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Fabrication of *b*-Oriented MFI Zeolite Films under Neutral Conditions without the Use of Hydrogen Fluoride**

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Abstract: *The fabrication of MFI zeolite films with particular b-axis orientation is especially fascinating. Unlike the conventional alkaline or hydrofluoric acid (HF) assisted neutral synthesis route, here we develop a novel neutral synthesis solution system of TPABr/fumed silica/H_2O without the use of HF and successfully synthesize highly b-oriented MFI zeolite films on glass-plate substrates by secondary growth. The localized weak alkaline environment created by the dissolved Na_2O species from the substrate is identified as the key factor for the depolymerization of fumed silica and subsequently the in-plane growth of zeolite seed layers. Continuous b-oriented MFI films can also be synthesized on other substrates in the presence of a glass plate or a trace amount of NaOH, which making our neutral synthesis route promising for the direct synthesis of MFI zeolite films and membranes on various substrates.*

MFI zeolite films and membranes have found many applications in the field of separation,[1–8] catalysis,[9,10] sensors,[11,12] and corrosion protection.[13,14] One particularly interesting but challenging issue is the fabrication of dominantly *b*-oriented pure silica MFI zeolite films. In 2001, Wang et al. for the first time reported that the delicate manipulation of the composition of the synthesis solution produced continuous *b*-oriented MFI thin films by in situ crystallization.[15] The film was then successfully used as a low-*k* intermetallic dielectric.[16] At present, one of the most important applications of *b*-oriented MFI membranes on porous supports is the separation of *p*-xylene from xylene isomers.[7,8] By using a specifically designed template of trimer-TPAOH (tetrapropyl ammonium hydroxide), highly *b*-oriented MFI membranes were synthesized on mesoporous-silica-coated alumina supports by Tsapatsis et al., which exhibited an excellent separation factor of 483 for *p*-/*o*-xylene separation.[7] Recently, an exceptionally high separation factor over 1000 was obtained by Yoon et al. on a perfectly *b*-oriented MFI membrane synthesized with TEAOH (tetraethyl ammonium hydroxide) and $(NH_4)_2SiF_6$ as co-templates.[8]

Generally, *b*-oriented MFI zeolite films/membranes are prepared under alkaline synthesis conditions by the secondary growth method.[7,8,17–21] To prevent Al leaching from the porous alumina supports, an intermediate silica layer should be precoated on the support surface.[7,19–21] This process is tedious and requires additional treatment steps prior to membrane synthesis. The silica layer may also dissolve in the alkaline synthesis solution. In addition, the intermediate layer would likely increase the transport resistance and therefore decrease the membrane flux. To avoid alkaline corrosion of the support/intermediate layer, a synthesis technique utilizing neutral or near-neutral conditions is an attractive alternative.

Lassinantti Gualtieri et al.[22,23] introduced hydrofluoric acid (HF) into the synthesis solution to adjust the pH to 6.7 ± 0.1. After optimizing the silica source, they successfully synthesized MFI membranes on alumina supports seeded with nanometer-sized MFI crystals. However, the SEM images and the XRD pattern showed that the zeolite membrane is (101)-oriented.[23] Very recently, using the identical synthesis protocol with HF as additive, Zhou et al. reported that *b*-oriented MFI membranes could be achieved on alumina supports that were precoated by *b*-oriented MFI seed layers.[24] Compared with randomly oriented MFI membranes, the *b*-oriented MFI membranes exhibited a higher CO_2/H_2 separation performance. It is worth noting that HF was used in these preparations.[22–24] Handling of HF in the laboratory synthesis or during the eventual large scale manufacturing is highly undesirable due to HF's corrosiveness. Therefore, the exploration of a new synthesis method without the need of HF is highly desired.

Here we demonstrate for the first time that under the neutral synthesis system of TPABr/fumed silica/H_2O, *b*-oriented MFI films can be easily synthesized on a glass plate support. Moreover, compared with other synthesis protocols, the employment of the inexpensive template of TPABr and fumed silica instead of TPAOH or trimer-TPAOH and TEOS (tetraethyl orthosilicate) can reduce the cost of membranes.

