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Nanoparticle Assembly of Mesoporous AlOOH (Boehmite)

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The first examples of a new mesoporous form of crystalline AlOOH (boehmite) were prepared using aluminum *sec*-butoxide as the alumina precursor and an amine surfactant as a hierarchical structure director. The hydrolysis of the alkoxide in the presence of various amine surfactants at ambient temperature afforded boehmite−surfactant nanocomposites, denoted MSU−S/B. TEM images of the as-made nanocomposites indicated the presence of a scaffold-like structure formed through the aggregation and intergrowth of boehmite nanofibers. Thermal treatment of the nanocomposite at 325 °C topochemically removed the surfactant component and afforded a surfactant-free boehmite phase, denoted MSU−B, with retention of the scaffold structure. The surface areas of the MSU−B products prepared at AlOOH:surfactant mass ratios of 1:1 were 1.27−1.43 times as large as the surface area obtained for boehmite prepared under equivalent hydrolysis conditions in the absence of an amine structure modifier. No correlation was found between the mesostructure pore size and the size of the structure-directing surfactant, which is consistent with a hierarchical scaffold structure formed through the assembly of nanoparticles of more or less uniform size. Both the surfactant−boehmite MSU−S/B nanocomposite and the surfactant-free MSU−B boehmite phase could be converted to mesostructured γ-Al_2O_3 through calcination at 500 °C. Substantially higher surface areas and pore volumes were obtained for the γ-Al_2O_3 phases derived from the nanocomposite, indicating that the surfactant mediates nanoparticle assembly even during the topochemical transformation of mesostructured boehmite to γ-Al_2O_3.

Introduction

Transition aluminas are disordered crystalline phases formed through the thermal dehydration of aluminum hydroxides and oxyhydroxides.[1] γ-Al_2O_3, the transition alumina most commonly used in heterogeneous catalysis,[2,3] is formed through the dehydration of the boehmite form of AlOOH at temperatures in the range 400−700 °C. In view of the improved surface areas and pore size distributions realized for mesostructured forms of silica,[4,5] one may anticipate similar improvements in the textural properties of mesostructured aluminas. Indeed, following the first reports of the supramolecular synthesis of mesostructured aluminas in 1996, [6−8] several additional mesostructured aluminas have been realized.[9−12] However, all of these early forms of mesostructured alumina were comprised mainly of amorphous framework walls, thus limiting their hydrothermal stability and greatly compromising their usefulness in catalytic applications.

More recently, we reported the first examples of mesostructured γ-Al_2O_3 from aluminum ions, cationic oligomers, and alkoxides as alumina precursors and PEO surfactants as structure directors.[13] The key to these novel compositions was the formation of an intermediate boehmite−surfactant nanocomposite upon the hydrolysis of the alumina precursor in the presence of the surfactant. Subsequent calcination of the intermediate nanocomposite simultaneously removed the surfactant and topochemically transformed the boehmite component to mesostructured γ-Al_2O_3. However, the removal of the PEO surfactant with retention of the

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boehmite phase proved to be difficult, typically resulting in products contaminated with carbonaceous residues and thwarting efforts to obtain a pure form of mesostructured boehmite.

In the present work we demonstrate for the first time a new approach to the synthesis of a mesostructured boehmite based on aluminum alkoxide as the AlOOH precursor and primary amine surfactants as structure directors. The use of an electrically neutral amine as a structure director allows for the assembly of a mesostructured boehmite through hydrogen bond formation to the surface hydroxyl groups of boehmite nanoparticles, while at the same time allowing for the clean removal of the surfactant through low-temperature calcination without the concomitant conversion of boehmite to γ-Al_2O_3.

Experimental Section

Aluminum *sec*-butoxide (Aldrich) and the amine surfactants (Aldrich and Akzo Nobel) were used as provided by the supplier without further purification. To a solution of the desired surfactant in ethanol−water at ambient temperature was added aluminum *sec*-butoxide under vigorous stirring through the use of a magnetic stirrer. The reaction mixture, which was sealed in a glass jar, was allowed to stir either at ambient temperature (20 °C) or at 45 °C in a controlled shaker bath for 20 h. The resulting surfactant−boehmite nanocomposites, denoted MSU−S/B, were recovered by vacuum filtration, washed with ethanol and water, and allowed to dry at ambient temperature. The reaction stoichiometries used to obtain the mesostructured MSU−S/B nanocomposites are provided in the following section. Surfactant-free mesostructured boehmites, denoted MSU−B boehmites, were obtained by calcining the amine MSU−S/B nanocomposite in air at 325 °C for 10 h.

