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Electronic Supplementary Information for

Manipulation of Amorphous Precursors to Enhance Zeolite Nucleation

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Supporting Tables

Table S1. Elemental composition of alkali-treated fumed silica (FS-a).

Composition[a]	Amount (wt%)[b]
SiO_2	86
Na	4
Br	10

a Obtained after soaking as received fumed silica in 2M NaBr solution for one week at room temperature;
b. Composition obtained by energy dispersive x-ray spectroscopy.

Supporting Figures

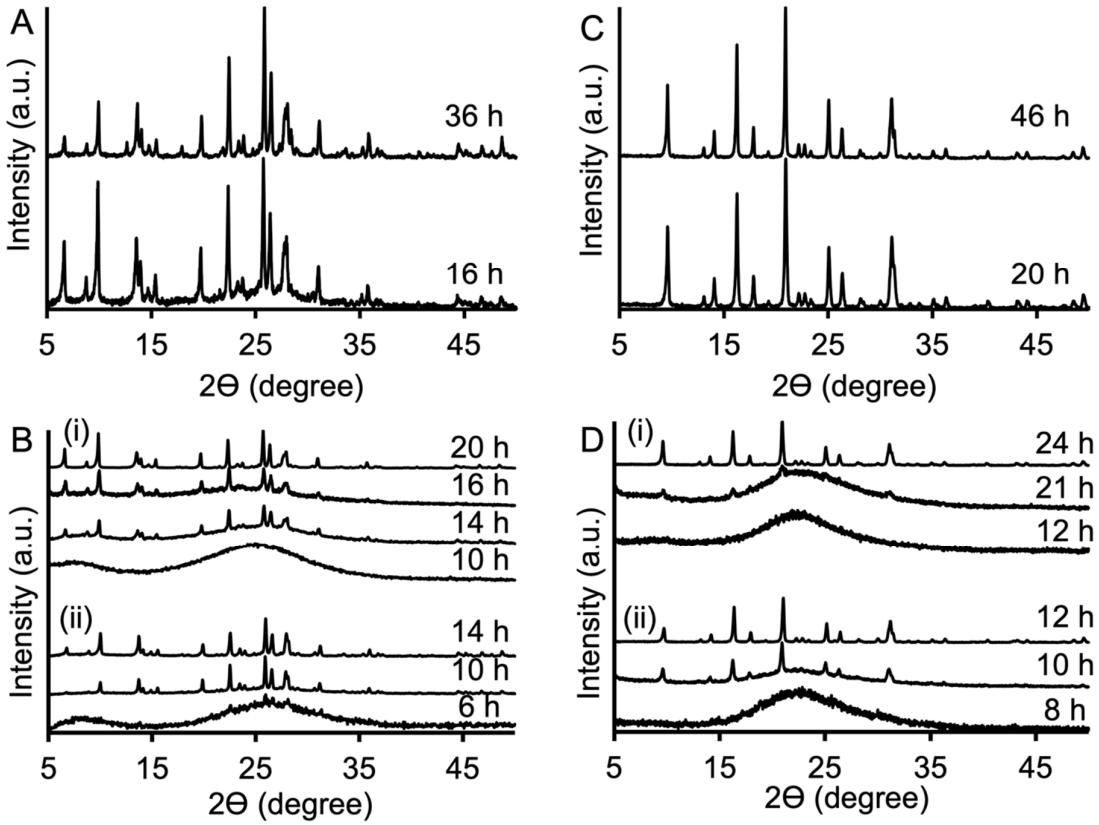

Fig. S1. Powder XRD patterns of solids extracted from (A, B) mordenite (MOR) and (C, D) SSZ-13 (CHA) synthesis prepared with (A, C) as received fumed silica (FS) and (B, D) colloidal silica (CS) at various times of hydrothermal treatment (labelled). (A and C) Syntheses were carried out with the addition of NaBr (equivalent to quantity in modified fumed silica, FS-a). (B and D) For studies with CS as the silicon source, syntheses were carried out without (i) and with (ii) the addition of NaBr. Hydrothermal synthesis was performed at 165 °C for mordenite and 180 °C for SSZ-13.

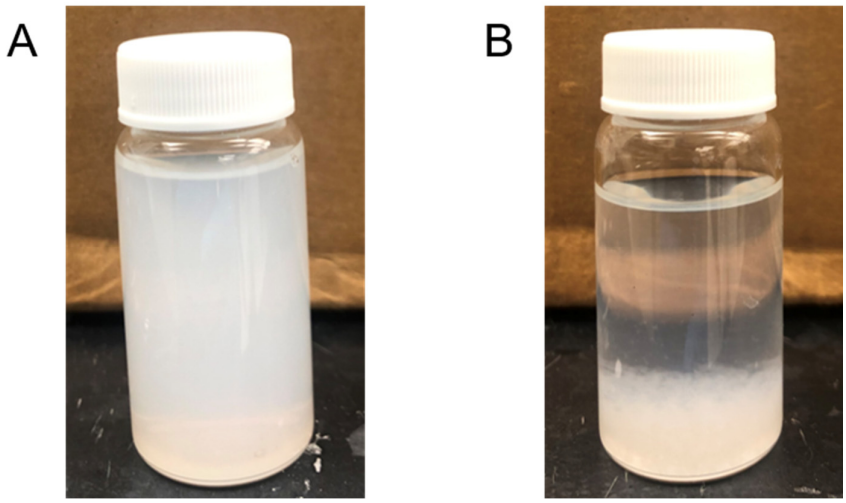

Fig. S2. The solutions used for DLS measurements with molar composition 1 SiO_2: 1 NaOH: 350 H_2O after 4 h of hydrothermal treatment at 180 ºC. (A) Solution made from as received fumed silica (FS) showing no phase separation or precipitation. (B) Solution obtained from alkali-infused fumed silica (FS-a) showing the precipitation of amorphous silica precursors. Prior to DLS analysis, all turbid solutions were filtered using a membrane (1 mm pore diameter) to prepare clear solutions.

