SYNCHROTRON RADIATION RESEARCH FOR PROGRESS OF SELF-REGENERATIVE FUNCTION TO Rh-, AND Pt-PEROVSKITE CATALYSTS

It is inevitable that the demand for precious metals, namely Pd, Rh, and Pt, for use as automotive catalysts has increased, in the absence of technological innovation, owing to the global strengthening of emission controls and to the increase in the number of automobiles particularly in China and India. Automotive catalysts deteriorate as a result of a decrease in the active surface area of precious metals induced by grain growth in high-temperature exhaust gas. To compensate for this deterioration, conventional catalysts are loaded with an excess amount of precious metals, which however leads to over-consumption and supply problems. A self-regenerative "intelligent catalyst," which suppresses the grain growth of Pd, was developed in 2002 and has been industrialized since then. This new technology is based on the reversible change of Pd with perovskite oxides between a solid solution and metallic nanoparticles under an inherent redox environment of exhaust gases during vehicle use [1,2]. Very recently, we have succeeded in realizing the self-regeneration function of an intelligent catalyst for Rh and Pt by utilizing synchrotron radiation research performed at beamlines **BL14B1** and **BL01B1** [3].

Figure 1 shows the powder X-ray diffraction pattern in the limited range of momentum transfer, Q, for $CaTi_{0.95}Rh_{0.05}O_3$ after oxidation. Two Bragg reflections from the sample are assigned to the pseudocubic cell of the ABO_3 perovskite structure. The structure factor for the (100) reflection can be expressed approximately as $F(100) \propto |f_A - f_B - f_O|$, where f_A, f_B, and f_O are the atomic scattering factors for the A-site, B-site, and oxygen atoms, respectively. The inset represents the energy dependence of the reflection intensity near the Rh K-edge (23.220 keV). The dip of the intensity at the edge energy clearly indicates that Rh occupies the B-site of the $CaTiO_3$-type perovskite structure, since $|f_{Ca}|$ is always smaller than $|f_{Ti}|$ in this energy range.

The self-regeneration function is analyzed by XAFS. The XAFS profile of $CaTi_{0.95}Rh_{0.05}O_3$ samples after oxidation (O), reduction (OR), and reoxidation (ORO) at 800 °C for 1 hour in each step are shown in Fig. 2. The edge shift towards lower energies for the OR sample indicates that a greater proportion of Rh is in the metallic state. The edge position for the O and ORO samples is slightly higher than that of the trivalent Rh seen in Rh_2O_3, implying an unusually higher valence state of Rh. The calculated radial structure function clearly shows a reversible change in the local structure around Rh. The first peak for the oxidized and re-oxidized samples corresponds to the 6 oxygen atoms of a RhO_6 octahedron. For the
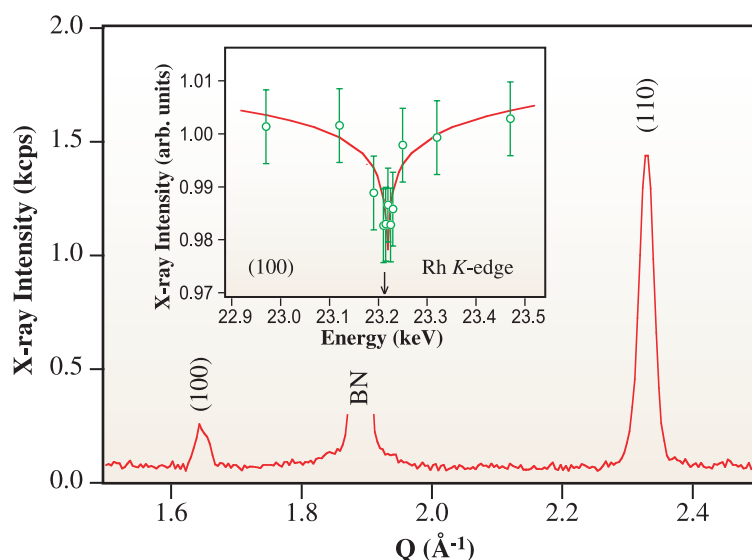

