Communications

Assembly of Hydrothermally Stable Aluminosilicate Foams and Large-Pore Hexagonal Mesostructures from Zeolite Seeds under Strongly Acidic Conditions

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Significant advances have been made recently in improving both the hydrothermal stability and acidity of Al−MCM-41 mesostructures through the use of protozeolitic aluminosilicate nanoclusters or “zeolite seeds” as framework precursors. These nanoclusters contain the secondary building blocks of the zeolite structures that they nucleate. The first demonstration of this approach to stable aluminosilicate mesostructures[1] utilized faujasitic zeolite seeds (FAU) to construct the walls of a hexagonal MCM-41 structure. More recently, we[2] and others[3] have used ZSM-5 (MFI) and zeolite beta (BEA) seeds to assemble steam-stable Al−MCM-41 derivatives containing the five-ring subunits of these pentasil zeolites. In an effort to assemble steam-stable framework structures with pore sizes substantially larger than those provided by MCM-41, we have examined the possibility of using zeolite seeds to assemble mesostructured cellular foams (MCF)[4,5] and very large pore hexagonal mesostructures that are structurally analogous to SBA-15.[4,6] Unlike MCM-41 mesostructures, which are assembled under basic pH conditions compatible with protozeolitic seeds formation, MCF and SBA-15 mesostructures require strongly acidic reaction conditions for assembly that may not be so favorable for the incorporation of zeolitic subunits into the framework walls. Our objective here was to determine whether the protozeolitic seeds that are formed initially under basic pH conditions could survive the strongly acidic conditions needed to assemble high-quality foams and large-pore hexagonal mesostructures.

Faujasitic zeolite Y (FAU), zeolite ZSM-5 (MFI), and zeolite beta (BEA) seeds (Si/Al = 50) were prepared using procedures analogous to those described previously.[1,7] FAU seeds (Si/Al = 5.6) were prepared by reacting sodium silicate and sodium aluminate at 100 °C for 12 h, diluting the mixture with sodium silicate solution to obtain a Si/Al ratio of 50, and then digesting the mixture an additional 12 h at 100 °C before use in preparing the desired mesostructure. MFI and BEA seeds were prepared using aluminum *sec*-butoxide and tetraethyl orthosilicate as precursors and tetrapropyl- and tetraethylammonium ions as structure directors, respectively. These latter solutions were digested at 100 °C for 3 h before use in constructing mesostructures. In agreement with earlier results,[2] the solids formed by the evaporation of the BEA and MFI seeds solutions exhibited IR bands in the 550−600-cm^{-1} region, indicative of the presence of five rings, but no phase formation was indicated in the XRD pattern. The FAU seeds also exhibited an amorphous XRD pattern. In addition, single tetrahedral ^{27}Al MAS NMR lines with the expected chemical shifts of 62, 54, and 53 ppm were observed for the FAU, MFI, and BEA seeds, respectively.

A mesostructured aluminosilicate cellular foam (Si/Al = 50) was prepared from FAU seeds by adding the seeds to a microemulsion containing Pluronic 123 surfactant, $(EO)_{20}(PO)_{70}(EO)_{20}$, and 1,3,5-trimethylbenzene (TMB) as a cosurfactant to provide a mixture with the molar composition 1.00:0.010:0.013:0.51:70.0 SiO_2:Al_2O_3:P123:TMB:H_2O. The pH of the mixture was adjusted to 4.5−6.5 by the addition of 1.7 M H_2SO_4, aged at 25−60 °C for 20−40 h and finally heated at 100 °C under static conditions for 24 h. Analogous foam compositions were prepared from MFI and BEA seeds by adding the seeds to an acidic emulsion of P123, TMB, and HCl to obtain a reaction mixture with the composition 1.00:0.010:0.017:0.79:4.95:158 SiO_2:Al_2O_3:P123:TMB:HCl:H_2O, stirring the mixture at 35 °C for 20 h, and then allowing the strongly acidic mixture ($pH < 2$) to digest under static conditions at 100 °C for 24 h. The as-made products were washed, air-dried, and calcined at 600 °C for 4 h to remove the surfactant. The mesostructured cellular foams constructed from FAU, MFI, and BEA seeds were denoted MSU−S/F_{FAU}, −S/F_{MFI}, and −S/F_{BEA}, respectively.

Each of the as-made MSU−S/F mesostructures exhibited ^{27}Al MAS NMR and IR spectra equivalent to the spectra observed for the initial protozeolitic seeds,

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(1) Liu, Y.; Zhang, W.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8791.

(2) Liu, Y.; Zhang, W.; Pinnavaia, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1255.

(3) Zhang, Z. T.; Han, Y.; Xiao, F. S.; Qiu, S. L.; Zhu, L.; Wang, R. W.; Yu, Y.; Zhang, Z.; Zou, B. S.; Wang, Y. Q.; Sun, H. P.; Zhao, D. Y.; Wei, Y. *J. Am. Chem. Soc.* **2001**, *123*, 5014. Zhang, Z. T.; Han, Y.; Zhu, L.; Wang, R. W.; Yu, Y.; Qiu, S. L.; Zhao, D. Y.; Xiao, F. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1258.

