International Journal of Chemical Sciences and Applications
ISSN 0976-2590, Online ISSN 2278 – 6015
Vol 5, Issue3, 2014, pp 126-131
http://www.bipublication.com

Effect of Chitosan on the Size Distribution of Alpha Alumina Nano Particles

Manjusha Hariharan[1*], Neethumol Varghese[1], A Benny Cherian[1], Jenish Paul[1] and Aneesh S. Benny[2].

[1]Department of Chemistry, Union Christian College, Aluva, Ernakulum, Kerala, India.
Department of Chemical Engineering, NIT Calicut, Kerala, India.
*Email:manjushahariharan@gmail.com, Tel: +919048547432, Fax: 04842607534

[Received-24/10/2014, Accepted-02/11/2014]

ABSTRACT

Metal oxide nano particles have been extensively synthesized because of its unique properties. In this paper nano alumina was synthesized using aluminum nitrate and citric acid as the reacting materials and biopolymer chitosan as precursor. Simple Sol-Gel method was used for the synthesis. Nano alumina synthesized using chitosan as precursor was compared with, nano alumina synthesized without using chitosan. The characterization was done using XRD, SEM, FTIR and UV-Visible Spectroscopy. The average grain sizes were estimated using Scherer's formula. Crystalline α-Al_2O_3 nano particles had a particle size distribution ranging from 30 to 32 nm. Nano alumina powder is extensively used in various fields such as electronics, composites, biocompatible implants, catalyst supports and high temperature applications. It is a biodegradable material, well tolerated by the biological environment.

Key words: Nanoparticle, α-alumina, synthesis, chitosan, sol-gel.

[I] INTRODUCTION

Al_2O_3 is extensively used and studied as high temperature structural material in electronic packaging, corrosion resistance ceramics and translucent ceramics. In general; alumina has many interesting properties such as high hardness, high stability, high insulation, and transparency [1]. Alumina has a high compression strength, high abrasion resistance, high chemical resistance, high thermal shock resistance, high degree of refractoriness and high dielectric strength, and is transparent to microwave radio frequencies and has a low neutron cross section capture area [2]. The importance of alumina as catalyst or catalytic support has also been widely recognized for many chemical reactions [3-5]. The transparency of alumina film and wide range of properties extend its application in optics as well [6]. The mechanical, chemical and electrical properties of alumina are often used in the ceramic industry. Alumina is also an inert substance, and at room temperature, it is insoluble in all ordinary chemical reagents. It also has excellent wear resistance and can be polished to high surface finish. These qualities make it useful as a biomaterial. Alumina is widely used in the fire retard, catalyst, insulator, surface protective coating, and composite materials [7-11]. Among different forms of this worthwhile material, ultrafine α-Al_2O_3 powder has

significant potential for a broad range of requests as high strength materials, electronic ceramics and catalysts.

Alumina (Al_2O_3) or aluminium oxide is the only oxide formed by the metal aluminium and it occurs in nature as the minerals *corundum* (Al_2O_3); *diaspore* ($Al_2O_3.H_2O$); *gibbsite* ($Al_2O_3.3H_2O$); and most commonly as *bauxite*, which is an impure form of gibbsite. It is a very hard material and this property of alumina lends itself for use as an abrasive material. Another useful property of the material is its high melting point, i.e., above 2000 °C (3632 °F), which makes it useful as a refractory and as linings of special furnaces. Alpha Al_2O_3 is generally refers to as corundum. The morphology of aluminium oxide nanoparticles is spherical, and they appear as a white powder. Alumina has several phases such as alpha, delta, theta and gamma. However, the alpha alumina phase is the most thermodynamically stable phase [12]. Conventional methods for synthesizing α -Al_2O_3 powder involve solid state thermally driven transformations from the hydrates of aluminum oxide. The extent of conversion to the corundum structure depends on the temperature and the time of thermal treatment. Total conversion occurs on heating above 1230 ^{0}C [13]. According to Gitzen [14], γ-Al_2O_3 transforms to δ-Al_2O_3 when calcined above 800 ^{0}C, the δ-Al_2O_3 transforms to θ-Al_2O_3 when calcined above 1000 °C, finally, θ-Al_2O_3 transforms to α-Al_2O_3 when calcined above 1100 °C. The benefits of nanoparticles can include increased electrical conductivity, toughness and ductility, and increased hardness and strength of metals and alloys.

