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Structural Transitions in Alumina Nanoparticles by Heat Treatment

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Abstract. γ-alumina nanoparticles were annealed sequentially at 800°C, 950°C and 1100°C and structural transitions as a function of heat treatment were studied by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS–NMR) methods.. XRD studies found that γ-Al_2O_3 is stable upto a temperature of at least 950°C and transforms to the thermodynamically stable α-phase after annealing at 1100°C. MAS–NMR revealed that γ–alumina contains AlO_4 and AlO_6 structural units in the ratio 1: 2, while α–phase contains only AlO_6 units. DSC confirmed that γ→ α transition initiates at 1060°C.

Keywords: Alumina nanoparticles, XRD, DSC, MAS–NMR.
PACS: 61.46.Df, 61.05.cp, 65.60.+a, 76.60.-k

INTRODUCTION

Aluminum oxide commonly known as alumina (Al_2O_3), is one of the most interesting ceramic materials both for its numerous applications and excellent physical properties [1]. Alumina exists in a several metastable polymorphs, the so-called transition alumina (such as γ, δ, θ, χ and κ) as well as its thermodynamically stable α-Al_2O_3 phase [2].

The metastable alumina polymorphs show structural transitions upon heating, with transformation sequence irreversibly ending in the α-phase at temperatures in the range of 1100 to 1200°C. The α-alumina transformation temperature is however, relatively high, and it is possible to form many of the metastable phases at synthesis conditions between room temperature and 1000 °C [3].

The metastable phases such as γ-alumina find use in numerous applications. The low surface energy and therefore the inherent high surface areas of γ-alumina have made it useful for catalysis applications. Furthermore, thin films of amorphous alumina have proved to be very useful as optical coatings and as a dielectric layers in microelectronics devices [4].

In this work, we report the study of phase transformations in γ–alumina nanoparticles. Nanoparticles were annealed at three temperatures and characterized by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and ^{27}Al MAS-NMR.

EXPERIMENTAL METHODS

γ-alumina nanopowder (Aldrich Inc., 99.9% particle size <50 nm) weighing 2 g was taken as a starting material. The powder was ground in an agate motor-pestle and subjected to heat treatment in the temperature range of 800-1100°C. X-ray diffraction and ^{27}Al MAS-NMR were performed after each annealing treatment to study the phase transformation properties. The initial sample (labelled as γ-Alumina-RT) was analysed by DSC to determine the temperature of structural transitions. Details of heat treatment of nanoparticles are given in Table 1.

X-ray diffraction studies were performed on Bruker D8 Focus X-ray diffractometer with Cu K_α radiation (λ =1.54056 Å) in the 2θ range of 10°-70°. Thermal studies were performed on the initial γ-Al_2O_3 sample on SETARAM SETSYS Evolution-1750 system in the temperature range of 200-1500°C at a heating rate of 10°C m^{-1} and airflow rate of 20 ml m^{-1} in Pt pans. ^{27}Al

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MAS-NMR spectra were collected with a 3.2 mm Varian MAS probe at room temperature on a Varian NMR spectrometer operating at 16.4 T corresponding to the Larmor frequency of 182.42 MHz for ^{27}Al nuclei. Chemical shifts was referenced to 1 M $Al(NO_3)_3$ (aq).

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of alumina nanoparticles annealed upto a maximum temperature of 1100°C.

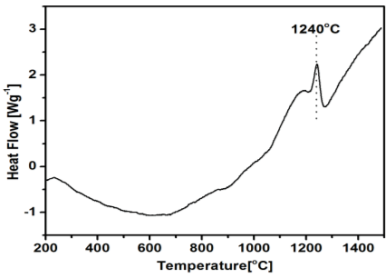

FIGURE 2. DSC thermogram of γ-Al_2O_3-RT sample.

TABLE 1: Details of annealing treatment of γ-Al_2O_3 powder and fraction of $^{[4]}Al$, $^{[5]}Al$ and $^{[6]}Al$ species as measured by ^{27}Al MAS-NMR.

