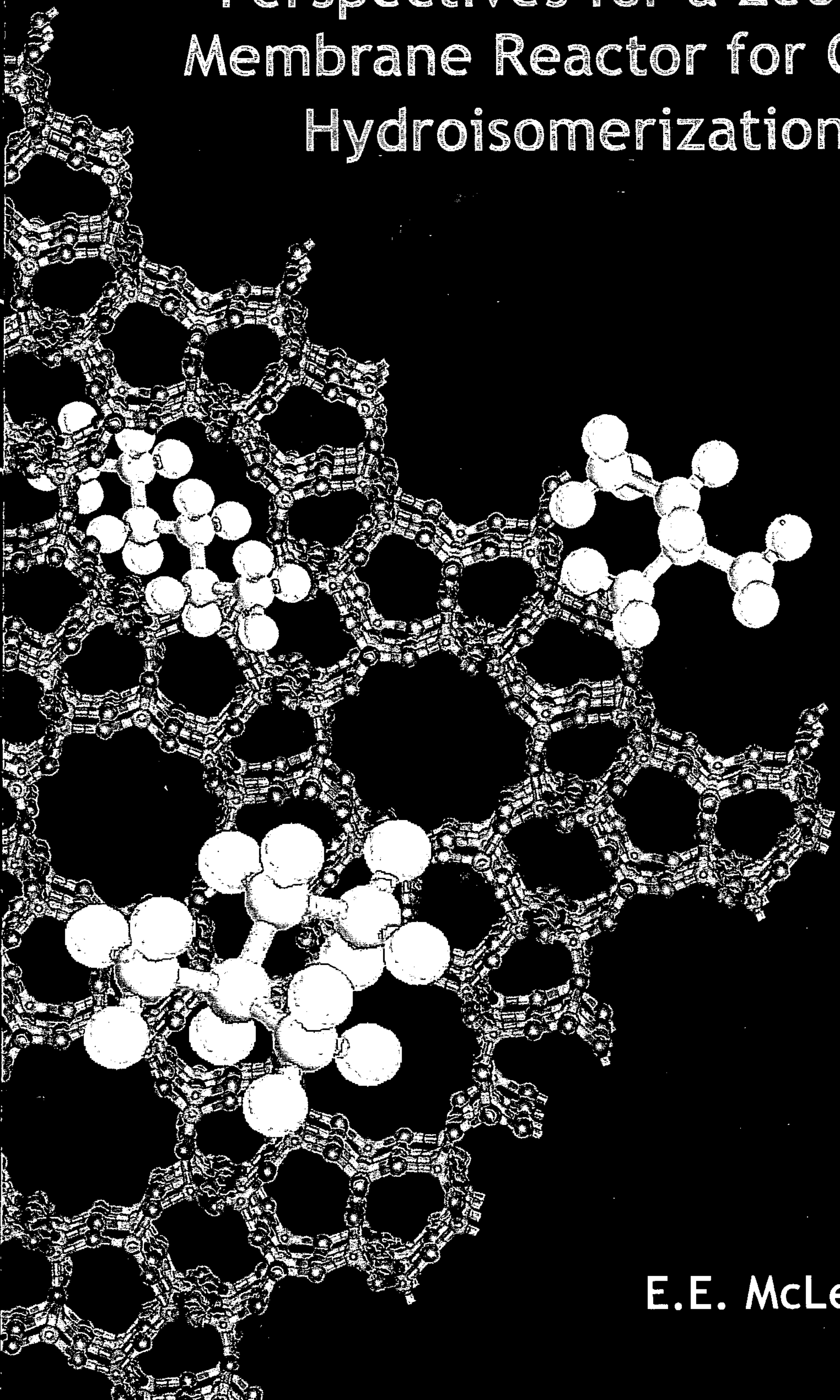
Perspectives for a Zeolite Membrane Reactor for C_5/C_6 Hydroisomerization



E.E. McLeary

Propositions

Belonging to the thesis:
'Perspectives on a Zeolite Membrane Reactor for C_5/C_6 Hydroisomerization'
by Engela Elizabeth McLeary-Diedericks

1. One should add to the basic adsorption properties of zeolites the flexibility of the framework- a fact that either opens unexpected opportunities or could cause failure in molecular separation.

   Koningsveld v. H., and Jansen J.C., *Mic.Mat. (1996), 6, 159-167, and this thesis*

2. Configurational entropy effects to separate linear from branched alkanes at high molecular loadings, as demonstrated by Krishna, could be used to effect separation at industrial scale using more attainable relatively thick, continuous zeolite membranes at higher pressures.

   Krishna, R., *et al.*, *Chem. Soc. Rev.*, **31**, (2002), 185–194

3. In contrast to the *in-situ* synthesis the use of a mesoporous silica precursor film provides a more viable way of synthesizing a zeolite membrane.

   Chapter 4 and 5 of this thesis

4. The use of "micro membrane reactors" produced by molecular sieve membranes coated onto catalyst particles, offers the greatest promise for industrial application of high temperature membrane reactors.

   Puil v.d. N., et al., *J.Chem.Soc.Farad.Trans.*, 93(1996), 4609, Zhong, Y. *et al. Chem. Commun.*, (2006), 2911–2912, Nishiyama, N., et al., *Mic. Mes. Mat.* 83, (2005), 244-250, and Van Vu, D. et al., J. of Catal. 243, (2006). 389-394

5. Clean cabinets, fundamentals of reactive precipitation and smooth, defect-free support surfaces are underexposed subjects in the preparation of continuous zeolite layers.

6. The state of world politics and societal relapse is symptomatic of a society that does not require any *education/examination for the two most influential jobs on earth: that of running a country and of being a* parent.

7. God was able to create the world in seven days largely because no-one was looking over His shoulder asking whether He had finished yet.

8. The institution of marriage and family life is the human right most often violated by the corporate world.

   Dawood v Minister of Home Affairs, 2000, 3, SA 936 (CC)

9. Without friction progress is not possible.

10. Success is not determined by the absence of problems but by one's reaction to them.

These propositions are considered defendable and as such have been approved by the supervisors Prof. J.C. Jansen and Prof. F. Kapteijn.

Stellingen

Behorende tot het proefschrift:

'Mogelijke configuraties van een Zeoliet Membraan Reactor voor C_5/C_6 Hydroisomerisatie '

van Engela Elizabeth McLeary-Diedericks

1. Men dient de flexibiliteit van het rooster aan de fundamentele adsorptie eigenschappen van zeolieten toe te voegen daar dit onverwachte mogelijkheden of obstructies geeft in moleculaire scheiding.

   Koningsveld v. H., and Jansen J.C., *Mic.Mat.* (1996), 6, 159-167, and this thesis

2. Configurationele entropy effecten in de separatie van lineaire en vertakte alkanen bij hoge moleculaire belading, zoals gedemonstreerd door Krishna, kunnen toegepast worden voor de scheiding op industriele schaal bij relatief dikke continue zeoliet membranen bij hoge druk.

   Krishna, R., *et al.*, *Chem. Soc. Rev.*, **31**, (2002), 185–194

3. In tegenstelling tot *in-situ* synthese biedt het toepassen van een mesoporeuze silica precursor film een meer levensvatbare weg om een zeoliet membraan te prepareren.

   Chapter 4 and 5 of this thesis

4. Het gebruik van "micro membraan reactoren" door moleculaire zeef membranen aan te brengen op catalysator deeltjes, biedt de grootste belofte voor industriele toepassing voor hoge temperatuur membraan reactoren.

   Puil v.d. N., et al., *J.Chem.Soc.Farad.Trans.*, 93(1996), 4609, Zhong, Y. *et al. Chem. Commun.*, (2006), 2911–2912, Nishiyama, N., et al., *Mic. Mes. Mat.* 83, (2005), 244-250, and Van Vu, D. et al., J. of Catal. 243, (2006). 389-394

5. Stof-arme ruimten, fundamentele kennis van reactieve precipitatie and gladde, defect-vrije drager oppervlakken zijn in aandacht onderbelicht in de synthese van continue zeoliet lagen

6. De toestand van de wereldpolitiek en de sociale terugval is symptomatisch voor een samenleving die geen opleiding/toetsing vereist voor de twee meest belangrijke taken op aarde: die van het besturen van een land en het ouderschap.

7. God was voornamelijk in staat de wereld te creeren in zeven dagen, omdat niemand over Zijn schouder keek en informeerde of Hij al klaar was.

8. Het instituut van huwelijk en familie leven is een menselijk recht dat het meest wordt geschonden in de universele samenleving.

   Dawood v Minister of Home Affairs, 2000, 3, SA 936 (CC)

9. Zonder wrijving is vooruitgang niet mogelijk.

10. Succes wordt niet bepaald door de afwezigheid van problemen maar door hoe men erop reageert.

Deze stellingen worden verdedigbaar geacht en zijn als zodanig goedgekeurd door de promotoren Prof. J.C. Jansen and Prof. F. Kapteijn.

Perspectives on a Zeolite Membrane Reactor for C_5/C_6 Hydroisomerization

Engela Elizabeth McLeary-Diedericks

Cover: Separation of linear from branched alkanes with MFI

Perspectives on a zeolite membrane reactor for C_5/C_6 hydroisomerization

Thesis

presented for the degree of doctor
at Delft University of Technology
under the authority of the Vice-Chancellor, Prof.dr.ir. J.T. Fokkema,
to be defended in public in the presence of a committee
appointed by the Board of Doctorates

on February 20, 2007 at 12.30 o'clock
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Prof.dr. R.D. Sanderson has provided substantial guidance and support in the preparation of this thesis.

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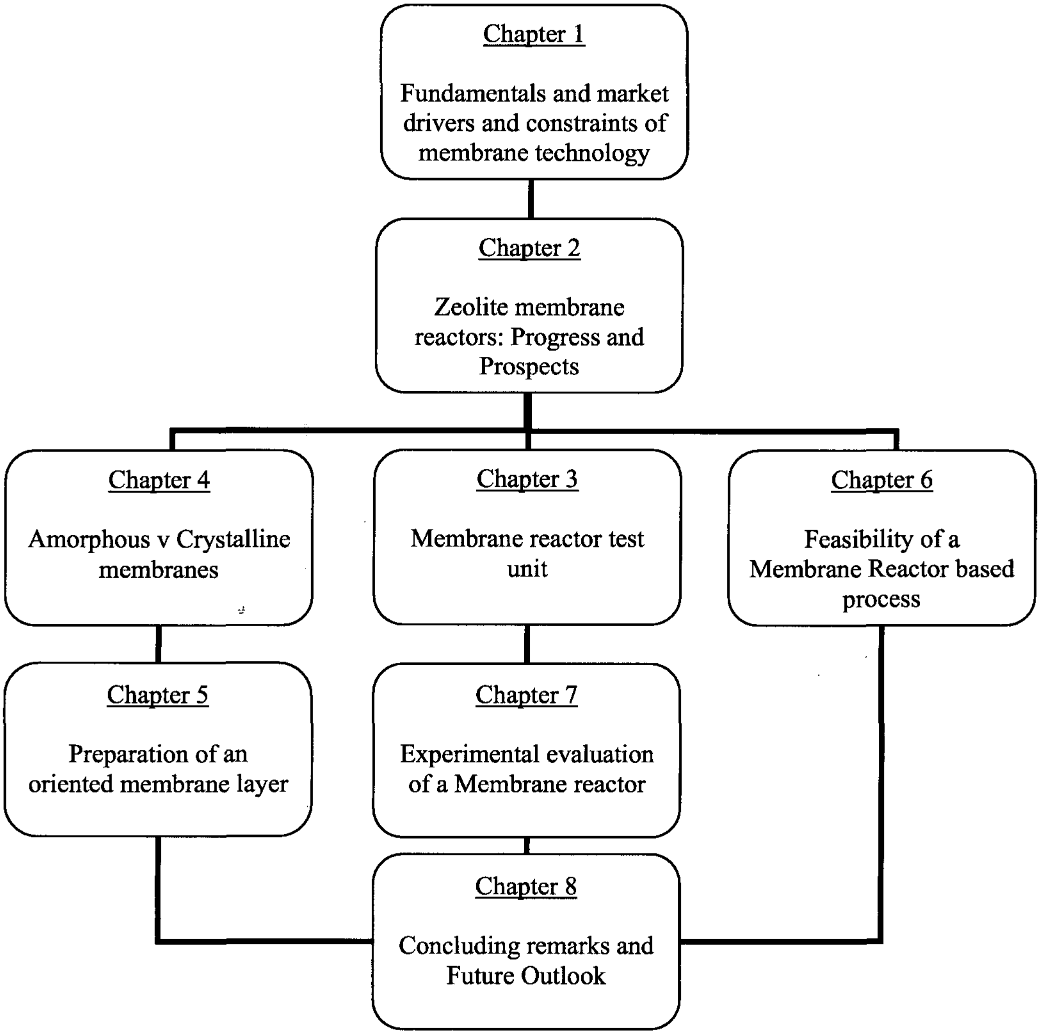
To James Breton
my personal saint

Preface and thesis outline

This dissertation follows a multidisciplinary approach exploring three avenues (see scheme), and describes an investigation into the intensification of the C_5/C_6 hydroisomerization process by combining the reaction and separation operations in a single membrane reactor unit. The successful commercial application of high temperature catalytic membrane reactors mainly depends on two determining factors: the catalytic reaction and the membrane separation. The task is further compounded by the fact that, especially for the petrochemical industry, the catalysts have been highly optimized. This thesis therefore places a strong emphasis on the one unresolved factor on which industrial application hinges, namely membrane separation.

Thesis outline:

- *Chapter 1* gives a short introduction and aims to draw the various strings on which the project is based together in order to provide the framework of the investigation.
- *Chapter 2* reviews membrane reactors, with specific attention given to the progress made and the road forward to the industrial realization of zeolite-based, catalytic membrane reactors.
- *Chapter 3* describes the test unit that was designed and installed to investigate the membrane reactor concept.
- *Chapter 4* critically evaluates the synthesis and mechanism of formation of amorphous and crystalline (zeolite) continuous membrane layers.
- *Chapter 5* investigates the preparation of an oriented, continuous silicalite-1 membrane.
- *Chapter 6* looks at the conceptual process design, and economic outlook for a membrane reactor based hydroisomerization process.
- *Chapter 7* gives an experimental investigation into the combination of the hydroisomerization reaction and separation of linear alkanes from the product, in a single membrane reactor unit.
- *Chapter 8* highlights some general conclusions and gives a future outlook.


Chapter 1
Fundamentals and market drivers and constraints of membrane technology
Chapter 2
Zeolite membrane reactors: Progress and Prospects
Chapter 4
Amorphous v Crystalline membranes
Chapter 3
Membrane reactor test unit
Chapter 6
Feasibility of a Membrane Reactor based process
Chapter 5
Preparation of an oriented membrane layer
Chapter 7
Experimental evaluation of a Membrane reactor
Chapter 8
Concluding remarks and Future Outlook

Contents

1

Membranes and membrane processes: the sustainable option

Abstract

Membrane technology is a vibrant industry which can play an important role in realizing global sustainability. This has given rise to an annual market valued at more than US$2 billion, growing at nearly 10% per annum. Applications abound in water and waste treatment, air pollution control, gas separations, fuel cells and product stream purification.

Amongst the various inorganic membranes being considered, the zeolitic systems show good promise. The commercial application of zeolites in separation processes as well as in the field of catalysis is already widespread on account of their intrinsic molecular sieving properties and catalytic activity. Furthermore, the combination of the zeolite properties with a membrane configuration has excellent potential for application in membrane reactors.

This dissertation provides a more in-depth look and critical evaluation of the application of zeolite membrane reactor technology to the skeletal hydroisomerization process used in gasoline pool octane management.

1.1 Introduction

It is an uncontested fact that chemistry and the chemical industry have had an enormous impact on virtually every aspect of life and irrevocably changed the quality of life for billions of individuals inhabiting this planet, for the better. However, it is equally unchallenged that these accomplishments have often come at a price. The process industry has therefore been under increased public scrutiny during the last few decades. This heightened awareness, coupled with changing economic circumstances and tightening environmental legislation, has mandated the industry to adopt a policy of sustainability. Process intensification, see Intermezzo I, is key to the realization of sustainable processes. It has the objective and potential to maximize process output with respect to the desired product, substantially decrease the equipment-size/production-capacity ratio, energy consumption, waste production, and ultimately result in cheaper, safer technologies[1].

Many separations that are currently carried out using distillation, crystallization and other conventional processes are criticized in a society that is aware of the huge amounts of energy used in separation technologies, see Intermezzo II. It is strongly recommended to apply much less energy-intensive and a.o. cleaner membrane-based separation processes to produce high-quality products. Due to its perfect fit with the requirements of sustainable development and process intensification in particular, membrane technology has already made inroads into numerous industrial processes including the petrochemical, food and pharmaceutical industries, in biotechnology and in a variety of environmental applications [2].

An example of process intensification is presented in this thesis. In general catalysis and separation functions can be combined provided that certain operational conditions can be fulfilled.

Intermezzo I

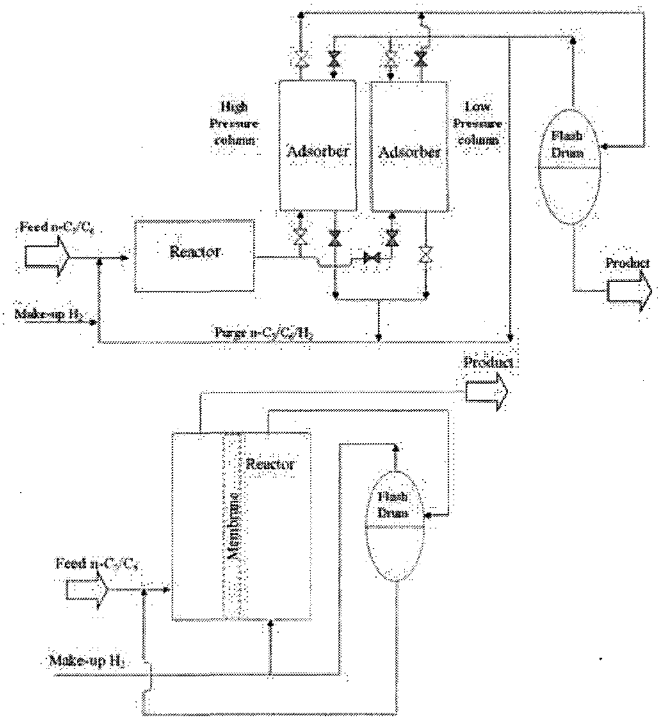


Figure 1.1: Schematic presentation of intensification.

A specific hybrid unit, already suggested two decades ago [3], pertains to the combination of separation and catalysis in the hydroisomerization process of C_5/C_6. The choice was made to use a membrane instead of a pressure swing adsorption unit combined with a catalyst all performing at a temperature that gives acceptable separations of linear and branched alkanes and yields. The state of the art process and the conceptual intensification are schematically illustrated in figure 1.1.

Intermezzo II

The Innovative Separation Technology Roadmap published in 2005 in The Netherlands concludes that 50 % of the energy supply in The Netherlands is needed for separation processes. It is advised to reduce the energy consumption for separation purposes with up to 75 % within the next 10 years. New separation technologies, probably based on materials development, are needed to fulfil the above requirements. It is envisaged that separations based on bulk properties such as boiling point (distillation) or freezing point (crystallization) might be gradually replaced, fig. 1.2 without *zeolite* and fig.1.3 *with zeolite*, by separation technologies in view of their improved process efficiency and reduction in energy costs, based on molecular size exclusion or other molecular properties. This might be possible with zeolites through adsorption or membrane operation. The performance of membranes, having advantages compared to pressure swing adsorption (PSA), is dependent on the quality of the membrane and costs of production/installation. The underlying material development has been accomplished to a large extent in the last 1-2 years [4, 5].

Krupp-Koppers process

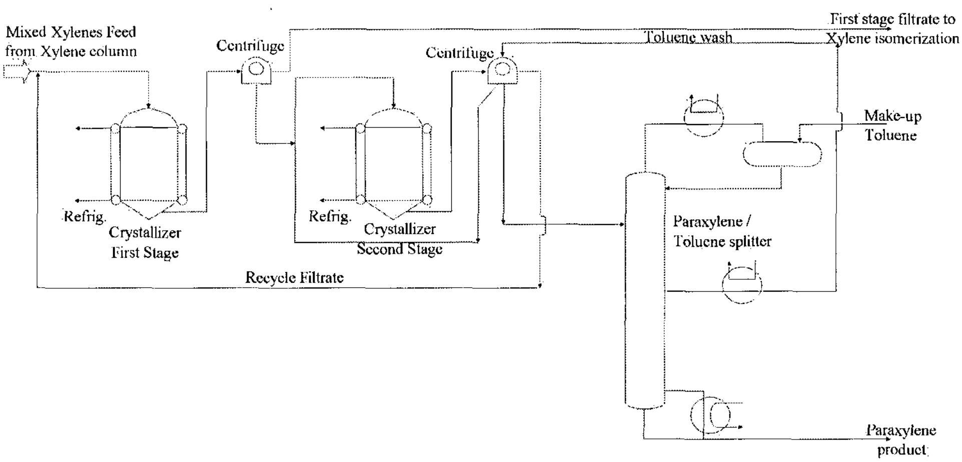


Figure 1.2. Crystallization process for paraxylene recovery

The separation of *p*-xylene from a mixed xylene feed, is a typical example of the application of the crystallization process. The C_8 aromatic isomers are very difficult to separate by conventional distillation processes because of their close boiling points, which in the particular case of *p*-xylene and *m*-xylene differ by less than 1°C. *p*-xylene can however, be readily separated from other xylene components taking advantage of its higher freezing point.

In the crystallization process (figure 1.2) the mixed xylenes are cooled and then charged to the first stage crystallization which consists of one or two crystallizers.

The first stage crystal slurry flows to a continuous centrifuge, where crystals of 80 – 90% *p*-xylene are removed from the filtrate. First stage filtrate is exchanged against the fresh feed, and then leaves the unit as feed for a xylene isomerization unit.

The first stage crystals are melted and then charged to a single second stage crystallizer which operates at -18°C to 0°C depending on the feedstock and desired purity. The combined crystal slurry flows from the crystallizer to a second stage continuous centrifuge which separates crystals from liquid. The liquid filtrate, which is fairly high in *p*-xylene content, is recycled to the first stage. The crystals are washed with toluene in the centrifuge, discharged from the centrifuge, and melted. The *p*-xylene stream is then fed to a final distillation step to yield high-purity *p*-xylene.

Parex process

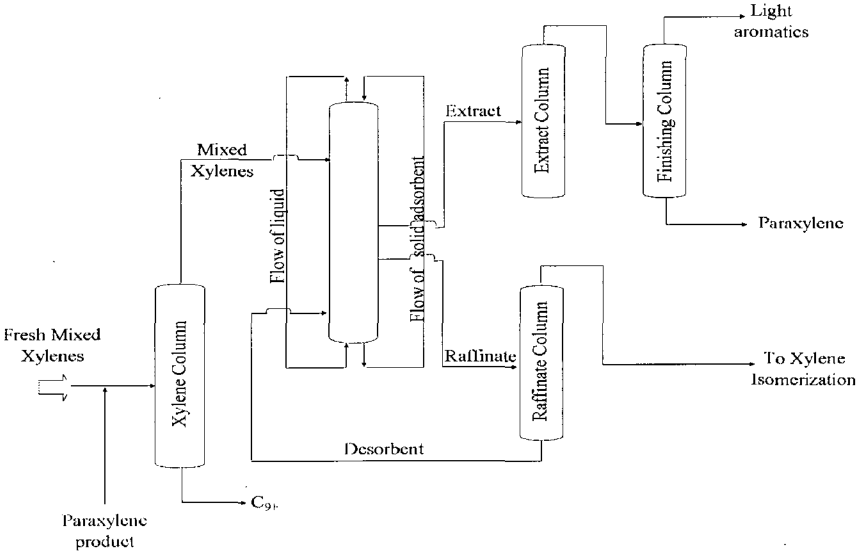


Figure 1.3: Moving bed adsorption system for separation of xylene isomers

Perhaps the most noteworthy development in *p*-xylene technology during the 1980's has exploited another characteristic of the xylenes, which is the molecular size. The C8 aromatic isomers have the alkyl groups at different positions, giving them different molecular diameters. In the Parex process (UOP) p-xylene is obtained in high purity from the isomer mixture by adsorption on a molecular sieve.

Figure 1.3 shows the basic flow scheme of the xylene isomer separations unit, based on adsorption over molecular sieves. A large fractionator removes the C_{9+} components from the feedstock and recycle streams. The xylenes go into the adsorption unit, where the paraxylene is selectively adsorbed onto the molecular sieve, and subsequently freed with a desorbent material. The stream with a depleted amount of *p*-xylene is returned to an isomerization unit, where thermodynamic equilibrium is re-established among the isomers. Finally the xylenes are sent back to the original C_8/C_9 fractionator until they are recycled to extinction.

Some of the most interesting developments in industrial membrane technology relates to the development of integrated membrane operations and multifunctional equipment capable of conducting several process steps synergistically. The integration of reaction and separation in a single multifunctional process unit especially gained recognition in the 1980's when methyl-tert-butyl ether (MTBE), for which there was a large demand due to its antiknock properties in fuel, was prepared in a reactive distillation unit.[6] Today the use of membrane reactors for the selective removal of one or more of the reaction products from equilibrium reactions is an established and rapidly expanding research field and has already been applied industrially in for instance the resolution of racemic mixtures using stereoselective enzymatic reactions in a membrane bioreactor.[7] Early studies and industrial applications of membrane reactors mostly dealt with low-temperature reactions or enzyme-catalyzed biotechnology applications since available organic polymer membranes can only withstand relatively mild conditions. Expanding the temperature range of operation as well as providing the capability for additional separations required new materials – a void that was filled by inorganic membranes with their increased stability at high temperatures and in harsh chemical environments. Amongst the various inorganic membranes being considered, the zeolitic systems show good promise. The commercial application of zeolites in separation processes as well as in the field of catalysis is already widespread on account of their intrinsic molecular sieving properties and catalytic activity. Zeolites also show immense capacity for application in environmentally benign processes. Furthermore, the combination of the zeolite properties with a membrane configuration has excellent potential for application in membrane reactors and could contribute to the efficiency enhancement thereof.

A sector of industry that has experienced the changing economic and environmental circumstances and more stringent legislation first hand is the refining industry. The oil refining industry is faced with important challenges, such as the processing of heavier and more contaminated crudes and the increasing demand for higher quality transportation fuels with reduced emissions of contaminants.[8] More than ever the named challenges are forcing the industry to consider new technologies for the production of clean, high-octane fuels. The isomerization of the light straight-run naphtha fraction (mainly C_5 and C_6) has been gaining popularity as a possible solution to the problem. However, there is more for refining industries to consider, particularly cost reduction and improved productivity, in order to guarantee their success. Following a process intensification approach and applying membrane technology to the posed problem holds enormous promise to deliver an improved product at reduced energy and environmental cost and certainly justifies further investigation. This dissertation provides a more in depth look and critical evaluation of the application of membrane reactor technology to the skeletal hydroisomerization process in specific.

1.2 The membrane alternative – implications for industry

Reactive membrane separation, which constitutes the subject matter of this dissertation, is part of the broader field of membrane separation. A brief overview of membrane-based separation processes and their role in industry will therefore be valuable in order to bring the subject in question into context.

1.2.1 Fundamentals

The period from 1960 to 1980 changed the status of membrane separation from a useful laboratory technique to a commercial separation technology. The turning point in membrane technology came when Loeb and Sourirajan developed an essentially defect-free, high-flux anisotropic cellulose membrane in the early 1960's, which was applied to water desalination[9]. Since then a number of breakthroughs in membrane applications have been achieved, first with the development of synthetic polymer membranes such as polyether sulfone, polycarbonate and polydimethylsiloxane (PDMS) in the late 1970's and then in the 1980's with the development and commercial utilization of inorganic membranes for gas separations such as the separation of nitrogen from air and carbon dioxide from natural gas, as well as the development of pervaporation systems for the dehydration of alcohol.

In layman's terms a membrane is a thin semi-permeable barrier that can separate substances based on physical and chemical properties when a driving force, such as pressure, concentration and temperature is applied across the membrane. According to the membrane pore size (or the size of the particles permeating through the membranes) and the driving force governing permeation, membrane separation processes can be classified as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), Reverse osmosis (RO), Electrodialysis, Gas separation (GS) and Pervaporation (PV) processes. The first four processes are all established industrial processes driven by a pressure differential while gas separation and pervaporation are fast developing technologies that have already found a number of industrial applications. Both gas separation and pervaporation are driven by a gradient in chemical potential across the membrane. Electrodialysis is driven by an electrical potential difference across the membrane and is also a fully developed industrial process. Table 1.1 lists the pore diameter range where each of the named membrane processes is applied as well as their classification according to IUPAC, the driving forces governing permeation, permeation mechanisms and their industrial applications and membrane materials.

Species permeate through membranes by different mechanisms, determined by factors such as membrane structure (dense or porous), the interactions between the membrane and permeating species and operating conditions.

Mass transfer through dense polymeric and metal as well as solid oxide membranes is typically described by a solution-diffusion mechanism. At the feed side, molecular species are adsorbed on the surface of the membrane and then dissolved in the membrane. Once dissolved, individual permeating molecules are transported according to a random process of diffusion. Separation results due to differences in solubility and diffusivity of the species in the membrane.

Table 1.1: Industrially membrane separation processes, their operating principles and applications

IUPAC Class.	Filtration process	Pore size	Driving Force	Permeation mechanism	Applications	Materials
Macro-porous (d>50 nm)	Micro-filtration	0.1 - 10µm	Pressure differential (10-500kPa)	Viscous flow, Knudsen diffusion	• Used in the pharmaceutical industry for production of injectable drug solutions • Filtration of bacteria in municipal water treatment •	Cellulose acetate-cellulose nitrate
Mesoporous (2 nm<d < 50 nm)	Ultra-filtration	2-100 nm	Pressure differential (0.1–1 MPa)	Viscous flow, Knudsen diffusion, Surface diffusion	• Separation of micro-organisms, bacteria and solids from liquid • Ultrafiltration of milk • Cheese production • Clarification of fruit juice	Polymeric materials eg. PTFE; Polysulfone; Polyvinylidene fluoride; Aromatic polyamides; Cellulose acetate
Miroporous (d < 2 nm)	Electro-dialysis		Electrical potential and concentration gradient	Ion transport	• Brackish water desalination • Salt recovery from seawater • Desalt whey • Remove tannic acid from wine and citric acid from fruit juice.	Palladium Polymers : sulfonated cross-linked polystyrene
Dense	Gas separation		Chemical potential gradient	Surface diffusion, Molecular sieving	• Sweetening of natural gas • Nitrogen removal from natural gas • Production of nitrogen from air • Recovery of organic vapours from waste air streams	Ceramics Polymers Silicone rubber Polyvinyl alcohol Palladium Silver
	Pervapora-tion			Solution-diffusion	• Dehydration of organic solvents • Separation of azeotropic mixtures • Desalination of sea and brackish water	
	Nano-filtration	5-10Å	Pressure differential (2-10MPa)		• Separation of small organics and multivalent ions from a solvent such as: - Separation of salts from dye solutions - Separation of acids from sugar solutions.	Polyacrylonitrile Polysulfone; Polyvinylidene fluoride; Aromatic polyamides; Cellulose acetate
	Reverse osmosis		Pressure differential (2-10MPa)		• Desalination of sea and brackish water. • Production of ultra-pure water for the electronics industry. • Removal of organic compounds from water. • Wastewater treatment • Separation of a solution of methyl ethyl ketone and lube oil	Polyamide membranes Cellulose acetates

The prevailing mass transport mechanism in porous membranes is determined by the membrane's mean pore size, and the size and type of the diffusing molecules, see Fig.1.4. If the pores are relatively large (macroporous and mesoporous membranes) compared to the size of the molecules, permeation through the membrane is governed by viscous flow, and Knudsen diffusion. For microporous membranes the interaction between the diffusing molecules and the membrane pore surface is of great importance to determine the transport characteristics. A number of mechanisms can be distinguished for gas or vapour permeation through the membrane. If the membrane diameter is the same size as or smaller than the mean free path of the permeating gas molecules, diffusion is governed by Knudsen diffusion, and the transport rate of any molecule is inversely proportional to the square root of its molecular weight. In membrane pores, which are only slightly larger than the molecular radius, molecular transport is a function of both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores and separation takes place due to molecular sieving. Mass transport in membrane processes involving liquids is more complex and interactions between the species present in liquid mixtures and the membrane could also include phenomena like electric, electrostatic and polarization effects.

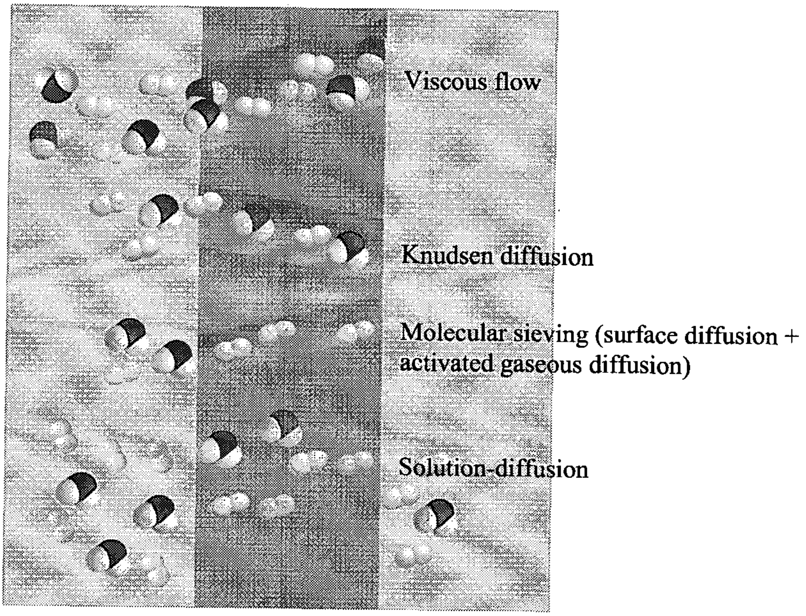


Figure 1.4: Mechanisms for permeation through porous and dense membranes.

Membranes are manufactured from a wide variety of materials, which include sintered metals, ceramics, polymers and even liquids. Polymeric membrane materials, including cellulose acetate, polysulfone, nylon and Nafion, have dominated the market up to now due to their flexibility, permeability and ability to be formed into a variety of membrane modules. However, there are many applications (for example, those in harsher environments of the oil and petrochemicals industries) in which those membranes are incapable of performing the desired separation because of thermal and structural instabilities. As a result, inorganic membranes such as zeolites with their superior stability are being pursued to perform many of these separations. Membrane geometry is diverse, as well, but commonly used forms include hollow fibres, films, tubes, composites and flat sheets configured as "plate and frame" or spiral wound" cartridges. The microstructure in cross-section can be homogeneous, asymmetric, or composite. The range of materials and membrane configurations used are continuously expanding in order to also increase the range of chemical compatibilities and physical conditions (including pressure, temperature and pH) at which these membrane systems can operate.

1.2.2 Present and future membrane market.

Whether isolating a substance of commercial interest, purifying a drug or food product, or cleaning industrial waste streams, the technology to separate and purify molecules of choice is of critical importance. As more and more industries are forced to re-evaluate the way they treat industrial processing, membranes are increasingly being seen as the future cornerstone for industrial separations.

Research conducted by US industrial research firm, The Freedonia Group Inc. forecasts that US demand for membrane materials will increase 8.4 % per annum to 2.7 billion US$ in 2008[10] while market research done by Frost and Sullivan suggested a annual growth rate of 7.8 % for the European membrane market for the period 2000 to 2007, translating to a value of US$ 1.49 billion in 2007[11]. McIlvaine Co predicts that globally the market for cross-flow membrane equipment and membranes is set to grow from about US$6.3 billion in 2004 to over US$8.4 billion in 2007.[12] Growth is expected to be fuelled by greater use of value-added, high performance membranes and membranes made from specialty materials such as ceramics.

Table 1.2 : Membrane materials demand (million US $)[10]

Annual Demand Item	1998	2003	2008
Membrane total demand	1190	1785	2675
Microfiltration	626	860	1175
Ultrafiltration	197	329	530
Reverse Osmosis	234	390	620
Pervaporation	24	52	81
Other	109	154	269

The market for membrane separation systems is governed by a series of drivers and restraints of which the most important is listed below.[13]

Market Drivers:

- Universal need for pure, clean water. Only 6% of the world's water is fresh, and according to the UN, about 1.2 billion people are without access to safe drinking water while an estimated 3 million people die ever year from diseases caused by unsafe water. Expected growth for Reverse osmosis, applied in water desalination, is nearly 10% per annum.[14]
- Environmental concerns and legislation, such as those set in motion by the Kyoto Protocol in 1997[15] stimulated research to find solutions, in which membrane separation technologies strongly feature, for the existing problems. An example of one such development is the removal of carbon dioxide from flue gas, which is then utilized in greenhouses to improve crop yields, by TNO in the Netherlands.[16]
- The crisis in energy security in all the major industrial countries has spurred efforts to reduce dependence on imported oil, contributing to fuel cell research and commercialization activity such as the study of polymer zeolite nanocomposite membranes for fuel cells at the University of California.[17]
- Desire to have a continuous rather than a batch process
- Increasing confidence in membrane technologies. A growing number of high quality reference plants are raising confidence in industrial customers for the use of membrane techniques.
- Traditional equilibrium-driven separation technologies (e.g., absorption, adsorption, distillation, extraction, ion exchange), suffer from inherent operational difficulties including lack of flexibility and modularity, slower rates, the need for hazardous chemicals, high capital costs, higher energy requirements and the need for large equipment, many which membrane-based separation technologies do not exhibit.

Market restraints:

- Concern about membrane integrity, long-term stability and fouling.
- Surface area to volume ratio. The production of large quantities of products in industrial installations or in waste treatments requires large membrane volumes. While large surface area to volume ratios can be obtained in polymeric membrane systems due to available membrane architectures such as spiral-wound systems, the ability to produce reliable ceramic membrane systems with a large surface area is still somewhat problematic.
- Difficulty to gain market share from competing, established and already proven technologies.
- Perceived cost of membrane separation
- Inadequate intrinsic membrane properties – low permeability and selectivity as well as low thermal and chemical resistance. Engineers are also often confronted with the demand for the combination of high separation factors with high permeation.

In emerging applications, solid polymer electrolyte membrane fuel cells are expected to grow rapidly with the drive to use alternative power sources to reduce the demand for oil in all the developed countries. Research have for instance been conducted at the University of California to incorporate zeolite nanocrystals into a polymer matrix to prepare membranes that will take advantage of the best properties of both polymers and zeolites in order to solve some of the major still existing problems with PEM fuel cells[18]. Gas separation technologies, with particular emphasis on hydrogen to power fuel cells, are also in demand. Medical applications are another major market for membranes. New membrane-based artificial organs, such as the liver, lung and pancreas, are undergoing clinical trials[19].

A shift away from more basic cellulose membranes towards membranes made from speciality polymers and to non-polymeric materials, including metal, ceramic and composite types, whose versatility and better performance at high temperatures and in corrosive environments is attracting interest and resources from both universities and industry, is foreseen[13].

The lab-on-a-chip is also a developing field that will receive more attention in future. It holds promise to achieve a drastic reduction of reactants and energy consumption and a resultant increase in safety.

1.3 Zeolites for green chemistry

The first definitive synthesis of an analogue of a natural zeolite reported by Richard Barrer in 1948, set in motion an important branch of chemistry, one that has become important in a number of major industries. These inorganic materials are crystalline microporous aluminosilicates, three-dimensional networks of AlO_4 and SiO_4 tetrahedra linked by their oxygen atoms. Due to the fact that aluminium atoms have only three electrons available for bonding with the oxygen atoms, compared to silicon's four, an imbalance of electrical charge exists. Cations (principally sodium, potassium, calcium, and magnesium), residing inside the network, neutralize the charge and are themselves, surrounded by loosely bound molecules of water. Why are zeolites commercially so attractive? Zeolites have crystalline structures with channels and cavities, which are all of the same shape and size allowing them to act as molecular sieves. Furthermore they provide large surface area on which chemical reactions can take place and therefore find use as catalyst supports and shape selective catalysts.

With the dawn of environmental awareness, zeolites have come of age. Their high efficiencies and ability to be regenerated repeatedly, the elimination of toxic and hazardous reagents, and the minimization of unwanted by-products, means that they are an essential ingredient for manufacturers trying to conform to the principles of green chemistry[20]. Environmental considerations to reformulate gasoline and reduce sulphur emissions have been responsible for the upsurge in the consumption of zeolites for catalytic applications. Average levels of zeolites in fluid catalytic cracking (FCC) catalysts have risen significantly. So also is the use of ZSM-5 as an additive to FCC catalysts to increase olefin production. Zeolite catalysts have experienced growth in their use for hydrocracking, isomerization of paraffins, dewaxing of lube oils, and conversion of low-value feedstocks to gasoline. Problems associated with traditional aluminium chloride and phosphoric acid catalysts in petrochemical processes have resulted in their replacement by zeolite catalysts.

