Electronic Supplementary Information for

Cooperative Effects of Inorganic and Organic Structure-Directing Agents in ZSM-5 Crystallization

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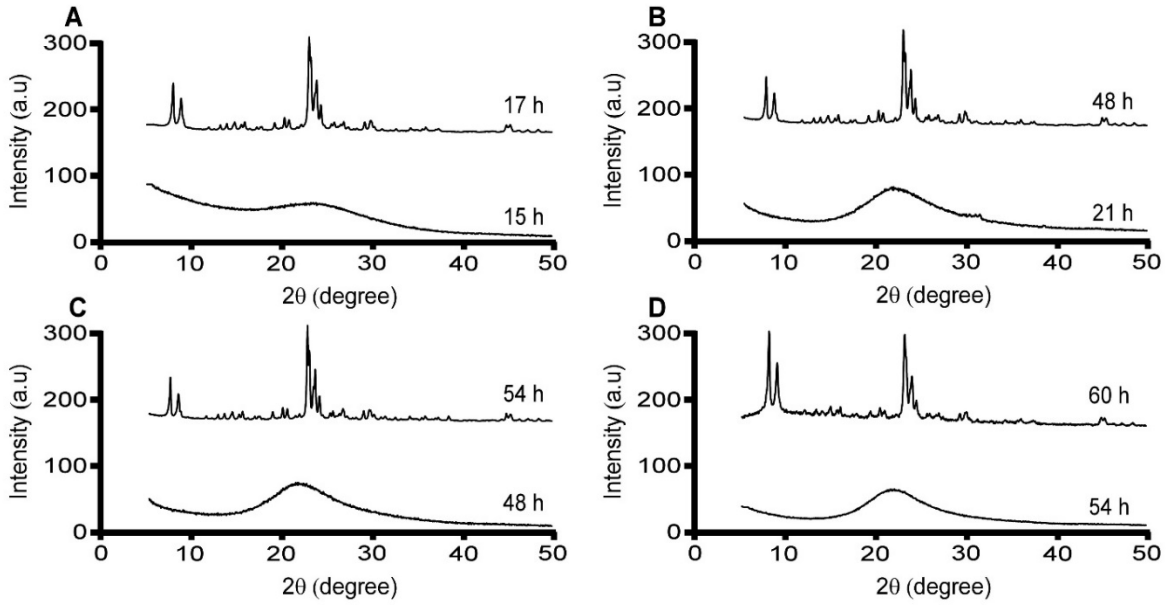

Figure S1. Time-elapsed powder X-ray diffraction patterns of solids extracted from ZSM-5 growth solutions containing CTA as the organic SDA and the following ratios of inorganic SDAs (listed as molar fractions of K:Na): (A) 1:0, (B) 0.75:0.25, (C) 0.5:0.5, and (D) 0:1.

