DESIGN OF A CERAMIC ZEOLITE MEMBRANE

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ABSTRACT

The step-wise preparation of a new type of ceramic zeolite membrane configuration, based on large silicalite (ZSM-5) crystals is reported on. The deposition of a gas tight matrix is crucial within the membrane preparation procedure. The consolidation of the zeolite crystals to the macroporous support by means of a porous interlayer facilitates the membrane preparation. The stacking of flat membrane elements for the production of zeolite membrane modules is discussed.

INTRODUCTION

In the field of ceramic membranes for gas separation, much research is directed towards a decrease of pore size in order to achieve separation factors above Knudsen selectivity. In addition, when combining gas separation membranes and chemical reactors, substantial improvement of present heterogeneous catalytic reactions are to be expected [1-3]. An overview of inorganic membranes is given by Hsieh [3].

Due to the narrow pore size distribution, the incorporation of zeolites in a separative film may lead to membranes with true molecular sieve characteristics. Moreover, the crystallinity of zeolites ensures the thermo-stability up to well specified conditions, allowing full regeneration in case of fouling. In contrast to crystalline materials, microporous amorphous materials will tend to degrade at high temperatures, resulting in either impermeable films or membranes showing Knudsen selectivity. Nonporous silica membranes may lead to very selective membranes for dehydrogenation, although selectivity and permeability were found to decrease in time [4].

Several procedures for preparing zeolite membranes have been patented. Filter cakes of zeolite crystallites were claimed to result into a zeolite membrane (e.g. [5]). However, if a true filter cake is considered, either a gas tight film or a porous film showing Knudsen selectivity is expected to be produced.

Several patents have been dedicated to in situ crystallization, either on top or within a macroporous support (e.g. [6]). As continuous zeolite films may be rather sensitive towards cracking, crystallization within a macroporous support is to be preferred. When dispersed in a mechanically stable macroporous support, the zeolite material will be resistant towards mechanical stress. Strong adherence has been achieved during in situ growth of zeolite crystals on various metal substrates [7]. Full coverage, however, may be hard to achieve. Stable silica membranes have been prepared as a thin

layer ($< 5 \mu\text{m}$) within a porous metal substrate [8].

A different approach starts from a monolayer of relatively large zeolite crystals, embedded in a gas tight matrix on a macroporous support. The gas tight matrix ensures mass transport to proceed exclusively via the zeolite micropores. In addition, the materials choice of zeolite crystals, gas tight matrix, and macroporous support can be optimized to produce a thermomechanically stable composite membrane. Here we report on the utilization of different deposition techniques in a step-wise production of ceramic zeolite membranes starting from large silicalite crystals.

STEP-WISE PREPARATION PROCEDURE

The present approach towards a ceramic zeolite membrane is a step-wise preparation, involving three separate stages (cf. Figure 1): (I) synthesis of zeolite crystals of equal shape and size, (II) orientation and fixation of zeolite crystals on top of a macroporous support, and (III) deposition of gas tight matrix material, either selectively in between the zeolite crystals, or as a homogeneous film covering both the zeolite crystals and the macroporous support. In the latter case a careful removal of matrix material from the zeolite crystals is required to renew mass transport through the membrane.

Figure 1: Step-wise preparation of the ceramic zeolite membrane.

I: ZEOLITE SYNTHESIS

Silicalite (ZSM-5, MFI-type, $\text{Si}/\text{Al} > 1000$) has been chosen as the starting zeolite material for a number of reasons: (1) silicalite crystals of equal shape and size can be synthesized in high quantities, (2) the three-dimensional pore structure in relation to the crystal shape is optimal for the present membrane concept, (3) silicalite is thermostable up to at least 900°C .

As MFI-type zeolites are widely applied catalysts (e.g. for catalytic alkylation), much research has been directed towards synthesis and characterization. The highly reproducible synthesis according to Sand [9] results in prismatic shaped crystals ($35 \times 30 \times 170 \mu\text{m}$). Recently, it has been shown that the addition of vanadium to the original synthesis mixture results in relatively flat crystals [10], generally referred to as cubic shaped crystals.

II: ORIENTATION AND FIXATION

Both crystal forms are readily oriented on any sufficiently flat surface at high surface coverages (up to 80% of the total surface area). A monolayer of zeolite crystals on top of a macroporous support is consolidated by means of an adhering film. An optimal procedure to fabricate the zeolite/macroporous support composite starts from a monolayer of silicalite crystals, oriented on a nonporous glass plate. On top of the macroporous support (e.g. α -alumina), an adhering film is deposited, in which the monolayer of zeolite crystals is impressed. Several routes for the preparation of the adhering film have been explored.

The deposition of a silicon rubber film can be applied to prepare thin silica films [8]. The general procedure is based on the temporary filling of a macroporous support with a liquid of high density. Upon calcination ($> 450^{\circ}\text{C}$), a very thin porous silica film with a narrow pore size distribution (diameter appr. 4 nm) results.

