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Alumina phase transformation behavior on titania-doped nano α-alumina by a solid liquid process

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Alumina phase transformation behavior on titania-doped nano α-Al_2O_3 powder by a solid liquid process was investigated under various conditions, such as different solvent concentrations and calcining temperatures. Three batches of the precursor powders were calcined at three different temperatures of 600 °C, 750 °C and 900 °C for 5 h and a final product of titania-doped nano α-Al_2O_3 powder was obtained. The product has been identified by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The XRD results show that the alumina phases of the powders were determined to be γ-Al_2O_3 and α-Al_2O_3. The optimum calcination temperature of the precursor powder for crystallization of nano α-Al_2O_3 was found to be 900 °C for 5 h. A higher concentration of solvent used for the sample preparation leads to the formation of a uniform and very smooth particle morphology, and smaller particle grains. The TEM images indicate that the average size of α-Al_2O_3 grains was ≤ 50 nm and larger grains of TiO_2 with 50-250 nm sizes.

Key words: Alumina, Phase transformation, Titania, Doping, Calcining temperature, Solvent concentration.

Introduction

Alumina (Al_2O_3) shows excellent physical and chemical properties, such as the highest strength among oxides, excellent abrasion resistance, heat resistance, high dielectric strength at high voltage, and high resistance to chemical attack [1]. Therefore, these characteristics have led to the wide use of Al_2O_3 in many applications as presented in Table 1.

The applications demand a particular nano-sized powder, so that nano-sized alumina powders will be indispensable for the manufacturing of various advanced materials and devices in the future [3]. The synthesis and control of materials in nanometre dimensions can access new material properties and device characteristics in unprecedented ways. Controlled structures, large interfaces, power density and other unique characteristics are examples of the superiority of nano-material properties, so that they can access new and improved properties and functionalities [4-6].

Table 1. Alumina functional ceramic and its applications [1, 2]

No.	Function	Application
1	Electronic function	IC-Board, Resistor substrates, Electron tube, and others
2	Optical function	High pressure sodium lamp non-volatile memory window
3	Chemical functions	Temperature sensor, catalytic converter, organic catalyst
4	Mechanical functions	Mechanical seals, ceramic liner
5	Biological function	Artificial teeth, artificial joints, artificial bones

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Some methods have been used to synthesize and to prepare nano and submicrometre alumina via a chemical route [7, 8]. Sarikaya and Akinc [9], prepared alumina microshells by calcining the precursor with an emulsion evaporation technique; on the other hand, Lin and Wen [10], used a chemical precipitation method to prepare an alumina precursor via an emulsified boehmite gel with oleic acid. Yu-Chen Lee, *et al*. [3], prepared nanoalumina powder by calcining an emulsion precursor derived from aqueous $Al(NO_3)_3$ solution that was mixed with oleic acid. Bastomi *et al.* [11], synthesized submicrometre α-Al_2O_3 using the precursor process method. Pati *et al.* [12], prepared nanocrystalline α-Al_2O_3 powder at 1150 °C for 2 h by the pyrolysis of a precursor material prepared by evaporation of an aqueous solution of sucrose with polyvinyl alcohol and a metal nitrate. Peng *et al*. [13], synthesized α-Al_2O_3 by combustion synthesis using glycine as a fuel and a nitrate as an oxidizer. Ding *et al.* [14], synthesized α-Al_2O_3 at 1250 °C via the reaction: $2AlCl_3 + 3CaO \rightarrow Al_2O_3 + 3CaCl_2$. Pati *et al.* [15], prepared nanocrystalline α-Al_2O_3 powder at 1025 °C by the pyrolysis of a complex compound of aluminum with triethanolamine (TEA) and the final material had particles with a 25 nm in size.

Most of the nano α-Al_2O_3 preparation methods mentioned are conducted at a relatively high temperature above

1000 °C. An alternative economical technique to reduce the α-Al_2O_3 crystallization temperature is by incorporating appropriate low-temperature crystallization additives such as titania [16, 17]. Therefore, 3% wt ultra fine titania powders were used as a dopant in this nano α-Al_2O_3 preparation.

The objective of this study is to evaluate the alumina phase transformation behavior on titania-doped nano a-Al_2O_3 powder by a solid liquid process under various conditions, such as different solvent concentrations and calcining temperatures. The products were evaluated by XRD analysis, SEM, and TEM. The scope of this study is limited, and it seems further experimentation and evaluation are necessary for a full understanding.

