Effects of preparation method of CeO_x–Al_2O_3 on the thermostability and activity of the monolith supported Pt–Rh catalysts for automotive exhaust control

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Various CeO_x–Al_2O_3 powders were prepared and the influence of the method of support preparation on the thermostability of the mixed alumina-supported Pt catalysts and on their oxidation of CO was investigated. It was found that the complexing agent-assisted sol–gel method is effective in improving the thermostability of the mixed alumina-supported Pt catalysts. Monolith Pt–Rh three-way catalysts were prepared using these aluminas and other thermostable alumina including Ba. Activity of the catalysts was also investigated after conducting accelerated thermal engine aging in order to test their durability. Under normal operating conditions of the automobile engine, the activity of the Pt–Rh three-way catalyst using the CeO_x–Al_2O_3 support prepared by the complexing agent-assisted sol–gel method is nearly equal to that of the catalyst using the CeO_x impregnated onto BaO–Al_2O_3 powder prepared by the same sol–gel method.

Keywords: support; cerium; alumina; sol–gel; thermostability; platinum; three-way catalyst

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1. Introduction

The three-way catalyst for automotive exhaust control consists of three principal components: supports, precious metals and metal oxide additives [1,2]. Alumina-based supports such as CeO_x–Al_2O_3 retaining high surface area at high temperature are widely used in automobile exhaust gas purification catalysts in order to stabilize precious metals [3]. One drawback of the catalysts is that they tend to suffer from thermal deactivation caused by surface area reduction of supports, sintering of precious metals and crystallization of additives [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 (AIP) using 2-methylpentane-2,4-diol (MPD) as a solvent has high thermal stability [6,7]. We have also reported that the platinum and palladium catalysts supported on this alumina show higher activity for carbon monoxide and methane oxidation than conventional catalysts [8]. However, supports of a two-component system (CeO_x–Al_2O_3) have not yet been prepared by the complexing agent-assisted sol–gel method and the influence of the support preparation method of CeO_x–Al_2O_3 on the thermostability of platinum catalysts supported on the alumina have not been investigated sufficiently. Moreover, the durability of monolith in Pt–Rh three-way catalysts using the CeO_x–Al_2O_3 and thermostable alumina including baria has also been investigated sufficiently, though it is known that baria is effective in improving the thermal stability of alumina [9–11]. We have prepared CeO_x–Al_2O_3 using the sol–gel method and carried out investigations on the thermostability of platinum catalysts supported on the alumina and the durability of monolith Pt–Rh three-way catalysts using the alumina and other thermostable aluminas.

2. Experimental

Preparation of CeO_x–Al_2O_3 support by the complexing agent-assisted sol–gel method. CeO_x–Al_2O_3 support was prepared by the complexing agent-assisted sol–gel method (fig. 1). 60.4 g of AIP (Wako) and 1.7 g of $Ce(C_5H_7O_2)_3$ (Dojin Kagaku) were added to 120 g of MPD (Tokyo Kasei) and stirred at 120°C for 4 h in an oil bath. AIP and MPD were used without further purification. After lowering the bath temperature to 100°C, 90 g of water was added to the stirred mixture, kept at this temperature for 2 h, and then aged for 12 h at 80°C. The gel obtained was dried at 120–150°C, followed by calcining at 300°C for 1 h and 450, 600, 800 and 950°C for 3 h each.

