulfide phases, see Table 2. In samples with a Mn loading above the stoichiometric amount present in MnAl\textsubscript{2}O\textsubscript{4}, 31.8 wt\% Mn, formation of a MnO phase occurred during regeneration with steam\textsuperscript{12}. Only above 35 wt\% Mn, this MnO phase could be detected by XRD, see Table 2. Samples prepared via deposition precipitation could not be fully regenerated; they still showed a large amount of MnS after regeneration with steam.

In Figure 6 the XRD spectra of an intermediate Mn-loading sample as function of the number of cycles are given. From the first to the fifth regeneration no significant change in the peak positions MnAl\textsubscript{2}O\textsubscript{4} is observed; but on the right side of three peaks, indicated with arrows, a small shoulder arises. The corresponding surface areas and sulfiding profiles are given in Figures 10 and 23, respectively.

\textsuperscript{11} After three cycles at 1123 K
\textsuperscript{12} See TEM and EDX analysis.
3.1.3 TEM and EDX

Typical TEM photographs are given in Figures 7-9, comparing the result of sulfiding and regeneration. For the sulfided sample also the EDX results are depicted in Figure 8b and 8c. The EDX results of the other samples are described but not shown in a figure.

Figure 7 shows the TEM picture of a high loading sample after steam regeneration that contains slightly more Mn than the stoichiometric amount to form MnAl₂O₄. Besides some amorphous material, indicated with (1) on the TEM photograph, some larger Mn-rich particles are found with EDX at the surface of the material; these particles can not be seen on this TEM photgraph.

![Figure 7. TEM photograph of (steam) regenerated high loading sample (IPS10). Besides to the crystalline (1) and amorphous material (2), some larger Mn-rich particles are found at the surface of the material; can not be seen at this photograph.](image)

TEM photographs and EDAX analysis have been made by P. Kooyman of the TU-Delft.

After sulfiding the sample is very inhomogeneous, see Figure 8. EDX shows that it contains separate particles of Mn-S-containing material with little Al-O present, see Figure 8b. Also Al-O-Mn-S-containing material with small quantities of Mn-S present, see Fig. 8c. The places of EDX measurements are indicated with (1) and (2) on the TEM photograph. The ratio between Mn and S does not vary much throughout the sample. The amorphous material at the surface looks somewhat different from the amorphous layer on the regenerated samples.

The medium loading sample contains slightly less Mn than the stoichiometric amount to form MnAl₂O₄. Figure 9 shows the TEM picture after regeneration. Although no clear separate phases are found, EDX showed inhomogenities with
Performance and characterization of manganese based sorbents in high temperature desulfurization

respect to the Mn/Al ratio. The sample also contains some amorphous material, indicated with (1) on TEM photograph. In the regenerated samples no S was found with EDX.

Figure 8a.
TEM photograph of a high loading sulfided sample (IPS10). Sample is very inhomogeneous. MnS rich (1) and MnS poor (2) spots and an amorphous phase (3) are present.

Figure 8b. EDX of sulfided high loading sample (IPS10). MnS rich spot; indicated on TEM picture in Figure 8a with (1). Peaks not indicated are from the copper in the sample grid.

Figure 8c. EDX of a sulfided high loading sample (IPS10). MnS lean spot; indicated with (2) on TEM picture. Unidentified peaks originate from copper grid.
3.1.4 BET surface area analysis

Figure 10 shows that the surface area decreases during cyclic operation with steam regeneration, mainly during the first cycles. For the sample considered it stabilizes at around 24 m²/g. In Table 3 the surface area for several samples is given; fresh, after impregnation and calcination, and after a number of cycles.

![Figure 10. BET surface area of a medium loading sample (IPL4) as a function of the number cycles at 1123 K. Regeneration with steam.]

For most impregnated samples which are regenerated with steam or with SO₂ the same behavior is observed as described above: a strong decrease of the surface area in
the first cycles, and stabilization between 13-24 m²/g. In general, sintering is more severe for samples with a high loading and samples which were regenerated with a SO₂/O₂ mixture.

Remarkably, only a small decrease in surface area is observed for the monolith sample, DM2, which was prepared via deposition precipitation, and regenerated with steam.

Table 3. BET surface area of different samples. Before and after use at 1123 K.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>referred to as</th>
<th>wt% Mn (gₘₙ/ g_active)¹</th>
<th>History</th>
<th>Regenerant</th>
<th>S_bet (m²/ g_active)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMW6</td>
<td>high</td>
<td>36</td>
<td>fresh</td>
<td>steam</td>
<td>76</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>after 75 cycles</td>
<td>steam</td>
<td>14</td>
</tr>
<tr>
<td>DM2</td>
<td>medium</td>
<td>19</td>
<td>fresh</td>
<td>steam</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after 9 cycles</td>
<td>steam</td>
<td>98</td>
</tr>
<tr>
<td>IPL4</td>
<td>medium</td>
<td>21</td>
<td>fresh</td>
<td>steam</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after 75 cycles</td>
<td>SO₂</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>after 80 cycles</td>
<td>SO₂</td>
<td>20</td>
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<td>13</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>after 50 cycles</td>
<td>SO₂/O₂²</td>
<td>6</td>
</tr>
</tbody>
</table>

¹) Mass of active phase = mass total sample - mass cordierite phase
²) Concentration O₂ is 1-8%

3.2 Isothermal cycles

3.2.1 Desulfurization depth

Typical curves for sulfiding with a dry feed and regeneration with steam at 1123 K for a high loading sample are presented in Figure 2a. The Figure is already discussed in the experimental section. During sulfiding the sample initially adsorbs all H₂S and essentially no H₂S is detected at the exit of the reactor¹³ (The detection limit was about 5 ppm).

In general, the outlet concentration of H₂S during sulfiding of high loading samples is between 5-50 ppm depending on the H₂S, CO, and H₂ concentrations, and the temperature.

Tests with simulated coal gas showed similar results (not depicted). No coke formation was observed.

¹³ As expected H₂O was released during sulfiding. H₂O could be condensed from the gas leaving the reactor by cooling of this gas in a cold trap.
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The typical sulfiding and regeneration curves for a low loading sample at 723 K are given in Figure 2b. Low loading samples, sulfided and regenerated at temperatures < 873 K, have been previously described by Wakker\textsuperscript{56} and Soerawidjaja\textsuperscript{7}. The desulfurization depth of these samples, if operated below 873 K, is < 10 ppm. At high temperatures (> 1023 K) the desulfurization depth of low and medium loading samples exceeds the 100 ppm H\textsubscript{2}S level within a relatively short time.

More details about sulfiding and regeneration are given in paragraphs 3.3 and 3.4.

3.2.2 Acceptor capacity

A typical sulfur uptake capacity\textsuperscript{14} for isothermal absorption and regeneration of a medium loading sample, at different temperatures (in temperature steps from 673 K to 1273 K and back to 673 K) is depicted in Figure 11. At all temperatures the same sample is used and at each temperature two cycles are performed. The acceptor capacity increases strongly from 873 K to 1123 K, and stabilizes. At the maximum of the curve the S/Mn ratio is around one. Going back from 1273 K to 673 K the same trend in the opposite way is observed. Below 1123 K, however, the sulfur uptake is less than the first measured capacity. This difference increases with decreasing temperature. At 673 K the capacity is even 3 times lower than the initial capacity at that temperature.

![Figure 11. Sulfur uptake capacity expressed in molar S/Mn-ratio for a medium loading sample (IPL2). Cycles from 723 K to 1223 K are indicated with ▲, and the cycles back to 723 K with ■.](image)

The acceptor sulfur uptake capacity at 1123 K as function of the manganese loading is shown in Figure 12. The uptake capacity has been measured after at least four absorption-regeneration cycles at 1123 K. The uptake acceptor capacity for all samples increases almost linearly with the manganese loading. The capacity for samples prepared via impregnation is, however, much higher than the capacity for samples

\textsuperscript{14} The acceptor capacity is based on the total amount of H\textsubscript{2}S absorbed and not on a certain breakthrough criterion. For reasons of convenience it is expressed as S/Mn ratio.
prepared via deposition precipitation. The sulfur uptake capacity for impregnated samples increases with the Mn loading. At a Mn loading of 1.4 and 35 wt% it amounts to 1.1 and 20 wt% sulfur, respectively. The manganese utilization, which is depicted in Figure 12b decreases somewhat with increasing Mn loading. For impregnated samples it starts with a S/Mn ratio around 1.2 and ends with a ratio around 0.9. For samples prepared via deposition precipitation the S/Mn ratio is around 0.3. No significant difference is observed in the S/Mn ratio for the different impregnated support types.

Figure 12a. Sulfur uptake capacity\textsuperscript{15} at 1123 K for different samples. The symbols are correlated to the sample codes as follows: \(\blacktriangle = \text{IPS, } \blacksquare = \text{DM, \(\bullet = \text{IMW, } + = \text{IPL, and } \blacklozenge = IM\)}\)

Figure 12b. Relative sulfur uptake capacity at 1123 K. See for the key Figure 12a.

3.2.3 Capacity development and mechanical stability
The acceptor sulfur uptake capacity as function of the number of cycles with standard sulfiding and standard steam regeneration is illustrated in Figure 13 for typical samples. During the first cycles the capacity, expressed in S/Mn ratio, decreases from 1.2 to 1. After this initial reduction hardly any further reduction is observed during the following 100 cycles.

In the same figure a test (35 cycles) with simulated coal gas for shows similar results. The initial reduction is less pronounced and the relative capacity is about 10% lower. No coke formation is observed during these tests.

The effective capacity\textsuperscript{16} during this experiment is around 75% of the theoretical maximum capacity (S/Mn = 1). During sulfiding of another high loading sample

\textsuperscript{15} weight % is based on Table 1 of Chapter 8 , excluding the mass of the cordierite.

\textsuperscript{16} Uptake capacity using a breakthrough criterion of 100 ppm H\textsubscript{2}S at the exit of the sorbent bed.
(IPL10) with simulated coal gas a somewhat lower effective capacity was measured; 68% of the maximum capacity.

Figure 13a. Capacity development during subsequent sulfiding and regeneration with steam for two high loading samples. IMW7 is sulfided with a simulated coal gas; see for feed gas composition Table 1.

Figure 13b. Capacity development of a medium and high loading sample during subsequent sulfiding and regeneration with SO₂.

Also cycling tests have been performed with standard sulfiding and standard SO₂ regeneration. This is shown in Figure 13b. Similar to the other experiments the intermediate loading sample shows practically no reduction. The capacity of the high loading sample declines with about 20% during 40 cycles. Addition of a small amount of oxygen, 1-5%, to the regeneration gas did not lead to a better regeneration performance (not depicted in the figure).

No mechanical damage was observed for any of the tested samples after prolonged operation. The washcoat layer on the washcoated samples was still intact. Generally, the mechanical strength of washcoated samples, both before and after isothermal cycles at 1123 K, was higher than for the pure γ-alumina samples. This was “measured” by crushing some fresh and sulfided samples in a mortar.
3.3 Sulfiding

3.3.1 Effect of H$_2$O on sulfiding
In Figure 14 the influence of H$_2$O on the sulfiding is illustrated with a low loading sample and a high loading sample.

![Figure 14a. Breakthrough curves during sulfiding of a medium loading sample, IPS3, with and without water in the sulfiding feed. 8 vol% H$_2$O and 0.7% H$_2$S in the wet feed.](image)

![Figure 14b. Breakthrough curves during sulfiding of a high loading sample, IPS10, with and without water in the sulfiding feed. The wet feed contains 4% H$_2$O and 0.7% H$_2$S.](image)

The curves for sulfiding without water are rather similar. The breakthrough of the low loading sample is only a little ahead of the high loading sample and somewhat less steep. The curves for "wet" sulfiding appear to be different from each other. The medium loading sample displays a fast breakthrough to a relatively high H$_2$S concentration followed by a slow approach towards the feed concentration. The [H$_2$O]/[H$_2$S] exit level ratio calculated from this breakthrough level is 16. The high loading sample shows two breakthrough levels. The first one is relatively low and constant; the second level is comparable to the one of the intermediate loading sample. The observed [H$_2$O]/[H$_2$S] exit level ratios for these regions are 220 and 10, respectively.

In Figure 15a sulfiding curves of an intermediate loading sample at different temperatures are given. Obviously, the [H$_2$O]/[H$_2$S] exit level ratio decreases with increasing temperature. The breakthrough time decreases with increasing temperature. In Figure 15b the numerical [H$_2$O]/[H$_2$S] exit level ratios are presented as function of the temperature. These ratio decreases from around 90 to 13 going from 973-1223 K. Also the theoretical thermodynamical equilibrium ratio is shown. This ratio decreases from 13 to 10.
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![Figure 15a](image)

**Figure 15a.** Examples of sulfiding curves for a medium loading sample (IPL4) at different temperatures. Standard sulfiding with 6 vol% H₂O in feed.

![Figure 15b](image)

**Figure 15b.** [H₂O]/[H₂S] exit level ratios for a medium loading sample (IPL4) as function of the temperature. Standard sulfiding with 6 vol% water. The theoretical thermodynamic equilibrium ratios of bulk MnAl₂O₄ as calculated with Chemsage 3.0 are also given.

In Figure 16 average[17] [H₂O]/[H₂S] exit level ratios at 1123 K for some other samples are depicted. The [H₂O]/[H₂S] exit level ratios vary from 6 to 17 for low and intermediate loading samples. Two breakthrough levels are observed for high loading samples. For very high loading samples only the low breakthrough level is observed. The [H₂O]/[H₂S] exit level ratios for these samples vary between 200 and 275.

![Figure 16](image)

**Figure 16.** [H₂O]/[H₂S] exit level ratios at 1123 K as a function of manganese content: ▲ and ■ are IPS and IMW samples, respectively. The [H₂O]/[H₂S] exit level ratios are calculated from average exit level ratios (feed up to 8 mol% H₂O). The exit level ratio for IPL4 from Figure 15b is indicated with ●.

[17] The [H₂O]/[H₂S] exit level ratios increase somewhat with increasing H₂O concentration in the feed.
Figure 17. The influence of the [CO]/[H₂] feed ratio on the sulfiding profile of a high loading sample (IMW6) at 1123 K. Feed 0.7 vol % H₂S and 2.5 vol % H₂O.

Figure 19. Influence of hydrogen concentration on sulfiding of a high loading sample (IMW5-1). Except for a variation in the amount of hydrogen the standard sulfiding procedure is used. The shaded area below the 0% H₂ curve represents SO₂ production.

3.3.2 Effect of CO, H₂, COS, and H₂S on sulfiding

The combined influence of CO and hydrogen on the sulfiding profile in the presence of water is shown in Figure 17. An increasing CO/H₂ ratio results in a lower breakthrough level and longer breakthrough time. The obvious reason is the occurrence of the water-gas-shift reaction. At the highest CO/H₂ ratio, 30% of the H₂O reacts away. Figure 18 shows the MS signal of CO, CO₂, H₂S, and COS during sulfiding with a simulated coal gas. The sulfiding starts without any water in the feed. At a certain moment, is indicated in the figure, water is added to the feed. From the start of the sulfiding CO is converted, and CO₂ is produced. After water addition, indicated with an arrow, the conversion of CO and the production of CO₂ increases. COS is detected simultaneously with the H₂S breakthrough.

Figure 19 and 20 show the effect of different concentrations CO and H₂ on the sulfiding profile without any H₂O present in the feed. Depending on the composition of the gas phase, the final H₂S concentration of the breakthrough is lower than the H₂S concentration in the feed. Obviously, under certain conditions a part of the H₂S is converted towards other components. In Figure 20 the amounts of H₂S converted, together with the products formed⁠¹⁸ are indicated by arrows.

If neither CO nor H₂ is present, the sulfiding profiles differ considerably from the other profiles and show two breakthrough levels. Some elemental sulfur deposits

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¹⁸ According to thermodynamical calculations.
at the end of the reactor tube during these experiments. Also a minor amount of SO₂ is formed. This is indicated by the shaded area in Figure 19.

No H₂S is converted if only H₂ and no CO is present, independent of the H₂ concentration. The breakthrough profiles during sulfiding with different concentrations H₂ are very much alike.

**Figure 18.** Qualitative MS signal during sulfiding of a high loading sample (IMW6) with simulated coal gas. During the first part of the sulfiding no water is added to the feed.

**Figure 20.** Influence of the H₂ and CO concentration on the sulfiding profile of a high loading sample (IPS8) during sulfiding without water, and with different CO and H₂ concentrations. 1 mol% H₂S in feed. The amount of H₂S converted together with the products formed are indicated by arrows.

Figure 20 shows that if only CO and no H₂ is added, a substantial amount of the H₂S is converted. Also some elemental sulfur was found at the end of the reactor tube after these experiments. After addition of hydrogen almost no H₂S is converted anymore. Furthermore, the H₂S conversion increases with an increase in CO concentration.

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19* In Figure 20 the UV measurements were performed at a wavelength where SO₂ does not absorb.
At high H$_2$S concentrations$^{20}$ and an Mn loading below 30 wt% two breakthrough levels are detected which are comparable to the sulfiding profile after addition of a small amount of water to the feed. An example is given in Figure 23 which is discussed in more detail in Section 3.3.4.

3.3.3 Effect H$_2$O and SO$_2$ regeneration on sulfiding
Besides H$_2$O, SO$_2$ was used as regeneration gas$^{21}$. In Figure 21 the acceptor capacities obtained after standard regeneration at several temperatures$^{22}$ with H$_2$O and SO$_2$ are compared. The difference is not large. For both methods the same capacity is observed at temperatures from 823 K to 923 K. Above this temperature the capacity of the steam regenerated sample is somewhat higher, about 5-10%.

![Figure 21. Sulfur uptake capacity as function of the temperature after respectively H$_2$O and SO$_2$ regeneration of a medium loading sample (IPLA).](image)

In Figure 22 the H$_2$S signal during H$_2$S absorption is shown after regeneration with SO$_2$ at several temperatures; i.e. from 673 to 1023 K. Below 873 K, with decreasing temperature, an increasing amount of H$_2$S is released during sulfiding. Above 873 K no H$_2$S is released and all the H$_2$S in the sulfiding feed is absorbed. After regeneration with steam no H$_2$S production is observed at any temperature.

3.3.4 Development of the sulfiding profile as function of the number of cycles
In Figure 23 typical sulfiding profiles of an intermediate Mn-loading sample are shown as a function of the number of cycles. During the first sulfiding one breakthrough is observed. In the other profiles also a second breakthrough is visible. The time between the start of the sulfiding and the steady state level of the 1$^{st}$ breakthrough decreases with increasing number of cycles.

