Effect of Concentration of $Al_2(SO_4)_3.18H_2O$ on the Synthesis of Nanosized Alumina

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Summary: Nanosized alumina has been prepared by the gelation of the solution containing aluminum sulphate and urea followed by low temperature calcination. The effect of different concentrations on pH and its ultimate effect on gelation were studied. Gel formation occurred in the solutions containing 1: 20 salt/urea ratio. Aluminum hydroxide and nanoparticles of alumina were characterized by SEM, DTA and TG. The process describes the formation of aluminum hydroxide $Al(OH)_3$ and its thermal decomposition to Aluminum hydroxyoxide AlOOH and finally to aluminum oxide Al_2O_3. Nanoparticles of alumina produced were spherical with average particle size of 200 nm.

Introduction

Nanomaterials have unique chemical, physical, optical and mechanical properties. A nanoparticle has as many as molecules on the surface as are hidden in its interior. Compared with micron sized particles nanocrystals have lower melting point and huge surface area i-e hundreds of square per gram.

The unusual and unexpected structure of the alumina nano particles, suggests a number of important applications. Nano sized particles of alumina are known for their ability to sinter at temperatures far lower than those for micron sized particles. This suggests their use as sintering aids. Chemical mechanical polishing slurries utilizing nano alumina particles have shown higher efficiencies, and easier cleaning compared to slurries utilizing conventional material. This is particularly useful in obtaining smoother wafer surfaces. The alumina nano particles dispersed in the solution and bonded to the surface of optics and display can provide the protective coating that exceeds current capabilities. The incorporation of alumina nanoparticle has provided desirable mechanical and bioactive properties for bone tissue engineering applications. Moreover, alumina nanoparticles are finding applications in ceramic ultra filters and membranes used for filtering viruses and bacteria, for gas separation processes, for the strengthening of composites where the matrix is ceramic, metal or plastic, also as a catalyst and preferably as catalyst substrate [1,2].

Various nanopowder technologies, evolved over the past two decades are spray pyrolysis, vapor phase condensation, emulsion process, microwave synthesis, flame process, laser abrasion, plasma synthesis, chemical vapor deposition, mechanical alloying or high energy milling and sol gel processing [3-7]. There is considerable interest today in the application of sol gel technology to produce powders, spheres, coating and fibers for a variety of applications [8,9].

In the present investigation an attempt has been made to synthesize nano sized alumina from aluminum sulphate and urea by sol gel process. The advantages of this technique include low capital cost equipment, room temperature processing, low sintering temperatures, high purity, three dimensional homogeneity, ease of making multi component and well distributed small particles [10,11].

Result and Discussion

The change in pH plays an important role to predict the rate and completion of the reaction (Fig 1). For convenience, abbreviations AS1, AS2, AS3 and AS4 are assigned to reaction mixtures containing 1.15, 0.5, 0.1 and 0.05 moles per liter aluminum sulphate. The initial pH of the four reacting solution is 2.5 (Fig 1). AS1 and AS2 did not show any change in pH whereas AS3 showed change after 200 minutes which was ceased at 3.3 after 75 minutes and remained same even after 24 hours. In case of AS4

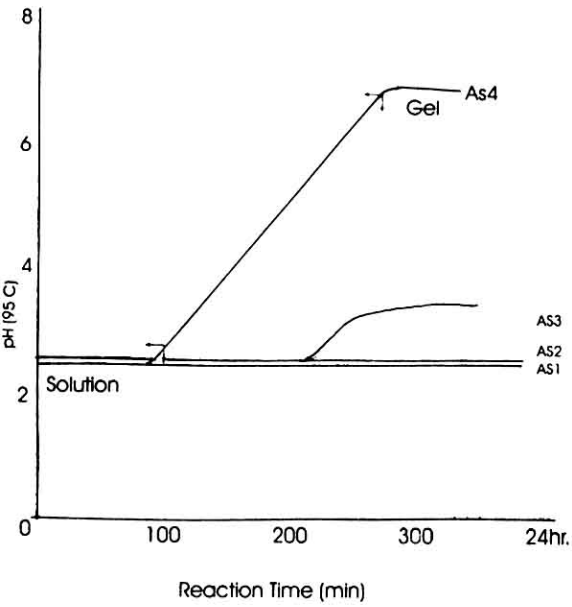

Fig. 1: The effect of reaction time on the pH behavior during sol gel processing

Reaction conditions:

$[Al_2(SO_4)_3.\ 18H_2O)]$ AS1 = 1.15 moles /l

AS2 = 0.5 moles / 1

AS3 = 0.1 moles /1

AS4 = 0.05 moles /1

[Urea] = 1 moles /1

Temperature = 95°C

pH slowly rose to 2.8 after heating and stirring for 100 minutes. The slow change is due to the acid base reaction. As the reaction proceeded the pH went to 6.8 after a time period of 275 minutes. The pH showed a linear change with respect to time and reached to 7.0 after 300 minutes showing complete conversion of the solution into gel.

As it is observed that the pH of the reaction mixture of aluminum sulphate and urea is acidic in the beginning. The acidic pH is solely due to aluminum salt solution as urea makes neutral solution. Aluminum sulphate gets dissociated in water to give Al^{3+} and SO_4^{2-} ions. Aluminum ion is amphoteric in nature. It can behave both as weak acid and weak base. On heating urea is hydrolyzed to NH_4OH and CO_2 gas is evolved. The hydrolysis can be written as follows:

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

It is suggested that sulphate being stronger base as compare to aluminum react with urea to give $(NH_2)_2SO_4$. The chemical equation for acid base neutralization reaction may be written as:

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

The difference in behavior of pH with respect to concentrations depends upon the availability of ammonium hydroxide in the solution to neutralize the sulphate ions. AS1 and AS2 did not show any change in pH due to the fact that sulphate being higher in concentration consumed all the urea and gel was not formed. In case of AS3 major part of urea was utilized in acid base reaction and it was not sufficient enough to raise the pH beyond 3.3 and ultimately resulted in incomplete conversion of solution into gel. On the contrary, in case of AS4 urea being sufficient in content completed the acid base reaction and afterwards conversion of solution into gel. Aluminum ions act as acid and react with water to give $Al(OH)_3$. The hydrolysis of urea is a slow process and gradually change the pH which ultimately leads to homogeneous precipitation of $Al(OH)_3$.

For thermal analysis of aluminum hydroxide produced, is evident from the DTA curve, first endothermic peak appeared at 95°C (Fig 2). It is a broad peak indicating slow and continuous dehydration of aluminum oxide hydrate, in good agreement with the observation of Houldsworth and Cobb [12]. The peak is not sharp probably because of poor crystalline nature of submicron sized aluminum hydroxide powder. Aluminum hydroxide decomposed at low temperature so it is predomnantly either gibbsite or bayerite [13]. The second peak appeared at 250°C. It is a small endothermic peak might be due to the decomposition of boehmite. The weight loss correspond these two peaks was found to be 37%. Thermal decomposition of $Al(OH)_3$ may be written as $2Al(OH)_3 \rightarrow 2AlOOH \rightarrow Al_2O_3 + 3H_2O \uparrow$, for which the theoretical weight loss is 34%. Theoretical weight loss is in accordance with the experimental weight loss. Last peak appeared at 920°C. It is a sharp endothermic peak and showed the decomposition of unreacted aluminum sulphate [14]. TG has

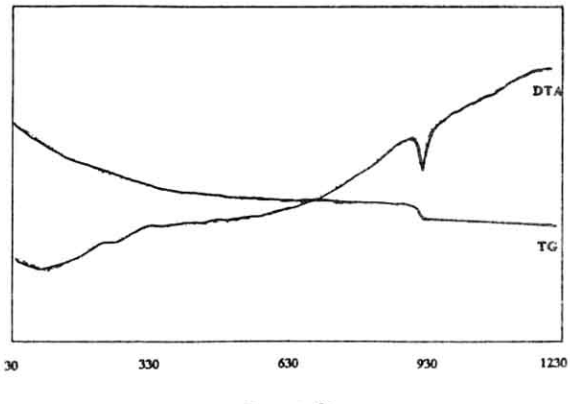

Fig. 2: DTA and TG traces of Aluminum Hydroxide Powder.

