Preparation of Pt-Co alloy nanoparticles supported on γ-Al_2O_3 and its application for automotive exhaust purification

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Abstract: Alloy nanoparticles consisting of trace amount of noble metal and other non-noble metal is expected as one of the potential strategies for reducing quantity of noble metal in the catalysts. In this research, we prepared Pt-Co alloy nanoparticles supported on γ-Al_2O_3 (Pt-Co/γ-Al_2O_3) and investigated catalyst performance for automotive exhausts purification. This Pt-Co/γ-Al_2O_3 has characteristic fine structure and electronic properties and showed good performance for automotive exhausts purification.
Keywords: alloy nanoparticle, bimetallic catalyst, elements strategy.

1. Introduction

Platinum (Pt) is one of the most important noble metals for industrial application. Catalysts are major use of Pt because Pt shows excellent performance for various chemical reactions. However, Pt is very scares and expensive element. Therefore development of an inexpensive and highly active catalysts including less amount of Pt is strongly demanded. It is well known that structural and electrical properties of metal are drastically changed by alloying with other kind of element, which results in drastic enhancement of the catalytic properties[1]. On the bases of such background, alloy nanoparticles consisting of trace amount of Pt and other non-noble metal is one of the potential strategies for reducing quantity of Pt in the catalysts. In this presentation, we report that Pt-Co alloy nanoparticle catalyst (Pt-Co/γ-Al_2O_3) has interesting fine and surface electronic structure and we applied this catalyst for automotive exhaust purification which is one of the most important applications of Pt as catalyst.

2. Experimental

γ-Al_2O_3 (Sumitomo Chemical) was suspended in aqueous solution including $Pt(NH_3)_4(NO_3)_2$ (Sigma-Aldrich) and $Co(NO_3)_2\ (H_2O)_6$ (Wako). After removing water and drying at 70 ºC for 12 h, the sample was calcined at 450 ºC for 5 h, reduced under flowing H_2 at 850 ºC, 1h and Pt-Co/γ-Al_2O_3 was obtained. Loading amounts of Pt and Co were set to 0.1 and 1.0 wt%, respectively. γ-Al_2O_3 supported monometal catalysts, 0.1 wt% Pt/γ-Al_2O_3 and 1.0 wt% Co/γ-Al_2O_3, were prepared as reference by same procedure.

X-ray absorption fine structure (XAFS) measurements of Pt-L_{III} edges and the infrared spectra of adsorbed CO were performed in order to investigate fine structure and surface electronic properties.

Catalytic activity tests for three-way reaction were carried out using a fixed-bed flow reactor. The reaction mixture simulates automotive exhaust with a theoretical air-to-fuel ratio. The catalyst bed was heated from room temperature to 600 °C, and the exit composition of the gases was continuously monitored with a chemiluminescence NO_x analyser and a non-dispersive infrared gas analyser.

3. Results and discussion

Pt L_{III}-edge XAFS spectra for Pt-Co/γ-Al_2O_3 and reference samples after H_2 reduction were examined. XANES spectra of Pt-Co/γ-Al_2O_3, Pt/γ-Al_2O_3 and reference Pt foil were almost same. On the other hand, EXAFS oscillation of Pt-Co/γ-Al_2O_3 was completely different from that of Pt foil and Pt/γ-Al_2O_3. In FT of EXAFS (Fig. 1), characteristic Pt-metal bond which is shorter than Pt-Pt bond appeared in Pt-Co/Al_2O_3 and is assignable to Pt-Co bond in hcp type structure by curb fitting of the spectra. These results suggest that major parts of Pt species in Pt-Co/γ-Al_2O_3 were reduced to Pt^0 and formed characteristic fine structure, i.e. Pt formed alloy nanoparticle with Co.

To understand surface electronic properties of the Pt-Co nanoparticles, we examined the states of adsorbed probe CO with using FI-IR (Fig. 2). Over Pt/γ-Al_2O_3, a sharp band appeared at 2079 cm^{-1}. It has been assigned to linear CO molecules adsorbed on Pt[2]. On the other hand, over Pt-Co/γ-Al_2O_3, this peak was shifted to lower wave number, 2059 cm^{-1}. This peak shift indicates that the strength of the carbon-oxygen bond of adsorbed CO was weakened. We considered such behavior of adsorbed CO is induced by electron enrichment of Pt in Pt-Co alloy. Pt has higher electronegativity compared to that of Co and thus charge transfer from Co to Pt occurred. Then back donation of d-electron from the electron enriched Pt to anti-bonding π orbital of CO occurred, which results in weakening of carbon-oxygen bond of CO.

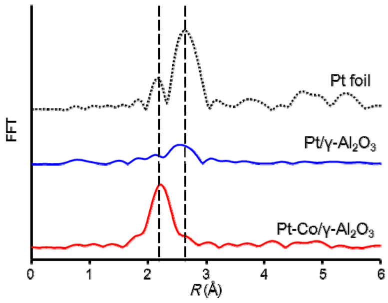

Figure 1. Pt L_{III}-edge Fourier transform of EXAFS spectra of Pt- Co/γ-Al_2O_3 and Pt-/γ-Al_2O_3.

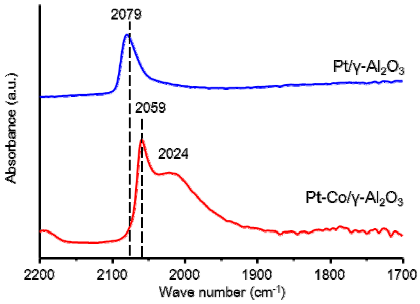

Figure 2. Difference IR spectra of CO molecules on Pt-Co/γ-Al_2O_3 and Pt-/γ-Al_2O_3.

The catalytic activity for automotive exhaust purification of Pt-Co/γ-Al_2O_3 and each monometal catalyst were measured in light-off mode. Here we focused on NO*x* reduction ability. As Fig. 3 shows, Pt-Co/γ-Al_2O_3 showed lowest light-off temperature, 200 ºC, and NO*x* conversion increased sharply. Furthermore, until 400 ºC, Pt-Co/γ-Al_2O_3 showed higher NO*x* conversion compared to that of Pt/γ-Al_2O_3 and Co/γ-Al_2O_3. These results suggest that synergistic effects between Pt and Co were induced by formation of alloy nanoparticle and enhanced catalytic activity of Pt-Co/γ-Al_2O_3.

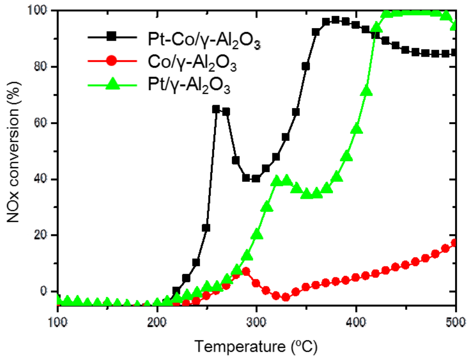

Figure 3. NO*x* reduction activity for Pt-Co catalyst and each monometal catalyst.

4. Conclusions

We prepared γ-Al_2O_3 supported Pt-Co alloy nanoparticle catalyst and revealed that this Pt-Co/γ-Al_2O_3 shows better catalytic performance for automotive exhaust purification. Over the surface of Pt-Co alloy nanoparticle, electron enriched Pt site was formed due to charge transfer from Co to Pt. We conclude such characteristic Pt site plays important roles for enhancing catalytic activity.

References

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