To investigate the reason for this behavior the XRD patterns and the surface area, as function of the number of cycles, were measured. These results are shown in

\[^{20}\text{E.g. 3 vol\% H}_2\text{S and no H}_2\text{O.}\]
\[^{21}\text{During some experiments also a SO}_2/\text{O}_2\text{ mixture or diluted O}_2\text{ was used.}\]
Figure 6 and Figure 10 and have been discussed in Section 3.1.2 and 3.1.4, respectively\textsuperscript{23}. The regeneration profiles during these experiments remain almost unchanged. Only the height of the initial H$_2$S production peak decreased 10-15% (not depicted).

![Diagram of temperature vs. time with H$_2$S concentration](image)

**Figure 22.** Sulfiding profile of a high loading sample (IPL9) after regeneration with SO$_2$ at several temperatures. The regeneration temperature is indicated. The actual sulfiding temperature is 50 K above the indicated regeneration temperature.

**Figure 23.** Sulfiding profiles during subsequent sulfiding of a medium loading sample (IPL4) with 3 vol% H$_2$S.

3.3.5 Partial regeneration

From a process point of view it might be attractive to regenerate a sample partially; e.g. because the regeneration time becomes much shorter without loosing too much of the acceptor capacity. Figure 24 depicts the effect of incomplete regeneration on the sulfiding profile of a low loading sample. Even with a small amount of non-

\textsuperscript{22} Below 823 K, the sulfur uptake capacity is not indicated because of severe sulfate formation during regeneration with SO$_2$.

\textsuperscript{23} No significant change in the peak positions of MnAl$_2$O$_4$ is observed but a small shoulder suggests the formation of another phase. The surface area decreases in 75 cycles to 20% of the initial value.
regenerated sample hardly any complete absorption occurs. The height of the first breakthrough level increases with decreasing regeneration time. The \([\text{H}_2\text{O}]/[\text{H}_2\text{S}]\) exit level ratio at the highest level of the first breakthrough corresponds to 5.

![Graph showing sulfiding profiles of a low loading sample (IPS1) with a decreasing time of regeneration with steam.](image)

**Figure 24.** Sulfiding profiles of a low loading sample (IPS1) with a decreasing time of regeneration with steam.

![Graph showing H_2S and SO_2 formation during regeneration of a medium loading sample (IPS5) with steam. During sulfiding the feed contained 4 mol% steam.](image)

**Figure 25.** H_2S and SO_2 formation during regeneration of a medium loading sample (IPS5) with steam. During sulfiding the feed contained 4 mol% steam.

### 3.4 Steam regeneration

For convenience, in most figures the relative regeneration time is used. The relative regeneration time for a sorbent is defined as: the absolute regeneration time divided by the time needed to completely sulfide the same, completely regenerated, sample with a gas with 1 vol.% H_2S. A S/Mn ratio of one is taken.

Figure 2a shows a typical H_2S production during regeneration with steam of a high loading sample. The regeneration starts with a very sharp and high H_2S production peak, after which the production tails off slowly. If almost all sulfur is removed the H_2S production rapidly drops to zero.

Figure 25 shows that besides H_2S a small amount of SO_2 is formed during regeneration. Also some condensed elemental sulfur was observed at the end of the reactor tube. The shape of the SO_2 production curve is clearly different from the H_2S production profile. The SO_2 production is “block shaped” without the initial high production peak.

In Figure 26 the H_2S production (regeneration) is compared to the H_2S absorption (sulfiding) at different temperatures. Above 900 K, the H_2S absorption is higher than the H_2S production. The difference between absorption and production increases with increasing temperature. During some experiments hydrogen was added to the regeneration gas (not depicted in a figure). During these experiments the H_2S
production was equal to the H$_2$S consumption at all applied temperatures (673 - 1223 K). The influence of hydrogen addition is discussed in more detail in Section 3.4.3.

Figure 27 shows the MS signal of H$_2$, H$_2$S and CO during steam regeneration of a medium Mn-loading sample. Besides the H$_2$S production peak$^{24}$ also some H$_2$ is produced. No CO production occurs.

**Figure 26.** H$_2$S absorption versus H$_2$S production during sulfiding with steam of an medium loading sample (IPL2). Isothermal sulfiding in different steps from 725-1225 K with two IPL2 samples.

**Figure 27.** MS signal of H$_2$S, CO and H$_2$ during regeneration with steam of a medium loading sample (IPS3).

**Figure 28.** Relative regeneration time at 1123 K as a function of the manganese loading. The sample numbers are indicated between brackets.

- ▲ = IPS samples (steam regeneration);
- ■ = IMW samples (steam regeneration);
- ● = IPL samples (steam regeneration);
- ○ = IPL samples (SO$_2$ regeneration).

**Figure 29.** Steam regeneration of a medium loading sample (IPL2) at different temperatures.

$^{24}$ The high H$_2$S production peak was present during this measurement but the strong signals were not correctly recorded due to the settings of the mass spectrometer.
3.4.1 Variation of Mn loading, bed length, and temperature
In Figure 28 the regeneration time as function of the manganese loading is given. It shows that, initially, with increasing manganese loading the relative regeneration time increases from 0.3 to around 1. Above 35 wt% Mn a strong increase in regeneration time is observed. At 53 wt% Mn it amounts to 3.

Figure 29 shows the result of temperature variation on the regeneration profile of a medium loading sample. With increasing temperature the regeneration time decreases strongly. At 1023 K the relative regeneration time is almost 0.7 while at 1223 K it is less than 0.2. The average H₂S concentration in the regeneration gas increases correspondingly. The height of the initial regeneration peak remains, however, unchanged (not shown).

In Figure 30 the effect of an increasing bed length is shown for a low loading sample. A less dispersed profile results. The height of the initial H₂S production peak more than doubles, with 2.5 times the initial sample weight. The relative regeneration time decreases with about 25%. For a high loading sample the height of the initial regeneration peak also doubles. The effect on the relative regeneration time with high loading samples is smaller (<10%; not depicted).

![Figure 30. Regeneration of two different amounts of a low loading sample (IPS1). Mass B = 2.5 * mass A.](image)

![Figure 31. Steam regeneration of a high loading sample (IMW6) without and with various amounts of hydrogen.](image)

3.4.2 Influence of hydrogen
The influence of hydrogen addition (0, 2.5, 5, and 10 vol%) on the regeneration is depicted in Figure 31. Addition of hydrogen to the regeneration gas results in an increase in the regeneration time of around 40%. Hereby the curve shape remains comparable, only the tailing becomes longer and the absolute H₂S concentration is lower. Increase of the H₂ concentration does not change the regeneration profile
further. No SO₂ or S₂ are formed if besides steam, hydrogen is present in the regeneration gas. Also less S and SO₂ formation occurred with increasing H₂O concentration in de regeneration gas (not shown).

3.4.3 Effect of partial sulfiding
During a practical application of an acceptor the sulfiding will be stopped as the H₂S concentration in the outlet exceeds a certain limit, e.g. 100 ppm. The sorbent will still be partially sulfided, and the regeneration profile may change, e.g. the regeneration time will be shorter. The effect on the regeneration of samples sulfided during increasing periods of time is depicted in Figure 32 for a high loading sample and in Figure 33 for a low loading sample.

Figure 32. H₂S production curves during steam regeneration of a high loading sample (IPS10) with an increasing degree of sulfiding.

Figure 33. H₂S production curves during steam regeneration of a low loading sample (IPS1) with an increasing degree of sulfiding.

With shorter sulfiding times, the absolute peak height in the regeneration curve decreases. As expected also the absolute regeneration time decreases. It is observed that with decreasing sulfiding time the H₂S production after the initial regeneration peak shows less tailing towards the constant H₂S level. The regeneration profile of the low loading sample also shows a disappearing regeneration peak. For low loadings no constant H₂S concentration level can be observed. The regeneration time decreases faster than at higher loadings.
3.5 Regeneration with SO₂, SO₂/O₂ or O₂

Figure 34 shows the SO₂ concentration profile during regeneration of an medium loading sample with SO₂ at 1123 K. Initially, a large part of the SO₂ is absorbed, after which the absorption tails off and reaches zero if all sulfur is removed from the acceptor. Elemental sulfur is formed as regeneration product, which is captured at the end of the reactor. This sulfur is bright yellow and does not contain significant contaminations.

Figure 13b shows that a high loading sample deactivates during prolonged operation. Therefore, during some experiments a small amount O₂ was added to the feed to regenerate the sample completely. The performance, however, did not improve. Only regeneration with a high oxygen concentration (8 vol%) could regenerate a deactivated sample almost completely.

XRD pointed out that, comparable with steam regeneration, MnAl₂O₄ is formed during regeneration. Below 873 K, however, some sulfate formation is observed. As shown in Figure 22 this results in H₂S production during the next sulfiding step.

After regeneration with oxygen or SO₂/O₂ XRD showed that a part of the manganese on the acceptor is present as MnO.

Table 4. Amount of sulfur recovered as elemental sulfur after regeneration with 50 mol% SO₂. If the recovery is 100% the only regeneration product is S.

<table>
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<th>Sample</th>
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<th>regeneration</th>
<th>S recovery %</th>
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<td>IPL4</td>
<td>standard</td>
<td>SO₂</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>sim. coal gas</td>
<td>SO₂</td>
<td>95</td>
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<td>IPL9</td>
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<td>99</td>
</tr>
<tr>
<td></td>
<td>standard</td>
<td>SO₂/O₂</td>
<td>94</td>
</tr>
</tbody>
</table>

1) 1.5 vol% O₂

Table 4 shows the sulfur production during regeneration of an intermediate and high Mn-loading sample. Standard sulfiding and regeneration results in a 100% recovery of the absorbed sulfur as elemental sulfur. Standard regeneration after sulfiding with simulated coal gas and regeneration with SO₂/O₂ result in about 95% recovery of the absorbed sulfur as elemental sulfur.

3.5.1 SO₂ regeneration at different temperatures for a medium and high loading sample

Figure 35 shows the SO₂ concentration profiles during regeneration of IPL4 for several temperatures. All samples show the same initial SO₂ absorption, but the remainder of the absorption is strongly dependent on the temperature. The relative regeneration time for IPL4 at 1223 K is 0.13 while at 1123 K it is two times longer. At 823 K it is much longer and the exact time could not be determined. A high loading
sample (IPL 9) showed the same picture as IPL4 but the regeneration is somewhat longer; 0.15 and 0.30 at 1223 K and 1123 K, respectively.

![Graph](image)

**Figure 34.** SO₂ profiles during regeneration of a medium loading sample (IPL4) with SO₂ at 1123 K.

![Graph](image)

**Figure 35.** SO₂ profiles during regeneration of a medium loading sample (IPL4) with SO₂ at different temperatures

### 4 Discussion

From the results presented it becomes clear that the developed acceptor is a rather complex system. Several chemical compounds are present in the solid phase, and both crystalline and amorphous phases co-exists. These components and phases behave differently under sulfiding and regeneration conditions. The resulting observed integral bed behavior can be understood if the separate contributions to this behavior are identified. In Section 4.1 the composition of the sorbent, and the sulfiding and regeneration mechanisms in the sorbent material are discussed. In Section 4.2-4.4 the performance is dealt with. Where possible the performance is related to the composition of the sorbent material.

An overview of the interpretation of the most important results is given in Figures 36 to 38. Figure 36 shows the overall sulfiding and regeneration cycle with the most attractive regenerant: SO₂. Figure 37a shows the acceptor composition coupled to the performance of the acceptor. Figure 37b shows the temperature dependence of a typical high loading sample during sulfiding and regeneration. Figure 38 shows the reactions during sulfiding on a molecular level within the acceptor. This is further elaborated in the following paragraphs.
4.1 Characterization; sulfiding and regeneration mechanisms

In the first part of this section the most important results are discussed. Then a more detailed discussion follows on the effect of manganese loading and operation temperature on the sorbent performance. Finally sulfiding and regeneration mechanisms within the acceptor are discussed.

\[ \text{Fresh acceptor} \quad \text{Mn}_x\text{O}_y / \gamma-\text{Al}_2\text{O}_3 \]
\[ \xrightarrow{H_2S, \text{ COS}} \]

\[ \text{1st sulfidation} \quad \text{MnS} / \gamma-\text{Al}_2\text{O}_3 \]
\[ \xrightarrow{\text{SO}_2 (> 823 K)} \]

\[ \text{Regenerated} \quad \text{MnAl}_2\text{O}_4 + \text{MnO} \quad \rightarrow S_2 \]
\[ \xrightarrow{\text{SO}_2} \quad \xrightarrow{H_2S, \text{ COS}} \quad \text{Sulfided} \quad \text{MnS} / \gamma-\text{Al}_2\text{O}_3 \]

Figure 36. "Life cycle" and product of a high loading acceptor with standard sulfiding and SO2 regeneration.

4.1.1 General

- From the XRD results it is clear that MnS/\(\gamma\)-Al2O3 is formed during sulfiding of calcined, fresh samples, and also after sulfiding of regenerated samples.
- Mainly MnAl2O4 is formed during regeneration with H2O or SO2. Furthermore, MnSO4 forms during regeneration with SO2 below 823 K. During regeneration with O2 always some MnO is formed, too. MnS/\(\gamma\)-Al2O3 and MnAl2O4 are seen by visual observation, XRD, and EDX. MnSO4 is observed by XRD and MnO by XRD and SEM. The formation of MnS during sulfiding, and of MnAl2O4 and MnO during regeneration is in accordance with the thermodynamic calculations as shown in Table 2 of Chapter 10. Also the formation MnSO4 below 823 K is predicted (Figure 11 of Chapter 10). Only the temperature at which the sulfate formation starts is experimentally about 100 K higher.
Manganese loading in relation to sorbent performance

**Sorbent**
- Deep removal sites
- Surface MnAl₂O₄
- Amorphous
- γ-Al₂O₃

**Performance**

**Sulfiding**
- Feed
- N-surf

**Regeneration**
- N-surf

Time/theoretical time (-)

0.0 0.5 1.0 1.5 2.0

Low loading sample (Mn < 8 wt%)

**Sulfiding**
- Feed
- N-surf

**Regeneration**
- N-surf
- Bulk MnAl₂O₄

Time/theoretical time (-)

0.5 1.0 1.5 2.0

Medium loading sample (8 < Mn < 32 wt%)
Performance and characterization of manganese based sorbents in high temperature desulfurization

**Sorbent**

- Deep removal sites
- Surface $\text{MnAl}_{2}\text{O}_{4}$ amorphous
- Bulk $\text{MnAl}_{2}\text{O}_{4}$
- Bulk removal of $\text{H}_2\text{S}$

**Performance**

- Sulfiding
- Regeneration
- $[\text{H}_2\text{S}]$ (a.u.)
- Time/theoretical time (-)

High loading sample ($32 < \text{Mn} < 40 \text{ wt\%}$) = actual sorbent

Very high loading sample ($\text{Mn} > 40 \text{ wt\%}$)

**Figure 37a.** Schematic representation of sulfiding and steam regeneration profiles as function of the manganese loading. See text for a detailed description. N-surf = surface sites.
During sulfiding the sorbent converts from a solid material containing mainly one crystalline phase (MnAl₂O₄; spinel) towards a material with two crystalline phases (γ-Al₂O₃; spinel, and MnS; rocksalt, see also Chapter 10).

Besides crystalline material, TEM showed amorphous material at the surface of the acceptor in both the regenerated and sulfided samples (Figures 7-9). The possible role of this material during sulfiding and regeneration will be discussed in Section 4.3.1.

The continuous change of the crystalline structure during subsequent sulfiding and regeneration, and not the high temperature, is the main mechanism for the observed decrease in surface area of the acceptor (Table 3). Impregnated samples, which can be fully regenerated, showed a strong decrease in surface area (Figure 10). Samples which were prepared via deposition precipitation could only partly regenerated (Figure 12) and only a minor decrease in surface area occurs.

Compared to other bulk sorbents the surface area of an impregnated and stabilized (at 1123 K) sample is still rather high, typically between 14-24 m²/gponder (Table 2), versus 0.2-1 m²/g for other bulk sorbents 8-10. This surface area is sufficiently high for high reaction rates at > 1073 K (see discussion on temperature dependency).

The distance between the atoms in the Mn-Al spinel crystal lattice varies with Mn loading. Low loading samples have a somewhat more compact spinel structure than stoichiometric MnAl₂O₄ samples. During XRD measurements this is shown by a shift in the MnAl₂O₄ peak position for samples with a lower (non-stoichiometric) manganese loading (Figure 5). It has been observed that this small difference in structure influences the water sensitivity of the sorbent (Figure 16). The compact structure seems thermodynamically more stable and thus the MnS on the γ-Al₂O₃ of a low loading sample is more sensitive towards H₂O. A small (partial) reduction in the cell volume of the MnAl₂O₄ spinel may also occur during subsequent cycling. This is indicated by the development of a shoulder in the XRD profile after some cycles (Figure 6). Possibly part of the Mn ions diffuse into the alumina carrier which results in slight differences in the lattice structure of the sorbent.

A small crystal size after synthesis is essential for MnAl₂O₄ formation during regeneration. In the samples prepared via deposition precipitation, most crystals are large compared to impregnated samples (Figure 5 of Chapter 8). This results in a large amount of irregenerable MnS and thus in a relatively low sulfur uptake capacity after the first cycle. The applied deposition precipitation method is, therefore, not suited for the preparation of a high capacity sorbent. See also Figure 8 of Chapter 8.

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4.1.2 Manganese loading and operation temperature

Variations of the Mn loading and the operation temperature give a good insight in the role of the various compounds in a sample. Below samples with different Mn loadings are discussed in detail. Figure 37a shows an overview. Also the temperature dependency is discussed. The temperature influence is schematically depicted in Figure 37b.

Low manganese loading (< 8 wt% Mn)

MnAl$_2$O$_4$ or MnAl$_2$O$_5$-like phases are present at the surface of the acceptor. These phases cannot be detected by XRD because of their high dispersion. Only a monolayer$^{25}$ or a few layers may be present. Moreover, part of the surface is amorphous as has been shown by TEM (see Figure 8 and 9a).

The reactions with the surface sites during absorption and regeneration are fast and can be described with an ion exchange model. In this model the concentration of solid phase is included in the equilibrium constant, See Eq. 4 in Chapter 9. Therefore, if a sample is fully regenerated, surface sites always adsorb some H$_2$S completely even when water is present in the feed. This can play an important role in removing H$_2$S to a sufficiently low level. Soerawidjaja$^7$ and Wakker$^5$ used this model to describe low loading samples being operated at temperatures below 873 K. During sulfiding the initial complete desulfurization is ascribed to surface sites (e.g. Figure 14a).

$^{25}$ A mono layer active material contains about 60 mg Mn.m$^{-2}$. 

