

Synthesis of MFI-type zeolite membranes on porous α -alumina supports by wet gel crystallization in the vapor phase*

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A new method has been developed for synthesis of MFI-type zeolite membranes on porous α -alumina supports. Using this method, a thin layer of wet-gel precursor precoated from a synthesis sol containing SiO_2 , tetrapropylammonium hydroxide (TPAOH), NaOH, and H_2O was converted to an MFI zeolite film by vapor-phase treatment at elevated temperatures. MFI zeolite films were formed on the α -alumina substrates, respectively, in the vapor phases of TPAOH solution and an ethylenediamine(EDA)/triethylamine (TEA)/water mixture, but an amorphous material was obtained in the vapor phase of pure water. Scanning electron microscopy and helium permeation examinations before calcination showed that the MFI membrane obtained in the vapor phase of the TPAOH solution was of higher quality than that synthesized in the vapor phase of the EDA/TEA/water mixture in terms of zeolite film integrity and compactness. It was also found that the existence of the template TPA^+ in the parental synthesis sol was critical to the formation of MFI zeolite under the investigated conditions. When precursor layers coated from a template-free colloidal silica system were used, the vapor-phase treatment resulted in formation of Na-P1 and ANA zeolite films, respectively, in the vapors of TPAOH solution and the EDA/TEA/water mixture. The method developed in this work has the advantages of improved controllability, minimal waste generation, and reduced chemical consumption that are desirable for large-scale production of zeolite membranes. © 2003 Kluwer Academic Publishers

1. Introduction

Supported polycrystalline zeolite membranes have been studied for more than a decade because of the increased interest in using these membranes in chemical reaction and separation processes [1]. To date, most of the resulting publications have focused on MFI-type zeolite membranes, ZSM-5 and silicalite-1 membranes in particular, because of their readiness to form polycrystalline films on different substrates [2–5], excellent performance in hydrocarbon separations [6–12], high thermal and chemical stabilities, and potential applications in membrane reactors [13–15]. However, industrial applications of zeolite membranes have been hindered due to some major disadvantages associated with current synthesis techniques that make large-scale production difficult and expensive. At present, zeolite membranes are

synthesized by liquid-phase hydrothermal treatment, including *in situ* crystallization and seeding/secondary growth methods [2, 16–19], and the vapor-phase transport (VPT) method [20–24]. Each of these two approaches has distinct advantages and disadvantages.

In the *in situ* crystallization method, one side of the substrate surface contacts an aluminosilicate-template synthesis sol or solution. During the early stage of hydrothermal treatment, a discrete layer of zeolite nuclei is formed on the support surface by heterogeneous nucleation and/or deposition of nuclei from the bulk liquid. The crystal nuclei continue to grow into an interlocked polycrystalline film with minimized intercrystal gaps [2, 25–27]. In seeding/secondary growth synthesis, small zeolite crystallites are pre-embedded in the support surface. The seeded surface is then brought into contact with a synthesis sol or solution under

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hydrothermal conditions to allow further growth of the crystallite seeds into a continuous film [18, 19, 28]. The various liquid-phase hydrothermal synthesis methods offer the advantages of a highly compact zeolite layer (minimized nonzeolitic gaps) and a short synthesis time (several hours). Furthermore, the crystallization process in these methods is better understood since it is similar to the traditional processes used for zeolite particle synthesis. The main drawbacks of these methods are (i) difficulty in ensuring the uniformity of the crystallization conditions and limited reproducibility of high-quality membranes [29]; and (ii) significant consumption of valuable chemicals such as tetrapropylammonium hydroxide (TPAOH), resulting in the generation of a large volume of waste and high processing costs.

In the VPT synthesis, the substrate surface is first coated with an aluminosilicate gel layer having a carefully controlled alkalinity and Si/Al ratio [20–22, 30]. The coated gel layer is dried and then converted to zeolite by contact with vapor phases of liquid mixtures containing water and organic compounds [23], such as the commonly used mixture of water, ethylenediamine (EDA), and triethylamine (TEA). The VPT process is carried out at an elevated temperature, normally in the range of 170–200°C, and requires a long synthesis time, which varies from two days to longer than a week to complete the crystallization. Important advantages of the VPT method include a controllable precursor coating process that can avoid uncovered areas in the synthesized zeolite film; a significant reduction in the consumption of valuable organic compounds (because the liquid phase is uncontaminated and may be reused directly); and minimal generation of waste by-products.