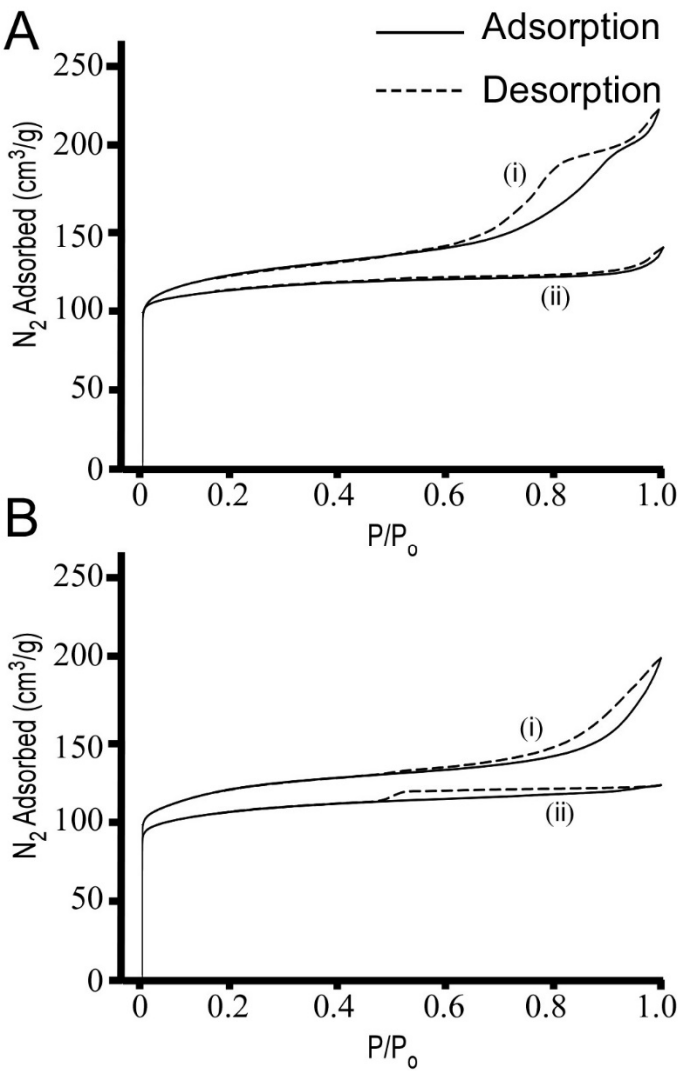

Figure S2. N_2 adsorption (solid line) and desorption (dashed line) isotherms of ZSM-5 crystals synthesized in the presence of (A) potassium and (B) sodium. Isotherms of samples prepared with CTA (*i*) are type IV, which indicates the presence of mesopores. Isotherms of samples prepared with TPA (*ii*) are type I, which is characteristic of microporous materials.

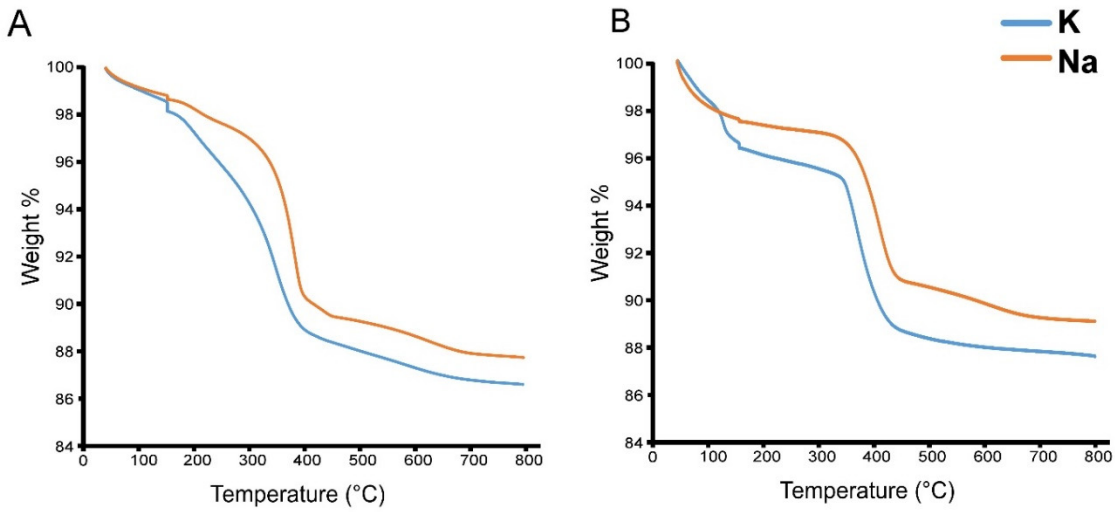

Figure S3. Thermogravimetric analysis (TGA) of ZSM-5 crystals prepared in the presence of (A) CTA and (B) TPA. Blue and orange lines denote samples prepared with potassium and sodium, respectively. TGA data were obtained using a 1 °C/min temperature ramp rate under the constant flow of N_2 gas.

