Supporting Information

for

Delamination of Layered Zeolite Precursors under Mild Conditions: Synthesis of UCB-1 via Fluoride/Chloride Anion-Promoted Exfoliation

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Experimental Methods

Materials. All reagents used in zeolite synthesis and delamination were of reagent-grade quality and were used as received. USY zeolite used in N_2 gas physisorption was purchased from Zeolyst International (CBV760, Si/Al ratio of 60). TON zeolite was synthesized at Chevron Energy Technology Company according to the literature method,[1] except that the starting gel composition used was SiO_2 : 0.10 NaOH : 0.01 Al_2O_3 (same ratio of H_2O/SiO_2 as that used in the literature).

Synthesis of MCM-22 (P). The zeolite was synthesized according to the literature method.[2,3] Fumed silica (Sigma Aldrich, 3.54 g) was added to an aqueous solution containing sodium hydroxide (EMD Chemicals, 97%, 0.372 g), hexamethyleneimine (Sigma Aldrich, 99%, 2.87 g), and sodium aluminate (Riedel-de Haen, 0.108 g) in deionized water (46.6 g) under vigorously stirring. After stirring the mixture for 6 h, the gel was divided into four portions and each portion was loaded into a 23 mL Teflon-lined Parr reactor. Each reactor was tightly sealed and heated in a convection oven at 408 K for 11 days with tumbling of the reactor. After 11 days of heating, the reactors were cooled down to room temperature, and the product was separated by centrifugation. The separated product was washed with deionized water thoroughly, and finally dried at 313 K overnight.

Delamination of MCM-22 (P) by the Conventional Method (Synthesis of ITQ-2 Zeolite). MCM-22 (P) synthesized according to the preceding section was delaminated by the literature method.[2] An aqueous slurry of MCM-22 (P) (3.00 g, 20 wt% solid) was mixed with cetyltrimethylammonium bromide (Sigma Aldrich, ≥98%, 3.38 g), deionized water (8.28 g), tetrapropylammonium hydroxide solution (Alfa Aesar, 40 wt%, 3.67 g), and the resulting mixture was heated at 353 K for 16 h. After 16 h of heating, the mixture was cooled to room temperature, and subjected to sonication for 1 h. The pH of the slurry was adjusted to 2 by adding concentrated HCl aqueous solution, upon which it was centrifuged to separate the product. Finally, the product was dried at 313 K overnight. The product yield was 75%.[4] The powder X-ray diffraction pattern of the product (Figure 1, pattern B) shows a

significant decrease of all peaks characteristic of a lamellar structure of MCM-22 (P), in agreement with the literature results.[2,6,7] ITQ-2 was calcined at 823 K in flowing N_2/O_2.

Synthesis of UCB-1 via delamination of MCM-22 (P). As-made MCM-22 (P) (1.00 g) was added to a mixture of cetyltrimethylammonium bromide (1.65 g), tetrabutylammonium fluoride (Fluka, ≥90%, 1.92 g) and tetrabutylammonium chloride (Sigma Aldrich, 1.68 g) in deionized water (25.9 g). The pH of the slurry was adjusted to approximately 9 by adding 40% tetrapropylammonium hydroxide solution, and the slurry was heated at 353 K for 16 h. After cooling, the pH of the mixture was adjusted to approximately 2 by adding concentrated HCl aqueous solution. The mixture was transferred to a centrifuge bottle with screw cap, and quickly centrifuged to separate solids. The supernatant solution was discarded, and the remaining solid was dried at 313 K overnight in the fume hood. The aluminosilicate product yield was 90%. UCB-1 was calcined at 823 K in flowing N_2/O_2.

Delamination of MCM-22 (P) without Chloride. Delamination of MCM-22 (P) was attempted under similar conditions to those described above, except without tetrabutylammonium chloride and with twice as much as tetrabutylammonium fluoride.

Delamination of MCM-22 (P) without Fluoride. Delamination of MCM-22 (P) was attempted under similar conditions to those described above, except without tetrabutylammonium fluoride and with twice as much as tetrabutylammonium chloride.

Characterization. Powder X-ray diffraction (XRD) patterns were collected on a Siemens D5000 diffractometer using a Cu Kα radiation. Transmission electron microscopy images were recorded on a Tecnai 20 at the University of California at Berkeley or a JEOL JEM-2010 (200 kV) at Chevron Energy Technology Company. Nitrogen gas adsorption isotherms[8] were measured on a Micromeritics ASAP2020 at 77 K. Prior to measurement, samples were evacuated at 623 K for 4 h. ^{29}Si solid-state MAS NMR spectra were measured using a Bruker Avance 500 MHz spectrometer with a wide bore 11.7 T magnet and employing a Bruker 4 mm MAS probe. The spectral frequencies were 500.23 MHz for the ^{1}H nucleus and 99.4 MHz for the ^{29}Si nucleus. ^{29}Si MAS NMR spectra were acquired after a 4

μs-90 degree pulse with application of a strong ^{1}H decoupling pulse. The spinning rate was 12 kHz, and the recycle delay time was 300 s. ^{29}Si CP MAS NMR spectra were collected on a Bruker DSX-500 spectrometer. The spectral frequency was 99.4 MHz for the ^{29}Si nucleus. The sample spinning rate was 8 kHz, and the cross polarization contact time was 2.0 ms. NMR shifts are reported in parts per million (ppm) when externally referenced to tetramethylsilane (TMS). One dimensional (1D) ^{27}Al MAS NMR spectra were recorded on a Bruker DSX-500 spectrometer (130 MHz for ^{27}Al) after a 0.5 ms single pulse ($< \pi/18$) with application of a strong ^{1}H decoupling pulse, at a sample spinning rate of 14 kHz. Mercury porosimetry was conducted according to Standard Test Method for Determining Pore Volume Distribution of Catalysts by Mercury Intrusion Porosimetry (ASTM D 428).