In the preparation of an all-ceramic zeolite membrane the application of a thin, commercially available clay suspension (De Porceleyne Fles, Manufacturer of Delft Blue, Delft, The Netherlands) has proven to be very successful. The thickness of the deposited clay film can be controlled by means of dipcoating. In order to obtain a stable composite, the clay has to be calcined at 900°C (rate $1^{\circ}\text{C}/\text{min}$, annealing for 1 hour).

III: GAS TIGHT MATRIX DEPOSITION

While depositing matrix material, deposition in between the zeolite crystals and the macroporous support must be avoided. The presence of a porous interlayer, partially incorporating the zeolite crystals, facilitates this critical preparative step significantly (cf. Figure 2).

Figure 2: Schematic representation of the present ceramic zeolite membrane configuration.

Two well-known deposition techniques have been applied: sol-gel and Chemical Vapour Deposition (CVD). As an alternative, the utilization of low melting glazes has been explored. These techniques may be applied in various manners, from which an optimal preparation strategy can be chosen.

For sol-gel techniques, good adhesion of the sol to the external zeolite surface is required in order to produce a gas tight film. This seems to contradict the requirement for selective deposition besides the zeolite crystals. In a separate study, however, it has been shown that selective deposition is possible by means of dip-coating [11]. A disadvantage of all

sol-gel techniques is that the deposited films are very sensitive to cracking upon drying and calcining [2,12].

Due to the fact that deposition by means of CVD proceeds via the gas phase, even very narrow spaces in between the zeolite crystals will be covered. As a macroporous substrate is involved, the alternative technique of Chemical Vapour Infiltration (CVI) will be most effective. It will be shown that selective deposition besides the zeolite crystals is feasible, applying a special CVI-technique. Obviously, a disadvantage of CVD-processes is that deposition on top of the zeolite crystals may occur.

An alternative for the techniques discussed above is the application of low temperature glazes. Generally, deposition is achieved by immersing a porous substrate in a glaze suspension, which resembles dip-coating. The use of glaze suspensions is advantageous, because severe shrinkage of the deposit does not occur. In addition, a thermomechanically stable system is obtained as the bonding process occurs at high temperature. Moreover, the optimal glaze composition can be varied with respect to the thermal expansion coefficients of the other materials.

With all three techniques selective deposition in between the zeolite crystals has been achieved, which is discussed in three examples.

1) Sol-gel of silica

On top of a porous sintered metal support a thin film of silicone rubber was applied, in which several silicalite crystals were impressed. On calcining (450°C, rate 100°C/h), a thin silica film resulted, from which the zeolite crystals were protruding. The metal support was filled temporarily with 1,1,1-trichloroethane, and successively a tetraethyl orthosilicate (TEOS) sol was spread over the support. The solvent (ethanol) is rapidly dissolving in 1,1,1-trichloroethane, thus resulting in fast gelation besides the zeolite crystals.

Deposited films obtained in this way turned out to be very sensitive towards cracking, even upon careful drying only. The optimal sol composition was found to be TEOS:H₂O:ethanol = 1:2:8. Figure 3 shows a SEM picture of two separate silicalite crystals on the support, embedded in a crack-free silica gel. If more crystals were grouped together on the support, cracking could not be avoided, in qualitative agreement with dip-coating experiments of γ -alumina [11].

15 μ m

Figure 3: Two silicalite crystals embedded in a silica gel using a sol-gel technique.

2) EVD of yttria-stabilized zirconia

By means of Electrochemical Vapour Deposition (EVD), yttria-stabilized zirconia (YSZ) films can be grown on top of a macroporous support [13,14]. YSZ-films are employed in Solid Oxide Fuel Cells (SOFC) as an oxygen ion conducting solid electrolyte. Briefly, chlorides of zirconium and yttrium, and a mixture of steam and oxygen are separately introduced on two sides of a macroporous support. During the first stage of the process (CVD-stage), reaction takes place within the macroporous support, resulting in a YSZ-deposit. This stage may be referred to as chemical vapour infiltration (CVI), as the reactants are diffusing into a porous substrate. The second stage (EVD) starts after a gas tight deposit is formed. Due to the oxygen ion conductivity, film growth on the metal chloride side proceeds while oxygen ions are conducted through the deposit from the oxygen/steam side. The EVD-process has been used to deposit selectively in between the zeolite crystals on a macroporous support. Silicalite crystals were fixed on a macroporous calcium-stabilized zirconia support by means of a thin clay film, as discussed previously.

The composite was fastened on an α -alumina tube with a gas tight kit (Aremco 569). The EVD-process was performed at 900°C for 1.5 hours. A YSZ-film (15 μm) in between the zeolite crystals was deposited (Figure 4), although some deposition had occurred on top of the zeolite crystals. Moreover, the silicalite crystals were cracked and partly transformed into a phase containing oxides of silicon, yttrium, and zirconium.

Figure 4: Silicalite crystal in a YSZ-film, as deposited by the EVD-process on a macroporous support; around the crystal a transformed phase is formed comprising silicon, yttrium, and zirconium oxides.