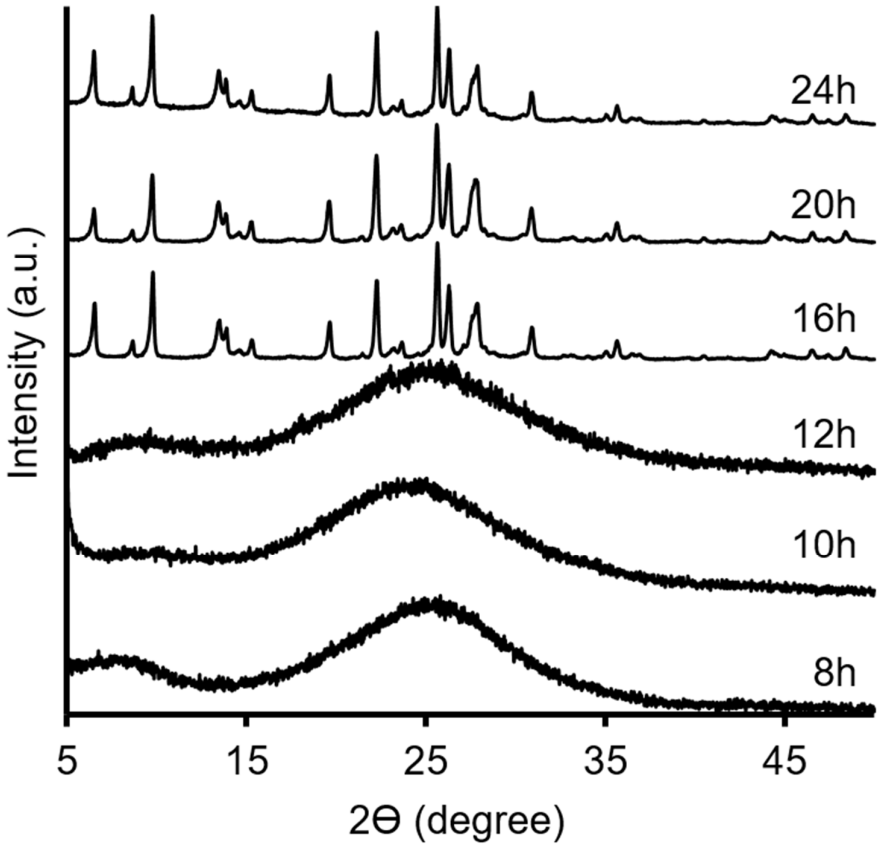

Fig. S3. Time-elapsed powder XRD patterns of solids extracted from a mordenite (MOR) synthesis prepared with water-treated fumed silica (FS-w) at various times of hydrothermal treatment (8, 10, 12, 16, 20, and 24 h) at 165 °C.

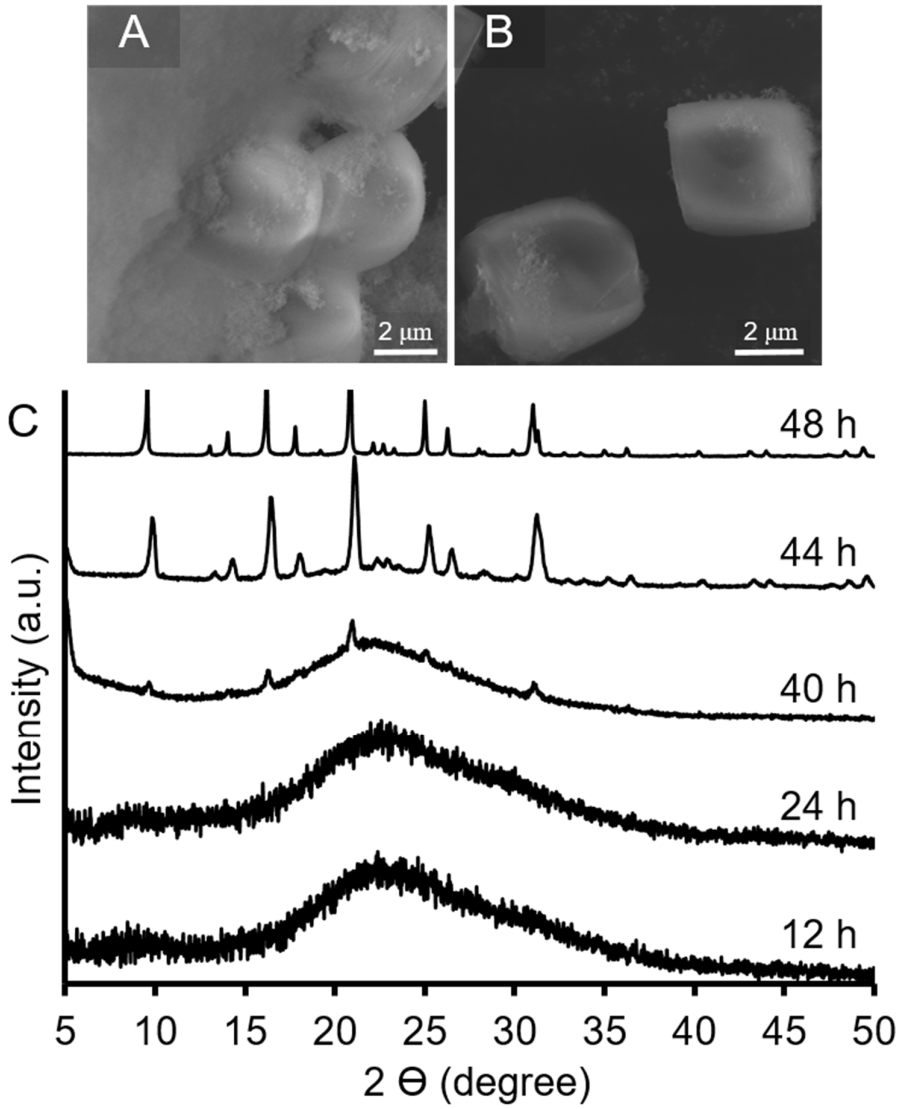

Fig. S4. Analysis of a SSZ-13 (CHA) synthesis using FS-w as the silicon source. (A and B) Scanning electron micrographs of (A) amorphous precursors and (B) fully crystalline product. (C) Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (12, 24, 40, 44, and 48 h) at 180 °C.

