In Situ Growth of Continuous *b*-Oriented MFI Zeolite Membranes on Porous α-Alumina Substrates Precoated with a Mesoporous Silica Sublayer

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Continuous *b*-oriented MFI membranes were prepared on a mesoporous silica sublayer-coated porous α-alumina substrate by in situ crystallization. Single gas permeation of butane isomers through the MFI membrane was carried out as a function of temperature from 298 to 473 K. A decreased permeance of butane isomers on the *b*-oriented MFI membrane with increasing temperature is observed in this temperature range, which is attributed to a weak adsorption effect. Meanwhile, it was revealed that the *b*-oriented membrane can maintain a high ideal selectivity of *n*-butane/*i*-butane at elevated temperatures. On the contrary, a discrete membrane with a randomly oriented top layer was obtained on the uncoated α-alumina substrate. Further investigation on the evolution of the MFI membranes on the two kind substrates was performed with the focus on the understanding of the oriented growth of zeolite crystals. The surface properties of the substrates used played an important role in the formation of MFI membranes with different morphologies.

Introduction

In the past decade, considerable research effort has been applied to the synthesis of high-performance zeolite membranes due to their great potential for application as selective membranes, catalytic membrane reactors, and chemical sensors.[1−5] Because many zeolites consist of microcrystals with an anisotropic structure, the orientation of the zeolite microcrystals can influence the membrane performance in most of these applications.[3,6−8] For the MFI (Silicalite-1 and ZSM-5) membranes, a particularly active research field mainly because of the crystal channel systems with pore diameter (about 0.55 nm) near the sizes of many industrially important organic molecules, the zeolite channel system is 2D: straight channels (*b*-direction) of elliptical cross section are interconnected with sinusoidal channels (*a*-direction) of circular cross section; the *c*-direction represents the tortuous path. There are mainly two approaches for the preparation of continuous, oriented, MFI zeolite membranes. One is the secondary growth technique,[7−11] and the other is the in situ crystallization technique.[12−18] The former involved the deposition of a seed layer (nanocrystals) on a substrate and then the secondary grain growth of the deposited nanocrystals. The membrane orientation can be controlled by the crystallization conditions and surface properties of the substrates. Xomeritakis et al. demonstrated that a MFI membrane with crystals oriented with their *c*-axis perpendicular to the substrate was formed at 448 K, whereas the MFI membrane exhibited [*h*0*h*]-orientation after secondary growth at 413 K.[9] Recently, Lai et al. reported the preparation of *b*-oriented MFI membranes by seeded growth of oriented particle monolayers and use of a certain structure-directing agent (*trimer*-TPAOH instead of *monomer*-TPAOH) as a crystal growth rate modifier to enhance the relative growth rate along the *b*-axis.[7,8] *b*-Oriented MFI membranes have also been prepared by this technique on a modified gold or silicon wafer surface.[10,11] The in situ crystallization technique uses direct crystallization of the zeolite crystals on the substrate. MFI crystals with their *b*-axis perpendicular to the substrate surface prepared by this approach are usually deposited on nonporous substrates such as stainless steel, aluminum alloy,

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(1) Tavolaro, A.; Drioli, E. *Adv. Mater.* **1999**, *11*, 975.
(2) Caro, J.; Noack, M.; Kaölsch, P.; Schäfer, R. *Microporous Mesoporous Mater.* **2000**, *38*, 3.
(3) Bein, T. *Chem. Mater.* **1996**, *8*, 1636.
(4) Li, S.; Wang, X.; Beving, D.; Chen, Z.; Yan, Y. *J. Am. Chem. Soc.* **2004**, *126*, 4122.
(5) Mintova, S.; Bein, T. *Microporous Mesoporous Mater.* **2001**, *50*, 159.
(6) Bernal, M. P.; Coronas, J.; Menéndez, M.; Santamaría, J. *Microporous Mesoporous Mater.* **2003**, *60*, 99.
(7) Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. *Science* **2003**, *300*, 456.
(8) Lai, Z.; Tsapatsis, M.; Nicolich, J. P. *Adv. Funct. Mater.* **2004**, *14*, 716.
(9) Xomeritakis, G.; Gouzinis, A.; Nair, S.; Okubo, T.; He, M.; Overney, R. M.; Tsapatsis, M. *Chem. Eng. Sci.* **1999**, *54*, 3521.
(10) Mintova, S.; Valtchev, V.; Engström, V.; Schoeman, B. J.; Sterte, J. *Microporous Mater.* **1997**, *11*, 149.
(11) Metzger, T. H.; Mintova, S.; Bein, T. *Microporous Mesoporous Mater.* **2001**, *43*, 191.
(12) Yan, Y.; Chaudhuri, S.; Sarkar, A. *Chem. Mater.* **1996**, *8*, 473.
(13) Koegler, J. H.; van Bekkum, H.; Jansen, J. C. *Zeolites* **1997**, *19*, 262.
(14) Wang, Z.; Yan, Y. *Microporous Mesoporous Mater.* **2001**, *48*, 229.
(15) Wang, Z.; Yan, Y. *Chem. Mater.* **2001**, *13*, 1101.
(16) Li, S.; Li, Z.; Bozhilov, K. N.; Chen, Z.; Yan, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10732.
(17) Seike, T.; Matsuda, M.; Miyake, M. *J. Am. Ceram. Soc.* **2004**, *87*, 1585.
(18) Vilaseca, M.; Mateo, E.; Palacio, L.; Prádanos, P.; Hernández, A.; Paniagua, A.; Coronas, J.; Santamaría, J. *Microporous Mesoporous Mater.* **2004**, *71*, 33.