Experimental Procedures

Materials used in this research were $Al(NO_3)_3 \cdot 9H_2O$, ultra fine titania powders, 5 M ammonia solution, and technical grade sucrose. All materials were obtained from Merck Inc. Germany; whereas instruments used were a pot mill, a Heraus electrical furnace, a Phillips X-Ray PANalytical, a JEOL JSM-35C SEM, and a JEOL TEM.

Methods

Preparation of titania-doped nano α-Al_2O_3

TiO_2-doped nano α-Al_2O_3 precursors were obtained by mixing 3% (w/w) ultra fine TiO_2 powders and 97% (w/w) aluminum nitrate in three different solvent concentrations (100 ml (A), 150 ml (B), 200 ml (C)) and milling the mixtures for 90 minutes. About 10% (w/w) sucrose was added appropriately into the mixture and milled until evenly mixed with the mixture. Five molar ammonia solution was added appropriately to the mixture, milled constantly to give an $Al(OH)_3$ gel, and heated slowly until a brownish concentrated gel was formed. The gel was then dried in an oven at 200 °C to produce black charcoal precursors. The precursors were milled in a non polar solvent for 24 hours and successfully calcined at 600 °C, 750 °C, and 900 °C in an electric furnace. The final products were identified using XRD, SEM, and TEM.

Characterization of titania-doped nano α-Al_2O_3

The crystalline phase and average crystallite size of calcined powder were determined by X-Ray Powder Diffraction (XRD Merck Phillips PW 3710 mpd control with a Cu target). A scanning electron microscope (SEM, JEOL JSM-35C) and transmission electron microscope (TEM, JEOL) studies were performed to verify the morphology and the grain sizes.

Results and Discussion

Alumina phase transformation behavior of titania-doped nano α-Al_2O_3 based on XRD analysis

Figs. 1-3 show typical XRD patterns of titania-doped nano α-Al_2O_3 calcined at the temperatures of 600 °C, 750 °C, and 900 °C, respectively. The XRD analysis

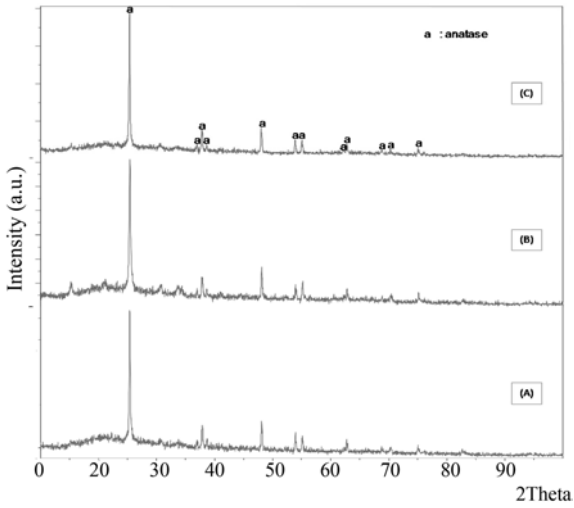

Fig. 1. XRD diffraction patterns of titania-doped nano alumina precursor for all batches namely A (100 ml of solvent), B (150 ml of solvent), C (200 ml of solvent), respectively at 600 °C.

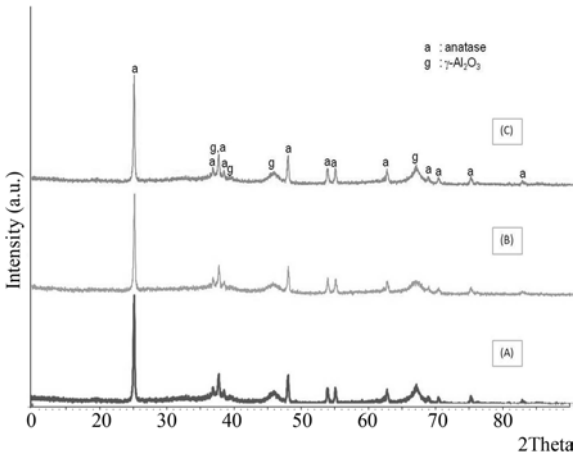

Fig. 2. XRD diffraction patterns of titania-doped nano alumina precursor for all batches namely A (100 ml of solvent), B (150 ml of solvent), C (200 ml of solvent), respectively at 750 °C.