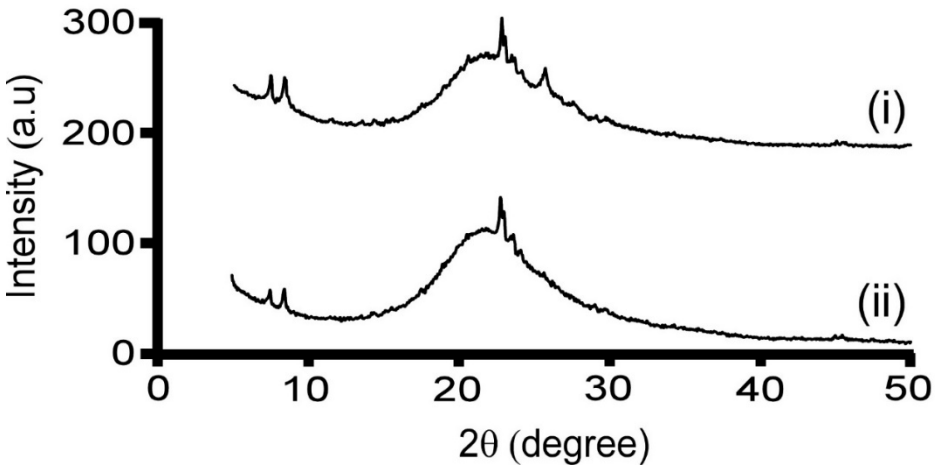

Figure S4. Powder X-ray diffraction patterns of solids extracted from growth mixtures after 72 h of hydrothermal treatment. The inorganic SDA in both samples is sodium. Here we compare a sample prepared with (*i*) tetramethylammonium (TMA) as the organic SDA to (*ii*) a sample prepared from an organic-free growth mixture.

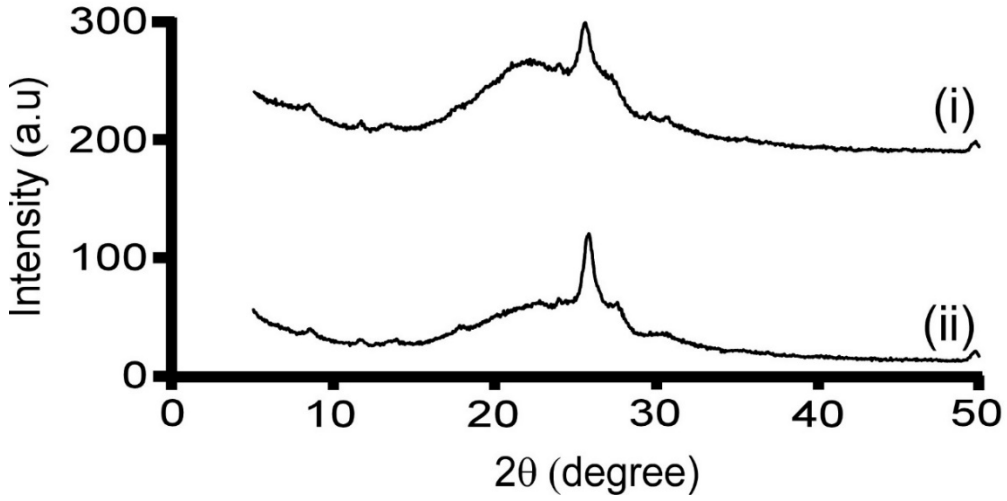

Figure S5. Powder X-ray diffraction patterns of solids extracted from growth solutions after 72 h of hydrothermal treatment. The inorganic SDA in both samples is potassium. Here we compare a sample prepared with (*i*) tetramethylammonium (TMA) as the organic SDA to (*ii*) a sample prepared from an organic-free growth mixture.