Table S1. Pore volume of MCM-22, UCB-1, and ITQ-2 determined from N_2 gas adsorption data.

range of relative pressure	pore volume (cm^3/g)		
	MCM-22	UCB-1	ITQ-2
$P/P_0 \leq 10^{-5}$	0.11	0.08	0.08
$10^{-5} < P/P_0 \leq 0.02$	0.08	0.09	0.17
$0.02 < P/P_0 < 1.0$	0.16	0.30	0.53

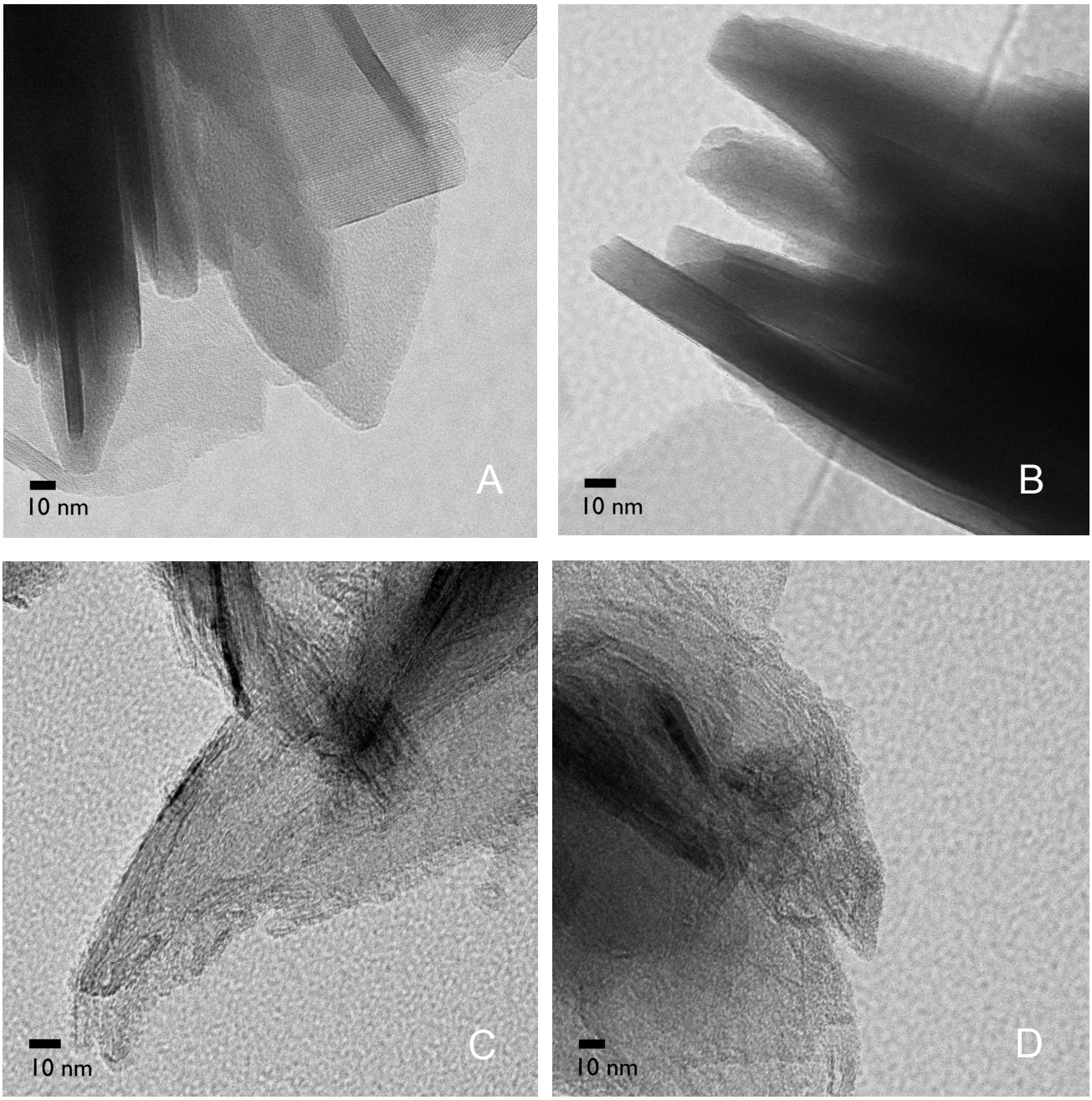

Figure S1. TEM images comparing MCM-22 (P) in (A) and (B) with as-made UCB-1 in (C) and (D) on similar length scales where MCM-22 (P) consists of an array of lamellar sheets, each of which consists of a rectilinear plate in (A) and (B). As-made UCB-1 consists of curved layers that have been split apart in (C) and (D), and lacks long-range order.

