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RESEARCH ARTICLE

Synthesis and characterisation of Al_2O_3 nanoparticles as catalyst prepared by polymer co-precipitation method

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Abstract: Alumina (Al_2O_3) is a very interesting material with broad applicability as a support for various catalytically active phases and ceramic materials. Aluminium oxide (Al_2O_3) nanoparticles were synthesized by aluminium chloride hexahydrate as precursor and polyvinylpyrrolydon (PVP) as surfactant and polymer agent. The samples were characterized by high resolution transmission electron microscopy (HRTEM), field effect scanning electron microscopy (FESEM), X-ray diffraction (XRD) and electron dispersive spectroscopy (EDS). XRD pattern exhibited gamma-Al_2O_3 to alpha-Al_2O_3 structural phase transition in the samples. The mean diameter of sphere-like as-prepared nanoparticles was around 26 nm and mean diameter of annealed sample was around 10 nm as estimated by XRD technique and direct HRTEM observation. The surface morphological studies from SEM depicted the size of alumina decreases with increasing annealing temperature. The effect of PVP surfactant on the morphology of the alumina nanoparticles has been investigated. EDS showed peaks of aluminium and oxygen in prepared Al_2O_3.

Keywords: aluminium oxide, nanoparticles, PVP, surfactant, synthesis

1 Introduction

Nowadays, metal oxide nanoparticles have found many uses in engineering, medicine and materials.[1–25] Al_2O_3 nanoparticles are used for a wide range of adsorbent and catalyst applications including the adsorption of catalysts in polyethylene production, in hydrogen peroxide production, as a selective adsorbent for many chemicals including arsenic, fluoride, in sulfur removal from gas streams. The oxides of aluminium materials are widely used in ceramics, refractories and abrasives due to their hardness, chemical inertness, high melting point, non-volatility and resistance to oxidation and corrosion.[26,27] The importance of alumina as catalyst or catalytic support has also been widely recognized for many chemical reactions[28] . The transparency of alumina film and wide range of properties extend its application in optics as well[29] . Aluminium oxide is the amphoteric oxide of aluminium with the chemical formula Al_2O_3 as shown in Figure 1. It is also commonly referred to as alumina or aloxite in the mining, ceramic and materials science communities. There are two forms of anhydrous Al_2O_3, namely, α-Al_2O_3 and γ-Al_2O_3. Alpha-Al_2O_3 is stable at high temperatures and also indefinitely metastable at low temperature. It occurs in nature as the mineral corundum and prepared by heating γ-Al_2O_3 or any hydrous oxide above 1000°C. α-Al_2O_3 is hard and is resistant to hydration and to attack by acids[26] . The density of α-Al_2O_3 is only about 0.595 g/cm3 with a hexagonal close packed, HCP array of anions. Although the anions are topologically arrayed as if they are in closest packing, they are really not contacting with one another. γ-Al_2O_3 is obtained by dehydration of hydrous oxides at low temperatures $\sim$ 450°C. Metastable γ-form aluminas have a cation deficient cubic spinel structure[27] . Calcination at increasing temperatures gives rise to the sequence γ-$Al_2O_3 \rightarrow$ δ-$Al_2O_3 \rightarrow$ θ-$Al_2O_3 \rightarrow$ α-Al_2O_3[28] . Alumina is a low cost material most widely used as a catalyst and catalyst support. In addition, it is also used as the starting material for the preparation of Al_2O_3 based ceramics[29] . Aluminas are extensively used as catalyst supports due to their favorable textural properties and intrinsic acid-base characteristics. In particular, γ-alumina which has a crystalline structure with large surface area is widely used as catalysts, catalysts support and adsorbents such as in automotive and petroleum industries. Alumina sup-

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ports with large surface areas, as well as suitable surface acidic–basic properties can often result in favorable enhancements in the catalytic performances. The catalytic properties of transition aluminas largely depend on their crystalline structures and textural characteristics. Controlling the morphological properties of materials during synthesis is of great importance, as these structural characteristics strongly influence the performance and purpose of the materials. There are several methods that have been used to synthesize the alumina particles in different classes of preparation alumina such as hydrothermal synthesis[30] , plasma synthesis[31] , the sol-gel method[32] , freeze drying of sulfate solutions[33] , controlled hydrolysis of metal alkoxide[34] , decomposition of organo metallic compounds in supercritical fluids and aerosol methods[35] and precipitation method[36] . Usually, conventional aluminas are manufactured by precipitation technique. In this paper, novel nanoporus alumina ceramic are fabricated by using precipitation method. Structural and morphological characterizations of the nanoparticles are carried out by using XRD, HRTEM and FESEM analyses.

