Chem. Mater. **2003,** *15,* 2803−2808

Synthesis and Characterization of Amorphous Nanostructured HAlO, a Novel Aluminumoxyhydride

Suwen Liu,[†] Ulrike Fooken,[†] Christopher M. Burba,[†] Margaret A. Eastman,[‡] and Rudolf J. Wehmschulte*[,†]

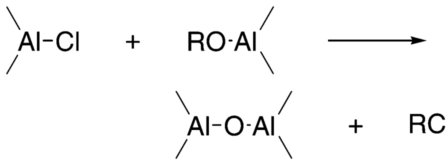
Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Room 208, Norman, Oklahoma 73019, and Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received January 29, 2003. Revised Manuscript Received May 6, 2003

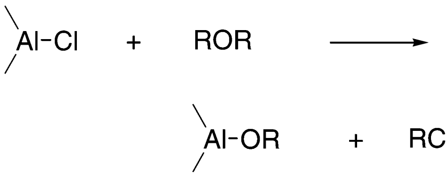
A novel material, amorphous nanostructured HAlO, has been synthesized by the reaction of various methylsiloxanes [e.g., $(Me_2HSi)_2O$] with the aluminum hydride $H_3Al{\cdot}NMe_3$ in ether or aromatic solvents under mild conditions. Its high surface area of ca. 250 m^2/g is due to both its small particle size of approximately 5 nm and its amorphous nanostructure. Its amorphous nature was demonstrated by TEM and XRD studies, and its composition was determined by elemental analysis, ^1H and ^{27}Al MAS solid-state NMR spectroscopies, and FT-IR spectroscopy. HAlO is an oxidic material that still contains a reactive aluminum hydride functional group. Prolonged heating at 200−250 °C causes it to slowly decompose to aluminum metal and amorphous Al_2O_3 without significantly changing the particle size or the BET surface area. This decomposition is accompanied by the loss of hydride and a decrease of the aluminum coordination number from five to four. HAlO reacts readily with protic reagents such as water or alcohols to give bayerite, $Al(OH)_3$, or alkoxy alumoxanes $(ROAlO)_n$. Annealing below its decomposition temperature led not to crystallization but rather to a dramatic decrease in reactivity. No reaction was observed between *n*-octanol and HAlO that had been annealed at 200 °C even after 17 h at 90 °C. HAlO cleanly reduces 2-cyclohexene-1-one to the corresponding alcohol, 2-cyclohexene-1-ol, and it converts Me_3SiCl to Me_3SiH, although with a yield of only 24% for the latter.

Introduction

High-surface-area aluminum oxide, Al_2O_3, is produced in large quantities each year and is used mainly as a support for catalysts or as an adsorptive material in separation applications. Micro- or nanocrystalline Al_2O_3 has also found widespread applications in the ceramics industry as a precursor for Al_2O_3-based ceramics.[1] Typically, the syntheses of these materials are based on hydrolysis of aqueous aluminum salt solutions, followed by high-temperature dehydration steps. These dehydration steps are energy-intensive and also lead to decreased surface areas in the products as a result of sintering. During the past decade, an alternative low-temperature approach to metal oxides has been developed, the so-called non-hydrolytic sol−gel process.[2,3] In this process, a metal halide is reacted with a metal alkoxide to give a metal−oxygen−metal linkage, accompanied by the release of a volatile alkyl halide (eq 1). Alternatively, a metal halide is reacted with an ether to give a metal alkoxide and an alkyl halide (eq 2).



(1)



(2)

General advantages of the non-hydrolytic sol−gel synthesis include low reaction temperatures, homogeneous reaction mixtures, high product surface areas, and generally very low hydroxyl contents. In the case of Al_2O_3, a high-temperature posttreatment (calcination) is often required to remove carbon and halide impurities.[4,5] Therefore, we were interested in developing a chloride-free non-hydrolytic sol−gel process for the synthesis of Al_2O_3, and on the basis of literature reports[6,7] and our own work,[8,9] we have begun to investigate the utility of aluminum hydrides as precursors for aluminum oxides. Here, we report the synthesis,

---

* Corresponding author. E-mail: rjwehmschulte@ou.edu.

[†] University of Oklahoma.

[‡] Oklahoma State University.

(1) Hudson, L. K.; Misra, C.; Wefers, K. In *Industrial Inorganic Chemicals and Products*; Wiley-VCH: Weinheim, Germany, 1999; Vol. 1, pp 26−83.

(2) Vioux, P. A. *Chem. Mater.* **1997**, *9*, 2292−2299.

(3) Lafond, V.; Mutin, P. H.; Vioux, A. *J. Mol. Catal. A* **2002**, *182−183*, 81−88.

(4) Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Lefevre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1994**, *170*, 234−242.

(5) De Hazan, Y.; Shter, G. E.; Cohen, Y.; Rottman, C.; Avnir, D.; Grader, G. S. *J. Sol−Gel Sci. Technol.* **1999**, *14*, 233−247.

10.1021/cm030191f CCC: $25.00

characterization, and initial reactivity studies of a novel material, HAlO, which is obtained by the reaction of $H_3Al{\cdot}NMe_3$ with various methylsiloxanes.

