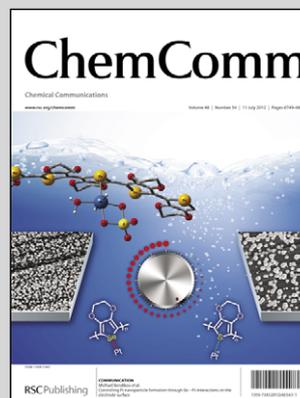


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Suppression of twins in *b*-oriented MFI molecular sieve films under microwave irradiation

Relying on the nucleation-related bottleneck effect, the undesired twin growth of an MFI zeolite seed layer can be effectively suppressed using microwave irradiation. The suppression of twins is very beneficial in improving the mobility of guest molecules through the zeolite film.

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Suppression of twins in *b*-oriented MFI molecular sieve films under microwave irradiation†Yi Liu,^{ab} Yanshuo Li,^{*a} Rui Cai^a and Weishen Yang^{*a}

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Twin growth in the synthesis of *b*-oriented MFI films is successfully suppressed by applying microwave irradiation on a *b*-oriented MFI seed layer, relying on the nucleation-related bottleneck effect. Electrochemical oxidation experiments demonstrated the importance of twin suppression in enhancing the diffusion of guest molecules in MFI films.

In recent years, there has been a growing interest in fabrication of high quality zeolite films with the aim of exploring their advanced applications, such as separation membranes,¹ selective sensors,² low-*k* materials,³ optical materials,⁴ and corrosion-resistant coatings.⁵ Improvement of the performance of zeolite films mainly depends on the optimization of their microstructures, including manipulation of grain size and shape, grain boundaries, and channel orientations. In particular, the preparation of dominantly *b*-oriented MFI (siliceous ZSM-5, [Si₁₀₆O₁₉₂]) molecular sieve films was highly significant.⁶ By accurate manipulation of thermodynamic and kinetic parameters of the crystal nucleation and growth during *in situ* synthesis, predominantly *b*-oriented MFI films have been grown on flat substrates but in a narrow synthesis window.⁷ By comparison, a secondary (seeded) growth method exerts more effective control over the membrane formation process by decoupling the nucleation and growth steps, which can significantly reduce the difficulty in manipulation of membrane orientation. Nevertheless, it is still very challenging to effectively suppress undesired twin growth of the seed layer, *e.g.* *a*-oriented twins in the case of MFI films, which often arises during secondary growth and severely degrades the performance of the final MFI films.¹

It is generally accepted that the adherence of new MFI nuclei in the bulk solution to the (0 *k* 0) faces of the original MFI seeds was the main cause of *a*-oriented twin growth during seeded growth.⁸ In view of this, H. K. Jeong *et al.* attempted to avoid the attachment of new nuclei by passivating the (0 *k* 0) faces of the *b*-oriented MFI seed layer with a coating

of Au/Pt.⁹ M. Tsapatsis *et al.* employed a specifically designed template *trimer*-TPA for secondary growth.¹ Besides the enhanced relative growth rate along the *b*-axis, the significantly retarded nucleation kinetics of MFI zeolite with *trimer*-TPA might be another plausible reason for the suppression of twin growth.¹⁰ Z. B. Wang *et al.* reported that the growth of twin crystals on a *b*-oriented MFI seed layer could be largely suppressed by reducing the TPAOH in bulk solution.¹¹ Very recently, K. B. Yoon *et al.* prepared perfectly *b*-oriented MFI film on a *b*-oriented seed monolayer with TPAOH and (NH₄)₂SiF₆ as co-SDAs. The precursor solution did not form new MFI crystals in the bulk during secondary growth, which may be the intrinsic mechanism for the effective suppression of twins.¹² In a previous study, we successfully suppressed undesired twin growth of MFI film by pre-heating the precursor solution.¹³ To summarize, a facile technique for controlling the bulk nucleation kinetics during secondary growth is of great importance for suppressing twin growth and achieving high performance of MFI films. A microwave technique is the ideal candidate.