Zeolite molecular sieves have also found application in several areas, such as the removal of radioactive isotopes from air streams and concentration of alcohols from dilute aqueous streams. The high cation exchange capacity of zeolites combined with their selective affinity for specific cations make them uniquely suited to various applications of water treatment. Natural zeolites are adsorbents of choice for many cost-effective air pollution control technologies treating the hazardous air pollutants and listed volatile organic compounds.

1.4 Exploring ways to synthesise high flux, selective zeolite membranes

The flux through a membrane is greatly dependent upon the film thickness and hence thin, continuous films are essential to obtain the permselectivity necessary to fully exploit the potentials of membrane applications such as membrane reactors.

There have been many attempts to meet the dual challenge of selectivity and permeability. The simplest and a regularly used approach to deposit a zeolite film on a porous support is to treat the support directly with a molecular sieve precursor solution, (in situ crystallization).

However, due to a relatively low nucleation site density, a considerable film thickness of several micrometers is often necessary to close all defects. The low nucleation site density often observed in membranes crystallized in situ can be improved by applying a thin layer of colloidal zeolite crystals to the support surface, followed by a crystallization step in order to grow the seeds into larger crystals that form a dense layer.

As a first approach several novel techniques were explored in this study to assemble nanometer-sized zeolite crystals on substrates (α-Al_2O_3 supports and silicon wafers) in order to grow continuous ultra thin (~200 nm) molecular sieve films (mainly silicalite-1) which could meet the demands placed on membranes for application in membrane reactors. What follows below is just a brief outline of the methods used and some of the results obtained. The layers obtained with the techniques were discontinuous and further optimisation was not pursued due to time constraints. The techniques however did allow a certain amount of control over the quantity of deposited crystals and do merit further investigation.

Discrete colloidal mono-disperse seed crystals (~200 nm) of TPA-siliclite-1 were synthesized in clear homogeneous solutions and purified by repeated centrifugation and re-dispersion following the method presented by A.E. Persson et al.[21]. According to this method a synthesis solution of TPAOH (25%):SiO_2:(TEOS):H_2O :Ethanol with the molar composition; 9:25:1500:100 was prepared and crystallization effected at 98°C. XRD and SEM confirmed that silicalite-1 particles were synthesized with an average particle size of 201.7 nm.

The sols containing discrete colloidal crystals were used to form dense mono-layers of zeolite crystals alumina substrates and silicon wafers making use of the following deposition techniques:

The Langmuir-Blodgett method was used to form ultrathin films of the zeolite seed crystals through self assembly on the α-Al_2O_3 tubular supports. This was done by floating an aqueous dispersion of silicalite-1 seed crystals on dichloromethane. A fluorinated soap from Du Pont was added to the dichloromethane to facilitate spreading of the silicalite-1 layer. Lastly an α-Al_2O_3 support tube was laterally immersed below the dichlormethane/silicalite phase boundery and finally withdrawn at a steady speed. Despite the fact that the described procedure was highly unoptimised interesting results were obtained as shown below. SEM images of the particles deposited on the support through the Langmuir-Blodgett technique show a very regular and continuous packing of the seed crystals in a monolayer (see fig. 1.5 below).

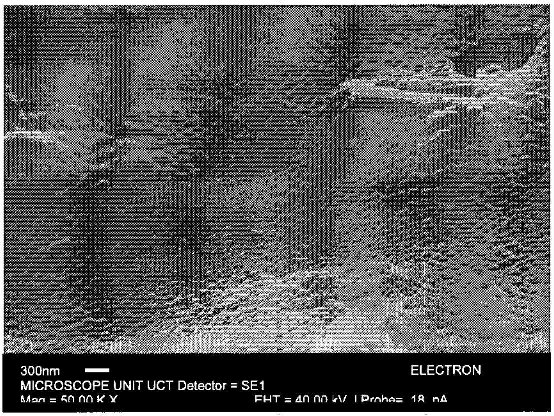


Figure 1.5: SEM image of LB deposited particles

In a second approach silicalite-1 seed crystals were deposited on the substrate (tubular α-Al_2O_3 as well as flat disk α-Al_2O_3) through the application of a pressure difference across the support. Figure 1.6 is a SEM image of the deposited silicalite-1 layer on a tubular α-Al_2O_3 support making use of a pressure difference across the support. This technique resulted in a closely packed coating.

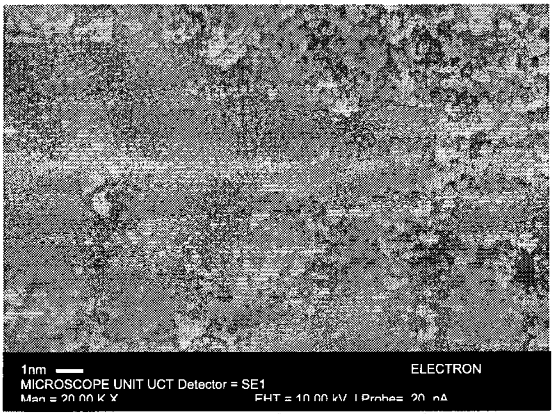


Figure 1.6: SEM image of particles deposited with pressure difference

When an electrical field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge. The zeta-potential of siliclite-1, TPA^+ and the α-alumina substrate in a solution with a pH of 10.5 – 12.5 was determined. Since the zeta-potential of TPA^+ is positive, a negative charge was applied to a copper rod placed on the inside of the α-alumina tube, i.e. to act as cathode. A platinum plate attached to the wall of the Teflon beaker placed inside the stainless steel autoclave in which the zeolite membranes synthesis was done, acted as anode. A filtered DC power supply was used to apply a potential difference between the two electrodes. The electrical potential was varied between 0.1 to 1.0 V in order to avoid hydrolysis.

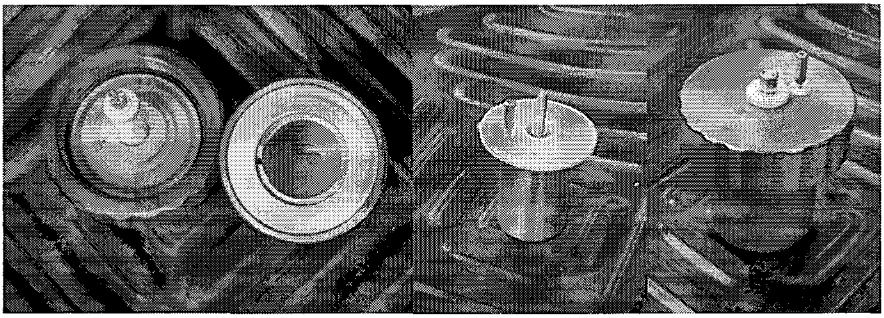


Figure 1.7: Apparatus used for electrophoretic deposition of seed crystals.

Figure 1.8 shows a sintered layer of the silicalite-1 seed crystals (sintering was effected at 1000°C for the duration of 30 minutes). Domains, 1-2 mm^2 in size, of continuous zeolite, large enough to bridge the pores in the macroporous support, can be seen.

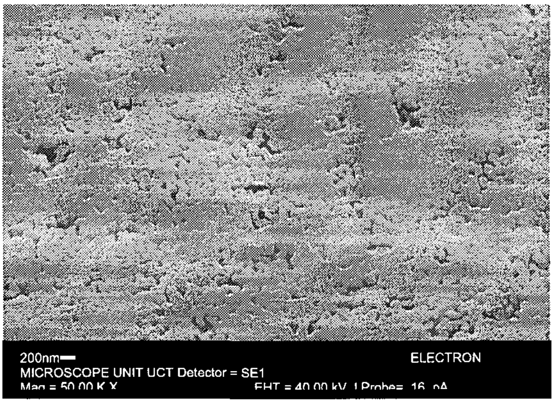


Figure 1.8: SEM image of sintered silicalite-1 layer.

1.5 Hydroisomerization – setting the scene

At present, the future of the oil refining industry, see Intermezzo III, hinges on several factors and challenges that will have to be addressed:

- the possible emergence of a production plateau for world crude oil.
- processing of heavier and more contaminated crudes,

- tight new fuel specifications in the United States and Western Europe which demand higher quality transportation fuels with reduced emission of contaminants,
- the need for more petrochemical feedstocks.

For gasoline the challenge is to maintain high octane, while meeting stricter requirements for Reid Vapour Pressure (RVP), removing lead-based antiknock agents like tetraethyl lead, removal of benzene, aromatics control, lower sulphur content and the impending ban of the gasoline oxygenate, MTBE and other homologues with longer alkyl side chains.

Intermezzo III

Figure1.5 is derived from the study: “Winning the oil end game”, of Amory B. Lovins et al. of the Rocky Mountain Institute, March 2005.

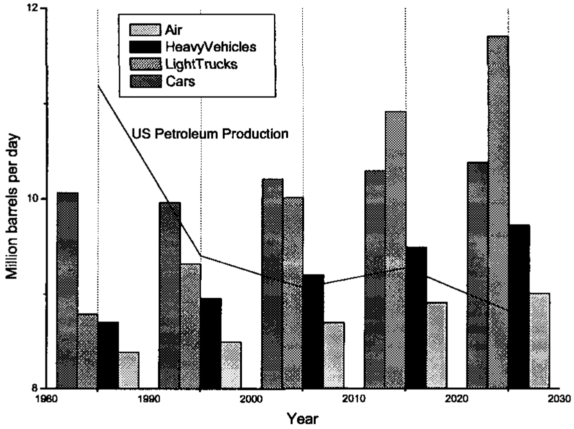


Figure 1.5: Transportation Petroleum Use in the USA by Mode

Figure 1.5, which is based on data of the Energy Information Administration, forecasts a substantial dependence on petroleum for transportation up to 2025. In contrast to this, the production of petroleum is declining, increasing the need to find additional feedstock and/or making the most of the available feedstock. Consequently there is still a huge market for gasoline additives such as i-alkanes. These octane boosters contribute only in a modest way to global pollution compared to alternatives like MTBE. The cleaning of MTBE pollution in the USA is estimated to amount to at least $ 140 billion!

Table 1.3: Gasoline specifications for 2005 in the US and Europe.

Fuel Parameter	US	Europe
RVP, kPa	<51.7	60
Oxygen, wt% max	2.7	2.7
Benzene, vol%	1.9	1.0
Aromatics, vol%	25-30	35.0
Olefins, vol%	<20	18
Sulphur, ppm	30 avg , 80 max	50

A report by Frost and Sullivan predicts that during the period 2004- 2008 just a little over US$ 100 billion will be invested in refining technology development, with the expenditure distribution as outlined in Table 1.4[22]

Table 1.4: Refining Markets worldwide, 2004-2008 (million US$)[22]

	2004-mid 2006	Mid 2006-2008
Alkylation	1575	2655
Isomerization	1525	3050
Catalytic Reforming	1355	1465
FCC & Hydrocracking	10700	11125
Desulfurization	16500	16050
Heavy Crude Upgrading	16500	18000
Total billion US$	48.16	52.3

Refinery processes that are used to improve RON include isomerization, reforming, alkylation and addition of oxygenates. Keeping in mind the Californian ban on MTBE and also the fact that the oxygenate content has to be reduced to half of the present value; the most favourable options are alkylation and isomerization.

Isomerization of C_5 and C_6 paraffins is a refinery process that generates high octane for the gasoline pool, while contributing no olefins or aromatics. Branched C_5 and C_6 paraffins have much higher octanes than normal pentane and normal hexane as indicted in Table 1.5. Furthermore, lower octane C_5 and C_6 isomers can be separated, and recycled.

Table 1.5: Octanes and boiling points for C_5 and C_6 paraffins

Paraffin	(RON*+MON†)/2	Boiling Point, °C
Isopentane	102.0	27.9
Normal Pentane	64.0	36.1
2,2-Dimethylbutane	93.0	49.7
2,3-Dimethylbutane	101.0	58.0
2-Methylpentane	80.0	60.3
3-Methylpentane	83.0	63.3
Normal Hexane	20.5	68.7

a) *Research Octane Number

b) †Motor Octane Number

Skeletal isomerization of n-paraffins is an acid-catalyzed reaction that is thermodynamically favoured at lower temperature. The goal therefore has to be to maximize gasoline octane with recycle flow schemes and with catalysts that are active at low temperatures. Catalysts also must have high selectivity to isomerization in order to maximize gasoline yield. Zeolitic molecular sieves can be utilized to recycle normal paraffins at high energy efficiency compared to fractionation.

Such a process (recycling of unconverted low-octane isomers) has already been implemented in industry. The Total Isomerization Process (TIP) is a combination of Shell's Hysomer process and Union Carbide's ISOSIV process. The Hysomer process is carried out using a Pt/HMOR catalyst and performs the hydro-isomerization of a mixture of C_6/C_5 at 250° and a hydrogen pressure of 10-30 bar. The ISOSIV process separates unreacted normal paraffins from their isomers by selectively adsorbing them on zeolite CaA (pressure swing adsorption). After desorption, the n-alkanes are recycled.

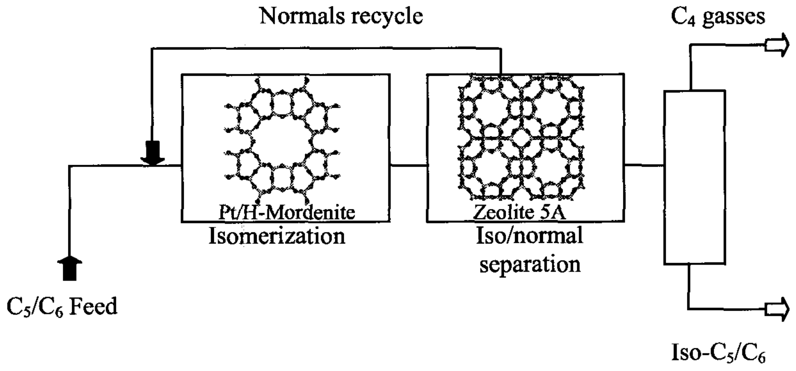


Figure 1.5: Total Isomerization Process (TIP)

Making use of a membrane as the separation phase will allow a continuous process, in contrast to the TIP process with adsorption and desorption cycles. The membrane reactor concept, combining the two different units, i.e. reactor and membrane separator, into a single unit is a natural design evolution that follows, with numerous benefits such as energy and cost savings[23].

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2

Zeolite based Films, Membranes and Membrane Reactors: Progress and prospects

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Abstract

The integration of reaction and separation in catalytic membrane reactors has received increasing attention during the past 30 years. The combination promises to deliver more compact and less capital-intensive processes with substantial savings in energy consumption. With the advent of new inorganic materials and processing techniques, there has been renewed interest in exploiting the benefits of membranes in many industrial applications. Zeolite membranes, however, have only recently been considered for *catalytic membrane* reactor applications. Despite the significant recent interest in these types of membranes there are relatively few reports of the application of such membranes in high temperature catalytic membrane reactor applications. This can be attributed to a number of limitations that still need to be addressed such as the relatively high price of membrane units, the difficulty of controlling the membrane thickness, permeance, high temperature sealing, reproducibility and the challenge of upscaling. A number of research efforts, with some degree of success have been directed to finding solutions to the remaining challenges. This review makes a critical assessment of what has been achieved in the past few years in terms of hurdles that still stand in the way of the successful implementation of zeolite membrane reactors in industry.

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2.1 Introduction

Increasingly stringent market and environmental demands, such as the minimization of energy consumption and ever-greater emphasis on process safety and superior product quality, mandate major revision of plant configurations. The manufacturing of fuel and chemicals has indeed been subject to large technological improvements during the past century. Headway has been made for instance in catalysis, heat integration, product purification and effluent clean-up. The new millennium, however, still needs further improvements in processes and catalysts as well as novel manufacturing technologies. Membrane reactors are one of such evolving technologies that have huge promise to deliver processes that are more compact, less capital intensive, offer improved conversion for equilibrium limited reactions, allow controlled operation and have substantial savings in energy and resultant costs due to feed/product separation at elevated process temperatures [1].

Although the concept of membrane reactors has already been introduced in the 1950's, it was only with the advent of new inorganic materials and high-temperature membrane systems [2, 3] in the last 30 years that considerable growth in the research and development of membrane reactor technology has been achieved. The significant interest in the field is demonstrated by more than a 100 scientific publications (fig. 2.1) on the subject per annum as well as several patents dealing with membrane reactors that have already been filed [4, 5].

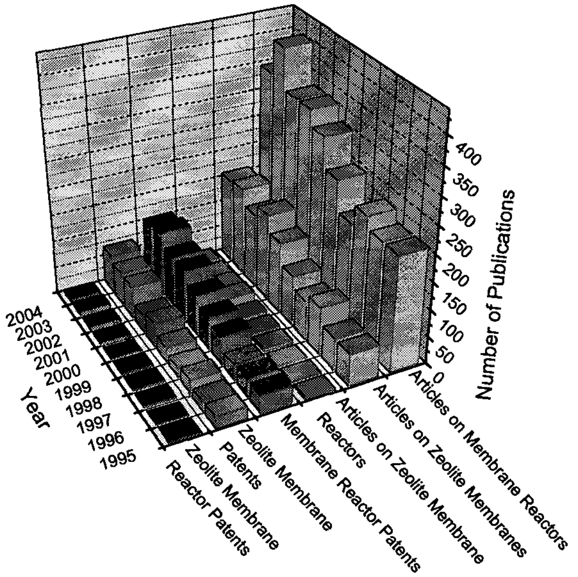


Figure 2.1: Scientific publications on Membrane Reactors and Zeolite Membrane Reactors respectively (Scifinder search)

Most publications highlight the remarkable potential of membrane reactors such as the ability to shift the overall conversion beyond thermodynamic equilibrium by selective product removal, improvement in selectivity by distributed addition of reactants alongside the reactor and safety improvement through controlled reactant contact. [6, 7] (table 2.1)

Table 2.1: Applications of Membrane reactor processes reported in recent literature.

Reaction type	Reaction	Reactor config.	Operating conditions	Membrane	Advantages sought/obtained	Ref.
Dehydrogenation	Methanol oxidative dehydrogenation to formaldehyde	PBMR	200 - 250° C Fe–Mo oxide	Non permselective 316L SS	Increased selectivity and yield due to distributed /controlled reactant addition	[8, 9]
	Oxidative dehydrogenation of butane to butadiene	CMR	550°C V/MgO	Alumina impregnated with MgO	Feed configurations that lead to a low partial pressure of oxygen also give rise to an improved selectivity.	[10]
Hydrogenation	CO_2 hydrogenation to methanol	CMR	210 - 230°C Pd	MOR/ZSM-5 /chabazite	Higher CO_2 conversion and CH_3OH selectivity	[11]
Oxidation	Oxidation of alkanes	PBMR	150 - 450°C	MFI/Al_2O_3, SiO_2/Al_2O_3 and $AlPO_4/Al_2O_3$	$AlPO_4$ membrane was the most efficient for O_2 distribution.	[12]
	Partial oxidation of ethane to syngas	CMR	800–900 °C LiLaNiO/γ-Al_2O_3	Dense ceramic membrane	Ethane conversion of ~100%, the selectivity of CO was higher than 91%	[13]
	Partial oxidation of methane to syngas	PBMR	875°C LiLaNiO/γ-Al_2O_3 catalyst	Dense ceramic membrane	94% methane conversion and higher than 95% CO selectivity	[14]
	Partial oxidation of methanol	NMR	Fe-Mo oxide catalyst bed 220-250°C	316L-SS membrane	Observed increased operational stability	[15]
	Selective oxidation of ethane to ethylene	CMR	825–875°C	Dense ceramic membrane	Ethylene yield of 56% with ethylene selectivity of 80%	[16]
	Selective oxidation of carbon monoxide	CMR	200–250°C PtY	Y-type zeolite / porous α-Al_2O_3	Selective oxidation of CO - the CO conc. on the permeate side decreased below the detection limit.	[17]
	Oxidation of benzene to Phenol	CMR	<250°C	Pd on Al_2O_3	phenol selectivities of 80 to 97% at benzene conversions of 2 to 16% below 250°C; WHSV of 1.5 at 150°C	[18]

Table 2.1(continued): Applications of Membrane reactor processes reported in recent literature.

Reaction type	Reaction	Reactor config.	Operating conditions	Membrane	Advantages sought/obtained	Ref.
Organic synthesis	liquid-phase oligomerization of *i*-butene	PBMR	20°C acid resin catalyst bed	MFI/ SS	significant increase in the selectivity, and as a consequence also in the yield of *i*-octenes	[19]
	Esterification between ethanol and acetic acid	CMR	60°C	Polyetherimide /γ-Al_2O_3	Almost complete conversion was reached.	[20]
	Metathesis of propene to ethylene and 2-butene	PBMR	Re_2O_7/ γ-Al_2O_3 catalyst, 23°C	Silicalite-1	Conversion could be increased above equilibrium to 38.4% with a *trans-2-butene* selectivity of 4.2	[21]

The clear advantages that exist for the combination of reaction and separation in a single unit and the multitude of possible applications reported in the scientific literature does not negate the fact that challenges remain which limits the large-scale industrial application of catalytic membrane reactors. This is acknowledged by several authors and evidenced by the shortage of commercialized high-temperature membrane reactor based processes (table 2.2).

Table 2.2: Industrial Membrane Reactor processes.

Company	Separation technique	Application	Materials	Reference
Degussa	Ultra-filtration	Production of enantiomerically pureL-amino acids	Acylase membrane	[22]
Air Products/ Ceramatec	Ion transport	Syngas process for synthesis gas production to be implemented by 2010	Dense Ceramic materials related to inorganic perovskite structures	[23]
Akzo Nobel	Micro-filtration	Polycondensation reaction	Microporous amorphous silica on alumina support, Polyvinyl alcohol/ nafion/	[24]

Several review papers have already been published, dealing with different aspects and applications of membrane reactors; Armor and Hsieh has published some of the earliest reviews in the field [2, 25] highlighting the advantages as well as the major challenges for inorganic membranes to be used in catalytic devices. Saracco and Specchia [6, 26] provided a survey on the reactions which have been performed in Catalytic Inert Membrane Reactors employing either dense (metals) or porous (mainly ceramic) membranes and also considered the practical difficulties to the commercialization of membrane reactors. In the more recent past, reviews on the subject were published by Sirkar *et al.* [27]; Dixon [7], Dalmon [28] and Tsotsis *et al.* [29-31]. Dittmeyer *et al.*[32] emphasized the role of palladium in a review on the subject and Noack *et al.*[33] looked at the developments in inorganic membranes and the implications for their practical application. Hsieh devoted the larger portion of a book to the subject of inorganic membrane reactors [34], while most recently, Marcano and Tsotsis authored a book, encompassing a broad treatment of catalytic membranes and membrane reactors [35].

Due to the multidisciplinary nature of membrane reactor technology, it is impossible to do justice to all aspects of the field in a single review article. It is also not the objective of the author to add to the already extensive list of reviews in the field but rather to focus on the progress made and the road forward to the industrial realization of zeolite-based, catalytic membrane reactors.

2.2 Zeolite-based membrane reactor configurations

In zeolite-based membrane reactors the membrane normally consists of a thin film of a mesoporous or microporous zeolite on a macroporous support, typically α-Al_2O_3, stainless steel or carbon. This thin film may simultaneously serve (i) as both a catalyst and a permselective membrane, (ii) as a permselective diffusion barrier or (iii) as an inert non-selective reactant distributor. Permselectivity depends on the size of the permeating molecules relative to the pore size of the membrane, the chemical nature of the permeating molecules and the membrane material as well as the adsorption properties of the membrane – in a mixture of components with different adsorption characteristics the stronger adsorbing compound will permeate preferentially [36].

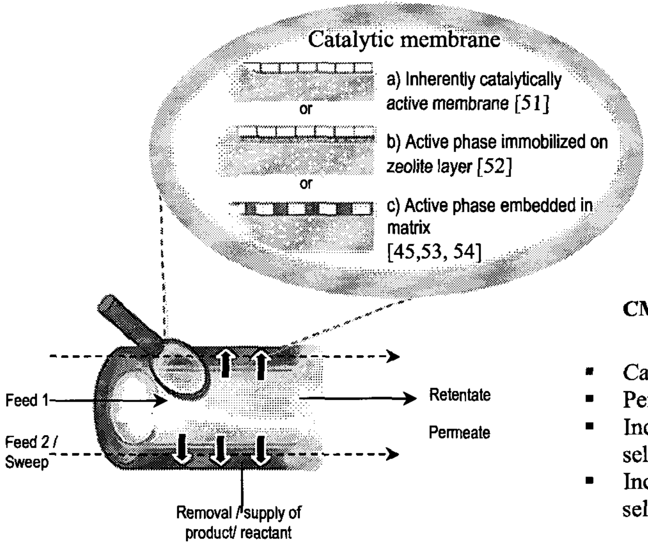
The common modes of application of zeolites in membrane reactors is; as a Catalytic Membrane Reactor (CMR), a Packed Bed Membrane Reactor, a Catalytic Non-permselective Membrane Reactor, a Non-permselective Membrane and a Reactant-Selective Packed Bed Reactor (RSPBR) (illustrated in table 2.3). The zeolite-based catalytic membrane reactor generally consists of a supported permselective layer (membrane) that simultaneously acts as catalyst (CMR). The aforementioned catalytic membrane:

- could be inherently catalytic due to the presence of catalytic sites (Brönsted acid sites; Lewis acid sites; metal ions in cationic positions; transition metal ions in zeolite lattice positions; extra-lattice transition metal compounds in channels and cavities of a zeolite, metal particles in zeolite cavities) [4, 37, 38]. Zhu *et al.* recently synthesized metal nanoparticles encapsulated in mesoporous silicates as model porous catalysts with the aim to improve reaction selectivity [39].
- could have a separate catalytic and permselective layer. Van der Puil reported a composite hydrogenation catalyst, in which the catalytic phase (TiO_2-supported platinum) was coated with a thin continuous layer of oriented silicalite crystals, creating separation selectivity and steric constraints at the zeolite/platinum interface [40].
- could have zeolite crystals with catalytic ability embedded in a matrix e.g. polymer membrane or another mesoporous zeolite/ceramic membrane. Baron *et al.* recently investigated the use of a polymeric membrane with dispersed zeolite crystals incapsulating immobilized metal-complexes, acting as an interphase contactor during alkene oxidation in a CMR [41].

When the reactor consists of a membrane that is permselective but not catalytic with a conventional catalyst present in the form of a packed bed of pellets/extrudates in the flow stream, it is termed a packed bed membrane reactor (PBMR). Caro *et al.* reported the application of MFI zeolite membranes in the dehydrogenation of iso-butane, for the selective removal of H_2, ultimately resulting in an increase in conversion. The catalytic reaction took place in a catalytic packed bed of Cr_2O_3 on Al_2O_3 spheres on the tube side of the membrane [42]. Although the majority of applications of zeolite membrane reactors reported in literature to date falls into the category of PBMR, more and more researchers are exploring the use of zeolite membranes as catalytically active centers and with different, more adventurous modes of operation. Sloot *et al.* introduced a novel membrane reactor (termed a Catalytic Non-permselective Membrane Reactor, CNMR) for the catalytic oxidation of H_2S to elemental sulfur, in which the membrane is although catalytically active, not permselective, and acts as reaction front, facilitating stoichiometrical feed rates of reactants [43]. When applied to the catalytic reduction of NO_x with NH_3 Sloot *et al.* obtained high conversions of NO_x despite fluctuating reagent concentrations [44]. Wu *et al.* also later used a composite membrane (titanium silicalite-1/polydimethylsiloxane) as a catalytic interphase contactor in the two-phase reaction of n-hexane oxidation by dilute aqueous hydrogen peroxide [45]. In this reactor, the catalytic membrane was placed at the interface between the H_2O_2 aqueous phase and the *n*-hexane vapor phase. The two reactants, H_2O_2 and *n*-hexane, reach the catalyst surface by diffusion through the membrane, thereafter reacting with each other. After their formation, the products diffuse out of the membrane. An additional advantage of using such a membrane interphase contactor is that it avoids the use of co-solvent at industrial scale. In a Non-permselective Membrane Reactor (NMR) the membrane does not have any catalytic activity, nor does it have permselectivity, it simply acts as a distributor of the reactant. Guizard and coworkers investigated the partial oxidation of alkanes in a membrane reactor where the membrane (MFI) acts as a O_2 distributor, allowing improved selectivity and preventing reaction run-away [12]. Increasing attention is being paid to Particle-Level Membrane Reactors (PLMR) which consists of catalyst particles coated with a permselective membrane layer allowing the selective addition of reactants to the reaction zone or the selective removal of products from the reaction zone when one product's diffusivity is much higher than those of the other products. The main benefit arising from this configuration is the increased membrane area per unit reactor volume compared to that of conventional membrane reactors. This is highly advantageous considering the difficulty to achieve a large membrane area with the absence of defects. Nishiyama *et al.* prepared a silica-alumina catalyst coated with a silicalite membrane and applied it to toluene disproportionation. Good selectivity for the *p*-xylene isomer, due to its selective removal, was achieved [46]. Nishiyama et.al. recently demonstrated the viability of membrane coated catalyst particles as a means to achieve selectivity again when they reported the use of spherical Pt/TiO_2 particles coated with a silicalite-1 for the selective hydrogenation of linear and branched alkenes. The composite silicalite-1/Pt/TiO_2 catalyst showed 1-Hexene/3,3-DMB hydrogenation selectivities of 12-20 at 50 °C and 18-30 at 100 °C due to the selective permeation of 1-hexene through the silicalite-1 layer [47].

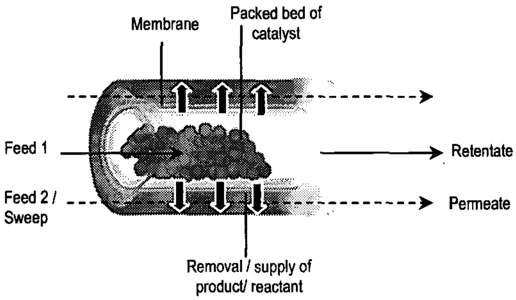
Sanchez Marcano and Tsotsis [35], Perez *et al.* [48, 49], Noble and Falconer [50] as well as Coronas and Santamaria [49] introduced similar acronyms for ease of reference to the different membrane reactor types.

Table 2.3: Classification of membrane reactor configurations according to membrane function and location. [51] [52] [45, 53, 54]



CMR

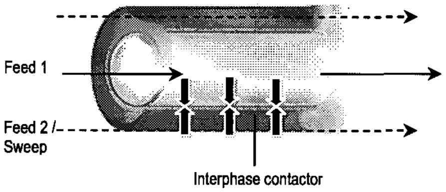
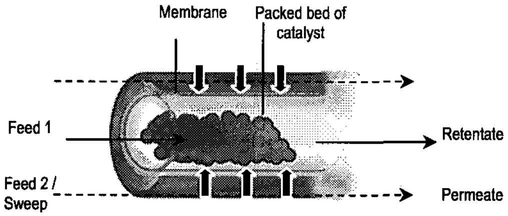
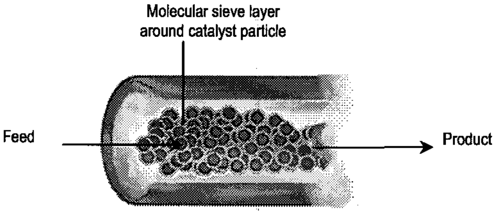
- Catalytic active membrane
- Permselective membrane
- Increase conversion through selective product removal
- Increase selectivity through selective reactant supply



PBMR

- Inert membrane
- Permselective membrane
- Increase conversion through selective product removal
- Increase selectivity through selective reactant supply

Table 2.3(continued): Classification of membrane reactor configurations according to membrane function and location.

	**CNMR** ▪ Catalyticly active membrane ▪ Non-Permselective membrane ▪ Interphase contactor ▪ Exclusion of solvents renders an environmentally attractive process ▪ Short contact time
	**NMR** ▪ Inert membrane ▪ Non-Permselective membrane ▪ Reactant distributor ▪ Improved selectivity ▪ Better controllability – for instance explosion limits
	**PLMR** ▪ Packed bed reactor consisting of permselective membrane-coated catalyst particles. ▪ Inert membrane ▪ Improved selectivity, through selective reactant supply or selective product removal ▪ Protection against catalyst poisoning.

2.3 Progress in zeolite membrane synthesis for membrane reactor applications

Polymeric membranes allow both high permselectivity and fast permeation, well-developed technology to produce thin polymeric membranes already exists and are also relatively cheap, yet these membranes have important drawbacks that limit their use in membrane reactors. The shortcomings, namely their limited resistance to temperature, solvents and corrosive environments, limits the application of polymeric membranes to bioreactor and liquid-phase reaction systems [55]. Inorganic membranes, such as ceramics and metals however, do promise significant payoff in chemical processing, owing to their superior characteristics of thermal, mechanical and structural stabilities as well as chemical and solvent resistance. Inorganic membranes also allow regeneration through the oxidative removal of carbonaceous species at 400-500°C and therefore have longer life expectations than their polymeric counterparts.

Inorganic membranes can be classified into two types: non-porous (dense) and porous membranes. Dense membranes prepared from palladium or perovskites only allow certain gases (such as H_2 or O_2) to permeate via mechanisms such as solution–diffusion or solid-state ionic conduction. Such nonporous systems exhibit extremely high selectivities but have limited permeabilities, although here, substantial research effort during the last decade have produced fluxes within reach of targets [56]. These membranes further require high capital investment due to the use of precious metals and/or extreme synthesis and operating conditions [57] and may be mechanically unstable [58]. In contrast, microporous silica membranes have proven to be promising for molecular sieving applications. Precise pore size control (0.3–0.4 nm in diameter) to allow for separation on the basis of size by molecular filtration or 'sieving' has however not yet been achieved for amorphous inorganic membranes and they are also chemically, mechanically and thermally less robust [59] than zeolite membranes.

Zeolite membranes form one of the newest branches of the inorganic membrane field. Unlike the most microporous metal oxides (e.g., SiO_2, Al_2O_3 and TiO_2) that have tortuous pore channels, zeolites are microporous aluminosilicate materials that have a well-defined, uniform pore system of molecular dimensions (enabling shape or size selective catalysis or separation) due to their porous crystalline structure. Zeolites are relatively stable at high temperatures, can be acidic or basic in nature and can exhibit hydrophilic or organophilic properties. These molecular sieves can be tailor made for a specific application through ion exchange, dealumination-realumination, isomorphous substitution and insertion of catalytically active guests such as transition-metal ions, complexes, basic alkali metal or metal oxide clusters. The molecular sieving abilities (figure 2.2) and selective sorption properties in combination with their catalytic activity, in addition to their thermal and chemical stability, make zeolites ideally suited for the combination of separation and reaction under process conditions.

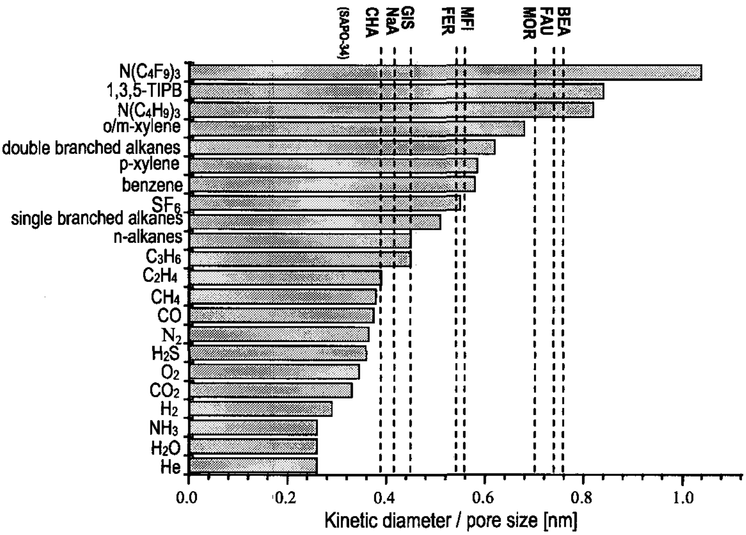


Figure 2.2: Comparison between the effective pore sizes of different zeolites and the kinetic diameters of gas molecules featured in reports on zeolite-based membrane reactor applications.

Total selectivity, or sieving, results when the size of the pore apertures is similar to the dimensions of the gas molecules. Even the very critical separation of propane-propene is possible in this way [60]. However very high selectivity is also possible with mixtures of gases when the zeolite pore sizes are significantly larger than the molecules, due to adsorption selectivities and/or the differences in diffusivities of the various components in the mixture [61, 62].

A great deal of progress in the science of zeolite membrane synthesis has been made since the first preparations of zeolite membranes by Suzuki in 1987 [37] the standalone, mechanically unstable membrane by Haag and Tsikoyiannis of Mobil in 1991 [4, 63] and the first supported silicalite-1 membrane reported in literature by Geus *et al.* [64]. Since then there has been an exponential growth in papers on the subject and literature abounds with reviews on zeolite membranes (van de Graaf *et al.* [65], Caro *et al.* [33, 66], Tsapatsis *et al.* [67] and Lin *et al.* who recently summarized the significant progress made in the synthesis of microporous membranes [68]).

MFI zeolite membranes (silicalite-1, ZSM-5), on flat or tubular supports, have been investigated extensively for application in gas separation, catalytic reactors and pervaporation. Silicalite-1 has for instance been applied in the separation of *n*-hexane from its branched isomers in a hydroisomerization membrane reactor [69]. The linear alkanes are preferentially adsorbed by the zeolite and supplied to a packed bed of catalyst. The control of the feed composition to the reaction resulted in an increased selectivity and conversion. Zeolite A membranes have often been the target of investigations because their small pore size would in principle exclude molecules with a size larger than 4.1Å thereby opening the field to highly selective separations in the gas and liquid-phases [70]. Other zeolite membranes that have been reported include FAU [71], MOR [72, 73], FER [74], GIS(P) [75], SAPO-34 [76], zeolite T [77, 78], BEA [51] and mesoporous UTD-1 [79]. The hydrophilic LTA zeolitic membrane has been the first to find industrial application. The first large-scale pervaporation plant, which produces 530 l/h of solvents (EtOH, IPA, MtOH, etc) at less than 0.2 wt.% of water from 90 wt.% solvent at 120°C, has been put into industrial operation recently by Mitsui Engineering and Shipbuilding Co. Ltd. [80]. The plant is equipped with 16 modules, each of which consists of 125 pieces of NaA zeolite membrane tubes. The excellent water separation is however based on the strong hydrophilic nature of the LTA membrane and not on molecular sieving [81]. Few reports exist for the successful application of zeolite A membranes to gas separation. Most authors report selectivities similar to those expected for Knudsen flow through the membrane – an indication of the presence of intercrystalline pores.

Despite the measurable success achieved in supported zeolite membranes during the past decade, few reports on the practical application of such membranes in high temperature catalytic membrane reactors exist. To some respect this can be contributed to the diminishing interest of industry in novel catalytic and separation materials and processes that provide only moderate performance improvements to established processes. The current economic climate and the fact that material uncertainties and associated development costs rarely counterbalance potential benefits fuel this somewhat discouraging view of industry. However, the lack of implementation of zeolite membrane reactor technology can't solely be blamed on industrial scepticism. In order to bring zeolite membrane reactors to commercial applications, there are a number of criteria that still have to be met and/or further explored:

a.) The synthesis of membranes with high permeability and selectivity, i.e. oriented, thin layers i.e. small effective thicknesses are required which must be highly uniform and free of defects. Optimal membrane reactor operation requires the membrane flux to be in balance with the reaction rate [82].

b.) Reproducibility and long-term stability of membrane performance. Coke deposition, triggered to a large extent by the acidic nature of the zeolite framework, necessitates the possibility of repeated membrane regeneration and a technology for repairing defective membranes.

c.) "Ultramicroporous" membranes, i.e. those with sufficiently small pores (~ 3Å) to allow separation on the basis of size exclusion, and without intercrystalline pores. The majority of the membranes synthesized so far are MFI-type zeolite membranes that have pore diameters (~5Å), which are still too big to selectively separate small gaseous molecules.

d.) The sealing of the membranes at high temperatures (> 250°C) and pressures.

e.) Scaling-up of membrane modules, requiring the ability to prepare large defect-free membranes at reasonable costs

f.) Cost of membranes and membrane modules,

g.) Clarification of multicomponent transport and separation behaviour through zeolitic and non-zeolitic pathways in the membranes at industrially relevant operating conditions.