The mechanism of zeolite film formation by the VPT method is not fully understood but is considered to be quite different from that of hydrothermal synthesis [31]. In VPT synthesis, crystallization is dominated by a dry-gel-crystallization mechanism [32]. In the conventional VPT method, a small number of tiny liquid puddles may be scattered in the coated precursor layer due to capillary condensation [31]; however, reconstruction of the dry gel network is difficult because the mobility of the precursor species is limited in the strong solid structure. This is evident by the much higher activation energy of ZSM-5 zeolite formation from amorphous dry gels (80 kJ/mol) than that of silicalite crystallization from an aqueous solution (40 kJ/mol) [32]. Therefore, the compactness of the resulting zeolite film is largely determined by the original packing density of the gel particles, and the VPT-derived zeolite membranes are likely to be less compact than membranes synthesized via hydrothermal treatments. Moreover, the structure-directing agents used in conventional VPT synthesis, including EDA and TEA, are highly hazardous to the human nervous system and may be a source of safety and environmental concerns.

In the present study, a new method of vapor-phase treatment of a template-containing wet gel layer was developed for synthesizing MFI-type zeolite membranes on porous α -alumina supports. Such a modified vapor-phase method uses TPAOH as the structure-directing

agent and, thus, can combine the advantages while avoiding the major disadvantages of conventional hydrothermal and VPT methods.

2. Experimental

2.1. Materials

α -alumina discs, 22 mm in diameter, 2 mm thick, and having an average pore size of about 0.19 μm , were used as substrates. The side of the disc used for membrane coating was polished with #600 sandpaper, washed with deionized water, and dried at 50°C overnight before use. Other chemicals used in this work included fumed silica (>99.99%, Aldrich), TPAOH (1 M solution, Aldrich), sodium hydroxide (>99.99%, Aldrich), EDA (>99%, Aldrich), TEA (>99%, Aldrich), and helium (>99.99%, Wright Brothers, Ohio). All the chemicals were used as received.

2.2. Membrane synthesis

The synthesis sol was prepared using the same procedure as reported previously [5, 33]. First, 0.33 g of NaOH pellets was dissolved in 16.7 ml of 1 M TPAOH aqueous solution. The solution was heated to 80–90°C while being stirred vigorously. Then 3.33 g of fumed silica was added to the solution with continued stirring until the system became visually transparent. The overall molar composition of the resulting synthesis sol was 7.0% SiO₂, 0.8% NaOH, 2.1% TPAOH, and 90.1% H₂O. The synthesis sol was aged for 3 h at room temperature in a capped Teflon flask. The polished side of the disc was dipped in the sol for 5–12 seconds to coat it with a uniform precursor layer. The disc was then placed with coated side upward on a Teflon stand in an autoclave.

The autoclave had an inner diameter of 25 mm and an inside height of 65 mm, providing a capacity of about 32 ml. The liquid volume in the autoclave was large enough (~15 ml) to avoid complete vaporization and to maintain a vapor-liquid coexisting state in the autoclave under the synthesis temperature and autogenous pressure. The disc was kept about 2 cm above the liquid level before being heated. Fig. 1 depicts the position of the alumina disc mounted in the autoclave. The autoclave

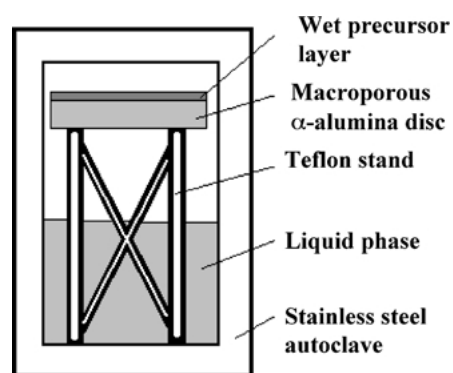


Figure 1 Schematic showing the α -alumina disc mounted in the autoclave.

was sealed immediately after the disc was mounted to prevent the loaded precursor layer from absorbing CO₂ from the air. Some liquid remained on the surface for 10–15 min before being completely soaked up by the substrate because of the high viscosity of the synthesis sol. After it had been placed at room temperature for 20–30 min to allow the remaining liquid to soak into the support pores, the autoclave was moved into the oven, which was preheated to 190°C for vapor-phase treatment.

