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TPA$^+$-Mediated Conversion of Silicon Wafer into Preferentially-Oriented MFI Zeolite Film under Steaming

Watcharop Chaikittisilp,[†] Mark E. Davis,[‡] and
Tatsuya Okubo*,[†]

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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Interactions with ions, molecules, and clusters both at external surface and inside the pores of zeolites can provide for well-ordered, multidimensional spatial arrangements on the nanometer length scale. This organization can be used not only for the well-established molecular sieve applications, i.e., ion exchange, adsorption, and catalysis, but also for emerging areas of application, such as membrane separations, chemical sensing, and optoelectronics.[1,2] For realizing such novel applications, the preparation of zeolites in the forms of layers, membranes, and thin films is a crucial step. Recently, zeolite thin films have been utilized as chemical sensors,[3] low-*k* materials for use as electrical insulator,[4] and hosts for organization of functional guest molecules.[5,6] Significant challenges to success in these areas are the control of film thickness and grain size, as well as zeolite crystal orientation. In particular, pore channels and grain boundaries should be controlled perpendicular to the support surface. Thus far, many attempts have been reported in controlling out-of-plane orientation; however, most of them require multistep procedures and thoroughly controlled synthesis parameters.[7−11] In-plane oriented zeolite layers have been prepared on large single crystals of zeolite by heteroepitaxial growth that opens the possibility of fabricating microporous-based heterojunctions with precise pore orientation; however, there are limitations to the structural match between the grown layers and substrates, and subsequent formation of twins.[12]

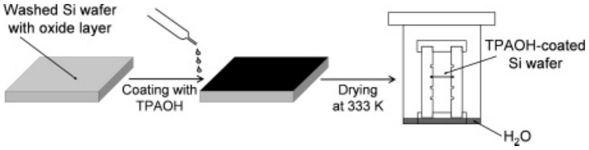

Figure 1. Schematic representation of the new SAC method for preparation of siliceous MFI zeolite films.

As an alternative method for synthesizing zeolite, the so-called dry gel conversion (DGC) method has been used for converting a dry (alumino)silicate gel to zeolite in the presence of vapors.[13] This method can be categorized into the vapor-phase transport (VPT), in which organic structure-directing agents (SDAs) are not occluded in the dry gel and are transported to the solid via the vapor phase, and the steam-assisted crystallization (SAC), in which the dry gel contains the SDAs and the vapor is only steam. For thin film preparation, the DGC method can show some advantages over solution methods because of the absence of the homogeneous nucleation in solution (localizes nuclei directly on substrates). Herein, we propose a new SAC method to prepare oriented zeolite thin films. A key aspect of the new SAC method is to utilize the chemical nature of the substrate, silicon wafers, as an atom source for the growing film.

In contrast to the conventional SAC method,[14] in which all nutrients (i.e., Si source, Al source, an SDA, a mineralizing agent, and water) are mixed together, coated on a substrate, and subsequently dried before steaming, here only the SDA was coated on a substrate; that is, besides serving as the support, the substrate itself was utilized as the source of tetrahedral atoms. In a typical method illustrated in Figure 1, a cleaned silicon wafer with an ca. 50 nm thick thermally oxidized layer was coated with 1.0 M tetrapropylammonium hydroxide (TPAOH) aqueous solution, the SDA for MFI-type zeolite, and then dried at 333 K for 1 h. Crystallization was carried out at 373−473 K for different periods of time under steaming in an autoclave, in which the TPAOH-coated silicon wafer was mounted horizontally on a Teflon holder. Finally, the product was thoroughly rinsed with distilled water, and subsequently dried at 333 K overnight (see further details in the Supporting Information).

Siliceous MFI zeolite films were prepared at various temperatures from 373 to 473 K; higher temperatures led to faster crystallization. X-ray diffraction (XRD) patterns of the samples crystallized at 423 K for different crystallization

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* To whom correspondence should be addressed. E-mail: okubo@chemsys.t.u-tokyo.ac.jp.
[†] The University of Tokyo.
[‡] California Institute of Technology.

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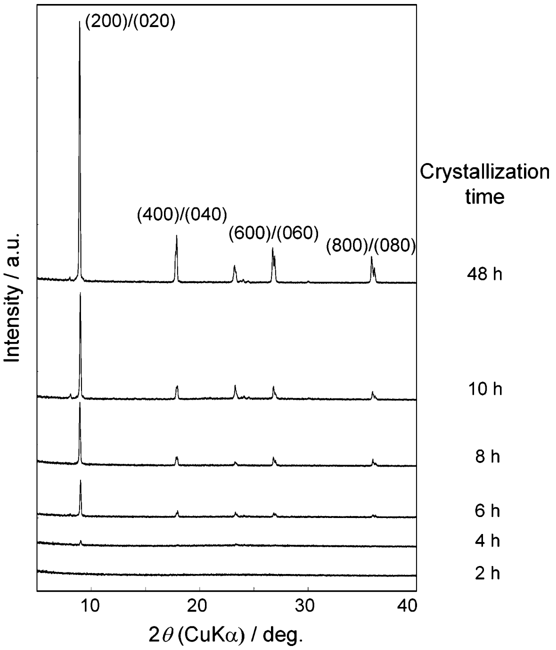

