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Effect of rare earth on the thermostability and the surface area of auto-catalyst washcoats

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Abstract

In this paper, the influence of rare earth on the thermostability and surface area of auto-catalyst washcoating was studied by XRD and BET analysis. The results showed that the modification of rare earth was positively effective for the thermostability of γ-alumina washcoating. With rare earth, the transformation temperature from γ-alumina to α-alumina was increased from 800°C to 1200°C. Rare earth oxides could improve the thermostability of γ-alumina washcoating better than rare earth nitrates. At the same time, the thermostability was also dependent on the loading amount of rare earth. To make the best thermostability of auto-catalyst washcoating, the additive content into γ-alumina was about CeO_2 6%wt, La_2O_3 8%wt. According to BET measurement, the biggest surface area of γ-alumina washcoating could be reached under the condition of CeO_2 10%wt, La_2O_3 2%wt. To modify auto-catalyst washcoating, the thermostability and surface area should be considered synthetically by adding the most appropriate amount of rare earth. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Auto-catalyst; Washcoating; Surface area; Thermostability

1. Introduction

It is popular that three-way catalysts (TWCs) are used to purify automotive exhaust gas emissions from internal combustion engines. The catalysts with precious metals (Pt, Rh or Pd) are the most widely used system, which have high catalytic activity for the oxidation of hydrocarbons, carbon monoxide and the reduction of NOx simultaneously. However, these catalysts are easily deactivated through surface area reduction in washcoating and precious metal sintering under high temperature. Therefore, it is necessary to improve their thermostability under high temperature condition.

Normally, catalyst consists of three principal components: washcoating, active elements (such as precious metals) and additives such as rare earth oxides. The efficiency of catalysts is strongly determined by the thermostability of alumina-based washcoating. There are two main ways to improve the thermostability of alumina washcoating. One is to prepare thermostable aluminas by adopting an appropriate procedure and controlling the structure and morphology of the aluminas. The other is to inhibit the sintering of active aluminas by adding some suitable additives. It has been reported that rare earth additives can improve the properties of catalysts and decrease the amount of precious metals at the same time [1–3].

The present paper mainly studied the effect of rare earth (RE) on the thermostability of alumina washcoating.

2. Experimental

2.1. Materials

The rare earth materials like $Ce_2(CO_3)_3$, La_2O_3, CeO_2 were used in the test. The surface area of alumina powder was 140 $m^2 g^{-1}$. A monolith cordierite having a honeycomb structure 62 square channels per cm^2 was taken as substrate.

2.2. Orthogonal experimental design

A three-level test, which studied the influence of rare earth on the thermostability of alumina, was designed on orthogonal method. Two parameters such as the additive amount of cerium (group P) and lanthanum (group Q)

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Table 1
Loading amount of rare earth for three-level experiments

	*P*1	*P*2	*P*3		*Q*1	*Q*2	*Q*3
CeO_2	2%	6%	10%	La_2O_3(%)	2%	5%	8%

were studied in the experiment. Based on rare earth oxides like CeO_2 and La_2O_3, an orthogonal table L_9 (3^4) (Table 2) was chosen and three levels of loading amount were listed in Table 1. A parallel experiment without any additives was studied at the same time.

Normally, the surface area (SA) and the amount of α-alumina (α-Al) were measured to quantitatively evaluate the thermostabilty of washcoating. Under the different loading amount of lanthanum and cerium oxides, the value of SA or α-Al was measured. And the mean value for each level of *P* or *Q* was demonstrated as *K*. To assess the effect of additive components on SA or the amount of α-alumina, the difference (*D*) of maximum *K* and minimum *K* among three levels of *P* or *Q* was calculated. The greater the value *D*, the more the effect. For example, a small value *D* meant that the effect was weak. By the way, $(P*Q)_1$ and $(P*Q)_2$ represented a combined effect of two parameters.

2.3. Preparation of $CeO_x/La_2O_3/Al_2O_3$ washcoating

$CeO_x/La_2O_3/Al_2O_3$ washcoating was prepared with two procedures of impregnation and kneading.