In our previous work, we found that a low TPA^+/Si ratio (typically lower than 0.1) with a OH^-/Si ratio of 0.1 is beneficial to the suppression of twin crystals on *b*-oriented MFI zeolite films.[25] In this work, we therefore first tried the synthesis with a composition of $0.1\,TPABr:SiO_2:165\,H_2O$ ($TPA^+/Si = 0.1$) for the secondary growth. Fumed silica was used as the silica source (Figure S1, see the Supporting

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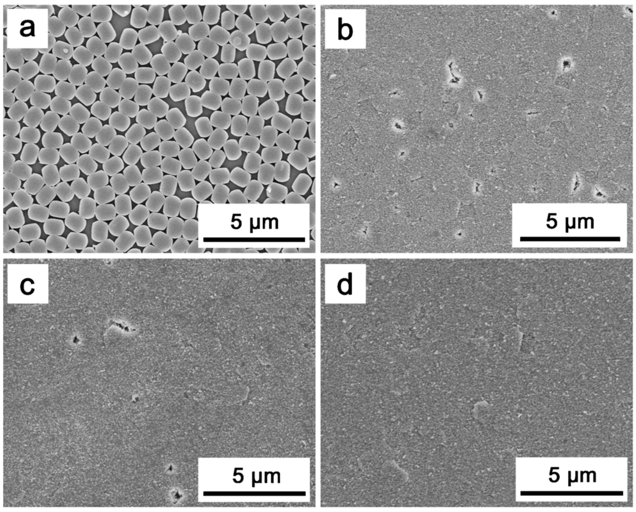


Figure 1. SEM images of a) *b*-oriented MFI zeolite seed layer on a glass plate and MFI films prepared by secondary growth on seeded glass plates at 175 °C for b) 12 h, c) 18 h, and d) 24 h.

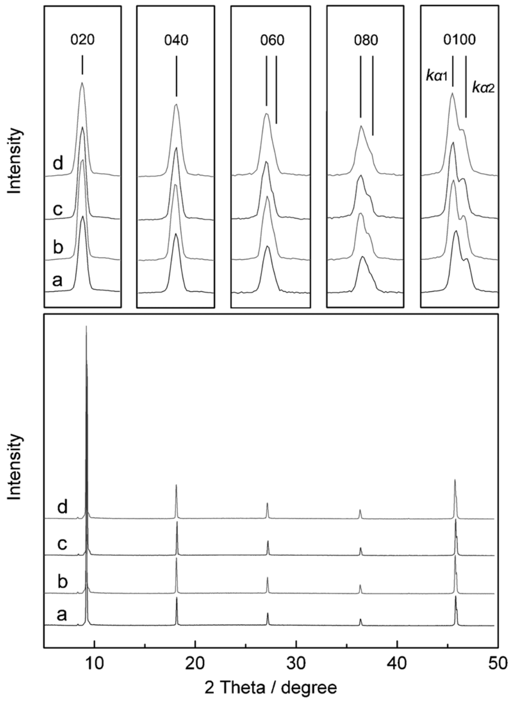


Figure 2. XRD patterns of a) MFI seed layer on a glass plate and zeolite films synthesized on seeded glass plates at 175 °C for b) 12 h, c) 18 h, and d) 24 h.

Information). The synthesis solution is neutral because no other chemical reagent is added. A detailed procedure on the preparation of MFI films is given in the Experimental Section. Figure 1 presents the SEM images of the *b*-oriented MFI zeolite seed layer on a glass plate prepared by hand-rubbing (Figure 1 a) and the evolution of the zeolite film morphology along with the crystallization time (Figure 1 b–d). It is seen that a long crystallization time is favorable for the improvement of continuity of the zeolite film. A continuous and twin-free *b*-oriented zeolite film can be achieved when the time is prolonged to 24 h (Figure 1 d). The crystal size along the *c*-axis is increased to about 2.4 µm (Figure S2c) from 1.0 µm (Figure 1 a) and the thickness of the film is about 380 nm (Figure S3) after the synthesis of 24 h. This synthesis time for obtaining continuous films is comparable with those preparation strategies employing fluoride media[22–24] and trimer-TPAOH templates.[7] Crystallization times less than 24 h are not adequate for the formation of continuous films (Figure 1 b,c). The crystal size is slightly increased to 1.6 µm and 2.0 µm (Figure S2a and S2b) after secondary growth for 12 h and 18 h, respectively. To analyze the channel orientation, the zeolite films were examined by X-ray diffraction (Figure 2). The diffraction patterns of the seed layer (Figure 2 a) and zeolite films (Figure 2 b–d) only show the diffraction peaks from the (020), (040), (060), (080), and (0100) planes, confirming that the synthesized films are highly *b*-oriented. The splitting of the latter three diffraction peaks is due to the presence of two different wavelengths in the X-ray source (Cu $K\alpha_1 = 1.54056$ and Cu $K\alpha_2 = 1.544$).[8,25]

