*Electronic Supplementary Information*

# Twin suppression effect of dihydroxy-benzene isomers during the secondary growth of two-dimensional *b*-oriented zeolite MFI nanosheet films

Ruilan Xu[a], Yong Peng[a,b,*] , Peng Lu[b], Yurun Miao[b], Xuekui Duan[c], Dennis T. Lee[b], Rui Wang[a], Zhengbao Wang[d,*], Michael Tsapatsis[b,e,*]

[a] *Nanchang Key Laboratory of Photoelectric Conversion and Energy Storage Materials, College of Science, Nanchang Institute of Technology, Nanchang 330099, PR China.*
[b] *Department of Chemical and Biomolecular Engineering and Institute for NanoBio Technology, Johns Hopkins University, Baltimore, MD 21218, USA.*
[c] *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA.*
[d] *College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China.*
[e] *Applied Physics Laboratory, Johns Hopkins University, Laurel, MD 20723, USA.*

**Corresponding author:** pengyong@nit.edu.cn (Y. Peng), zbwang@zju.edu.cn (Z.B. Wang), tsapatsis@jhu.edu (M. Tsapatsis)

**Materials**: Stainless steel plates (2 cm × 2 cm) and silicon wafers (2 cm × 2 cm) were rinsed with deionized water, and dried at 60 °C before the synthesis of zeolite films. For the secondary growth of bulky coffin-shape MFI seed monolayer, Tetraethyl orthosilicate (TEOS, 98%), 1,2-dihydroxybenzene (1,2-$C_6H_6O_2$, 99%), 1,3-$C_6H_6O_2$ (99%) and 1,4-$C_6H_6O_2$ (99%) were purchased from J&K Scientific Ltd.; Tetrapropylammonium hydroxide (TPAOH, 25%) was supplied by Sachem Wuxi. For the secondary growth of MFI nanosheet monolayer, TPAOH (20%), TEOS (98%), 1,2-$C_6H_6O_2$ (99%), 1,3-$C_6H_6O_2$ (99%) and 1,4-$C_6H_6O_2$ (99%) were purchased from Sigma-Aldrich.

**Preparation of bulky coffin-shaped MFI zeolite seeds**: The synthesis mixture of molar composition 0.17 TPAOH:1 TEOS:165 $H_2O$ was prepared by slowly adding TEOS to a solution of TPAOH and water under stirring. A clear synthesis mixture was obtained after stirring at room temperature for 4 h. Then the synthesis mixture was directly loaded into a Teflon-lined stainless steel autoclave. The autoclave was sealed and fixed in the rotation shaft of a convection oven. It rotated at 20 rpm in the oven at 175 °C for 130 min. 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 film supports by rubbing MFI zeolite crystals with a finger in latex glove and then heat treated at 165 °C for 4 h. The seeded support was vertically placed in a Teflon-lined stainless

steel autoclave for secondary growth. The synthesis mixture was prepared by slowly adding TEOS to a solution of TPAOH and water under stirring. After the mixture was clear, 1,3-dihydroxybenzene was added to it. The molar composition of the resulting mixture was 0.2TPAOH : 1TEOS : 200$H_2O$ : (0.1~1.0)1,3-$C_6H_6O_2$. The same procedure were used to prepare synthesis mixture with composition: 0.2TPAOH : 1TEOS : 200$H_2O$ : (0.1~0.5)1,2-$C_6H_6O_2$ and 0.2TPAOH : 1TEOS : 200$H_2O$ : (0.1~1.5)1,4-$C_6H_6O_2$. The seeded growth was carried out at 165 $^oC$ for 4 h. After synthesis, the film was rinsed with deionized water and dried at 60 $^oC$. The calcination of the film was carried out at 450$^oC$ with a ramp rate of 1$^oC$/min.

