Synthesis of Silicalite Tubular Membranes by *In Situ* Crystallization

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Silicalite membrane preparation conditions related to membrane separation properties were studied focusing on in situ crystallization to prepare highly selective silicalite membranes on porous tubular supports by a single hydrothermal treatment. The membranes morphologies prepared under typical synthesis conditions were characterized by scanning electron microscopy. The silicalite membrane, well-oriented with c axis normal to the support surface, could be prepared by in situ crystallization and a seeding method. The membrane separation properties were controlled by synthesis conditions such as seeding, temperatures, supports, and silica sources. Under certain conditions, such factors as tube pore size, played an important role. Silicalite membranes would be prepared better by in situ crystallization than by a seeding method under the same conditions. For example, the highest ethanol/water separation factor of 106 with a flux of 0.9 kg/m^2·h for a feed concentration of 5 wt. % ethanol at 60°C was obtained for the silicalite membrane prepared on an unseeded mullite tube at 175°C for 16 h with colloidal silica, whereas the membranes prepared on the silicalite-seeded tubes had separation factors up to 70. The higher separation selectivity for ethanol over water would be attributed to reduction in nonzeolitic pores, supported by gas permeations of n-butane and i-butane.

Introduction

Since the first report on the preparation of zeolite membranes on inorganic porous supports (Suzuki et al., 1990), many efforts have been paid to synthesize zeolite membranes for applications in gas separation, pervaporation, and membrane reactors. Now, more than a decade later, the first zeolite (zeolite A) membranes commercialized on a large scale by Mitsui Engineering and Shipbuilding Co. Ltd., in cooperation with Yamaguchi University, are available on the market (Morigami et al., 2001). However, the zeolite A membranes have only been successfully applied to remove water from aqueous solutions via pervaporation or a vapor permeation process on a larger scale. As in our previous article (Okamoto et al., 2001), the completely dried zeolite A membranes exhibited Knudsen diffusion, even though they displayed the excellent water-permselective performance, indicating that they are not completely defect-free such as nonzeolitic pores. Therefore, for more practical applications, it is still challenging work to prepare reproducible and high performance zeolite membranes such as MFI (ZSM-5 and silicalite) on porous tubular supports on a large scale, when the cost is greatly reduced.

The membrane separation performance (permeability and selectivity) is related to the quality of the zeolite layer formed on a porous support. In an ideal case, this layer with high crystallinity should be thin and defect free. In general, the preparation of zeolite membranes requires the control of zeolite crystal growth on porous supports. It is known that the formation of zeolite layers is involved in complex chemical reactions, which are affected by many interacting factors such as the chemical composition, silica source, hydrothermal synthesis conditions, seeds, and so on. Under certain conditions, some factors play a more important role. There are two typical techniques which are often used to synthesize zeolite membrane on a flat or tubular porous support under hydrothermal reaction conditions: (1) *in situ* crystallization, crystal growth on an untreated support from a solution or a gel of aluminosilicate; and (2) seed-enhanced crystallization (a seeding method), formation of a crystal layer on a seeded support.

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The *in situ* crystallization has the strong advantage of simplicity, namely, without pretreatment of porous supports such as water slurring or dip coating for seeding. This method may also benefit scaling up synthesis of zeolite membranes in a reproducible manner and mass production. This method was widely used to prepare MFI membranes, especially in the earlier research works (Bai et al., 1995; Geus et al., 1992, 1993; Jia et al., 1994; Kusakable et al., 1996; Sano et al., 1994; Suzuki et al., 1990; Vroon et al., 1996; Yan et al., 1995). However, the main disadvantage of this method is that it is very difficult to find the suitable conditions under which nucleation and crystal growth with an interlocking fashion occur preferentially on the support surface rather than in the bulk solution. More difficulties arise from the complex chemical reactions involved in a process of crystal growth, which are affected by many interacting factors. Due to heterogeneous nucleation and a relatively low nucleus concentration, the crystals must be grown large enough to form a continuous and defect-free membrane, and, as a result, it is very difficult to control the thickness and orientation of the crystal layer. Besides, it is common that repeated *in situ* crystallization processes are required to reduce defects (Jafar and Budd, 1997; Tuan et al., 1999; Vroon et al., 1998).

Our laboratory first developed a seeding method to prepare zeolite A membranes on tubular supports and first presented their excellent pervaporation properties in 1993 (Horii et al., 1993). Up to now, this seeding method has been successfully adopted to synthesize not only zeolite A (Kita et al., 1995; Kondo et al., 1997; Okamoto et al., 2001), but also zeolite Y (Kita et al., 1997), X (Kita et al., 2000), T (Tanaka et al., 2001), and MFI (silicalite) membranes (Lin et al., 2000, 2001). Our seeding method indicates that the main advantage of the seed-enhanced crystallization is to fasten preferential crystal growth onto the support surface and shorten a synthesis time similar to synthesis of zeolite powders. For example, zeolite A membranes with a water flux of 2.2 kg/m^2 h and a water/alcohol separation factor of more than 10,000 were prepared on seeded tubes for 3 h of hydrothermal treatment. This was the much shorter synthesis time than those prepared on unseeded tubes by a two-times synthesis for more than 48 h with the similar pervaporation performance (Jafar and Budd, 1997). On the other hand, secondary growth was also developed to control membrane microstructure (Bernal et al., 2001; Lovallo et al., 1998; Xomeritakis et al., 1999, 2000). For example, silicalite membranes preferentially oriented with c axis normal to the support surface were prepared on porous α-Al_2O_3 disks coated with an aqueous suspension of silicalite-seed nanocrystals (~ 100 nm). In this approach, nanoscale seeds grew directly to form the oriented silicalite membranes with columnar microstructures. However, the mass production by this method may still be disadvantageous, both economically and practically.

In our previous article (Lin et al., 2000, 2001), we reported the preparation of silicalite membranes on porous tubular supports using the seeding method. Silicalite crystals slowly grew onto the unseeded and nanoscale-silicalite-seeded supports with tetraethylorthosilicate (TEOS), leading to the formation of an incompact crystal layer, especially on the unseeded support. On the other hand, silicalite crystals preferentially grew onto the support tubes seeded with silicalite powders (particle size up to 4 μm) under the same synthesis condition. The silicalite membranes with the good pervaporation performance were synthesized within the shortest time of 5 to 6 h at 185°C in the literature. As mentioned above, the zeolite A membranes, as well as the silicalite membranes prepared by our seeding method, still have defects although they exhibit very good pervaporation separation properties. Therefore, the main objective of the current work is to further improve a separation property of silicalite membranes. The *in situ* crystallization was considered another way to reach this aim. Besides, to the best of our knowledge, zeolite growth is not yet fully understood, especially in the case of *in situ* crystallization on porous tubular supports. It is also the purpose of the present study to gain more insight on the conditions that control the crystal orientation and thickness of the crystal layer by *in situ* crystallization.

