A Soft-Chemical Method to Synthesize Lewis Acid Surfaces of Aluminum Oxide

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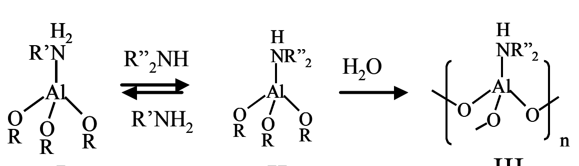
Introduction

Alumina is prepared conventionally by hydrolysis of either aluminum ions in an aqueous solution or aluminum alkoxides in an organic solution. In these preparations, the surface of the resulting aluminum oxide is covered with hydroxyl groups. Thus, in order to generate a surface of the desired properties for the various applications, such as adsorption, separation, ion-exchange, and catalysis, post-synthesis treatments are commonly applied, 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 novel method to generate an alumina surface that possesses a high density of surface Lewis acid sites without post-synthesis high-temperature calcination, and few hydroxyl groups relative to the conventional preparation. The alumina was shown to be an active catalyst for the aminolysis of epoxide.

The main idea employed is to protect the Lewis acid sites of Al with a base during hydrolysis to form the oxide by forming an amine-aluminum adduct (Eqn. 1) . After the oxide was formed, the bound amine could be exchanged with other bases. This approach 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-inorganic complexes are utilized to form structure-directing templates around which gelation of the inorganic precursor occurs. However, the chemistry of the gelation process remains largely the same as 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.



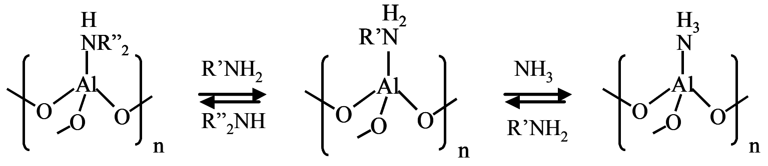
I II III

Eqn. 1

Results and Discussion

The amine-aluminum alkoxide adduct monomer was prepared by reaction of Al *t*-butoxide with an amine in a toluene solution. The reaction could be followed by ^{1}H NMR, and the monomer **I** showed only one singlet at about 1.47 ppm instead of the two singlets at 1.39 and 1.51 ppm for the alkoxide dimer. However, if a primary amine was used, the NMR peaks of the α carbon showed detectable broadening, suggesting that there was rapid exchange of the bound amine with free amine in solution. On the other hand, the binding of a secondary amine, such as piperidine, was stronger and offered sufficient protection of the Al Lewis acid site.

The hydrolysis of the piperidine-Al alkoxide adduct **II** in toluene using water introduced via the gas phase resulted in the Al oxide complex **III**. The DRIFT spectrum of the dried solid (Fig. 1, spectrum a) showed strong peaks at 1462, 1388, and 1250 cm^{-1} due to piperidine bound to Lewis acid sites. The bound piperidine can be displaced by propylamine and ammonia (Spectra 1b and 1c). Thus, the amine coordinated to the Al Lewis acid center can be exchanged with other bases, as illustrated in Eqn. 2. In all these spectra, the absorption in the 3500cm^{-1} region was low, indicating that there were few hydroxyl groups in the samples. These solids were XRD amorphous. The alumina prepared using piperidine **III** was tested as a catalyst for the aminolysis of epoxide by amine, a class of reactions that may be useful in drug synthesis. After refluxing cyclopentane oxide (1.0 mmol) and piperidine (1.0 mmol) in acetonitrile for 4 days in the absence of **III**, no reaction was observed. However, in the presence of **III** (27 mg), 77% conversion quantitatively to the 1,2-amino alcohol was obtained.



IV

V

Eqn. 2

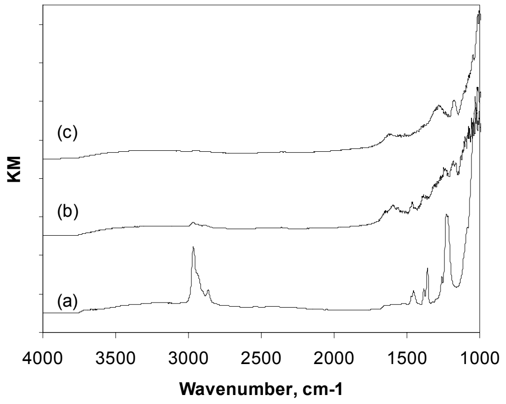


Fig. 1: DRIFT spectra of: (a) dried $C_5H_{10}NH$-Al_2O_3 formed from hydrolysis of $C_5H_{10}NH$-$Al(OBu^t)_3$; (b) sample a exchanged with n-$C_3H_7NH_2$; (c) sample b

References

1. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 1992, 359, 710.
2. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B.; Higgins, J.L.Schlenker, *J. Amer. Chem. Soc*. 1992, 114, 10834.