**Preparation of MFI nanosheet seeds**: The MFI nanosheet seeds were synthesized following the reported procedure [1]. Briefly, the nanoseeds were firstly prepared from a clear sol with the molar composition of 10$SiO_2$ : 2.4TPAOH : 0.87NaOH : 114$H_2O$, which was then heated at 50 $^oC$ for 6 days and then at 100 $^oC$ for 3 days under static condition in oil bath. The nanoseeds were washed thrice with DI water and re-dispersed in DI water to obtain nanoseeds suspension, and the content was determined by drying a small portion of the suspension. Then the MFI nanosheets were synthesized using a molar composition of 80TEOS : 3.75dC5 : 20KOH : 9500$H_2O$ with the addition of nanoseeds suspension, where the nanoseeds to precursor ratio is 1:1000 (based on silica). The clear sol was heated at 140 $^oC$ for 7 days to obtain a white gel containing MFI nanosheets, which were then purified using centrifugation followed the reported procedure [1], to obtain MFI nanosheets water suspension to be used for the preparation of MFI films.

**Preparation of *b*-oriented MFI nanosheet films**: *b*-oriented MFI seed monolayers were prepared on silicon wafer supports by a floating-particle coating method [2] and then heat treated at 165 $^oC$ for 4 h. The seeded hydrothermal growth of the nanosheet film is the same as that of the regular film described in **Preparation of *b*-oriented MFI zeolite films**. The pH values of the synthesis mixtures (0.2TPAOH : 1TEOS : 200$H_2O$, 0.2TPAOH : 1TEOS : 200$H_2O$ : 0.3 1,2-$C_6H_6O_2$, 0.2TPAOH : 1TEOS : 200$H_2O$ : 0.6 1,3-$C_6H_6O_2$, 0.2TPAOH : 1TEOS : 200$H_2O$ : 1.0 1,4-$C_6H_6O_2$) were tested before hydrothermal growth.

**Characterization**: The top and cross-sectional images of the zeolite films were obtained with scanning electron microscope JSM-6701F (JEOL), Helios G4 (Thermo-Fisher), Sigma 300 (ZEISS) and TM3030 (Hitachi). X-ray diffraction (XRD) patterns were collected on Bruker D8 Advance diffractometer and PANalytical X'pert X-ray diffractometer with Cu *K*α radiation. Liquid-state $^{29}$Si-NMR spectra of the mother solutions for MFI film synthesis were recorded on a Bruker Avance III HD 500 spectrometer. Solid-state $^{29}$Si-NMR spectra of the precipitations were recorded on a Bruker 400 MHz spectrometer. AFM images were collected on a Bruker Multimode 8 under tapping mode.

