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Steam-Stable Aluminosilicate Mesostructures Assembled from Zeolite Type Y Seeds

Yu Liu, Wenzhong Zhang, and Thomas J. Pinnavaia*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

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Soon after the discovery of mesoporous MCM-41 molecular sieves,[1] it was found that the incorporation of aluminum into the framework introduced mild acidic functionality. However, the long range order and tetrahedral siting of the aluminum was compromised,[2] especially at aluminum loading above $\sim$8 mol %. Mild acidity and loss of structural integrity, together with poor steam stability under regeneration conditions made hexagonal Al−MCM-41 compositions unattractive candidates for the processing of high molecular weight petroleum fractions. More recently, important advances have been made in improving the structural integrity of Al−MCM-41 through direct assembly[3] and postsynthesis modification methods.[4] However, the low acidity and poor steam stability still limit potential applications in petroleum refining.[5]

We report here that the structural order, acidity, and steam stability of hexagonal aluminosilicate mesostructures all can be substantially improved through the assembly of nanoclustered precursors that normally nucleate the crystallization of microporous zeolites. These precursors, also known as "zeolite seeds", are presumed to promote zeolite nucleation by adopting AlO_4 and SiO_4 tetrahedra connectivities that resemble the secondary structural elements in a crystalline zeolite.[6] Assembling these same zeolite seeds into a mesostructure imparts acidity and hydrothermal stability that begin to approach zeolites, even though the framework walls remain atomically disordered.

We describe here the synthesis and properties of a typical hexagonal aluminosilicate mesostructure (Si:Al = 9:1) derived from seeds that normally nucleate the crystallization of faujasitic zeolite type Y.[6,7] Nanoclustered zeolite Y seeds were prepared by reacting NaOH (0.088 mol) and $NaAlO_2$ (0.10 mol, Strem Chemicals) in H_2O (8.5 mol) with silicate anions (0.90 mol) in the form of a sodium silicate solution containing 27 wt % SiO_2 and 14 wt % NaOH (Aldrich Chemicals) under vigorous stirring at 100 °C overnight. ^{27}Al NMR indicated the exclusive presence of tetrahedral aluminum ($\delta = 60$ ppm), and the XRD pattern of a thin film sample obtained by evaporation of the seeds solution showed no Bragg peaks. The formation of a hexagonal mesostructure, rather than a zeolite, was achieved by lowering the pH of the seeds solution to a value of $\sim$9 and introducing a surfactant after the initial aging period. Thus, the addition of cetyltrimethylammonium bromide (0.20 mol), sulfuric acid (0.52 mol) and water (127 mol) to the seeds solution, followed by an additional aging period of 20 h at 100 °C afforded a hexagonal aluminosilicate mesostructure, which we denote generally as MSU−S, or, more specifically, 10%Al−MSU−S.

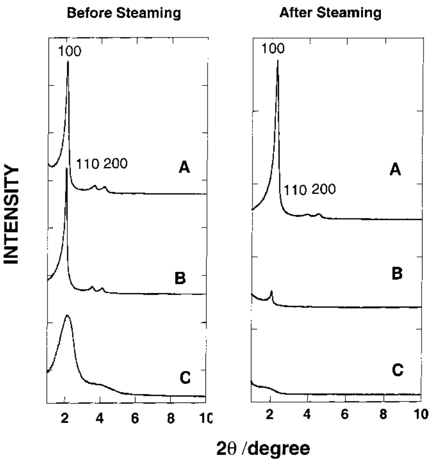

Figure 1. XRD patterns of calcined (540 °C, 7 h) mesoporous aluminosilicate molecular sieves before and after steaming (800 °C, 5 h): (A) hexagonal 10%Al−MSU−S; prepared from zeolite Y seeds; (B) "ultrastable" hexagonal 14%Al−MCM-41 prepared by grafting; (C) disordered 10%Al−MCM-41 prepared by direct synthesis from conventional silicate and aluminate precursors. The intensity scale is the same for the samples before and after steaming. Hexagonal unit cell parameters are provided in Table 1.