Experimental Section

Starting Materials. The aluminum hydride $H_3Al{\cdot}NMe_3$ was prepared according to a literature method.[10] 1,1,3,3-Tetramethyldisiloxane, $(Me_2SiH)_2O$, was purchased from Gelest. Hexamethylcyclotrisiloxane $(Me_2SiO)_3$, >98%, was purchased from Aldrich and was purified by sublimation prior to use. Polymethylhydrosiloxane, $Me_3SiO(MeHSiO)_xSi(Me)_3$, was purchased from Hüls America and used as received.

Synthesis. All manipulations were performed under a dry, oxygen-free nitrogen gas atmosphere using modified Schlenk techniques and an Innovative Technologies drybox. Solvents were freshly distilled from sodium, potassium, or sodium/potassium alloy and degassed twice prior to use.

Reaction of $H_3Al{\cdot}NMe_3$ with $(Me_2SiH)_2O$. A sample of $H_3Al{\cdot}NMe_3$ (2.0 g, 22 mmol) was dissolved in benzene (200 mL) in a Schlenk flask, and $(Me_2SiH)_2O$ (3.96 mL, 22 mmol) was added to the stirred $H_3Al{\cdot}NMe_3$ solution slowly via syringe at room temperature. The mixture was then heated to 65 °C. After 0.5 h, the solution became cloudy; it was stirred overnight (19 h), during which time a white precipitate formed. The resulting colorless solid was collected on a glass frit, washed with hexanes (5 × 40 mL), and dried in vacuo at 65 °C for 3 h to obtain a fine colorless powder. Yield: 0.90 g. Anal. Found C 9.96%, H 4.20%, N 2.68%, Al 43.10%; 18.7 mmol of hydrolyzable hydrogen per gram of HAlO. Analytical data for another sample: Anal. Found C 9.04%, H 3.24%, N 2.20%; 19.4 mmol of hydrolyzable hydrogen per gram of HAlO. Annealed samples were prepared in a nitrogen atmosphere by heating at a specified temperature for 3 h. Data for a sample annealed at 200 °C: Anal. Found C 4.57%, H 2.18%, N 1.17%; 14.2 mmol of hydrolyzable hydrogen per gram of HAlO.

Reaction of $H_3Al{\cdot}NMe_3$ with $(Me_2SiO)_3$. A mixture of $H_3Al{\cdot}NMe_3$ (2.4 g, 26.9 mmol) and $(Me_2SiO)_3$ (2.0 g, 9.0 mmol) was dissolved in toluene (90 mL), and the resulting solution was stirred for ca. 12 h at room temperature. This was followed by heating at 60 °C for 1.5 days. Cooling to 4 °C resulted in the precipitation of a fine colorless powder that was isolated by careful decantation of the supernatant liquid and dried in vacuo. Yield: 1.2 g. Anal. Found C 12.83%, H 4.56%, N 3.10%, Al 43.24%. FT-IR (CsI plates, mineral oil) ν(Al−H): 1890 cm^{-1} (st). TGA: steady weight loss of ca. 12% between 50 and 300 °C, followed by two more steps contributing an additional 5% loss.

Reaction of $H_3Al{\cdot}NMe_3$ with $Me_3SiO(MeHSiO)_nSiMe_3$. A similar procedure was followed using $Me_3SiO(MeHSiO)_nSiMe_3$ as the starting material. A mixture of $H_3Al{\cdot}NMe_3$ (0.445 g, 5 mmol) and $Me_3SiO(MeHSiO)_nSiOMe_3$ (0.3 g) was dissolved in benzene, and the resulting solution was stirred for 1.5 days at 65 °C. Cooling to room temperature resulted in the precipitation of a fine colorless powder that was isolated by careful decantation of the supernatant liquid, washed with hexanes (3 × 20 mL), and then dried in vacuo. Yield: 0.172 g. FT-IR (CsI plates, mineral oil) ν(Al−H): 1886 cm^{-1} (st).

Reaction of HAlO with Alcohols. Ethanol, *i*-propanol, or *n*-octanol (30 mL each) was added to HAlO [0.12 g, from the reaction of $H_3Al{\cdot}NMe_3$ with $(Me_2SiO)_3$], and the resulting mixture was heated to 60, 80, or 90 °C, respectively, for 14 h. Similarly, *n*-octanol (3 mL) was added to HAlO [0.10 g, from the reaction of $H_3Al{\cdot}NMe_3$ with $(Me_2SiH)_2O$ before and after annealing at 200 °C], and the resulting mixture was heated for 14 h at 95 °C. The volatile materials were removed under reduced pressure, and the resulting colorless powders (or sticky solids in the case of *n*-octanol) were investigated by IR and ^1H NMR spectroscopies and also by ^{27}Al NMR spectroscopy for one of the *n*-octanol reactions.

