Dispersion state and oxygen storage capacity properties of ceria and zirconia nanoparticles supported on alumina by the impregnation process

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Abstract. The characterization of the phase and oxygen storage capacity of ZrO₂, CeO₂, and mixed oxides, which were supported on Al₂O₃ by the impregnation method, was performed for the development of a better sub-catalyst in the exhaust treatment. Regarding the dispersion on the alumina support, the behavior of ZrO₂ is different from that of CeO₂; CeO₂ becomes crystalline nanoparticles on Al₂O₃, while majority of ZrO₂ do not form well-structured particles. We found that the oxygen storage capacity of cerium was improved by the addition of ZrO₂ to CeO₂ in the case of alumina-supported mixed oxides.

1. Introduction

In the field of environmental technologies, the treatment of the engine exhaust is an important issue which should be resolved to control air pollution. The three way catalyst (TWC) is used to remove carbon monoxide, hydrocarbons, and nitrogen oxides, emitted during the high- and low-temperature operation of an engine. The best performance of TWC is shown around a certain oxygen pressure corresponding to the ideal air/fuel (A/F) condition. The role of a sub-catalyst of the oxygen storage capacity (OSC), such as CeO₂ and CeO₂-ZrO₂, is very useful in order to maintain the partial pressure of oxygen with fluctuation of A/F. Therefore, Ce and Zr are the most important elements of a sub-catalyst in TWC with dispersed Pt and other noble metals on the support.[2,3] In addition, the OSC should be improved by surface and bulk properties as well as the interface in the system of CeO₂ by the addition of ZrO₂.[4] However, the dispersed state of CeO₂ and ZrO₂ themselves, when they are supported on alumina, has not been characterized even though the two metal oxides have similar fluorite structures. Since the catalyst is generally a composite powder with multi-components as well as the preparation process, the characterization of the fundamental microstructure about the nanoparticle materials is important for advanced performance and optimization of catalysts. The impregnation method using aqueous salts and support is widely used in preparing catalysts. In this work, we compare the phase and coordination state of CeO₂, ZrO₂, and CeO₂/ZrO₂, which were...
dispersed and supported on alumina via the impregnation process, using XRD, Raman scattering, and TEM, as well as OSC catalytic properties.

2. Experimental

2.1. Synthesis and characterization of catalyst

γ-Al2O3-supported Ce1-xZrxO2/Al2O3 (x=0, 0.2, 0.8, and 1.0) catalysts were prepared by the impregnation method, using a mixed aqueous solution of cerium nitrate Ce(NO3)3·6H2O (Wako, 99.9% purity), zirconyl nitrate ZrO(NO3)2·6H2O (Wako, 99.9% purity), and the γ-Al2O3 powder (Sumitomo chemical, surface area: 105 m²/g), followed by drying and calcination at 600°C for 5 h in air. The mixture was then calcined at 800°C for 5 h in air. The mixing molar ratio of alumina:ceria and/or the zirconia catalyst was 100:30. Pt/Ce1-xZrxO2/Al2O3 catalysts were prepared by impregnation of a solution of Pt(NO3)2(NH3)2 to three supports, alumina, CeO2/Al2O3, and ZrO2/Al2O3, followed by drying and calcination at 600°C for 5 h in air. Catalyst samples were further heated at 1000°C for 5 h in air to examine the dispersion effect of CeO2 and ZrO2 and also the catalytic performance of Pt.

2.2. Characterization

XRD patterns were recorded using a Rigaku Rint X-ray diffractometer (Japan). Samples were scanned using CuKα radiation with a Ni filter over the range of 2θ from 20 to 80° at 40 kV and 20 mA. JCPDS cards were used for identification of the crystals. Clustered species in the powders were identified by laser Raman spectroscopy (JASCO NRS-3100) using a 532 nm laser. A transmission electronic microscope (TEM, Jeol JEM2000EX) was used to observe the morphology of dispersed CeO2 and ZrO2 in the samples.

2.3. Evaluation of catalytic properties

The OSC was measured by injecting an O2 gas pulse of 1.0 ml at 600°C on 0.1 g of the catalyst samples preheated in flowing H2/Ar at 800°C. The temperature programmed reduction with hydrogen (H2-TPR) was monitored using a TCD-type detector during heat treatment of the sample in flowing H2/Ar up to 800°C at a rate of 10°C min⁻¹. The specific surface area was measured by the nitrogen gas adsorption at 77 K after heat treatment at 200°C in flowing nitrogen for 2 h. The reaction conditions for the Pt catalyst was as following: 0.1 g of the catalyst at temperatures of 50-600°C, after heat treatment of catalysts under 10% H2/N2 up to 600°C, at a flow rate of 500 ml min⁻¹ of mixed gases containing 3345 ppm of C3H6, 0.5 vol% of O2, and a N2 balance under a space velocity of 300,000 lkg⁻¹h⁻¹.

