研 究

Effect of Lanthanum Modification on Thermal Stability of γ - Al_2O_3 Layers Fabricated by Suspension-dip Process

Masakuni Ozawa

Ceramics Research Laboratory, Nagoya Institute of Technology, Tajimi 507-0017, Japan.

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SYNOPSIS

The forming and thermal stability of a coat layer was investigated through a simple suspension-dipping procedure of aqueous La-modified γ - Al_2O_3 suspension. The effect of La on the stabilization of surface area for powder, and the morphology of coat layers, which are heated at elevated temperatures, were examined by X-ray diffraction, nitrogen adsorption and scanning electron microscopy. The La-addition stabilized the metastable phases of Al_2O_3 at temperatures up to 1200 °C, and induced the increase of phase-transformation temperature to α - Al_2O_3 . The surface area of pure Al_2O_3 layer decreased after heat treatment at 900–1200 °C. Several factors for controlling the formation of a coat layer from La-modified γ - Al_2O_3 suspension were discussed. A fabricated La-modified alumina layer was stable to realize high surface area as well as homogeneous shape without large cracks after heat treatment under heating condition at 1100 °C in air.

KEYWORDS

ceramics, alumina, catalyst, lanthanum, powder, suspension

1 Introduction

The catalytic layer of gamma-alumina (γ - Al_2O_3) is very important in an automotive catalyst converter for air pollution control. In the catalytic treatment of high-temperature engine exhaust, the thermal durability of a coat layer is essential, because a porous surface coat must support the catalytic composition of precious metals without sintering^{1–4}. The loss of surface area of this layer has resulted in large degeneration of whole catalyst containing alumina support, metals and promoters. In addition, the destruction of a porous layer is improper phenomenon to the performance and durability of a device, which was designed toward the harsh condition of high temperature and high flow rate in exhaust treatment. Therefore, heat-stable catalytic supports (powder as well as layer) are required with different viewpoints of both surface area and shape stability in practical catalysis operation. Recently, the washcoat process using alumina powder has been refocused regarding with several viewpoints such as suspension control, powder loading, porosity, as well as catalytic performance^{5–12}. In a present study, we describes the effect of La-addition in γ - Al_2O_3 coat layer on crystal phase and morphology stabilization at elevated temperatures, which is fabricated through a simple suspension-dip process, without organic additives, toward

catalytic components in exhaust treatment at around 1000–1100 °C.

2 Experimental

Pure and La-modified γ - Al_2O_3 powders for catalytic support were supplied from Sumitomo Chemicals Co., Japan. The fraction of La in Al_2O_3 was set at 1 mol%, since our previous study indicated that the surface area stabilization appeared most effectively at 1–2 mol% La for γ - Al_2O_3 ^{13,14}. Starting surface area of powders was 125 m²/g for γ - Al_2O_3 and 105 m²/g for La- γ - Al_2O_3 , respectively. Aqueous suspensions were prepared with deionized water at room temperature. The pH was controlled by adding aqueous solution of ammonia and acetic acid. For the preparation of the coating layers, thin alloy substrates were dipped into the suspensions, and then withdrawn. We applied many conditions of solid concentration, a withdrawing rate and pH of solution. The as-dipped sample was dried in an oven at 120 °C for 1 h in air, and then heated at temperatures up to 1300 °C. Also, raw powders and dried slurries as references were heated at various temperatures.

Powder X-ray diffractometry (XRD; Rigaku Rint2000, Tokyo, Japan) with Cu-K α source (20 kV–30 mA) was used for characterizing crystalline phases in the samples after heat treatment at various temperatures. The surface

areas of the powder and dried slurries were evaluated from nitrogen adsorption at 77 K. The zeta potentials of powders were measured using the ultrasonic vibration potential (UVP; PemKem system7000, New York, USA) for the aqueous suspensions. Scanning electron microscopy (SEM; JEOL, JEM8000, Tokyo, Japan) was used to observation of morphology of coated layers. Differential thermal analysis (DTA; Seiko Instruments, SSC580, Tokyo, Japan) was applied to detect the phase transformation temperature of aluminas.

3 Results and discussion

3.1 Phase transformation

Fig. 1 and 2 show the XRD powder patterns for γ - Al_2O_3

Fig. 1 The change of XRD patterns for pure γ - Al_2O_3 heated at (a) 900°C, (b) 1100°C and (c) 1200°C. (○) γ - Al_2O_3 ; (●) α - Al_2O_3 .

