Modified Aluminum Oxide

A "Soft-Chemical" Method To Synthesize Lewis Acid Surfaces of Aluminum Oxide**

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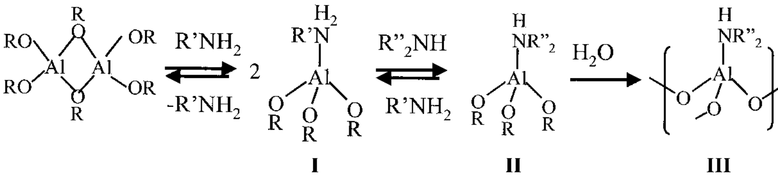
Many applications of metal oxides such as adsorption, separation, ion-exchange, and catalysis depend critically on surface properties, which include Brønsted acidity or basicity, Lewis acidity, and coordination unsaturation or redox properties of the surface metal ions. In order to generate the desired surface, it is common to perform postsynthesis treatments such as high-temperature calcination to dehydroxylate the surface or functionalization by reaction of the surface hydroxyl groups with various reagents. Here we report a method to generate a metal oxide with a specific surface property through synthesis instead of by postsynthesis treatment. We have synthesized an alumina that possesses a high density of surface Lewis acid sites, without resorting to postsynthesis high-temperature calcination, and has few hydroxyl groups relative to the material resulting from conventional preparation. The strategy is to protect the Lewis acid sites of Al with a base during hydrolysis to form the oxide. After the oxide is formed, the bound amine can be exchanged with other bases. The resulting alumina was an active catalyst for the aminolysis of epoxide. This concept of protecting the desired functionality during synthesis is applicable generally to other oxides having other surface properties.

This approach of protecting the Lewis acid site of an Al ion by forming an amine–aluminum adduct differs from the concept used in preparing oxides of uniform pore structures such as the M41S family of mesoporous siliceous oxides.[1,2] In those methods the self-assembly properties of the surfactants or surfactant–metal complexes are utilized to form structure-directing templates around which gelation of the inorganic precursor occurs. Various types of interactions between surfactants and inorganic species have been explored, including the direct charge–charge interaction between cationic surfactant and anionic inorganic species (and the counterpart anionic surfactant–cationic inorganic species), mediated charge–charge interaction in which the like-charged surfactant and inorganic species are separated by a mediator of opposite charged,[3] and hydrogen bonding between a neutral surfactant and neutral inorganic precursor.[4] By means of these techniques, transition[5–7] and post-transition metal oxides with structured mesopores have been prepared. Aluminum oxide has been prepared using these methods, and materials containing mesopores with narrow pore-size distributions can be obtained.[8–10]

In these methods the function of the surfactants is to provide structural templates around which the inorganic oxyhydroxy polymeric gel is formed. The chemistry of the gelation process remains largely the same as that in the hydrolysis of the inorganic metal ions in the absence of the surfactants, and the resulting surface properties of the final oxides are similar. In other cases, the surfactant ligand was employed to moderate the hydrolysis rate of the metal ion.[5] There has been no attempt to control the surface properties of the final oxide.

The common aluminum oxide precursors such as $AlCl_3$ and $Al(OR)_3$ are Lewis acids that exist as dimers (e.g., Al_2Cl_6) and oligomers (e.g., Al alkoxides). In the presence of a strong Lewis base such as an amine, these dimers and oligomers can be transformed into monomeric amine–Al acid–base adducts **I**. Thus, instead of serving as a structure-directing agent in the synthesis process, an amine can be used as a Lewis base to protect the Lewis acid site of Al by forming an adduct. After hydrolysis (→**III**), the resulting oxide surface would retain a high density of the amine-protected Al ions and be different from a hydroxyl-covered surface obtained by the conventional hydrolysis procedure. Equation (1) summarizes the steps involved.



