Pak. J. Sci. Ind. Res. 2005 **49**(2) 77-81

Development of Nanoparticles of Alumina by Sol-Gel Method Using Inorganic Aluminum Salts as Precursors

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(received January 3, 2005; revised December 27, 2005; accepted December 30, 2005)

Abstract. Alumina nanoparticles were synthesized by homogeneous precipitation method from inorganic aluminum salt solutions using urea followed by calcination. The nanoparticles so produced were spherical and acicular with uniform particle size distribution. The process describes synthesis of aluminum hydroxide $Al(OH)_3$ and boehmite AlOOH, and their thermal decomposition into alumina (Al_2O_3). The structural and morphological properties of the prepared aluminum hydroxide and nanocrystalline powders were characterized by scanning eletron microscopy, differential thermal analysis and thermogravimetric analysis.

Keywords: nanoparticles, alumina, aluminum salts, sol-gel, homogeneous precipitation, aluminum hydroxide, nanocrystalline powder

Introduction

There is a considerable current interest in the application of sol-gel technology to produce powders, spheres, coatings and fibres for a variety of applications (Sakka, 2005).The advantages of this technique include: low capital cost of the equipment, room temperature processing, low sintering temperatures, high purity, three-dimensional homogeneity, and ease of making multicomponent and well distributed small particles (Ovecoglu and Mandal, 2004).

The preparation of metal oxide powders by sol-gel technique generally involves two-stage processes, the formation of hydroxide from the metal salt solution and its subsequent decomposition. In previous investigations, aluminum metal (Cossa, 1870), aluminum salts (Russell *et al*., 1970), and aluminum alkoxides (Yoldas, 1975) have been used as precursors to synthesize aluminum hydroxide. The materials produced as a result range from fibrous gels (Bugosh *et al*., 1962) to monosized spheres (Maitijevic, 1981). The structures include all the varities of crystalline, more or less amorphous aluminum trihydroxides, $Al(OH)_3$ and monohydroxides, AlOOH (Papee *et al*., 1958; Imelik *et al*.,1954). An attempt has been made in the present study to synthesize nanoparticles of alumina from three different aluminum salts, viz., aluminum sulphate, aluminum chloride, and aluminum nitrate under identical reaction conditions.

Materials and Methods

Synthesis of nanoalumina. Reagent grade aluminum chloride $AlCl_3{\cdot}6H_2O$ (BDH), aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ (PCSIR), aluminum sulphate $Al_2(SO_4)_3{\cdot}18H_2O$ (PCSIR), and urea $(NH_2)_2CO$ were used as starting reagents. Aluminum salts were dissolved in distilled water and the concentrations of the stock solutions were adjusted to 1.0 mol. l^{-1}, 1.0 mol. l^{-1}, and 0.5 mol. l^{-1} of the three aluminum salts, respectively, and that of urea to 1.0 mol. l^{-1}. Each aluminum salt solution was mixed with urea solution separately to prepare three reacting systems. The starting pH of each reacting solution, i.e., aluminum salt and urea, was adjusted at 2.5 by using either NHO_3 or ammonia. The sols were first heated in a 2 litre glass flask at 50 °C for 1 h, and subsequently heated at the reaction temperature of 90 °C with constant stirring on a hot plate. During the reaction, the solutions were stirred with magnetic stirrer and volume (2 litre) was maintained throughout the reaction by manually adding distilled water when required. The pH change was continuously measured till it reached 7.0 at which the solution vessels were cooled in a waterbath to stop the reaction. The gels were then atomized by sublimation, followed by cooling at 40 °C, and finally calcination at 600 °C in an isothermal fur-nace for 2 h.

Characterization of the products. The products were characterized by scanning electron microscope (SEM), Hitachi S-2700. To study the morphology and particle size distribution, a thin layer of the sample was prepared by dispersing it in isopropyl alcohol. Differential thermal analyzer and thermogravimetric analyzer (DTA-TG), Shimadzu DT-40, was used to study the physical and chemical changes on heating up to 1200 °C at the rate of 10 °C per min.