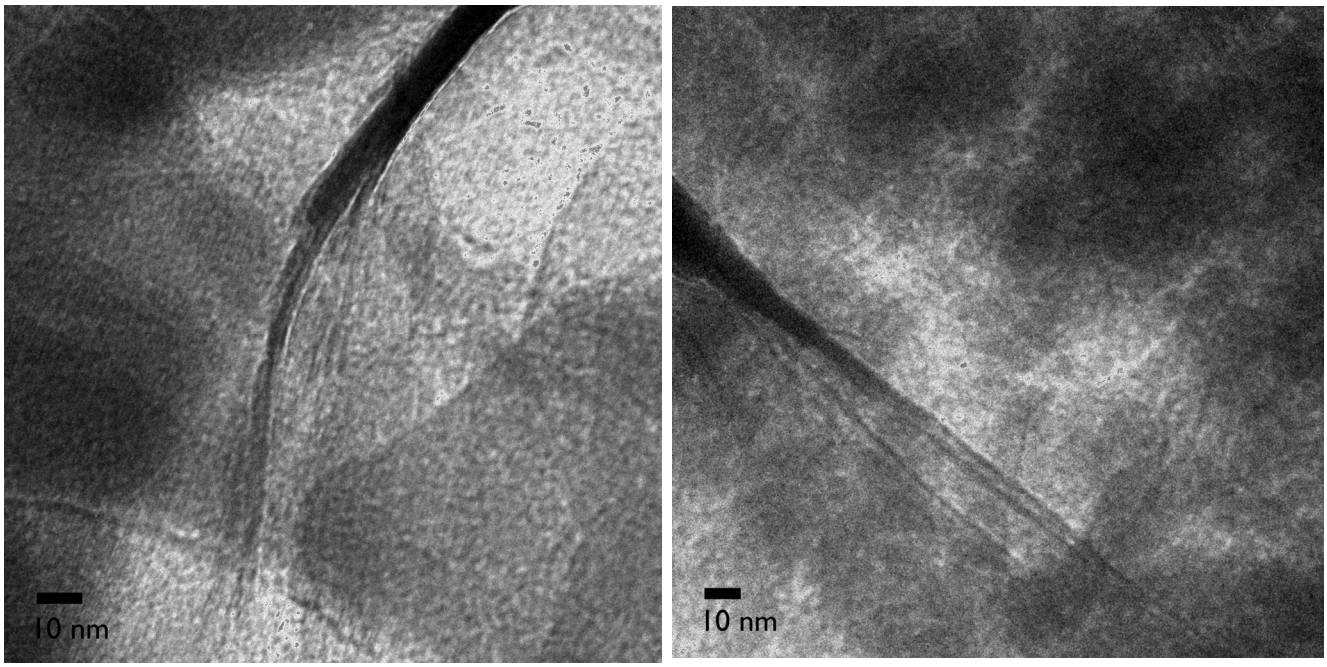

Figure S2. TEM images characterizing the splitting off of a layer as a consequence of the delamination process in as-made UCB-1.

