Preparation of a Completely Oriented Molecular Sieve Membrane

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It would be of significant interest if the microstructure of materials could be controlled by modification of the molecular structures of the starting materials. It has been shown that organic compounds influence the crystallization of zeolites.[1–7] For instance, the addition of triethanolamine (TEA) to the reaction mixture for the synthesis of LTA-type zeolite ($NaAlSiO_4 \cdot x H_2O$) allows the growth of giant crystals[4–7] as a result of modification of the molecular structure of the Al species by TEA.[6, 7] Zeolites are especially interesting because they can provide unique molecular selectivity to devices such as chemical sensors and catalyst membranes.[8–11] If a continuous zeolite coating with oriented channels were realized, a novel device in which the oriented channels could effectively control the access of molecules to the underlying surface could be constructed. So far, most zeolite films and membranes have random or partial orientation[12–23] or large voids between oriented particles.[24–26] The control of nucleation and crystal growth of zeolites is of great importance for the preparation of continuous oriented zeolite films and membranes. This objective may be achieved by introducing organic compounds that modify the molecular structure of the starting materials and lead to better control of crystallization.

Here we show that a completely oriented and continuous LTA-type zeolite membrane can be prepared by intergrowth of oriented seed crystals, which were attached to a glass plate by dip-coating from a suspension of seed crystals (Figure 1). An organic ligand was then used to preferentially enhance the growth of the seeds.

The seed crystals of LTA-type zeolite were prepared from an aqueous mixture of $NaAlO_2$, $Na_2SiO_3 \cdot 9H_2O$, and $N(C_2H_4OH)_3$ (TEA) by hydrothermal treatment. Only loose crystals were formed when the aqueous mixture was used without addition of an organic ligand such as TEA. The addition of TEA led to the formation of crystals with a cubic morphology. The size distribution of the particles was uniform, and the average edge length of the cubes was about 10 μm. The powder X-ray diffraction (XRD) pattern of the product (see Figure 3a) was consistent with that of LTA-type zeolite.

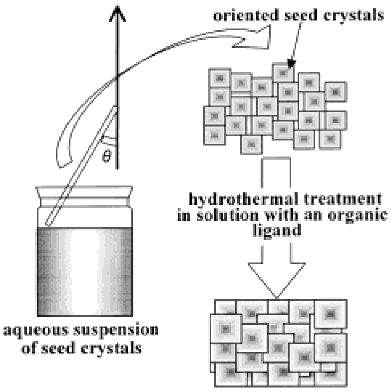

Figure 1. Schematic diagrams of the attachment of seed crystals to the substrate and the growth of oriented seeds to give a completely oriented molecular sieve membrane.

The seed crystals were attached to a glass substrate (Corning #1737) by the dip-coating method. The substrate was dipped into an aqueous suspension of seed crystals with a concentration of 180 g L^{-1}, withdrawn at a rate of 2 cm min^{-1}, and then dried at 110 °C for 10 min. To increase the number of crystals attached to the plate and thus maximize the coverage of the plate, the dip coating was conducted on a tilted substrate as shown in Figure 1. Figure 2 shows optical micrographs of seed layers that were dip-coated onto substrates tilted by 0 to 45°. The number of seeds attached to the substrates increased with increasing tilt angle of the substrate. Large interparticle voids were no longer observed at a tilt angle of 45°. Attachment of the seeds occurred only on the upper side of the substrate. Therefore, the substrate was coated once on each side. In the second coating step, no seeds were removed from the lower surface of the substrate. Scanning electron microscopy (SEM) showed that a single layer of seeds was attached to the substrate with good orientation of the (100) plane parallel to the substrate surface. This indicates that the bonding between the substrate and the seeds is much stronger than that between the seeds. As shown in Figure 3b, the XRD pattern of the seed-coated substrate exhibited only the peaks with (h00) plane indices; this supports the above observations. The LTA-type zeolite has a channel in the ⟨100⟩ direction, which is perpendicular to the (100) plane due to the cubic symmetry of LTA-type zeolite.[27]

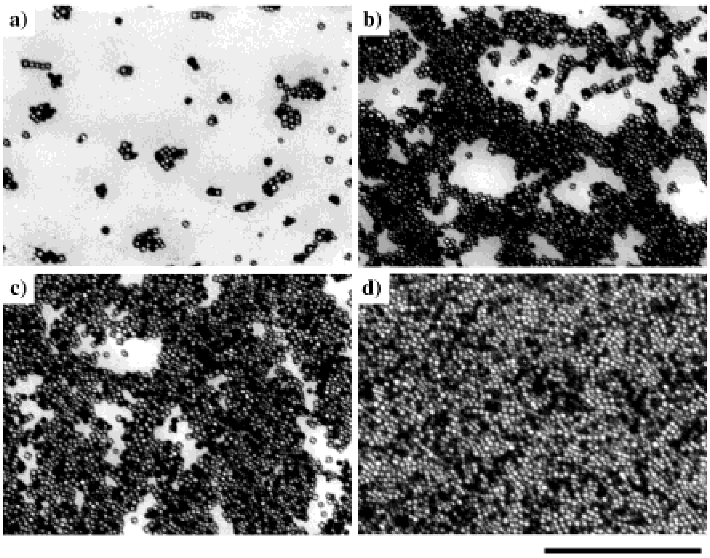

Figure 2. Variation of the amount of seed crystals attached to the substrate with the tilt angle of the substrate in the dip coating process. a) 0°, b) 15°, c) 30°, and d) 45°. Scale bar: 300 μm.