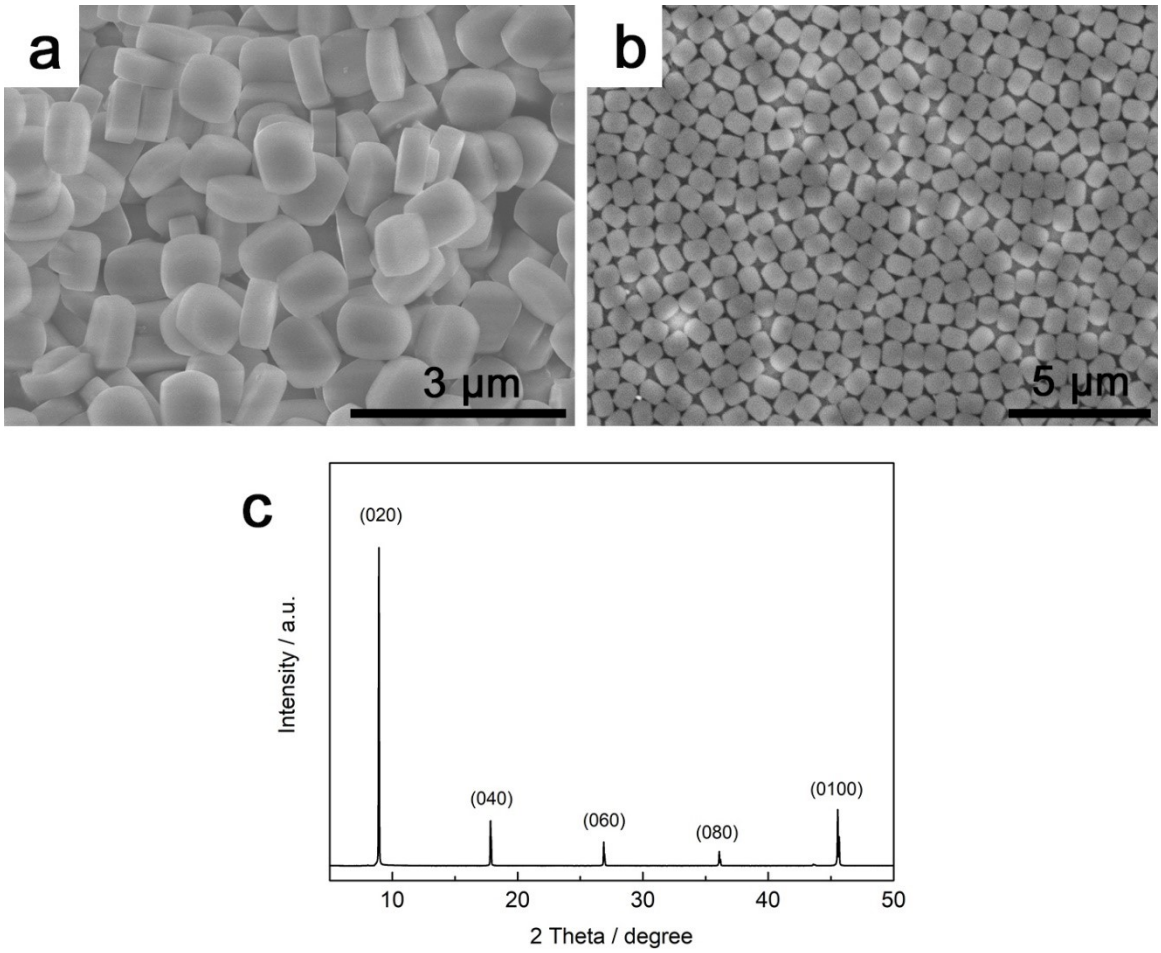


Figure S1 SEM image of (a) zeolite MFI seeds and (b) their monolayer on stainless steel support. (c) XRD pattern of the MFI seed monolayer. Results are cited from Ref [3].

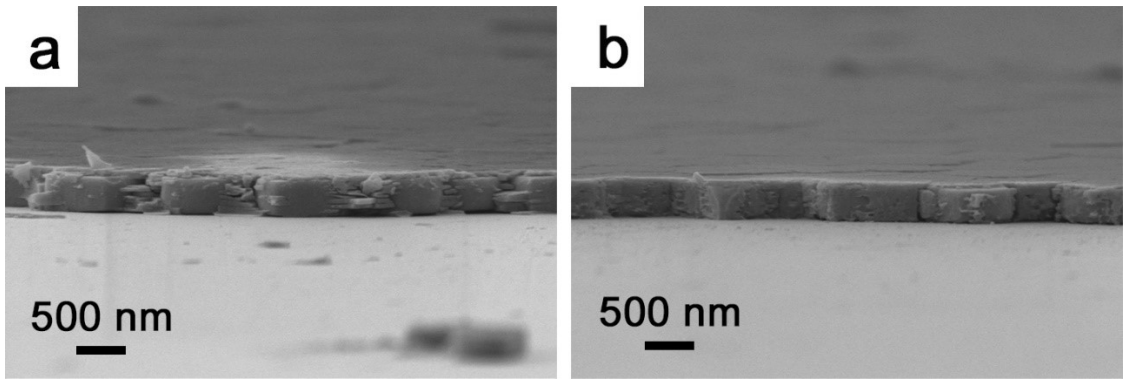


Figure S2 Cross-sectional SEM images of MFI zeolite films synthesized in mixtures with composition: (a) 0.2TPAOH : 1TEOS : 200$H_2O$ : 0.6-(1,3-)$C_6H_6O_2$ and (b) 0.2TPAOH : 1TEOS : 200$H_2O$ : 1.0-(1,4-)$C_6H_6O_2$.