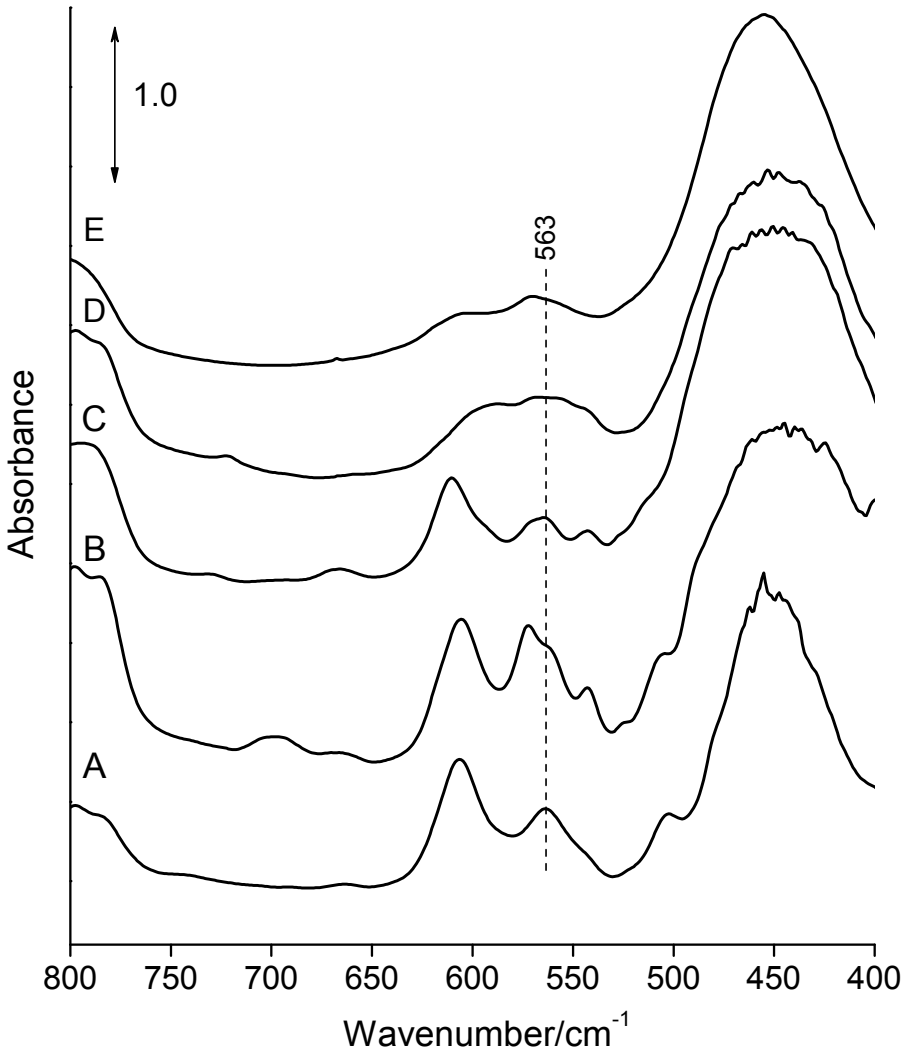

Figure S3. Fourier transform infrared (FTIR) spectrum of (A) MCM-22 (P) with Si/Al ratio of 50, (B) as-made UCB-1, (C) calcined UCB-1, (D) as-made ITQ-2, and (D) calcined ITQ-2. The labeled band at 563 cm^{-1} corresponds to a pentasil structure in the framework, which is slightly shifted from its previously reported value of 550 cm^{-1}.[9] This shift is due to the differing Si/Al ratios between MCM-22 in reference [9], which consists of a Si/Al ratio of 15, and materials investigated in Figure S3, which all consist of a Si/Al ratio of 50. Synthesis of both UCB-1 and ITQ-2 involved steps consisting of swelling of MCM-22 (P) at 353 K for 16 h, and acidification to pH 2. Both as-made UCB-1 and ITQ-2 were calcined at 823 K for 12 h in N_2/O_2.

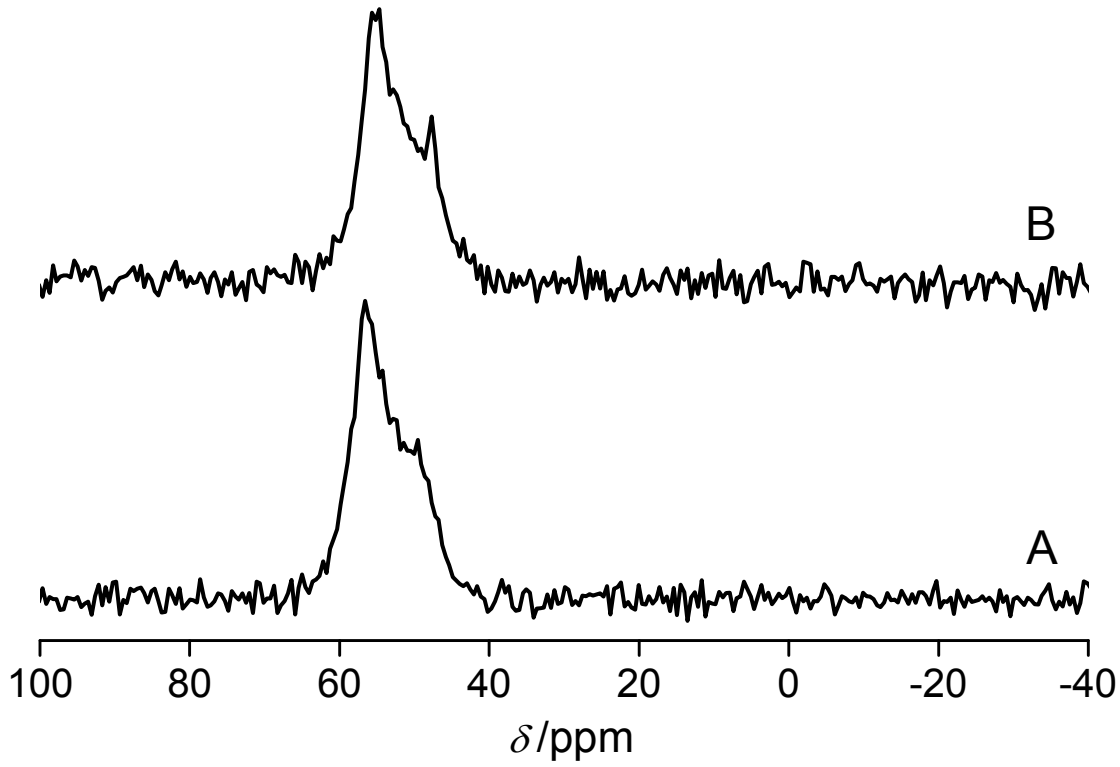

Figure S4. ^{27}Al MAS NMR spectra characterizing (A) MCM-22 (P) (Si/Al ratio = 50) and (B) the as-made UCB-1. The as-made UCB-1 was washed according to procedures described by Bein *et al*.[10] in order to remove templates.