Results and Discussion

The changes in the pH predict the rate and completion of the reaction. The relationship of pH with reaction time is given in Fig. 1. It may be noted that the initial pH of the three reacting

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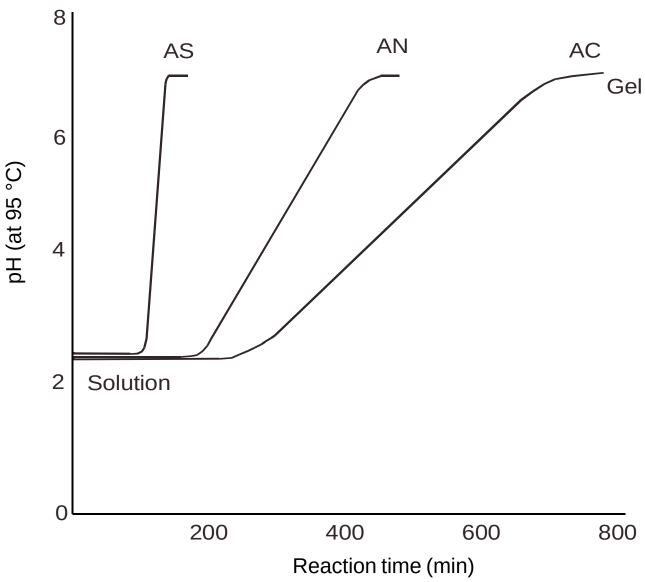

Fig. 1. The effect of reaction time on the pH behaviour during sol-gel processing; reaction conditions: [$Al_2(SO_4)_3$. $18H_2O$] (AS) = 0.5 mole/litre; [Al)$NO_3)_3$. $9H_2O$] (AN) = 1.0 mole/litre; [$AlCl_3$. $6H_2O$] (AC) = 1.0 mole/litre; [Urea]= 1.0 mole/litre; temperature = 95 °C.

solutions was 2.5. It was observed that aluminum sulphate (AS) showed change in pH from 2.5 to 7.0 after 100 min, aluminum nitrate (AN) after 170 min, whereas aluminum chloride (AC) took 285 min. The slow change was due to the acid-base neutralization reaction. As the reaction proceeded, pH showed a linear rise in all the three cases. However, the rate of change of pH with respect to time was the slowest in AC, rather slow in AN, and comparatively fast in the case of AS. Afterwards, the reaction slowed down and only slight changes in pH were observed.

The pH of the reacting mixture of aluminum salt and urea is acidic in the beginning. The acidic pH is solely due to aluminum salts, as urea makes neutral solution.

Aluminum salts get dissociated in water to give Al^{+3} and the respective anions, viz., $SO4^{-2}$, Cl^{-1} or NO_3^{-1}. On heating, urea is hydrolyzed. The reaction may be written as:

$$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4OH + CO_2\uparrow$$

It is suggested that prior to sol-gel reaction, the reacting solution undergoes acid-base neutralization reaction.The chemical equation for the respective acid-base neutralization reaction may be written as:

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 3(NH_4)_2SO_4 + 2Al(OH)_3$$

$$Al(NO_3)_3 + 3NH_4OH \rightarrow 3NH_4NO_3 + Al(OH)_3$$

$$AlCl_3 + 3NH_4OH \rightarrow 3NH_4Cl + Al(OH)_3$$

The difference in time taken by the AC, AN and AS to initiate changes in pH depends upon the neutralization of the stoichiometric chloride, nitrate, sulphate ions, and the free acid as well. Aluminum sulphate took the least time to initiate rise in pH, whereas aluminum chloride took the maximum time. This shows that the free acid contents were low in the former and comparatively very high in the latter. Aluminum ion is amphoteric in nature, which can thus act both as a weak acid and a weak base. It acts as acid in water and yields aluminum hydroxide. The hydrolysis of urea is slow and changes the pH gradually, which ultimately leads to homogenous precipitation.