Sample Code	Annealing Temperature [°C]	$^{[4]}Al$	$^{[5]}Al$	$^{[6]}Al$
γ–Alumina-RT	-	0.330	0.022	0.646
γ–Alumina–800	800	0.343	0.020	0.635
γ–Alumina–950	950	0.357	0.017	0.625
γ–Alumina–1100	1100	0	0.022	0.978

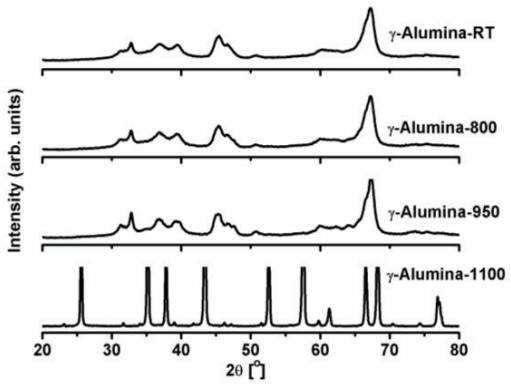

FIGURE 1. XRD patterns of initial γ–alumina powder (Sample Code: γ-Alumina-RT) and annealed samples.

XRD pattern of the initial Al_2O_3 powder (γ-Alumina-RT) shows two prominent but broad peaks centered at 45.9° and 67.1° corresponding to γ-alumina [5]. XRD patterns of the samples annealed at 800°C and at 950°C, do not show any significant changes and match with those of the initial γ-Al_2O_3 sample (Figure 1), whereas after annealing at 1100°C, sharp peaks are detected due to its transformation to α-Al_2O_3 [6]. Peak positions in the XRD patterns of all samples are presented in Table 2.

DSC studies confirm that transition of γ-alumina into α-phase occurs at 1240°C with onset point of 1064°C. Hence the transformation to α-phase after heat treatment at 1100°C can be understood [Figure 2].

^{27}Al MAS-NMR spectra are shown in Figure 3. The spectra consist of four peaks centered at ~8, 14, 35 and 70 ppm. Peaks at ~8 ppm and ~14 ppm are due to AlO_6 structural units, AlO_5 and AlO_4 produce resonance peaks at ~35 and 70 ppm respectively [7]. The initial sample (γ–Alumina-RT) has two peaks at ~8 and 70 ppm due to γ–phase, that is normally formed by thermal decomposition of aluminum oxy-hydroxide at 400°C [7]. The fractions of tetra, penta and hexa coordinated Al-O units are determined from the tatios of areas under the resonance peaks and their values are given in table 1.

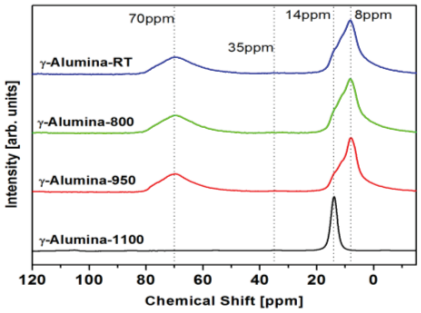

FIGURE 3. ^{27}Al MAS-NMR spectra of γ–alumina powder heat-treated upto 1100°C.

Table 2: XRD peak positions of γ–Alumina-RT and the sample annealed at 1100°C. Corresponding crystalline phases are also listed

Sample no.	2θ [°]	Crystalline phases
γ-Alumina-RT	32.7	γ
	36.8	γ
	39.5	γ
	45.4	γ
	67.2	γ
	84.6	γ
	100.7	
γ-Alumina-1100	25.6	α
	35.2	α
	37.8	α
	43.4	α
	52.6	α
	57.5	α
	61.3	α
	66.5	α
	68.2	α
	76.9	α
	77.1	α
	80.7	α

From the data given in table 1, it can be concluded that the initial γ-Al_2O_3 nanoparticles contain 33% of AlO_4 units and 66% of six-coordinated, AlO_6 units. On annealing γ-Al_2O_3 powder upto 950°C, no significant changes take place in the concentration of short-range structural units. After annealing at 1100°C, the sample contains ~98% of AlO_6 units. Hence, the initial γ-Al_2O_3 powder transforms almost completely to the rhombohedral α-phase of Al_2O_3 with heat treatment at 1100°C for 6 h.

CONCLUSIONS

γ–Alumina nanoparticles were heated in the temperature range of 800-1100°C. Phase transitions after heat treatment at 800, 950 and 1100°C are studied by XRD and ^{27}Al MAS-NMR. Sharp peaks in XRD pattern of the sample annealed at 1100°C confirm the transformation to the thermodynamically stable α–phase. The fraction of AlO_6 units is maximizes in this sample. The exothermic peak at ~1240°C in the DSC thermogram is due to γ → α transition.

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