

Full Length Research Paper

Synthesis and Characterization of Cr-Doped Al_2O_3 Nanoparticles Prepared Via Aqueous Combustion Method

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Chromium-doped Alumina was synthesized via combustion technique. Nanoparticles were produced from aluminum nitrate, ammonium dichromate, and sucrose. Silver nitrate was used as catalyst. The use of sucrose ($C_{12}H_{22}O_{11}$) as dispersion agent and ammonium dichromate both as fuel and a doping agent source are new techniques in the synthesis of Cr-doped Al_2O_3 nanoparticles. The heat-treated powders were characterized by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Heat treatment of the nanoparticles was performed at temperatures of 900 °C, 1000 °C, and 1100 °C, which resulted in the formation of porous agglomerated chromium-doped alumina nanoparticles. Chromium-doped alumina with an average crystalline size of 35 nm was successfully synthesized via combustion technique with sucrose as fuel.

Key words: Chromium Doped Alumina; Combustion Synthesis; Heat Treatment; Nanoparticles.

1. INTRODUCTION

The combustion synthesis method was first reported in 1993 by Holt et al (Holt *et al.*, 1993). It is a safe, simple, and the rapid fabrication process that saves both time and energy (Edrissi et al., 2007; Deraz et al., 2009; Naskar, 2010). This quick and simple method can be used to synthesize highly pure, homogeneous, and crystalline oxide ceramic powders, including ultrafine nanoparticles with broad particle size distributions (Mukasyan et al., 2007; Epherre et al., 2011; Timmaji et al., 2011; Wang et al., 2011). Combustion synthesis is based on thermochemical concepts in explosives theory. The method is successfully performed because the components are thoroughly blended together with the use of a suitable fuel or a complexing agent (e.g., urea, glycine, and citric acid) in an aqueous environment. Exothermic redox reaction occurs between the fuel and the oxidizer (nitrates) (Toniolo et al., 2005; Toniolo et al., 2007; Deraz et al., 2009; Ahmed et al., 2010). The main parameters that control the reaction include type of the main fuel, the ratio of the fuels, fuel to oxidizer ratio, pH of the solution, amount of excess oxidizer, and rate of calcination. A good fuel neither react violently nor produces toxic

gases, and it must act as a complexing agent for metal cations (De Andrade et al., 2006; Lima et al., 2006; Edrissi et al., 2008). Alumina nanoparticles are very important materials because of their technological applications and interesting properties (Zhai et al., 2006; Naskar, 2010). Alumina, $\alpha-Al_2O_3$ (corundum), has been studied widely because of its widespread applications in different fields. Cr-doped Al_2O_3 has been proposed in laser application in different studies (Hirai et al., 1987; Makhov et al., 2008; Mi et al., 2009; Xiaoyun et al., 2009).

Dopants confer new properties to Al_2O_3 nanoparticles by changing the mass transport properties of Al_2O_3 (Wang et al., 2008). Mi et al. were the first to prepare Cr-doped Al_2O_3 nanoparticles via low-temperature combustion synthesis using glucose as dispersion agent. They found that Al_2O_3 crystals were formed when the calcination temperature was increased to 1000 °C and 1100 °C. Moreover, the lattice positions of Al^{3+} ions in the Al_2O_3 crystals were occupied by Cr^{3+} ions, which induced

Cr^{3+} luminescence. Luminescent intensity did not increase further when the temperature was higher than 1100 °C. This result indicated that the concentration of the luminescent centers in the

Al_2O_3 crystals was saturated (Mi et al., 2009). When the ratio of fuel/oxidizer in the precursor materials was fixed, and the reaction occurred under the same conditions, the heat of combustion remained constant (Cordier et al., 2006; Kishan et al., 2010).

In this study, sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) was used as a dispersing agent. Ammonium dichromate is used instead of common chromium nitrate, which is hygroscopic and quite expensive. Ammonium dichromate functioned both as fuel and chromium source. The effectiveness of different heat treatment temperatures on the properties of the synthesized α -alumina powders was investigated. The synthesized nanopowders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA), and energy-dispersive X-ray spectroscopy (EDX).