Fig. 1. X-ray powder diffraction patterns of $CaTi_{0.95}Rh_{0.05}O_3$ around Bragg reflections (100) and (110) for pseudocubic cell of perovskite structure. The oxidized sample contained BN as a binder. The inset gives the energy dependence of the (100) reflection intensity near the Rh K-edge.
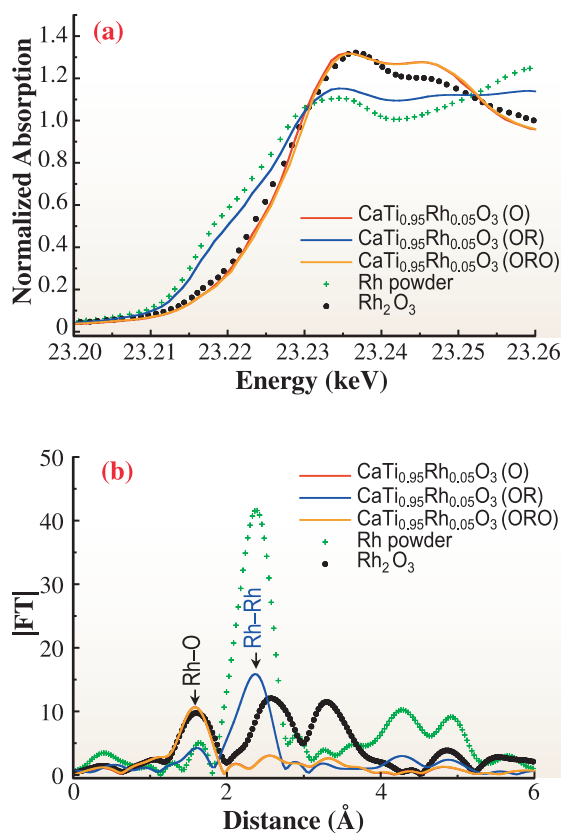
Fig. 2. **(a)** XANES profile near the Rh *K*-edge for CaTi$_{0.95}$Rh$_{0.05}$O$_3$ after oxidization (O), reduction (OR), and re-oxidization (ORO), together with Rh$_2$O$_3$ and Rh powders as reference materials. **(b)** The radial structure function around Rh calculated as magnitude of the Fourier transform of k^3-weighted EXAFS oscillations.
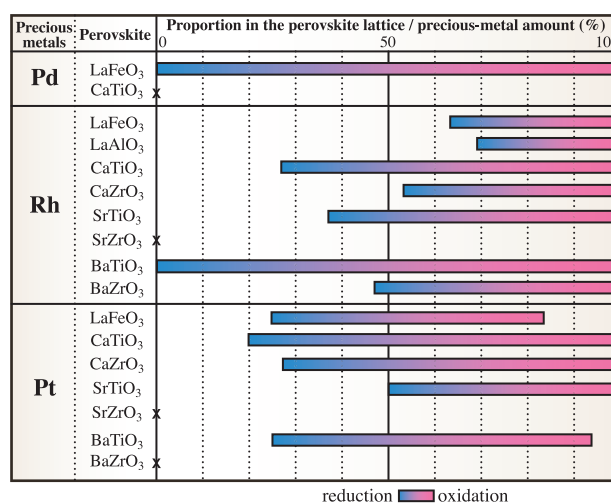

Fig. 3. Comparison of solid solution of precious metal for various perovskites. A longer bar indicates better self-regeneration performance. X indicates that the precious metal forms no solid solution with perovskite.

intelligent catalyst, which regenerates itself to maintain a high catalytic activity even in a harsh redox environment at high temperatures. Such technology is expected as a solution to precious-metal reduction. A DXAFS experiment is now in progress to investigate the real time-dependent behavior of precious metals.

reduced sample, the coordination number of the oxygen atoms decreases and the Rh-Rh bond appears due to the formation of metallic clusters or nanoparticles. At the same time, the perovskite oxide releases oxygen and retains its electro-neutrality.

We have successfully realized the self-regeneration function for Pt in the same way as that for Pd and Rh. The proportion of precious metal present in the perovskite lattice as a solid solution was estimated from the coordination number of the first nearest neighbor with oxygen (Pd-O, Rh-O, or Pt-O bonds) and is given for various combinations in Fig. 3. In a reductive atmosphere, precious metals emerge from oxides to form metallic nanoparticles that demonstrate a higher catalytic activity. Perovskite oxides should maintain a stable structure so that they can capture and release precious metals at high temperatures under a redox environment.

We have demonstrated that a precious-metal-containing perovskite catalyst can behave as an

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