Experimental Studies

Membrane preparation

Silicalite membranes were prepared by a single hydrothermal treatment on three types of porous tubular supports with 5 or 10 cm in length:

(1) Mullite tube with 1 μm diameter pore
(2) α-Al_2O_3 with 1 μm diameter pore
(3) α-Al_2O_3 with 0.1 μm diameter pore.

Most of the membrane preparation was carried out with mullite tubes, except for study on the effect of supports in which membranes were prepared on α-Al_2O_3 tubes. The surface of the mullite tube was very rough so that the outer surface was polished with SiC paper. All the types of tubes were cleaned with water three times by ultrasonic cleaner. The silicalite (Si/Al $= \infty$) powders were provided by Toso, Ltd. Seeding was carried out by the method reported in our previous article. The outer surface of the support tube was simply rubbed with a water slurry of zeolite silicalite particles. After seeding, the support tubes were first dried at room temperature and then dried at 100°C for 15 to 30 min.

Colloidal silica (Nissan Chemical Ltd.), TEOS (Aldrich), Ludox AS30 (Aldrich), Ludox AS40 (Aldrich), and fumed silica (Aldrich) were used as silica sources. Without indication, colloidal silica (Nissan Chemical Ltd.) was used to prepare silicalite membranes. Except for fumed silica, a clear solution for synthesis of silicalite membranes was prepared by mixing and stirring a silica source, tetrapropylammonium hydroxide and deionized water at room temperature for 1 h. All the resultant molar composition is SiO_2:TPAOH:H_2O = 1:0.17:120, which is our standard recipe. Two support tubes were vertically placed in a stainless steel autoclave containing 200 g synthesis solution. It is noted that the outer and inner surfaces of the tube were contacted with the synthesis solution, so that silicalite crystals could form on both sides of the tube. The dense layer was formed on the outside of the tubular supports. The autoclave was placed in a convection oven preheated at the synthesis temperature from 145 to 185°C for a given time. After crystallization, the autoclave was removed from the oven and cooled with water. The sample was taken out, washed carefully with hot distilled water, dried at 100°C for several hours, and then calcined at 400°C for 60 h with a heating rate of 0.5°C/min.

Characterization and permeation experiments

SEM observation of the membrane surface and cross section was carried out with scanning electron microscopy (SEM) Hitachi S-2300. The compositions of the cross section were analyzed by electron probe microanalysis (EPMA; JEOL, JXA-8800R) with wavelength dispersive spectrometer (WDS).

Pervaporation experiments were carried out with a batch system illustrated in our previous article (Lin et al., 2001). The inside of the membrane tube was evacuated through a vacuum line. The permeate vapor was collected by a cold trap cooled with liquid nitrogen. The downstream pressure was maintained below 0.1 torr. The effective membrane areas were about 10 cm^2. The compositions of the feed and permeate were analyzed by a gas chromatograph (Shimalite F) equipped with 3 m column packed with Polarpack Q poly (ethylene glycol)-1000. The flux was calculated by weighing the condensed permeate. The separation factor was determined as

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

where X_A, X_B, Y_A, and Y_B denote the mass fractions of components A (ethanol) and B (water) in the feed and permeate sides.

To carry out gas permeation tests, silicalite membranes were prepared on mullite tubes with 10 cm in length (an effective area of 19 cm^2). Single-gas permeation experiments were conducted for *n*-butane and *i*-butane using the permeation module described in our previous article (Okamoto et al., 2001). The feed gas was introduced to the outside of the membrane at a feed pressure of about 1 atm, and the gas permeation was measured by a vacuum time-lag method, namely, recording pressure increase using a pressure transducer.

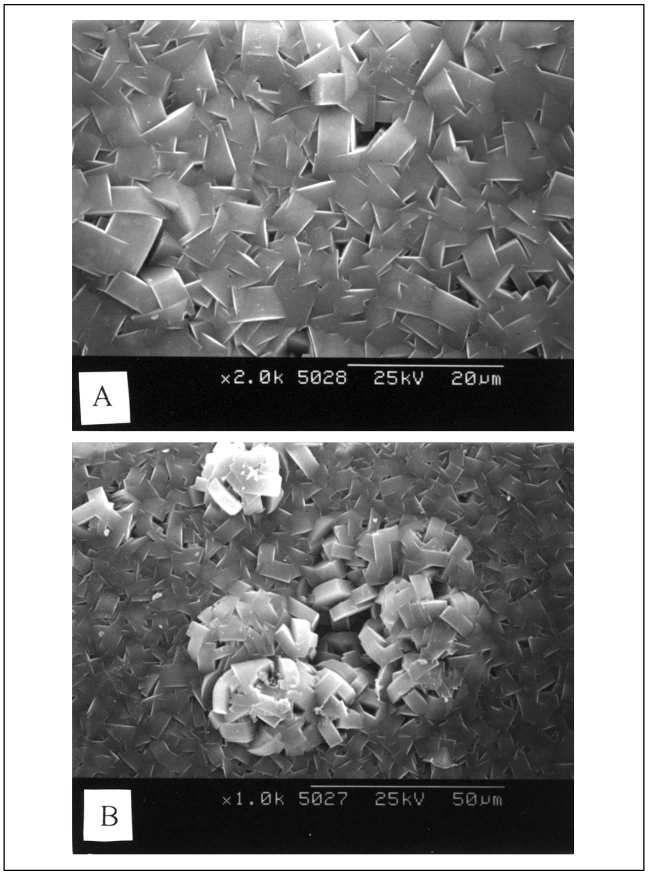

Figure 1. SEM surface of the membrane prepared on silicalite-seeded mullite tube at 175°C for 16 h using colloidal silica.

