

Highly Acidic Mesostructured Aluminosilicates Assembled from Surfactant-Mediated Zeolite Hydrolysis Products

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The surfactant-mediated hydrolysis of ZSM-5 zeolite affords five-membered ring subunits that can be readily incorporated into the framework walls of a hexagonal mesostructured aluminosilicate, denoted MSU-Z. The five-membered ring subunits, which are identifiable by infrared spectroscopy, impart unprecedented acidity to the mesostructure, as judged by cumene cracking activity at 300 °C. Most notably, MSU-Z aluminosilicate made through the base hydrolysis of ZSM-5 in the presence of cetyltrimethylammonium ions exhibits a cumene conversion of 73%, which is 6.7-fold higher than the conversion provided by a conventional MCM-41. This approach to stabilizing zeolitic subunits through surfactant-mediated hydrolysis of zeolites appears to be general. The hydrolysis of USY zeolite under analogous hydrolytic conditions also affords zeolitic fragments that boost the acidity of the mesostructure in comparison to equivalent compositions prepared from conventional aluminosilicate precursors.

The high surface areas and large pore sizes of mesostructured aluminosilicates¹ have been recognized as desirable properties for the catalytic processing of high molecular weight petroleum fractions.² However, due to the absence of atomic order in the mesostructured framework, these compositions lack the desired hydrothermal stability and acidity. In 2000, a novel approach to the preparation of mesostructured derivatives with improved hydrothermal stability and acidity was reported based on the incorporation of protozeolitic nanoclusters or “zeolite seeds” in the framework.³ This was accomplished by quenching a zeolite synthesis gel prior to the onset of zeolite crystal formation and then transforming the quenched gel into a mesostructure. The generality of this approach and the spectroscopic evidence supporting the presence of zeolitic subunits in the mesostructured framework has been substantiated by several subsequent studies.^{4–11}

In the present work we describe the surfactant-mediated transformation of ZSM-5 zeolite into a MCM-41 aluminosilicate mesostructure with retention of the five-ring subunits (zeolite fragments) found in the starting zeolite. This “top-down” approach to incorporating zeolitic subunits into the framework walls of a mesostructure substantially boosts the acidity of the mesostructure far beyond the levels achievable through the “bottom-up” methodology based on the formation of protozeolitic seeds.³ Evidence for the effectiveness of this new approach to incorporating zeolitic subunits into a mesostructure framework is provided by FTIR spectroscopy and by the activity of the mesostructures as cumene cracking catalysts. An analogous surfactant-mediated transformation of USY zeolite into MCM-41 also substantially increases the acidity of the resulting mesostructure, suggesting that zeolitic fragments other than five-membered rings also can be incorporated into the framework of a mesostructure.

Our “top-down” approach to improving the incorporation of zeolitic subunits into the framework walls of a mesostructure is based on the hydrolysis of a pre-formed zeolite (ZSM-5) in the presence of a cationic surfactant that stabilizes the zeolitic subunits through ion pairing. The cationic surfactant also serves as a structure-directing porogen for the assembly of the mesostructure. Thus, in the case of zeolite ZSM-5 as a precursor, 2.0 g (33.3 mmol) of the zeolite (Zeolyst, Si/Al = 40) was dispersed in a solution containing 55 mL of 0.45 M NaOH ($\text{OH}^-/T = 0.75$, where $T = \text{Si} + \text{Al}$) and 2.45 g (6.7 mmol) cetyltrimethylammonium bromide (CTAB) under vigorous stirring for 60 min. The resulting mixture was transferred into a Teflon-lined autoclave and heated at 100 °C for 24 h to degrade the zeolite. The mixture was cooled to room temperature and the pH was adjusted to 9.0 through the addition of dilute sulfuric acid. The mixture was then aged at 100 °C for another 24 h to form a hexagonal MCM-41 mesostructure. The product, denoted MSU-Z, was washed with distilled water, air-dried, and calcined at 600 °C for 4 h to remove the surfactant. The protonated form of MSU-Z was obtained by duplicate ion-exchange with 0.5 M NH_4NO_3 solution at 60 °C for 2 h and then calcining the product at 550 °C. An equivalent procedure was used in forming hexagonal MSU-Z using USY zeolite (Zeolyst, Si/Al = 40) as a precursor, except that the hydrolysis solution contained 0.10 M NaOH ($\text{OH}^-/T = 0.17$).