Powder diffraction patterns were collected on a Rigaku Rotoflex Diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm). Peak intensities were obtained by counting every 0.02° 2θ at sweep rates of 2.0° 2θ/min.

Nitrogen adsorption−desorption isotherms were collected on a Micromeritics TriStar 3000 sorptometer at 77 K. Samples were degassed under a vacuum of 10^{-6} Torr for at least 12 h at 150 °C prior to analysis. Surface areas and pore sizes were determined by the BET and BJH methods, respectively.

TEM images were collected on a JEOL 100CX microscope equipped with a CeB_6 filament. The accelerating voltage was 120 kV. Samples were prepared by sonicating a suspension of the powder in ethanol for 20 min. One to two drops of the suspension were then placed on a carbon-coated holey film that was supported on a 3-mm, 300-mesh copper grid.

^{27}Al NMR spectra were collected on a Varian 400 VRX solid-state NMR spectrometer. Samples were placed in a zirconia rotor and spun at 4 kHz with a pulse width of 0.5 μs and a pulse delay of 0.5 s. Chemical shifts were referenced to $Al(H_2O)_6^{3+}$, which was assigned a value of 0 ppm.

Results and Discussion

The hydrolysis reaction of aluminum *sec*-butoxide in an ethanol−water solution of an amine surfactant results in the formation of a mesostructured surfactant−boehmite phase, denoted MSU−S/B. Although the hydrolytic conversion of aluminum *sec*-butoxide to boehmite according to the reaction

$$Al(O-{}^{s}Bu)_3 + 2H_2O \rightarrow AlOOH + 3(s\text{-}BuOH)$$

is normally accomplished under hydrothermal conditions,[2] boehmite formation will occur even at ambient temperature, provided the reaction time is adequate. In the present work a reaction time of 20 h at ambient temperature (20 °C) was sufficient to convert all of the precipitated alumina to a crystalline boehmite−surfactant nanocomposite. The presence of an amine surfactant in the reaction mixture increases the pH and shortens the reaction time needed for boehmite formation. Increasing the reaction temperature to 45 °C also shortens the reaction time needed for boehmite formation. In addition to promoting boehmite formation, the amine surfactant also mediates mesostructure formation by regulating the growth and aggregation of the boehmite nanoparticles through hydrogen bond formation with surface hydroxyl groups, as will be discussed in further detail below. The conversion of the MSU−S/B surfactant−boehmite nanocomposites to surfactant-free MSU−B boehmites was cleanly and conveniently achieved through the topochemical removal of the surfactant through calcination at 325 °C for a period of 10 h.

The hydrolysis of aluminum *sec*-butoxide in the absence of an amine surfactant leads to the formation of boehmite nanoparticles with a high fraction of the hydroxyl groups at the surface of the particles. The small particle size and high fraction of surface hydroxyl groups allows the boehmite to be peptized to a sol in dilute acidic solution. This latter form of boehmite is typically referred to as “pseudoboehmite”. However, neither the MSU−S/B nanocomposites nor the corresponding surfactant-free MSU−B boehmites prepared in the present work undergo peptization in dilute nitric acid. This indicates that the amine surfactant fosters the intergrowth of the boehmite nanoparticles formed in the hydrolysis reaction, as was verified by transmission electron microscopy (see below).

Several amines can be used to mediate the assembly of boehmite nanoparticles, including C_8 to C_{18} primary alkylamines, as well as polyfunctional tallow amines of the type $RNH(CH_2CH_2CH_2NH)_xH$, where the R group contains 16−18 carbon atoms and $x = 1-3$. Reaction mixtures with aluminum to surfactant molar ratios were investigated over the range 10:1 to 1:1, as well as 1:0, but ratios in the range 2:1 to 7:1 typically afforded MSU−B mesostructures with the highest surface areas and pore volumes.

