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Effects of alkaline earths and rare earths added to sol–gel alumina on the thermostability and the oxidation activity of the mixed alumina-supported Pt catalysts

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Various alumina-based supports were prepared by adding metal elements such as alkaline and rare earths to sol–gel alumina synthesized from aluminium isopropoxide using 2-methylpentane-2,4-diol as a solvent and the influence of the additives on the thermostability of the supports was investigated. It was found that Ba and Sr are the most effective in improving the thermostability of the alumina, La is moderately effective while Zr, Mg and Ca are ineffective. The influence of the additives on the catalytic activities of $Pt/CeO_x/MO_y–Al_2O_3$ (M = Ba, Sr, La) after the calcination at 1273 K was also investigated. $Pt/CeO_x/BaO–Al_2O_3$ and $Pt/CeO_x/La_2O_3–Al_2O_3$ showed higher catalytic activity than $Pt/CeO_x/Al_2O_3$, while $Pt/CeO_x/SrO–Al_2O_3$ showed lower catalytic activity. The activity order was Ba > La = none > Sr in terms of CO and C_2H_4 oxidation.

Keywords: alumina; carbon monoxide oxidation; ethylene oxidation; platinum; cerium; sol–gel; thermostability

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1. Introduction

Alumina is widely used as a catalyst support [1]. In particular, alumina-based supports holding high surface area at high temperature are used for automobile exhaust gas purification catalysts. The recent automobile exhaust gas purification catalysts consist of three principal components: supports, precious metals and additives such as cerium oxide [2,3]. One drawback of these catalysts is that they tend to give rise to thermal deactivation caused by surface area reduction of the supports, sintering of precious metals and crystallization of additives such as cerium oxide [4].

It has been reported that the complexing agent-assisted sol–gel method is effective in obtaining thermostable aluminas [5] and the alumina synthesized from aluminium isopropoxide using 2-methylpentane-2,4-diol as a solvent has high thermal stability [6,7].

We have also reported that the iridium catalyst supported on this alumina shows higher catalytic activity for the decomposition of hydrazine than conventional catalysts [8] and the platinum and palladium catalysts supported on this alumina show higher activity for carbon monoxide and methane oxidation than conventional catalysts [9]. On the other hand, many oxides, such as baria, are effective in improving the thermal stability of alumina [10–12] and Ce is commonly included in automobile exhaust gas purification catalysts for other purposes [13]. However, the activities of precious metal catalysts supported on supports composed of a three-component system where Ce is impregnated have not been investigated systematically. The present work reports the properties of sol–gel alumina-based supports by adding metal elements such as alkaline earths and rare earths and discusses the catalytic activities of platinum catalysts supported on supports composed of a three-component system where Ce is simply impregnated.

2. Experimental

Preparation of two-component supports by impregnation. A sol–gel alumina was prepared from aluminium isopropoxide (AIP) using 2-methylpentane-2,4-diol (MPD) as a complexing agent [7]. Aluminium isopropoxide (AIP; 108 g) was added to a solution of MPD (120 g) and stirred at 393 K for 4 h in an oil bath. After lowering the bath temperature to 373 K, 90 g of water was added to the stirred mixture, kept at this temperature for 2 h, and then aged for 12 h at 353 K. The gel obtained was dried at 393–423 K, followed by calcining at 573 K for 1 h and 723, 873, 1073 and 1223 K for 3 h each.

The additives were introduced into the sol–gel alumina at 8 mol% content by a conventional impregnation technique using metal nitrates as raw materials. After drying overnight at 383 K, the nitrates were decomposed by calcination in air at 873 K for 2 h.

Thermal deterioration of the supports was investigated by calcining them at 1273 K for 20 h.

Preparation of three-component system (CeO_x/MO_y–Al_2O_3*) supports.* Supports composed of three components (CeO_x/Mo_y–Al_2O_3) were prepared as shown in fig. 1. The preparation of (CeO_x/*BaO*–Al_2O_3) is described below as typical example.

Aluminium isopropoxide (AIP; 60.4 g) and 1.7 g of $Ba(acac)_2 \cdot 2H_2O$ were added to a solution of MPD (120 g) and stirred at 393 K for 4 h in an oil bath. After lowering the bath temperature to 373 K, 90 g of water was added to the stirred mixture, kept at this temperature for 2 h, and then aged for 12 h at 353 K. The gel obtained was dried at 393–423 K, followed by calcining at 573 K for 1 h and 723, 873, 1073 and 1223 K for 3 h each. CeO_x was introduced into this BaO–Al_2O_3 at 8 mol% content by a conventional impregnation technique using $Ce(NO_3) \cdot 6H_2O$ as raw material. After drying overnight at 383 K, the composite was calcined at 873 K for 2 h to decompose the nitrate.