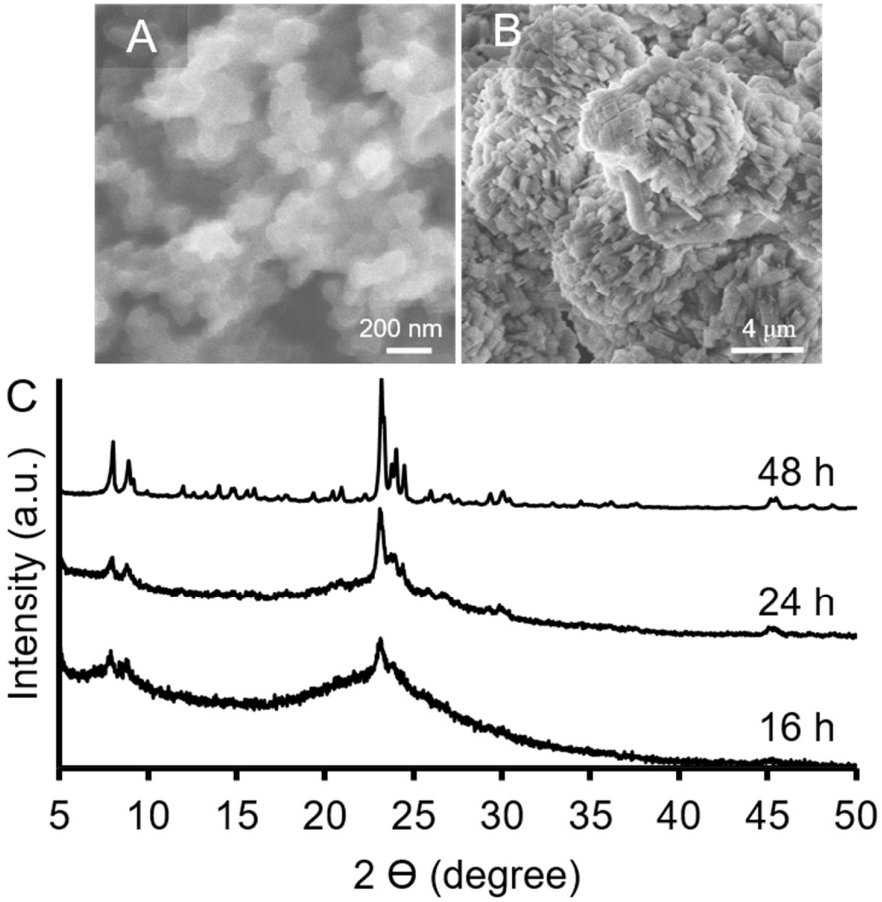

Fig. S5. Analysis of a ZSM-5 (MFI) synthesis using FS-w as the silicon source. (A and B) Scanning electron micrographs of (A) amorphous precursors and (B) fully crystalline product. (C) Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (16, 24, and 48 h) at 170 °C.

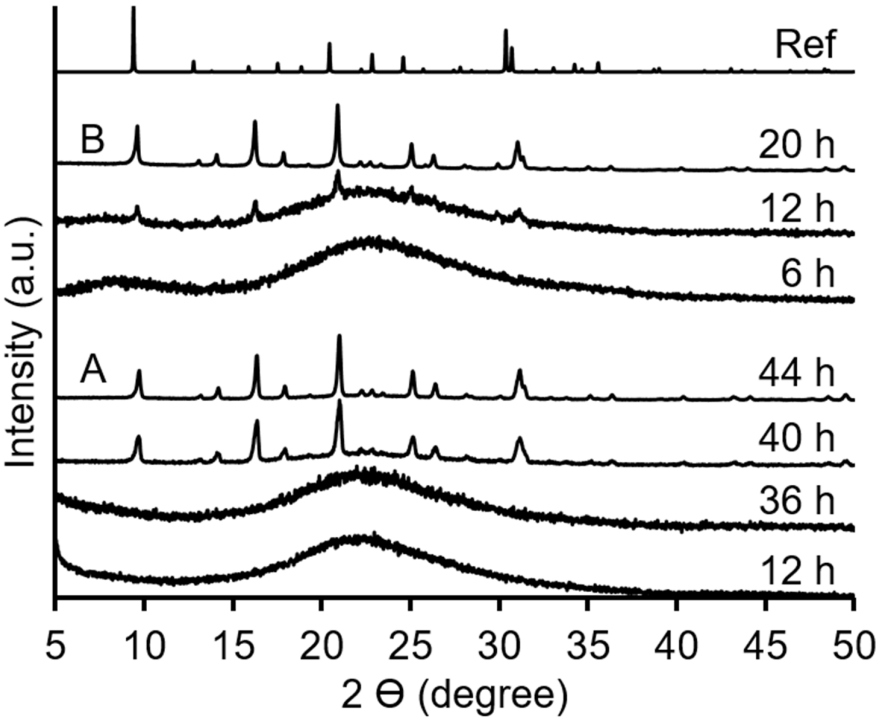

Fig. S6. Time-elapsed powder XRD patterns of solids extracted from a SSZ-13 (CHA) synthesis prepared using (A) as received fumed silica (FS) and (B) alkali-treated fumed silica (FS-a) at various hydrothermal treatment times (labeled) at 180 °C. Reference XRD pattern for SSZ-13 is shown at the top.[1]

