

Synthesis of Oriented Zeolite Molecular Sieve Films with Controlled Morphologies

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Received August 18, 1995. Revised Manuscript Received October 27, 1995⁸

Zeolite molecular sieve films (MFI-topology) consisting of one or more layers of pure-silica ZSM-5 crystals have been hydrothermally synthesized on the surfaces of fused silica glass. The resulting films have been characterized by field emission scanning electron microscopy, X-ray diffraction, energy-dispersive X-ray analysis, and Fourier transform infrared spectrometry. At the early stage of reaction a porous gel layer spontaneously condenses on the substrate surface, within which the zeolite crystals are nucleated and grown as mediated by the structure-directing agent. Notable shifts of the C–H stretching vibrations are observed on the tetrapropylammonium cations attached to the gel layer compared to those enclathrated in the crystal frameworks. The zeolite crystals are preferentially oriented with their *b* axis perpendicular to the substrate surface. The crystal orientation is also strongly dependent on the roughness of the underlayer surface and consequently the thickness of the zeolite film. By control of the synthesis conditions, the individual crystals constituting the zeolite films can be prepared either smaller than 500 nm or as large as 30 μ m. Those zeolite films grown *in situ* on the silica glass also show some unique properties and new potential applications.

Introduction

Zeolite molecular sieves are crystalline materials and possess ordered and interconnected microporous channels. The discrete crystals are commonly synthesized in powder form, and the crystal size can be varied in the range of several tens of nanometers to several millimeters.^{1,2} Two distinct methods, namely *ex situ* zeolite-composite coating and *in situ* crystal growth, have been developed to prepare zeolite films. The *ex situ* method consists of pregrown crystals and a porous bonding phase which can be applied as membranes or film coatings.^{3–5} In the latter method the crystals grow *in situ* on different substrate surfaces in a precursor solution,^{6–8} which is normally accompanied by the formation of powder crystal. The films prepared by the two methods can result in different intercrystal porosity, molecular accessibility to intracrystal micropores, and bonding strengths between the crystals and the support substrates.⁹

In the rapidly developing area of advanced porous materials science, the preparation of zeolite films for membrane catalysis and separation is well-known.^{10–13} Considerable attention has also been given to zeolite film-based novel optics,^{14,15} microelectronics, and sensor devices.^{5,9,16–21} It has been shown that the bulk alignments of individual guest molecular dipoles could be realized by adsorption of the molecules in oriented zeolite crystals aligned in a strong electric field.^{14,15} If the intercrystal porosity can be avoided, zeolitic films could act as idealized molecular sieve membranes. Such membranes would have the capability to recognize and control the access of the guest molecules according to their molecular sizes, shapes, and/or sorption affinities, since the intracrystal porosity can be finely tuned with a precision of less than 1 \AA with tailored surface properties.^{22–24} The presence of intercrystal porosity is

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Abstract published in *Advance ACS Abstracts*, December 1, 1995.

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also required to prepare catalytic coatings. Those larger pores can effectively reduce the pressure drop and intercrystal diffusion time. In zeolite film-based piezoelectric sensor devices, it has also been demonstrated that the intracrystal porosity does not adversely influence their selectivity and sensitivity. This is because the vapor sorption at low concentration is energetically favored in the intracrystal microporosity over both the zeolitic external surfaces and the macroporosity.^{9,18,19}

Zeolite crystals have been grown or deposited on large varieties of supports, including metallic,^{25–27} inorganic,²⁸ organic,^{29,30} and self-assembled molecular layers.³¹ Much experimental effort has been directed toward achieving dense-packed films and membranes. Unfortunately, such materials are very difficult to obtain, particularly for oriented or pinhole-free ultrathin film. Permeability studies of the membranes indicate that the molecular sieving effect and/or intracrystal microporosity-controlled diffusion can be observed only when the film is thicker than ten to several hundreds of microns. Those materials are normally formed by growth and precipitation of randomly oriented polycrystals aided by gravitation.^{10–12} It continues to be a key technical hurdle to develop very thin molecular sieve membranes, in order to enhance the permeability of such materials. Due to the complex chemical reactions occur through the heterogeneous synthesis mixtures during the crystallization process,¹ it is not yet fully understood why some of the zeolites grow on the surface of the supported substrates, whereas the majority are hydrothermally crystallized as powder forms. Therefore, more synthetic efforts are required to assemble the zeolite crystals into a two-dimensional scale with desired properties.

The synthetic strategy of this work is to elucidate the processes that influence the nucleation and growth kinetics of the Si-ZSM-5 on the silica surface under well-defined conditions. It is also the purpose of the present study to gain more insight on the conditions that govern the crystal orientation, surface coverage density, and thickness of the zeolite film. This work will hopefully lead to a new synthetic approach which is suitable for designing novel zeolite film-based devices and/or chemical processes.