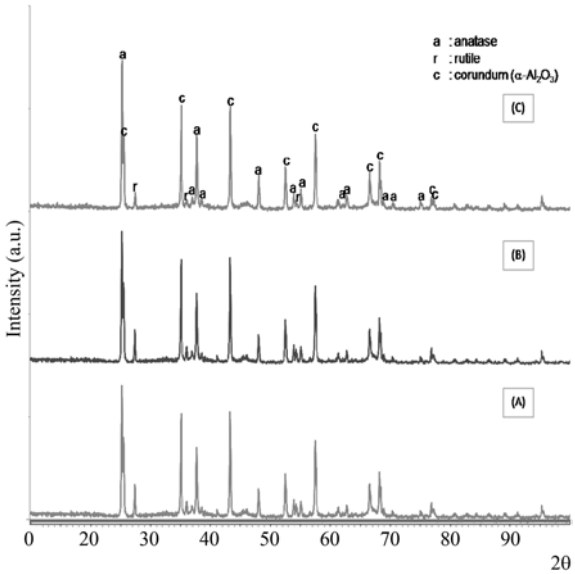

Fig. 3. XRD diffraction patterns of titania-doped nano alumina precursor for all batches namely A (100 ml of solvent), B (150 ml of solvent), C (200 ml of solvent), respectively at 900 °C.

indicates that at a temperature of 600 °C, anatase is the only phase present in all the samples whereas no phases of any alumina transition have been identified in this temperature. At the higher temperature, at 750 °C, the predominant phases in all the samples are anatase, and γ-Al_2O_3; and at 900 °C, the phases identified in all the samples are slightly different than at a temperature of 750 °C, where α-Al_2O_3, the most stable alumina phase has been identified with the strong peaks of α-Al_2O_3 main crystal planes at diffraction angles of 25.581° [012], 35.156 [104], 43.363 [113], and 57.511 [116]. Therefore, the crystal phase transformation of alumina occurred was γ-Al_2O_3 (cubic) $\rightarrow$ α-alumina (trigonal). According to the result of the XRD analysis, the addition of 3% wt ultra fine titania powder as a dopant on this nano α-Al_2O_3 preparation has reduced the crystallization temperature of α-Al_2O_3 from above 1000 °C to 900 °C because the normal crystallization temperature of α-Al_2O_3 is above 1000 °C [18]. However, the effect of solvent concentrations is not significantly shown in the alumina phase transformation behavior of titania-doped nano α-Al_2O_3.

Crystallite sizes of α-Al_2O_3 based on XRD analysis

Based on the α-Al_2O_3 peaks of XRD patterns from Figs. 1, 2 and 3, the crystallite sizes of α-Al_2O_3 for all the samples can be calculated using the Scherrer equation [3, 19]:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

where D is the crystallite size, K is a shape factor with a value of 0.9-1.4, λ is the wavelength of the X-rays (1.54056 Å), θ is Bragg's angle and β is the value of the *full width at half maximam* (radian). According to the Scherrer equation, the crystallite sizes of three alumina samples were calculated and are presented in Table 2.

Effect of solvent concentrations to morphology and particle size characteristic

According to the SEM micrographs as presented in Fig. 4, the particle sizes of the TiO_2-doped nano α-Al_2O_3 were found to be 50-275 nm at 900 °C. The brighter particles in the SEM micrographs show the titania present on the

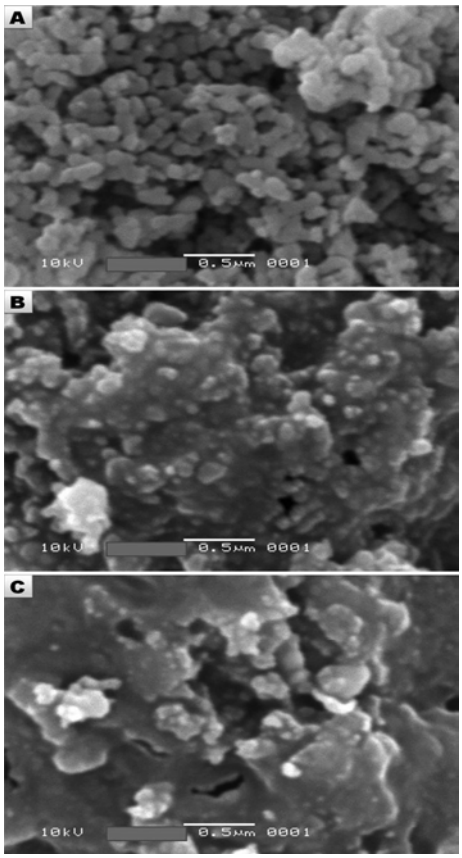

Fig. 4. Scanning electron microscope micrographs of TiO_2-doped nano α-Al_2O_3 powders calcined at 900 °C for 5 hours for all batches namely A (100 ml of solvent), B (150 ml of solvent), C (200 ml of solvent), respectively.

