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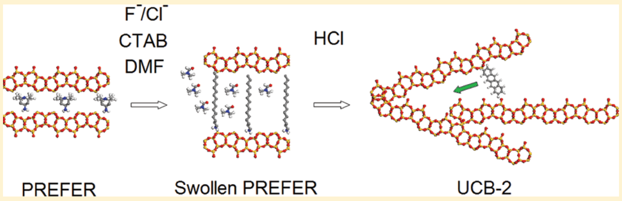
Nonaqueous Fluoride/Chloride Anion-Promoted Delamination of Layered Zeolite Precursors: Synthesis and Characterization of UCB-2

Einar A. Eilertsen,[†,¶] Isao Ogino,[*,†,¶] Son-Jong Hwang,[§] Thomas Rea,[‡] Sheila Yeh,[‡] Stacey I. Zones,[*,†,‡] and Alexander Katz[*,†]

[†]Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, California 94720, United States
[‡]Chevron Energy Technology Company, Richmond, California 94804, United States
[§]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

S *Supporting Information*



ABSTRACT: The delamination of layered zeolite precursor PREFER is demonstrated under mild nonaqueous conditions using a mixture of cetyltrimethylammonium bromide, tetrabutylammonium fluoride, and tetrabutylammonium chloride in *N*,*N*-dimethylformamide (DMF) as solvent. The delamination proceeds through a swollen material intermediate which is characterized using powder X-ray diffraction (PXRD). Subsequent addition of concentrated HCl at room temperature leads to synthesis of UCB-2 via delamination of the swollen PREFER material and is characterized using PXRD, transmission electron microscopy (TEM), and argon gas physisorption, which shows lack of microporosity in UCB-2. ^{29}Si magic angle spinning (MAS) NMR spectroscopy indicates lack of amorphization during delamination, as indicated by the entire absence of Q^2 resonances, and ^{27}Al MAS NMR spectroscopy shows exclusively tetrahedral aluminum in the framework following delamination. The delamination process requires both chloride and fluoride anions and is sensitive to solvent, working well in DMF. Experiments aimed at synthesizing UCB-2 using aqueous conditions previously used for UCB-1 synthesis leads to partial swelling and lack of delamination upon acidification. A similar lack of delamination is observed upon attempting synthesis of UCB-1 under conditions used for UCB-2 synthesis. The delamination of PREFER is reversible between delaminated and swollen states in the following manner. Treatment of as-made UCB-2 with the same reagents as used here for the swelling of PREFER causes the delaminated UCB-2 material to revert back to swollen PREFER. This causes the delaminated UCB-2 material to revert back to swollen PREFER. Altogether, these results highlight delamination as the reverse of zeolite synthesis and demonstrate the crucial role of noncovalent self-assembly involving the zeolitic framework and cations/anions/structure-directing agent and solvent during the delamination process.

KEYWORDS: delamination, exfoliation, layered zeolite precursor, PREFER

INTRODUCTION

The delamination of layered zeolite precursors[1−8] synthesizes well-ordered two-dimensional materials consisting of microporous frameworks. Catalytic sites incorporated within these micropores are accessible to bulky reactants that would otherwise be unable to diffuse into a three-dimensional microporous framework, and titration of these acid sites is possible using bulky base molecules that would otherwise be unable to diffuse into micropores.[9,10] This has led to new applications in adsorption and catalysis, involving cracking,[1] alkylation,[11,12] disproportionation,[13] epoxidation,[2,6] and Beckmann rearrangement.[14] We recently reported synthesis of UCB-1,[8] corresponding to delaminated zeolite precursor MCM-22(P), using a fluoride/chloride-promoted exfoliation in aqueous solution at near-neutral pH. Such conditions were chosen to obviate the significant amorphization of the zeolite framework that usually accompanies conventional delamination when high pH aqueous solution (above 13.5 typically) is employed as solvent.[5−7] The lack of amorphization in UCB-1 was demonstrated using ^{29}Si magic angle spinning (MAS) NMR and infrared spectroscopies, which demonstrate a higher retention of structural integrity relative to ITQ-2,[1] which results from conventional delamination of the same zeolite precursor. Here, we demonstrate the synthesis of UCB-2, consisting of delaminated PREFER,[15] which is a precursor to ferrierite zeolite that consists of 8 and 10 MR microchannels. Delamination is accomplished using a nonaqueous solution containing fluoride and chloride anions. The resulting material, UCB-2, is characterized throughout the synthesis process comprising swollen and final delaminated states and is compared with delamination under previously described aqueous conditions employing fluoride/chloride at pH 9 as well as highly basic conditions of pH 12.5, which synthesize the previously reported conventionally delaminated material ITQ-6.[2]

EXPERIMENTAL SECTION

Materials. All reagents used in zeolite synthesis and delamination were of reagent-grade quality and were used as received.