The vapor phase was provided by a 1 M TPAOH aqueous solution, which had never been used before in conventional VPT synthesis. We used TPAOH as the structure-directing agent in this study because it is (i) the most effective template for formation of MFI-type zeolites [34] and (ii) less toxic than the commonly used amines. Other liquids, including an EDA/TEA/water mixture with a composition of 8.1 mol% EDA/30.7 mol% TEA/61.2 mol% H₂O and pure water, were also used to investigate the effects of these vapor phases on zeolite crystallization. The composition of the EDA/TEA/water mixture was the same as that previously used by Dong *et al.* [20] in VPT synthesis. The time of vapor-phase treatment was 6 d in every case in this study. After synthesis, the discs were washed several times with deionized water and dried/stored in an oven at 50°C.

Experiments were also carried out using colloidal silica for the gel coating to study the effect of the template in the parental sol on the resulting zeolite structure. The colloidal silica suspension was prepared by adding 3.33 g of fumed silica to 17.3 ml of 1.37 M NaOH solution at 80°C under rigorous agitation. The overall molar composition of the final colloidal system was 7.0% SiO₂, 2.9% NaOH, and 90.1% H₂O. The overall molar fraction of NaOH was determined by equalizing the total molar numbers of the hydroxide group introduced into the colloidal silica system and the silicate-TPA⁺ synthesis sol. The 1 M TPAOH solution and the 8.1% EDA/30.7% TEA/61.2% water mixture were used in the vapor-phase treatment. All the other conditions were identical to those of the previous synthesis performed in this study.

2.3. Membrane characterization

The crystal structures of the resulting films were identified by X-ray diffraction (XRD) (Scintag XDS 2000, Cupertino, California), and the morphology of the top layer was observed by scanning electron microscopy (Philips XL 30/FEG SEM, the Netherlands). The zeolite crystalline structures were analyzed based on the XRD data using Jade software (Materials Data, Inc., Livermore, California). The permeation of pure helium was measured before membrane activation to evaluate the integrity and compactness of the zeolite film. Helium permeation was determined by a transient single-gas-permeation setup, which was described in detail in a previous paper [35]. The membranes were further dried at 100°C for at least 4 h prior to helium permeation measurement.

3. Results and discussions

3.1. Results

XRD patterns of the discs after vapor-phase treatment are shown in Figs 2 and 3. Table I summarizes the synthesis conditions and results of the present work. For the gel layers coated from the parental synthesis sol containing template TPAOH, the XRD patterns (Fig. 2)

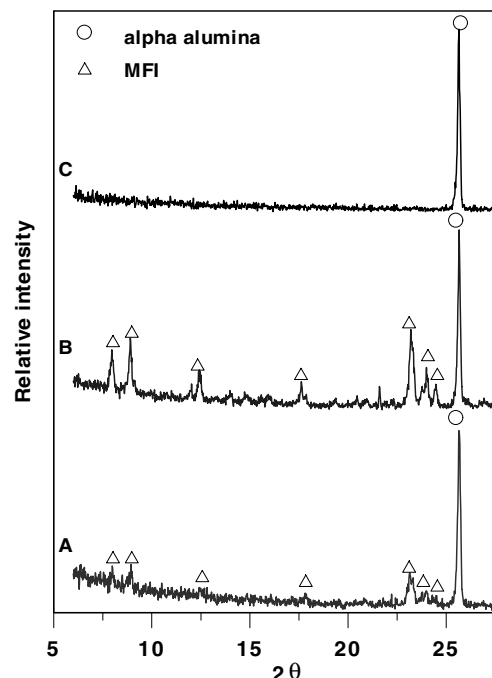


Figure 2 XRD patterns of the membranes after treatment in different vapor phases. (A) treated in vapor of 1 M TPAOH aqueous solution; (B) treated in vapor of EDA/TEA/water mixture; (C) treated in water vapor.

