



Formation of featured nano-structure in thermal stable La-doped alumina composite catalyst

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ABSTRACT

Nanometer-order structural changes of lanthanum-modified γ -alumina at elevated temperature were examined for application toward heat-stable catalytic support. The composite powder was prepared by aqueous process using lanthanum (III) nitrate and alumina. The La added aluminas were heated in the temperature range of 600–1200 °C, and then characterized by surface area measurement, X-ray powder diffraction, scanning electron microscope (SEM), and transmission electron microscope (TEM). The solid-state reaction between lanthanum oxide and alumina lead to the nano-structure where the nanometer-size particles of LaAlO_3 are dispersed in the secondary particles of alumina. The tailored microstructure provides a new nano-structured catalyst of La-alumina, which is stable catalytic support at high temperatures.

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1. Introduction

For catalytic combustion, especially for the automotive three-way catalytic (TWC) processes, $\gamma\text{-Al}_2\text{O}_3$ is required to maintain a high surface area for dispersion of the precious metals [1]. The thermal stabilization is important even if the temperature in the catalyst bed rises to over 1000 °C. The phase transformation of $\gamma\text{-Al}_2\text{O}_3$ to thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ is observed at around 1100 °C and the sintering behavior of alumina itself decreases the surface area. Therefore, the stabilization of $\gamma\text{-Al}_2\text{O}_3$ support is vital to high temperature applications. The previous results of transition aluminas have showed that the impurities or the additives greatly influence the sintering and phase transformations of aluminas. Lanthanum has extremely positive effect of inhibition on the sintering and α -phase transformation [2–16]. However, the chemical state of this additive in aluminas and the formation of microstructure of La-aluminas are still of open question, so that the mechanism of stabilization has not been fully established regarding with the nanometer-level microstructural assessment of lanthanum-modified aluminas. When the high-temperature interaction between $\gamma\text{-Al}_2\text{O}_3$ and La_2O_3 results in the other phase, the morphology and stability of structure are also the subject on heat-stable support. The stabilization of transition aluminas concerns the dependence of processing such as pre-heat treatment.

Here we study the nanometer-ordered structural feature and its development in lanthanum-modified alumina after high temperature treatment around at 1000 °C, regarding with nanometer-size LaAlO_3 formation. Based on the solid-state reaction at the interface between $\gamma\text{-Al}_2\text{O}_3$ and La_2O_3 at high temperature, we provide the controlled nano-composite catalytic alumina support, which is heat-stable at around 1000 °C.

2. Experimental

2.1. Sample preparation

The starting powder of $\gamma\text{-Al}_2\text{O}_3$ is a sample from Sumitomo chemical (Japan), and lanthanum nitrate is high grade reagent of Wako chemicals (Japan). The La-modified samples with different atomic ratios of lanthanum to aluminum (La/Al) were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ with aqueous lanthanum nitrate. The obtained La-modified products were then freeze-dried after freezing at -30 °C, and heated at 600 °C for 3 h in air, and then heated at 800–1200 °C for 3 h in air.

2.2. Characterization

The measurements of BET specific surface areas of samples were performed by nitrogen adsorption of N_2 at 77 K after pre-heat treatment of powders at 200 °C for 1 h to remove adsorbed water. The X-ray powder diffraction (XRD) data were measured with a Rigaku rint-2000 diffractometer using $\text{Cu K}\alpha$ radiation, operated at 40 kV and 40 mA. X-ray photoemission spectra were measured using JEOL Jump10 spectrometer for the heat-treated samples. The surface atomic ratio was calculated by software from the each XPS intensity. The microstructure was investigated by transmission electron microscopy (JEOL 2000FX) at 160 kV and a scanning electron microscopy (JEOL JSM6000F) with EDS element analysis apparatus.