Ethanol Reaction. ^1H NMR (400 MHz, C_6D_6): 1.08 (s, br), 1.376 (s, br), 1.540 (s, br), 3.51 (s, br), 3.78 (s, br), 4.02 (s, br), 4.141 (s, br), 4.25 (s,br), 4.35 (s, br). IR (KBr, mineral oil): 2955 (s), 2925 (s), 2854 (s), 1461 (m), 1389 (m), 1291 (w, sh), 1258 (m), 1163 (s), 1112 (s), 1073 (s), 912 (m, sh), 859 (s), 829 (s), 805 (s), 748 (m), 683 (s), 665 (s), 626 (s, sh), 543 (m, sh).

i-Propanol Reaction. ^1H NMR (400 MHz, C_6D_6): 0.92 (s, br), 0.985 (s,br), 1.33 (s, br), 1.352 (s, br), 1.48 (s, br), 3.70 (s, br), 4.52 (s, br). IR (KBr, mineral oil): 2953 (s), 2921 (s), 2852 (s), 1486 (w), 1392 (w), 1361 (w), 1255 (m), 1169 (m), 1133 (m), 1028 (s), 995 (s, sh), 859 (s, sh), 816 (s), 804 (s), 692 (s).

n-Octanol Reaction. ^1H NMR (400 MHz, C_6D_6): 0.962 (s, br), 1.289 (s, br), 1.389 (s, br), 1.50 (s, br), 1.913 (s, br), 2.17 (s, br), 3.52 (s, br), 4.245 (s, br). ^{27}Al NMR (130.25 MHz, C_6D_6): 65.0 (s, br), $w_{1/2} = 1500$ Hz; 36.0 (s, br), $w_{1/2} = 3000$ Hz; 8.5 (s, br), $w_{1/2} = 1200$ Hz; relative intensity 1:2:2. IR (KBr, mineral oil): 2961 (s), 2919 (s), 1258 (m), 1145 (m), 1088 (m), 1022 (m), 865 (s), 820 (s, sh), 802 (s), 668 (s), 626 (s, sh).

n-Octanol Reaction with Annealed HAlO. No reaction occurred.

Reaction of HAlO with 2-Cyclohexene-1-one. 2-Cyclohexene-1-one (0.20 mL, 2.0 mmol) was added to a suspension of HAlO (0.20 g, 3.9 mmol of hydrolyzable hydrogen) in THF (20 mL) at room temperature. The reaction mixture was heated to reflux for 17 h and then cooled to room temperature, and the resulting yellow reaction mixture was quenched with water (0.15 mL). The insoluble material was separated by filtration, and the solvent was distilled off the yellow filtrate in vacuo (0.05 Torr). The remaining yellow oil (1.5 mL) was shown to be a mixture of THF and 2-cyclohexene-1-ol by ^1H NMR spectroscopy.

Reaction of HAlO with Me_3SiCl. A resealable NMR tube was charged with HAlO (10 mg, 0.19 mmol of hydrolyzable hydrogen), C_6D_6 (1.0 mL), and Me_3SiCl (20 μL, 0.16 mmol) and shaken for 3 days at room temperature. The ^1H NMR spectrum showed a 10% conversion of Me_3SiCl to Me_3SiH. Subsequent heating to 70 °C for 15 h resulted in an overall conversion of 24%.

Characterization. Infrared spectra were recorded in the range 4000−200 cm^{-1} using a Nicolet Nexus 470 FT-IR spectrometer. The samples were prepared either as mulls between KBr or CsI plates or as KBr pellets. Transmission electron microscopy (TEM) was performed on a JEOL TEM-2000 instrument at 200 kV. Specimens for TEM experiments were sonicated in benzene for 15 min and then loaded onto copper grids (200 mesh). ^1H and ^{27}Al solid-state MAS NMR spectra were recorded at ambient temperature on a Varian/Chemagnetics CMX-II 300 MHz NMR spectrometer using a double-resonance 7.5-mm MAS probe. Samples were packed in airtight Kel-F ampules, which were inserted into silicon nitride rotors for magic-angle spinning. ^1H-decoupled ^{27}Al NMR MAS spectra were obtained with a 1 μs $\pi/20$ pulse on ^{27}Al and a decoupling radio-frequency field strength of 27 kHz. Solid-state spectra were referenced to aqueous $Al(NO_3)_3$ (^{27}Al) or tetramethylsilane (^1H), both at 0 ppm. Additional details are given in the figure legends. Solution NMR spectra were recorded on a Varian Unity Plus 400 MHz, a Varian Mercury 300 MHz, or a Varian VXR-500S spectrometer. ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 as the internal reference ($\delta = 7.15$ ppm). ^{27}Al NMR spectra were referenced to an aqueous $Al(NO_3)_3$ solution as the external standard ($\delta = 0$ ppm). X-ray diffraction (XRD) patterns were recorded with a SCINTAG XRD Xtra X-ray diffractometer (Cu Kα radiation, 45 kV and 40 mA). BET measurements were recorded on a NOVA 1200 Quantachrome BET analyzer. The specific surface area was derived via a six-point analysis with P/P_0 ratios of 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3. TGA measurements were carried out with a DuPont 2000 thermogravimetric analyzer using a heating rate of 5 °C/min. Elemental analyses were performed

---

(6) Fritz, G. *Z. Naturforsch.* **1955**, *10b*, 423−424.

(7) McMahon, C. N.; Bott, S. G.; Alemany, L. B.; Roesky, H. W.; Barron, A. R. *Organometallics* **1999**, *18*, 5395−5408.

(8) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387−8388.

(9) Fooken, U.; Khan, M. A.; Wehmschulte, R. J. *Inorg. Chem.* **2001**, *40*, 1316−1322.

(10) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141−2144.