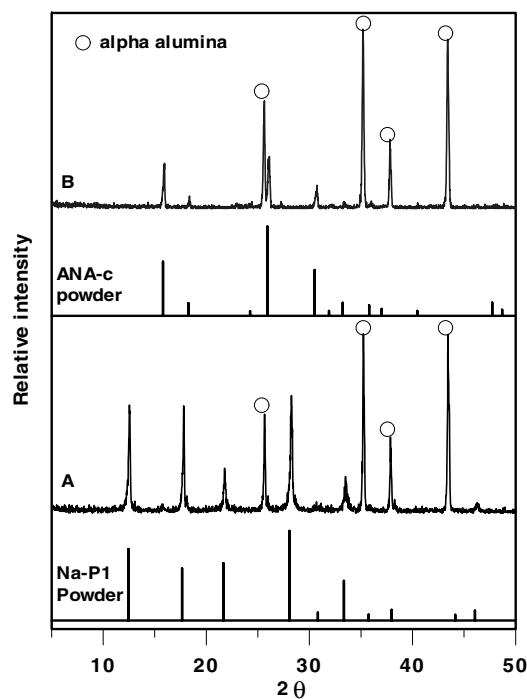


Figure 3 XRD patterns of the materials synthesized from the TPA⁺-free wet gel and the standard patterns of cubic NaP and cubic ANA zeolites. (A) Na-P1 film synthesized in the vapor of TPAOH solution; (B) ANA-c film synthesized in the vapor of the EDA/TEA/water mixture.

TABLE I Results of zeolite membrane synthesis under different conditions

Exp.	Synthesis sol	Liquid phase	T ($^{\circ}\text{C}$)	Time (d)	Top layer	Thickness (μm)	Quality
1	7.0% SiO_2 + 2.1% TPAOH + 0.8% NaOH + 90.1% H_2O	1 M TPAOH	190	6	MFI	3	Good
2	7.0% SiO_2 + 2.1% TPAOH + 0.8% NaOH + 90.1% H_2O	EDA/TEA/ H_2O (8.1/30.7/61.2)	190	6	MFI	12	Poor
3	7.0% SiO_2 + 2.1% TPAOH + 0.8% NaOH + 90.1% H_2O	H_2O	190	6	Amorphous	–	–
4	7.0% SiO_2 + 2.9% NaOH + 90.1% H_2O	1 M TPAOH	190	6	NaP-cubic	–	–
5	7.0% SiO_2 + 2.9% NaOH + 90.1% H_2O	EDA/TEA/ H_2O (8.1/30.7/61.2)	190	6	ANA-cubic	–	–

indicate that MFI-type zeolite crystallites are formed on the α -alumina supports after being treated in the vapor phases of the TPAOH solution and the EDA/TEA/water mixture. However, the gel layer remained in an amorphous phase after treatment in the vapor of pure water.

Interesting results were obtained when the precursor layers were coated from the TPA^+ -free colloidal silica suspension. In these experiments, MFI zeolite was not formed in either one of the vapor phases of the TPAOH solution or the EDA/TEA/water mixture. A cubic Na-P1 (GIS) zeolite phase was formed on the support after treatment in the vapor phase of the TPAOH solution, and a cubic analcime (ANA) phase was formed in the vapor phase of the EDA/TEA/water mixture. Fig. 3 shows that the XRD patterns of the two synthesized materials match perfectly the standard patterns of cubic Na-P1 and cubic ANA powder, respectively. These results indicate that the structure-directing organic molecules play a key role in determining the crystallization of the precursor layer and utilization of template TPAOH in the parent synthesis sol is critical to the formation of the MFI zeolite films.

3.2. Discussion

3.2.1. Precursor layer from the silicate- TPA^+ sol

Fig. 4 shows schematically the wet precursor gel layer loaded on the porous α -alumina substrate. A substantial volume of liquid from the synthesis sol was retained in the porous structure of the precursor gel and the support pores after the dip-coating process. Since a liquid phase existed in the autoclave at the synthesis temperature, a significant quantity of liquid could be retained in the gel layer throughout the heat treatment because of the capillary condensation effect. When the TPAOH solution or the EDA/TEA/water mixture was used, a definite level of the organic concentration was maintained in the liquid phase of the gel layer by reaching a vapor-liquid

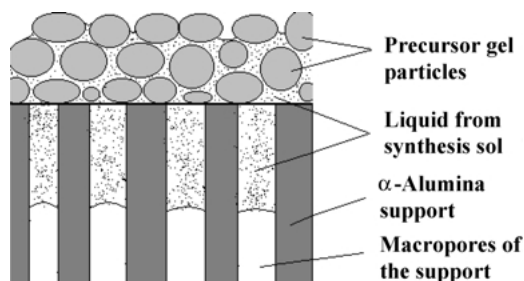


Figure 4 Schematic showing of the wet gel layer loaded on the porous α -alumina support.

equilibrium state with the vapor phase. The presence of the liquid containing template and silicate species in the gel structure not only promoted crystal nucleation but also helped densify the zeolite film. This is because the ionic precursor species could efficiently diffuse to the crystallite surface, allowing growth of the crystals and eventual closure of the intercrystal gaps.