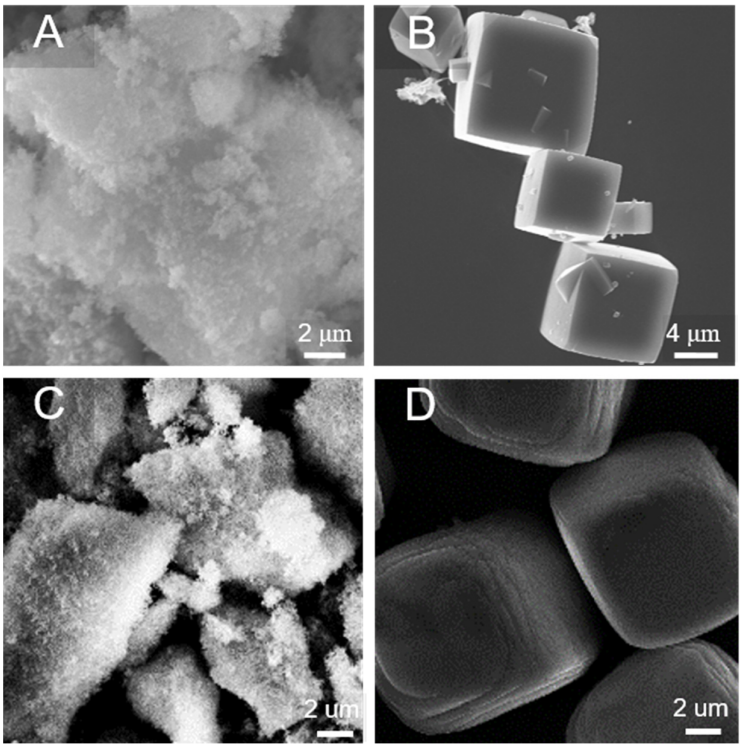

Fig. S7. Scanning electron micrographs of solids extracted from a SSZ-13 (CHA) synthesis prepared with (A,B) FS and (C,D) FS-a as the silicon sources. Images show solids prior to nucleation (A, C) and once fully crystalline (B, D). Growth mixtures were heated at 180 °C and solids were removed at the following times: (A) 12 h, (B) 44 h, (C) 6 h, and (D) 20 h.

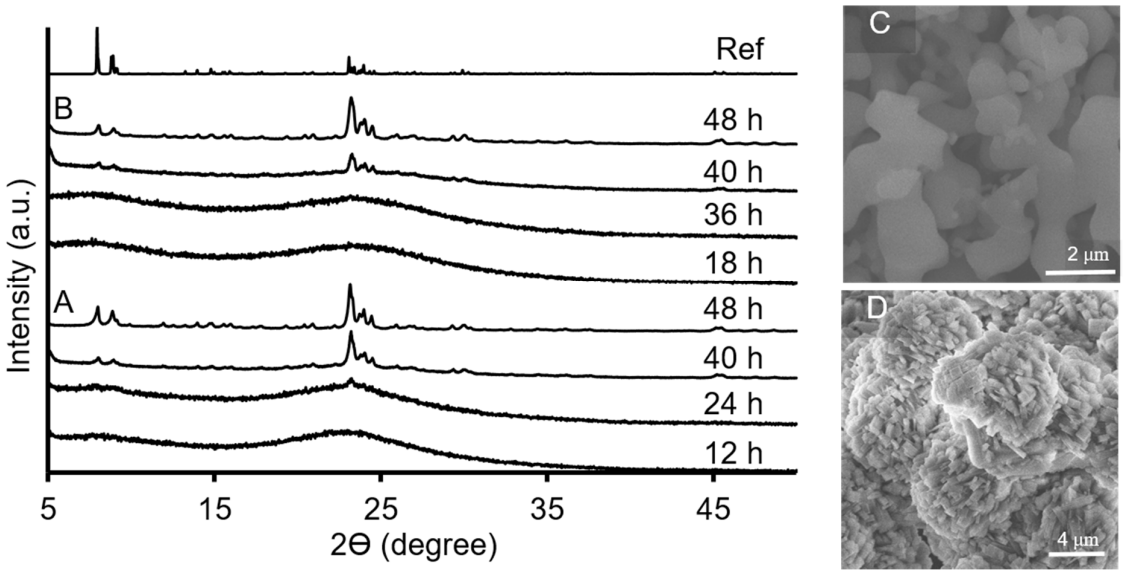

Fig. S8. Time-elapsed powder XRD patterns of solids extracted from a ZSM-5 (MFI) synthesis prepared using (A) as received fumed silica (FS) and (B) alkali-treated fumed silica (FS-a) at various hydrothermal treatment times (labeled) at 170 °C. Reference XRD pattern for MFI (Ref) is shown at the top.[1] (C and D) Scanning electron micrographs of (C) amorphous precursors and (D) fully crystalline product for ZSM-5 synthesized using FS-a.

