

## Oxygen-diffusion-driven oxidation behavior and tracking areas visualized by X-ray spectro-ptychography with unsupervised learning

Three-way exhaust catalysis is a key reaction in automobile systems, and cerium-containing mixed oxides have been widely used as the support for exhaust catalysts. The oxygen storage and release capacity (OSC) of cerium-containing mixed oxides associated with the reversible oxidation and reduction of Ce<sup>3+</sup> and Ce<sup>4+</sup> ions enables widening of the operation window of three-way catalysts. In particular, Ce<sub>2</sub>Zr<sub>2</sub>O<sub>x</sub> (denoted CZ-x, where x = 7–8) solid solutions with an ordered arrangement of Ce and Zr atoms exhibit high OSCs. The reversible oxygen storage and release processes erase the oxygen diffusion track in the bulk of the CZ-x particles, and consequently, the details of the oxygen storage pathways in the CZ-x particles remain unclear.

X-ray spectro-ptychography (XSP), a combination of XAFS spectroscopy and X-ray ptychography, is a promising tool for visualizing both the structures and chemical states of bulk materials at the nanoscale beyond the limitation of an X-ray lens. Recently, 2D XSP in the hard X-ray region has been reported, which provided 2D maps of the Ce density and valence state, suggesting the existence of several 2D domains with different oxygen storage behavior in Pt-supported CZ-x (Pt/CZ-x) catalyst particles [1]. However, significant ambiguities, especially regarding the 3D oxygen-diffusion-driven Ce oxidation tracking areas in individual CZ-x particles during the heterogeneous oxygen storage process, remain in the 2D images derived from the projection of the structure and valence state along the optical axis.

In this study, we propose the approach of 3D hard X-ray spectro-ptychography (HXSP) imaging coupled with unsupervised learning [2]. The 3D HXSP method combined with computed tomography (CT) allowed the realization of 3D nanoscale imaging of the structure and valence state inside individual Pt/CZ-x solid solution particles during the oxygen storage process. Unsupervised data mining of the visualized 3D nanoscale chemical maps then successfully revealed the concealed heterogeneous oxygen-diffusion-driven 3D nanoscale Ce oxidation tracking areas inside the individual mixed-oxide particles during the oxygen storage process.

3D HXSP (5.708–5.770 keV, which includes the Ce  $L_{III}$ -edge) was conducted at SPring-8 **BL29XUL**. For the CT measurement, the sample was rotated from –75 to 75° via 61 evenly spaced angles at each X-ray energy. The projected amplitude and phase images at each angle were reconstructed. Then, 3D image

reconstruction was accomplished using the filtered back projection algorithm at each X-ray energy. The voxel size of the reconstructed 3D HXSP images in real space was as low as 14 nm, in contrast to the size of single CZ-x particles of ~500 nm to 1  $\mu$ m, enabling the determination of the 3D oxidation reaction tracking areas in individual catalyst particles during the oxygen storage process.

Figure 1(a) shows the isosurface rendering of the reconstructed 3D HXSP phase images of six CZ-x particles in the field of view. The facet structures on the surfaces of the CZ-x particles can be clearly visualized in the 3D HXSP image. The Ce  $L_{III}$ -edge ptychographic-XAFS spectra allowed discrimination of Ce<sup>3+</sup> and Ce<sup>4+</sup>, whose linear combination fitting at each voxel afforded a 3D map of the Ce oxidation state in (*x*,*y*,*z*) real space. The resulting 3D cross-sectional images of the Ce valence are presented in Fig. 1(b),



Fig. 1. (a) Isosurface rendering of the reconstructed 3D phase map of partially oxidized Pt/CZ particles. (b) Series of slices of the 3D Ce valence image along the z direction. Scale bars correspond to 700 nm.

showing the heterogeneous variation of the Ce oxidation state inside individual CZ-x particles where oxygen storage partially proceeded via the oxidation of CZ-7 with  $O_2$  at 423 K for 1 h. The surfaces of the solid particles appeared blue (Ce<sup>4+</sup>) and wide color variation inside the solid particles was observed in a heterogeneous manner.

