

Aluminosilicate Nanoparticles for Catalytic Hydrocarbon Cracking

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The replacement of amorphous aluminosilicates by derivatives of zeolite Y in gas oil cracking catalysts 40 years ago resulted in better product distributions, less coke formation, better stability, and lower catalyst consumption rates.¹ Zeolites continue to be the major active component of present-day refining catalysts.² As more emphasis is placed on the conversion of a higher fraction of petroleum into clean fuels, there is a desire to crack the vacuum residual oil fractions (bp > 565 °C), which typically constitute ~10–25% of crude oil assays in comparison to ~30% for the gas oil fraction. Zeolite-based catalysts are capable of cracking these high molecular residual oils, but, because the reaction is limited to the external surfaces of the zeolite particle, the activity is greatly reduced, and the catalyst usage rate is substantially increased.

Although aluminum-substituted derivatives of mesostructured M41S silicas³ were immediately recognized as having the large pore sizes and surfaces needed to accommodate high molecular weight petroleum fractions, initial studies indicated that they lacked the intrinsic acidity and hydrothermal stability for hydrocarbon cracking applications.⁴ More recently, the incorporation of protozeolitic nanoclusters (so-called “zeolite seeds”) into the framework of mesostructured aluminosilicates has been shown to greatly improve both the acidity and the hydrothermal stability of these structures.^{5–9} Although protozeolitic mesostructures are stable to exposure to 20% steam at 750–800 °C and exhibit acidities comparable to those of zeolites, the hydrothermal stability, impressive as it is, remains inadequate for sustained large-scale hydrocarbon cracking. Substantially improved hydrothermal stability comparable to the stability exhibited by ultrastable zeolite Y (USY) and rare earth exchanged zeolite Y (REY) is needed for the processing of high molecular weight petroleum fractions.

The present work reports the first example of a nanosized mesoporous aluminosilicate with the hydrothermal stability and acidity needed for the cracking of high molecular weight hydrocarbons. All previously reported mesostructures lack this unique combination of physical and chemical properties so vital to large hydrocarbon processing. Our approach is based on the use of protozeolitic aluminosilicate nanoclusters for the construction of acidic pore walls and starch as a porogen. Under appropriate reaction conditions, these reagents afford nanoparticles that contain mesopores with exceptionally thick walls between the pores.

In a typical synthesis, zeolite Beta seeds were prepared by mixing fumed silica, sodium aluminate, tetraethylammonium hydroxide (TEAOH), and water at a mole ratio of 1.00 SiO₂:0.01 Al₂O₃:0.54 TEAOH:16.7 H₂O at room temperature under vigorous stirring and by aging them at 135 °C for 4 h. The presence of five-membered ring subunits in the zeolite seeds solution was confirmed by IR spectroscopy, as judged by the presence of a vibrational band in the 550–600 cm⁻¹ region.^{10,11} The synthesis of a nanosized mesoporous aluminosilicate was accomplished by adding 1.50 g of corn starch to 9.0 g of the zeolite Beta seeds solution and allowing the mixture to age at 100 °C for 24 h under stirring. The resulting gel was dried in the open atmosphere at 75 °C and then transferred to

a Teflon-lined autoclave for reaction at 175 °C for 3 days. The starch was removed by calcination at 650 °C for 10 h. The proton exchanged form of the resulting product **1**, denoted 2%Al-MSU-AS, was obtained by the ion exchange reaction with 0.1 M NH₄NO₃ at 100 °C for 3 h and then by calcining the product at 550 °C for 4 h. The XRD pattern of the calcined product showed no low angle Bragg reflections, indicating a disordered pore structure, as expected on the basis of the use of nonsurfactant starch as a porogen. Also, the absence of Bragg reflections at wide angles verified the presence of atomically amorphous pore walls and the absence of a crystalline zeolite component. However, a vibrational band between 550–600 cm⁻¹ was observed in the IR spectrum, which is indicative of a five-membered ring subunit, the same subunit found in zeolite Beta and related pentasil zeolites.

The ²⁷Al MAS NMR spectrum of calcined **1** indicated that >95% of the aluminum centers were in tetrahedrally coordinated sites, which is characteristic of aluminosilicate frameworks assembled from zeolite seeds. Thus, the ²⁷Al MAS NMR results, together with the IR results, verify the incorporation of zeolite Beta subunits into the pore walls.

As shown by the TEM images in Figure 1, the calcined **1** is comprised almost entirely of irregular nanoparticles with a serpentine-like hierarchical structure permeated by 9–20 nm mesopores. Equivalent reaction conditions in the absence of starch exhibited only monolithic particles with little or no mesoporosity. Table 1 reports the Langmuir surface area obtained from the Type I N₂ isotherm over the partial pressure range $P/P_0 = 0–0.45$, along with the total pore volume and the BJH mesopore size obtained from the desorption leg at $P/P_0 = 0.6–0.9$. To our knowledge, this is the first reported example of an amorphous aluminosilicate phase with a hierarchical nanostructure penetrated extensively by mesopores. There has been only one earlier report of starch-generated mesoporosity in an aluminosilicate,¹² and in that case the phase was crystalline, and the pore volume was substantially lower than the porosity achieved in the present work. Table 1 also reports the textural properties of **1** after exposure to different hydrothermal treatments. Exposure to 20% steam at 800 °C for 2 h and to boiling H₂O for 96 h resulted in negligible structural degradation. Under more severe conditions, at 800 °C for 4 h in pure steam, **1** retained a surface area of 321 m²/g or 60% of its initial surface area before steaming. In comparison, USY zeolite containing 1.0 mol % framework Al retains a surface area of 213 m²/g, corresponding to only 39% of its initial surface area under a comparable steaming condition.⁴ At a 2.5% Al content, an even lower fraction (25%) of the initial surface area is retained for USY. Thus, **1** retains substantially more surface area and porosity than the major zeolite component of a commercial cracking catalyst after high-temperature exposure to pure steam.