Experimental Section

Synthesis. Si-ZSM-5 crystals are hydrothermally synthesized using tetrapropylammonium bromide (TPABr, Aldrich) as the organic structure-directing agent, and tetraethyl orthosilicate (TEOS, Aldrich) as the silica source. The substrate for growing zeolite crystals is fused silica glass (25 × 50 mm) polished on both sides. Three substrates 10 mm apart facing each other are mounted in a Teflon holder. This set of substrates is first cleaned in an ultrasonic bath containing 1 2-propanol–2 ethanol–2 water–0.1 HCl for 15 min, then rinsed with deionized water, and blow-dried with nitrogen before being transferred to a precursor reactant solution.

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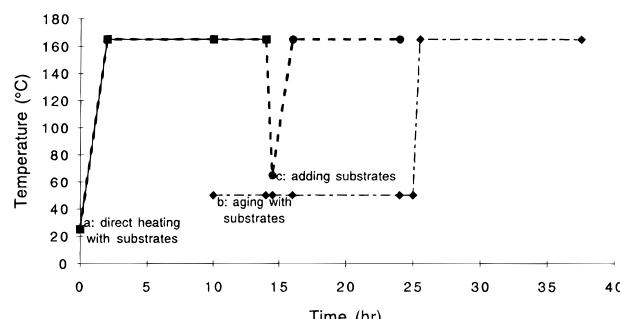


Figure 1. Crystallization processes used for growth of zeolite films on the surface of silica substrates.

The zeolite reactant solution is prepared by dissolving TPABr and sodium hydroxide in a stirred water solution in a 125 mL Teflon sleeve. After a clear solution is obtained, the silica substrates with Teflon holder are vertically immersed in this solution and to which TEOS is added. Some oily TEOS floats to the top, while some is mixed as small droplets in the aqueous solution. The prepared hydrogel solution has a composition of 1 SiO₂–0.15 TPABr–0.05 Na₂O–60 H₂O. The samples are sealed in the autoclave and placed in a convection oven at 165 °C (*Caution*: do not open the autoclave if the inside temperature is above 90 °C). With a fixed composition and crystallization temperature, zeolite films with different morphologies are obtained by controlling the solution aging process and/or adding the silica substrates in the precursor solutions at different times. Two kinds of heating programs are used for the crystallization. The hydrogel sealed in the autoclave is either aged at 50 °C for 15 h, then heated to 165 °C at a rate of 230 °C/h, or directly heated to the crystallization temperature at a rate of 70 °C/h without aging. Figure 1 shows the typical processes used for the film growth. Those processes have been found to influence the coverage density of zeolite crystals on the substrate surface, the extent of crystal intergrowth, and crystal size.

Characterization. The process of zeolite nucleation and crystallization on the surface of silica substrate is studied by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6401F). Prior to microscopic examinations the samples are sputter-coated with a conducting layer of chromium under 6–10 mTorr argon atmosphere. The thickness of the chromium is about 50 Å as calibrated on a reference substrate and monitored by a quartz microbalance. Depending on the extent of surface charging, accelerating voltages between 1 and 5 kV is used. The elemental analysis of the zeolite films and amorphous gel layer is studied by energy-dispersive X-ray (EDX) analysis (Oxford Microanalysis Group) attached to the FE-SEM chamber. A fine beam of 400 × 400 nm with 5 kV is used to analyze the selected areas on the surface of zeolite crystal or amorphous gel formed on the substrates.

The crystallization behavior of the hydrogel film and zeolite film is studied by X-ray diffraction (XRD) with Cu K α radiation (Philips PW 3020). The substrate surface is placed perpendicular to the plane of the X-ray beam and detector. All the XRD patterns of the zeolite films, ranging from single-layer crystal to multilayer, are recorded by using $\theta/2\theta$ scan with a $1/4^\circ$ divergence slit and 0.02° step size. Owing to the relatively rough surface of the substrate caused by the presence of amorphous hydrogel and zeolite crystals, this method gives both higher resolution and peak intensities compared to the measurement obtained by a 2θ scan at a fixed grazing angle ($<3^\circ$) of incidence.

The C–H stretch vibrations of TPA cations, incorporated in the zeolite crystal and/or attached to the hydrogel films, are obtained on a Nicolet 740 FTIR instrument. Due to the surface roughness of the coated substrates, only absorbency FTIR spectra are collected at a resolution of 4 cm⁻¹. After drying at 100 °C for 1 h, the substrates are transferred into the spectrometer under dehydrated-nitrogen flow so as to minimize the attachment of other contaminants.