The weight loss as determined by thermogravimetric analysis (TG) and differential thermal analysis (DTA) graphs of aluminum hydroxide powders prepared using the three different precursors are shown in Fig. 2. It is evident that AN and AC

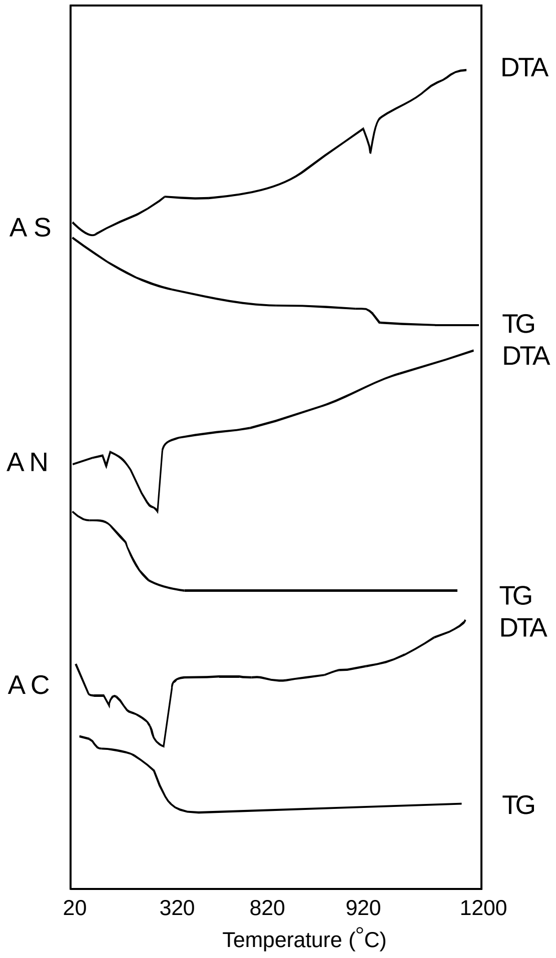

Fig. 2. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) graphs of aluminum hydroxide powders obtained from aluminum sulphate (AS), aluminum nitrate (AN) and aluminum chloride (AC).

samples behaved similarly, while AS behaved in a different manner. In the case of both AN and AC, the loss of water below 100 °C was 1.0% and 2.4%, respectively, and was due to the evaporation of the surface adsorbed water. Further, the loss of weight up to 300 °C was 26% for AN and 38% for AC. This weight loss was due to chemically combined water. The DTA curves were consistent with the dehydration of boehmite reported in litrature (Wefers and Bell, 1972). Its peak appeared at 280 °C in the case of AN, and at 300 °C in the case of AC. The peaks were sharp and distinct showing the crystalline nature of boehmite. Dehydration of boehmite may be written as:

$$2AlOOH \rightarrow Al_2O_3 + H_2O$$

for which the theoretical weight loss was 15%.

The theoretical value was not in accordance with the experimental value. Since boehmite contains variable amounts of additional water molecules, it is called as pseudoboehmite (Temuujin *et al.*, 2000). On the contrary, in the case of AS, first endothermic peak appeared at 95 °C, which was a broad peak (Fig. 2), indicating slow and continuous dehydration of aluminum oxide hydrate. The peak was not sharp, probably due to the poor crystalline nature of the submicron sized aluminum hydroxide powder. Aluminum hydroxide decomposed at low temperature, so it was predominantly either gibbsite or bayerite (Wefers and Bell, 1972). The second peak appeared at 250 °C (Fig. 2), which was a small endothermic peak due likely to the decomposition of boehmite. The weight loss corresponding to these two peaks was found to be 37%. Thermal decomposition of $Al\,(OH)_3$ may be written as:

$$2Al(OH)_3 \rightarrow 2AlOOH + 2H_2O\uparrow \rightarrow Al_2O_3 + H_2O\uparrow$$

for which the theoretical weight loss was 34%.

The theoretical weight loss was in accordance with the experimental weight loss. The last peak appeared at 920 °C (Fig. 2), which was a sharp endothermic peak and showed the decomposition of unreacted aluminum sulphate. The weight loss corresponding to this peak was 9%.

The particle size distribution of nanoparticles of the alumina synthesized, using three aluminum salts, is shown in Fig. 3. The nanoparticles obtained from aluminum chloride had an average size of 60 nm and those obtained from aluminum nitrate had the average size of 100 nm. In both the cases, the particle size distribution was narrow, whereas the particles obtained from aluminum sulphate had an average size of 200 nm with a wide range of size distribution. It seems that molecular weight of the anion may have an effect on the particle size of alumina. Apparently, aluminum salt with lighter anion resulted in obtaining finer particle size as shown in Fig. 4.

