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Controlling Crystal Orientation in Zeolite MFI Thin Films by Direct In Situ Crystallization

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A systematic study was carried out on the synthesis of oriented continuous zeolite MFI thin films on stainless steel substrate by direct in-situ crystallization, and clear correlation was obtained between crystal orientation in the zeolite film and the composition of the synthesis solution. Within the synthesis system of TPAOH:NaOH:TEOS:H_2O:NaCl, OH^-/Si and Na^+/TPA^+ ratios play a critical role in controlling crystal orientation. For sodium-free or low sodium syntheses, only random-oriented films are formed at $OH^-/Si \geq 0.64$, (*a*, *b*)-oriented films at $0.64 > OH^-/Si > 0.5$ or at $0.2 \geq OH^-/Si > 0.1$, and *b*-oriented films at $0.5 \geq OH^-/Si > 0.2$. For a given OH^-/Si ratio, addition of Na^+ leads to change of crystal orientation from *b*-oriented, to (*a*, *b*)-oriented, to (*a*, *b*, *c*)-oriented, and eventually to random-oriented.

1. Introduction

Zeolite thin films and layers (film for continuous and layer for noncontinuous[1]) have been widely synthesized and shown to have interesting properties as membranes and membrane reactors,[1−15] chemical sensors,[1,16,17] heat pumps,[18] catalytic coating reactors,[19] and corrosion-resistant coatings.[20] One important but difficult task in the synthesis of a zeolite film or layer has been the control of crystal orientation in the film or layer.[1,14,15,21−30] Thus far demonstrated approaches include templated in-situ growth,[21,22] assembly of preformed zeolite crystals,[23−26] and seeded growth[14,15] which is a combination of assembly of preformed crystals and in-situ growth. Using templated in-situ growth, Bein and co-workers[21,22] showed that perfectly oriented metallophosphate (e.g., zincophosphate and $AlPO_4$-5) molecular sieve crystals could be synthesized on organophosphonated gold surfaces. They associated the crystal orientation to the templating effect of the organophosphonate film and its favorable interaction with growing phosphate surfaces. Highly oriented $AlPO_4$-5 crystal bundles were obtained by using nanoporous anodic alumina membrane as template.[23] Although still not continuous, the layer so obtained has substantial surface coverage. Using assembly of preformed zeolite crystals, orientated ZSM-5 crystals were prepared on a microstructured silicon wafer (e.g., with etched grooves),[24] and the crystal layer so obtained contained both *a*-oriented (*a*-axis perpendicular to substrate surface) and *b*-oriented crystals. Oriented crystals inside a metal film were obtained by alignment of crystals with an electrical field followed by electroplating.[25] For this method to function, the preformed crystals must have large aspect ratio.

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Table 1. Effect of Solution Composition on Crystallization of MFI on Stainless Steel Substrate at 165 °C with Solution Loading of 4 g

						crystals on substrate		
sample no.	solution composition TPAOH:NAOH:TEOS:H_2O:NaCl	OH^-/Si	Na^+/TPA^+	pH	cryst time (h)	orientation	size[a] (μm)	inter-growth
S01-0	1:0:1:165:0	1.0	0		18	random	19.1	good
S02-0	0.82:0:1:165:0	0.82	0		13[b]	random	16.7	good
S02-1	0.32:0.50:1:185:0	0.82	1.56		6[b]	random	14.0	good
S03-0	0.64:0:1:165:0	0.64	0	11.22	7	random	7.1	good
S03-1	0.64:0:1:165:0.25	0.64	0.39		5	random	9.4	good
S04-0	0.60:0:1:165:0	0.60	0	11.09	2	*a*, *b*-oriented	0.9	good
S05-0	0.57:0:1:165:0	0.57	0	11.01	2	*a*, *b*-oriented	0.8	good
S05-1	0.57:0:1:165:0.38	0.57	0.67	11.05	2	*a*, *b*-oriented	1.2	good
S05-2	0.32:0.25:1:165:0	0.57	0.78		2	*a*, *b*-oriented	2.3	good
S05-3	0.57:0:1:165:0.45	0.57	0.79		2	*a*, *b*-oriented	1.1	good
S05-4	0.57:0:1:165:0.57	0.57	1.0		4	random	1.5	bad
S05-5	0.32:0.25:1:165:0.25	0.57	1.56		5	random	3.2	bad
S06-0	0.50:0:1:165:0	0.50	0		1.7	*b*-oriented	0.6	good
S06-1	0.32:0.50:1:185:0[c]	0.50	1.56		4	random	3.0	bad
S07-1	0.32:0.04:1:165:0	0.36	0.13		2	*b*-oriented	1.0	good
S08-0	0.32:0:1:165:0	0.32	0	10.7	2	*b*-oriented	1.0	good
S08-0*	0.32:0:1:165:0[d]	0.32	0		2	*b*-oriented	0.5	good
S08-1	0.32:0:1:165:0.10	0.32	0.31		3	*b*-oriented	1.1	good
S08-2	0.32:0:1:165:0.15	0.32	0.47		3	*a*, *b*-oriented	1.9	good
S08-3	0.32:0:1:165:0.25	0.32	0.78		3	*a*, *b*-oriented	2.6	good
S08-4	0.32:0:1:165:0.32	0.32	1.0		3	*a*, *b*, *c*-oriented	2.7	good
S08-5	0.32:0:1:165:0.38	0.32	1.19	10.88	3	random	4.4	bad
S08-6	0.32:0:1:165:0.50	0.32	1.56	10.94	4	random	5.1	loose
S09-0	0.20:0:1:165:0	0.20	0	10.41	3	*a*, *b*-oriented	2.7	good
S09-1	0.20:0:1:165:0.25	0.20	1.25	10.58	4	random	8.8	loose
S10-1	0.17:0:1:165:0.10	0.17	0.59	10.36	4	*a*, *b*-oriented	5.8	good
S11-0	0.10:0:1:165:0	0.10	0	9.57	15.5[b]	*a*, *b*-oriented	15.5	good