When TPAOH solution was used to provide a vapor phase (Exp. 1 in Table I), the nucleation and crystal growth mechanism of the wet-gel vapor-phase treatment was thought to be similar to that of the *in situ* crystallization method. Zeolite nuclei could form in gel particles and in the liquid phase between the particles as well [36]. The nucleation process could be greatly facilitated by the existence of synthesis solution directly from the aged sol because the preassembled organic-inorganic building blocks, which serve as nucleation centers [36, 37], were preserved in the wet gel. These crystal nuclei were able to grow because the ionic species such as silicate and TPA^+ were efficiently supplied by the liquid phase in the coated layer. The silicate species in the liquid of the gel pores could be those originally dissolved in the synthesis sol when it was first prepared, or those redissolved from the solid gel particles in the process of crystallization.

We believe that the crystallization mechanism of the current vapor-phase treatment method helps increase the compactness of the zeolite layer because the redissolution-crystallization process can completely reconstruct the original gel network. Thus, the effect of the packing density of the gel layer on the zeolite film compactness became less significant. In fact, some small zeolite crystals (0.1–0.2 μm) with typical MFI morphology were found on the zeolite film surface (see the magnified section in Fig. 5a). This suggests that small liquid puddles existed even at the gel surface during the vapor-phase treatment because such small MFI crystals with well-defined morphology were most likely formed in a liquid phase.

Fig. 5 shows scanning electron microscopy (SEM) images of the zeolite membrane synthesized in the vapor of TPAOH solution. These images clearly show a compact zeolite film, composed of intergrown crystals, which is estimated to be ~ 3 μm thick. The zeolite particles (Fig. 5a) are about 1.5–2 μm in size and have a cauliflower-like structure. These particles appear to be aggregates consisting of numerous smaller, intergrown crystallites. This observed particle morphology is consistent with that reported in the VPT synthesis in which a well-defined single crystal shape is unable to develop because of the mechanism of gel particle crystallization in the absence of a bulk liquid

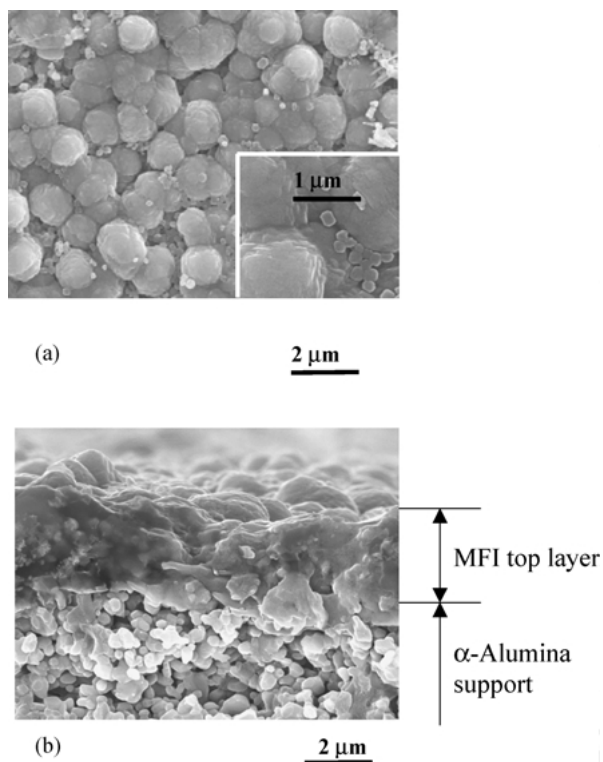


Figure 5 SEM images of the MFI zeolite membrane synthesized in vapor of the TPAOH solution. (a) surface of membrane; (b) cross-sectional view.

phase. The helium permeance of the membrane before calcination was $3.8 \times 10^{-9} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$, which is less than 0.1% of the permeance through the uncoated α -alumina support (helium permeance $4.1 \times 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$). This indicates that the membrane is of good quality, with minimized macrodefects.