Results and Discussion

SEM characterization

Crystal Growth on Mullite Tube. Figure 1 shows SEM surface views of the silicalite membrane prepared on a silicalite-seeded mullite tube with a colloidal silica source at 175°C for 16 h of hydrothermal treatment. From this SEM surface view in Figure 1a, it is clearly seen that silicalite crystals showed a good intergrowth behavior with less interzeolitic spaces. However, a lot of dome-like defects similar to the previous report (Xomeritakis et al., 1999) were observed, as shown in Figure 1b. In addition, these SEM surface views suggested that silicalite crystals oriented with c axis normal to the support surface were formed on the seeded mullite tube. In Figure 2a, the SEM cross-sectional views further supported the orientation of the crystal layer. The crystal layer had columnar microstructures exhibiting an increase in grain size with increasing crystal layer thickness, which was a typical morphology of the silicalite membranes oriented with the c axis. The thickness of the top crystal layer was about 10 μm, which was estimated from Figure 2a. On the other hand, as shown in Figure 2b, there was a continuous intermediate layer with about 10 to 20 μm in thickness between the top crystal layer and support, while a lot of big cavities were observed in the cross section of the mullite tube. In addition, a lot of smaller silicalite crystals were observed in the depths of the support.

Figure 3 shows the SEM surface and cross-sectional views of the silicalite membrane prepared on an unseeded mullite tube with a colloidal silica source at 175°C for 16 h of hydrothermal treatment. After hydrothermal treatment, the unseeded mullite tube was fully covered with silicalite crystals. From Figure 3a, it seems that the crystal intergrowth was poorer than that on the silicalite-seeded tube in Figure 1a under the same synthesis conditions. Also, silicalite crystals randomly grew onto the unseeded tube in contrast to the seeded tube. In Figure 3b, the SEM cross-sectional view supported a random orientation of an incompact top crystal layer. It was also found that silicalite crystals were formed inside the support. It was very difficult to determine the interface between the mullite support and the silicalite crystal layer not only because of the very rough surface of the support, but also the formation of the silicalite crystals inside the support. Compared with the cross section of the mullite tube, the thickness of the intermediate layer was estimated about 5 to 10 μm, which was thinner than that on the silicalite-seeded mullite tube in Figure 2b.

Figure 4 shows the SEM surface and cross-sectional views of the silicalite membrane prepared on an unseeded mullite tube with TEOS as a silica source at 175°C for 30 h of hy-

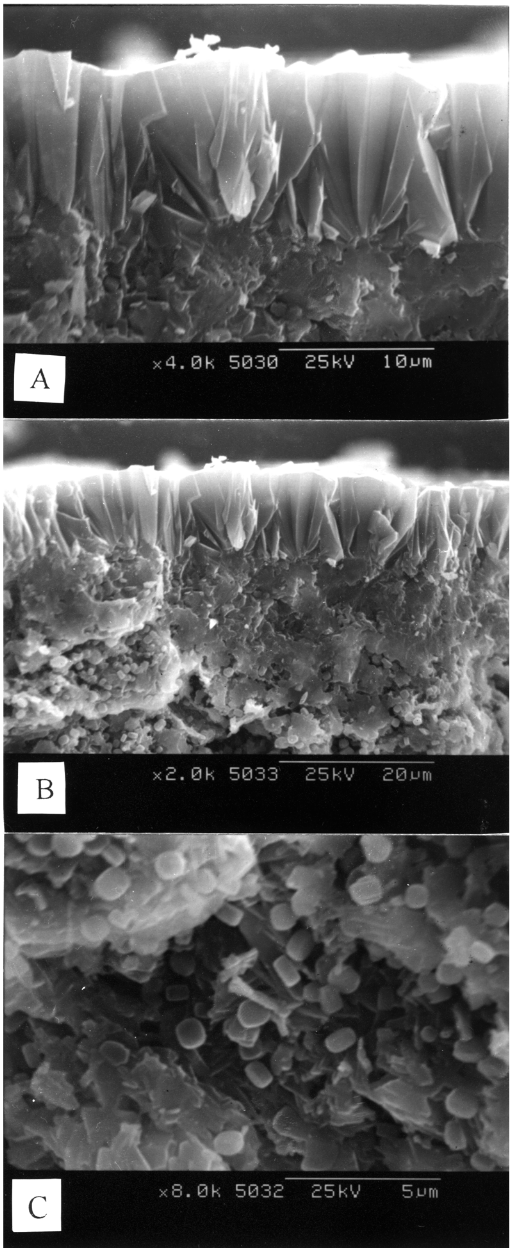

Figure 2. SEM cross section of the membrane prepared on silicalite-seeded mullite tube at 175°C for 16 h using colloidal silica.

drothermal treatment. From this figure, not only good coverage is seen by silicalite crystals on the unseeded tube, but also good orientation of the crystal layer is clearly seen. As reported in our previous article (Lin et al., 2001), in the absence of seeds, silicalite crystals with a size less than 1.5 μm could not form a continuous layer on the tube surface for 16 h of hydrothermal treatment. However, after 30 h of the hydrothermal treatment, the membrane with crystal thickness of about 18 μm had the typical morphology of the columnar microstructures for the well-oriented silicalite membranes, which is similar to that of the membrane prepared on the silicalite-seeded tube with the colloidal silica, as shown in Figures 1 and 2. On the other hand, Figure 5 shows the SEM surface and cross-sectional views of the silicalite membrane prepared on an unseeded mullite tube with TEOS at 185°C for 24 h of hydrothermal treatment. It can be seen that, when the synthesis temperature increased from 175°C to 185°C, the more randomly oriented silicalite membrane with larger size crystals was obtained on the unseeded tube instead of the well-oriented membrane. In the case of the seeded tube, more crystals with smaller sizes grew around the silicalite seeds under the same synthesis conditions except for 5.5 h (Lin et al., 2001).

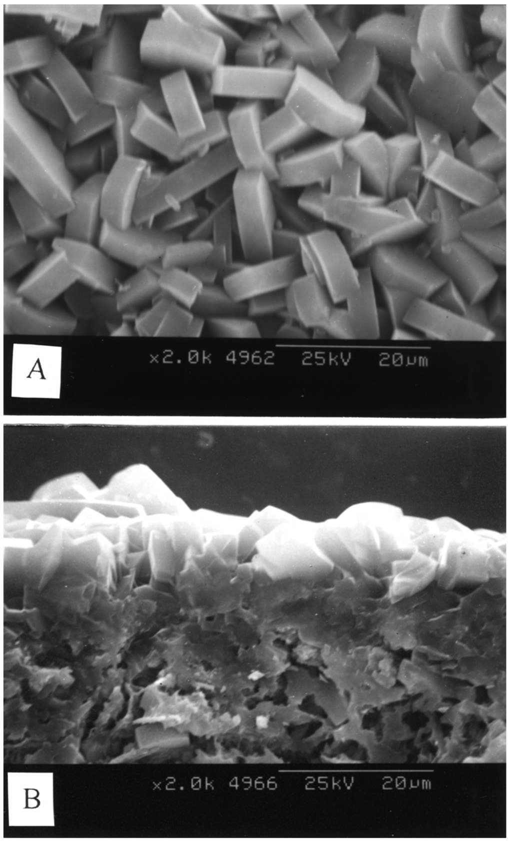

Figure 3. SEM surface and cross section of the membrane prepared on unseeded mullite tube at 175°C for 16 h using colloidal silica.