Treatment of the as-made mesostructure with 0.1 M NH_4NO_3 at 100 °C displaced exchangeable sodium ions, as well as 50% of the surfactant from the mesostructure. The product then was calcined at 540 °C for 7 h to remove the remaining surfactant and to convert NH_4^+ at exchange sites to protons. Chemical analysis indicated a Si:Al molar ratio of 9:1, along with the presence of carbon (0.80 wt %) formed through the cracking of surfactant during calcination. Figure 1 illustrates the XRD patterns of calcined 10%Al−MSU−S before and after exposure to 20% (v/v) water vapor in N_2 at 800 °C for 5.0 h. Included in Figure 1 are the corresponding patterns for 14%Al−MCM-41 prepared by a very recently reported postsynthesis grafting reaction between a sodium-free MCM-41 silica and Al_{13} oligocations.[8] This grafted form of Al−MCM-41 has been described as being "ultrastable" in comparison to all previously reported Al−MCM-41 derivatives. Also, included in Figure 1 are the patterns for disordered 10%Al−MCM-41 obtained by the same direct assembly route and postsynthesis NH_4^+ exchange reaction used to prepare 10%Al−MSU−S, except that the 100 °C aging step leading to the formation of zeolite type Y seeds was eliminated. The broadening of the diffraction lines for this calcined sample is indicative of the disorder that normally accompanies the assembly of Al−MCM-41 from conventional precursors.

The XRD results clearly indicate that the Al−MSU−S mesostructure assembled from nanoclustered zeolite seeds retains a well-ordered hexagonal structure upon steaming at 800 °C. In comparison, the mesostructures prepared from conventional silicate and aluminate precursors or by ultrastable grafting reaction are almost totally destroyed by steaming. These observations are supported by a comparison of the N_2 sorption isotherms shown in Figure 2 for the same series of mesostructures. The surface areas, framework pore sizes, and pore volumes derived from these sorption isotherms are provided in Table 1. The 10%Al−MSU−S retains more than 90% of it surface area and about 75% of its framework pore volume after steaming. In addition, the steam treatment improves the textural porosity of the mesostructure as

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[1] Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olsen, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 4, 10834.

[2] (a) Chen, C.-Y.; Li, H. -X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17. (b) Borade, R. B.; Clearfield, A. *Catal. Lett.* **1995**, *31*, 267. (c) Luan, Z. H.; Cheng, C. F.; He, H. Y.; Klinowski, J. *J. Phys. Chem.* **1995**, *99*, 10590.

[3] Janicke, M. T.; Landry, C. C.; Chistiansen, S. C.; Brirtalan, S. B.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater*. **1999**, *11*, 1342.

[4] (a) Hamdan, H.; Endud, S.; He, H.; Mohd Muhid, M. N.; Klinowski, J. *J. Chem. Soc., Faraday Trans* **1996**, *92*, 2311 (b) Mokaya, R.; Jones, W. *Chem. Commun*. **1997**, 2185. (c) Ryoo, R. Jun, S.; Kim, J. M.; Kim, M. J. *Chem. Commun*. **1997**, 2225.; (d) Ryoo, R.; Ko, C. H.; Howe, R. F. *Chem. Mater*. **1998**, *9*, 1607;

[5] Corma, A. *Chem. Rev.* **1997**, 2373

[6] Robson, H. *ACS Symp. Ser.* **1989**, *398*, 436.

[7] Lechert, L.; Staelin, P.; Wrobel, M.; Schimmel, U. *Stud. Surf. Sci. Catal.* **1994**, *84*, 147.

[8] Mokaya, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 2930

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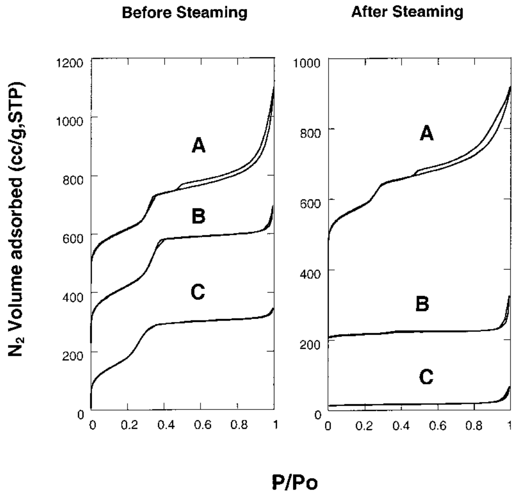

Figure 2. N_2 adsorption/desorption isotherms for calcined (540 °C, 7 h) mesoporous aluminosilicate molecular sieves before and after steaming (20 vol % H_2O in N_2, 800 °C, 5h): (A) 10%Al−MSU−S; (B) "ultrastable" 14%Al−MCM-41 prepared by grafting; (C) 10%Al−MCM-41 prepared by direct synthesis. The isotherms are offset by 200 cm^3/g for clarity.

