Introduction of Bridging and Pendant Organic Groups into Mesoporous Alumina Materials

Stacy M. Grant,[†] Stephan M. Woods,[†] Arne Gericke,[‡] and Mietek Jaroniec[*,†]

[†]Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44242, United States

[‡]Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, United States

ABSTRACT: Incorporation of organic functionalities into soft-templated mesoporous alumina was performed via organosilane-assisted evaporation induced self-assembly using aluminum alkoxide precursors and block copolymer templates. This strategy permits one to obtain mesoporous alumina-based materials with tailorable adsorption, surface and structural properties. Isocyanurate, ethane, mercaptopropyl, and ureidopropyl-functionalized mesoporous alumina materials were synthesized with relatively high surface area and large pore volume with uniform and wormhole-like mesopores. The presence of organosilyl groups within these hybrid materials was confirmed by IR or Raman spectroscopy and their concentration was determined by elemental analysis.

KEYWORDS: mesoporous alumina, organosilane-assisted synthesis, soft templating, block copolymers
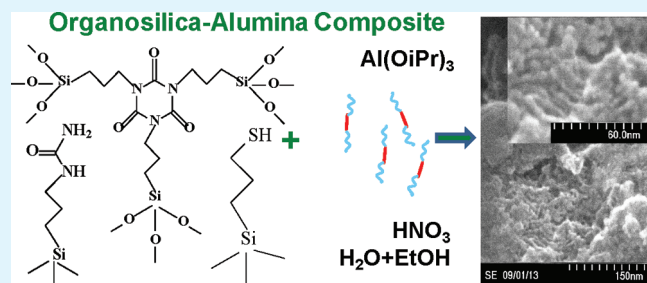
1. INTRODUCTION

Aluminum oxide is a subject of significant interest in part due to its utility in a vast number of applications (e.g., gas sensors, chemiresistors, adsorbents, catalysts for the degradation of pollutants and chemical warfare agents and materials for fuel cells).[1] This material possesses interesting catalytic,[2−4] optical,[5] electronic,[6] and biomedical properties,[7,8] which can be tuned depending on the synthesis method and additives used. Recently, there has been a great interest in the development of well-defined mesoporous aluminum oxides with high surface area and large pore volume.[2,3,9] Of particular note are aluminum oxide materials synthesized in a facile and reproducible way through evaporation induced self-assembly (EISA) in the presence of block copolymers.[10−12] The use of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers $[(EO)_x(PO)_y(EO)_x]$ as soft templates attract a lot of attention because they are inexpensive, commercially available, biodegradable and afford materials with relatively large and ordered/uniform mesopores. The first successful synthesis of ordered mesoporous alumina (OMA) in the presence of block copolymers used as soft templates was reported by Niesz et al.;[13] however, their procedure required a strict control of experimental conditions. A major leap in the preparation of γ-Al_2O_3 with ordered mesopores has been achieved by self-assembly of the $(EO)_{20}(PO)_{70}(EO)_{20}$ triblock copolymer and alumina precursors in ethanolic solution in the presence of additives such as citric or nitric acids.[10] This route has been found to be reproducible and avoids the need for controlling hydrolysis conditions, such as the amount of water and humidity.

Several papers have been devoted to altering mesoporous aluminum oxides in an attempt to tune their properties and expand their utility in various applications. Most noted is the development of mixed metal aluminum oxides in which a portion of aluminum atoms have been replaced with another metal such as nickel, magnesium, chromium, calcium and titanium.[12,14] Addition of a new level of modification, in the form of organic functionality, would allow one to alter the surface properties of mesoporous aluminum oxides and to expand the utility of these materials.

The incorporation of organic functionalities into soft templated mesoporous aluminas is an interesting challenge. In siliceous materials, the class of mesoporous organosilicas, in which an organic group is incorporated into the siliceous framework or added as a hanging group, have been shown to be useful in a broad range of applications such as adsorbents for the removal of heavy metals from aqueous solutions,[15] as sensors to detect heavy metal ions[16] and as catalysts.[17,18] A major hurdle in adding organic groups to aluminum oxide materials is the limited capability of this oxide for direct attachment of organic groups and because of this shortcoming, organosilane molecules were used in this work to incorporate organic functionality into mesoporous alumina.