Figure 2. XRD patterns of MFI films after steaming at 423 K for 2−48 h. Peaks are indexed with the crystallographic planes of MFI structure.

periods are shown in Figure 2. Peaks corresponding to the reflections arising from the (*h*00) and (0*k*0) planes of MFI-type zeolite are dominant, indicating that the obtained films show preferential *a* and *b* out-of-plane orientations. The first visible Bragg diffraction appears after steaming for 4 h. After prolonging crystallization time, the intensities of the peaks are increased, which reveals that MFI zeolite films have grown over this period (4−48 h). Both *a* and *b* out-of-plane orientations were found from the beginning of crystallization. Such imperfect out-of-plane orientation might be caused by the 90° twinning intergrowth,[15] in which substantial (*h*00) twins are epitaxially formed on the top of the (0*k*0) faces of crystals.

In control experiments where silicon wafers with a natively oxidized layer (a few nanometers) were used as supports and Si source instead of those with a thermally oxidized layer, similar *a* and *b* out-of-plane oriented MFI films were obtained without any significant differences (see Figure S1 in the Supporting Information). However, MFI films prepared on silicon wafers with a natively oxidized layer consisted of larger crystal size than those prepared on wafers with a thermally oxidized layer. Such larger sizes are likely due to a smaller number of nuclei. These results suggest that tetrahedral atoms for constructing a zeolite framework were supplied not only by the silicon oxide layer but also by silicon in the wafers that could easily be oxidized by the aqueous hydroxide solution and subsequently converted to zeolite under steaming.

To understand the conversion process, we observed the textural evolution of the obtained MFI films by field-emission scanning electron microscopy (FE-SEM). After 2 h of crystallization, small particles and their agglomerates, which should be TPA^+/SiO_2 composites, were observed on the surface (Figure 3a). Consistent with the XRD pattern, no crystal-like particles were present at this stage. Figure 3b shows an FE-SEM image of the obtained product after steaming for 4 h. Isolated MFI crystals with smooth, rounded faces appear on the surface. Clear observation of twinning intergrowths at this stage supports the XRD patterns, in which *a* and *b* orientations were the results of such crystal defects. As shown in Figure 3c, the MFI crystals are overgrown and formed a connected layer after steaming for 6 h. Figure 3d represents an almost continuous MFI film grown after 8 h of crystallization. At this stage, amorphous-like particles are still observed on the top of surface. The morphology of the crystals is slightly changed to well-faceted MFI shape after prolonging crystallization time to 48 h (Figure 3e). Figure 3f reveals the cross-sectional FE-SEM image of the MFI film after 48 h of crystallization. The zeolite film is in close contact with the silicon wafer; no oxide layer is apparently observed at the interface. However, there might be a very thin layer of amorphous TPA^+/SiO_2 composite at the interface because of the inaccessibility of steam. The thickness of the film is estimated to be ca. 2.5 μm. The silicon wafers were coated with approximate 8×10^{-3} g of TPAOH cm^{-2}; hence the amount of coated TPA is about a hundred times higher than the required amount for crystallizing MFI zeolite.[16]

SDAs were removed by calcination at 823 K with a slow heating rate in a muffle furnace. The FT-IR spectrum, the XRD pattern, and the FE-SEM image of the calcined product are shown in the Supporting Information. The removal of organic SDA was evidenced by FT-IR spectra in the C−H stretching vibrations region (2800−3100 cm^{-1}; see Figure S2 in the Supporting Information). The as-prepared MFI film reveals the peaks assigned to the methylene and methyl groups. After calcination, on the contrary, no noticeable peaks attributed to the C−H stretching vibrations are observed. The XRD pattern of the calcined film shown in Figure S3 in the Supporting Information reveals that the peak intensities are as high as those observed from the as-prepared sample and confirms that the MFI structure is maintained upon calcination. However, the positions of peaks were slightly changed after calcination. In particular, the reflections arising from the (200) and (020) can clearly be distinguished in the calcined sample. Such changes in the XRD patterns are probably due to the orthorhombic to monoclinic phase transition upon calcination.[17] As shown in the FE-SEM image (see Figure S4 in the Supporting Information), neither significant changes in the film morphology nor the formation of cracks are observed.

The XRD patterns and the FE-SEM images suggest that the assembly of the siliceous MFI zeolite films prepared by the SAC method is as follows. First, the oxide layer on the surface of the silicon wafer is dissolved, and subsequently the top surface of the silicon is oxidized by TPAOH(aq). As a result, hydrated TPA^+/SiO_2 composite particles are

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(16) The amount of TPA occluded in the zeolite films was calculated from the crystal structure of MFI zeolite and was about 7.45×10^{20} molecules cm^{-3}.

