The Effect of Lanthanum and Barium Additives on the Thermal Stabilization of γ-Al$_2$O$_3$

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The effect of La and Ba additives on the thermal stabilization of γ-Al$_2$O$_3$ was investigated through total-surface-area measurements. The parameters considered were additive content, calcination temperature, and calcination period. The effect of precalcination was also studied. It was found that thermal stabilization caused by 3 wt% La and Ba is superior to 6 wt % La or Ba, and the positive effect of 3 wt% La and 3 wt% Ba are almost identical. The nearly threefold increase in the total surface area of 3 wt% La or Ba doped samples calcined above the $\gamma - \alpha$ phase-transition temperature indicates that the aluminate complexes formed with La or Ba during phase transition impart thermal resistance to sintering. Aluminate formation at these temperatures is verified by XRD measurements. Precalcination at 723 K stabilizes the γ-Al$_2$O$_3$ structure, leading to higher surface areas in the undoped sample upon sintering.

Keywords: γ-Al$_2$O$_3$, thermal stabilization, lanthanum additive, barium additive, calcination.

Introduction

The support materials used in catalyst preparation play a crucial role in determining the physical characteristics and performance of the catalysts. Alumina is one of the best known catalyst-support materials frequently used in both research and industrial applications[1-6]. It is also widely used in industry for the drying of liquid or gaseous hydrocarbons produced by the thermal cracking of petroleum fractions. In the preparation of catalysts, alumina, especially γ-Al$_2$O$_3$, is used not only for its very high surface area on which active metal atoms/crystallites can spread out as reaction sites[1,2,5], but also for its enhancement of productivity and/or selectivity through metal-support interaction and spillover/reverse-spillover phenomena[7-9].

In catalytic reactions having environmental and industrial applications, γ-Al$_2$O$_3$ has to start with a high surface area and also to retain as much of it as possible during the reaction period. However, it has been reported that the rate of surface-area loss in alumina exhibits an Arrhenius-like relationship with temperature[10]. Some additives have been used in order to impart thermal resistance for retaining the high surface area of the γ-Al$_2$O$_3$ support under reaction conditions. Several elements (Ce, Ba, Sr, La, Sm, Si, Pr and P), when added to γ-Al$_2$O$_3$, markedly increase the thermal stability of the support and prevent the loss of surface area[3,10,11,12]. The addition of silicon enhances thermal stability in the 1596-1766 K range[13].

When lanthanum is used as an additive, the formation of lanthanum aluminate upon calcination at 1073 K is reported to decrease the surface energies of γ-Al$_2$O$_3$, which lowers the driving force for sintering[14]. BaO has also been proposed as the most effective stabilizing agent due to the formation of barium aluminate phases that make the γ-Al$_2$O$_3$ structure more resistant to sintering[15].

In this study, the effect of La and Ba additives on the thermal stabilization of γ-Al$_2$O$_3$ was investigated through total-surface-area and XRD measurements. The concentration of each additive was changed between 0 and 6 wt% in impregnated samples, and calcination temperatures between 723 and 1423 K were used. The time of exposure to elevated temperatures was also changed to see the effect of the calcination period on the stability of total surface area. La and Ba were impregnated on both fresh and precalcined γ-Al$_2$O$_3$ samples in order to investigate the effect of precalcination.

Materials and Methods

The support material γ-Al$_2$O$_3$ (Alcoa) was ground and the particles sieved to 250-355 μm (45-60 mesh). Impregnated samples containing 3 wt% and 6 wt% La and Ba on γ-Al$_2$O$_3$ were prepared using the incipient wetness method. These weight percentages correspond to 2.2 mol% and 4.5 mol% for both mixtures, La and Ba on γ-Al$_2$O$_3$. The impregnation equipment consisted of a Masterflex computerized-drive peristaltic pump, a vacuum pump, a flask and an ultrasonic mixer. During impregnation, analytical grade La(NO$_3$)$_3$.6H$_2$O (Riedel) and Ba(NO$_3$)$_2$ (Merck) were used to prepare the aqueous nitrate solutions, whose concentrations were determined according to the target La or Ba loadings of the samples.