The kneading $CeO_x/La_2O_3/Al_2O_3$ (Sample A) was prepared by mixing the three oxides. The usable slurry was obtained by ballmilling three oxides with water. Some slurry was dried for 1 h at 400°C, then calcined in air at high temperatures for 2 h to get powder samples.

The impregnation $CeO_x/La_2O_3/Al_2O_3$ (Sample B) was prepared by impregnation of $La(NO_3)_3$ and $Ce(NO_3)_3$ into commercial pure alumina powder. With appropriate H_2O they were ball-milled. The slurry was dried for 1 h at 400°C, then calcined in air at high temperatures for 2 h to get powder samples. The nitrates were decomposed into oxides at high temperature.

The washcoatings were impregnated on monolith samples in slurries, with a length of 40 mm and a diameter of 16 mm, which were cut from honeycomb cordierite.

Table 2
Orthogonal experimental design (L_9 (3^4))

Sample	*P*	*Q*	$(P*Q)_1$	$(P*Q)_2$
0#	–	–	–	–
1#	1	1	1	1
2#	1	2	2	2
3#	1	3	3	3
4#	2	1	2	3
5#	2	2	3	1
6#	2	3	1	2
7#	3	1	3	2
8#	3	2	1	3
9#	3	3	2	1

Table 3
Effect of rare earth on the surface areas

	γ-Al_2O_3	γ-$Al_2O_3+Ce_2O_3$	γ-$Al_2O_3+La_2O_3$
T,°C	950	950	950
SA, $m^2\ g^{-1}$	19.2	132.5	135.7

2.4. X-ray powder diffraction (XRD) measurements

A Japan Science D/max-RB instrument was used for XRD test. Samples were scanned over the range $2\theta=20$–80° at 4° 2θ min^{-1}. For quantitative estimation of α-alumina, TiC was chosen as an internal standard. At 41.8° 2θ, TiC could give a clear peak, that was independent to all peaks of various forms of Al_2O_3. At the same time, the chosen peak of TiC was closed to the prime peak of α-alumina at 43.3° 2θ. The intensity of peaks was measured by step scanning in the 2θ range between 40° and 45° at 2° 2θ min^{-1}.

2.5. Surface area measurements

The specific surface area was determined by Brunauer–Emmett–Teller (BET) method from N_2 adsorption data at −196°C with a CHEMBET-3000 instrument.

3. Results and discussion

3.1. Effect of RE on the properties of alumina washcoating

The surface area of three alumina powder samples was listed in Table 3. At 950°C, the surface area increased with cerium oxide or lanthanum oxide added, which demonstrated that the thermostability of washcoating was improved by adding rare earth.

Fig. 1 showed the amount of α-alumina in Sample B5

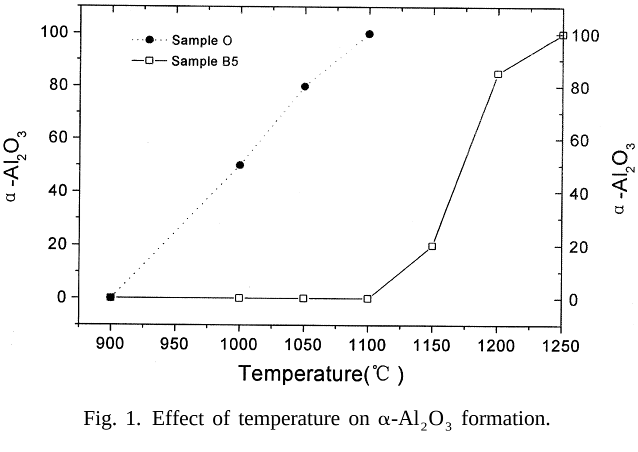


Fig. 1. Effect of temperature on α-Al_2O_3 formation.

(impregnation with 6%CeO_2, 5%La_2O_3) and Sample 0 (without rare earth additives) calcined at different temperatures for 2 h. It was calculated through XRD analysis. The XRD patterns of the two samples were similar below 900°C and no α-alumina was found. After heated at 1050°C for 2 h, the undoped-alumina converted to a great deal of α-alumina. And by 1100°C, it was totally transformed into α-alumina. In doped-alumina, however, δ- and θ-alumina were the main phases at 1100°C. A small quantity of α-alumina appeared by 1150°C, then a drastic increase of α-alumina happened in the range between 1150°C and 1200°C. So 1200°C was chosen as the calcining temperature in orthogonal experiments to find the effect of RE amount on the properties of supports. It also indicated the same result as Table 3 that RE oxides were effective additives for improving the thermostability of aluminas.