2. METHODOLOGY

The synthesis of the Cr-doped Al_2O_3 nanoparticles was performed at a low temperature via aqueous combustion method. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used as Al source. Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) was used as a dispersion agent (carbon source). About 14.7 g of aluminum nitrate and 12.86 g of sucrose were separately mixed with deionized water. The two solutions were mixed together to obtain a stable suspension. About 0.1 g of ammonium dichromate (as fuel and Cr source) was then dissolved in the mixture.

A hot plate was used to evaporate the excess water, and a gelatinous mixture was formed. The as-prepared powders were then subjected to three thermal treatments (900 °C, 1000 °C, and 1100 °C) in flowing air. The powders had a dwell time of 5 h and were cooled down to room temperature. The heating rate was 5 °C/min. The chromium-doped alumina powders were ground with an agate pestle and mortar to break the agglomerates.

All nanoparticles were characterized by XRD with Cu-K α radiation (Bruker D4 Endeavor). XRD was performed to detect and identify the phases in the powders. DTA was performed in flowing air (heated from 25 °C to 1100 °C) with a heating rate of 10 °C/min. Finally, all calcined powders were characterized by SEM.

3. RESULTS AND DISCUSSION

The XRD patterns of the powders calcined at 900 °C, 1000 °C, and 1100 °C for 5 h are shown in Figure 1, α - Al_2O_3 phase was found in all nanoparticles calcined in three different temperatures.

The average crystalline size was calculated via peak broadening method. The full width at half maximum (FWHM) of the peak was measured. The average nanoparticles sizes were determined according to Scherrer formula: (1)

$$D = \frac{0.9\lambda}{(\cos\theta)\sqrt{B^2 - b^2}}$$

Where D is the average nanoparticle size, λ the wavelength of the radiation, θ is Bragg's angle and B and b are the FWHMs measured for the sample and standard, respectively. Terms B and 2θ were obtained from XRD pattern. The crystal diameters of the powders calcined at 1100 °C were calculated on each diffraction peak also via peak broadening method. The average particle size of the nanoparticles was about 35 nm.

As shown in Figure 1, gamma-aluminum oxide was detected in the Cr-doped alumina sintered at 900 °C, whereas aluminum chromium oxide was observed in the Cr-doped alumina sintered at 1000 °C. At a calcination temperature of 1000 °C, the Cr ions reacted with alumina to form an aluminum chromium oxide, which has a formula of $\text{Al}_{1.98}\text{Cr}_{0.02}\text{O}_3$. In addition, the result indicated that the aluminum chromium oxide was observed in the Cr-doped alumina calcined at 1100 °C, which is similar to the Cr-doped alumina calcined at 1000 °C. The broadening in the diffracted peaks was distinct because of the reduction in particle size (Salah et al., 2011). There is a phase transition between the γ - and α -alumina structures around 1000–1200 °C. The chemisorbed water at the sample surface will be completely eliminated at these temperatures (Ardizzone et al., 2000).