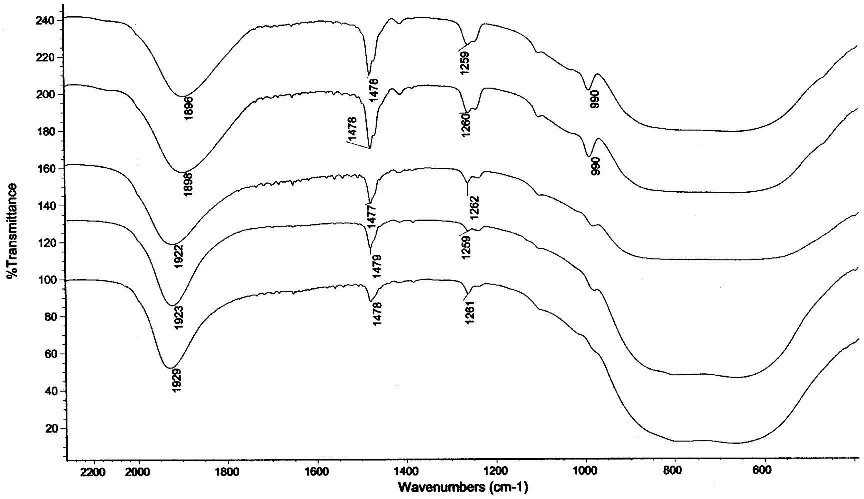


Figure 1. FT-IR spectra for HAlO samples with different annealing temperatures. From top to bottom: as-prepared sample; treated at 100, 180, 200, and 250 °C.

at Complete Analysis Laboratories, Inc., in Parsippany, NJ, and at Desert Analytics in Tucson, AZ.

Results and Discussion

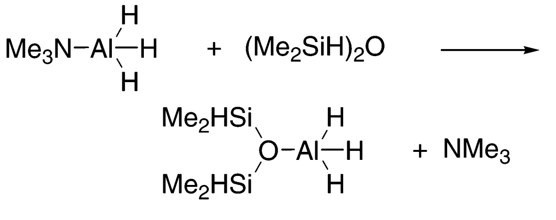
Synthesis of HAlO. The reaction of $H_3Al{\cdot}NMe_3$ with the simple siloxanes 1,1,3,3-tetramethyldisiloxane, $(Me_2SiH)_2O$, hexamethylcyclotrisiloxane, $(Me_2SiO)_3$, or poly(methylhydrosiloxane), $Me_3SiO(MeHSiO)_nSiMe_3$, in aromatic solvents at room temperature afforded a novel, amorphous, nanostructured powder of the approximate composition HAlO. Idealized equations are given below.

$$H_3Al{\cdot}NMe_3 + {}^1/_3(Me_2SiO)_3 \rightarrow HAlO + Me_2SiH_2 + NMe_3 \quad (3)$$

$$(n + 1)H_3Al{\cdot}NMe_3 + Me_3SiO(MeHSiO)_nSiMe_3 \rightarrow (n + 1)HAlO + nMeSiH_3 + 2Me_3SiH + (n + 1)NMe_3 \quad (4)$$

$$H_3Al{\cdot}NMe_3 + (Me_2SiH)_2O \rightarrow HAlO + 2Me_2SiH_2 + NMe_3 \quad (5)$$

When these reactions were conducted in NMR tubes and directly monitored by NMR spectroscopy, the silane products Me_2SiH_2 or $MeSiH_3$ and free NMe_3 were detected and identified. The reaction rates depend on the type of siloxane employed. Reaction 4 is the fastest, with the precipitate appearing within 5 min, followed by reaction 3 (ca. 20 min) and reaction 5 (ca. 30 min). Although the exact mechanisms of the above reactions are not yet known, the first step most likely involves adduct formation between the aluminum hydride and the siloxane (eq 6).



(6)

We propose that the observed reactivity differences are mainly due to steric effects, with the oxygen center being most accessible in the polymeric $Me_3SiO(MeHSiO)_nSiMe_3$. This notion is further supported by the fact that no reaction was observed when $(Me_3Si)_2O$ was employed, even in refluxing toluene. Notwithstanding the different reaction rates, the use of $(Me_2HSi)_2O$ routinely afforded the cleanest product and most facile workup.

The new compound, HAlO, was obtained as a very fine colorless powder. To elucidate the structure and properties of this novel material, it was subjected to annealing processes at 100, 180, 200, and 250 °C in a vacuum and was then analyzed using FT-IR and ^1H and $^{27}Al\{^1H\}$ MAS NMR spectroscopies, TEM, X-ray diffraction, BET measurements, and elemental analysis.

IR Spectroscopic Results. The FT-IR spectra of the HAlO samples after annealing at various temperatures are displayed in Figure 1. These spectra are dominated by a strong Al–H stretch between 1896 and 1929 cm^{-1} and a very strong and broad absorption between 1000 and 500 cm^{-1}. This band is probably due to Al–O stretching and bending[11] and Al–H bending vibrations.[12] The ν(Al–H) band is found at the upper range of Al–H absorptions reported to date.[13–15] The broad and featureless Al–O absorption indicates disorder and corresponds well with the IR spectrum of γ-Al_2O_3.[11] Furthermore, additional bands at 1478, 1260, and 990 cm^{-1} are clearly discernible and are caused by solvent and reagent residues (benzene, trimethylamine, siloxane), which are probably adsorbed on the surfaces or trapped within the pores of the amorphous particles. Heat treatment causes these bands to decrease in intensity. Annealing of the sample at various temperatures leads to a narrowing of the Al–H band and a shift to higher wavenumbers (Figure 1, Table 1). At the same time, the intensity of the Al–H band relative to the Al–O band decreases with higher annealing temperature. This is accompanied by a color change of the

---

[11] Baraton, M. I.; Quintard, P. *J. Mol. Struct.* **1982**, *79*, 337–340.