Preparation of CeO_x–Al_2O_3 support by impregnation technique. A sol–gel alumina was prepared from AIP using MPD as a complexing agent [7]. 108 g of AIP was added to 120 g of MPD and stirred at 120°C for 4 h in an oil bath. After lowering the bath temperature to 100°C, 90 g of water was added to the stirred mixture,

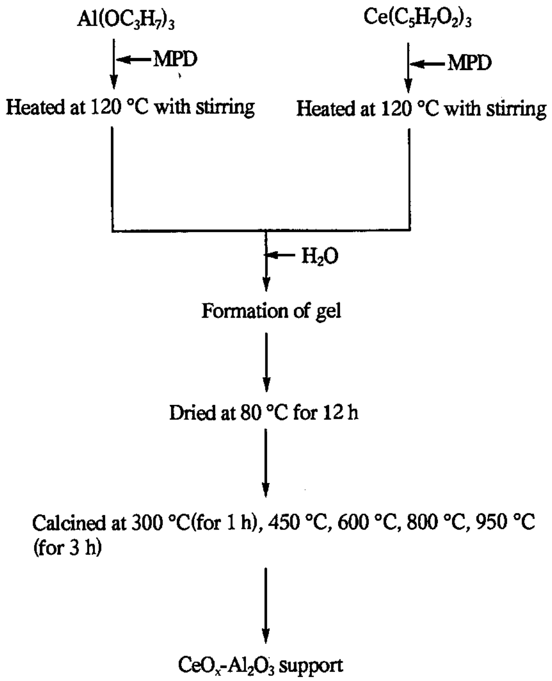

Fig. 1. Procedure for preparation of CeO_x–Al_2O_3 support by the complexing agent-assisted sol–gel method.

kept at this temperature for 2 h, and then aged for 12 h at 80°C. The gel obtained was dried at 120–150°C, followed by calcining at 300°C for 1 h and 450, 600, 800 and 950°C for 3 h each. The cerium was introduced into the sol–gel alumina at 8 mol% content by a conventional impregnation technique using $Ce(NO_3)\cdot 6H_2O$ (Wako) as the raw material. After drying overnight at 110°C, the nitrate was decomposed by calcination at 600°C for 2 h.

Preparation of the Ce-impregnated BaO–Al_2O_3 support. 60.4 g of AIP and 1.7 g of $Ba(C_5H_7O_2)_2\cdot 2H_2O$ (Soekawa Rikagaku) were added to 120 g of MPD and stirred at 120°C for 4 h in an oil bath. After lowering the bath temperature to 100°C, 90 g of water was added to the stirred mixture, kept at this temperature for 2 h, and then aged for 12 h at 80°C. The gel obtained was dried at 120–150°C, followed by calcining at 300°C for 1 h and 450, 600, 800 and 950°C 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 110°C, the composite was calcined at 600°C for 2 h to decompose the nitrate.

Preparation of Pt catalysts. The 1 wt% Pt/CeO_x–Al_2O_3 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 absorption analysis. To evaluate the thermostability of the catalysts, they were calcined at 1000°C for 4 h before measuring the catalytic activity.

Preparation of monolithic Pt–Rh three-way catalysts. The catalyst was prepared by washcoating a 400 cell per cm^2 cordierite monolith body. The washcoat composition consisted of a combination of platinum and rhodium in a 5 : 1 weight ratio. Monolith cores of 120 cm^3 volume were used for the engine experiments.

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.

Activity of Pt catalysts. CO oxidation reactions over the alumina-supported Pt catalysts (0.10 g) were carried out in a conventional fixed bed flow-type reactor. The catalysts were first treated in a hydrogen stream with a flow rate of 100 ml/min at 400°C 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 CO conversion calculated.

Activity of monolithic Pt–Rh three-way catalysts. In order to study the durability of the monolithic Pt–Rh three-way catalysts using thermostable aluminas such as CeO_x–Al_2O_3 support by the complexing agent-assisted sol–gel method, they underwent an accelerated aging whose mode is 60 s cruising + 5 s fuel cut [12]. The monolithic catalysts were then evaluated in engine A/F perturbation test. The test adapted a 2 ℓ in-line six-cylinder EGI engine. The evaluation temperature was 400°C and the perturbation was a frequency of 1 Hz and an amplitude of 1.0 A/F.