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3. Results and discussion

3.1. Specific surface area

Table 1 summarizes the BET specific surface areas of some samples that vary with lanthanum content and heat treatment temperature. The effect of La_2O_3 on stabilizing alumina appeared at the temperatures over 1100°C , however at 1000°C the surface area decreased as the La content increased. The thermal stabilization strongly depended on the adding content of lanthanum species, and the optimal content of lanthanum was the La/Al of 0.003–0.015 regarding with surface area if we selected heat treatment temperature at 1200°C . Such results indicate the effect of small amount and well-dispersed lanthanum species on alumina surface to inhibit surface area loss of aluminas. An optimal content of lanthanum modification located in small amount range of La/Al atomic ratio is also observed in practice, depending on processing catalytic powders and operation temperature. As lanthanum content increases to La/Al = 0.05, the retarding influence of lanthanum species relatively decreases at lower temperatures, however the surface area is as high enough as over $70\text{ m}^2/\text{g}$ if a support is used at around 1000°C . The effect of La at around La/Al = 0.05 at elevated temperatures is not a simple inhibition to sintering and transformation but the interaction between alumina and La added. Thus, it suggests the influence of microstructure of La-modified alumina support, which can have surface modified structure and/or complex nanostructure from solid-state reactions.

3.2. Solid-state reaction

Fig. 1 is the XRD patterns of a series of samples heated at 1000°C . The bulk phase changes of aluminas and solid phase interaction between $\gamma\text{-Al}_2\text{O}_3$ and La_2O_3 at high temperature was characterized by XRD. Up to La/Al = 0.015 only γ phase was observed at 1000°C . It should be noted that no reflection characteristic of lanthanum-containing species in XRD patterns for a sample below La/Al = 0.015 was observed at 1000°C . However, for a series of La-modified samples when La/Al is over 0.03 after 1000°C heat treatment, a new phase corresponding to LaAlO_3 was found as in Fig. 1. The LaAlO_3 phase is derived from the solid-state reaction between Al_2O_3 and La_2O_3 at these temperatures, when La content is large. For La-modified alumina with La/Al = 0.05, LaAlO_3 appeared at 800°C , and the content increased as heat treatment temperature was elevated. The crystallite size, which was measured by XRD peak width using the Scherrer's equation was 13 nm at 800°C , 19 nm at 1000°C , and 21 nm at 1100°C . Even when the La/Al goes up to 0.1, the XRD pattern corresponding to crystalline phase is LaAlO_3 at 1000°C . No other phase due to lanthanum species was observed from XRD patterns for these samples at 1000°C . Fig. 2 is the XRD patterns of a series of samples heated at 1200°C . Up to La/Al = 0.03 the other phase corresponding to $\text{LaAl}_{11}\text{O}_{18}$ was formed through further solid-state reaction between Al_2O_3 and LaAlO_3 . However, since the diffraction lines from $\text{LaAl}_{11}\text{O}_{18}$ phase are weak, the main phases are still γ phase and LaAlO_3 phase at these samples. The result should suggest that LaAlO_3 strongly influence both the stability of

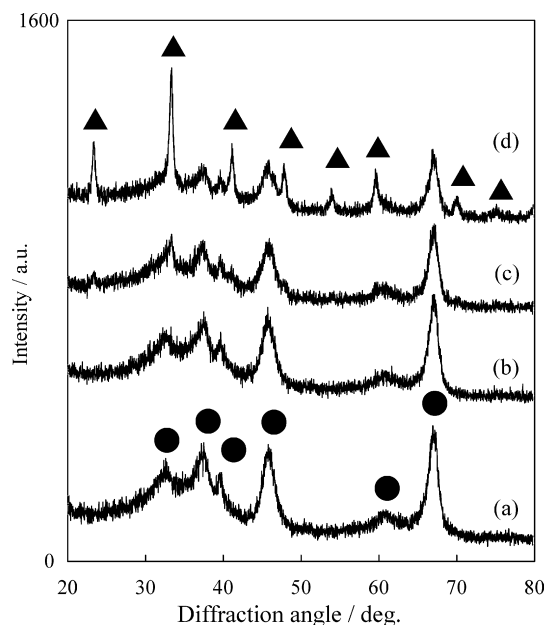


Fig. 1. XRD (Cu K α radiation source) patterns of La-modified aluminas heated at 1000°C ((●) $\gamma\text{-Al}_2\text{O}_3$, (▲) LaAlO_3). La/Al ratio; (a) 0, (b) 0.015, (c) 0.03, (d) 0.05.