The transition from γ-alumina to α-alumina was a progress of phase nucleation and growth, and the nucleation sites were usually in oxygen vacancies or dislocations. [3] It was possible that the rare earth cations went into the interstitial positions of the alumina lattice and the oxygen vacancy concentration was decreased, so as to increase the temperature of phase transformation. At the same time, the size of rare earth cations was larger than Al^{3+}, which inhibited the transport of Al^{3+} and O^{2-} and retarded the sintering of washcoating as well as the phase transformation.

It had been reported that there was intensive reaction between lanthanum and alumina too [2]. The stabilization of γ-alumina by lanthanum was also supposed to be caused by the nucleation of the $LaAlO_3$ on the alumina surface [4–7]. $LaAlO_3$ interacted with the γ-alumina phase and inhibited its transformation toward α-alumina.

The XRD patterns of Sample B5 calcined at different temperatures, however, didn't show the presence of $LaAlO_3$ phase and La_2O_3 phase. Even at 1200°C, the crystalline phases observed were α-alumina and CeO_2. When the samples doped with cerium were calcined at high temperatures, a segregation of CeO_2 was found from XRD pattern instead of any Ce–Al–O compound. At the same test condition, the segregation of lanthanum oxide was not observed.

3.2. Effects of RE form added into washcoatings

Powder Samples A5 (mixing with 6%CeO_2, 5%La_2O_3) and B5 (impregnation with 6%CeO_2, 5%La_2O_3) were prepared. Rare earth oxides were added directly in Sample A5, and rare earth nitrates added in Sample B5. After calcined at high temperatures, in fact, nitrates were decomposed and rare earth oxides formed. Fig. 2 was the effect on the thermostability of washcoatings when rare earth oxides and rare earth nitrates added respectively. The results showed that the amount of α-alumina in Sample B5 was a bit larger than in Sample A5 at 1150°C and 1200°C. It meant that rare earth oxides improved the thermostability of washcoatings better than rare earth nitrates. Ce_2O_3 and CeO_2 were discovered in the XRD patterns, suggesting that the growth of cerium oxides in Sample A5 was much faster than in B5.

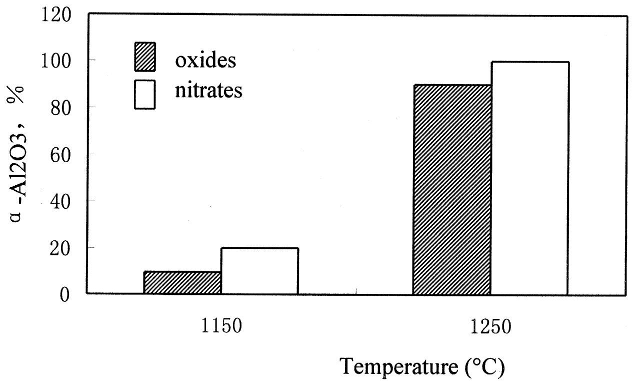
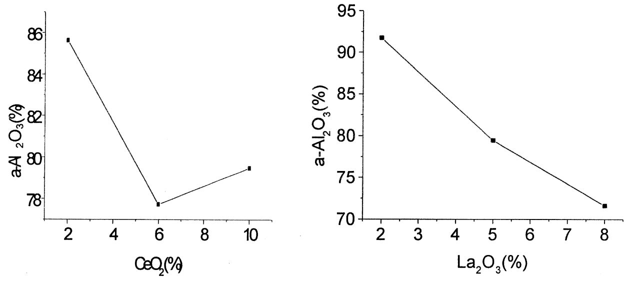


Fig. 2. The effect of RE forms on thermostability of washcoatings.