Recently many researchers are showing interest on the preparation and application of nano-sized alumina or alumina composites considering their diverse properties [15-18]. The properties of alumina particles are largely governed by the particle size, morphology, surface and phase homogeneity and these can be controlled by selecting a proper synthetic route. Rodica Rogogan *et al.* had prepared alumina powder by sol- gel method can be done using organic precursors and inorganic precursors [19]. In 2004, Macêdo *et al*. reported the synthesis of γ -alumina by sol-gel method from a saturated aqueous solution of aluminum nitrate using urea as neutralizing and hydrolysis control agent [20]. Hamed Sadabadi *et al.* had synthesized high purity crystalline alpha alumina (α -Al_2O_3), platelet powder, synthesized by the combustion synthesis; aluminum nitrate was used as the source of aluminum and urea as oxidizer in an aqueous medium [21].

Chitosan is a biopolymer and obtained as a byproduct from seafood industry. In this work, simple, sol–gel method was adopted to synthesize nano-sized alumina particles, chitosan used as the precursor for the synthesis, aluminum nitrate and citric acid was used as the reacting materials. This method has many advantages over the other methods as it is low-cost, easy to control particle size, simple processing and ecofriendly.

[II]. MATERIALS AND METHODS

2.1 Materials

Analytical grade citric acid and aluminum nitrate, procured from Merck Specialty Chemicals Limited, Mumbai (India), Acetic acid glacial obtained from Nice Chemicals Pvt, Ltd, Edapally, Cochin (India), Chitosan provided by CIFT Cochin, were used as the raw materials for the synthesis of nano alumina.

2.2 Synthesis

The sol–gel method is an important technique for the processing of metal oxides and the technology has been known for two centuries. Since the first reports on preparation of inorganic monoliths in the early 1970s, the interest for the method has increased tremendously. The process can be divided into the following general stages: a) hydrolysis of precursors-sol formation b) poly condensation of hydrolyzed precursors-gelation c) aging d) drying e) calcinations. In this work, two methods were adopted for the synthesis of nano alumina.

2.2.1 Synthesis of nano alumina

Aluminium nitrate 158 gram in 100 ml water mixed with Chitosan 1 gram in 3% acetic acid, the mixture was blended with citric acid 105 gram in 100 ml water, the resultant mixture was digested for 4 hrs at 80 °C with constant stirring. The solution turned into a transparent gel. The gel was calcined at 1200 °C for 2 hrs in a muffle furnace to get nano alumina powder (Kar et al 2008). The same procedure was repeated without chitosan and the results were compared.

[III]. RESULTS AND DISCUSSION

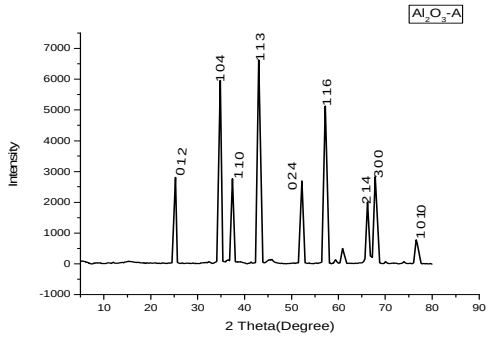
3.1 XRD

The size of the nano alumina powder synthesized with chitosan and without chitosan were demonstrated [XRD, PANalytical, (model: DY-1656)] machine (position 2θ, range 5-80)]. The scintillation instrument present in the machine moves through the required angle at specific counts and scans. The output was obtained in the form of a graph with 2θ on X axis and intensity on Y axis. The peaks obtained from graph corresponding to different planes were compared with the standard data in JCPDS files. The XRD pattern is shown in Figure 1. The analysis of crystal structure using XRD illustrates that the nano powder synthesized were α-Al_2O_3. The strong and sharp peaks showed that the α-Al_2O_3 was well crystalline. It also exhibits that the most stable phase, α-Al_2O_3, was obtained at1200 °C. Hyuk-Joon *et al.* [11] reported that completion of the most stable phase of α alumina occurs at this temperature.