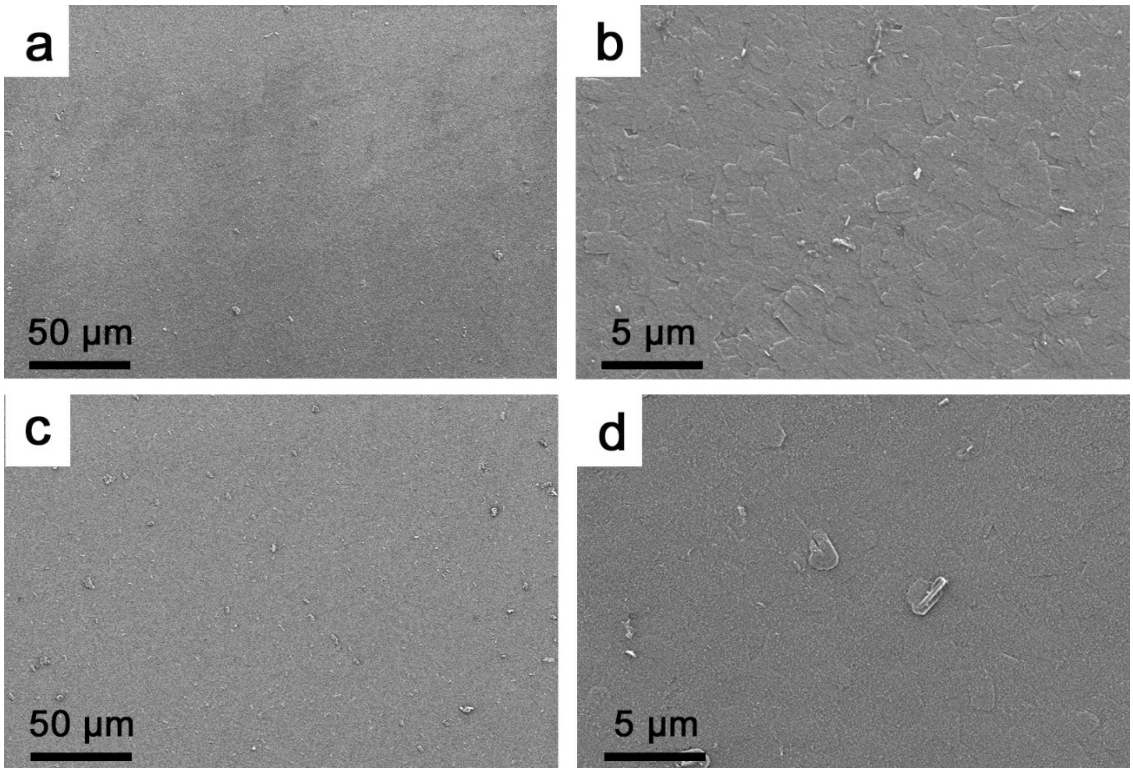

Figure S3 SEM images of calcined films in Fig. 1c (a, b) and 1g (c, d).