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The sharp high regeneration peak is also ascribed to surface sites. Therefore, the height of the regeneration peak is dependent on the amount of acceptor present and can vary with the amount of sorbent and the degree of sulfiding. This has been shown in Figures 30, 32, and 33.

During prolonged operation at high temperatures (> 873 K) also some Mn diffuses into the bulk of the acceptor and, simultaneously, a decrease of the surface area occurs. This decrease in surface area and the diffusion into the acceptor decreases the number of surface sites and thus the capacity of surface sites. This has been observed in Figure 23 and Figure 10. Also the height of regeneration peak is lower due to a lower amount of surface sites.

Medium manganese loading (8-32 wt% Mn)

With increasing Mn loading the formation of multi-layer or bulk MnAl2O4 is inevitable. The higher the manganese loading the lower the relative contribution of the surface sites to the total acceptor capacity. At intermediate loadings bulk MnAl2O4 is responsible for the largest part of the acceptor capacity.

Diffusion limitation can play an important role during sulfiding and regeneration. It has been shown that diffusion in the bulk is a strongly activated process (Figure 11). Only at temperatures > 1073 K the sorbent is sulfided and regenerated completely. Thermodynamically, sulfiding is possible over the whole temperature range as has been shown in Figure 6 of Chapter 10. The tailing after the first regeneration peak (e.g. Figure 2) is, at least partly, ascribed to diffusion limitation. Samples which were only partly sulfided showed less tailing because less bulk sites are sulfided and thus less diffusion limitation occurs (Figure 32).

High manganese loading (32-40 wt%)

This is the actual sorbent which has been developed for the desulfurization of dry ("Shell type") coal gas. The crystals in these samples still have a relatively small crystal size (< 20 nm; Figure 4) and can be fully sulfided and regenerated above 1073 K. The minor amount of MnS which is sometimes observed after regeneration of impregnated samples (Figure 4-3) may be attributed to large MnS crystals which are very difficult to regenerate. These MnS crystals may originate from large Mn2O3 crystals formed after improper impregnation; e.g. because the excess solution was not removed effectively.

MnAl2O4 contains 31.7 wt% Mn. So, it is not surprising that formation of MnO occurs during regeneration if the amount of Mn on the support is higher. The dispersion of the MnO phase is very high when a few percent overstoichiometric Mn is present. MnO in sample IPS10 is only detected with TEM/EDX and not by XRD

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because of the small crystals (Figure 7). Thermodynamically, MnO is relatively insensitive to H₂O if it has to convert to MnS. It, therefore, enhances the desulfurization depth of the acceptor, even in an H₂O containing atmosphere. The amount of MnO should preferably not be higher than the amount needed to obtain the desired desulfurization depth. As shown in Table 4 of Chapter 10 the bulk thermodynamics for regeneration with SO₂ or H₂O are unfavorable and would require extra regeneration gas. Alternatively, addition of a few percent of oxygen to the regeneration gas may, theoretically, solve this problem. However, the first experiments showed deactivation of the sorbent if oxygen was added to the regeneration gas. Moreover, oxygen will not selectively regenerate the MnS from the MnO, but also stemming originally from the MnAl₂O₄. So if necessary the addition of O₂ should take place in the final stages of the regeneration. More research in this field is needed.

Very high Mn loading (> 40%)
For some washcoated samples the Mn loading is very high. XRD could clearly detect MnO crystals after regeneration. As expected these sample have a good sulfiding depth, they are very difficult to regenerate and large amounts of regeneration gas is required. Again, theoretically, oxygen can reduce the regeneration time. Except from deactivation also a solution should be found for the excessive heat production.

Temperature dependence
The temperature has a large influence on the absorption and regeneration characteristics of the sorbent, see Figure 37b. The most important is the fact that bulk diffusion is strongly activated with increasing temperature. It has been shown that a temperature > 1073 K is needed for complete and fast absorption and regeneration of the sorbent, see Figure 11. At high temperatures a high surface area is favorable because of the good desulfurization depth of surface sites; not because of the uptake capacity. At low temperatures (< 873 K) only the surface sites can be effectively used, and thus the capacity is directly coupled to the available surface area. At intermediate temperatures part of the bulk material can be sulfided and regenerated. To avoid sintering and diffusion of the Mn into the alumina support stabilization of the sorbent seems sensible for application at low temperatures. It should, however, be kept in mind that Mn itself is a stabilizer for γ-Al₂O₃ and that commercially stabilized alumina is already available. At High temperatures stabilization may even decrease the reaction rate, which is of course not desired.

The washcoated monolith samples are commercial materials with a stabilized alumina layer.
4.1.3 Sulfiding mechanisms

To our knowledge little has been published on the sulfiding and regeneration mechanisms within or at the surface of a solid acceptor. The acceptor step may, however, be compared with sulfiding of high-temperature catalysts\textsuperscript{11-14}. From the results presented in this thesis some details about these mechanisms become clear. Below they are explained using MnAl\textsubscript{2}O\textsubscript{4}, prepared according to the impregnation method. Figure 38 shows a simplified representation of the proposed sulfiding process.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sulfiding_process.png}
\caption{Schematic representation of the sulfiding process within the acceptor. \(M\) = metal ion. Mn\textsuperscript{2+} diffuses out of the spinel and Al\textsuperscript{3+} into the spinel. O\textsuperscript{2-} becomes available for exchange with S\textsuperscript{2-}.}
\end{figure}

In Section 4.1.1 of the discussion the most important results are summarized. Also the following should be kept in mind to understand the sulfiding and regeneration process.

- Metal ions in the spinel structure are relatively mobile because many unoccupied octaeder en tetaeder holes are present, see Figure 4 of Chapter 10. In the rocksalt structure all places are occupied and metal ions are less mobile (Figure 5 of Chapter 10).
- S ions are 30% larger than oxygen ions and do not fit in the spinel structure.
- During regeneration with steam, hydrogen, SO₂ and S₂ formation is observed (Figures 25 and 27). COS formation occurs during sulfiding (Figure 18).
- The presence of a small amount of hydrogen suppresses SO₂ and S formation (Figure 19 and 20). Furthermore, it enhances the desulfurization depth and increases the regeneration time (Figure 19 and 31, respectively).
- The acceptor surface catalyses dissociation and shift reactions, e.g. the water-gas-shift reaction.

Table 4. Elementary reactions during sulfiding and regeneration. Bulk, amor, crys refer to the bulk, amorphous, and crystalline, respectively. F. and S. refer to Figure and Section, respectively.

<table>
<thead>
<tr>
<th>Eq.</th>
<th>sulfiding reactions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>H₂S ⇌ 2 H⁺ + S⁺</td>
<td>H₂S dissociation</td>
</tr>
<tr>
<td>4</td>
<td>O⁺ + S⁺ ⇌ S⁺</td>
<td>O-S exchange</td>
</tr>
<tr>
<td>5</td>
<td>O⁺ + 2H⁺ ⇌ H₂O⁺</td>
<td>H₂O formation</td>
</tr>
<tr>
<td>6</td>
<td>O⁺ + CO⁺ ⇌ CO₂⁺</td>
<td>CO₂ formation</td>
</tr>
<tr>
<td>7</td>
<td>O₉ bulk ⇌ O₉ amor</td>
<td>γ-Al₂O₃ formation</td>
</tr>
<tr>
<td>8</td>
<td>Mn₉ bulk ⇌ Mn₉ amor</td>
<td>MnS formation</td>
</tr>
<tr>
<td>9</td>
<td>S⁺ amor + Mn₉ amor</td>
<td>MnS formation</td>
</tr>
</tbody>
</table>

**Side reactions**

<table>
<thead>
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<th>Eq.</th>
<th>sulfiding reactions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>S⁺⁺S⁺ ⇌ S₂</td>
<td>S₂ formation</td>
</tr>
<tr>
<td>11</td>
<td>S⁺ + 2 O⁺ ⇌ SO₂⁺</td>
<td>SO₂ formation</td>
</tr>
<tr>
<td>12</td>
<td>CO⁺⁺S⁺ ⇌ COS⁺</td>
<td>COS formation</td>
</tr>
<tr>
<td>13</td>
<td>H⁺⁺H⁺ ⇌ H₂</td>
<td>H₂ formation</td>
</tr>
</tbody>
</table>

**Regeneration**

<table>
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<th>Eq.</th>
<th>sulfiding reactions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>SO₂ ⇌ SO⁺ + O⁺</td>
<td>SO₂ dissociation</td>
</tr>
<tr>
<td>11a</td>
<td>SO⁺ ⇌ S⁺ + O⁺</td>
<td>dissociation</td>
</tr>
<tr>
<td>11b</td>
<td>H₂O⁺ ⇌ 2 H⁺ + O⁺</td>
<td>H₂O dissociation</td>
</tr>
<tr>
<td>14</td>
<td>O₂ ⇌ 2 O⁺</td>
<td>O₂ dissociation</td>
</tr>
<tr>
<td>7a</td>
<td>MnS_crys ⇌ S⁺ amor + Mn⁺ amor</td>
<td>MnS₉ bulk deformation</td>
</tr>
<tr>
<td>4a</td>
<td>S⁺ amor + O⁺ ⇌ O⁺ + S⁺</td>
<td>O-S exchange</td>
</tr>
<tr>
<td>10a</td>
<td>S⁺ + S⁺ ⇌ Sx</td>
<td>Sx formation</td>
</tr>
<tr>
<td>8a</td>
<td>O⁺ amor ⇌ O⁺ bulk</td>
<td>MnAl₂O₄ formation</td>
</tr>
<tr>
<td>9a</td>
<td>Mn⁺ amor ⇌ Mn⁺ bulk</td>
<td>MnAl₂O₄ formation</td>
</tr>
</tbody>
</table>

**Side reactions**

<table>
<thead>
<tr>
<th>Eq.</th>
<th>sulfiding reactions</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>11c</td>
<td>SO⁺⁺S⁺ ⇌ S₂O</td>
<td>S₂O formation</td>
</tr>
<tr>
<td>11d</td>
<td>SO⁺⁺O⁺ ⇌ SO₂</td>
<td>SO₂ formation</td>
</tr>
</tbody>
</table>

* = activated at surface
** = predicted by Figure 11 in Chapter 10
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Sulfiding
During sulfiding H₂S dissociates to H⁺ and S⁺. The acceptor surface catalyses this reaction. S⁺ enters the amorphous phase, e.g. by exchange with O⁺ₐₘ. The presence of H₂ or CO favors the sulfiding process, because O⁺ reacts with H⁺ or CO which accelerates the formation of vacatures for S⁺ in the solid phase. Mn²⁺ diffuses from the spinel into the amorphous phase. Al³⁺ diffuses into the spinel and Al₂O₃ is formed. A surplus of oxygen remains and leaves the sorbent by exchange with sulfur. A separate MnS phase is formed. Diffusion of sulfur into the spinel structure will not occur because it is too large. Diffusion of oxygen into the spinel structure will be limited because of its low diffusivity compared to the metal ions. Theoretically this process continues until thermodynamic equilibrium is reached. At low temperatures the sulfiding may, however, stop because of diffusion limitations. In that case only the sites near or at the surface are sulfided.

Regeneration
During regeneration SO₂, H₂O or O₂ dissociates and O⁺, S⁺ or H⁺ is formed. Sulfur at the surface of MnS or in the amorphous phase is exchanged with O⁺ and, depending on which regenerant is used, S₂, H₂S or SO₂ is formed. If hydrogen is present in the regeneration gas, it will lower the S⁺ concentration and the regeneration process becomes relatively slow. Mn²⁺ diffuses from the MnS crystal into the amorphous phase and the alumina spinel. It will partly replace the Al³⁺, which diffuses into the amorphous phase. Due to favorable thermodynamics, MnAl₂O₄ is formed. Again the process continues until equilibrium is reached or stops in case of severe diffusion limitation. Especially large MnS crystals will not be fully regenerated because of diffusion limitation in the MnS crystal. The diffusion in this crystal is relatively slow because of its compact lattice structure (rocksalt structure, see Figure 5 in Chapter 10). In the case an over-stoichiometric amount of Mn is present, MnO is also formed. This is relatively difficult because MnO also have the compact rocksalt structure.

4.2 Acceptor performance during isothermal cycles

The results show that a manganese based sorbent can be made which is a good acceptor for high temperature desulfurization of dry coal gas. The preparation method and the manganese loading is, however, rather critical for successful operation within a specific application. The sulfiding performance with different samples and under varying conditions is discussed below.

---
27* Direct exchange with the crystalline phase will also occur but less frequently.
4.2.1 Desulfurization depth

Impregnated high loading samples (> 32 wt% Mn) appear to be good acceptors for hot gas desulfurization. If no water is present in the feed the sorbent can reduce the amount of H₂S to a level between 5-50 ppm (@1123 K; Figure 1). Also the desulfurization of simulated coal gas down to a level between 10-50 ppm H₂S is satisfactory if a desulfurization down to 100 ppm is desired (Chapter 7). This desulfurization level is in accordance with thermodynamical calculations for bulk MnO which predict a removal down to 40 ppm\textsuperscript{28*}

Samples with Mn loading below 32 wt% show in many cases a satisfying capacity but at temperatures above 1023 K insufficient desulfurization depth. In combination with sorbents with a better desulfurization depth they still can be attractive at high temperatures because they form elemental sulfur during regeneration relatively easy.

4.2.2 Optimal operation temperature

The highest capacity is obtained between 1123 and 1223 K. Below 1123 K the capacity decreases (Figure 11). In Chapter 7 it was argued that the optimal operation temperature for desulfurization was at temperatures between 1000-1200 K. The highest capacity is thus obtained around the optimal operation temperature which is, of course, satisfactory. At 723 K the capacity is only 0.1-0.3 times the maximum capacity but the desulfurization depth at that temperature is sufficient. The low sulfur uptake capacity at 723 K after heating towards 1273 K can be explained by surface loss caused by the sintering of the sorbent. At low temperatures only the surface sites can be sulfided\textsuperscript{3} and sintering causes a direct decrease in the sulfur uptake capacity.

4.2.3 Sulfur uptake capacity

The sulfur uptake capacity of pure alumina supported samples (sample codes IPS, IPL, IM) is high and increases to 20 wt% sulfur at the maximum applied manganese loading of 36 wt% (Figure 12). The maximum sulfur uptake capacity of the coated samples (IMW) is even higher. Based on the total mass the capacity of the IMW samples is of course lower (9 wt% S), but still satisfactory.

The S/Mn ratio decreases a little with increasing Mn loading (Figure 12b). This may be explained by the formation of an increasing amount of (large) irregenerable MnS crystals with increasing Mn loading. A large amount of irregenerable MnS crystals also explains the low capacity of samples prepared via deposition precipitation (Figure 12).

\textsuperscript{28*} Assuming a [H₂O]/[H₂S] equilibrium ratio for IMC 7 and IPL10 of 225 (Figure 16) and a \(K^b_{eq}\) of 1 for the WGS reaction (see Table 2 of Chapter 10).
4.2.4 Optimal manganese loading

A high manganese loading and thus, for impregnated samples, a high sulfur uptake capacity is not necessarily the optimal manganese loading. The maximum capacity is always lower than the practical capacity (= capacity which can be used in an industrial desulfurization process).

According to previous work\cite{5,6} the optimum performance is reached with a manganese loading of 8 wt% at 873 K. This resulted in a practical sulfur uptake capacity between 0.5 and 1.5 wt% sulfur. Higher loadings did not result in a higher capacity at this temperature and it was believed that, although higher temperatures increased the S/Mn ratio, excessive sintering during prolonged operation would destroy the acceptor capacity.

Indeed, severe sintering and deactivation at low temperatures is observed after cycles at high temperatures, see Figure 10 and 11. However, for desulfurization at high temperatures the following was overlooked: solid state diffusion is an activated process and, as a consequence, with increasing temperature, diffusion in the solid phase, at least partly compensates the decrease in reactivity by the loss in surface area. The formation of an amorphous phase at high temperatures may also enhance the reaction rate as diffusion in an amorphous phase is, in general, relatively fast. Above 1100 K the loss in surface area is completely compensated by a higher solid state diffusion rate (Figure 11). At low temperatures a high surface area is still important since the capacity is then directly related to the surface area, and thus always relatively low.

The current manganese based sorbent has been designed for desulfurization of dry coal gas (0.4-2 vol\% H\textsubscript{2}O) down to a level of below 100 ppm H\textsubscript{2}S. At 1123 K bulk MnAl\textsubscript{2}O\textsubscript{4} can remove about 90\% of the H\textsubscript{2}S from our simulated dry coal gas\cite{29}. The remaining 10\% should be removed in an alternative way. Surface sites can remove H\textsubscript{2}S to a very low level. This has been shown in e.g. Figure 14a and by Wakker and Soerawidjaja\cite{57}. Also MnO can remove H\textsubscript{2}S to a sufficient low level if the water content in the feed is relatively low; < 2.5 vol\% after the WGS reaction, see Figure 14b and 16.

Thus, if sufficiently available, MnO and surface sites remove the H\textsubscript{2}S which is not absorbed by MnAl\textsubscript{2}O\textsubscript{4}. A disadvantage of MnO is that it is difficult to regenerate with steam or SO\textsubscript{2} after sulfiding (Figure 28). The amount of MnO should, therefore, be minimized. Sulfided surface sites are easy to regenerate. Their availability is, however, limited. It has been shown in Table 3 that the surface area at 1123 K stabilizes around 20 m\textsuperscript{2}.g\textsuperscript{-1active}. The maximum absorption capacity at 1123 K of surface sites is, therefore, only about 1 wt\% sulfur. Theoretically, 2-4 wt\% MnO is required additionally. As MnAl\textsubscript{2}O\textsubscript{4} contains 32 wt\% Mn the optimal Mn loading of a
sorbent is around 35 wt% Mn. So IPS10, IPL10 and IMW6 have an optimal Mn loading. To avoid excessive usage of SO$_2$ or H$_2$O additional regeneration with oxygen may be useful, especially for samples with a high amount of MnO. Different process options are discussed in Chapter 12.

4.2.5 Practical sulfur uptake capacity
During sulfiding the full capacity of the sorbent cannot be used because the sulfiding is stopped if the maximum H$_2$S concentration is reached. The practical sulfur uptake capacity during sulfiding with simulated coal gas for IMW7 and IPL10 is with 7$^{30\text{a}}$ and 14 wt% sulfur, respectively, is very satisfactory, see also Table 5 in Chapter 7.

4.2.6 Acceptor stability, mechanical strength and influence of impurities in feed
Stability
The stability tests indicate that the sorbents have a stable performance during prolonged operation (40-110 cycles; Figure 13). Little or no deactivation during the first cycles (< 20%) or no deactivation has been observed. An exception is IPL10; if it is regenerated with SO$_2$ a continuous deactivation takes place, see Figure 13b. Possibly, the regeneration of high loading samples leads to the formation of relative large crystals which are difficult to sulfide after regeneration.