It is well known that the nucleation and crystallization rate and growth morphology of zeolite depend on not only the chemical composition of the synthesis mixture, but also the silica source. As presented above, the silicalite membranes prepared with the colloidal silica (di-trimeric Si source) and TEOS (monomeric Si source) had the different morphologies such as orientation and crystal layer thickness. On the other hand, the preferentially oriented silicalite membranes have so far been prepared only on the porous supports seeded with an aqueous suspension of silicalite nanocrystals (~ 100 nm) by repeated dip coating (Bernal et al., 2001; Lovallo et al., 1998; Nair et al., 2001; Xomeritakis et al., 1999). In their cases, nanocrystal seeds coated on the support surface grew directly

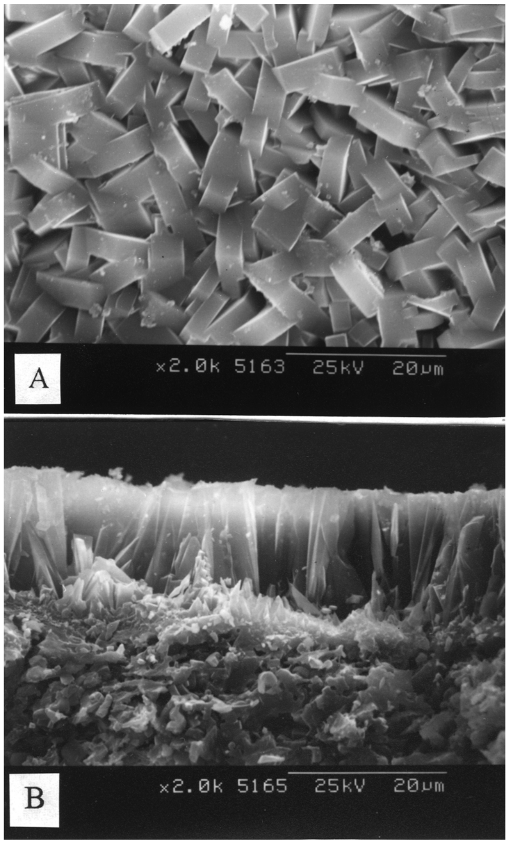

Figure 4. SEM surface and cross section of the membrane prepared on unseeded mullite tube at 175°C for 30 h using TEOS.

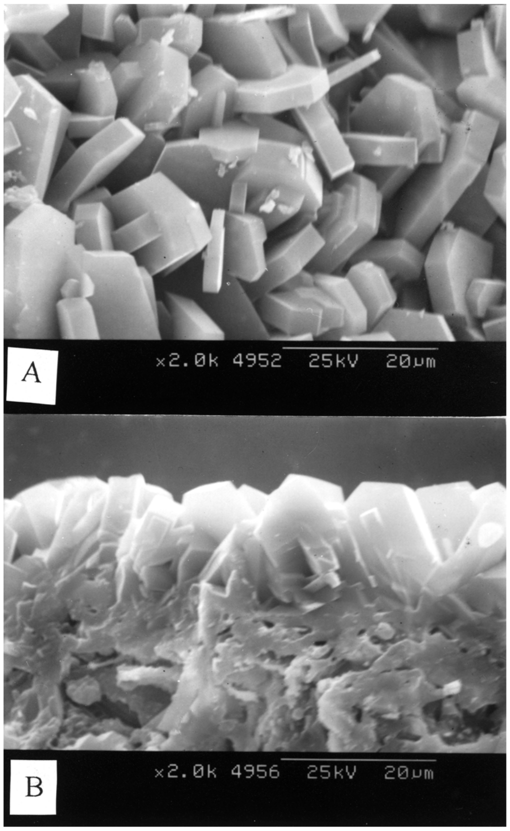

Figure 5. SEM surface and cross section of the membrane prepared on unseeded mullite tube at 185°C for 24 h using TEOS.

to form the oriented silicalite membranes with columnar microstructures. The present formation of the oriented layer is apparently different from theirs. In our case, the silicalite seeds mainly provided the nucleation sites (Loos, 1997; Warzywoda et al., 1991) instead of direct seed growth. This result is not surprising, because it is well known that the faster growth direction of silicalite crystals is c axis at high temperature than other axes, which is essential to preparation of oriented silicalite membranes. Therefore, the well oriented silicalite membranes were also obtained by *in situ* crystallization at the present study.

Crystal Growth on α*-Al*$_2$*O*$_3$ *Tube.* Figure 6 shows SEM surface and cross-sectional views of the silicalite membrane prepared on an unseeded α-Al$_2$O$_3$ tube with the same average pore size of 1 μm as the mullite tube. The hydrothermal synthesis conditions were the same as in the case of the unseeded mullite tube (175°C for 16 h with the colloidal silica source). In Figure 6a, it can be seen that silicalite crystals grew with well-interlocking fashion onto the support surface and the α-Al$_2$O$_3$ tube surface was entirely covered with random silicalite crystals. This crystal growth behavior was similar to the case of the unseeded mullite tube. However, tiny silicalite crystals were observed for the sample prepared on the unseeded α-Al$_2$O$_3$ tube, indicating the secondary nucleation of new crystals on the first formed ones. This behavior might be the same as the role of the silicalite seeds, which provides nucleation sites (Loos, 1997; Warzywoda et al., 1991). On the other hand, there is a larger difference of the cross-sectional structure found between these two membranes. First, as shown in Figure 6b, silicalite crystals were hardly observed inside the α-Al$_2$O$_3$ tube, and, also, it was more difficult to determine the intermediate layer between the top crystal layer and the porous support compared with Figure 3b. It seems that silicalite crystals were only formed in the pore mouth of the α-Al$_2$O$_3$ tube. Secondly, the thickness of the crystal layer including the top crystal layer and the estimated intermediate layer was 10 μm, which was much thinner than that on the unseeded mullite tube with about 15 to 20 μm in thickness.