5-gram batches of catalyst were prepared in each case. The required amount of γ-Al$_2$O$_3$ support was weighed and dried for 1h at 378 K. In the preparation of precalcined alumina samples, the drying step was followed by calcination at 723 K for 4h. Calculated amounts of the additive and water were introduced through ultrasonic mixing under vacuum, and ultrasonic mixing was continued for an additional 20 minutes. The impregnated samples were first dried at 323 K for 15h and then at 393 K for 3h in all cases. Subsequently, 500 mg portions of each batch were calcined at different temperatures (723 K, 873 K, 1023 K, 1423 K) for different periods (3h, 5h, 10h). A muffle furnace was used for the calcinations at 723 K, 873 K and 1023 K, while those at 1423 K were calcined in a tube furnace (Lenton LFT 1200) equipped with a temperature-control unit (Eurotherm 91e). Samples were put into the latter furnace in platinum crucibles when the furnace temperature reached the desired level.

The total-surface-area (TSA) values were determined on a Micromeritics Flowsorb II 2300 system by N$_2$ adsorption from N$_2$-He mixtures at 77 K using a multipoint technique together with the BET equation. Samples were degassed at 523 K for 3h prior to each total-surface-area measurement. A Rigaku RINT x-ray diffractometer with Co Kα radiation (λ = 1.7A$^\circ$) was used in the X-ray powder-diffraction (XRD) measurements of doped samples calcined at different temperatures.

Results and Discussion

The thermal stabilization of γ-Al$_2$O$_3$ by the addition of La and Ba was investigated on the basis of total-surface-area measurements using samples subjected to different levels of heat treatment. The parameters considered were the weight percent of the additives doped into γ-Al$_2$O$_3$, the calcination temperature and the calcination period. The effect of precalcination prior to the impregnation of the additive was also studied.

Effect of Additives

Previous reports of the thermal stabilization of γ-Al_2O_3 indicate that both the type and the amount of additive used are important[10,11,12,14,16]. In this study, two different additives that are frequently included in the alumina support of vehicle exhaust catalysts, namely, La and Ba, were added to γ-Al_2O_3. 3 wt% and 6 wt% loadings were examined in each case. γ-Al_2O_3 samples both with and without La or Ba additive were calcined at different temperatures for different periods. The total surface areas of the samples are presented in Table 1, and the percent loss in total surface area is plotted versus calcination temperature for each sample in Figure 1. In each case, the total surface area of the sample calcined at 723 K was taken as the basis for the calculation of percent loss, which was defined as the difference in the total surface area between the samples calcined at T and 723 K divided by the total surface area of the sample calcined at 723 K.

Table 1. The effect of additive content, calcination temperature and calcination period on the total surface area at temperatures below the $\gamma - \alpha - Al_2O_3$ phase-transition level

Calcination Temperature (K)	wt% of additive	TSA (m^2/g) $\pm$ 2%			
		3h Calcination		5h Calcination	
		Ba-γ-Al_2O_3	La-γ-Al_2O_3	Ba-γ-Al_2O_3	La-γ-Al_2O_3
723	0	222	222	196	196
	3	230	222	201	203
	6	212	225	204	221
873	0	157	157	144	144
	3	184	194	178	182
	6	170	173	157	154
1023	0	123	123	116	116
	3	155	148	132	137
	6	132	121	118	117

