ABSTRACT

A crylamide (as monomer), N,N’-methylene-bis-acrylamide (as cross-linker), ammonium persulphate (as initiator), N,N,N’,N’-tetramethylethyldiamine (as accelerator), and aluminium nitrate salt were used to produce a low temperature polymeric gel-net, in order to tailor the particle size of alumina powder. The monomers/salt ratio, metal ion/monomers interaction, furnace atmosphere, thermal stability and pore size of polymeric gel-net are the key factors to control the alumina particle size. Mercury porosimetry data and transmission electron microscopy (TEM) micrographs indicated that increasing the monomers/salt ratio from 1/1 to 3/1 resulted in polymeric gel-net with smaller pore size, and hence, nanopowders with narrower particle size distribution. The X-ray diffraction (XRD) patterns for nanopowders exhibited the amorphous phases below 1100°C and a single phase α-Al2O3 above 1100°C. Thermal analysis showed that for pre-oxidized samples below 200°C polymeric gel-net possesses better thermal stability at higher temperature in the presence of inert gas. Trapping of metal ions, with specific coordination numbers, into polymeric gel-net pores prevents their migration and reduces the nanopowder particles agglomeration. These observations were also confirmed by Fourier transform infrared (FTIR) and UV-vis spectrometry measurements. Polymeric gel-net inhibits the aggregation of Al2O3 nanopowder, improves its homogeneity, and provides a powder with narrower particle size distribution.

INTRODUCTION

In recent years, there has been a rising interest in the synthesis of nanocrystalline metal oxides. It is widely accepted that the properties of nanocrystalline materials can be dramatically different from those of the parent bulk materials which offers a new scope for their novel technological applications [1,2].

One of the critical factors in advanced ceramic technology is the synthesis of the starting powders. The initial powder plays an important role in determining the properties of the final product [3,4]. Nanoscale powders with high performance are required to obtain nano-structural ceramics. The nanocrystals are important for a variety of applications, e.g., fabrication of metal ceramic laminate composites or as a reinforcement phase in brittle polymer matrix composites.

Alumina (Al2O3) is an important industrial and structural ceramic
material which some of its properties are controlled by its microstructure and matrix stability [5]. Alumina has many applications both as structural and functional materials due to its proper hardness, mechanical strength, excellent biocompatibility, good corrosion resistance and low cost [6,7]. It is also used to improve the mechanical properties, thermal stability, barrier properties and dielectric enhancement of polymeric systems [8-11].

It is well known that the physical and mechanical characteristics of alumina ceramic articles depend strongly on their microstructure, which it closely reflects the shape and size of the raw alumina particles. In recent years, substantial research works have been conducted for the preparation of nano-size alumina particles [12-14]. Higher densification rate and lower sintering temperature have been encountered in nano-structured ceramics as compared with conventional counterparts [15]. However, there are two main reasons why it is difficult to obtain nano-scale \(\alpha\)-\(\text{Al}_2\text{O}_3\) powder. The first reason is the phase stability of \(\alpha\)-\(\text{Al}_2\text{O}_3\) after calcination at high temperature which easily prompts the grain growth of particles and hard to acquire the nanoscale powder. The second reason is the tendency of \(\alpha\)-\(\text{Al}_2\text{O}_3\) particles to aggregate during dehydration process in wet chemistry method [16,17].

Conventional method for synthesizing \(\alpha\)-\(\text{Al}_2\text{O}_3\) powder involves the thermally driven transformation of the hydrates of aluminium oxide into solid state. The extent of hydrated aluminium oxide conversion to corundum structure depends on the temperature and duration of thermal treatment. Total conversion occurs on heating above 1230°C [18].