Wacker$^{6}$ performed deactivation tests of 50 cycles at 873 K with a low loading sample (8 wt% Mn) behind a pilot coal gasifier of ECN in The Netherlands. He also observed only initially deactivation, followed by a stable performance. It is advised to test the current high capacity sorbent in a similar way.

Mechanical strength
The higher mechanical strength of the washcoated cordierite monolith compared to alumina monoliths is not surprising, because it is designed for application in car exhaust systems in which it should resist not only mechanical stress caused by sudden movements of the car but also a high thermal stress. In future research the mechanical strength of the sorbents should be investigated in more detail. Especially, when particles are used in a fluidized bed or moving bed reactor this is an important issue.

Impurities
Besides H$_2$S the coal gas contains other impurities like dust, HCl, HF and alkali metals, see Table 2 of Chapter 7. As shown in Figure 8 in Chapter 10, theoretically, HCl and HF are also adsorbed by MnAl$_2$O$_4$. These components cannot be removed

$^{30\text{a}}$ 2% H$_2$O and 0.7% H$_2$S; $K_{WGS}$ ≈ 1, [H$_2$O]/[H$_2$S] equilibrium ratio =1

$^{30\text{b}}$ Based on the total sample weight. If based on weight of active phase about 3 times higher.
with SO₂ but they can be removed relatively easy with H₂O. This difference can be beneficial during regeneration of the sample, see also Chapter 12. HCl or HF will not be released during SO₂ regeneration and thus the product gas will not be contaminated with these components. In a practical application the sorbent will be treated with steam after a number of cycles to remove the absorbed HCl and HF. Furthermore, some deactivation might occur by volatilization of MnCl₂ at 1123 K. The amounts are, likely, small because of the high boiling point of MnCl₂.

Also alkali metals have to be removed from the coal gas. No data are available of the influence of these metals on the manganese sorbent. Removal of alkali metals at high temperatures, up to 1223 K, can be performed with an other sorbent e.g. with "Fullers earth" as described by Schulz.

### 4.3 Sulfiding

In this paragraph the influence of the feed composition and the manganese loading are discussed. In Figure 37 an overview is given.

#### 4.3.1 H₂O concentration in feed and amount of Mn on acceptor

The amount of water present in the feed and the manganese loading of the sorbent are key factors in the sulfiding behavior of the sorbent (Figures 14 and 16). Besides direct influence on the sulfiding, other components, such as hydrogen, carbon monoxide, and H₂S influence the amount of water in the feed and thus indirectly the sulfiding, see Eqs. 1 and 15 in Chapter 10.

As has been discussed in Section 4.1, a sorbent can contain different types of active material, MnAl₂O₄ and MnO, in different morphologies (crystalline and amorphous) and at different locations (surface and bulk). The amount of surface sites is correlated to the surface area, see Figures 10 and 11. These surface sites can remove H₂S and COS to very low levels even in the presence of water. This is shown in Figure 14 in which, initially, all the H₂S is absorbed by surface sites. The capacity of these sites is, however, limited (< 1% S for samples stabilized at 1123 K) and decreases with increasing amount of water. The behavior of these sites can be compared with the sorption behavior of an ion exchange column. If the column is fully regenerated always some ions can be exchanged. This behavior has been used in a model developed by Soerawidjaja to describe regenerative desulfurization at a temperature of 673-873 K. Empty surface sites play a role in the thermodynamic equilibrium between the gas phase and the solid surface sites according to Eq. 4 in Chapter 10.

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* The presence of hydrogen and carbon monoxide have an influence on the sulfiding mechanism. The concentrations are, however not important (Figures 19 and 20).
The two breakthrough levels in Figure 14b are assigned to bulk sites of MnO and MnAl₂O₄, respectively. In low and intermediate loading samples only a bulk MnAl₂O₄ phase is present which explains that only one level before final breakthrough can be seen, see Figure 14a.

With very high MnO loadings, > 40 wt% Mn, only one breakthrough is observed, see Figure 16. This is explained by the occurrence of integral bed behavior. All H₂S that is not taken up by MnAl₂O₄ is taken up by MnO and the breakthrough of MnAl₂O₄ is not observed separately anymore.

The absorption of H₂S produces an equivalent amount of H₂O according to Eq. 1 in Chapter 10. Therefore, with increasing H₂S concentration its removal becomes less efficient and more H₂S has to be removed by surface sites or, if present, by MnO. If not sufficient surface sites are available a second breakthrough level will become visible. This is clearly demonstrated in Figure 23. With increasing number of cycles the surface area (see Figure 10) decreases. Moreover, a certain amount of Mn will diffuse into the alumina which also decreases the amount of available surface sites. This explains the development of a second breakthrough level which starts earlier after every cycle. The height of regeneration peak is also somewhat lower due to a lower amount of surface sites.

4.3.2 Thermodynamic equilibrium ↔ [H₂O]/[H₂S] exit level ratio

Theoretically, H₂S absorption in the bulk of the sorbent occurs only if the [H₂O]/[H₂S] exit level ratio in the gas phase is lower than the theoretical equilibrium ratio Kₘ. The [H₂O]/[H₂S] exit level ratios for low loading samples at 1123 K are around the theoretical equilibrium ratio; 5-17 compared to 12, see Figures 16 and Figure 6 of Chapter 10. The variation in the [H₂O]/[H₂S] exit level ratio can be explained by a changing interaction of Mn within the spinel structure with varying Mn loading. XRD (Figure 5) showed that low loading samples have a somewhat more compact structure. This should have an influence on the mutual interactions. Apparently, this results in a more stable structure for which sulfiding is less favorable. For IPS3 and 4 the opposite holds.

The theoretical equilibrium [H₂O]/[H₂S] ratio for MnO is much higher than for MnAl₂O₄ and, therefore, for high loading samples which contain (disperse) MnO, high [H₂O]/[H₂S] exit level ratios are measured (200-275). These exit level ratios are near the theoretical [H₂O]/[H₂S] equilibrium ratio of MnO (375, Figure 6 in Chapter 10). The [H₂O]/[H₂S] exit level ratio for high loading samples increases with increasing Mn loading towards the [H₂O]/[H₂S] equilibrium ratio of pure MnO. This

₃₂ In reality O-S exchange with the bulk phase occurs via the surface sites of the sorbent. The question is whether the [H₂O]/[H₂S] equilibrium ratios between surface sites and bulk phase sites can be compared with the equilibrium ratios between the bulk and gas phase.
can be explained if it is assumed that MnAl₂O₄ has a stabilizing effect on MnO. With an increasing amount of MnO this interaction decreases, and the formation of MnO during regeneration is less favorable.

4.3.3 Shift reactions
The water gas shift reaction, Eq. 11 of Chapter 10, is an important reaction during sulfiding. It has been shown in Figure 17 that a large amount of water can be shifted away by this reaction. As is predicted from the reaction equation an increase of the [CO]/[H₂] leads to a decrease of the amount of water and thus to a decrease in the H₂S breakthrough level.

From thermodynamic calculations it is known that at 1123 K, the water gas shift reaction proceeds to an equilibrium in which \( K_{eq} = 1 \) (Table 3 in Chapter 10). The experimental exit level ratio of 2 is thus in reasonable agreement with the theoretical equilibrium ratio.

Besides the WGS reaction, the occurrence of some other reactions has been found. MS showed that COS is formed in the sulfiding mixture (Figure 18). The difference with the feed signal indicated as "COS" in Figure 20 is also due to COS formation. As predicted, COS is very well adsorbed by the sorbent (Eq. 6 in Table 3). Only as breakthrough occurs COS could be detected with MS. As the equilibrium shifts, the amount of COS formed increases with increasing amount of CO.

Figures 19 and 20 show that a considerable amount of H₂S is converted if no hydrogen is present in the feed. Simultaneously some sulfur is detected at the end of the reactor tube. This can be explained by the conversion of H₂S in H₂ and S₂ according to reaction 18 in Chapter 10. The equilibrium constant for both the formation of COS and S₂ is about 5 times higher than expected from the equilibrium ratios given in Table 3 of Chapter 10. This difference is somewhat high. No clear explanation for this difference was found.

An extra breakthrough occurs if no hydrogen or CO are present in the feed, see Figures 19 and 20. Also some SO₂ is formed during the sulfiding if no hydrogen is present in the feed, see Figure 19. Furthermore, besides the influence of the presence of H₂, the sulfiding behavior is not a function of the H₂ concentration during a standard sulfiding (Figure 19). The extra breakthrough, the SO₂ formation, and the independence of the H₂ concentration can be explained by the sulfiding mechanisms which is discussed in Section 4.1.3.

4.3.4 Incomplete regeneration
During sulfiding the initial complete desulfurization is ascribed to surface sites. If the sample is not fully regenerated no complete desulfurization is possible as has been
shown in Figure 24. Surface sites are in equilibrium with the bulk sites and in principle S-O exchange takes place via the surface of the sorbent. If a sample is not fully regenerated, the surface sites at the end of the bed still contains sulfur which will be removed by the H₂O which is produced during sulfiding at the beginning of the bed. The amount of H₂S released is dependent on the concentration of sulfided surface sites on the acceptor. With a decreasing degree of regeneration the amount of non-regenerated sites increases and thus the concentration of H₂S released increases. Counter current regeneration will make incomplete regeneration possible because the completely regenerated sites are at the end of reactor. This will be subject of future research.

4.3.5 H₂S formation

The formation of H₂S during sulfiding of samples which have been regenerated with SO₂ below 823 K can be explained by the regeneration of sulfates by the sulfiding gas (H₂). Sulfates are formed during regeneration with SO₂ at temperatures below 823 K. See Section 4.1.1.

4.4 Regeneration

Regeneration of sulfided acceptors with H₂O, SO₂, O₂ or a mixture of SO₂ and O₂ is possible. Especially the good results obtained with SO₂ regeneration are interesting because of the production of elemental sulfur. Below the different regeneration experiments are discussed.

4.4.1 Steam regeneration

The main product during regeneration of sulfided samples with H₂O is H₂S. Figure 25 shows that at 1123 K besides H₂S also some SO₂ is formed. The formation S₂ is indirectly proven by the production of H₂ during regeneration as shown in Figure 27. The formation of SO₂, S₂ and H₂ is predicted by reactions in Eqs. 16 and 17 in Chapter 10. With increasing temperatures these reactions shift towards these products. This explains that with increasing temperature the H₂S production decreases compared to the amount absorbed, see Figure 26. Consequently, the amount of SO₂, S₂ and H₂ in the regeneration gas increases.

The regeneration time is a function of the manganese loading and the regeneration temperature, Figure 29. Three aspects are important with respect to the regeneration time. The [H₂O]/[H₂S] equilibrium ratio for MnAl₂O₄, the relative amount of surface sites and the presence of Mn which has to be regenerated towards MnO.

Surface sites are regenerated fast compared to bulk sites. This results in high H₂S concentrations in the regeneration gas. The initial high regeneration peak is ascribed to surface sites. The height of this peak is directly related to the amount of sulfided
surface sites. This is shown in Figure 30, 32 and 33. A clear example of fast regeneration is IPS1. This sample has a relatively high amount of surface sites and also a low \([\text{H}_2\text{O}] / [\text{H}_2\text{S}]\) equilibrium ratio which makes regeneration relatively easy. This results in a relative regeneration time of only 0.3.

Regeneration of samples with high a manganese loading requires a longer regeneration time because of the formation of MnO. It has been shown that this is thermodynamically less favorable than the formation of MnAl2O4 (high \([\text{H}_2\text{S}] / [\text{H}_2\text{O}]\) ratio; Figure 7 in Chapter 10). The regeneration of the high loading IM samples is still relatively easy compared to "unsupported" MnS16 (Figure 9 in Chapter 9) and MnS on samples prepared via deposition precipitation. see Figure 12. This may be explained by the existence of interaction of dispersed MnS with γ-Al2O3 which makes the regeneration thermodynamically more favorable (Figure 16). Moreover, the crystals on IM samples are relatively small which results in less diffusion limitation.

4.4.2 Regeneration temperature

Also the regeneration temperature is a very important parameter. This is shown by the \([\text{H}_2\text{O}] / [\text{H}_2\text{S}]\) exit level ratios which are measured during sulfiding experiments as function of the temperature (Figure 29). The \([\text{H}_2\text{O}] / [\text{H}_2\text{S}]\) exit level ratio decreases strongly with increasing temperature. Remarkably, the thermodynamic calculations predicts a less strong dependence of the temperature (see Figure 15b). This is not fully understood. A decrease in diffusion limitation with increasing temperature may play a role but can only partly explain the observed behavior.

The presence of hydrogen increases the sulfiding time considerable. The reason of this is given by the sulfiding mechanism which is explained in Section 4.1.3. Furthermore, no SO2 and S2 formation occurs in the presence of hydrogen. The latter can be explained by a shift of the reaction described in Eqs. 16 and 17 of Chapter 10 towards H2S.

The difference in shape between the SO2 production curve and the H2S production curve (Figure 25) indicate that the formation H2S from (some of) the surface sites follows a different mechanism than with the regeneration of bulk material. E.g., the reaction rate of H2S formation from surface sites might be much higher than the SO2 formation via surface sites, so the thermodynamic equilibrium for SO2 is not reached.

4.4.3 SO2 regeneration

Regeneration with SO2 is successful at temperatures above 873 K. Below that temperature sulfate formation occurs which results in H2S release during sulfiding (Figure 22). Direct formation of sulfur takes place and the mass balance indicates that the conversion to S2 is near to 100% (Table 3). Thermodynamic calculations predict (Figure 11 in Chapter 10) that around 10% of the regeneration products is S2O.
Apparently, none or less S\textsubscript{2}O is formed than predicted. This will be a point for future investigations.

The regeneration time using SO\textsubscript{2} is shorter than with H\textsubscript{2}O regeneration (Figures 28-35). For IPL10 the regeneration is even two times faster than with steam. This is in accordance with calculations which predict that regeneration of MnS on Al\textsubscript{2}O\textsubscript{3} at high temperatures is more favorable with SO\textsubscript{2} than with H\textsubscript{2}O (Chapter 10 Figure 9). It is not clear why for IPL10 the difference between steam regeneration and SO\textsubscript{2} regeneration is larger than for low loading samples. The durability test with IPL10 indicates that not all MnS is regenerated (Figure 13b). Possibly, some of the over-stoichiometric MnS is not converted by SO\textsubscript{2} to MnO which results in a shorter regeneration time.

The observed temperature dependency can be explained in a similar way, as described above for steam regeneration.

The direct production of elemental sulfur during regeneration with SO\textsubscript{2} is in most cases preferred over the production of SO\textsubscript{2} or H\textsubscript{2}S. Regeneration of MnS to MnO in high loading samples with SO\textsubscript{2} or H\textsubscript{2}O is difficult and requires large amounts of regeneration gas. Therefore, in practical applications some of the material might preferably will be regenerated with oxygen. However, it has been shown that regeneration with a SO\textsubscript{2}/O\textsubscript{2} mixture results in relative severe sintering (Table 2). Furthermore, it was observed that MnS on γ-Al\textsubscript{2}O\textsubscript{3} after regeneration with diluted O\textsubscript{2} contained a relatively large amount of MnO. Possibly, the formation of MnO instead of MnAl\textsubscript{2}O\textsubscript{4} accelerates sintering. It is expected\textsuperscript{33} that regeneration with diluted O\textsubscript{2} (typically 2-3 %) of the remaining MnS after regeneration with SO\textsubscript{2} is a more successful method, and will result in less sintering compared to direct addition of oxygen to SO\textsubscript{2}. An advantage of direct addition of O\textsubscript{2} to SO\textsubscript{2} is that the exothermal reaction with oxygen can compensate the endothermal regeneration with SO\textsubscript{2} (Table 4 in Chapter 10). High oxygen concentrations should be avoided as that leads to unacceptable temperature rise in the acceptor bed and requires additional cooling\textsuperscript{10}. In Figure 8 of Chapter 12 possible process schemes for regeneration with SO\textsubscript{2} and O\textsubscript{2} are depicted.

\textsuperscript{33} Only the sites most difficult to regenerate sites need oxygen. The other sites should preferably be regenerated with SO\textsubscript{2}.
5 Conclusions

A stable high capacity manganese based sorbent for high temperature desulfurization of dry coal gas has been developed. Wet impregnation of $\gamma$-Al$_2$O$_3$ with a manganese acetate solution appears to be a good method for the preparation of a high capacity manganese based sorbent with a, compared to other bulk sorbents, high surface area. Both particles and monoliths are suitable as support, and regeneration with SO$_2$ with direct production of elemental sulfur is well possible. The active material consists of two manganese phases: bulk manganese aluminate which provides the high sulfur uptake capacity and a disperse manganese oxide phase which provides the desulfurization to a low H$_2$S level. Also surface sites play a role for the desulfurization depth of the sorbent. The amount of water in the feed gas and the Mn loading are the key elements in the sulfiding behavior.

Thermodynamic calculations appeared to be a useful tool to estimate gas phase and solid phase compositions, at high temperatures, during both sulfiding and regeneration. A sulfiding mechanism within the sorbent has been proposed to explain the observed sulfiding and regeneration behavior.

6 Literature

2. International center for powder diffraction data, database (1992)
Continuous regenerative desulfurization with a rotating monolith reactor

Abstract
The development of a rotating (monolith) reactor is described. The aim is to continuously operate cyclic processes in corrosive gas environments at unusually high temperature, i.e. up to 1273 K. For certain applications this new reactor type is attractive. Compared to other continuous reactors it is very flexible towards flow variations, has a low pressure drop, shows little maldistribution, and is insensitive to dust. Under the severe operation conditions of high temperature desulfurization only ceramics are applicable as construction material. Unlike metal alloys, no separate sealing materials are required between the rotating parts, because of the high stability of ceramics at an atomic level. A reactor has been built on a pilot scale (0.1-20 m³ gas.hr⁻¹). It has been successfully tested under non-rotating conditions up to 1273 K and under rotating conditions up to 973 K. The application of the manganese based sorbent on a monolith structure in a rotating reactor is feasible. 90% of the reactor volume can be used for absorption. For the removal of H₂S from the coal gas of a 250 MW gasification unit about 0.9 m³ sorbent material is needed, and an open cross-sectional area of 0.55 m². Hereby, the reactor makes 18 revolutions per hour. Compared to a sequentially operated fixed bed reactor, the reactor volume can be over 80 times smaller. A new process configuration for fuel gas cleaning and sorbent regeneration is proposed. It should, however, be stressed that the process designs in this chapter are conceptual and that more studies are required for a detailed and accurate process design.
1 Introduction

The development of corrosion resistant moving parts with good sealing properties at high temperature is one of the challenges in present day process industries. Also continuous operation of cyclic processes, such as regenerative desulfurization, selective oxidation, and methane conversion is considered an important new development. In this chapter the development of a new reactor (concept) is presented in which continuous operation of cyclic processes and good sealing of rotating parts at high temperatures are combined.