[a] Dimension estimated along *c* axis. [b] Solution loading was 12 g. [c] TPABr was used instead of TPAOH. [d] TPABr was added to S08-0, and the molar composition is 0.68TPABr:0.32TPAOH:TEOS:165H_2O.

Very recently, oriented zeolite layers also were obtained through assembly of preformed crystals using organic linkers between zeolite crystals and glass substrates.[26]

All of the highly oriented zeolite layers mentioned above may have potential applications as chemical sensors and in optical devices, but their application as membranes are limited because they are not continuous, and in most cases, the crystal adhesion to substrate is not strong (e.g., merely surviving ultrasonication). Very recently, continuous oriented zeolite films were successfully prepared on porous supports with seeded-growth method in which a zeolite seed layer was deposited on the substrate prior to hydrothermal treatment.[14,15] In one example, zeolite A film with two-dimensional preferential orientation was obtained by aligning the seed crystals accordingly.[14] In another example, a *c*-oriented silicalite film was prepared from a randomly oriented seed layer by taking advantage of the preferential crystal growth along *c*-axis.[15] Essentially, the high seed density combined with the limited growth space forced the fastest growth direction (*c*-direction in this case) to align up. Similar mechanism also appears at work for a recently reported oriented UTD-1 layer.[27]

We are interested in controlling crystal orientation of a continuous MFI thin film by direct in-situ crystallization. The benefit of direct in-situ method is its simplicity; it is a one-step process where the need is eliminated for specially designed substrates (e.g., organic-functionalized or microstructured) and for preparation of a seed crystal layer by dip- or spin-coating.[20] In-situ crystallization also has the advantages that it produces excellent adhesion to a wide variety of substrates and can easily coat surfaces of complex shape and in confined spaces.[20] Direct in-situ crystallization has been widely used for preparation of zeolite films and membranes.[1−13] Although partially oriented zeolite layers have been occasionally achieved,[28−30] at present, in-situ crystallization mostly produces thick (>10 μm) zeolite films with random orientation,[1−13] and there is no systematic study on the correlation between the crystal orientation in MFI film and the composition of the synthesis solution. The goal of this study is to show that manipulation of crystal orientation in a continuous thin film can be achieved with in-situ crystallization through systematic optimization of the synthesis composition. We focused on stainless steel as the substrate because it offers many desirable properties such as high chemical and thermal stability and the possibility of forming modules of arbitrary shape.[31]

2. Experimental Section

Pure silica MFI films on stainless steel substrates were prepared as follows. Stainless steel 304 plates (16 × 16 mm) were polished sequentially by abrasive paper (600, 1200, and 2000 grit, 3M Co.) and α-Al_2O_3 suspension (1, 0.3, and 0.05 μm, EXTEC Co.) using a Buehler polisher followed by thorough washing in deionized water under ultrasonication. The substrates were then cleaned with hydrogen peroxide solution, rinsed with deionized water, and blow-dried with air. The synthesis mixture was made by slowly adding tetraethyl orthosilicate (TEOS, Aldrich) to a solution of tetrapropylammonium hydroxide (TPAOH, Sachem), sodium hydroxide, sodium chloride, and water under stirring. After the solution is aged for 4 h under stirring, the synthesis mixture becomes a clear solution. Then 4 g of synthesis solution was directly