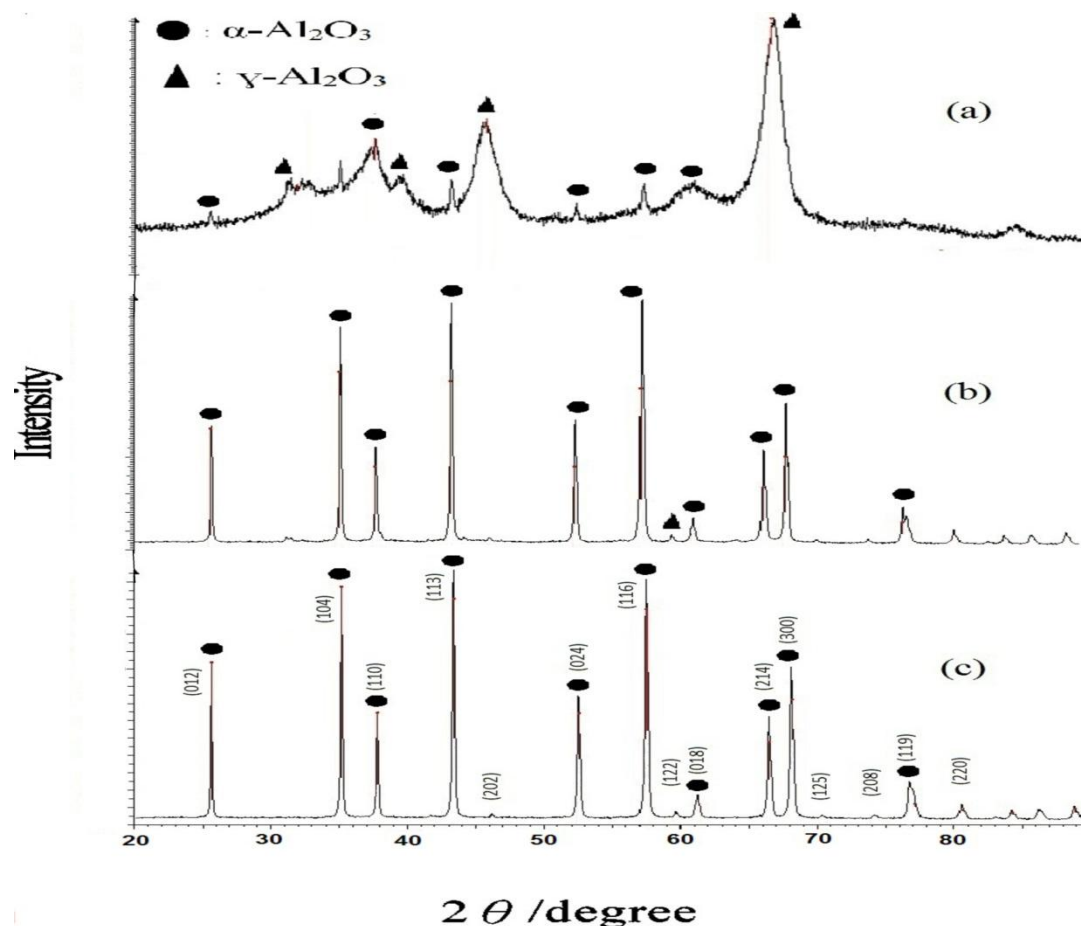


Fig. 1: XRD pattern of Chromium doped Alumina ($\text{Al}_{1.98}\text{Cr}_{0.02}\text{O}_3$) at a) 900 °C b) 1000 °C c) 1100 °C ; $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ are depicted in this figure.

DTA analyses were then performed on the chromium-doped alumina nanoparticles. The chromium-doped alumina calcined at 1100 °C was used to investigate phase transformations. In Figure 2, the DTA curve shows an exothermic peak at 949 °C. This result indicated that a thermodynamically stable crystallographic alpha alumina can be found at about 1100 °C.

The FESEM micrographs of the powders calcined at 900 °C, 1000 °C, and 1100 °C for 5 h are shown in Figure 3. The synthesized products were agglomerated and foamy. The formation of voids in their structures was caused by the evolution of high amounts of gases during combustion and heat treatment. The size of the void in the $\text{Al}_2\text{O}_3\text{:Fe}$ powders increased as the heat treatment temperature was increased. This result was due to the increase in the amount of gas in the structure. As shown in Figure 3 (a, b, and c), the agglomerates breaking and gases exiting made the

material porous. Toniolo et al.⁹ and Kishan et al.²¹ also reported that the void size increased as the amount of gases increased.

The FESEM micrograph of the chromium-doped alumina calcined at 1100 °C under a magnification of 50 kX is shown in Figure 3 (c). A growth of particles was observed on the surface because sintering occurred during calcination at 1100 °C, which initiated the diffusion process. Therefore, the particles melted on the surface. The mixture in the compound could be estimated with EDX. As shown in Figure 4, the distribution of Al, O, and Cr was homogenous. The atomic content of Cr^{3+} ions was 0.81%, and the mass content was 1.89%. This result indicated that the content of Cr^{3+} ions in the samples was close to the calculated value. The EDX curve also confirmed that no carbon was found in the sample, and all carbon evaporated during the heating process at a temperature of 1100 °C.

