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Barium oxide as a modifier to stabilize the γ-Al_2O_3 structure

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This research concentrated on the structural stability of γ-alumina (γ-Al_2O_3) was investigated by a combination of differential thermal analysis, X-ray diffractometry and surface-area measurements. The γ –to– θ and then α phase transitions were observed as an exothermic peak at 1000°C–1400°C in the DTA curves. The role of barium oxide as a modifier to stabilize γ-Al_2O_3 structure has been investigated. XRD measurements show that after calcination at 1000°C for 2 h, a significant fraction of the pure γ-Al_2O_3 (BaO-free) transformed to θ-Al_2O_3 while that the transition phase in alumina samples modified by BaO have been reduced significantly. Barium oxide, eliminate pentacoordinated aluminum ions through coordinative saturation and alter these ions into octahedral cations and effectively suppressed the γ –to– α phase transition in Al_2O_3, which concluded as improving the thermal stability and porous properties of the experimental samples.

Keywords: γ-Al_2O_3, thermal stability, phase transition, barium oxide, pentacoordinated Al^{3+} ions.

INTRODUCTION

γ -Alumina, one of the metastable "transition" alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for catalytically active phases. Regarding to high level of commercial position and due to wide applications of this material, the bulk and surface structure of γ -alumina and its formation and thermal stability have been and continue to be subjects of many investigations[1]. The γ -to- θ and then α phase transition temperature is important for catalyst and catalyst-support materials used at high temperature, because the specific surface area decreases drastically at the transition, and catalytic activity is lost. Many investigators have reported the effects on the transition temperature of adding various cations[2, 3]. There have also been numerous studies dedicated to improving the thermal stability of γ-Al_2O_3 because its phase transformations are thought to directly affect both the surface area and the number of active sites, which are very important with respect to its practical application. For example, previous studies have shown that the addition of Mn^{2+} and Cu^{2+} accelerate the phase transition, Co^{2+}, Ni^{2+}, Mg^{2+}, and Zn^{2+} have little or no effect, but Ca^{2+}, Sr^{2+}, and Ba^{2+} have retarding effect on the γ -to- α phase transition in Al_2O_3.

Extensively the subject has been studied in the nature of the surfaces is Lewis acidity. The Lewis acid sites are generated after dehydroxylation of the surfaces and present in the form of coordinatively unsaturated aluminum ions. A large body of studies on this aspect with a variety of techniques such as solid state NMR, FT-IR and theoretical calculations have revealed the presence of three-, four-, and five-coordinate Al ions in alumina as Lewis acid sites[4]. The removal of OH groups during high temperature treatment creates coordinatively unsaturated surface cations where tetrahedral (Al^{IV}) and octahedral (Al^{VI}) aluminum coordinations are the most widely accepted[5]. Furthermore, several amounts of pentahedral coordinated aluminum (Al^{V}), concentrated at the surface, have also been found[6]. It has been reported that the Al^{V} content is directly related to the pore-size distribution, crystallinity, and surface area[7]. Regarding to acid and base definition of Lewis, uncoordinated metal cations and oxide anions on the surface of γ-Al_2O_3 can act as acids and bases, respectively[8]. The strongest acid sites are considered to be the Al^{IV} coordinatively unsaturated surface ions, which are responsible for the high catalytic activity of highly dehydrated alumina. Up to now, the most accepted and frequently used empirical model to describe γ-Al_2O_3 surfaces was that developed by Knözinger and Ratnasamy[9]. Accordingly, five different types of OH groups are present on the surface that exhibit a distinct "net electric charge" (σ), depending on the number of Al neighbors and on Al coordination. Recently, using density functional theory (DFT) calculations, realistic models of the γ-Al_2O_3 surface have been proposed that account for the above process[10]. Behavior of various types of surface hydroxyl groups is shown in this model depends on the local chemical environment, morphology (exposed surfaces), and composition of the oxide, which are greatly influenced by the alumina precursors and synthetic methods used.

The ability to control the dispersion and morphology (typical characteristics that determine the performance of catalysts) of oxide-supported metal catalysts is a primary goal of catalyst design and can be enabled by understanding the nature of metal–support surface interactions[11]. Precious metals (e.g., Pt, Pd, Ir and Rh) supported on oxide surfaces are the most widely used industrial catalyst materials. For these classes of catalysts, dispersion of the precious metal on the oxide support is an especially critical factor due to the expense of the metal. One of these catalysts is Ir/γ-Al_2O_3 for hydrazine decomposition in gas generators and monopropellant systems. Because of hydrazine decomposition is a highly exothermic reaction to elevate the temperature up to 1000°C[12–14], Therefore, the catalyst should be durable at such high temperature. So the stability of γ-Al_2O_3 is a critical point for hydrazine decomposition. The γ-Al_2O_3 phase transforms into the δ- and θ-Al_2O_3 polymorphs with increasing calcination temperature and finally forms α-Al_2O_3, the thermodynamically stable structure[9].