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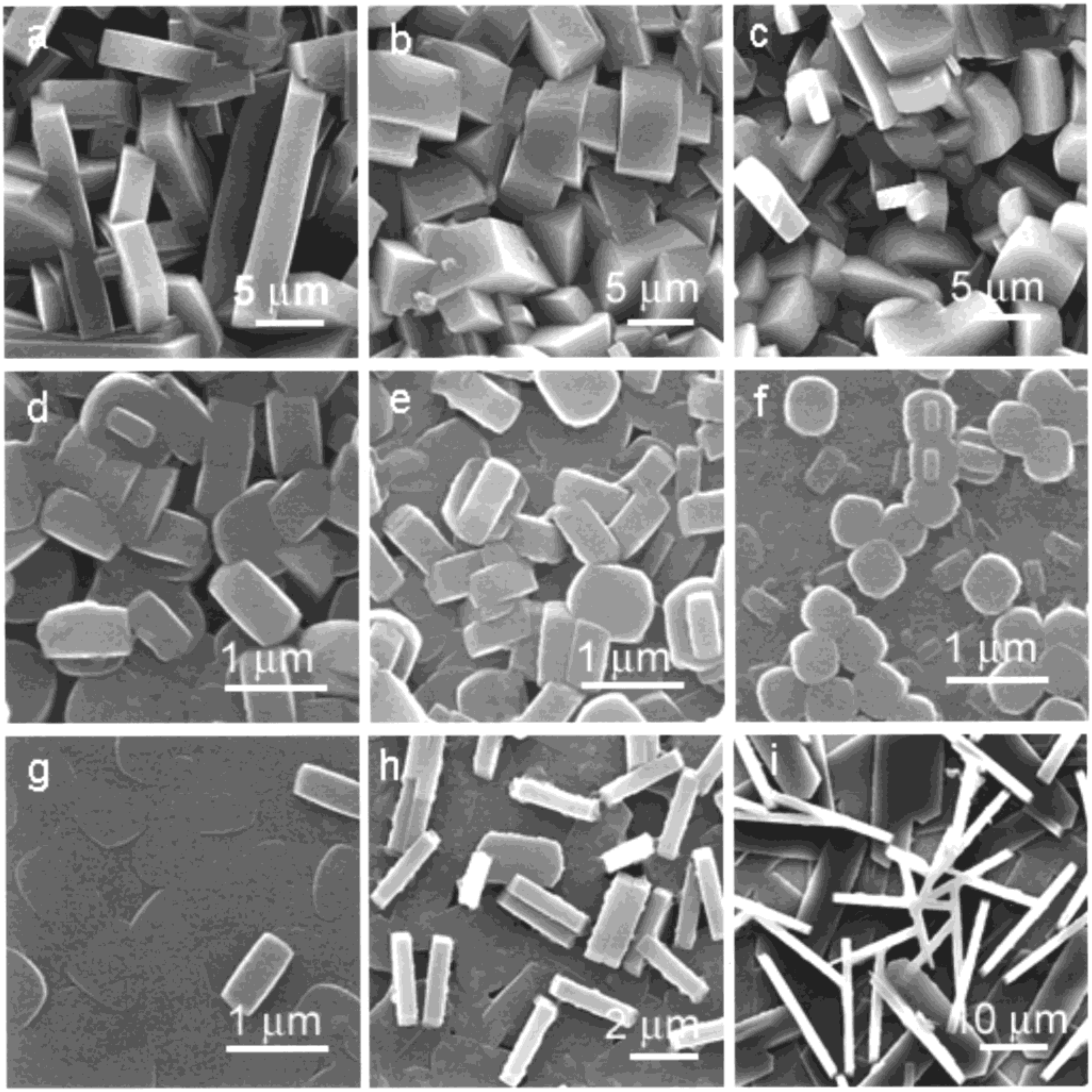

Figure 1. Effect of OH$^-$/Si ratio (x) of synthesis solution on MFI film morphology. x = (a) 1.0 (S01-0), (b) 0.82 (S02-0), (c) 0.64 (S03-0), (d) 0.60 (S04-0), (e) 0.57 (S05-0), (f) 0.50 (S06-0), (g) 0.32 (S08-0), (h) 0.20 (S09-0), and (i) 0.10 (S11-0).

loaded without filtering into a 45 mL Teflon-lined Parr autoclave. A stainless steel substrate was placed horizontally at the bottom of the autoclave. The autoclave was then sealed and placed in a convection oven at 165 °C for 1−18 h (see detailed synthesis solution composition and synthesis conditions in Table 1). Then the samples were recovered and thoroughly washed with deionized water. All samples were dried at room temperature, and some are calcined at 500 °C for 2 h. The films were stable under calcination conditions.

The morphology of silicalite films synthesized was examined by scanning electron microscopy (SEM) at 20 kV, using a Philips XL-30 instrument. Both the top and the bottom surfaces of the substrate were examined, and similar films were obtained for *b*-oriented films. Only SEM images of the top surface are reported here as we normally only polish the top surface. X-ray diffraction (XRD) patterns of the films were collected on a Siemens D-500 diffractometer using Cu Kα radiation.