(1)

Aluminum *tert*-butoxide exists as dimer in a toluene solution. Its ^1H NMR spectrum exhibits two singlets at $\delta =$ 1.39 and 1.51 ppm with a peak area ratio of 2:1 due to the terminal and bridging butoxy groups, respectively.[11] Addition of a primary amine such as propylamine, butylamine, or octylamine at room temperature resulted in the formation of a monomeric amine aluminum *tert*-butoxide adduct such as **I** ($R = t$Bu). The ^1H NMR spectrum of the monomer showed only one singlet at about $\delta = 1.47$ ppm (Figure 1). The transformation to the monomer was also supported by ^{13}C NMR spectroscopy. For the dimer $[Al(OtBu)_3]_2$ in toluene, the bridging *tert*-butyl groups gave rise to resonances at $\delta = 31.5$ and 76.2 ppm due to the methyl groups and the tertiary carbon, respectively, whereas the terminal *tert*-butyl groups gave rise to resonances at $\delta = 34.0$ and 69.1 ppm. For the monomer **I** only one type of *tert*-butyl groups was observed with resonances at $\delta = 34.3$ and 67.7 ppm. ^{27}Al NMR spectroscopy provided additional evidence. The peak at $\delta = 48.7$ ppm for the tetrahedral Al center in a dimeric species was replaced

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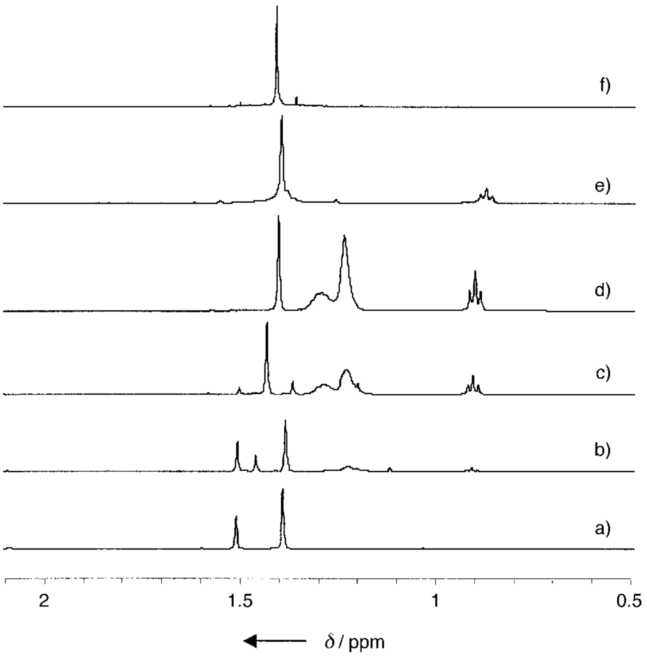


Figure 1. ^{1}H NMR spectra of solutions of $Al_2(OtBu)_6$ alone and as an adduct with various amines in [D$_8$]toluene. a) 6.4 wt% $Al_2(OtBu)_6$; b) adduct with *n*-octylamine (N/Al = 1.0); c) adduct with *n*-octylamine (N/Al = 4.7); d) adduct with *n*-octylamine (N/Al = 9.6); e) adduct with *n*-propylamine (N/Al = 3.0); f) adduct with piperidine (N/Al = 1.5).

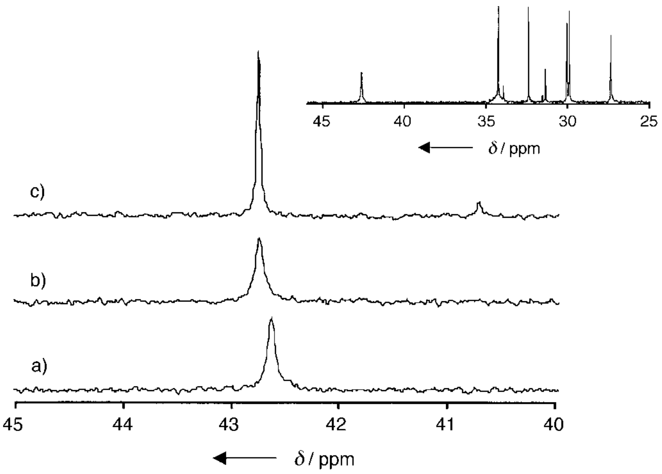


Figure 2. Variable-temperature ^{13}C NMR spectra of the $Al(OtBu)_3$–*n*-octylamine adduct at a) 20 °C, b) −30 °C, and c) −75 °C. Spectra recorded on dilute solutions of 0.4 M ($Al(OtBu)_3$) and 2 M octylamine in [D$_8$]toluene by using gated technique. The insert is the spectrum at 20 °C.

by a peak at $\delta = 62.9$ ppm with the formation of the monomeric species.