Preparation of Pt catalysts. The 1 wt% $Pt/CeO_x/MO_y$–Al_2O_3 (M: metal additives) catalysts were prepared by impregnating the supports with an aqueous solution of $Pt(NO_3)_2(NH_3)_2$. The metal contents of these catalysts were measured by atomic adsorption analysis. To evaluate the thermostability of the catalysts, they were calcined at 1273 K for 4 h before measuring the catalytic activity.

Surface area measurements. The specific surface area was determined by the BET method from N_2 adsorption data at −196°C using a Micromeritics AccuSorb 2100.

X-ray diffraction (XRD) measurements. The XRD patterns were obtained on a MAC Science MXP-18 instrument using Cu Kα radiation with Ni filter. The extent of the crystallinity, i.e. wt% of α-alumina content, was calculated from the integrated intensity of the (113) reflection from γ-alumina and of broad reflections near 44–48° from transition aluminas by comparison with a calibration curve of known MPD alumina at 1273 K and a fully crystallized one. Broadness of the latter peak and small (202) reflection from α-alumina prevented the determination of the accurate value over 90% of crystallization.

Catalyst activity. CO oxidation reactions over the alumina-supported Pt catalysts (0.10 g) were carried out in a conventional fixed bed flow-type reactor. The

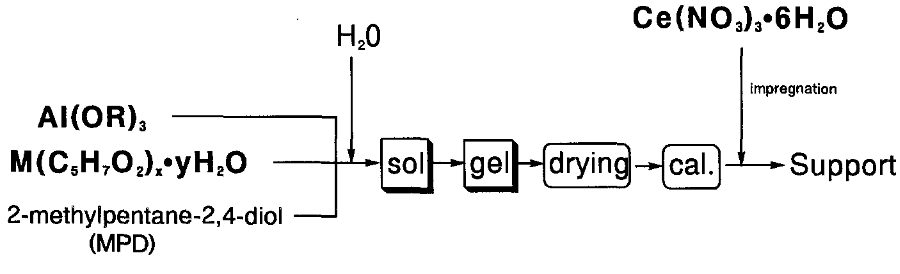

Fig. 1. Support preparation procedure by the complexing agent-assisted sol–gel method.

catalysts were first treated in a hydrogen stream with a flow rate of 100 ml/min at 673 K for 1 h, and then the reaction gas, a mixture of CO, O_2 and He in a ratio of 0.5 : 0.25 : 99.25, was allowed to flow through the catalyst bed. The effluent gas was led directly to sampling valves of a gas chromatograph for analysis. The catalytic activity was estimated from the calculated CO conversion.

X-ray photoelectron spectropy (XPS) measurements. The catalysts were analyzed by X-ray photoelectrons using VG ESCA Lab MK II.

3. Results and discussion

As it has been reported that MPD alumina is one of the thermostable aluminas [7] and that the addition of alkaline and rare earths is one of the effective ways to inhibit the sintering of alumina [10–12], a series of MPD alumina-based supports were prepared by a conventional impregnation technique using nitrates of alkaline and rare earths. The supports calcined at 1273 K for 20 h were compared with the corresponding non-impregnated MPD alumina in terms of the BET surface area and the extent of the crystallinity of the aluminas.

Fig. 2 summarises the results with four alkaline earth (Ba, Sr, Ca, Mg), five rare earth (La, Ce, Sm, Eu, Ho) and two other (Y, Zr) elements. Higher BET surface areas were seen for MPD alumina-based supports except Zr, Mg, Y and Ca than for the non-impregnated MPD alumina. Ho, Sm, Eu, Ba, Sr and Ce were effective in point of BET surface area and La was a little effective. The transformation temperature to α-alumina is higher for all the additive-impregnated aluminas than for non-impregnated MPD alumina. Among them, Ho, Sm, Eu, Ce, Y, Mg and Ca were a little effective, La and Zr were moderately effective while Ba and Sr were the most effective. These results indicate that the addition of Ba, Sr and La improves the thermostability of the supports.