It is clear from the above results that corn starch, which contains branched amylopectin chains (73%) and linear amylose chains (27%),¹³ is capable of providing mesoporous protozeolitic aluminosilicate compositions with exceptionally thick walls (7–15 nm)

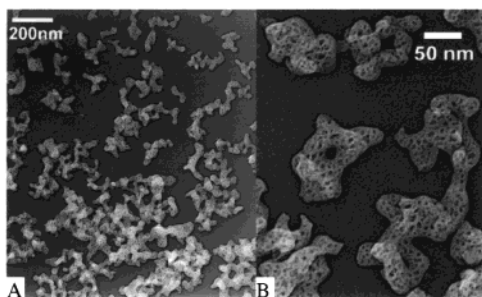


Figure 1. (A) Low and (B) high magnification TEM images of **1**.

Table 1. Textural Properties of 2% Al-MSU-AS, Freshly Calcined and after Different Hydrothermal Treatments

sample treatment	Langmuir S.A. (m ² /g)	pore size (nm)	pore volume (cc/g)
freshly calcined	532	9–20	0.86 ^a
20% steam at 800 °C for 2 h	537	9–20	0.83
boiling water for 96 h	521	9–20	0.84
100% steam at 800 °C for 4 h	321	7–20	0.34

^a Approximately 33% of the initial pore volume is due to micropores, as judged from t-plots.

between the mesopores that contribute to the remarkable steam stability. Amylopectin and amylose undergo hydrolysis reactions under the hydrothermal assembly and pH conditions (> 13) needed for the formation of zeolite seeds. The hydrolysis products may well contribute to the pore-forming properties of starch.

The ²⁷Al MAS NMR spectrum of **1** indicated that essentially all of the aluminum centers occupied tetrahedrally coordinated sites, which presages the presence of a high fraction of Brønsted acid sites. Moreover, in accord with the high hydrothermal stability of the mesophase, the ²⁹Si MAS NMR spectrum exhibited a single resonance at –114 ppm, indicating that nearly all of the SiO₄ units are fully cross-linked in Q⁴ sites in which all of the oxygen atoms are bridging.

Using the cumene conversion reaction as a well-established test of hydrocarbon cracking activity,¹⁴ we compared the acidic reactivity of **1** with the reactivity of previously reported 2% Al-MSU-S_{BEA}, 2% Al-MCM-41, and 2% Al-HMS mesostructures. Although 2% Al-MSU-S_{BEA} also is assembled from zeolite Beta seeds, it structurally degrades in pure steam at 800 °C. The latter two mesostructures, made from conventional aluminosilicate precursors, are even less stable, degrading completely in 20% steam at 800 °C.¹⁵

As illustrated in Figure 2, **1** showed an initial cumene cracking activity corresponding to 56% conversion, whereas MCM-41, HMS, and MSU-S at the same Al-loading afforded conversions of only 22, 26, and 40%, respectively. Most importantly, **1** still exhibited 41% cumene conversion even after a 110 h time-on-stream, while 2% Al-MCM-41 and 2% Al-HMS decayed to cumene conversions of 7 and 13% after 72 h, respectively. The 2% Al-MSU-S_{BEA} mesostructure made from zeolite seeds also showed a comparatively low 29% cumene conversion after a reaction time of 100 h. Although USY zeolite afforded an initially high cumene conversion of 86% (not shown), the activity rapidly decayed to 6% conversion within 48 h due to extensive coke formation.

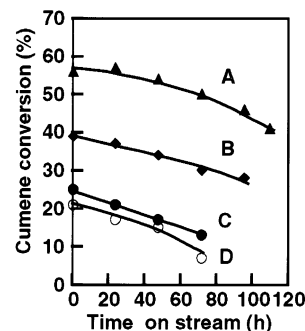


Figure 2. Cumene cracking activity of (A) mesoporous 2% Al-MSU-AS (**1**) in comparison to the activity of (B) hexagonal 2% Al-MSU-S_{BEA},⁶ (C) wormhole 2% Al-HMS,¹⁷ and (D) hexagonal 2% Al-MCM-41¹⁷ aluminosilicates.

The remarkable hydrothermal stability and catalytic reactivity of the new nanoparticles are attributable to a unique combination of two factors, the presence of protozeolitic nanoclusters in the pore walls and the unprecedented pore wall thickness (7–15 nm) provided through the use of starch as a porogen. In addition, the excellent longevity of **1** is most likely facilitated by the small domain size of the nanoparticles that greatly improves access to the acid sites on the pore walls and minimizes the diffusion length of coke precursors out of the pores.

In summary, **1** and related nanosized MSU-AS compositions possess the unique combination of mesoporosity, hydrothermal stability, acidity, and longevity that is desired for the efficient cracking of high molecular weight hydrocarbons. Future work will examine the properties of these materials as acid catalysts for the processing of residual petroleum fractions with kinetic diameters too large for efficient cracking over conventional zeolite catalysts.

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