Neiman et al. [19] obtained nano-sized \(\text{Al}_2\text{O}_3\) powders by electrical explosion of metal wires in an oxidizing atmosphere. Wu et al. [17] prepared the alumina gel from \(\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) by \(\text{NH}_4\text{OH}\), where plate-like nano \(\alpha\)-\(\text{Al}_2\text{O}_3\) particles were crystallized by heating around 900°C. Pathak et al. [20] synthesized the nanocrystalline alumina powder by a chemical reaction using citric acid and ammonia at 1200°C. Wen et al. [21] and Yen et al. [22] prepared \(\alpha\)-\(\text{Al}_2\text{O}_3\) nanopowder using \(\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) and \(\text{NH}_4\text{OH}\) as precursors. Yen et al. [23] and Yü et al. [24] reported \(\text{Al}_2\text{O}_3\) nanopowder preparation by calcination of boehmite. Takatori et al. [7] fabricated the hollow alumina submicron size particles with extremely thin wall by emulsion-combustion process. Pang et al. [25] synthesized alumina nanopowder with \(\text{AlCl}_3\) using aqueous \(\text{NH}_4\text{OH}\) as precipitant. Pacheco et al. [26] reported \(\alpha\)-\(\text{Al}_2\text{O}_3\) nanopowder prepared by sol-gel method. Noda et al. [27] synthesized nano-sized \(\text{Al}_2\text{O}_3\) particles by metal organic chemical vapour deposition (MOCVD) method with \(\text{Al(CH}_3\text{)}_3\).

Wang et al. [16] synthesized \(\alpha\)-\(\text{Al}_2\text{O}_3\) at 1100°C via accelerator-free polyacrylamide gel system, prepared at 80°C, and compared their route with other methods such as precipitation and calcination methods. They observed the particle size of nanopowders produced by gel method was smaller than that of the nanopowders made by other methods. The polymeric gel-net method has attracted more attention since then and has been used to prepare both ceramic articles [28] and oxide nanoparticles such as; \(\text{SnO}_2/\text{Eu}\) [29], \(\text{Bi}_2\text{O}_3\) [30], and \(\text{BiFeO}_3\) at 60-80°C [31].

The aim of the present work was to control the size of alumina nanopowder particles using polymeric gel-net formation at low temperature. It is believed that by this method the polymerization rate can be properly controlled in a manner to prevent the aggregation of nanopowder particles at its minimum. The effect of polymeric gel-net pore size on powder particle size has been investigated, as well. Furthermore, it is demonstrated that the metal ions in polyacrylamide gel-net are not only entrapped but also coordinated with the pendant groups. UV-vis spectrometry, FTIR spectroscopy, XRD, simultaneous thermal analysis/thermal gravimetry analysis (STA/TGA), mercury porosimetry and TEM techniques were employed in order to characterize the produced alumina nanopowder.

**EXPERIMENTAL**

**Materials and Methods**

Acrylamide (\(\text{C}_2\text{H}_3\text{CONH}_2\), AM, Merck, Germany) and \(\text{N,N'}\)-methylene-bis-acrylamide (\(\text{CH}_2\text{CH}_3\text{CONH})_2\text{CH}_2\), MBAM, as a cross-linker, (Merck, Germany) monomers (AM+MBAM denoted by M) easily dissolve in aqueous solution of aluminium.
nitrate (Al(NO$_3$)$_3$.9H$_2$O denoted by S, Merck, Germany) with various weight ratios of M/S (1/1, 2/1, and 3/1). Then, 2 mL ammonium persulphate aqueous solution ((NH$_4$)$_2$S$_2$O$_8$ (APS) as an initiator, 10 wt%, Merck, Germany) was added to the mixture followed by 1 mL N,N,N',N'-tetramethylethyldiamine (TEMED as an accelerator, Merck, Germany) at low temperature of 4°C (Scheme I). The polymerization was initiated by APS via free radical mechanism and a semi-transparent gel was rapidly produced. The gel was transferred to crucible, put in a ventilated furnace and heated to a temperature which practically all the water and the organic species were removed.

The heating process was carried out in three steps: first, the temperature increased to 200°C at a constant heating rate of 15°C/min under air atmosphere, then kept constant at this temperature for 5 h. Second step was followed from 200°C up to 1100°C under inert gas. At the final step the samples were kept at 1100°C under air stream for 1 h to remove all the organic materials still left.

Interactions between the metal ions, polymer and monomers were investigated by a FTS-7, BIO-RAD (USA) FTIR spectrophotometer using the KBr pellet method and a DR5000, HACH (USA) UV-vis spectrometer using quartz cells of path length of 1.0 cm, at 190-300 nm wavelength range and a 0.1 nm/s sweep rate.

