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Catalytic aminolysis of epoxide by alumina prepared from amine-protected Al precursor

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Abstract

The catalytic activities of alumina prepared from an Al alkoxide-amine adduct monomer for the reaction of cyclopentene oxide with piperidine was determined after various pretreatments, including calcination and exposure to moisture. They were compared with the activity of alumina prepared by the conventional hydrolysis method. It was found that the as-prepared sample from the alkoxide-amine monomer preparation was five times more active than a conventional preparation, suggesting that it has a higher density of surface Lewis acid sites. However, its activity was much more severely suppressed by exposure to moisture.

Keywords: Alumina; Aminolysis; Epoxide; Piperidine; Lewis acid

1. Introduction

Lewis acids are catalysts and cocatalysts for various chemical reactions, such as Friedel–Craft, dehydration of alcohol, aminolysis, and polymerization. Aluminum chloride is one of the most common Lewis acids, which is used either in the liquid phase or as a supported liquid phase. Although effective, aluminum chloride is often not efficiently used because it exists as a dimer; an electron lone pair of the chlorine atom in one molecule is coordinated to the Al ion of another molecule to satisfy the coordination unsaturation of the Al ion. This situation applies to other aluminum compounds, such as aluminum alkoxides, which exist as dimers or larger oligomers for similar reasons. Thus, the concentration of monomeric aluminum compound in a reaction mixture is limited by the extent of dissociation of the dimers or oligomers.

Aluminum oxide is also a Lewis acid. Being a solid, it can be much more easily separated from the reaction mixture than the liquid aluminum compounds for reuse. Thus, it is a more environmentally friendly catalyst. In the common methods of preparation of alumina, aluminum ions are hydrolyzed to form a solid oxyhydroxy aluminum compound, which has no Lewis acidity. The solid is calcined to form the oxide by condensation of neighboring hydroxyl groups. Upon exposure to moisture, the surface of the oxide is rehydroxylated, such that the surface Al ions are covered by hydroxyl groups. Lewis acidity is generated by dehydroxylation to create surface coordinatively unsaturated Al ions. Thus, the concentration of Lewis acid sites depends on the calcination temperature; the higher is the temperature, the greater extent is the degree of dehydroxylation and the higher is the Lewis acidity.

Recently, we reported a new preparation method that results in an aluminum oxide containing a much lower concentration of hydroxyl groups without

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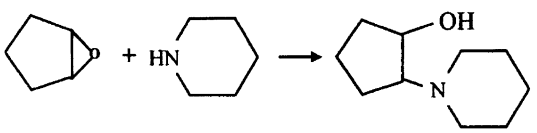
calcination than conventional preparation [1]. In this method, the coordination unsaturation site of an Al ion is protected with a strong Lewis base throughout the preparation, especially during hydrolysis, by converting the Al precursor compound into a monomer of an Al-amine adduct. By following the interaction of Al *t*-butoxide with amine with NMR, it was found that for this Al precursor, primary amines are not sufficiently strong Lewis bases for this purpose, whereas a secondary amine such as piperidine is satisfactory. Upon controlled hydrolysis of a piperidine-Al *t*-butoxide adduct monomer, a solid containing a rather low concentration of hydroxyl groups is formed. There is a significant amount of piperidine remained bound to Al ions in the as-prepared solid. It was shown furthermore that these bound piperidine can be exchanged with other amines, including propylamine, butylamine, and ammonia. Thus, the Lewis acid site of Al where piperidine is bound to is accessible to other Lewis bases.

In this paper, we report the results of our study of the catalytic activity of these alumina prepared from the piperidine-Al *t*-butoxide monomers for the aminolysis of epoxide [2,3], which may be useful in drug synthesis [4]. Specifically, the reaction between cyclopentene oxide and piperidine was studied (Eq. (1)). Aluminum oxide has been shown to be a catalyst for this reaction. The activity was compared to that of a sol–gel alumina prepared by hydrolysis of the Al *t*-butoxide.



(1)

2. Experimental

Three types of alumina were used for comparison: PPD-Al_2O_3 prepared from a piperidine-Al *t*-butoxide monomer, PA-Al_2O_3 by exchanging PPD-Al_2O_3 with propylamine, and SG-alumina from Al *t*-butoxide without amine. Preparation of PPD-Al_2O_3 has been described previously [1]. Briefly, the Al *t*-butoxide dimer was first converted to a propylamine-Al *t*-butoxide monomer by reacting the alkoxide with excess amine in a toluene solution. Then the monomer was converted to piperidine-Al *t*-butoxide monomer by adding piperidine to this mixture. After removing the propylamine and toluene by purging the vessel and drying in vacuo, the monomeric piperidine-Al *t*-butoxide monomer solid was redispersed in toluene. The alkoxide was hydrolyzed slowly by passing a stream of N_2 saturated with water over the solution, until no monomer could be detected in the solution by ^{1}H NMR. The solid was dried in vacuo at 60 °C and kept in a moisture-free atmosphere.