(4) Zhao, D. Y.; Feng, J. L.; Huo, Q. S.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548;

(5) Schmidt-Winkel, P.; Lukens, W. W.; Zhao, D. Y.; Yang, P. D.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1999**, *121*, 254. Schmidt-Winkel, P.; Glinka, C. J.; Stucky, G. D. *Langmuir* **2000**, *16*, 356.

(6) Zhao, D.; Hou, Q. S.; Feng, J. L.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(7) Lechert, L.; Staelin, P.; Wrobel, M.; Schimmel, U. *Stud. Surf. Sci. Catal.* **1994**, *84*, 147. Robson, H. *ACS Symp. Ser.* **1989**, *398*, 436. Kirschhock, C. E. A.; Ravishankar, R.; Jacobs, P. A.; Martens, J. A. *J. Phys. Chem. B* **1999**, *103*, 11021. Kirschhock, C. E. A.; Ravishankar, R.; Verspeurt, F.; Grobet, P. J.; Jacobs, P. A.; Martens, J. A. *J. Phys. Chem. B* **1999**, *103*, 4965. Kirschhock, C. E. A.; Ravishankar, R.; Van Looveren, L.; Jacobs, P. A.; Martens, J. A. *J. Phys. Chem. B* **1999**, *103*, 4972. Perez-Pariente, J.; Martens, J. A.; Jacobs, P. A. *Appl. Catal.* **1987**, *31*, 35.

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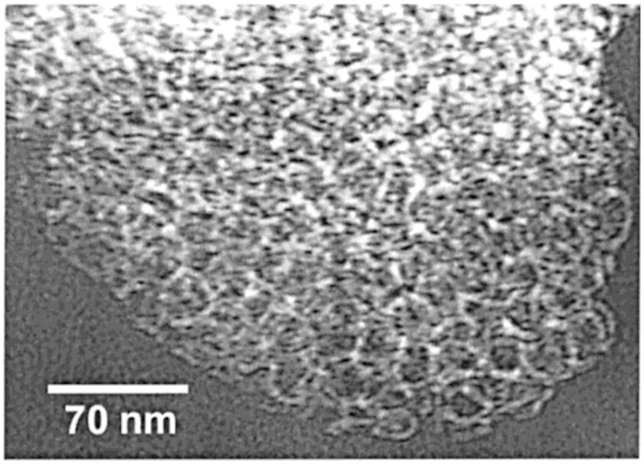

Figure 1. TEM image of a MSU−S/F_{FAU} aluminosilicate foam assembled from faujasitic zeolite seeds.

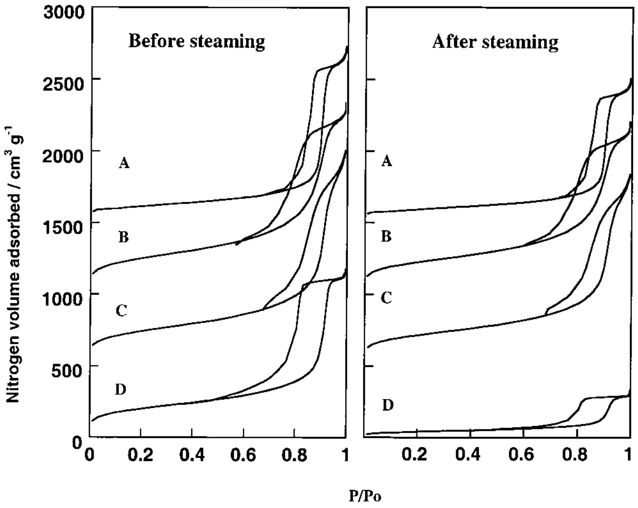

Figure 2. N_2 adsorption−desorption isotherms of mesostructured aluminosilicate foams before and after exposure to 20% steam in nitrogen at 800 °C for 2 h: (A) MSU−S/F_{FAU}, (B) MSU−S/F_{MFI}, (C) MSU−SF_{BEA}, and (D) MCF. Each isotherm is offset by 500 cm^3 g^{-1}.

Table 1. Textural Properties of Calcined Mesostructured Aluminosilicate Foams (Si/Al = 50) before and after Hydrothermal Stability Tests[a]

sample	window size (nm)	cell size (nm)	surface area (m²/g)	pore vol. (cm³/g)
MSU−S/F_{FAU}				
before steaming	132	208	570	1.79
after steaming	126	204	462	1.46
boiling H_2O	118	196	273	0.78
MSU−S/F_{MFI}				
before steaming	102	201	888	1.95
after steaming	95	195	748	1.68
boiling H_2O	90	187	463	0.96
MSU−S/F_{BEA}				
before steaming	128	220	861	2.18
after steaming	124	215	737	1.86
boiling H_2O	117	210	647	1.87
MCF				
before steaming	110	228	715	1.79
after steaming	105	220	147	0.44
boiling H_2O			103	

[a] Calcined samples were exposed to 20% steam in nitrogen at 800 °C for 2 h or to boiling water for 250 h.