Recent research efforts have therefore been directed to finding solutions to the above challenges. For this reason the advances made in the in the field of membrane reactors mirror the advances made in the production of new and improved membranes.

2.3.1 The synthesis of high-flux, selective membranes.

The quality of zeolite membranes is determined by intercrystalline porosity (defects) [83], the crystal orientation relative to the membrane layer [84], size of the crystals [85] and the thickness and uniformity of the zeolite layer [86]. In recent years, several groups have reported preparations of high quality zeolite membranes: MFI [87, 88], mordenite [89, 90], Y-type [91], A-type [92] and ferrierite [93]. A variety of methods for the fabrication of zeolite thin films exists which includes dip coating, spin coating, sputtering, chemical vapour deposition (CVD) and laser ablation [94]. The three most common methods used to produce membranes for gas separation have been (a) the formation of a composite, by embedding zeolite crystals in a matrix, such as a polymer, (b) in situ crystallization in the presence of a substrate, such as a porous ceramic, to give a supported zeolite membrane and (c) the more recently developed secondary growth process which involves the deposition of colloidal zeolite crystals on a macroporous support followed by hydrothermal synthesis.

Most papers written on zeolite membranes, and most development in the field have been targeted at MFI type molecular sieves. Table 2.4 gives a summary of recent progress made in the synthesis of silicalite-1 membranes.

Table 2.4: Overview of synthesis for thin, high flux, oriented silicalite-1 membranes

Ref.	OH^-/Si	Na^+/TPA^+	Synthesis temp. [°C]	Synthesis method	Support	Membrane thickness [μm]	Crystal Orientation	Membrane performance
[95]	0.32	0.00	165	in situ, hydrothermal, horizontal placement of support at bottom of autoclave, clear solution	SS 304 plates	1	b-oriented	Not determined
[95]	0.50	0.00	165	in situ, hydrothermal, horizontal placement of support at bottom of autoclave, clear solution	SS 304 plates	0.6	b-oriented	Not determined
[96]	0.32	0.00	165	in situ, hydrothermal, horizontal placement of support at bottom of autoclave, clear solution	SS 304 Aluminium alloy	<0.4	b-oriented	Not determined
[97]	4.23	0.00	175 and 140	secondary growth of precursor layers with no calcination step prior to secondary growth.	non-porous glass slides	4 / 7.5 / 13	primarily c-oriented / or c-axis tilted by 35°	Not determined
[98]	0.44	1.00	175	seeded synthesis, by two successive secondary synthesis for 24 hours, from clear solution	α-Al_2O_3 disks	25-40	primarily c-oriented	50% mixture binary para:ortho xylene flux ratio <4 as opposed to almost 40 for the single-component
[84]	0.23	1.00	140/175	secondary growth procedure consisting of deposition of MFI microcrystals from a colloidal suspension on the substrate to form seed layers, followed by hydrothermal growth of the seed crystals to form a film.	α-Al_2O_3 disks and non-porous glass	12-15	c- or [h0h]-out-of-plane	N_2 : SF_6 single-component selectivity is 8-10, flux of n-C_4H_{10} and the n-C_4H_{10} : i-C_4H_{10} flux ratio from 50/50 mixtures at 223°C is in the range 1.5-5.5x10^{-3} $molm^{-2}$ s^{-1} and 28-62, respectively. N-butane/i-butane selectivity of 50-90
[99]	4.00	0.00	175	Sol-gel dipcoating of mesoporous silica, followed by the covalent linking of oriented seed layer and secondary growth.	α-Al_2O_3 disks	1	a and b-oriented	2.5 x 10^{-7} $mol/m^2s \cdot Pa$ p-xylene/o-xylene selectivity of 300
[99]	4.20	0.00	175	Sol-gel dipcoating of mesoporous silica, followed by the covalent linking of oriented seed layer and secondary growth.	α-Al_2O_3 disks	1	primarily b-oriented	High flux + o/p-xylene selectivity >4

Table 2.4: Overview of synthesis for thin, high flux, oriented silicalite-1 membranes

Ref.	OH^-/Si	Na^+/TPA^+	Synthesis temp. [°C]	Synthesis method	Support	Membrane thickness [μm]	Crystal Orientation	Membrane performance
[100]	0.25	0.00	130	seeded, secondary growth	γ/α-Al_2O_3 disks	2	101	Single gas permeation tests performed at 323 K and 1.2 bar for SF_6 = 200 mol^{-1}s^{-1}Pa^{-1}m^{-2}
[100]	0.28	10.00	150	seeded, secondary growth	γ/α-Al_2O_3 disks	3	002	Single gas permeation tests performed at 323 K and 1.2 bar for SF_6 = 280 mol^{-1}s^{-1}Pa^{-1}m^{-2}
[101]	0.13	0.00	175	In situ, hydrothermal	silicon disks	Not determined	(0 2 0) plane parallel to the surface initially	Note determined
[101]	0.25	0.00	125	charge reversal with 3-mercapto propyl trimethoxy silane, seeded, secondary growth	silicon disks	1.1-12	*c*-axis nearly normal	Not determined
[102]	4.12	0.00	100	seeded, secondary growth, hydrothermal	silicon wafers	0.5	*b* oriented, however in thick films, most of the crystalline material is *a*-oriented	Not determined
[103]	4.12	0.00	100	Masking of support followed by seeded, secondary growth, hydrothermal	silicon wafers	240, 500, 1200 nm	a and b-oriented	3.2 for 0.27 kPa p-xylene/0.59 kPa o-xylene
[104]	0.64	0.00	180	Aging followed by in situ hydrothermal growth	Stainless steel disks with TiO_2 coating	32 - 40	unorientated	50/50 mixture of n/i-butane gave a selectivity 55 at 30°C n-butane flux of 2.75 mmol/m^{2}s

In order to control and direct the synthesis of thin, oriented, selective zeolite membranes, crucial to the success of membrane reactors, a fundamental understanding of the mechanism of zeolite crystallization *and* membrane growth needs to be gained. The preparation of zeolite membranes is still often conducted in conditions similar to zeolite powder synthesis, which are not optimized for membrane formation. Finding the proper conditions to prepare a desired zeolite membrane is often largely based on trial and error, limiting the reproducibility of membrane preparation. As a result, substantial effort has recently been put into the elucidation of the mechanism of crystal growth [105] and zeolite film formation [106-108], as well as the role of structure directing agents (SDA's) in the assembly of long-range ordered materials. More importantly the correlation between the mechanism, the membrane synthesis procedure and composition and the resulting zeolite film has been investigated. De Moor *et al.* [109], using a combination of *in situ* SAXS, USAXS and WAXS (ultrasmall and wide-angle X-ray scattering), found the nucleation of Si-TPA MFI to be a two-step process: first nutrients must assemble into composite species (~2.8nm). Aggregation of these nanometer-scale primary units to 10-15-nm-sized particles is found to be an essential step in nucleation of the zeolite since it enhances the nucleation rate. By varying the alkalinity, it was found that 2.8 nm particles were always present unlike their aggregates which weren't formed at high alkalinities (Si/OH ratio > 2.65) [110]. Although the size of the primary units for MFI was shown to be independent of the structure-directing agent used (a dimer of TPA, a trimer of TPA or trimethylene-bis(N-hexyl, N-methyl-piperidium)), the organic species does have a pronounced influence on the crystal growth step and, therefore, on the crystal growth rate, size, and morphology [111]. The suggested growth mechanism agrees with a mechanism proposed earlier by Schoeman et. al. [112] essentially the same growth mechanism was also suggested by den Exter *et al.* [113].

Although most of the earlier molecular sieve membranes prepared was freestanding, the vast majority of zeolite membranes prepared today are supported, owing to their greater structural stability and reduced mass-transfer resistance. Two critical stages can be distinguished during the formation of supported zeolite membranes, namely nucleation on the support followed by crystal growth to form a continuous zeolite film covering the support. Nucleation and crystal growth processes during zeolite membrane synthesis are very sensitive to experimental conditions such as synthesis solution/gel composition (which Wang *et al.* proved can be manipulated to control the crystal growth orientation [95]), pH, temperature, chemical and structural nature of the support [114], support position [75, 115], structure directing agents (SDA's) [116] used to assemble long-range ordered materials and even nutrient sources [117, 118].

Synthesis of zeolite membranes or thin films on a support can broadly be classified as either *in-situ*, a one-step hydrothermal synthesis where the support is placed in direct contact with the alkaline precursor solution, or *secondary (seeded) growth* in which an existing zeolite phase (seed crystals), is attached to the support followed by hydrothermal growth of the applied seeds to a continuous layer. In essence both these techniques involve nucleation and crystal growth steps, although nucleation sites are created and applied separately and with more control to the surface of the support during secondary synthesis. Since secondary growth techniques enable improved control of nucleation site location and density, it renders the nature of the support less important for membrane growth with growth proceeding from a layer of seed crystals covering the support [119]. Nevertheless good adherence of the zeolite seed crystals (nucleation sites), as well as the zeolite film to the support is still as important as is the case for in-situ synthesis in order to guarantee the mechanical, thermal and chemical stability of the composite membrane.

The above constitutes the main difference between zeolite powder and zeolite membrane synthesis as well as one of the difficulties inherent to the preparation of zeolite membranes, namely the existence of an additional parameter, the substrate and the linking of zeolite crystals to that substrate so as to obtain a continuous thin composite zeolite membrane. Various techniques have been developed to facilitate nucleation and crystal growth on the substrate and to tailor the interaction between the zeolite layer and the substrate.

It has been well established that the quality of the underlying support determines, to a high degree, the quality of the selective membrane layer on top. A thin zeolite film is less likely to adhere in a continuous fashion to a rough or large-pore substrate, therefore whenever attempting to prepare a supported zeolite membrane; one of the first steps taken is to ensure that the substrate surface is smooth. Smooth porous surfaces for deposition of a zeolite layer could be created in its simplest form by mechanical polishing of the substrate [84, 120]. However this method is tedious and repetitive while more importantly, the polishing of tubular support interiors are unfeasible. More recently the deposition of a thin meso-/ micro-porous film on the support have been used to create a smooth surface for zeolite film growth. The layer has the additional benefit of serving as a diffusion barrier, preventing the zeolite layer from penetrating the support, which would result in a longer effective diffusion path, whilst also protecting the support against possible leaching [64]. Lai *et al.* [116] dip-coated an α-alumina support with a mesoporous silica layer according to the method developed by Tsai *et al.* [121] to improve the surface finish of the substrate for seed crystal deposition. They reported not only and improved flux due to a shorter effective diffusion path, but also increased selectivity partly due to the elimination of stress-induced crack formation during calcinations. A *p*-xylene/*o*-xylene selectivity as high as ~400 at a *p*-xylene permeance of $3\text{x}10^{-7}$ mol/(m^2 s Pa) with an essentially b-oriented MFI film of 1μm was obtained.

Hedlund *et al.* [103, 122] reported what they termed "a two-step support masking technique" to prevent support invasion and leaching. They applied a coating of PMMA on the surface of the support and plugged the pores of the support with a polyethylene wax. The PMMA layer was removed by rinsing in acetone for a week while the polyethylene wax was later removed during calcination. A monolayer of colloidal nucleation seeds was adsorbed electrostatically on the support, followed by hydrothermal growth, producing a defect-free film, although grain boundaries are still clearly visible, with a thickness of 0.5 μm. High-pressure xylene separation tests were carried out at 400 °C at 100 kPa hydrocarbon partial pressure (200 kPa total pressure). The *p*-xylene/*m*-xylene selectivity was 13 at a *p*-xylene permeance of $1,1 \times 10^{-7}$ mol/(m^2 s Pa).

One of the challenges faced during *in situ* synthesis is ensuring a high nucleation site density on the support, often giving rise to higher film thickness than desired to close all defects. Techniques that have been used to ensure that nucleation takes place on the support are multitude.

The adherence of the zeolite crystals to the support surface is to a large extent determined by the hydrophilicity of the support surface, eg. the number of OH-groups per nm^2. Treatment of the support with NaOH in order to increase the number of surface hydroxyl groups would therefore impart the support with more nucleation points as well as sights where crystals could adhere by means of Van der Waals interactions and H-bonding. Kim. *et al.* reported treatment of the support with trimethylchlorosilane to create Si-Cl bonds on the surface of the support in order to enhance adhesion of a mesoporous layer to the support [123]. Pretreatment of the support surface by impregnation or spin-coating with the appropriate template was also shown to direct the formation of crystallites on the support. Chau *et al.* found that a coating of a metal oxide (eg. Fe_2O_3) on the support surface provided a simple technique to controle the number and type of nucleation sites available on the support surface [119]. Their results indicated that there was a direct correlation between the number of nucleation sites and the amount of iron(III)oxide present on the surface of the support and allowed the synthesis of a more complete and uniform zeolite film. Synthesis conditions, such as a highly alkaline synthesis mixture, have also been shown to favor a high nucleation density [120, 124]. In a more recent report of Van den Berg *et al.* UV-radiation was used to increase the number of defect sites and hydroxyl groups to promote the hydrophilicity of a TiO_2-coated support. The authors reported an increased nucleation and the resultant formation of a uniform, monolithic zeolite A film, well attached to the support [125, 126].

Other approaches that rely on limiting/directing nutrient sources or other conditions necessary for synthesis, to the surface of the support have also been examined. Electrophoretic deposition can be used to coat substrates with charged particles from colloidal suspension. Zeolite particles formed during hydrothermal synthesis assume a negative/positive charge due to electrical double layer effects. These charged zeolite particle would be attracted to a support to which an opposite charge is applied. Oonkhanond *et al.* made use of this principal to attract ZSM-5 particles to the surface of a porous alumina tube in order to obtain a 10-15 μm thick, continuous layer [127]. Mohammadi *et al.* synthesized a zeolite A membrane from Kaolin that was electrophoretically deposited on a cylindrical anode and treated hydrothermally [128]. Heating only the support while the rest of the synthesis solution is cooled would rule out nutrient depletion by competing nuclei and crystal growth in the bulk solution and result in crystallization being limited to the support surface. Yamazaki *et al.* used a plate heater to apply heat to the substrate area alone with a static solution, as well as a circulated solution system [129]. In both scenarios zeolite membrane formation was not accompanied by powder formation in the bulk solution. Deposition of films within a substrate can be achieved by using the countercurrent reactor configuration, where each reagent enters from the opposite side of the substrate. This method would effectively eliminate nucleation and growth from occurring outside the support [130]. The vapor phase transfer synthesis method is a variation of the in situ synthesis method, developed by Xu *et al.* that consists of two steps: covering the support with a synthesis gel and crystallization of the dried gel under autogeneous pressure. Since one of the nutrient sources is limited to the support surface, zeolite membrane formation would also be limited to the support surface [131, 132].

Seeded synthesis tends to produce continuous films a lot more readily and with better reproducibility due to better control over nucleation site density. One of the determining factors for the successful synthesis of a thin, defect-free zeolite film on the support with this two-stage method, is the application of a thin, uniform and continuous layer of seed crystals to the support. The simplest and often used method is to apply seed crystals to the substrate with mechanical rubbing [132] [92]. This method is not ideal however since it is quite difficult to obtain a continuous and even seed layer. Several authors applied seed crystals to the support by dipcoating the substrate in a suspension of zeolite particles, followed by drying at room temperature and calcination in order to fix the crystrals to the support surface. This process is often repeated a few times in order to ensure a sufficiently high coverage of the support with zeolite seed crystals [84, 133, 134]. Electrostatic attraction could be used to limit the number of times the dipcoating procedure has to be repeated. This involves charge modification of the substrate surface by adsorption of an anionic or cationic polymer, which would then effect the electrostatic attraction of colloidal zeolite particles in suspension to the surface of the support [117]. The electrostatic deposition process generally achieves a high coverage of the substrate with well-adhered particles and is one of the most-effective techniques developed to date for seed crystal deposition. Electrophoretic deposition (EPD) offers a way to coat a substrate uniformly with a variety of charged particles without the need to pretreat the substrate. Seike *et al.* [135] prepared a zeolite Y membrane through EPD of NaY zeolite seed crystals on a stainless steel support. Shan *et al.* [136] were recently able to prepare zeolite films through electrophoretic deposition in a non-aqueous medium, allowing the application of a higher voltage and better control over the thickness and density of the prepared films. The self-assembly of micrometer-sized zeolite crystals on supports via covalent linkers has received increasing attention during the last five years. This method of preparation, although promising for yielding well-oriented monolayers, is however rather complicated and to date no membrane suitable for gas separation has been obtained. [137, 138] Other methods that have been investigated for the deposition of oriented monolayers of zeolite seed crystals include Langmuir-Blodgett deposition [139] and Pulsed laser ablation [79].

The MFI crystal has an anisotropic two-dimensional channel network consisting of straight channels of elliptical cross-section (0.51 x 0.54 nm) along the *b*-direction and sinusoidal channels of nearly circular cross-section (0.54 nm) along the *c*-direction (Fig.2.3). Due to the anisotropic nature of this zeolite, the orientation of the crystals will have a significant influence on the molecular sieving performance.

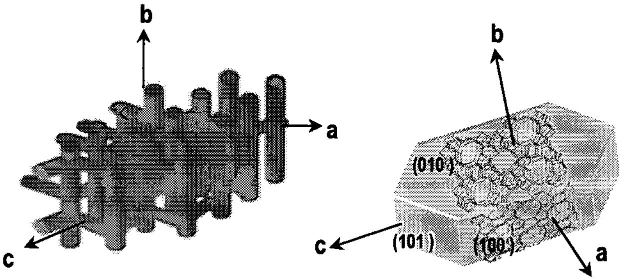


Figure 2.3: MFI crystal with stylistic pore structure and crystallographic axis**[66]**

Preferred crystal orientation could impact the molecular sieving and permeation of the zeolite film that are crucial for their application in membrane reactors. Due to the attractive features of oriented thin films, there has been intense effort during the last ~5 years to prepare zeolite films with controlled orientation and several approaches have been developed:

a) Identifying and controlling conditions to promote growth rates along certain crystallographic directions. Progress towards the fundamental understanding of the origin of shape and habit of zeolite crystals will greatly facilitate the task of engineering zeolite film microstructure according to design. Some degree of preferred orientation could always be expected since most of the zeolite structure types have anisotropic growth rates. MFI crystals most often have a coffin shape, elongated along the *c*-crystallographic direction, indicative of fast growth along the *c*-axis. Many authors have noted that the growth morphology of zeolite varies with the composition of the synthesis mixture, i.e. composition of the starting mixture, as well as the synthesis temperature. This means that the growth process for each crystal face is strongly dependent on the synthesis conditions. Systematic variations of MFI synthetic conditions can lead to particle shapes ranging from symmetric to elongated needle or coffin. Iwasaki *et al.* [140] and Wang *et al.* [95] performed a systematic study on the correlation between the crystal orientation in MFI films on stainless steel plates and the composition of the synthesis solution. The goal of their respective studies was to show that manipulation of crystal orientation in a continuous thin film could be achieved with in-situ crystallization through systematic optimization of the synthesis composition. They found that within the synthesis system of TPAOH:NaOH:TEOS:H_2O:NaCl, OH^-/Si and Na^+/TPA^+ ratios play a critical role in controlling crystal orientation. For sodium-free or low sodium syntheses, only random-oriented films are formed at OH-/Si ≥ 0.64, (*a*,*b*)-oriented films at 0.64 > OH-/Si > 0.5 or at 0.2 ≥ OH-/Si > 0.1, and *b*-oriented films at 0.5 ≥ OH-/Si > 0.2. For a given OH-/Si ratio, addition of Na^+ leads to change of crystal orientation from *b*-oriented, to (*a*, *b*)-oriented, to (*a*, *b*, *c*)-oriented, and eventually to random oriented. Wang *et al.* explained this by the fact that Na^+ tends to cause agglomeration of silicate precursors leading to large aggregates of random-oriented crystals. Wang *et al.* also found that the crystallization temperature and time as well as the chemical nature and roughness of the support are important for orientation and film continuity.

By studying the nucleation and growth rates of MFI crystals along different crystallographic directions, Lai *et al.* were able to manipulate relative growth rates along different crystallographic directions of MFI, and by doing so, obtained highly selective oriented molecular sieve films. [99, 141] Membranes of the high silica molecular sieve MFI with c-out-of-plane preferred orientation showed low selectivity for *p*-/*o*-xylene (Fig. 2.4, left) due to the presence of grain boundary defects. MFI membranes with a small difference in preferred orientation (*c*-axis inclined by about 35°, (h0h) plane normal to the support) showed no evidence for the presence of similar defects at the grain boundaries. These membranes show excellent selectivity for p-xylene. The relationship between membrane microstructure and the transport properties of ZSM-5 membranes were also investigated by Au *et al.* [100]. Experiments conducted by the authors suggested that grain boundaries form the main non-zeolitic pathway in the membrane diffusion and their elimination through grain growth can result in better membrane performance.

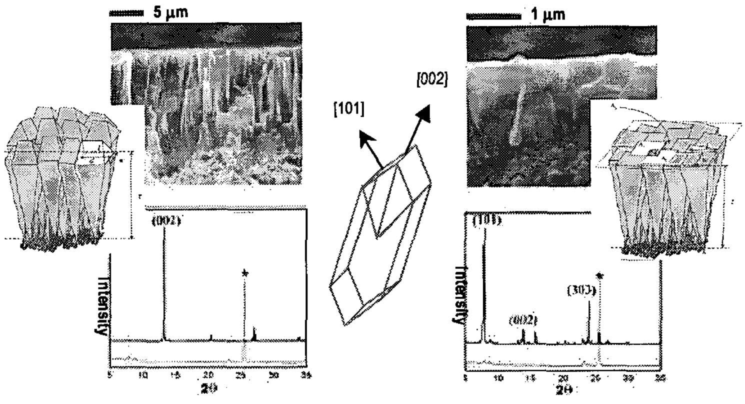


Figure 2.4: Molecular sieve membranes with small differences in microstructure showing drastically different performance.[97, 100]

b) The second approach involves starting the membrane synthesis with oriented seeds and proceeding with the seeded growth in the absence of further nucleation. Several different strategies have been used for oriented seed layer deposition. These include dip coating [133], charge reversal of the support with a cationic polymer followed by seed deposition [101, 142], and recently there has been a trend to make use of chemical linkers such as iso-cyanates to covalently bind the seed crystals to the support [137].

Tsapatsis *et al.* [143] prepared a silicalite membrane by growing a layer of oriented silicalite-1 crystals on a composite precursor nanocrystalline silicalite/alumina unsupported film using controlled secondary growth. The orientation of the crystals was primarily with the *c*-direction perpendicular to the support, in other words both straight and sinusoidal channel networks ran nearly parallel to the membrane surface. Although oriented seed crystals give rise to a zeolite layer of the same orientation initially, it was found that as the film grew thicker during secondary growth, randomly oriented films formed due to anisotropic growth rates of the different crystal faces. In 1998 Tsapatsis and coworkers [97] further studied the growth of an oriented zeolite layer. They succeeded in manipulating the out-of-plane grain orientation by secondary growth conditions, in such a way that the *c*-axis of the grains range from being oriented perpendicular to the substrate to being oriented at and angle of ~35° from the direction normal to the substrate. More recently Lai *et al.* [99] succeeded in preparing a primarily *b*-oriented layer on α-Al_2O_3 disks, by following a three-step approach. First the supports were coated with a mesoporous silica layer, masking the support and providing a smooth layer for membrane growth. This was followed by the deposition of an essentially single layer of seed crystals through the use of chemical linking groups according to the method of Ha *et al.* [137]. Finally the seeded supports were hydrothermally treated at 175°C for 24 hours in a synthesis solution containing trimer TPA as structure directing agent. Lai *et al.* obtained supperior *o*-xylene/*p*-xylene separation whilst maintaining high permeances with the above described membrane.

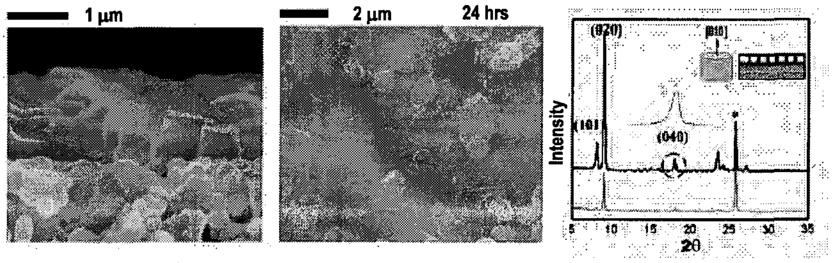


Figure 2.5 : Cross section and top view of the primarily b-oriented silicalite-1 membrane, and corresponding XRD trace of the seed layers (bottom trace) and the membranes (top trace) [99].

Hedlund *et al.* [144] treated an alumina support with a cationic polymer in order to reverse the charge of the support. They subsequently deposited the negatively charged LTA seed crystals electrostatically on the support. Film crystallization on the seeded substrate was effected by hydrothermal treatment in synthesis solution with the same composition that was used for the seed crystal preparation. They obtained an essentially continuous 280 nm LTA film with the (100) plane of the crystals primarily oriented parallel to the substrate surface. In 1998 Mintova, Hedlund and Sterte [145] reported the synthesis of ZSM-5 films on quartz substrates from template free precursors. The substrates were covered with a monolayer of seed crystals. These crystals were grown into continuous films with thicknesses in the range 230 – 3500 nm by hydrothermal treatment. The preferential orientation of the crystals constituting the film was initially with the *c*-axis close to parallel to the substrate surface. During the course of crystallization this orientation changed to one with the most of the crystals having the axis directed (as in the case of Tsapatsis *et al.* [97]) approximately 35° from perpendicular to the substrate surface. In 1999 Hedlund, Mintova and Sterte [102] investigated certain parameters in the film formation process These included the seed crystal size, amount of adsorbed seed crystals and film thickness after hydrothermal treatment of the seeded substrates. They concluded that the shape and orientation of the adsorbed seed crystals and their growth rate in different directions determine the orientation of the final film. By controlling the seed size and amount of seed crystals they could attain some control of the orientation of the crystals constituting the film.

In 2001 Yeung *et al* [86] also succeeded in preparing a (101)-oriented MFI zeolite membrane on seeded supports by tailoring the synthesis conditions and composition.

c) Changing the direction of the highest nutrient concentration from the out-of-plane to the in-plane direction. The presence of a precursor gel can be used to provide high nutrient concentrations on the surface of the substrate. Direct hydrothermal synthesis with this approach can lead to *a* and/or *b*-out –of-plane oriented films since the fastest growing crystallographic plane (along the c-axis) is now *in-plane*, confined by nutrient availability. Essentially *b*-oriented MFI films, prepared according to this approach were previously reported on silicon wafer and glass supports by Jansen *et al.* [146], den Exter *et al.* [113] and Koegler *et al.* [107]. However, these films were often non-continuous.

2.3.2 Reproducibility and long-term stability of membranes

Reliability and durability are key criteria in the process industry and one of the main obstacles for industrial zeolite membrane reactors. It is well-known that poor reproducibility of zeolite membrane preparations is a commonly encountered problem [83] due to the large number of factors that play a role in zeolite membrane formation. Van de Graaf *et al.* for instance reported that only 4 out of 12 silicalite-1 membranes had an acceptable quality. Noack *et al.* [147] also concluded that reproducibility of membrane preparation was severely lacking with only 10-30% of preparations producing high quality membranes. By varying the synthesis composition and conditions, the authors could however increase the yield of high-quality membranes to 70% of their preparations.

One of the key contributing factors to the difficulty of obtaining reproducibility is the lack of attention that has been paid to temperature trajectories within synthesis reactors. Several authors have shown that the synthesis temperature and profile has a significant influence on the microstructure and the overall quality of the membrane [100, 148]. Li *et al.* [149] obtained notably improved results when use was made of a two-stage temperature synthesis, allowing the formation of a larger amount of nuclei and a resultant continuous membrane. Even though temperature profiles within reactors clearly have a major influence on the final quality of the membrane, very few authors have mentioned synthesis reactor characteristics or temperature profiles within those reactors. This necessitates the re-optimization of synthesis procedures whenever the experimental setup and conditions are slightly altered.

For the successfully implementation of zeolite membranes in industrial processes, permeances and selectivities should also be maintained over long periods of time. Coronas *et al.* [85] studied the separation properties as a function of time on stream for several membranes and observed a reduction in the n-hexane permeance and *n*-hexane/2,2-dimethylbutane selectivitiy that increased with increasing operating temperature. The degraded membranes could however be regenerated by calcination at elevated temperature to obtain their original permeances and selectivities. Van den Broeke *et al.* [150] studied the reproducibility of permeation results for carbon dioxide and the robustness of silicalite-1 membranes prepared by them with a time span of about a year between runs. During this period a large number of temperature and pressure cycles were performed, with various gases. Their results indicated only minor changes in performance. Van de Graaff *et al.* [83] investigated the long-term stability of a silicalite-1 membrane using the *n*-butane/*i*-butane permselectivity at 30 °C as a standard test and found that there was only a slight decrease in selectivity over a period of two years. Studies on the reliability of membrane syntheses and the reproducibility of membrane performance has also been conducted by Gora *et al.* [104] and Hedlund *et al.* [151] Current efforts to produce reproducible high quality membranes overall indicates that a satisfactory success rate could be obtained with optimization of conditions and compositions for zeolite membrane formation.

2.3.3 "Ultramicroporous" membranes.

Zeolite molecular sieves, having high porosities and well-defined pore sizes in the range of 3-12Å, are clearly good candidates for membrane reactors. The difficulty to produce ultramicroporous zeolite membranes however remains and is of dual-nature: firstly zeolite membranes with pores in the ~ 3 Å range to separate small gas molecules on the basis of size exclusion should be produced, and secondly a method to produce zeolite membranes without non-zeolite pores or defects has to be found.

Until recently the attention of the research community had been focused on MFI zeolites due to its suitability for the separation of several industrially important raw materials. The development of zeolite membranes with channel sizes small enough to achieve high separation factors for gas mixtures is however also attractive for the separation of small gas molecules such as carbon dioxide (CO_2) and methane (CH_4) which typically have small differences in adsorption strengths. The small pore size of, for instance, zeolite NaA (0.41 nm) could improve separation of small gas molecules such as nitrogen (0.364 nm) and oxygen (0.346 nm) by exploiting differences in size between them. Xu *et al.* [152] made use of this fact in order to separate nitrogen and oxygen and achieved a permselectivity of 1.8 for O_2/N_2. Further investigation however indicated the presence of defects with a larger diameter than the pore size of zeolite NaA. More recently Kazemimoghadam *et al.* [153] investigated the dehydration of water/1-1-dimethylhydrazine mixtures by zeolite NaA and hydroxy sodalite membranes. Separation factors of >10 000 were obtained for both NaA and hydroxy sodalite membranes at 25°C and a pressure of 1.5 mbar on the permeate side. The hydroxysodalite membrane had a slightly lower flux but also a higher selectivity due to its smaller pore size. Other small pore zeolite membrane that have been investigated include the zeolite P membrane (examined by Dong *et al.* [75] for the separation of H_2/Ar, CH_4/Ar and H_2/SF_6), zeolite T [154] and a DDR type zeolite membrane, examined by Tomita *et al.* [155]. Tomita *et al.* concluded that the prepared DDR membrane had few defects and worked well as molecular sieving membrane, obtaining a separation factor of 220 for a 1:1 CO_2/CH_4 mixture at 28 °C and 0.5 MPa total gas feed pressure. Poshusta *et al.* [76] demonstrated that a SAPO-34 membrane also hold promise for the separation of light gas molecules. The authors achieved a CO_2/CH_4 separation factor of 30 at 27 °C.

The intercrystalline diffusion via defects in the structure of the zeolite membrane has a large negative impact on the performance of the membrane. In figure 2.6, Nelson *et al.* [156] showed that the flux through the imperfect membrane has a similar functional form to that for the perfect membrane, but with a maximum flux that is about ten times larger. This increase in flux was attributed to the decrease in the effective thickness of the membrane due to the presence of voids. Since the effective membrane thickness is much smaller than the actual thickness Nelson *et al.* also predict lower permselectivities for this imperfect, anisotropic membrane compared to those for defect-free membranes.

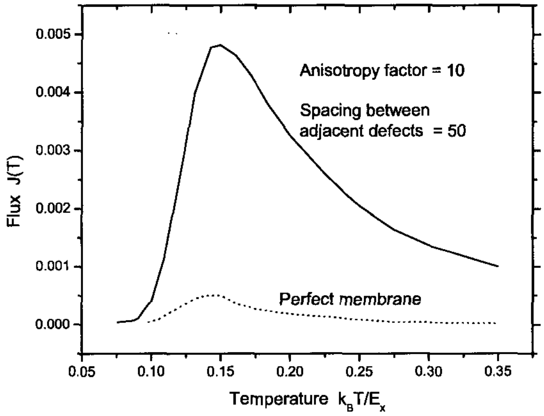


Figure 2.6: Comparison of fluxes through an anisotropic imperfect membrane with nanoscopic defects and a perfect membrane as a function of temperature [154].

Since defect size and defect density determines the separation performance of the membrane, the number and size of defects that form during membrane crystallization and post-synthesis thermal treatment have to be limited to a minimum. The defects that do form should be repaired through a suitable technique.

Several groups have shown the deleterious effect of calcination on the membrane quality and performance. Den Exter *et al.* [113], Geus *et al.* [157] and Dong *et al.* [158] found that compression stresses that developed during cooling after calcination induced cracks in the supported zeolite film. In response to the mentioned findings, endeavors to prepare zeolite membranes in the absence of an organic template have been reported by for instance Mintova *et al.* [145] and Hedlund *et al.* [151] reported the in situ synthesis of a MFI membrane while

Lai *et al.* [159], Pan *et al.* [160] and Lassinanti *et al.* [161] reported the preparation of a MFI membrane according to the secondary growth method. Most authors reported reduced flux and slightly increased selectivity.

Efforts that have been made to eliminate defects that did form during synthesis, include post-synthetic coke treatment, [162] chemical vapor deposition of silica by reaction with silicon alkoxide or silylation agents and treatment with a silane coupling reagent [163]. In a study performed by Nomura *et. al.*, the separation selectivity for a *n*/*i*-C_4H_{10} mixture increased from 9.1 to 87.8 after modification of the membrane pore structure by a TEOS-O_3 counter-diffusion chemical vapor deposition technique [164, 165]. Van den Broeke et al. also demonstrated that the permeation behaviour of a silicalite-1 membrane can be modified selectively by the reaction of a silane, $(CH_3)_3ClSi$ (TMCS), with accessible zeolitic OH-groups [150]. Xomeritakes *et al.* [166, 167] selectively sealed cracks that formed during the calcination of MFI membranes by dip-coating the membranes in a surfactant-templated silica. After drying, the mesostructured surfactant-silica layer that formed on top of the MFI membrane exhibited extensive cracking and could be easily peeled off by blowing the membrane surface with compressed air. However, the sol infiltrated inside large cracks during dip-coating, permanently plugged the cracks after transformation to an impervious surfactant-silica composite and improved the membrane selectivity. Although this method is successful in increasing the selectivity, it could lead to pore blocking and is therefore done at the cost of the flux. Van den Broeke *et al.* reported a reduction in *n*-butane flux by a factor 17 after silanation.

Lai *et al.* [99] recently made a large contribution to the art of membrane synthesis when the authors showed that it is possible to prepare highly selective zeolite membranes with a very low defect density. They were the first to report a zeolite membrane showing excellent separation with high permeance that relies on discrimination between molecules on the basis of differences in size and shape. The oriented film of the siliceous zeolite ZSM-5 prepared, showed para-xylene/ortho-xylene selectivities of ~200 – 800 whilst maintaining high flux.

2.3.4 Addressing the problem of sealing

The property of inorganic zeolite membranes that set them apart from polymeric and amorphous membranes is their thermostability, which allows operation under severe conditions as well as the ability to be reactivated which in turn gives rise to increased life expectancies for these membranes. It is however, generally acknowledged that the high-temperature application of zeolitic membranes is strongly limited by high-temperature resistant sealing of the module by which feed and permeate are separated from each other [168]. Despite the technical importance of high temperature seals for zeolite membrane research, studies with emphasis on high temperature seals themselves are seldom reported in literature.

One possibility is the parting of the locations of sealing and separation in order to be able to apply already known technology for sealing at low temperature. This however necessitates a much more complex membrane module in which a large temperature gradient exists over the different sections (that for separation and that for sealing) of the equipment. This has been achieved by providing a cooling system (e.g. water cooling) in a fully heated apparatus [169].

Of the many joining processes available, brazing is one of the most established techniques for ceramic to metal joining. In its simplest form, a brazing alloy that wet ceramics is applied to the support surface and subsequently heated in a controlled atmosphere such as nitrogen or argon [26]. Due to large differences in thermal expansion coefficients between the brazing material and the ceramic, this process often generates high residual stresses in the ceramic with resultant cracking and an inability to form gas impermeable seals. Another innovation has a ceramic incorporated in the braze alloy, to both increase its strength and reduce its coefficient of thermal expansion [170].

Ceramic glazes can also be used to seal the porous surface around the ends of a ceramic membrane. Ceramic glazes will limit the difference in thermal expansion coefficients between the seal and the membrane and reduce the development of thermal stresses. However some ceramic glazes have a lower chemical resistance and could dissolve in the high pH zeolite synthesis solution. Reed *et al.* [171] addressed the dilemma in their patent for a gas impermeable, glass-based glaze that can withstand high temperatures, for sealing the ends of a porous tubular alumina support containing a microporous separation membrane on the inside.

Geus *et al.* [114] solved the problem by preparing MFI membranes on porous, sintered stainless steel supports within stainless steel membrane modules in order to perform (high-temperature) permeation experiments whilst avoiding high-temperature sealing by the formation of the zeolite layer on both porous and non-porous stainless steel parts. Although the as-synthesized layers were found to be gas-tight, even for small molecules such as neon, this method severely complicates the synthesis procedure. Later Gora *et al.* [104] obtained a gas-tight seal by preparing zeolite A and MFI membranes on porous stainless steel supports to which swagelok connections had been welded.

Another approach, often used for lab-scale reaction systems, involves the lamination of the ends of the membranes combined with the use of graphite O-ring seals. The high temperature enamel (Aremco 617) that can tolerate temperatures up to 1100 K was for instance used by

Wong *et al.* to coat the tube ends while viton or graphite O-rings were used along with modified compression fittings to provide leak-free sealing [148]. The major problem of this technique is that, if not properly designed, the system can experience substantial thermally induced stress due to the differences in the thermal expansion coefficients between the seal, the ceramic support and the zeolite membrane and this could cause the membrane to crack during heating or cooling.

Recently Min *et al.* [172] reported a new approach to membrane module design using a porous metal support and a tapered sealing technique. To perform the permeation measurements of single gases and xylene isomers at temperatures of up to 723 K, Min *et al.* developed an all-stainless steel module in which the membrane module was constructed by tightly mounting the sintered metal support into a tapered hole to fasten the metal support in the module as shown in Figure 2.7. Afterwards the membrane module and support was placed in a stainless steel autoclave and a hydrothermal synthesis repeatedly carried out at 180°C until the zeolite membrane was rendered impermeable to N_2. By following the tapered sealing method, no special sealant was needed to seal the metal support and membrane module in order to perform the permeation experiments above 473 K.

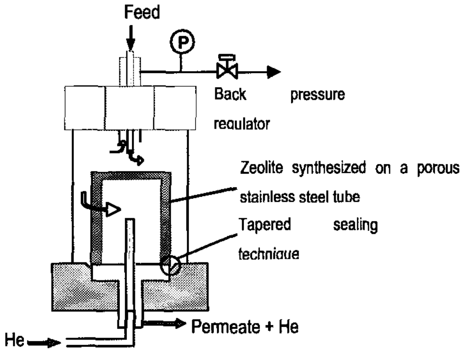


Figure 2.7: Schematic cross-sectional view of the membrane module [172].

It does seem as if some progress has been made in the high-temperature sealing of zeolite/ceramic membranes, especially at laboratory scale. The gas-tight, high-temperature resistant sealing of tubular zeolite membranes in an industrial scale module, where each individual tube in a tube bundle has to be sealed and fixed to metal tube sheets in the module, with differences in thermal expansion, whilst still preserving the integrity of the membrane film on the ceramic support, remains problematic and a possible bottleneck for this technology.

2.3.5 Up-scaling

Up-scaling is faced with a number of challenges; such as the synthesis of large continuous membranes. Although seeded synthesis may improve nucleation density and therefore increase the ease of synthesizing a large continuous membrane, the two-step synthesis procedure also poses problems and decreased ease of synthesis when one considers for instance the application of the seed layer in a uniform and continuous way on a large scale.