The thermal stability and pore size distribution of polymeric gel-net were analyzed by a STA-1500 thermal analyzer (PL-Thermal Sciences, UK) and a Pascal 440 Series mercury porosimeter (Thermo-ﬁnnigan, Italy), respectively. The phase identification of synthesized powder was obtained by XRD (X’pert, Philips, Netherlands) using CuK$_\alpha$ radiation in the range of 2$\theta$ =10-80°. Morphology and particles size of the synthesized powder were determined by an EM-900, Zeiss, TEM microscope (Germany).

**RESULTS AND DISCUSSION**

The polymeric gel-net method takes advantage of the polymerization of MA [32] initiated by free radicals...
which are formed by ammonium persulphate. The polyacrylamide chains are cross-linked by two functional groups of MBAM (Scheme II, part a). If the solution contained only acrylamide monomers, the chain would be linear and unbranched. However, a MBAM molecule can incorporate into two chains simultaneously and forms a permanent link between them. As a result, the polyacrylamide chains grow into a complex network of interconnected loops and branches.

The first step in free-radical polymerization is the decomposition of the initiator molecule into two free radicals with a constant initiation rate of $k_i$. The free radicals can then react with double bonds of vinyl monomers, with one electron remaining unpaired. In a few seconds or less, many monomers are added successively to the growing chains with a constant propagation rate of $k_p$. Finally each two chains with radicals at their ends react with each other to end the chain growth and form a polymer molecule. This bi-molecular process known as "termination" is identified with the constant termination rate of $k_t$ [33-35].

Owing to the form of the three-dimensional (3D) polyacrylamide gel-net, the $\text{Al}^{3+}$ ions in aqueous solution are trapped within gel-net pores. They coordinate to primary and secondary amine groups of polymer (Scheme II, part b). Therefore, the mobility of $\text{Al}^{3+}$ ions is limited.

The FTIR spectra of polyacrylamide gel with and without aluminium nitrate salt are shown in Figure 1. In the FTIR spectrum of polyacrylamide gel (Figure 1,

Scheme II. Preparation of (a) polyacrylamide gel-net and (b) the trapped and coordinated ions in gel-net pores.

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Figure 1. FTIR Spectra of polyacrylamide gel-net: (a) without salt and (b) with salt.

spectrum a) two strong intense bands appeared around 3500 and 3200 cm\(^{-1}\) are undoubtedly associated with the N-H stretching vibrations (related to primary and secondary amines) [36].

Comparing spectra a and b in Figure 1 reveals that new bands are appeared around 3050 and 2450 cm\(^{-1}\) in the presence of Al\(^{3+}\) which implies that Al\(^{3+}\) is coordinated with primary and secondary amine groups. The strong and sharp bands at 3500 and 3200 cm\(^{-1}\) in the spectrum a in Figure 1 are due to the presence of NH shifts towards lower frequency, which reveal the involvement of amine groups in complexation. The splitting of the C=O band of the polyacrylamide gel around 1650-1750 cm\(^{-1}\) upon complexation is a further support of nitrogen coordination with Al\(^{3+}\).

A new band at 1350-1450 cm\(^{-1}\) is related to aluminum nitrate. A much lower frequency of this absorption band may be attributed to metal ions coordination through amine nitrogen atoms with a strong bonding between the same ions and the polyacrylamide gel [37].

The UV-vis spectrum (Figure 2) confirms the FTIR results and shows interactions between unpaired electrons of AM and Al\(^{3+}\), since the absorption peak of AM has been shifted to lower wavelength or higher energy in the presence of Al\(^{3+}\) [38]. All the above mentioned parameters reduce the chance of Al\(_2\)O\(_3\) molecules to aggregate during drying and calcination processes, and increase the probability of obtaining nanopowder with narrower distribution size with minimum aggregation.

In order to prevent the aggregation of nanopowders, it is required to enhance thermal stability of polymeric gel-net to maintain its 3-D structure throughout the calcination process. Figure 3 shows the TGA curves of polymeric gel-net in the presence of air and/or an inert gas. It is evident in Figure 3 that in region below 200°C the thermal stability of polymeric gel-net under air atmosphere is better than its stability under inert argon atmosphere. The presence of air increases intermolecular cross-linking during oxidation by forming ether links (C-O-C) which produce higher thermal stability in polymeric gel-net at higher temperature [39,40]. However, beyond 200°C, using argon atmosphere is essential in lowering the rate of thermal degradation.