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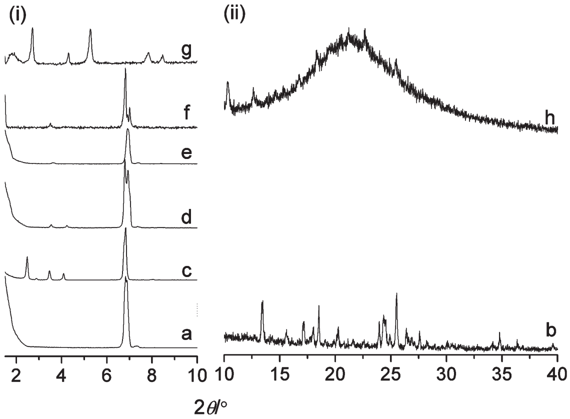

Figure 1. Powder XRD patterns in (i) low-angle region and (ii) high-angle region, respectively, characterizing (a and b) PREFER and swollen materials in the following solvents: c, water; d, CH_2Cl_2; e, ethanol; f, 4-methylmorpholine *N*-oxide; g and h, *N,N*-dimethylformamide.

Synthesis of PREFER. A typical synthesis of PREFER was made by mixing 1.60 g of fumed silica with 0.38 g of alumina (bohemite, Catapal B). A mixture of 1.47 g of NH_4F and 0.50 g of HF (49%) was added subsequently, and the highly viscous gel was stirred using a spatula until it was homogeneous. A mixture of 4.16 g of 4-amino-2,2,6,6-tetramethylpiperidine (Aldrich, 98%) and 4.43 g of H_2O (deionized) was added, and the gel was stirred until it was homogeneous. The gel was transferred to a 25 mL Teflon lined Parr stainless steel autoclave and heated at 175 °C for 5 days in a tumbling oven at 60 rpm.

Synthesis of UCB-2 via Delamination of PREFER. PREFER was swollen by mixing 10.00 g of *N,N*-dimethylformamide (DMF), 0.85 g of cetyltrimethylammonium bromide (CTAB), 0.85 g of tetrabutylammonium fluoride trihydrate (TBAF), 0.85 g of tetrabutylammonium chloride (TBACl), and 0.50 g of PREFER in a 25 mL Teflon lined Parr stainless steel autoclave. The mixture was heated for 16 h at 100 °C in a tumbling oven at 60 rpm. After swelling, approximately 20 drops of concentrated HCl aq. was added and the product was recovered by filtration through a fine glass filter.

Delamination of PREFER without Chloride. Delamination of PREFER was attempted under similar conditions to those described above, except without tetrabutylammonium chloride and with twice as much as tetrabutylammonium fluoride.

Delamination of PREFER without Fluoride. Delamination of PREFER was attempted under similar conditions to those described above, except without tetrabutylammonium fluoride and with twice as much as tetrabutylammonium chloride.

Reversibility Test between Swelling and Delamination. To test whether the acidification step leads to irreversible condensation of the layers, the delaminated UCB-2 was washed thoroughly in water 5 times and subjected to a new delamination process with CTAB, TBAF, and TBACl. The objective was to see if this treatment was able to swell the material. Washed UCB-2 (0.50 g) was mixed with 0.85 g of CTAB, 0.85 g of TBAF, 0.85 g of TBACl, and 10.00 g of DMF in a 25 mL Teflon lined Parr stainless steel autoclave. The mixture was heated for 16 h at 100 °C in a tumbling oven at 60 rpm.