There are numerous reports showing that microwave heating can greatly accelerate the growth of zeolite crystals in the form of powders or films.^{14,15} Nevertheless, strong experimental evidence suggests the existence of a nucleation-related bottleneck in the microwave synthesis of zeolite crystals¹⁶ and films.¹⁷ In this communication, we report that highly *b*-oriented MFI films without *a*-oriented twins can be rapidly synthesized under microwave irradiation *via* positive utilization of the bottleneck effect. This is the first report showing that microwave irradiation exerts a significant influence on twin growth of zeolite films. Moreover, compared with other methods, the shortest time (~30 min) was required to obtain a compact and *b*-oriented MFI film.

A detailed procedure on preparation of MFI films is given in the ESI† (S-1). Microstructures of the prepared MFI films were studied with an X-ray rocking curve (XRC) technique to achieve a better resolution for near neighbour peaks, *e.g.* the (2 0 0) and (0 2 0) diffraction peaks, which overlap each other with commonly used X-ray diffraction (PXRD) (as shown in the insets of Fig. 1).¹⁹ For the sample subjected to direct microwave irradiation, the related 3D contour pattern showed that only the (0 2 0) diffraction peak was present (shown in Fig. 1a). However, under conventional hydrothermal growth conditions, both the (0 2 0) and (2 0 0) diffraction peaks were clearly visible (shown in Fig. 1b) and well separated from each other, implying that substantial *a*-oriented twin growth had

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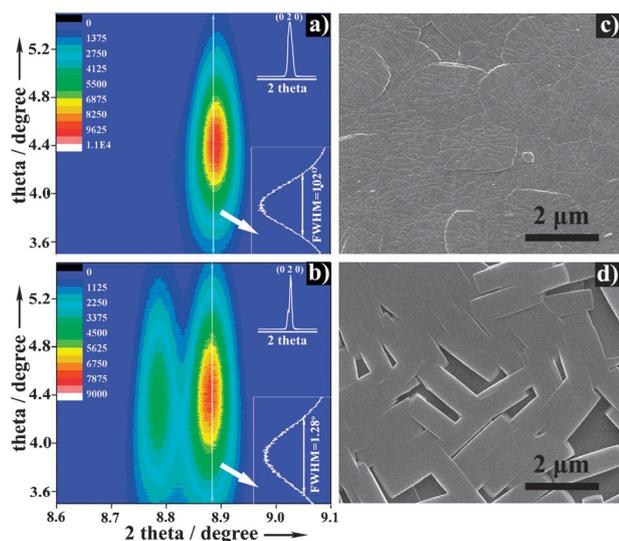


Fig. 1 The X-ray rocking curve patterns of MFI films obtained through (a) direct microwave-assisted heating at 150 °C for 30 min, and (b) conventional hydrothermal growth at 150 °C for 5 h. The 2 theta value was set between 8.6 and 9.1°. Inset (top): XRD patterns of the (0 2 0) diffraction peak obtained with the conventional XRD technique. Inset (bottom): FWHM values of MFI films obtained by fixing 2-theta angle and doing a theta scan. SEM images of MFI films (c) prepared by direct microwave-assisted synthesis at 150 °C for 30 min, and (d) under conventional hydrothermal conditions at 150 °C for 5 h.

been promoted. Meanwhile, the SEM results illustrated that after microwave-assisted secondary growth for 30 min, the MFI film had become compact, and the original *b*-oriented MFI seeds were well-merged with each other with no obvious twin crystals (Fig. 1c). In contrast, substantial *a*-oriented twin crystals had formed before the complete sealing up of the intercrystalline gaps between pre-deposited MFI seed crystals under conventional hydrothermal conditions (shown in Fig. 1d). Furthermore, XRC could be used as a gauge of the quality of crystalline film.²⁰ As shown in the insets (bottom) of Fig. 1a and b, at a fixed 2θ angle ($\sim 8.88^\circ$), the full width at half maximum (FWHM) value for the MFI film prepared by microwave heating (1.02°) was lower than the film prepared by conventional heating (1.28°), implying that the MFI grains were more regularly arranged on the substrate in the former case. Therefore microwave heating offers a special advantage for achieving highly ordered *b*-oriented MFI grains, which may be beneficial for improving the lattice matching and reducing potential inter-crystalline defects.²¹ More detailed elucidation of the XRC method can be found in ESI† (S-2).