powders of TiO_2-doped nano α-Al_2O_3. The particle sizes of the powders are sensitive to the solvent concentrations in the feedstock for preparation. The effect of the solvent concentration is significantly shown in the particle morphology of titania-doped nano α-Al_2O_3. This is shown by the different SEM micrographs for each sample. A SEM micrograph of a sample using 100 ml of solvent (Fig. 4(A)) shows a homogenous particle morphology and larger grain size of particles, whereas a SEM micrograph of a sample using 150 ml of solvent (Fig. 4(B)) shows a homogenous and smooth particle morphology, and a

Table 2. The XRD Identification and Average Crystallite Size of α-Al_2O_3 by the Scherrer Method

Samples	Phases			Average Crystallite Size of α-Al_2O_3 (nm)	PDF 2 No.
	600 °C	750 °C	900 °C		
A	Tetragonal Anatase (TiO_2)	Tetragonal Anatase (TiO_2) Cubic γ-Al_2O_3	Tetragonal Anatase (TiO_2) Tetragonal Rutile (TiO_2) Trigonal α-Al_2O_3	50.5	21-1272 (Anatase) 75-1754 (Rutile) 10-0425 (γ-Al_2O_3) 83-2080 (α-Al_2O_3)
B	Tetragonal Anatase (TiO_2)	Tetragonal Anatase (TiO_2) Cubic γ-Al_2O_3	Tetragonal Anatase (TiO_2) Tetragonal Rutile (TiO_2) Trigonal α-Al_2O_3	56.5	
C	Tetragonal Anatase (TiO_2)	Tetragonal Anatase (TiO_2) Cubic γ-Al_2O_3	Tetragonal Anatase (TiO_2) Tetragonal Rutile (TiO_2) Trigonal α-Al_2O_3	53.1	

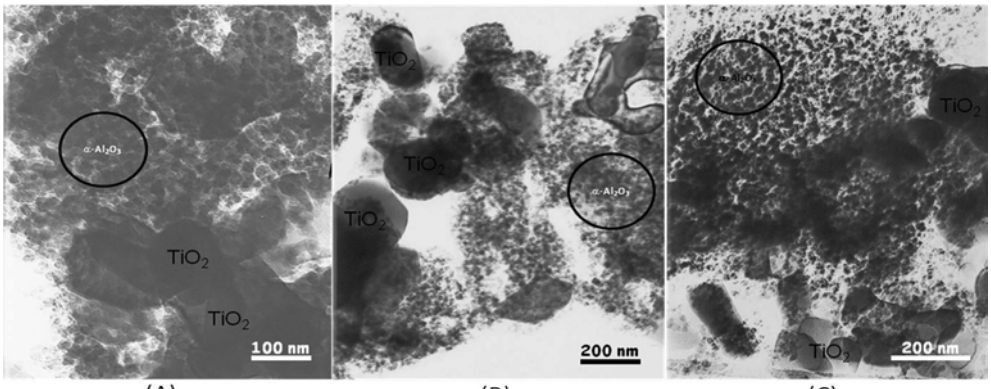

Fig. 5. TEM images of TiO_2-doped nano α-Al_2O_3 powders calcined at 900 °C for 5 hours for all batches namely A (100 ml of solvent), B (150 ml of solvent), C (200 ml of solvent), respectively.

small grain size of particles. Fig. 4(C) shows a SEM micrograph of a sample using 200 ml of solvent in the preparation process, showing a uniform and very smooth particle morphology, and a smaller grain size of particles. The higher concentration of solvent leads to the formation of quite unsaturated Al^{3+} ions in the solution, thus the binding distance among them or the particle density will be wider; so that as the calcined temperature increases, the contact among the nucleated α-Al_2O_3 grains will occur slowly, leading to the formation of smaller particles.

Typical TEM images of TiO_2-doped nano α-Al_2O_3 powders for all the samples at 900 °C for 5 h are given in Fig. 5(A)-(C). The images represent small grains of α-Al_2O_3 had an average size $\leq$ 50 nm and larger grains of TiO_2 with 50-250 nm sizes.

Conclusions

The optimum calcination temperature of the precursor powder for crystallization of nano α-Al_2O_3 on a titania-doped nano α-Al_2O_3 preparation by a solid liquid process was found to be 900 °C for 5 h.

The effect of solvent concentration is significantly shown in the particle morphology of titania-doped nano α-Al_2O_3 powder. A higher concentration of solvent used in the sample preparation leads to the formation of a uniform and very smooth particle morphology, and a smaller grain size of particles as given by SEM.

The TEM results show small grains of α-Al_2O_3 had an average size $\leq$ 50 nm and larger grains of TiO_2 with 50-250 nm sizes.

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