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New pore structure of nano-alumina (Al₂O₃) prepared by sol gel method

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Nano-porous alumina ceramics were fabricated using a simple and new sol-gel method. Aluminium oxide (Al_2O_3) nanoporous templates were synthesized by iron (III) nitrate 9-hydrate and aluminium isopropoxide as precursor. The samples were characterized by high resolution transmission electron microscopy (HRTEM), field effect scanning electron microscopy (FESEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and UV-Vis spectrophotometer. XRD technique was used to identify α -alumina and γ -alumina. XRD pattern exhibited gamma-Al₂O₃ to alpha- Al₂O₃ structural phase transition in nanoporous. The particle size of spherical as-prepared Al₂O₃ was measured around 20 nm by direct HRTEM observation. The surface morphological studies depicted the samples changed from sphere-like shaped to sponge-like pore structure by increasing annealing temperature. The sharp peaks in FTIR spectrum determined the purity of Al₂O₃ nanoparticles and absorbance peak of UV-Vis spectrum showed the small bandgap energy of 2.61 ev.

Key words: Aluminium oxide, Nanoporous, Phase transition, Synthesis.

Introduction

Porous ceramics have become increasingly important in industry recently due to their numerous applications and utilizations involving different materials like metals, ceramics, polymers, composites, semiconductors and biomaterials [1]. Porosity can affect performance, properties, strength (both flexural and compressive), and density of materials. There has been a long tradition in producing porous materials, mainly for structural applications which include concrete, cements, bricks and refractories [2]. In all applications of porous material, transport through the pore phase is very important which can be achieved if the materials contain more than 10% connected porosity and pore volume. This type of porous ceramics finds key applications as supports for heterogeneous catalysts, membranes for bioreactors, environmental filters for hot flue gases and diesel engine emissions etc [3]. Alumina is used for making porous ceramics because most of the alumina-based ceramics possess relatively high strength along with improved thermal and chemical stability [4]. Porous alumina materials are used in various forms, e.g. as polymeric foams for packaging and porous ceramics for water purification [5]. Because of their inherently brittle nature, pores have been traditionally avoided in ceramic components because pores reduce the material's strength. However, applications of porous ceramics have increased in the last decades, especially for environments where high temperatures, excessive wear and corrosive environment are involved [6]. Such applications include the

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filtration of molten metals, high-temperature thermal insulation, filtration of particulates from diesel engine exhaust gases, support for catalytic reactions, and filtration of hot corrosive gases in various industrial operations [5-7]. Porous ceramics are used in these applications due to the following advantages like high melting point, high corrosion resistance and wear resistance along with the features gained by the replacement of solid material by voids in the material. Such features include low thermal mass, low thermal conductivity, controlled permeability, high surface area, low density, high specific strength, and low dielectric constant. These properties can be modified for each specific application by controlling the composition and microstructure of the porous ceramic [7]. Fluctuations in open and closed porosity, pore size distribution, and pore morphology can have a major effect on a material's properties. These microstructural features are in turn greatly influenced by the processing route used for the production of the porous material. Alumina exists both in the transition or metastable and stable forms. Of the different forms of aluminas $(\alpha, \gamma, \eta, \delta, \kappa, \theta, \gamma, \rho)$, all are in the transition forms except for α -alumina. γ -alumina and α -alumina are the only two types of commercial alumina that are produced. The crystal structure of γ alumina is that of hexagonal plate with large surface area. This made the alumina used being mainly in catalysis and in absorbent applications. There are different crystal structures of α -alumina most of which are rounded shape and hexagonal. The crystals also have small surface area. In recent years, attention has been focused on the preparation of high-purity α -Al2O3 nano-powders by various routes such as gas phase deposition, hydrothermal synthesis [8], plasma synthesis [9], the sol-gel method [10-13], freeze drying of sulfate

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solutions [14], controlled hydrolysis of metal alkoxide [15], decomposition of organo metallic compounds in supercritical fluids and aerosol methods [16] and precipitation method [17]. In this paper, novel nanoporus alumina ceramic are fabricated by using sol-gel method. Structural, optical and surface morphological properties are discussed by XRD, HRTEM, FESEM, FTIR and UV-visible analyses.

Experimental Detail

Aluminium oxide nanoporous were synthesized by a new synthesis route. In the first stage, 18.75 g $Al(NO_3)_3 \cdot 9H_2O$ was completely dissolved in 100 mL pure water with stirring at room temperature. 28 g aluminium isopropoxide was then added to the solution. After 5 min, 5 mL 2-ethilenglycole was added drop by drop to the solution and synthesis temperature was increased to 90 °C. The color of solution changed from orange color to dark brown color. The Ph was adjusted to 3 during the synthesis. During synthesis, the white color of solution changed to yellow color. The product was evaporated for 3 hours, cooled to room temperature and finally calcined at 500 °C and 1000 °C in air for 4 hours. The novelty of this article is that the samples were analyzed without any washing and more purification. The specification of the size, structure and optical properties of the as-synthesis and annealed Al₂O₃ nanoparticles were carried out to specify alumina morphology. 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 ° with type X-Pert Pro MPD, Cu-K_{α}: $\lambda = 1.54$ Å. 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 optical properties of absorption were measured by ultraviolet-visible spectrophotometer (UV-Vis) with optima SP-300 plus, and Fourier transform infrared spectroscopy (FTIR) with WQF 510. All the measurements were carried out at room temperature.