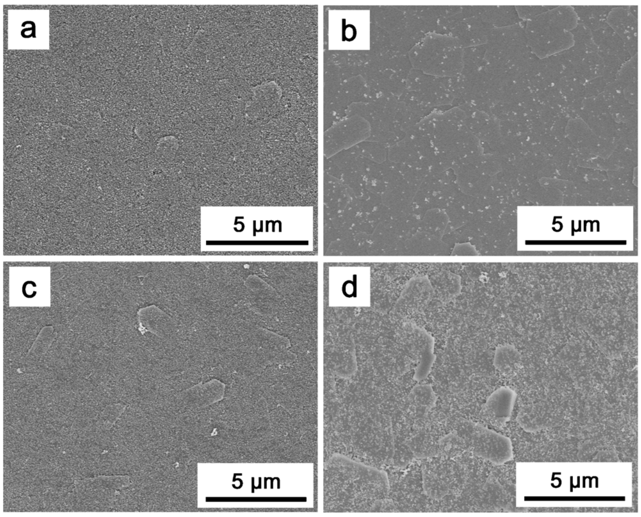


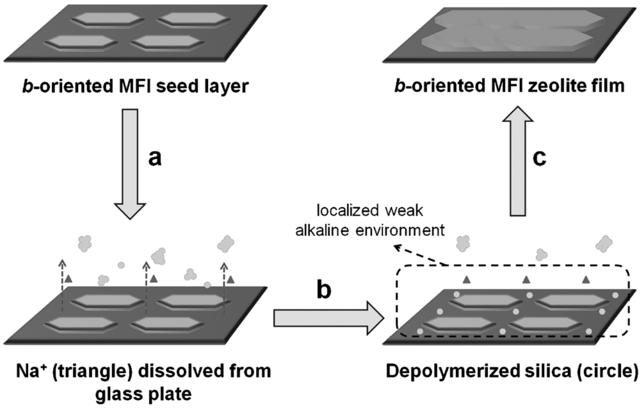
Figure 3. SEM images of *b*-oriented MFI films synthesized a–c) using the synthesis solution of $0.1\,TPABr{:}0.1\,SiO_2{:}165\,H_2O$ at 175 °C for 24 h, a) on a seeded glass plate, b) on a seeded stainless-steel plate in the presence of an extra bare glass plate, c) on a seeded glass plate in the presence of an extra bare glass plate, and d) using the synthesis solution of $0.1\,TPABr{:}0.1\,SiO_2{:}165\,H_2O{:}0.001\,NaOH$ on a seeded stainless-steel plate at 175 °C for 24 h.

Due to the aggregation of undissolved fumed silica during hydrothermal synthesis, a semi-solid gel was formed after crystallization. The solidification of the synthesis solution is relatively alleviated when the molar amount of silica source in the synthesis solution is decreased to 0.1 and 0.5 (i.e., the synthesis solution composition is $0.1\,TPABr{:}0.1\,SiO_2{:}165\,H_2O$ and $0.1\,TPABr : 0.5\,SiO_2{:}165\,H_2O$). Although the available "active species" (i.e., active silica nanoparticles)[25] for crystal growth in the synthesis solution is simultaneously decreased with the decrease of the silica amount, the synthesized *b*-oriented zeolite films are still continuous. The crystal size of zeolite film synthesized at a lower silica ratio in Figure 3 a (3.6 µm, see Figure S4a) is even larger than that obtained at the higher silica ratio (2.4 μm, Figure S2c). This may be attributed to the fact that the increased mobility of the "active species" in the synthesis solution accelerated the zeolite seed growth. In addition, despite the TPA^+/Si ratio being 1.0, no clear twin crystals can be observed on the zeolite film (Figure 3a), which is mainly a result of the very low concentration of "active species" when using fumed silica as silica source compared with hydrolyzed TEOS. XRD patterns shown in Figure S5 suggest that the synthesized MFI zeolite films are still highly *b*-oriented when altering the amount of fumed silica in the synthesis solution. Compared with previous work,[25] the operation window of the TPA^+/Si ratio is therefore significantly extended. By contrast, increasing the amount of fumed silica has no promotion effect on the crystal size in the zeolite film. Instead, a distinct hindering effect on "active species" occurs, which is ascribed to much more solidification of the synthesis solution.