The Si/Al ratios for the mesostructured products (Table 1) are equivalent to those of the initial zeolite precursors. Also, after ammonium ion exchange, only a trace amount of Na^+ is present in the mesostructure.

Figure 1 illustrates the XRD patterns of MSU-Z materials assembled from ZSM-5 and USY fragments. Both samples show the same hexagonal symmetry characteristic of MCM-41, but no Bragg peaks indicative of a zeolite phase. Also, we were unable to observe lattice fringes indicative of atomic order by

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TABLE 1: Textural Properties and Cumene Cracking Activity of Hexagonal Mesostructured Aluminosilicates

mesostructure	Si/AlZeolite precursor	Si/Al mesostructured product	NaOH concentrated ^a (mol/L)	unit cell size (nm)	BJH pore size (nm)	BET surface area (m ² /g)	pore vol. (cm ³ /g)	Cumene conv. ^b (%)
MCM-41 (conventional)		50		4.64	2.4	1135	0.87	11
MSU-Z from ZSM-5	40	42	0.45	4.98	2.4	1160	0.86	74
MSU-Z from USY	40	43	0.10	4.98	2.5	1051	0.86	37
mesostructure formed from over-hydrolyzed ZSM-5	40		0.91	4.75	2.2	1114	0.73	17

^a Concentration of base used to hydrolyze the zeolite precursor. ^b Cumene cracking reaction was carried out at 300 °C in a 6 mm i.d. fixed bed quartz reactor; 200 mg catalyst; cumene flow rate, 4.1 μ mol/min; N₂ carrier gas, 20 cm³/min; time-on-stream, 3 h.

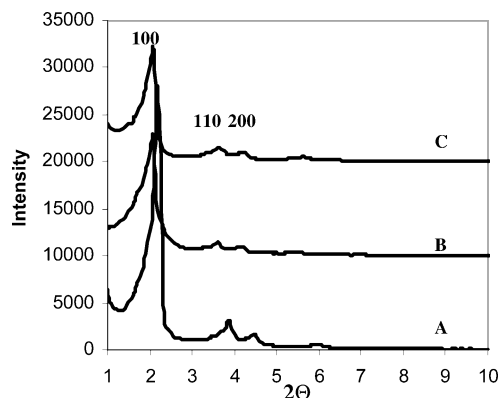


Figure 1. X-ray powder diffraction patterns of calcined mesostructured aluminosilicates: (A) MCM-41 (Si/Al = 50) assembled from conventional silicate and aluminate precursors; (B) MSU-Z (Si/Al = 40) assembled from zeolitic fragments formed by hydrolysis of USY zeolite in 0.10 M NaOH ($\text{OH}^-/\text{T} = 0.171$); (C) MSU-Z (Si/Al = 40) assembled from zeolite fragments generated from ZSM-5 in 0.45 M NaOH ($\text{OH}^-/\text{T} = 0.75$).

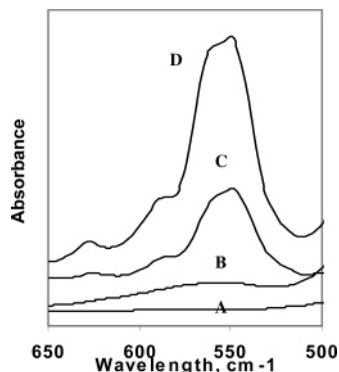


Figure 2. FT-IR spectra of calcined mesostructured aluminosilicates (2 mg per 400 mg KBr) for (A) MCM-41 assembled from conventional precursors; (B) MSU-S assembled from protozeolitic ZSM-5 seeds; (C) MSU-Z assembled from zeolite fragments generated through the surfactant mediated hydrolysis of ZSM-5 zeolite in 0.45 M NaOH ($\text{OH}^-/\text{T} = 0.75$); and (D) pristine ZSM-5, respectively.

