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Core-shell type ceria zirconia support for platinum and rhodium three way catalysts

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ABSTRACT

Ceria zirconia support with core-shell structure was investigated as a novel item for platinum and rhodium three way catalysts (TWC). Core-shell type CeO_2/ZrO_2 nanocomposite support was obtained by precipitation of CeO_2 nanoparticle followed by heat treatment at 800 °C on pure zirconia surface. A novel support was characterized by X-ray diffraction, Raman spectra, transmission electron microscopy and energy dispersive spectroscopy. The interesting morphology and dispersion were observed for pure CeO_2 nanoparticles on pure ZrO_2; thus, it can provide a number of active sites, resulting in the total oxygen storage capacity (OSC) value of 2.7 ml/g when Ce/Zr = 1/9. As to supported catalysts, the repeated TPR induced high dispersion and reducibility of Pt and Rh supported on present CeO_2/ZrO_2 support. The TWC activities of Pt catalyst are enhanced by a designed core-shell type ZrO_2/CeO_2 support. In addition to enhanced CO oxidation, C_3H_6 oxidation was promoted immediately to produce intermediate reductant species for NO reduction, resulting in the enhancement of TWC performance. It was confirmed that a new support does not have a negative effect on the TWC of Rh/ZrO_2.

1. Introduction

The incorporation of ceria and stabilized ceria into automotive catalyst was a major advance in the ability of three way catalyst (TWC) to perform at high efficient pollution control [1–15]. The TWC requires totally high catalytic activity in various operating parameters under steady state, dynamic or transient condition. The ability to storage/release oxygen through redox processes involving the Ce^{4+}/Ce^{3+} couple enables CeO_2-based materials to possess oxygen storage capacity (OSC), which is very effective for higher removal efficiencies under A/F (air/fuel) variation. For this, many studies have been carried out about ceria, and especially OSC materials using ceria zirconia based composite supports. Essentially, when the selected ceria zirconia catalysts depending on Ce/Zr ratio in solid solution are used, they can buffer most effectively A/F fluctuation under various conditions. Although OSC is the most important factor besides catalytic metal itself, other factor is the synergistic interactions between the ceria or ceria zirconia and the dispersed precious metals. During the exposure to a cyclic gas feed with alternating O_2 and CO or H_2, the dynamic behavior of ceria containing catalysts must be considered regarding with reversible change of component (both metal and OSC catalysts) and removal reaction performance [15–21]. Recent industrial requirement is the reducing of the noble metals contents towards saving resources and lowering cost of catalyst, which will be applied to small engine cars and motorcycles using the modified TWC technology. For this purpose, pure ceria is very effective and of capability to control the interaction of Ce-O-M(metal) on support surface [22–32]. In addition, it has been recently reported that CeO_2 nanoparticles (NPs) and low dimensional nanorods show the high activities in redox behavior [33–40]. However, CeO_2 with nanometer dimensions in size cannot be effectively stabilized at elevated temperatures in general; thus, there has been a problem that ideal property of CeO_2 NPs catalyst will not be realized as “practical NPs”. The impact of Ce to TWC has been discussed with mixing of Ce-Zr composition, nanoparticle state and the interaction with noble metals so far. The OSC is one successful example of the established design concept which is based on novel materials invention and their combination using ceria zirconia solid solution. Other desirable trend is

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to provide novel item and such nanomaterials, and their design technique with practical level, including proposed composition and microstructures as supports and catalysts.

Along this context, we will propose a novel composite support of CeO_2-NPs dispersed on ZrO_2, and demonstrate its application to three way catalysts. Contrasting to famous CeO_2-ZrO_2 solid solution, there are a few studies that focus on heterogeneous state in the system of CeO_2-ZrO_2 [41–46]. The interface between CeO_2 and ZrO_2 plays some role for stabilization and dispersion for CeO_2 NPs which will be structured on coherent ZrO_2 surface. Such stabilized CeO_2 NPs will provide better interaction of noble metals (Pt) with pure CeO_2, leading to characteristic TWC activities, which are more effectively improved by ZrO_2/CeO_2 NPs/metal nanostructure. Based on this idea for a new ceria zirconia, we examine core-shell type support for platinum and rhodium three way catalysts in this work. In addition to materials characterization of the prepared core-shell type CeO_2/ZrO_2 support, the light-off TWC performance over Pt and Rh catalysts supported are examined under dynamic model mixed gas flow. The results are useful to provide a new model and a support material toward development of future TWC catalysts using CeO_2 NPs.