[12] Kurth, F. A.; Eberlein, R. A.; Schnoeckel, H.; Downs, A. J.; Pulham, C. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1302–1304.

[13] Nöth, H.; Schlegel, A.; Knizek, J.; Krossing, I.; Ponikwar, W.; Seifert, T. *Chem. Eur. J.* **1998**, *4*, 2191–2203.

[14] Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 5611–5612.

[15] Nöth, H.; Schmidt, M.; Treitl, A. *Chem. Ber.* **1995**, *128*, 999–1006.

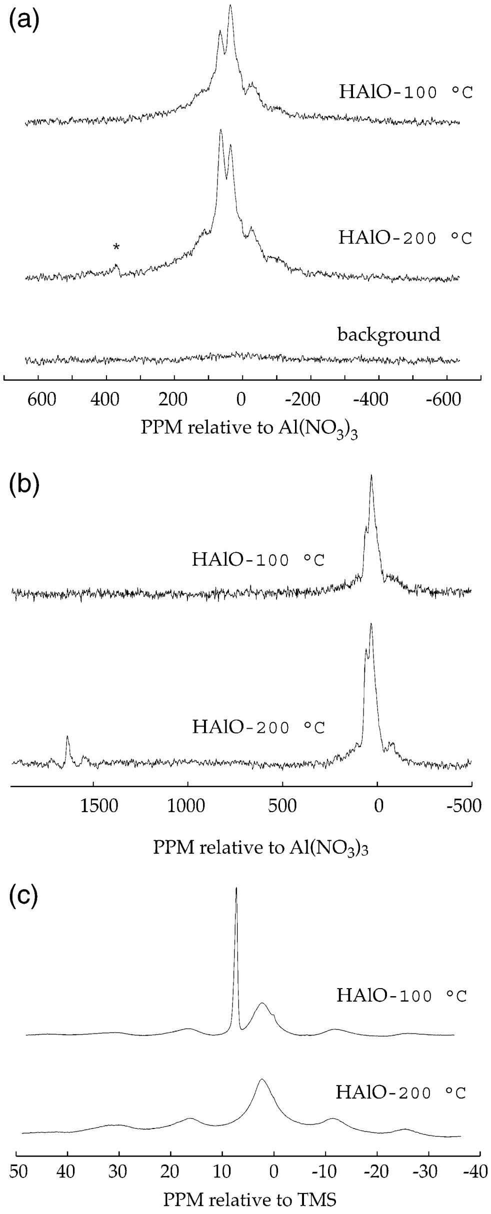


Figure 2. (a) $^{27}Al\{^1H\}$ MAS NMR spectra of the two samples and a background spectrum of an empty rotor (30600 scans). (b) $^{27}Al\{^1H\}$MAS NMR spectra taken with a much wider spectral range to show both Al and Al−O peaks (5000 scans). (c) ^1H MAS NMR spectra (512 scans). The top spectrum is from the sample treated at 100 °C, and the bottom is from the sample heated at 200 °C. Magic-angle spinning speeds are 4.0 kHz for a and c and 6.0 kHz for b.

Table 1. IR Characteristic Peaks (Al−H) and Surface Areas of HAlO Prepared at Different Temperatures

		annealing temperature (°C)			
	as-prepared	100	180	200	250
peak position (cm^{-1})	1896	1898	1922	1925	1929
surface area (m^2/g)	257.2	269.2	−	247.1	−

solid from white to gray, which indicates a partial decomposition of HAlO.

Solid-State NMR Spectroscopy. Figure 2a shows $^{27}Al\{^1H\}$ MAS spectra of two HAlO samples (one annealed at 100 °C, the other at 200 °C). There are two main peaks in both spectra, at about 34 and 64 ppm. The additional smaller peaks are spinning sidebands of the main peaks, except for the one marked with an asterisk, which is the Al metal signal folded in from outside the spectral width. Figure 2b shows $^{27}Al\{^1H\}$ MAS spectra taken with a much wider spectral width to include both the Al metal and Al oxide peaks. Clearly, the HAlO sample that was heated at 200 °C for several hours contains Al metal (δ = 1637 ppm),[16] but no detectable Al metal signal is found in the sample that was heated at 100 °C. ^{27}Al NMR chemical shifts depend greatly on the coordination number.[17] This has been well established in studies of zeolites where both AlO_4 and AlO_6 units have been identified. The tetrahedral unit appears between +50 and +80 ppm and the octahedral unit between −10 and +20 ppm. AlO_5 resonances have been observed in aluminosilicate glasses,[18] thermal decomposition products of aluminosilicate minerals,[19] and amorphous alumina.[20] The peaks from these sites tend to appear in the range 35−25 ppm with some field dependence from the residual second-order quadrupolar shift.[21]

Thus it appears that both samples contain Al with coordination number 4 [i.e., Al(4)], 5 [i.e., Al(5)], and very little with coordination number 6 [i.e., Al(6)]. The relative intensity of the Al(4) and Al(5) peaks varies with sample spinning speed (4 kHz in Figure 2a, 6 kHz in Figure 2b), thus preventing a quantitative analysis (higher spinning speeds were not possible with the instrumentation available). Nevertheless, the spectra clearly show a relative increase of Al(4) sites with increasing annealing temperature and concomitant formation of Al metal. Given that the IR data show a decrease of the aluminum hydride band with increasing annealing temperature, we tentatively propose that the Al(5) sites are associated with the Al−H group.