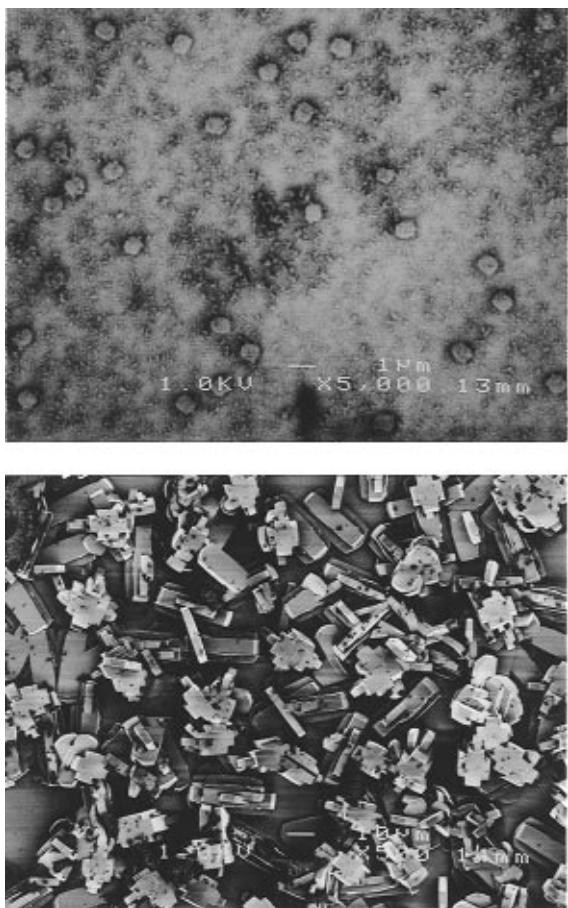


Figure 2. FE-SEM micrographs of Si-ZSM-5 films grown on the silica substrates after 2 (a, top) and 12 h (b, bottom) of reaction. Scale bars are 1 and 10 μm , respectively.

Results and Discussion

Orientation and Intergrowth of the Zeolite Films. Figure 2 shows FE-SEM micrographs of the zeolite crystals grown at 165 $^{\circ}\text{C}$ for 2 and 12 h, respectively. The samples were thoroughly washed with deionized water immediately after the substrates were removed from the aqueous solution, so as to eliminate any loosely contacted species or surface attachments resulting from the substrate-withdrawing process. The silica glass is slightly translucent after 2 h of reaction and covered with irregularly globular species. These globules range from smaller than 20 nm to about 100 nm in diameter. Some nearly cubic, regular-shaped crystals about 400–600 nm in size are strewn on the coatings. X-ray diffraction indicates the appearance of long-range order indicative of ZSM-5 structure on the coated surfaces. Some other areas examined by the FE-SEM show that the crystals are embedded in a porous gel layer composed of the aggregated globular gels. In a comparison study, when no soluble silica source, i.e., TEOS, is added to the precursor solution, no surface coatings on the silica glass could be observed by FE-SEM after washing. This implies that the hydrogel coating is not caused by dissolution of the fused silica substrate. Such coatings, therefore, can be attributed to the formation of silicate gel layer and ZSM-5 crystals on the substrate resulted from the condensation of the readily hydrolyzed TEOS. The nuclei probably evolved from the supersaturated silicate gel layers. In the early stage of the reaction, the rate of surface condensation of the globular-shaped

hydrogel is apparently much faster than that required for zeolite nucleation and crystal growth. The crystal growth on the substrate surface is possibly controlled by a solid-phase transformation process,³² in which the solid hydrogel is reorganized for the formation of zeolite crystal mediated by the structure directing agent, TPA. The gel layer can coexist with the zeolite crystals on the substrate surface even after 4 h of reaction.

After 12 h of reaction, the silica glass withdrawn from the precursor solution has a visual appearance similar to that of ground glass. The micrograph (Figure 2b) shows that multiple intergrown, elongated cubic crystals about 20–30 μm (*c* axis) are formed on the substrate. The first layer of the crystals grows with a maximum contact area, i.e., with its largest face (010) parallel to the substrate surface. The second layer typically grows on top of the underlayer crystals. This intergrowth has been characterized as a 90° rotation of the (100) faces around the *c* axis and nucleation on the (010) faces of the growing crystals.³³ Optical microscopy, using polarized light, has revealed the 90° intergrowth as an hourglass pattern.^{34,35} The intergrowth has been observed to be initiated at a small region near the center of the growing crystals with only alternate pentasil chains linked across the boundary.³⁶ Indeed, the intergrowth can also be clearly seen even on the crystals grown on the silica surface after 2 h of reaction (not shown). It can also be observed that some crystals are laterally connected with each other along the *c* axis. Those crystals are impinged by their grain boundaries as a result of growth of individual crystals with non-parallel *c*-axis orientation. The 90°-intergrown crystals formed on the substrate surface can still be observed after several hours of ultrasonication of the samples. The growth of subsequent layers of the crystals is dominated by a complex and multiple intergrowth, which can occur on all developing (010) faces of the sublayer crystals in this reactant system.