The differential scanning calorimetry (DSC) technique provides a powerful tool to monitor the nucleation process of zeolites in bulk solution, as there exists a remarkable endothermic peak due to the release of OH^- into solution during nucleation.¹⁸ To verify the effect of bulk nucleation on twin growth, DSC curves measured under different secondary growth conditions were shown in Fig. 2. Analogous to the conventional secondary growth condition for MFI films (Fig. 2a), the nucleation took place at about 60 min, prior to the minimum time required for compact MFI film formation (at around 180 min). In the case of a pre-heated precursor solution, nucleation was still observed at around 60 min (Fig. 2b). However, intensity of the endo-peak

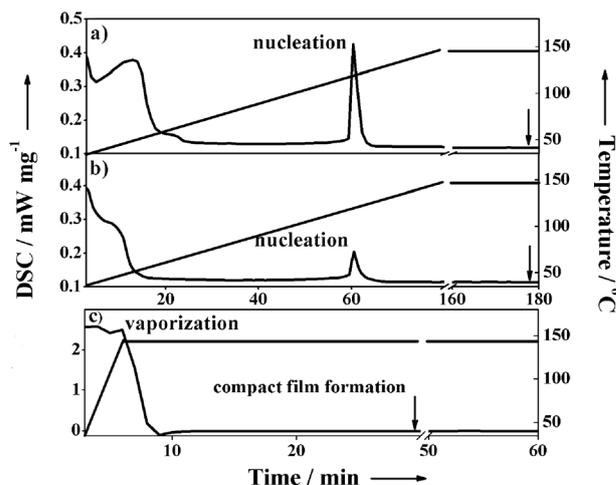


Fig. 2 DSC curves of the hydrothermal crystallization of MFI zeolites. (a) Hydrothermal synthesis, (b) hydrothermal synthesis with pre-heated (150 °C, 2 h) precursor solution, and (c) simulated microwave-assisted synthesis. Arrows denote the times when compact MFI films were formed. Temperature variation during DSC tests was analogous to real reaction conditions in the vessel (shown in S-3, ESI†).

was greatly reduced, demonstrating that MFI nucleation was effectively suppressed, probably due to over-consumption of nutrients (especially TPAOH) by pre-heating. To simulate rapid microwave heating, the DSC autoclave was heated at a heating rate of $25^\circ\text{C min}^{-1}$. As shown in Fig. 2c, no nucleation peak was observed from 0 to 60 min, even though this duration was long enough to completely seal the intercrystalline gaps between *b*-oriented MFI seeds, thanks to the accelerated growth rate under microwave irradiation. The DSC result indicated that the recognized nucleation-related bottleneck might not originate from the non-thermal microwave effect and the rapid temperature increase *via* microwave heating accounts for this. The effect of heating rate on the nucleation kinetics of MFI zeolite is unclear at present. Nevertheless, microwave dielectric heating is the most reliable and facile way to achieve volumetric and fast heat-up. More extensive discussion of the nucleation-related bottleneck effect under microwave irradiation is given in S-4 (ESI†).

Selective sensor applications have been one of the major motivations for developing zeolite thin films.² When integrated with a sensor substrate, an appropriate zeolite film can improve both the selectivity and sensitivity of the original sensor, owing to its unique molecular sieving ability. Taking zeolite-modified electrodes (ZMEs) as an example, numerous studies have showed that microstructures of the zeolite films, such as continuity, thickness, and preferential orientation of the grains, can greatly influence their electrochemical performance.²² In the current study, we fabricated *b*-oriented (by microwave-assisted growth) and *a*-twinned MFI films (by conventional hydrothermal growth) on Pt electrodes, respectively, and investigated the effect of twins on the electrochemical response of ZMEs (details shown in S-5, ESI†).