On the other hand, it is surprising that silicalite crystals could not grow well onto the surface of an unseeded α-Al$_2$O$_3$ tube with an average pore size of 0.1 μm under the same hydrothermal synthesis conditions, even after prolonged hydrothermal treatment of 24 h. A SEM surface view of this sample is shown in Figure 7. An isolated silicalite crystal growth behavior was observed for the pore size of 0.1 μm, leading to the formation of a discontinuous crystal layer, so that the bare α-Al$_2$O$_3$ surface was clearly observed. It is apparent that much fewer nuclei were directly formed on the surface or attached from the solution onto the support sur-

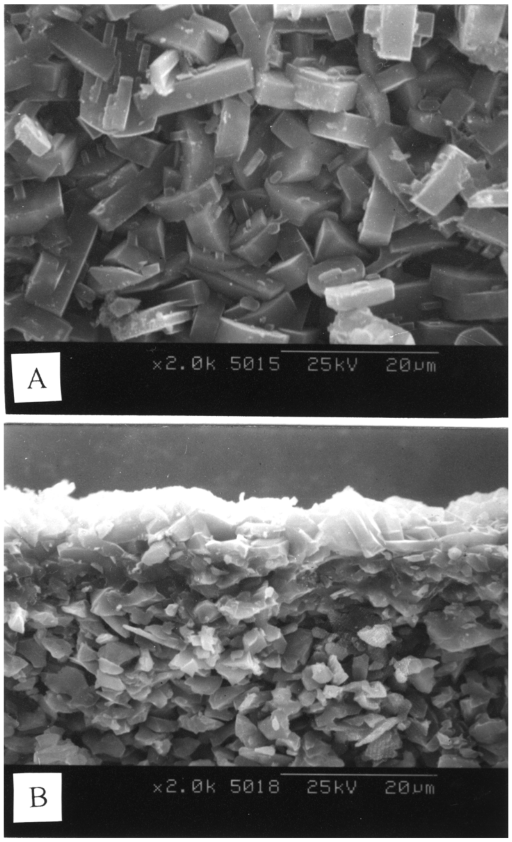

Figure 6. SEM surface and cross section of the membrane prepared on unseeded α-Al_2O_3 tube with 1 μm pore size at 175°C for 16 h using colloidal silica.

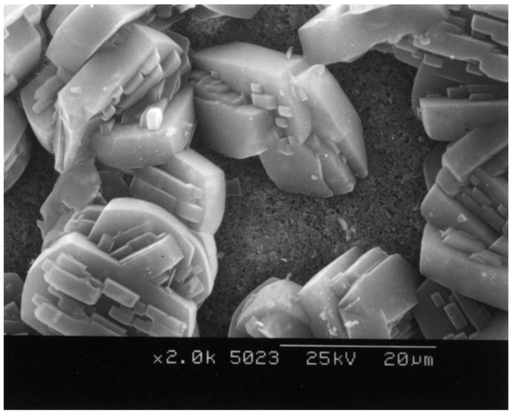

Figure 7. SEM surface of the membrane prepared on unseeded α-Al_2O_3 tube with 0.1 μm pore size at 175°C for 24 h using colloidal silica.

face. At the present time, it is not clear why the pore size of the support strongly affects the crystal growth behavior. However, it would be considered that the porous tube surface provided the nucleation sites and fasten the crystallization. The different crystal growth behavior on the α-Al_2O_3 tubes with the different pore sizes might result from the different surface area and roughness of the tube.

The silicalite membranes reported in the literature are generally prepared on porous supports including flat disks and tubes with pore sizes of less than 1 μm, and some membranes showed good separation properties. Compared with those membrane preparation methods, we focused on the composition of the synthesis solution, especially a molar ratio of H_2O/SiO_2. In order to obtain reliably comparable information, the typical molar chemical compositions applied to prepare the silicalite membranes on porous tubes were chosen and are listed in Table 1. The silicalite membranes were already prepared on the unseeded supports with the smallest pore size of 0.005 μm among the used supports, but with the much more concentrated synthesis solution ($H_2O/SiO_2 = 23$) and longer synthesis treatment (Tuan et al., 1999). In addition, the silicalite membranes were prepared on the seeded supports also using the concentrated solution ($H_2O/SiO_2 = 60$) (Bernal et al., 2001). Our synthesis solution has the highest H_2O/SiO_2 ratio of 120, so that the isolated silicalite crystal growth behavior on the α-Al_2O_3 tube with the pore size of 0.1 μm may not unreasonable.

In this section, the SEM characterization results of the samples prepared under the typical synthesis conditions were presented and discussed, not including the results concerning the time course for each sample preparation. In order to understand the silicalite crystal growth process on the support, these results will be presented in detail in another article.

Pervaporation performance

The membrane separation performance (permeability and selectivity) is related to the quality of a zeolite layer formed on a porous support. Under the certain gel composition for synthesis of zeolite membranes, a crystal growth behavior such as growth rate, morphology, and orientation of crystals is

Table 1. Typical Synthesis Conditions for Preparation of Silicalite Membranes on Tubular Supports

Molar Chemical Composition		Support		Synthesis Conditions		
SiO_2:TPAOH:H_2O	H_2O/SiO_2	Pore Size (μm)	Seeding	Temp. (°C)	Time (h)	Ref.
(a)	98	0.2	Yes	130–150	16+7	Lai and Gavalas (1998)
1:0.0514:23(b)	23	0.005 or 0.2	No	170	72+72	Tuan et al. (1999)
1:0.12:60	60	0.2	Yes	175	20–24	Bernal et al. (2001)
1:0.17:120	120	1	No	175	16	This work

Note: (a): SiO_2:TPABr:H_2O:Na_2O = 1:0.15:98:0.35; (b) Small amount of Al_2O_3 added ($Al_2O_3/SiO_2 = 0.00083$).

Table 2. PV Performance of Silicalite Membranes for 5 wt. % Ethanol Feed Solution at 60°C

Memb. No.	Seeding	Synthesis Time (h)	Flux kg/m^2·h	α
M1-1	Yes	4	—	—
M2-1	″	8	1.28	65
M3-1	″	10	1.17	49
M4-1	″	12	1.12	57
M5-1	″	14	0.60	49
M6-1	″	16	0.67	49
M7-1	″	18	0.74	53
M8-1	″	20	0.87	67
M9-1	″	24	0.88	69
M1-2	No	4	—	—
M2-2	″	8	—	—
M3-2	″	10	1.17	64
M4-2	″	12	1.33	83
M5-2	″	14	0.76	96
M6-2	″	16	0.93	106
M7-2	″	18	0.83	95
M8-2	″	20	0.96	96
M9-2	″	24	0.93	96

Note: (a) Mullite tube; (b) SiO_2:TPAOH:H_2O = 1:0.17:120; (c) colloidal silica; (d) synthesis temperature of 175°C.