With prolonged reaction, the surface coverage by zeolite is slightly increased as a result of crystal growth of (010) faces along the substrate surface. The substrate surface covered by the crystal is less than 60%. Since the substrates are placed vertically in the precursor solution, gravitation-aided precipitation of the zeolite crystals cannot occur, and no smaller crystals nucleate on the silica surface. Whereas, the thickness of the film increases at a much faster rate by intergrowth or nucleation on the underlayer crystals. This phenomenon indicates that the crystal nucleation on zeolite surface has a lower activation energy than on silica surface in the reactant system. This also indicates that once the nuclei are in sufficient concentration on the silica surface, crystallization will possibly occur much more rapidly than nucleation.

On the surface of the film consisting of multiple-layer crystals, the irregular particles which appeared at the early stage of nucleation have decreased dramatically as examined by FE-SEM. This phenomenon can be

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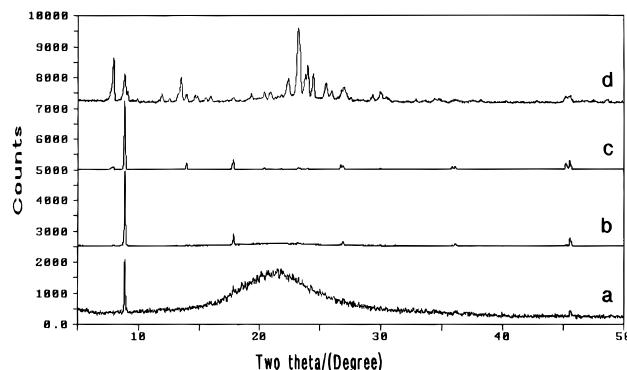


Figure 3. XRD patterns of oriented Si-ZSM-5 films grown on the silica substrates after 2 h (a, offset is $8.3\times$), 4 h (b, $0.6\times$), and 12 h (c, $0.11\times$) and of powder-formed crystals after 12 h of reaction (d, $3.3\times$).

attributed either to a decrease in the aggregation rate of the irregular, globular species on the crystal surface as a result of the consumption of the nutrient or to fast crystal growth in which the globular species attached to the crystal surface are immediately transformed to the crystalline phase. The first hypothesis can be completely eliminated, because more zeolite crystals can be grown on bare silica substrates from this solution (refer to following sections). Therefore, the crystal growth possibly involves the diffusion of silicate and TPA species from the liquid phase to the nucleation site. The crystal growth at this stage is similar to the solution-mediated transport mechanism as has been found in the crystallization process of powder zeolite.^{1,32}

The X-ray diffraction patterns of the zeolite films are also consistent with the ZSM-5 structure (Figure 3), but with most significant absence or considerable weakness in the intensities corresponding to $(h0l)$ planes, such as the reflection at $2\theta = 7.95^\circ$ (correlates to (101) reflection), 13.40° (002), 23.12° (501), 23.95° (303), and 45.20° (804).³⁷ It is suggested that those faces of the ZSM-5 crystals are oriented parallel to the plane of the X-ray beam and the detector. This result is also in agreement with the FE-SEM observations that the crystals grow with their elongated *c* axis parallel to the silica substrate. The relative intensity of diffraction peaks at $2\theta = 7.95^\circ$ vs 8.90° , which correspond to the (101) and (020) faces of the oriented zeolite,³⁸ is $<0.5\%$ on the zeolite films after 2 h of reaction. This value increases slightly to 1.0% after 4 h and to 3.6% after 12 h of reaction. Whereas, the ratio of those peaks is 1.908 on the bulk powder crystals synthesized from the same batch. After increasing the coating thickness with a 12 h reaction, the reflections at 13.94° (102) and 45.20° (804) are also present in the X-ray diffraction patterns. This implies that with increasing surface roughness of the top layer of the zeolite film as a result of increased coating thickness, some crystals begin to tilt from the substrate surface (for cubic or prismatic ZSM-5 crystal the *a*, *b*, and *c* axes are parallel to the crystal's width, height, or thickness of the film, and length, respectively). Although the micrographs show the crystal sizes (*c* axis)

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grow from $0.5\text{ }\mu\text{m}$ in 2 h to $>25\text{ }\mu\text{m}$ after 12 h, no significant narrowing of the widths of the diffraction peak (8.90°) at the half height is observed. This indicates that the thickness (*b* axis) of crystals formed on the substrate is almost unchanged, i.e., the zeolites show pronounced growth in the *a* and *c* axes compared to the *b* axis. The strong affinity to grow the (010) faces of the crystals on the substrate surface is possibly responsible for the preferential orientation of the zeolite films. In deep contrast, the width of the reflections obtained on the zeolite films are much narrower than those of the bulky powder forms. This is directly related to the relatively smaller crystal sizes of zeolite powder formed in solution.