The corresponding ^1H MAS NMR spectra are shown in Figure 2c. The broad peak centered around 2.5 ppm is due to the hydridic hydrogen bound to aluminum. The top spectrum also shows a sharp intense peak at ca. 7.5 ppm and a weaker one around 0 ppm. The 7 ppm peak can be attributed to residual solvent (benzene), which might be adsorbed on the surface of the particles or, more likely, trapped in pores given that the sample had been annealed at 100 °C under reduced pressure for several hours. The weaker peak at ca. 0 ppm is probably due to $Al-O-SiMe_2H$ groups bound to aluminum. Annealing at 200 °C removes the solvent, but the peak at ca. 0 ppm is still visible, albeit weaker, supporting the notion that it is caused by covalently attached $Al-O-SiMe_2H$ groups.

TEM and XRD Analyses. TEM results show that the as-prepared sample is composed of connected nanoparticles with an average size of about 5 nm (Figure 3a). At high magnification, no crystal lattice fringes were found. The particles were also characterized by selected area electron diffraction (SAED), as illustrated in the inset of Figure 3a. The SAED pattern revealing

---

(16) Andrew, E. R.; Hinshaw, W. S.; Tiffen, R. S. *J. Magn. Reson.* **1974**, *15*, 191−195.

(17) MacKenzie, K. J. D.; Smith, M. E. *Multinuclear Solid-State NMR of Inorganic Materials*; Pergamon Press: New York, 2002.

(18) Sato, R. K.; McMillan, P. F.; Dennison, P.; Dupree, R. *J. Phys. Chem.* **1991**, *95*, 4483−4489.

(19) Smith, M. E.; Neal, G.; Trigg, M. B.; Drennan, J. *Appl. Magn. Reson.* **1993**, *4*, 157−170.

(20) Farnan, I.; Dupree, R.; Forty, A. J.; Jeong, Y. S.; Thompson, G. E.; Wood, G. C. *Philos. Mag. Lett.* **1989**, *59*, 189−195.

(21) Chee, K. S.; Cheng, Y.-B.; Smith, M. E. *Chem. Mater.* **1995**, *7*, 982−988.

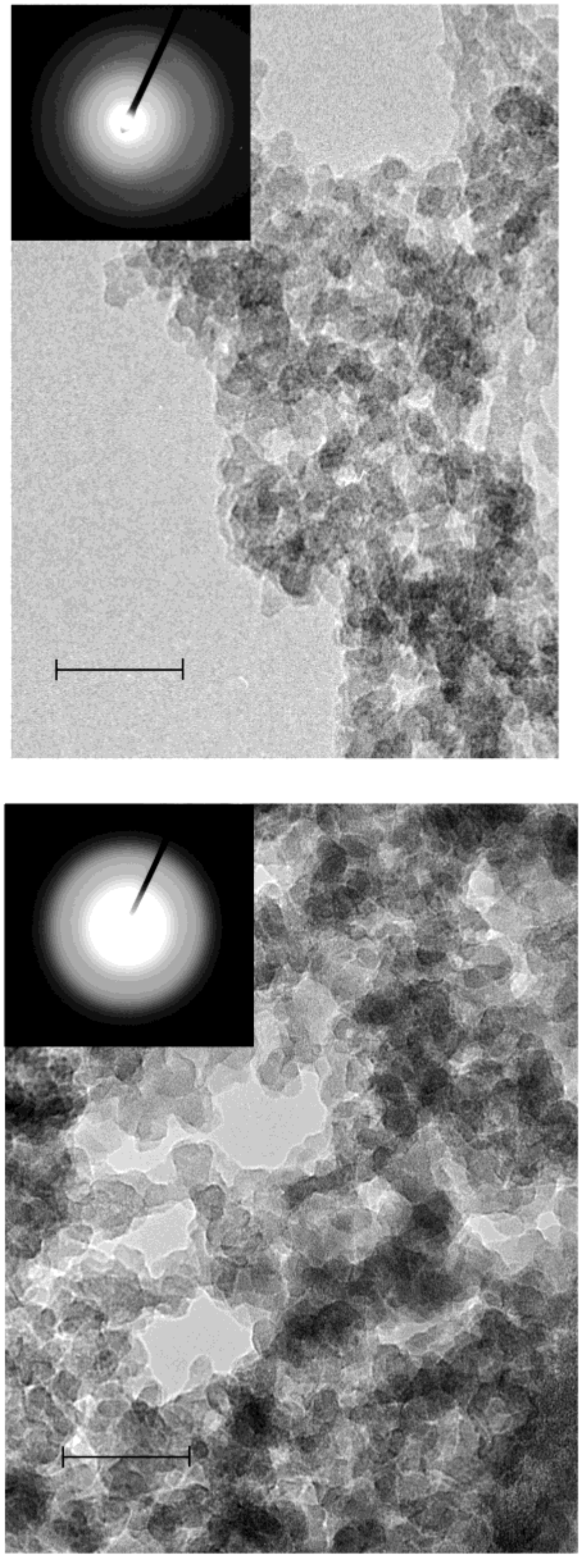


Figure 3. TEM images of the HAlO samples. Top: as-prepared sample; a selected area electron diffraction (SAED) pattern is shown in the inset. The scale bar is 20 nm. Bottom: sample annealed at 200 °C for 3 h; the inset is the SAED pattern. The scale bar is 20 nm.