3. Results and discussion

Conversion efficiencies of the mixed alumina-supported platinum catalysts (Pt/CeO_x–Al_2O_3) for carbon monoxide were investigated after calcination at 1000°C. Fig. 2 shows the carbon monoxide conversion efficiencies obtained with the platinum catalysts supported on CeO_x–Al_2O_3 prepared by the complexing agent-assisted sol–gel method (Pt/sol–gel CeO_x–Al_2O_3), platinum catalysts supported on CeO_x–Al_2O_3 prepared by impregnation using MPD-Al_2O_3 (Pt/impreg CeO_x–Al_2O_3 (MPD)) and platinum catalysts supported on CeO_x–Al_2O_3 prepared by impregnation using commercial Al_2O_3 (Pt/impreg CeO_x–Al_2O_3 (commercial)). For the catalysts, the Pt/sol–gel CeO_x–Al_2O_3 catalyst showed much higher activity than the Pt/impreg CeO_x–Al_2O_3 (MPD) and Pt/impreg CeO_x–Al_2O_3 (commercial). Next, as baria is known to form thermostable oxides on account of the ion radius and electric charge [13], BaO–Al_2O_3 was prepared by the complexing agent-assisted sol–gel method and CeO_x was impregnated onto the BaO–Al_2O_3 support (impreg-sol–gel CeO_x–BaO–Al_2O_3). The monolith Pt–Rh three-way catalyst was prepared using this alumina in order to test its durability and compare with the catalyst using sol–gel CeO_x–Al_2O_3. Monolithic Pt–Rh three-way catalysts were also prepared using impreg CeO_x–Al_2O_3 (MPD) and impreg CeO_x–Al_2O_3 (commercial)

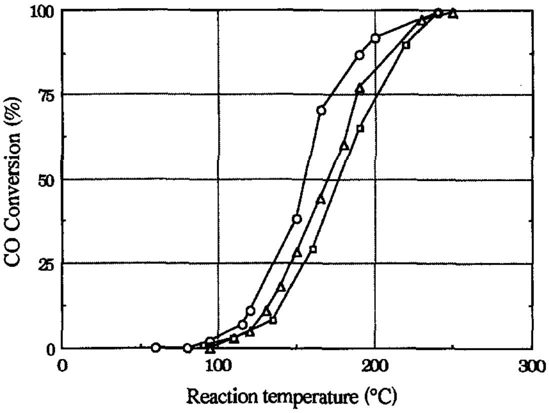

Fig. 2. Oxidation of CO with three mixed alumina-supported Pt catalysts calcined at 1000°C for 4 h. (○) Pt/sol–gel CeO_x–Al_2O_3, (△) Pt/impreg CeO_x–Al_2O_3 (MPD), (□) Pt/impreg CeO_x–Al_2O_3 (commercial).

in order to test their durability. Activity of the catalysts was investigated after conducting accelerated thermal engine aging at 850°C. The HC, CO and NOx conversions at 400°C for these catalysts under normal operating conditions of the automobile engine are shown in fig. 3. Higher CO and NOx conversions were seen for the catalyst using the sol–gel CeO_x–Al_2O_3 and the catalyst using the impreg-sol–gel CeO_x–BaO–Al_2O_3 than for the catalyst using impreg CeO_x–Al_2O_3 (MPD) and impreg CeO_x–Al_2O_3 (commercial). HC, CO and NOx conversions of the catalyst using the sol–gel CeO_x–Al_2O_3 are nearly equal to those of the catalyst using the impreg sol–gel CeO_x–BaO–Al_2O_3.