Characterization. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer using a Cu Kα radiation. Transmission electron microscopy images were recorded on a JEOL JEM-2010 (200 kV) at University of California, Davis. Argon gas adsorption isotherms were measured on a Micromeritics ASAP2020 at 86 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. Elemental analysis was performed at Galbraith Laboratories Inc.

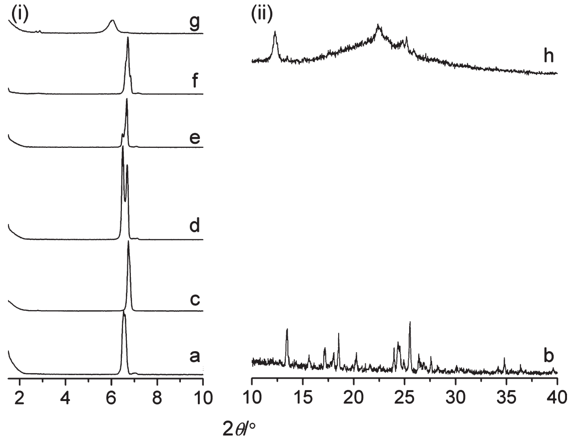

Figure 2. Powder XRD patterns in (i) low-angle region and (ii) high-angle region, respectively, characterizing (a and b) PREFER and acidified materials in the following solvents: c, water; d, CH_2Cl_2; e, ethanol; f, 4-methylmorpholine *N*-oxide; g and h, *N,N*-dimethylformamide.

RESULTS AND DISCUSSION

Synthesis of layered zeolite precursor PREFER is confirmed by the powder X-ray diffraction (PXRD) patterns in Figure 1a,b, which exhibit prominent peaks corresponding to 200 (*d* spacing, 13 Å) and 400 (*d* spacing, 6.6 Å) planes within the lamellar structure.[15] Consistent with previously described syntheses of PREFER,[15] scanning electron microscopy (SEM) shows large crystals (>20 μm in the longest dimension in Figure S1 in the Supporting Information), and transmission electron microscopy (TEM) clearly shows the expected rectilinear morphology of PREFER layers.

Initial attempts to delaminate PREFER used conditions that are similar to those previously described for synthesis of UCB-1, which employs a mixture of cetyltrimethylammonium bromide (CTAB), tetrabutylammonium fluoride (TBAF), and tetrabutylammonium chloride (TBACl) in aqueous solution.[8] This treatment partially swells PREFER, as shown by the PXRD pattern in Figure 1c consisting of decreased 200 peak intensity along with appearance of relatively small peaks at low angles of 2.5° (*d* spacing, 35 Å), 3.5° (25 Å), and 5.3° (17 Å), which are consistent with expanded layers.[2] However, addition of an aqueous solution of concentrated HCl aqueous to the swollen PREFER-containing slurry results in a full recovery of the 200 peak intensity in Figure 2c. This indicates lack of exfoliation, with formation of a PREFER-like material upon acidification, when UCB-1-type synthesis conditions for PREFER delamination are used.

We hypothesized that the use of organic solvents may facilitate delamination of PREFER in a manner that cannot be achieved in aqueous solution, on the basis of previous examples employing organic solvents for successful exfoliation of layered materials such as hydrotalcites[16−21] as well as the dissolution of hydrogen-bonded networks such as cellulose. A set of organic solvents consisting of ethanol (EtOH), dichloromethane (DCM), 4-methylmorpholine *N*-oxide (NMMO), and *N*-dimethylformamide (DMF)

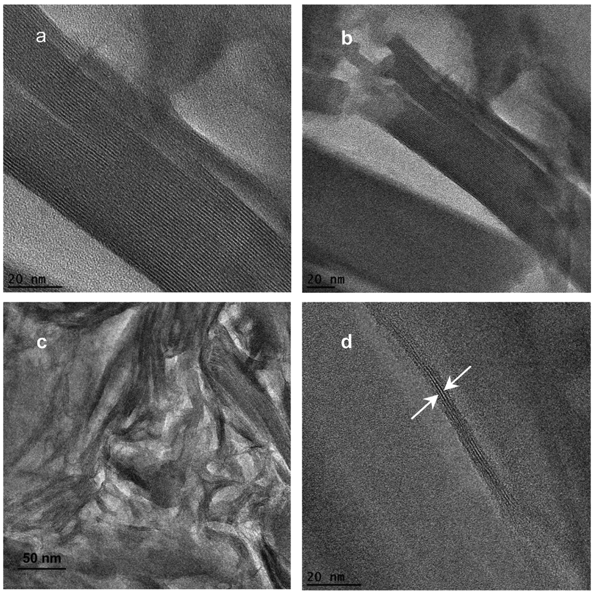

Figure 3. TEM images characterizing (a, b) PREFER and (c, d) UCB-2. The arrows in d indicate exfoliated layers.