the amorphous nature of the nanoparticles is faint and displays broad diffraction rings. Annealing at 200 °C (Figure 3b) does not significantly affect the particle size, and the diffraction ring in the inset of Figure 3b is broad. We conclude that both samples are amorphous nanostructured materials. In comparison with the as-prepared sample, the sample annealed at 200 °C began to aggregate slightly. In addition, the TEM results also show that both samples are composed of nanoparticles that are connected and form a three-dimensional web-like nanostructure. The amorphous nature of HAlO and the lack of any long-range order were further confirmed by powder XRD.

Adsorption of N_2. The TEM and XRD results suggested that these samples might exhibit a high surface area. Therefore, the BET surface areas of the as-prepared sample and two samples annealed at 100 and 200 °C were determined by nitrogen adsorption. The results are listed in Table 1. At ca. 250 m^2/g, the BET surface area of the HAlO nanostructured particles is somewhat larger than that of commercial activated alumina (Aldrich, 155 m^2/g) and less than the up to 800 m^2/g found for Al_2O_3 nanoparticles formed by modified aerogel synthesis.[22] Furthermore, the BET surface area is largely independent of the heat treatment of the samples investigated in this study.

Composition and Purity. Elemental analysis results (C, H, N) are in agreement with the spectroscopic results discussed before, with values of 9.96% C, 4.20% H, 2.68% N, and 43.10% Al for the as-prepared sample and 4.57% C, 2.18% H, and 1.17% N for the sample annealed at 200 °C indicating residual hydrocarbons. The Al results were low at 43.10 and 43.24% for the as-prepared samples obtained from the reactions of $H_3Al{\cdot}NMe_3$ with $(Me_2HSi)_2O$ and $(Me_2SiO)_3$, respectively. These values correspond to about 70% of the amount expected for pure HAlO. To obtain a reliable estimate of the hydride content, samples were hydrolyzed with H_2O, and the volume of the resulting H_2 gas was determined. One g of HAlO as-prepared contained approximately 18.7 mmol of hydrolyzable hydride, which corresponds to 82% of the value expected for pure HAlO. Although the reason for the low aluminum content is not fully understood at present, the hydrolyzable hydride content agrees reasonably well with the observed carbon, hydrogen, and nitrogen contents. The IR and ^1H NMR spectroscopic results indicate the presence of benzene, trimethylamine, and either free $(Me_2HSi)_2O$ or Me_2HSiO- groups covalently bound to surface aluminum sites. In fact, the volatile material that distilled off the HAlO powder during the annealing process was trapped and identified as a mixture of mainly benzene and trimethylamine by ^1H NMR spectroscopy. The organic impurities are rather tightly bound, since even after a several hour annealing process at 100 °C benzene can be identified in the HAlO sample by solid-state ^1H NMR MAS spectroscopy. Annealing at 200 °C removed all of the benzene (see Figure 2c), but the C, H, N analysis still showed the presence of organic materials. The IR and ^1H NMR spectroscopic data indicate that these are due to trimethylamine and Me-Si groups. Unfortunately, the organic materials could not be removed completely because of the aforementioned thermolability of HAlO. This thermolability leads to a decrease of hydrolyzable hydrogen. Only 62% of the value expected for pure HAlO was found for the sample annealed at 200 °C for 3.5 h.

---

[22] Carnes, C. L.; Kapoor, P. N.; Klabunde, K. J.; Bonevich, J. *Chem. Mater.* **2002**, *14*, 2922−2929.

Despite the relativley large amount of organic impurities, the presented data are in agreement with the description of the new material as an aluminumoxyhydride, HAlO. The presence of the hydridic hydrogen is demonstrated by the hydrolysis experiments and the ν(Al−H) band in the IR spectra, as well as the reactivity studies described below.

Reactivity and Thermal Stability. HAlO is thermally labile. Prolonged heating at temperatures in excess of ca. 150 °C leads to a slow decrease in the amount of hydride hydrogen, i.e., the Al−H bond is broken. This is typical for aluminum hydrides. For example, $H_3Al{\cdot}NMe_3$ decomposes at 105 °C[23] and $LiAlH_4$ around 125 °C.[24] The thermal decomposition of HAlO results in the formation of metallic aluminum, which was detected by ^{27}Al MAS NMR spectroscopy or, more simply, by the color change from white to gray. An idealized equation is given below.