Previously reported studies have shown that the ambient temperature hydrolysis of aluminum alkoxides in the presence of poly(ethylene oxide) surfactants can result in the formation of one of two possible forms of mesostructured aluminas. One form is a wormhole framework with essentially amorphous framework walls (i.e., MSU−X aluminas), as was initially reported by Bagshaw and Pinnavaia[6] and more recently confirmed by Shanks and co-workers.[14] The second type of mesostructured alumina made from PEO surfactants is in the form of mesostructured boehmite nanoparticles, as was demonstrated recently by Zhang et al.[13] In these PEO-mediated systems, the composition and structure of the mesostructured product is determined in large part by the reaction stoichiometry, the ratio of water to alcohol in the solvent, and the method used to combine the reagents. A high aluminum-to-surfactant ratio (e.g.,

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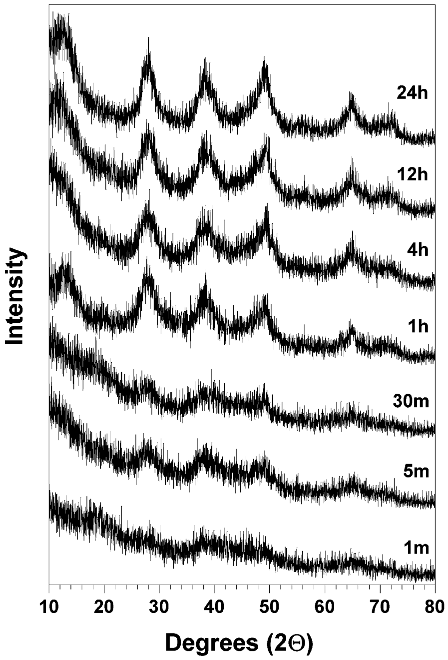

Figure 1. Wide-angle XRD patterns of MSU−S/B surfactant−boehmite nanocomposites prepared from a 5:1 molar ratio of aluminum *sec*-butoxide and dodecylamine at 20 °C showing the evolution of the boehmite phase with reaction time.

≈10:1), a low ratio of Al:H_2O (e.g., 1:2), and a high ethanol content in the solvent favors the formation of a wormhole gel, whereas lower aluminum-to-surfactant ratios and higher water levels in the solvent favor the formation of boehmite. The use of primary amines as the structure-directing surfactant in the present work increases the pH of the reaction mixture in comparison to that of a PEO reaction mixture. This increase in pH strongly favors boehmite formation.

As is shown by the X-ray powder patterns in Figure 1, the initial precipitate formed in the hydrolysis of aluminum *sec*-butoxide in the presence of dodecylamine as the structure at 20 °C is largely amorphous. Just the onset of boehmite formation can be discerned in the XRD pattern of the product after 1 min of reaction time. However, as the reaction mixture ages, more of the amorphous alumina in the initial precipitate is converted to boehmite in the form of an MSU−S/B nanocomposite. Boehmite formation is nearly complete after 4 h of reaction time at ambient temperature.

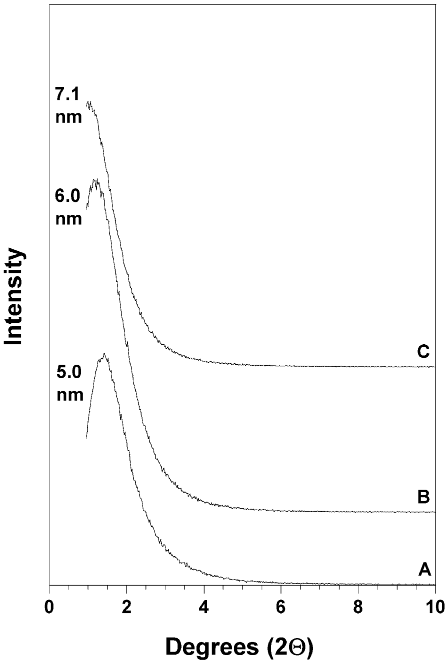

Figure 2. Low-angle XRD patterns of surfactant-free MSU−B boehmites prepared from aluminum *sec*-butoxide at (A) a 5:1 molar ratio of Al:dodecylamine, (B) 3.1:1 molar ratio of Al:dodecylamine, and (C) a 5:1 molar ratio of Al:octylamine in 75:25 (v/v) ethanol−water solvent.

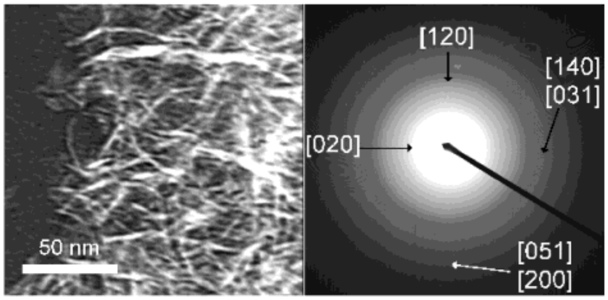

Figure 3. Bright field TEM image (left) and electron diffraction pattern (right) of a MSU−B scaffold structure prepared from aluminum *sec*-butoxide and dodecylamine at a Al:surfactant ratio of 5:1. The electron diffraction pattern shows diffuse rings which are indexed to boehmite.