Temperature control in large synthesis reactors is another subject that needs more thorough investigation. Larger volumes would lead to the existence of a large temperature trajectory within the reactor, which means that synthesis conditions will have to be optimized for larger volume preparations. Obtaining a clear picture of the effect of synthesis temperature as a parameter on the nucleation and crystal growth rate of zeolites on a support is very difficulty due to insufficient/incomplete information that are given regarding the subject in reports of membrane syntheses. Microwave heating could provide better control over the temperature-time profile. Compared to conventional hydrothermal synthesis, microwave synthesis of zeolite membranes provide fast homogeneous heating throughout a reaction vessel and more simultaneous nucleation on the support surface, uniform small zeolite crystals and a resulting thin membrane, as well as a reduction in processing time and energy cost compared to conventional heating [173].

Membrane reactor modules will have to be designed in order support large surface area membranes, especially when dealing with potentially fragile ceramic units. Ease and effectiveness of sealing inside the module will also need attention.

2.3.6 Cost considerations

The estimation of the feasibility of a membrane reactor process is not merely as straightforward as the comparison of yield and selectivity with that of a fixed bed process (although this is the approach generally used) and actually requires a full economic assessment. However, due to the fact that zeolite membrane technology is relatively new and very few long-term commercial processes exist, an economic evaluation of a zeolite membrane reactor process is very difficult and reports of such evaluations in literature are scarce.

An initial study of the limited number of cost assessments of zeolite membranes and zeolite membrane reactors that have been reported in literature, paints a rather gloomy picture for the future of zeolite membrane reactor technology. Costs of about US$ 3000/m^2 for zeolite modules of which 10-15% is contributed to the membrane itself has been reported by Caro et.

al. [66]. When considering specifically zeolite membrane reactors, the problem is further intensified by the fact that the supports have not been designed and optimized for use as supports for zeolite membranes. Meindersma and de Haan [174] concluded in a feasibility study done by them for the separation of aromatics from Naphtha feedstocks, that unless membrane module costs were reduced by a factor of 10 and the flux were increased by a factor of 25 the investments would be uneconomical. Tennison reported that due to selectivity limitations of zeolite membranes, membrane processes are uneconomical and a considerable reduction in membrane costs is required to make such processes feasible [175]. Tennison emphasized that very few processes would be able to tolerate costs of more than €1000/m^2 and operation would also occur under far more demanding conditions than were generally used in modelling studies [176].

Besides variable and fixed costs in processes, increasing consideration will have to be paid in future to the costs for minimizing the environmental damages of manufacturing. The disposal of toxic or dangerous waste, such as spent catalysts and chemicals, easily amounts to US$250–US$750 per ton [177]. It is therefore critical to minimize waste production and emission, both from a conservation responsibility as well as a cost perspective. Zeolites and zeolite membrane reactors are ideally suited for environmentally friendly operation and their respective properties suggest that they will have a key role to play in sustainable process technology in the new millennium.

The economics of a plant could be improved by improving the overall selectivity and the productivity of the plant. Zeolite membrane reactors are known to be beneficial for product selectivity and using zeolite membranes/catalysts, which have an improved resistance to deactivation and could already separate species that could lead to deactivation, before reaching the catalyst, could limit plant downtime - thereby increasing productivity. The losses and transfers of energy, which dictate the investment costs, can be potentially minimized by zeolite membrane reactor technology by maximizing the reaction selectivity and the concentration of the various streams, and by minimizing changes in temperature.

Therefore, although at first glance economic feasibility of zeolite membrane reactors seems unattainable, there are a lot of possible benefits that should be taken into careful consideration and which will play an increasingly important role in future developments. In light of the above as well as the recent reports of submicron, highly selective, high flux, [99, 103, 144] reproducible, and reduced cost membranes [178], economic feasibility might well be reached.

2.3.7 Multicomponent transport and separation behaviour

Transport in zeolite membranes is a complex process that is governed by adsorption and diffusion. The irregular nature of the zeolite membrane with intercrystalline pores [156], and the further contribution of a support layer to the permeation resistance [179] add to the complexity of the process. In order to employ zeolite membranes on a large scale, improved experimental methods for the measurement of intracrystalline diffusion has to be developed and our understanding of the mass transport properties, the factors governing separation behaviour and our ability to predict the permeation of molecules through these membranes have to be increased.

The diffusivity in zeolites depends strongly on the pore diameter, the structure of the pore wall, the interactions between the surface atoms and the diffusing molecules, the shape of the diffusing molecules and the way the channels are connected as well as, most important in mixtures, adsorbate-adsorbate interactions [180]. The quantitative prediction of diffusion rates inside zeolites with modelling techniques is often hard to relate to the aforementioned properties and the underlying microscopic mechanisms [181, 182]. A contributing factor to the difficulty of diffusion prediction is the large discrepancies that often exist between diffusivities determined from different experimental techniques [183-185].

When used as a catalyst or molecular sieve, at least two, and often more, species are present inside the zeolite pore structure. A number of studies have indicated that mixture separation selectivities could not be predicted from the permeances of single components alone since competitive adsorption, pore mouth blocking and/or single file diffusion may govern the molecular transport through the zeolite channels (fig 2.8.) [179, 186-188]. However despite its practical importance, mixture transport through zeolites and zeolite membranes has only recently received more substantial attention. This can be contributed to the difficulty of experimentation with mixtures as well as the exponential increase in complexity of simulations with an increasing number of components.

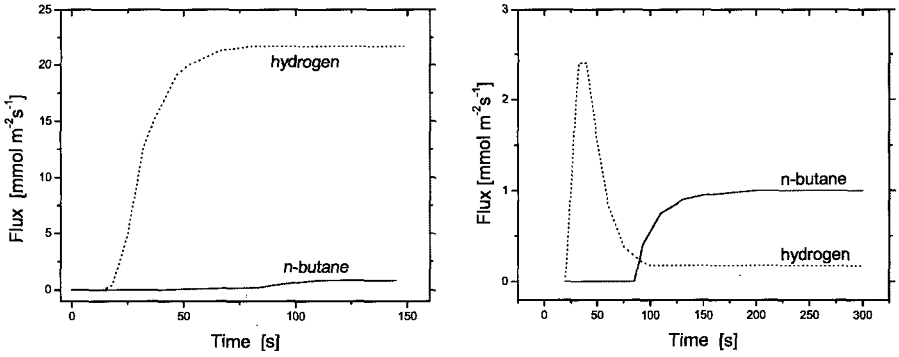


Figure 2.8: Breakthrough curves of the (a) single components hydrogen and n-butane and a hydrogen/n-butane mixture (95 kPa/5 kPa, T = 295 K) indicating the difference in fluxes of components in single component and mixture permeation [179, 186].

Currently two classes of experiments to measure intracrystalline diffusion through zeolites can be distinguished; macroscopic techniques, or visible uptake measurements [gravimetry, volumetry, Fourier transform infrared (FTIR) spectroscopy], including the frequency response technique and zero-length-column chromatography and secondly microscopic techniques such as Pulsed Field Gradient NMR (PFG NMR) [189, 190]and Quasi Electron Neutron Scattering (QENS)[191]. Unlike macroscopic techniques, the microscopic techniques take place under equilibrium conditions. The difference in diffusivities obtained by these two classes of techniques has sparked further development of experimental techniques to measure diffusion such as the fast pulse technique for the simultaneous determination of both the pore diffusion coefficients in, and the rate constants for adsorption and desorption at zeolitic materials reported by Nijhuis *et al.* [192]; Schumacher *et al.* [193] reported Tracer-Exchange experiments with Positron Emission Profiling (TEX–PEP) which allowed the measurement of self-diffusion coefficients of adsorbates in zeolites on a macroscopic time-scale and at elevated temperature; while Zhu *et al.* [194] used the novel tapered element oscillating microbalance (TEOM) technique to determine the intracrystalline diffusivities of n-hexane, 2-methylpentane, 3-methylpentane and 2,3-dimethylpentane in silicalyte-1 and obtained good agreement with ZLC results.

A number of simulation techniques have been used and sometimes combined to describe mixture transport through zeolites and zeolite membranes such as Monte-Carlo [195], Molecular dynamics (MD), Transition-State Theory (TST), Fick and Onsager formulations and the Maxwell-Stefan model to name a few. Among these it is generally accepted that the Generalized Maxwell-Stefan formulation offers the most convenient and the nearest quantitative prediction of multicomponent diffusion through zeolite membranes [61, 182]. This model is based on the principle that frictional interactions (characterized by Maxwell-

Stefan diffusivities) experienced between different molecules in a mixture as well as with a solid matrix, balances the driving force (often the chemical potential gradient in the case of membranes) exerted on each molecule and gives rise to the different velocities of molecules. The strength of this model lies in the fact that it intrinsically encompasses intra-crystalline diffusion phenomena as well as sorption processes, allowing it to predict multicomponent diffusion based on pure component Maxwell-Stefan diffusivities and mixture adsorption isotherms. Configurational-bias Monte-Carlo (CBMC) simulations demonstrated that due to the inefficient packing of higher branched alkanes and aromatic molecules, their saturation loadings will be lower than that of linear short alkanes and these molecules might even be expelled from the zeolite, as a result of configurational entropy effects [196]. Adsorption isotherms of mixtures consisting of components with widely different saturation loadings would therefore show an inflection, which is not described by multicomponent Langmuir isotherms in a thermodynamically consistent way. Kapteijn *et al.* [197] extended the Generelized Maxwell Stefan equations for multi-component diffusion to also account for molecules with different saturation loadings by using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz [198] which shows good agreement with adsorption isotherms predicted from CBMC simulations [199]. Krishna *et al.* [200] made use of CBMC simulations to develop the required mixture isotherms and followed the approach of Kapteijn *et al.* [197] using the Maxwell-Stefan theory for describing hydrocarbon mixture diffusion across a silicalite-1 membrane. Both authors emphasized the influence of mixture non-ideality effects on separation selectivities and recommended the use of the IAST in the Maxwell-Stefan formulation in order to account for size and configurational entropy effects.

2.4 Catalytic activity of zeolites in membrane reactors.

The high internal surface area of zeolites, coupled with the ability to control the number and strength of acid sites and shape and size selective effects, allow the application of zeolites as versatile heterogeneous catalysts and catalyst supports. The intrinsic catalytic activity of zeolites coupled with the possibility to tune adsorptive properties makes them good candidates for bringing about simultaneous reaction and separation. The symbiosis that exists between the catalyst and membrane in the membrane reactor however also limits the degrees of freedom of both the membrane and the catalyst. Besides an appropriate membrane, membrane reactors will therefore also require the design of a customized catalyst, owing to the different conditions that catalysts are exposed to in membrane reactors compared to conventional reactors.

One of the main aspects that received attention is the correlation of the membrane throughput with the catalyst activity. Van Dyk *et al.* [201] did a comparative study of the dehydrogenation of isobutane in an extractor-type CMR fitted firstly with a MFI membrane and secondly with a Pd-membrane, which showed superior performance compared to the zeolite membrane, and found that the reactor performance was in fact limited by the catalyst. The authors concluded that in order to draw the full benefit of the separation-reaction synergism, very active catalysts that were able to comply with the high extraction ability of the membrane had to be developed. Also Miachon *et al.* [202] highlighted that although a catalyst could be active enough to achieve equilibrium in a conventional reactor this was not necessarily the case in an extractor type membrane reactor. Membrane reactors might also require catalysts with improved stability. Such is the case for catalysts used for dehydrogenation reactions in an extractor-type membrane reactor, where selective hydrogen removal might in fact promote coke formation due to a decrease in the H/C ratio and result in a decrease in catalytic activity. Larachi *et al.* [203] for instance reported that an increase in conversion during methane aromatization due to hydrogen removal from the reaction zone was offset by a drop-off ascribed to a carbon build-up on catalytic active sites. The authors were however able to regenerate the catalytic sites by an interruption in permeation with either autogeneous hydrogen or an external source of hydrogen to reduce the deposited carbon.

The presence of a membrane however does not always adversely affect the catalyst function. It could also protect the catalyst from poisons and increase selectivity by suppressing undesirable side reactions from taking place. Lai *et al.* [204] reported one such case when they investigated the Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate to produce ethyl 2-cyano-3-phenylacrylate. Here, the presence of a ZSM-5 membrane in a PBMR and microreactor enabled the continuous and selective removal of water during the reaction, protecting the Cesium-exchanged NaX faujasite catalyst from deactivation by the water which is formed as byproduct during the reaction. Espinoza *et al.* [205] applied the same principle to the Fischer-Tropsch process, protecting the cobalt and iron-based catalysts from deactivation by water produced during the reaction. An increase in the contact time or effective reactor volume due to product extraction from the reactive zone and a resultant improvement in conversion and yield could also be affected by the presence of a membrane. The dimerization of *i*-butene into branched octenes not only produces *i*-octenes, but also undesired C_{12} or even C_{16} species. Piera *et al.*[19] reported that by removing the C_8 intermediate product from the reaction environment through a silicalite-1 membrane further reaction to give undesired C_{12} and C_{16} compounds was prevented, and an increased residence time of the reactants effected, consequently, increasing both the *i*-butene conversion and *i*-octene reaction selectivity considerably with respect to a conventional FBR.

Although inert membranes simply function as a distributor of reactants or a separator of products, inorganic membranes with catalytic activity are able to simultaneously function as a distributor, a separator and a catalytic reactor. The benefit most often reported by authors is the improved selectivity and resistance to deactivation of catalytic membranes as compared to the same catalyst, employed in a packed bed configuration. In a study by Yeung *et al.* [82]

the effect of catalyst location in membrane reactors was investigated. The authors demonstrated that for a PBMR, a CMR and a fixed bed reactor (FBR), for a first-order reversible reaction, a non-uniform distribution of catalyst, located on the feed/external side in either the membrane (CMR) or the pellet (PBMR and FBR) gave superior performance compared to uniformly distributed catalyst. In addition it was found that the performance of the CMR and PBMR was identical when the catalyst location is at the feed side of the membrane (for the CMR) or at the external surface of the pellet (for the PBMR), due to the absence of mass transfer resistance. These two membrane configurations exceeded the performance of the FBR configuration over the full range of residence times.

Santamaria and coworkers [206] also compared three reactor configurations for the catalytic esterification of ethanol with acetic acid, loaded with the same amount of catalyst, namely: (i) packed bed reactor, with the H-ZSM-5 catalyst packed as powder inside an impervious tube. (ii) packed bed membrane reactor (PBMR), with the H-ZSM-5 catalyst packed as powder inside a tubular Na-ZSM-5 membrane which acted as an extractor of product(iii) a catalytic membrane reactor (CMR), where there was no catalyst other than the H-ZSM-5 membrane itself resulting in the efficient integration of product extraction and reaction. As a result the conversion obtained at the same feed rate and catalyst loading was greater than in conventional fixed bed reactors, or even in reactors where the zeolite membrane was kept separated from the catalyst.

When Liu *et al.*[52] applied a La_2NiO_4/NaA zeolite composite membrane to CH_4/CO_2 reforming, the conversions of CH_4 and CO_2 in a catalytic membrane reactor (CMR) were remarkably higher than those over a fixed-bed reactor, while coke deposition was lower. Here the membrane also acted as an extractor of the products CO and H_2 resulting in a decrease of carbon deposition although the separation selectivity was quite low. *Masuda et al.* [207] applied a ZSM-5 type zeolite membrane to the catalytic dehydrogenation of methanol to olefins. In this instance the membrane served as a contactor, allowing the control of the residence time of species inside the reactive zone. Optimising the reaction rate and the diffusion rate in the membrane could minimize further dehydrogenation of the olefins to aromatics. A selectivity of 80–90% for high methanol conversions of 60–98% was obtained. Torres *et al.* [208] made use of a zeolite-β membrane for the oligomerization of iso-butene, which is an acid catalysed reaction. Also in this application, the membrane didn't function as a separator, but was used as a contact medium, with which the residence time could be controlled, limiting secondary reactions and improving selectivity. Compared to a conventional fixed-bed zeolite catalyst, here too, the beta membrane reactor showed improved performance and resistance to deactivation.

The development of mesoporous molecular sieve films, such as MCM-41 and UTD-1 in the past decade has made the encapsulation of nanometer size guest compounds or clusters possible. Furthermore, the reactive hydroxyl groups on the internal surface of these mesoporous hosts could be easily modified by covalently anchoring of organometallic complexes or grafted by silane coupling agents. These mesoporous membranes expand the range of reactions that can be catalyzed by zeolite membranes and the possible applications in Membrane reactors.

2.5 Applications of zeolite membrane reactors

In the majority of zeolite-based membrane reactor applications, the zeolite membrane used, is only applied to separation and is not catalytically active. An example of this is the dehydrogenation of isobutane to isobutene reported by Dalmon and [209]. They applied a MFI zeolite membrane supported on a mesoporous alumina tube to the dehydrogenation reaction of iso-butane to isobutene with modest gains in yield; in 1999 Casanave *et al.* [210, 211] resumed their study on the dehydrogenation of isobutene this time making use of two sweeping modes: co-current and countercurrent and varying the sweep and flow rates. The lower the feed and the higher the sweep flow, the higher the conversion. High sweep flows is however economically unfavourable for industrial applications and therefore not recommended. Their studies indicated that the limiting parameter could be either the membrane or the catalyst depending on the sweeping configuration that is used. Although Dalmon and coworkers obtained a certain degree of success applying MFI membranes (10-membered oxygen ring zeolite with 0.56 nm pore diameter) to the dehydrogenation of alkanes, it seems difficult to get high enough hydrogen separation factors to make the process industrially viable. Since the zeolite membrane membranes have pore diameters larger than the sizes of the components to be separated, separation will not be based on molecular exclusion but on the combination of competitive adsorption and the different mobilities of molecules, arising from differences in molecular shape, within the zeolite pore [61, 197]. Small pore, defect-free zeolite membranes with pore sizes between the size of hydrogen (0.29 nm) and n-alkanes (0.45 nm) have yet to be developed to a satisfactory extent. Possible candidates, in addition to LTA, include the 8 membered ring zeolites such as GIS, CHA and SOD.

Van de Graaf *et al.* applied an inert stainless steel supported, silicalite-1 membrane in a packed bed membrane reactor to study the effect of selective product removal in the equilibrium limited metathesis of propene to ethene and 2-butene and of cis-2-butene to trans-2-butene [212, 213]. Depending on the operating conditions that were used, the propene conversion was 13% higher than the thermodynamic equilibrium conversion obtained in a conventional packed bed reactor. Van de Graaf *et al.* showed in their study, that when the separation selectivity of the membrane is not absolute, the performance of the membrane reactor is a balance between reactant loss and sufficient removal of the products. They compared the flux through the reactor wall (Areal Time Yield, ATY) to the productivity per unit volume (Space Time Yield, STY) for the silicalite-1 membrane reactor and found the values to be between 20 and 5000. This represents the necessary volume to area ratio of the reactor. For a cylinder this implies diameters of ~0.1-20 cm – a good perspective for the application of zeolite membranes in industrial reactors.

A zeolite membrane (mordenite or NaA zeolite) was recently employed by Santamaria and coworkers [214] to selectively remove water during the gas-phase synthsis of MTBE obtaining higher performances than in a traditional reactor. An increase of conversion in the Fischer–Tropsch process by selective water removal with a ZSM5 membrane was reported (Espinoza *et al.* [205]). In this case the reason for the conversion increase is not the shifting of an equilibrium through product removal; the presence of water decreases the reaction rate by dilution of the gases and causes deactivation of the Mordenite catalyst. Nomura *et al.* [215] selectively extracted ethanol from an ethanol fermentation broth through a silicalite membrane. A high separation factor of 218 for ethanol over water was obtained and maintained for at least 48 h.

The dimerization of isobutene in a zeolite membrane reactor, recently studied by Santamaria *et al.* [19], involved the removal of a valuable intermediate product before it reacted further in consecutive reaction networks. In this case, a considerable increase in the yield to the desired product can be obtained, provided that the membrane is sufficiently selective to the intermediate product under reaction conditions.

The ability of a membrane reactor to control the addition and mixing of reactants, and the selective removal of products, results in better material utilization, less waste and pollution, and safer operation. Zeolite membrane reactors, when applied to the oxidative dehydrogenation of alkanes, are potentially useful to (a) control the oxygen feed, thereby limiting highly exothermic, total combustion [216] and (ii) improving the contact between the reactant and the catalyst. Zeolite membranes can be used as active contactors if they are catalytically active. Immobilizing transition metal ions in zeolites by ion exchange or by incorporation into the lattice leads to stable isolated and well-defined redox active catalytic sites. Julbe *et al.* [38] compared the catalytic performance of MFI and V-MFI membrane reactors for the oxidative dehydrogenation of propane. Better conversion was obtained with the V-MFI membrane. The NCMR configuration was however, not found to improve the reactor performance compared to the conventional flow through one.

2.6 Outlook of zeolite based membrane reactors

Significant progress has been made during the last decade in the understanding of separation mechanisms of zeolite membranes and the synthesis of thin, high flux, defect-free zeolite membranes. The reproducible preparation of superior quality membranes seems to finally be within reach. As a result of the groundwork made numerous new prospective applications of zeolite membrane reactors have emerged. The end line has however not yet been crossed. More studies on the economic feasibility of zeolite membrane reactor processes, long-term stability of membranes and up-scaling are needed. A closer look at temperature profiles and control within the synthesis autoclave is necessary for large-scale membrane production, here microwave heating might be a solution to the problem although this should be further explored. Further improvements in especially cost reduction and membrane reliability should still be endeavoured to facilitate the wide introduction of zeolite-based membrane reactors into industrial practice.

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3

Membrane reactor test unit for membrane and integrated process evaluation

Abstract

The design and the construction of a membrane reactor test unit for the objected use in separation and hydroisomerization experiments in this thesis are explained in detail in this chapter.

The main focus point was to investigate the overall performance of separation and catalysis integrated in one unit. Therefore a tubular reactor concept was chosen with a membrane layer on the outside and a catalyst phase on the inside. The membrane layer, support and catalyst bed for this reaction is allowed to all be based on ceramics as hardly any reaction heat is produced which needs to be transferred.

3.1 Introduction and System description

The critical assessment of the membranes prepared in this study and more importantly, the membrane reactor concept investigated in this work, requires the analysis of membrane and catalyst performance respectively as well as overall performance of the integrated unit at various reaction conditions in a continuous flow system. In view of the above a complete gas/liquid phase membrane-reactor test unit was designed and constructed, allowing online analysis of the feed, permeate and retentate streams at different reaction conditions.

It is comprised of three basic modules: the reactor module, control module and an analytical module.

The reactor module contains an asymmetric tubular membrane filled with catalyst. Since hardly any heat, which needs to be transferred, is produced during the hydroisomerization reaction, the membrane layer, support and catalyst bed for this reaction can all be based on ceramics. Linear hydrocarbons will be continuously separated from their branched isomers with the help of a selective zeolite membrane coated on the feedside of the support (α-Al_2O_3). Depending on the selective layer, a reactant enriched stream of mainly linear alkanes or linear and monobranched alkanes, will therefore reach the catalyst where it will be isomerized. The final product consists of two streams:

- the retentate containing mainly branched isomers that have been separated by the zeolite membrane and
- isomers from the hydro-isomerization reaction unit.

During an experiment the amount of specific hydrocarbon species (n-C_6, 2,2-dimethylbutane, 2-methylbutane, hydrogen) present will be measured on the tube and shell side of the membrane reactor in order to determine diffusion and reaction conversion.

For the separation of linear and branched C_5/C_6 isomers zeolite CaA and silicalite-1 are possible membrane candidates:

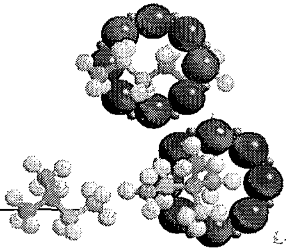
Zeolitea CaA: pore diameter of 0.46, separating the linears from the branched. The difference in molecular size of linear and iso-paraffins is the basis for separation through CaA. In theory, therefore, 100 % separation selectivity should be possible. Work done in our laboratory as well as reports in literature, however suggests that it will be extremely difficult to obtain gas separation on the principle of size exclusion. Most studies done on gas separation with zeolite A, obtained Knudsen type diffusion suggesting the presence of intercrystalline pores.

Silicalite-1: The selectivity arises from the fact that the linear molecules are preferentially adsorbed by the silicalite membrane, thus excluding the branched from permeating through the membrane.

The catalyst used in for the integrated unit investigation is a chlorinated Pt-Al_2O_3 catalyst (AT-20) supplied by Akzo Nobel. The extrudated particles consist of an active phase, platinum oxide, on a porous alumina suppor (composition 94 wt% alumina, 0.25wt% platina and 5 to 6wt% chlorine). This catalyst allows reaction at the relatively low temperature of 120°C, which yields superior membrane performance. The catalyst is however sensitive to water, necessitating moisture traps in all feeding lines.

Table 3.1: Pore/kinetic diameters of zeolites/alkanes

Species	denoted as	Diameter [nm]
Zeolite KA	3A	0.32 x 0.32
Zeolite NaA	4A	0.41 x 0.41
Zeolite Ca,Na-A	5A	0.46 x 0.46
Silicalite-1		0.56 x 0.53
n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14}		0.43
i-C_4H_{10}, i-C_5H_{12}, i-C_6H_{14}		0.50



The measurements will be done at different temperatures (25 - 120°) and pressures (1-5 bar with a pressure differential <1) in order to find optimum conditions for the integrated system.

Quantification of the hydrocarbons present in the specific process stream is done with a Gas chromatograph equipped with a Thermal Conductivity Detector (TCD) as well as a Flame Ionization Detector (FID).

Overall Specifications

Maximum operation temperature	: 120 °C
Maximum operating pressure	: 5 bar
Reactor type	: Inert membrane packed bed reactor (IMPBR), 28 mm O.D., 300 mm long
Materials of construction	: Stainless steel 316SS $^1/_8$" and ¼" tubing.

3.2 Reactor module

At the heart of the test unit is the reactor module. A schematic depiction of the reactor can be seen in Figure 3.1. The reactor consists of a tubular 316 stainless steel vessel with a 28 mm outer diameter and a total length of approximately 300 mm. Inside the reactor is a membrane (zeolite on alumina support) that is typically 10 mm in diameter and 250 mm long. The reactor module has two inlets: feed and sweep gas, and two outlets: one from the inside of the membrane and the other from the annular space around the membrane (permeate and retentate). The tubing configuration creates downward flow, i.e. in the top and out the bottom.

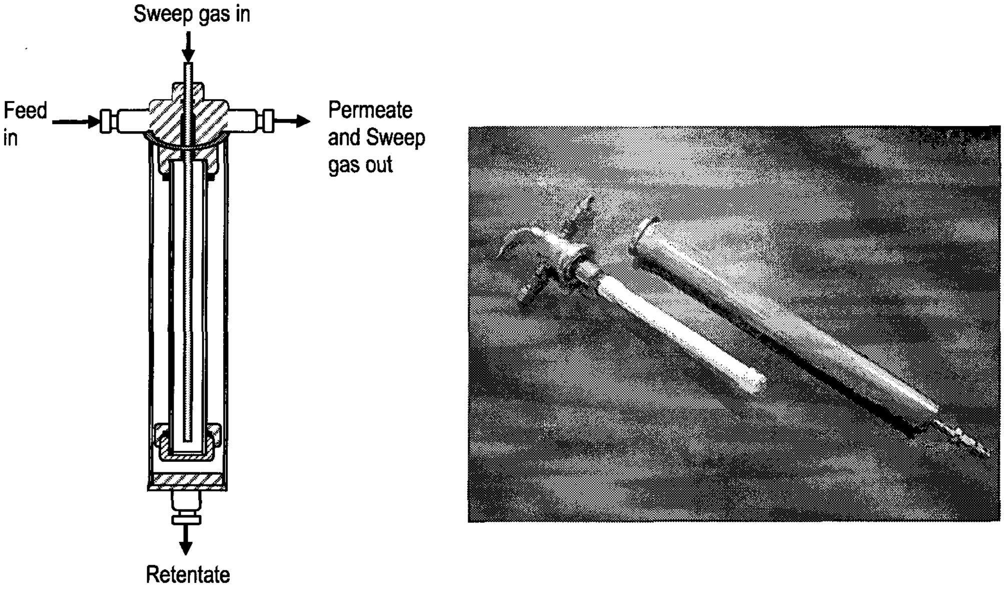


Figure 3.1: Reactor configuration

The reactor, as well as the selection and status valves, is mounted within a 34 H 49.5 W 36.5 cm oven isothermally thermostated up to 200°C. A forced convection blower provides heating for the oven. This totally heated environment will ensure that undesirable condensation is minimized, ensuring performance and reproducibility from the reactor system.

Operating conditions:

Temperature : 25°C - 120°C

Pressure in annular space around tube : 0 – 5 bar

Pressure inside tube : 0 – 5 bar

Maxim pressure differential across membrane : 1 bar

3.3 Equipment

3.3.1 Reactant stream preparation

The reactant preparation module is capable of handling up to 6 inputs. Five of these inputs are gas delivery lines while the sixth is a controlled liquid feed to the reactor provided by a HPLC pump.

Gas feed

Of the five gas feed lines, one line is used for the sweep gas (hydrogen/helium) and one is used for the purge gas (nitrogen) and another for the carrier gas (helium). The remaining two lines are used for reactant feed (n-butane and iso-butane). The five gas feed streams consists of a filter, manual stop valve, mass flow controller, reverse-flow check valve to ensure flow in one direction, solenoid valve for automatic shut-off (This safety feature provides for positive shut-off of reactants in the case of a system failsafe or upon receipt of a zero set point by a mass flow controller), and a diverter valve to direct flow away from the system if needed.

Liquid feed

The liquid feed stream consists of a filter (2 m), manual stop valve, HPLC pump, check valve to ensure flow in one direction, solenoid valve for automatic shut-off, and a diverter valve to direct flow away from the system if needed.

3.3.2 Reactor status valves

Two 8-port 2-position micro-electric actuated valves that can be manually operated or digitally controlled are included to permit reactant bypass of the reactor. The valves provide a convenient means of performing analytical sampling of the feed material and also act as an additional safety feature. When the reactor is placed in the "by-pass" position, an inert gas (nitrogen) is directed through the reactor to purge the reactor contents to a vent.

The micro-electric actuated valves are located in the oven, in order to prevent condensation within the lines.

Reactor status valve 1

This 8-port 2-position micro-electric actuated valve is used to supply the sweep gas (hydrogen) to the inside of the membrane in the tubular membrane reactor (*Position A)* or to bypass the reactor and direct the sweep gas to the GC selection valve (*Position B*) where it is either vented or sent to the GC.

The permeate gas is directed to the GC selection valve (*Position A)* to be analysed or vented or in the case of *(Position B)*, when the system is purged it would be directed to a vent.

Simultaneously it will also direct the purge gas, nitrogen, to the GC selection valve/vent (*Position A)* or in the case of *Position B* to the inside of the reactor.

Reactor status valve 2:

This 8-port 2-position micro-electric actuated valve is used to supply the Feed gas (Hydrocarbons) to the shell side of the membrane in the tubular membrane reactor (*Position A)* or to bypass the reactor and direct the hydrocarbon feed to the GC selection valve (*Position B*) where it would be either vented or sent to the GC for analysis.

Simultaneously the retentate gas will be directed to the GC selection valve (*Position A)* to be analysed or vented or in the case of *(Position B)*, when the system is purged, it is directed straight to a vent.

3.3.3 GC selection valve

This 6-port 2-position micro-electric actuated valve is used to direct the Sweep gas (Hydrgen)/Permeate to the GC (*Position B)* or to the vent (*Position A*). Simultaneously the Hydrocarbon feed/Retentate is directed to the GC (*Position A*) or to the vent (*Position B*).

3.3.4 Pressure control and measurement

Two pressure relief valves (one in the sweep gas line and one in the feed line) are installed upstream of the reactor to eliminate the risk of over pressurization. The two pressure relief valves have cracking pressures of between 0.65 and 15 bar. The pressure relief valves have been designed such that the cracking pressure is only sensitive to the upstream pressure and is not influenced by downstream pressure.

Pressure control is maintained by a spring-loaded manually controlled back pressure regulator with a pressure range of 0–34.5 bar, both on the tube-side and shell side of the membrane reactor.

Pressure measurement upstream from the backpressure regulator and downstream from the reactor is performed via a pressure transducer (Cole-Parmer) and digital indicator (able to sustain operation between 0–121°C).

3.4 Analysis

A heated $^{1}/_{8}$" SS transfer line transports the gas that has to be analysed to the sampling valve and sample loop which is located on the inside of the GC oven.

A PerkinElmer Autosystem XL with pneumatic control is used for online GC-analysis. In order to enable the separation of hydrocarbon isomers as well as H_2 and He, a combination of

Thermal Conducting Detector (TCD) and a Flame Ionisation Detector (FID) is used in series. A capillary column : 100% dimethylsiloxane, 100 m L x 0.25 mm ID is used for separation of the isomer mixture.

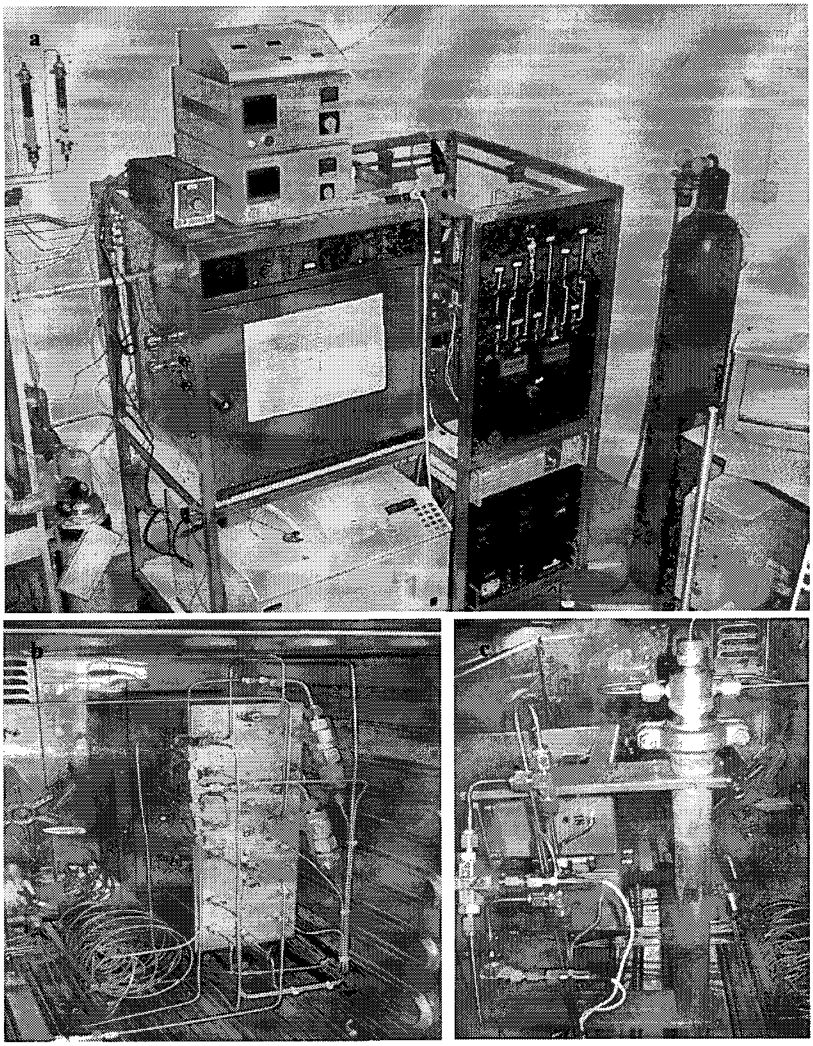


Figure 3.2: (a)Reactor set-up (b) Multi-position valves and heating coils (c) Reactor and pressure transducers

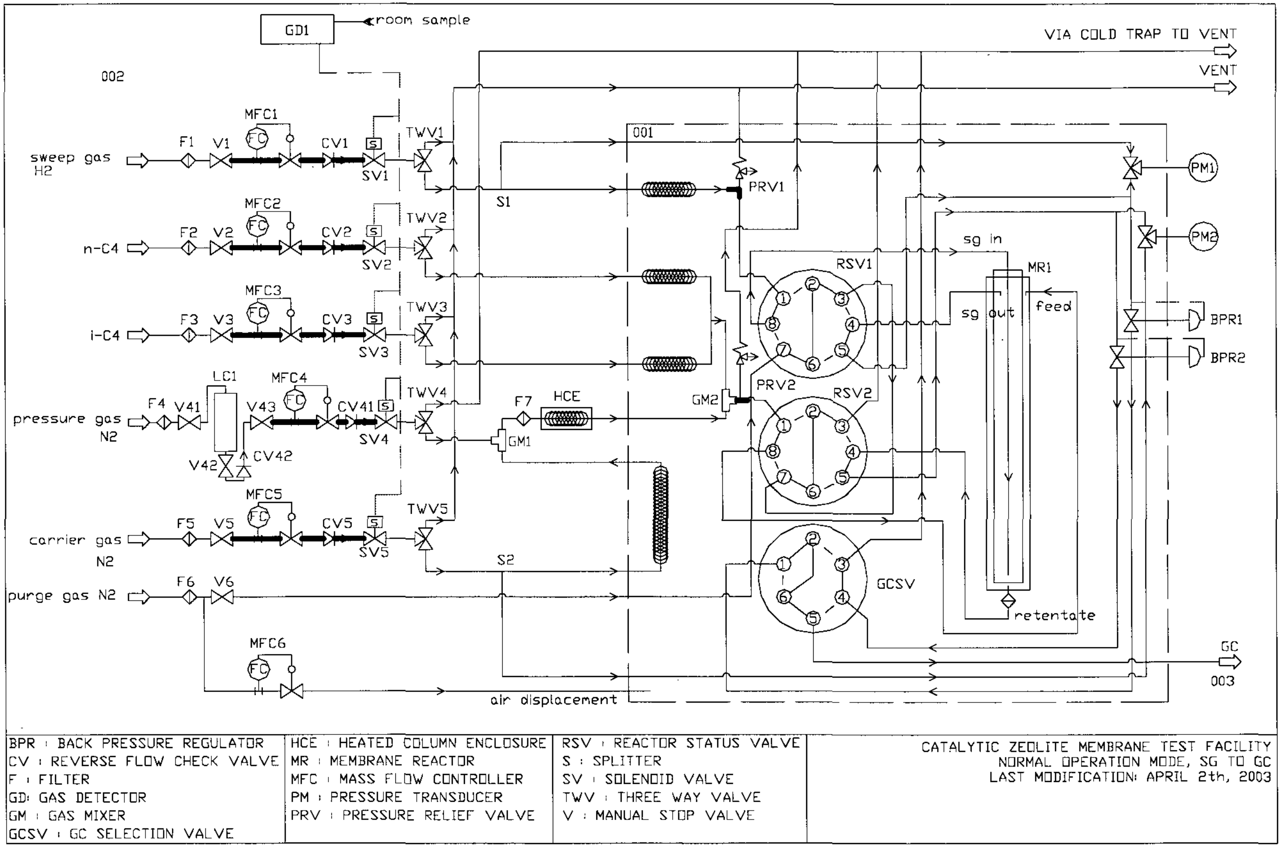
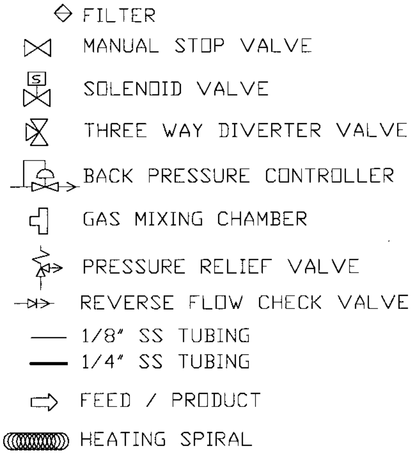


Figure 3.3: Flow scheme of reactor set-up



3.5 Permeation measurements

The driving force for permeation is a partial pressure gradient across the membrane, maintained by a sweep gas at the permeate side. From the composition and total flow it is possible to calculate the permeance and the separation factor α:

$$\alpha = \frac{(x_i / x_j)_{Permeate}}{\left(x_i / x_j\right)_{Feed}}$$

where x_i and x_j are molar fractions of the two components *i* and *j* in the mixture .

Separation of three hydrocarbon isomer mixtures were studied; *n*-/iso-butane, *n*-hexane/ 2,2-DMB and 2-MP/2,2-DMB, at various temperatures.

3.6 Sealing

A not to be underestimated challenge is the gas tight and temperature resistant sealing of the membrane modules in the setup. Torr Seal, Aremco 630 two component resin or glazed support ends in combination with Viton O-rings were used in the respective studies.