Crystal Size and Coverage Density of the Zeolite Films.

Increased zeolite coverage density on the substrate surface can be achieved by increasing the nucleation rates prior to the rapid growth of the crystals. One of the approaches is to age the precursor solution with the silica substrates immersed. Figure 4 shows the films after 2 h of reaction at 165°C , during which the zeolite precursor solution has been aged at 50°C for 15 h. A monolayer of crystals uniformly covers the surface of the silica substrate (Figure 4a). Each individual crystal is about $400\text{--}600\text{ nm}$ in diameter, and the impinged crystals are composed of dense packed $10\text{--}40\text{ nm}$ globular species (Figure 4b). Despite the irregular shapes of the individual crystals, the 2-dimensional coating already shows a long-range order indicative of the oriented, crystalline ZSM-5 structure similar to that shown in Figure 3a. The occlusion of the organic structure-directing agent TPA inside the crystal is also evidenced by the presence of the carbon $\text{K}\alpha_1$ peak according to the EDX analysis. The TPA cations enclathrated in the coating layer cannot be removed by washing with either water or alcohol. The monolayer zeolite crystal indicates it is possible to obtain more densely packed crystals and thinner zeolite films by tuning the reaction conditions. It also suggests strongly that there is a preferential interaction between the substrate surface and the zeolite self-assembled on top of the surface. Since the thickness of the film is less than 250 nm as examined at the cross section, the coated substrates are expected to have a little scattering effect on visible light. The oriented zeolite molecular sieve films devised here may have great potential for optical sensor and nonlinear optics applications. To our knowledge, these results represent the first examples of growth of oriented zeolite monolayer consisting of the closest packed small crystals on support substrates.

Three distinct processes may occur during the aging of the precursor solution: hydrolysis of TEOS,³⁹ condensation on the substrate surfaces, and interaction of the TPA molecules with the soluble silicate species. Such inorganic-organic interactions are thought to be necessary for the formation of the nuclei in the solution.^{32,40} The presence of TPA ions also mediates the hydrolysis-condensation process of TEOS molecules. Rather than forming spherical silica particles, the hydrolyzed TEOS is ready to interact with the TPA ion, yielding soluble silicate species. Due to the low solubility of TEOS in water, the hydrolysis of the silicon alkoxide occurs only

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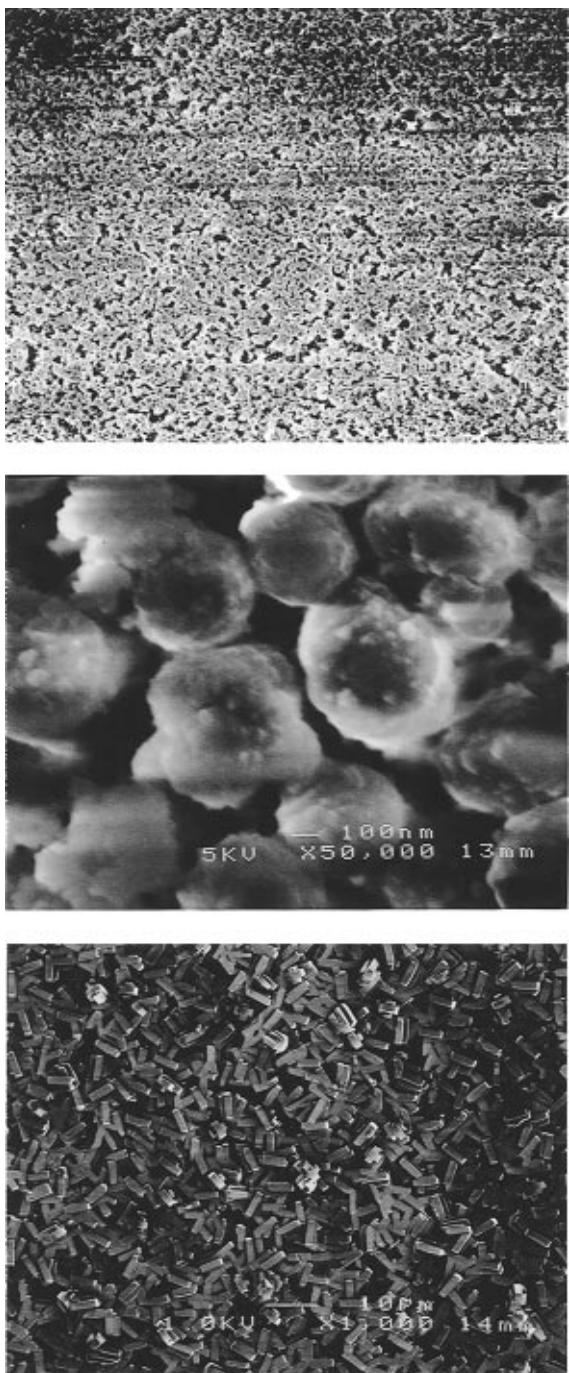