Fig. 2 The change of XRD patterns for 1 mol% La-modified γ - Al_2O_3 heated at (a) 900°C, (b) 1100°C and (c) 1200°C. (▽) LaAlO_3 .

and 1 mol% La- γ - Al_2O_3 heated at various temperatures up to 1200 °C for 3 h in air, respectively. The sequence of transformation (with or without LaAlO_3) is simply as follows; γ - $\text{Al}_2\text{O}_3 \rightarrow (\delta$ - $\text{Al}_2\text{O}_3) \rightarrow \alpha$ - Al_2O_3 , where θ - Al_2O_3 did not appear. The α -phase transformation temperature (T_c) increased by La-addition; DTA data with a heat-rate of 10 °C/min indicated $T_c = 1290$ °C for γ - Al_2O_3 and 1450 °C for 1 mol% La- γ - Al_2O_3 , respectively. Since the transformation to α - Al_2O_3 induces the rapid loss of surface area with grain growth^{2,15}, the increase of T_c corresponds to an improvement of the thermal stability for catalytic layer. The XRD showed larger amount of α - Al_2O_3 for pure alumina than La-modified alumina at 1200 °C. The appearance of α - Al_2O_3 at lower heat treatment temperatures than T_c (measured by DTA) is due to α -transformation depending on time in this temperature range. When La-modification was applied, γ -(or δ) phase of alumina was stabilized at 1100 – 1200 °C although small amount of LaAlO_3 appeared above 850 °C. Thus, the La- γ - Al_2O_3 is expected to realize heat-stability as support if it is used as a coat layer under catalytic operation at < 1100 °C.

3.2 Zeta potential and characteristics of suspensions

The powders of both γ - Al_2O_3 and La- γ - Al_2O_3 consist of primary crystallites with 8 – 15 nm in diameter, however the secondary particles of 150 – 300 nm in size were often observed by electron microscopy. After ultrasonic vibration of suspension, it changes to the mixture of large and very small aggregates (from transmission electron microscopy observation). The “particle” seems to have porous structure and wide size distribution in suspension.

Fig. 2 compares the data of zeta-potential that was

Fig. 3 Zeta potential versus pH for Al_2O_3 powders. (□) pure γ - Al_2O_3 ; (■) 1 mol% La-modified γ - Al_2O_3 .

evaluated from UVP amplitude at 100 kHz. The pH dependence of zeta-potential of γ - Al_2O_3 was largely different from that of $\text{La-}\gamma\text{-Al}_2\text{O}_3$. The point of zero charge in pH appears at 8.5 for γ - Al_2O_3 and 9.5 for $\text{La-}\gamma\text{-Al}_2\text{O}_3$. The isoelectric point in previous reports^{16,17} is 8.0–8.5 for Al_2O_3 and 9.6 for La_2O_3 . The shift of the zero charge pH value of 8.5 to 9.5 (by La-modification) means that the powder surface become slightly basic. Thus, the surface of $\text{La-}\gamma\text{-Al}_2\text{O}_3$ is fully covered by La_2O_3 which isoelectric point is larger than that of Al_2O_3 .

All suspensions showed thixotropic behavior. When $\text{pH}=7\text{--}10$, they become rather stable and well-dispersed suspension with proper viscosity so that it can be well applied to dip-coating procedure. In present experiment, the concentration of powder was selected in 4.8 vol %, with no organic additive, and at a withdrawing rate of 3.9×10^{-3} m/sec, and $\text{pH}=9$.

3.3 Surface area

The relationship of BET surface area vs. temperature for powders and dried slurry of pure alumina is illustrated in Fig. 4. The surface area values gradually decreased with heat treatment temperature. After heat treatment at $900\text{--}1100^\circ\text{C}$, the surface area of pure Al_2O_3 powder was higher (ca. $20\text{ m}^2/\text{g}$) than the dried slurry sample. This behavior essentially is caused by the degree of agglomeration, i.e. the difference of contact fraction between primary particles in the samples. In drying process, the capillary force between neighboring primary particles should make the particle-particle distance smaller, leading the tight connectivity in the microstructures of pure Al_2O_3 aggregates. Also, the increase of contact number among

the primary particles accelerates its local sintering, as well as following grain growth phenomenon, at elevated temperatures. These factors should affect on the decrease of surface area, when the dried slurry is subjected to heat treatment at high temperatures.