The compactness of the prepared MFI films was first verified by cyclic voltammetry² with $[\text{Fe}(\text{CN})_6]^{3-}$ as probing molecules. The results showed that no obvious intercrystalline defects existed in either MFI film (S-6, ESI†). Subsequently, the electrochemical

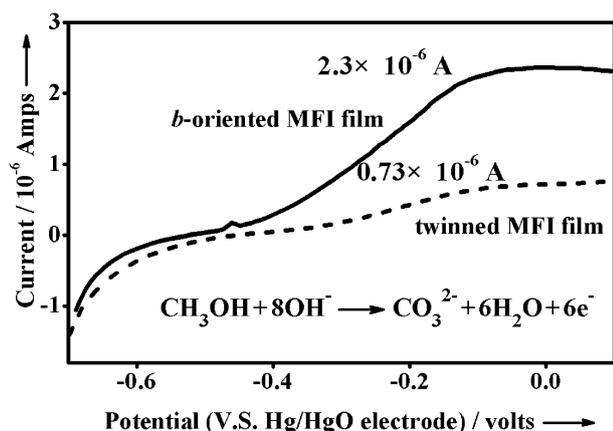


Fig. 3 Linear sweep voltammograms of MeOH oxidation on a *b*-oriented MFI film-modified Pt plate (black line) and a twinned MFI film-modified Pt plate (dotted black line).

oxidation behaviour of methanol (MeOH) molecules on bare and MFI film-modified Pt electrodes was investigated by linear sweep voltammetry (LSV). Results showed that peak currents for methanol electrochemical oxidation on *b*-oriented MFI film-modified and twinned MFI film-modified Pt electrodes were 2.3×10^{-6} A and 0.73×10^{-6} A, respectively (Fig. 3), demonstrating that methanol molecules diffuse notably faster in the *b*-oriented MFI film than in the twinned one.

The results can be rationalized by considering the microstructure discrepancy between the two films. Twin crystals may increase the film thickness; however, the extra mass transfer resistance may largely arise from the grain boundary barrier, as was confirmed by D. A. Newsome and D. S. Sholl²³ and L. Karwacki *et al.*²⁴ Therefore, effective suppression of twin growth during secondary growth paves the way for the performance optimization of MFI films.

In summary, we found that microwave irradiation can effectively suppress the undesired twin growth of an MFI seed layer, relying on the unique nucleation-related bottleneck effect. X-Ray rocking curve characterization further demonstrated that *b*-oriented MFI grains showed higher regularity in comparison with those obtained by a conventional hydrothermal method. Electrochemical oxidation of methanol on MFI film-modified Pt electrodes vividly illustrated that suppression of twin growth was very beneficial in improving the mobility of guest molecules through the nano-channels of zeolite film.

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Notes and references

- Z. P. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis and D. G. Vlachos, *Science*, 2003, **300**, 456; J. Choi, H. K. Jeong, M. A. Snyder, J. A. Stoeger, R. I. Masel and M. Tsapatsis, *Science*,