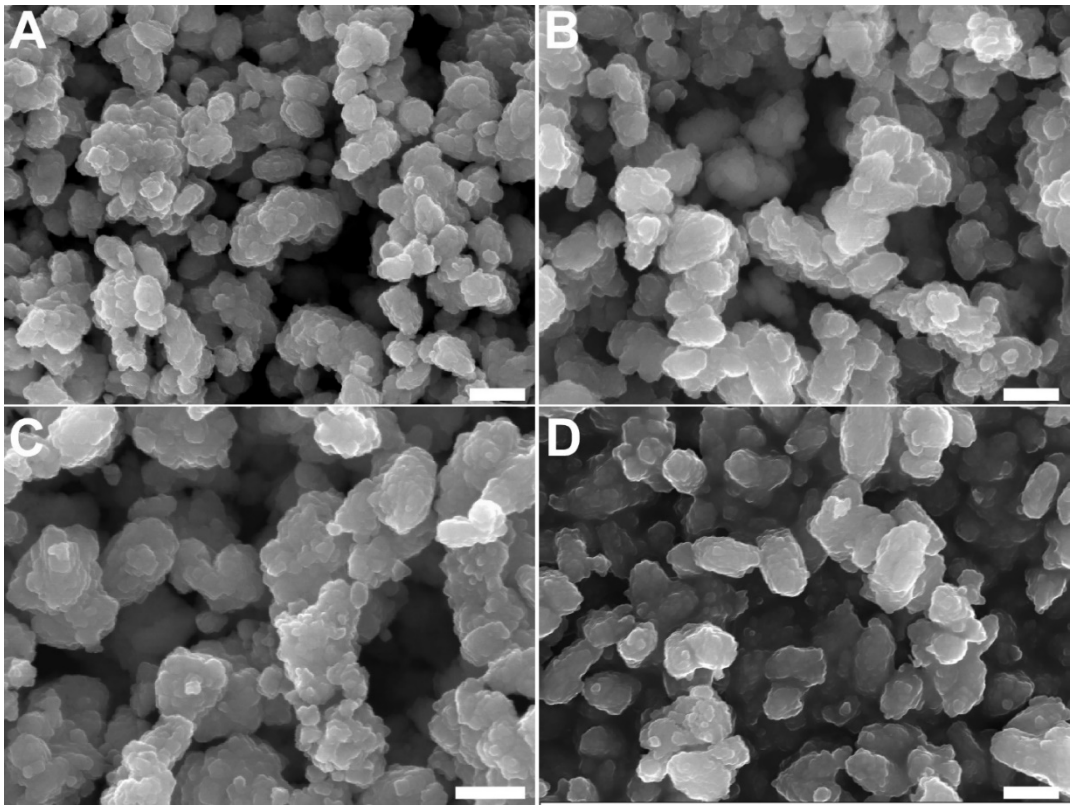

Figure S6. Scanning electron micrographs of ZSM-5 samples prepared with CTA as the organic SDA in the presence of the following molar percentages of potassium relative to the total alkali content (K + Na): (A) 0%, (B) 50%, (C) 75%, and (D) 100%. Scale bars equal 1 μm.

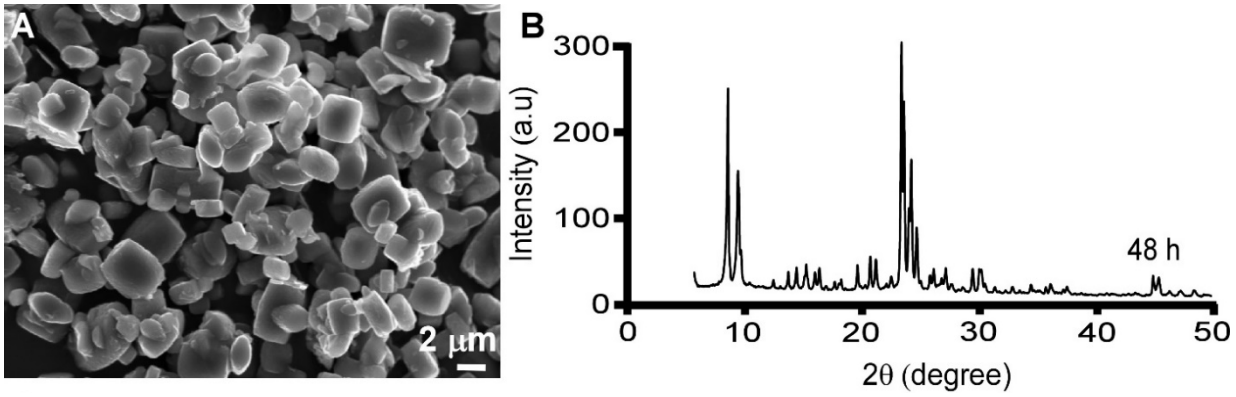

Figure S7. ZSM-5 crystals synthesized with TEOS as an alternative silica source. (A) Scanning electron micrograph revealing crystals grown from TEOS are larger than those from colloidal silica. (B) Powder X-ray diffraction pattern of solids extracted from a growth mixture prepared with TEOS reveals that crystallization is complete within 48 h of hydrothermal treatment.