were selected for PREFER delamination. Neither DCM nor EtOH swells PREFER according to data in Figure 1d,e, respectively. Although NMMO is known to dissolve cellulose, it is unable to swell PREFER, as shown in Figure 1f, which may be the result of its hampered hydrogen-bond accepting ability in the presence of water.[22,23] However, strong hydrogen-bond acceptor DMF completely swells PREFER, as shown by the disappearance of the 200 peak and the appearance of peaks at 2.3° (*d* spacing of 33 Å), 4.3° (21 Å), 5.3° (17 Å), and 1.8° (broad at 49 Å) in the PXRD data of Figure 1g, h. This result indirectly suggests the incorporation of DMF between PREFER layers in the swollen material and the crucial nature of interactions involving DMF during the delamination process. Addition of concentrated HCl to the swollen PREFER in DMF leads to the complete disappearance of these peaks in the PXRD pattern, and the appearance of small peaks at 6.1° (15 Å) and 12.3° (7.3 Å) in Figure 2g,h. This indicates the loss of long-range order along the *a*-axis (i.e., direction perpendicular to lamellae in the precursor material) as expected for delaminated layers. The integrity of order within each two-dimensional lamellae represented by *0kl* planes is consistent with small-intensity diffraction peaks in the vicinity of 23° in Figure 2h.

The material formed by delamination of PREFER in DMF (i.e., after swelling and subsequent acidification in DMF) is designated as UCB-2. TEM images of UCB-2 are shown in Figure 3 in comparison to PREFER. Figure 3c clearly shows the lack of rectilinear morphology and presence of curved layers, in contrast to Figure 3a,b for PREFER. The measured feature thickness in Figure 3d is consistent with a distance of approximately 1.1 nm, which is commensurate to two layers and indicative of PREFER delamination, since structures consisting of such a small number of layers are not observed prior to delamination (Figure 3a,b).

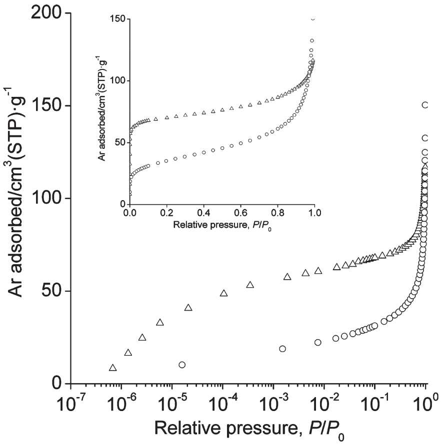

Figure 4. Argon gas adsorption characterizing (△) calcined PREFER (ferrierite) and (○) UCB-2 in a semi-logarithmic scale. The inset shows the same data in a linear scale.

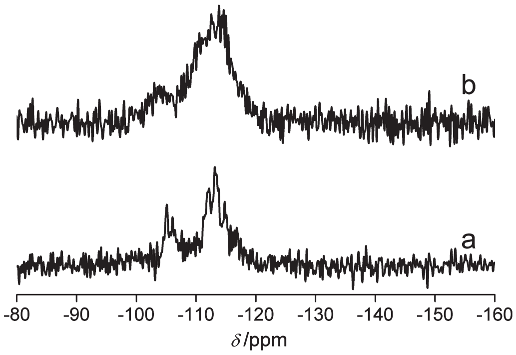

Figure 5. Solid-state ^{29}Si MAS NMR spectra characterizing (a) PREFER and (b) as-made UCB-2.