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silicon wafer, and yttria stabilized zirconia (YSZ). Orientation is thought to be determined by the preferential growth of (010) crystal faces on the flat surface. To our knowledge, there has been no test of the potential of the in situ crystallization technique for the preparation of a *b*-oriented MFI membrane on porous substrates. In this study on the use of porous α-alumina substrates to prepare MFI membranes, we report that *b*-oriented membranes can be grown by in situ crystallization on porous α-alumina precoated with a mesoporous silica sublayer. In contrast, a membrane with a randomly oriented top layer is obtained on the uncoated α-alumina substrate using the same preparation conditions. To understand the oriented growth of the zeolite crystals, a detailed investigation of the evolution of MFI membranes on the two kind substrates is further performed.

Separation by MFI zeolite membranes are studied most often with respect to the mixtures N_2/SF_6, H_2/*n*-butane, *n*-butane/*i*-butane, *n*-hexane/2,2-dimethylbutane, and *p*-xylene/*m*-xylene.[1,2] In general, there are three kinds of models for describing the permeation behaviors of zeolite membranes according to the mixture components with different properties. There are (i) shape selective permeation by molecular sieving for the permeation of mixture with different size, (ii) diffusion-controlled permeation for the permeation of mixture with similar adsorption but different diffusion properties, and (iii) adsorption-controlled separation for the permeation of a mixture with different adsorption and diffusion behavior.[2] Because of the different molecular sizes of *n*-butane (0.43 nm) and *i*-butane (0.50 nm), large differences in the diffusivity of *n*-butane/*i*-butane can be expected for the MFI membrane. The ideal selectivity of *n*-butane/*i*-butane has been established as a criterion for the quality of MFI membranes. Many factors can influence the *n*-butane/*i*-butane permeation performance of zeolite membrane, such as the measurement method[19] and the location and the orientation of the crystal deposits.[6,20] Here, the single gas permeation of butane isomers is carried out to investigate the characteristics of the obtained MFI membranes. A proposed explanation for the permeation behavior of the MFI membranes is presented.

Experimental Section

Preparation of the Mesoporous Silica Sublayer and MFI Zeolite Membranes. Porous asymmetric α-alumina disks were fabricated by a gel-casting technique developed in our group.[21,22] The α-alumina disks, with a porosity of 62.5%, consist of a thin fine-layer (150 μm) with 0.15 μm pores and a large-pore body with 150 μm pores. A mesoporous silica sublayer was deposited on the surface of the thin fine-layer by a sol−gel dip-coating technique.[23,24] Precursor silica sols were prepared by addition of CTAB (cetyltrimethylammonium bromide) to prehydrolyzed polymeric silica sols from TEOS (tetraethyl orthosilicate), ethanol, water, and HCl. The final molar ratios of the dipping sols were 1TEOS:20ethanol: $5H_2O$:0.004HCl:0.16CTAB. After dip-coating, the samples were dried in a laminar flow cabinet at 298 K for 12 h and then calcined at 723 K in air for 2 h.

Silica powders were obtained by casting the dipping sol in a glass Petri-dish, drying in the laminar flow cabinet, and calcining under the same conditions as the dipped silica layer.

The MFI membranes were prepared by in situ crystallization on uncoated and silica sublayer-coated substrates. TEOS, TPAOH (tetrapropylammonium hydroxide), and deionized water were used as raw materials for the preparation of precursor sols. The molar ratio of the precursor sols was 1TEOS:0.17TPAOH:$120H_2O$. The precursor sols were made by slowly adding TEOS to a solution of TPAOH and water under stirring. To prepare Al-containing precursor sols, a measured amount of $Al(NO_3)_3\cdot 9H_2O$ was first dissolved with water, and then the required amount of TPAOH and the balance of water were added. After the solution was stirred for a few minutes, a measured amount of TEOS was added dropwise under stirring. The substrates with fine-layer were placed vertically in a Teflon-lined stainless steel autoclave which was kept in an oven at 453 K. The membranes were calcined at 723 K in air for 12 h (heating/cooling rate 0.5 K/min) for removing the organic templates.