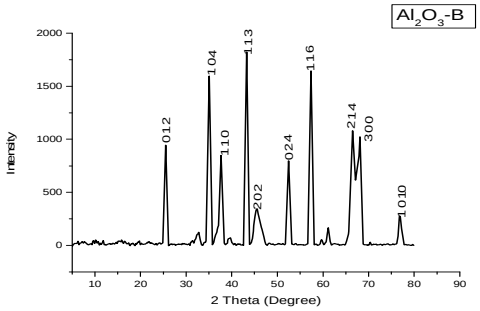
The Average crystallite size (D) of the α-Al_2O_3 was calculated using Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

D = shape factor, λ = x-ray wavelength, β = FWHM of diffraction peak, θ = Bragg angle. The grain size was estimated to be in the range of 30-32 nm for synthesized alumina using chitosan as precursor and synthesized alumina using conventional methods having grain size in the range of 40 – 45 nm. However, the nano Al_2O_3 obtained in both cases at 1200 ^{0}C calcination was mainly in the form α-Al_2O_3. The α-Al_2O_3 is the most thermodynamically stable form. It was concluded that all of the peaks obtained in the XRD pattern of alpha alumina nano powder matched perfectly with the standard corundum or α-Al_2O_3 pattern (JCPDS 81-2267)



(Al_2O_3) -A



(Al_2O_3) –B

Figure 1

Figure 1 shows the XRD pattern of α -Al_2O_3 synthesis by sol-gel method of aluminum nitrate and citric acid without chitosan (Al_2O_3-A) and with chitosan (Al_2O_3-B)

3.2 Fourier Transform Infrared Spectroscopy

The phase of the nano alumina powder was further confirmed by FTIR. Fourier transform infrared spectra were recorded in a FTIR (Shimadzu IR Affinity-1 Spectrophotometer) machine. An FTIR spectrum was generated by the absorption of electromagnetic radiation in the frequency range 400 – 4000 cm^{-1}. The obtained spectrum is shown in figure 2. According to FTIR spectra, the bands in the region of 400-1000 cm^{-1} were generally associated with stretching vibrations of Al-O

bonds. There were some wide and high peaks of Al-O stretching in the range of 500 – 1000 cm^{-1} that were related to the transitional phases of alumina and stable phase of alpha alumina .The broad band at 589 cm^{-1} and 848 cm^{-1} corresponds to the vibrational frequencies of co-ordinate ν-AlO_6 and ν-AlO_4 respectively. The peaks at 3468 cm^{-1} and 1645 cm^{-1} were assigned to stretching and bending modes of absorbed water. The bands at around 500 cm^{-1} and 850 cm^{-1} from FT-IR analysis confirmed that the nano powder synthesized, using chitosan precursor and conventional method had the characteristic peak of alpha alumina.

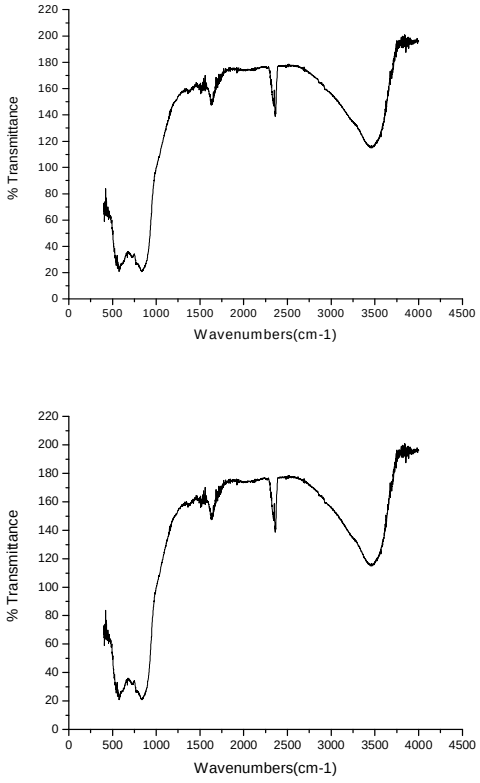
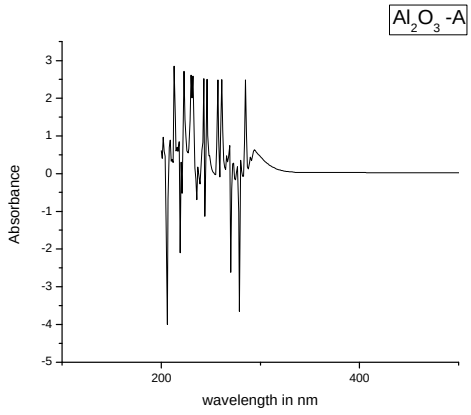