Investigations on the basis of NMR and IR spectroscopic measurements, showed that the two characteristic ^{27}Al NMR features of γ-Al_2O_3 at 13 and 70 ppm represent Al^{3+} ions in octa-hedral (Al^{3+}octa) and tetrahedral (Al^{3+}tetra) coordination, respectively. The NMR peak at 35 ppm chemical shift has been assigned to Al^{3+} ions in pentahedral coordination (Al^{3+}penta)[15, 16]. These pentacoordinate sites are created on the γ-Al_2O_3 surface by dehydration and dehydroxylation at elevated temperatures. The number of Al^{3+}penta sites increases with increasing annealing temperature[6].

Due to the phase transformations affect on both the surface area and number of active sites, improving the thermal stability of γ-Al_2O_3 for hydrazine decomposition is very important[17]. The role of barium oxide as a modifier to stabilize the γ-Al_2O_3 structure (and Ir/γ-Al_2O_3 catalyst) is investigated in this paper. In this contribution, relation exits between pentacoordinated aluminum ions and the thermal stability of γ-Al_2O_3. In particular, the specific interaction of barium oxide with these pentacoordinated Al^{3+} ions is shown to correlate with the observed enhancement of the thermal stability of γ-Al_2O_3[18].

DETAILS EXPERIMENTAL

The γ-Al_2O_3 samples used in this work were purchased from Sasol Company. The 2, 6 and 10 wt% BaO/γ-Al_2O_3 samples were prepared by the impregnation method, using an aqueous solution of Ba $(NO_3)_2$ (Aldrich) and a γ-Al_2O_3 support. After impregnation, the samples dried at 120°C and calcined in a furnace at 600, 800 and 1000°C for 2 hours.

Supporting Ir catalysts were synthesized using pure γ-Al_2O_3 (BaO-free) and promoted γ-Al_2O_3. The preparation method of catalysts is impregnation with H_2IrCl_6 (aq) solution.

To determine the γ -to- α phase transition temperature, differential thermal analysis (DTA) measurements conducted (using a Thermo-Plus Model No. TG8120, Rigaku Co.) at a heating rate of 10°C/min, under flowing air (50 mL/min), using about 10 mg samples.

The DTA measurements also performed at heating rates of 1°, 2°, 5°, and 20°C/min, to obtain the nonisothermal activation energy for nucleation growth of α-Al_2O_3 from the Kissinger equation[19].

The crystalline phases in the heated samples determined by powder X-ray diffractometry. XRD analysis carried out on a Philips PW3040/00 XPert powder X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å) in step mode between 2θ values of 10 and 75°, with a step size of 0.02°/s.

To examine the changes in the specific surface area, values of the heated samples were determined by the BET method using an automated adsorption instrument (Nova Station A).

SEM analysis was employed to compare dispersion of two types of catalysts (Ir/γ-Al_2O_3 and Ir/Bao/γ-Al_2O_3) after heated at high temperature. Scanning electron micrographs (SEM) were obtained with Philips XL30 ESEM instrument.

RESULTS AND DISCUSSION

The γ -to- α phase transition was observed as an exothermic peak at around 1000°–1400°C in the DTA curves. The temperatures of the exothermic peaks in the no-additive alumina, 2, 6, 10% wt BaO/γ-Al_2O_3 were 1208, 1320, 1355 and 1300°C respectively.

DTA runs show an increase in the BaO concentration initially causes a corresponding increase in α – Al_2O_3 transformation temperature (Fig. 1).

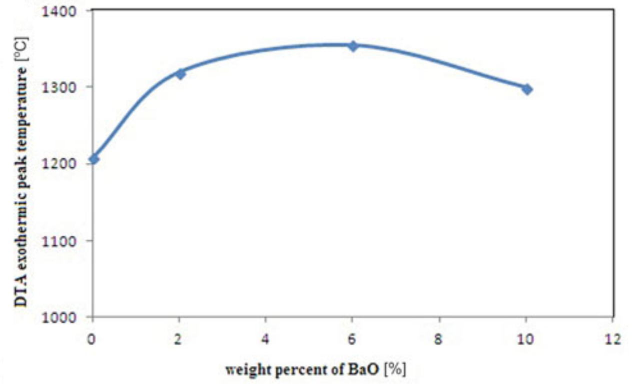

Figure 1. Relationship between the DTA exothermicpeak temperature of the γ – to – α phase transition and weight percent of barium oxide