$$3HAlO \xrightarrow{200-250\ ^\circ C} Al_2O_3 + Al + {}^3/_2H_2 \qquad (7)$$

The observation that the amorphous nanoparticle structure of HAlO remained essentially unchanged after annealing at 200 °C suggests that the facile decomposition of HAlO under these conditions might lead to interesting Al/Al_2O_3 nanohybrids.[25,26] Because of the hydridic character of the hydrogen in HAlO, the latter reacts readily with protic reagents with the evolution of H_2 gas. Addition of water resulted in a brief but intense reaction that produced microcrystalline bayerite, $Al(OH)_3$. Similarly, reaction of HAlO with various alcohols gave colorless powders or oils that no longer contained the Al−H functional group. Judging from the similarity of the solution ^{1}H and ^{27}Al NMR spectra of the products discussed here with those reported for the reaction of methylalumoxane $(MeAlO)_n$ with *i*-propanol, we propose those products to be alkoxy alumoxanes $(ROAlO)_n$.[27] This interesting class of compounds is usually prepared by careful hydrolysis of trisalkoxyalanes and is known to consist of mixtures of Al−O clusters and cage structures featuring aluminum coordination numbers between four and six.[28] An alternative approach to these compounds consists of the thermolysis of trisalkoxyalanes $[(RO)_3Al]_n$.[29] The fact that the ^{27}Al NMR spectrum of the oily product obtained from the reaction of HAlO with 1-octanol revealed the presence of four-, five-, and six-coordinated aluminum sites supports its preliminary identification as $(n\text{-}C_8H_{17}\text{-}OAlO)_n$.[27] The exact structure of this and the related compounds is currently under investigation.

The reactivity of HAlO decreases strongly with increasing annealing temperature. This can best be illustrated by the reaction of excess octanol with HAlO that had been annealed at 200 °C. Remarkably, even after treatment of this HAlO with excess octanol at 90 °C for 17 h, unreacted starting material was still present. This is shown by the presence of the characteristic Al−H band in the IR spectrum. The reasons for this are not yet known, but we suggest that the structural change that occurs along with the partial decomposition of HAlO during annealing at 200 °C is accompanied by a decrease in pore size so that the Al−H sites are not as accessible for the relatively large *n*-octanol molecule.

The hydridic nature of the hydrogen in HAlO was further demonstrated by the clean reduction of 2-cyclohexene-1-one to the corresponding unsaturated alcohol 2-cyclohexene-1-ol. The C−C double bond was not reduced under these conditions. The reduction of Me_3SiCl to Me_3SiH with HAlO (20% excess) was only partially successful. Even after 15 h at 70 °C, a conversion rate of only 24% was obtained. Although the exact reasons are not yet known, we suggest that some hydridic sites in the interior of the HAlO particles are not accessible to Me_3SiCl under the conditions applied.

Summary

The reaction of $H_3Al{\cdot}NMe_3$ with methylsiloxanes in aromatic or ether solvents under mild conditions (20−60 °C) afforded the novel material HAlO as an amorphous, high-surface area solid. IR and ^{1}H and ^{27}Al NMR spectroscopic data and elemental analysis results strongly suggest that its composition is HAlO, i.e., an oxidic material containing a reactive hydridic functional group. Although its empirical formula is similar to those of aluminumoxychloride ClAlO[30] or boehmite HOAlO,[1] the aluminum center in HAlO was found to be four- and five-coordinate unlike the six-fold coordination found in ClAlO and HOAlO. Attempts to induce crystallization by annealing at elevated temperatures were unsuccessful because of the compound's thermal lability. On the other hand, its decomposition into Al metal and amorphous Al_2O_3 at ca. 250 °C provides a convenient entry for the facile preparation of metal−metaloxide nanohybrids, which so far requires more elaborate CVD processes.[25]

Initial reactivity studies show HAlO to be reactive toward protic reagents such as water or alcohols. In the case of alcohols, the reactions afford hydroxide-free alkoxy alumoxanes $(ROAlO)_n$. In addition, the ketone 2-cyclohexene-1-one was cleanly reduced to the corresponding alcohol, and Me_3SiCl was converted to Me_3SiH, although with a yield of only 24% for the latter. Further investigations of the reactivity of HAlO toward a variety of organic substrates with the aim of developing it as an easily obtainable reducing or hydride-transfer reagent are in progress.

Acknowledgment. Financial support for this work from the University of Oklahoma and the donors of the American Chemical Society Petroleum Research Fund is gratefully acknowledged. We are also thankful to Professor Allen Apblett, OSU Stillwater, for the BET measurements; to Nathan Hesse for the TGA results; and to Greg Strout for the TEM pictures.

CM030191F

---

(23) Stecher, O.; Wiberg, E. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 2003−2012.

(24) Finholt, A. E.; A. C. Bond, J.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 1199−1203.

(25) Veith, M.; Faber, S.; Hempelmann, R.; Janssen, S.; Prewo, J.; Eckerlebe, H. *J. Mater. Sci.* **1996**, *31*, 2009−2017.

(26) Veith, M.; Kneip, S.; Faber, S.; Fritscher, E. *Mater. Sci. Forum* **1998**, *269*−*272*, 303−306.

(27) Kimura, Y.; Tanimoto, S.; Yamane, H.; Kitao, T. *Polyhedron* **1990**, *9*, 371−376.

(28) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Chem. Mater.* **1992**, *4*, 167−182.

(29) Inoue, M.; Kimura, M.; Inui, T. *Chem. Mater.* **2000**, *12*, 55−61.

(30) *Structure Reports* **1959**, *23*, 310.