The 3D HXSP imaging results provided a 3D nanoscale Ce valence map of the solid particles with  $452 \times 450 \times 136$  voxels. To characterize each voxel, we considered the surrounding binning of  $3 \times 3 \times 3$  voxels  $(42 \times 42 \times 42 \text{ nm}^3)$  in the 3D map and used the local mean (m(x,y,z)) and local standard deviation (sd(x,y,z)) of the Ce valence state in each binning domain as descriptors. Note that m(x,y,z) corresponds to the degree of oxygen storage (Ce<sup>3+</sup>  $\rightarrow$  Ce<sup>4+</sup>) and sd(x,y,z) corresponds to the variation of oxygen storage in the local domains. Using these descriptors, we observed a volcano-type correlation between m(x,y,z) and sd(x,y,z), as shown in Fig. 2(a). By minimizing the Bayesian information criterion, a



Fig. 2. (a) Scatter plot of mean Ce valence (m) and its standard deviation (sd) for  $42 \times 42 \times 42$  nm<sup>3</sup> ( $3 \times 3 \times 3$  voxels) domains of partially oxidized Pt/CZ-x particles, and classification of correlation trends using a Gaussian mixture model. (b) Series of slices showing the 3D distributions of the four correlation groups along the z direction. The scale bar corresponds to 700 nm.

Gaussian mixture model approximating the 2D plot of (m, sd) revealed that the actual distribution was a mixture of four Gaussian components denoted  $G_1$ ,  $G_2$ ,  $G_3$ , and  $G_4$ . The volcano-type pattern was related to the course of the oxygen storage process during Ce oxidation from  $Ce^{3+}$  to  $Ce^{4+}$  via the  $G_1$ ,  $G_2$ , and  $G_3$  domains in the CZ-x particles concealed in the bulk. The Ce oxidation in the  $G_1$  domains proceeds in the CZ-7 phase with a pyrochlore structure, whereas the Ce oxidation in the  $G_2$  domains is considered to occur in the disordered (mixed) phases accompanied by the transformation of the pyrochlore phase to the CZ-8  $\kappa$ -phase with a fluorite structure and showing a larger sd. Further oxygen storage proceeds in the Ce oxidation states above +3.7 and forms the  $G_3$ domains with a maximum Ce valence population. The  $G_3$  domains, considered to be nearly a fluorite phase, readily converge to the Ce4+ valence state in the G<sub>4</sub> domains and the final CZ-8 phase. We classified the locations of the four groups in (x, y, z) real space and present a 3D map and cross-sectional images in Fig. 2(b). This figure clearly shows that the locations of the four groups were dependent on the morphological characteristics of the particles: the domains belonging to  $G_4$  (blue) were observed at the outermost surfaces of the particles, whereas those belonging to  $G_1$ (red) were predominantly located in the cores of the particles.

3D HXSP is expected to be an indispensable tool for determining reaction tracking areas and the relationships between the structure and function of heterogeneous functional materials. In particular, in next-generation synchrotron facilities where fluxes with much higher coherence will be achieved, the present approach will be applied to *in situ* 3D measurements, which can be expected to significantly accelerate progress in chemistry and materials science.

Yukio Takahashi<sup>a,b,c,\*</sup>, Hieu Chi Dam<sup>d</sup> and Mizuki Tada<sup>e</sup>

- <sup>a</sup> Institute of Multidisciplinary Research for
- Advanced Materials, Tohoku University
- <sup>b</sup> Department of Engineering, Osaka University
- <sup>c</sup> RIKEN SPring-8 Center
- <sup>d</sup> Japan Advanced Institute of Science and Technology
- <sup>e</sup> Department of Chemistry, Nagoya University

\*Email: ytakahashi@tohoku.ac.jp

## References

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