Representative low-angle diffraction patterns are shown in Figure 2 for surfactant-free MSU−B boehmites made from aluminum *sec*-butoxide and dodecylamine and octylamine as structure directors. The presence of a diffraction peak at 2θ values corresponding to basal spacing between 6.0 and 8.5 nm are indicative of mesostructure formation. However, the positions of the diffraction line are not correlated with the amount of the surfactant used in the synthesis or with the size of the surfactant. TEM micrographs, such as the representative micrograph shown in Figure 3, indicate that the structure is a consequence of the hierarchical ordering of fibrous boehmite nanoparticles into a scaffold-like array. Mesopores are formed through the scaffold-like aggregation and intergrowth of the boehmite nanoparticles. Thus, MSU−S/B nanocomposites derived from amines as structure directors share the same scaffold-like structure previously reported for MSU−S/B materials assembled using PEO surfactants.[13] The great advantage of amine surfactants in comparison to PEO surfactants, however, is their ability to be removed cleanly and efficiently from the pores of the MSU−S/B composite structures without contaminating the MSU−B boehmites with surfactant decomposition products. That is, in comparison to amine surfactants, PEO surfactants are more difficult to remove from the mesopores and undergo decomposition under similar thermolysis conditions.

The accompanying electron diffraction pattern in Figure 3 verifies that the particles forming the hierarchical scaffold structure in the image are indeed comprised of crystalline boehmite. Thus, the low-angle reflections observed in the XRD pattern are a consequence of the assembly of nanoparticles of more or less regular size. The fact that boehmite has a pleated layer structure with a repeat distance of 1.2 nm along the 020 stacking direction most likely facilitates regular nanoparticle formation. In addition, the amine surfactant

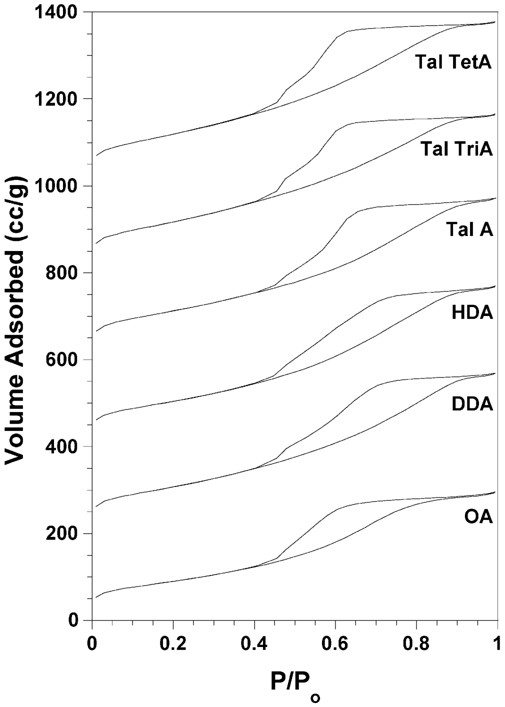

Figure 4. Nitrogen adsorption−desorption isotherms for MSU−B aluminas prepared through the hydrolysis of aluminum *sec*-butoxide in the presence of different amine surfactants at a 5:1 molar ratio. OA = octylamine, DDA = dodecylamine, HDA = hexadecylamine, Tal A = tallow amine, Tal TriA = tallow triamine, and Tal TetA = tallow tetraamine. The isotherms are offset by 200 cm^3/g for clarity.

also mediates the size and intergrowth of the boehmite nanoparticles. There is little doubt that the regularity of the nanoparticles is an important aspect of the observed scaffold mesostructure. We have observed low-angle diffraction lines even for boehmites formed through the hydrolysis of aluminum *sec*-butoxide even in the absence of an amine structure director. As expected, however, it is much more difficult to control the size of the nanoparticles formed in the absence of surfactant to the point where a low-angle peak can be reproducibly observed in the XRD pattern. Thus, a low-angle XRD peak is much more likely to be observed when an amine structure director is present to mediate nanoparticle growth and assembly. A nanoparticle assembly mechanism, as opposed to a supramolecular assembly process, most likely also operates in the formation of previously reported mesostructured forms of SnO_2,[15] ZrO_2,[16] and certain mixed metal oxides.[17]