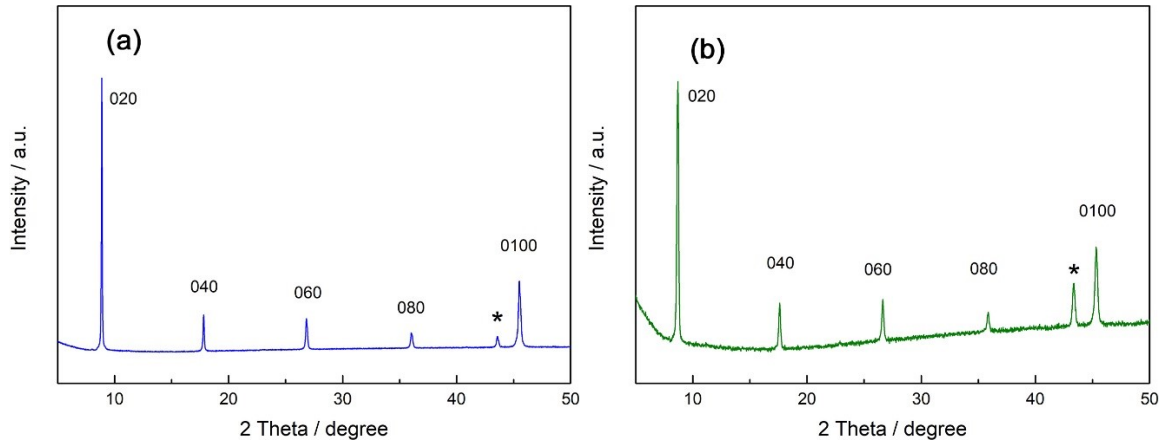

Figure S4 XRD patterns of calcined films in Fig. 1c (a) and 1g (b). (*) Peaks from the SS plate.