4

Amorphous v crystalline films and the effect of a mesoporous precursor layer on film orientation and morphology of MFI membranes

Abstract

The preparation of silica-based supported microporous membranes depends on nucleation and solidification/crystal growth rates, i.e. both should be as high as possible. Most important for the membrane phase is its continuity, which is easily achieved for amorphous materials and extremely difficult to accomplish for crystalline materials. This paper outlines how, in a combination of steps, an amorphous phase can be converted into a crystalline phase, providing membrane continuity as well as unique pore size distribution and high stability

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4.1 Introduction

Siliceous microporous membranes are based on one of the most versatile inorganic building blocks, i.e. silica tetrahedral units, and are comprised of amorphous and crystalline materials, which are both typically created by hydrolysis/condensation, sol-gel and solidification or crystallization processes. On the one hand, amorphous materials, characterized by a moderately narrow pore size distribution as well as modest (hydro)thermal stability, offer the possibility to produce in a facile way, thin as well as defect-free membranes.

On the other hand, zeolites allow the precise control of the pore size, offer high stability as well as high specific surface areas and are, therefore, also promising candidates for the preparation of inorganic membranes. Applications of zeolite membranes in industry in, e.g., gas separation has, however, been limited mainly because of difficulties in producing ultra-thin, defect-free (composite) zeolite membranes on a large scale. The most successful case to date is given by pervaporation units comprising zeolite membranes for the industrial separation of alcohol from water.

The more recently developed three-dimensional mesoporous material, denoted as TUD-1, synthesized from triethanolamine/silica solutions, exhibits properties somewhat in between those of crystalline and amorphous materials. During the course of membrane syntheses, TUD-1 materials have been shown to be a promising bridging phase between a macroporous support and a microporous top layer. In addition, such a mesoporous layer can be used as a precursor-building phase for zeolites, thus being converted completely into a continuous microporous phase, *vide infra.*

The synthesis and mechanism of formation of supported amorphous and crystalline ceramic membranes differs distinctly. In general, heterogeneous nucleation rates are higher for the building species of the amorphous phase than for the different types of building units and ions in the crystalline phases. Consequently, the solidifying rate of amorphous material is typically orders of magnitude higher than that of the corresponding crystalline material. Upon preparing an amorphous layer by, e.g. dip-coating, the thickness of the entrained layer and the evaporation rate establish the time-scale of the film formation, which is typically around several seconds. This relatively short time scale for film formation means that the time available for reacting species to rearranging into thermodynamically stable configurations is limited and that film formation is, therefore, often a more kinetically rather than a thermodynamically controlled process. In contrast, the crystallization process of zeolites is more thermodynamically controlled as it can be described as reactive precipitation, requiring more time for the rearrangement of the different building units from solution and gel into a typical zeolite structure.

Well-known theoretical concepts provide unique opportunities to develop synthetic procedures for coatings. Fundamentals on coating formation for both crystalline and amorphous materials are based on theories of nucleation, crystal growth/solidification and the well-established views on island-and layer-growth.

In a recently developed method of converting a continuous mesoporous coating prepared from dipcoating into a continuous microporous film, the above arguments were also taken into account. However, in contrast to the island growth, the Ostwald rule of successive phase transformation was more applicable to describe the growth phenomena. The advantages of both amorphous and crystalline layer growth methods are discussed in terms of high nucleation rates and crystal growth rates, vide infra.

4.2 Amorphous microporous ceramics

An amorphous silica film is commonly prepared with tetraethylorthosilicate, TEOS, as silica source [1-3]. The silica sol is applied to a macroporous support by dip-coating or spin-coating at a relatively low temperature. At elevated temperatures the liquid film, provided that the temperature is constant over the film during phase transitions, is homogeneously converted into a gel phase. After gelation, the amorphous silica layer on the support is by no means a stagnant, dry system. A wide variety of chemical and physical changes still takes place, such as (i) polymerization, increasing the connectivity of the gel network, (ii) syneresis, resulting in a reduction of the solid/liquid surface areas, and (iii) coarsening and phase separation. It is envisaged that in the coated layer on the support an equilibrium exists between the monomeric/ oligomeric species and the gel network. Monomeric silica species can be released from the gel via hydrolysis reactions to form $Si(OH)_3O^-$ and $Si(OH)_2O_2^{2-}$ that will in turn preferentially react with OH^- groups on the support in order to decrease the interfacial energy [4]. This process leads to the formation of a homogeneous amorphous layer on the support, which exhibits an increasing degree of order with time/ aging.

In this way a relatively thin and continuous amorphous silica layer can be achieved, since the gel network has the ability to ''bridge'' the alumina support surface macropore openings (diameter ca. 2.5 nm). The thickness of the coating applied can be as small as 30 nm [5]. It has been well-established that the thinner the silica layer, the fewer the chances of crack development, since strong interactions of the silica layer with the support prevent lattice relaxation in the plane of the coating.

In sol-gel-derived oxides, neither the oxide framework nor the pore structure is ordered, whereas the surface of the support tubes is often composed of sintered α-alumina. In contrast to crystalline coatings like zeolites, amorphous phases like silica can accommodate such a lattice on an atom-length-scale. Based on the high concentration of silica on the support (close to smelt or even solid) and the fact that there is no need of other building blocks (as would be the case for zeolite coatings), extremely high condensation rates and continuous phases can be achieved. Mesoporous oxide sieves resemble sol-gel-derived oxides in that they have non-crystalline, amorphous oxide frameworks, but differ in that their mesopores are uniform and ordered. TUD-1 is a recently reported siliceous mesoporous material, which can be prepared using triethanolamine (TEA) as an organic template. During hydrolysis and condensation reactions of the silica species the TEA is forced into meso-sized aggregates that templates the mesopores. The pore size distribution could be manipulated by varying the temperature and time of heating, similar to microporous amorphous sieves [6]. Although these ordered mesoporous materials have less hydrothermal stability than zeolites, they offer tailorability of their pore size as well as easier processability. In short, structured mesoporous materials provide a promising way of combining the best properties of amorphous and crystalline materials.

4.3 Crystalline microporous ceramics

TEOS, a frequently applied silica source for the preparation of crystalline material like zeolites, together with a template, e.g. tetrapropylammonium-ions (TPA) can be used to synthesize MFI-type zeolites. Typically a macroporous support is coated with a synthesis liquid/gel comprising at least TEOS and an aqueous TPA solution both mixed at a molecular level. At elevated temperature, phase transitions occur, ultimately leading to the formation of a supported zeolite membrane. In contrast to the amorphous silica phase, the crystalline silicalite layer is formed via a complicated mechanism in which a nucleation step and a crystallization step can be identified. The relationship between relevant parameters determining the heterogeneous nucleation rate is given in equation (1). Variables such as (i) supersaturation, (ii) number of potential sites (OH, see table 4.1) for nucleation on the support surface as well as (iii) interfacial energy and (iv) building unit volume, regarding a distribution of silica species from monomers to polymers, play a relevant role in the quality of the zeolite layer formed.

Table 4.1: Currently applied supports in porous ceramic membranes

Material	Surface area [m^2/g]	Stability at high pH and Temperature	OH-groups [n/nm^2]	Ref.
α-alumina[b]	<1	++	<1	[7-9]
γ-alumina	>10	--	11 – 14.5	[10]
quartz	<1	+	4.6	[11]
Cr_2O_3 on stainless steel	<1	+	10.0	
rutile (TiO_2)	<1	++	10.4	[12, 13]
Fe_2O_3/FeO(OH)	<1	±	9.0	[14]
ZrO_2	>10	+	9.8	[15, 16]

[a] + stable; ± some stability (time and surface area dependent dissolution); - unstable

[b] supports of α-alumina are usually fired at temperatures above 1200 °C. Terminal OH-groups can be re-established upon boiling in 0.5 m NaOH. The material is now hydrophilic and contains more than 9 OH/nm^2[17].

In particular, the interfacial energy and building unit volume have a strong contribution to the nucleation rate. There exists interdependency between the number of OH-groups, the interfacial tension at the solid/liquid surface and the wettability of the support. Even under optimized conditions the heterogeneous nucleation rate of crystalline material, when compared to amorphous material, is relatively low. This results in the distance between nuclei on the support being much larger than the distance between potential nucleation sites on the support, or the distance between nuclei of amorphous material. The types of building blocks are an important parameter. The smaller the block, the higher not only the intrinsic concentration in solution, but also the diffusion rate as well as the nucleation rate. However, there are several views on the type of building blocks for the zeolite reactive precipitation mechanism. Next to monomeric species, so-called secondary building units (SBU's) even polyhedralike sodalite cages are suggested [18-20]. A schematic view of the complexity of zeolite building blocks that might precipitate on support is given in figure 4.1.

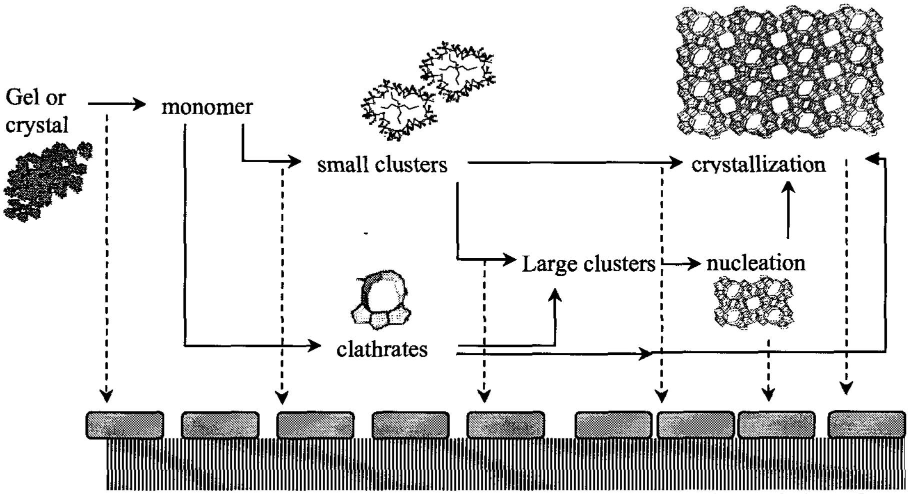

Figure 4.1: Representation of building units and successive steps in the evolution of a crystalline zeolite membrane.

The zeolite layer can be grown over 2.0 nm pores on a silica mesoporous supported coating or on an a alumina support containing pores of 20 nm. Depending on the crystal size the layer thickness is typically ~0.2 – 1 µm. Plate shaped crystals, lying flat on the support with their pores perpendicular to the support surface would therefore be ideal, if the plate thickness is in the order of tens of nanometers. In this case the plate length and width are in the order of hundreds of nanometers, typically 0.1-0.2 µm. This should be at least the distance of the nuclei on the support. Apart from MFI and ferrierite, which can be crystallized close to a plate shape, most zeolite frameworks do not grow in such ideal plate shapes. In a more frequently observed isotropic form, like zeolite A and faujasite, it is clear that a continuous layer with a thickness of tens of nanometers could only be achieved with crystal sizes of the same order of magnitude. The nucleation rate must then be extremely high to achieve closest packing of crystallites and optimal film formation.

$$J = n_0 \cdot f^* \cdot Z \cdot e^{\frac{-\beta \cdot V_m^2 \cdot \sigma_{eff}^3}{\Delta\mu^2}} \tag{4.1}$$

where

J = nucleation rate (number of nuclei/s)

n_0 = number of active sites (kinks, steps) per surface area

f^* = attachment frequency of atoms on surface

Z = Zeldovich factor (constant)
β = form factor (related to form of nucleus)
V_m = volume of one atom, molecule or building unit
σ_{eff} = effective interfacial tension
$\Delta\mu$ = supersaturation

As mentioned earlier, a dominant factor for the nucleation rate on the support surface is the interfacial energy. The interfacial tension is largest when the liquid phase has no interaction with the support surface. Upon improved wettability the interfacial energy drops to the power three and, thus, a steep increase in the J value is expected. To improve the wettability of the support, the terminal groups on the support surface could be functionalised before commencement of the hydrothermal zeolite synthesis. In a previous study [21] on the preparation of a zeolite A coating, the support chosen was a titania-coated metal which was irradiated by UV-light. This increased the population of functional groups. Indeed, upon using the support surface after this treatment for zeolite synthesis, abundant zeolite A crystals (shaped in a monolithic phase as indicated in figure 4.2) appeared on the surface. This increased the population of functional groups. Indeed, upon using the support surface after this treatment for zeolite synthesis, abundant zeolite A crystals (shaped in a monolithic phase as indicated in figure 4.2) appeared on the surface.

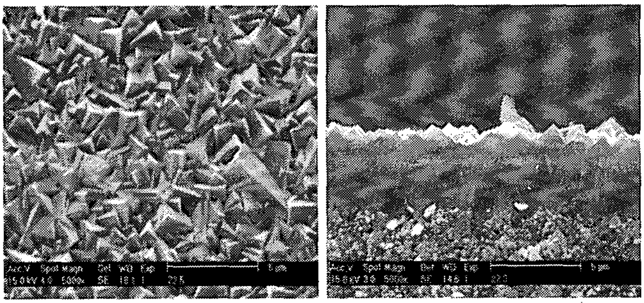

Figure 4.2: Abundant amount of crystals of zeolite type A in top view and cross-section on UV irradiated support [21].

Continuous layers of crystalline zeolite material are extremely difficult to realize. Promising SEM pictures from the top or of a cross-section of the crystalline layer are often published. However, artificial and systematic failures in the layer are frequently reported and have been well analyzed [22]. The continuity of the layer, which is rather invisible with microscopic imaging, is more reliably determined from permeation experiments, which in contrast to the microscopic observations often indicate imperfections in the microporous phase. Hurdles to overcome in the preparation of a continuous layer are, in particular, the systematic imperfections. One of the most crucial of these is the ever-occurring triangularly shaped gap between growing crystals on the support. In the frequently occurring event that three crystallites do not grow parallel to each other on the support this gap will form.

The mass of nutrient supplied to this gap will preferentially attach on the closest and fastest growing crystal faces, see figure 4.5(b), increasing the nucleation rate and, thus, decreasing the crystal size, reduces these gaps. In the same experiment it was observed that upon the highest experimentally feasible crystal growth rate, the crystallites, better defined as grains without recognizable facets[23], grew together.

In order to obtain a continuous layer of zeolite crystallites, it is important to address the well-developed theories on the preparation of continuous phases of metal oxides and silica as coatings [24].In particular, the theory of island growth of Volmer and Weber is relevant, at least as a point of departure for practical work [25]. Here it is important that a crystal growth rate from high supersaturation, almost a smelt, can be achieved which allows for crystal growth roughening, a condition needed to obtain a continuous layer. B&S growth (according to a birth and spread mechanism) and spiral growth at lower supersaturation should be avoided as crystals with well-developed facets will not grow into a continuous layer.

The dramatic changes in the crystal form as a function of the supersaturation are illustrated in figure 4.4, and are related to the growth modes shown in figure 4.3.

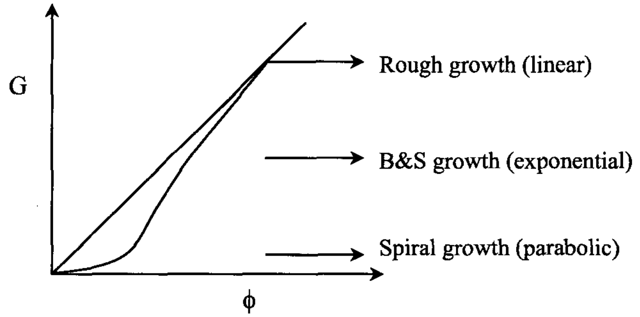

Figure 4.3: Illustrating in a schematic way the various crystal growth modes as a function of the supersaturation.

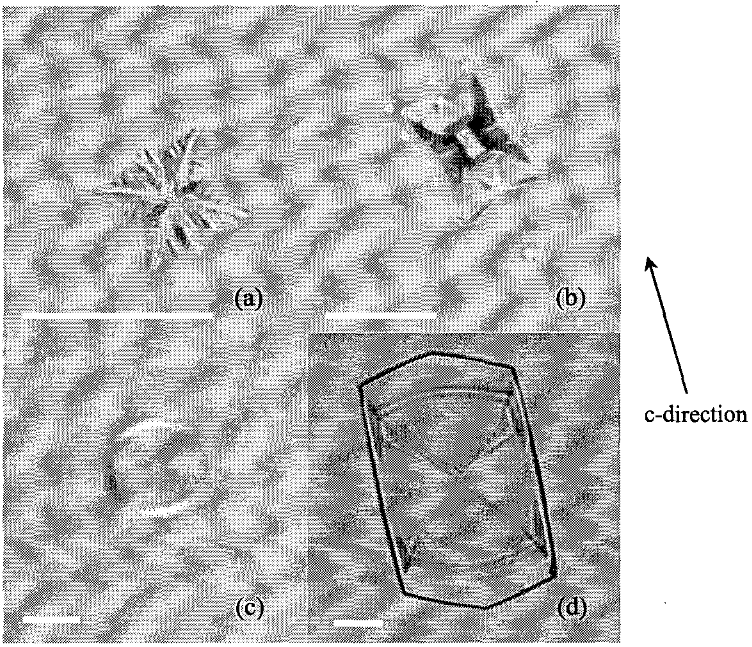

Figure 4.4: The various stages of formation of crystals of zeolite type MFI, bar = 5 μm, all crystals are oriented in the c -direction as indicated by the arrow, (a) crystal formation when a high initial supersaturation is present and (b) dendritic growth, close to smelt growth, (c) smooth curved surface, actually crystal growth roughening, in the c-direction and (d) completely faceted crystal in an almost exhausted synthesis mixture, however, the preceding growth mode (c) is observed due to poor calcination of the template.

At the early stages of the zeolite synthesis (MFI) in high supersaturation conditions, dense gel spheres without template are formed. At the interface of these gel spheres and the surrounding solution (i.e. where sufficient template molecules are adsorbed onto the dense gel phase) the supersaturation is the highest and 3-D nucleation of zeolite occurs. Small dendrites are first developed as shown in figure 4.4(a).

The smoothly curved branches of these dendrites strongly resemble those of dendrites of organic compounds grown from their smelts. It looks as if also for this case the crystal faces grow above their thermal roughening temperature. Although the density of the gel is not equal to that of the melt, it comes close to that of the zeolite phase, and the interfacial tension between the zeolite crystal and the gel could be very low just as for smelts. Enlargement of the interface for rapid release of the heat of reaction (reactive precipitation) can therefore occur at low energy costs, which causes the development of dendrites.

The surrounding gel phase is then rapidly consumed, and a liquid layer is formed around the dendrites akin to a "womb ". The interfacial tension of the crystal against the liquid phase increases to high values, and growth proceeds above the thermal roughening temperature. In fact, these species are identified as the grains/ islands necessary to obtain a continuous layer. However, the supersaturation is still very high and it is maintained by the dissolution of the surrounding meta-stable gel phase. In this liquid layer the zeolite particles change their shape into forms equivalent to those of mineral dendrites grown from a highly supersaturated solution, see figure 4.4(b). Under such conditions the sizes of the 2-D nuclei are only one or a few building blocks in diameter. Importantly, 2-D nucleation is particularly promoted at corners or edges of the crystals that protrude into the supersaturated solution. Lateral spreading of the 2-D nuclei by step propagation is not fast enough to develop faceted crystal faces. If the supersaturation is further lowered by consumption of the silica released by the gel phase, a sphere could be formed if all the crystal faces are still growing as rough faces because the supersaturation is above the kinetic roughening value for all faces. Soon, however, the crystal faces with the lowest attachment energy become faceted and the prism faces parallel to the c -axis, see figure 4.4(c). The top faces are still roughened, and therefore curved. Only when most of the gel phase is dissolved the top faces become faceted too, and the crystal shape approaches that of the final aspect ratio, see figure 4.4(d).

4.4 Various ways to prepare zeolite membrane layers

4.4.1. In situ crystallization

The support is immersed in a synthesis mixture of zeolite. In the heating ramp during synthesis, a higher temperature exists initially in the autoclave wall and the solution with respect to the support surface. Based on the reactive crystallization of the zeolite, the temperature gradient also induces crystallization in the solution, thus, exhausting the nutrient pool towards the support surface. Transport from the solution to the support surface is determined by the relatively low concentration in solution. The heterogeneous nucleation on the support, although facilitated by the wetting properties of the support, is relatively low. Typically the smallest speciation of crystal centers is ~100 nm. Because the crystal growth rate is relatively low, spiral growth is expected which results in well-developed crystal faces. Under these prevailing conditions crystals systematically pack with triangular holes, figure 4.5(a), between the crystals. This phenomenon is intrinsic to the packing of well faceted crystals, independent of their size. It is extremely difficult to close the space between the crystals as nutrient moves preferentially to the closest crystals facets and not into the triangular shaped holes, figure 4.5(b).

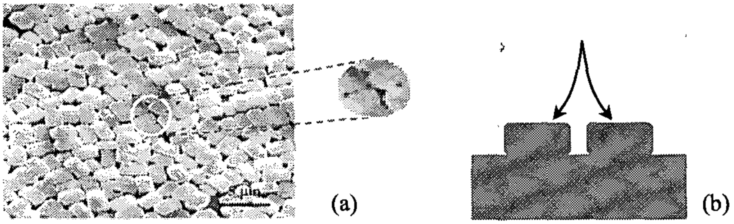

Figure 4.5: MFI crystals oriented with triangular shaped macropores. To illustrate the systematic phenomenon of the macropore shape between well-formed crystals, the crystals are deliberately presented in an unfinished membrane configuration. However, in a final stage of the membrane synthesis triangular macropores on a relatively small scale are still observed [26].

4.4.2. Seeding

Seeding is a step, which provides zeolitic material on the support surface from a slurry of crystallites with a size between 80 and 200 nm by dip-coating of the support. Subsequently the crystallite coating is anchored *via* a high temperature step. Then the coated support is immersed in a zeolite synthesis mixture. It is envisaged that the seed layer will be closed. Although a step forward compared to the *in situ* crystallization, the principle problem of closing pinholes between crystals seems to be identical.

4.4.3. Monolayered nutrient phases

Monolayered nutrient phases prepared by dip-coating, provide an amorphous silica layer on the support surface in a more continuous mode than can be found in the above mentioned techniques. The concentration of silica is extremely high and continuous over the support surface and can be used in a dissolution process with a template to prepare, in successive steps, a continuous zeolite phase. The diffusion and concentration limited transport phenomena regarding silica from solution are avoided in this case. However, the nucleation rate, although the silica concentration is high, might still be relatively low based on the concentration of the template diffusing to the surface from the solution and based on the specific interface area between the two nutrients.

An interesting approach to achieve a microporous as well as an oriented layer is the crystal growth from an extremely dense bi-layer of nutrients. By coating the support firstly with a nutrient e.g. silica (from solution, or gel), which is next immersed in a 40% template solution, a high nucleation rate can be achieved together with an oriented crystal/grain growth. As depicted schematically in figure 4.5, the nucleation occurs at the interface of the two nutrient phases. The two relatively fastest growth directions of the crystal that are parallel to the interface determine the crystallite growth. The third direction, in the case of MFI the b-direction (0 1 0), is poor in one of the two nutrients and develops only to a limited extent, giving rise to plate-shaped oriented crystals with the b -direction perpendicular to the support figure 4.6.

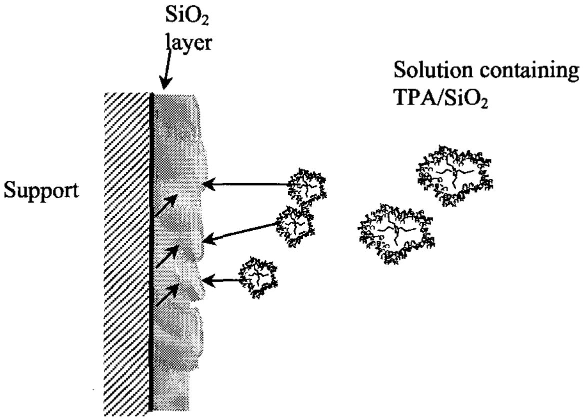

Figure 4.6: Schematic presentation of the crystallization at the interface of both reactants needed to prepare oriented crystals on the support. At the interface the fastest growing directions of the crystals grow parallel to the interface of the reactants, thus, providing the source of orientation for the individual developing crystals.

Crystal growth should proceed dominantly along the support surface induced by modification of the support. This modification refers to the type and number of potential sites on the support for nucleation as well as to the wettability. With regard to this, it has been shown that when an α-alumina support was coated with a TiO_2 layer, the TiO_2 -promoted crystallization on the support leads to the formation of a continuous ordered layer of silicalite-1. Another factor that demands careful consideration during membrane synthesis is the need for the grains to be large enough to bridge the macropores of the support. The macropores of the support must be either small, e.g. a few nm, or closed in a precursor step and activated after the zeolite crystallization. Various attempts with this concept showed the feasibility, however, always on a relatively small scale. At high supersaturations of the nutrient species, such as experienced at the interface of an amorphous silica layer and in a highly concentrated template solution, roughening of the crystal facets or grain-growth will take place. In any real physical situation, imperfections of some type are always present. At various stages during the growth process, these imperfections will cause small perturbations in the shape of the growing crystal. Under stable conditions the perturbation will decay with time and the crystal will return to a smooth shape. For unstable conditions, such as experienced at high supersaturation, the perturbations will be enhanced in amplitude; this will cause a still greater distortion and corrugated crystal facets. It is our postulate that this crystal growth, with undefined crystal facets, is necessary to achieve a pinhole-free continuous zeolite layer.

4.5 A new method to prepare microporous crystalline membrane layers

Mesoporous silica precursor layers seem to facilitate and promote the formation of a continuous layer of zeolite in the best way. A precursor phase of a mesoporous layer of TUD-1 was prepared on a tubular alumina support. Subsequently this phase was activated by calcination and then impregnated by a 25 % aqueous solution of TPA^+. This template-loaded mesoporous coating was immersed in a standard MFI synthesis solution of TPA/silica in an autoclave for a few hours at elevated temperature. After cooling and washing a continuous layer of oriented crystallites of zeolite type MFI could be observed, the first image of which is depicted in figure 4.7. The mesoporous phase had completely disappeared, in contrast to similar routes for preparation of hierarchically structured catalysts[27]. The reasons for the formation of this apparently perfect layer might be the following: To obtain a continuous layer, the nucleation and crystal growth rate must be extremely high in order to grow small crystallites with rough surfaces in such a way that they form a continuous phase. The nucleation and crystallization rate could indeed be extremely high at the support surface as this was achieved with the high concentration of silica nutrient of the solid mesoporous material with a thickness of a few micrometers. This material had a specific surface area of ~1000 m^2/g. The interface between the silica and the TPA^+ solution was, thus, high. Additionally, the pore wall being curved provides a higher degree of supersaturation of nutrient locally and, therefore, a higher nucleation rate compared to that associated with surfaces of lesser curvature. As the layer is relatively thin, the crystals orient during growth according to their aspect ratio along the largest crystal dimension, i.e. *c*-direction parallel to the support. The complete disappearance of the mesoporous phase is most probably due to Ostwald's rule of successive phase transformation. Indeed, zeolites are more stable than amorphous mesoporous materials.

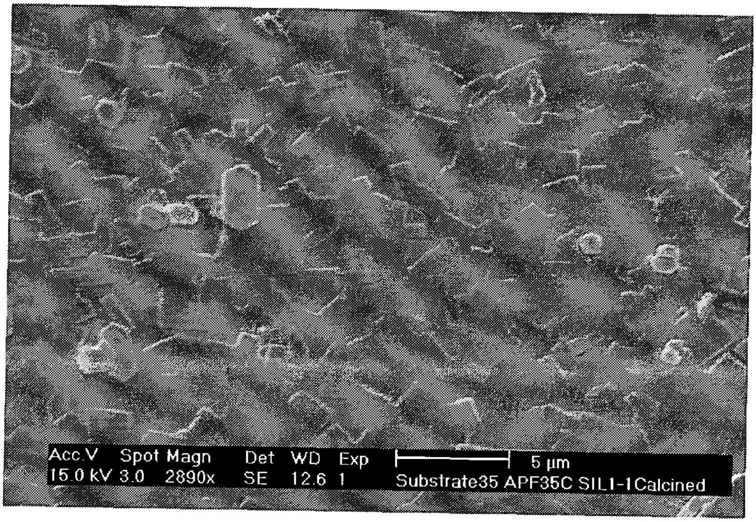

Figure 4.7: Top view of a continuous crystal layer of MFI type zeolite prepared through conversion of an activated mesopore layer impregnated with TPA^+ template at zeolite synthesis temperature. The thickness of this layer is about 1 *µm*

4.6 Conclusions

The preparation of supported silica-based microporous membranes depends mainly on nucleation rates. Crystal growth rates should be relatively high in order to achieve rough/linear crystal growth. Still under the extreme conditions mentioned, the continuity of the membrane phase, which is easy to achieve for amorphous materials is difficult to accomplish for crystalline materials. This chapter concludes that a combination of steps, i.e. an amorphous phase that is next converted into a crystalline phase, provides a new method for the synthesis of zeolite membranes characterized by continuity, a unique pore distribution and high stability.

4.7 References

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5

Oriented zeolite membrane through successive phase transformation

Abstract

A membrane of MFI-type zeolite was made from a precursor phase of the 3-D amorphous, mesoporous layer, denoted as TUD-1, on a tubular alumina support. Subsequently this phase was activated and impregnated with a 25% aqueous solution of TPA$^+$. This template-loaded mesoporous coating was immersed in a standard MFI synthesis solution of TPA/silica in an autoclave for a few hours at elevated temperature. After cooling and washing a continuous phase of oriented crystallites of zeolite type MFI was obtained. Results on *i*/*n*-butane mixture permeation and separation confirmed the performance as a silicalite-1 membrane.

The contents of this chapter have been submitted as:

McLeary, E.E., Correia, L., Friedrich, A., Sanderson, R.D., Kapteijn, F. and Jansen, J.C., *Micropor. and Mesopor. Mater.*

5.1 Introduction

Those active in membrane science would agree that the "ultimate" membrane constitutes a membrane that has a high/economically feasible permeability and can bring about the desired separation. In fact, the successful industrial application of membrane technology often hinges on this very challenge. Chemical sensors, zeolite-modified electrodes and membrane-reactor applications have been major driving forces for the development of zeolite thin films and layers. Although zeolite membranes offer considerable promise to industry on account of their unique properties, such as uniform pore size and high specific surface area as well as high thermal, chemical and structural stability, the demonstration and scaling-up of selective, high throughput zeolite films remains a somewhat elusive goal to which many research efforts have been directed. Mainly three factors determine the performance of the zeolite membrane, namely the film thickness, the continuity and the orientation of the zeolite crystals, which the film is composed of, on the support. The orientation of the crystals constituting the film determine the orientation and type of the pores perpendicular to the support through the membrane and therefore the flux properties of the film.[1]

During the past decade a number of scientific reports have been devoted to the preparation of oriented, MFI membranes, frequently oriented in the *c*-direction perpendicular to the support surface.[1-5] Xomeritakis et al. took advantage of the preferential crystal growth along the c-axis to prepare essentially 101 and *c*-oriented MFI membranes on α-Al_2O_3 disks. [3, 4, 6] However, the MFI framework consists of sinusoidal channels in the a-direction interconnected with straight channels in the *b*-direction. A tortuous path, actually comprising a- and b-channel fragments, is present along the *c*-direction. For a translation of the unit cell in the c-direction, i.e. 1.4 nm, it is thus needed to go through 2x 1.0 nm in the straight and 2x 1.1 nm in the sinusoidal channels together with 4x 90° corners. It would therefore be beneficial to align the crystals with the *a*- and/or *b*-direction perpendicular to the support in order to allow the molecules to traverse the film directly through sinusoidal and/or straight pores.

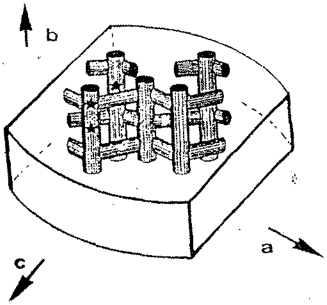


Figure 5.1: typical cubic shaped crystal form of MFI type zeolite. Orientation of the sinusoidal- and straight pore is schematically presented in the crystal drawing. Propagation of molecules through the sinusoidal- and/or straight channels is straightforward. However, any propagation in the c-direction proceeds via a detour along the a- and b-direction which is about 4 times more than a straightforward displacement of the guest in the c-direction.

When considering permeation, through the sinusoidal channel and/or the straight channel, only two weak s-curves and straight channel elements, equaling a distance, 1.4 nm are present. In that respect the majority of reports focus on a so-called secondary synthesis of oriented zeolite membranes from a *b*-oriented layer of seed crystals. In addition to the memory effect induced by the seeds oriented with the *b*-direction perpendicular to the support, the proceeding growth is expected to have some degree of preferred orientation as well. This orientation is brought about by the anisotropic growth rate exhibited by the MFI zeolite structure type, actually with the fastest growth along the c-axis and the slowest growth along the *b*-axis. Recently Lai *et al.* [1] reported the preparation of highly selective and permeable *b*-oriented MFI membranes, demonstrated by *p*-/*o*-xylene separation. These membranes were prepared by the hydrothermal growth of an oriented seed layer deposited on porous alumina disks coated first with a mesoporous silica layer. The authors prepared the *b*-oriented film making use of dimer- and trimer-TPAOH as structure directing agents in order to achieve an appropriate balance between the rates of growth in, and perpendicular to the plane of the membrane.

The numerous studies presented in literature on oriented, thin films illustrate the large number of factors and degrees of freedom that are at work in zeolite membrane growth. The substrate surface is clearly an important factor. Surface smoothness plays an important role in the formation of *b*-oriented continuous zeolite thin films. Wang et al. were for instance, able to obtain zeolite films with much improved quality on polished stainless steel substrates as opposed to unpolished substrates[7]. Another factor that in membrane synthesis is the need for the grains to be large enough to bridge the macropores of the support. The macropores of the support must therefore be either small, e.g. a few nm, or closed in a precursor step. The nutrient composition and location plays an important role as well in, for instance, determining the aspect ratio of the formed crystals which in turn has a pronounced effect on the crystal orientation and continuity of the deposited film.

Most of the reported successes pertaining to the *in situ* synthesis of oriented zeolite films have been, however, on *in situ* syntheses on non-porous supports such as silicon wafers[8] or polished metals. Wang *et al.* were able to prepare good quality b-oriented ZSM-5 coatings by *in situ* growth on stainless steel plates by manipulating synthesis composition and conditions[7, 9]. In membrane preparation, on the other hand, the substrates are porous and have a certain intrinsic roughness that cannot be eliminated by polishing, which greatly enhances the difficulty to obtain oriented, continuous films.[7] Earlier work performed suggests that mesoporous material, i.e. MCM-41, loaded with the appropriate template at adequate concentration can be partly or completely transformed into zeolite upon heating.[10]

Recently we first reported the *in situ* preparation of an oriented MFI layer on a porous tubular α-Al_2O_3 support utilizing a mesoporous TUD-1 precursor layer.[11] Applying a precursor layer of amorphous, porous silica on an alumina support to promote a zeolite membrane configuration with oriented crystals was thereafter studied in more detail taking the following arguments into consideration.

- The porous precursor layer can be used to provide a high concentration of silica on the surface of the support. Subsequently the zeolite template can be adsorbed after activation of the mesopore phase. Compared to crystallization from solution, an unprecedented high concentration of reactants for the zeolite membrane, is locally present. The stoichiometry of the amorphous phase can be easily fine-tuned for the zeolite type envisaged.
- Amorphous coatings can provide continuous (porous) precursor layers; a prerequisite for making a zeolite membrane.
- The thickness of the amorphous coating governs the zeolite membrane layer thickness since the zeolite crystal sizes are mainly determined by the amorphous coating present. Thin films, < 0.1 μm, are envisaged.
- The amorphous mesoporous precursor phase, on the relative rough surface of the macroporous alumina support forms a smooth layer which improves the prospects to prepare a continuous zeolite layer with oriented crystals and reduces stress-induced crack formation upon calcination when a thin layer is prepared.
- Comparatively an extremely large interface (specific surface area of 1000 m^2/g) is obtained between the activated mesopore material and the template for the zeolite which in turn promotes a high nucleation and crystal growth rate of the zeolite crystallites. This growth condition is mandatory to prepare a continuous film.
- Comparable densities of the mesoporous silica and the zeolite avoid the formation of cavities during the transformation of the mesopore phase to the zeolite. As a result pinhole formation upon calcinations is reduced.

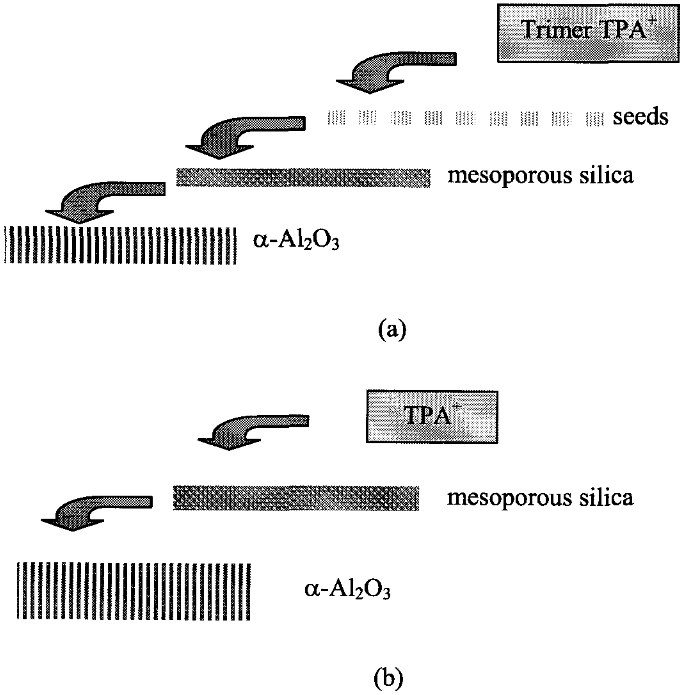
- There is no need for orientation of the mesopores as the TUD-1 precursor has a 3-D configuration.[12]
- Gradual transition between micro-, meso-, and macropores promotes permeation.
- The precursor phase acts as a barrier layer which protects the support from leaching and crystal deposition inside the macropores.[1]
- The number and type of terminal groups, i.e. SiOH, and the external as well as internal surface are most susceptible/reactive to connect zeolite building blocks.

The final observation in the efforts to make continuous oriented zeolite crystals layers is that the preparation in particular in scaling up should be economically feasible.

At present there are two avenues to prepare *b*- and/or *a*-oriented MFI zeolite type crystal films indicating membrane configurations.

(a) Extremely well prepared, continuous film based on an amorphous silica layer on alumina support that is coated with oriented seeds; actually with the *b*-direction perpendicular to the support. Subsequently the *b*-direction growth is strongly promoted with a solution containing a trimer of TPA^+, scheme 1a.

(b) The relatively simple and cheaper oriented growth by organizing an interphase of the template solution and mesoporous silica phase, scheme 1b. At the interphase the crystals grow with *a*- and/or *b*-orientation in a continuous film, *vide infra*.



Scheme 5.1: a) complicated, extremely well prepared layers of zeolite oriented with straight pores in the b-direction and b) relatively simple prepared layers of zeolite with the a- and/or b-direction.

5.2 Experimental

5.2.1. Membrane synthesis

Porous asymmetric α-Al_2O_3 tubes from ECN were used as supports. Theses tubes consist of a large-pore (3.5 μm) layer and a thin (90 μm), smooth outside coating with a mean pore size of 150 nm. The tubes have an inner diameter of 10 mm and total thickness of 3.9 mm. The synthesis procedure consisted of two steps:

First a precursor phase of a mesoporous layer of TUD-1 was deposited on the tubular alumina support via sol-gel dip-coating. In a typical synthesis of the TUD-1 sol, triethanolamine (TEA, 97%, ACROS) and deionized water were added together and thoroughly mixed for 1 hour. This was followed by the dropwise addition of tetraethylorthosilicate (TEOS, +98%, ACROS) and tetraethylammoniumhydroxide (TEAOH, 35%, Aldrich) to the continuously stirred mixture. Finally a homogeneous sol was obtained with a molar ratio of

SiO_2:TEA:0.1TEAOH:33H_2O. The dip-coating was carried out by inserting the alumina support, connected to a mechanically movable rod, in the homogeneous sol and retracting the support at an electronically controlled rate of 16 mm/min in order to achieve a final layer thickness of 1.0(3) µm after activation. Subsequently the samples were aged at room temperature for 24 h, dried at 100°C for 24 h and hydrothermally treated in Teflon-lined stainless steel autoclaves at 180 °C for 4 h. Finally the coated tubes were activated by calcination at 600°C for 10 h at a rate of 1°C/min in air.