Table 1. Textural Properties of Mesoporous Aluminosilicate Sieves Before and After Steaming

sample	unit cell dimension, a_o (Å)	surface area (m^2/g)	pore vol. (cc/g)	pore dia. (Å)
		10% Al−MSU−S		
calcined	48.6	713	0.56	32.1
steamed	44.5	652	0.42	30.3
		14%Al−MCM-41[a]		
calcined	49.6	760	0.58	29.8
steamed		62	0.07	
		10% Al−MCM-41[b]		
calcined	45.5	721	0.53	33.4
steamed		31	0.03	

[a] Prepared by grafting. [b] Prepared by direct synthesis from conventional silicate and aluminate precursors.

evidenced by the hysteresis behavior at partial pressures above 0.50. In contrast, little or no surface area or framework pore volume is retained in either of the Al−MCM-41 samples after steaming.

We attribute the unique hydrothermal stability of Al−MSU−S at least in part to the retention of a zeolite-like connectivity of AlO_4 and SiO_4 tetrahedra upon assembling the zeolite seeds into a mesostructure. Also, the occluded carbon contributes to the structural stability, because calcined samples with lower carbon content exhibited a substantially greater loss in surface area and pore volume upon steaming. However, in support of the importance of a zeolite-like connectivity, we note that the ^{27}Al chemical shift of tetrahedral aluminum in as-made and calcined Al−MSU−S occurs at $\delta = 60$ ppm, the same value as the seeds solution and within the 59−65 ppm range observed for most zeolites.[9] This chemical shift value is unique among aluminosilicate mesostructures. All previously reported mesostructured aluminosilicates, including the Al−MCM-41 samples of the present work, exhibit a chemical shift in the range 53−56 ppm. On the basis of the relationship between ^{27}Al chemical shift and the mean bond angle in framework aluminosilicates,[9] the mean Al−O−Si angle is substantially smaller (by ~8°) in Al−MSU−S than in previously reported forms of Al−MCM-41.

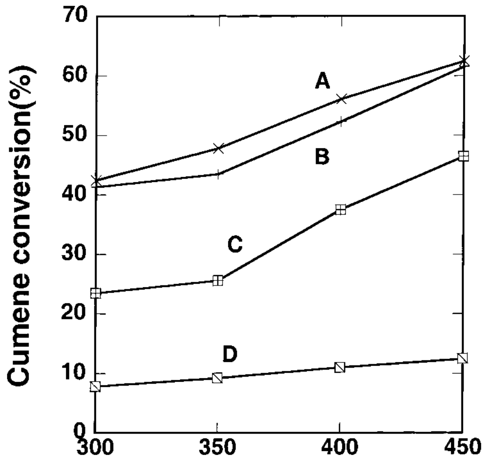

Figure 3. Cumene conversions over mesoporous aluminoslicates in the temperature range 300−450 °C: (A and C) conversions obtained for calcined and steamed samples of 10%Al−MSU−S, respectively; (B and D) conversions for calcined and steamed samples, respectively, for 10%Al−MCM-41 prepared by direct synthesis. Reaction conditions: 6 mm i.d. fixed bed quartz reactor; 200 mg catalyst; cumene flow rate, 4.1 μmol/min; N_2 carrier gas, 20 cm^3/min; conversions reported after 60 min on stream.

The acidic properties of 10%Al−MSU−S for cumene cracking over the temperature range 300−450 °C are compared in Figure 3 with those of 10%Al−MCM-41 assembled from conventional aluminate and silicate precursors. Although the two calcined mesostructures are nearly equivalent in activity, 10%Al−MSU−S is a far more active catalyst after exposure to steam. This result illustrates the potential importance of nanoclustered zeolite seeds as precursors for the design of hydrothermally stable mesostructures for catalytic applications.

The use of zeolite seeds as precursors for the assembly of steam stabile aluminosilicates mesostructures is not limited to compositions containing 10 mol % aluminum. We also have used zeolite Y seeds to prepare Al−MSU−S compositions containing 0.01−38 mol % Al with retention of the structural, steam stability, and acidic properties found for 10%Al−MSU−S. In addition, our approach is not limited to the use of type Y zeolite seeds. Using 2.8 nm ZSM-5 seeds templated by tetrapropylammonium ions,[10] we also have assembled related hexagonal aluminosilicate mesostructures. Future studies will report on mesostructures derived from these and other nanoclustered zeolite seeds.

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(9) Lippma, E.; Samoson, A.; Mägi, M. *J. Am. Chem. Soc.* **1986**, *108*, 1730.

(10) (a) Watson, J. N.; Brown, A. S.; Iton, L. E.; White, J. W. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2181. (b) de Moor, P. P. E. A.; Beelen, T. P. M.; Komanschek, B. U.; van Santen, R. A. *Microporous Mesoporous Mater.* **1998**, *21*, 263.