Table 2. Textural Properties of Calcined Large-Pore Hexagonal Mesostructured Aluminosilicates (Si/Al = 50) before and after Hydrothermal Stability Tests

sample	surface area (m²/g)	*d* spacing[b] (Å)	unit cell size[c] (Å)	pore size[d] (Å)	pore vol. (cm³/g)
MSU−S/H_{MFI}					
before steaming	886	102	118	77	0.93
after steaming[a]	701	95	110	69	0.78
MSU−S/H_{BEA}					
before steaming	849	101	117	76	0.90
after steaming	687	96	111	70	0.77
MSU−S/H_{FAU}					
before steaming	653	110	127	90	0.85
after steaming	421	95	110	80	0.57
SBA-15					
before steaming	823	101	117	77	0.89
after steaming	305	86	96	60	0.31

[a] Steaming conditions: 800 °C, 2 h, 20% H_2O in N_2. [b] $d(100)$ spacing is the reflection of calcined samples. [c] Unit size was calculated from the relationship $a = 2d_{100}/\sqrt{3}$. [d] Determined by the BJH method using the adsorption branch of the N_2 isotherm.

indicating that the same subunits present in the seeds were incorporated into the mesostructures. TEM images of the calcined derivatives verified the formation of a reticulated foamlike structure. As is illustrated in Figure 1 for MSU−S/F_{FAU}, these structures are defined by strutlike walls that frame windows opening into spherical cells.

Figure 2 shows the N_2 adsorption and desorption isotherms for the calcined MSU−S/F foams before and after exposure to 20% steam at 800 °C for 2 h. Included for comparison are the corresponding isotherms for a MCF assembled from conventional aluminosilicate precursors. Table 1 provides the BJH window and cell sizes deduced from the desorption and adsorption branches of the isotherms, along with the BET surface areas and pore volumes. Included in the table are the textural properties for the foams after exposure to boiling water for 250 h. Clearly, the MSU−S foams assembled from zeolite seeds, which retain at least 80% of their initial surface area and pore volume after steaming, exhibit greatly improved hydrothermal stability in comparison to a foam assembled from conventional aluminosilicate precursors (<25% retention of surface area and pore volume after steaming).

The as-made MSU−S/F mesostructures each exhibited the same ^{27}Al NMR chemical shifts as the starting seeds solutions, indicating that all of the aluminum adopted tetrahedral positions in the framework walls. Upon calcination at 600 °C, the MSU−S/F foams retained between 80 and 95% of the aluminum centers in tetrahedral framework sites after calcination, as evidenced by the relative intensities of the tetrahedral and octahedral ^{27}Al resonances in the 52−62 and 0−10 ppm regions, respectively. In contrast, almost all the aluminum centers in the conventional MCF derivative occupy extraframework octahedral sites in both the as-made and the calcined forms. However, the use of protozeolitic precursors effectively integrates tetrahedral aluminum centers into the walls of MSU−S foams and imparts exceptional hydrothermal stability to the mesostructures. This dramatic difference in the siting of aluminum centers in the as-made forms of MSU−S/F and conventional MCF mesostructures points to the benefit of utilizing preformed protozeolitic nanoclusters in the assembly of aluminosilicate mesostructure even under strongly acidic conditions.

Extending the use of zeolite seeds to the assembly of large-pore hexagonal structures, we prepared SBA-15 analogues using the same FAU, MFI, and BEA seeds, reaction conditions, and procedures that were used to prepare the above MSU−S/F mesostructures, except that the TMB cosurfactant was eliminated from the reaction mixtures. The hexagonal long-range structure of the calcined mesostructures, which we denote MSU−S/H, was verified by XRD, and the hydrothermal stability of each mesostructure was tested against 20% steam at 800 °C for 2 h.

The textural properties of the MSU−S/H mesostructures (Si/Al = 50) before and after hydrothermal testing are provided in Table 2. The properties of a compositionally equivalent SBA-15 mesostructure assembled from conventional aluminosilicate precursors are included for comparison. After exposure to steam, MSU−S/H$_{FAU}$ retains >65% of its initial surface area and pore volume. MSU−S/H$_{MFI}$ and MSU−S/H$_{BEA}$ are even more stable to steam, retaining >80% of the initial surface areas and pore volumes with little pore contraction. In contrast, a conventional SBA-15 retains only ≈35% of its mesostructure and undergoes substantial pore contraction upon steaming. Equally dramatic differences in hydrothermal stability are observed between MSU−S/H and a conventional SBA-15 aluminosilicate after exposure to boiling water.

Although the construction of MSU−S/F and MSU−S/H mesostructures from zeolite seeds required the pH of the initial seeds mixtures to be lowered from initially basic values to acidic values in the range from <2 to 6.5, protozeolitic nanoclusters clearly persist under acidic conditions and can be incorporated into the final mesostructures. Thus, the concept of incorporating zeolite seeds into the walls of an aluminosilicate mesostructure as a means of improving hydrothermal stability is quite general and applies even to mesostructures that require strongly acidic conditions for assembly.

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