The extent of delamination is quantified using argon gas physisorption of calcined PREFER and UCB-2. Calcined PREFER exhibits measurable argon uptake at a relative pressure of as low as approximately 5×10^{-6} in Figure 4. This corresponds to filling of 10 MR pores by argon, as previously described in the literature.[2] Argon physisorption data shown in Figure 4 demonstrate significantly diminished uptake in micropore region ($P/P_0 < 0.02$) for UCB-2. The total micropore volume using data in Figure 4 and the *t*-plot method is 0.02 cm^3/g for UCB-2 and 0.08 cm^3/g for PREFER. The significant decrease in microporosity in UCB-2 relative to calcined PREFER indicates successful PREFER delamination in DMF using fluoride/chloride anions, since delaminated PREFER in the calcined form has been shown previously to possess essentially no microporosity.[2]

^{29}Si MAS NMR data of PREFER in Figure 5a show Q^3 resonances at approximately −105 and −106 ppm, and Q^4 resonances between −111 and −117 ppm, which match well with literature data.[15] The corresponding spectrum for UCB-2 in the as-made form retains Q^3 and Q^4 resonances observed for PREFER, as shown in Figure 5b. The lack of Q^2 resonances (expected at −90 ppm)[2] in Figure 5b indicates lack of amorphization in UCB-2, in contrast to results obtained previously for ITQ-6,[2] when the conventional delamination method is used. The high pH used in this latter method is likely responsible for the amorphization.[5] ^{27}Al MAS NMR spectroscopy of UCB-2 shows a single resonance corresponding to tetrahedral Al, which is similar to the spectrum previously reported for ITQ-6 (see Supporting Information Figure S2).[2] Elemental analysis of PREFER and UCB-2 show essentially no change in Si/Al ratio before and after delamination (74 for PREFER and 69 for UCB-2), indicating lack of dealumination upon exfoliation and delamination of what is a highly siliceous framework by composition. This is also illustrated by the following control experiment

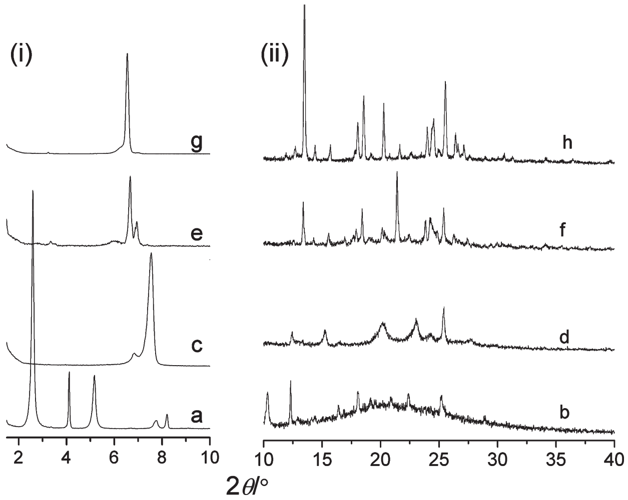

Figure 6. Powder XRD patterns in (i) low-angle region and (ii) high-angle region, respectively, characterizing (a−h) materials treated in *N*,*N*-dimethylformamide as follows: a and b, swelling PREFER with fluoride alone without chloride; c and d, acidifying material obtained in a and b; e and f, swelling PREFER with chloride without fluoride; g and h, acidifying material obtained in e and f.

employing zeolite ZSM-5 with a Si/Al ratio of 43 as a model, since PREFER is known to contain a significant amount of extra-framework aluminum.[15] This ZSM-5 was treated according to the same conditions as used for synthesis of UCB-2 from PREFER. The zeolite Si/Al ratio after this treatment remained unchanged via elemental analysis, indicating lack of Al leaching under delamination conditions.

To investigate necessity of fluoride and chloride anions during delamination of PREFER in DMF, delamination was attempted similarly to as that described above except in the absence of either fluoride or chloride anion. In the absence of chloride, PREFER is swollen, as indicated by the disappearance of the 200 peak and the appearance of three new peaks at 2.6° (*d* spacing, 34 Å), 4.1° (22 Å), and 5.2° (17 Å) in the PXRD pattern shown in Figure 6a, b. However, addition of concentrated HCl to this slurry leads to the complete disappearance of these new peaks and appearance of peaks resembling calcined PREFER, as shown in Figure 6c,d. These results indicate that absence of chloride results in the condensation of layers upon acidification and suggests a role for chloride that prevents this when DMF as solvent is used. Such a role for chloride is different from the one observed when aqueous fluoride/chloride in the synthesis of UCB-1 via delamination of MCM-22(P) is used. In that system, conducting delamination in the absence of chloride resulted in the entire absence of swelling and suggested a role for chloride as an essential species for facilitating interactions in the swollen material state. Fluoride is also a necessary component for delamination because treating PREFER with DMF in the absence of fluoride results in a lack of PREFER swelling. This is indicated by a nearly intact 200 peak in pattern in Figure 6g.