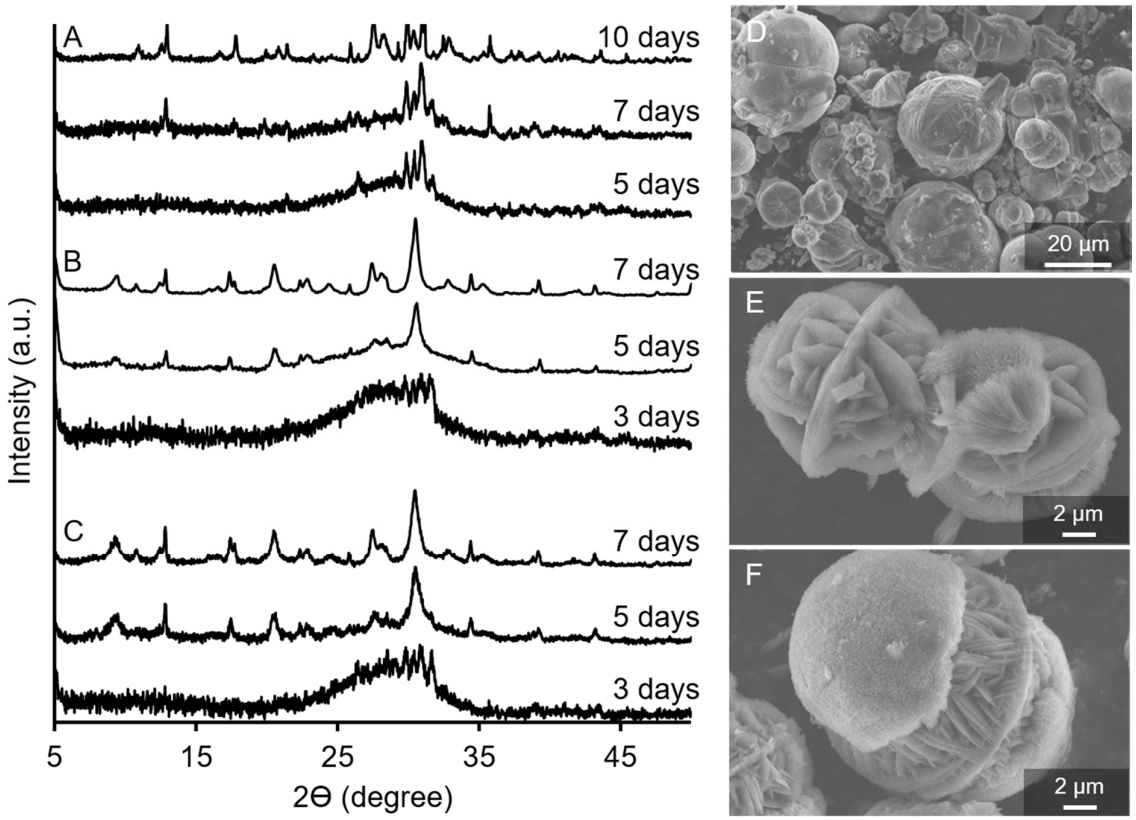

Fig. S9. (A-C) Time-elapsed powder XRD patterns of solids extracted from a K-SSZ-13 (CHA) synthesis prepared using (A) as received fumed silica (FS), (B) alkali-treated fumed silica using KBr (FS-a) and (C) fumed silica (FS) with the addition of KBr (equivalent to quantity in modified fumed silica, FS-a) at various hydrothermal treatment times (labeled) at 100 °C. (D-F) Scanning electron micrographs of fully crystalline materials synthesized using fumed silica (D), alkali-treated fumed silica (E) and fumed silica with addition of KBr (F).

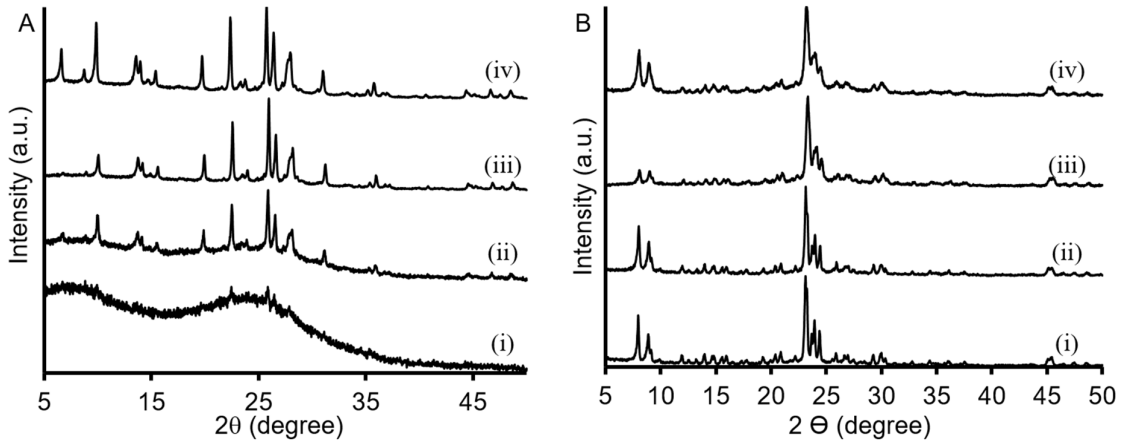

Fig. S10. Powder XRD patterns of solids extracted from (A) mordenite and (B) ZSM-5 (MFI) synthesis prepared using fumed silica (FS) with PDDA/SiO_2 molar ratios of (i) 2.4×10^{-5}, (ii) 1.8×10^{-5}, (iii) 1.2×10^{-5}, and (iv) 6.0×10^{-6}. Hydrothermal synthesis was done for 24 h at 165 °C for mordenite and for 20 h at 180 °C for ZSM-5. The optimum PDDA/SiO_2 ratios resulting in the fastest zeolite crystallization time are 6.0×10^{-6} and 2.4×10^{-5} for mordenite and ZSM-5 (based on diffraction peaks intensity) synthesis, respectively.

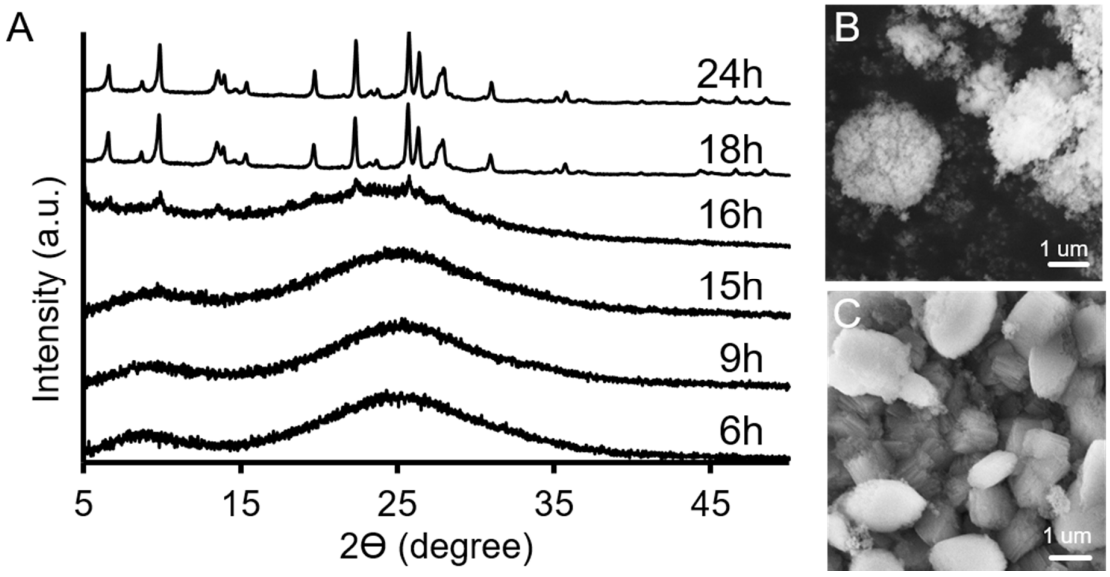

Fig. S11. (A) Time-elapsed powder XRD patterns of solids extracted from a mordenite (MOR) synthesis prepared using FS as the silicon source and PDDA with PDDA/SiO_2 molar ratio of 6.0×10^{-6} at various times of hydrothermal treatment (6, 9, 15, 18, and 24 h) at 165 °C. (B and C) Scanning electron micrographs of solids extracted after (B) 6 h and (C) 18 h of hydrothermal treatment.