3. Results and Discussion

3.1. Effect of OH$^-$/Si Ratio. To facilitate discussion, we define the film as *b*-oriented when all or almost all MFI crystals have their *b*-axis perpendicular to the substrate surface. A film is defined as (*a*, *b*)-oriented if both *a*-oriented and *b*-oriented crystals appear in significant numbers inside the film. Several syntheses consistently produce MFI films containing *a*-oriented, *b*-oriented, and roughly *c*-oriented (by SEM) crystals simultaneously in one film, and these films are defined as (*a*, *b*, *c*)-oriented. We have systematically varied synthesis composition to carefully examine the effects of each component of the synthesis solution and found that the crystal orientation is most sensitive to the ratios of OH$^-$/Si and Na$^+$/TPA$^+$. A selected set of compositions is presented in Table 1. For each composi-

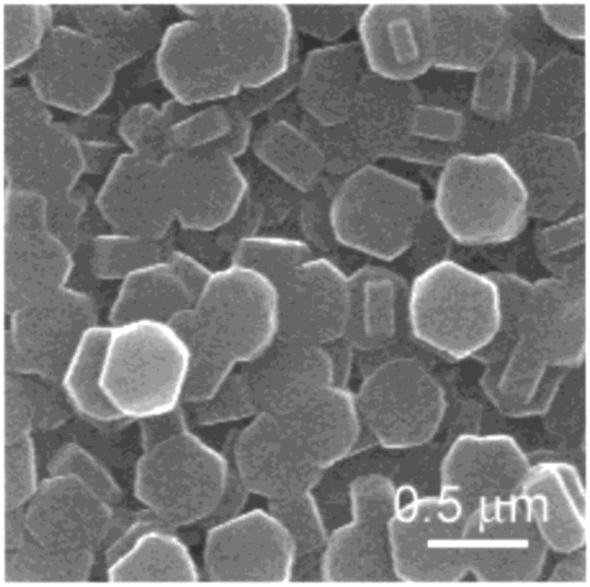

Figure 2. SEM micrograph of MFI zeolite film S08-0* (TPAOH/Si = 0.32, TPABr/Si = 0.68).

tion, we have also examined the effect of crystallization time and temperature, the aging time, and the position and the chemical nature of the substrate on crystal orientation and continuity. However, these data are beyond the scope of this study and thus not included here. Instead, these data and a detailed discussion of film formation mechanism have been reported elsewhere.[13] Briefly here, crystallization time affects the film continuity. The film becomes continuous once certain crystallization time is reached, and it undergoes little change afterward (the time shown in Table 1 is this threshold time).

To examine the effect of OH^-/Si ratio, we first focused on a simple synthesis system in which TPAOH is the only alkaline source (TPAOH:TEOS:H_2O; the "-0" series from S01-0 to S11-0 in Table 1). Figure 1 shows the SEM micrographs of MFI films formed on stainless steel using synthesis solution with different OH^-/Si ratios. Random-oriented crystals are obtained when the OH^-/Si ratio is higher than 0.64 (Figure 1a−c). When OH^-/Si is between 0.64 and 0.5 (Figure 1d,e) or between 0.2 and 0.1 (Figure 1h,i), (*a*, *b*)-oriented crystals are obtained. When the ratio of OH^-/Si is between 0.5 and 0.2 (Figure 1f,g), predominantly *b*-oriented crystals result although some twin crystals are present in the film.

Crystal orientation information and crystal size are also summarized in Table 1. It is interesting to notice that the crystal size goes through a minimum at OH^-/Si = 0.5 as OH^-/Si changes from 1 to 0.1 (Figure 1 and Table 1). It is noted that some of the films shown in Figure 1 (Figure 1a−c,i; see Table 1 for crystallization time) have longer crystallization time than others (Figure 1d−h; see Table 1 for crystallization time). And this leads to the question whether longer crystallization time may have been responsible for the larger crystal observed. Experiments with longer crystallization time (e.g., 18 h) were performed for the latter group of samples, and only slight further growth was observed, suggesting that crystallization time was not a major factor. One plausible explanation is that nucleation is