Regarding to increase temperature, γ – Al_2O_3 changed gradually to θ – Al_2O_3 and, then, α – Al_2O_3 as already reported in many papers[20]. Figure 2 represents the XRD patterns of the as-received γ – Al_2O_3 at 600°C (a), 800°C (b) and 1000°C. No noticeable structural changes are observed after extended calcination at either 600°C (a) or 800°C (b). However, several new peaks at 2θ values of 31.8°, 32.9°, 51.1°, and 60.3°, assigned to θ – Al_2O_3, are observed in the XRD pattern of the alumina calcined at 1000°C for 2 h.

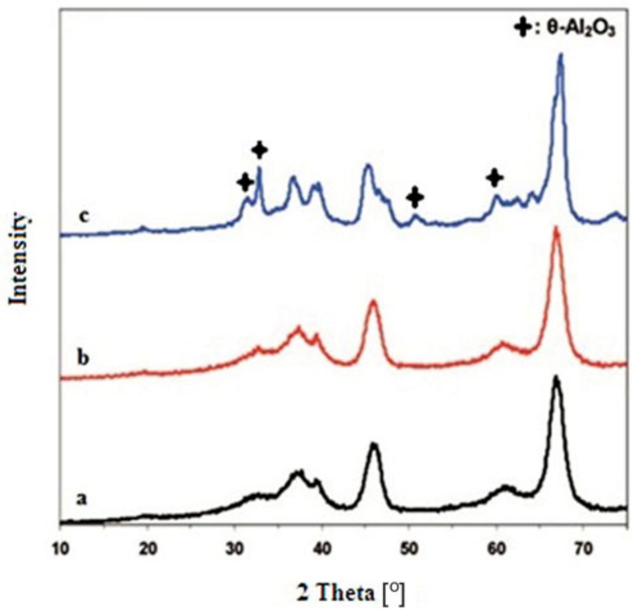

Figure 2. XRD patterns of γ-Al_2O_3 samples calcined for 2 hrs at (a) 600ºC, (b) 800ºC, and (c) 1000ºC

Figure 3 shows the XRD patterns samples containing different weight percent of BaO calcined at 1000°C for 2h. Figure 3(a) indicates the BaO-free samples. The angles belonging to θ – Al_2O_3 is reduced in Figure 3(b) (2 wt% BaO-loaded γ-Al_2O_3). In 6 wt% BaO-loaded γ-Al_2O_3 sample, peaks related to θ-Al_2O_3 (Fig. 3(c)) are eliminated. By the results of DTA and XRD techniques, the 6 wt% loading of BaO is optimized amount to thermal stabilization of γ-Al_2O_3.

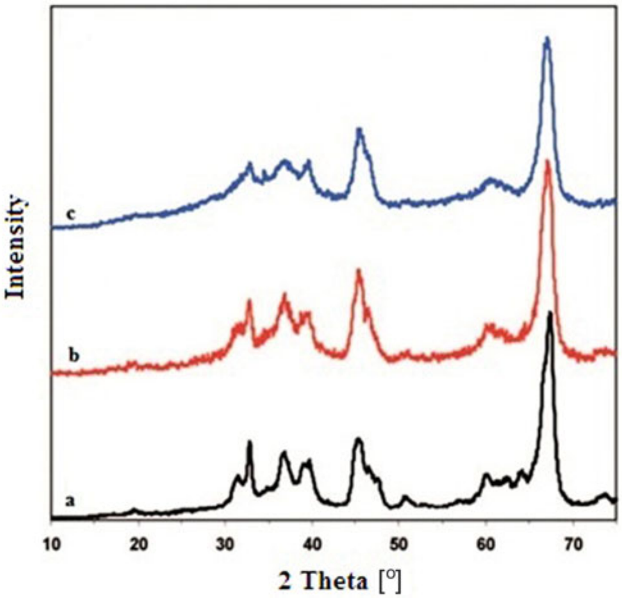

Figure 3. XRD patterns after being calcined at 1000°C for 2 hrs: (a) γ-Al_2O_3, (b) 2% wt BaO/Al_2O_3, and (c) 6% wt BaO/Al_2O_3

Pentacoordinated aluminum (Alp) ions exist on the surface of γ-Al_2O_3 can dramatically influence on its structural stability and participate in transition phase from γ to θ-Al_2O_3. The role of barium oxide as a modifier retards this phenomenon by saturated the Alp ions and converts them into octahedral ones.