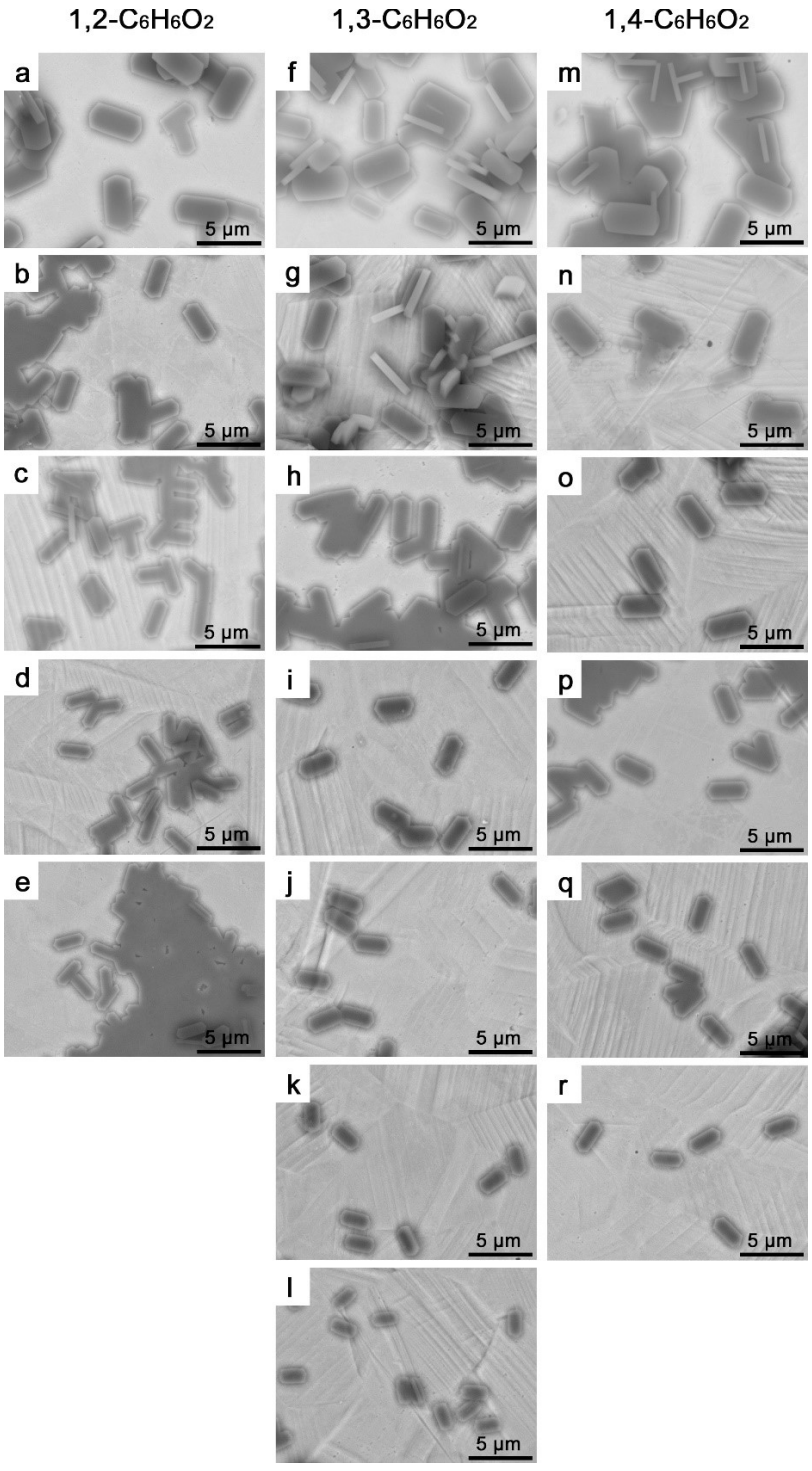


Figure S5 MFI zeolite crystals at the edge of the films synthesized with different molar amounts of dihydroxy-benzene isomers, left column: 1,2-$C_6H_6O_2$ (a-0.1, b-0.2, c-0.3, d-0.4, e-0.5), middle column: 1,3-$C_6H_6O_2$ (f-0.1, g-0.3, h-0.4, i-0.5, j-0.6, k-0.8, l-1.0), right column: 1,4-$C_6H_6O_2$ (m-0.1, n-0.3, o-0.5, p-1.0, q-1.2, r-1.5).

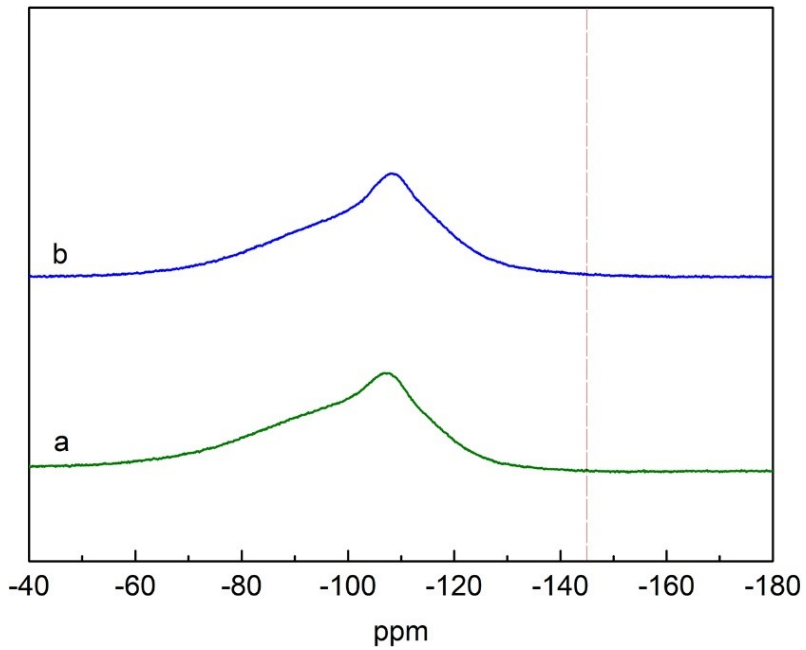


Figure S6 Liquid-state $^{29}$Si-NMR for the mother solution synthesized at 165°C for 2 h, (a) 0.2TPAOH: 1TEOS : 200$H_2O$: 0.6(1,3-)$C_6H_6O_2$ and (b) 0.2TPAOH: 1TEOS : 200$H_2O$: 1.0(1,4-)$C_6H_6O_2$. The vertical line indicates the chemical shift of -144.1 ppm.