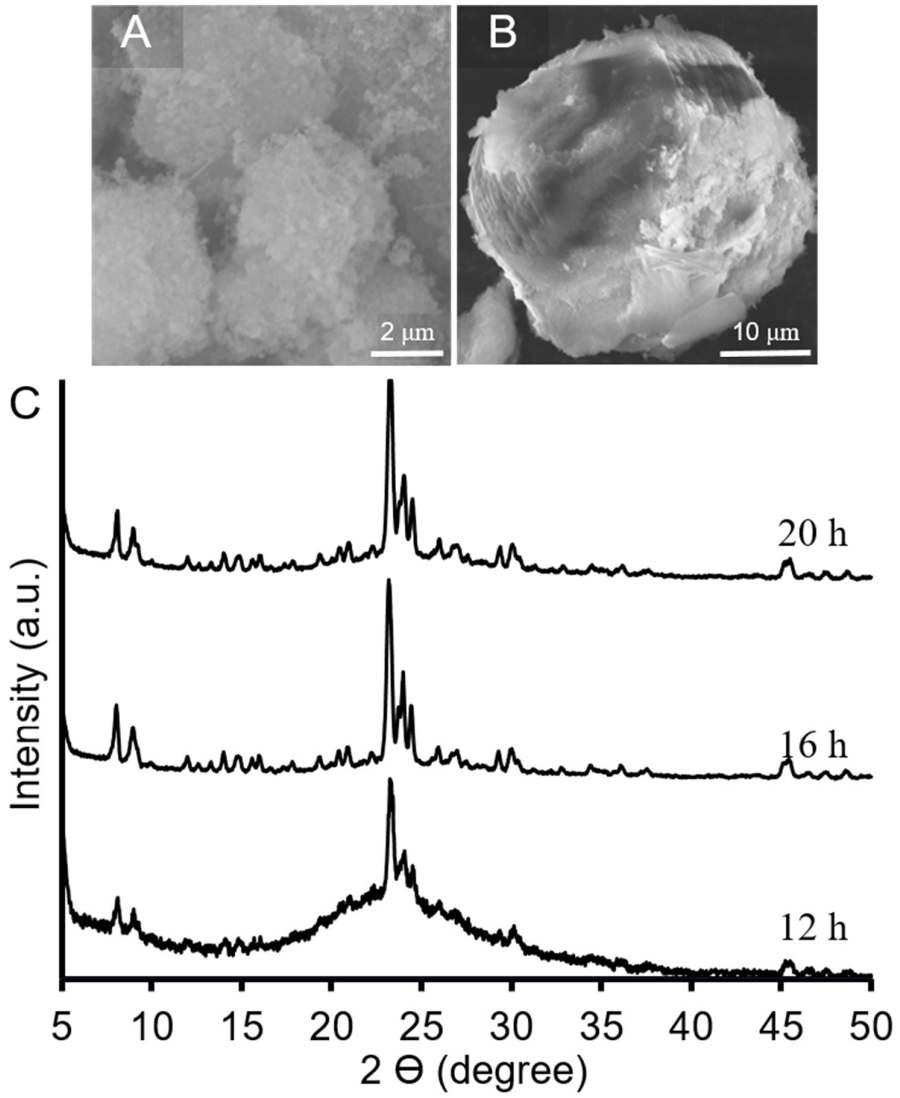

Fig. S12. Analysis of a ZSM-5 (MFI) synthesis using FS as the silicon source and PDDA with PDDA/SiO_2 molar ratios of 2.4×10^{-5}. (A and B) Scanning electron micrographs of (A) amorphous precursors and (B) fully crystalline product. (C) Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (12, 16, and 20 h) at 170 °C.

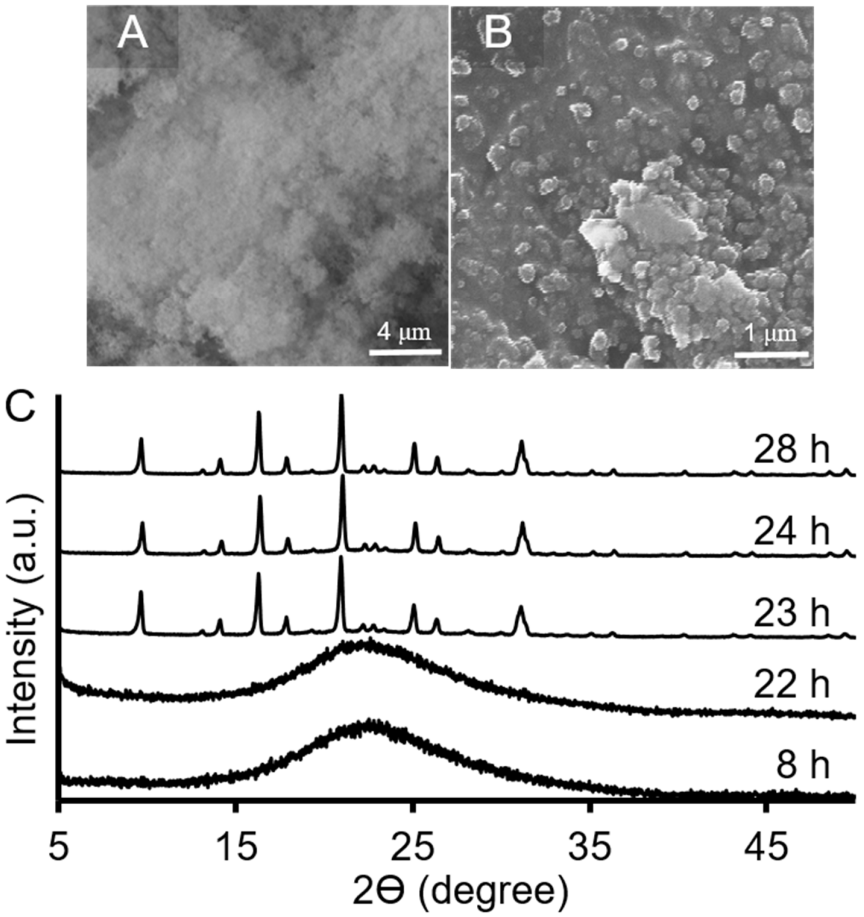

Fig. S13. Analysis of a SSZ-13 (CHA) synthesis using FS as the silicon source and PDDA with PDDA/SiO_2 molar ratios of 1.2×10^{-5}. (A and B) Scanning electron micrographs of (A) amorphous precursors and (B) fully crystalline product. (C) Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (8, 22, 24, and 28 h) at 180 °C.