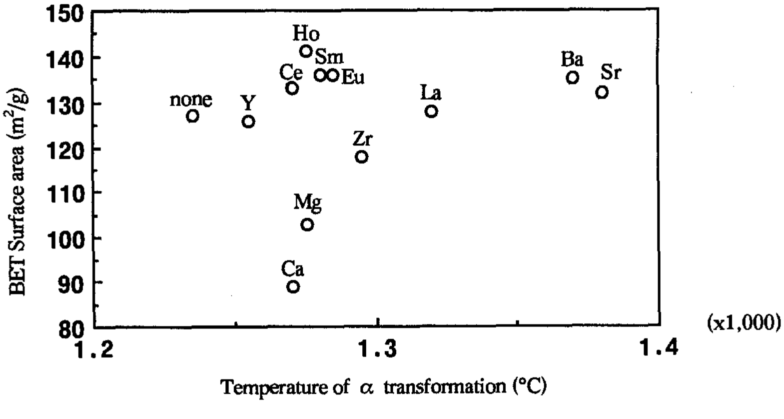

Fig. 2. BET surface area and α-alumina transformation temperature of sol–gel alumina added with 8 mol% of various oxides and calcined at 1273 K for 20 h.

On the basis of this and the above results, alumina-based supports containing Ba, Sr or La were prepared by the complexing agent-assisted sol–gel method and Ce was introduced at concentrations of 8 mol% by a conventional impregnation technique using nitrate. After that, the 1 wt% $Pt/CeO_x/MO_y–Al_2O_3$ (M: Ba, Sr or La) catalysts were prepared by a conventional impregnation technique using the aqueous solutions of $Pt(NO_3)_2(NH_3)_2$. Activities of the alumina-supported Pt catalysts ($Pt/CeO_x/MO_y–Al_2O_3$) for CO and C_2H_4 oxidation were investigated after calcination at 1273 K for 4 h. Fig. 3 shows the CO oxidation reactions with the $Pt/CeO_x/BaO–Al_2O_3$, $Pt/CeO_x/SrO–Al_2O_3$, $Pt/CeO_x/La_2O_3–Al_2O_3$ and $Pt/CeO_x/Al_2O_3$ catalysts calcined at 1273 K for 4 h. Higher activity was seen for $Pt/CeO_x/BaO–Al_2O_3$ than for $Pt/CeO_x/Al_2O_3$, but lower activity was seen for $Pt/CeO_x/SrO–Al_2O_3$ than for $Pt/CeO_x/Al_2O_3$. The activities of $Pt/CeO_x/La_2O_3–Al_2O_3$ and $Pt/CeO_x/Al_2O_3$ were almost the same. The activity order was $Ba > La = none > Sr$ in terms of CO oxidation. Fig. 4 shows the C_2H_4 oxidation reactions with $Pt/CeO_x/BaO–Al_2O_3$, $Pt/CeO_x/SrO–Al_2O_3$, $Pt/CeO_x/La_2O_3–Al_2O_3$ and $Pt/CeO_x/Al_2O_3$ catalysts calcined at 1273 K for 4 h. $Pt/CeO_x/BaO–Al_2O_3$ also showed the highest level of activity, but the differences among the catalysts were larger than those seen for CO conversion.

The following investigations were carried out to elucidate the reasons for the differences in conversion efficiencies with respect to Pt and CeO_x. The Pt dispersion of both the $Pt/CeO_x/BaO–Al_2O_3$ and $Pt/CeO_x/SrO–Al_2O_3$ catalysts was measured by the CO adsorption method. The value of these two catalysts was 0.04 ml/g. Accordingly, from these results it was impossible to discern why the catalytic activity of $Pt/CeO_x/SrO–Al_2O_3$ is low. Therefore, the cerium oxides of both the

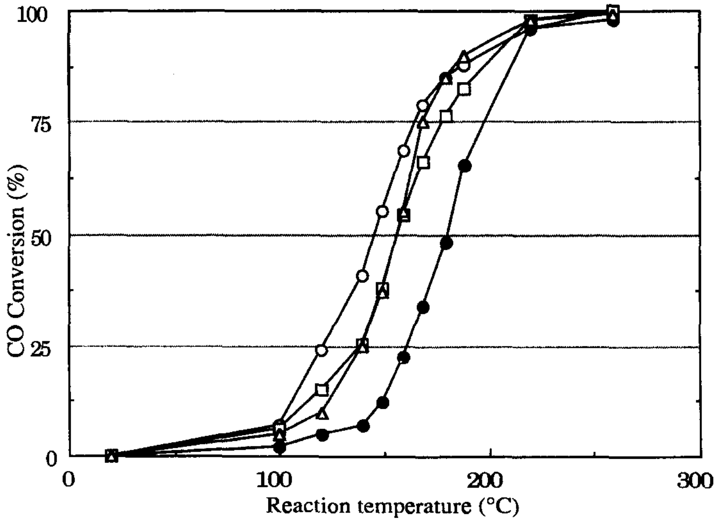

Fig. 3. Oxidation of CO with four alumina-supported Pt catalysts calcined at 1273 K for 4 h. (○) $Pt/CeO_x/BaO–Al_2O_3$, (△) $Pt/CeO_x/La_2O_3–Al_2O_3$, (□) $Pt/CeO_x/Al_2O_3$, (●) $Pt/CeO_x/SrO–Al_2O_3$.