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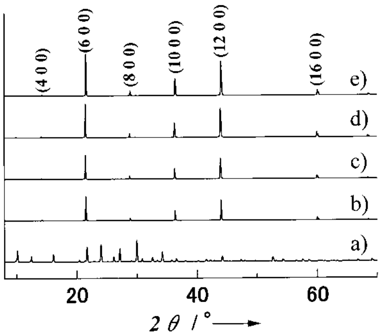

Figure 3. XRD patterns of the seed crystals (a), of the seed crystals attached to the substrate (b), and of the specimens heat-treated in the suspension with bis-tris/Al ratios of 0 (c), 2 (d), and 4 (e).

Therefore,in such an arrangement of the seed crystals on the substrate, the channels are normal to the surface.

The substrates with oriented seeds were hydrothermally treated in the aqueous reaction mixture to fill the spaces between the seeds by intergrowth. The chemical composition of the synthesis mixture was the same as that of the seeds, except that instead of TEA, 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol (bis-tris) was used as the organic ligand. The bis-tris/Al molar ratio was varied from 0 to 4. Our preliminary study showed that the addition of bis-tris to the starting mixture led to greater growth of zeolite particles than TEA because the ability of bis-tris to form an aluminum complex is greater. This result was confirmed by liquid-state NMR measurements on a suspension containing the precipitate of silica gel. After the precipitate had settled, the seeded substrate was placed horizontally and was hydrothermally treated without stirring at 90 °C for one week. On the upper side of the substrate, deposition of the particles that formed in solution onto the substrate prevented the growth of the attached seed crystals.

Figures 3 c – e show the XRD patterns of the lower surfaces of the hydrothermally treated substrates. All patterns exhibited intense peaks for (*h*00); this indicates that the orientation of the zeolite was retained. The intensities of the (*h*00) peaks increased with increasing amount of bis-tris; hence the addition of bis-tris facilitated the growth of the seed crystals. For the specimens obtained with bis-tris/Al ratios of 0 and 2, peaks due to planes other than (*h*00) and products other than LTA-type zeolite were observed, though they were very weak.

Figures 4 a – c show the SEM images of the lower surfaces of the substrates treated hydrothermally at different bis-tris/Al ratios, and Figure 4 d shows the image of the fractured cross section for the specimen obtained with a bis-tris/Al ratio of 4. For the specimen obtained with a bis-tris/Al ratio of 0, very limited growth of the seed crystals occurred, and some aggregates of very small randomly oriented zeolite particles were observed on and between the oriented zeolite crystals, probably due to the occurrence of homogeneous nucleation and deposition of the crystals in the solution. Although some growth of seeds occurred at a bis-tris/Al ratio of 2, spherical secondary particles also were observed on the substrate surface between the oriented zeolite crystals. On the basis of the XRD data, these particles are not LTA-type zeolite, and they may have formed by leaching of the substrate under the strongly alkaline conditions. With a bis-tris/Al ratio of 4, well-developed continuous films consisting exclusively of intergrown oriented zeolite crystals were obtained (Figure 4 c). Despite the growth of faces other than (100), the orientation was maintained. Neither other products nor voids were observed in the interparticle spaces. As shown in Figure 4 d, the membrane is uniform, continuous, and about 15 μm thick. This suggests that intergrowth of the oriented seeds was rapid enough to prevent leaching of the substrate.

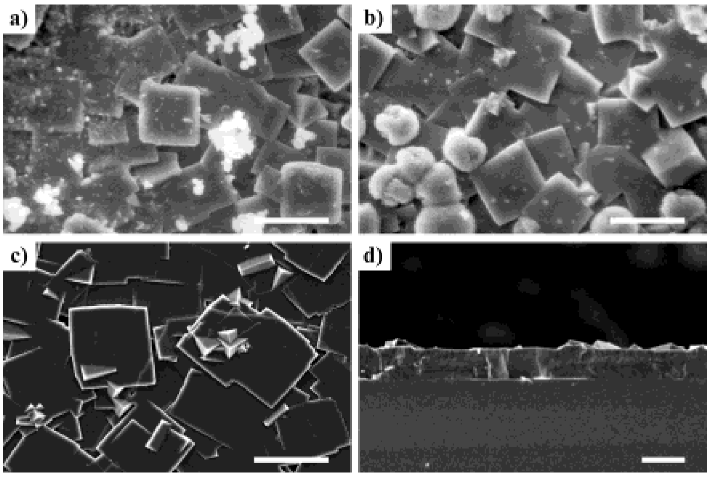

Figure 4. SEM images of the surface of the specimens heat-treated in the suspension with bis-tris/Al ratios of 0 (a), 2 (b), and 4 (c) and the fractured cross section of the specimen with bis-tris/Al = 4 (d). All scale bars: 20 μm.