When using stainless-steel plates instead of glass plates as film supports, however, the crystal size of the *b*-oriented MFI zeolite is only slightly increased and the film is not continuous at the identical composition of the synthesis solution ($0.1\,TPABr:0.1\,SiO_2:165\,H_2O$) as presented in Figure S6. Interestingly, when an extra bare glass plate is placed near the seeded stainless-steel plate in the synthesis solution (detailed procedure is given in the Experimental Section), MFI zeolite crystals on the stainless-steel plate grew significantly larger (4.5 μm, see Figure S7a) and a continuous *b*-oriented MFI film is obtained (Figure 3b). We also found that the presence of an extra bare glass plate in the synthesis solution accelerates the growth of MFI seeds on a glass plate (Figure 3c) and that the crystal size of the resulting MFI zeolite film (6.8 μm, see Figure S7b) is significantly larger than that synthesized without an extra glass plate (3.6 μm, Figures 3a and S4a).

From the above results, we can conclude that the glass plate plays an important role in the seeded growth in the neutral synthesis solution. It is possible that the glass plate plays a role of second silica source during secondary synthesis. Kida et al. reported that large silicalite-1 crystals can be obtained using a quartz glass plate as single silica source, which may slowly dissolve in the synthesis solution.[26] Actually, an EDX spectrum (Figure S9) indicates that the glass plate employed in the present work contains a significant amount of Si. Note that the fumed silica in the synthesis solution is indispensable, because the seed crystals on the glass plate cannot grow without fumed silica (data not shown). This indicates that the Si species from the glass plate for seeded growth can be ignored. It is known that glass materials usually contain some Na_2O. EDX results indeed confirmed the presence of a significant amount of Na in the glass plate (Figure S9). As revealed by ICP-AAS analysis, the Na^+ concentration in the synthesis solution is significantly enhanced from $0.15\,mg\,L^{-1}$ to $18.2\,mg\,L^{-1}$ after the synthesis of the seeded glass plate at 175 °C for 24 h. Note that the fumed silica employed in this work is a polymeric silica source, which could not be completely dissolved under the neutral synthesis condition. The dissolution of Na^+ into the synthesis solution from the glass plate during seeded growth would result in the generation of a localized weak alkaline environment, which then promotes the depolymerization of fumed silica. Therefore, the available amount of "active species" for seeded growth is considerably increased. However, the dissolved Na^+ amount is still low because no change of pH value is observed in the solution after crystallization, i.e., the synthesis solution is still neutral. To verify the effect of the dissolved Na^+, we intentionally added a very small amount of NaOH (molar amount: 0.001) in the synthesis solution. As seen in Figure 3d, on the stainless-steel plate, a continuous *b*-oriented MFI film (XRD, Figure S10) with large crystals (10 μm, Figure S11) is obtained. This confirms that a trace amount of Na_2O in the synthesis solution can facilitate the secondary growth of MFI seeds.

On the basis of the above results, we put forward a secondary growth mechanism for preparing *b*-oriented MFI films on glass plates in a neutral synthesis solution of $TPABr/fumed\ silica/H_2O$ (Scheme 1). There are two key elements to obtain highly *b*-oriented MFI films: 1) Due to the employment of a polymeric silica source of fumed silica and the neutral synthesis environment, the growth rate of oriented zeolite seeds is very slow, which allows the fine-control of the growth rate. 2) The dissolved Na_2O species from the glass support (Scheme 1a) provide a localized weak alkaline environment near the seed crystals to depolymerize fumed silica (Scheme 1b), offering more "active species" to accelerate the growth rate. Because the "active species" is still at a low concentration level for forming nuclei in the synthesis solution, the appearance of twin crystals is suppressed. Finally, a continuous highly *b*-oriented MFI film is achieved (Scheme 1c).



