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A novel method for the synthesis of ZSM-5 zeolite membranes on a porous alumina tube: the role of a dry-gel barrier in pores

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An aluminosilicate gel barrier as a zeolite precursor is first incorporated in the pores of an alumina support tube and then subjected to hydrothermal crystallization, leading to ZSM-5 zeolite membranes with high compactness at the molecular level.

The potential industrial applications of zeolite membranes in continuous separation and reaction–separation processes on the basis of molecular sieving have recently motivated many attempts and efforts in zeolite membrane preparation. The last ten years have witnessed significant progress in the demonstration of the potential of zeolite membranes to separate hydrocarbon gas mixtures and organic/aqueous mixtures using MFI and A type zeolite membranes.[1,2] *In situ* hydrothermal crystallization in solution or the vapor phase is mainly applied in zeolite membrane synthesis.[3–5] However, presently good quality zeolite membranes are obtained in plate form rather than in tube form though the latter is preferable for industrial applications owing to its large volume/area ratio. It appears to be difficult to adapt a synthesis method applied to plate-form zeolite membranes for tubular zeolite membranes since the membrane quality is sensitive to the geometry of a substrate (plate *vs*. tube) and the manner of contacting a substrate with a zeolite synthesis mixture. Therefore, synthesis of tubular zeolite membranes is still a subject of importance and remains to be addressed.

We note in the literature[6–10] that the separation performance of zeolite membranes is strongly related to the degree that zeolite crystallites are incorporated in the pores of the substrate during hydrothermal crystallization. In addition, in view of the methodology for zeolite membrane preparation it seems that plugging pores of a substrate with inter-grown zeolite crystals is easier to achieve than growing a continuous defect-free zeolite layer on top of a substrate. Therefore, based on the concept of pore plugging, we anticipated developing a novel synthesis method for tubular zeolite membranes.

Here we outline such a method by the synthesis of ZSM-5 zeolite membranes using a tubular substrate. Our synthetic strategy was to incorporate a highly dense aluminosilicate gel barrier in the substrate pores followed by hydrothermal crystallization. The method can generate a compact zeolite barrier and appears to be reproducible.

In our synthesis, a commercial porous alumina tube of 10 mm outside diameter and 7 mm inside diameter and *ca*. 50 mm length was employed as the substrate. The tube has a multilayer structure with a 0.1 μm porous outer layer. One end of the tube was sealed and the other end was connected with a dense alumina tube *via* a high-temperature glaze. The synthesis procedure consisted of two sequential processes. The first was to incorporate an aluminosilicate gel barrier in the outer layer pores by the urea technique. The substrate was first impregnated *in vacuo* with an alcohol-based solution containing $Si(OEt)_4$, $Al(NO_3)_3$, $CO(NH_2)_2$, H_2O (EtOH as balance). The impregnated substrate was dried at *ca*. 50 °C to such an extent that all the solution was sucked by and further concentrated in the outer layer pores by capillary action. The sample was then placed in a closed glass vessel at 90 °C. Thus, precipitation of $Si(OEt)_4$ and $Al(NO_3)_3$ occurred exclusively in the pores by homogeneous alkalinization from decomposition of $CO(NH_2)_2$ [$CO(NH_2)_2 + 3H_2O \rightarrow 2OH^- + 2NH_4^+ + CO_2$]. The above steps were repeated until the N_2 gas flow of the sample was below 10^{-9} mol m^{-2} s^{-1} Pa^{-1} at room temperature. The second process was to convert the aluminosilciate gel barrier to a desired zeolite barrier by hydrothermal treatment. The modified substrate tube was filled with $Si(OPr)_4$ (bp 225 °C) and then placed into a solution of composition $0.005NaAlO_2 : 0.55TPABr : 0.42NaOH : 100H_2O$ in a Teflon vessel. In this arrangement, a reactive interface at the incorporated gel barrier was developed between the two separate liquids. Thus, during hydrothermal treatment, hydrolysis of $Si(OPr)_4$ supplied an additional silica source to the crystallization front while the gel barrier was being converted to zeolitic materials. Hydrothermal treatment was performed in a stainless steel autoclave at 190 °C for 10 days. When the hydrothermal treatment was complete, the sample was thoroughly washed with H_2O and dried at 50 °C overnight and then carefully calcined at 400 °C for 12 h to remove the TPA occluded within the zeolite channels.