Organosilane is the general name used here in relation to either bridged silsesquioxanes, $(R'O)_3$-Si-R-Si-$(OR')_3$ (having bridging groups) or trialkoxyorganosilanes, $(R'O)_3$-Si-R (having pendant groups), in which R represents an organic group. These compounds were first used for the synthesis of organosilicas, giving materials with tunable properties by varying the R group.[19−21]
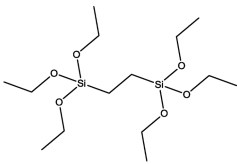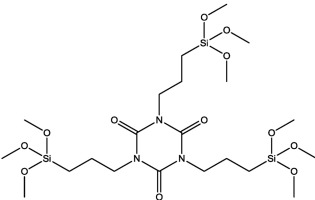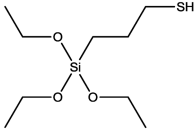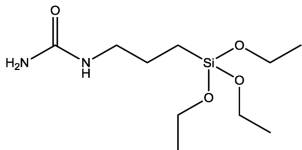
Since their introduction, a number of different organosilanes are available commercially and have been used for the synthesis of various organosilicas, many of which are ordered and have been studied in depth.[22,23] These materials can be prepared in a one-pot synthesis by co-condensation of organosilane and metal oxide precursors. The incorporation of various organic groups has been used to alter the surface and chemical properties (optical, magnetic, electric, hydrophobicity/philicity, acidity/basicity) and consequently, to enhance their catalytic, adsorption, separation, and other applications.[24]

Organosilanes with N-, O-, and S-containing groups have been used for their ability to chelate and adsorb heavy metal ions such as Hg^{2+}, Pb^{2+}, and Cd^{2+} in aqueous media. Monofunctional and bifunctional organosilicas with pendant and/or bridging organic groups, such as mercaptopropyl, ureidopropyl and isocyanurate, have been explored as adsorbents for heavy metal ions and related environmental remediations.[25−29] Postsynthesis chemistry can also be employed to further functionalize materials, as in the case of the oxidative conversion of mercaptopropyl groups to sulfonic groups for use in acid−base catalysis.[30,31] Ethane-functionalized organosilica has been suggested to be beneficial when used individually (addition of hydrophobicity) or in tandem with other functional groups such as when combined with sulfonic groups (obtained by oxidative conversion of mercaptopropyl groups) for improved catalytic activity in the esterification of acetic acid with ethanol and hydrolysis of cycloacetonate. It has also been suggested that the addition of ethane bridging groups in lieu of tetraethyl orthosilicate can facilitate the synthesis of multifunctional organosilicas with enhanced surface area.[32]

The recent study by Yang et al.[33] shows that the postsynthesis functionalized γ-alumina nanofibers obtained by refluxing with 3-mercaptopropyltrimethoxysilane in toluene solution can be used to effectively remove Pb^{2+} and Cd^{2+} from water at a high flux rate. The authors also grafted octyl groups in order to adsorb hydrophobic 4-nonylphenol molecules from dilute aqueous solutions. The resulting grafted fibers had final surface areas of about 135 and 240 m^2/g for mercaptopropyl and octyl-functionalized nanofibers.[33] The use of mesoporous alumina powders with large pores and accessible organic functionality can enhance the adsorption properties of such materials for removal of heavy metal ions or organic pollutants.

The one-pot self-assembly of organosilane and aluminum alkoxide compounds in the presence of block copolymer templates seems to be an attractive strategy for the development of various mesoporous organosilica−alumina hybrids with tunable surface chemistry and porosity. The potential of this synthesis strategy to achieve high loadings of organic groups in mesoporous alumina is demonstrated for isocyanurate and ethane bridging groups as well as mercaptopropyl and ureidopropyl pendant groups. The resulting materials exhibited the potential for high organic loading (up to 30% for the smaller ethane bridging group), large specific surface area, significant pore volumes and uniform worm-like mesopores as evidenced by pore size distributions and nitrogen adsorption isotherms. It was suggested elsewhere[34] that wormlike mesostructures are often preferred over ordered ones for catalytic applications because of branching, which improves the access of molecules to active sites. The retention of organic groups within materials was confirmed by IR or Raman spectroscopy and elemental analysis data.[35] The aforementioned recipe represents an important step toward the synthesis of mesoporous organosilica−alumina hybrid materials

Table 1. Organosilanes Used in the Synthesis of Mesoporous Organosilica—Alumina Composites

Functional Group (Abbreviation)	Organosilane Structure
Ethane (E)	
Isocyanurate (IC)	
Mercaptopropyl (MP)	
Ureidopropyl (U)	

for various applications where large and accessible mesopores with high loading of organic functionality are required.

