

In situ and Time-Resolved Observation of RedOx Reactions of Pd/Sr-Fe-O Catalysts for Automotive Emissions

We investigated changes in structure of a new type of Pd/Sr-Fe-O catalyst for automobile exhaust emissions during reduction and oxidation. *In situ* and time-resolved XAFS techniques (QXAFS and DXAFS) showed changes in palladium states and oxygen concentrations simultaneously during reduction and oxidation reactions. Quantitative analysis showed that palladium atoms change their states between Pd(II) and Pd(0) reversibly, according to the gas atmosphere, accompanying changes in the oxygen concentration. This reaction explains the high performance of the catalyst used.

Gasoline engines generally operate near the stoichiometric air-to-fuel ratio, and three-way catalysts (TWCs) are used to convert pollutant emissions—carbon monoxide (CO), unburned total hydrocarbons (THC), and nitrogen oxides (NO_x)—into carbon dioxide (CO₂), water (H₂O), and nitrogen (N₂) [1]. In an actual engine, the time lag of the gas control system results in the fluctuation of exhaust emissions between the reduction and oxidation condition. In these catalysts, therefore, structural changes in precious metals and oxygen deficiency during reduction and oxidization (RedOx) reactions are of great importance in understanding the mechanism itself.

In this study, a new type of Pd/Sr-Fe-O perovskite catalyst for exhaust emissions was developed [2]. The catalyst is composed of nano-sized domains of perovskite phases, such as Pd/SrFeO₃, and showed low emissions of CO, THC, and NO_x in the exhaust gas from two-wheeled vehicles. In this instance, the catalytic performance of the new catalyst was the same as or better than that of conventional TWCs, even though the amount of loaded precious metals was reduced by 70%.

In situ and time-resolved observation of palladium states were carried out using a reaction cell with quick-

scanning XAFS (QXAFS [3]) and dispersive XAFS (DXAFS [4]) techniques. *In situ* QXAFS and DXAFS measurements [5] around the Pd K-edge were carried out at BL-9C, 12C and AR-NW2A, respectively.

In situ QXAFS measurement was carried out to investigate the reproducibility of change in structures of catalyst during RedOx reactions. The change of palladium state in the catalyst during RedOx reactions was investigated by switching the flow gas between 4 vol.%H₂-He and 20 vol.%O₂-He [2]. The typical XANES spectra are shown in Fig. 1, while Fig. 2 shows the atomic fraction $x_{\text{val}} = [\text{Pd(II)}]/([\text{Pd(II)}] + [\text{Pd(0)}])$, which was determined by fitting each XANES spectrum with a linear combination of the spectrum of as-prepared (fully oxidized) specimens and that of fully reduced specimens (the same as that of the metal). In H₂-He gas, x_{val} became less than 0.05 in the short time of less than 50 s. In O₂-He gas, the reduced Pd(0) atoms were oxidized into Pd(II) for a longer time of ca. 1,000 s, and returned to Pd(II) in the catalyst. The RedOx behavior between Pd(0) and Pd(II) was repeated during more than five RedOx cycles, which is similar to that reported for Pd-doped perovskite oxides [6].

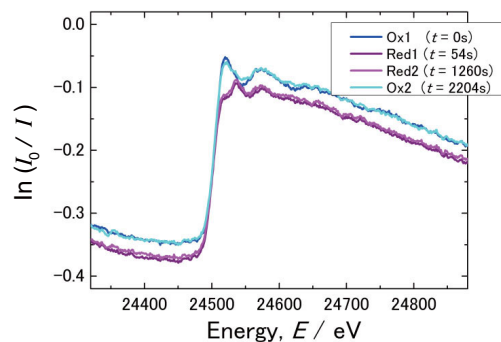


Figure 1
Typical XANES spectra obtained by *in situ* measurements at $T = 673$ K in 4 vol.%H₂-He and 20 vol.%O₂-He; each spectrum (Ox1, Red1, Red2, and Ox2) corresponds to a state shown in Fig. 2.

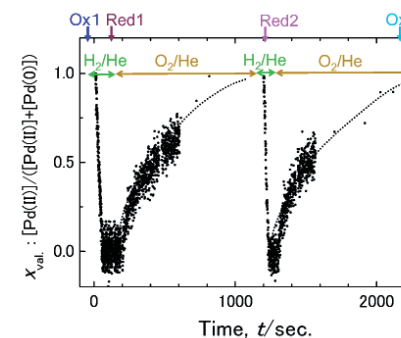


Figure 2
Tim-evolution of the atomic fraction by *in situ* QXAFS measurements during RedOx reactions.

In situ DXAFS measurement was carried out for an early stage of reactions just after switching the gas between H₂/He and O₂/He. Here, the change of oxygen content, as well as the change of Pd valence, could be monitored simultaneously by monitoring the change of the average density of the specimen through the X-ray absorbance in the pre-edge region. Thus, it was found that the average density also showed reversible changes and that the starting and ending times of this change were synchronized with those of the palladium states between Pd(II) and Pd(0). This kind of change in density, corresponding to changes in oxygen deficiency, was not observed during *in situ* observation of a Pd/Al₂O₃ catalyst, which was examined as a reference.

These results can explain the high performance of the new Pd/Sr-Fe-O catalyst in spite of the smaller amount of Pd. The complete reverse change in palladium states between Pd(II) and Pd(0) suppresses the large growth of Pd particles during the cycles, resulting in the best usage of a small amount of palladium. This reversible reaction, furthermore, may be enhanced by "active" oxide support, where oxygen atoms go in and

out according to the change of the gas atmosphere.

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BEAMLINES

9C, 12C and AR-NW2A

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