When a mixture of EDA/TEA/water was used as the vapor source (Exp. 2 in Table I), the crystallization and the zeolite film formation mechanisms appeared similar to those observed when a TPAOH solution was used. However, the organic compounds in the vapor phase were ETA and TEA instead of TPAOH. In the first stage of vapor-phase treatment, a significant fraction of the TPAOH molecules in the original liquid of the wet gel should have been removed via vaporization because both the vapor and liquid phases in the autoclave initially did not contain TPAOH. Meanwhile, EDA and TEA molecules were continuously absorbed/dissolved by the liquid in the wet gel from the vapor phase until a vapor-liquid equilibrium state was reached.

A cross-sectional SEM image of the MFI membrane synthesized in the vapor of an EDA/TEA/water mixture is shown in Fig. 6. It is evident from such images that the compactness and continuity of the zeolite membrane are not as good as was observed for the membrane obtained in the vapor phase of TPAOH solution. Helium permeance of the membrane measured before calcination was $1.9 \times 10^{-7} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$, which was about 5% of the permeance on the uncoated support and was 50 times higher than that of the membrane synthesized in the TPAOH vapor.

There are two possible reasons for the lower quality of the membrane synthesized in the vapor phase

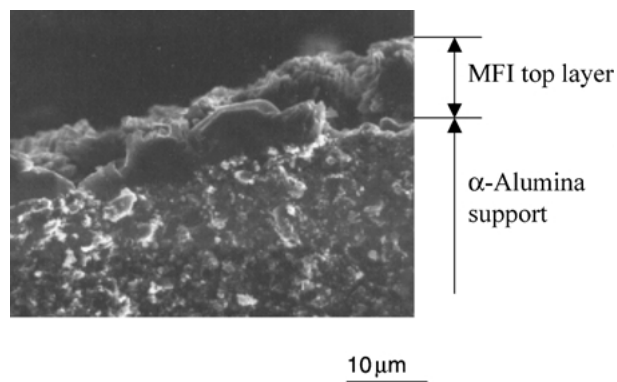


Figure 6 Cross-sectional SEM picture of the MFI zeolite membrane synthesized in the vapor of EDA/TEA/water mixture.

of EDA/TEA/water. The first is that the two types of organic molecules (i.e. EDA/TEA and TPAOH) may have different degrees of effectiveness as promoters of zeolite crystallization due to their different molecular structure, basicity, hydrophilicity, and polarity [34, 38, 39]. TPA⁺ has been demonstrated to be the most effective template for the synthesis of MFI-type zeolites in both the initial nucleation and the late crystallization stages [34]. The second is that the silicate-TPA⁺ nucleation centers carried over from the original synthesis sol may be partly disbanded when the TPAOH molecules are vaporized from the gel layer, thus decreasing the population of the crystalline nuclei generated in the early stage.

An experiment was also conducted using pure water as the vapor source and the precursor layer coated from the silicate-TPA⁺ parental sol (Exp. 3 in Table I). No zeolite crystalline phase was found by XRD examination after vapor-phase treatment. This result indicates that, under the present synthesis conditions, a vapor phase containing template molecules with an appropriate concentration is necessary for zeolite crystallization. Although the wet gel originally contained silicate-TPA⁺ composites and TPA⁺ ions with concentrations suitable for zeolite formation under hydrothermal condition, a large fraction of the TPAOH molecules necessary for MFI zeolite formation was removed from the gel by vaporization during the process of being heated to 190°C. The vaporized TPAOH molecules were dissolved into the water phase in the autoclave. It is likely that the pre-organized silicate-TPA⁺ clusters (nucleation centers) were dissociated and the concentration of TPAOH in the liquid of the gel layer became too dilute to serve effectively as structure-directing agent in zeolite crystallization. The results of this experiment are consistent with the findings reported in the literature that, in many systems, amorphous or dense nonzeolitic materials were formed in the absence of templating agents [40].

3.2.2. Precursor layer from colloidal silica

When the precursor layers were obtained from the template-free colloidal silica system, cubic Na-P1 zeolite and cubic ANA zeolite were formed in the vapor phases of the TPAOH solution and the EDA/TEA/water mixture, respectively (Exp. 4 and Exp. 5 in Table I).

These results demonstrate that the silicate-TPA⁺ nucleation centers preorganized during the synthesis sol preparation and preserved in the wet gel thereof play a key role in the crystallization of MFI-type zeolite under the present synthesis conditions.

