

Mesostructured Forms of γ -Al₂O₃

Zhaorong Zhang, Randall W. Hicks, Thomas R. Pauly, and Thomas J. Pinnavaia*

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

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Transition aluminas are disordered crystalline phases formed through the thermal dehydration of aluminum hydroxides and oxyhydroxides.¹ These oxides are used as adsorbents and catalysts or catalyst supports in many chemical processes, including the cracking, hydrocracking, and hydrodesulfurization of petroleum feedstocks.² At least seven transition aluminas have been reported. Of these, γ -Al₂O₃ is perhaps the most important for catalytic applications.¹ The γ -phase is formed upon the dehydration of the aluminum oxyhydroxide boehmite at temperatures ranging from 400 to 700 °C.² The utility of γ -Al₂O₃, as well as other transition aluminas, can be traced to a favorable combination of textural properties (i.e., surface area, pore volume, and pore size) and acid–base characteristics. Conventional forms of γ -Al₂O₃ typically exhibit a BET surface area below 250 m²/g and a pore volume less than 0.50 cm³/g. The properties of these materials for applications in catalysis and adsorption are determined in large part by these textural parameters.

In view of the recent advancements realized for mesostructured forms of silicas,^{3–7} one may anticipate similar improvements in the properties of mesostructured aluminas. However, comparatively limited progress has been made in this area. Although mesostructured aluminas with amorphous framework walls have been assembled in the presence of ionic^{8–10} and nonionic^{11–13} surfactants, these materials have limited thermal and hydrothermal stability, which greatly compromises their usefulness. A mesostructured alumina containing a transition alumina phase has been reported recently,¹⁴ but well-expressed alumina mesostructures with atomically ordered walls have yet to be demonstrated.

Here we report a general route to mesostructured aluminas, denoted MSU- γ , composed of γ -Al₂O₃ walls. The key to obtaining these structures is the formation of a mesostructured surfactant/boehmite precursor, denoted MSU-S/B, assembled through the hydrolysis of an aluminum cation, oligomer, or molecule in the presence of a nonionic surfactant. The assembly of a MSU-S/B mesostructure was achieved by aging an aqueous mixture of [Al₁₃O₄(OH)₂₄(H₂O)₁₂]Cl₇ (21.78 g of a 12.5 wt % Al solution, 100 mmol Al) and the tri-block (EO)₁₉(PO)₃₉(EO)₁₉ surfactant Pluronic P84 (4.2 g, 1.0 mmol) at 45–80 °C for 6–10 h and then hydrolyzing the mixture with concentrated NH₄OH (3.02 g 50 mmol). The precipitate was aged at 80 °C for 6 h and then at 100 °C for 24 h, and air-dried. The resulting mixture of MSU-S/B and NH₄Cl was calcined at 325 °C for 3 h and then at 550 °C for 4 h, to form MSU- γ . Analogous procedures were carried out using AlCl₃ and aluminum 2-butoxide in place of the Al₁₃ oligomer as the alumina precursor, but in the case of the alkoxide, water was used as the hydrolysis agent in place of ammonia and 2-butanol was used as a cosolvent.

Representative XRD patterns are shown in Figure 1 for the as-made MSU-S/B and MSU- γ products prepared from aluminum 2-butoxide and Al₁₃ oligomers. The presence of a single diffraction

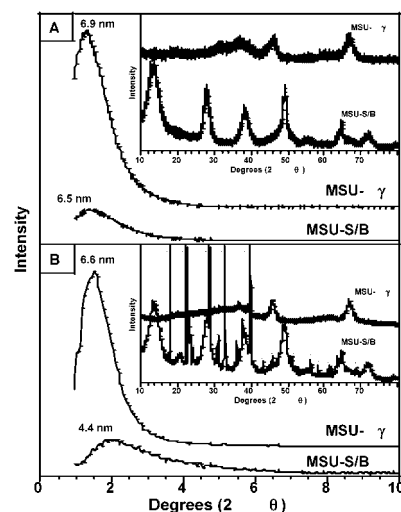


Figure 1. Powder XRD patterns of as-made MSU-S/B and calcined MSU- γ aluminas prepared from (A) Al(OC₄H₉)₃ and (B) Al₁₃ precursors and Pluronic P84 surfactant. The very narrow diffraction lines in the inset to (B) are attributable to the NH₄Cl byproduct.