PA-Al_2O_3 was prepared by refluxing twice a dried PPD-Al_2O_3 dispersed in toluene in propylamine followed by drying in vacuo at 60 °C. The final solid was kept in a moisture-free atmosphere. SG-Al_2O_3 was prepared using the conventional method of hydrolysis of Al *t*-butoxide in a methanol/toluene solution using excess water (9.33 g Al alkoxide, 130 ml toluene, 10 ml methanol, and 5 ml water). The hydrous gelatinous solid was dried in vacuo at 60 °C.

Some of these samples were calcined to various temperatures before use. They are identified by appending the calcination temperature to their designation. For example, PA-Al_2O_3-500 is one that was calcined to 500 °C. Any other additional treatments are similarly appended. Calcination at 200 °C was performed in situ in the reaction vessel without exposing the catalyst to air afterwards. PA-Al_2O_3-500 and SG-Al_2O_3-500 were calcined in flowing O_2 with a temperature ramp of 1 °C/min until 500 °C and held at 500 °C for 2 h. The calcined solids were transferred to a closed container immediately before being loaded into the reaction vessel in a glove box. Table 1 shows the BET surface areas of these samples.

Catalytic reaction was carried out in a Schlenk flask and all material was handled in a glove box. Typically, 5 ml acetonitrile, 0.366 ml (5 mmol) of piperidine, 0.405 ml (5 mmol) cyclopentene oxide and 40 μl (0.19 mmol) hexamethyldisiloxane (as internal standard) were added to a Schlenk flask. The acetonitrile, cyclopentene oxide, and piperidine were dried by standard methods [5]. Then, a weighed amount of Al_2O_3 equivalent to 12.7 m^2 of surface was added. The mixture was stirred at 77 °C, and the reaction was followed by withdrawing samples with a syringe for ^{1}H NMR analysis. The identity of the reaction product was confirmed by ^{1}H and ^{13}C NMR, and GC–MS using a Zebron ZB-5 capillary column (30 m, 250 μm ID, 0.25 μm film thickness).

Table 1
Surface area and catalytic activity

Catalyst	Surface area (m^2/g)	Induction time (min)	Initial rate ($\times 10^{-3}$ mol/g h)	Initial rate ($\times 10^{-6}$ mol/m^2 h)
PPD-Al_2O_3	254	0	12	50
PPD-Al_2O_3-200	[a]	–	∼0	∼0
PA-Al_2O_3	225	0	11	50
PA-Al_2O_3-200	[a]	–	∼0	∼0
PA-Al_2O_3-500	226	0	2.1	9
PA-Al_2O_3-500-H_2O	[b]	–	∼0	∼0
PA-Al_2O_3-500-H_2O-200	[b]	–	∼0	∼0
SG-Al_2O_3	326	15 ± 5	3.4	10
SG-Al_2O_3-200	[a]	15 ± 5	3.8	11
SG-Al_2O_3-500	452	0	5.4	10
SG-Al_2O_3-500-H_2O	[b]	100 ± 20	2.3	5
SG-Al_2O_3-500-H_2O-200	[b]	40 ± 10	4.6	10

[a] The surface area was assumed to be the same as the as-prepared samples.
[b] The surface area was assumed to be the same as the 500 °C calcined samples.

3. Results and discussion

The catalysts studied are listed in Table 1. They include as-prepared samples that had not been heated to higher than the reaction temperature, samples that had been calcined to 200 or 500 °C and without further treatment, as well as the 500 °C calcined samples after further exposure to moisture and with or without subsequent heating to 200 °C in vacuo. Exposure to moisture was performed by putting the sample in a constant humidity chamber.