In conclusion, we have discovered a new technique to prepare completely oriented and continuous zeolite membranes having channels normal to the surface of substrate. Controlled crystallization of LTA-type zeolite enabled both the preparation of seed crystals suitable for oriented attachment and homoepitaxial growth of the seeds. Organic ligands such as bis-tris and TEA decrease the degree of supersaturation of $[Al(OH)_4]^-$ and thus facilitate homogeneous nucleation of the zeolite by an equilibrium reaction such as Equation (1).[6, 7] Recently, Boudeau et al.[28, 29] attempted to prepare continuous oriented LTA-type zeolite films by the intergrowth of seed crystals with a method similar to that described here. However, they used starting solutions without organic ligands for seed preparation and intergrowth, and the films had a rough surface due to multiple coating of seeds[28] or a partially random orientation due to insufficient intergrowth.[29]

$$N(C_2H_4OH)_3 + [Al(OH)_4]^- \rightleftharpoons [Al(OH)(OC_2H_4)_3N]^- + 3\,H_2O \qquad (1)$$

Gouzinis and Tsapatsis[30] and Lovallo et al.[31] prepared continuous and oriented membranes of MFI-type zeolite. Although the straight and sinusoidal channels were parallel to the substrate surface, highly selective gas permeation was exhibited. Our LTA-type zeolite membrane with channels normal to the substrate surface may have similar properties. Investigations on selective gas sensing and permeation are in progress. For application to other zeolite types, our method may require modification, because unlike LTA-type zeolite, which is homogeneously nucleated,[32] some other zeolites are nucleated inhomogeneously.[33]

The materials prepared in this study could offer applications such as controlled access of molecules with selected size and shape to a sensor surface, membranes for catalysis and for separations with true molecular selectivity, and orientation of molecules for nonlinear optical applications.

Experimental Section

The seed crystals of LTA-type zeolite were prepared from an aqueous mixture of $NaAlO_2$, $Na_2SiO_3 \cdot 9H_2O$, and $N(C_2H_4OH)_3$ by hydrothermal treatment. Before mixing the starting materials, the aqueous solution of $NaAlO_2$ was filtered through a membrane filter with pore size of 0.2 µm to remove impurities such as $Fe(OH)_3$. The other reagents were used as received. The composition of the aqueous mixture was adjusted to Na_2O:Al_2O_3:SiO_2:TEA:H_2O = 1.88:1:0.88:8:106. During mixing, precipitates formed. The resulting suspension was transferred to a teflon-lined stainless steel autoclave and heated at 110 °C under autogenous pressure for one week. The product was filtered, washed with 1000 mL of distilled water, and dried at 70°C in air for 12 h.

The chemical composition of the solid component in the starting suspension was derived from that of the liquid component and the initial composition. The chemical composition of the liquid component was determined by ICP analysis (JICP-PS-1000UV · AT, Leeman Labs). The samples were diluted with milli-Q water.

The crystalline phase and the orientation in the specimens were examined by X-ray diffraction measurements (Rigaku Geigerflex) with graphite-monochromated $Cu_{K\alpha}$ radiation at a scan rate of $2^\circ \min^{-1}$ in the range $5 < 2\theta < 70^\circ$.

The microstructure of the membranes was observed by SEM (Philips XL30) at an acceleration voltage of 10 kV after deposition of a carbon layer with a thickness of about 15 nm on the specimen.

The formation of complexes from Al compounds and alkanolamines was examined by ^1H, ^{13}C, ^{23}Na, ^{27}Al, and ^{29}Si NMR spectroscopy (JEOL α400) at 20 °C and 9.4 T.

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Nickel-Assisted Carbon–Fluorine Bond Activation of 2,4,6-Trifluoropyrimidine: Synthesis of New Pyrimidine and Pyrimidinone Derivatives[**]

Thomas Braun, Simon P. Foxon, Robin N. Perutz,[*] and Paul H. Walton

Several methods have been described for the activation of carbon–fluorine bonds of fluoroaromatic and fluoroaliphatic compounds by reaction at transition metal centers.[1–3] One of the most striking is the fast oxidative addition of pentafluoropyridine at a nickel center to give *trans*-$[NiF(2\text{-}C_5F_4N)(PEt_3)_2]$.[3] Here we report 1) the activation of a carbon–fluorine bond of 2,4,6-trifluoropyrimidine by a nickel center under mild conditions, 2) the conversion of the nickel fluoride compound into a bifluoride complex, and 3) the selective substitution of the 4-fluoro substituent of 2,4,6-trifluoropyrimidine by a hydroxyl group through reaction at nickel.

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