Figure 4 provides nitrogen adsorption−desorption isotherms for a series of MSU−B boehmites derived from the hydrolysis of aluminum *sec*-butoxide at ambient temperature in the presence of various amine surfactants at an aluminum-to-surfactant molar ratio of 5:1. The primary alkylamine surfactants contained between 8 and 18 carbon atoms and the multifunctional $RNH(CH_2CH_2CH_2NH)_xH$ tallow amines contained 16−18 carbon atom alkyl chains and two and three aminopropyl segments in the hydrophilic block (i.e., $x = 2$ and 3). Each mesostructure exhibits a broad type IV adsorption isotherm indicative of mesoporosity and a H2 hysteresis loop that closes at a partial pressure near 0.40. The BJH pore size distributions determined from the adsorption branch of the isotherm are shown in Figure 5. As might be expected for a mesostructure formed through a particle assembly pathway, the pore size distributions are broad, much broader than would be anticipated for mesostructures formed through a supramolecular pathway. Also, the average pore sizes show no relationship to the size of the amine surfactant used in the formation of the MSU−S/B nanocomposite. Analogous isotherms and pore size distributions were obtained for MSU−B boehmites formed at a AlOOH-to-surfactant mass ratio of 1:1.

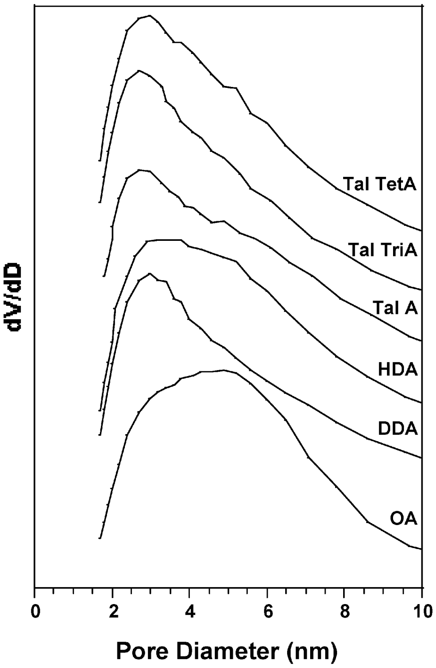

Figure 5. BJH adsorption pore size distribution curves of MSU−B boehmites prepared from aluminum *sec*-butoxide and various amine surfactants at an Al:surfactant molar ratio of 5: 1.

The data in Table 1 report the pore sizes, surface areas, and pore volumes for surfactant-free MSU−B boehmites derived from MSU−S/B nanocomposites that were assembled at ambient temperature from various amines at an Al-to-surfactant molar ratio of 5:1, as well as at a constant AlOOH-to-surfactant mass ratio of 1:1. For both reaction stoichiometries there is no correlation between the size or amount of the surfactant and the textural properties of the resulting mesostructures. This behavior is consistent with a hierarchical particle assembly mechanism in which the role of the surfactant is primarily to mediate the size and intergrowth of the boehmite nanoparticles responsible for the formation of a scaffold-like structure. Increasing the temperature for the assembly of the MSU−S/B precursors to 45 °C improved the textural parameters somewhat, but no further improvement in textural properties was realized upon increasing the assembly temperature to 65 or 95 °C, at least when dodecylamine was the structure director. Also, varying the ethanol-to-water ratio of the solvent used to form the MSU−S/B precursors over the

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Table 1. Synthetic Parameters and Textural Properties for MSU−B Aluminas

surfactant[a]	Al/surf./EtOH/H_2O molar ratio	AlOOH/ surf. mass ratio	S_{BET} (m^2/g)	pore size[b] (nm)	pore volume (cm^3/g)
OA	5:1:20.0:21.6	2.33	325	4.7	0.47
DDA	5:1:28.7:31.0	1.62	378	3.0	0.59
HDA	5:1:37.4:40.4	1.24	391	4.0	0.59
Tal A	5:1:46.2:49.9	1.24	410	2.7	0.60
Tal TriA	5:1:64.0:69.0	0.85	429	3.0	0.60
Tal TetA	5:1:72.8:78.7	0.73	436	3.1	0.61
OA	2.2:1:20.0:21.6	1.00	452	5.0	0.81
DDA	3.1:1:20.0:21.6	1.00	418	5.0	0.63
HDA	4.0:1:20.0:21.6	1.00	434	3.2	0.64
Tal A	4.0:1:20.0:21.6	1.00	410	3.0	0.60
Tal TriA	5.9:1:20.0:21.6	1.00	462	3.1	0.63
Tal TetA	6.9:1:20.0:21.6	1.00	459	3.1	0.61
none	5:0:28.7:31.0	∞	322	4.0	0.71