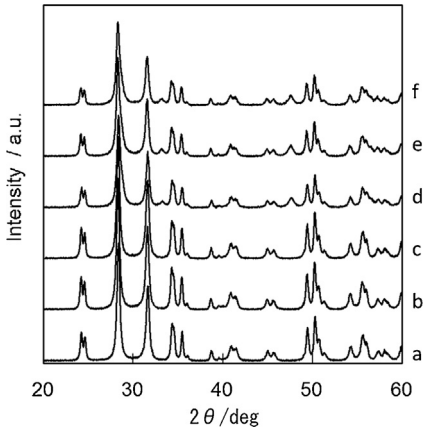

Fig. 1. XRD patterns of supports and catalysts; (a) ZrO_2 (monoclinic), (b) Pt/ZrO_2, (c) Rh/ZrO_2, (d) CeO_2/ZrO_2, (e) Pt/CeO_2/ZrO_2, (f) Rh/CeO_2/ZrO_2.

2. Experimental

2.1. Catalyst preparation

In the preparation of ceria-zirconia support, Ce species was mixed by pure zirconia powder (Toso TZ-0, Japan) with an aqueous mixed solution an equimolar of diammonium cerium(IV) nitrate ($(NH_4)_2Ce(NO_3)_6$, 95 +%, Wako Pure Chemical, Japan) and potassium oleate ($C_{33}H_{17}COOK$, 19% solution, Wako Pure Chemical, Japan). The mixture of Ce/Zr = 1/9 (molar ratio) as the solution was agitated for 1 h in air, followed by addition of excess amount of ammonia aqueous solution (NH_3, 25% solution, Wako Pure Chemical, Japan) under a vigorously stirred condition for 1 h. The related preparation method of CeO_2 nanoparticles has been examined by other works [47]. The powder was separated from the solution by centrifugation and then washed with distilled water three times and dried at 90 °C for 15 h in air. It was heated at 600 °C, and fol-

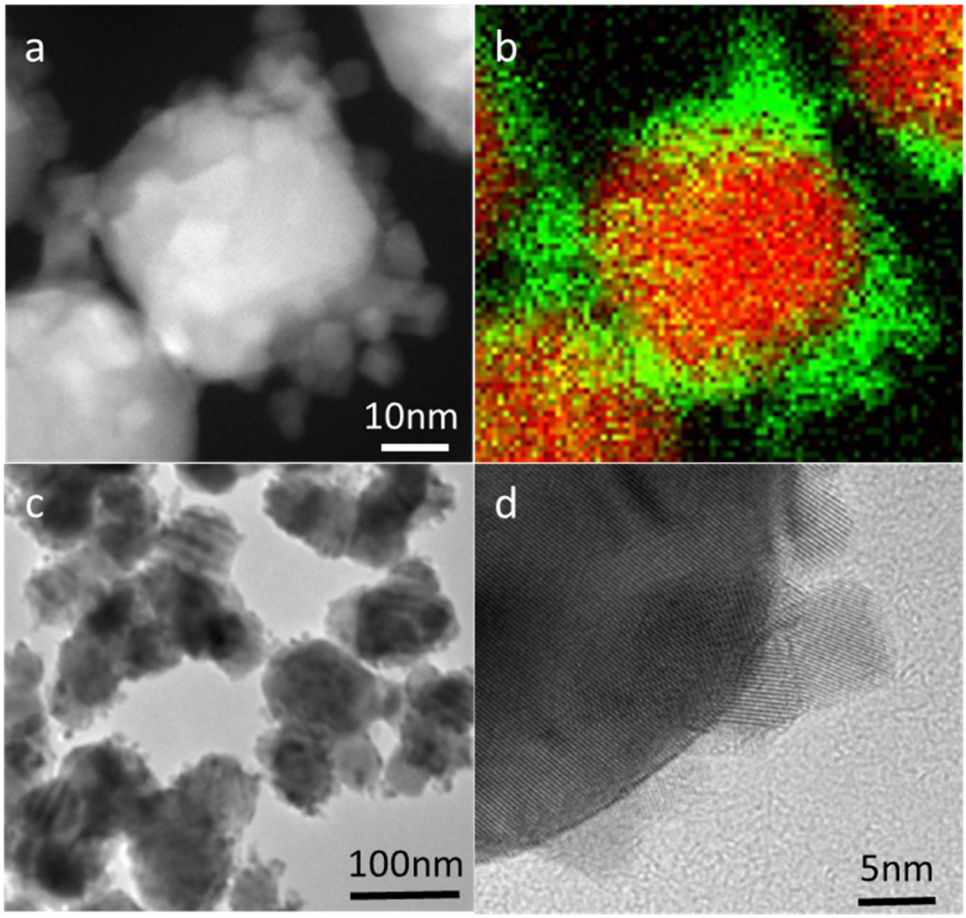

Fig. 2. Transmission electron analysis of CeO_2/ZrO_2 support; (a) STEM image of a core-shell type CeO_2/ZrO_2 particle, (b) EDS elemental mapping of corresponding area to (a), (c) TEM image of CeO_2/ZrO_2 samples under low magnification, (d) TEM image of interface region in a composite particle.

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