line in the small-angle region is indicative of a disordered mesostructure. In the wide-angle regions of the XRD patterns (Figure 1, insets) the as-made products exhibit diffraction lines assignable to boehmite, whereas the calcined MSU- γ products show broad, small-angle reflections consistent with γ -alumina.

The negative bright-field TEM images in Figure 2, A and B, show that MSU- γ mesostructures are formed from porous lath- to rod-shaped nanoparticles (light areas). The nanoparticles are thicker and longer for the product made from the Al₁₃ oligocation than from the Al(s-OC₄H₉)₃ molecule. Also, as shown by the lower-magnification images in Figure 2, C and D, the nanoparticles are assembled into a scaffoldlike array in the product made from the alkoxide, whereas in the alumina made from the ionic Al₁₃ oligomer the nanoparticles are intergrown into parallel arrays to form a hierarchical sheetlike morphology. A mesostructure made of parallel laths also was observed for the MSU- γ assembled from aluminum chloride. The selected area electron diffraction patterns, shown as insets to Figure 2, C and D, verified the presence of crystalline γ -alumina in the mesostructured framework. The crystallinity of the lathlike walls was further verified by the dark-field images in Figure 2, E and F. A projection of the scattered electrons defining a 7° segment of the 440 diffraction ring was used to form these images. The bright regions in these later images identify the lath orientations that meet the Bragg condition for scattering in the selected region of diffraction. These results clearly show that the mesostructures are assembled from γ -Al₂O₃ nanoparticles. Further evidence for γ -Al₂O₃ walls was provided by ²⁷Al NMR which showed the presence of four- and six-coordinate Al in ~25:75 ratio,

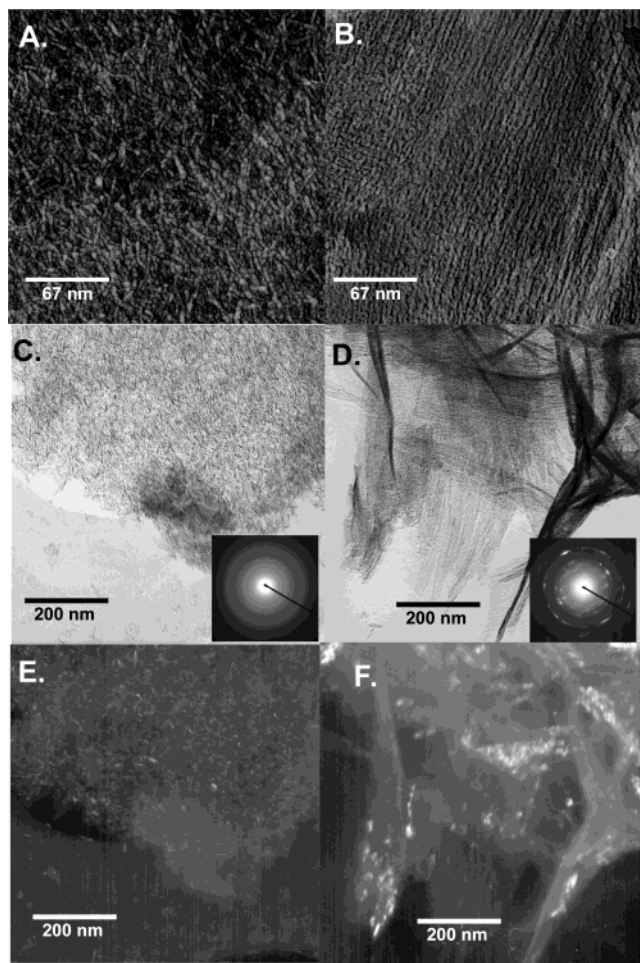


Figure 2. Negative bright-field TEM images of MSU- γ aluminas prepared from (A) $\text{Al}(\text{OC}_4\text{H}_9)_3$ and (B) Al_{13} oligocations with Pluronic P84 as the nonionic surfactant; (C) and (D) show lower-magnification images for the respective samples, along with their electron diffraction patterns; (E) and (F) are the dark-field images of the same particles in (C) and (D), but formed from a $\sim 7^\circ$ arc of the 440 diffraction ring.