2. EXPERIMENTAL SECTION

The organosilica−alumina hybrid samples were synthesized by using a recipe analogous to that elaborated for the preparation of mesoporous alumina[10,12] and adjusted for the addition of organosilanes. In a typical synthesis, approximately 1.0 g of $(EO)_{106}(PO)_{70}(EO)_{106}$ triblock copolymer (Pluronic P123 from BASF, Co.) was dissolved in 15 mL of 99.5 $^+$% anhydrous ethanol (Acros Organics), and allowed to stir at room temperature for 4 h. Then, 1.8382 − 1.4298 g (depending on the molar fraction required) of 98 $^+$% aluminum isopropoxide (Acros Organics) was added, followed by 1.6 mL of 68−70 wt % nitric acid (Acros Organics) and 5 mL anhydrous ethanol. Finally, 0.001−0.003 mols (depending on the desired molar fraction) of organosilanes were added in a dropwise fashion (see Table 1). The organosilanes used in this study include tris(3-trimethoxysilypropyl)isocyanurate, bis(triethoxy-silyl)ethane, 3-mercaptopropyl-triethoxysilane and ureidopropyltriethoxysilane; all silanes were used as received from Gelest, Inc. The synthesis mixture was continuously stirred at room temperature for 5 h. Next, solvent was evaporated at 60 °C for 48 h in air without stirring. The polymeric template was removed using ethanol extraction or controlled thermal treatment. Ethanol extraction was performed by agitating 100 mL of 95% ethanol (Acros Organics) with approximately 0.25 g of the sample in an oven at 60 or 100 °C for 24 h. Once cooled, the resulting samples

were washed with 95% ethanol, filtered and dried overnight at 60 or 100 °C. The samples were alternatively thermally treated in flowing nitrogen in a quartz tube furnace by heating at 1 °C/min to 315 °C and then held at that temperature for 4 h. The molar compositions of the samples studied were 1.7×10^{-4} moles of the polymer template:0.01 mols (combined) of aluminum isopropoxide and organosilane:3.6×10^{-2} moles of nitric acid:0.34 mols of ethanol.

The resulting samples were labeled starting with mesoporous organosilica—alumina (A), followed by the molar fraction percentage (10, 20, 30) of organosilane per aluminum atom and the organosilane used (E for ethane, MP for mercaptopropyl, IC for isocyanurate, or U for ureidopropyl) and finally, temperature used in template removal method (60 for extraction at 60 °C, 100 for extraction at 100 °C or 315 for thermal treatment in flowing nitrogen up to 315 °C for 4 h); for instance, A-10IC-60 denotes the sample obtained using 10% of isocyanurate silane and extracted with ethanol at 60 °C.

Nitrogen adsorption measurements were measured using ASAP 2010 (Micromeritics, Inc.) volumetric analyzers at −196 °C with ultra high purity nitrogen gas. All samples were outgassed under vacuum at 100 °C for 3 h prior to each measurement.

Samples were imaged using a Hitachi HD-2000 Scanning and Transmission Electron Microscope (STEM). A lacy carbon coated, 200-mesh, copper grid was dipped into the sample suspension (sample in ethanol) and then dried under vacuum at 100 °C for 12 h prior to analysis. The unit was operated at an acceleration voltage of 200 kV and an emission current of 30 μA in the scanning electron (SE) mode or transmission electron (TE) mode.

Adsorption parameters for the samples were determined from the collected nitrogen adsorption data. The specific surface area (S_{BET}) was calculated using the BET method in the relative pressure range of 0.05 to 0.2.[36] The single-point pore volume (V_{sp}) was calculated from the adsorption isotherm at a relative pressure of 0.98. Pore size distributions (PSDs) were calculated from adsorption branches of nitrogen adsorption—desorption isotherms using an unpublished extension of the KJS method, calibrated for cylindrical pores up to 19 nm.[37] The pore width (w_{KJS}) was obtained at the maximum of the PSD curve. The volume of fine pores, mainly micropores (V_{mi}), was evaluated by integration of the PSD curve up to ~3 nm.