The transformation from dimer to monomer was slow at room temperature, and the equilibrium conversion increased when the ratio of amine to aluminum was increased. For octylamine, it took over 10 h to achieve equilibrium conversion, and a ratio of about 10 was required for complete conversion (Figure 1, spectrum d), whereas a lower ratio was sufficient for the reaction with propylamine (spectrum e). This method of preparing the amine–aluminum alkoxide monomer **I** is significantly simpler than the previously reported alcoholysis of $[Al(NMe_2)_3]_2$.[12,13]

At 25 °C primary amines bound to Al *tert*-butoxide exchange rapidly with the free amine in solution [Eq. (1)]. For example, the ^{13}C NMR resonance of the α carbon of octylamine at $\delta = 42.7$ ppm showed detectable broadening in the presence of Al *tert*-butoxide (Figure 2, spectrum a). The peak broadened further at −30 °C (spectrum b). When the sample was cooled further to −75 °C (spectrum c), the exchange was sufficiently slow that the resonances due to the bound amine and the free amine became distinguishable at $\delta = 40.7$ ppm and 42.8 ppm, respectively. A similar observation was obtained when propylamine was used instead of octylamine.

The rapid exchange between the free species and the bound species suggests that primary amines do not provide the desired protection of the Al coordination site. When the free amine was removed by purging with a flow of N_2 or by evacuation, $Al_2(OtBu)_6$ could be recovered. On the other hand, the more strongly basic piperidine can provide the protective function. However, piperidine does not react directly at a convenient rate with $Al_2(OtBu)_6$, probably due to steric hindrance. An adduct between piperidine and $Al(OtBu)_3$, **II,** can be obtained by reacting piperidine (piperidine/Al = 20) with $[Al(OtBu)_3(nPrNH_2)]$ in toluene (propylamine/Al = 10) at room temperature [Eq. (1)]. After 2 h the propylamine and most of the excess piperidine were removed by purging with N_2 for 12–20 h. The product was dried in vacuo at 25 °C for 2 h and then at 50 °C for 2 h. Throughout the process, the ^{1}H and ^{13}C NMR spectra of the mixture showed the presence of monomeric $Al(OtBu)_3$ and the absence of the dimer. The final solid could be redispersed in toluene. Its ^{1}H NMR spectrum shows new features not present in free piperidine. These peaks (and their assignments) are: a doublet at about $\delta = 3.1$ ppm (equatorial H of α-C), a quartet at about $\delta = 2.5$ ppm (axial H of α-C), a quartet at about $\delta = 0.95$ ppm (axial H of γ-C), a quartet at $\delta = 0.75$ ppm (axial H of β-C), and a broad doublet at $\delta = 1.25$ ppm. The α carbon atom of piperidine in this sample gives rise to two peaks at $\delta = 47.1$ and 45.96 ppm in the ^{13}C NMR spectrum. Their relative integrated areas are 1 and 0.46, respectively. From the ratio of the peak intensities of the piperidine and alkoxide, the N/Al ratio in this solution is close to 1.5, which suggests that some free piperidine remains.

Hydrolysis of the piperidine/Al alkoxide adduct **II** in toluene was conducted by introducing water to the gas phase with a stream of N_2 (100 mL min^{-1}) saturated with water at 30 °C until no Al *tert*-butoxide could be detected in solution by ^{1}H NMR spectroscopy. The resulting Al complex **III** was dried in vacuo at 60 °C to remove the toluene solvent, released *t*BuOH, and free piperidine. The ^{27}Al MAS NMR spectrum (MAS = magic angle spinning) of the dried solid showed a very pronounced peak at $\delta = 30$ ppm that could be due to pentacoordinated Al, in addition to the peaks at $\delta = 0$ ppm due to octadedral Al, and $\delta = 60$ ppm due to tetrahedral Al (Figure 3, spectrum a). The ratio of the peaks due to the tetrahedral and octahedral Al centers was much higher than that in a sample prepared without the formation of