In Figure 1 it is clear that thermal treatment leads to a reduction in total surface area, even at temperatures below the $\gamma - \alpha$ phase-transition temperature of alumina (below 1273 K). All samples were found to lose surface area with increasing calcination temperature, but samples doped with 3 wt% La or Ba exhibited the lowest percent loss in total surface area. It can be said that the thermal stabilization caused by the addition of 3 wt% La or Ba is superior to that of 6 wt% La or Ba additive. Table 1 indicates that almost all the samples reached their highest total-surface-area values with 3 wt% additive content, which is in accordance with the results obtained by Church et.al.[12] in their study on the stabilization of γ-Al_2O_3 as a function of sintering time at 1373 K. Church et.al.[12] found that a sample with 2 mol% La outperformed a sample with 5 mol% La. A possible explanation for the additional loss of surface area in samples impregnated with higher additive loadings (even at low calcination temperatures such as 873 K) may be the coverage of the pore walls of the γ-Al_2O_3 with the La and Ba. This conclusion is supported by the experimental results obtained by Church et.al.[9] They compared the TSA measurements of 2 and 5 mol% La/γ-Al_2O_3 samples at 1373 K and observed that the 2 mol% La doped sample retained a higher surface area after heat treatment. It can be said that there is a critical additive concentration below which an additive can be efficiently used in surface-area enhancement, whereas, above this concentration, it can produce a negative effect on the TSA by filling up the pores of the alumina particles.

The results presented in Table 1 and Figure 1 indicate that it is not possible to choose the best additive on the basis of calcination experiments conducted at moderate thermal-treatment temperatures. Therefore, additional experiments were carried out at 1423 K with γ-Al$_2$O$_3$ and γ-Al$_2$O$_3$ containing 3 wt% La or Ba. After observing the sintering of the samples and the transition to the α-phase at 1423 K, it can be said that the positive contributions of 3 wt% La and Ba (2.2 mol% for each) to the thermal stabilization of γ-Al$_2$O$_3$ are almost identical (Table 2). This is in agreement with the results reported by Johnson et.al.[10], who stated that equimolar amounts of additives such as P, Si, Sr, Sn, Ba and La show similar thermal-stabilization effects on γ-Al$_2$O$_3$, which implies a similarity in the nature of the interaction between the inorganic additive and the alumina surface.
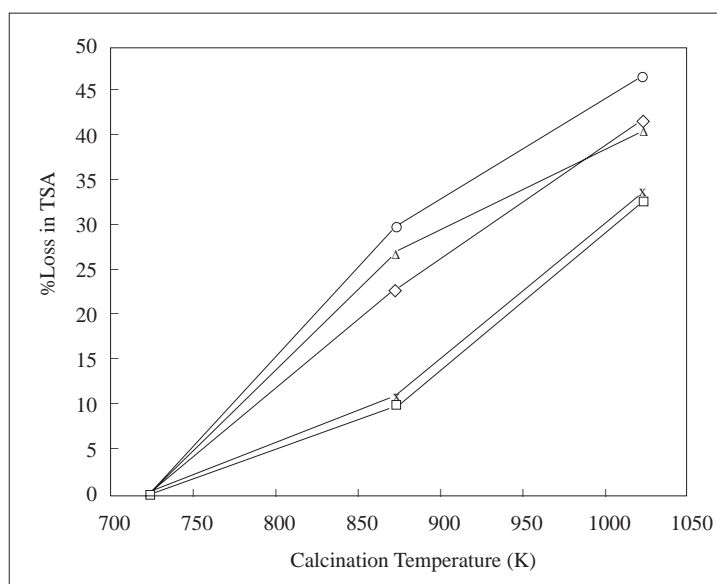

Figure 1. The effect of additive loading on the loss of total surface area in samples subjected to heat treatment at different temperatures for 5 hrs $-\Delta-$ Al$_2$O$_3$; $-X-$ 3wt% Ba/Al$_2$O$_3$; $-\square-$ 3wt% La/Al$_2$O$_3$; $-\diamond-$ 6wt% Ba/Al$_2$O$_3$; $-\circ-$ 6 wt % La/Al$_2$O$_3$)

Table 2. Comparison of the total surface areas of 3 wt% La- or Ba-doped samples calcined for 5h at different temperatures.