3. Results and discussion

3.1. Characterization of microstructure

Figure 1 shows the XRD patterns for the Ce1-xZrO2/Al2O3 (x=0, 0.2, 0.8, and 1.0) catalysts. The XRD patterns of the samples heated at 800°C showed the formation of crystalline metal oxides and γ-Al2O3 in the catalysts. For the powders with x=0 and 0.2, the XRD showed the strong diffraction intensities of a cubic symmetry corresponding to fluorite-type oxides. Broad tetragonal phase patterns appeared in the composition of x=0.8 and 1.0, which were indicated by weaker diffraction intensities with broaden peaks of γ-Al2O3. In addition, the diffraction angle of all fluorite peaks was observed to shift to higher angles with decreasing CeO2. The peaks of the present samples are not symmetrical because of the inhomogeneous mixed state of Ce and Zr oxides.[5] The fact that peak intensities decreased with increasing ZrO2 suggested higher dispersion of Ce-Zr oxides on alumina when the ZrO2 content becomes dominant.
Figure 1. X-ray diffraction patterns of Ce$_{1-x}$Zr$_x$O$_2$/Al$_2$O$_3$: (a) $x=0$, (b) $x=0.2$, (c) $x=0.8$, (d) $x=1.0$, and (e) $\gamma$-Al$_2$O$_3$.

Figure 2. Raman spectra of Ce$_{1-x}$Zr$_x$O$_2$/Al$_2$O$_3$: (a) $x=0$, (b) $x=0.2$, (c) $x=0.8$, (d) $x=1.0$, and (e) $\gamma$-Al$_2$O$_3$.

Figure 2 shows the Raman spectra for Ce$_{1-x}$Zr$_x$O$_2$/Al$_2$O$_3$ ($x=0$, 0.2, 0.8, and 1.0). Raman scattering reveals more detailed information on the whole evolution about the symmetry of the coordinated complex between the metal and oxygen in Ce$_{1-x}$Zr$_x$O$_2$ on $\gamma$-Al$_2$O$_3$. Since the average arrangement of atoms for coherent lattice larger than ca.5 nm can be observed in the XRD, Raman scattering is preferable to detect the atomic scaled structure. The scattering intensity of the Al$_2$O$_3$ support was very weak because of the defective gamma-phase (spinel structure), as well as the very small (distorted) crystal less than 10 nm in diameter. In the present catalysts, the intensity of Raman scattering was very weak for the ZrO$_2$-rich samples ($x=1.0$, 0.8), while that of the CeO$_2$-rich samples showed clear scattering amplitude from highly symmetrical fluorite (CeO$_2$). The results suggest that the formation of the crystalline CeO$_2$-based solid solution occurs only in the CeO$_2$-rich sample, but major parts in the ZrO$_2$-rich sample or very small particles of the solid solution in which the coordination is disordered are in the non-crystalline state. Thus, majority of ZrO$_2$ exist as a highly dispersed and defective state.
with fluctuation of coordination between Zr and O, so that symmetry uncertainty for Zr-O interaction is assumed.

Figure 3 shows the TEM images of Al₂O₃ nanoparticles in Ce₁₋ₓZrxO₂/Al₂O₃ (x=0 and 1.0). For CeO₂/Al₂O₃, the nanoparticles of CeO₂ are observed as the coverage on Al₂O₃ decreases. However for ZrO₂/Al₂O₃, there are dark grains with no particulate shape of ZrO₂ on Al₂O₃. The TEM observation is consistent with the results of Raman scattering spectra, by which a clear symmetry of Zr-O was not observed due to very low Raman intensities. The measured specific surface area (SA) was 105.1 m²/g for a pure alumina support, 63.1 m²/g for x=0, 63.5 m²/g for x=0.2, 80.1 m²/g for x=0.8, and 85.8 m²/g for x=1.0 in Ce₁₋ₓZrxO₂/Al₂O₃. The SA suggests that the coating (adsorbed) layer of ZrO₂ on the Al₂O₃ surface corresponds to a small decrease of SA. For CeO₂/Al₂O₃, the formation of CeO₂ particles on Al₂O₃, with a single nanometer size, may lead to a decrease of SA more than that of ZrO₂/Al₂O₃. The impregnation process is different from the coprecipitation of mixed oxides, because the absorption properties of each species should influence the final microstructure. In the present case, the stronger interaction (adsorption) of Zr on alumina seems to cause more dispersed ZrO₂ with a non-crystalline state which creates layer coverage on alumina.