Figure 4. FE-SEM micrographs of Si-ZSM-5 films grown from aged solutions after 2 (a, top, full scale of the micrograph is 43 (W) \times 34 (H) μm) and (b, middle) and 8 h (c, bottom) of reaction. Scale bars are (4a) 10 μm , (4b) 100 nm, and (4c) 10 μm .

at the interface of the two phases. The rate of hydrolysis is consequently very slow. Considerable amount of TEOS can still be found floating on top of the aqueous solution upon stirring, after the precursor solutions have been aged at 50 $^{\circ}\text{C}$ for 3 h or at 165 $^{\circ}\text{C}$ for 1 h. As the active silicate species are continuously produced during aging, a higher concentration of silica-TPA composites are consequently available for the nucleation.

It is observed that a layer of amorphous hydrogel always condenses on the substrate surface prior to the formation of zeolite crystal. It can, therefore, be deduced that the decrease in the specific free energies in the system, particularly at the interfaces between the

smaller silicate species and the substrate in the solution, probably provides the primary thermodynamic driving force for the formation of gel layers. Formation of the amorphous layer prior to the zeolite growth has also been reported by van Bekkum and co-workers.^{7,20} The condensation not only reduces the surface area of the silicate species, but also preorganizes them as the precursor necessary for the nuclei formation as mediated by the structure directing-agent. The zeolite crystals are believed to nucleate within the gel layer which is supersaturated with silicate and TPA molecules. The crystallization process may also be accelerated by the presence of the sodium ion.¹ Aging the solution provides a higher concentration of the soluble silicate species and consequently results in a smaller and more homogeneous crystal layer.

With increasing crystallization time, larger multilayer crystals are formed on the zeolite film. Figure 4c shows the films grown from the aged solution after 8 h of reaction. The coverage density of the zeolite crystal is markedly increased. The top layer crystal grows to about 5–8 μm , and the extent of crystal intergrowth is decreased compared to those grown from unaged solutions. It has also been observed previously by other authors that the size of the zeolite crystal increases with increasing crystallization time, as seen by examining different portions of the cross section of much thicker films.^{10,12} The X-ray diffraction pattern of this film shows that the ratios of the reflection intensities at 2 θ = 7.95 $^{\circ}$ and 23.12 $^{\circ}$ to that at 8.90 $^{\circ}$ is about 0.7% and 1.7%, respectively. This indicates the preferred orientation of the zeolite crystals. Despite the highly crystalline morphology of the zeolite film, some amorphous hydrogel can still be observed on the dried zeolite powder precipitated at the bottom of the Teflon sleeve.

Another method to tailor the properties of the films is to place the substrate into the precursor solution after some of the zeolite crystals have been formed. Figure 5 shows the films obtained after 8 h of reaction, in which the solution had been previously heated at the crystallization temperature for 12 h. The silica substrate is covered by more than one layer of elongated prismatic zeolite crystals up to 25 μm in length. The coverage density by zeolite is higher than 90%. The elongated, very thin prismatic forms clearly indicate that the crystal growth occurred in a less supersaturated system. The first layer crystals orient with their *a* axis (width) and *c* axis (length) parallel to the surface of the substrate. The second layer grows with randomly oriented crystals. Some crystals grow axially from the substrate and some grow with their *a* and *c* axis perpendicular to the underlayer zeolite crystals. The thickness (*b* axis) of the single crystal is in the range of 300–600 nm. An interesting feature demonstrated by these samples is that the *zeolite films can be polished using abrasive paper*. After polishing, the randomly oriented crystals are broken along the *b*-axis direction, whereas the horizontally oriented crystals remain attached to the substrates.