Scheme 1. Schematic illustration of the film formation mechanism of the HF-free neutral synthesis route: a) dissolution of Na^+ species from the glass plate, b) depolymerization of large fumed silica particles in the localized weak alkaline environment, and c) growth of seed crystals.

In summary, we have developed a neutral synthesis solution system without fluoride for the preparation of highly *b*-oriented MFI zeolite films. When using glass plates as film supports, the dissolved Na_2O from the glass plate facilitates the secondary growth of MFI seed crystals in the synthesis system of $TPABr/fumed\ silica/H_2O$. Continuous *b*-oriented MFI films can also be synthesized on other supports (e.g., stainless steel plate) in the presence of a glass plate or a trace amount of NaOH. The absence of HF during crystallization avoids the undesirable operation conditions. The TPA^+/Si ratio can be operated in a wide range due to the utilization of fumed silica instead of TEOS. The film/membrane cost may decrease due to the employment of inexpensive raw materials. The novel neutral synthesis system (TPABr/fumed silica/H_2O) without fluoride with a trace amount of NaOH or in the presence of glass materials may provide us a new route for the direct synthesis of *b*-oriented MFI zeolite films and membranes on various substrates.

Experimental Section

Materials: Glass plates and stainless steel 202 plates (20 × 20 mm) were immersed in hydrogen peroxide solution for 45 min, then rinsed with deionized water, and dried at 60 °C before the synthesis of zeolite films. Tetrapropylammonium bromide (TPABr, 99 %) and sodium hydroxide ($\geq 96\,\%$) were purchased from Sinopharm. Fumed silica (99.8 %) was purchased from Xi'ya Reagent.

Preparation of MFI zeolite seeds: Synthesis solution of molar composition 0.32 TPAOH:1 TEOS:165 H_2O was prepared by slowly adding TEOS to a solution of TPAOH and water under stirring. A clear synthesis solution was obtained after stirring at room temperature for 4 h. Then the synthesis solution was directly loaded into a Teflon-lined stainless steel autoclave. The autoclave was sealed and fixed in the rotation shaft of a convectional oven. It rotated with the axis at 20 rpm in the oven at 175 °C for 2 h. After synthesis, the mixture was quenched. The sample was recovered, thoroughly washed with deionized water, and dried at 60 °C. The size of the MFI zeolite seed crystals is ca. 1 μm.

Preparation of *b*-oriented MFI zeolite films: Perfectly *b*-oriented MFI seed monolayers were prepared on the supports of glass plates and stainless-steel plates by rubbing MFI zeolite crystals with a finger in latex glove. The seeded support was vertically placed in a Teflon-lined stainless steel autoclave for secondary growth. The synthesis solution was prepared by slowly adding fumed silica to a solution of TPABr and water under stirring. The molar composition of the resulting gel was 0.1 TPABr:(0.1–2.0) SiO_2:165 H_2O. The gel was aged for 1 h prior to use at room temperature. The seeded growth was carried out at 175 °C for 12 to 24 h. After synthesis, the film was rinsed with deionized water and dried at 60 °C. When an extra bare glass plate was placed in autoclave, it was also vertically placed and the distance between this glass plate and the seeded support was ca. 3 mm. To prepare the synthesis solution containing NaOH, NaOH was added to a solution of TPABr and water under stirring prior to introducing fumed silica.

Characterization: The top and cross-sectional images of the zeolite films were obtained with a scanning electron microscope TM-1000 and SU-70 (Hitachi). Elemental analysis of glass plates was performed by energy-dispersive X-ray (EDX, Horiba EX350). X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert-Pro diffractometer using Cu $K\alpha$ radiation. The ICP-AAS analysis was carried out on Thermo X Series 2 and the solution tested was from the synthesis during which a seeded glass plate was vertically placed in the solution.

Keywords: hydrothermal synthesis · MFI · oriented film · thin films · zeolites

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