Figure 2. UV-vis Spectra for AM and AM + Al(NO\(_3\))\(_3\).

Figure 3. TGA Curves of polymeric gel-net in the presence of air and argon (Ar).
Figure 4. FTIR Spectra of polyacrylamide gel-net: (a) before and (b) after oxidation.

Figure 4 shows the FTIR spectra of polymeric gel-net before (spectrum a) and after oxidation (spectrum b), indicating to a strong and sharp ether band at around 1190 cm\(^{-1}\) for acrylamide gel-net after oxidation at 200°C for 5 h. We observed that by extending the oxidation time to 5 h, due to the formation of higher number of ether cross-links, the intensity of ether band increases.

As stated earlier, the heating process was carried out in three steps: in the first step, the temperature raised to 200°C at a constant heating rate of 15°C/min under air atmosphere. In the second step, from 200°C up to 1100°C, the heating process was followed under inert argon gas in order to protect 3-D structure of the polymeric gel-net. The prevention of polymeric gel-net from degradation can guarantee the production of Al\(_2\)O\(_3\) nanopowders with narrow particle size distribution and minimum aggregation. In the third step, the temperature of heating process was kept at 1100°C for 1 h under air to remove (if any) all the remaining organic materials and obtain pure alumina nanopowder.

The XRD patterns (Figure 5) of the calcined powder after subsequent heat treatment show diffraction peaks corresponding to δ-Al\(_2\)O\(_3\) and θ-Al\(_2\)O\(_3\) for calcination under 700°C. By increasing the temperature up to 900°C, the intensity of peaks attributed to θ-Al\(_2\)O\(_3\) increases while the others are disappeared. Finally, the peak of single phase α-Al\(_2\)O\(_3\) can be observed for the sample calcined at 1100°C for 2 h. This temperature is less than that of the conventional methods [18]. At 700°C or higher, some particles can be formed and at the same time, the following transformations can take place [16, 41]:

\[
\begin{align*}
\gamma - AlOOH(s) & \rightarrow \gamma - Al_2O_3(s) \\
\gamma - Al_2O_3(s) & \rightarrow \delta - Al_2O_3(s) \\
\delta - Al_2O_3(s) & \rightarrow \theta - Al_2O_3(s) \\
\theta - Al_2O_3(s) & \rightarrow \alpha - Al_2O_3 \\
\end{align*}
\]

Al\(_2\)O\(_3\) powder samples produced at 700°C (Figure 6a), 900°C (Figure 6b) and 1100°C (Figure 6c) have reflected the basic powder morphologies as obtained by TEM, where the smallest visible particles could be identified either as crystallites or their aggregates. The micrograph in Figure 6c exhibits a sharp distribution of the particles with an average particle diameter of less than 10 nm. Low temperature (i.e., 4°C) used for preparation of the gel inhibits the particle growth and aggregation.

The TEM micrographs show that by increasing the ratio of M/S from 1/1 (Figure 7a), to 2/1 (Figure 7b), and 3/1 (Figure 7c) the average particle size of powders decreases from 50 nm to 30 nm and 10 nm,
Figure 6. TEM Micrographs of $\text{Al}_2\text{O}_3$ powder samples; heat treated at (a) 700°C, (b) 900°C and (c) 1100°C.

Figure 7. TEM Micrographs of $\text{Al}_2\text{O}_3$ nanopowders at M/S ratios of: (a) 1/1, (b) 2/1, and (c) 3/1.
We put forward two arguments to interpret the particle size reduction by increasing the M/S ratio: (i) the enhancement of thermal stability of polymeric gel-net, as thermal stability curves imply in Figure 10 and (ii) pore size reduction of 3-D polymeric gel-net as it is observed in Figures 9 and 10.

**CONCLUSION**

Al₂O₃ nanopowder can be successfully prepared by formation of polymeric gel-net at low temperature. Particle growth and polymer network aggregation are inhibited at low temperature. The polymeric gel-net traps metal ions to come into coordination with them and limits their movement thus, inhibits the aggregation of Al₂O₃ nanopowder particles, improves their homogeneity, decreases their agglomeration, and enhances narrow particle size distribution of the produced nanopowders. By changing the monomer to salt ratio, it is possible to tailor the size of Al₂O₃ nanopowder particles due to improved thermal stability and reduced pore size of 3-D polymeric gel-net.

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