

In-situ XAFS Analysis on Redox Dynamics of Precious Metal-supported Ce Complex Oxides

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Significance and Relevance

In-situ XAFS studies on the fine structure and oxygen storage dynamics of CeO_2 -based complex oxides with precious metals were performed at the BL14B1 and BL14B2 beamlines at SPring-8. H₂ and CO were used as reducing gases, and their differences were analyzed. The results showed no change in the fine structure of Ce and near elements after reduction by either gas, though CeO₂ was reduced faster by H₂ than CO. These results indicated the need for evaluation using real vehicle model gases due to differences in reduction rates and the many species of emissions gases in real vehicle environments_{[1][2]}.

Introduction and Motivations

The automotive industry has reached a turning point, and emissions regulations for internal combustion engine vehicles are being further tightened. In Europe, On-Board Monitoring (OBM) regulations are scheduled to be introduced in EURO7 from 2025 onward, creating an immediate need for technological innovation in internal combustion engine vehicles. In particular, On-Board Diagnostics (OBD) standards will be tightened, requiring precise management of the deterioration of the Oxygen Storage and release Capacity (OSC) of precious metal-loaded ceria-based complex oxides.

Materials and Methods

In this study, oxygen storage and release dynamics and the fine structure of CeO₂-based complex oxide with Pd were analyzed by Conventional and Dispersive XAFS at

| Table 1. Percentage | of sample | contained in | n the sam | ple |
|---------------------|-----------|--------------|-----------|-----|
| Table III Clecifuge | or sample | eonica n | | P |

| Sample | Oxide weight ratio | | | Composition (Atomic ratio) | |
|-------------------|--------------------|------|-------------------------------|--|--|
| Pd(0.5 wt%)/CZY40 | CeO ₂ | ZrO2 | Y ₂ O ₃ | $Ce_{0.32}Zr_{0.62}Y_{0.06}O_{2\cdot\delta}$ | |
| | 40 | 55 | 5 | | |

Ce K-edge in BL14B1 and BL14B2, SPring-8[3][4].

Samples were heat treated at high temperatures to reproduce the degraded catalyst. This method allowed us to evaluate the robustness of the catalysts and the dynamics of the OSC as actually degraded. *In-situ* EXAFS and Dispersive XAFS measurements were carried out at Ce *K-edge* (40,443 eV) using the high energy of SPring-8. White X-rays dispersed by Si (311) curved crystals were incident on the sample, and the X-ray intensities before and after transmission were measured by an ion chamber. *K-edges* of Pd, Zr, and Y were measured by the transmission method. All samples were pretreated for oxidation. O₂ 20% (N₂ balance) was used as the oxidizing gas. H₂ 5% (N₂ balance) or CO 10% (N₂ balance) was used as the reducing gas. During the measurement, the oxidizing and reducing gases were alternately flowed at 400 °C.

Results and Discussion

DXAFS analysis showed that H_2 reduction proceeded faster than CO until 40 to 50 seconds. However, the reduction rate decreased after that, and the final reduction reached at 100 s was found to be similar for both gases (Fig. 1).

On the other hand, the reduction rate by CO showed a steady rate until the switch to the oxidation process. No difference in oxidation rate was observed between H_2 and CO. These results indicate that there is a clear difference in the reduction rates depending on the species of reducing gases, and provide important knowledge in the reactivity of the catalysts.



Furthermore, the structural changes of Ce crystals during the transition from the oxidation state to the reduction state were investigated by Conventional XAFS using the same sample (Fig. 2) [5].

As a result, a decrease in the Ce-Ce bond distance (about 3 Å), a shift of the peak position to the left, and a decrease in the Ce-O bond (about 1.6 Å) were observed during the transition from the oxidation state to the reduction state.

This suggests that CeO_2 releases oxygen between Ce and Ce during the reduction process, which shortens the Ce-Ce bond distance. These results observed the difference in the reaction rate depending on the species of reducing gas, but also observed that there is no clear difference in the structural change of CeO_2 .

The results of this research are expected to provide new knowledge on the mechanisms of reaction rates and fine structure of Ce and near elements changes with reducing gas species and contribute to the development of catalyst design for refined redox characteristics.



reducing gas species

References

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Acknowledgements

The synchrotron radiation experiments were performed at SPring-8 beamlines BL14B1 and BL14B2 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2023B3618, 2024A3618 and 2024B1634). A part of this work was supported by the Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM Japan) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Grant Nos. JPMXP1223AE0021 and JPMXP1224AE0003) and the Shared-Use Program of JAEA Facilities (Proposal Nos. 2023B-E04 and 2024A-E06).