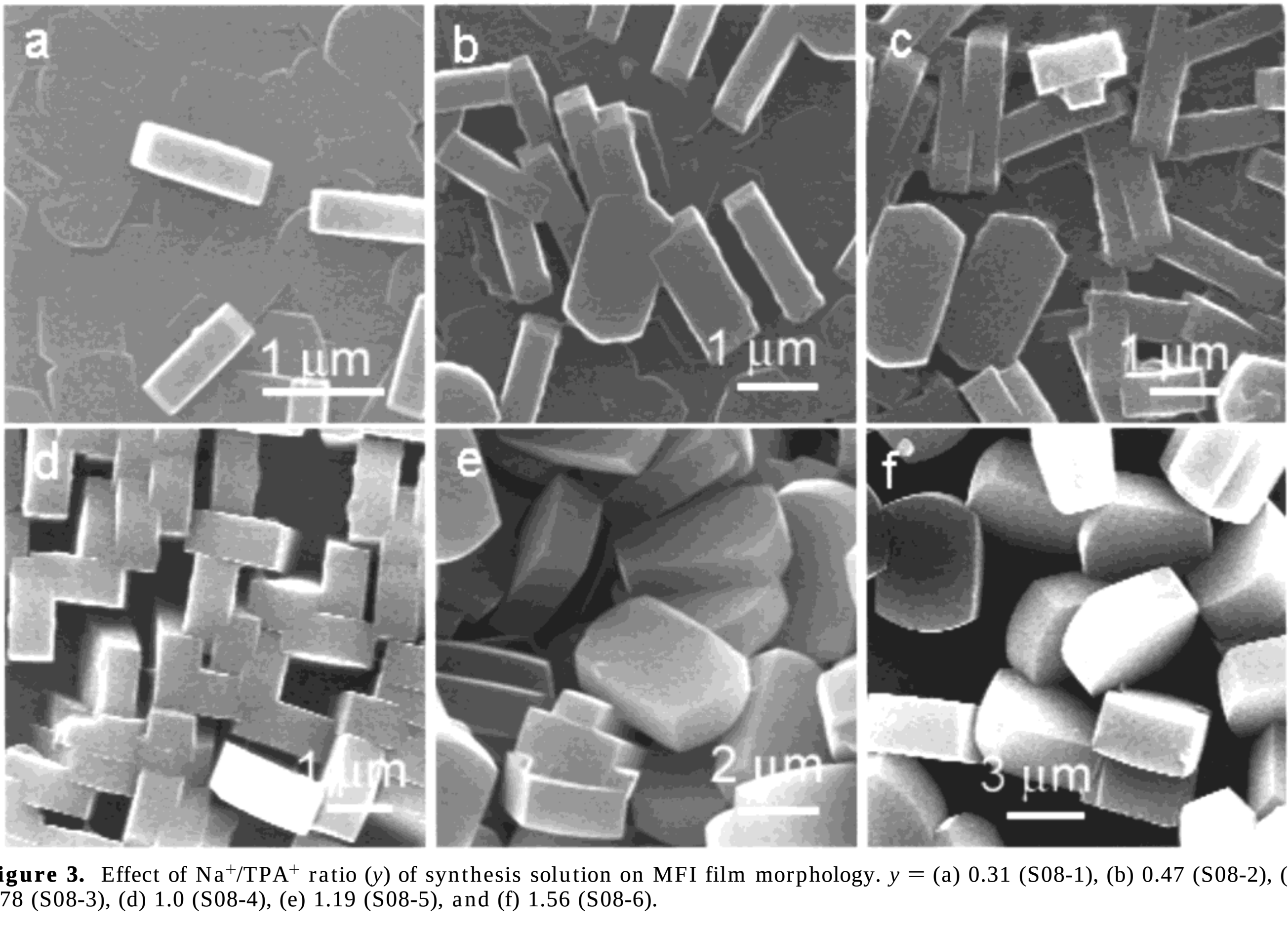

Figure 3. Effect of Na^+/TPA^+ ratio (*y*) of synthesis solution on MFI film morphology. *y* = (a) 0.31 (S08-1), (b) 0.47 (S08-2), (c) 0.78 (S08-3), (d) 1.0 (S08-4), (e) 1.19 (S08-5), and (f) 1.56 (S08-6).

suppressed at both high and low TPAOH concentrations leading to fewer and larger crystals. The suppression mechanisms are likely to be different for the two conditions, however. It is speculated that at high TPAOH concentrations the suppression is a result of high alkalinity while at low TPAOH concentrations the lack of TPA molecules is responsible.

It has also been observed that no crystals form in the bulk phase when OH$^-$/Si is higher than 0.64 or lower than 0.2 while abundance of crystals appear in the bulk when OH$^-$/Si is between 0.5 and 0.32. In all these cases, however, continuous zeolite films are obtained on stainless steel substrate although much longer crystallization time is needed for high and low OH$^-$/Si ratios. Blank crystallization experiments were attempted without using substrate, and no crystals formed for OH$^-$/Si $>$ 0.64 and OH$^-$/Si $<$ 0.2 for crystallization time up to 20 h. These data again seem to suggest that nucleation is severely suppressed at very high and very low TPAOH concentrations. It also shows that the presence of a stainless steel surface plays an important role in the film formation process.