alumina and its microstructure during solid-state reactions. The XPS data indicated that surface La can react with alumina resulting in nanometer bulk phase when the surface coverage of La exceeds a content of a monolayer oxide (La_2O_3). If the high-temperature interaction between $\gamma\text{-Al}_2\text{O}_3$ and La_2O_3 results in the LaAlO_3 , the morphology depends on the stability of LaAlO_3 on alumina support. Actually, since some amount of La has to be often contained in catalysts as a component besides stabilization additives, this question is important. The XRD suggests that the LaAlO_3 exist as the crystal with a certain volume including spheres with a few nm in diameter, which is corresponding to the coherent length of X-ray wave to produce diffraction amplitude. The practical surface coverage content of La on alumina particles is much lower than

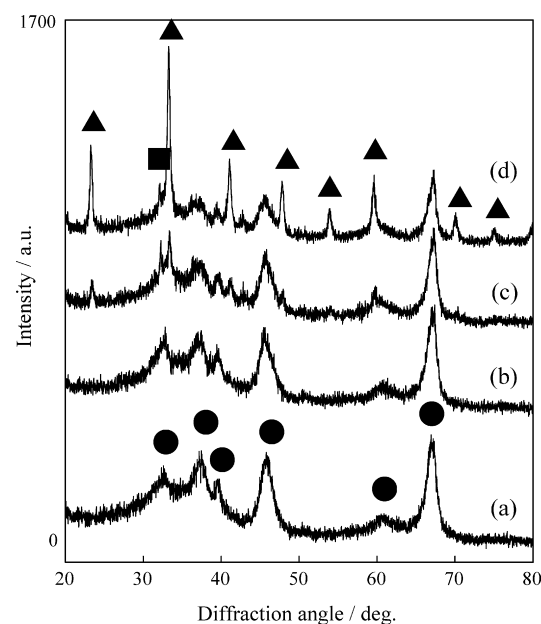


Fig. 2. XRD (Cu K α radiation source) patterns of La-modified aluminas heated at 1200°C ((●) $\gamma\text{-Al}_2\text{O}_3$, (▲) LaAlO_3 , (■) $\text{LaAl}_{11}\text{O}_{18}$). La/Al ratio; (a) 0, (b) 0.015, (c) 0.03, (d) 0.05.

Table 1
Specific surface area of La-modified alumina heated at various temperatures.

Temperature ($^\circ\text{C}$)	Surface area (m^2/g)				
	La/Al				
	0	0.3	1.5	5	10
800	104	95	96	76	–
1000	103	95	92	74	55
1200	45	82	82	59	48

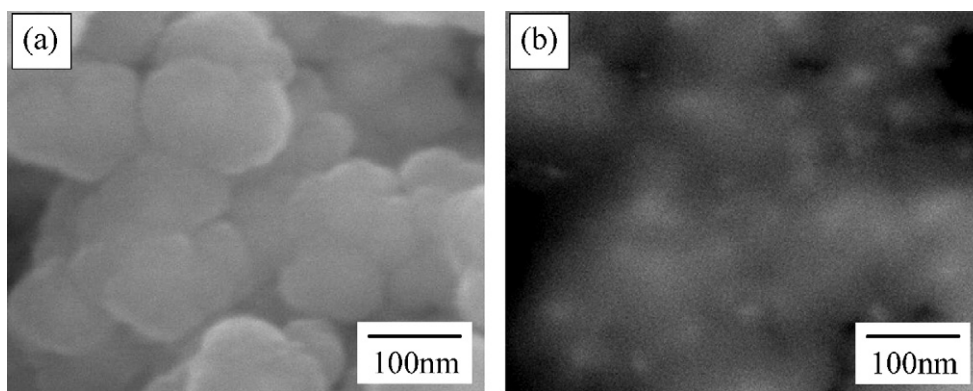


Fig. 3. SEM image of La-modified aluminas with La/Al = 0.05, heated at 1000 °C. (a) Secondary electron image, (b) reflection electron image.