Fig. 5 compares the heat-temperature dependence of the surface area for both the powder and the dried slurry of La-modified alumina. In the case of La-modified sample, no difference of surface area between two samples was observed. Both the powder and dried slurry (layer) represented the high surface area of $85\text{--}90\text{ m}^2/\text{g}$ at $900\text{--}1100^\circ\text{C}$ and $55\text{ m}^2/\text{g}$ at 1200°C . The fabrication process of La-modified alumina seems to result in the stable agglomeration of primary particles (with post-heat treatment). The La-modified powder in water is expected to maintain the structure of agglomeration even if the drying process of slurries is applied. In addition, the La-modification has the large effect to inhibit sintering, and lead the heat-stabilization of primary particles below 1100°C .

The thermal behavior of a dried slurry (layer) for two aluminas at $900\text{--}1200^\circ\text{C}$ is summarized and expected as follows. Below 1000°C , pure alumina shows a large shrinkage, while La-modified alumina is very stable without shrinkage (without the decrease of surface area) because of the stable agglomeration of primary particles. At $1000\text{--}1200^\circ\text{C}$, the sintering of both the dried slurries is initialized so that their resultant shrinkage will be large. However, the extent of shrinkage will be far smaller for La-modified alumina than pure alumina, because of the effective inhibition of α -transformation with La-modification at around 1100°C .

Fig. 4 BET surface area of a powder (●) and a dried slurry (■) of pure Al_2O_3 versus temperature in heat-treatment at $900\text{--}1200^\circ\text{C}$ for 3 h in air.

Fig. 5 BET surface area of a powder (○) and a dried slurry (□) of 1 mol% $\text{La-Al}_2\text{O}_3$ versus temperature in heat-treatment at $900\text{--}1200^\circ\text{C}$ for 3 h in air.

Fig.6 SEM photograph of the surface morphology of the coated layers from (a) pure Al_2O_3 and (b) La-modified Al_2O_3 subjected to heat-treatment at 1100°C for 3h in air.

3.4 Morphology of coated layers

As discussed above, the shrinkage of a formed body using La-modified Al_2O_3 as raw powder will be effectively inhibited during both drying process and heat-treatment. The layer which is made from its suspension should also be stable, when the coat layer is used below 1100°C . Then, the morphology of layers from both aluminas (with or without La) was compared by selecting the heat treatment temperature of 1100°C . Fig. 6 shows the SEM photograph of the surfaces of (a) pure Al_2O_3 and (b) La-modified Al_2O_3 layers on alloy substrate heat-treated at 1100°C . The coating condition and heat treatment were as follows solid concentration, 4.8 vol%; pH = 8; withdrawing rate, 3.9×10^{-3} m/sec; heat-treatment at 1100°C for 3h in air. In pure Al_2O_3 layer, large amount of cracks appeared after heat-treatment over 900°C . After heat treatment at 1100°C , the layers did not maintain a good contact with substrate. On the other hand, La-modified Al_2O_3 layer showed partially the sintering areas with small pores, however whole shape of the layer on substrate was reserved even after heat treatment at 1100°C . This result well demonstrates both effects; the inhibition of sintering in heat-treatment as well as the reduction of capillary force in post-dipping (drying) process, when La-modified Al_2O_3 is used as a starting powder. The La-modified $\gamma\text{-Al}_2\text{O}_3$ layer, which is fabricated through slurry-coat process, is stable, and maintains high surface area (over $85\text{ m}^2/\text{g}$) and good shape of the layer, even if it is subjected to high temperatures up to 1100°C .

4 Summary

This work examines the effect of La on the stabilization of surface area and morphology of alumina coat-layer. The following conclusions can be drawn:

- (1) La-modification of powder stabilized the metastable phases of Al_2O_3 at temperatures up to 1200°C . The increase of α -transformation temperature lead to the maintenance of high surface area at high temperatures. The surface area of the dried slurry become lower than that of powder after heat treatment in the case of pure alumina, however in La-modified Al_2O_3 , this influence was not found.
- (2) The layer from a suspension dip-coat process using La-modified $\gamma\text{-Al}_2\text{O}_3$ was morphologically stable, and maintained the surface area of over $85\text{ m}^2/\text{g}$ and homogeneous surface shape even when it was subjected to high temperatures up to 1100°C .

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