Figure 2

Figure2 shows the FTIR spectra of α -Al_2O_3 synthesis by sol-gel method of aluminum nitrate and citric acid without chitosan (Al_2O_3-A) and with chitosan (Al_2O_3-B)

3.3 UV -Visible Spectroscopy

The obtained alpha alumina nano powders were again confirmed by taking UV spectra using (Shimadzu UV 1800) spectrophotometer. Alpha alumina nano powders were partially dissolved in deionized water to obtain the UV absorption bands. Obtained spectra are given in the figure 3. Particular absorbance will produce a band in UV spectrophotometer. The strong absorbance peak obtained for alpha alumina nano powders were in the range of 243,380 nms for the alpha alumina powder synthesized without applying chitosan and 243,375 for the alpha alumina powder synthesized by applying chitosan as precursor. A strong absorption peak between 200 nm and 400 nm was clearly observed which confirmed the presence of Al_2O_3 nano particles. UV- visible absorption spectroscopy was one of the important tools to probe the energy band gap. The absorption peak of synthesized alpha alumina nano particles without chitosan was found at around 243 nm and 380 nm. Chitosan assisted synthesis of alpha alumina nano particles had absorption peaks at 243 nm and 375 nm. There was an appearance of blue shift at 5nm with the addition of chitosan. Band gap of the nanoparticles was calculated from E = hc / λ where, E = Band gap energy, h = Planck's constant, c = velocity of light; λ = wavelength of absorption edge in reflectance spectra. Band gap energy of chitosan assisted synthesis of alumina nano particles (3.31eV) was slightly greater than for the conventional synthesis alumina nanoparticles (3.26eV). It has to be confirmed that there was a decrease in particle size of alumina in presence of chitosan.



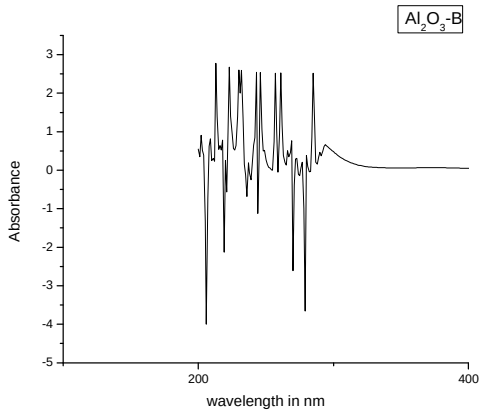
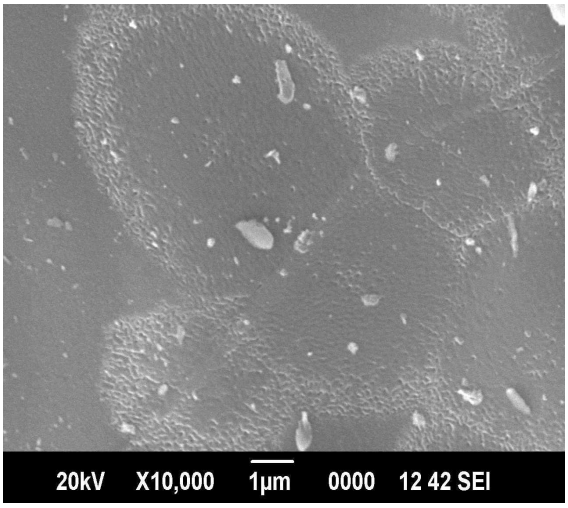


Figure 3.