Calcination Temperature (K)	TSA (m^2/g) $\pm$ 2%		
	γ-Al$_2$O$_3$	3% Ba-γ-Al$_2$O$_3$	3% La-γ-Al$_2$O$_3$
723	196	201	203
873	144	178	182
1023	116	129	137
1423	25	63	72
*1423	38	69	70

* Precalcined at 723 K for 4h.

Effect of Calcination Temperature and Calcination Period

The total surface areas of γ-Al$_2$O$_3$ samples both without and with two different levels of La and Ba loading calcined at three temperatures in the 723-1023 K range for 3h and 5h periods are presented in Table 1. For the samples doped with 3 wt% Ba or La, a 150 K increase in temperature caused about a 10% decrease in total surface area, while a 300 K increase caused the same samples to lose about 30 % of their initial total surface area. 6 wt% La- or Ba-doped samples lost almost 20% of their initial total surface area when the calcination temperature was increased by 150 K, and losses of more than 40 % were observed when the calcination temperature was increased by 300 K. The plots in Figure 1 indicate that the loss of surface area in samples doped with 6 wt% Ba or La are similar or even somewhat above those in the γ-Al$_2$O$_3$ itself at calcination temperatures below 1273 K. This might be an indication of the fact that the formation of La- or Ba- aluminate phases is almost negligible at temperatures below 1273 K. Therefore, the mechanism that leads to thermal stabilization and hence to total surface area enhancement in doped γ-Al$_2$O$_3$, when compared to γ-Al$_2$O$_3$ alone, cannot be clearly observed at these temperatures.

Table 2 shows the total surface area of 3 wt% La- or Ba-doped samples calcined for 5 hrs at temperatures including 1423 K, which is above the temperature at which the phase transition of alumina from the thermodynamically unstable γ-phase to the stable α-phase occurs. A comparison of the samples treated at 1023 K and 1423 K shows that the additional loss in total surface area is nearly 80 % in γ-Al$_2$O$_3$, whereas this additional decrease is only 51 % in the 3 wt% Ba-doped sample and 47 % in 3 wt% La/γ-Al$_2$O$_3$. When the different samples calcined at 1423 K are compared, it can be seen that the total surface area of 3 wt% La/γ-Al$_2$O$_3$ is almost 3 times that of γ-Al$_2$O$_3$ alone, and the total surface area of 3 wt% Ba/γ-Al$_2$O$_3$ is about 2.5 times that of γ-Al$_2$O$_3$.

The total surface areas of samples both with and without additive were adversely affected by an increase in the calcination period from 3h to 5h at all calcination temperatures (Table 1). Figure 2 presents a plot of the change in total surface area of undoped and 3 wt% La- or Ba-doped samples with calcination periods at 1423 K. Following the $\gamma - \alpha$ phase transition, the total surface area of the undoped sample decreased to 25 m^2/g in 5 hrs and to 20 m^2/g in 10 hrs. The sample with 3 wt% Ba-content shows stabilization at 60 m^2/g for 5-10 h of calcination, while the total surface area of the 3 wt% La/γ-Al$_2$O$_3$ sample fluctuates between 60 and 70 m^2/g for calcination periods up to 5h and then declines with further calcination. The results presented in Figure 2 clearly reveal the drastic enhancement in total surface area caused by the addition of La or Ba to γ-Al$_2$O$_3$. A nearly threefold increase in the total surface area of doped samples calcined above the phase-transition temperature indicates that both La and Ba form aluminate complexes with alumina during the phase-transition mechanism, and that these complexes give thermal resistance to the catalyst samples[3,15,17]. The results obtained in the 723-1423 K temperature range indicate that the stabilization effect of additives via the formation of aluminate complexes is less pronounced at temperatures below 1023 K.