Furthermore, a new process option is discussed for coal gas cleaning at very high temperatures. The regenerative high temperature desulfurization of the coal gas from a 250 MW gasification unit is used to illustrate the typical properties of the new rotating reactor.

1.1 Reactors for regenerative gas cleaning

For high temperature desulfurization of coal gas from a gasifier the following reactor characteristics are preferred: continuous but flexible operation, constant composition of the cleaned gas and regeneration product, low pressure drop, low dust sensitivity, and little attrition of the sorbent.

In principle, several reactor types can be used. The most simple reactor set-up for regenerative gas cleaning is two or three sequentially operated fixed bed reactors. In these reactors either pellets or more structured acceptors, like monoliths, can be used. In treating large volumina of gas, structured sorbents are preferred over conventional particles. Not only because of the low pressure drop and dust low sensitivity of these sorbent materials, but also because less maldistribution occurs. Moreover, the gas diffusion path, in particles used for packed beds, is a factor 10-50 longer, than in e.g. monoliths because of the thin walls in the monolith. Switching of valves leads to instabilities in the system of typically 15 minutes. To avoid unacceptable system instabilities 2-4 hours is a preferred minimum switching time. This leads to large reactor volumina. Furthermore, a major drawback of the fixed bed reactor is that the composition of the gas leaving the absorption and regeneration reactor changes with time.

To overcome the disadvantages of the discontinuous operation many options are available, the most important being: a fluidized bed reactor, a moving bed, a riser or downer, and a rotating reactor.

In a fluidized bed the sulfur removal efficiency is lower than in a fixed bed because of extensive mixing of the acceptor bed and the bypassing of acceptor particles by bubbles. Staging of a fluidized bed can (partly) overcome this problem. Sorbent
attrition is, however, relatively high. The use of an interconnected fluidized bed system reduces sorbent attrition as it eliminates transport of solids through tubings. Figure 2 shows the principle of this new type reactor\(^5\). A drawback of fluidized bed reactors that they are not flexible with respect to flow variations as they should operate within a rather strict flow regime.

\[ \text{MnAl}_2\text{O}_4 + \text{H}_2\text{S} \rightarrow \text{MnS}/\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \]

\[ \text{fuel gas} + \text{H}_2\text{S} \rightarrow \text{clean fuel gas} \]

\[ \text{S}_2 \rightarrow \text{SO}_2 \]

\[ \text{MnS}/\text{Al}_2\text{O}_3 + 0.5 \text{SO}_2 \rightarrow \text{MnAl}_2\text{O}_4 + 0.75 \text{S}_2 \]

\[ \text{H}_2\text{S} \text{ flush} \text{ SO}_2 \text{ flush} \]

**Figure 1. Principle of the rotating reactor. No flushing is indicated.**

**Figure 2. Principle of the interconnected fluidized bed.**

A moving bed reactor is a solution to sorbent mixing and attrition. It combines the advantages of fixed bed and fluidized bed operation.

The rotating reactor is a new type of reactor. The principle of this reactor for high temperature desulfurization is shown in Figure 1. In the rotating reactor practically no attrition of the sorbent occurs while the removal efficiency can, in principle, be more constant than in a normal fixed bed reactor. In Figure 3 the preliminary design for the rotating monolith reactor is shown. The sorbent material is subsequently exposed to a "sulfidation" and "regeneration" gas by continuous rotation of the reactor part which contains the sorbent. Unlike the other continuous reactors a structured packing, such as a monolith, can be used to reduce pressure drop and dust sensitivity. Furthermore, this reactor can very easily adapt to flow or concentration variations by variation of its rotation speed. The rotating reactor for high temperature applications\(^2\) is, however, in the conceptual/development phase and thus far from commercialization. Below the rotating reactor is discussed in detail.

\(^2\) For low temperature applications large rotating reactors exist. e.g. in Heidelberg a 3000 tons rotating reactor is used for deNOx.
1.2 Rotating monoliths reactor: Principle

Figure 3 shows the preliminary design of the rotating monolith reactor. The reactor is divided in different sections, an uptake and regeneration section is separated by a purge section (not shown). In the uptake section the sorbent is loaded with sulfur. Due to the rotation of the reactor this sorbent enters a purge section to remove the remaining coal gas before it enters the regeneration section. The rotation speed is adjusted in such a way that the sorbent is transported out of the uptake sections before $\text{H}_2\text{S}$ breaks through. The division between uptake and regeneration section depends on the relative time needed for regeneration compared to sulfiding. A structured reactor is needed for this purpose which consists of sufficient sections separated from each other along the length of the reactor. A single monolith would be the ultimate structure to achieve this, with the additional advantage of low pressure drops. However, no proper sealing of the brittle monolith structure is possible. Therefore, a special device had to be designed in which the different sections are separated in such a way that proper sealing is achieved.

![Figure 3. Preliminary design of the rotating reactor](image)

1.3 Modeling

The separation between the sections implies that the reactor can be described as a number of parallel plug flow reactors, each of which operates in a distinct state of uptake and regeneration at a certain time. The reactor modeling then reduces to
describe the cyclic operation of a single reactor. To obtain modeling data a separate large fixed bed reactor has been built. For details see Section 2.5.

2 Design and construction of pilot rotating monoliths reactor

2.1 Concept

The aim of the pilot reactor is to demonstrate the principle of the rotating reactor at high temperatures, up to 1223 K, and in a corrosive coal gas environment. For this, the reactor construction is kept simple, although it is in principle, suitable for scale up. The conceptual design is shown in Figure 3. It consists of parallel tubes filled with acceptor. These tubes end at both sides in a disk which rotates against static disks for gas supply and removal. Gas may only be transported from the distinct sections for gas supply and removal in the non rotating disks, towards the tubes in the rotating disk, covered by these sections. Special attention should thus be given to proper sealing between the disks.

2.2 Materials selection

Given the extreme operation conditions and the required proper sealing between the disks it may be obvious that the most important issue for the reactor design is the material selection. Below the materials selection is discussed. First the most important material requirements are summarized:

- temperature resistant up to 1223 K
- corrosion resistant in a coal gas environment up to 1223 K
- good sealing possibilities and wear resistance; no or very little gas transport may occur between the different sections, and no gas transport from the inside to the outside of the reactor system.
- sufficient mechanical strength
- good resistance to cyclic variation in stress and temperature
- reliable operation over a long period
- simple construction and joining to other equipment
- reasonably priced

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2 For a detailed description of the device see Bakker et al.
3 e.g. > 99% total flow
4 In practice the reactor will be placed in a pressure vessel
Potential construction materials for the rotating reactor are: metals (alloys), inorganic materials like ceramics and carbon, or combination materials like ceramic coated metals. In general, organic materials can only be applied below 500 K and are, therefore, not considered. In the next section the properties of the different materials are discussed.

2.2.1 Metal alloys

Many current high temperature metal alloys have been designed to resist corrosion in atmospheres with low oxygen activities; for instance an oxygen pressure of $1 \times 10^{-4}$ Pa. However, most do not provide resistance to attack by higher sulfur/lower oxygen activity cases as, for example, generated during the gasification of fossil fuels.

With respect to high temperature corrosion, classical thermodynamics can be used to determine the temperature at which the following reaction occurs:

\[
M + X \rightarrow MX
\]  

(1)

where M is the base material and X the component in the atmosphere. The extent of corrosion is very dependent on the temperature. For example, Figure 1 in Chapter 10 demonstrates the “corrosion behavior” of manganese.

The occurrence of a reaction with the gas phase in general leads to corrosion but in several cases it is favorable. e.g. CrO$_2$ and Al$_2$O$_3$, act as a barrier between the atmosphere and the metal. Sometimes the protective nature of the scale is destroyed, due to development of growth stresses in the scale. These stresses can, for example, be caused by difference in volume or expansion coefficient between the corrosion product and the base material.

Combined erosion-corrosion conditions, such as between the rotating parts of the reactor, can cause extra severe degradation of materials. This is because the erosive component often adversely affects the protective properties of the corrosion product. In general, rotating metal parts need a lubrication and sealing material to avoid erosion. At temperatures above 873 K sealing is very difficult if the environment is oxidative because the most convenient high temperature packing material graphite cannot be used. This applies to the SO$_2$/O$_2$ regeneration mixture that is oxidative.

The presence of H$_2$S and alkali metal salts accelerates the attack on materials; no protective sulfide scale is formed, because of the large size of sulfur and difference in expansion. Also the diffusion rates in sulfides are much higher than in oxides.
which causes sulfiding to proceed orders of magnitude faster than oxidation.\textsuperscript{8,13,14} The attack is particularly severe in the temperature range 1023-1273 K, which is typically the proposed operation temperature of the high temperature desulfurization process, see section 1.4 in Chapter 7. In the strongly reducing coal gas environment also protective oxides can be reduced by \textit{e.g.} carbon monoxide to form lower oxides or carbides.

\textbf{Types of metals}

For use in coal gasification processes, alloys should preferably be low in iron and manganese, relative to nickel and cobalt, as iron and manganese are strong sulfide formers.\textsuperscript{11,15,16} Cobalt alloys appear to be intrinsically more resistant to sulfidation than nickel alloys. This is mainly due to the higher melting point of Co-S compared to Ni-S. Also the diffusion of sulfur in a cobalt alloy is about 100 times slower than in nickel.

A variety of elements may be added to base metals in order to improve their properties:\textsuperscript{12,17} chromium, aluminum, silicon, carbon, rare earth metals, and refractory metals. Chromium, aluminum and silicon form a protective scale. Carbon and refractory metals, \textit{e.g.} Mo, W, Ta, Rh, Nb, V, Zr, T, increase the strength of the alloy. Rare earth metals, \textit{e.g.} Sc, Y, La, Ce etc., or their oxides have, amongst others, beneficial effect on the scale adherence.

An example of an alloy which is reasonably resistant to sulfiding and other aggressive environments is the Haynes alloy HR-160\textsuperscript{18}. This is attributed to its high Co-level (29 wt\%) in combination with Cr and Si, which forms a very protective oxide scale. The alloy is easily fabricated and is weldable with \textit{e.g.} the TIG (tungsten inert gas) method.

\textbf{2.2.2 Surface coatings on metal alloys}

The shortcomings of high strength high temperature metals with respect to resistance to the corrosion can in some cases be overcome by the application of a surface coating with a corrosion protective material.\textsuperscript{9,16,19,20} These coatings can be metals which have the ability to form protective oxide scales like chromium, aluminum or silicium. Also non-metallic coatings such as oxides, nitrides, or carbides are possible. Besides a protection against corrosion, coatings may also form a thermal barrier coating. In general, no protection against erosion corrosion is obtained.

\textbf{2.2.3 Ceramics}

Ceramics are all inorganic non-metallic solids which are characterized by covalent and ionic bonding. Extensive research over the past twenty years has led to
improved properties and therefore increased usage of these materials\textsuperscript{7,18,21-24}. They may be used at high temperatures as monolithic parts replacing superalloys, as thermal barrier coatings, or as coatings protecting metallic alloys from environments which cause severe corrosion problems. Ceramics have the hardness and corrosion resistance necessary for wear applications. An advantage is also that no lubrication is needed whereas metallic components do. To obtain minimal wear and heat-build-up surface finish is crucial.

The most important commercial ceramic materials can be divided according to their chemical composition: oxide-, nitride-, carbide, graphite, and carbon ceramics.

The oxides often have a much higher melting point than the metals from which they are derived, but are usually less refractory than the corresponding nitrides and carbides. Alumina, magnesia, silica and zirconia are examples of single oxides. Mixed oxides have most often a lower melting point than single oxides, but may have performance and cost advantages in a specific application. Examples are zircon (ZrO\textsubscript{2}SiO\textsubscript{2}) and cordierite (2MgO.2Al\textsubscript{2}O\textsubscript{3}.5SiO\textsubscript{2}). Glass ceramics contain lithium or magnesium alumina-silicate phases. These materials have relatively high bending strengths, 500 N/mm\textsuperscript{2}, and are very resistant to thermal shock.

Nitrides are more difficult to fabricate than oxides but they generally have better thermal shock properties and can bear high engineering stresses up to 1673 K\textsuperscript{17}. Carbide ceramics, for example silicium carbide, show excellent oxidation-, thermal-shock-, abrasion- and chemical attack resistance. Carbons and graphites can be used in the absence of oxygen up to very high temperatures, over 2773 K, and they are unique in strengths that increase with temperatures\textsuperscript{24}. However, in oxidizing atmospheres like the SO\textsubscript{2}/O\textsubscript{2} regeneration gas they are limited to about 773 K and are thus not suitable for application in the rotating reactor.

Although most ceramics are very inert some corrosion may occur. E.g. cations may be oxidized to a higher state. An other possibility is that molecules in the gas reacts with cations in the ceramic. E.g. siliconnitride may react with oxygen to silicndioxide.

Fabrication of ceramics is complex and highly specialized\textsuperscript{21,22}. Most high temperature ceramics are also materials of high hardness and, consequently, machining and polishing pose problems. Diamond grinding of the hot pressed sintered components is widely practiced and where high accuracy of the finished dimensions is required laser machining of ceramics is being seriously evaluated for cutting and drilling operations.

Because of the costs of fabrication, ceramics in most cases are only placed in the area of high wear. Therefore, they must be joined to other materials in the construction in most cases metals. Significant thermal expansion differences exist
between metals and ceramics. If a flexible joining can be made that allows wear loads to be distributed, improved results can be expected because surface microcracks are minimized.

2.2.4 Comparison of construction materials
In Table 1 an overview is given for the most important materials properties for application in the rotating reactor of metal alloys, ceramics and coated metals. From the table and the above discussions it follows that ceramics are the only suitable construction materials for the rotating reactor. In terms of materials properties, the advantages of ceramics over alloys are:

- higher upper temperature limits
- greater corrosion resistance
- higher wear resistance
- longer term mechanical and thermal stability
- lower density

In terms of process design further advantages are:
- lower costs over the raw materials
- less cooling equipment required, which is often needed in metallic equipment
- cost savings over the use of lighter weight ceramic components

On the other hand, there is much more experience in machining metals, and metals have better thermal shock properties. Also the strength of most ceramics is lower than most metallic materials. Therefore, it was decided to construct the shaft of the rotating reactor, which is not in contact with the corrosive gas, from a high temperature resistant alloy. One should however account for differences in the expansion coefficient.

To improve the corrosion resistance of alloys a coating on the alloys can be applied. Coatings have, however, a poor impact resistance which makes coated alloys vulnerable. Further comparison of coated alloys show that coatings are by far superior over uncoated alloys.

Although the price of mechanical processing is high, the application of most ceramics is technically attractive. Alumina ceramics are most widely used and their properties fit the requirements. Therefore, high purity alumina was chosen as construction material. Only for the place where the driving shaft is coupled to the reactor silicium nitride was chosen as it is extremely strong and tough.
Table 1. Comparison of possible construction materials for the rotating (monoliths) reactor if applied up to 1223 K and in a coal gas environment. Abbreviations: e = excellent, vg = very good, s = satisfactory, and p = poor.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Ceramics</th>
<th>Alloys</th>
<th>Coated alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature resistance (fixed shape)</td>
<td>e</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>e</td>
<td>p</td>
<td>s</td>
</tr>
<tr>
<td>Wear resistance</td>
<td>e</td>
<td>p</td>
<td>s</td>
</tr>
<tr>
<td>Impact resistance</td>
<td>s</td>
<td>e</td>
<td>p</td>
</tr>
<tr>
<td>Inertia (weights)</td>
<td>e</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>Surface finish</td>
<td>vg</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>Price raw materials</td>
<td>vg</td>
<td>p</td>
<td>-</td>
</tr>
<tr>
<td>Experience mechanical processing</td>
<td>s</td>
<td>e</td>
<td>s</td>
</tr>
<tr>
<td>Price mechanical processing</td>
<td>p</td>
<td>vg</td>
<td>-</td>
</tr>
</tbody>
</table>

The most suited construction material is without doubt silicon carbide because of its extreme strength, its good heat conduction properties, and fixed shape up to extremely high temperatures. However, this material is much more expensive than alumina.

2.5 Reactor⁵ and equipment construction

A pilot scale rotating reactor has been constructed, consisting of sixteen parallel reactor tubes, which can be filled with monolithic samples or particles, in a circular arrangement. The reactor has a diameter of 0.15 m and a length of 0.4 m. Depending on the pressure and temperature the gas flow through the reactor can be 0.1-20 m³/kw·h⁻¹ (STP). Figures 4a-f show the reactor set-up and some relevant reactor parts. The disks in which the reactor tubes are mounted are pressed to the other disks by means of an adjustable spring to allow for materials expansion during heating. The middle disk serves to distribute gas flows in the four sections, uptake, regeneration, and two flushing sections. This section can be replaced to vary the distribution between uptake and regeneration section. The outer disks contain four connections for gas supply and removal at each side. The flow system is designed for countercurrent operation but in principle also cocurrent operation is possible.

One of the main concerns were temperature and corrosion resistance and effective sealing at high temperatures, up to at least 1173 K. This is achieved by the use of alumina ceramics. This material is highly corrosion, wear, and temperature resistant and no separate lubrication is necessary. So, practically the whole reactor section is

⁵ For details on the reactor construction see Bakker et al. 31
constructed out of this material and no separate sealing material is needed. During construction the disks of the reactor were lapped on to each other with diamond powder to obtain a perfect fit. The roughness of the disk surface was less than 0.2 μm. After construction the reactor was two times heated up to 1273 K. Some additional lapping of the disks was performed after the first heating cycle. After the second heating cycle no additional lapping was necessary. The drive shaft, which was made of a high temperature resistant steel, contains a double Cardan coupling to minimize stresses on the reactor construction. Figures 4d and e shows the reactor placed in an oven which is mounted in the experimental set-up. This set-up includes facilities for gas supply and removal. Analysis can be performed with a UV spectro-photometer and a mass spectrometer. The data acquisition and operation are fully automated. A flow scheme of the experimental set-up is depicted in Appendix 1.

In the same set-up also a large fixed bed reactor is present to obtain accurate data for modeling. The maximum length and diameter of this reactor are 1 m and 0.04 m, respectively. Operation is possible up to 1273 K and 11 bar with both cocurrent and countercurrent regeneration. The operation pressure of the rotating reactor is, in principle, not higher than two bar although the reactor can withstand higher pressures (up to 30 bar). The maximum operation temperature for the rotating reactor is 1223 K (oven limit) and for the fixed bed reactor 1273 K.