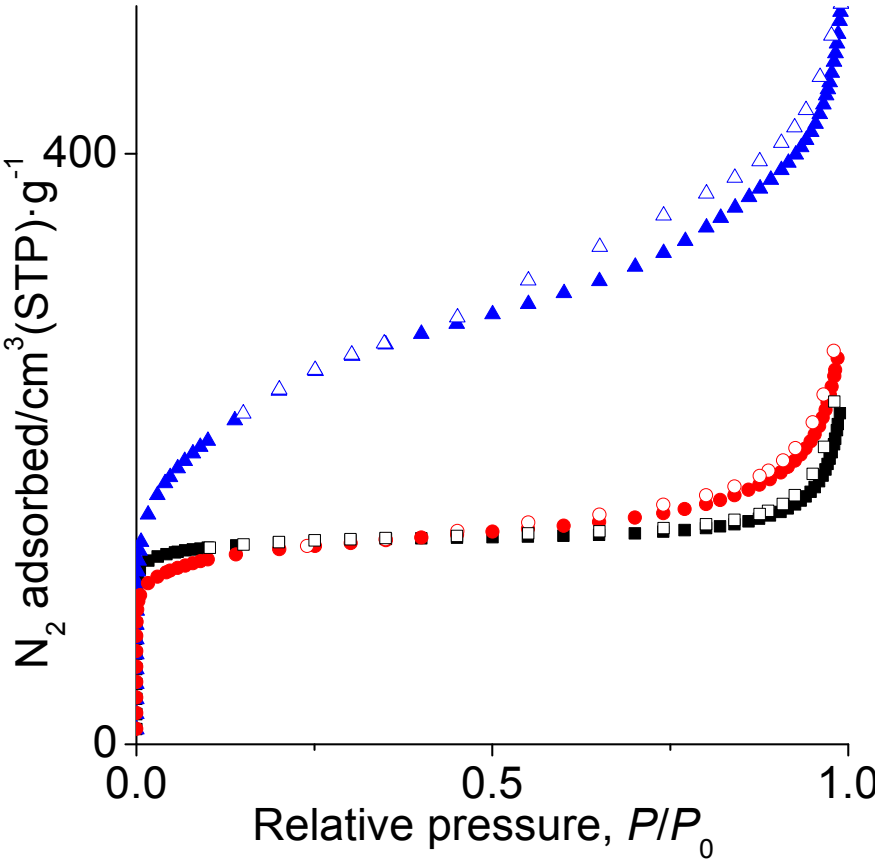

Figure S5. Adsorption-desorption isotherms of (▲: adsorption, ∫: desorption) ITQ-2, (●: adsorption,○: desorption) UCB-1, and (■: adsorption, □: desorption) MCM-22.

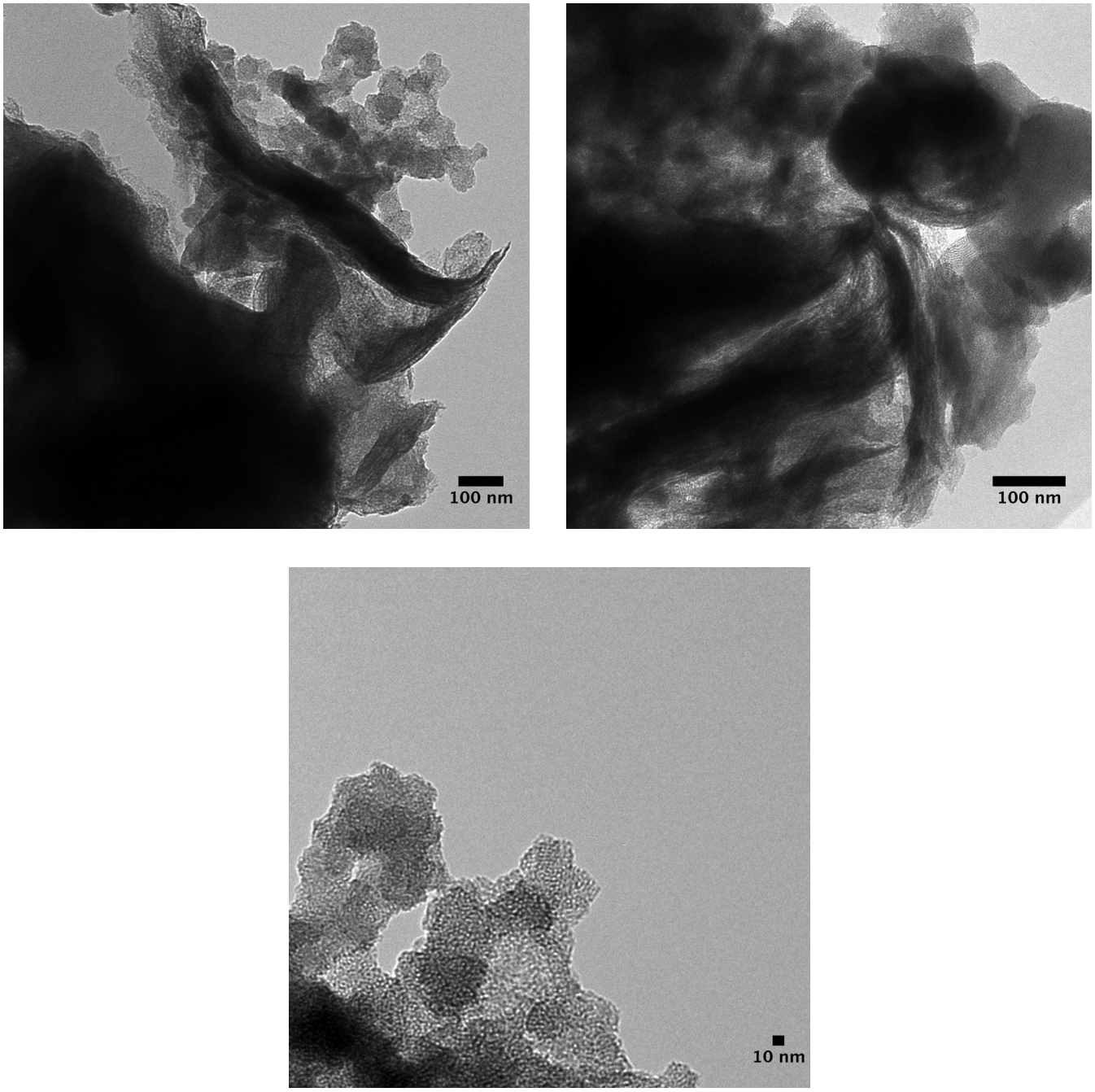

Figure S6. TEM images charactering as-made ITQ-2 zeolite show mesoporosity that is likely a consequence of silica amorphization during delamination.