Figure 3. TEM images of (a) CeO₂/Al₂O₃ and (b) ZrO₂/Al₂O₃.

3.2. OSC and catalytic properties

Table 1 lists the total OSC for the catalysts which are measured by TPR up to 800°C, followed by oxygen pulse absorption at 600°C. The results indicate that the OSC becomes larger following the order of Ce₀.₈Zr₀.₂O₂/Al₂O₃ > CeO₂/Al₂O₃ > Ce₀.₂Zr₀.₈O₂/Al₂O₃ > ZrO₂/Al₂O₃ > Al₂O₃. The OSC should first depend on the content of CeO₂ in composite powders. On the other hand, ZrO₂ addition has improved the OSC because the best OSC is observed in Ce₀.₈Zr₀.₂O₂/Al₂O₃ in this work. Although this indicates the positive effect of ZrO₂ addition when co-impregnated to an alumina support on the OSC per Ce of Ce₁₋ₓZrxO₂/Al₂O₃, more studies should be conducted by comparing the results of the bulk-state CeO₂-ZrO₂ (with no alumina). In fact, the OSC per Ce is a half of the bulk state of Ce₀.₂Zr₀.₈O₂ from the coprecipitation process [6]. It will be caused by the incomplete (noncrystalline) solid state of Ce₀.₂Zr₀.₈O₂ on Al₂O₃. The OSC is essentially the property of the bulk state to release and store oxygen in the crystal lattice when the solid solution of CeO₂-ZrO₂ is effectively used. A previous paper has proposed special crystal structures depending on the mixing of Ce and Zr and the synthesis method [7]. However, the best crystal structure has not been clear so far in the case of very small and dispersed particles on Al₂O₃. In the microstructure driven by the usual impregnation process, followed by heat treatment, all nanoparticles do not have an ideal crystal structure. Majority of the ZrO₂ species exist as a highly dispersed state on the alumina support in this work. However, with regards to the oxygen storage capacity (OSC), higher capacity properties are expected by doping ZrO₂, such as in Ce-Zr to complete the oxide solid solution. Although a more detailed examination is required for a better composite catalyst and shorter processing time when using this system in future work, the present study has clarified the state of character about the nanoparticles dispersion or symmetry of the
metal and oxygen of CeO₂ or ZrO₂ on Al₂O₃ via the simple impregnation process. The effect of ZrO₂ addition to CeO₂ on the alumina support will improve the CeO₂ catalyst for realizing the dispersed state of a catalytic composition.

Table 1. Oxygen storage capacity of catalysts

| X in Ce₁₋ₓZrxO₂ | 0.0 | 0.2 | 0.8 | 1.0 | Al₂O₃ |
|-----------------|-----|-----|-----|-----|-------|
| OSC (ml/g) *₁    | 4.0 | 4.7 | 1.7 | 0.1 | <0.1 |

*₁ oxygen storage capacity per gram of Ce₁₋ₓZrxO₂/Al₂O₃

Finally, the performance of the Pt catalyst using three supports, Al₂O₃, CeO₂/Al₂O₃, and ZrO₂/Al₂O₃, was compared by the complete oxidation activity of propylene. The conversion efficiency to CO₂ was 91% for CeO₂/Al₂O₃, 20% for ZrO₂/Al₂O₃, 8% for Al₂O₃ at 400°C, and 100% for CeO₂/Al₂O₃, 51% for ZrO₂/Al₂O₃, and 48% for Al₂O₃ at 500°C. The result indicated that the best removal performance was obtained by the Pt/CeO₂/Al₂O₃ catalyst. It suggests that the strong interaction between Pt and CeO₂ improves the catalytic performance of the total oxidation of hydrocarbons. The effect of Ce, Zr, and Al oxides on oxidation over Pt is becoming an open question within the aspect of an atomic scale [8]. However, the microstructural feature of these compositions in the present work could become a useful basis to reveal the microstructure of nanometer-scale materials in complex compositions of Ce, Zr, and Al₂O₃, as well as Pt.

4. Summary
We have performed a comparative study on the phase and dispersion of CeO₂, ZrO₂, and ZrO₂-CeO₂ which are supported on alumina. Novel result on the dispersion of ZrO₂ in alumina was found using Raman scattering and TEM observation. With regards to the dispersion on the alumina support, the behavior of ZrO₂ is different from CeO₂: CeO₂ becomes crystalline nanoparticles on Al₂O₃, while majority of ZrO₂ do not form well-structured particles. The results of the catalytic performance concluded that the OSC was improved by mixing ZrO₂ to CeO₂ in the present system of Ce₁₋ₓZrₓO₂/Al₂O₃.

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