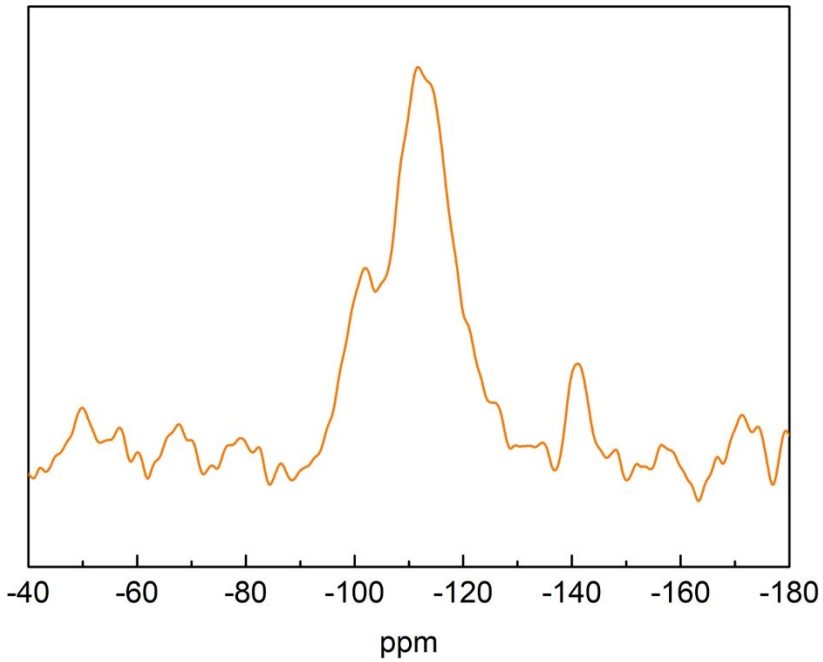


Figure S7 Solid-state $^{29}$Si-NMR of the precipitate synthesized at 165°C for 2 h. Synthesis mixture composition: 0.2TPAOH: 1TEOS : 200$H_2O$: 0.3(1,2-)$C_6H_6O_2$. Scanning time: 2 hours.

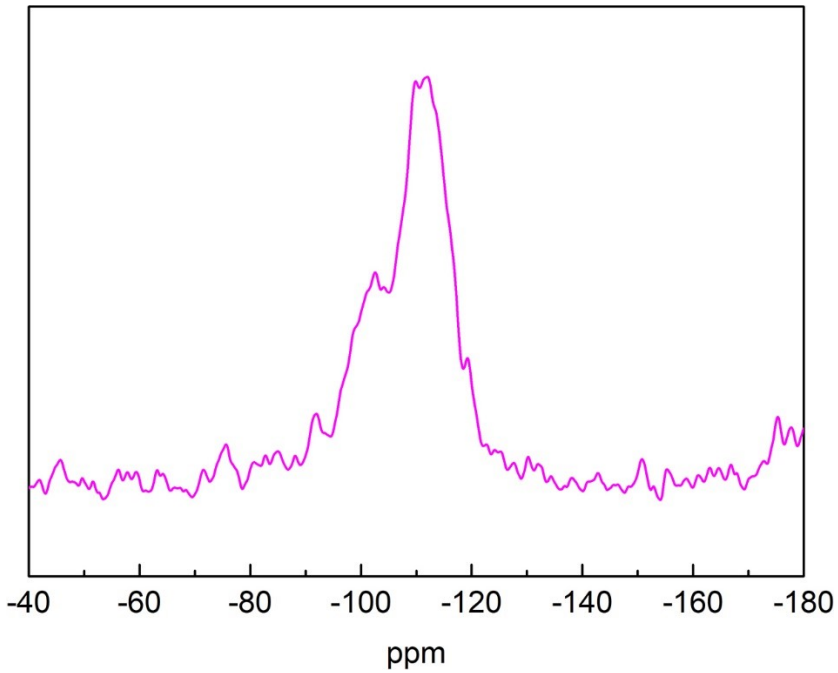


Figure S8 Solid-state $^{29}$Si-NMR of the precipitate synthesized at 165°C for 2 h. Synthesis mixture composition: 0.2TPAOH: 1TEOS : 200$H_2O$: 0.6(1,3-)$C_6H_6O_2$. Scanning time: 10.5 hours.

Reference

[1] M. Y. Jeon, D. Kim, P. Kumar, et al., Nature 543 (2017) 690-694.

[2] D. Kim, M.Y. Jeon, B.L. Stottrup, M. Tsapatsis, Angew. Chem. Int. Ed. 57 (2018) 480-485.

[3] R.L. Xu, Y. Peng, Ceram. Int. 44 (2018) 22352-22356.