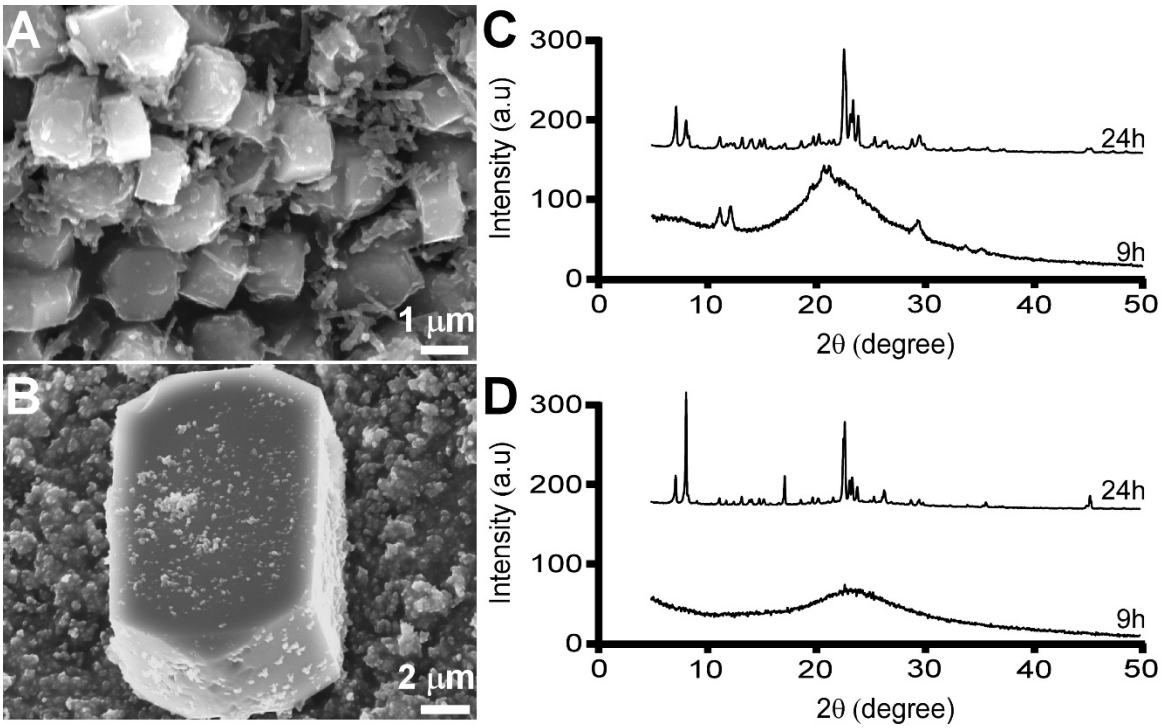

Figure S8. Characterization of ZSM-5 crystals synthesized using TPA as the organic SDA. (A and B) Scanning electron micrographs of ZSM-5 crystals after 72 h of hydrothermal treatment. Growth mixtures were prepared with (A) lithium and (B) cesium. (C and D) Powder X-ray diffraction patterns of solids extracted from ZSM-5 syntheses after listed times of hydrothermal treatment corresponding to growth mixtures prepared with (C) lithium and (D) cesium.