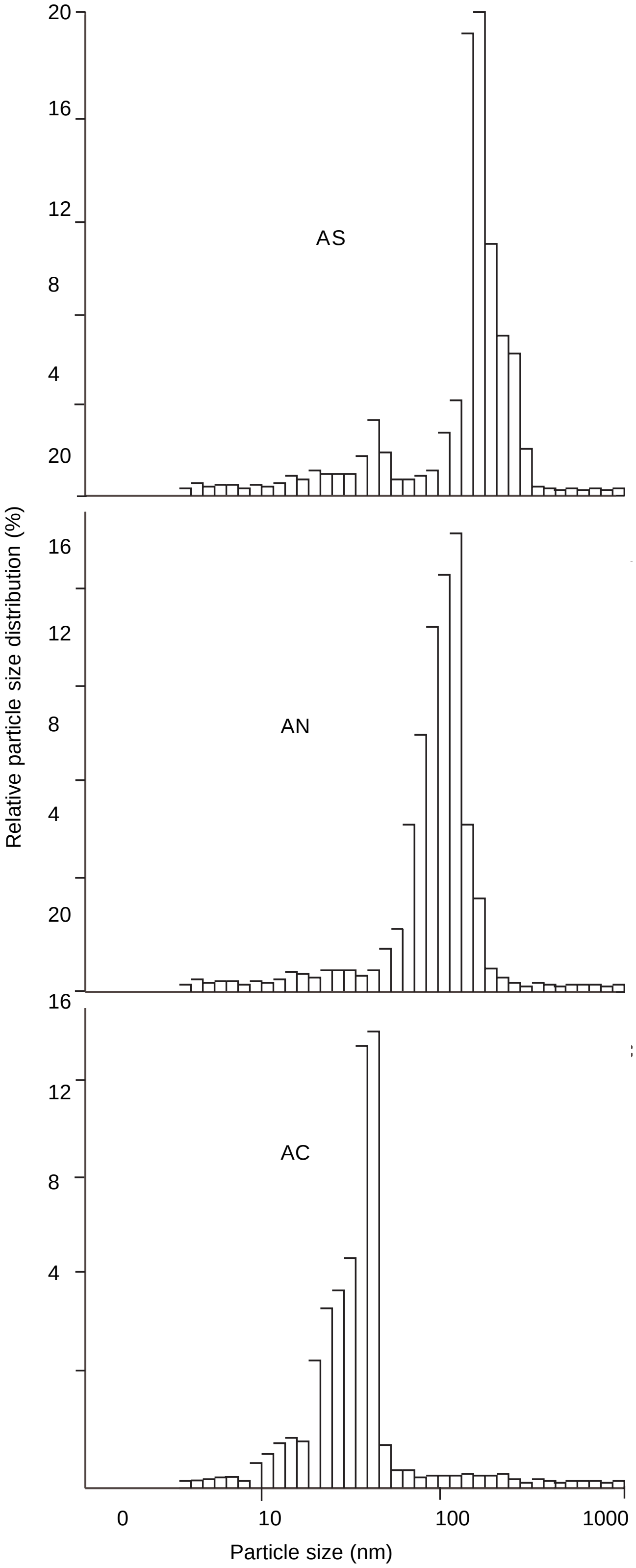

Fig. 3. Relative particle size distribution (%) of alumina obtained from aluminum sulphate (AS), aluminum nitrate (AN), and aluminum chloride (AC).

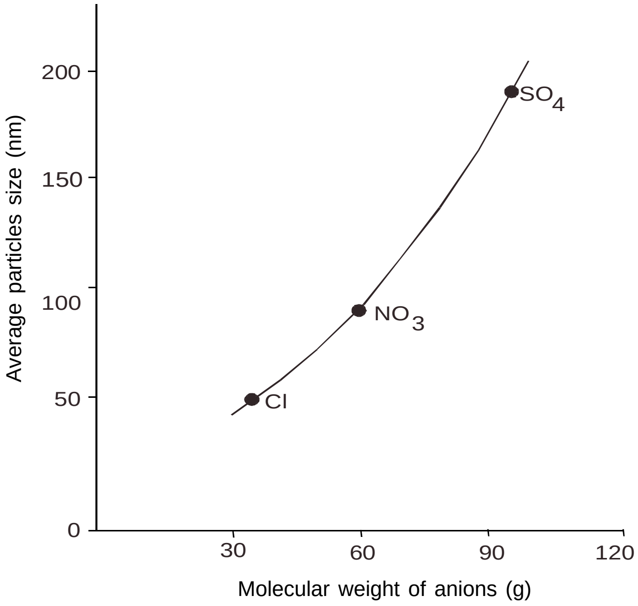

Fig. 4. The effect of molecular weight of anions on the particle size of nanoalumina.