It is noted here that within this simple system change of OH$^-$/Si results in change of TPA$^+$/Si ratio, and this leads to the question of whether the observed change in film morphology is a result of changing TPA$^+$/Si. To clarify this point, we have carried out experiments in which we keep OH$^-$/Si of the synthesis solution constant while changing TPA$^+$/Si by adding TPABr into the synthesis solution (most of these data are not shown). For example, TPABr was added to synthesis composition S08-0 (TPA$^+$/Si = 0.32, OH$^-$/Si = 0.32, Table 1) to make a new composition S08-0* (TPA$^+$/Si = 1, OH$^-$/Si = 0.32, Table 1). As shown in Figure 2, crystals in the film formed from this new solution are still *b*-oriented as at TPAOH/Si = 0.32. This suggests that crystal orientation is primarily determined by the ratio of OH$^-$/Si, not TPA$^+$/Si. Compared with sample S08-0, sample S08-0* contains more (in terms of number density) and smaller crystals (0.5 μm vs 1.0 μm), and this is consistent with the general observation reported in the literature that more TPA molecules usually lead to more nuclei and therefore smaller crystals.[32,33]

3.2. Effect of the Na$^+$ Content. Sodium ions are often used in the synthesis solution for preparation of MFI zeolite films and membranes.[1−13] Thus, it is important to clarify the effect of sodium ions in controlling crystal orientation. Since *b*-oriented MFI films (only *b*-direction has straight channels) have special importance from the viewpoint of both practical application and fundamental studies, we have focused our effort on the effect of Na$^+$ in sample S08-0 (OH$^-$/Si = 0.32, Figure 1g) where *b*-oriented films are obtained. To avoid changing OH$^-$/Si, the content of Na$^+$ ions was adjusted by addition of sodium chloride into the synthesis solution. The result is shown in Figure 3 and Table 1 (sample series S08-*m*, *m* = 0−6). With increasing amount of Na$^+$, crystal orientation changes from *b*-orientation (Figure 3a), to (*a*, *b*)-orientation (Figure 3b,c), to (*a*, *b*, *c*)-orientation (Figure 3d), and to random orientation (Figure 3e,f). The loss of crystal alignment (orientation) can be explained by reported trend that Na$^+$ tends to cause agglomeration of silicate precursors, leading to large aggregate of random-oriented crystals.[34]

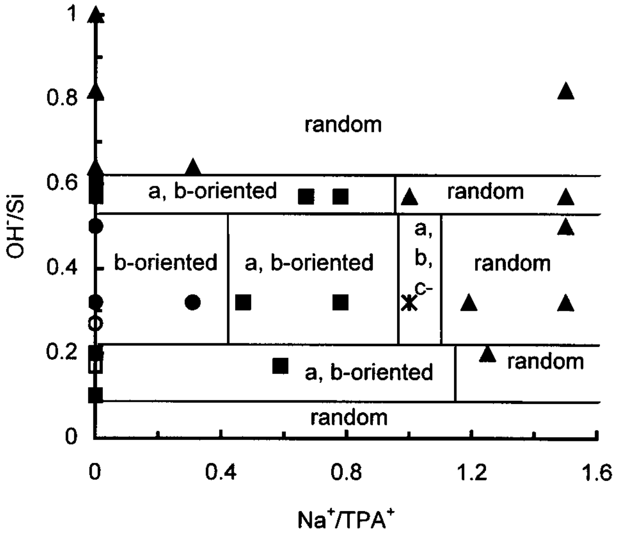

Figure 4. Crystal orientation−synthesis composition (OH$^-$/Si and Na$^+$/TPA$^+$ ratios) map.

We have also examined the effect of sodium concentration for other OH$^-$/Si ratios, and a similar trend was observed. The effect of different forms of sodium (NaOH or NaCl) was also examined. For example, in the sample series S05-*m*, *m* = 0−5 (OH$^-$/Si = 0.57, Table 1), the content of sodium ions was adjusted by addition of sodium chloride or sodium hydroxide into the synthesis mixture while keeping the ratio of OH$^-$/Si constant (i.e., OH$^-$/Si = 0.57). It is found that (*a*, *b*)-orientation changes to random orientation if the ratio of Na$^+$/TPA$^+$ is more than 1 (S05-4 and S05-5) regardless of the sodium source (sodium chloride or sodium hydroxide) (Table 1). It is again found that more TPA$^+$ in the synthesis solution results in smaller crystals (S05-3 vs S05-2). It is noted that the pH value of the synthesis mixture increases with the addition of sodium chloride due to the aggregation of the silica gel.[34]