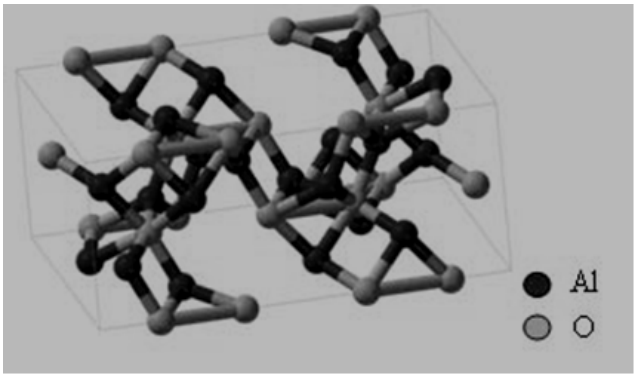

Figure 1. Molecular structure of alumina

2 Experimental detail

The γ-Al_2O_3nanoparticles were synthesized by polymer-mediated synthesis using aluminium chloride hexahydrate as precursor and polyvinylpyrrolydon (PVP) as surfactant. First, 8 g PVP was completely dissolved in 100 mL pure water with stirring at room temperature and 24 g $AlCl_3.6H_2O$ was added to the solution under stirring and synthesis temperature was increased to 90^0C. The Ph=1 was maintained during the synthesis. The product was evaporated for2 hours, cooled to room temperature and finally calcined at 1000^{o}C for 4 hours. All analyses were done for samples without any washing and more purification. The specification of the size, structure and optical properties of the as-synthesis and annealed Al_2O_3 nanoparticles were carried out. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2θ in the range of 4-85^o with type X-Pert Pro MPD, Cu-K_α: λ = 1.54 $\mathring{A}$. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV. The Al and O elemental analysis of the samples was performed by energy dispersive spectroscopy (EDS) type VEGA, 15 kV. All the measurements were carried out at room temperature.

3 Result and discussion

X-ray diffraction (XRD) at 40Kv was used to identify crystalline phases and to estimate the crystalline sizes. Figure 2 shows the X-ray diffraction patterns of the powder before and after heat treatment at 1000^{o}C. As you can see, the broad γ picks were appeared with increasing temperature. A $\gamma \rightarrow$ α-Al_2O_3 phase transformation took place at calcination more than 1000 ^{o}C. α-Al_2O_3 was the only phase present for the powder calcined above 1000^{o}C. The exhibited picks correspond to the (012), (104), (110), (113), (024), (116), (018), (300) and (119) of a rhombohedral structure of α-Al_2O_3 is identified using the standard data. The mean size of the ordered Al_2O_3 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula[37] according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared Al_2O_3 nanoparticles was around 20 nm from this Debye-Sherrer equation.

SEM analysis was used for the morphological study of nanoparticles of Al_2O_3 samples. With increasing temperature the mean particle size decreases from 26 nm to 10 nm because of PVP surfactant.[38–47] Figure 3(a) shows the SEM image of the as-prepared spherical shape Al_2O_3 nanoparticles with mean diameter size of 26 nm and Figure 3(b) shows the SEM image of the annealed Al_2O_3 with mean diameter of 10 nm at 1000^{o}C for 4 hours.

Energy dispersive spectroscopy (EDS) of the Al_2O_3 prepared by wet synthesis is shown in Figure 4 which confirms the existence of Al and O with weight percent. EDS was used to analyze the chemical composition of a material under SEM. EDS shows peaks of aluminium