TPA Interaction with Gel Layer and Crystal Occlusion. The interaction between the silicate species and the TPA molecules, and consequently the formation of the organic-containing zeolite crystals, was studied by EDX using a finely aligned electron beam. Figure 6 shows the EDX spectra of the surface condensed with

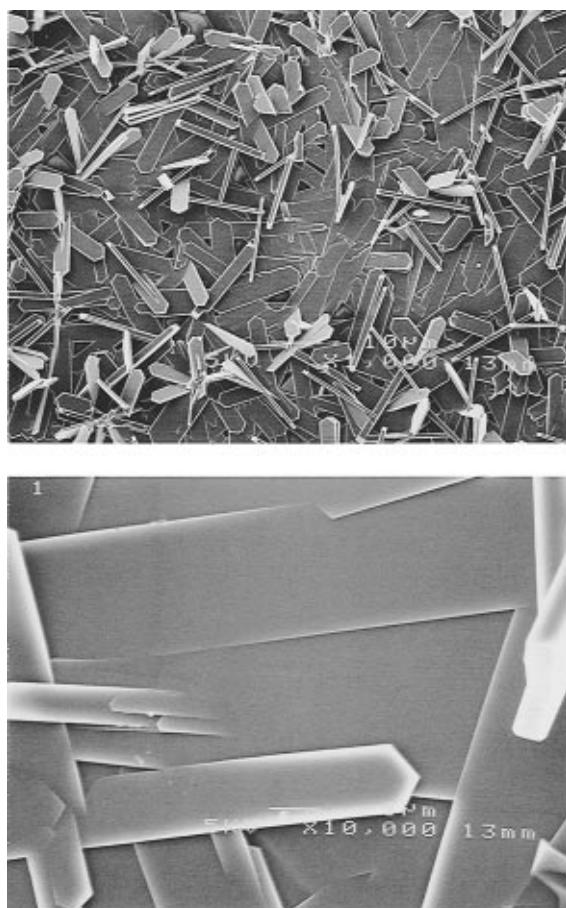


Figure 5. FE-SEM micrographs of SI-ZSM-5 films grown from low supersaturated solutions after 8 h of reaction. Scale bars are (a, top) 10 and (b, bottom) 1 μ m.

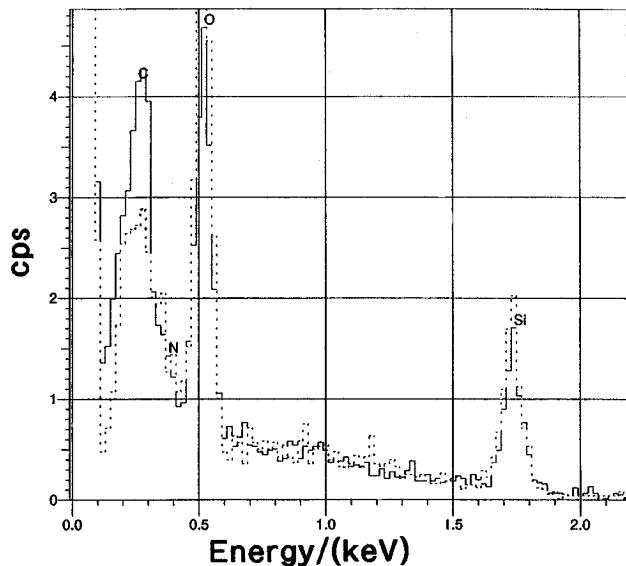


Figure 6. EDX spectra of amorphous gel (dashed line) and zeolite crystal surface (solid line).

amorphous, irregular globular particles, and the single-crystal surface. The presence of carbon $K\alpha_1$ can be attributed to TPA cations attached to the silicate layer through the formation of an inorganic-organic composite on the surface of the globular particles or to TPA enclathrated in the zeolite channel during the process of crystal growth, respectively. For similar Si and/or O peak intensities, the concentration of carbon and consequently the amount of TPA ions in the amorphous

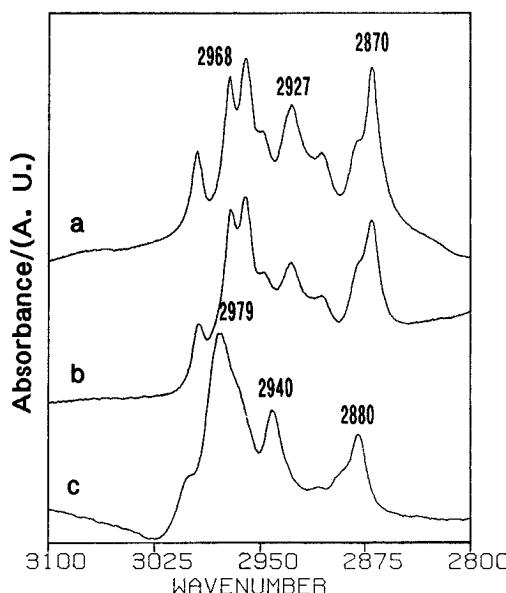


Figure 7. IR spectra of bulk TPA (a) in KBr pellet, (b) attached to amorphous gel layer, and (c) enclathrated in zeolite structures.

hydrogel layer are much lower than that enclathrated in the channel intersection of the zeolite structure. The relatively lower intensities of the carbon can also be related plausibly to the thickness of the areas analyzed, since the zeolite crystal is much thicker than the surrounding amorphous areas. This is a subject for further investigations.