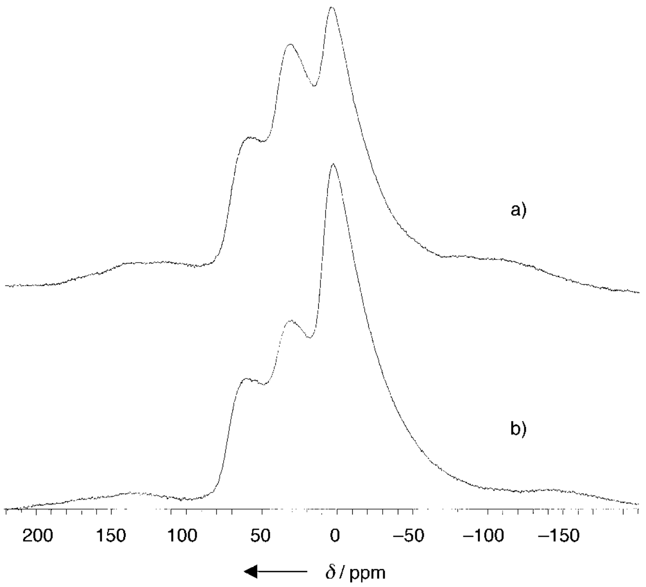


Figure 3. ^{27}Al MAS NMR spectra of the solids obtained from hydrolysis of a) piperidine-protected Al(O*t*Bu)$_3$; b) Al *tert*-butoxide in the presence of piperidine (unbound).

amine–Al alkoxide adduct (Figure 3, spectrum b). The dried solid had a BET surface area of 250 m^{2}g^{-1}. The DRIFT spectrum of the dried solid (Figure 4, spectrum a) showed strong peaks at $\nu = 1462$, 1388, and 1250 cm^{-1} due to piperidine bound to Lewis acid sites.[14,15] Peaks in the region $\nu = 2900$ cm^{-1} indicated that some *tert*-butanol or butoxide remained. After this dried solid had been refluxed in propylamine twice and then dried, a propylamine-exchanged sample (**IV**) was obtained, which gave the DRIFT spectrum in Figure 4b. The intensity of the C–H stretching band decreased substantially, although residual *t*Bu groups were still evident in the ^{13}C MAS NMR spectrum. The peaks at $\nu = 1595$, 1463, 1280, and 1253 cm^{-1} could be assigned to propylamine bound to Lewis acid sites.[14] If this solid, in turn, was exposed to a stream of NH$_3$/He for 5 h at 25 °C, a solid (**V**) characterized by the spectrum in Figure 4c was obtained. Bands at 1615 and 1280 cm^{-1} indicated Lewis acid bound NH$_3$ group.[14,16] Thus, the amine coordinated to the Al Lewis acid center can be exchanged with other bases, as illustrated in Equation (2). In all these spectra, the absorption in the region near 3500 cm^{-1} was low, indicating that there were few hydroxyl groups in the samples. These solids were amorphous by X-ray diffraction.

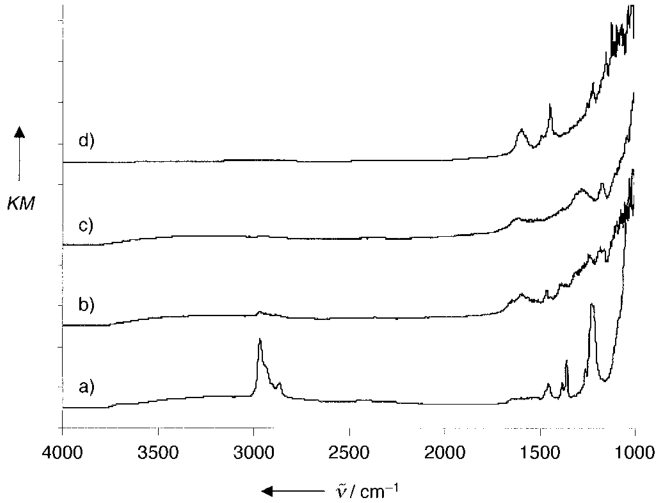
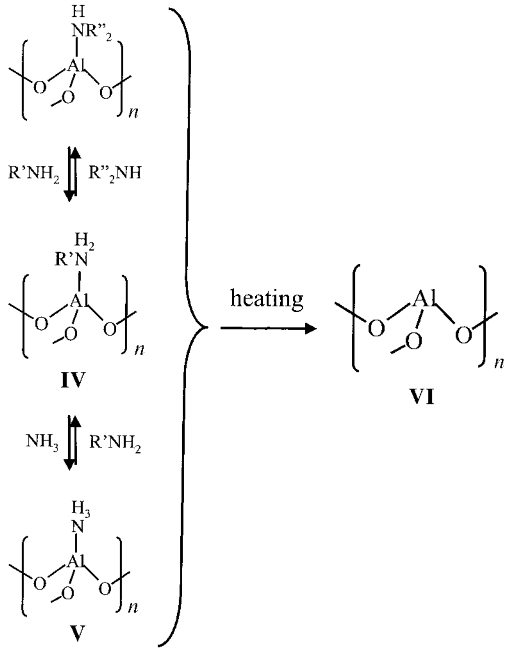