Organic group concentrations were obtained experimentally through CHNS elemental analysis. In the case of ethane groups, carbon percentages were used. To correct for any residual polymer template in the final material, pure alumina was synthesized in a manner analogous to the organosilica—alumina composites and these values (2.373 and 1.269% for extraction at 60 and 100 °C, respectively) were subtracted from the elemental analysis carbon percentage values. Thermogravimetric analysis (not shown) was used to monitor template removal. In general, the as synthesized samples had ~35 wt % polymer template and after extraction had ~10 wt %. Full polymer removal was only achieved with calcination. To eliminate this problem from the other samples, N percentages were used for isocyanurate and ureidopropyl-containing samples and sulfur percentages for mercaptopropyl-containing materials. Calculations were performed by dividing the elemental percentage by 100 and then the molar mass of that element found in the organic group. For example, in A-10MP-60 there is 2.25% sulfur (average value of two runs). Dividing 2.25 by 100 gives the sulfur content in 1 g of the sample, and next dividing the resulting value by 32.065 g/mol (the molar mass of one sulfur atom) gives an experimental organic group concentration of 0.70 mmol of mercaptopropyl group per gram of the sample.

The calculated organic group concentration was determined based on the molar quantities of the precursors added to the synthesis mixture. This concentration was calculated by dividing the moles of organic group added (0.001 for 10% molar fraction; see the molar composition of the synthesis mixture) by the total mass of the resulting sample (organosilica and alumina) in grams. The mass of an organic group was
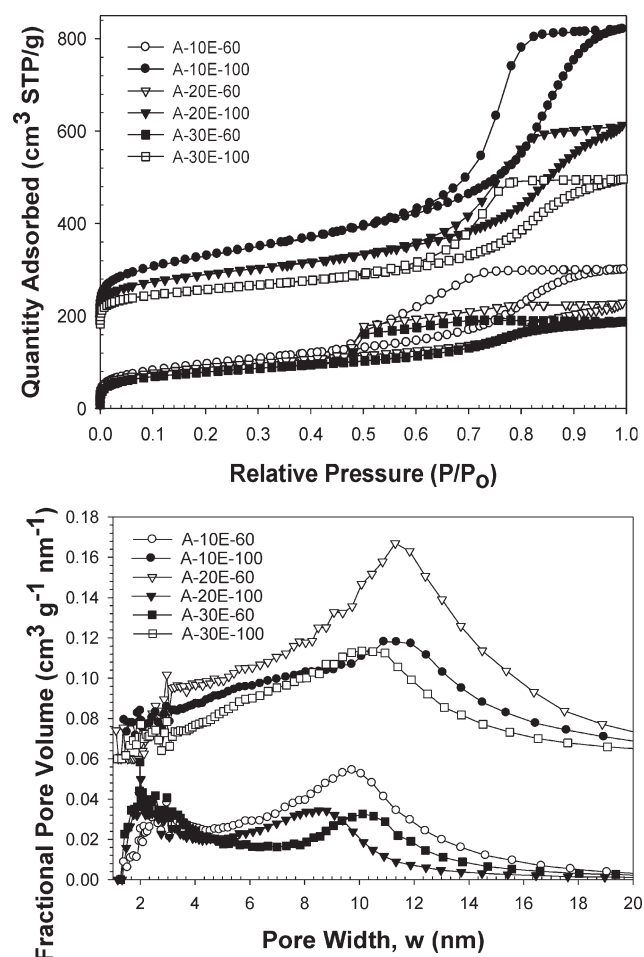

Figure 1. N_2 adsorption isotherms (top) and PSDs (bottom) for mesoporous organosilica—alumina composites with ethane bridging groups (E) at 10, 20, and 30% (molar) of organosilane to aluminum; the samples were extracted at 60 and 100 °C. Isotherms for the samples extracted with ethanol at 100 °C are offset by 175 cm^3 STP/g. PSDs for these samples are offset by 0.06 cm^3 g^{-1} nm^{-1}.

obtained by excluding half of the oxygen atom per silicon atom and the entire pendant group or half of the bridging group (1/3 in the case of isocyanurate group). This calculation assumes a complete conversion of aluminum isopropoxide into alumina and a complete incorporation of all organosilanes into the sample, and excludes all polymer templates from the material. Carbon, nitrogen and sulfur (CNS) analysis was performed using a LECO model CHNS-932 elemental analyzer from St. Joseph, MI.

IR data were acquired using a Bruker vector 33 FTIR spectrometer, equipped with a DTGS detector and a ZnSe ATR attachment. 256 interferograms were co-added and Fourier transformed with 4 cm^{-1} spectral resolution using a Blackmann-Harris 3-Term apodization function and a zerofilling factor of 2. Raman data were obtained using a Horiba Jobin Yvon LabRam HR 800 Raman spectrometer with an Olympus IX 71 microscope attachment, and a symphony CCD detector. Spectra were acquired with a 632.81 nm laser and 180 s acquisition times. A 40× air objective was utilized in all measurements.