Table 1 also compares the surface area of pure and modified γ-Al_2O_3 at different temperatures. Pure γ-Al_2O_3 (without barium oxide) has a specific surface area of 176 m^2/g after calcination at 600°C for 2 h. while that at the same conditions the specific surface area of γ-Al_2O_3 modified by 6 wt% BaO is 170 m^2/g.

Table 1. BET Surface Areas for Alumina Samples as a Function of Calcination Temperature

Sample	Specific surface area [m^2/g]		
	600°C for 2 h	800°C for 2 h	1000°C for 5 h
γ-Al_2O_3	176	172	103
6 wt % BaO/ γ-Al_2O_3	170	168	115

Increasing the calcination temperature to 800°C resulted in very similar decreases in the specific surface areas of both of these materials, regardless of the presence or absence of BaO. Specific surface areas of γ-Al_2O_3 and 6 wt% BaO-doped γ-Al_2O_3 at 800°C were 172 m^2/g and 168 m^2/g respectively. Further calcination at 1000°C for 2 h significantly reduced the specific surface areas of both of these samples. Increasing the calcination temperature to 1000°C showed the specific surface area of 103 m^2/g for γ-Al_2O_3 and 115 m^2/g for BaO/γ-Al_2O_3. However specific surface area of promoted sample is more than γ-Al_2O_3.

The iridium supported on γ-Al_2O_3 and BaO/γ-Al_2O_3 catalysts were prepared by the impregnation method[14] for decomposition of hydrazine. To compare the thermal stability of these catalysts, the samples were heated at 1000°C for 2 hours. SEM and BET measurements were employed to determine their changes.

As it may be seen in Figure 4, after heated at 1000°C for 2 hours, the dispersion of particles in iridium based on promoted gamma alumina support is better.

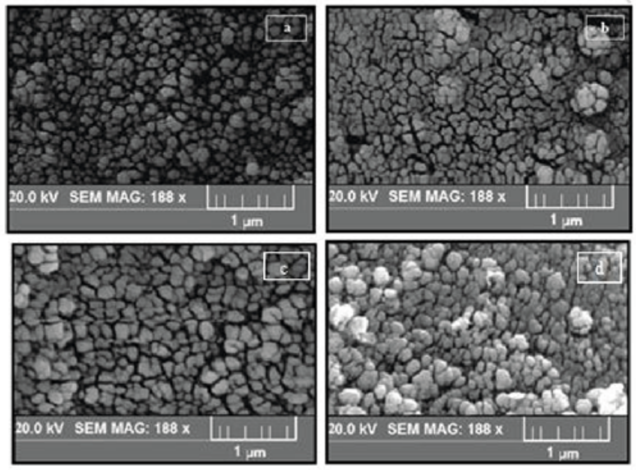

Figure 4. Micrographs of Ir/BaO/γ-Al_2O_3 and Ir/γ-Al_2O_3 catalysts a, c) before, and b, d) after being heated at 1000°C for 2 hrs

Table 2 indicates the specific surface area of two catalysts before and after heated at 1000°C for 2 hours. Specific surface area of Ir/γ-Al_2O_3 catalyst is much more decreased after being heated at 1000°C than Ir/ BaO/γ-Al_2O_3.

Table 2. specific surface area before and after heated at 1000°C for 2 hrs

Sample	Before	After
Ir/ γ-Al_2O_3	139	70
Ir/ BaO/ γ-Al_2O_3	130	84

CONCLUSIONS

The effects of barium oxide on γ- to θ and α phase transition for Al_2O_3 were examined by using a combination of DTA, XRD and BET techniques. DTA analysis show that the α-Al_2O_3 transformation temperature is increased from 1200°C to about 1360°C at 6% barium oxide doping. The results of the XRD indicate that at about 1000°C γ-Al_2O_3 alters to θ-Al_2O_3 phase, but addition of BaO prevents the γ phase and has retarding effect.

Regarding to experimental results, it may propose that formation temperature of θ-Al_2O_3 is about 900–1000°C. At high temperature (>950°C) pentacoordinated aluminum ions became unstable, so transition to θ-Al_2O_3 occurred. In the other words the transformation from γ- to θ and then α-Al_2O_3 happens only in the presence of Alp (Pentacoordinated aluminum ions) sites. In case of the addition of BaO, coordination of pentahedral aluminum ions saturated and therefore instability of γ-Al_2O_3 reduced. The addition of barium oxide effectively suppressed the γ -to- α phase transition in Al_2O_3 and increased its thermal stability and porous properties in iridium catalyst.

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