[a] DDA = dodecylamine, OA = octylamine, HDA = hexadecylamine, Tal A = tallow amine, Tal TriA = tallow triamine, and Tal TetA = tallow tetraamine. The tallow amine structure is generalized by the following formula, $RHN(CH_2CH_2CH_2NH)_xH$, where R is a mixture of alkyl groups ranging from C_{16} to C_{18} and x = 0, 2, or 3 for tallow amine, triamine, and tetraamine, respectively. [b] BJH pore diameter as determined from the adsorption branch.

Table 2. Textural Properties of Mesostructured γ-Al_2O_3 Prepared through the Calcination (500 °C) of MSU−S/B Surfactant−Boehmite and MSU−B Boehmites[a]

precursor	temp (°C)	surface area (m^2/g)	pore size[b] (nm)	pore volume (cm^3/g)
MSU−S/B	20	440	7.3	1.07
	45	529	4.0	0.86
MSU−B	20	385	7.1	0.97
	45	431	5.0	0.89

[a] The MSU−S/B and MSU−B precursors were prepared from aluminum *sec*-butoxide and dodecylamine. The Al:DDA:EtOH:H_2O reaction stoichiometry was 5:1:68.0:73.4 for all samples.

range 75:25 to 25:75 (v/v) had little effect on the textural properties of the final MSU−B boehmite mesostructures.

It is particularly noteworthy that the MSU−B aluminas reported in Table 1 have BET surface areas that are generally superior to those of conventional boehmites prepared without the aid of a surfactant. For instance, the MSU−B boehmites prepared using AlOOH: surfactant mass ratios of 1:1, the surface areas are 1.27 to 1.43 times as large as the surface area of 322 m^2/g obtained for the boehmite prepared under equivalent hydrolysis conditions in the absence of an amine structure modifier.

Since boehmite is the preferred precursor to γ-Al_2O_3, it was of interest to us to evaluate the relative merits of MSU−S/B and MSU−B for this application. As shown by the data in Table 2, the conversion of MSU−B boehmites to mesostructured γ-Al_2O_3 at calcination temperatures above 500 °C occurs with the retention of a substantial fraction of the surface area and pore volume. Even better textural properties are realized for a γ-Al_2O_3 prepared through the calcination of a MSU−S/B nanocomposite, further illustrating the particle-mediating properties of the amine surfactant (see Table 2). Increasing the assembly temperature of MSU−S/B from 20 to 45 °C results in even higher surface areas for the resulting γ-Al_2O_3 products (cf., Table 2). Future work will examine the catalytic properties of γ-Al_2O_3 compositions made from MSU−S/B precursors.

One additional area of potential application for mesostructured boehmites is as vaccine adjuvants.[18] Although the mechanism of adjuvant function is not well-understood, the high surface area associated with MSU−B boehmites may lead to increased vaccine potency.

Conclusions

The formation of mesostructured MSU−S/B nanocomposites through the hydrolysis of aluminum *sec*-butoxide in the presence of amine surfactants proceeds through a particle assembly mechanism wherein the amine mediates the size and intergrowth of the boehmite nanoparticles. The particle assembly pathway results in a hierarchical scaffold-like framework with pore sizes, surface areas, and pore volumes that do not correlate with the molecular size of the amine. Thus, the assembly mechanism parallels the pathway recently reported for MSU−S/B nanocomposites prepared in the presence of PEO surfactants as structure directors.[13] Unlike PEO surfactants, however, the amine surfactants can be topochemically removed from the boehmite−surfactant nanocomposites through calcination, affording the first examples of mesostructured MSU−B boehmites that are free of surfactant decomposition products. The mesostructured boehmites may be used as precursors to mesostructured γ-Al_2O_3. They may also find other materials applications (e.g., vaccine adjuvants) that are dependent on the textual properties of boehmite.

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