In the second step the deposited mesoporous layer was first heated to 95°C and subsequently immersed in a 25% aqueous solution of TPA^+ at ambient temperature. It is expected that TPA^+- solution is sucked into the mesopores upon cooling. The template-loaded mesoporous-coated tubular support was vertically immersed in a MFI synthesis solution in a Teflon-lined autoclave. A MFI synthesis solution with a molar composition of 0.32TPAOH:SiO_2:165H_2O was used to avoid dissolution of the amorphous TUD-1 in the subsequent synthesis. The only hydroxyl source used in this work was tetrapropylammonium hydroxide (Chemische Fabriek Zaltbommel CFZ B.V., 20% in water) and the silica source was SiO_2 (Aerosil 200, Degussa). The synthesis solution was allowed to hydrolyze for 4h prior to hydrothermal treatment. In situ crystallization of the membrane on the support was affected at 175°C for 4 h under autogenous pressure. After crystallization the membranes were rinsed with deionized water and dried in air. Subsequently the membranes were calcined in air at 450°C for 12 h in order to remove the organic templates. Heating and cooling rates of 1°C/min were applied. A silicalite-1 layer on an uncoated support was also synthesized in-situ, making use of the same MFI synthesis solution as above i.e. of 0.32TPAOH:SiO_2:165H_2O optimized for b-oriented growth, for calibration purposes.

5.2.2. Characterization

A scanning electron microscope (SEM) Phillips XL20 was used to record images of the samples which in turn, were used to determine the crystal orientation as well as the continuity of the zeolite layer.

Powder and thin layer XRD were recorded in order to examine the crystal structures as well as the crystal orientation using Cu-$K_{\alpha 1}$ radiation on a Philips PW 1840 diffractometer equipped with a graphite monochromator. The samples were scanned over the range of 0.1–60° 2θ with steps of 0.02°.

The quality of the synthesized silicalite-1 layer was also measured with a helium-1-point test developed by ECN[13]. The helium-1-point test gives an indication of the defect density of the membrane. In this method, the He flow which is necessary to maintain a pressure differential of 3 bar, is measured. It is assumed that the pores of a microporous hydrophilic membrane will be filled with water molecules that are present in the atmosphere. Adsorption data confirm that this is the case at *P/Po* of ~ 0.1 (10% relative humidity). Therefore when a non-condensable gas such as He is fed to the membrane, the He molecules will not be able to permeate through the micropores. A microporous membrane without any defects will consequently not show any He permeance. In experiments carried out by ECN it was found that the probability for sufficient gas separation was high if per membrane length of 10 cm (14 mm diameter) the He flow is less than 100 ml/min when a pressure differential of 3 bars is maintained across the membrane.

5.2.3. Permeation

The quality of the synthesized tubular membrane of the current study was characterized by measuring the permeation of a 50:50 binary mixture of n/i-butane introduced at 100 ml/min to the tube side (retentate) of the membrane via mass flow controllers according to the Wicke-Kallenbach method. [14] Permeation experiments were performed between 30 and 150°C. Helium was used as a sweep gas on the permeate side at a flow rate of 100 ml/min in order to remove the permeating components. The pressure on both sides of the membrane was kept at atmospheric pressure (101 kPa). Feed, retentate, and permeate streams were analyzed with an online GC (Perkin-Elmer Autosystem XL, equipped with an Elite-Petro (dimethyl polysiloxane) column, 100 m, i.d. 0.25 mm and a FID as well as TCD detector).

5.3 Results and Discussion

5.3.1. Membrane morphology

In this synthesis we followed an integrated approach using a synthesis solution optimized for b-oriented growth. The SEM image shown in fig. 5.2 indicates that some degree of orientation on the porous support was obtained with the used synthesis solution in the absence of a TUD-1 precursor layer. It is, however, evident that no continuity was obtained and that the obtained layer would not give any selectivity.

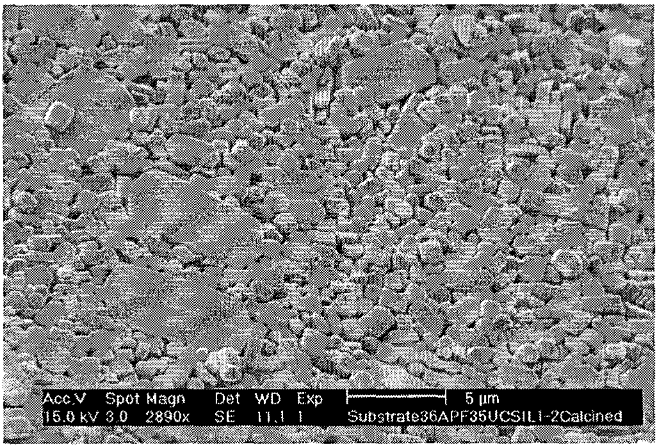


Figure 5.2: Silicalite-1 layer synthesized in-situ in the absence of a TUD-1 precursor layer.

Direct hydrothermal synthesis with the precursor approach led to *a* and/or *b*-out-of-plane oriented films since the relatively fastest growing the *c*-direction is now in-plane, and promoted by nutrient availability. The synthesis performed in the presence of a mesoporous TUD-1 precursor layer additionally also resulted in the formation of a continuous thin film (~ 1µm) of tightly packed, preferentially oriented MFI crystals that, at least within the SEM resolution, possess a high degree of intergrowth necessary for membrane applications (fig. 3). The continuity of the prepared layer was confirmed with the Helium-1-point test performed by ECN. A flow of 122.69 ml/ min He was necessary for a tube of 10 cm to maintain a pressure differential of 3 bar. This flow is close to the 100 ml/min flow of He specified by ECN for a continuous membrane, indicating a relatively high degree of continuity.

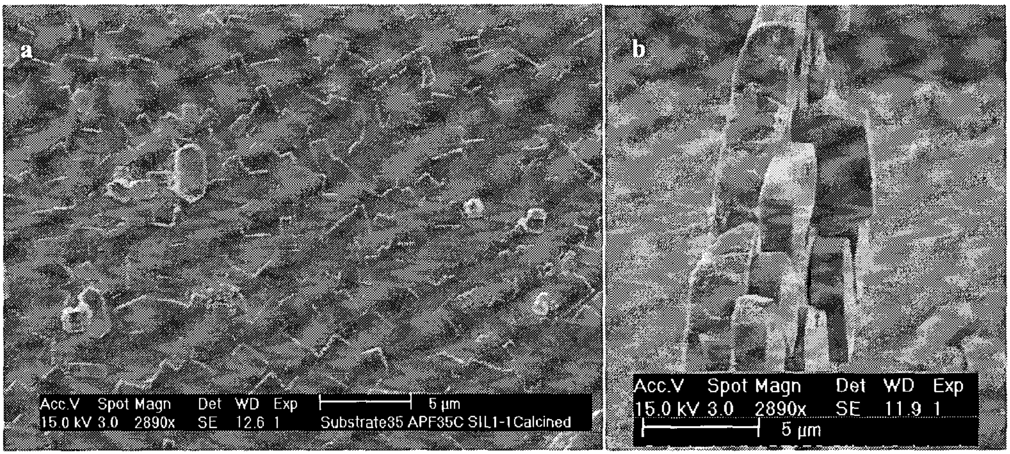


Figure 5.3: Top view (a) and cross-section (b) of a continuous crystal layer of MFI type zeolite prepared through conversion of an activated mesoporous layer impregnated with TPA$^+$ template.

The formation of this apparently continuous layer could be ascribed to an extremely high nucleation and crystal growth rate in the mesoporous layer due to (a) the presence of a high concentration of silica nutrient, formed by the solid mesoporous material, and the highly concentrated TPA^+ solution and (b) the specific surface area of ~1000 m^2/g of the mesoporous layer resulting in a large interface between the silica and the TPA^+ solution. fig.5.4 gives the XRD pattern of the deposited layer, indicating that a layer of TUD-1 was indeed formed on the α-Al_2O_3 support. The orientation of the crystals is most probably dependent on the relatively fastest zeolite growth locations and on the aspect ratio of the zeolite crystal.

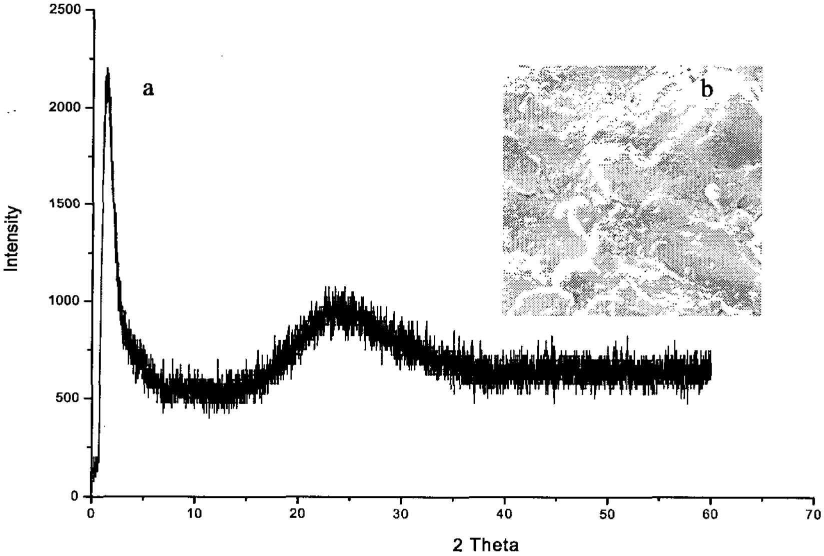


Figure 5.4: (a) XRD pattern of deposited calcined TUD-1 precursor layer and (b) 1μm thick mesoporous TUD-1 layer on α-Al_2O_3 substrate

At the interface of the solution and the external hydroxylated surface of the mesoporous layer, the highest concentration of TPA^+ is present while the highest concentration of silica is available in the mesoporous film. Nucleation occurs at the interface and subsequently crystal growth as well. In particular the *c*-direction, actually the dendritic growth direction, which is very sensitive to nutrient concentrations, is most abundantly provided with nutrient from solution and silica solid. Therefore the growth in the *c*- direction proceeds in the plane of the interface. Further orientation in the *a*- or *b*-direction is apparently influenced by equal drivers. The XRD pattern of fig. 5.6 demonstrate that the TUD layer-supported MFI membrane yields relatively intense (OkO) and (hOO) peaks. The intensity ratio of the (101) peak to that of the (020) peak in is about 0.2, which indicates that a significant amount of crystals are orientated with their *b* axis perpendicular to the substrate. The complete disappearance of the mesoporous phase is most probably due to Ostwald's rule of successive phase transformation.

A similar observation, regarding crystal orientation, was made by Koegler *et al.*[15] when they prepared an oriented layer of silicalite-1 on a silicon wafer. The authors placed a silicon wafer in a concentrated solution of TPAOH. The oxide layer at the support surface was consumed during synthesis with crystallization taking place at the support/solution interface.

5.3.2. Membrane performance

The *n*/*i*-butane mixture selectivity is generally used as a measure of membrane quality [4, 5, 16-18]. At 303 K, the mixture selectivity of a 50:50 *n*/*i*-butane mixture was 25 and dropped to 5.5 at 420 K (Fig. 5.5) with increasing temperature, a trend normally observed for this separation [19].

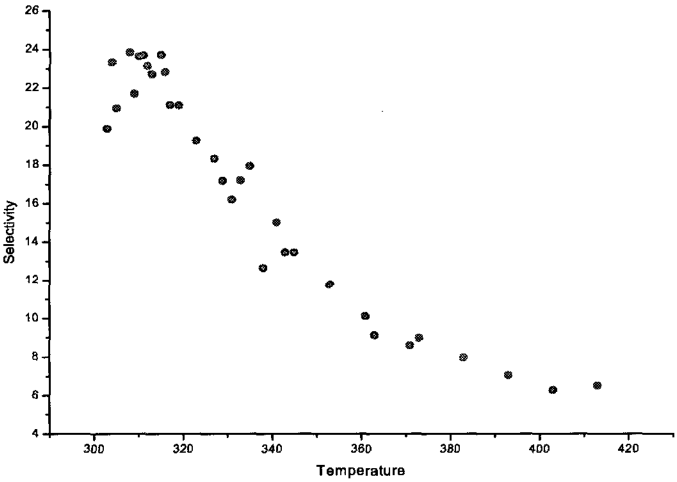


Figure 5.5: Change in selectivity as a function of temperature (K).

The flux is comparable to literature, 0.6mmol/m^2.s although a factor 2 lower. Most probably the mesopore phase is not completely converted between the zeolite and the support, resulting in an amorphous silica, indicated in fig. 5.6, thus obstructing free passage under the conditions prevailing.

The separation between *n*/*i*-butane is determined by the preferential adsorption of n-butane at the feed-side of the membrane, which at low temperatures is able to load the zeolite pores.

Combined with its faster diffusion this results in a good selectivity [20]. At higher temperatures the activated diffusion of the *i*-butane increases faster than *n*-butane, while the adsorption of the latter decreases, so there is a rapid drop in selectivity. It is therefore rather common to find in the literature MFI-type membranes that perform well at low temperatures, for this separation, but show almost no selectivity above a certain temperature.

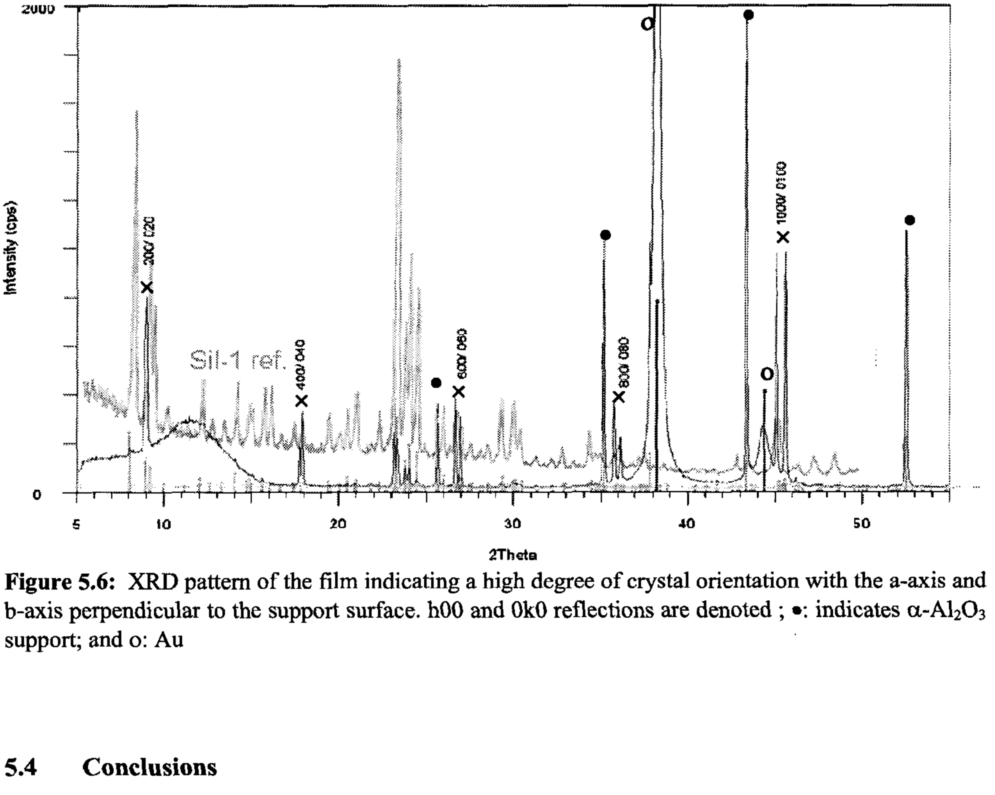


Figure 5.6: XRD pattern of the film indicating a high degree of crystal orientation with the a-axis and b-axis perpendicular to the support surface. h00 and 0k0 reflections are denoted ; •: indicates α-Al_2O_3 support; and o: Au

5.4 Conclusions

A continuous MFI membrane that is uniquely *a*-/*b*-oriented has been prepared on a porous α-Al_2O_3 substrate pre-coated with a TUD-1 precursor layer. The mesoporous precursor phase is mainly converted during the formation of the MFI-layer, most probably due to Ostwald's rule of successive phase transformation. In the separation of *n*/*i*-butane mixtures, demonstrating its integrity as a membrane, the membrane exhibited the selectivity performance characteristic for a silicalite-1 membrane.

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6

Evaluation of a zeolite membrane reactor based C_5/C_6 hydroisomerization process

Abstract

This chapter presents the conceptual design of two membrane-reactor-based processes for the hydroisomerization of C_5/C_6 (one with a recycle stream, where both normal and single branched alkanes are sent to the catalyst bed and a single-pass process which allows only normal alkanes to reach the catalyst bed) and an economic evaluation of the two processes which were compared to state-of-the-art technology. The recycle and single-pass process, delivered a product stream with a RON value of 87.9 and 87.2. An investment cost of 77.2 and 33.5 MUS$ were obtained. Membrane reactor reforming still faces an uphill battle towards commercialization. It will probably only gain wide acceptance if the membrane fluxes are improved significantly as compared with the assumptions used in this work while maintaining a high selectivity, and if furthermore the membrane costs are reduced by at least a factor 10.

The contents of this chapter have partly been based on:

McLeary, E.E., Sanderson, R.D., Luteijn, C., Buijsse, E.J.W., Gora, L., Maschmeyer, T. and Jansen, J.C., Stud. Surf. Sci. Catal., (2001), 3273-3280

6.1 Introduction

Refining is an industry that is continuously evolving in order to handle changes in both the quality and quantity of product demand. Currently the refiner is faced with increasingly stringent fuel specifications as environmentally driven regulations are enacted worldwide. The hydrocarbon composition of fuel will shift away from aromatics and olefins to hydrocarbon types such as naphthenes and paraffins that burn more cleanly.

One of the main responses of the refining research and development community to the challenges posed by environmental and market demands, is a renewed interest in paraffin hydroisomerization technology [1, 2]. The installed isomerization capacity in Europe increased from 20 000 m^3/day in 1980 to 80 000 m^3/day in 2000, representing a four-fold increase in capacity[3]. It is well recognized that the hydroisomerization of linear alkanes to their higher branched isomers provides an economic means for reducing benzene content of gasoline pools while upgrading light hydrocarbon octane values to make up for octane and feedstock lost due to benzene and MTBE reduction[1].

Not only are refiners faced with the challenge of producing environmentally friendly, high-octane gasoline but they will also find it increasingly important to reduce cost and improve productivity in order to stay competitive. These are difficult objectives to achieve in a mature industry like refining. In this context process integration has an important role to play.

This study aims to investigate the competitiveness and economic feasibility of the hydroisomerization process applicable to the C_5/C_6 cut of Naphtha, incorporating a zeolite membrane reactor. The high selectivity and high thermal and chemical stability of zeolite membranes make them extremely attractive for membrane reactor applications. Membrane based reactors have shown enormous potential in optimising the yield of desired products and reducing the overall costs. Another major advantage arising from the combination of reaction and separation is an improvement in the conversion and selectivity of the reactions.

The acid-catalyzed hydroconversion of paraffins can be described as a series of consecutive, equilibrium reactions, followed by cracking reactions as indicated by figure 6.1.

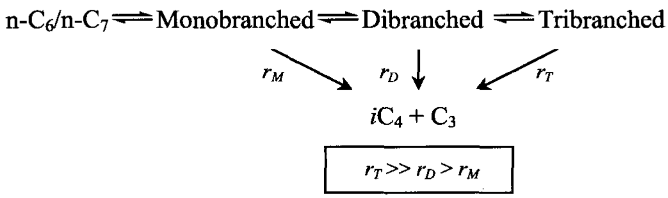


Figure 6.1: Reaction scheme for the formation of isomers and cracked products during the hydroconversion of linear hydrocarbons where r_M, r_D and r_T are the cracking reaction rates of monobranched, dibranched and tribranched isomers respectively.

The thermodynamic equilibrium distribution between the isomers for the C_5, C_6 and C_7 alkanes are represented in figure 6.1[4]. These graphs indicate that a lowering of the reaction temperature favors the formation of highly branched hydrocarbons. As a result, the octane number of the equilibrium products increases by decreasing the reaction temperature. For the C_5-C_6 hydrocarbons, this variation of the octane number is indicated in Figure 6.3. It is clear that there is a strong incentive to convert the alkanes at the lowest possible temperatures, which requires more active catalysts. Other reactions that also have to be considered, includes benzene saturation, which is highly exothermic and which is responsible for the temperature increase in the reactor, together with naphthenes ring opening which is slightly exothermic as well.

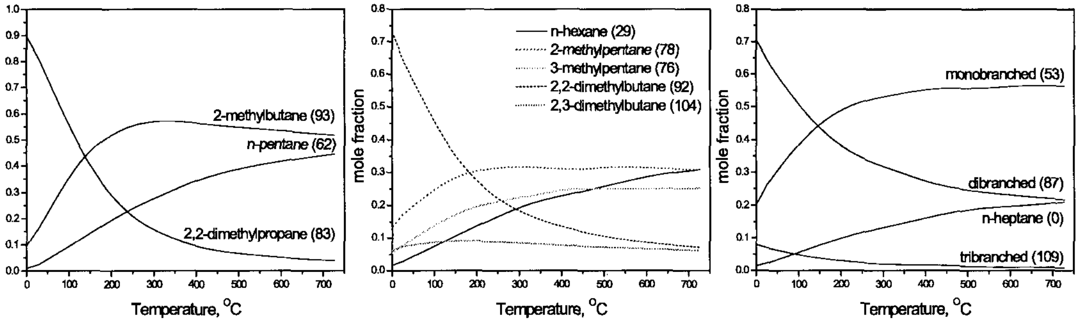


Figure 6.2: Thermodynamic distribution of C_5, C_6, and C_7 with RON values in parenthesis.

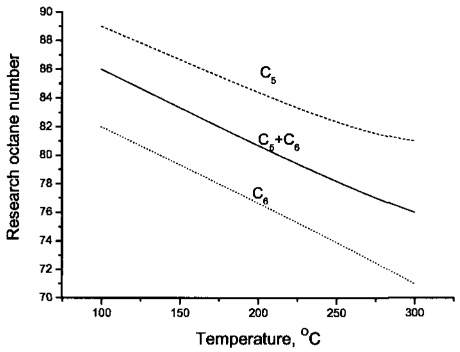


Figure 6.3: Research octane number for the C_5-C_6 equilibrium mixtures.

At present, the state-of-the-art process TIP (Total Isomerisation Process) uses two units, a reaction unit with Pt-H-Mordenite as a catalyst, and a separation unit using pellets of zeolite 5A to adsorb the linear alkanes and later desorbs them under vacuum in order to recycle them back to the feed. A zeolitic membrane reactor can achieve the same or higher conversion than the TIP-process and can be operated in a single unit and in continuous mode, which could give rise to substantial operational cost savings.

The hydroisomerization process is a good candidate process for the application of a zeolite membrane reactor mainly due to three reasons:

- The products and reactants differ in properties relevant for membrane separation.
- Furthermore, the heat of reaction, ΔH, for the hydroisomerization of C_5/C_6 paraffins is negligible, making this particular process ideally suited for execution in a single unit all-ceramic membrane reactor with possible heat transfer limitations.
- Thermodynamic constraints for the hydroisomerization reaction of linear alkanes can be surpassed by the combination of reaction and separation.

Further advantages that will be obtained by the combination of reaction and separation include:

- Reduced catalyst deactivation due to the fact that only a selected reactant stream is sent to the catalyst bed. Feed components such as benzene and naphthene which can lead to coke formation due to preferential adsorption on the catalyst and ensuing hydrogenation and cracking reactions, are separated by the membrane.
- The amount of branched and C_{7+} components that reach the catalyst bed will be limited by the membrane, decreasing the amount of cracking and the reactant space velocity which in turn has a favorable affect on process yields.

6.2 Process concept

Two process variants will be considered in the following communication:

In the first process (recycle process), a hydrocarbon feed, consisting mainly of C_5 and C_6 isomers is supplied to the tube side of a shell and tube membrane reactor. Use is made of a silicalite-1 membrane, which will separate the linear and monobranched alkanes from the dibranched alkanes (product stream). The linear and monobranched alkanes are subsequently converted to higher branched alkanes on the packed bed of Pt-H-β catalyst, located on the shell side of the tubular membrane. Pt-H-β shows an increased selectivity for higher branched products as well as good resistance against feed contaminants and allows operation at 230°C.[5] After reaction the effluent stream from the reactor (catalytic packed bed) is recycled back to the separation/catalytic unit to achieve complete hydroisomerization to dibranched paraffins. The recycle stream to the reactor is sent through a de-isopentanizer in order to remove the i-C_5 to the product stream and avoid the build-up of this species within the system.

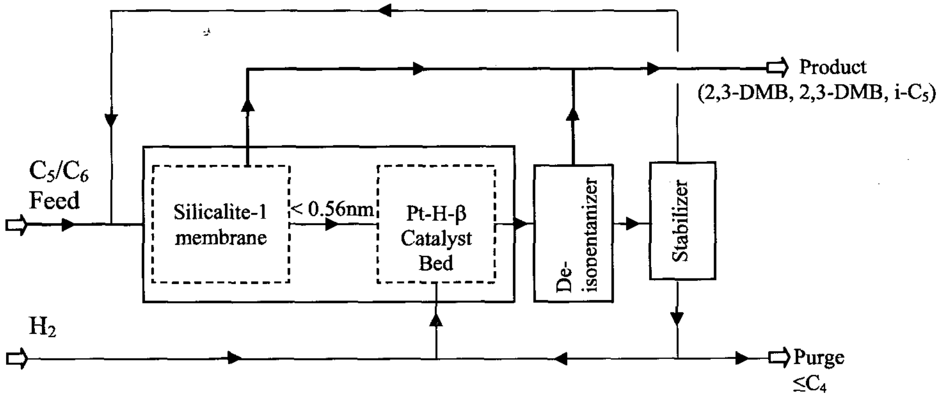


Figure 6.4: Block scheme of hydroisomerization process utilizing silicalite-1 membrane and recycle

In the second process (single-pass process), a representative feed is supplied to the shell side of a shell and tube membrane reactor. Use is made of a zeolite 5A membrane, which will separate the linear from the mono- and dibranched alkanes (product stream). The linear alkanes are subsequently converted to branched alkanes on the packed bed of AT-20 catalyst, located in the annulus of the tubular membrane (see figure 6.5). No recycle is present.

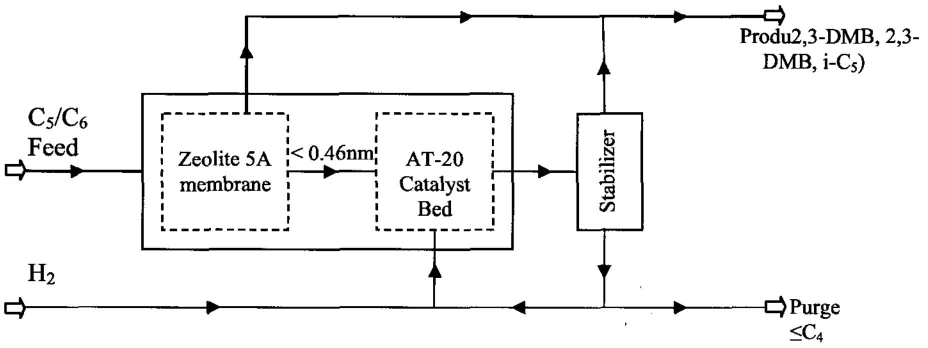


Figure 6.5: Block scheme of hydroisomerization process utilizing zeolite 5A membrane without recycle

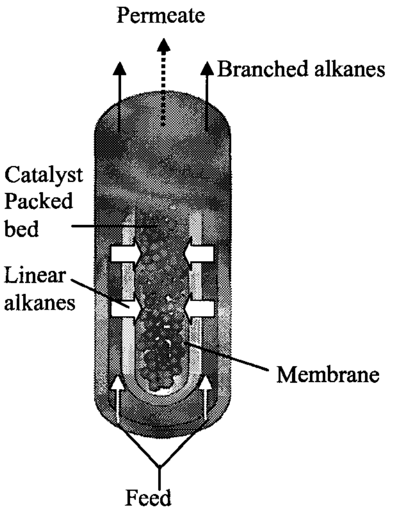


Figure 6.6: Single pass membrane reactor

The membrane reactor configuration considered in both processes for the hydroisomerization of n-C_5/n-C_6 to their higher branched isomers in a membrane reactor, is illustrated in figure 6.6. A hydrocarbon feed (consisting of linear and/or branched alkanes) is selectively supplied through an inert tubular membrane, to a packed bed of catalyst located in the core of the tubular membrane. This limits possible cracking of branched alkanes present in the feed, as well as allowing higher conversion by controlling the feed composition to the reaction. When no recycle is present, the named configuration will mainly be suited for operation at low temperatures (120°C) when the amount of linear alkanes, remaining in the product stream, is less than 6%.

For the process a catalyst is required which is sufficiently active and selective for the hydroisomerization reaction at the optimum process conditions: low hydrogen to hydrocarbon ratio at the optimum process temperatures and pressures.

The molar ratio H_2/feed prevents in an important way the deactivation of the catalyst by decreasing coke deposits. Kouwenhoven [6] ascribed the positive influence of platinum on catalyst stability and isomerization selectivity to the hydrogenation activity of platinum causing alkenes to be saturated before they can form dimers with carbenium ions, which leads to deactivation and enhanced cracking selectivity. Commercial hydroisomerization units operate at molar ratios between 2 and 6. The increase of the molar ratio requires the increase of the hydrogen recycle, which influences the economic parameters of the process. A balance therefore has to be found between decreasing the molar ratio H_2/feed and the desired hydrogen partial pressure that ensures a long catalyst life.

The catalyst should furthermore be resistant to the contaminants present in the feedstock after feedstock cleaning. Based on the activity, selectivity and sulfur resistance, two catalysts were considered in this study. The first catalyst is a chlorinated Pt/Al_2O_3 catalyst that has high activity and will allow operation at the relatively low temperature of 120-130°C, favoring thermodynamic product distribution, and requires a low hydrogen to hydrocarbon ratio. Adversely, these chlorinated Pt/Al_2O_3 processes are more difficult to operate, and are substantially more vulnerable to contaminants and catalyst deactivation.[7] The second catalyst considered is Pt-H-β which shows an increased selectivity for higher branched products, compared to for instance Pt-H-Mordenite allowing operation at 230°C but does not provide the level of catalyst activity of chlorinated Pt/Al_2O_3. However, the high temperature catalyst is much more resistant to contaminants such as sulfur and water.

Table 6.1: Concept Materials

Membrane/ Permeate	Diameter [nm]	Temperature [°C]	Catalyst	Remark
Zeolite 5A	0.46*0.46	120, 250, 230	AT-20 Pt, Pt-H-Mordenite, Pt-H-β	absolute separation
Silicalite-1	0.56*0.53	120, 250, 230	AT-20 Pt, Pt-H-Mordenite, Pt-H-β	Competitive adsorption and size exclusion
Paraffins:				
linears	0.43			
monobranched	0.50			
double branched	0.62			

The selectivity of the membrane depends on the pore size of the zeolite (molecular sieving), its adsorption properties and difference in diffusion of components. Application of a zeolite membrane can translate the selectivity properties already in use with the pressure swing adsorption / desorption steps to a real continuous process. Two types of membranes are interesting for selective separation of the molecules to be isomerised.

Zeolitea 5A: pore diameter of 0.46, separating the linears from the branched. The reactants and products of the hydroisomerization: pentane and isopentane or hexane and its mono and di-branched isomers should thus separate using a zeolite 5A membrane. The difference in molecular size of linear and iso-paraffins is the basis for separation by the zeolite 5A membrane. Linear alkanes are able to enter the zeolite 5A pore, whilst branched isomers are excluded. In theory, 100 % separation selectivity should be possible.

Silicalite-1: pore diameter of 0.56, separating the double branched from the single branched and linear molecules on the basis of size exclusion. The less branched molecules will furthermore be preferentially adsorbed in the zeolite pore, and will therefore diffuse faster and be separated from the higher branched molecules.

The characteristics of the microporous silicalite-1 and zeolite 5A membranes have been used for further evaluation of the process concepts. It is recognized that obtaining a combination of an acceptable permeability with an acceptable selectivity, remains somewhat troublesome, however vast progress has been made in the past decade in achieving this goal [8-10].

6.3 Process design considerations

Feedstock composition is a key determinant with regard to catalyst selection and process design. Catalyst contact with known isomerization poisons such as sulfur, nitrogen, and water can result in irreversible catalyst deactivation and poor product yields. Catalyst contact with heavy components with 7 or more carbon atoms or cyclics of 6 carbon atoms or more can result in adverse competitive reactions that either result in a lower octane product or in interference with the isomerization reactions by adsorption on the catalyst. The presence of benzene in the feedstock, for example, results in strong adsorption on the catalyst acid sites which interferes with normal pentane and normal hexane isomerization. The benzene itself is saturated to form cyclohexane which has a substantially lower octane value.[11] The presence of heavy components with 7 or more carbon atoms also strongly inhibits the normal pentane and normal hexane isomerization reaction and increases reaction space velocity in the process due to being substantially hydrocracked to lower value propane and butane products. While essentially inert to the isomerization reaction, the processing of lighter hydrocarbons of 4 carbon atoms or less in an isomerization unit adversely affects isomerization yields of normal pentane and normal hexane by increasing reactor space velocity (WHSV).

The feedstock used for the conceptual process designs is a representative light straight run naphtha stream obtained from Shell. Table 6.2 gives the feedstock composition.

Table 6.2: Straight Run Naphtha feed composition

Components	Symbols	Wt%	RON
<=C_4 components		3.99	>92
n-Pentane	nC_5	38.90	62
2-Methylbutane	2-MB	23.41	93
2,2-Dimethylpropane	2,2-DMPr	0.03	83
Cyclopentane	$c\text{-}C_5$	3.02	102
n-Hexane	nC_6	6.78	29
2-Methylpentane	2-MP	12.67	78
3-MethylPentane	3-MP	5.81	76
2,2-Dimethylbutane	2,2-DMB	0.68	92
2,3-Dimethylbutane	2,3-DMB	1.74	104
Benzene	$a\text{-}C_6$	0.68	120
Cyclohexane	$c\text{-}C_6$	0.04	84
Methyl-cyclopentane	$M\text{-}C_5$	0.74	96
C_7+ alkanes		0.86	0-109
Methyl-cyclohexane	$M\text{-}C_6$	0.05	75
Toluene	$a\text{-}M\text{-}C_6$	0.01	115
Straight Run Naphtha	SRN		73.51

The design concept for each process was formulated based on the following assumptions:

The feed stream to the membrane reactor hydroisomerization plant is assumed to be a 1000 ton/day. It is furthermore assumed that the plant operates continuously for 8000 hours/annum (333 days) and that hydrogen is available to the processes at a purity of 99.99% by weight. It is further assumed that the feed streams are free of contaminants such as sulfur and water

6.3.1. Reactor design

The membrane reactor in process 1 and 2 is considered as an annulus, divided into two compartments (figure 6.1):

- The inner tube (permeate side) formed by the membrane, packed with catalyst where a sweep gas is fed to, being enriched with the separated gases all the way to the outlet (permeate stream) and where the reaction takes place
- The space between the tubes (feed side) where a gas mixture (consisting of feed /and recycle in the case of the recycle process) is fed to.

The systems are designed for reactor conditions to be closer to equilibrium, thus improving conversion into the direction of product formation.

In the recycle process the concentration of reactant is maximally chosen by separating the dibranched alkanes first via the silicalite-1 membrane layer and consequently providing a pure normal and mono-branched alkane feed to the catalyst phase. The catalyst volume is comprised of a packed bed of α-alumina spheres coated with 1.5 wt% Pt-H-zeolite-β.

In the single-pass process single and double-branched alkanes are separated by the zeolite 5A membrane, consequently providing a pure linear alkane feed to the catalyst bed. Here the catalyst bed is comprised of cylindrical Pt-chlorinated Al_2O_3 particles.

The driving force for transmembrane mass transport is the partial pressure difference of the components across the membrane. To enhance the driving force and thus the separation efficiency:

- A pressure differential across the membrane is maintained,
- A sweep gas is introduced on the permeate side of the membrane to lower the partial pressure of the components on this side. Hydrogen is chosen as sweep gas, to remove the permeate since it has the dual functionality of limiting cracking whilst also taking part in the reaction.

The design and dimensions of the membrane reactors have been established by closely evaluating the necessary membrane surface area and catalyst volume.

The assumptions made for the development of the reactor models are as follows:

- The reactor operates at steady state.
- The flux along the membrane is considered to be constant. Furthermore the flux is chosen as the maximum flux achievable using the partial pressures at the inlet of the reactor and the partial pressures after reaction at the outlet of the reactor to determine Δp_i.
- Diffusion through the membrane is considered as rate limiting for the process and the factor that will govern reactor performance and size.
- Benzene as well as all the naphthenes are separated by the membrane and will therefore not reach the catalyst bed, subsequently the hydrogenation/cracking reactions undergone by these reactants as well as the ensuing catalyst deactivation will not be considered. This assumption is supported by the findings of Funke et al.[12]; although the pure components, despite their kinetic diameters do in fact permeate through silicalite-1 on account of the zeolite framework flexibility (Table 6.3 vide infra) it was found that mixtures of cyclic molecules with linear alkanes were readily separated with high selectivities (over 200 for n-hexane/benzene) due to preferential adsorption.

Table 6.3: Kinetic diameters of SRN compounds

Compound	Kinetic diameter [nm]
n-hexane	0.43
3-methylpentane	0.50
benzene	0.59
cyclohexane	0.60
methylcyclohexane	0.60
2,2-dimethylbutane	0.62

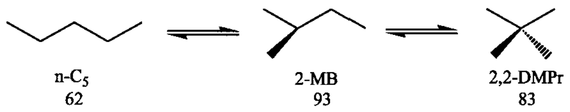
- The isomerization reactions over Pt-chlorinated Al_2O_3 at 120°C and Pt-H-β at 230°C is assumed to be sufficiently fast to reach local chemical equilibrium [5, 13-15] and conversion will therefore be transport limited. The assumed equilibrium distribution in terms of mole fraction at 120 and 230°C is listed in Table 6.4.

Table 6.4: Equilibrium distribution as a function of temperature[16]

Temp [°C]	n-C_4	i-C_4	n-C_5	i-C_5	2,2-DMPr	n-C_6	2-MP	3-MP	2,2-DMB	2,3-DMB	n-C_7	Monobranched C_7	Dibranched C_7	Tribranched C_7
120	0.30	0.70	0.11	0.64	0.25	0.08	0.28	0.15	0.40	0.09	0.04	0.28	0.60	0.08
230	0.44	0.56	0.22	0.56	0.22	0.15	0.32	0.21	0.23	0.09	0.11	0.51	0.35	0.03

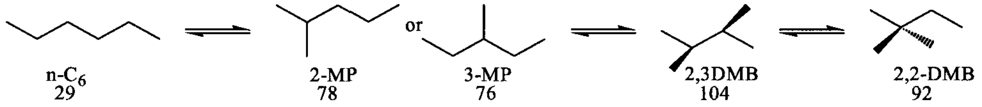
- It is assumed that the ceramic membranes will allow no heat flux across the membrane.
- Hydrocracking products for C_5-C_7 are negligible at 100-150°C whilst hydrocracking products for C_5 and C_6 are negligible at 230-250°C [4]. The rates of the secondary reactions of hydrocracking and coking decrease with lower molecular mass.[11]
- The reactor is assumed isothermal for this study – the isomerization reaction is isothermal[17-19]
- Pressure drop in the packed bed takes place according to Ergun's equation.
- The conversions obtained with 1.5 wt% Pt/H-β at 230 °C are the same as those obtained with Mordenite as catalyst at 250°C. This assumption is based on the higher catalytic activity of Pt/H-β compared to Mordenite [18, 20, 21].

The equilibrium reactions that have been considered for the reactor design, with their blending RON values, are shown below.

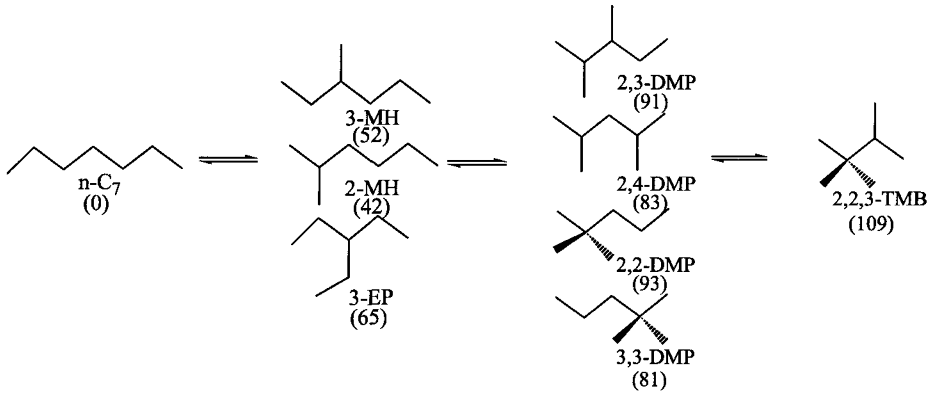


(6.1)

The isomerization of normal hexane occurs in two steps: The first step is the isomerization of normal hexane into 3-methylpentane, 2-methylpentane, and 2,3-dimethylbutane. These three components are rapidly inter-converted and are in near equilibrium with each other[13]. Formation of 2,2-dimethylbutane occurs in a second step.[22]



(6.2)



(6.3)

The cracking reactions considered are listed in table 6.5.