Although the originally template-free liquid phase of the precursor gel could absorb TPAOH or EDA/TEA molecules from the vapor phase in the process of vapor-phase treatment, these organic molecules were unable to direct an MFI structure during crystallization. A possible reason is the significant change in the Si/Al ratio of the precursor layer during the vapor-phase treatment. Although no aluminum source was introduced to the original sol and the colloidal silica, a substantial amount of Al³⁺ could enter the gel layers via dissolution of the alumina support into the highly alkaline liquids [5, 22]. Since the NaOH concentration in the colloidal silica (2.9 mol%) was much higher than that in the silicate-TPA⁺ sol (0.8 mol%), much more alumina would be dissolved in the wet gel from the colloidal silica than in the gel from the silicate-TPA⁺ sol.

It is difficult to accurately quantify the Si/Al ratios of the alumina-supported layers during or after the vapor-phase treatment due to the influence of the alumina support. However, the Si/Al ratios of the identified Na-P1 and ANA zeolite structures were 1.67 and 2.0, respectively, suggesting that an Si/Al ratio near the range of 1.6–2.0 was attained in the precursor layers of the colloidal silica due to dissolution of the alumina support. Such a low Si/Al ratio is unfavorable to the formation of MFI-type zeolite but favors crystallization of low silica zeolites such as ANA and MOR [22, 31]. According to Ostward's law of successive transformation, dense phases (structure with small ring numbers such as Na-P1 and ANA) are thermodynamically favored as final results when a long synthesis time is used [41], which may help explain the experimental observations made during this study.

Both the Na-P1 (GIS) and ANA zeolitic channels are defined by an eight oxygen-ring structure with different secondary building units. Their channel sizes are not large enough to accommodate any of the organic molecules involved in this work. This suggests that the organic compounds currently being used could not play a templating role in the crystallization of Na-P1 and ANA zeolites. However, these organic molecules may function as space-filling agents, which reduce the energy barrier to organization of the zeolite structure [42]. Differences in the molecular geometry, polarity, and hydrophilicity of TPAOH and EDA/TEA molecules may account for the variety of zeolite structures synthesized in their vapor phases. The acidity of the synthesized Na-P1 zeolite is higher than that of the ANA zeolite because of the higher aluminum content of its framework. As expected, the more acidic Na-P1 zeolite was formed in the presence of the more basic TPAOH molecules.

4. Conclusions

A new method that takes advantages of both *in situ* crystallization and VPT processes has been developed for the synthesis of MFI-type zeolite membranes on porous alumina support. The synthesis process is com-

prised of two major steps. In the first step, a thin layer of precursor gel is loaded onto the surface of the support from an aged synthesis sol containing silica and template TPAOH but no aluminum. The amorphous gel layer is converted to an MFI zeolite film by a vapor-phase treatment during the second step, which was performed immediately after the first step without drying the gel. The synthesis method can be characterized as a wet-gel crystallization process. MFI films have been synthesized successfully in the vapor phases of TPAOH solution and a EDA/TEA/water mixture but not in pure steam. The synthesis method developed in this study shows promise in applications in the large-scale production of zeolite membranes.

The MFI membrane synthesized in the vapor of the TPAOH solution was of higher quality, in terms of zeolite film continuity and compactness, than that obtained in the vapor of the EDA/TEA/water mixture. It has also been demonstrated that the silicate-TPA⁺ nucleation centers preorganized during the synthesis sol preparation and preserved in the wet gel thereof play a key role in the crystallization of MFI-type zeolite under the present synthesis conditions. Cubic Na-P1 zeolite and cubic ANA zeolite crystallites were formed in the vapor phases of the TPAOH solution and the EDA/TEA/water mixture, respectively, when the precursor layers were coated from the template-free colloidal silica system.

The new synthesis method offers the following advantages:

- (i) The synthesis process is well controllable. A uniformly coated thin precursor layer can be obtained by a dip-coating or slip-casting technique even on complex geometry. The uniformity of the crystallization conditions for the entire precursor layer can be ensured in a vapor environment at vapor-liquid equilibrium state.
- (ii) Consumption of the valuable organic compounds can be significantly reduced. Since the liquid phase in the autoclave is kept away from the membrane support, contamination is avoided and the liquid phase can be reused multiple times.
- (iii) The volume of waste by-products generated by this method can be minimized, and the less toxic compound, TPAOH, can be used as the template instead of the highly hazardous amines (e.g. EDA and TEA).

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