General Characterization. The crystal structures of zeolite membranes and powder were examined by X-ray diffraction (XRD, RIGACU RINT1100) using Cu Kα radiation. The morphologies of the substrates and zeolite membranes were characterized by scanning electron microscopy (SEM, JEOL JSM-6100) at 15 kV. The porous texture of the calcined silica powder was measured with an N_2 adsorption/desorption isotherm using a micromeritics apparatus (GEMINI 2375) at 77 K.

Gas Permeation Test. Gas permeation tests were performed by a pressure gradient (PG) method, which was operated in a batchwise manner. The MFI membrane was placed in a Cu module with a cylindrical geometry. O-rings were used as sealing between the membrane and the module. The active membrane area was 6.4×10^{-4} m^2. Before each permeation experiment, the MFI membrane was calcined at 673 K for 4 h to remove adsorbed components. In the PG method, the permeation side was evacuated to less than 0.133 Pa. Gas permeation tests were carried out in the temperature range of 298−473 K. The permeances of butane isomers were determined by using the rate of pressure decrease of the feed side from 101 to 91 kPa. Ideal selectivity was calculated from the ratio of permeances.

Results and Discussion

Oriented Growth of MFI Membrane. Before being used as substrate, the α-alumina disks were coated with a mesoporous silica sublayer on the thin fine-layer by a sol−gel dip-coating technique.[23,24] SEM micrographs revealed that the reflectivity of the silica layer surface is greater than that of the α-alumina surface, indicating the high smoothness of the precoated silica layer. The silica layer is approximately 2 μm thick. The N_2 adsorption/desorption isotherm of the calcined silica powder indicates the lack of hysteresis and absence of any appreciable adsorption at relative pressures above 0.3, which suggests a unimodal porosity with no

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(19) Gump, C. J.; Lin, X.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **2000**, *173*, 35.

(20) Coronas, J.; Falconer, J. L.; Noble, R. D. *AIChE J.* **1997**, *43*, 1797.

(21) Takahashi, M.; Mizuno, T.; Shiroki, Y.; Yokoyama, T.; Abe, H.; Naito, M. In *Ceramic Powder Science VI, Ceramic Transactions*; Hirano, S., Messing, G. L., Claussen, N., Eds.; American Ceramic Society: Westerville, OH, 2001; Vol. 112, p 559.

(22) Izuhara, S.; Kawasumi, K.; Yasuda, M.; Suzuki, H.; Takahashi, M. In *Ceramic Powder Science VI, Ceramic Transactions*; Hirano, S., Messing, G. L., Claussen, N., Eds.; American Ceramic Society: Westerville, OH, 2001; Vol. 112, p 553.

(23) Lu, Y.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W.; Guo, Y.; Soyez, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364.

(24) McCool, B. A.; Hill, N.; DiCarlo, J.; DeSisto, W. J. *J. Membr. Sci.* **2003**, *218*, 55.

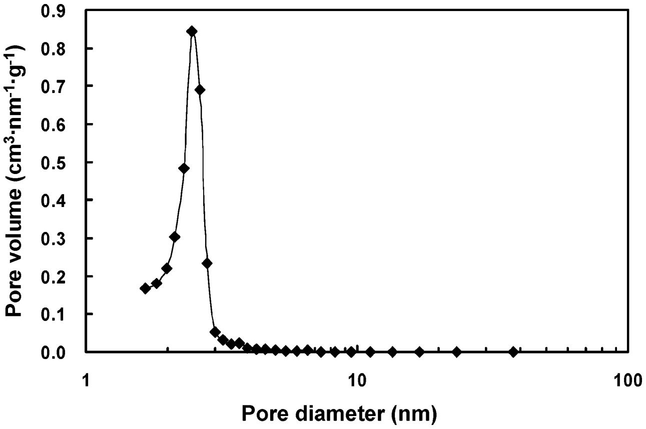

Figure 1. Pore size distribution of calcined silica powder.

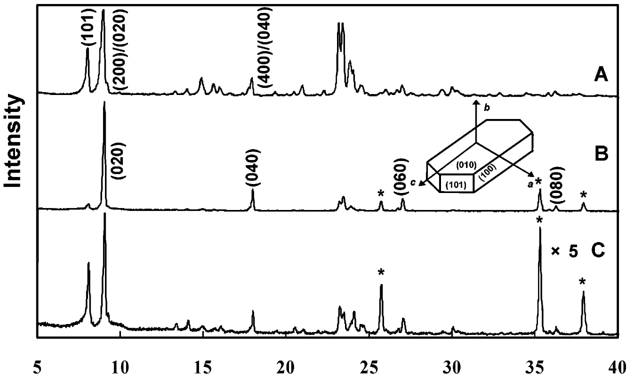

Figure 2. XRD patterns of MFI powder at the bottom of the autoclave when using silica sublayer-coated substrate (A), MFI membranes on silica sublayer-coated substrate (B), and uncoated α-alumina substrate (C) with a crystallization time of 10 h. Inset: Schematic diagram of the MFI zeolite crystal. "∗" indicates peaks from α-alumina substrate.

interpartical meso- or macroporosity.[23] The calcined silica powder has a unimodal pore size distribution centered at 2.5 nm (Figure 1). The specific surface area, determined by the five point BET method, is about 1050 m^2 g^{-1}.