transmission electron microscopy. Thus, we conclude that an authentic atomically ordered zeolite phase is absent. The ²⁷Al MAS NMR chemical shifts of the as-made MSU-Z indicate that all of the aluminum in the mesostructures is in tetrahedral coordination. Upon calcination, some octahedral aluminum is observed at ~3 ppm, but the majority of aluminum centers remain in tetrahedral coordination.

As shown in Figure 2, the IR spectrum of MSU-Z formed from ZSM-5 fragments (curve C) exhibits an intense band near 550 cm⁻¹, indicative of five-membered ring subunits¹² analogous to those subunits found for the pristine zeolite (curve D). This band is absent in the spectrum of MCM-41 prepared from conventional aluminosilicate precursors (curve A) and comparatively weak in the spectrum of MSU-S made from pro-

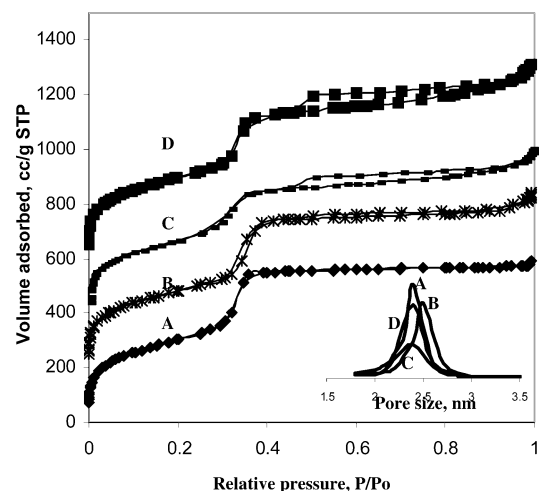


Figure 3. N₂ adsorption/desorption isotherms for mesostructured aluminosilicates: (A) MCM-41 synthesized from conventional precursors (B) MSU-Z made from zeolite fragments generated from USY in 0.10 M NaOH ($\text{OH}^-/\text{T} = 0.17$); (C) MSU-Z assembled from surfactant-mediated ZSM-5 hydrolysis products (zeolite fragments) formed in 0.45 M NaOH ($\text{OH}^-/\text{T} = 0.75$), and (D) mesostructured aluminosilicate formed through over-hydrolysis of ZSM-5 in 0.91 M NaOH ($\text{OH}^-/\text{T} = 1.50$). The curves are offset by 200 units along the y-axis. Inset: BJH pore size distributions obtained from the adsorption isotherms.

tozeolitic ZSM-5 seeds⁴ (curve B). As expected, this band is absent from the spectrum of MSU-Z made from hydrolyzed USY zeolite, as this zeolite does not contain five-ring subunits. On the basis of these FTIR results for MSU-Z made from hydrolyzed ZSM-5 fragments, it is clear that the “top-down” degradation of a zeolite in the presence of a fragment-stabilizing surfactant is superior to our earlier “bottom-up” approach to generating zeolite subunits from conventional aluminosilicate precursors.

Figure 3 provides the nitrogen adsorption–desorption isotherms and framework pore size distributions for MSU-Z made from surfactant-mediated ZSM-5 and USY zeolite fragments (curves C and B, respectively) in comparison to conventional MCM-41 (curve A). We emphasize that it is possible to over-hydrolyze the zeolite precursor to the point where the concentration of zeolitic fragments available for mesostructure formation is compromised despite the presence of a cationic surfactant. Curve D in Figure 3 is the isotherm for a mesophase formed from ZSM-5 that was deliberately over-hydrolyzed by using an excessive concentration of sodium hydroxide. Table 1 provides the textural properties of the MSU-Z mesostructures made from ZSM-5 and USY zeolite fragments.