3.3. Crystal Orientation−Synthesis Composition Map. As discussed above, ratios of OH$^-$/Si and Na$^+$/TPA$^+$ significantly affect the crystal orientation of a pure-silica MFI film on stainless steel substrate. We have examined an extensive list of compositions (Table 1), and Figure 4 shows the crystal orientation as the function of the ratios of OH$^-$/Si and Na$^+$/TPA$^+$. It should be noted that this map is generated by using TEOS as the silica source and may not be directly applicable to composition in which other silica source (e.g., colloidal silica) is used.[33,34] It is also noted that the hydrolysis of TEOS produces ethanol (1 TEOS to 4 H$_2$O). But it is expected that ethanol only plays a minor role in the synthesis because the solution is rather dilute (the ratio of H$_2$O to ethanol is about 40:1). The synthesis compositions reported in the literature for MFI film/membranes were examined, and it was found that synthesis solutions with Na$^+$/TPA$^+$ $>$ 1.2 or OH$^-$/Si $<$ 0.1 or OH$^-$/Si $>$ 0.8 are often used. Consistent with the map in Figure

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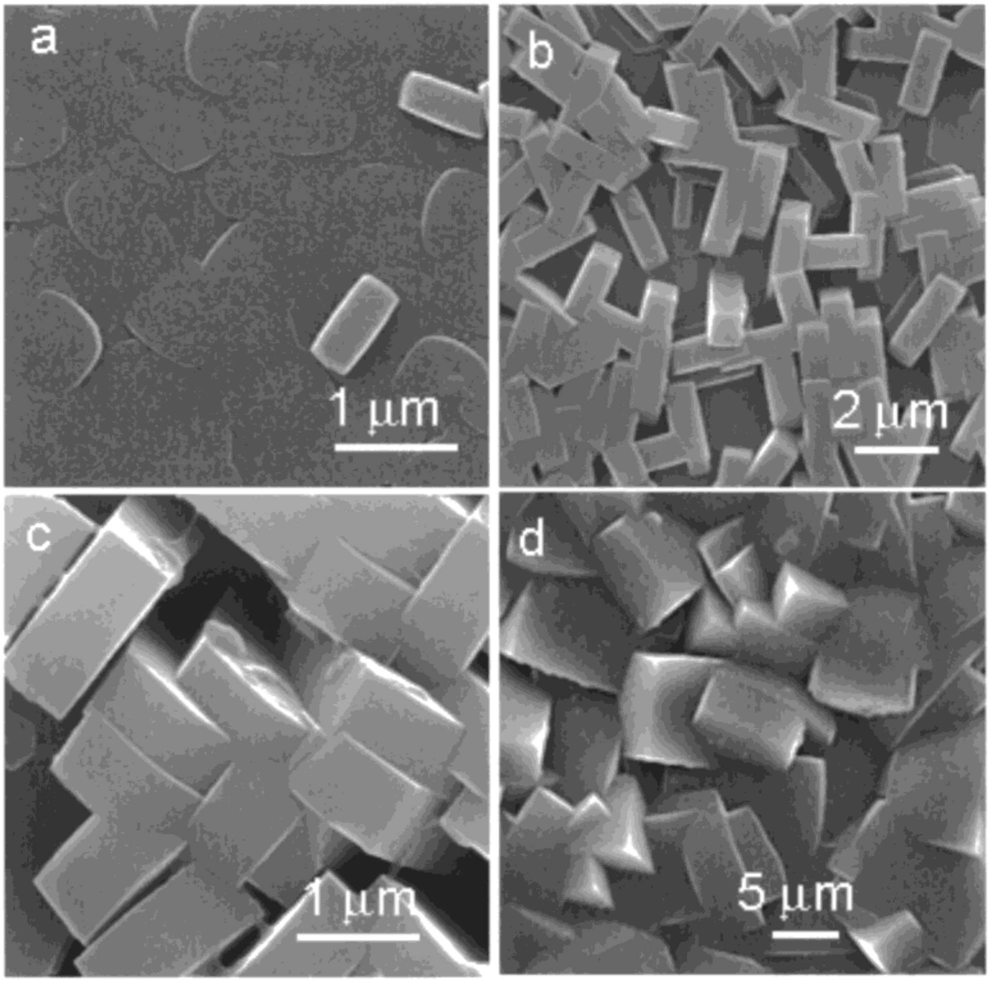

Figure 5. SEM micrographs of MFI zeolite films: (a) *b*-oriented (S08-0), (b) (*a*, *b*)-oriented (S05-2), (c) (*a*, *b*, *c*)-oriented (S08-4), and (d) random-oriented (S02-1).