3. RESULTS AND DISCUSSION

Nitrogen adsorption isotherms for mesoporous organosilica—alumina hybrid samples with ethane (E) bridging groups are shown in Figure 1. Those after template removal at 100 °C show

Table 2. Adsorption Parameters Obtained by Analysis of Nitrogen Adsorption Isotherms and the Corresponding Pore Size Distributions for Mesoporous Organosilica−Alumina Composites with Various Organosilica Groups at 10% Molar Fraction of Organic Group to Aluminum Atom; Ethane Organic Group Is Also Shown at 20 and 30% Molar Fractions[a]

sample	V_{sp} (cm^3/g)	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	w_{KJS} (nm)
A-10E-60	0.46	348	0.04	9.7
A-10E-100	0.99	563	0.02	11.3
A-20E-60	0.34	321	0.06	10.1
A-20E-100	0.66	451	0.03	10.9
A-30E-60	0.29	285	0.05	8.6
A-30E-100	0.49	298	0.02	10.1
A-10IC-60	0.15	141	0.01	5.1
A-10IC-315	0.33	338	0.04	5.6
A-10MP-60	0.25	193	0.05	10.2
A-10MP-100	0.68	491	0.04	11.7
A-10U-60	0.28	202	0.02	11.8
A-10U-100	0.72	396	0.02	14.5

[a] V_{sp}, single point pore volume calculated from adsorption isotherm at P/P_o = 0.98; S_{BET}, BET specific surface area obtained from the adsorption data in the P/P_o range from 0.05 − 0.2; V_T, total pore volume calculated by integration of the PSD curve; V_{mi}, micropore volume calculated by integration of the PSD curve up to ~3 nm; w_{KJS}, pore width calculated at the maximum of PSD.

Table 3. Organic Group Concentrations (exptl and calcd) and Elemental Analysis Data for Mesoporous Organosilica−Alumina Composites with Various Organic Groups at 10% Molar Fraction of Organic Group to Aluminum Atom; Ethane Organic Group Is Also Shown at 20 and 30% Molar Fractions[b]

sample	%C, [%N], or (%S)	exptl C_{org} (mmol/g)	calcd C_{org} (mmol/g)
A-10E-60	3.04	1.3	2.1
A-10E-100	2.96	1.4	2.1
A-20E-60	7.85	3.3	3.5
A-20E-100	7.41	3.1	3.5
A-30E-60	11.87	4.9	4.6
A-30E-100	11.75	4.9	4.6
A-10IC-60	[3.46]	0.82	0.98
A-10IC-315	[3.40]	0.81	0.98
A-10MP-60	(2.25)	0.70	1.6
A-10MP-100	(2.32)	0.72	1.6
A-10U-60	[2.66]	0.95	2.1
A-10U-100	[2.28]	0.81	2.1

[b] Exptl C_{org}, millimoles of organic group (C data used for ethane, N for isocyanurate, and ureidopropyl or S for mercaptopropyl groups) per gram of the sample, calculated from CHNS elemental analysis data; carbon from polymer template remaining in pure alumina samples extracted at 60 or 100 °C (2.373 and 1.269%, respectively) was subtracted from the ethane-containing samples; calculated C_{org}, millimoles of organic group per gram of the sample calculated from quantities added to the synthesis mixture.
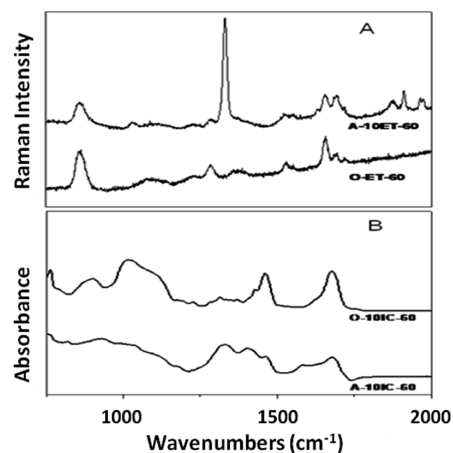
higher overall adsorption of nitrogen, larger BET surface areas and single-point pore volumes (Table 2). Samples have small quantities of fine micropores, which decreased as the ethanol extraction temperature was increased. This series of samples was expanded from 10% molar fraction of ethane bridging groups to 20 and 30% molar fractions with retention of favorable characteristics such as high BET surface areas and pore volumes. In fact, the BET surface areas (348 and 563 m^2/g for A-10E, 321 and 451 m^2/g for A-20E and 285 and 298 m^2/g for A-30E samples extracted with ethanol at 60 and 100 °C, respectively) of the hybrid samples are much larger in comparison to that of pure alumina previously synthesized (228 m^2/g when calcined at 400 °C).[12] The overall adsorption characteristics decreases as the organic loading increases from 10% molar fraction of the ethane bridging group to 30%. PSDs show that pore sizes are large (8.6−11.3 nm) and increase further when the extraction temperature is raised from 60 to 100 °C.