Considering the presence of steam and metal chlorides at high temperature, the EVD-process may not be the optimal route to a ceramic zeolite membrane. Nevertheless, the possibility to control the film growth to a selected area is shown. Provided that local deposition on top of the macroporous support can be strictly controlled, the porous interlaying clay film will avoid the deposition of matrix material in between the zeolite crystals and the macroporous support. Other CVI-processes can be performed under less severe conditions, resulting in a gas tight film as well [4].

3) Dip-coating of a lead-boron glaze

On top of a two-layer α -alumina support, silicalite crystals were oriented [11]. The crystals were consolidated with a thin clay film by means of dip-coating. After calcining at 900°C, a lead-boron silicate powder (Ferro, Rotterdam, The Netherlands) was deposited besides the crystals, again, by means of dip-coating, and calcined at 550°C (rate 1°C/min, annealing for 1 hour). A thin glaze film on top of the clay interlayer was obtained (Figure 5). Good adherence is achieved, due to the occurrence of a melting phase at high temperature.

Figure 5: Four silicalite crystals on top of a two-layer α -alumina support, embedded in a clay film. A thin glaze film is deposited on top of the clay film.

IV: MEMBRANE MODULE DESIGN

The construction of a membrane module may be referred to as the fourth stage in the production of ceramic zeolite membranes. A high membrane surface to module volume ratio is a prerequisite as low permeabilities are expected for this type of membrane. Therefore, the effective membrane surface area should be maximal. The production of flat membrane elements is favoured, because the orientation of zeolite crystals on flat surfaces leads to a high surface coverage. Stacking of these membrane elements (Figure 6) leads to a relatively high membrane surface to module volume ratio.

Figure 6: Schematic view of the ceramic zeolite membrane module design.

A similar design has been suggested for Solid Oxide Fuel Cells [15]. The construction of ceramic zeolite membrane modules will, however, be less complex, because lower process temperatures are involved. In addition, the materials choice can be exclusively based on thermomechanical considerations.

CONCLUSION

Within the present step-wise preparation of a ceramic zeolite membrane, starting from large silicalite crystals, various supports and gas tight matrix materials may be used. A porous interlayer to consolidate the zeolite crystals on top of the macroporous support facilitates the selective deposition of the gas tight matrix besides the zeolite crystals. The application of sol-gel techniques is limited due to the fact that the gas tight matrix is deposited under ambient conditions. During heat treatment, cracking of the composite film may be difficult to avoid. Both CVD-techniques and the application of glaze powders are more appropriate as the gas tight matrix is produced at high temperature. For the preparation of model membranes, in order to study the membrane characteristics, the application of low temperature glazes is preferred.

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LITERATURE

1. J.N. Armor, Appl. Catal. **49**, (1989), 1-25.
2. M.A. Anderson, F. Tiscareno-Lechuga, Q. Xu, C.G. Hill, A.C.S. Symp.Ser. **437**, "Novel Materials in Heterogeneous Catalysis", (Ed. R.T.K. Baker, L.L. Murrell), (1990), 198-215.
3. H.P. Hsieh, Inorganic Membrane Reactors - A Review, AIChE Symp.Ser. **5**, **85**, No. 268, (1989), 53-67.
4. C.E. Megiris, S.W. Nam, G.R. Gavalas, Proceedings of ICIM-1, Montpellier, France, (1989), 355-360.
5. G. Bellussi, F. Buonomo, A. Esposito, M. Clerici, U. Romano, Eur. Patent Appl. No. 265 018 (27 April 1988).
6. H. Suzuki, U.S. Patent No. 4 699 892 (13 October 1987).
7. K.E. Creasy, Y. Deng, J. Park, E.V.R. Borgstedt, S.P. Davis, R. Grosso, S.L. Suib, B.R. Shaw, paper presented at MRS Spring Meeting, Anaheim, California, U.S.A., 1-3 May 1991.
8. A. Mulder, E.R. Geus, P.A. Dekker, J.W. Geus, paper to be published in ICIM2-91 proceedings.
9. M. Ghamami, L.B. Sand, Zeolites **3**, (1983),
10. M.S. Rigutto, H. van Bekkum, Appl. Catal. **68**, (1991), L1-L7.
11. E.R. Geus, H.M. van Veen, H.J. Veringa, J. Schoonman, H. van Bekkum, paper to be published in ICIM2-91 proceedings.
12. G.J. Brinker, G.W. Scherer, Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing, (Academic Press, London, 1990), 453.
13. U.B. Pal, S.C. Singhal, proceedings of 1st Int.Symp.on Solid Oxide Fuel Cells, Volume 89-11, The Electrochemical Society, (1989), 41-56.
14. J. Schoonman, J.P. Dekker, J.W. Broers, N.J. Kwiwet, Mat.Res.Soc.Symp.Proc. Vol. 210, Materials Research Society, (1991), 13-29.
15. P.A. Lessing, L.W. Tai, K.A. Klemm, proceedings of 1st Int.Symp.on Solid Oxide Fuel Cells, Volume 89-11, The Electrochemical Society, (1989), 337-360.