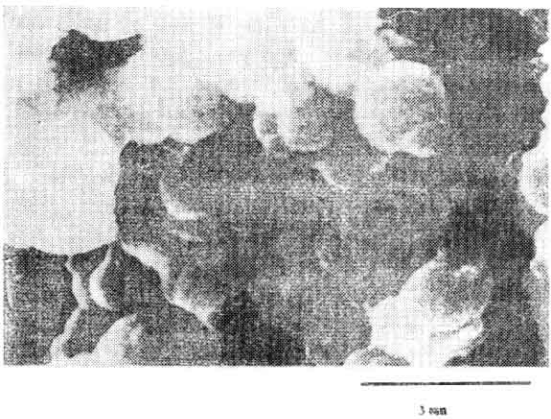

Fig. 3: Micrograph of Nanoparticles of Alumina

shown 9% of weight loss. The sulphate ions in the system might be problematic in the sintering of aluminum hydroxide to α alumina. The explanation to this probability is that SO_4^{2-} is very difficult to eliminate as the valence bond it forms with Al is covalent in nature [15]. The free sulphate however can be reduced to certain extent by the optimizing the concentration of urea and aluminum sulphate solution. Attempt can also be made to neutralize the excess sulphate at least partially with ammonia.

The morphology of nanoparticles of alumina shows that the particles were spherical in shape and well dispersed (Fig 3). The average particle size of alumina was 200nm (Fig 4). However range of particle size distribution was quite wide.

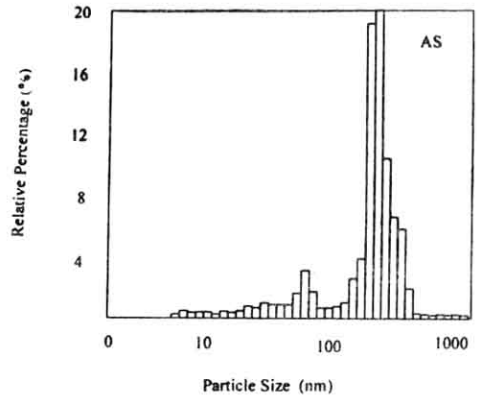

Fig. 4: Particle size distribution of alumina obtained from Aluminum Sulphate (AS)

Experimental

Synthesis of nano alumina

Reagent grade aluminum sulphate $Al_2(SO_4)_3.18H_2O$ (PSCIR) and urea (Pak Agro) were used as starting reagents. Aluminum salt was dissolved in distilled water and the concentration of the stock solutions were adjusted to 1.15, 0.5, 0.1, 0.05 $mol.l^{-1}$ and that of urea to 1.0 $mol.l^{-1}$. The starting pH of each solution was adjusted at 2.5 by using either HNO_3 or ammonia. The reacting solutions were preheated in a glass flask at 50°C for 1 hr, and subsequently heated at the reaction temperature of 95 °C on hot plate. During the reaction the solutions were stirred with magnetic stirrer at constant volume (2000ml) through out the reaction. The change in pH was measured with a pH meter. When the pH of the reacting solution reached 7.0 the solution vessel was cooled in water to stop th reaction. The resulting gel was washed five times with distilled water to eliminate excess of free acid. The gel was then atomized by its sublimation below freezing point at –40°C and finally calcined at 600 °C in an isothermal furnace for 2 hrs.

Characterization of Product

The products were characterized by Scanning Electron Microscope (SEM) Hitachi S-2700 to study morphology and particle size distribution. A thin layer of the sample was prepared by dispersing it in isopropyl alcohol. Thermal Analyzer (DTA-TG) Shimadzu DT-40 was used to study the physical and chemical changes on heating up to 1200°C @ 10°C per minute.

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