XRD measurements of 3 wt% La-doped γ-Al$_2$O$_3$ samples calcined at 873, 1023 and 1423 K show that aluminate formation began above 1023 K. The formation of barium aluminate can also be observed from the XRD pattern of 3 wt% Ba-doped γ-Al$_2$O$_3$ calcined at 1423 K, given in Figure 3 together with the XRD pattern of 3 wt% La-doped γ-Al$_2$O$_3$. In both graphs, it was not possible to obtain high and distinct peaks with such a low additive concentration. The aluminate structure is obvious in both the 5h- and 10h-calcined 3 wt% Ba-doped γ-Al$_2$O$_3$ samples; in addition α-Al$_2$O$_3$ and θ-Al$_2$O$_3$ peaks are more frequent than the small number of γ-Al$_2$O$_3$ peaks. Even though there is α-Al$_2$O$_3$ in the structure of this support, its surface area is high. This shows the contribution of Ba additive as Ba-aluminate to surface-area stabilization. The

XRD traces of samples calcined at 873 K and 1023 K for 5h do not have peaks due to La-aluminate. Again, 1423 K samples calcined for 5h and 10h exhibit peaks due to La-aluminates in 3 wt% La-doped γ-Al$_2$O$_3$ samples. In these 3 wt% La-doped samples, γ-Al$_2$O$_3$ peaks begin to disappear at 1423 K, and, instead, α-Al$_2$O$_3$ and θ-Al$_2$O$_3$ peaks start to rise. It was observed that there was very low α-Al$_2$O$_3$ formation in La-doped samples compared to Ba-doped ones. It has been proposed by Bettman et.al.[14] that the high degree of stability of γ-Al$_2$O$_3$ is caused by a substantial lowering of the surface energies of γ-Al$_2$O$_3$ with the addition of La, which is in parallel with the observations of the present work.
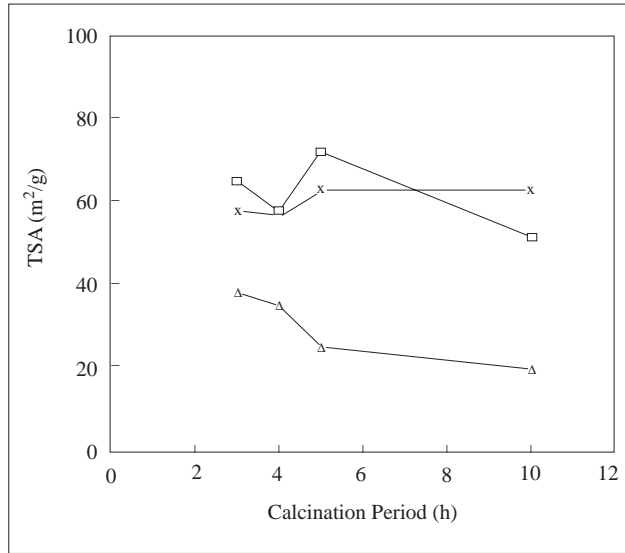

Figure 2. The effect of calcination period on total surface area at 1423 K. ($-\Delta-$ Al$_2$O$_3$; $-X-$ 3wt% Ba/Al$_2$O$_3$; $-\square-$ 3wt % La/Al$_2$O$_3$)
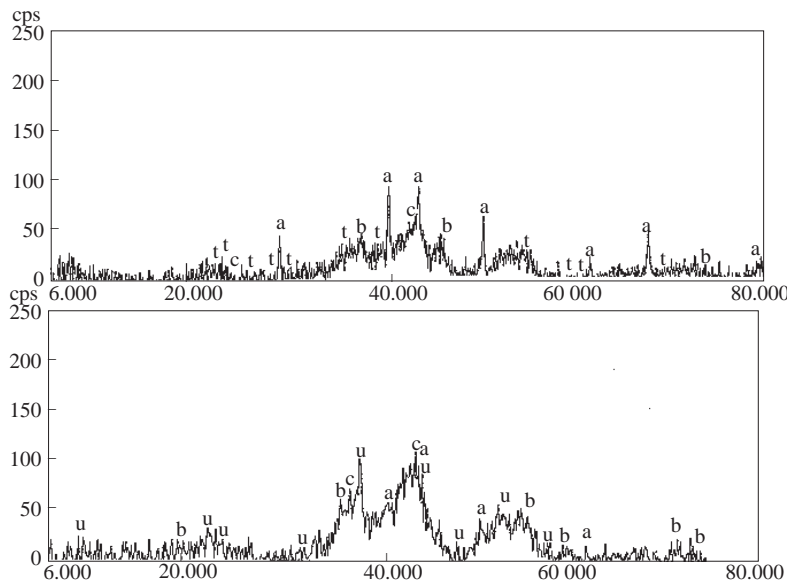