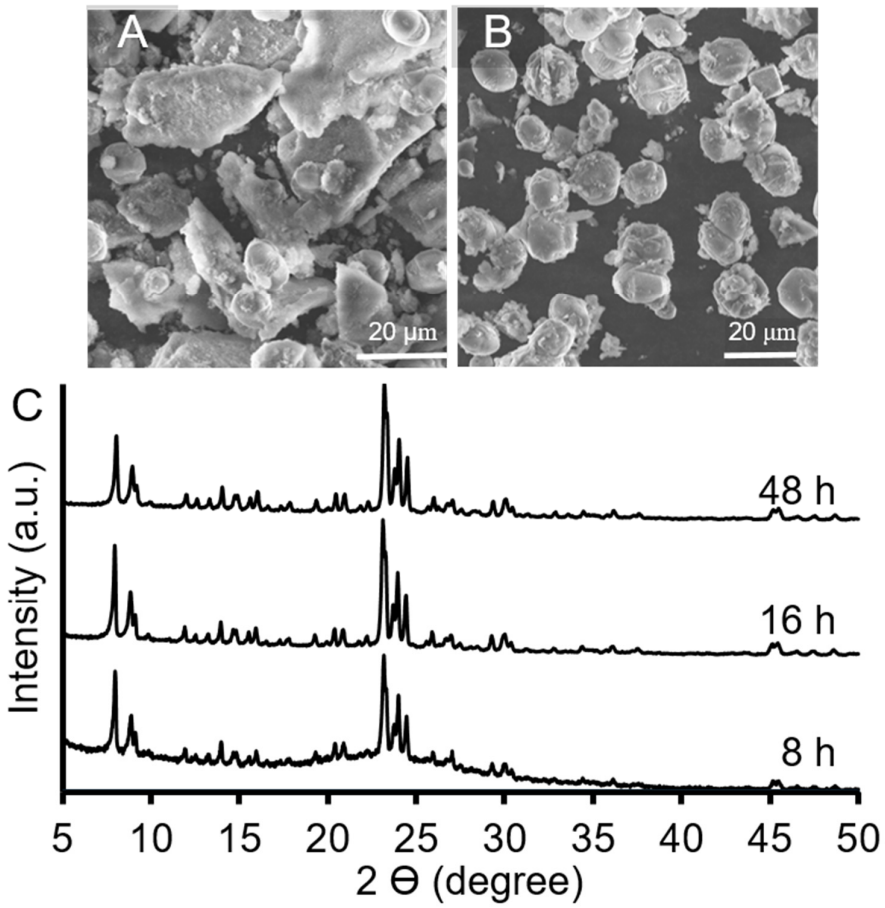

Fig. S14. Analysis of a ZSM-5 (MFI) synthesis using FS-a as the silicon source and PDDA with PDDA/SiO_2 molar ratios of 2.4×10^{-5}. (A and B) Scanning electron micrographs of (A) amorphous precursors and (B) fully crystalline product. (C) Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (8, 16, and 48 h) at 170 °C.

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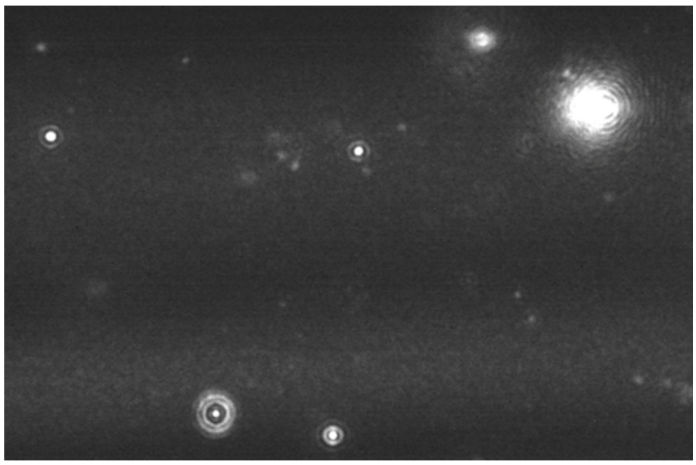

Fig. S15. OIM studies in clear solutions prepared from soluble silica source (sodium silicate) at a molar composition of 1 Na_2SiO_3: 1760 H_2O: 0.1 TPAOH with 0.05 wt% PDDA after 30 min.

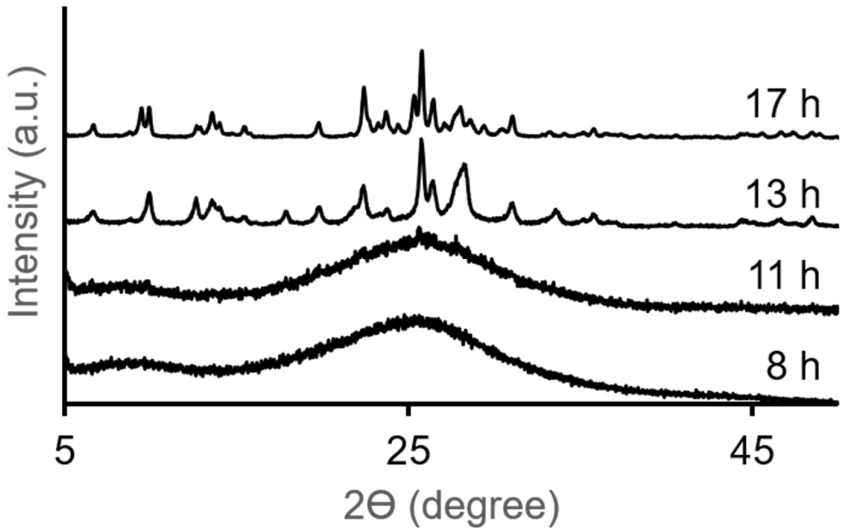

Fig. S16. Analysis of a mordenite (MOR) synthesis using FS-a as the silicon source and PDDA with PDDA/SiO_2 molar ratios of 6.0×10^{-6}. Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (8, 11, 13, and 17 h) at 165 °C.