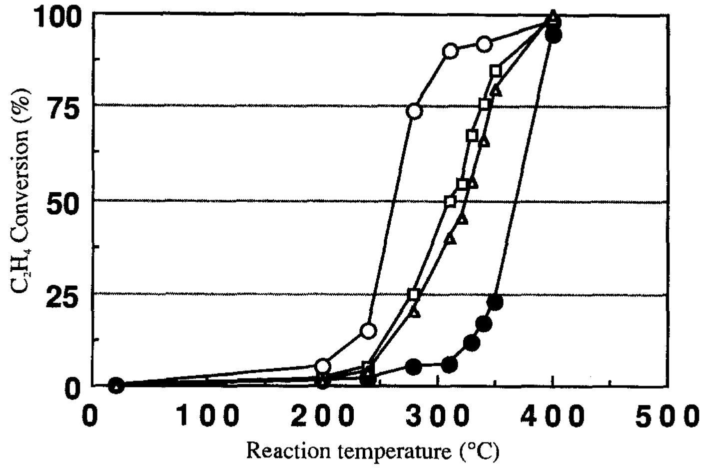

Fig. 4. Oxidation of C_2H_4 with four alumina-supported Pt catalysts calcined at 1273 K for 4 h. (○) Pt/CeO_x/BaO–Al_2O_3, (△) Pt/CeO_x/La_2O_3–Al_2O_3, (□) Pt/CeO_x/Al_2O_3, (●) Pt/CeO_x/SrO–Al_2O_3.

Pt/CeO_x/BaO–Al_2O_3 and Pt/CeO_x/SrO–Al_2O_3 were also investigated by XRD. Table 1 shows the crystallite size and lattice constant of cerium oxide of these catalysts. It is seen that the crystallite size of cerium oxide of Pt/CeO_x/SrO–Al_2O_3 is larger than that of the Pt/CeO_x/BaO–Al_2O_3 and the cerium oxide lattice constants of these catalysts are unchanged. These results suggest that a substantial solid solution does not occur, but crystallization of cerium oxide of Pt/CeO_x/SrO–Al_2O_3 occurs much higher than crystallization of cerium oxide of Pt/CeO_x/BaO–Al_2O_3. It is deduced that the low activity of Pt/CeO_x/SrO–Al_2O_3 is mainly due to the prevention of the redox interaction between Pt and Ce. Furthermore, the catalysts were investigated using XPS with respect to the Pt. In general, it is possible to obtain information within about 3 nm from surface by XPS. The content of Pt at surface of the Pt/CeO_x/BaO–Al_2O_3 and Pt/CeO_x/Al_2O_3 catalysts was 0.08–0.09 at%, while the content of Pt at surface of Pt/CeO_x/SrO–Al_2O_3 was 0.06 at%. These results show that the Pt amount of Pt/CeO_x/SrO–Al_2O_3 at surface was a little smaller than the others. As already reported by us [8], the catalytic activity for the decomposition of hydrazine is dependent on the surface amount of Ir. It is also

Table 1
Crystallite size and lattice constant of cerium

Catalyst	Cerium oxide crystallite (Å)	Lattice constant (Å)
Pt/CeO_x/BaO–Al_2O_3	130	5.413
Pt/CeO_x/SrO–Al_2O_3	150	5.413
Pt/CeO_x/Al_2O_3	140	5.414

deduced that the low activity of $Pt/CeO_x/SrO–Al_2O_3$ is due to the small amount of Pt at surface.

4. Conclusion

The addition of Ba, Sr and La improves the thermostability of sol–gel aluminas synthesized from aluminium isopropoxide using 2-methylpentane-2,4-diol as a solvent. The addition of Ba improves the catalytic activities of the mixed alumina-supported Pt catalyst where Ce is included while the addition of Sr does not improve the catalytic activities of the mixed alumina-supported Pt catalyst. The activity order of the mixed alumina-supported Pt catalysts was found to be $Ba > La = none > Sr$ for CO and C_2H_4 oxidation. The support composed of a three-component system($CeO_x/BaO–Al_2O_3$) prepared by the complexing agent-assisted sol–gel method is concluded to be one of the most thermostable supports for automotive catalysts.

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