The as-prepared PPD-Al_2O_3 had a surface area of 254 m^2/g. Exchanging piperidine with propylamine did not result in a significant change in surface area. The as-prepared SG-Al_2O_3 had a somewhat higher surface area. The difference in surface areas was more significant after calcination to 500 °C. For the SG-alumina sample, calcination removed water from the network of the gel and caused condensation of hydroxyls and collapse of the pores. Apparently, the gain in the measured surface area by removing the occluded water was more than the loss due to collapse of the pores. On the other hand, calcination of a PA-alumina did not increase its surface area much. This may be due to the fact that in the amine preparation, the aluminum coordination sites are occupied by the amine adducts. Thus, there is less condensation of aluminum hydroxyl groups, and the network is less extensive. Consequently, the structure of the alumina gel is less rigid and there is more extensive collapse of the structure upon calcination. In addition, the PA-Al_2O_3-500 sample was slightly yellow in color, suggesting that the some carbonaceous residue remained even after 2 h at 500 °C in O_2. The carbonaceous residue could be removed eventually after prolonged heating.

The as-prepared samples were amorphous to X-ray diffraction. Transmission electron micrographs of PPD-Al_2O_3 showed the presence of small particles less than 20 nm in size (Fig. 1). The particles were better formed after calcination to 500 °C but without significant increase in size. Previously, we have shown by FTIR that PPD-Al_2O_3 possesses a much lower density of hydroxyl groups than a conventional preparation [1].

The reaction results are shown in Figs. 2 and 3. Without any catalyst, there was no detectable reaction after 3 h. This is consistent with the literature results that alumina promotes this reaction [2,3]. In all cases, the aminocyclopentanol was the only product detected (Eq. (1)), and its yield equaled the epoxide conversion. Thus, the selectivity was 100% for this product. For the as-prepared PPD-Al_2O_3 and PA-Al_2O_3, the reaction proceeded immediately, and the conversion of epoxide increased linearly initially. The rate of increase of conversion declined with increasing time-on-stream due to consumption of the reactants. From these initial conversions, the activities of these samples could be calculated, and they are shown in Table 1. Within experimental error, the two samples had identical areal

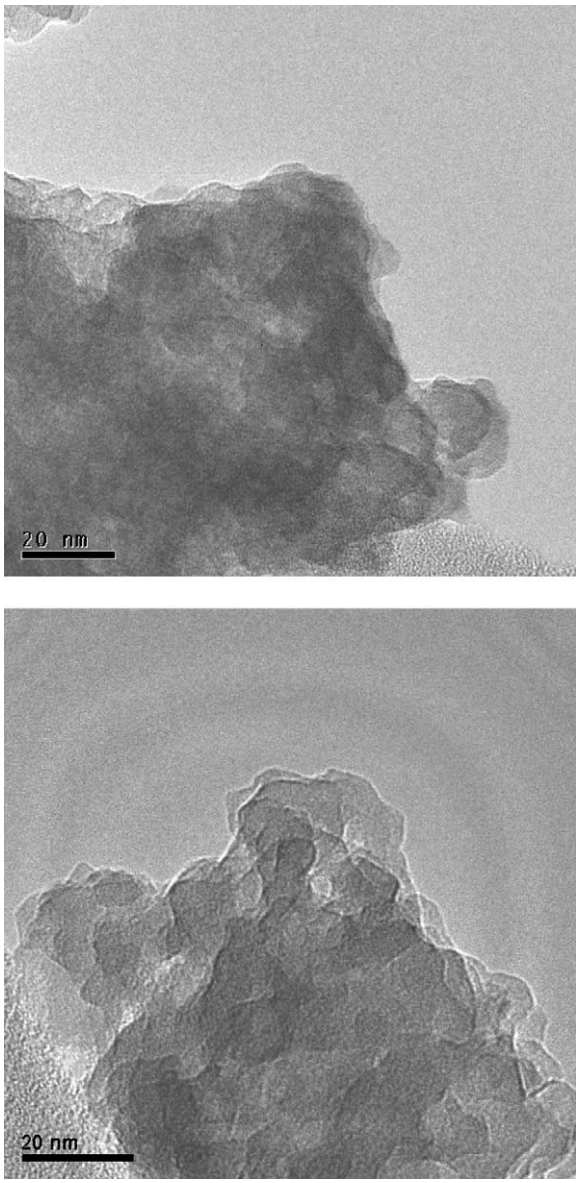


Fig. 1. TEM images of PA-Al_2O_3 (top) and PA-Al_2O_3-500 (bottom).

activity. The as-prepared SG-Al_2O_3 also showed reasonable activity. However, there appeared to be a short induction period of about 15 min before the catalyst attained the full activity, which was still lower than the activity of PPD-Al_2O_3. On a surface area basis, PPD-Al_2O_3 and PA-Al_2O_3 were about five times more active than SG-Al_2O_3. The much higher activity of PPD-Al_2O_3 was not due to a significant difference in the concentration of piperidine in these experiments due to the piperidine introduced with PPD-Al_2O_3. In this experiment, 5 mmol of piperidine and 50 mg of PPD-Al_2O_3 were used. The quantity of alumina corresponded to about 0.45 mmol. Since the piperidine to Al mole ratio was about 1:5 as determined by chemical and NMR analyses, there were only about 0.1 mmol of piperidine added to the mixture with the alumina.