Figure 3. Shows the UV-Visible spectra of α -Al_2O_3 synthesized by sol-gel method of aluminum nitrate and citric acid without chitosan (Al_2O_3-A) and with chitosan (Al_2O_3-B)

3.4 Scanning Electron Microscopy

Information on morphological and textural characteristics of the synthesized powders was made by scanning electron microscopy analysis. The surface morphology of the Al_2O_3 nano powder synthesized was examined by SEM (JEOL-JSM 5800) scanning electron microscope operating at 20 kV accelerating voltage. The Al_2O_3 nano powder was a conducting powder therefore the SEM images were taken at high vacuum mode to obtain sharp images. The images were shown in Figure 4. The SEM results clearly indicated the formation of spherical shape of alumina nano particles with its size in nano metric scale.



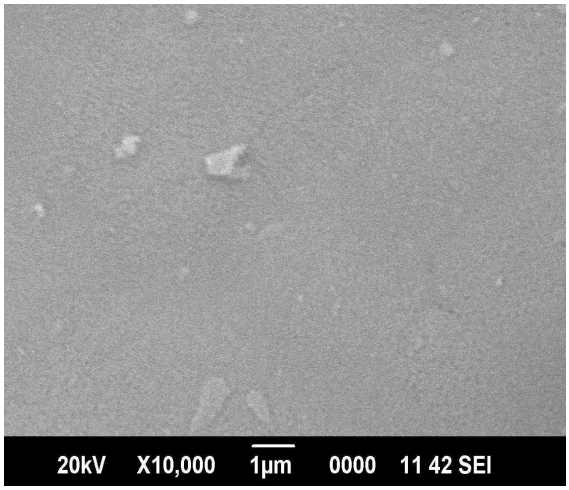


Figure 4.

Figure 4 shows the SEM images of α -Al_2O_3 synthesized by sol-gel method of aluminum nitrate and citric acid without chitosan (Al_2O_3-A) and with chitosan (Al_2O_3-B)

[IV] CONCLUSION

It is to be concluded that, the chitosan have great influence in the size reduction of alpha alumina nano particles. Using sol-gel method and by applying Chitosan; the obtained alumina was in nano meter range. XRD analysis showed that the alumina nano powder synthesized had more stable alpha alumina phase. FT-IR analysis showed a characteristic peak at 848 cm^{-1} and 589 cm^{-1}, which confirmed the formation of nano alumina. SEM images also revealed that the synthesized alumina nano powder have alpha phase. Alpha alumina powders obtained at the nano metric scale may have superior properties as compared to the powders obtained in larger particle sizes and this can be used in various applications.

ACKNOWLEDGEMENT

Sophisticated Analytical Instrument Facility (SAIF) STIC, Cochin and Department of Chemistry, Union Christian College, Aluva for their valuable support and financial assistance.

REFERENCE

1. A. Laachachi, M. Ferriol, M. Cochez, J.-M. Lopez Cuesta, and D. Ruch, (2009), “A comparison of the

role of boehmite (AlOOH) and alumina (Al_2O_3) in the thermal stability and flammability of poly (methyl methacrylate), Polymer Degradation and Stability, vol-94, no. 9, pg 1373–1378. View at Publisher· View at Google Scholar. View at Scopus.