Table 3. PV Performance of Silicalite Membranes for 5 wt. % Ethanol Feed Solution at 60°C

Memb. No.	Synthesis Temp. (°C)	Synthesis Time (h)	Flux (kg/m^2·h)	α
M10	145	24	—	—
M11	155	24	1.29	67
M12	165	24	1.06	78
M13	175	16	0.93	96

Note: (a) Unseeded mullite tube; (b) SiO_2:TPAOH:H_2O = 1:0.17:120; (c) colloidal silica.

strongly related to the crystallization temperature and time, seeds, supports, and so on. Consequently, the membrane separation properties are affected by these factors. In this section, the pervaporation (PV) performance of silicalite membranes corresponding to the synthesis conditions was presented.

Effect of Synthesis Time. Table 2 shows the PV performance of the silicalite membranes prepared on unseeded and silicalite-seeded mullite tubes with the colloidal silica at 175°C as a function of different treatment time. As mentioned in the experimental section, two membranes were once prepared with one autoclave. One formed on the seeded tube and another formed on the unseeded tube were called M1-1 and M1-2, respectively. After 4 h of hydrothermal treatment, silicalite crystals formed could not fully cover all the pores of the support, especially on the unseeded one. Both of the samples did not have a separation property. After 8 h, the silicalite membrane prepared on the seeded tube had a separation factor of 65 for ethanol over water. For further treatment, the separation factors and fluxes did not show dramatic changes. On the other hand, the silicalite membrane prepared on the unseeded tube for 8 h of hydrothermal treatment was still leaking, but after 10 h, had a separation factor of 64, which was comparable to that prepared on the seeded tube. For further treatment, the separation factors first increased, combining with a decrease in the fluxes. After 14 h, the separation factors almost kept constant, although the highest separation factor of 106 was obtained for 16 h of hydrothermal treatment. However, with much prolonged treatment of 48 h, the membrane had a lower separation factor of 70, as will be shown in Table 7, which results from the formation of defects during calcinations (Vroon et al., 1998) or for other unknown reasons. On the other hand, the membranes prepared on the seeded tube with the colloidal silica had the pervaporation separation properties similar to those with TEOS (Lin et al., 2001). A dramatic difference was found on the unseeded tube. The silicalite membranes prepared on the unseeded tube with TEOS at 175°C for 16 h did not show the separation property (Lin et al., 2001). It indicates that the crystal growth rate was faster with the colloidal silica than with TEOS under the present synthesis conditions, as also confirmed by the SEM characterizations.

Effect of synthesis temperature

Table 3 shows the PV performance of the silicalite membranes prepared on unseeded mullite tubes with the colloidal silica at different synthesis temperatures from 145 to 175°C. It can be seen that the separation factors increased with increasing synthesis temperature. At 145°C, the crystal growth rate was so low that the compact crystal layer could not be formed on the support. Even after 24 h of hydrothermal treatment, the sample was still leaking before calcination, while the membrane prepared on the seeded tube under the same hydrothermal synthesis conditions with TEOS had the separation factor of about 40 (Lin et al., 2001). This is the advantage of seeding, in which silicalite crystal seeds can promote the crystal growth onto the support, even at low temperature (Lai and Gavalas, 1998). At 175°C, the highest separation factor of about 95 was obtained. The results suggest that the synthesis temperature is one of the most important variable factors, which strongly affects the quality of the membrane. The faster crystal growth rate at higher temperature is more effective in closing a pore between the silicalite grains (Gora et al., 1999, 2001). Vroon et al. (1998) found that the separation factor of n-C_4H_{10}/i-C_4H_{10} increased with increasing synthesis temperature from 98 to 180°C, although the good MFI membrane was also prepared at low temperature of 120°C. Tuan et al. (1999) also reported that ZSM-5 membranes prepared at higher temperature exhibited better gas separation performance at high temperature compared with those prepared at lower temperature.

Effect of H_2O/SiO_2 ratio

Table 4 shows the PV performance of the silicalite membranes prepared on the unseeded mullite tubes with different H_2O/SiO_2 ratios. All the sample preparation was carried out at 175°C for 16 h of hydrothermal treatment with the colloidal silica. From Table 4, the more diluted or the more concentrated synthesis solution was not suitable for preparation of the silicalite membranes with higher separation factors compared with the H_2O/SiO_2 ratio of 120. The sample prepared with a H_2O/SiO_2 ratio of 200 was leaking after 16 h of hydrothermal treatment, suggesting that under the present synthesis conditions the solution was too diluted. These two samples repeated by one hydrothermal treatment

Table 4. PV Performance of Silicalite Membranes Prepared with Different H_2O/SiO_2 Ratios

Memb. No	H_2O/SiO_2 (Molar Ratio)	Synthesis Time (h)	Flux (kg/m^2·h)	α
M14	80	16	1.15	59
M15	120	16	0.93	96
M16	160	16	0.97	62
M17	200	16	—	—
M17*	200	16 + 24	0.89	80

Note: (a) Unseeded mullite tube; (b) SiO_2:TPAOH:H_2O = 1:0.17:X; (c) colloidal silica; (d) synthesis temperature of 175°C; (e) PV: 5 wt. % ethanol feed solution at 60°C. M17*: prepared by repeating one more hydrothermal treatment for 24 h to M17.

for 24 h under the same conditions showed good separation ($\alpha_{\text{ethanol/water}} = 80$), but still lower than those ($\alpha_{\text{ethanol/water}} = 96$) prepared with the H_2O/SiO_2 ratio of 120 by a single hydrothermal treatment. It is clear that the high H_2O/SiO_2 ratio would not result in a continuous crystal layer because fewer nuclei were directly formed on the surface or attached from the solution onto the support surface, and also the limited nutrient was provided for their growth. On the other hand, the lower H_2O/SiO_2 ratio might change the crystal growth form such as crystal sizes, leading to the formation of more defects.

Effect of aging

Table 5 shows the PV performance of the silicalite membranes prepared with the synthesis solution aged for different time. It can be seen that the separation factors for ethanol over water decreased with an increase in aging time. It is known that during aging, nucleation takes place. The longer the solution is aged, the more nuclei are created in the solution. Consequently, more crystallization occurs in the solution during crystallization. It is noted that the clear synthesis solution used in our experiments contained more water than others, as listed in Table 1. The formation of more crystals in the solution depressed crystal growth or changed crystal growth fashion onto the support, especially longer aging. It is indeed the case that the separation factors of the membranes decreased with an increase in aging. This result suggests that when the diluted solution is adopted to synthesize silicalite membranes, it cannot be ignored that crystallization takes place in the solution.