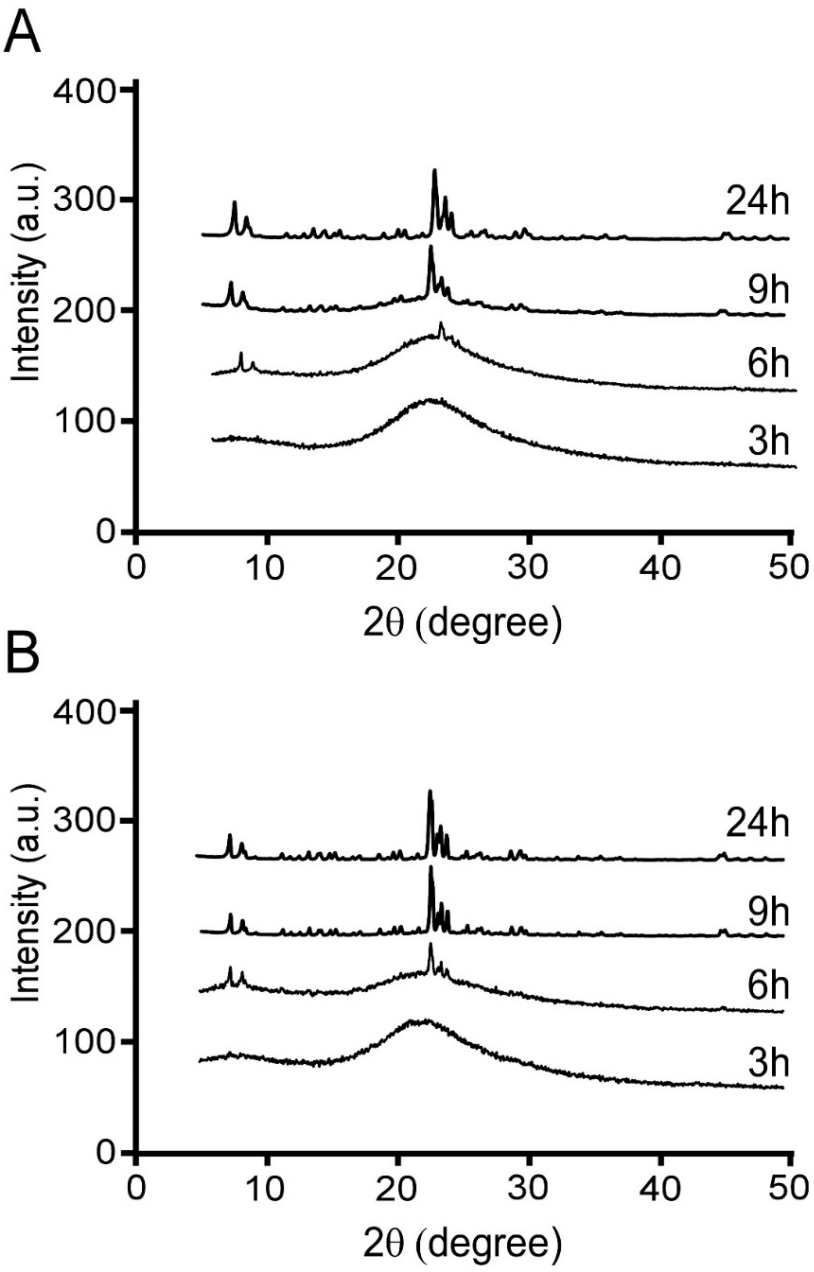

Figure S9. Comparison of powder X-ray diffraction patterns of solids extracted from ZSM-5 growth mixtures after specified heating times. Growth mixtures were prepared with TPA as the organic SDA and the following inorganic SDAs: (A) sodium and (B) potassium