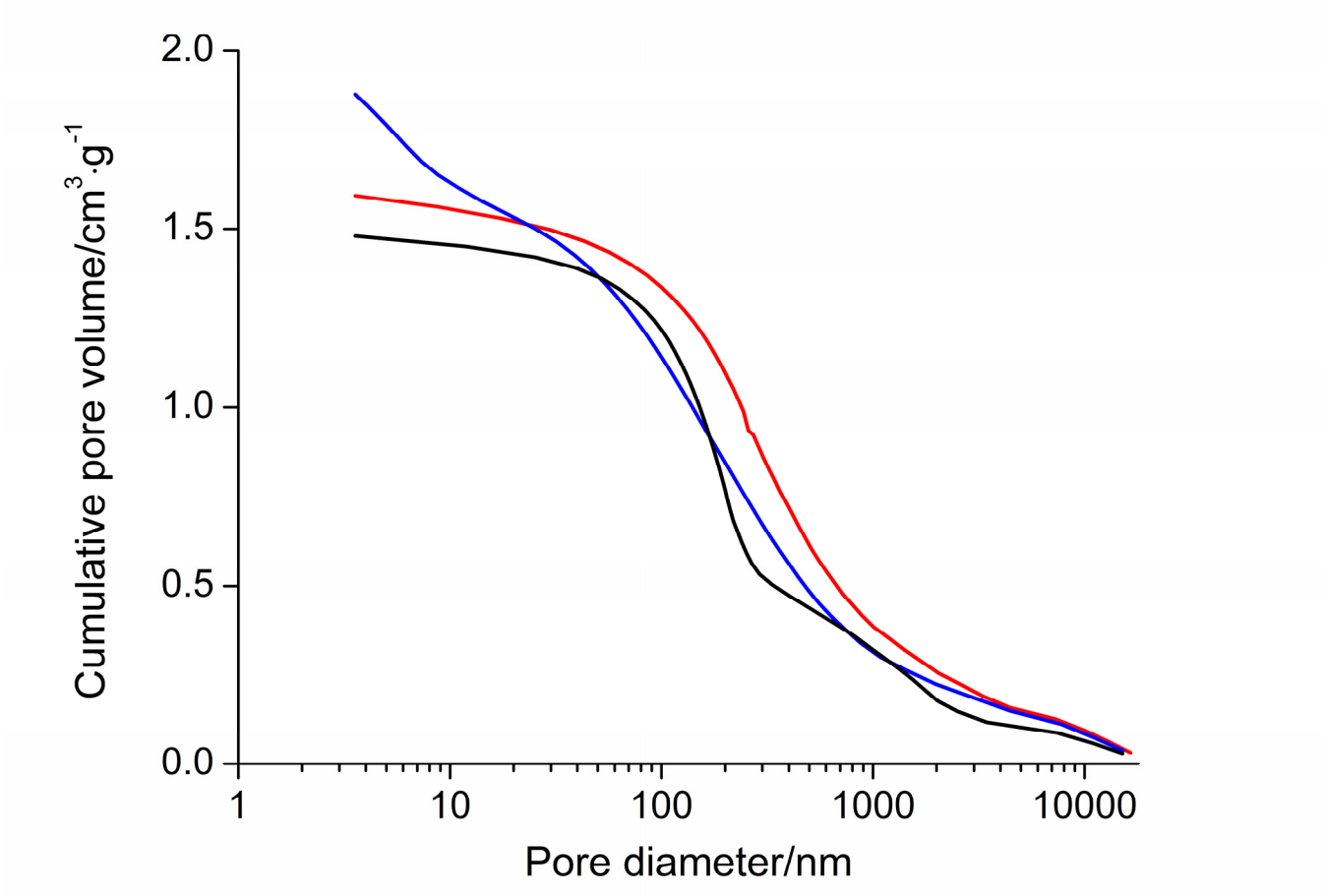

Figure S7. Cumulative pore volumes measured via mercury porosimetry for the following samples: black line, MCM-22 zeolite; blue line, ITQ-2 zeolite; red line, new material.