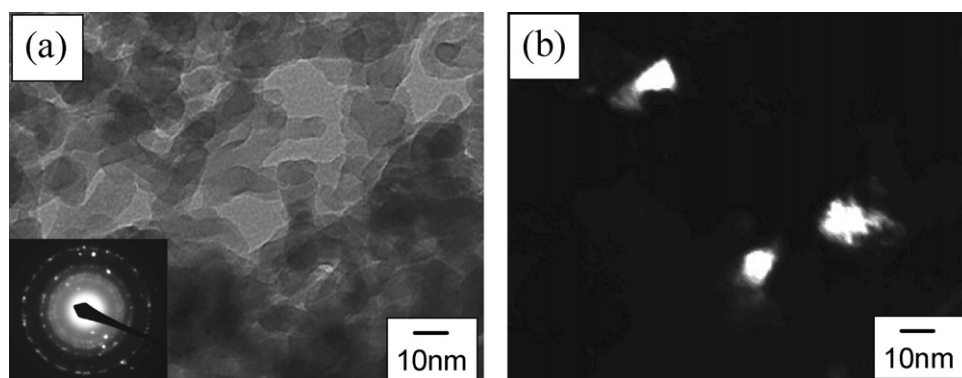


Fig. 4. TEM image of La-modified aluminas with La/Al = 0.05, heated at 1000 °C. (a) Bright field image, (b) dark field image.

La content when La/Al = 0.05, the sample has two parts of purely La-modified alumina and LaAlO₃ particle. This indicates that the small amount of lanthanum can effectively retard the sintering between alumina particles as well as phase transformation of γ to α phase of Al₂O₃. In addition, the LaAlO₃ as particulate state should have some role to maintain the microstructure of alumina catalyst, because LaAlO₃ thus its complex microstructure is thermodynamically stable phase. We have examined the effect of lanthanum to stabilize alumina catalyst support regarding on microstructural aspect, using the data of SEM and TEM, which are newly observed.

3.3. Microstructure

Fig. 3 shows the secondary electron (SEM) and reflection electron images (REM), which are carefully taken using SEM apparatus with high magnification and electron beam width of <3 nm in diameter. The sample is La-modified alumina with La/Al = 0.05 which was heated at 1000 °C for 3 h in air. The SEM indicates the microstructure of the agglomeration of alumina with 100 nm in size after heat treatment. The microstructure is the same as of the initial sample, however the grain growth is slightly higher as the effect of heat treatment. The REM image provided the novel information on microstructure, because the emission efficient of reflection electron is different between the elements including Al and La. In Fig. 3, the bright particles are observed only in the reflection electron image. The bright contrast suggests the high concentration of La, which is a heavier metal element than Al. The particle-size was determined as 10–20 nm in diameter, and existed at the inner part of the secondary particle of alumina. These particles are dispersed in the matrix of alumina, as in (b) of Fig. 3, which demonstrates the novel structure of alumina/LaAlO₃ nano-composite. Since the XRD indicates the crystalline phases of γ -Al₂O₃ and LaAlO₃, this

bright contrast should correspond to LaAlO₃. The solid-state reaction between Al₂O₃ and La₂O₃ lead to thermodynamically stable LaAlO₃. Then, the structure was analyzed by TEM as in Fig. 4. The TEM micrograph shows a set of bright and dark field image with high magnification. The electron diffraction contains ring-type polycrystalline patterns and some reciprocal lattice spots that correspond to γ -Al₂O₃ and LaAlO₃, respectively. The dark field image is obtained using a diffraction spot from (0 1 2) of LaAlO₃, so that the LaAlO₃ particle is highlighted as a bright area. The corresponding microstructure to both image are agreed as that the particles of LaAlO₃ exist in the nanometer particulate matrix of γ -Al₂O₃. Both phases consist of small grains in nanometer-size and combined each other to make a composite where particles with 10–20 nm in size are intersecting LaAlO₃ phase and its dispersing structure become due to the solid-state reaction after heat treatment, so that the composite catalyst is stable and heat resistant with respect of microstructure. The nano-composite, where LaAlO₃ particles have dispersed to stabilize the metastable γ -Al₂O₃ matrix, and its formation process are revealed for the first time in our study. Thus we propose an interesting nano-structured alumina catalytic material that is novel, stable and providing possible catalytic function.

4. Conclusion

Nanometer-ordered structural changes of lanthanum-modified γ -alumina at elevated temperature were examined for application toward novel heat-stable catalytic support. The SEM and TEM determined that the solid-state reaction between lanthanum oxide and alumina lead to the nanometer-ordered structure, where LaAlO₃ particles are dispersed in the secondary particles of alumina after heat treatment. The tailored La-modification to alumina support and its processing provides a novel nano-structured catalyst in

the system of La and alumina, which is very stable catalytic support at elevated temperatures.

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