A comparison of the experimental C_{org} (Table 3) with the calculated C_{org} of the final products shows that for the 10% ethane samples, extracted at 60 and 100 °C, there was a loss of the ethane organosilane (~38 and 33% loss, respectively) but for the 20 and 30% ethane samples, the majority of the ethane bridging groups were retained after template removal. There is most likely an overestimation in the organic group concentration in these samples (especially, the 30% ethane group-containing samples with 107% of the calculated organic group concentration) due to the assumption that the error introduced from polymer template remaining in the final sample was removed from the elemental analysis data by determining the quantity remaining in pure alumina samples. The final samples (extracted at 100 °C) contain 1.4, 3.1, and 4.9 mmol of ethane groups per gram of the sample with 10, 20, and 30% molar equivalent, respectively, added to the synthesis mixture.

Figure 2. Raman (panel A) and IR (panel B) spectra for mesoporous organosilica−alumina composites with 10% (molar) of ethane (sample A-10ET-60) and isocyanurate (sample A-10IC-60) bridging groups compared to those of the pure organosilica material (O-ET-60 and O-10IC-60, respectively).

The presence of ethane groups within the alumina framework was confirmed by Raman spectroscopy, which was performed on bis(triethoxysilyl)ethane containing A-10E-60 and compared to that of pure bis(triethoxysilyl)ethane organosilica (O-Et-60), Figure 2A. Spectral changes were seen in the region of 1000−1800 cm^{-1}. The appearance of bands at 1051, 1660, 1701, and 1767 cm^{-1} are associated with aluminum oxide and are observed in other aluminum oxide-containing samples. A change in the intensity ratio was seen in the bands at 1417 and 1457 cm^{-1}, which
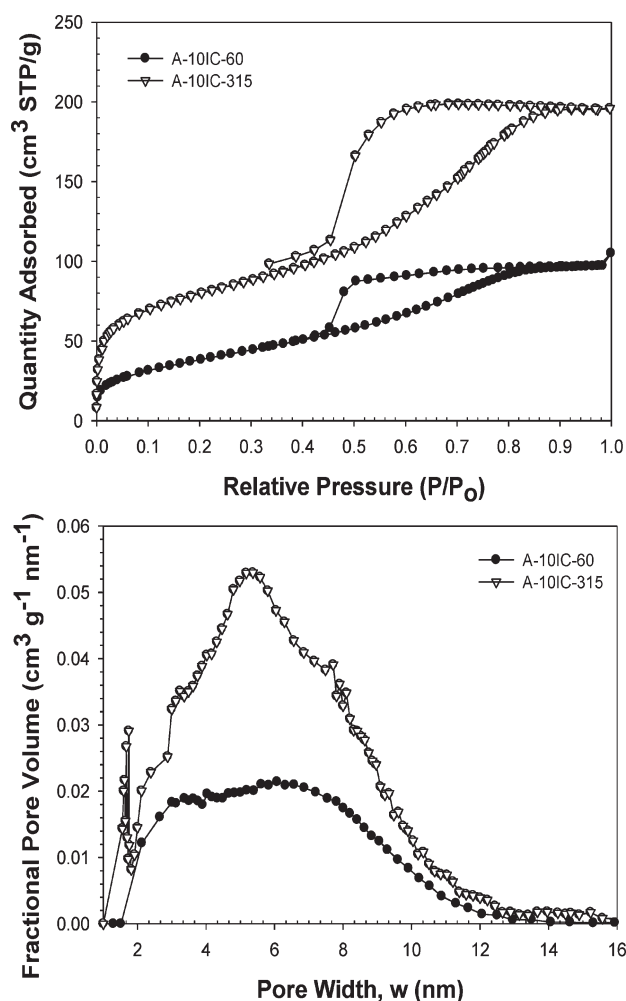
Figure 3. N_2 adsorption isotherms (top) and PSDs (bottom) for mesoporous organosilica—alumina composites with isocyanurate bridging groups (IC) via ethanol extraction at 60 °C, and calcination in flowing nitrogen from room temperature up to 315 °C.