The silica sublayer-coated α-alumina was adopted as a substrate to prepare MFI membrane by in situ crystallization. The XRD patterns of Figure 2 demonstrate that the silica sublayer-supported MFI membrane gives relatively intense single (0*k*0) peaks. The intensity ratio of the (101) peak at around 9° to that of the (020) peak ($I_{(101)}/I_{(020)}$) for the MFI membrane is about 0.08, whereas the ratio of these peaks is 0.72 for the MFI powders at the bottom of the same autoclave. This indicates the MFI crystals with their *b*-axis perpendicular to the substrate surface are deposited on the silica sublayer surface. In a comparison study using uncoated α-alumina as substrate, the ratio of $I_{(101)}/I_{(020)}$ for the supported MFI membrane is 0.61. The other MFI structure peaks such as (002), (012), and (031) peaks around 13−14° and (051), (−501), and (033) peaks around 23−24° show considerably strong intensities in the α-alumina-supported MFI membrane. The above results demonstrate the presence of MFI crystals with random orientation on the α-alumina substrate. SEM photograph of the MFI membrane (Figure 3A) shows that the MFI crystals on the silica sublayer-supported membrane have a columnar shape and show a good intergrowth behavior. Also, it is seen that some small crystals that exhibit twinning appear. The cross-section micrograph of Figure 3B shows that the zeolite membrane is about 2−3 μm thick. Two or three levels of crystals are grown on the substrate with their *b*-axis perpendicular to the substrate surface. In contrast, the crystals on the α-alumina-supported membrane are obviously discrete. On the other hand, it can be observed that a gel layer occurs among some crystals. The crystallization is not completed at this point. The zeolite layer with random orientation on the α-alumina substrate has a thickness of about 8 μm and appears to be much rougher than that of the silica sublayer-supported membrane.

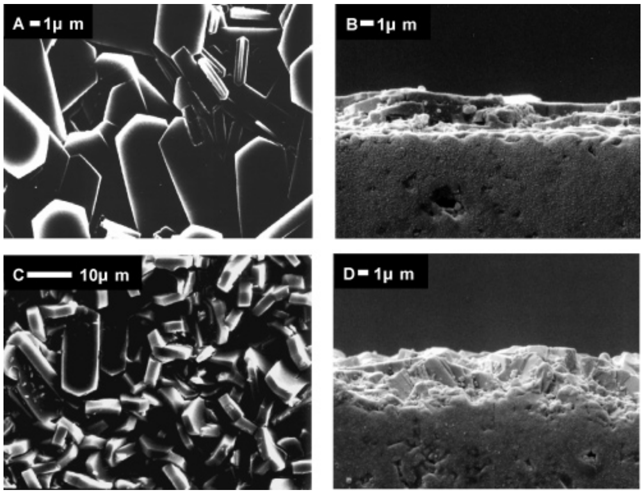

Figure 3. SEM photographs of the surface and cross section of MFI membranes on silica sublayer-coated substrate (A, B) and on uncoated α-alumina substrate (C, D) with a crystallization time of 10 h.

Gas Permeation Test. The single gas permeation of butane isomers through the obtained MFI membranes was carried out to investigate the characteristics of the obtained MFI membranes. Table 1 shows the temperature dependence of the permeances of butane isomers for the silica sublayer-supported membrane. The permeances of the butane isomers decrease with increasing temperature. This tendency has not been previously reported for MFI zeolite membranes in the temperature range of 298−473 K. In the literature, several behaviors of permeance-temperature dependency have been revealed, depending on the membrane morphology and experimental conditions.[6,19,20,25] At the lower temperature range, the *n*-butane permeance increases with temperature due to the enhancing of the mobility of adsorbed species. Subsequently, a maximum can be reached, above which a decline in occupancy prevails, resulting in a decrease in permeance. A stronger adsorption would shift the maximum toward higher temperatures.[6] According to the literature, most of the high-selectivity gas separations are adsorption-controlled, while there are fewer separations by molecular sieving or diffusion-controlled permeation.[2,19] Adsorption may destroy the intrinsic selectivity of the zeolite membranes. For example, Gump et al. reported that ZSM-5 membranes with nonzeolite pores can separate *n*-butane/*i*-butane mixtures

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(25) Bakker, W. J. W.; Kapteijn, F.; Poppe, J.; Moulijn, J. A. *AIChE J.* **1997**, *43*, 2203.