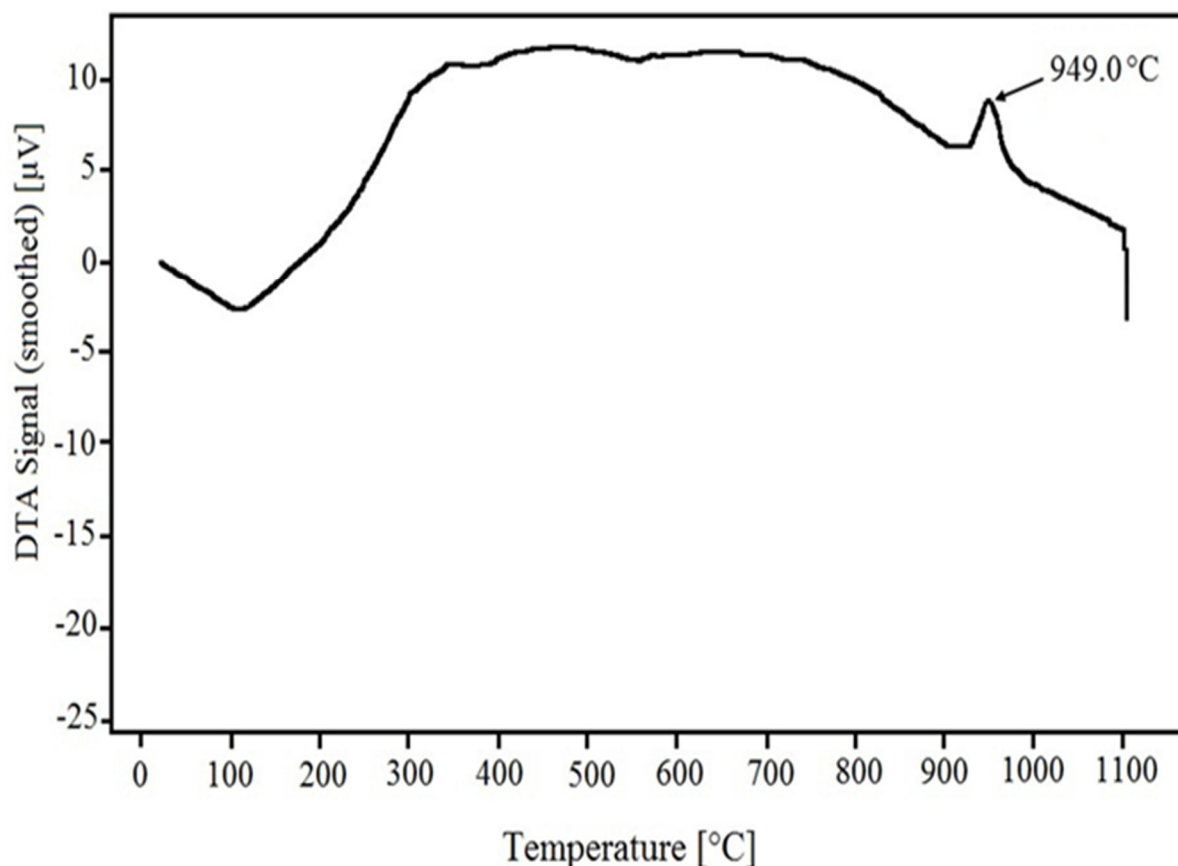


Fig. 2: DTA curve for Chromium doped Alumina sintered at 1100°C

The infrared spectrum of the synthesized Cr-doped alumina nanoparticles calcined at 1100 °C is shown in Figure 5. Three absorption peaks at 443, 587, and 827 cm^{-1} were observed. These peaks correspond to the Al-O peaks of $\alpha-Al_2O_3$.¹⁵ Thus, Al_2O_3 nanoparticles with significant Al-O peaks could be prepared by calcination at 1100 °C. This result was confirmed using the XRD results.