To test the acidity of MSU-Z mesostructures made from surfactant-mediated zeolite hydrolysis products, cumene cracking was carried out as a probe reaction. The results are included in Table 1. For comparison, cumene cracking also was carried out over ammonium exchanged conventional MCM-41, which showed a cumene conversion of 11%, consistent with previously

reported results.⁴ The MSU-Z mesostructure prepared from USY fragments showed a substantial 3.4-fold increase in cumene conversion to in comparison to MCM-41. This high cumene activity value is similar to the activity observed for MSU-S aluminosilicates assembled from faujasite zeolite seeds.¹³ The 73% conversion found for MSU-Z made from the surfactant-mediated hydrolysis of ZSM-5 is 6.7-fold higher than observed for a conventional MCM-41. This level of cumene cracking activity is unprecedented among mesostructured aluminosilicates. The highest cumene conversion previously observed under analogous reaction conditions (57%) was for a MSU-S made from faujasite seeds at a Si/Al of 5.7.⁵

The cumene cracking activity of MSU-Z made from surfactant-mediated ZSM-5 fragments approaches the 90–95% conversions observed for the pristine ZSM-5 at the same Si/Al ratio. This extremely high acidity cannot be attributed to the presence of residual ZSM-5 crystals in the mesostructured product, because the presence of such crystals is precluded by the absence of wide angle Bragg peaks in the XRD powder pattern and the lack of TEM lattice fringes.

Several composite compositions containing mixtures of zeolite and mesostructured aluminosilicate phases have been reported previously.^{14–18} These mixtures show wide angle Bragg X-ray reflections characteristic of the zeolite phase. Also, the zeolite component of these mixtures typically exhibits lattice fringes in the bright field TEM mode and dense nanocrystallite domains in dark field mode.¹⁵ None of these XRD or TEM features representative of a zeolite phase were observed for MSU-Z made from surfactant-mediated ZSM-5 fragments. Moreover, the absence of zeolitic microporosity was verified through t-plots of the nitrogen adsorption data, as expected for a framework that contains the secondary building units of a zeolite, but not zeolite cavities.

When the hydrolysis of ZSM-5 was carried out in the absence of surfactant and the pH adjusted to 9.0, a low surface area aluminosilicate gel was obtained which had no 550 cm⁻¹ IR band and virtually no activity for cumene cracking. Thus, ion pairing to the cationic cetyltrimethylammonium ion surfactant plays an essential role in stabilizing the anionic zeolitic fragments formed upon hydrolysis. Even in the presence of the surfactant, however, it is possible to over-hydrolyze the zeolite fragments. For instance, increasing the NaOH concentration for ZSM-5 hydrolysis to 0.91 M affords a mesostructure with no 550 cm⁻¹ band and little improvement in cumene conversion compared to MCM-41 (cf. Table 1).

We note that MCM-41 aluminosilicates containing zeolitic fragments have been assembled from solutions formed through the partial hydrolysis of ZSM-5 in the absence of a surfactant.¹⁹ This approach not only makes incomplete use of the zeolite

but also affords a mesostructure with a Si/Al ratio that is 30-fold larger than the initial zeolite. Moreover, the incorporation of five-membered ring subunits into the framework walls of the mesostructure, as well as the cracking activity of the mesostructure, is no better than what can be achieved through the direct assembly of aluminosilicate mesostructures from protozeolite seeds formed in the presence of a zeolite template. The surfactant-mediated hydrolysis of ZSM-5 described in the present work is far more effective than direct zeolite hydrolysis for the preparation of mesostructures with high levels of five-ring subunits and high acid cracking activity. The improved cumene cracking activity observed for MSU-Z made by surfactant-mediated hydrolysis of USY zeolite also suggests that our “top-down” approach to the incorporation of zeolitic subunits into the framework walls of a mesostructure is general and most likely applicable to other zeolite precursors.

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