Table 1. Permeance of Butane Isomers and Ideal Selectivity of *n*-Butane/*i*-Butane through Different MFI Membranes[a]

thickness (μm)	orientation	preparation method	measurement method	temp (K)	permeance (10^{-9} mol s^{-1} m^{-2} Pa^{-1})		ideal selectivity	ref
					n-butane	*i*-butane		
2−3	*b*	ISC	PG	298	2.0	0.64	3.1	this work
				323	1.4	0.41	3.4	this work
				373	0.75	0.05	15	this work
				423	0.28	0.04	7	this work
				473	0.09	0.01	9	this work
3	random	(multi)ISC	WK	298	30	0.3	100	26, Table 4
				473	50	4	12.5	26, Table 4
1.5	random	SG	PG	298	0.05	0.04	1	27, Table 3
0.75	*c*	SG	PG	423	3.1	1.6	2	28, Table 1
60	[*h*0*l*]	ISC	PG	378	0.5	0.6	0.8	29, Figure 3

[a] ISC, in situ crystallization; SG, secondary growth; PG, pressure gradient method; WK, Wicke−Kallenbach method.

with high selectivity by preferential adsorption of *n*-butane.[19] However, these membranes lost most of their selectivity at higher temperature at which the adsorption coverages are low. Bernal et al. reported that the morphologies of the zeolite crystals strongly affect the adsorption performance of the MFI zeolite membrane. A MFI membrane with a large amount of zeolite material inside the substrate pores gave rise to a large proportion of intercrystalline micropores and/or grain boundaries, leading to a stronger adsorption of organic gas than those with a thin layer of randomly or *c*-oriented crystals on the top of the substrate.[6] In our study, the permeances of butane isomers in the silica sublayer-supported membrane decrease in the temperature range studied, indicating a weaker adsorption effect of the MFI membrane. It can be inferred from the SEM photographs of the *b*-oriented MFI membrane that the increase of the lateral sizes of the crystals results in the loss of the perfect morphology of the MFI crystals. The dense stacks of two or three levels of crystals on the substrate surface could decrease the amounts of intercrystalline micropores. Additionally, the large in-plane grain size (about 20 μm) reduces the density of grain boundaries.

For the separation controlled by the adsorption effect, the gas selectivity decreased with an increase in the temperature because of the occupancy decline at higher temperatures. Table 1 shows that the ideal selectivity of *n*-butane/*i*-butane increases as the temperature increases. Because the adsorption effect in the silica sublayer-supported membrane is rather weak, the difference in the diffusion rates of the butane isomers controls the permeation performance. In the temperature range studied, the permeance of *i*-butane decreases quickly as compared to that of *n*-butane. As expected, the ideal selectivity was retained at a higher temperature.

For comparison, Table 1 also shows data for single gas permeation of butane isomers through different thin and/or oriented membranes reported by other groups. The membrane thickness and orientation are given in the table. It should be noted that the tests reported have been carried out under different measurement conditions and that the membranes have been prepared by different methods. We can see that the random MFI membrane prepared by multi in situ crystallization shows significantly larger *n*-butane permeance and ideal selectivity of *n*-butane/*i*-butane at 298 K. As the temperature increases, however, the ideal selectivity drops from 100 to 12.5 at 473 K.[26] For the MFI membrane synthesized without organic template using a secondary growth technique, very low permeances of *n*-butane and *i*-butane were reported, even though the membrane was relatively thin (1.5 μm).[27] Nevertheless, this membrane showed high separation factors for binary mixtures of N_2/SF_6 and H_2/*i*-butane. Both the *c*- and the [*h*0*l*]-oriented MFI membranes show relatively low permeance and ideal selectivity as compared to the results in ref 26. The crystals in the *c*-oriented MFI membrane are oriented with their straight and sinusoidal channels parallel to the membrane surface. According to Lovallo et al., transport through the *c*-oriented membrane should occur by successive jumping between the two channel networks. In this respect, the MFI membrane performs as a small pore material rather than a medium pore zeolite.[28] The parallel orientation of the *b*-axes with the support plane as well as the relatively thicker membrane layer may result in the lower permeation performance of the [*h*0*l*]-oriented MFI membrane. In the present work, the permeance of butane isomers is still not spectacular as compared to the results for the random MFI membrane prepared by multi in situ crystallization. However, the ideal selectivity for the silica sublayer-supported membrane was retained at a higher temperature. The adsorption effect in the *b*-oriented MFI membrane is rather weak, as discussed earlier, which may lead to the relatively low permeance of butane isomers.

As mentioned above, after 10 h of hydrothermal crystallization, the MFI crystals formed cannot fully cover all of the surface of uncoated α-alumina substrate. The uncalcined membrane was permeable to N_2 for a 101 kPa-pressure drop at 298 K. We repeated the preparation procedure five times to get a N_2-tight membrane prior to calcinations (crystallization time of 24 h for the last four times). The ideal selectivity of *n*-butane/*i*-butane is 0.92 with *n*-butane permeance of 34×10^{-9} mol s^{-1} m^{-2} Pa^{-1} and *i*-butane permeance of 37×10^{-9} mol s^{-1} m^{-2} Pa^{-1}, indicating that their transport occurs mainly through some nonzeolite pores.