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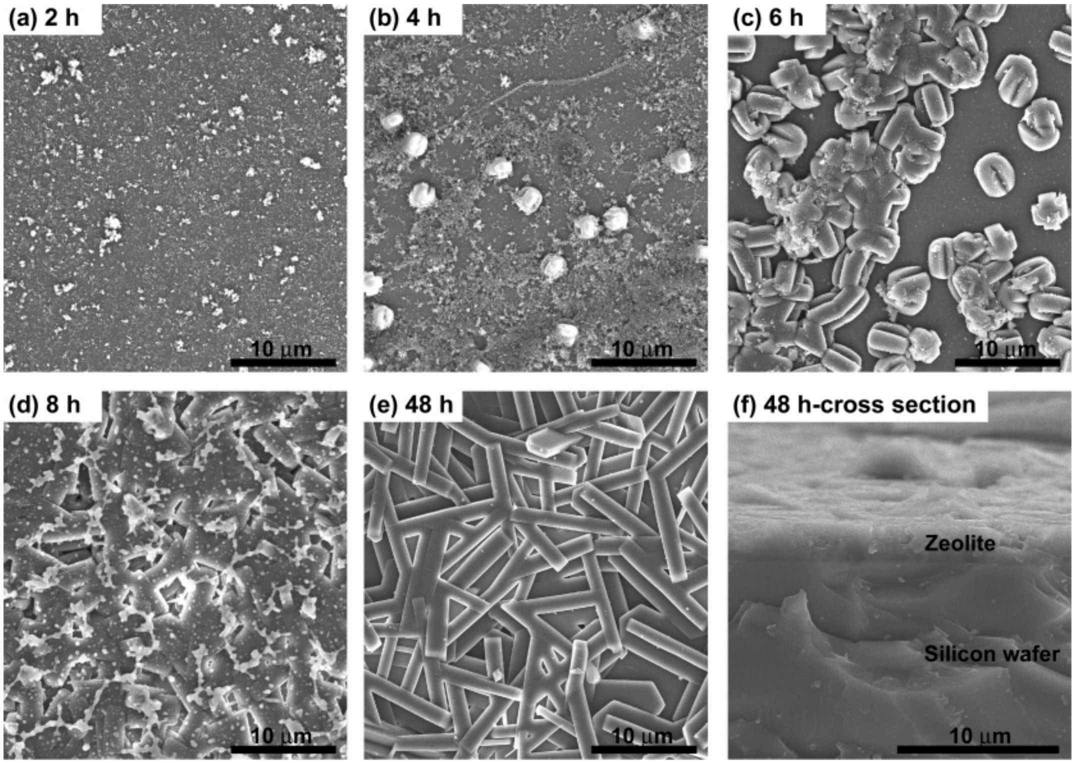

Figure 3. Top-view FE-SEM images of obtained products after steaming at 423 K for (a) 2, (b) 4, (c) 6, (d) 8, and (e) 48 h, and (f) a cross-sectional view of (e).

formed on the substrate surface. Nucleation should occur at such composite particles, and then discrete crystals are developed throughout the crystal growth process. Because of mobility of individual small composite particles, such particles are supplied as the nutrients for crystal growth. The developed crystals are overgrown and subsequently connected with neighboring crystals. Water should serve as a local pool for the long-range transport of the nutrients needed for intergrowth,[18] resulting in a continuous film after prolonging crystallization time. *b* Oriented MFI films are easily formed because of the coffin shape of crystals, i.e., the *ac* plane is much larger than others. Besides the *a* and *b* orientations, a small amount of other orientations are observed by FE-SEM and are speculated to be due to the evolutionary selection or competitive growth process.[19] It is evident that the 90° twinning intergrowth causes the imperfect out-of-plane orientations. Because such intergrowth is formed at the early stage of crystallization, the secondary (or surface) nucleation should occur on the *b* plane of crystals and lead to the formation of the *a* and *b* oriented film. Attempts to minimize such intergrowth, leading to the formation of completely *b* oriented films, are currently underway.

In conclusion, a new method (SAC) in which silicon wafers serve as both the support and Si source for the formation of the continuous siliceous zeolite films has been developed. The MFI zeolite films with preferential *a* and *b* out-of-plane orientations are obtained by conversion of TPA$^+$-mediated layer on the top of silicon wafers under steaming. It is expected that the truly simple SAC method may provide opportunities for the preparation of the films of other zeolite frameworks.

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Supporting Information Available: Experimental details; XRD pattern and FE-SEM image of the product prepared on the silicon wafer covered with a natively oxidized layer; FT-IR spectrum, XRD pattern, and FE-SEM image of the calcined product compared with those of the as-prepared one (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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