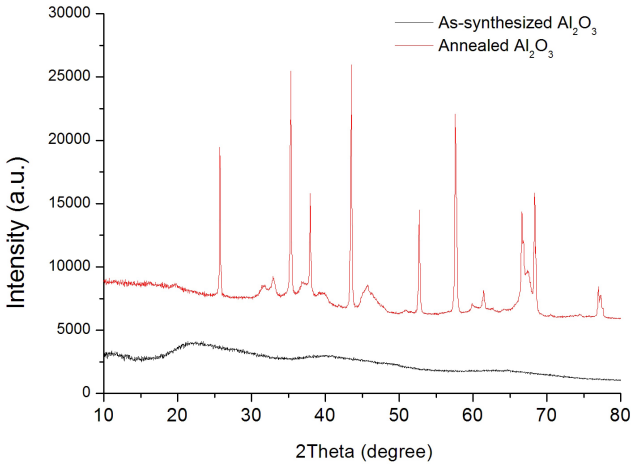

Figure 2. XRD pattern of as-synthesixed and annealed alumina at 1000^{o}C

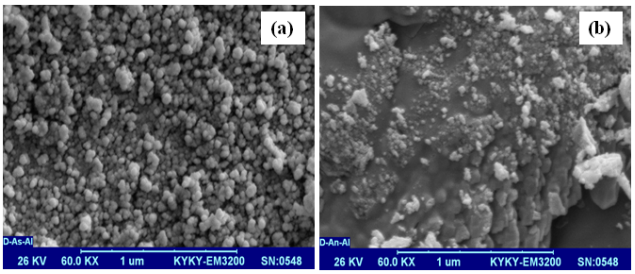

Figure 3. SEM images of the (a) as-prepared (b) annealed Al_2O_3 nanoparticles at 1000^{0}C

and oxygen and indicates fewer impurities in prepared Al_2O_3.

TEM analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. Figure 5 shows the as-synthesized TEM image of sphere-like shaped of Al_2O_3 nanoparticles prepared by precipitation route. The alumina nanoparticles were formed with size in the range of 20-50 nm.

4 Conclusion

Polymer-mediated alumina ceramic nanoparticles were successfully prepared using aluminium chloride and PVP surfactant. XRD spectrum shows rhombohedral (hexagonal) structure of α-Al_2O_3 annealed at 1000^{o}C. The size of alumina decreased from 26 nm to 10 nm with increasing annealing temperature from SEM images observations. TEM image exhibited that the size of as-synthesized Al_2O_3 nanospheres decreased to 20 nm because of PVP surfactant.

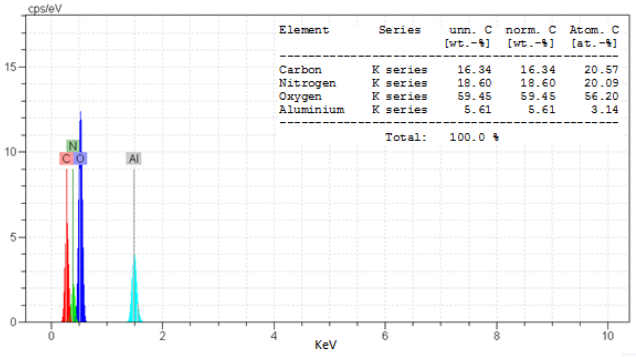

Figure 4. EDS spectra of the as-synthesized Al_2O_3

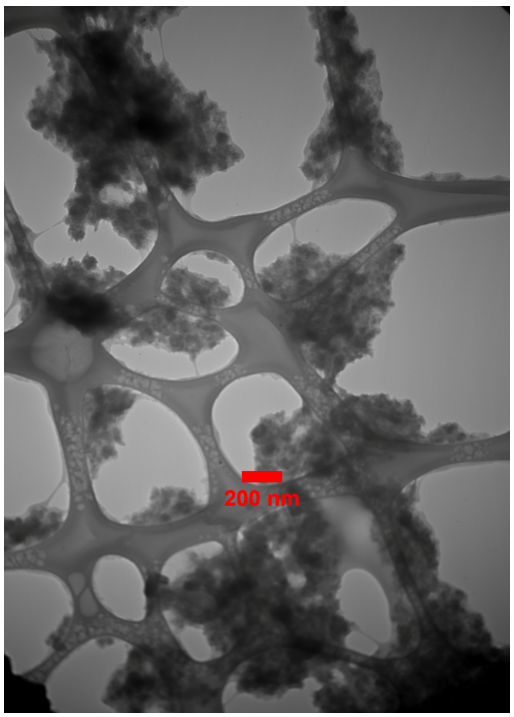

Figure 5. TEM images of the as-prepared Al_2O_3 nanoparticles

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