Figure 3. XRD patterns of I- 3 wt% Ba-doped γ-Al$_2$O$_3$, and II- 3 wt% La-doped γ-Al$_2$O$_3$ calcined at 1423 K for 10h. (a: α-Al$_2$O$_3$, b: θ-Al$_2$O$_3$, c: γ-Al$_2$O$_3$, t: Barium Aluminate, u: Lanthanum Aluminate).

Effect of Precalcination

The effect of precalcination on undoped and doped γ-Al$_2$O$_3$ samples was tested at calcination temperatures in the 723-1023 K range by comparing the total surface areas of samples which were not subjected to calcination before the impregnation step (Table 3). No positive effects of precalcination were observed in the 6 wt% La- or Ba-doped γ-Al$_2$O$_3$ samples. However, it can be said that the total surface area of the γ-Al$_2$O$_3$ itself was stabilized by precalcination. Similar behavior can also be seen in Table 2, where precalcined samples sintered at 1423 K are compared with those that were not precalcined. A comparison of the total surface area of fresh and precalcined γ-Al$_2$O$_3$ samples after sintering at 1423 K reveals that precalcination at 723 K stabilized the structure of γ-Al$_2$O$_3$, which resulted in the retention of higher total surface areas at higher calcination temperatures or upon sintering at 1423 K. Again, the effect of precalcination was not significant in the 3 wt% Ba- and 3 wt% La-doped γ-Al$_2$O$_3$ samples under the same conditions.

Table 3. The effect of precalcination on the total surface areas of γ-Al$_2$O$_3$ and 6 wt% La- or Ba-doped γ-Al$_2$O$_3$ calcined for 5h.

Calcination Temperature (K)	TSA (m^2/g) $\pm$ 2%					
	γ-Al$_2$O$_3$	γ-Al$_2$O$_3$(*)	6% La-γ-Al$_2$O$_3$	6% La-γ-Al$_2$O$_3$(*)	6% Ba-γ-Al$_2$O$_3$	6% La-γ-Al$_2$O$_3$(*)
723	196	200	221	183	204	190
873	144	167	154	161	157	161
1023	116	122	117	120	118	117

* Precalcined at 723 K for 4h.

Conclusions

The results presented show that the additive content, calcination temperature and calcination period are major parameters that affect the thermal stabilization of γ-Al$_2$O$_3$. Lower La or Ba concentrations impart better thermal resistance for retaining higher surface area, and equal amounts of La and Ba show similar thermal-stabilization effects. 3 wt% La- or Ba-doped γ-Al$_2$O$_3$ samples calcined above the $\gamma - \alpha$ phase-transition temperature had total surface areas that were nearly three times that of the undoped γ-Al$_2$O$_3$ sintered at high temperatures. The aluminate complexes formed with La or Ba during phase transition provide the thermal resistance to sintering which leads to lower surface-area losses. X-ray powder-diffraction measurements proved the presence of aluminates at temperatures above the phase transition, i.e., at 1423 K, in this study. Finally, precalcination at 723 K before the impregnation of the La or Ba additive stabilizes the γ-Al$_2$O$_3$ itself but does not lead to any significant change in the total surface areas of La- or Ba-doped γ-Al$_2$O$_3$ samples.

Acknowledgement

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