2.5.1 Tests to determine temperature resistance and gas tightness of the rotating reactor

To test if the reactor was gastight, experiments with nitrogen were performed with a rotating, 0.1-2 rpm, and a non-rotating reactor, at different temperatures, up to 973 K, and gas flows of 0.1 - 5 l/min. The length of the test varied from several hours to several days. Hereby, the in- and outlet gas flow was measured with a calibrated flow meter. Different flow meters were used depending on the gas flow to obtain maximum accuracy. The disk pressure should be adjusted to the pressure in the reactor. If the correct disk pressure was chosen no gas leakage could be observed from one section to an other section, or from the sections to the outside of the reactor.\textsuperscript{7,8}

\textsuperscript{6} The rotating reactor has been constructed by Ceratec Technical Ceramics in Geldermalsen.

\textsuperscript{7} The accuracy of the flow measurement was 1-2% of the total flow.

\textsuperscript{8} In a practical application the rotating reactor will be mounted in a pressure vessel. Especially for applications at high pressures this will reduce the mechanical requirements on the construction.
Figure 4. "Snap-shots of the rotating reactor with additional equipment.

a. Parts of the rotating reactor. From left to right:
- Disk with tubes for gas supply and removal.
- Gas distribution disk; contains 2 small sections for flushing and 2 large sections for sulfiding and regeneration; variation of the gas distribution is possible by replacement of this disk.
- Rotating reactor with 16 tubes which can be filled with a monolith shaped sorbent.

Gas distribution disk. Disk with tubes for gas supply and removal and a central tube in which the shaft rotates.
b. (Left) All ceramic rotating reactor in horizontal position. Gas supply and removal and tube for axis. Length rotating part 40 cm, diameter 15 cm.
c. (Left below) Detail of the reactor axis. The connection with ceramics is flexible to avoid stresses
d. Rotating reactor in oven. On top of the oven the drive for the axis with momentum limiter is installed.
2.5.2 Regenerative desulfurization with the rotating reactor

Due to time constraints no experiments under reaction conditions could be performed with the rotating reactor. The performance of the rotating reactor has, therefore, been simulated using the data of a single tube experiment in the TPS experimental set-up, see Chapter 8 and 11. The results are shown in Figures 5a-c. In the first case the reactor, which contains 16 tubes, is divided in 6 tubes for the regeneration and 6 tubes for the sulfiding section. 30 kPa steam is used as regenerant. Figure 5a shows an almost constant low H₂S concentration of the simulated coal gas leaving the sulfiding section. Fluctuation in the gas outlet composition is moderate compared to a single bed operation because variations in the gas from a single tube are averaged by the gas leaving the other tubes⁹. The gas outlet, see Figures 5b and 5c, of the regeneration section shows a periodical character, although also in this case the variation is less

⁹ At time x the sorbent is sulfided up to a different degree for all tubes in the sulfiding section. A tube is in the sulfiding section until the H₂S concentration in this tube exceeds 100 ppm.
strong than with a single bed, see for example Figure 2 in Chapter 11. In Figure 5c the regeneration section is shown if it contains 25 tubes. In that case the H₂S outlet concentration is almost constant. In a practical application an optimum should be found between the degree of periodicity in the regeneration off gas and the number of tubes in a sections.

Figure 5. Desulfurization simulation of coal gas with 0.64% H₂S and regeneration with 30% steam in the rotating reactor at 1123 K. Monolith shaped sorbent with high loading Mn. The H₂S concentration in the feed of the sulfiding gas is indicated at the left side of the figures.

a. H₂S concentration in cleaned coal gas; 6 tubes for uptake. The maximal H₂S concentration is about 65 ppm.

b. H₂S concentration in the regeneration gas leaving the reactor; 6 tubes for regeneration.

c. H₂S concentration in the regeneration gas leaving the reactor; 25 tubes for regeneration.

3 Case study: High Temperature Desulfurization of a 250 MWe Coal gasifier

For two practical cases a conceptual design study was performed. First the operation the application of a full scale rotating reactor in a 250 MWe gasification unit is discussed, and second our pilot rotating reactor in a side stream of a gasification unit. Furthermore, a comparison is given of the rotating reactor versus a sequentially
operated fixed bed reactor and a new process for high temperature coal gas cleaning is proposed.

3.2 Desulfurization of the coal gas of a 250 MWe coal gasification unit

A coal gas of the 250 MWe power plant in Buggenum (the Netherlands) is chosen as an example. In this power plant Shell gasification technology is used. The coal produced has a low water content and is strongly reducing, see Table 2 of Chapter 7. About 0.5 kg sulfur/s has to be removed from this gas stream.

The operation temperature and pressure is 1123 K and 30 bar, respectively. In the rotating reactor pure SO₂ is used as regenerant. As a sorbent a high Mn loading monolith with a effective sulfur uptake capacity of 14 wt% is taken. To avoid contamination of the cleaned gas or the regeneration product, flushing occurs with e.g. nitrogen between the sulfiding and regeneration step. Table 2 gives an overview of the operation and boundary conditions. These conditions are based on calculations and experimental results of the previous chapters.

The calculated dimensions and operation limits of the rotating reactor are given as “results” in the same Table. It appears that about 90% of the sorbent can be used for the uptake of H₂S. Furthermore, only 0.9 m³ sorbent is needed for complete desulfurization. The uptake capacity is not the most important factor for the reactor volume. So maximizing the sorbent capacity is not necessary. Hydrodynamics and kinetics require about 1.5 meter length sorbent material and a cross-sectional area of at least 0.55 m². If the 60 rpm is taken as the maximum rotation speed of the reactor the required sorbent uptake capacity is only 4.2 wt% sulfur.

No significant temperature change occurs during sulfidation because of the relatively small amount of H₂S and the low heat of reaction. The regeneration is endothermic and a temperature drop of the regeneration gas of around 40 K will occur. A somewhat higher inlet temperature e.g. 1173 K can compensate for this effect. Possibly, for the regeneration of absorbed HCl and HF an extra section can be included in the reactor. This section would be placed after the regeneration section for sulfur regeneration.

3.2 Operation of the pilot rotating reactor in a side stream of a coal gasification unit

The current rotating reactor can be used as a pilot reactor for several applications. Below some characteristics are discussed in case it is used in a side stream of a coal gasifier and using the outcomes and boundary conditions of the case discussed above. The design data and some of the results are given in Table 2.

---

10 5% of the reactor volume is reserved for flushing.
The rotating reactor contains 16 tubes, 2 flushing sections and a sulfiding and a regeneration section. To avoid pressure fluctuations the minimum of tubes per section is two. If the current rotating pilot reactor would be used in a pilot installation to desulfurize dry “Buggenum” coal gas the sulfiding section would contain 10 tubes, the regeneration section11 2, and each flushing section 2 tubes. The reactor would be able to desulfurize 21 m³ (NPT) coal gas per hour. The rotation speed would be 50 rotations per hour.

3.3 Rotating reactor versus sequentially operated fixed bed reactor

A conventional method for operation of cyclic processes is a sequentially operated fixed bed reactor. Generally, the construction of a fixed bed reactor is simple and relatively inexpensive. However, as mentioned in the introduction it has some disadvantages; especially in treating large volumes of gas at high temperatures. To avoid unacceptable system instabilities 2-4 hours is a preferred minimum switching time; switching valves in these large systems leads to instabilities of typically 15 minutes. To minimize the reactor volume of a fixed bed reactor a high capacity sorbent is important. For example, with a three hours sulfiding time and a 14 wt% S uptake capacity of the sorbent, about 75 m³ of sorbent material is required12. For the rotating reactor only 0.92 m³ is needed, see Table 2.

The construction of corrosion resistant and gas tight valves, which are necessary for application at high temperatures and high gas volumes, is still extremely difficult. The construction of the rotating reactor is, of course, also difficult. An advantage is, however, that this is one system and that it rotates continuously. Large pressure variations which cause instabilities do not occur.

The performance of the fixed bed reactor is not constant because the composition of the gas leaving the reactor changes in time. As shown in figure 5 the performance of the rotating reactor is less periodical, depending on the number of tubes in one section. Also the sorbent can be used more effectively during absorption because high H₂S concentrations in the outlet of one tube can be compensated by the (still) lower outlet concentrations of the other tubes.

3.4 New process proposal for coal gas cleaning

In this paragraph the implementation of high temperature gas cleaning in a conceptual process is discussed. The regeneration process for the sulfided sites is discussed in more detail in Section 3.4.1.

11" A minimum of two tubes is required to avoid pressure build up in a supply up during rotation of a tube to an other section.
12" For this it is assumed that two reactors are used for sulfiding and one for regeneration.
Table 2. Boundary and operation conditions, and typical dimensions of high temperature desulfurization in a 250 MWt coal gasification plant.

<table>
<thead>
<tr>
<th>Basis of design</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>25,26</td>
</tr>
<tr>
<td>CO, H2, H2S, H2O</td>
<td>Ch.7</td>
</tr>
<tr>
<td>other</td>
<td>Ch.7</td>
</tr>
<tr>
<td>sulfiding temperature</td>
<td>Ch.11</td>
</tr>
<tr>
<td>regeneration temperature</td>
<td>Ch.11</td>
</tr>
<tr>
<td>pressure</td>
<td>25,26</td>
</tr>
<tr>
<td>max. gas velocity in monolith</td>
<td>27</td>
</tr>
<tr>
<td>uptake rate</td>
<td>Ch.11</td>
</tr>
<tr>
<td>estimation rate constant</td>
<td>Ch.11</td>
</tr>
<tr>
<td>minimal residence time sulfiding gas</td>
<td>Ch.11</td>
</tr>
<tr>
<td>effective sulfur uptake capacity sorbent</td>
<td>27, Ch.11</td>
</tr>
<tr>
<td>regeneration time/sulfiding time</td>
<td>Ch.11</td>
</tr>
<tr>
<td>open cross-sectional area monolith</td>
<td>Ch.8</td>
</tr>
<tr>
<td>density sorbent including open space</td>
<td>Ch.8</td>
</tr>
<tr>
<td>channel diameter in monolith</td>
<td>Ch.8</td>
</tr>
<tr>
<td>high loading sorbent</td>
<td>Ch.8</td>
</tr>
<tr>
<td>Δ Hf,°(T) sulfiding with H2S</td>
<td>Ch.9</td>
</tr>
<tr>
<td>Δ Hf,°(T) regeneration with SO2</td>
<td>Ch.9</td>
</tr>
</tbody>
</table>

| Results full scale RMR                       | full scale | pilot |
| rotation speed reactor                       | rph        | 18    | 50    |
| sorbent sulf. section/sorbent reg. Section  | -          | 21:1  | 5:1   |
| total weight of sorbent material             | kg         | 730   | 0.4   |
| total volume of sorbent material             | m³         | 0.92  | 5 10⁴ |
| SO₂ flow                                     | m³ s⁻¹     | 0.35  | 3.7 10⁴ |
| minimal cross-sectional area total reactor   | m²         | 0.55  | -     |
| length for given capacity at 60 rpm          | m          | 0.5   | -     |
| length for minimal residence time            | m          | 1.5   | -     |
| ΔT sulfiding gas                             | K          | < 2 K | < 2 K |
| ΔT regeneration gas                          | K          | - 35 K| - 35 K|
| ΔT reg. gas if 1/3 of S₂ is burned for SO₂   | K          | 170 K | 170 K |
| production (total 15 vol.% S₂ in reg. Gas)   | bar        | 0.21  | -     |
Continuous regenerative desulfurization in a continuous (monolith) reactor

As has been shown in Chapter 11, the application of the developed manganese based sorbent is feasible for high temperature desulfurization of dry coal gas. For convenience the schematic representation of the sorbent is shown in Figure 6. Theoretically, also the regenerative removal of HCl and HF is possible with this sorbent. An interesting feature is that the regeneration of the sulfided sites can occur independently from the regeneration of the chlorinated and the fluoridated sites. While SO₂ regenerates the sulfided sides it does not regenerate the other sites\(^{28}\). These sites can be subsequently regenerated with steam. Besides the removal of the above mentioned components, also a small amount of alkali metals have to be removed from the fuel gas. Absorbents\(^{29}\) have been reported, which absorb alkali metals very efficiently, also at very high temperatures e.g. Fullers earth. However, no regeneration of these sorbents is possible.

![Figure 6. Schematic representation of the manganese based sorbent developed. The combination of three types of sites ensures a good desulfurization depth and a high capacity. Besides the direct sulfur production during regeneration the applicability without significant deactivation up to very high temperatures is an attractive characteristic.]

The current method for removal of various components is cooling of the coal gas in a huge syngas cooler followed by wet scrubbing at temperatures below 350 K and heating up again\(^{30}\). Usually, the H₂S is recovered from the liquid sorbent during regeneration and sent to a Claus unit where H₂S is converted to elemental sulfur.

Figure 7 shows a proposal for a new gas cleaning process at high temperature. The gas leaving the gasifier is not cooled and flows directly to the cleaning section. First the alkali metals are removed\(^{13}\) in a fixed bed absorber. H₂S, COS, HCl and HF are removed in a rotating monolith reactor. Regeneration of the sulfided sites occurs with SO₂ or with a mixture of SO₂ and O₂. The other sites are regenerated with steam after the regeneration of the sulfided sites to minimize contamination with H₂S. The regeneration products are pure elemental sulfur, and steam with HCl and HF. After cleaning the gas flows (preferably) without heat exchange to the conversion section.

\(^{13}\) In a practical process the removal of the alkali metals usually should occur before the other components because the interaction with the Mn sorbent is unknown. To our knowledge alkali absorption is non regenerative and the sorbent should, therefore, be replaced from time to time, e.g. during maintenance stops.
The outcomes of the conceptual study indicate that ("compared to a system with a "low temperature gas cleaning process"):
- Less heat exchange equipment is required (smaller syngas cooler)
- No separate Claus plant is needed
- The inlet temperature in the gas conversion unit can be higher than in the current IGCC unit, e.g. 900 K. This unit may be new generation gas turbine, a SOFC, or another device. For a discussion on optimal operation temperature see Chapter 7.

**Figure 7.** Simplified representation of the proposed coal gas cleaning and conversion process. Dust removal is not indicated separately in the gas cleaning section.

### 3.4.1 Regeneration of the sulfided sites
In Figure 8 the simplified regeneration process is depicted. The previous chapters show that the sorbent can be regenerated in several ways to obtain elemental sulfur as regeneration product, including regeneration with SO₂, SO₂ in combination with a small amount of O₂, or SO₂ followed by SO₂ with a small amount of O₂. The addition of oxygen improves the regeneration of sites which are difficult to regenerate. On the other hand experiments indicated that direct addition of oxygen lead to some deactivation. The best regeneration method is, therefore, likely the regeneration with pure SO₂, followed by regeneration with a SO₂/O₂ mixture. The SO₂ can be obtained by the oxidation of a small amount, typically 1/3, of the produced sulfur (15% in SO₃).

The regeneration gas leaving the rotating reactor contains a mixture of SO₂ and S₂. The SO₂ is reused and most of the S₂ is condensed from this mixture. To obtain liquid sulfur the condensation temperature should be between 400 and 700 K. After condensation, the remaining SO₂ is reheated to the required inlet temperature of the regeneration section. The required heat can be partly supplied by the exothermic
oxidation of sulfur. In the process scheme part of the liquid sulfur is fed back to a oxidation section. The sulfur is also partially supplied via the gas phase with SO₂.

![Diagram showing process scheme for the regeneration of the sulfided sites.]

**Figure 8.** Process scheme for the regeneration of the sulfided sites.

![Diagram showing the uptake of MnAl₂O₄ and MnO, MnS + Al₂O₃, and MnS with SO₂ and SO₂/O₂.]

**Figure 9.** Operation principle of a "two sorbent" desulfurization process in a rotating or fixed bed reactor.

The developed sorbent contains different manganese phases to ensure a good capacity and desulfurization depth. Another option for effective desulfurization is the use of different sorbents, e.g., MnO in combination with MnAl₂O₄, see Figure 9. During sulfiding MnAl₂O₄ captures the bulk of the H₂S while MnO captures the remainder. During regeneration, in the counter current mode, MnS is efficiently converted to MnO with O₂ from an O₂/SO₂ mixture. The remaining SO₂ regenerates the MnS on Al₂O₃ to MnAl₂O₄. For the most effective desulfurization if different absorption materials are used, a fixed bed or rotating reactor is required. In a fluidized bed the use of two separate sorbents will not be less effective.

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14° The heat of sulfur combustion to produce SO₂ can be used to partially reheat the regeneration gas, ΔT about 150 K.
4 Conclusions

The results obtained for the pilot rotating reactor and the conceptual process designs show that:

- The concept of the rotating reactor is feasible for high temperature coal gas desulfurization.
- The rotating reactor allows a flexible operation and is very small compared to swing operation of fixed bed reactors.
- A rotating reactor has been developed and built on a pilot plant scale, 0.1-21 m³ h⁻¹ (NTP), for continuous operation of cyclic processes, at high temperatures, and in corrosive environments.
- Ceramics are the only feasible construction material for operation up to 1223 K.
- A good sealing between the rotating parts and non-rotating parts is obtained with the use of alumina ceramics.
- The reactor has been successfully heated under non-rotating conditions up to 1273 K and under rotating conditions up to 973 K.
- No leakage could be observed during operation from 300-973 K
- A new conceptual process configuration is proposed for the high temperature desulfurization of coal gas. In this configuration less heat exchange equipment is required.
- The removal of H₂S, COS, HCl and HF can possibly take place simultaneously in a rotating reactor. Alkali metals have to be removed in a separate fixed bed reactor which is placed before the rotating reactor.
- More detailed studies are necessary

5 Literature

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11. Stephenson, D.J., Predicting the high temperature erosion behavior of materials used in gas turbines, Corrosion Science, 29 (1989) 647-656


Gestructureerde Systemen voor Gasscheiding

Samenvatting

Dit proefschrift bestaat uit twee delen welke afzonderlijk van elkaar gelezen kunnen worden.

Deel 1
Silicaliet-1 zeolietmembranen


In het eerste hoofdstuk is een korte inleiding gegeven over membranen en membraanreactoren. Het silicaliet-1 zeolietmembran is een microporouso anorganisch membraan waar de scheiding van gassen en vloeistoffen op moleculair
niveau plaatsvindt. Een typische poriegrootte van het membraan is 0.55 nm. Het selectief verwijderen of toevoeren van reactanten en producten met behulp van een anorganisch membraan in een membraanreactor is een aantrekkelijke methode om chemische processen efficiënter en schoner te laten verlopen.