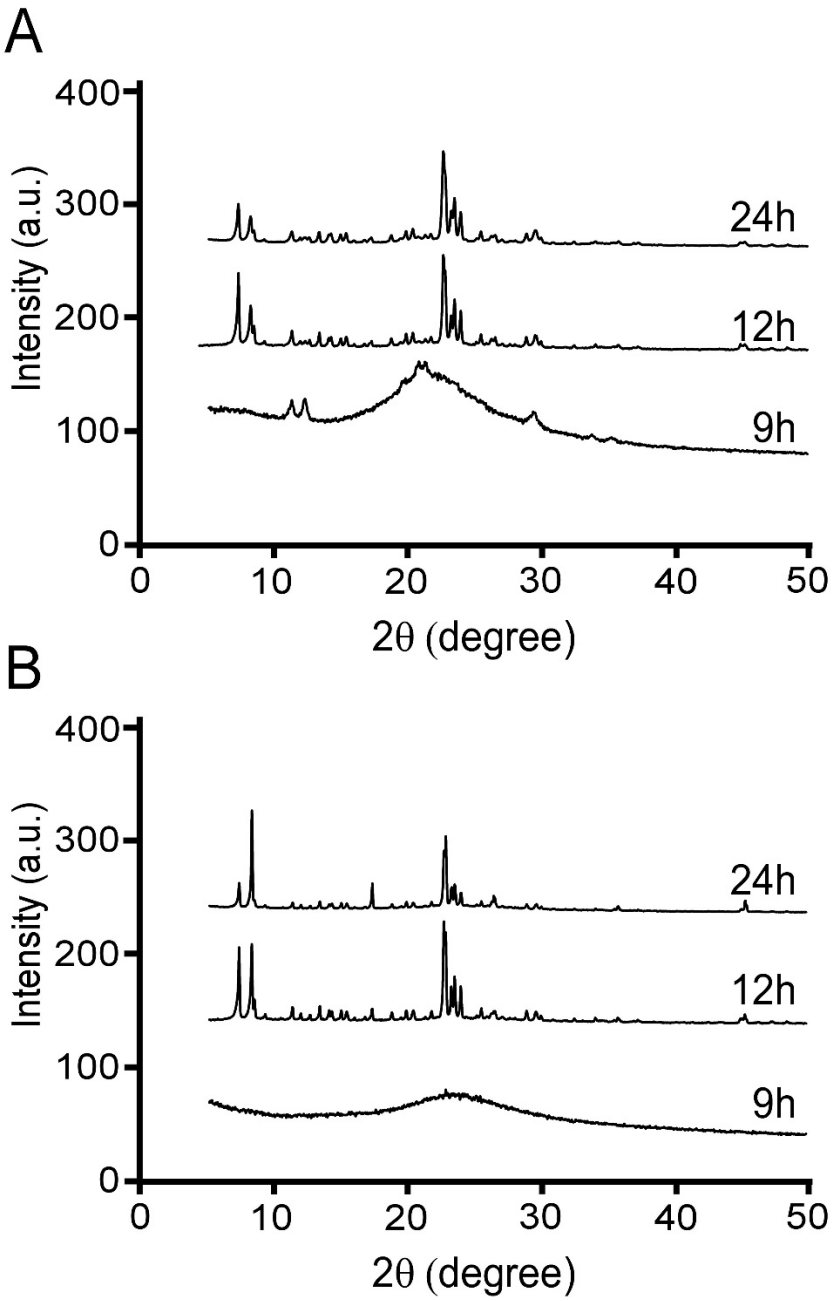

Figure S10. Comparison of powder X-ray diffraction patterns of solids extracted from ZSM-5 growth mixtures after specified heating times. Growth mixtures were prepared with TPA as the organic SDA and the following inorganic SDAs: (A) lithium and (B) cesium

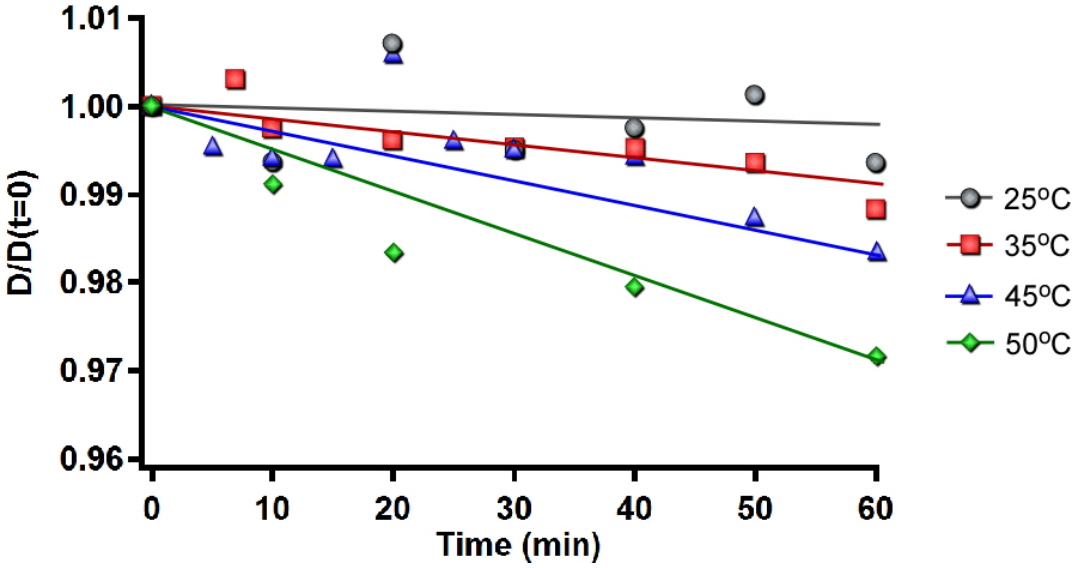

Figure S11. Dissolution of colloidal silica (LUDOX AS-40) in NaOH solution (pH 12) with a molar composition of 20 SiO_2: 0.2 NaOH: 1030 H_2O at temperatures between 25 and 50 °C. The average hydrodynamic diameter of silica particles D_H scaled by the initial size $D_H(t=0)$ (measured at t = 0 min) is plotted as a function of time. Solid lines are linear regression with slopes equaling the kinetic rate of dissolution. The experiment details are consistent with what is reported in the manuscript (Figure 9).