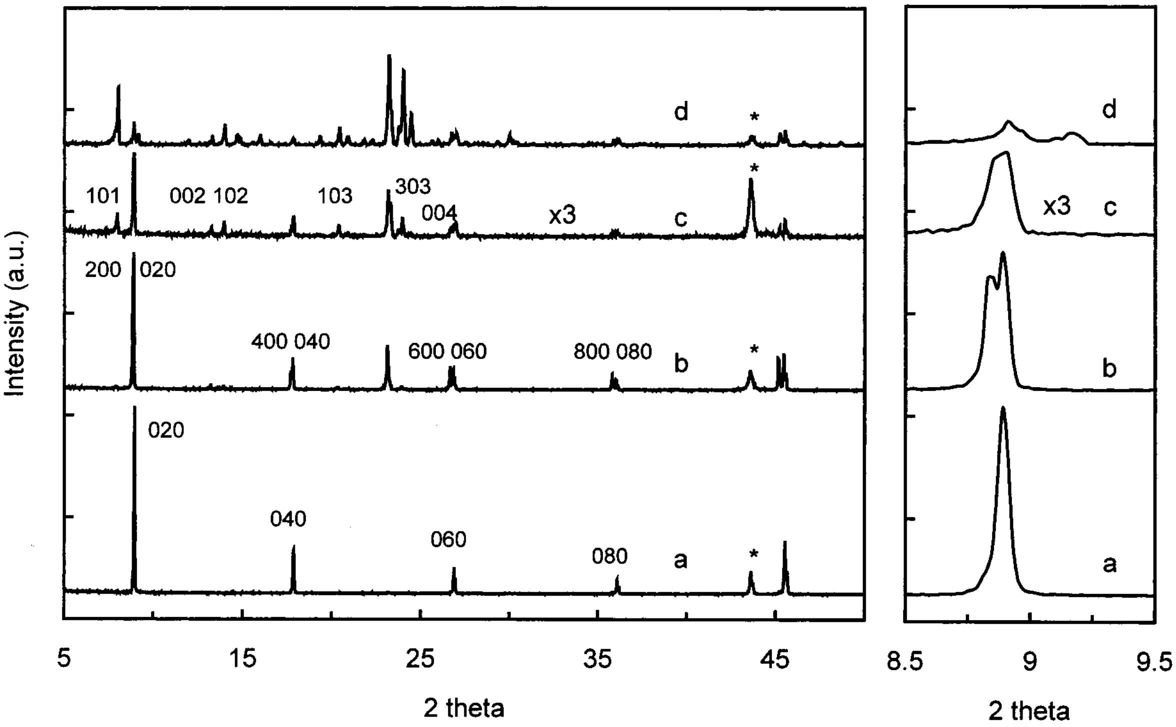

Figure 6. XRD patterns of zeolite films (a) *b*-oriented (S08-0), (b) (*a*, *b*)-oriented (S05-2), (c) (*a*, *b*, *c*)-oriented (S08-4), and (d) random (S02-1). (*) Peak from stainless steel substrate.

4, all of the films so obtained are random oriented.[35−37] We have also included in our map the data points from previous publications on oriented MFI layers (*b*-oriented, ○, and (*a*, *b*)-oriented, □).[38] Again, their results appear consistent with our orientation−composition map.

From Table 1, it is clear that four distinctive orientations (i.e., *b*-oriented, (*a*, *b*)-oriented, (*a*, *b*, *c*)-oriented, and random-oriented) of a thin continuous MFI film on stainless steel substrate can be obtained using direct in-situ crystallization, and these orientations are exemplified in Figure 5. To confirm the orientation, the films were examined by XRD (Figure 6). For *b*-oriented film (Figure 6a), only (0*k*0) lines are observed, confirming that *b*-axis is perpendicular to the substrate surface. Similarly, only (0*k*0) and (*h*00) are observed for a (*a*, *b*)-oriented film (Figure 6b). On the side chart, the area near (020) line was magnified, and it shows clearly that *b*-oriented sample has a single peak and (*a*, *b*)-oriented sample has doublet. The XRD pattern of (*a*, *b*, *c*)-oriented film (Figure 6c) shows (0*k*0), (*h*00), (*h*0*l*), and (00*l*) reflections, and it is clearly different from the XRD pattern of a random-oriented film (Figure 6d). The presence of *c*-oriented crystals in the film is clear in the SEM image in Figure 5c, and the XRD pattern is consistent with that of reported *c*-oriented MFI films.[15]

4. Summary

We have demonstrated that crystal orientation control in a continuous MFI thin film can be achieved by simple adjustment of synthesis compositions using direct in-situ crystallization. Clearly highly *b*-oriented MFI film is favored by medium OH^-/Si (e.g., $OH^-/Si = 0.32$) and low Na^+/TPA^+ ratios (e.g., $Na^+/TPA^+ < 0.31$). The comprehensive orientation−synthesis composition map developed in this study may prove useful for preparing thin continuous MFI films with specified orientations. The ultrathin ($<0.4\ \mu$m) continuous *b*-oriented films obtained are particularly promising for many applications including chemical sensors, membrane separation, and as components in electronics. This simple direct in-situ synthesis also holds great potential for forming oriented zeolite films on 3-D objects and therefore could open up doors for many new applications.

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