The outlook color was different between the samples added with rare earth oxides and rare earth nitrates. The former was pale yellow and the latter was yellow. It had been reported that Ce^{4+} was yellow after calcined in air [3], so it seemed that the amount of Ce^{4+} in B5 was more than in A5. On the contrary, there was more Ce^{3+} in A5 than in B5. It was reported that the thermostability increased with increasing ions size of the Ce in Ce-doped alumina [3]. As the size of Ce^{3+} was larger than Ce^{4+}, sample A5 had better thermostability.

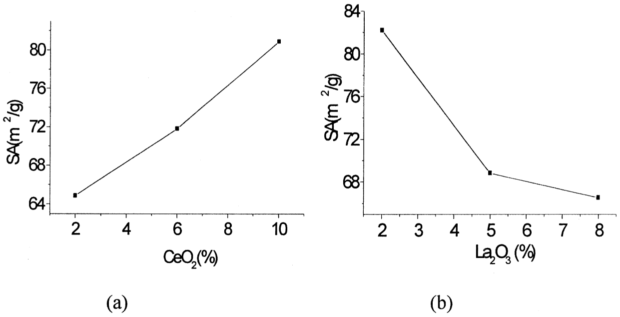
3.3. Effect of the amount of RE on thermostability

Fig. 3 showed the effect of rare earth loading quantity on the amount of α-alumina in washcoatings. The amount of α-alumina was obtained through XRD analysis of the powder samples calcined at 1200°C for 2 h. Fig. 3(a) presented that the amount of α-alumina decreased when the amount of cerium increased from 2 to 6%(CeO_2). If more cerium was added, however, the amount of α-alumina increase. Fig. 3(b) described that the influence of lanthanum on α-alumina formation was lightly different from that of cerium. With the increase of lanthanum



(a) (b)

Fig. 3. Effect of the amount of rare earth on the amount of α-alumina.



(a) (b)

Fig. 4. Effect of the amount of rare earth on the surface areas.

additives, the amount of α-alumina decreased continually. The results showed that the best thermostability of washcoatings could be made with 6%wt CeO_2 and 8%wt La_2O_3 in γ-alumina.

Fig. 4 presented the effect of rare earth loading quantity on the surface areas of washcoatings. With BET method, the surface areas were measured for $CeO_x/La_2O_3/Al_2O_3$ washcoatings calcined at 780°C. It could be found from Fig. 4 that the more cerium added, the larger the surface area of washcoatings. On the contrary, the more lanthanum, the smaller the surface area. It was probably that the formation of $LaAlO_3$ not only at the surface but also in the interior of the support made the amount of γ-alumina lessen. The results suggested that the biggest surface area of γ-alumina washcoatings after sintered could be reached with 10%CeO_2 and 2%La_2O_3 in γ-alumina.

According to the values of $D_{\alpha\text{-Al}}$ in Table 4, the biggest difference is found in $D_{Q,\ \alpha\text{-Al}}$, which suggests that lanthanum has more significant effect on the amount of α-alumina than cerium. At high temperatures, a segregation of cerium oxides occurred and the process was not happened for lanthana. Therefore, the alumina-dopant interaction was stronger for La-doping. The D_{SA} data showed that both lanthanum and cerium had significant effect on the surface area. However, cerium has a positive affection, and lanthanum shows a negative one. The results in Table 4 also suggest that the influence of the interaction between cerium and lanthanum was weak on the amount of α-alumina and surface area.

Table 4
Analysis of orthogonal experimental results

	P	Q	$(P \times Q)_1$	$(P \times Q)_2$
$D_{\alpha\text{-Al}}$	7.90	20.11	6.43	1.99
D_{SA}	16.053	15.638	5.255	6.340

4. Conclusions

1. Both lanthanum and cerium could contribute to the thermostability of aluminas. The thermostability of γ-alumina washcoatings could be improved by rare earth oxides better than by rare earth nitrates.
2. The thermostability was also dependent on the loading amount of rare earth. With the increase of cerium and lanthanum, the amount of α-alumina decreases. The best thermostability of washcoatings could be made with 6%wt CeO_2 and 8%wt La_2O_3 in γ-alumina.
3. The surface area increased when more cerium was added; but when too much lanthanum was added, the surface areas decreased. The biggest surface area of γ-alumina washcoatings after sintered could be reached with 10%CeO_2 and 2%La_2O_3 in γ-alumina.

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