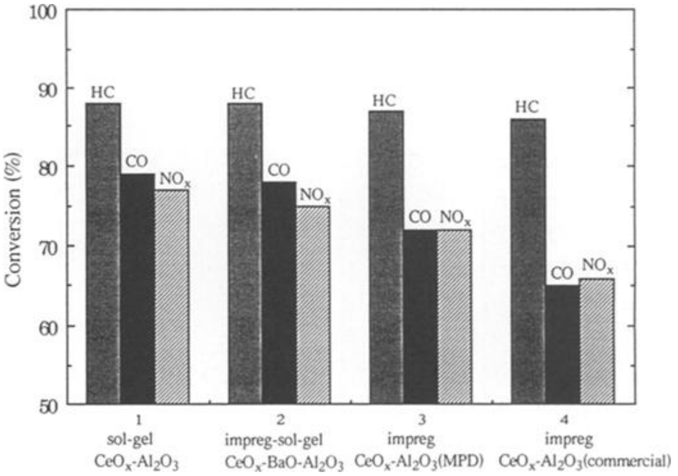

Fig. 3. Activity of four monolith Pt–Rh catalysts using various thermostable aluminas under normal operating conditions of the automobile engine at 400°C after accelerated thermal engine aging at 1000°C for 50 h.

The following investigation was carried out to elucidate the reasons for the differences in conversions with respect to the alumina structure. It is well known that the change of alumina structure is often accompanied with the change of surface area [8]. Fig. 4 shows the specific surface areas of the platinum catalysts after calcination at 1000°C for 4 h. The specific area of Pt/sol–gel CeO_x–Al_2O_3 was similar to that of Pt/impreg-sol–gel CeO_x–BaO–Al_2O_3 and the specific surface areas of the two catalysts were much higher than those of Pt/impreg CeO_x–Al_2O_3 (MPD) and Pt/impreg CeO_x–Al_2O_3 (commercial). From the foregoing results, it was found that the activity ranking of the Pt–Rh three-way catalysts using the sol–gel CeO_x–Al_2O_3, Pt–Rh three-way catalysts using the impreg-sol–gel CeO_x–BaO–Al_2O_3, Pt–Rh three-way catalysts using impreg CeO_x–Al_2O_3 (MPD) and Pt–Rh three-way catalysts using impreg CeO_x–Al_2O_3 (commercial) corresponded with the surface areas of the aluminas used.

4. Conclusion

The complexing agent-assisted sol–gel method was shown to improve the thermostability of CeO_x–Al_2O_3. Under normal operating conditions of the automobile engine, higher activity was seen for the Pt–Rh three-way catalyst using the sol–gel CeO_x–Al_2O_3 and the catalyst using the impreg-sol–gel CeO_x–BaO–Al_2O_3 than for the catalyst using CeO_x–Al_2O_3 (MPD) and CeO_x–Al_2O_3 (commercial) after conducting accelerated thermal engine aging. The activity of the Pt–Rh three-way catalyst using the sol–gel CeO_x–Al_2O_3 was nearly equal to that of the catalyst using the impreg-sol–gel CeO_x–BaO–Al_2O_3.

It was concluded that the sol–gel CeO_x–Al_2O_3 is one of the most thermostable supports for automotive three-way catalysts.

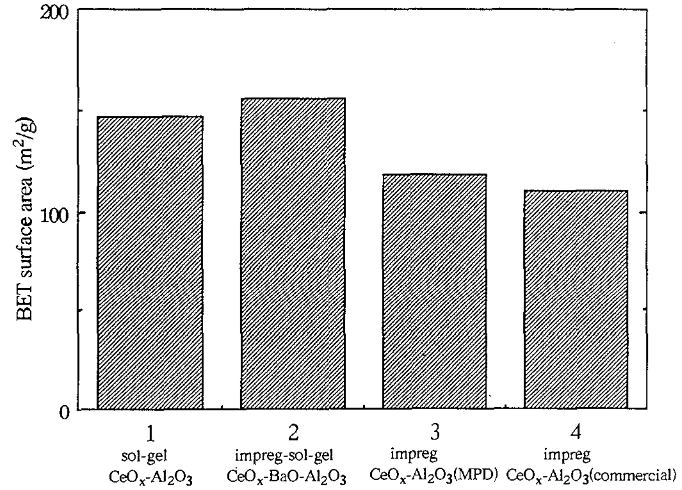

Fig. 4. BET surface area with four mixed alumina-supported Pt catalysts calcined at 1000°C for 4 h.

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