4. COCLUSION

In this study, Cr-doped alumina nanoparticles with an average crystalline size (35 nm) were

successfully synthesized using sucrose as fuel. The results show that combustion synthesis is an easy and cheap method to synthesize Cr-doped alumina nanoparticles compared with other conventional methods. The properties of the final products depend on the combined effects of the amount of gas generated and heat. Crystalline growth and agglomeration occurred at higher calcination temperatures. Furthermore, no reaction occurred at a calcination temperature of 900 °C. The onset reaction between Cr ions and alumina occurred at 1000 °C to form aluminum chromium oxides.

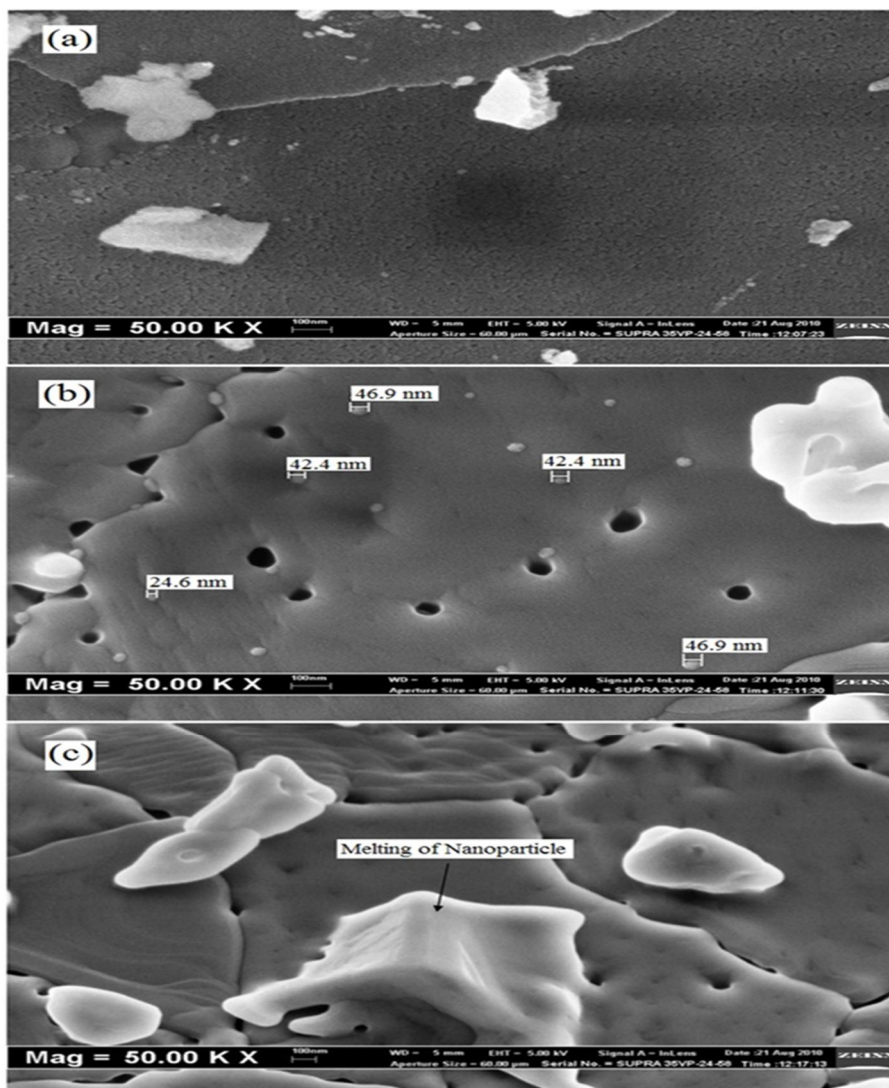


Fig. 3: FESEM micrograph of Chromium doped Alumina calcined at a) 900 °C b) 1000 °C c) 1100 °C