Table 5. PV Performance of Silicalite Membranes Prepared with Aged Clear Solution

Memb. No	Aging Time (h)	Flux (kg/m^2·h)	α
M18	1	0.93	96
M19	12	1.22	63
M20	24	1.31	47

Note: (a) Unseeded mullite tube; (b) SiO_2:TPAOH:H_2O = 1:0.17:120; (c) colloidal silica; (d) synthesis conditions: 175°C for 16 h; (e) PV: 5 wt. % ethanol feed solution at 60°C.

Table 6. PV Performance of Silicalite Membranes Prepared by Different Preparation Procedure

Memb. No.	Crystal Layer	Flux (kg/m^2·h)	α
M21	Inner surface	—	—
M22	Outer surface	1.13	93

Note: (a) Unseeded mullite tube; (b) SiO_2:TPAOH:H_2O = 1:0.17:120; (c) colloidal silica; (d) synthesis conditions: 175°C for 16 h; (e) PV: 5 wt. % ethanol feed solution at 60°C.

Effect of membrane preparation procedure

Silicalite crystals also grew onto the inner surface of the unseeded mullite tube using the standard membrane preparation procedure. In order to investigate the effect of the inner crystal layer on the membrane separation property, silicalite membranes were also prepared by controlling the formation of a crystal layer on the tube surface, specifically, the only outer surface or the only inner surface of the tube. When both ends of the mullite tube were blocked by wrapping Teflon tape, crystals were formed only on the outer surface of the mullite tube. Meanwhile, the outer surface was wrapped by Teflon tape; crystals were formed only on the inner surface. PV performance of the membranes is listed in Table 6. The membranes prepared by the formation of the crystal layer on the outer surface of the mullite tube had a separation factor of 94 for ethanol over water and flux of 1.1 kg/m^2 h. The separation factor was similar to that prepared by the formation of the crystal layer on both sides of the mullite tube, as shown in Table 2, while the flux was little bit larger. On the other hand, the membranes prepared by the formation of the crystal layer on the inner surface of the tube were leaking. Presently, the reason is not clear. However, the concentration of the nutrient for the crystal growth may be different between the inside and outside of the tube. The pervaporation results indicate that the compact layer was apparently the outer layer, and the inner layer also did not strongly affect the flux. In addition, our results were different from the previous reports (Jia et al., 1994; Tuan et al., 1999). In their cases, the membranes were prepared only by the formation of the crystal layer on the inner surface of the tube. Also, the good membranes were obtained only by repeated hydrothermal treatment.

Table 7. PV Performance of Silicalite Membranes

Memb. No.	Silica Source	Synthesis Condition Temp. (°C)	Synthesis Condition Time (h)	Flux (kg/m^2·h)	α
M23	Fumed SiO_2	175	16	—	—
M24*	Fumed SiO_2	175	16	1.97	56
M25	Ludox-30	175	16	1.17	60
M26	Ludox-40	175	16	1.13	79
M27	TEOS	175	30	1.23	46
M28	TEOS	185	20	1.31	76
M29	TEOS	185	24	1.22	85

Note: (a) Unseeded mullite; (b) SiO_2:TPAOH:H_2O = 1:0.17:120; (c) M24* prepared on silicalite-seeded tube; (d) PV: 5 wt. % ethanol feed solution at 60°C.

Effect of silica source

Table 7 shows the PV performance of the silicalite membranes prepared on the unseeded mullite tubes with different silica sources. The membranes formed on the unseeded mullite tube with fumed silica did not have a separation property, while the membrane formed on the seeded tube had a separation factor of 56. As mentioned above, all of the synthesis solution was prepared with the same molar chemical composition. The fumed silica could not be completely dissolved under the present conditions, resulting in the formation of a milk-like gel. During the crystallization process, most of crystals were precipitated to the bottom as a result of the formation of the bulk powder in the solution instead of the support surface. Consequently, the crystal layer formed on the unseeded tube was not continuous, as evidenced by the observation of the bare surface of the mullite. The silicalite membranes prepared with Ludox AS30 and Ludox AS40 showed lower separation properties than those with the colloidal silica. The most important information from this table is about TEOS. While using TEOS as a silica source at synthesis temperature of 175°C, it took a longer time to prepare the membrane on the unseeded tube than at 185°C. Moreover, the membrane prepared at 185°C for 24 h had the much higher separation factor of 85 than that prepared at 175°C for 30 h. On the other hand, the PV performance of the membranes prepared on the unseeded tubes at 185°C for 24 h was comparable to that of the membranes prepared on the seeded α-Al_2O_3 tubes at 185°C for 5.5 h (Lin et al., 2001). It is further supported that the faster crystal growth rate at higher temperature is more effective in closing a pore between the silicalite grains, as discussed above. Gora et al. (1999, 2001a, 2001b) studied the effect of various silica sources on the flat membrane formation and the resulting membrane separation properties. They found that TEOS was the better source for making dense, well-intergrown silicalite membranes. Tuan et al. (1999) also reported that the membranes prepared with the different silica sources exhibited the different separation performance. Under the strongly alkaline condition, the fumed silica (polymeric Si source) could be completely dissolved, so that the good MFI membranes were obtained (Vroon et al., 1998).

Table 8. PV Performance of Silicalite Membranes Prepared on Unseeded α-Al_2O_3 Supports

Memb. No.	Pore Size (μm)	Synthesis Time (h)	Flux (kg/$m^2\cdot$h)	α
M30	0.1	24	—	—
M31	1	14	2.07	78
M32	1	16	1.91	69
M33	1	24	1.16	66
M34	1	48	0.72	72

Note: (a) SiO_2:TPAOH:H_2O = 1:0.17:120; (b) colloidal silica; (c) synthesis temperature: 175°C; (d) PV: 5 wt. % ethanol feed solution at 60°C.