Figure 4. STEM image of mesoporous organosilica—alumina composite with 10% (molar) of isocyanurate (A-10IC-315) bridging group calcined in flowing nitrogen up to 315 °C, held for 4 h. Mesochannels are uniform but wormholelike. Inset is of the same sample at an additional magnification.

are associated with deformation CH_2 and CH_3 mode. The change in the intensity ratio depicts a change in the vibrational modes, which are indicative of the binding to aluminum oxide.

Nitrogen adsorption isotherms for organosilane-alumina samples with 10% molar fraction of isocyanurate bridging groups with template removal by ethanol extraction at 60 °C and calcination at 315 °C are displayed in Figure 3. Calcination at 315 °C is possible in the samples with isocyanurate groups due to the retention this group to temperatures of 315 °C as shown in siliceous materials[38] and confirmed by thermogravimetric analysis in which the polymer template removal was monitored (~180 °C) and the isocyanurate peak was retained. The sample with ethanol extraction at 60 °C has decreased overall adsorption and a delayed hysteresis loop, which may be indicative of pore blockages by the bulky isocyanurate bridging group. The calcined sample has a larger surface area (338 m^2/g), pore volume (0.33 cm^3/g), slight increase in the pore width (5.6 nm), and a small decrease in the desorption delay.

The pore size distributions for the samples show that they have mesopores of varying sizes. The sample with template removal by ethanol extraction at 60 °C has a broad peak covering the range from micropores to approximately 10 nm and the
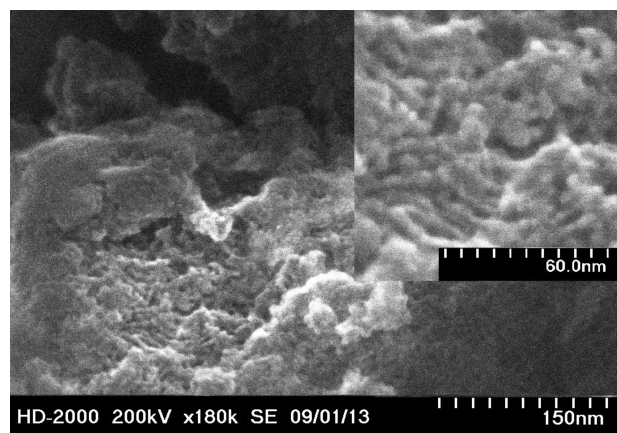
calcined sample has one primary peak at 5.6 nm with shoulders on either side indicating the presence of micropores and larger mesopores.

The calculated and experimental C_{org} values show that the majority of isocyanurate groups remained in the alumina material after template removal (~83%, Table 3). The quantities of nitrogen present, from nitrogen elemental analysis data, in the samples extracted at 60 °C and calcined at 315 °C are virtually the same (0.82 and 0.81 mmol/g, respectively). This finding further supports the ability to retain isocyanurate in the alumina matrix with complete polymer removal when calcined up 315 °C in flowing nitrogen.

Connection of isocyanurate unit within the alumina structure was confirmed by infrared spectroscopy. IR spectra, Figure 2B, were taken of A-10IC-60 and compared against the IR spectra of a pure organosilica sample of tris(3-trimethoxysilylpropyl)isocyanurate (O-10IC-60). The data showed significant changes in the spectral range of 1300—1600 cm^{-1}, in particular the shifts of the bands at 1330 and 1405 cm^{-1} and the appearance of a band at 1581 cm^{-1} indicating an association with aluminum. The method of IR was chosen over Raman due to the strong fluorescence produced by the isocyanurate group in A-10IC-60, which prevented acquisition of Raman spectra.

Structural ordering of the samples was performed by STEM analysis, Figure 4. The mesopores were found to be organized in a wormhole-like fashion as opposed to a hexagonal ordering of the mesopores, found in alumina and mixed-metal alumina samples.[10,12,14] This ordering has been suggested to be beneficial over hexagonal ordering because of the potential for improved access of molecules to the active sites in catalytic applications.[34,35] The same was observed for other samples studied as well as the mesoporous organosilica—alumina sample with bridging 10% isocyanurate calcined at 315 °C by both STEM analysis and small-angle X-ray diffraction (not shown).