2. Suchanek, W.L., (2010), hydrothermal synthesis of alpha alumina (α-Al2O3) powders: Study of the processing variables and growth mechanisms. J. Am. Ceram. Soc., vol-93, pg 399–412.
3. Bujdák, J.; Rode, B.M., (2003), Alumina catalyzed reactions of amino acids, J. Thermal Anal. Calorim, Vol-73(3), pg 797-805.
4. Elinaga, H.; Futamura, S, (2004) Comparative study on the catalytic activities of alumina-supported metal oxides for oxidation of benzene and cyclohexane with ozone. React. Kinet. Catal. Lett., vol-81 (1), pg.121-128.
5. Lang, Wang, Xing, Zhang, Liu, (2008) Preparation of magnetic α -Al_2O_3 supported palladium catalyst for hydrogenation of nitrobenzene. Process Syst. Eng., vol-54(9), pg 2303-2309.
6. Kobayashi, Y.; Ishizaki, T.; Kurokawa, Y. (2005), Preparation of alumina films by sol-gel method. J. Mater. Sci., vol-40, issue (2), pg. 263-283.
7. I. Lukić, J. Krstić, D. Jovanović, and D. Skala, (2009) "Alumina/silica supported K_2CO_3 as a catalyst for biodiesel synthesis from sunflower oil," Bioresource Technology, vol. 100, no. 20, pg 4690–4696. View at Publisher . View at Google Scholar . View at Scopus
8. M. Touzin, D. Goeuriot, C. Guerret-Piécourt, D. Juvé, and H. J, (2007) Fitting, "alumina based ceramics for high-voltage insulation," Vacuum, vol- 81, pg 762–765.
9. A. Keyvani, M. Saremi, and M. Heydarzadeh Sohi, (2010) "Microstructural stability of zirconia-alumina composite coatings during hot corrosion test at 1050 °C," Journal of Alloys and Compounds, vol- 506, issue -1, pg 103–108. View at Publisher . View at Google Scholar . View at Scopus
10. R. Lach, K. Haberko, M. M. Bućko, M. Szumera, and G. Grabowski, (2011) "Ceramic matrix composites in the alumina 5-30 vol. % YAG system," Journal of the European Ceramic Society, vol-31, issue-10, pg 1889–1895. View at Publisher · View at Google Scholar . View at Scopus
11. Hyuk-Joon Y., Jin W.J., Iu T.K., Kug S.H.: J. (1999) Colloid and Interface Science 211, pg 110.
12. L.D. Hart, (1990), Alumina Chemicals: Science and Technology Hand book, American Ceramic Society, Columbus, Ohio, USA.
13. R.K. Pati, J.C. Ray, P. Pramanik, (2000) A novel chemical route for the synthesis of nano crystalline alpha-Al2O3, Mater. Lett; vol - 44, pg 299–303.
14. Gitzen, W.H. , (1970) Alumina as a Ceramic Material; American Ceramic Society: Columbus, Ohio, USA.
15. Bahlawane, N.; Watanabe, T., (2000), New sol-gel route for the preparation of pure α-alumina at 950 °C. J. Am. Ceram. Soc., vol- 83 issue 9, pg 2324-2326.
16. Jun, C.J.; Choi, J.H.; Lim, Y.M.; Jeun, J.P.; Kang, P.H.; Nho, Y.C, (2006), "Preparation and characterization of polypropylene nanocomposites containing polystyrene-grafted alumina nanoparticles. J. Ind. Eng.Chem., vol 12 issue 6, pg 900-904.
17. Siengchin, S.; Karger-Kociss, J.; Thomann, R, (2007), Alumina-filled polystyrene micro- and nanocomposites prepared by melt mixing with and without latex precompounding: structure and properties, J. Appl. Polym. Sci., vol-105 issue 5 pg 2963-2972.
18. Ash, B.J.; Rogers, D.F.; Wiegand, C.J.; Schadler, L.S.; Siegel, R.W.; Benicewicz, B.C.; Apple, T, (2002), Mechanical properties of Al_2O_3/polymethyl methacrylate nanocomposites. Polym. Composites, vol 23, issue 6, pg 1014-1025.
19. Rodica ROGOJAN, Ecaterina ANDRONESCU (2011) Synthesis and Characterization of alumina nano powder obtained by sol-gel method. U.P.B. Sci. Bull., Series B, Vol. 73, Issue. 2.
20. Macêdo, M.I.F.; Osawa, C.C.; Bertram, C.A, (2004), Sol-gel synthesis of transparent alumina gel and pure gamma alumina by urea hydrolysis of alumina nitrate. J. Sol-gel Sci. Tech., vol-30, issue 3, pg 135-140.
21. Hamed Sadabadi, Adeleh Aftabtalab, Shirzad Zafarian, Sarah Shaker, Mohsen Ahmadipour, and K. Venkateswara Rao, (2013), High purity Alpha Alumina nanoparticles: Synthesis and characterization, International Journal of Scientific & Engineering Research, Volume 4, Issue 4, pg 1593.