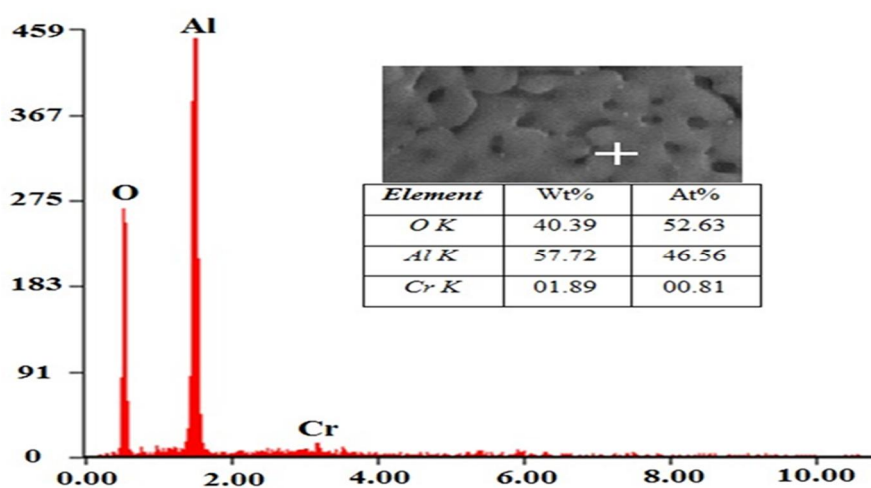


Fig. 4: EDX result of Chromium doped Alumina calcined at 1100°C

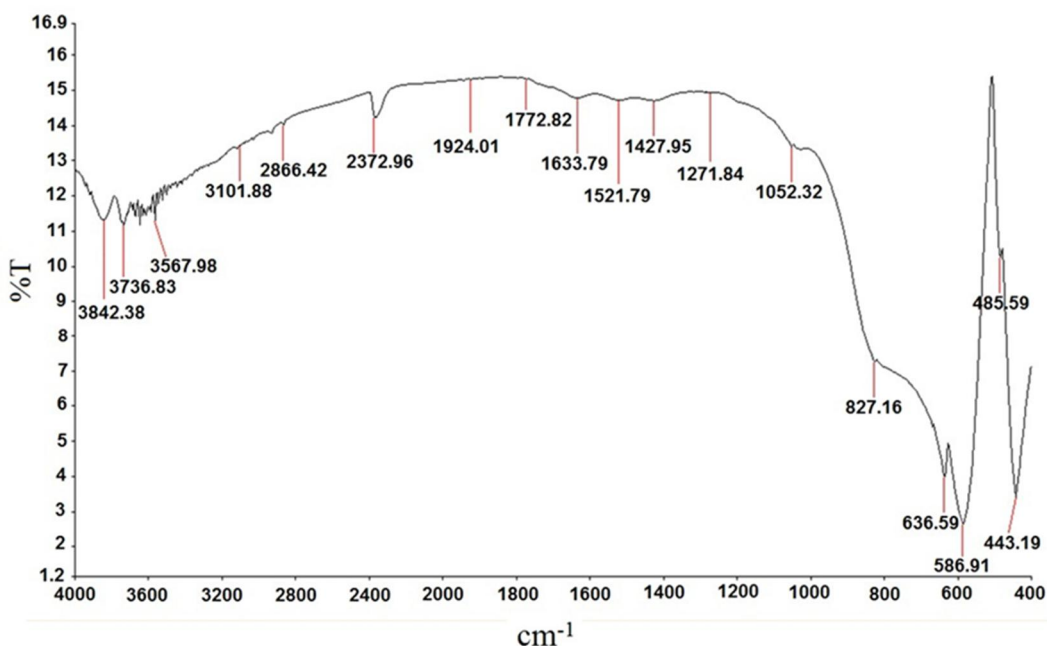


Fig. 5: Fourier Transform Infrared Spectrum of Cr-doped Alumina nanoparticles calcined at 1100°C

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