- 2009, **325**, 590; W. H. Yuan, Y. S. Lin and W. S. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 4776; M. A. Carreon, S. Li, J. L. Falconer and R. D. Noble, *J. Am. Chem. Soc.*, 2008, **130**, 5412; X. C. Xu, W. S. Yang, J. Liu and L. W. Lin, *Adv. Mater.*, 2000, **12**, 195; Y. S. Li, H. L. Chen, J. Liu and W. S. Yang, *J. Membr. Sci.*, 2006, **277**, 230.
- 2 S. Li, X. Wang, D. Beving, Z. W. Chen and Y. S. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 4122; L. Gora, J. Kuhn, T. Baimpos, V. Nikolakis, F. Kapteijn and E. M. Serwicka, *Analyst*, 2009, **134**, 2118.
- 3 S. Li, Z. J. Li and Y. S. Yan, *Adv. Mater.*, 2003, **15**, 1528; J. L. Wang, M. E. Davis and Y. S. Yan, *Adv. Funct. Mater.*, 2008, **18**, 3454.
- 4 H. S. Kim, S. M. Lee, K. Ha, C. Jung, Y. J. Lee, Y. S. Chun, D. Kim, B. K. Rhee and K. B. Yoon, *J. Am. Chem. Soc.*, 2004, **126**, 673; H. S. Kim, T. T. Pham and K. B. Yoon, *J. Am. Chem. Soc.*, 2008, **130**, 2134.
- 5 R. Cai, M. W. Sun, Z. W. Chen, R. Munoz, C. O'Neill, D. E. Beving and Y. S. Yan, *Angew. Chem., Int. Ed.*, 2008, **47**, 525; R. Cai and Y. S. Yan, *Corrosion*, 2008, **64**, 271.
- 6 M. A. Snyder and M. Tsapatsis, *Angew. Chem., Int. Ed.*, 2007, **46**, 7560; J. Caro and M. Noack, *Microporous Mesoporous Mater.*, 2008, **115**, 215; E. E. McLeary, J. C. Jansen and F. Kapteijn, *Microporous Mesoporous Mater.*, 2006, **90**, 198.
- 7 Z. B. Wang and Y. S. Yan, *Chem. Mater.*, 2001, **13**, 1101; Z. B. Wang and Y. S. Yan, *Microporous Mesoporous Mater.*, 2001, **48**, 229.
- 8 D. G. Hay, H. Haeger and K. G. Wilshier, *Zeolites*, 1990, **10**, 571; A. Iwasaki, M. Hirata and I. Kudo, *Zeolites*, 1996, **16**, 35.
- 9 I. Lee, J. L. Buday and H. K. Jeong, *Microporous Mesoporous Mater.*, 2009, **122**, 288.
- 10 G. Bonilla, I. Diaz, M. Tsapatsis, H. K. Jeong, Y. Lee and D. G. Vlachos, *Chem. Mater.*, 2004, **16**, 5697.
- 11 X. M. Li, Y. Peng, Z. B. Wang and Y. S. Yan, *CrystEngComm*, 2011, **13**, 3657.
- 12 T. C. T. Pham, H. S. Kim and K. B. Yoon, *Science*, 2011, **334**, 1533.
- 13 Y. Liu, Y. S. Li and W. S. Yang, *Chem. Commun.*, 2009, 1520; Y. Liu, Y. S. Li and W. S. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 1768; Y. Liu, Y. S. Li and W. S. Yang, *J. Mater. Sci.*, 2011, **46**, 3942.
- 14 J. Motuzas, A. Julbe, R. D. Noble, A. van der Lee and Z. J. Beresnevicius, *Microporous Mesoporous Mater.*, 2006, **92**, 259.
- 15 Y. S. Li and W. S. Yang, *J. Membr. Sci.*, 2008, **316**, 3.
- 16 P. M. Slangen, J. C. Jansen and H. van Bekkum, *Microporous Mater.*, 1997, **9**, 259; L. Bonaccorsi and E. Proverbio, *Microporous Mesoporous Mater.*, 2008, **112**, 481; C. S. Cundy, R. J. Plasted and J. P. Zhao, *Chem. Commun.*, 1998, 1465.
- 17 X. M. Li, Y. S. Yan and Z. B. Wang, *Ind. Eng. Chem. Res.*, 2010, **49**, 5933.
- 18 L. Lang, X. F. Liu, H. Y. Jiang, J. Y. S. Lin and B. Q. Zhang, *Langmuir*, 2010, **26**, 5895.
- 19 I. Lee and H. K. Jeong, *Microporous Mesoporous Mater.*, 2010, **141**, 175.
- 20 T. N. Blanton, M. Lelental and C. L. Barnes, *Phys. C Supercond.*, 1991, **184**, 119; S. Zhu, C.-H. Su, S. L. Lehoczy, M. A. George and D. H. Lowndes, *J. Mater. Res.*, 2000, **15**, 1125.
- 21 Y. Yoo, Z. P. Lai and H. K. Jeong, *Microporous Mesoporous Mater.*, 2009, **123**, 100.
- 22 S. Senthilkumar, A. Adisa, R. Saraswathi and R. A. W. Dryfe, *Electrochem. Commun.*, 2008, **10**, 141; Y. H. Zhang, F. Chen, W. Shan, J. H. Zhuang, A. G. Dong, W. B. Cai and Y. Tang, *Microporous Mesoporous Mater.*, 2003, **65**, 277; S. Kornic and M. Baker, *Chem. Commun.*, 2002, 1700.
- 23 D. A. Newsome and D. S. Sholl, *J. Phys. Chem. B*, 2006, **110**, 22681.
- 24 L. Karwacki, M. H. F. Kox, D. A. Matthijs de Winter, M. R. Drury, J. D. Meeldijk, E. Stavitski, W. Schmidt, M. Mertens, P. Cubillas, N. John, A. Chan, N. Kahn, S. R. Bare, M. Anderson, J. Kornatowski and B. M. Weckhuysen, *Nat. Mater.*, 2009, **8**, 959.