The applicability of this organosilane-assisted synthesis for the incorporation of pendant and bridging organic groups into alumina-based materials was demonstrated by the synthesis of mesoporous organosilica—alumina composites with 10% mercaptopropyl and 10% ureidopropyl surface groups (see Table 1). The resulting isotherms for the hybrid samples obtained by using
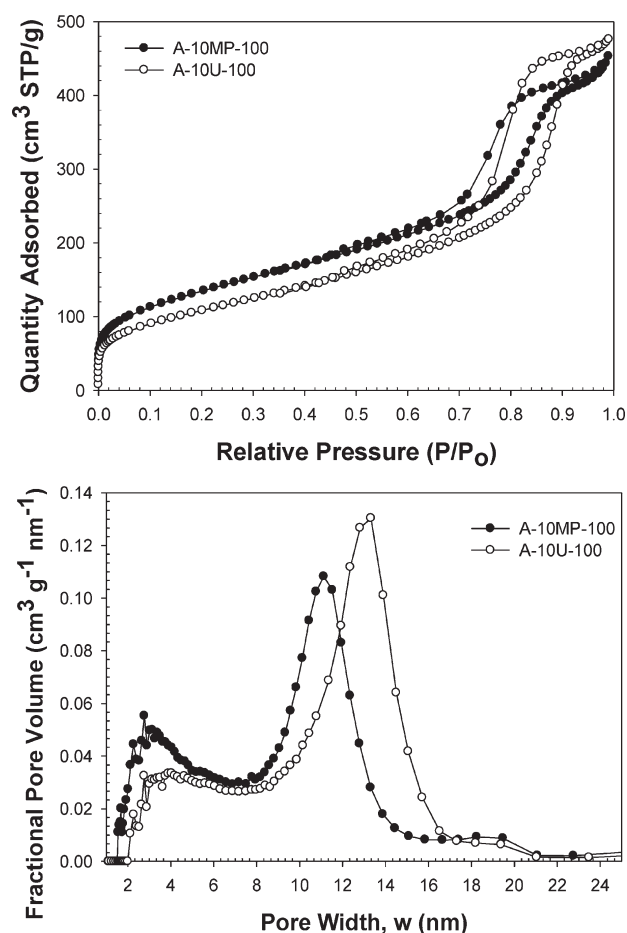
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dx.doi.org/10.1021/am2011788 |*ACS Appl. Mater. Interfaces* 2011, 3, 4480–4486

Figure 5. N$_2$ adsorption isotherms (top) and PSDs (bottom) for mesoporous organosilica—alumina composites with pendant groups.

that of pure mesoporous alumina, similarly high pore volumes, and uniform wormhole-like mesopores. Significant attention must be paid in selection of the template removal process for each organosilane introduced and the effects of such processes (i.e., lower organic loading for the samples prepared at higher temperatures, and the lack of structural condensation for those obtained at lower temperature). The presence of bridging organic groups within the hybrid samples was confirmed by IR or Raman spectroscopy and organic group concentrations were determined on the basis of elemental analysis data. The feasibility of this approach to organosilanes in general (with bridging and pendant groups) was shown through the synthesis of mercapto-propyl and ureidopropyl-functionalized mesoporous organosilica—alumina composites with similar properties to those with bridging groups. The materials synthesized and characterized within represent a new subclass of mesoporous alumina materials as potential candidates for use in applications in which desired organic functionalities are desirable.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: jaroniec@kent.edu. Phone: 001-330-672-3790.

■ ACKNOWLEDGMENT

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10% (molar) of the organosilane with pendant group and extracted in ethanol at 100 °C are shown in Figure 5. The resulting samples, see Table 2, have high overall BET surface area (both samples extracted in ethanol at 100 °C have significantly higher surface area than that of pure alumina), large pore volumes and show uniform mesopores, confirmed by the corresponding PSDs. The mesopore sizes for these samples are very large with mercaptopropyl-containing alumina having 11.7 nm and ureido-propyl-containing alumina having 14.5 nm. In addition to these mesopores, both samples contain a significant amount of small mesopores (~3−4 nm) which contribute to the large surface area of these materials. The samples extracted in ethanol at 100 °C have more favorable characteristics than those prepared at 60 °C (not shown), see Table 2. This is most likely due to structural organization and condensation occurring at the higher temperature. Approximately 40−45% of the organic group added to the synthesis mixture was retained after template removal. This is most likely due to the fact that pendant-type organic groups have only one silicon atom in which to bond to the alumina framework and thus are the least retained of the organosilanes used in this work.

4. CONCLUSIONS

The one-pot organosilane-assisted synthesis of organosilica—alumina composites with bridging organic groups afforded mesoporous materials with much higher BET surfaces area than

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