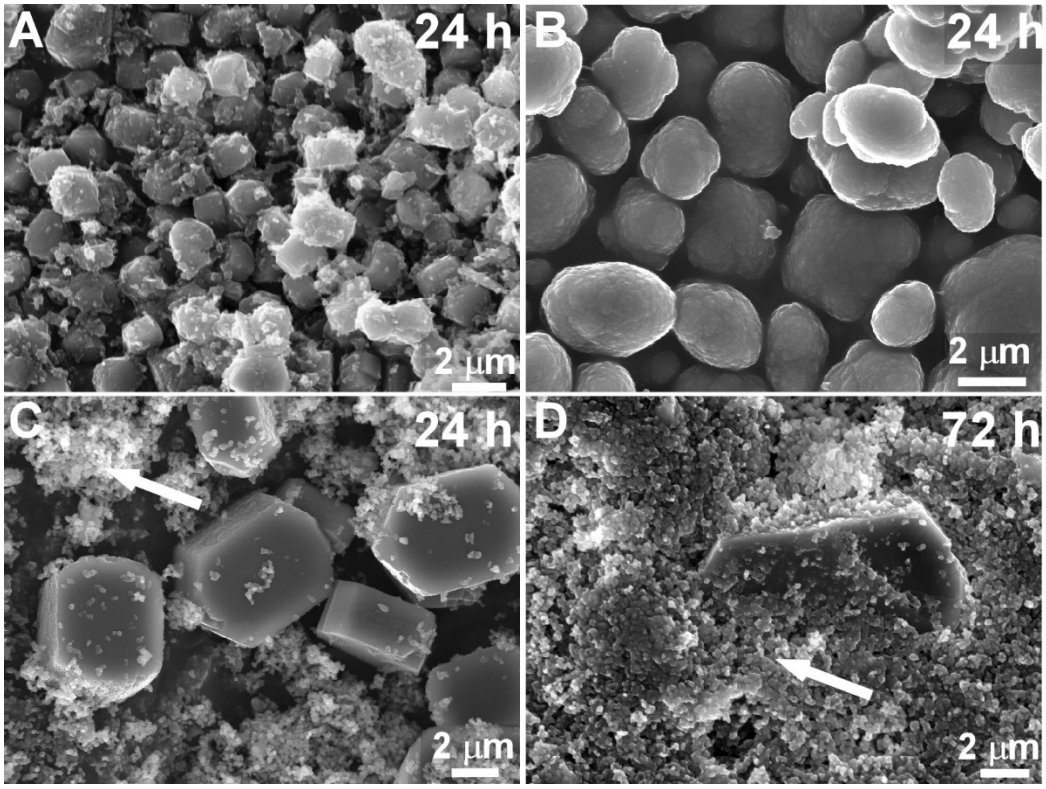

Figure S12. Scanning electron micrographs of ZSM-5 samples prepared with TPA as the organic SDA after specified heating times in the presence of (A) lithium, (B) sodium, (C) potassium, and (D) cesium cations. An arrow indicates the presence of residual amorphous precursors in TPA/K-MFI and TPA/Cs-MFI samples. Note that the times account for both induction (nucleation) and crystal growth.

Table S1. t-plot analysis of ZSM-5 crystals using N_2 adsorption/desorption data.

SDA Combinations	Total surface area (m^2/g)	Micropore surface area (m^2/g)	External surface area (m^2/g)
CTA/Na	443	305	139
TPA/Na	398	311	87
CTA/K	450	316	134
TPA/K	423	346	77

Table S2. t-plot analysis of N_2 adsorption/desorption data for ZSM-5 crystals prepared with CTA/Na.

Si Source	Total surface area (m^2/g)	Micropore surface area (m^2/g)	External surface area (m^2/g)
LUDOX	443	305	139
TEOS	409	319	90