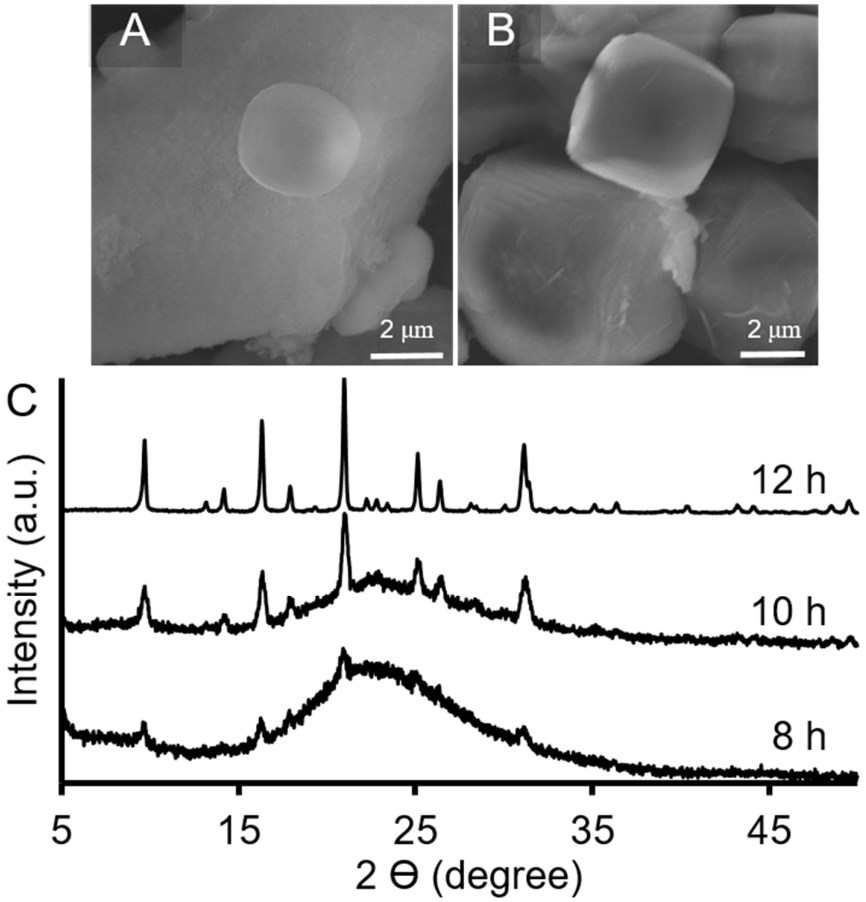

Fig. S17. Analysis of a SSZ-13 (CHA) synthesis using FS-a as the silicon source and PDDA with PDDA/SiO_2 molar ratios of 1.2×10^{-5}. (A and B) Scanning electron micrographs of (A) amorphous precursors and (B) fully crystalline product. (C) Time-elapsed powder XRD patterns of solids extracted from Patterns are shown for samples extracted at various times of hydrothermal treatment (8, 10, and 12 h) at 180 °C.

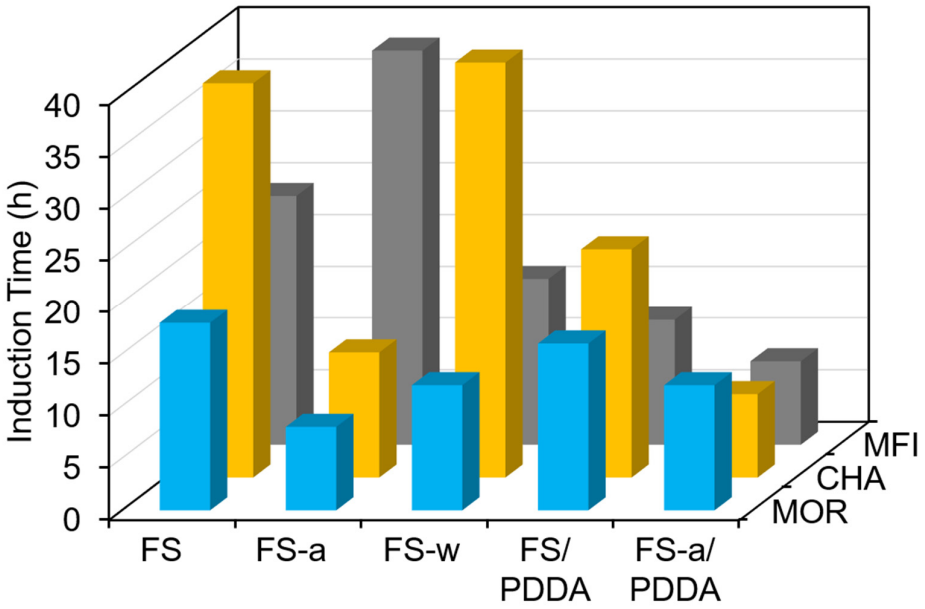

Fig. S18. Three dimensional plot of zeolite induction times for all three structures (MOR, CHA, MFI) for the five synthesis conditions tested: FS, FS-a, FS-w, FS/PDDA, and FS-a/PDDA. The induction times (i.e. first appearance of Bragg peaks in powder XRD patterns) listed here are evaluated from powder XRD patterns of solids extracted at periodic synthesis times.

References

1 C. Baerlocher and L. McCusker, Database of Zeolite Structures: http://www. iza-structure.org/databases. (2013).