Shota Hamada[1], Daiju Matsumura[2], Shinya Uegaki[1] , Hidetaka Tanabe[1] , Tomohito Nakayama[1], Itsuki Jinjo[1], Seita Kurono[1], Masami Nakamoto[3], Tomohisa Mizuno[4],Takashi Goto[4], Hirohisa Tanaka*[1]
[1]*Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Hyogo, Japan.*
[2] *Japan Atomic Energy Agency, SPring-8., 1-1-1 Koto Sayo, Sayo, Hyogo, Japan.*
[3]*Daihatsu Motor Co., Ltd., 2-1-1 Momozono, Ikeda, Osaka, Japan.*
[4]*Cataler Corporation, 1905-10 Shimonobe, Iwata, Shizuoka, Japan.*
* *e-mail corresponding :* hirohisa.tanaka@kwansei.ac.jp

Oxygen Storage Materials in Automotive Catalysts : Composition of CZY

Significance and Relevance

The optimal composition of ceria-based composite oxides was investigated for oxygen storage capacity (OSC), which is important for automotive catalysts. Weight changes due to oxygen storage capacity were measured using thermogravimetric balance, and valence changes of ceria and other elements were observed at the K-edge of Ce, Zr, and Y using dispersive X-ray absorption fine structure (DXAFS) at SPring-8. Some interesting results were obtained, such as the Ce valence change slowing down when the amount of precious metal was increased. Observations of changes in the weight of the catalyst and changes in the valence of elements make this discovery possible.

Introduction and Motivations

The upcoming Euro 7 regulations will be stricter than ever before, and automakers will need to take on more challenging challenges. In order to comply with these strengthened regulations, automobile manufacturers need to conduct research into catalysts that can meet the strengthened regulations. In this study, we studied what changes occur when the ceria ratio in automobile catalysts is changed, in order to provide a guideline for future catalyst development.

Materials and Methods

A composite oxide with different ceria ratios was prepared as an automobile catalyst with OSC. As a durable product, it was subjected to durability in a rich (CO) and lean (O2) atmosphere as a driving treatment of a car, and the temperature was lowered in a lean atmosphere. In addition, in the initial product, it was treated in a model gas with A/F = 14.4 to stabilize the initial state.

This time, samples with different ceria ratios were prepared. The powder was prepared so that the weight ratio of ceria in the CZY powder composition was 20, 40, and 57%, and precious metals were supported.

The experiment was performed by flowing reducing gas and oxygen alternately five times every 100 seconds to observe the changes caused by releasing and storing oxygen.

Table 1. types of ceria-based complex oxides

Code	Oxide weight ratio			Composition (Atomic ratio)
	CeO_2	ZrO_2	Y_2O_3	
CZY20	20	73	7	$Ce_{0.15}Zr_{0.77}Y_{0.08}O_{2-\delta}$
CZY40	40	55	5	$Ce_{0.32}Zr_{0.62}Y_{0.06}O_{2-\delta}$
CZY57	57	39	4	$Ce_{0.49}Zr_{0.46}Y_{0.05}O_{2-\delta}$

Results and Discussion

To observe the weight change of the catalyst and the local structural change of cerium due to H_2 or CO reduction and O_2 oxidation, we performed experiments to observe the mass change using a thermogravimetric balance and analysis by time-resolved dispersive X-ray absorption fine structure (DXAFS) near the Ce *K*-edge at the BL14B1 beamline of SPring-8[3][4].

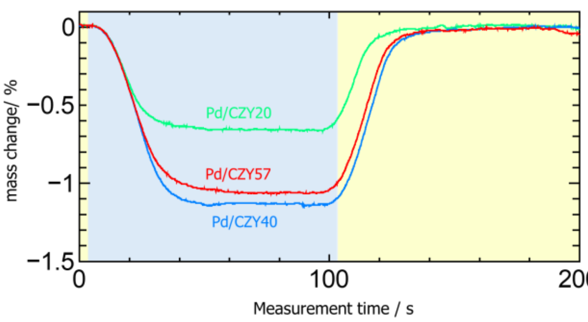

Figure 1. Comparison of ceria ratios using a thermogravimetric device

First, Pd/CZY20, Pd/CZY40, and Pd/CZY57, which have different ceria ratios, were reduced with hydrogen and oxidized with oxygen, and the mass change was observed using a thermogravimetry balance (Figure 1). When reduced with hydrogen, oxygen is released and the mass decreases, and when oxidized with oxygen, oxygen is absorbed and the mass increases. Figure 1 shows the percentage of mass that is reduced when reduced, based on the oxidized state.

In this study, the mass change was greatest for Pd/CZY40, where the ceria mass ratio was 40, followed by Pd/CZY57 and Pd/CZY20. This suggests that the difference in ceria ratio has a significant effect on the amount of oxygen stored.

Next, using the same sample, we observed CO reduction and O_2 oxidation in an experiment using time-resolved dispersive X-ray absorption fine structure (DXAFS) near the Ce K-edge at the BL14B1 of SPring-8 (Figure 2).

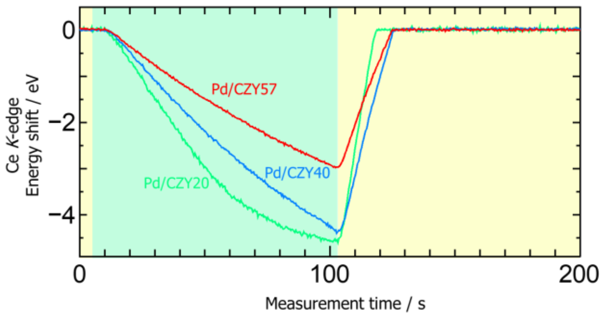

Figure 2. Comparison of ceria ratios by DXAFS

Unlike the thermogravimetric balance used earlier, we found that the lower the cerium ratio, the faster the reaction. What is noteworthy here is that as the cerium ratio decreases, the zirconium-yttrium ratio increases. This shows that as the zirconia ratio increases, the reduction and oxidation rates of ceria become faster[5]. As such, the OSC and reaction rate change depending on the ratio of cerium to zirconium, so when designing a catalyst or sensor, it is necessary to take into account the balance between the required OSC and reaction rate.

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