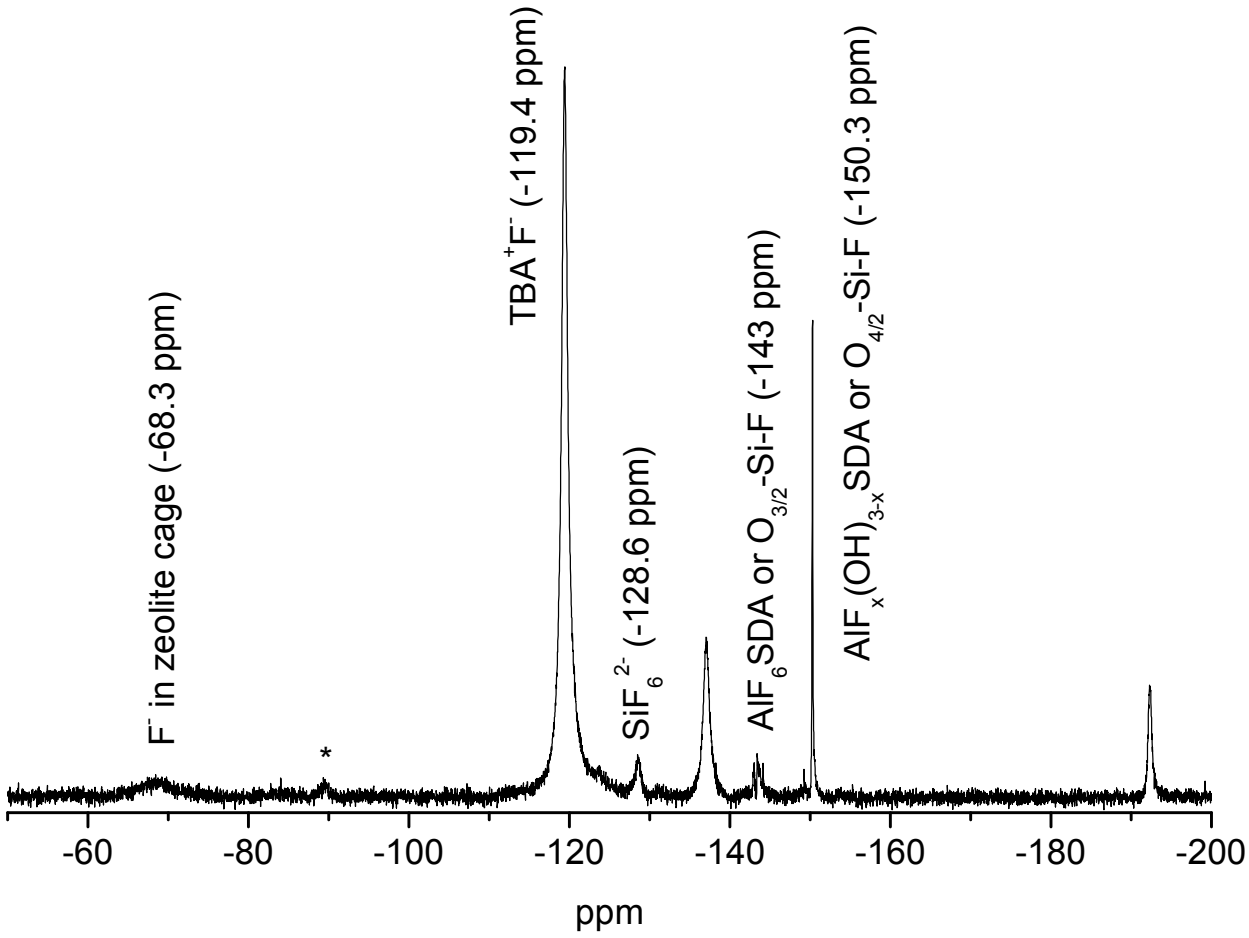

Figure S8. ^{19}F MAS NMR spectra characterizing the as-made UCB-1.

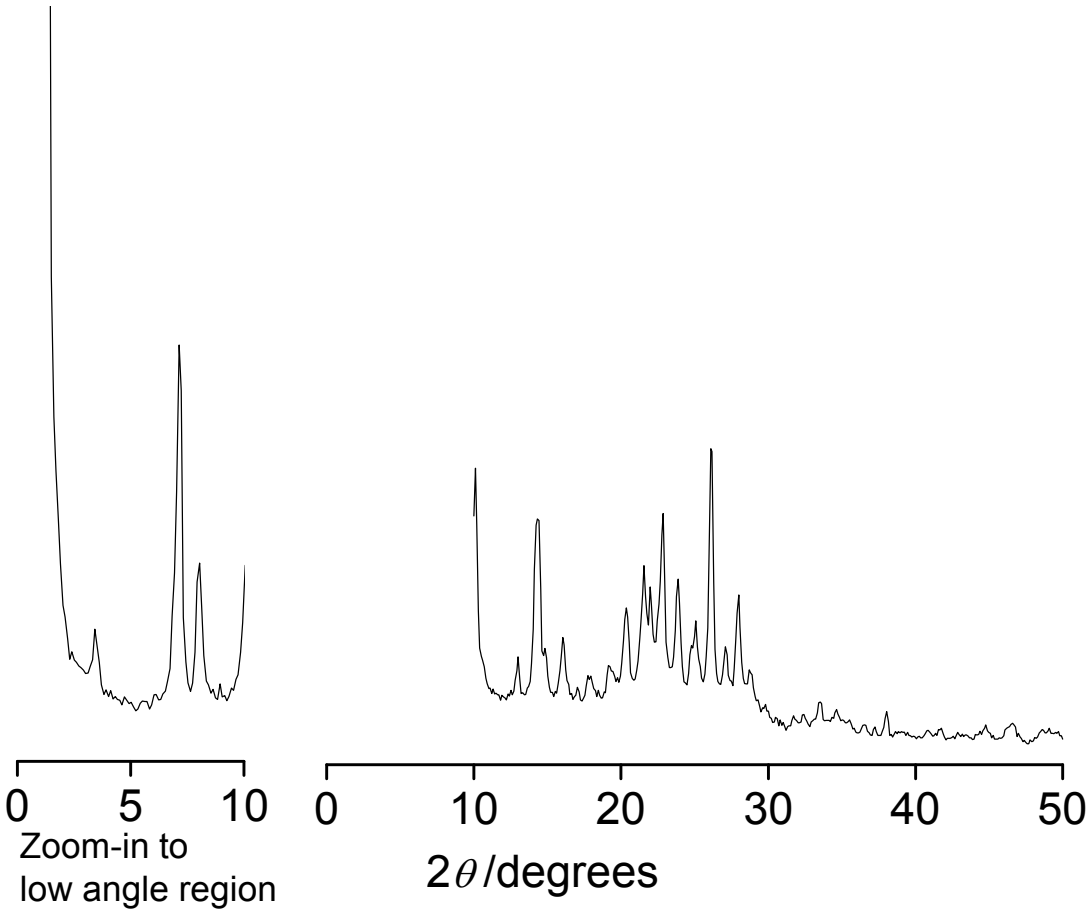

Figure S9. Powder X-ray diffraction pattern characterizing MCM-22 after the sample was treated under the same conditions as those used to synthesize UCB-1.