In hoofdstuk 2 wordt de ontwikkeling van het silicaliet-1 membraan en het groeien van een dergelijk membraan in een membraanmodule beschreven. Ook wordt een introductie gegeven over zeolieten. Een continue zeolietlaag met een dikte van ongeveer 50 μm wordt verkregen vanuit een waterige synthese oplossing bij een temperatuur van rond de 458 K. De synthese vindt plaats in de een geheel roestvrijstalen membraanmodule. Bijzonder is dat de silicalietlaag zelf de afdichting vormt tussen het poreuze en het niet poreuze gedeelte van de module. Tijdens de synthese vindt kristalgroei plaats, zowel vanuit een gellaag die op het metaaloppervlak wordt gevormd, als direct vanuit de oplossing. Na de synthese is de zeolietlaag gasdicht, zelfs voor kleine moleculen zoals neon. Het malmolecule tetrapropyllumonium dat de zeolietporiën blokkeert wordt verwijderd door calcinatie op een temperatuur van 673 K. Het verkregen membraan heeft naast zeolietporiën een klein aantal iets grotere poriën. Slechts een zeer klein gedeelte van het transport vindt plaats door deze grotere poriën.

Hoofdstuk 3 beschrijft het massatransport door poreuze media. Ook wordt de proefopstelling en een aantal systeemkarakteristieken besproken. Het massatransport door poreuze media is sterk afhankelijk van de poriegrootte, druk en temperatuur. Hoe kleiner de poriën worden des te belangrijker is de interactie met de poriewand. Voor transport door zeolietporiën is zowel adsorptie als groeot en vorm van het molecuul belangrijk, bovendien is het transport geactiveerd. De flux door het membraan is afhankelijk van de meetmethode. De gemeten flux moet daarom in veel gevallen gecorrigeerd worden om een juist beeld van de membraaneigenschappen te verkrijgen. Zo blijkt bijvoorbeeld de positionering van het membraan ten opzichte van de voeding een invloed te hebben op de flux door het membraan. In deze studie is de Wicke-Kallenbach meetmethode gebruikt voor het meten van het massatransport van een groot aantal componenten en mengsels door het zeolietmembraan. Naast edelgassen waren dat koolwaterstoffen (C1-C8) en enkele anorganische componenten zoals H₂, CO₂ en SF₆. Helium werd gebruikt als draaggas. De temperatuur werd hierbij gevarieerd tussen de 190 en 700 K en de druk tussen 5-1000 kPa.

Hoofdstuk 4 beschrijft een studie naar het permeatiegedrag van enkele componenten over een groot temperatuurgebied. Over het algemeen wordt er met toenemende temperatuur een maximum en een minimum in de permeatie waargenomen. Voor sterk adsorberende gassen is echter alleen een maximum waarneembaar en voor zwak absorberende gassen is alleen een minimum.
verschillen in permeatieflux voor de verschillende gassen zijn groot, voor een voedingsdruk van 101 kPa ongeveer een factor 10000. De hoogste permeatieflow werd waargenomen voor metaan: een permeance van \(10 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}\) op 240 K en de laagste voor iso-butaan op 300 K: \(0.07 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}\). De waargenomen temperatuurafhankelijkheid van de permeatie kan alleen verklaard worden met het optreden van twee verschillende diffusiemechanismen. Voor een hoge bezettingsgraad (lage temperatuur) kan het massatransport beschreven worden met evenwichtsadsorptie en oppervlakte diffusie en bij een lage bezettingsgraad (hoge temperatuur) met geactiveerd gasachtig transport (geactiveerde Knudsendiffusie). Met toenemende temperatuur verschuift het massatransportmechanisme van oppervlakte diffusie naar de geactiveerde gasachtige diffusie. Met een mathematisch model waarin beide diffusie mechanismen zijn opgenomen zijn de experimentele resultaten goed te beschrijven.

Het permeatiegedrag van mengsels is beschreven in hoofdstuk 5. In de meeste gevallen is de scheidingsselectiviteit niet gelijk aan de permeatie van de enkele componenten permeatieverhouding. Naast het "moleculaire zeefmechanisme" en verschil in mobiliteit tussen de verschillende moleculen blijkt adsorptie een sleutelrol te spelen in de scheidingsselectiviteit. Zo kan de permeatie van zwak absorberende component (bijvoorbeeld waterstof) makkelijk een factor 100 dalen door de aanwezigheid van een sterk absorberende component (bijvoorbeeld butaan). Dit resulteert in zeer selectieve scheidingen in het voordeel van de sterkst absorberende component. Typische scheidingsselectiviteiten zijn 125, 27 en >300 voor, respectievelijk, \(n\)-butaan/waterstof (@295 K, 95 kPa/5 kPa), \(n\)-butaan/iso-butaan (295 K, 50 kPa/50 kPa) and metaan/iso-octaan (@423 K, 25 kPa/5 kPa). Bij toenemende temperatuur wordt draait in veel gevallen de scheidingsselectiviteit om. Dit kan verklaard worden door de temperatuurafhankelijkheid van adsorptie en diffusie. De scheidingsselectiviteit is ook een functie van de samenstelling van een mengsel en de voedingsdruk. Hieruit blijkt dat de binaire evenwichtsadsorptie niet beschreven kan worden met het uitgebreide Langmuir model.

Tot slot wordt in hoofdstuk 6 de kwaliteit en modificatie van het metaalgedragen silicaleit-1 membraan besproken. Ook de commerciële status en potentie van zeolietmembranen komen aan de orde. Het membraan is opmerkelijk stabiel. Voor individuele membranen werd na twee jaar testen bij temperaturen tussen de 200 en 700 K geen significante verandering van het massatransport waargenomen. Vooral de thermische stabilité van het membraan is opmerkelijk omdat de uitzettingscoëfficiënt van silicaleit-1 en roestvrij staal verschillend is. Ook regeneratie van een membraan met koolafzetting resulteerde in het terugkeren van de oorspronkelijke permeatie eigenschappen. Permeatiedata voor verschillende membranen liggen dicht bij elkaar. Dit geeft een goede reproduceerbaarheid van de membraansynthese aan. Silaneren is een goede methode om selectief de permeatie-

Deel 2  
**Mangaan absorbentia voor hoge temperatuur H₂S verwijdering**

Ongeveer eenderde van de brandstoffen worden wereldwijd gebruikt om elektriciteit op te weken. Omdat de wereldvoorraad van olie en gas afneemt wordt verwacht dat de rol van kolen voor elektriciteitsopwekking en als grondstof voor chemicaliën gaat toenemen. Een efficiënte manier om kolen te gebruiken voor elektriciteitsopwekking is ze om te zetten, via een vergassingsproces, naar een mengsel van waterstof en koolmonoxide en daarna elektriciteit op te weken door dit gas te verbranden in een gasturbine en geproduceerde warmte te gebruiken om een stoomturbine aan te drijven. Kolen en ook kolengas bevatten relatief veel verontreinigingen. Voor kolengas zijn stof en H₂S de belangrijkste. Maar ook alkalimetalen, zware metalen, HCl, HF en ammoniak moeten vaak verwijderd worden. Reiniging is niet alleen belangrijk om milieuvervuiling te voorkomen maar ook om de apparatuur te beschermen tegen corrosie. In de huidige lage temperatuur reinigingsprocessen wordt het kolengas voordat het gereinigd wordt gekoeld naar een temperatuur iets boven kamertemperatuur. Hierna worden via verschillende wasprocessen de verontreinigingen verwijderd met vloeibare absorbentia. Het zwavel komt vrij in de vorm van H₂S en wordt in een Claus fabriek omgezet naar elementaire zwavel. Door bij een hogere temperatuur de verontreinigingen te verwijderen kan bespaard worden op de kosten van warmtewisselaars en kan het elektrisch rendement van de centrale omhoog met enkele procenten. Het tijdens de regeneratie direct vormen van elementaire zwavel is ook aantrekkelijk omdat geen Claus installatie nodig is voor de productie van elementaire zwavel. Het doel van het onderzoek, in het tweede deel van dit proefschrift, is het ontwikkelen van een lage drukval sorbent voor hoge temperatuur onttwaveling waarbij bij tijdens regeneratie van dat sorbent direct elementair zwavel wordt gevormd. Een tweede doel is de ontwikkeling van een roterende reactor om cyclische processen, zoals regeneratieve hoge temperatuur onttwaveling, continue te laten verlopen.

In hoofdstuk 7 wordt een introductie gegeven over kolenvergassing en kolengasreiniging. Speciale aandacht wordt hierbij besteed aan de selectiecriteria voor sorbentia voor regeneratieve hoge temperatuur onttwaveling. In het algemeen
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geldt dat de keuze van het sorbent sterk afhankelijk is van de specifieke toepassing (bijvoorbeeld nat of droog kolengas) en het gewenste regeneratieproduct. Mangaan werd uitgekozen als een potentieel geschikt sorbentmateriaal voor ontzwaveling van droog (Shell type) kolengas bij zeer hoge temperatuur (boven 873 K) en de mogelijkheid van directe productie van elementair zwavel tijdens regeneratie. Hierbij moet worden opgemerkt dat toepassing van het sorbent mogelijk ook interessant kan zijn voor andere gasstromen die ontzwaveld moeten worden.

Hoofdstuk 8 beschrijft de bereiding van op mangaan gebaseerde sorbentia. Zowel deeltjes als monolieten zijn hiervoor gebruikt. Herhaalde natte impregnering met een mangaanacetaat oplossing gevolgd door droging en calcinatie bleek een geschikte methode om hoge belading (typisch 36 gewicht %) monsters te verkrijgen met een goede uniforme mangaanverdeling. Bij deze monsters was na calcinatie zowel Mn₂O₃ als Mn₃O₄ aanwezig. Depositiепrecipitatie resulteerde in monsters met een slechte mangaanverdeling. Het gebruikte meertap impregneringproces is tijdrovend en dus relatief duur. Voor commerciële productie van het mangaansorbent heeft een eenstaps proces de voorkeur, bijvoorbeeld het meeextruderen van mangaanacetaat bij de productie van deeltjes of monolieten.

In hoofdstuk 9 wordt een algemeen overzicht gegeven van de verschillende typen inzwavelingsreacties van metalen en metaaloxideën. Hiervoor worden zowel literatuurgegevens van molybdeen-, wolfram- en nikkeloxideën, nikkel en metingen aan verschillende mangaan(alumina)oxideën. Voor de metingen werd gebruik gemaakt van temperatuur geprogrammeerde inzwaveling (TPS) met H₂S en temperatuur geprogrammeerde regeneratie met stoom (TPReg). De apparatuur die hiervoor nodig is wordt ook beschreven in dit hoofdstuk. Metaloxideën zwavelen meestal in door middel van zuurstof-zwavel uitwisseling en metalen via oxidatie. Bij reductie van metaloxideën is de temperatuur zeer belangrijk naast de aanwezigheid van H₂S en H₂. Tijdens inzwaveling is de kristalgroottes (dispersie) van grote invloed op de mate van inzwaveling. Bij kleine kristallen treedt minder diffusielimitering op waardoor de inzwaveling beter verloopt. Omdat vaste stofdiffusie een sterk geactiveerd proces is, wordt bij toenemende temperatuur een vollediger inzwaveling bereikt. Bij 1200 K is de inzwaveling meestal compleet. Naast de bekende TPS techniek blijkt TPReg een waardevolle aanvullende methode om inzwavelingsreacties te bestuderen.

Hoofdstuk 10 beschrijft de thermodynamische eigenschappen en kristalstructuur van mangaanoxideën, mangaansulfideën, en mangaan-aluminaat (MnAl₂O₄). Ook de thermodynamica van inzwaveling en regeneratie met verschillende reactanten, te weten zuurstof, stoom, zwaveloxide, kooldioxide en waterstof, komt aan de orde. Er is gekeken naar de reactie met andere componenten in kolengas zoals HCl, HF, NH₃ en HCN. Ook belangrijke reacties in het kolengas, zoals de water-gas-shift reactie worden besproken. Alle mangaanverbindingen
absorberen COS en H$_2$S. Vergeleken met mangaan-aluminaat absorberen mangaanoxiden deze verbindingen sterker. Als gevolg daarvan zijn ze moeilijker te regenereren en is zuurstof nodig voor een efficiënte regeneratie. Behalve dat dit een zeer exotherme reactie is, wordt hierbij zwaveldioxide gevormd wat in de meeste gevallen een ongewenst product is. Mangaanaluminaat kan worden geregenererd met SO$_2$ en H$_2$O waarbij respectievelijk elementair zwavel en H$_2$S worden gevormd. Met name elementair zwavel is een aantrekkelijk regeneratie product. NH$_3$ en HCN reageren niet met de mangaanverbindingen. HCl en HF daarentegen wel. Bij hoge temperatuur (> 800 K) reageren COS en H$_2$S preferent met het sorbent. Het sorbent kan dus in principe gebruikt worden voor zowel het afvangen van zwavelhoudende verbindingen als van HCl en HF. Regeneratie van MnCl$_2$ is niet mogelijk met SO$_2$ maar wel met stoom. Dit maakt aparte regeneratie mogelijk. Mangaanaluminaat is vooral aantrekkelijk als (deel van) een sorbent als het gewenste regeneratieproduct zwavel is en het kolengas relatief droog is. Bovendien maakt de relatief goede stabiliteit van MnCl$_2$ toepassing bij zeer hoge temperatuur mogelijk.

In Hoofdstuk 11 worden de mangaansorbentia, waarvan de bereiding in hoofdstuk 8 is beschreven, getest op hun geschiktheid voor toepassing in een hoge temperatuur ontwavelingsproces. Ook wordt veel aandacht besteed aan de karakterisering van de sorbentia en inzwanings en regeneratie mechanismen. Het blijkt dat een "duo" sorbent dat bestaat uit kristallijn MnAl$_2$O$_4$ en enkele procenten dispers verdeelde MnO het meest geschikt is voor de ontwaveling van droog kolengas. De mangaanbelading van dit sorbent is typisch 36 gewicht % en de concentratie H$_2$S na ontwavelen van (een gesimuleerd) kolengas is kleiner dan 50 ppm. Naast de kristallijne fases is ook een amorfe fase aanwezig op het oppervlak van het sorbent. Tijdens regeneratie met SO$_2$ is elementair zwavel het enige regeneratie product. Bij regeneratie met stoom wordt H$_2$S gevormd en boven 1000 K ook enig SO$_2$ en zwavel. Het sorbent kan gebruikt worden tussen 673 en 1273 K maar de capaciteit is sterk temperatuur afhankelijk. De hoogste capaciteit wordt bereikt tussen 1100 en 1200 K. De acceptor capaciteit is hoog, tot 20 gewichts % zwavel bij een mangaanbelading van 35 gewichts %. De praktische capaciteit bij een ontwaveling tot 100 ppm H$_2$S ligt rond de 14 gewichts % zwavel. Bij een test bij 1123 K van 110 cyc ni bleef de performance van het sorbent stabiel. Het oppervlak van het sorbent is na stabilisatie relatief hoog: 13-24 m$^2$ na meer dan 50 cycli op 1123 K. Op hoge temperatuur, > 1100 K, blijken de thermodynamische berekeningen van hoofdstuk 10 in overeenstemming met de waargenomen (vaste) fases. Thermodynamische berekeningen zijn daarom een bruikbaar hulpmiddel om de gas en sorbent samenstelling te voorspellen op hoge temperatuur. Het gedrag van oppervlaktiesites is echter niet te voorspellen met de gebruikte methode. Oppervlakteplaatsen spelen een belangrijke rol tijdens ontwaveling. Op "lage" temperaturen, < 700 K, vindt zwavelabsorptie voornamelijk plaats op deze sites. Op
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grond van de resultaten in dit hoofdstuk is het volgende inzwavelings- en regeneratiemechanisme voorgesteld. Tijdens inzwaveling diffundeert Mn$^{2+}$ uit de spinel structuur, terwijl Al$^{3+}$ een deel van de vrijgekomen plaatsen opvult. Hierdoor ontstaat een aparte Al$_2$O$_3$ fase. De zuurstof ioni en die overblijven worden uitgewisseld met zwavelioni en verlaten het sorbent uiteindelijk in de vorm van H$_2$O. De zwavelioni reageren met Mn tot MnS met een steenzoutstructuur. Tijdens regeneratie diffundeert een deel van de Mn$^{2+}$ weer terug in de spinelstructuur en diffundeert een deel van het alumina uit het rooster. Na wat herstructurering is ook O$^2-$ weer opgenomen en vormt zich weer MnAl$_2$O$_4$. Naast de kristallijne fasen is ook altijd een amorfe fase aanwezig die waarschijnlijk een belangrijke versnellende rol speelt in het hierboven genoemde diffusie proces.

Hoofdstuk 12 beschrijft de ontwikkeling van een roterende (monoliet) reactor voor continue operatie van cyclische processen. Ook wordt de toepassing van deze reactor voor hoge temperatuur reiniging van kolengas conceptueel behandeld. Het bijzondere van deze reactor is dat hij bedreven kan worden tot op ongewoon hoge temperaturen (1273 K) en in een corrosieve gasomgeving. Het voordelen ten opzichte van andere continue reactoren is dat hij zeer flexibel is met betrekking tot variaties in het gasdebiet en gasconcentratie. Als een monoliet wordt gebruikt als reactorvulling dan heeft het systeem bovendien een zeer lage drukval, geen maldistributies en is ongevoelig voor stof. Voor toepassing voor hoge temperatuur ontswaveling is keramiek het enige geschikte constructiemateriaal voor de reactor. Een reactor op pilotschaal is gebouwd met een capaciteit van 0.1-20 m$^3$.h$^{-1}$ (STP). Deze reactor is succesvol getest (zonder reactie) onder niet roterende condities tot 1273 K en onder roterende condities tot 973 K. De toepassing van het ontwikkelde monoliet sorbent voor hoge temperatuur ontswaveling in de roterende reactor is in principe mogelijk. 90% van het reactorvolume (en het sorbent materiaal) kan continue worden gebruikt voor absorptie van H$_2$S. De overige 10% wordt gebruikt voor regeneratie met SO$_2$ en spoelen. vergeleken met sequentieel bedreven vastbed reactor met dezelfde monoliet sorbent kan het reactor volume meer dan 80 maal kleiner zijn. Als de reactor zou worden opgeschaald voor het ontswavelen van een 250 MWe (Shell type) kolenvergasser dan bevat de reactor slechts 0.9 m$^3$ sorbent materiaal en is het open doorstroomd oppervlak van 0.55 m$^2$. De rotatie snelheid zou 18 rpm bedragen. Benadrukt moet worden dat de uitkomst is van een conceptueel ontwerp en dat nadere studies noodzakelijk zijn voor een nauwkeurig en gedetailleerd procesontwerp.

Wridzer J.W. Bakker
Structured Systems for Gas Separation

Summary
A subdivision into two parts have been made for this thesis. Each part can be read separately.

