Nanoparticles catalyst for reducing Pt and Pd by using nano-structured CeO_2/ZrO_2 materials in exhaust treatment

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Abstract:

Ceria zirconia support with core-shell structure was investigated for possible exhaust treatment by low-content Pt and Pd catalysts. A novel CeO_2/ZrO_2 nanocomposite support was obtained by precipitation of CeO_2 nanoparticle followed by heat treatment on pure zirconia surface. The support was characterized by X-ray diffraction, Raman spectra, transmission electron microscopy and energy dispersive spectroscopy. The improvement of composite catalysts in oxidation and three way catalytic (TWC) activities was explained because of surface modified structures which prefer to make better interaction for catalytic activity. Improvement of conversion was speculated due to the modification of surface modification with CeO_2 nanoparticles and thin layers, so that the controlled dispersion of metals on CeO_2/ZrO_2 nanocomposite would accelerate to reactions even when the amount of precious metals was reduced.

Keywords

Three-way catalyst, ceria, ceria-zirconia, core-shell, support, oxygen storage capacity

1. Introduction

The precious metals including Pt, Rh ad Pd are among the rarest metals on earth, and have always been reflected by present and future demand in industries toward environmentally conscious vehicle manufacture. They have been widely employed as three way catalysts (TWCs) and diesel oxidation catalysts so far, and recent technology has achieved the recycle in the spent catalysts for recovering original resources. However, since the wider use of such catalysts and future industrial requirement will bring the requirement of essentially reducing the noble metals contents, it is important to examine the catalysts with better combination between ceria-based support and metals in exhaust treatment. In this work, we examined the stabilized CeO_2 nanoparticles (NPs) as a support for low-content precious metal catalyst.

2. Experimental

Cerium salts solution was prepared at room temperature under a stirred condition followed by addition of ammonia aqueous solution, then the produced precipitates was transferred to heat at 200°C for 48 hours. The composite support of CeO_2-NPs/ZrO_2, which was demonstrated for application as new type CZ was prepared by the same process in a previous paper.[3)] Pt and Pd catalysts, supported by CeO_2 nanoparticles and the prepared CeO_2/ZrO_2 composite support, were prepared by the impregnation process. The catalysts were characterized by XRD, Raman spectra, and TEM-EDS and other techniques. The H_2 temperature programmed reduction (H_2-TPR) experiments were performed from 30 to 600 °C at a heating rate of 10 °C/min in flowing 5 vol% H_2/Ar as a reducing gas. The CO chemisorption was measured at 25 °C after the sample was treated by flowing H_2/He at 400 °C. TWC activity (light off) was evaluated in a continuous flow reactor under a model exhaust gas mixture with space velocity of 300,000 ml g^{-1} h^{-1}.

3. Results and discussion

The starting CeO_2 nanoparticles (NPs) support was originally isolated nanocrystals one another, but partially coalescences microstructure among NPs resulting in micrometer-sized aggregates after heat

treatment at elevated temperatures. The diameter of CeO_2 NPs was ca.6 nm after heat treatment at 400 °C, followed by treatment at 600 °C. The effect of CeO_2 NPs in different supports on Pt catalysts will be discussed regarding with reduced Pt amount. The novel CeO_2/ZrO_2 (CZ) support contained CeO_2 particles of ca.5-8 nm in diameter on the surface of ZrO_2. Each CeO_2 NPs were coated and dispersed with one or less than two layers at the least and covering the ZrO_2 surface. There is no evidence regarding with the formation of complete solid solution by both XRD and Raman scattering.

H_2-TPR measurements of supports showed that OSC value (at 600 ℃) increased with CeO_2 content and mixing of CeO_2 and ZrO_2 induced effective increase of OSC per Ce fraction in support powders. Also, H_2-TPR measurements revealed that the reducibility of Pt and Pd species supported is different among CeO_2 and other CZs, and the addition of small amount CeO_2 induced lower temperature reducibility. The H_2 consumption in TPR appeared in the low temperature region below 100 °C and H_2 was associated with the effectively metallic Pt and Pd combined with lattice oxygen in CeO_2 NPs after the cycled TPR treatment. However, the reduction profiles of Pt/CZ and Pd/CZ with very low metal contents showed almost single peak in each reaction temperature, and carried with metals content from low to high temperatures with decreasing metals content. The behavior was different from those of Pt and Pd/CeO_2(NPs), and peak temperatures were lower than those of Pt/CeO_2 when the same loading samples were compared.

The light-off removal properties of NO, CO and C_3H_6 were compared among different amount of Pt and Pd which were doped on CeO_2 and CZ. The catalysts showed that CO oxidation was first enhanced, and then C_3H_6 oxidation and NO reduction occur simultaneously. In addition to enhanced CO oxidation, C_3H_6 oxidation was promoted immediately to produce intermediate reductant species to NO resulting in the enhancement of three-way catalytic performance. Both 1.0 wt% metal catalysts using two different suppors (CeO_2 and core-shell CZ) showed the same performance in light-off TWC profiles. When the content was lower to 0.1wt%, a novel CZ showed better TWC performance than that of CeO_2 (NPs). Thus, it was found that TWC activity was enhanced by designed nanostructured core-shell type CeO_2/ZrO_2 support.

4. Conclusions

Novel nanostructured ceria-zirconia support with core-shell structure has been investigated for Pt and Pd three way catalysts. The nanocomposite support was obtained by precipitation of CeO_2 nanoparticle followed by heat treatment on pure zirconia surface, allowing us to obtain interesting morphology and the stabilized dispersion observed for CeO_2 nanoparticles. The present CeO_2/ZrO_2 will provide the improved OSC properties, and H_2-TPR indicated the better reducibility of Pt and Pd catalyst supported by present CeO_2/ZrO_2. It was found that novel CeO_2/ZrO_2 support lead to better activity for as low content Pt and Pd catalyst, and nanoparticles-based catalyst was possibly useful for reducing Pt and Pd by using nano-structured CeO_2/ZrO_2 materials in exhaust treatment

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