In each synthesis experiment, the membranes were shown by XRD to be highly crystalline, pure zeolite ZSM-5. Fig. 1 shows SEM micrographs of the cross-section of a representative ZSM-5 zeolite membrane. From the micrographs, the following two points can be made. (a) As seen in Fig. 1A, the substrate outer layer displays an SEM contrast comparable to those of the ZSM-5 zeolite films indicating that some zeolitic materials were formed from the aluminosilicate gel barrier incorporated in the pores. (b) It was observed that 10 and 100 μm ZSM-5 zeolite films grew on the inner and outer surface, respectively (Fig. 1B and C). These films showed significant morphological differences. The crystals of the inner zeolite film were essentially parallelepipeds of size *ca*. 30 μm and well intergrown. In contrast, those of the outer zeolite film were coffin-shaped and much larger being *ca*. 80 μm along the *c*-axis. It was also observed that few non-zeolitic pathways existed in both the inner and outer zeolite film, which act as defects for gas separation.

A dead-end method was applied for gas permeation measurements with pure He, N_2, CO_2, *n*-butane and isobutane. The permeation measurements were performed at room temperature with the permeation side set at an atmospheric pressure. The gas flow rates were measured with a mass flow meter. The flow rates were plotted *vs*. the kinetic diameters of gas molecules in Fig. 2. As seen, the permeance of all the gases showed a good correlation with their kinetic diameters except for *n*-butane and isobutane. Noble's group reported that an MFI zeolite membrane on a 5 nm γ–alumina tubular substrate showed a *n*-butane/isobutane perm-selectivity of 3–20 and a *n*-butane permeance of

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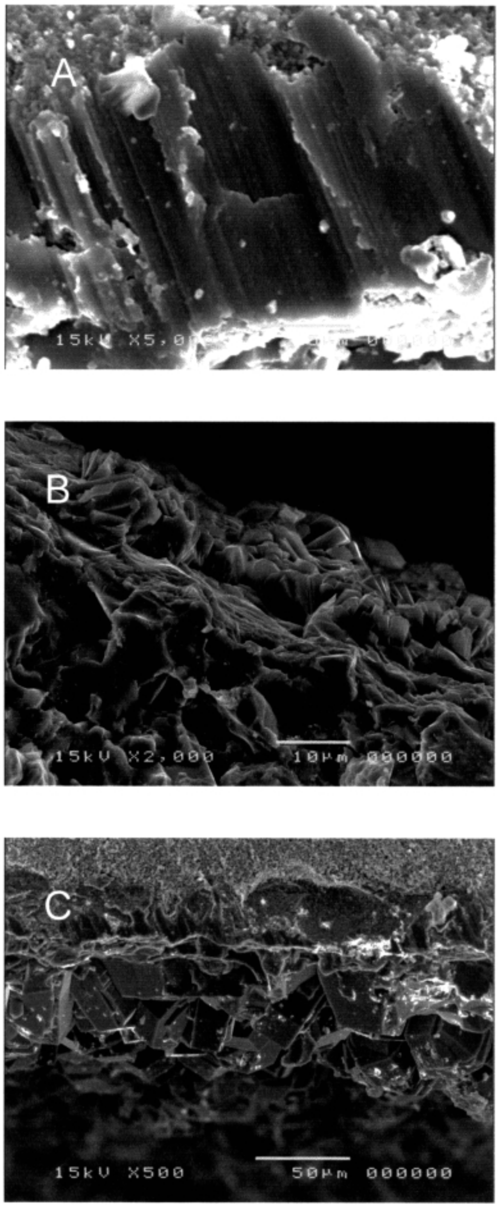

Fig. 1 SEM micrographs of a cross-section of the ZSM-5 zeolite membrane: (a) the 0.1 µm porous outer layer, (b) the inner layer and (c) the outer layer.

ca. 10^{-9} mol m^{-2} s^{-1} Pa^{-1}. The ZSM-5 zeolite membrane in the present study showed a comparable permeance although it exhibited no *n*-butane/isobutane perm-selectivity.

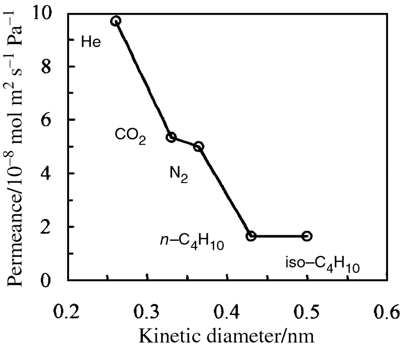

Fig. 2 Permeance of pure gases through the ZSM-5 zeolite membrane *vs.* their kinetic diameters.

Accordingly, a highly compact zeolite barrier with few defects has been formed within and on the substrate. Further, on the basis of SEM observations, zeolite barriers, mainly that in the pores, led to a significant contribution to gas separation. The reason for the formation of defects could be that the reactive interface has insufficient additional aluminosilicate at the crystallization front during crystallization and contracting of the gel barrier, or/and the gel barrier was partially dissolved during hydrothermal treatment.

In summary, the present study has explored a new route for the preparation of tubular zeolite membranes. The resulting ZSM-5 zeolite membrane shows the potential of the novel preparation method. However, improvement of the membrane integrity with regard to separation performance is underway by studying the process kinetics of the preparation method.

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