Effect of support

Table 8 shows the PV performance of the silicalite membranes prepared on the unseeded α-Al_2O_3 tubes using the colloidal silica. The membranes formed on the tubes with 1 μm pore size showed the good separation for ethanol over water. In contrast, the membranes formed on the unseeded α-Al_2O_3 tubes with 0.1 μm pore size after 24 h of hydrothermal treatment were leaking, as confirmed by the SEM as shown in Figure 5. In our previous article (Lin et al., 2001), the silicalite seeds with a size up to 4 μm could not be planted into 0.1 μm pore of the stainless steel tube. Then, the crystals only grew on the surface, resulting in the formation of crystal layers with defects. Consequently, the membranes showed the PV performance with low separation factors, but high fluxes when compared with those formed on other supports with 10 times larger pores. On the other hand, more silicalite seeds could be planted into the 2 μm pores of α-Al_2O_3 tubes compared with 1 μm pores of the mullite tube and, as a result, the better membranes were prepared on the α-Al_2O_3 tubes under the same synthesis conditions in our previous work. The present results further support that the membrane preparation conditions should be also optimized regarding the state of supports.

Comparison of separation performance among silicalite membranes

The pervaporation performances of silicalite membranes in the literature are listed in Table 9. Sano et al. (1994) re-

Table 9. Pevaporation Performance of Silicalite Membranes for Ethanol/Water Mixtures

	Synthesis Condition			Feed Conc.	PV Temp.	Flux		
Support	Seeding	Temp. (°C)	Time (h)	(EtOH wt. %)	(°C)	(kg/$m^2\cdot$h)	α	Ref.
M1-tube	No	175	16	5	60	0.93	106	This work
α-tube	No	185	24	5	60	1.22	85	This work
M1-tube	Yes	175	8	5	60	1.28	65	This work
M1-tube	Yes	175	12	5	60	1.41	72	Lin (2001)
M1-tube	Yes	185	5.5	5	60	2.23	62	Lin (2001)
α-tube	Yes	185	5.5	5	60	1.81	89	Lin (2001)
SS-disk	No	170	48	4	60	0.78	58	Sano
α-disk	No	170	48	4	30	0.1	24	Sano
SS-disk	No	170	144	4	30	0.29	120	Matsuda
				4	60	0.97	84	Matsuda
SS-disk	No	170	48	4.7	30	0.50	64	Nomura
M1-tube	No	170	148	5	50	0.34	51	Kondo
α-tube	No	170	48	10	75	2.29	25	Kita (1998)
γ-tube	No	170	24	9.7	24	0.1	12	Liu

Notes: M1-tube: mullite tube; α-tube: α-Al_2O_3 tube; SS-disk: stainless steel disk; α-disk: α-Al_2O_3 disk; γ-tube: γ-Al_2O_3 tube.

ported that the separation factor of about 60 for ethanol (EtOH)/water mixtures was obtained for their silicalite membrane formed on a stainless steel disk with crystal layer thickness of 400–500 μm. Several years later (Matsuda et al., 1998), they further improved the separation factor from 60 to 120 by using a small amount of diluted gel for prolonged hydrothermal treatment (144 h) and calcination at a low temperature of 375°C, leading to the formation of a more dense crystal layer with higher crystallinity. However, the silicalite membranes prepared on alumina disks or tubes showed much lower separation, as listed in Table 9, due to the incorporation of Al leached from the supports into crystal layers under strongly alkaline conditions (Liu et al., 1996; Sano et al., 1994; Sasaki et al., 2000). In our previous work (Lin et al., 2001), the different approach such as seeding, TEOS with alkali-free medium, and high temperature was adopted to quickly synthesize silicalite membranes, so that Al leaching was depressed. The silicalite membranes with higher Si/Al ratio showed both high separation factor and flux.

Considering the kinetic diameter of water, ethanol, and silicalite pore size, the separation is not based on molecular sieving, but preferential adsorption, in which ethanol molecules preferentially adsorbed block water from entering the pores and permeating through the membrane. The higher the Si/Al ratio, the stronger hydrophobicity would result in the higher separation factor. However, if silicalite membranes had more nonzeolitic pores, a high separation factor would not be expected, even with the high Si/Al ratio. Based on this notion, *in situ* crystallization was considered another way to prepare silicalite membranes with fewer defects. The better separation properties of the present silicalite membranes prepared by *in situ* crystallization were not attributed to the higher Si/Al ratio of 960, but to reduced defects such as nonzeolitic pores compared with our previous membranes (Si/Al ratio more than 2000). This was also supported by gas permeation tests of *n*-butane and *i*-butane. From gas permeation results, the higher *n/i*-butane ideal separation factor is, the higher ethanol/water separation factor is. For example, the silicalite membrane with the ethanol/water separation factor of 90–95 at 60°C with a 5 wt. % ethanol feed solution showed an *n*-butane/*i*-butane ideal separation factor of more than 30 at 200°C.

On the other hand, the oriented silicalite membranes had the lower separation factor for ethanol over water compared with the randomly oriented membranes. It is suggested that under the present synthesis conditions, the oriented membrane had more defects than the randomly oriented membrane. It is apparent that the uniform seed layer could not be prepared by our seeding method due not only to silicalite powder with a size up to 4 μm, but also the very rough surface of the support, leading to the formation of a lot of dome-like defects evidenced by the SEM characterization. In addition, the thickness of the crystal layer with preferential one direction growth (c axis) should be thick enough to close systematic pinholes between the crystals when the crystals had sufficient time to grow in lateral directions (Jansen et al., 1999). The thickness of less than 20 μm for the oriented membranes prepared in the present study would be too thin. In the case of *in situ* crystallization, the crystals grew in all directions onto the support and formed the more incompact top crystal layer compared with that for the oriented membranes. However, the silicalite membranes showed the better pervaporation performance. The higher separation factors for the membranes prepared on the unseeded tubes indicate that the effectively selective layer was not the top crystal layer, but the intermediate layer between the top crystal layer and support.

Our results also indicate that the formation of the zeolite layer is involved in the complex chemical reactions, which are affected by many interacting factors. The membrane formation on porous supports and the membrane structures related to the membrane qualities are still not well understood. In order to prepare the better membranes, this issue combined with considering support structures needs to be further elucidated in future work.

Conclusions

(1) Well-oriented silicalite membranes with the c axis normal to the tube surface could be obtained on tubular supports not only by the seeding method, but also *in situ* crystallization.

(2) Randomly oriented membranes with a dense intermediate layer had the higher separation selectivities than the oriented membranes. This results from fewer defects.

(3) The present results further supported that, for preparation of good silicalite membranes, not only synthesis conditions should be optimized, but also the state of supports should be considered.

(4) The main advantage of seeding was to shorten the synthesis time. In the present results, the better silicalite membranes, specifically, higher separation selectivities, were prepared by *in situ* crystallization using the colloidal silica.

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