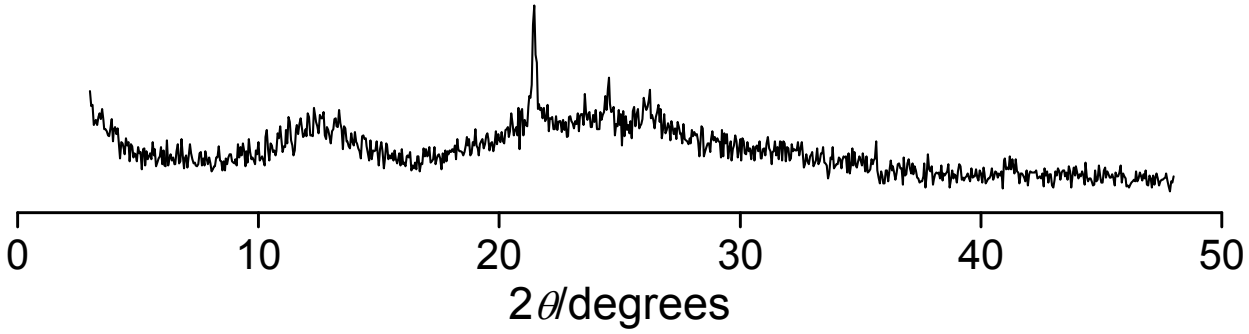

Figure S10. Powder X-ray diffraction pattern characterizing MCM-22 after the sample was treated under the same conditions as those used to synthesize ITQ-2 zeolite.

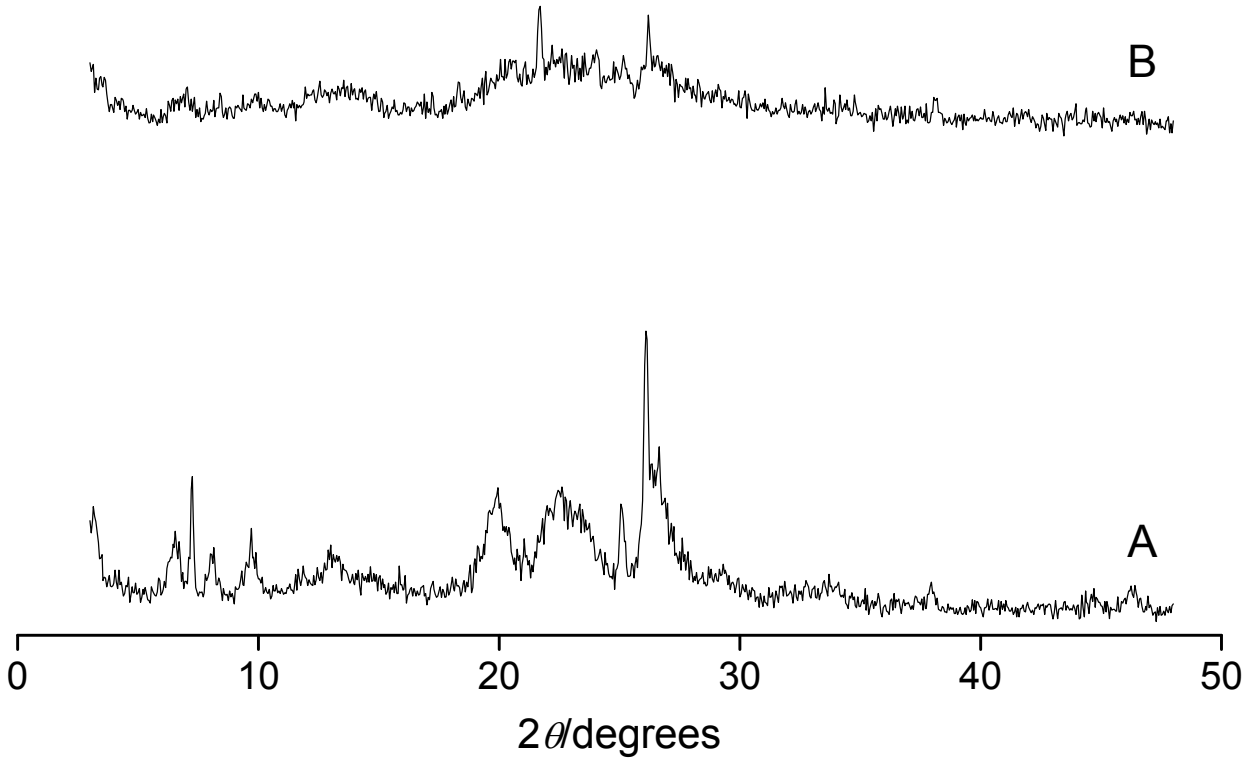

Figure S11. Powder X-ray diffraction patterns characterizing (A) MCM-22 (P) (Si/Al ratio = 20) and (B) the same sample after delamination by the fluoride/chloride anion-promoted method.

References

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