Figure 4. DRIFT spectra of: a) dried C$_5$H$_{10}$NH–Al$_2$O$_3$ formed from hydrolysis of C$_5$H$_{10}$NH–Al(O*t*Bu)$_3$; b) sample a exchanged with *n*C$_3$H$_7$NH$_2$; c) sample b exchanged with NH$_3$.



(2)

Alumina **III** prepared using piperidine was tested as a catalyst for the aminolysis of epoxide by amine,[17,18] a class of reactions that may be useful in drug synthesis.[19] After cyclopentene oxide (5.0 mmol) and piperidine (5.0 mmol) had been heated in acetonitrile at reflux for 8 h in the absence of **III**, only 3 % conversion of the epoxide was observed. However, in the presence of **III** (50 mg), 50 % conversion quantitatively to the 1,2-amino alcohol was obtained after the same time period. On a per unit surface area basis, **3** was five times more active than conventional γ-Al$_2$O$_3$ activated in vacuo at 500 °C.

The bound amine in **IV** could be removed at elevated temperatures. A sample characterized by spectrum a in Figure 5 was obtained after **IV** had been heated in oxygen and then in vacuo at 400 °C for 30 min. Peaks due to coordinated piperidine disappeared. However, small peaks possibly due to surface nitro/nitrato groups remained, suggesting that some of the amine was oxidized. Pyridine was adsorbed on this sample readily to exhibit peaks at $\nu = 1445$ and 1615 cm^{-1} due to coordination to Lewis acid sites. A similar observation was made with the ammonia-exchanged sample **V**.

The alumina prepared using the amine–Al adduct contained a much higher ratio of Lewis acid sites to hydroxyl groups than conventionally prepared alumina. A sample (**VI**) prepared by thermally removing the bound propylamine was

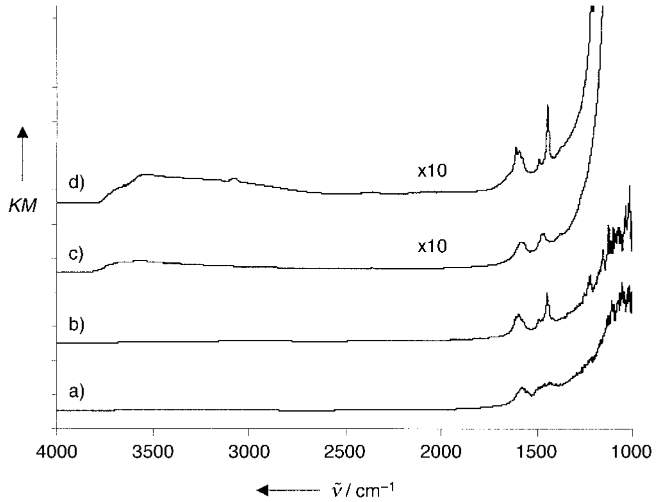


Figure 5. DRIFT spectra of pyridine adsorption on aluminas: a) $nC_3H_7NH_2$-exchanged sample **IV** after heating in O_2 and then in vacuo at 400 °C; b) sample a after pyridine adsorption; c) conventional γ-alumina after heating in vacuo at 400 °C; d) sample c after pyridine adsorption.

heated further in an O_2 stream containing 1.5 % H_2O for 30 min. After the sample had been dried in He at 400 °C for 5 h, pyridine was adsorbed at 25 °C. The DRIFT spectra of the sample before and after pyridine adsorption (very similar to Figure 5, spectra a and b) showed rather low absorption in the OH stretching region (around 3500 cm^{-1}). The adsorbed pyridine showed bands at $\nu = 1612$, 1447, and 1223 cm^{-1}, indicative of adsorption on Lewis acid sites. On the other hand, a conventionally prepared γ-Al_2O_3 after the same water treatment and adsorption of pyridine exhibited spectra c and d, showing much more intense absorption in the OH region and much lower intensity of the peaks from adsorbed pyridine. Thus, the results reported here demonstrated that it is possible to exercise control of the surface properties of an oxide through the synthesis method.

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