Result and Discussion

X-ray diffraction (XRD) at 40 Kv was used to identify crystalline phases and to estimate the crystalline sizes. Fig. 1 shows the X-ray diffraction patterns of the powder before and after heat treatment. Fig. 1(a) shows the XRD pattern of aluminium oxide before annealing process. Fig. 1(b) shows the XRD pattern of aluminium oxide at 500 °C. As you can see, the broad ã picks were appeared with increasing temperature. Fig. 1(c) shows the annealed samples at temperature 1000 °C for 4 hours. A $\gamma \rightarrow \alpha$ Al₂O₃ phase transformation took place after calcination more than 1000 °C. α -Al₂O₃ was the only phase present for the powder calcined up to temperature



Fig. 1. XRD pattern of alumina (a) as-synthesized (b) at 500 $^{\circ}$ C and (c) at 1000 $^{\circ}$ C.

1000 °C. The exhibited picks correspond to the (012), (104), (110), (113), (024), (116), (018), (300) and (119) of a rhombohedral structure of α -Al₂O₃ is identified using the standard data. The mean size of the ordered Al₂O₃ nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \tag{1}$$

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 Al₂O₃ nanoparticles was around 20 nm from this Debye-Scherer equation.

SEM analysis was used for the morphological study of nanoparticles of Al_2O_3 samples. These analyses show high porosity structure emerged in the samples surface by increasing annealing temperature. Fig. 2(a) shows the SEM image of the as-prepared Al_2O_3 nanoparticles with formation of clusters. Fig. 2(b) shows the SEM image of the annealed sponge-like shaped nanoporus Al_2O_3 at 500 °C for 4 hours. SEM results also indicate that with increasing temperature the morphology of the particles change to the sponge-like shaped. The diameter of Al_2O_3 nanoporous is in the range of 10-300 nm with a wide size distribution.

TEM analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. Fig. 3 shows the assynthesized TEM image of pore structure of Al_2O_3 nanoporus prepared by sol-gel route. The sponge-shape structure of the alumina are formed. The novelty of this work is the formation of pore structure by this sol-gel method.

According to Fig. 4, the infrared spectrum (FTIR) of the synthesized Al_2O_3 nanoparticles was in the range of 400-4000 cm⁻¹ wavenumber which identify the chemical bonds as well as functional groups in the compound. The large broad band at 3464 cm⁻¹ is ascribed to the O-H groups. The absorption picks around 1623 cm⁻¹ is due to the asymmetric bending vibration of C = O and absorption



Fig. 2. SEM images of the (a) as-prepared (b) annealed Al_2O_3 nanoparticles at 500 °C.



Fig. 3. TEM images of the as-prepared Al₂O₃ nanopores.

picks around 1383 and 1353 cm^{-1} are ascribed to C-N group. The broad absorption picks around 612 cm^{-1} is assigned Al-O or Al-O-Al stretching mode.

UV-visible absorption spectral study may be assisted in understanding electronic structure of the optical band gap of the material. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. UV-Vis absorption spectra of asprepared and annealed Al_2O_3 are shown in Fig. 5. For assynthesized Al_2O_3 nanoparticles, the strong absorption band at low wavelength near 475 nm correspond to bandgap energy of 2.61 ev and for annealed Al_2O_3 at



Fig. 4. FTIR spectrum of Al₂O₃ sample.



Fig. 5. UV-Vis absorption spectra of Al₂O₃ nanoparticles.

500 °C and 1000 °C the strong absorption band at low wavelength near 399 nm and 405 nm correspond to 3.10 ev and 3.06 ev respectively. In comparison with UV-visible absorption spectrum of Al_2O_3 nanoparticles reported in the literature [18], band/peak in the spectrum located at around 400-700 nm are observed to be shifted towards lower wavelength side, which clearly shows the blue shift. It indicates the absorption positions depend on the morphologies and sizes of Al_2O_3 . The UV absorption ability of Al_2O_3 is related with band gap energy.

Conclusions

New nanoporous alumina ceramic were successfully prepared using aluminium nitrate and aluminium isopropoxide precursor in presence of 2-ethylenglycole surfactant. XRD spectrum showed rhombohedral (hexagonal) structure of α -Al₂O₃ annealed at 1000 °C. From SEM images, with increasing temperature the morphology of the particles changed from sphere-like shaped to sponge-like shaped. TEM image exhibited the as-synthesized Al₂O₃ nanoporous prepared by solgel route. FTIR measurement showed the presence of

Al-O stretching mode of Al_2O_3 . The UV-vis absorption indicated the small band gap of 2.61 eV for the asprepared samples.

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