

## In Situ Time-Resolved Energy-Dispersive X-ray Study on the reaction mechanism on Ce/Zr

A. Suzuki<sup>1)</sup>, Y. Inada<sup>2)</sup>, T. Yamamoto<sup>1)</sup>, Y. Nagai<sup>2)</sup>, M. Nomura<sup>4)</sup>, and Y. Iwasawa<sup>1)</sup>

1) Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

2) Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan

2) Toyota Central R&D Labs. Inc., Nagakute, Aichi 480-1192, Japan.

3) Photon Factory, Institute of Materials Structure Science, KEK, Ibaraki 305-0801, Japan.

### Introduction

Oxygen storage/release capacity (OSC) of automobile three-way catalysts (TWCs) is one of the important issues to improve the overall catalytic efficiency of TWCs. However, the detail of the dynamic OSC process and the key issue to regulate it are not clear yet because of lack of the information on structural dynamics of Ce and Zr coordination spheres. In the present study we have successfully characterized the time scale and sequence of the structural and electronic changes at Zr and Ce sites in the OSC processes of CeZrO<sub>4</sub> and Pt(1 wt%)/CeZrO<sub>4</sub> by the time-resolved DXAFS technique for the first time.

### Experimental

DXAFS measurements at the Ce L<sub>3</sub>-edge and Zr K-edge in the energy ranges 5.67-5.87 and 17.8-18.8 keV, respectively, were carried out in KEK-PF. A four-point supporting crystal bender was developed for Si(111) (Ce L<sub>3</sub>-edge) and Si(311) (Zr K-edge) bent-crystal polychromators (Bragg-type) to achieve an elliptical optics for focusing incident X-rays at the sample. A self-scanning photodiode array was used as a position-sensitive linear detector. The DXAFS spectra every 100-300 ms for the oxygen sorption into the Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (oxidation with O<sub>2</sub>) and oxygen removal from the CeZrO<sub>4</sub> (reduction with H<sub>2</sub>) were analyzed by the similar procedure to that in the literature.

### Results and Discussion

Fig.1 shows the time-resolved DXANES spectra at Ce L<sub>3</sub>-edge during the reduction of Pt/CeZrO<sub>4</sub> at 573 K. The characteristic doublet peaks for the CeZrO<sub>4</sub> changed to the single peak for the Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, and the reduction is indicated to occur directly from Ce<sup>4+</sup> to Ce<sup>3+</sup> according to the existence of the isosbestic point in the inset of Fig.1. It is concluded from the two-states fitting of the DXANES spectra, at 773 K about 90% of Ce<sup>4+</sup> were converted to Ce<sup>3+</sup> within 2 s. Similarly, the oxidation of Pt/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (about 75% of Ce<sup>3+</sup>) by oxygen sorption was also completed within 2 s. The Ce reduction rate increased with temperature. In contrast, the DXANES

spectra at Zr K-edge in both reduction and oxidation steps at 773 K did change. After the oxidation state of Ce changed, the DXANES spectra at Zr K-edge began to change and continued over 10 s.

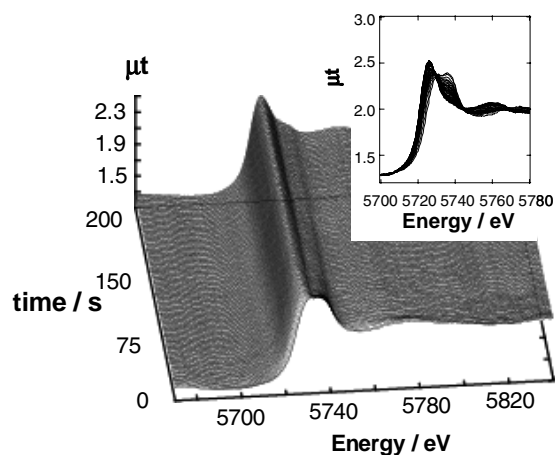


Fig.1 A series of the DXANES spectra at Ce L<sub>3</sub>-edge during the reduction of Pt/CeZrO<sub>4</sub> with H<sub>2</sub>(26.7 kPa) at 573 K

[1] Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda and M. Sugiura, Catal. Today, 74 (2002) 225.