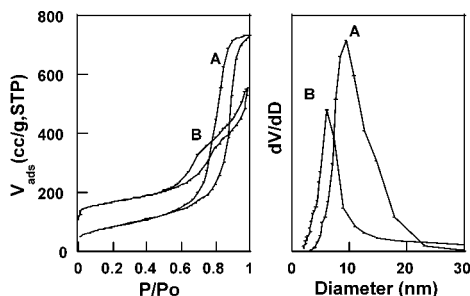


Figure 3. Nitrogen adsorption/desorption isotherms (left) and BJH pore size distributions (right) for MSU- γ aluminas prepared from (A) $\text{Al}(\text{OC}_4\text{H}_9)_3$ and (B) Al_{13} precursors and Pluronic P84 surfactant.

as expected for the γ -phase.¹⁵ Mesoporous aluminas with amorphous walls exhibit an observable five-coordinate resonance near 35 ppm, in addition to four- and six-coordinate Al.^{11,13} Little or no five-coordinate Al was observed for MSU- γ , signifying the absence of appreciable quantities of amorphous domains in the walls.

Representative N_2 adsorption/desorption isotherms and pore-size distributions for MSU- γ aluminas are provided in Figure 3. Table 1 lists the textural properties for the derivatives prepared from $\text{Al}(\text{s-OC}_4\text{H}_9)_3$, Al_{13} oligocations and AlCl_3 and Pluronic P84 surfactant. Included for comparison are the textural properties of MSU- γ

Table 1. Properties of MSU- γ Aluminas

precursor	surf	d_{100} (nm)	S_{BET} (m^2/g)	pore vol (cc/g)	pore size (nm) ^a
$\text{Al}(\text{O}^i\text{Bu})_3$	P84	6.9	306	1.15	9.0
Al_{13}	P84	6.6	299	0.73	6.4
AlCl_3	P84	6.5	311	0.69	6.3
$\text{Al}(\text{O}^i\text{Bu})_3$	P123	8.5	370	1.51	13
Al_{13}	L64	5.1	307	0.53	4.4

^a BJH desorption.

aluminas formed from tri-block surfactants that are larger and smaller than P84, namely, P123 and L64, with compositions $(\text{EO})_{20}(\text{PO})_{69}(\text{EO})_{20}$ and $(\text{EO})_{13}(\text{PO})_{30}(\text{EO})_{13}$, respectively. Note that the pore volumes and pore sizes are larger for the scaffoldlike mesostructures derived from the alkoxide than for the parallel lath frameworks assembled from the cationic forms of aluminum. This suggests that 2-butanol may function in part as a cosurfactant or, more likely, that the rapid hydrolysis rate of the alkoxide limits the lath size of the boehmite precursor, creating a scaffold structure with greater mesostructured space between the randomly intergrown particles. Also, the data in Table 1 show that the pore size is correlated with the size of the surfactant molecule as expected for surfactant-mediated assembly of nanoparticles.

The surface areas of MSU- γ aluminas (299–370 m^2/g) are substantially larger than those normally observed for conventional γ - Al_2O_3 (185–250 m^2/g).² The observed surface areas are compatible with the values expected for a mesostructure with thick walls. SBA-15 silica with 3.5 nm walls has a mesoporous surface area estimated to be between 450 and 620 m^2/g .¹⁶ Correcting for differences in wall density (3.3 g/cm^3 for γ - Al_2O_3 vs 2.2 for amorphous silica), we expect MSU- γ with similarly thick walls to have a surface area in the range 300–413 m^2/g , as observed.

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