Heating the as-prepared samples to 200 °C had very different effects on the various aluminas. SG-Al_2O_3-200 behaved very similarly to the as-prepared sample. It was as active and showed a short induction time. On the other hand, PPD-Al_2O_3-200 and PA-Al_2O_3-200 lost all their activities. The epoxide conversions in these experiments were similar to the blank experiment. Solid state ^{13}C MAS NMR of PA-Al_2O_3-200 showed a substantial decrease of the propylamine resonances compared with PA-Al_2O_3. However, no new peaks of significant intensities could be detected. It is probable that heating in vacuo to 200 °C caused decomposition of the adsorbed amines to a surface deposit that blocks the Al site. These decomposed products cannot be displaced easily by the reactants. That is, the alumina was poisoned.

Heating the as-prepared samples to 500 °C resulted in active catalysts. SG-Al_2O_3-500 was slightly more active than SG-Al_2O_3 or SG-Al_2O_3-200, but the difference was small. More interestingly, the sample did not show an induction period. For the PA sample, calcination at 500 °C restored a large fraction of the activity. PA-Al_2O_3-500 was about as active as the SG samples and it did not show any induction.

Exposing the 500 °C calcined samples to moisture suppressed the activities. For the SG alumina (sample SG-Al_2O_3-500-H_2O), adsorbed water increased the induction time and lowered the activity. These effects could be removed by heating to 200 °C to remove the adsorbed water (sample SG-Al_2O_3-500-H_2O-200). In contrast, the sample PA-Al_2O_3-500-H_2O showed no detectable activity above the blank, and heating to 200 °C could not restore any of the lost activity.

The aminolysis of epoxide is catalyzed by alumina although its detailed role is not known. A possible mechanism involves the binding of epoxide to the

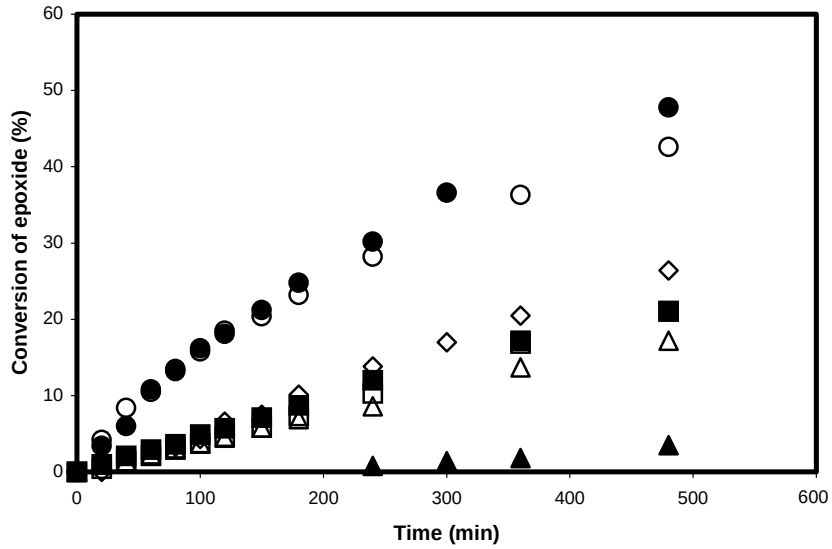


Fig. 2. Conversion of cyclopentene oxide in reaction with piperidine catalyzed by various aluminas. (●) PPD-Al_2O_3, (○) PA-Al_2O_3, (◇) SG-Al_2O_3-200, (■) SG-Al_2O_3-500, (□) SG-Al_2O_3, (△) PA-Al_2O_3-500, (▲) PA-Al_2O_3-200.

Lewis acid center to form an acid–base adduct:

$$(O\text{–})_3Al \leftarrow NR'_2H + (OC_2)R_2 \rightarrow (O\text{–})_3Al^{\delta-}(OC_2)^{\delta+}R_2 + NR'_2H \qquad (2)$$

The nucleophilic nitrogen of the amine then attacks the electrophilic carbon of the epoxide, causing opening of the oxide ring. According to this mechanism, a catalyst that has more Lewis acid centers would be more active.