It may be noted from Fig. 5 that the nanoparticles of alumina synthesized using aluminum sulphate were circular in shape, while these were acicular and spherical in the case of aluminum nitrate. The particles in these two cases were well dispersed. On the contrary, the nanoparticles obtained form aluminum chloride were not discrete and showed agglomeration and coalescence due to the fineness of the particle size.

The present studies suggest that aluminum nitrate may be the best of the three aluminum salts to be used for the synthesis of nanoparticles of alumina. The explanation to this conclusion is that NO_3 ion is the easiest to eliminate in the final sintering of aluminum hydroxide to á-alumina because of more ionic character of its bond than the other two ions (Cotton and Wilkinson, 1988). The unreacted sulphate, as indicated by DTA, can be reduced to a certain extent by optimizing the concentrations of urea and aluminum sulphate solutions. Attempt can also be made to neutralize the excess sulphate, at least partially, with ammonia.

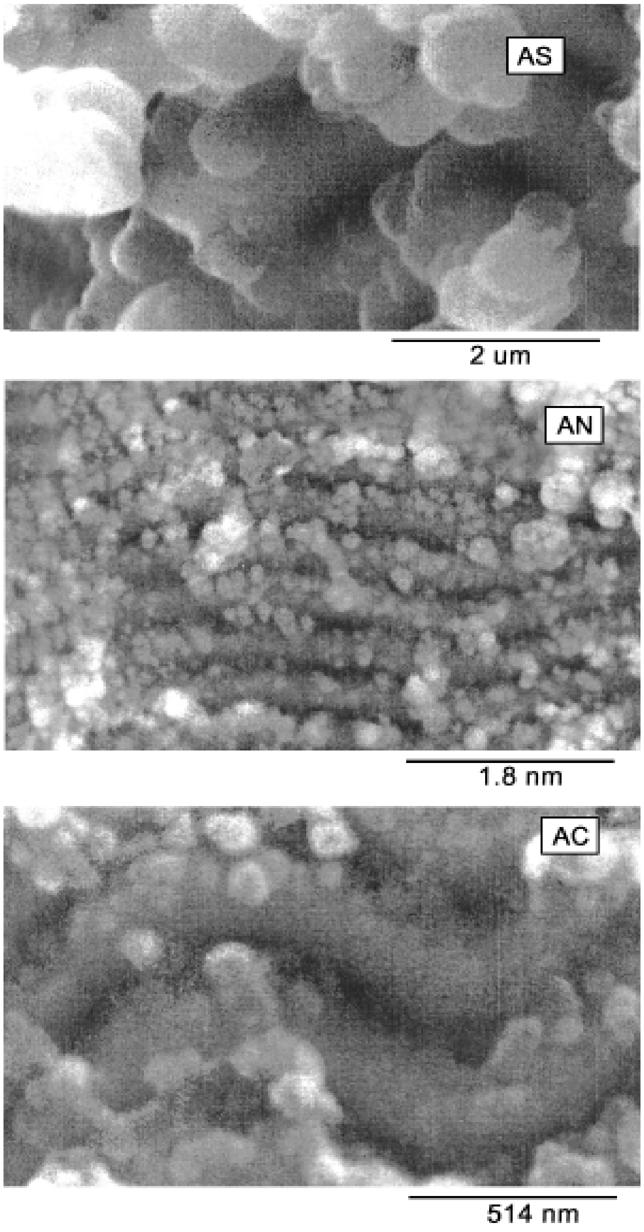

Fig. 5. Nanoparticles of alumina synthesized from alminum sulphate (AS), aluminum nitrate (AN), and aluminum chloride (AC).

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