Evolution of the Oriented Growth. To understand the controlling of MFI crystal orientation, we investigated the growth of MFI membranes on the uncoated and silica sublayer-coated substrates. Figure 4 presents XRD patterns

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(26) Vroon, Z. A. E. P.; Keizer, K.; Burggraaf, A. J.; Verweij, H. *J. Membr. Sci.* **1998**, *144*, 65.

(27) Hedlund, J.; Noack, M.; Kölsch, P.; Creaser, D.; Caro, J.; Sterte, J. *J. Membr. Sci.* **1999**, *159*, 263.

(28) Lovallo, M. C.; Tsapatsis, M. *AIChE J.* **1996**, *42*, 3020.

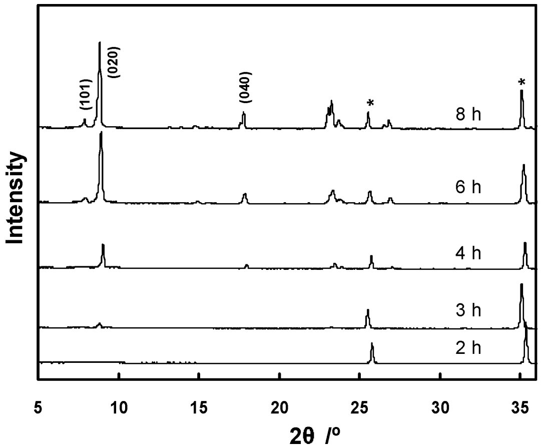

Figure 4. XRD patterns of MFI membranes on silica sublayer-supported substrates after different crystallization times. "∗" indicates peaks from α-alumina substrate.

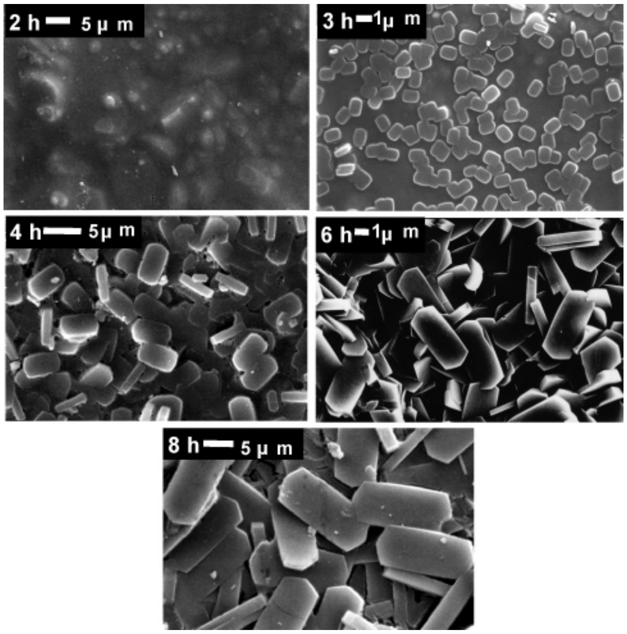

Figure 5. SEM surface of MFI membranes on silica sublayer-supported substrates after different crystallization times.

of MFI membranes on silica sublayer-coated substrates with crystallization times of 2, 3, 4, 6, and 8 h. For the sample after 2 h, no obvious diffraction peaks of MFI zeolite were recorded, besides background from substrate. The diffraction peaks of the *b*-oriented MFI crystal, with a characteristic intense single (020) peak and a very weak (101) peak as shown in Figure 2B, were observed after 3 h. The peak intensities of the *b*-oriented MFI membrane increase with crystallization time, which coincides with the growth of the MFI membrane. SEM micrographs of the MFI membranes with different crystallization times are shown in Figure 5. For the 2 h-obtained sample, the SEM micrograph does not show any significant difference from the substrate with the silica sublayer. The substrate surface is covered with a layer of disk-shaped crystals with a size of 1 μm after 3 h. Most crystals are discrete and settled with the (010) face parallel with the substrate surface. After 4 h, a rather dense crystal layer with crystals of large sizes (ca. 5 μm) has been formed. Meanwhile, a second layer with loose crystals is stacked on the first layer. The coexistence of crystal growth and nucleation on both the substrate and the crystals after certain crystallization times is thought to be responsible for the structure of the MFI layer with several levels of crystals.

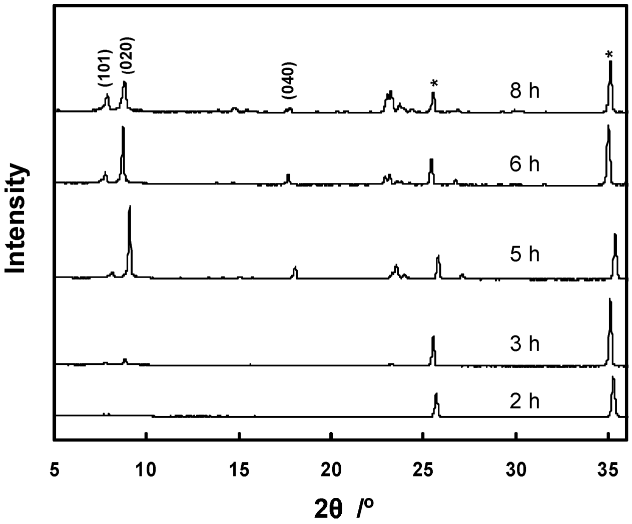

Figure 6. XRD patterns of MFI membranes on uncoated α-alumina substrates after different crystallization times. "∗" indicates peaks from α-alumina substrate.