Table 6.5: Cracking reactions

Cracking reactions:	Conversion	Reference
1.00 2-MC_6 + 0.02 H_2 → 0.58 i-C_4 + 0.44 C_3	62.20	[23]
1.00 n-C_7 + 0.02 H_2 → 0.58 n-C_4 + 0.44 C_3	62.20	[23]
1.00 2.2-DMC_5 + 0.02 H_2 → 0.58 i-C_4 + 0.44 C_3	62.20	[23]

6.3.2. Flux through the zeolite membrane

The permeate flux is the determining parameter for the reactor design since it is considered to be the limiting factor for conversion in the reactor and is inversely proportional to the membrane area. The features of paraffin permeation through the membrane can only be described adequately with a model based on at least two contributions to overall permeation, i.e. surface diffusion and activated gaseous diffusion. Figure 6.7 gives an indication of the dependence of the flux due to activated gaseous and surface diffusion, on temperature and feed pressure

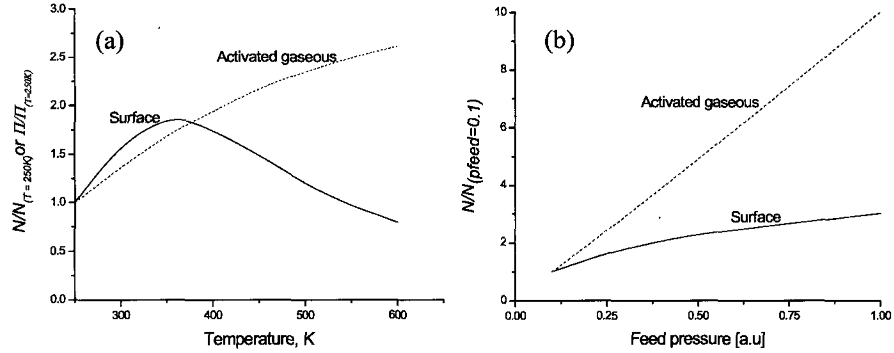


Figure 6.7: Trends in (a) the permeance and flux due to activated gaseous diffusion (Ng) and surface diffusion (Ns) as a function of temperature and (b) the flux due to activated gaseous diffusion and surface diffusion as a function of feed pressure.[24]

Recycle process:

The Straight Run Naphtha (SRN) feed to the membrane reactor is heated up to 200°C whilst the feed pressure is maintained at 25 bars. Therefore, the stream destined for membrane separation is in the vapour phase and, as indicated by figure 6.7, activated gaseous diffusion will provide the largest contribution to the flux.

The following equations were used to describe the activated gaseous diffusion of the different components through the membrane:

$$N_i^g = -\frac{1}{RT}\cdot\frac{g}{\delta}\cdot D_i^g \Delta p_i \qquad (6.4)$$

In this D_i^g is the corrected transport diffusivity and N_i^g is the flux for gaseous activated diffusion. The parameter δ is the effective thickness of the zeolite layer. The shape factor, g, includes the porosity of the support top layer and the porosity and tortuosity of the membrane. The factor $(g\cdot d)/\delta$, where d is the diffusional length for activated gaseous diffusion, has experimentally been determined with helium.[24]

Table 6.6 lists transport diffusivities (D_i^g) for the relevant components, obtained from literature as well as the corresponding calculated fluxes and required membrane areas at

200°C. Values of parameters used in the calculation of the flux, membrane area and amount of catalyst required are listed in table 6.7.

The membrane area is calculated according to:

$$\text{Area} = F_i/N_i \tag{6.5}$$

with F_i, the flow in mol/s through the membrane.

Table 6.6: Diffusivities, calculated fluxes and corresponding membrane areas for C_6 isomers

Component	Diffusivity (D_i^g) $\times 10^{-11}$ (m^2/s)	Calculated Flux $\times 10^{-4}$ ($mol/m^2\cdot s$)	Membrane area $\times 10^4$ (m^2)	Reference
n-C6	2.50	6.12	1.8	[25]
2-MP	0.50	2.03	0.82	[25]
3-MP	0.25	0.70	1.70	[25]

Table 6.7: Model parameters: Recycle process

Parameter	Units	Values & Assumptions
g		1.2
δ	m	1.00×10^{-6}
$(g\cdot d)/\delta$		2.4×10^{-2}
Δp_{tot}	bar	20
$T_{\text{feed side}}$	°C	200
$T_{\text{permeate side}}$	°C	230
Catalyst WHSV	h^{-1}	1
Catalyst particle shape		Spherical
Catalyst particle size	mm	4
Loading density	kg/m^3	1000

Since the largest surface area needed for diffusion, required by 3-MC_5 (17.0×10^3 m^2), is sufficient to allow the rest of the components to diffuse through the membrane the surface area needed for the reactor was taken as 17.0 x 10^3 m^2. This area is used in further calculations of the dimension of the reactor as well as process economic calculations. When the flux for 3-MP is calculated by substituting a permeance of 8.5 x 10^{-10} $mol/m^2\cdot s$ Pa for 3-MP reported by Flanders et al. [26] in equation 6.6 a value of 7.8×10^{-5} $mol/m^2\cdot s$ and a corresponding membrane area of 15.3×10^3 m^2 is obtained for a membrane thickness of 100μm.

$$N_i = \Pi_i \Delta p_i \tag{6.6}$$

where Π_i is the permeance of component i.

The difference in flux and corresponding area can partially be attributed to the contribution of surface diffusion to the total flux through the membrane which is neglected in the calculated flux given in table 6.5.

Single-pass process:

The Straight Run Naphtha (SRN) feed to the membrane reactor is heated up to 90°C whilst the feed pressure is maintained at 22 bars. Therefore, the stream destined for membrane separation is in the liquid phase and pervaporation through the membrane will take place. The flux due to pervaporation is calculated according to:

$$J_i = \Pi_i (x_i \gamma_i p_i^{sat} - y_i p) \tag{6.7}$$

with

J_i : flux due to pervaporation

Π_i : permeance

x_i : feed molar composition in the liquid phase

γ_i : activity coefficient of component *i* in liquid stream

y_i : permeate molar composition in the gas phase

p : pressure on permeate side

p_i^{sat} : vapour pressureof component *i* in liquid stream given by the equation of Antoine:

$$\log p_i^{sat} = A - \frac{B}{T+C} \tag{6.8}$$

Intracrystalline permeation is governed by surface diffusion as shown in figure 6.7 [24]. The permeance can therefore be calculated by:

$$\Pi_i = \rho . q_{sat,i} . D_i^s . \frac{\nabla Ln(1-\theta_i)}{\Delta p_i} \tag{6.9}$$

$$\theta_i = \frac{q_i}{q_{sat,i}} \tag{6.10}$$

Where $q_{sat,i}$, is the adsorbed phase concentration at saturation, D_i^s , the corrected transport diffusivity and θ_i, the percentage occupancy of the adsorbed phase.

Values for D_i^s for n-C_{4-7} are listed in table 6.8.

Table 6.8: Corrected transport diffusivities [27]

Components	D_i^s $\times 10^{-11}$ (cm^2/s)
n-C_4	1.60
n-C_5	1.28
n-C_6	0.80
n-C_7	0.45

All relevant parameters used in the model calculations are listed in table 6.9.

Table 6.9: Model parameters: Single-pass process

Parameter	Units	Values & Assumptions
$q_{sat,i}$	g/g	13 [28]
Δp_{tot}	bar	2
$T_{feed\ side}$	°C	90
$T_{permeate\ side}$	°C	120
Catalyst WHSV	h^{-1}	2
Catalyst particle shape		Cylindrical
Catalyst particle diameter	mm	1.4
Catalyst particle length	mm	3-5
Loading density	kg/m^3	795

For n-C_6 a permeance of 3.1×10^{-2} mol/m^2·s Pa and a corresponding flux of 3.68×10^{-4} mol/m^2·s was obtained. Since n-C_6 requires the largest surface area for diffusion, compared to the rest of the components, the membrane area required for the reactor is equal to the area required by n-C_6 for diffusion and amounts to 21.3×10^3 m^2.

The main design characteristics for the reactor in the concept processes are summarized in table 6.10. The membrane area needed by both process is comparable to that determined by Meindersma et al.[29] for the separation of aromatic compounds from a naphtha feedstream of ~7000 ton/day with a zeolite membrane.

Table 6.10: Reactors characteristics

Reactor Dimensions	Units	Recycle process	Single pass process
Membrane area needed for separation	m^2	17000	21300
Number of units	m	2	2
Diameter of tube	m	0.04	0.04
Unit dimensions	m	3 × 12	3 × 15
Diameter of tube	m	0.04	0.04
Amount of catalyst needed	kg	29138	11509
Volume of catalyst	m^3	29.1	14.5

6.3.3. Process simulation results

The proposed processes were simulated with the process flow sheet simulator Aspen Plus 10.2. Material balances were set up in Excel, making use of the available Solver utility to converge recycle streams in the process. Process flow schemes of process 1 and 2 are shown sequentially in figures 6.8 and 6.9.

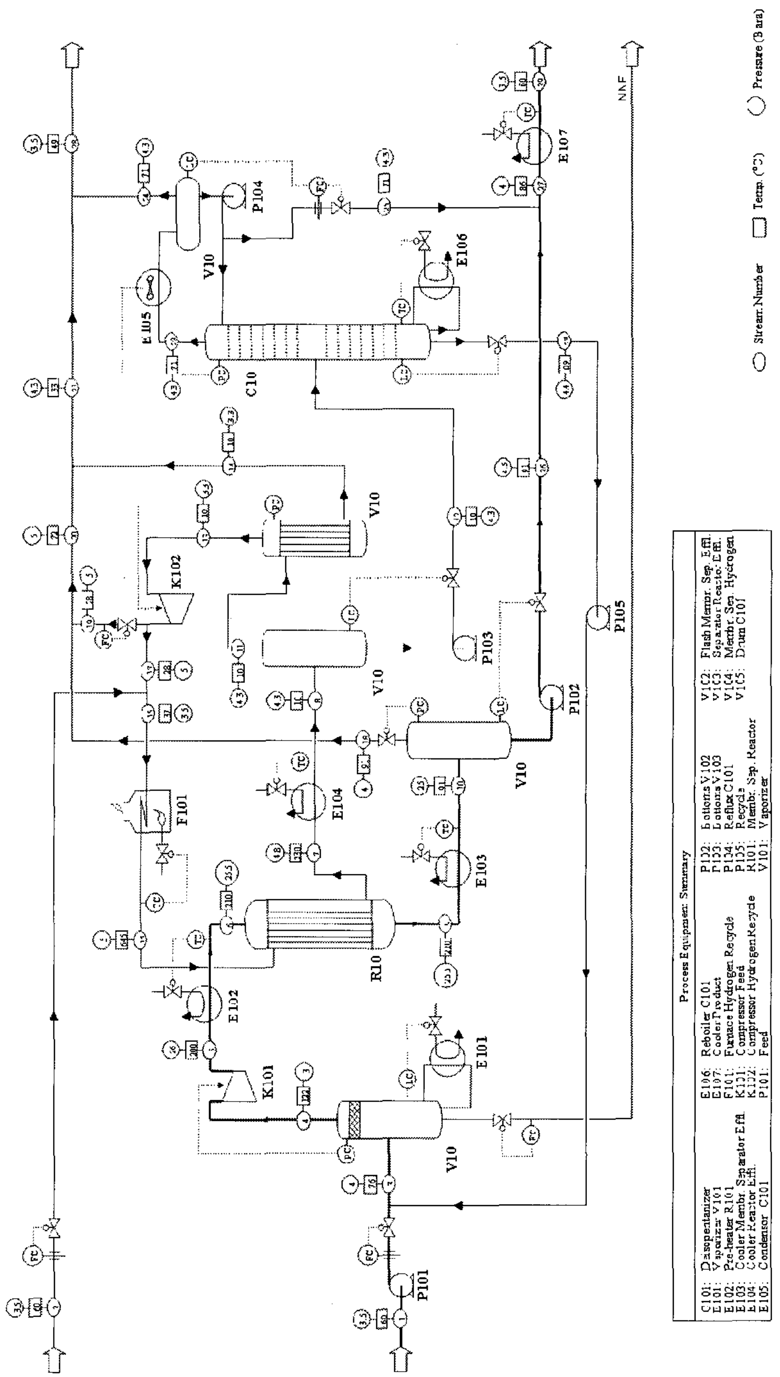


Figure 6.8: Process flow scheme of hydroisomerization process utilizing silicalite-1 membrane and recycle

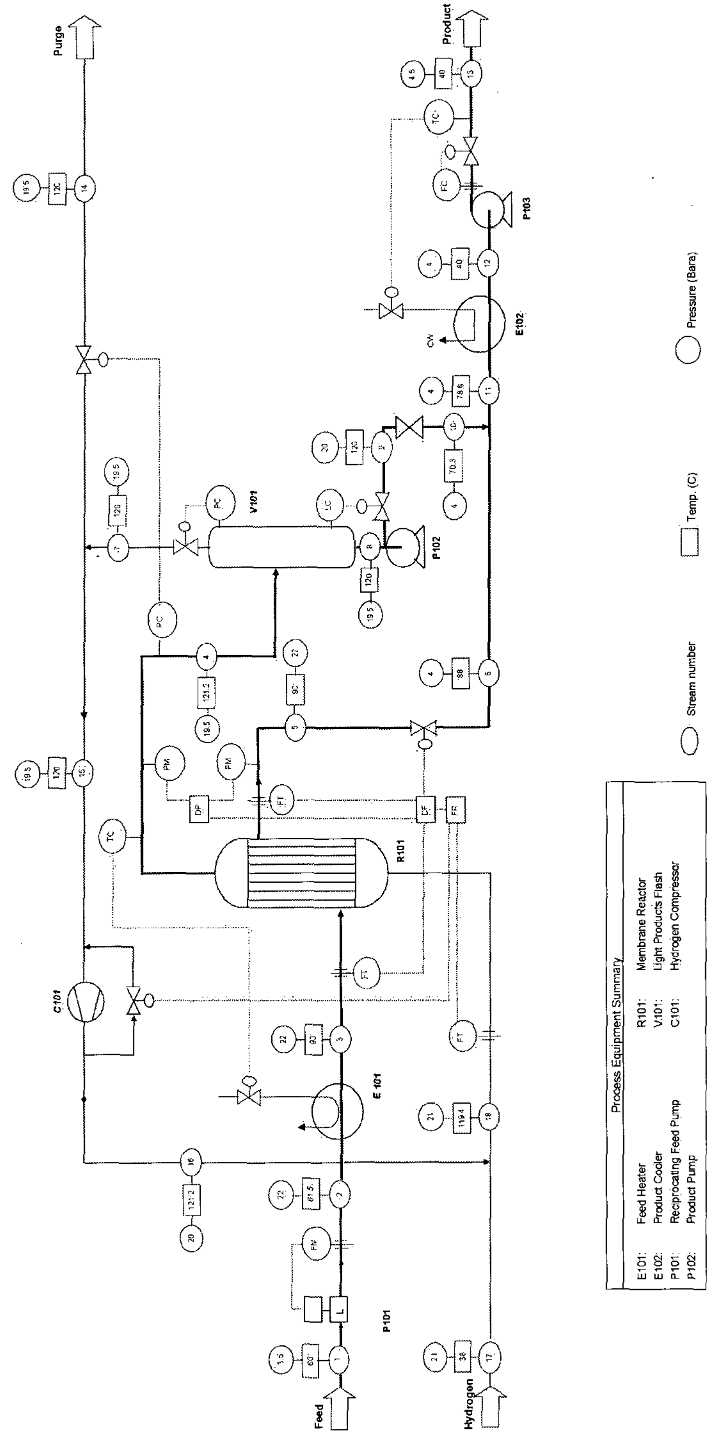


Figure 6.9: Process flow scheme of hydroisomerization process utilizing zeolite 5A membrane without recycl

Table 6.11 summarizes the results obtained in the conceptual process design of the Packed bed membrane reactor plant in the recycle and single-pass process. Results obtained from a conceptual design of the state of the art TIP Process is also listed for comparison.

Table 6.11: Comparison of State-of-the-art and Membrane technology

	State-of-the-Art	Recycle process	Single-pass process
RON:			
Feed	73.51	73.51	73.51
Final Product	86	87.92	87.20
C_{5+} Yield (%)	95	79	97

6.4 Process economics

The introduction of membrane reactors in an industrial context is strongly dependent on the economics of the membrane process. Gaining a foothold in the refining industry is made more complex by the fact that existing classical processes are mature and highly optimized, and the generally low process return of investments (ROI's) does not provide much leeway in terms of additional initial capital investment.

In order to determine the economic feasibility of the proposed membrane-reactor-based hydroisomerization processes an estimate of the investment needed for the individual processes was made using the Lang factorial method of cost estimation. According to this method the fixed capital (C_f) is calculated as a function of the total purchase cost of equipment (PCE)[30]:

$$C_f = 3.7\text{PCE} \qquad (6.11)$$

The cost of the purchased equipment is projected with an accuracy of ±25% from sized equipment lists with base date mid-1998[30]. The Marshall and Swift index was used to account for inflation between 1998 and 2004 (see table 6.12).

Table 6.12: Marshall & Swift index

Year	Index
1998	1061.90
2004	1275.04

The cost data shown in Table 6.13 were taken into account for the economic evaluation.

Table 6.13: Assumed costs for the economical analysis

	Unit	Cost
Catalyst: Pt chlorinated Al_2O_3	\$/kg	40
Catalyst Pt-H-β zeolite	\$/kg	372
Zeolite membrane	\$/m^2	300
SRN	\$/ton	180
H_2 make-up	\$/ton	165
Isomerized product	\$/RON·ton	5.85
C_{4-} purge	\$/ton	173
LP Steam	\$/ton	5.51
Electricity	\$/ kWh	0.06
Cooling water	\$/ton	0.01

The total investment was calculated as the sum of the fixed capital and the working capital. The latter was considered to be 15% of the fixed capital. Table 6.14 summarizes the results of the economic evaluation for the two new process options considered in this study.

Table 6.14: Comparison of State-of-the-art and Membrane technology

	Recycle process (MUS\$)	Single-pass process (MUS\$)
Total investment	77.2 MUS\$	33.5 MUS\$
Annual Operating Cost	94.8 MUS\$	69.3 MUS\$
Pay-back time	4 years	2.25 years

Compared to the total investment costs reported for C_5/C_6 hydroisomerization plants (23 million euros for a UOP/Molex plant), the capital investment needed for the recycle and the single-pass process is considerably greater. This can be contributed in large to the membrane cost which constitutes the largest fraction of the purchased equipment cost. The payback times take into consideration the main economic factors such as capital and operating costs together with process performance, covering product octane and yield. Figure 6.10 shows the estimated payback times for some of the state-of-art isomerisation processes [31] as well as the recycle and single-pass processes of the current study. The recycle process and the single-pass process payback times are comparable when it is assumed that the cost of the membrane is \$300/m^2 (a factor 10 lower than the current price for zeolite membrane modules [32]) and furthermore when the octane index cost is high - 5.85 \$/RON point / ton in stead of the present European value of ~ 3.5 \$/RON point/·ton [33].

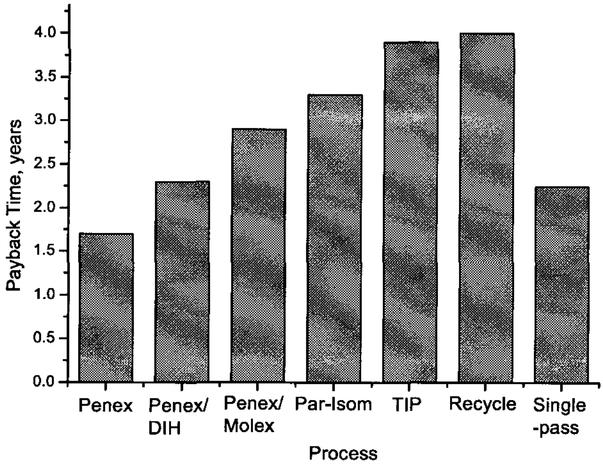


Figure 6.10: Payback time of isomerization processes [31]

6.5 Conclusions

This paper presents the results of a membrane reactor analysis and an economic evaluation of two membrane reforming processes which were compared to state-of-the-art technology for the hydroisomerization of C_5/C_6. Even for rather optimistic assumed fluxes and selectivities, the calculated required membrane areas were quite significant. Coupled with the current high cost for zeolitic membrane modules (\$ 3 000/m^2) [32] membrane reactor reforming still face an uphill battle towards commercialization, and will probably only gain wide acceptance if the membrane fluxes are improved significantly as compared with the assumptions used in this work, while also maintaining a high selectivity, and if furthermore membrane cost are reduced by at least a factor 10.

The proposed processes are still not optimised and plenty of scope for the latter still remains. Optimization could have a significant impact on the utilities and resulting operating costs and ultimately the financial feasibility. The possibility for optimisation of the reactor design also still remains. Keeping in mind that the linear alkanes are the fastest diffusing species which will preferentially diffuse through the membrane, resulting in a drop in concentration of these species on the feed side along the length of the reactor, it can for instance be considered to remove the isomerised product at several points along the length of the reactor in order to maintain a higher partial pressure difference across the membrane and thus a higher flux across the membrane (see figure 6.11) which would ultimately result in a decreased required membrane area and a reduced capital investment.

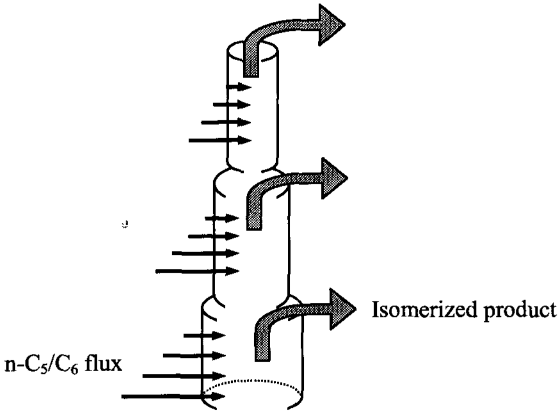


Figure 6.11: Possible membrane reactor design

6.6 References

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Pushing the limits on C_5/C_6 hydroisomerization utilizing membrane reactor technology

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Abstract

In this communication we propose an improved hydroisomerization process making use of membrane reactor technology. Linear alkanes are selectively supplied from a hydrocarbon feed (consisting of branched and linear alkanes) through an inert tubular membrane, to a packed bed of catalyst. This prevents possible cracking of branched alkanes present in the feed, as well as allowing higher conversion by controlling the feed composition to the reaction. The results indicate that linear molecules can be separated from mono- and di-branched components in a gas mixture with a selectivity factor of > 20 with a zeolite membrane under dedicated parameter settings. The RON-value of the product was calculated to be 68 – this is 28 points higher than the feed value. Further investigation indicated that the STY/ATY ratio for the reactor could fall within the limits of technical feasibility with optimised membrane preparation. The results indicate that a membrane reactor based process is a promising option for C_6 hydroisomerzation and certainly justifies further investigation.

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7.1 Introduction

Economics and government regulation are as much a driving force for technological development as innovation. Relevant examples of this can be found in the area of petroleum refining catalyst and process development. Worldwide gasoline specifications are continuing to move towards cleaner burning gasoline. Changes in Reid vapour pressure, reductions in olefins, sulphur, aromatics, as well as the controversy surrounding the use of MTBE [1] and the pending petroleum deficit [2] are all driving forces for the development of new technology that fit the requirements of an increasingly value conscious and environmentally aware society.

One of the main responses by the refining research and development community to the challenges posed by environmental and market demands, is a renewed interest in paraffin hydroisomerization technology. It is well recognized that the hydroisomerization of linear alkanes to their higher branched isomers offers a valuable blendstock to produce high octane, clean burning gasoline. Many of the recent attempts to improve this process have been focused on the development of Pt/sulphated zirconia or similar solid super acids as a means to achieve activity nearly commensurate with the conventional Pt/chlorided alumina catalysts, but without the need for continuous chloride injection that is required by these catalysts [3, 4]. Other areas of interest include the development of new paraffin isomerization catalysts that can selectively carry out the isomerization of longer chain paraffins such as n-C_7 [5-7].

In this communication we propose an improved hydroisomerization process making use of membrane reactor technology. The number of studies on catalytic membrane reactors (CMR) has grown considerable in the last twenty years, but the majority of them have been devoted to dehydrogenation/hydrogenation [8-10] and oxidation reactions [11]. Membrane based reactors have shown enormous potential in optimising the yield of desired products and reducing the overall costs [12, 13]. This is mainly because of the synergy that is being realized between separation and conversion. This synergy immediately comes into play for reactions limited by thermodynamic equilibrium, as is the case for the hydroisomerization of straight chain paraffins. Currently in industry, thermodynamic constraints for the hydroisomerization reaction of linear alkanes are overcome with recycle schemes using fractionation, adsorption, or both to separate the lower-octane components for recycling. For example, the Penex-DIH option uses a deisohexanizer (DIH) column for fractionation and recycle; the Penex-Molex and Total Isomerization process (TIP) use adsorptive separation; UOP's Penex-DIH-Pentane PSA system combines fractionation with adsorptive separation to recycle the low-octane components [14]. Membrane reactors have the ability to shift the overall conversion above thermodynamic equilibrium and increase selectivity by selective product removal and selective reactant addition [15]. Additional advantages that result from the physical combination of the separation module and reactor into the same unit include compact design and capital and operating (energy) savings realized by the elimination of intermediate processing steps.

All the various configurations in membrane reactor design have their merits and need to be optimized for a specific reaction. For the hydroisomerization of n-C_6 to its branched isomers in a membrane reactor, four configurations were considered using a specific sweep gas (hydrogen) in combination with a selective membrane (Fig. 7.1).

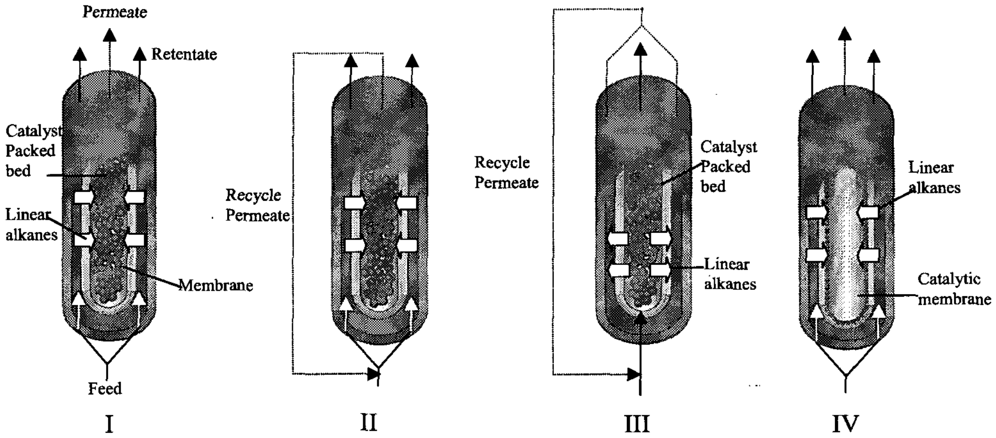


Figure 7.1 Scheme of possible reactor configurations for paraffin hydroisomerization.

In reactor I linear alkanes are selectively supplied from a hydrocarbon feed (consisting of branched and linear alkanes) through an inert tubular membrane, to a packed bed of catalyst. This prevents possible cracking of branched alkanes present in the feed, as well as allowing higher conversion by controlling the feed composition to the reaction. Since no recycle is present, the named configuration is mainly suited for operation at low temperatures (< 130°C) when the amount of linear alkanes, remaining in the product stream, is less than 6%. Reactor II makes use of a recycle, and will therefore be beneficial when the reaction takes place at high temperatures (~ 250°C) i.e. with Pt/H-mordenite as the catalyst, thermodynamically limiting the amount of linear alkanes that will be converted to their branched isomers per pass. By controlling the feed composition to the catalyst bed and recycling the unconverted linear alkanes the overall conversion can be increased[16]. In reactor III the feed is first supplied to the catalyst bed and the final equilibrium is separated into linear and branched products followed by the recycling of the linear product back to the catalyst bed at operating temperatures around 230°C with zeolite β as the catalyst. Pt-H-β shows an increased selectivity for higher branched products as well as good resistance against feed contaminants and allows operation at a slightly lower temperature then Pt/H-mordenite[17]. The primary advantage of configuration III is that it 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 and increasing the energy efficiency. Since only a reduced amount of linear alkanes that have to be separated for recycling remain, the surface area needed for the membrane is also reduced. Unlike the inert membrane reactors in scheme I – III, in which the role of the membrane is limited to add or remove products/reagents to or from the reaction environment, the catalytic membrane reactor in configuration IV contains the catalytic material on which reaction takes place, in the membrane itself. This configuration could allow increased process efficiency, limiting the amount of pressure drop and unwanted cracking reactions taking place. However, since reaction and separation are integrally linked, it will be very difficult to find optimum conditions for both selectivity and conversion.

In this paper we focus our attention on reactor configuration I. The catalyst and membrane are the key components that determine the successful application of the membrane reactor process and therefore require careful consideration. The catalyst that was used in this study is a chlorinated Pt/Alumina catalyst that will allow operation at the relatively low temperature of 120°-130°C [18], favouring the thermodynamic product distribution.

It is apparent that the effective use of membranes with catalytic reactors is dependent on understanding their strengths as well as their limitations. The permselectivity has to be coupled with high enough permeability so as to avoid large areas of expensive membranes. Thermal stability of the membrane is a further important issue to consider. To this extent inorganic membranes are superior to organic membranes since they are stable at relatively high temperatures (> 373 K) and have good chemical and mechanical resistance. [19] In particular zeolite membranes lend themselves very well to application in membrane reactors due to their unique molecular sieving ability stemming from their well-defined microporous structure and ability to be tailor made for a specific application. In this study we employ the MFI membrane silicalite-1 as selective permeation barrier. The structural porosity of MFI zeolite consists of channels of about 5.5Å in diameter, the silica rich composition induces hydrophobic properties and also stability at high temperature (at least 600°C). In the case of *n*-hexane/2,2dimethylbutane separation, linear alkanes have a smaller kinetic diameter (0.43 nm for n-hexane, 0.5 nm for iso-pentane and 0.62 nm for 2,2-dimethylbutane), therefore one would expect that size exclusion will control transport. At low temperatures, however the governing separation mechanism is that of surface diffusion in the zeolite. The normal alkanes are preferentially adsorbed because of configurational entropy effects; they "pack" more efficiently within the channel structures of silicalite. Since branching destroys the symmetry of the paraffins the linear paraffin molecules stack more easily and will therefore preferentially diffuse through the membrane.

7.2 Experimental

7.2.1 Materials

High silica MFI membranes were prepared on disk-shaped (2.5 cm in diameter) as well as tubular (1 cm in diameter with a membrane area of 29.8 cm^2) Trumem supports (manufacturer: Trumem International, Russia) consisting of a 180 μm sintered stainless steel layer (mean pore size 2-5 μm) coated with a ~15 μm TiO_2-layer (mean pore size of 0.10 μm). The chemicals used in this work were tetraethoxysilane (TEOS, 99% Merck), tetrapropylammonium hydroxide (TPAOH, 25 wt% in water, Chemische Fabriek Zaltbommel CFZ B.V.), tetrapropylammonium bromide (CFZ B.V.) and distilled water. All the chemicals were used as received with no additional purification. All the gases used during permeability tests were at least 99.9% pure. The hydrocarbon feeds used during the testing of the membrane reactor had a purity of at least 99% with the exception of 2,3-dimethylbutane that was 98% pure. n-Hexane was supplied by J.T. Baker, 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane by Acros and 2,2-dimethylbutane by Aldrich. The catalyst that was used during hydroisomerization was a chlorinated Pt/alumina catalyst. (AT-2, Akzo Nobel)

7.2.2 Membrane preparation

The membranes were prepared according to the secondary growth method previously reported by Gora et al. [20] The method consists of (i) preparation of a precursor suspension of MFI crystals of nanometer size dimensions, (ii) deposition of a thin film of seeds onto the substrate, and (iii) secondary grain growth of the deposited seed crystals to a continuous film [21, 22]. The silicalite-1 seed crystals (700 nm) were prepared from a synthesis solution with a molar composition of 107.7 SiO_2: 32.68 TPA: 32.68 OH: 12000 H_2O that was aged for 1.5 hrs at room temperature and subsequently treated hydrothermally at 433 K for 3 hrs and finally dried at 373K. Growth of a continuous zeolite film was facilitated by vertical immersion of the seeded supports in a clear solution with molar composition 100 SiO_2: 123 TPA: 63.7 OH: 14200 H_2O followed by hydrothermal treatment under autogenous pressure in a Teflon-lined autoclave at 453 K for 17 hours. After the synthesis, the autoclave was removed and quenched to room temperature. Subsequently, the samples were rinsed in distilled water and calcined in air at 673 K for 17 hrs at a heating and cooling rate of 1 K/min.

7.2.3 Characterization of the supported MFI zeolite membranes

The morphology and structural integrity of the synthesized membranes were examined with scanning electron microscopy (SEM) using a Philips XL20 microscope. Permeation measurements with a 1:1 mixture of n/i-butane were performed on the air-calcined samples according to the Wicke-Kallenbach method [23] at 303K. The feed and permeate sides were kept at atmospheric pressure. Helium was used as sweep gas with a flow rate of 100 ml/min. Feed, retentate and permeate streams were analyzed with a mass spectrometer (Quadrupole mass analyzer, Ledamass), which is placed on line. The zeolite layer was placed in the module facing the feed side. The flux through the membrane was calculated from the mass balance by determining the concentration of n-butane or i-butane in the permeate stream and that of the sweep gas (helium) in the retentate.

Prior to calcination the tubular membranes were tested for helium permeation. Since the zeolite pores are inaccessible to diffusing gas molecules, any diffusion of helium through the uncalcined zeolite membranes, would be due to interparticle porosity, defects in the membrane or insufficient sealing of the membrane to the reactor module.

For design and performance examination of a membrane reactor unit containing a zeolite membrane, the quantitative description of both fluxes and separation factors as a function of operating conditions is indispensable. Therefore the flux and selectivity of the tubular membranes were determined as a function of temperature, pressure gradient, hydrocarbon flow rate, and sweep flow rate respectively, in the membrane reactor test unit.

7.2.4 Membrane reactor test unit

The membrane reactor test unit is a stand-alone system for the testing and evaluation of the membrane and catalyst performance as well as the continuous flow combined process analysis. Figure 7.3 shows the schematic drawing of the experimental setup. At the heart of the test unit is the reactor module. A schematic depiction of the reactor can be seen in Figure 7.2 [24]. The reactor has two inlets: feed and sweep gas, and two outlets: one from the inside of the membrane and the other from the annular space around the membrane (permeate and retentate). The tubing configuration creates downward flow, i.e. in at the top and out at the bottom. A packed bed of catalyst pellets is present on the inside of the membrane.

A HPLC pump (Micrometrics 760) that allows slow, constant flow rates, pumps the organic feed into the system. The feed liquid is mixed with a preheated helium carrier stream and vaporized while passing through a heated zone at a temperature well above its boiling point. Dilution with helium guarantees a steady flow rate, prevents condensation on cold spots, and allows the investigation of different feed concentrations. A helium stream was used to remove the permeating compounds from the sweep side during permeability tests, whilst hydrogen was used as a sweep gas during combined process analysis. During the testing of the inert membrane catalytic reactor, the roll of the hydrogen is twofold: (i) it is used as a sweep gas and (ii) takes part in the hydroisomerization reaction (it has been shown by various authors that hydrogen limits the amount of cracking that takes place) [25, 26]. Both the feed and the permeate were analyzed on-line by a HP gas chromatograph 5890 with a flame ionization detector and a capillary column (CP-Sil PONA CB, 50 m x 0.25 mm; df = 0.5μm). A feed bypass line allows analysis of the feed before entering the module. The pressures of the feed and permeate sides are adjusted separately by two backpressure regulators and monitored by pressure transducers. The helium sweep/carrier flow rates are controlled by mass flow controllers (Bronkhorst, 0-500 ml/min).

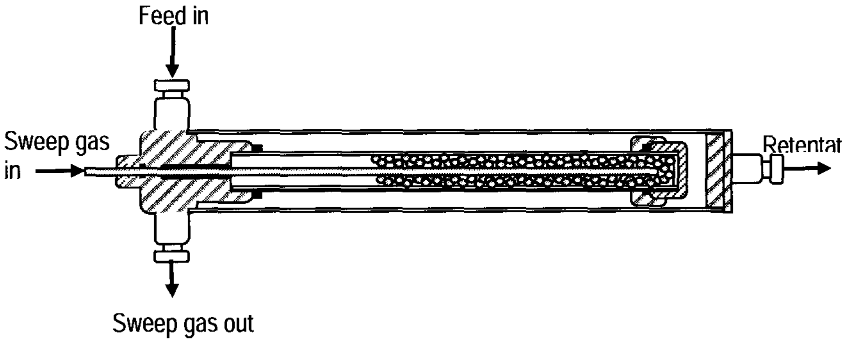
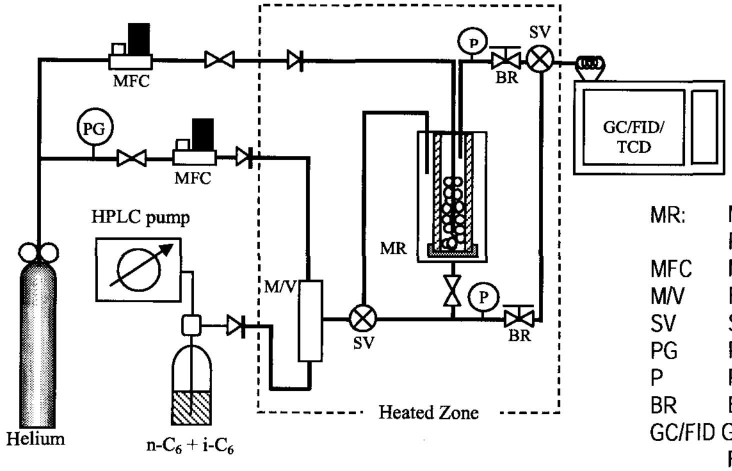


Figure 7.2: Design of the membrane reactor module



MR:	Membrane reactor with Packed catalyst bed
MFC	Mass flow controller
M/V	Feed mixer and vaporizer
SV	Selection valve
PG	Pressure gauge
P	Pressure Transducer
BR	Back Pressure Regulator
GC/FID	Gas chromatograph with Flame Ionization Detector

Figure 7.3: Schematic illustration of the Membrane reactor test unit

7.2.5 Determination of Membrane reactor performance

The tube (volume 7.46×10^{-6} m^3) was filled with 5.39 g of chlorided Pt/Al_2O_3 (AT-2), packing 7.22×10^5 g catalyst/m^3 reactor under N_2 (in order to prevent catalyst deactivation due to moisture). A molar feed ratio of 21.5 H_2/n-C_6, was used. The H_2-sweep flow rate, *n*-C_6 flow rate and He carrier gas flow rate were set to 5 ml/min, 0.073ml/min and 50 ml/min respectively. The hydrocarbon feed, a n-C_6/2-methylpentane/2,2-dimethylbutane-mixture (80/15/5 wt%), were supplied with a flow rate of 0.073 ml/min. A Weight Hourly Space Velocity (WHSV) of 0.954 g of feed/h·g of catalyst was used. A pressure difference of 0.5 bar was applied across the membrane, $P_{shell} > P_{tube} = 4$ bar.

7.3 Results and Discussion

7.3.1 Morphology and nature of the prepared Silicalite-1 membranes

The membrane grown on the disk shaped Trumem support is shown in figure 7.4. The image shows a dense intergrown layer consisting of randomly oriented silicalite-1 crystals. From the SEM image of the cross section, it is estimated that the grown silicalite-1 membrane has a thickness of ~16μm.