We wish to also investigate whether it is possible to synthesize UCB-1 using DMF rather than aqueous solution as solvent. The PXRD pattern of MCM-22(P) treated under similar conditions as used for synthesis of UCB-2 shows a sharp peak at 2.0° (44 Å) (see Figure S3 in the Supporting Information). This means that MCM-22(P) can be swollen in DMF. However, addition of concentrated HCl to the resulting slurry containing the swollen material leads to the complete recovery of 001 and 002 peaks at 3.3° (27 Å) and 6.6° (13 Å) (see Figure S4 in the Supporting Information), respectively, which are attributable to MCM-22(P) and indicate lack of delamination in DMF. These observed differences in requirements for synthesis of UCB-1 and UCB-2 could be due to either the different framework topologies or the different SDA employed in zeolite precursor syntheses. Both this result and the inability to synthesize UCB-2 under conditions used for UCB-1 (vide supra) implicate the importance of self-assembly and noncovalent interactions between the layered zeolite precursor framework and participating cations/anions and solvent during delamination via swelling and acidification.

The reversibility of the interactions involved in swelling and acidification during synthesis of UCB-2 is investigated by the following experiment. After acidification, the slurry consisting of delaminated PREFER in the form of UCB-2 is treated once more with fluoride/chloride and surfactant in DMF. Our hypothesis is that if no irreversible damage (i.e., amorphization or intralayer bond cleavage) has occurred in UCB-2, then a material similar to swollen PREFER should result. This should occur presumably via F^--promoted cleavage of any covalent Si−O−Si connectivity formed after acidification. The PXRD pattern in Figure S5 (Supporting Information) after addition of fluoride/chloride and surfactant in DMF following acidification closely matches the pattern observed for swollen PREFER. This result provides evidence for the reversibility of the delamination process as well as confirms the hypothesis above. It also lends credence to the view of delamination as the microscopic reverse of zeolite synthesis and suggests that the same noncovalent interactions between organic and inorganic species are involved in both.

■ CONCLUSION

The results presented here demonstrate the successful delamination of PREFER under mild conditions using fluoride and chloride anions in DMF. DMF facilitates swelling of PREFER more efficiently than other polar solvents including water and NMMO. Both fluoride and chloride anions are required for complete delamination of PREFER layers. Results from ^{29}Si and ^{27}Al MAS NMR spectroscopy of the delaminated PREFER material show retention of structural integrity of PREFER layers and incorporation of tetrahedral aluminum atoms. In particular, the entire lack of a Q^2 resonance in the ^{29}Si MAS NMR spectrum for the delaminated PREFER material highlights the lack of amorphous silica phase with the current synthetic method, which is in stark contrast to reported results with the conventional method at high pH. Reversibility experiments reinforce the concept of delamination as the reverse of zeolite synthesis, and the importance of organic−inorganic self-assembly. The new synthetic method comprising fluoride/chloride anion-promoted delamination is anticipated to be generalizable to other structures and to find widespread use for the synthesis of new classes of delaminated layered zeolite precursor materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. SEM of PREFER, ^{27}Al MAS NMR spectrum of UCB-2, and PXRD patterns of MCM-22(P), MCM-22(P) treated with fluoride/chloride-promoted method in DMF, and swollen or acidified PREFER (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: iogino@eng.hokudai.ac.jp (I.O.); sizo@chevron.com (S.I.Z.), askatz@berkeley.edu (A.K.).

Present Addresses

¶Centre for Materials Science and Nanotechnology/InGAP/Department of Chemistry, University of Oslo, Postbox 1033, Blindern, 0315 Oslo, Norway. (E.A.E). Division of Chemical Process Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo, 060-8628, Japan. (I.O.)

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