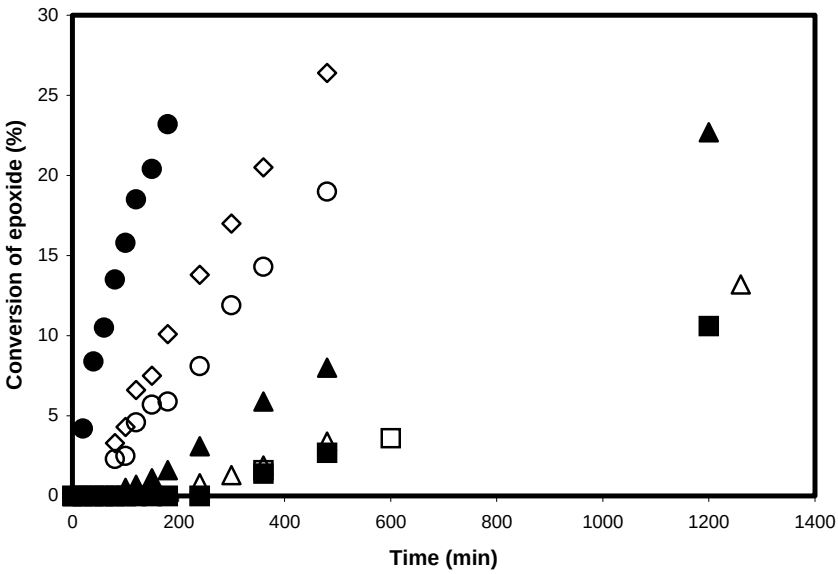


Fig. 3. Conversion of cyclopentene oxide in reaction with piperidine catalyzed by various aluminas. (●) PPD-Al_2O_3, (◇) SG-Al_2O_3-200, (○) SG-Al_2O_3-500-H_2O-200, (▲) SG-Al_2O_3-500-H_2O, (△) PA-Al_2O_3-500-H_2O-200, (■) PA-Al_2O_3-500-H_2O, (□) blank.

The much higher activity of PPD-Al_2O_3 than the SG alumina suggests that this catalyst has a much higher density of surface Lewis acid sites. If we assume that calcination of the SG alumina at 500 °C removes about 70% of the surface hydroxyl groups from its surface [6–8], and one surface Lewis acid site is formed from condensation of two hydroxyls, then about 1/3 of the surface Al ions on SG-Al_2O_3-500 would be available as Lewis acid sites. Since PPD-Al_2O_3 is about five times more active than SG-Al_2O_3-500, it implies that practically every Al ions on the surface of PPD-Al_2O_3 is an active Lewis acid site. This is consistent with our model that all, if not most of the surface Al ions in PPD-Al_2O_3 are coordinated to a piperidine molecule and available for reaction.

Adsorbed water suppresses the activity on all aluminas. However, on SG alumina, its effect is relatively small. Samples SG-Al_2O_3 and SG-Al_2O_3-200 have activities comparable to SG-Al_2O_3-500. The only difference is that the latter sample shows no induction time. The short induction times of the former two samples may be due to the need to displace the adsorbed water from the surface Al ions by piperidine. Similarly, exposing SG-Al_2O_3-500 to water suppresses its activity by about half and lengthens the induction time. The effect was removed by heating the sample to 200 °C. In contrast, the effect of adsorbed water on PA-Al_2O_3-500 was much more severely, and the lost activity could not be recovered by heating the sample to 200 °C.

In addition to the density of surface Al Lewis acid sites, the strength of these sites may also affect the activity. Unfortunately, at present we do not have direct information on the acid strength. Judging from the fact that water poisons PA-Al_2O_3-500 much more severely than SG-Al_2O_3-500, which implies that the former sample adsorbs water more strongly, it is possible that the amine preparation generates stronger surface Lewis acid sites than a conventional preparation. However, direct measurements on the strength of bonding of Lewis base on these sites are needed to be certain of any differences.

In summary, we have demonstrated that alumina prepared by controlled hydrolysis of an amine-Al monomeric complex is a more active catalyst than sol–gel alumina prepared by hydrolysis of Al alkoxide for the Lewis–acid catalyzed reaction of aminolysis of epoxide. The sample is active as-prepared. This implies that such a preparative method generates alumina with a much higher density of surface Lewis acid sites. In fact, the results are consistent with the assumption that every surface Al ion is a Lewis acid site. In contrast, the surface density of Lewis acid sites of a conventional preparation is limited by the extent of dehydroxylation, as well as the fact that stoichiometrically, condensation of two hydroxyl groups generate only one Lewis acid center. Therefore, the amine preparation represents alumina with a new type of surface.

Acknowledgements

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