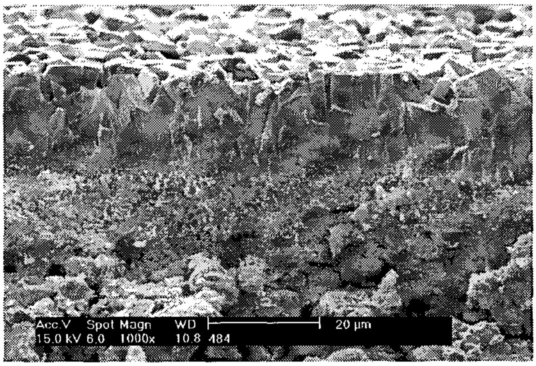


Figure 7.4: Cross section silicalite-1 membrane before calcination

The silicalite membrane was prepared on a tubular support in a way analogous to the membrane preparation on the Trumem disks. Figure 7.5 shows the tubular support with the silicalite-1 membrane after calcination at 673 K.

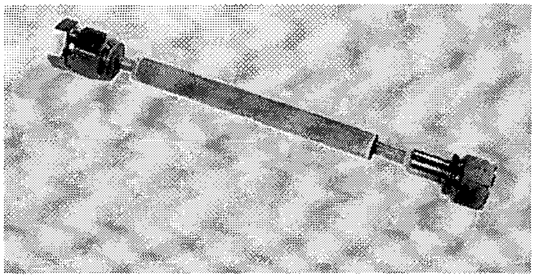


Figure 7.5: Silicalite-1 membrane on tubular TRUMEM support after calcination at 673 K

Ideally, membranes should exhibit high selectivity and high flux, which in practice means that the zeolite film should be as thin as possible and free of defects, in order to assure optimal performance of the membrane reactor. The presence of a dense layer of precursor seeds on the substrate, at the onset of membrane synthesis, ensures to a large extent, the production of a defect-free membrane [27] whilst still allowing the fulfillment of the requirements on film thickness. The film should have a sufficiently low defect density to be isomer selective. The helium leak test that was performed indicated that the membrane was impervious to helium prior to template removal. It can therefore be assumed that the membrane was free of macroscopic defects and the system was well sealed.

7.3.2 Gas permeation and butane isomer selectivities

Table 7.1 shows data for gas permeabilities at room temperature and selectivities of a 1:1 mixture of n/i-butane from this work as well as literature data, included for comparison. It should be noted that the tests reported have been performed at quite different conditions and that the membranes have been prepared by various methods. Butane isomer separation is believed to be based on adsorption at low temperatures and on molecular sieving at high temperatures resulting in a strong dependence of the separation performance on the membrane composition and test conditions [28].

Table 7.1: Comparison of obtained n-butane flux and n/i-butane selectivity with reported n-butane fluxes and selectivities for MFI-type zeolite membrane at room temperature, Wicke-Kallenbach method

Membrane	*n*-butane flux [mmol/m^{2}s]	Selectivity *n*-butane/*i*-butane	Reference
Silicalite/Al_2O_3	2.7	84	[29]
ZSM-5/Al_2O_3	0.9	14	[30]
Silicalite/Al_2O_3	5.9	20	[31]
ZSM-5/Al_2O_3	1.3	7.6	[32]
Silicalite/SS	6.7	23	[33]
Silicalite/TiO_2/SS	10	41	[34]
Silicalite/TiO_2/SS	4.58	32.10	Present work

7.3.3 Membrane Reactor performance

In order to examine the performance of the membrane reactor, optimal conditions concerning temperature, pressure differences, flow rate of the hydrocarbons as well as of the sweep gases were determined.

7.3.3.1 Influence of n-C_6 and sweep flow through the membrane

The influence of the sweep gas flow rate on the permeation of pure n-C_6 at 120°C and 101kPa is presented in figure 7.6. The helium carrier gas flow rate was fixed at 50 ml/min whilst the flow of the sweep gas was varied, between 50 and 200 ml/min, for two different hydrocarbon flow rates (set: 0.073 and 0.564 ml/min, respectively).

As indicated in figure 7.6, the flux of *n*-C_6 is higher with a high *n*-C_6 flow rate, 0.564 ml/min, than the flux for the low feed rate, 0.073 ml/min. It is also observed that an increase in sweep gas flow rate increased the *n*-C6 flux, which is consistent with data in literature [11, 35]. At higher sweep flow rates more of the component (*n*-C_6) is effectively removed from the tube side, thus increasing the concentration gradient across the zeolite membrane, resulting in an increase in the driving force for permeation, and therefore also an in increase in the flux. This results in a simultaneous increase in partial pressure at the permeate site and consequently a decrease in driving force. The observed flux is therefore a balance of the above effects. Counter-diffusion of the sweep gas also plays a definitive role in the n-C_6 flux. It has been shown that this counter-diffusion is, at a given temperature, less significant when the occupancy of the feed component in the membrane is higher [36]. This could be a contributing reason for the lower flux of the 0.073 ml/min C_6 stream as compared to the 0.564 ml/min C_6 flow. Since Helium adsorbs very weakly on silicalite-1, the effect of counter-diffusion on the flux should however be limited. The permeation fraction, which is defined by:

$$Permeation\ \ fraction = \frac{c_{HC_i,permeate}}{c_{HC_i,feed}} \tag{7.1}$$

shows an expected increase in the fraction of the component present in the feed, that is permeating through the membrane.

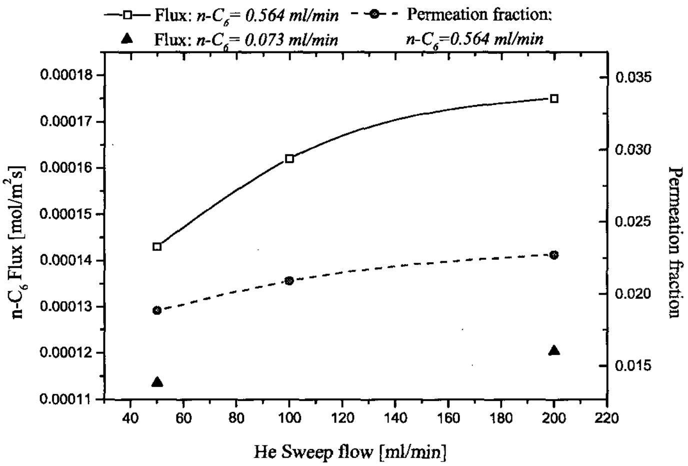


Figure 7.6: Flux *n*-C_6 vs. time different sweeping flow rates (50, 100 and 200 ml/min) with 0.564ml/min and 0.073 ml/min *n*-C_6 feed flow rate at 120°C and 101kPa.

7.3.3.2 Influence of pressure differential across the membrane

Besides the effect of the sweep gas flow rate on the permeance through the membrane, the influence of the differential pressure ($P_{shell} > P_{tube} =$ atm. Pressure) across the membrane on permeation was also studied for different flow rates of *n*-C_6 (0.07 and 0.58 ml/min). A reactor temperature of 120°C, a He carrier gas flow rate of 50 ml/min and a He sweep gas flow rate of 200 ml/min was employed. As table 7.2 indicates, applying a pressure difference across the membrane causes a marginal increase in the flux of *n*-C_6 as well as the permeation fraction of *n*-C_6. This is indicative of the fact that permeation through this membrane is governed by surface diffusion, which is valid for C_6 isomers at these relatively low temperatures [37]. The low permeation fraction of *n*-C_6, can be attributed to poor mass transfer from the feed flow to the membrane inside the membrane reactor due to dimensional constrains and therefore could still be optimised. Results from further investigations done by this laboratory indicate that better permeabilities could be obtained when the membrane calcination procedure was changed. This indicates that the incomplete removal of the template molecule could be a contributing factor to the poor permeability.

Table 7.2: Flux and permeation fraction of *n*-C_6 at *high* and *low* *n*-C_6 feed flow and sweep flow rate of 200 ml/min, applying a Δp of 0 and 0.5 bar at 120°C.

Press. diff. [bar]	Flow,$_{n\text{-}C6}$ [ml/min]	Flux $_{n\text{-}C6}$ [mmol/m^{2}s]	Permeartion fraction
0	0.071	0.122	0.0404
0.5	0.073	0.151	0.0488
0	0.581	0.559	0.0227
0.5	0.589	0.562	0.0224

7.3.3.3 Influence of temperature on flux through membrane

The influence of the temperature on the *n*-C_6 permeation was examined by varying the reactor temperatures (100, 120, 140 and 160°C) with a He carrier gas flow rate of 50 ml/min, a He sweep gas flow rate of 200 ml/min and a n-C_6 flow rate set to 0.073 ml/min.

In a predictable fashion, the flux as well as the permeation fraction increased with rising temperature, see figure 7.7. The hydrocarbon molecules vibrate more vigorously at higher temperatures and have reduced interaction with the pore wall and will therefore diffuse faster through the membrane yielding a higher flux and permeation fraction. Increased temperature will therefore improve flux across the membrane and could thus be considered to be favourable for membrane reactor operation. However, as will be discussed in (3.2.4) an increased temperature is less favourable for membrane selectivity.

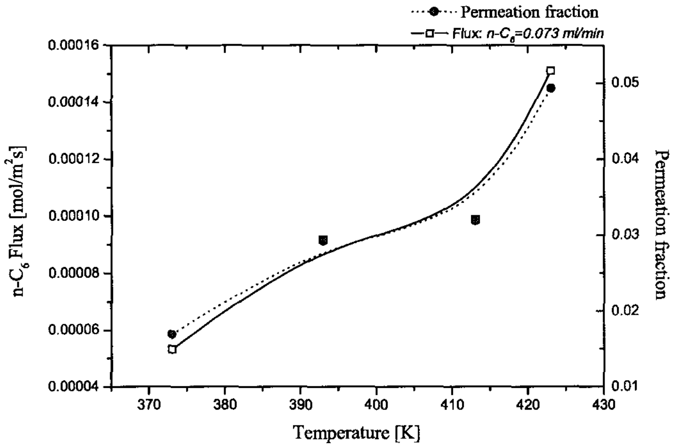


Figure 7.7: Flux n-C_6 through the membrane and Permeation fraction vs. temperature

7.3.3.4 Influence of temperature on selectivity of membrane

The influence of temperature on the permeation and selectivity of a n-C_6/2-MP/2,2-DMB-mixture (80/15/5) was examined by varying the reactor temperatures between 100 and 160°C, with a He carrier gas flow rate of 50 ml/min, a He sweep gas flow rate of 200 ml/min and a n-C_6 flow rate set to 0.070 ml/min. The selectivity decreased with rising temperature (fig. 7.8) in contrast to the flux, which increased at higher temperatures (fig. 7.9). This strongly points out towards competitive adsorption and blockage of zeolite channels as the mechanism controlling permeation. n-Hexane is able to adsorb preferentially on silicalite-1, hindering the pass of the other components in the mixture. As temperature increases, the surface coverage declines, and the n-C_6/i-C_6 selectivity decreases. This trend is also reported in literature [38, 39]. Thus, when higher selectivity is the objective, a lower temperature, in this case 120°C is favourable. This is clearly shown in figure 7.9. The high selectivities observed for n-C_6/2,2-DMB and n-C_6/2-MP also clearly indicates the difference in pakcing efficiency between the linear and branched molecules respectively. Almost no selectivity is observed for 2-MP/2,2-DMB due to the fact that there is a very small difference in their configurational entropy i.e. their packing efficiencies and their maximum loadings within the zeolite framework.

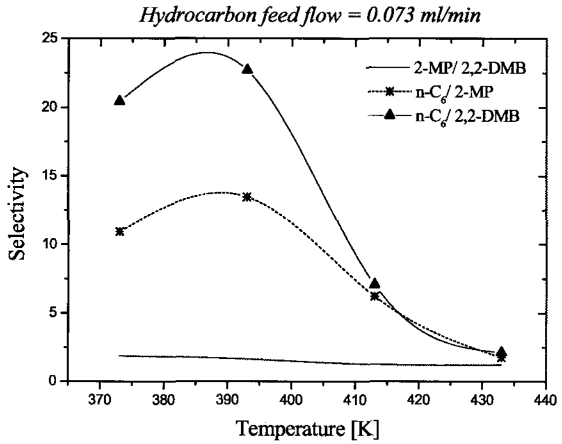


Figure 7.8: Selectivity vs. temperature of 80/15/5 mixture of *n*-C_6/2-MP/2,2-DMB

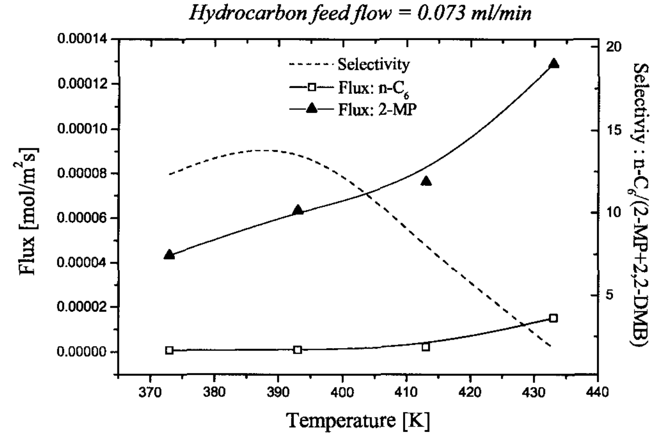


Figure 7.9: Flux and Selectivity vs. temperature of 80/15/5 mixture of *n*-C_6/2-MP/2,2-DMB

7.3.3.5 Influence of pressure differential on selectivity and permeation fraction of mixture

The influence of the pressure differential across the membrane on the flux and selectivity of a *n*-C_6/2-MP/2,2-DMB-mixture (80/15/5) was examined by applying a pressure difference of 0.5 bar over the membrane ($P_{shell} > P_{tube} =$ atm. pressure) with a He carrier gas flow rate of 50 ml/min, a He sweep gas flow rate of 200 ml/min and a hydrocarbon mixture flow rate set to 0.070 ml/min. An increase pressure differential caused an increase in the n-C_6 flux whilst the n-C_6 selectivity and the 2-MP flux remained more or less constant (table 7.3). The permeation fraction of n-C_6 also increased with an increased pressure differential, while the change in pressure difference across the membrane had little effect on the permeation fraction of 2-MP and 2,2-DMB.

Table 7.3: Flux and Selectivity of 80/15/5 mixture of *n*-C_6/2-MP/2,2-DMB with and without pressure difference (Δp = 0.5 and 0 bar respectively) across the membrane

Differential pressure [bar]	Flux [mol/m²s]		Selectivity		
	n-C_6	2,2-DMB	*n*-C_6/2-MP	*n*-C_6/2,2-DMB	2-MP/2,2-DMB
0	5.05×10^{-5}	7.51×10^{-7}	13.742	23.180	1.687
0.5	1.08×10^{-4}	1.99×10^{-6}	12.085	14.835	1.228

7.3.3.6 Combined separation and reaction performance

The combined separation and reaction performance was finally investigated, employing a pressure difference of 0.5 bar over the membrane and a pressure inside the tube of 4 bar ($P_{shell} > P_{tube}$), a He carrier gas flow rate of 50 ml/min, a H_2 sweep gas flow rate of 50 ml/min and a *n*-C_6/2-MP/2,2-DMB-mixture (80/15/5) flow rate of 0.073 ml/min. Our studies indicated that the use of H_2 instead of He as a sweep gas hardly influences the flux or the permeation fraction and therefore also has very little influence on the selectivity (table 7.4), *n*-C_6 flux (mmol/m²s) He = 4.38×10^{-2}, H_2 = 4.49×10^{-2}, Selectivity: *n*-C_6/2-MP (He as sweep gas) = 12.085, *n*-C_6/2-MP (H_2 as sweep gas) = 12.880. The replacement of helium with H_2 was required as hydrogen also takes part in the hydroisomerization reaction. Counter diffusion of H_2 is expected to be very limited since hydrocarbons will be effectively blocking the pores of the zeolite [40] at the operational temperature.

Table 7.4: Flux and permeation fraction of *n*-C_6/2-MP/2,2-DMB-mixture applying a Δp of 0.5 bar, using He or H_2 as sweep gas

Sweep gas	Flux [mmol/m²s]			Permeation fraction		
	n-C_6	2-MP	2,2-DMB	*n*-C_6	2-MP	2,2-DMB
He	4.38×10^{-2}	6.69×10^{-4}	1.82×10^{-4}	1.82×10^{-2}	1.59×10^{-3}	1.29×10^{-3}
H_2	4.49×10^{-2}	6.32×10^{-4}	1.89×10^{-4}	1.89×10^{-2}	1.48×10^{-3}	1.29×10^{-3}

Hydroisomerization of the normal alkanes to their branched isomers as well as a minor amount of cracking takes place inside the catalyst bed. The distribution of hexane isomers in the feed, the permeate, isomerised product and at thermodynamic equilibrium is tabulated in table 7.5. Using permeate and isomerised-product distributions of *n*-hexane in table 7.5 the conversion of *n*-hexane was calculated and found to be equal to 86.5 %. The table also shows that the obtained isomerised product was close to thermodynamic equilibrium.

Table 7.5: Distribution of hexane isomers at T = 120 °C, Δp = 0.5 bar, P_{tube} = 4 bar

	Distribution (%)				
	n-C_6	3-MP	2-MP	2,3-DMB	2,2-DMB
Feed	80	0	15	0	5
Permeate	97.93	0	1.61	0	0.45
Isomerised product	13.31	13.66	37.60 *		35.43
Equilibrium$^+$	7.72	15.00	28.45	8.83	40.00

* 2-MP + 2,3-DMB

$^+$ Thermodynamic equilibrium at 120°C[41]

Branched hydrocarbons are preferred as ingredients in gasoline because of their higher octane number. Considering the isomers of hexane: *n*-Hexane has a research octane number (RON) of 30, whereas the corresponding RON values for its isomers are as follows: 2-methyl pentane (2-MP) = 74.5; 3-methylpentane (3-MP) = 75.5; 2,2-dimethylbutane (2,2-DMB) = 94; and 2,3-dimethylbutane (2,3-DMB) = 105. During conversion of n-C_6, the reaction was more selective towards 2-methylpentane (+ 2,3-dimethylbutane) and 2,2-dimethylbutane than towards 3-methylpentane, with production selectivities of 41.3, 40.2 and 15.7 % respectively thus favouring a higher RON. Less than 3 % of the converted *n*-hexane was cracked into smaller components. The RON-value* of the total product, which is a blend of retentate from the membrane and the permeate, of a reactor configuration such as depicted in scheme I of figure 7.1, was calculated to be 68 (see table 7.6). Since the RON value of the hydrocarbon feed (calculated from the feed composition) to the reactor was 40, this means that the process led to a rise in RON of 28 points.

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* RON = $\sum$(%composition × RON $\text{value}_{\text{component i}}$)

Table 7.6: RON of Feed, Permeate, Retentate and Total product streams. H_2/n-C_6=21.5 *n*-C_6/2-MP/2,2-DMB-mixture (80/15/5) flow rate of 0.073 ml/min, 120°C

Component	Distribution (%)				
	Feed	Permeate	Reaction product	Retentate	
	100.0	62.6	62.6	37.4	
n-C_6	80.0	97.9	13.0	49.5	
3-MP			13.3		
2-MP	15.0	1.6	28.0	37.8	
2,3-DMB			8.7		
2,2-DMB	5.0	0.5	34.5	12.7	RON of combined streams
Cracked (<C_6)			2.5		
RON	40	31	76	55	**68**

Table 7.7: Molar flow through the membrane (1), molar flow of permeate (2) and the production selectivities of the components in the membrane reactor

Component *i*	$\phi_{i,1}$ (mmol/s)	$\phi_{i,2}$ (mmol/s)	$\Delta\phi_i$ (mmol/s)	$S_{prod,i}$ (%)
n-C_6	9.07×10^{-5}	1.21×10^{-5}	-7.68×10^{-5}	-
2-MP	1.57×10^{-6}	3.43×10^{-5} *	3.27×10^{-5}	41.3
3-MP	0	1.24×10^{-5}	1.24×10^{-5}	15.7
2,2-DMB	4.41×10^{-7}	3.23×10^{-5}	3.18×10^{-5}	40.2
Cracked (< C_6)	0	2.24×10^{-6}	2.24×10^{-6}	2.83

(+ 2,3-DMB)

7.3.3.7 Feasibility of industrial application

In order for membrane reactor processes to be established as viable industrial processes, numerous hurdles still need to be addressed such as: the development of high-surface-area-per-volume-systems, long-term stability of the membranes materials, scale-up and high temperature sealing of the membranes in the modules. Insight in some of the challenges and barriers that still remain is offered in a number of recent published reports [18, 42].

Proving whether a membrane reactor based process is technically and economically feasible is a complex undertaking involving many other factors beyond a straightforward comparison between the yield and selectivity of the membrane reactor and the competing state of the art systems. Cost of the membranes and membrane robustness for example are as critical in determining process success as selectivity and yield. Nevertheless, as a first attempt to estimate the technical feasibility of the suggested membrane reactor process for C_6 hydroisomerization in this study, we calculated the Space Time Yield (STY) to Areal Time Yield (ATY) ratio (STY/ATY). Van de Graaf et. al., [43] specified that feasible industrial application is indicated by a STY value within the range of 1- 10 mol/m^{3}s for catalytic reactors and a STY/ATY or Area/Volume (A/V) ratio, in the range of 20-5000 m^{-1} for porous inorganic membranes. An A/V value of 32 895m^{-1} is obtained for an STY value of 1mol/m^{3}s and the ATY value of 3.04 x 10^{-5} mol/m^{2}s obtained for the membrane in this study. However, results from further investigations done by this laboratory indicate that fluxes of 1.14 x 10^{-3} mol/m^{2}s and a A/V ratio of 877 m^{-1} could be obtained when the membrane calcination procedure is improved. This results in a ~4.5 mm tube which falls within the range of technical feasibility signifying that the application of membrane reactor technology to improve C_5/C_6 hydroisomerization could be realized in future. Furthermore, results indicate that linear molecules can be separated from mono- and di-branched components in a gas mixture with a selectivity factor of > 20 with a zeolite membrane under dedicated parameter settings. The RON-value of the total product was calculated to be 68 – this is 28 points higher than the feed value.

7.4 Conclusions

The influence of various process conditions on the single gas as well as hydrocarbon mixture permeation through an asymmetric supported silicalite-1 membrane has been studied and the relative importance of a number of operating modes has been presented. The flux of *n*-C_6 through the membrane is proportional to both the *n*-C_6 feed flow rate as well as the sweep gas flow rate. In this study, the highest flux of 0.562 mmol/m^{2}s was obtained at a *n*-C_6 feed rate of 0.581 ml/min and sweep gas flow rate of 200 ml/min. The flux of the ternary mixture of *n*-hexane, 2-methylpentane and 2,2-dimethylbutane (80/15/5) compared to the single gas flux of *n*-hexane is a factor 0.2 lower. This is due to blocking of the adsorbed *n*-hexane by other components in the ternary mixture resulting in a decreased flux. The flux of *n*-C_6 through the membrane is also proportional to temperature. The highest flux (0.199 mmol/m^{2}s) was obtained at the highest temperature (160°C). As opposed to the flux, the selectivity is inversely proportional to temperature. Therefore, on the basis of higher selectivity, lower temperatures are preferred. The application of a pressure difference across the membrane causes a marginal increase in the flux of *n*-C_6 indicative of the fact that permeation through the membrane at 120°C is governed by surface diffusion.

The results indicate that linear molecules can be separated from mono- and di-branched components in a gas mixture with a selectivity factor of > 20 with a zeolite membrane under dedicated parameter settings. The RON-value of the total product was calculated to be as high as 68 – this is 28 points higher than the feed value. The STY/ATY for the reactor could fall within the limits of technical feasibility with optimised membrane preparation. The above results indicate that a membrane reactor is a promising process option for C_6 hydroisomerzation and certainly justifies further investigation.

7.5 Acknowledgement

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8

Concluding remarks and Future outlook

Membrane reactors offer clear advantages such as improved yield and energy savings. More specifically Zeolite Membrane Reactors offer unique opportunities owing to the exceptional properties of zeolite membranes which include their (i) size and shape selective separation behaviour and their (ii) thermal and chemical stability and (iii) the ability to couple the discrimination between molecules to catalytic conversion. However it is clear that in order to capitalize on these benefits a substantial reduction in membrane module cost and further improvements on the integrity (selectivity and permeability) of the molecular sieve films to facilitate a reduction in surface area requirements is mandatory.

The conversion of linear alkanes into their branched isomers in the hydroisomerization process produces a mixture of isomers that requires separation and recycling. Traditionally, only the normal alkanes would be separated from the mixture by adsorption and recycled to the isomerization reactor, and any mono-methyl alkanes would be collected with the di-methyl alkanes as product. The octane number, however, increases with the degree of branching and therefore di-branched isomers are the preferred products. It would consequently be advantageous to separate the di-branched isomers from the reaction products and recycle the mono-branched and linear alkanes back to the reactor. .In contrast to the flux and absolute separation properties of zeolite Ca-Na-A in the TIP-process, zeolite MFI shows higher fluxes and broader separation capabilities for the C_6 isomers. The MFI morphology in the ZSM-5 morphology appears to be able to separate mono- from dibranched C_6 (Table 6.1) and consequently provides the ability to increase the RON number even further. This separation is however no easy feat when relying on the principle of molecular sieving, as evidenced by several authors. It has been the general belief that zeolites have uniform, rigid and robust framework structures of molecular dimensions and are, therefore, ideally suited to separate molecules on the basis of their size. Hence, silicalite with elliptical pore openings of 0.51 x 0.57 nm should be able to separate mono-branched (0.56 nm) and di-branched (0.62

nm) alkanes on the basis of molecular sieving. The truth however seems to be far more complex as illustrated by Van Koningsveld *et al.* [1] who adsorbed naphthalene in the pores of silicalite-1. Naphthalene is almost 1.5 times larger than the zeolite pore diameter and its adsorption within the framework would not be predicted if the zeolite framework is viewed as being rigid. On closer examination it seems as if zeolites can change the pore shape and size in response to external stimuli such as temperature and pressure, to allow certain molecules to diffuse/be absorbed. In future work the MFI framework could be rendered more rigid through ion-exchange and subsequently used to affect the separation of mono- and di-branched alkanes.

Various synthesis techniques have been applied in this thesis to provide working membranes. Although the membrane behavior in terms of permeance and separation is acceptable, there remains scope for improvement when the membranes are applied in the context of membrane reactors. The flux can be improved, for example, by orientation of the MFI crystals with their straight pore channels perpendicular to the support while the integrity of the layer can be improved with the use of seed crystals. When use is made of oriented seed crystals the two approaches for improved performance can be combined.

The ability to engineer surfaces to allow oriented crystal growth is crucial. The work of Lai *et al.*[2] revealed the importance of integrating the concepts of crystal orientation, film thickness, and the use of a mesoporous silica barrier layer. Such an oriented crystal membrane indeed gave superior performance when applied in the xylene separation process.

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Summary

This dissertation pertains the investigation of a zeolite membrane reactor based process for the hydroisomerization C_5/C_6 paraffins. The introduction of zeolite membrane reactors in an industrial context is strongly dependent on the economics of the process. Despite successes already achieved and the great potential that exist, membrane technology is still far from meeting expectations. To overcome the existing barriers, more systematic analysis of possible advantages or drawbacks due to the introduction of a membrane stage instead of a conventional unit, and considerable multidisciplinary research efforts are needed. Therefore, in order to establish full insight in the possibilities of the application of a zeolite membrane reactor, a multidisciplinary study has been carried out comprising membrane synthesis and performance testing, integration studies and conceptual process design.

Membrane technology is a vibrant industry which can play an important role in realizing global sustainability. This has given rise to an annual market valued at more than US$2 billion, growing at nearly 10% per annum. In *chapter 1* a brief overview of the fundamentals of membrane technology and the key constraints as well as the factors that drive this market, are reviewed. Specific examples of process intensification are given. Furthermore the energy and other environmental benefits that can be realized through the use of zeolites and especially zeolite membranes for separation are outlined. Finally the energy /oil challenges that face modern society, as highlighted by "*Winning the oil end game*", of Amory B. Lovins et al. and how the use of hydroisomerization and process intensification could help relieve some of the difficulties that are experienced, are given.

Despite the significant recent interest in zeolite membranes there are relatively few reports of the application of these membranes in high temperature catalytic membrane reactor applications. *Chapter 2* reviews the progress that has been made in terms of hurdles, such as the relatively high price of membrane units, the difficulty of controlling the membrane thickness, permeance, high temperature sealing, reproducibility and the dilemma of upscaling, that stand in the way of the successful implementation of zeolite membrane reactors in industry.

Chapter 3 describes the test unit that was designed and installed to investigate the membrane reactor concept.

Chapter 4 compares and evaluates the synthesis and mechanism of formation of amorphous and crystalline (zeolite) *continuous* membrane layers. Although continuity is easily achieved for amorphous materials, it is extremely difficult to accomplish for their crystalline counterparts. Crystalline layer formation proceeds along a complicated mechanism involving a nucleation and crystallization step. The nucleation rate must be extremely high to achieve

closest packing of crystallites and optimal film formation. It is furthermore argued that crystal growth rates should be relatively high in order to achieve rough/linear crystal growth which is mandatory for continuous membrane layer formation. The best solution still may however be a combination of steps, i.e. converting an amorphous phase into a crystalline phase, providing membrane continuity as well as unique pore size distribution and high stability.

The successful industrial application of membrane technology hinges on the ability to produce a membrane exhibiting a high/economically feasible permeability which can bring about the desired separation. *Chapter 5* investigates a new approach to prepare an oriented, continuous silicalite-1 membrane which could meet the demands placed by industry. Here the preparation of a continuous MFI membrane which is primarily a- and b-oriented on a porous α-Al_2O_3 substrate utilizing a pre-coated TUD-1 precursor layer, is reported. The precursor layer in this work was completely consumed during the synthesis of the MFI layer most probably due to Ostwald's rule of successive phase transformation. In contrast, only a discontinuous MFI membrane was obtained on an uncoated α-Al_2O_3 substrate.

The refiner is currently faced with increasingly stringent fuel specifications as environmentally driven regulations are enacted worldwide. One of the main responses of the refining research and development community to the challenges posed by environmental and market demands, is a renewed interest in paraffin hydroisomerization technology. *Chapter 6* investigates the competitiveness and economic feasibility of the hydroisomerization process applicable to the C_5/C_6 cut of Naphtha, incorporating a zeolite membrane reactor. The conceptual design of two membrane-reactor-based processes for the hydroisomerization of C_5/C_6 (one with a recycle stream, where both normal and single branched alkanes are sent to the catalyst bed and a single-pass process which allows only normal alkanes to reach the catalyst bed) and an economic evaluation of the two processes which were compared to state-of-the-art technology, are presented. The recycle and single-pass process, delivered a product stream with a RON value of 87.9 and 87.2. An investment cost of 77.2 and 33.5 MUS$ were obtained. It is concluded that membrane reactor reforming still face and uphill battle towards commercialization, and will probably only gain wide acceptance if the membrane fluxes are improved significantly as compared with the assumptions used in this work whilst also maintaining a high selectivity and if furthermore membrane cost are reduced by at least a factor 10.

Chapter 7 gives an experimental investigation into the combination of the hydroisomerization reaction and separation of linear alkanes from the product, in a single membrane reactor unit. The influence of various process conditions on the single gas as well as hydrocarbon mixture permeation through an asymmetric supported silicalite-1 membrane was studied and the relative importance of a number of operating modes presented. The results indicate that linear molecules can be separated from mono- and di-branched components in a gas mixture with a selectivity factor of > 20 with a zeolite membrane under dedicated parameter settings. The RON-value of the product was calculated to be as high as 68 – this is 28 points higher than the feed value. Further investigation indicated that the STY/ATY ratio for the reactor could fall within the limits of technical feasibility with optimised membrane preparation.

Finally some general conclusions and the future outlook for a membrane reactor based hydroisomerization process are highlighted in *Chapter 8.*

Samevatting

In hierdie tesis word die aanwending van 'n zeoliet-membraanreaktor in die hidro-isomerisasieproses van C_5/C_6 paraffiene, ondersoek. Die invoering van zeoliet-membraanreaktore in die industriële konteks is grootliks afhanklik van die ekonomiese lewensvatbaarheid van die proses. Ten spyte van welslae reeds behaal en die enorme potensiaal wat bestaan, is membraantegnologie nog vêr daarvan om verwagtinge te ewenaar. 'n Meer sistematiese analiese van moontlike voor- en na-dele voortvloeiend uit die inkorporering van 'n membraanstap in stede van 'n konvensionele eenheid, en aansienlike multi-dissiplinêre navorsing word benodig. Dus, ten einde volledige insig in die moontlikhede wat die toepassing van zeoliet-membraanreaktore bied te verkry, is 'n multi-dissiplinêre studie uitgevoer wat insluit membraan-sintese en –prestasie evaluering, integreringstudies en konseptuele prosesontwerp.

Membraantegnologie is 'n opwindende industrie wat 'n baie belangrike rol kan speel in die realisering van lewensvatbaarheid. Dit het aanleiding gegee tot 'n jaarlikse mark ter waarde van US$2 biljoen, wat 'n groei toon van om en by 10%/jaar. In *Hoofstuk 1* word 'n kort oorsig gegee oor die grondbeginsels van membraantegnologie, terwyl die sleutelbeperkings sowel as die faktore wat hierdie mark aandryf ook hersien word. Spesifieke voorbeelde van proses-intensifisering word gegee. Verder word die energie en omgewingsvoordele wat bereik kan word deur die gebruik van zeoliete en meer spesifiek, zeolietmembrane vir skeiding uitgelig. Laastens word die energie/olie uitdagings wat die moderne samelewing in die gesig staar, soos beklemtoon deur "*Winning the oil end game*" van Amory B. Lovins et al., en hoe die gebruik van hidro-isomerisasie en prosesintensifisering kan help om sommige van die probleme te verlig, gegee.

Ten spyte van die aansienlike belangstelling wat huidiglik getoon word in zeoliet-membrane is daar relatief min verslaggewings van die toepassing van hierdie membrane in hoë-temperatuur katalitiese membraanreaktore. *Hoofstuk 2* gee 'n oorsig van die vordering wat gemaak is in terme van struikelblokke, soos die relatief hoë prys van membraanmodules, die moeilike taak om membraandeursnee en permeansie te beheer en hoë-temperatuur seëling te verkry, herhaalbaarheid en die dilemma van opskallering, wat in die pad staan van die suksesvolle implimentering van zeoliet-membraan-reaktore in die industrie.

Hoofstuk 3 beskryf die toetsingseenheid wat ontwerp en opgestel is om die membraanreaktor-konsep te ondersoek.

Hoofstuk 4 vergelyk en evalueer die sintese en vormingsmeganisme van amorfe en kristallyne (zeoliet), *kontinue* membraanlae. Alhoewel kontinuïteit maklik verkry kan word met amorfe materiale, is dit uiters moeilik om te verkry met hul kristallyne ekwivalente. Die kristallynelaag vormingsproses vind plaas volgens 'n komplekse meganisme wat 'n nukleasie en kristallisasie stap insluit. Die nukleasie-snelheid moet uitermate hoog wees om die naaste pakking van kristalle en optimale filmvorming te verkry. Dit word verder geargumenteer dat die snelheid van kristalgroei, relatief hoog moet wees om rowwe/lineêre kristalgroei te verkry wat noodsaaklik is vir die vorming van 'n kontinue membraanlaag. Die beste oplossing steeds mag egter 'n kombinasie van stappe wees, m.a.w. die omskakeling van 'n amorfe fase in 'n kristallyne fase, wat membraankontinuïteit sowel as 'n unieke porie-grootte verspreiding en hoë stabiliteit sal bied.

Die suksesvolle industriële toepassing van membraantegnologie berus op die vermoë om 'n membraan wat oor 'n hoë/ekonomiese uitvoerbare permeabiliteit beskik te produseer, wat die verlangde skeiding kan teweegbring. *Hoofstuk 5* ondersoek 'n nuwe benadering om so 'n georiënteerde, kontinue silikaliet-1 membraan te produseer, wat eise gestel deur die industrie kan bevredig. Hier word die sintese van 'n kontinue MFI membraan wat hoofsaaklik a- en b-georiënteerd is, op 'n porieuse α-Al_2O_3 substraat, deur gebruik te maak van 'n voorafbedekte TUD-1 voorgangerlaag, gerapporteer. Die voorgangerlaat in hierdie werk is geheel en al verteer deur die sintese van die MFI-laag waarskynlik as gevolg van Ostwald se reël van opeenvolgende fase transformasie. In teenstelling, is slegs 'n diskontinue MFI-membraan verkry op 'n onbedekte α-Al_2O_3 substraat.

Die raffineerder word tans gekonfronteer met toenemende streng brandstofspesifikasies soos wat omgewingsaangedrewe regulasies wêreldwyd verorden word. Een van die hoof reaksies van die raffinerings navorsings- en ontwikkelings- gemeenskap op die uitdagings gestel deur omgewings- en mark- eise, is 'n hernude belangstelling in paraffien-hidroisomerisasietegnologie. Hoofstuk 6 ondersoek die mededingbaarheid en ekonomiese uitvoerbaarheid van 'n hidro-isomerisasieproses wat 'n zeoliet-membraan-reaktor inkorporeer, soos toegepas op die C5/C6 segment van Nafta. Die konseptuele ontwerp van twee membraanreaktor-gebasseerde prosesse vir die hidro-isomerisasie van C_5/C_6 (een met 'n hersirkuleringstroom, waar beide lineêre en enkelvertakte alkane na die katalisbed gestuur word, en 'n enkel-deurvloei proses wat slegs lineêre alkane toelaat om die katalisbed te bereik) en 'n ekonomiese evaluasie van die twee prosesse 'n vergelyking díe van kontemporêre tegnologie, word voorgelê. Die hersirkulering- en enkel-deurvloei- proses, het 'n produkstroom met RON-waarde van 87.9 en 87.2 onderskeidelik gelewer. 'n Investeringskoste van 77.2 en 33.5 MUS$ is opgelewer. Daar word tot die gevolgtrekking gekom dat membraanreaktor-omvorming nog steeds 'n opdraende stryd in die gesig staar ten opsigte van kommersialisering, en sal waarskynlik slegs breë aanvaarding geniet indien membraanflukse merkwaardig verbeter kan word in vergelyking met die aannames wat in die studie geneem is terwyl hoë selektiwiteit behoue bly en membraankoste verder verminder word met ten minste 'n faktor 10.

Hoofstuk 7 loods 'n eksperimentele ondersoek na die kombinasie van die hidro-isomerisasie reaksie en die skeiding van lineêre alkane van die produk, in 'n enkel-membraanreaktor-eenheid. Die invloed van verskeie proseskondisies op die enkelgas- sowel as koolwaterstofmengsel-permeasie deur 'n assimetriese ondersteunde silikaliet-1 membraan is bestudeer en die relatiewe belang van werkskondisies word gegee. Die resultate dui aan dat n-, mono- en di-vertakte komponente in 'n gasmengsel geskei kan word met 'n selektiwiteitsfaktor van > 20 met behulp van 'n zeolietmembraan onder toegewyde parameterstellings. Die RON-waarde is bereken om so hoog te wees as 68 – dit is 28 punte hoër as die toevoerwaarde. Verdere ondersoek het aangetoon dat die STY/ATY verhouding vir die reaktor binne die grense vir tegniese uitvoerbaarheid kon val met ge-optimaliseerde membraanbereiding.

Ten slotte word 'n paar algemene gevolgtrekkings en die toekomsuitkyk vir 'n membraanreaktor-gebasseerde hidro-isomerisasie proses uitgelig in *Hoofstuk 8*.

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E.E. McLeary

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Curriculum Vitae

Engela Elizabeth McLeary was born on the 30th of June 1974 in Lichtenburg, South Africa. In 1992 she obtained her matriculation certificate at the Bergvlam High School, with distinction. In 1995 she obtained a B.Sc. in chemistry and computer science, cum laude at the University of Potchefstroom. At this point she was asked to specialize in Polymer Science by the Atomic Energy Coorporation with whom she held a bursary. In 1996 she obtained a B.Sc hons (Polymer Science), cum laude at the University of Stellenbosch. In 1997 she started her M.Sc. (Polymer Science) studies which she carried out under supervision of Prof. R.D. Sanderson (University of Stellenbosch) and Prof. W.F. Maier (Max Planck Institute, Mülheim-an-der-Ruhr, Germany). She obtained her M.Sc. (Polymer Science), cum laude from the University of Stellenbosch in 1999. On the 28th of August 1999 she married James Breton McLeary and in September 1999 began her Ph.D. studies under supervision of Prof. Dr. J.C. Jansen at the Technical University of Delft on "C_5/C_6 hydroisomerization in a zeolite membrane reactor". In 2001 she was employed as lecturer by the University of Stellenbosch and continued her Ph.D. studies on a part-time basis. On the 2nd of January 2005 she welcomed her first born, James Hendrik McLeary into the world. The results of the research carried out during her Ph.D. studies are described in this dissertation.