Although the EDX measurements provide information on the coexistence of the TPA in the coatings, this information reflects only indirectly the possible attachments of the organic cations on the surface-bound silicate species. To examine the changes in intermolecular and intramolecular interactions between the TPA ions and/or with silicate species, FTIR was used to characterize the C-H stretch vibrations of TPA attached to the amorphous film obtained after 1 h of synthesis, and to the ZSM-5 film after 8 h of reaction. Figure 7 presents such results. For comparison purposes, the bulk spectrum of solid TPABr in KBr pellets is also included. A substantial number of silanol groups at 3666 cm^{-1} are already present at the silica substrate before the formation of the hydrogel layer (not shown). The CH_3 stretching vibrations ($v_a(\text{CH}_3)$ at 2968 cm^{-1} and $v_s(\text{CH}_3)$ at 2870 cm^{-1}) and a peak at 2927 cm^{-1} appear in the spectra, after a hydrogel layer has heterogeneously covered the silica substrate. The latter vibrational band can be assigned to the asymmetric CH_2 stretch, $v_a(\text{CH}_2)$, of the propyl chains of the TPA molecules by comparison with assignments for long alkyl chains at 2929 cm^{-1} .⁴¹

One prominent feature of the spectrum of the TPA cations attached to the gel layer is that it has a similar band width, relative intensity, and frequency to that obtained on solid bulk spectrum (in KBr). This implies that the TPA molecules tend to build up bulk film on the silicate gel layers. The intermolecular interaction between the organic species is still dominant feature of the spectrum rather than the organic-inorganic interaction. Indeed, the intensity of these peaks decreases

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after washing with deionized water, which suggests that the organic cations are not occluded inside the silicate gels. For the zeolite film formed on the silica substrate, we observe shifts toward higher frequencies of the C–H vibrations by more than 10 cm^{−1} from the positions in the bulk spectrum. The $\nu_a(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$ are shifted to 2979 and 2880 cm^{−1} and $\nu_a(\text{CH}_2)$ to 2940 cm^{−1}, respectively. This effect can be attributed to the formation of a more liquidlike, relatively disordered environment for the propyl chains extended into both the linear and sinusoidal channels of the zeolite framework. Parallel frequency shifts have also been obtained between the liquid and solid phase of long-chain alkanes.⁴² It is apparent that the TPA attached to the amorphous silicate hydrogel does not have a similar environment compared to that enclathrated in the zeolite channel. The latter has a liquidlike phase imposed by the large distance between each TPA cation separated by the silicate framework. Nevertheless, the TPA attachment on the amorphous layer also suggests that the TPA ions have a high affinity for the silicate species condensed on the substrate surface. The propyl chains of TPA may interact preferentially with the hydrophobic silicate species at an appropriate van der Waals contact distance.⁴⁰ The interaction may also involve a weak Coulombic attraction between the organic TPA cations and the Q³ sites of $\text{Si}(\text{OSi})_3\text{O}^-$ species. Such interactions ultimately lead to the enclathration of the TPA molecules into the extended silicate structure.⁴³ The

extent of the inorganic–organic interaction and the rate of the gel condensation on the substrate surfaces can influence the crystal size and coverage density of zeolite films. The orientation of the zeolite crystal is influenced by the surface roughness of the underlayer substrate which can be mediated by the surface hydroxyl groups and by the TPA cations assembled on the substrate surface.

Conclusion

Several methods have been reported here to grow zeolite films with different surface coverage densities and morphologies on silica substrates. The decrease in the specific free energy of the system may provide the driving force for the spontaneous condensation of a gel layer on the substrate surface. The preferential growth of (010) crystal faces on the flat surface determines the zeolite film orientation. Experimental results also indicate that the tunable crystal size and intercrystal porosity offers some potential for the development of zeolite film-based catalysis and new optical sensor devices.

Acknowledgment. The authors wish to acknowledge D. Meyers (YTCA), Prof. T. Bein (Purdue University), and Dr. H.-X. Li (APCI) for many useful discussions. CM950393E

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