Further investigations of the growth of the MFI membrane were performed on the uncoated α-alumina substrates. The XRD diffraction peaks of the MFI zeolite are observed after 3 h (Figure 6). The larger (020) peak than the (101) peak on the three samples with crystallization times of 3, 5, and 6 h reflects that the MFI crystals are deposited on the substrate surface with *b*-orientation at the initial stage. However, the $I_{(101)}/I_{(020)}$ ratio improves rapidly from 0.09 in 6 h to 0.62 after 8 h, confirming that the membrane loses its *b*-orientation for a relatively long crystallization time. On the contrary, the $I_{(101)}/I_{(020)}$ ratio for the silica sublayer-supported MFI membrane can be maintained at a quite low value of 0.08 for longer crystallization times of 8 h (Figure 4) and 10 h (Figure 2B). Recently, the grazing incidence diffraction (GID) technique has been used to characterize the crystal orientation in MFI membranes, which is shown to be a more powerful means to permit a detailed analysis of the orientation of zeolite crystal as a function of the film depth, as compared to the standard X-ray diffraction technique.[11,30] This issue will be addressed in our continuing investigation. SEM photographs show that, with a crystallization time of 2 h, a gel layer is observed on the surface of the uncoated α-alumina substrate (Figure 7). It is well-known that aluminum can be leached from an alumina support during the zeolite crystal growth procedure.[31,32] Lai et al. found that leached aluminum has dual roles during the zeolite membrane growth, to facilitate the formation of the hydrogel layer on

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(29) Noack, M.; Kölsch, P.; Caro, J.; Schneider, M.; Toussaint, P.; Sieber, I. *Microporous Mesoporous Mater.* **2000**, *35*−*36*, 253.

(30) Mintova, S.; Metzger, T. H.; Bein, T. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *200*, 160.

(31) Lai, R.; Yan, Y.; Gavalas, G. R. *Microporous Mesoporous Mater.* **2000**, *37*, 9.

(32) Sano, T.; Ejiri, S.; Yamada, K.; Kawakami, Y.; Yanagishita, H. *J. Membr. Sci.* **1997**, *123*, 225.

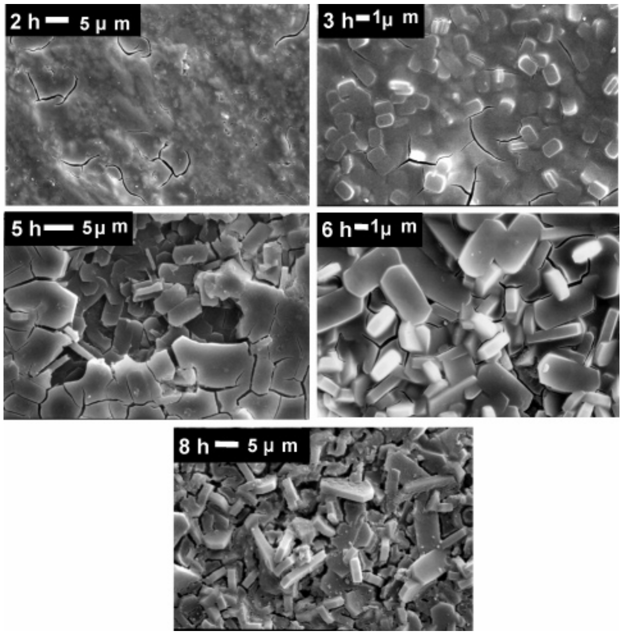

Figure 7. SEM surface of MFI membranes on uncoated α-alumina substrates after different crystallization times.

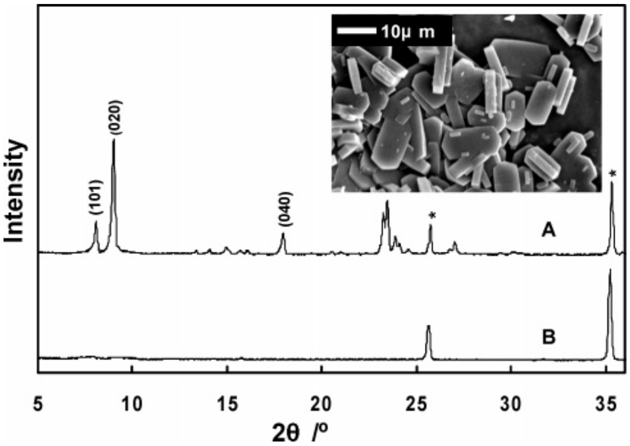

Figure 8. XRD patterns of MFI membranes on silica sublayer-coated substrates with a crystallization time of 10 h in a solution with Si/Al = 100 (A) and 12.5 (B). Inset: corresponding SEM surface of a MFI membrane prepared in a solution with Si/Al = 100.