Part 1.
Silicalite-1 zeolite membranes
Separation of liquid and gas mixtures are essential steps in many (petro) chemical processes. For these separations many techniques have been developed. Distillation, adsorption and extraction are the most important ones. Membrane separation is a relative new technology with a rapidly growing importance. Membrane processes are attractive because of the low energy costs, ease of operation and compactness of the membrane unit. Currently, most membranes are polymeric membranes. The polymers applied have, however, some disadvantages: a limited thermal, chemical and mechanical stability. For example: a thermal cleaning procedure is not possible and the membrane material is pressed together at high pressures. The attractive application of membranes in multi-functional reactors is in most cases not possible because of the limited temperature resistance, typically 437 K. Inorganic membranes, in principle, can be used under extreme conditions. Therefore, the development of inorganic membranes received much attention in the last decade. In this respect inorganic membranes based on zeolites are attractive because of their well defined pore structure of molecular dimensions. The first part of the thesis focuses on the development and characterization of a metal-supported silicalite-1 zeolite membrane. Special attention has been given to the mass transport through this type of membrane.

In Chapter 1 a short introduction has been given on membranes and membrane reactors. Separation of gases and liquids with a silicalite-1 zeolite membrane takes place on a molecular level. A typical dimension of the pores is 0.55 nm. The selective removal or addition of components with the add of an inorganic membrane is a very attractive method to increase process efficiency and to obtain cleaner processes.

In Chapter 2 an introduction is given on zeolites and the preparation of zeolite membranes in Chapter 2. A continuous layer with a thickness of about 50 μm is obtained during a hydrothermal synthesis in an all stainless steel membrane module at around 458 K. Crystal growth occurs from a gel layer which is formed on the
metal and directly from the solution. No separate sealing is needed in this membrane module as the membrane layer itself seals the transition from porous to non-porous steel. It is shown that several formulations lead to continuous zeolite layers. These layers appeared to be gas tight before calcination and only opened up above 623 K after the template molecule TPA (tetrapropylammonia) decomposes. Besides zeolite pores the membrane also contains a small amount of somewhat larger pores. Only a very small part of the total mass transport takes place through these pores. The membrane is remarkably stable upon thermal cycling.

Chapter 3 qualitatively describes mass transport through porous media, focusing on micropore/zeolite diffusion. Also the experimental set-up for permeation and adsorption measurements and some system characteristics are discussed. Mass transport through porous media is strongly dependent on pore size, pressure, pressure difference, and temperature. The smaller the pore size the more important the interaction with the pore walls. Also the size and the shape of the molecules are important; in general an activated mass transport is observed. For micropores, at low temperatures, strong adsorption dominates and permeation is described by a combination of adsorption and surface diffusion. At high temperatures the mass transport is described by an activated type of gaseous diffusion. The flux through the membrane is dependent on the experimental method and should be corrected to obtain the real membrane characteristics. In this work the Wicke-Kallenbach method has been used to measure the mass transport of single components and binary mixtures. Helium has been used as carrier gas and the temperature and pressure have been varied between, respectively, 190 and 700 K and 0.05 and 10 bar. Components under investigation were the noble gases, linear and branched alkanes (C₁-C₈) and several inorganic gases like H₂, CO₂, CO, N₂ and SF₆.

In Chapter 4 one-component permeation characteristics of the silicalite-1 membrane over a broad temperature range (190-680 K) are presented. Large differences have been found between the one-component permeation fluxes: up to a factor of about 500 between methane and the bulky i-butane at room temperature. Generally, the permeation and diffusion coefficient decrease with increasing molecular size. A remarkable temperature dependency has been observed. In general, with increasing temperature the permeance shows a maximum followed by a minimum. For gases which are weakly adsorbed at 300 K, such as hydrogen, the permeance has only a minimum, for gases which are strongly adsorbed at 300 K, such as butane, only a maximum is observed in the permeance. For i-butane the permeance only increases steadily with temperature. A comparison between the adsorption isobars and the temperature dependence of the steady state permeance shows that at the temperature where the amount adsorbed decreases strongly a maximum in permeation occurs and that where the amount adsorbed vanishes the
permeance starts to increase. The temperature dependence of the steady state fluxes through the silicalite-1 membrane can only be described if two diffusion mechanisms are taken into account. For high occupancies the mass transport can be described by equilibrium adsorption and surface diffusion and for low occupancies the mass transport can be described by activated gaseous diffusion. With increasing temperature the mass transport mechanism shifts from the surface diffusion regime to the activated gaseous diffusion regime. Using these two diffusivities good agreement is obtained between the modeling and the experimental results for the one-component flux through the silicalite-1 zeolite membrane. In agreement with the one-component permeation results for the silicalite-1 membrane, as presented in this work, a general model for mass transport is micropores is available.

In Chapter 5 permeation data are presented of several mixtures, which give an overview of the separation characteristics of the metal-supported silicalite-1 membrane over a broad temperature and pressure range. In many cases the separation selectivity of a mixture does not reflect the one-component permeation ratio. Besides molecular sieving and difference in diffusivity, difference in adsorption appears to be a key factor in separation selectivity. The permeation of weakly adsorbing molecules, e.g. hydrogen at 295 K, can drop over two orders of magnitude in the presence of strongly adsorbing molecules, e.g. n-butane at 295 K. This results in high separation selectivities favoring the strongest adsorbing component. Typical separation selectivities for n-butane/hydrogen (@295 K, 95 kPa/5 kPa), n-butane/i-butane (@295 K, 50 kPa/50 kPa), and methane/iso-octane (@423 K, 25 kPa/5 kPa) mixtures, are 125, 27 and >300, respectively. An inversion in separation selectivity is observed during a temperature programmed permeation which is explained from the temperature dependence of adsorption and diffusivity. The separation factor is also a function of the composition and the feed pressure. It is concluded that the binary equilibrium adsorption can not be described with the extended Langmuir model.

The application potential and the quality of the metal-supported silicalite-1 zeolite membrane is discussed in Chapter 6. Also the commercial status of zeolite membranes and the results of zeolite pore modification via silanation with TMCS are given. The membrane is remarkably stable. For individual membranes the transport characteristics remained unchanged during a testing period of up to 2 years at a temperature between 200 and 700 K. It can withstand a pressure difference of at least 10 bar and a heating rate of over 15 K/min.1. Regeneration of the membrane after deliberate coking results in the recovery of the original properties. Permeation results are reported for two different silicalite-1 membranes. Only a small difference is observed, indicating a high reproducibility of the zeolite membrane synthesis. It has been demonstrated that silanation is a way to influence, selectively, the permeation behavior. Larger and strongly adsorbed molecules are more affected by the
modification than smaller and weakly adsorbed molecules. The first commercial zeolite membrane modules are available. They are used for pervaporation applications.

Part 2
Manganese based sorbents for high temperature H₂S removal

About one-third of the world’s energy fuels consumption is in generating electricity of which almost 60 % is produced from fossil fuels. The role of coal in electricity production and the production of chemicals is expected to become more and more important, as the world supply of oil and gas is diminishing. A efficient way to convert coal to electricity is via a gasification process. In this process coal is converted to hydrogen en carbon monoxide and burned in a gas turbine. The heat produced is used to produce steam for a steam turbine. Coal and coal gas contain impurities. In coal gas, dust and H₂S are the most important ones. But, in most cases, also a significant amount of alkali metals, heavy metals, HCl, HF and NH₃ are present. Gas cleaning is not only necessary to prevent pollution of the environment, but also to protect the equipment against corrosion. For the currently used low temperature cleaning processes the gas is cooled with a large syngas cooler from about 1750 K to about room temperature. The impurities are removed in several washing steps with liquid sorbents. During regeneration of these sorbents, in most cases, H₂S sets free and is converted in a Claus plant towards elemental sulfur. High temperature gas cleaning is attractive as it enhances the electrical efficiency. Direct sulfur production during regeneration is attractive as the expensive Claus plant becomes redundant. The objective of the research, described in part two of the thesis, is to develop a low pressure drop sorbent for high temperature desulfurization. Also, direct sulfur production during regeneration is desired. The second objective is the development of a rotating reactor for continuous operation of cyclic processes, e.g. high temperature regenerative desulfurization.

In Chapter 7 a short introduction is given on coal gasification processes and gas cleaning processes. Special attention has been given to sorbents for high temperature desulfurization and the selection aspects of these sorbents. In general, the choice of the sorbent is dependent on the type of coal gas, e.g. wet or dry coal gas, and the preferred regeneration product. An overview is presented of regenerable metal oxide acceptors which are currently under investigation or being applied. Zinc ferrite and zinc titanate have received much attention over the last 15 years and it has become clear that besides advantages they also exhibit some limitations. Other
sorbents are promising at temperatures at which the often commercially used zinc based sorbents cannot be applied, T > 973 K, and if direct sulfur production during regeneration is desired. It is discussed that the ideal hot gas cleaning process operates at a temperature around 1100 K. Application of this gas can be attractive in (future) gas turbines suitable for a very hot fuel gases, e.g. 900 K, or as fuel for solid oxide fuel cells. Manganese based sorbents are attractive as they can be applied at very high temperature. Moreover, direct sulfur production during regeneration seems possible.

Chapter 8 describes the preparation of manganese based sorbents for high temperature desulfurization (> 873 K) via wet impregnation and deposition precipitation. Both γ-Al2O3 particles (50-7000 μm) and monoliths (pure γ-Al2O3 and γ-Al2O3 wash coated) are used as support. Wet impregnation with manganese acetate appears to be a good method to prepare high loading samples, typically 36 wt.% manganese, with a relatively good manganese distribution. Hereby, the type of γ-Al2O3 support is of minor importance. Deposition precipitation resulted in samples with a poor manganese distribution. Mn3O4 and, at high manganese loading, also Mn2O3 is formed after impregnation and calcination at 873 K. For the samples prepared via deposition precipitation only Mn2O3 was observed. The applied multi-step impregnation is labor intensive and, therefore, expensive. For the production of a commercial sorbent a one step method is preferred. For example, the co-extrusion of manganese acetate during the production of particles or monoliths.

In Chapter 9 sulfiding reactions have been elucidated using temperature programmed sulfiding profiles of MoO3, WO3, Ni, NiO and several manganese oxides on γ-Al2O3, and manganese aluminate (MnAl2O4). Also the temperature programmed steam regeneration profiles of MnS and MnS on γ-Al2O3 are discussed in relation to their sulfiding behavior.

Metal oxides sulfide mainly via O-S exchange and metals via oxidation. In the reduction of oxides the temperature is the most important factor, but the concentration of H2S and H2 is also important. During sulfiding the dispersion (crystal size) plays a major role. Solid state diffusion is slow, although strongly activated. Therefore, only at very high temperatures, typically 1200 K, the samples are completely sulfided. It is concluded that temperature programmed steam regeneration is a useful additional tool to clarify sulfiding reactions.

Furthermore, the experimental set-up for TPS, and isothermal sulfiding and regeneration experiments is discussed.

In Chapter 10 the thermodynamical properties and structure of supported and unsupported manganese oxides, manganese sulfides and manganese aluminate (MnAl2O4) have been reviewed. Also the thermodynamics of sulfidation and regeneration with different reactants, viz. O2, H2O, SO2, CO2, and H2 are
summarized. Furthermore, the reactions with other components, such as HCl, HF, NH₃, HCN, H₂ and CO, present in coal gas are dealt with. Compared with MnAl₂O₄, manganese oxides H₂S and COS absorb more strongly. Consequently, regeneration is relatively difficult and oxygen is needed for regeneration. The resulting regeneration product, SO₂, is in most cases not desired. Sulfided MnAl₂O₄ can be regenerated with SO₂ and H₂O leading to elemental sulfur and H₂S, respectively. Especially, elemental sulfur is an attractive regeneration product. It is concluded that MnAl₂O₄ is an attractive material for desulfurization of dry coal gas, eventually in combination with another sorbent, because elemental sulfur can be produced during regeneration. HCl and HF are also absorbed by MnO and MnAl₂O₄ but at high temperatures H₂S and COS absorb preferentially. An advantage from a process point of view is that MnCl₂ on Al₂O₃, in principle, does not react with SO₂ but relatively easy with steam. This enables a component specific regeneration.

In Chapter 11 the applicability of a manganese based sorbent for high temperature desulfurization of dry coal gas has been studied. It appears that a “duo” sorbent consisting of crystalline MnAl₂O₄ and a small amount of disperse MnO performs best in the desulfurization of a dry type coal gas (desulfurization depth lower than 50 ppm H₂S). Beside these phases also an amorphous Mn-Al-O phase is present at the surface of the sorbent. Elemental sulfur is the only observed regeneration product during regeneration with SO₂. H₂S, and above 1000 K also some sulfur and SO₂ are formed during steam regeneration. The sorbent can be used in the temperature range between 673 to 1273 K but the optimum capacity is obtained between 1100 and 1200 K. For regeneration with SO₂ the regeneration temperature should be > 873 K to avoid sulfate formation. The acceptor capacity is high, up to 20 wt.% sulfur, and the sample appears to be stable during at least 110 sulfiding and regeneration cycles at 1123 K. The practical capacity, with a desulfurization depth of 100 ppm H₂S is up to 14 wt.%. The surface area is relatively high after stabilization. It amounts to 13-24 m²/g after more than 50 cycles at 1123 K. At high temperatures, > 1100 K, the thermodynamic calculations in Chapter 10 are in accordance with the observed (solid) phases after sulfiding and regeneration. It is concluded that thermodynamic calculations are a helpful tool to predict the actual gas and solid phase compositions at high temperatures. The performance of the surface sites can, however, not be predicted with the applied method. These surface sites play an important role during desulfurization. At “low” temperatures, below 700 K, absorption occurs mainly on these sites. Furthermore, a sulfiding and regeneration mechanism within the sorbent material is proposed. It is discussed that during sulfiding the Mn²⁺ diffuses out of the spinel structure, while Al³⁺ diffuses into the spinel structure and fills the created vacatures. The resulting oxygen is exchanged with sulfur and MnS with a rock salt crystal structure is formed. During
regeneration most of the Mn$^{2+}$ diffuses back into and Al$^{3+}$ out of the spinel structure. After some rearrangements the O$^{2-}$ is included and a MnAl$_2$O$_4$ phase is formed. Also an amorphous phase is present on the sorbent which seems to enhance the mass transport within the sorbent during sulfiding and regeneration.

In Chapter 12 the development of a rotating (monolith) reactor is described. The aim is to continuously operate cyclic processes in corrosive gas environments at unusually high temperature, i.e. up to 1273 K. For certain applications this new reactor type is attractive. Compared to other continuous reactors it is very flexible towards flow variations, has a low pressure drop, shows little maldistribution, and is insensitive to dust. Under the severe operation conditions of high temperature desulfurization only ceramics are applicable as construction material. Unlike metal alloys, no separate sealing materials are required between the rotating parts, because of the high stability of ceramics at an atomic level. A reactor has been built on a pilot scale (0.1-20 m$^3$ gas.h$^{-1}$). It has been successfully tested under non-rotating conditions up to 1273 K and under rotating conditions up to 973 K. The application of the manganese based sorbent on a monolith structure in a rotating reactor is feasible. 90% of the reactor volume can be used for absorption. For the removal of H$_2$S from the coal gas of a 250 MW gasification unit about 0.9 m$^3$ sorbent material is needed, and an open cross-sectional area of 0.55 m$^2$. Hereby, the reactor makes 18 revolutions per hour. Compared to a sequentially operated fixed bed reactor, the reactor volume can be over 80 times smaller. A new process configuration for fuel gas cleaning and sorbent regeneration is proposed. It should, however, be stressed that the process designs in this chapter are conceptual and that more studies are required for a detailed and accurate process design.

Widmer J.W. Bakker
Symbols and Definitions

Symbols

\( b^0 \) = limiting value of the Langmuir adsorption parameter (100 kPa)\(^{-1} \)
\( d_p \) = pore diameter, m
\( M \) = molar mass, g.mol\(^{-1} \)
\( R \) = gas constant, J.Mol\(^{-1} .K\(^{-1} \)
\( R_m \) = diameter of zeolite membrane layer, m
\( v \) = gas velocity, m.s\(^{-1} \)
\( V \) = diffusional volume, m\(^3\)
\( x \) = space coordinate, m
\( \alpha \) = constant in Fuller equation, \( 9^{0.5} .m^2.s^{-1}.N.K^{-1.75}.mol^{1.16} \)
\( \Delta \) = thickness of support, m

Subscripts and superscripts

avg = average amount adsorbed
D = diffusion
F = Fick diffusion
max = maximum in potential energy
min = minimum in potential energy
sat = saturation capacity

Abbreviations

IGCC = Integrated Gasification Combined Cycle
PFBC = Pressurized Fluidized Bed Combustion
Me = Metal
TP = Temperature Programmed
TPS = Temperature Programmed Sulfiding
TPR = Temperature Programmed Reduction with H\(_2\)
TPReg = Temperature Programmed Regeneration with steam
**Definitions**

Theoretical sulfiding time: Time needed to sulfide all the manganese present with the chosen feed composition. Hereby, a $S/Mn$ ratio of 1 is taken.

Relative regeneration time: Regeneration time/time needed for complete sulfiding with 1 vol% $H_2S$ in the feed. Hereby, a $S/Mn$ ratio of 1 is taken.

Active phase
- greyscale

Low loading sample: $Mn < 8 \text{ wt.\%}$
- greyscale

Medium loading sample: $8 < Mn < 32 \text{ wt.\%}$
- greyscale

High loading sample: $32 < Mn < 40 \text{ wt.\%}$
- greyscale

Very high loading sample: $Mn > 40 \text{ wt.\%}$
- greyscale
Publications and Patents

Publications


Patents/ patent applications


Presentations at international conferences

About 20 (oral and poster)
Dankwoord

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Wridzer, 11 november 1998
Curriculum Vitae

Equipment for temperature-programmed and isothermal sulfiding and regeneration experiments.
TPS and Regeneration Unit
Pressure: around 1 bar
Design and Drawing: Wridzer J.W. Bakker
Copyright: TU-Delft; may 1994
Cross-sectional overview of the silicalite-1 membrane, SS-1, by SEM (left) and EDAX elemental image (right). Blue refers to metals, red to silicon (Chap. 2, Fig. 9d).

Cross-section of an impregnated and calcined washcoated monolith acceptor. The dark brown part is the washcoat layer, the white part is the cordierite support (Chap. 8, Fig. 3).
Colors of different high loading monolith samples. 1) upper left, fresh unloaded (IM0), 2) upper right, fresh impregnated and calcined at 973 K; 3) lower left, regenerated with steam at 1123 K after sulfiding at 1123 K; 4) lower right, sulfided after two sulfiding and regeneration cycles at 1123 K (Chap. 11, Fig. 3).