the support and to retard zeolitization in this hydrogel layer.[31] Subsequently, nucleation and crystallization occur at the interface of the gel layer and the synthesis solution. The crystals sink to the substrate surface by consuming the gel. The gel layer is retained on some areas of the substrate surface after a crystallization time of 10 h, in which crystals are embedded (Figure 3C). The relatively low growth rate along the *b*-direction and the simultaneous slow consumption of nutrients may lead to the secondary nucleation in the neighboring gel. As a result, new crystals with random orientation are incorporated inside the preliminary crystal layer.

For comparison purposes, hydrothermal synthesis was also carried out in a synthesis solution of Si/Al = 100 using the silica sublayer-coated substrate under otherwise similar conditions, to study the effects of the aluminum on the preparation of an oriented MFI membrane. The relatively higher intensity of the (101) XRD peak indicates that the MFI crystals grow with random orientation on the substrate surface (Figure 8A, $I_{(101)}/I_{(020)} = 0.3$). The absence of close-packed crystals throughout the area of the substrate can be observed by the surface SEM photograph. No zeolite crystals were formed on the substrate surface when a synthesis solution of Si/Al = 12.5 was used.

On the other hand, at the early stage of membrane formation on the silica sublayer-coated substrate, the substrate surface is covered with a layer of disk-shaped MFI crystals instead of a gel layer in the present study (Figure 5). In earlier work involving the preparation of polycrystalline ZSM-5 membranes with random orientation on α-alumina substrates by in situ crystallization, Yan et al. also evidenced a heterogeneous nucleation process involving a gel layer when an Al-containing precursor solution was used and a homogeneous nucleation process when an Al-free one was used, respectively.[33] Recently, a homogeneous nucleation model has been proposed and clearly established by TEM for the growth of *b*-oriented pure silica MFI membranes by in situ crystallization on nonporous metal substrates.[14,16] According to this model, the MFI membranes form through homogeneous nucleation and crystal growth in the bulk solution to form disk-shaped crystals, followed by self-assembly of these crystals onto the substrate to produce a two-dimensional close-packed structure. This model suggests that the chemical properties of the substrate surface are important for the adsorption of preliminary submicrometer crystals in appropriate numbers to cover the substrate surface. In fact, inert substrates can hardly be used by in situ crystallization. It is clear that the sol−gel silica membrane has a surface covered by Si−OH groups.[34,35] For the silica sublayer-coated substrate, these Si−OH groups may provide a strong interaction between the silica sublayer surface and the silicate species, which leads to sufficient coverage of the substrate surface with preliminary crystals. Subsequently, the preferential growth of the (010) crystal faces on the substrate surface produces the MFI crystals with a *b*-orientation.

Additionally, we cannot exclude the possibility that the surface smoothness of the silica sublayer also plays an important role in the formation of a *b*-oriented MFI membrane. The elimination of intrinsic defects on the porous substrate by the silica sublayer provides a smooth surface for the adsorption and growth of the submicrometer crystals with their (010) faces parallel to the substrate surface. It should be noted that several groups have made efforts to adopt asymmetric alumina substrates with a γ-alumina layer (pore size 5 nm) to prepare MFI membranes by in situ crystallization.[36,37] A smooth planar surface of the alumina substrate can also be created by this kind of γ-alumina layer. However, a large amount of aluminum could be leached easily from the γ-alumina layer during the zeolite crystal

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(33) Yan, Y.; Davis, M. E.; Gavalas, G. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 1652.

(34) Lenza, R. F. S.; Vasconcelos, W. L. *J. Non-Cryst. Solids* **2003**, *330*, 216.

(35) Jal, P. K.; Patel, S.; Mishra, B. K. *Talanta* **2004**, *62*, 1005.

(36) Bai, C.; Jia, M.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **1995**, *105*, 79.

(37) Piera, E.; Giroir-Fendler, A.; Dalmon, J. A.; Moueddeb, H.; Coronas, J.; Menéndez, M.; Santamaría, J. *J. Membr. Sci.* **1998**, *142*, 97.

growth procedure, due to the relatively poor chemical stability of the γ-alumina layer, which might lead to the similar course of crystallization discussed above for the uncoated α-alumina substrates.

Conclusions

Continuous *b*-oriented MFI membranes have been prepared on mesoporous silica sublayer-coated substrates by in situ crystallization. Single gas permeations of butane isomers show that the *b*-oriented MFI membrane can retain high ideal selectivity at elevated temperature. The difference in the diffusion rate is proposed to control the permeation performance. The investigation of growths of MFI membranes on the uncoated and silica sublayer-coated substrates suggests that the surface properties of the substrates have significant effects on the membrane orientation.

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