In situ observation of RedOx reactions of Pd/Sr-Fe-O catalysts for automotive emission

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Abstract. We investigated the change in structures during reduction and oxidation of a new type of Pd on Sr-Fe-O catalyst for exhaust emission. In situ DXAFS techniques have shown changes in palladium states and oxygen concentration simultaneously during reduction and oxidation reactions. Quantitative analysis has shown 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.

Introduction
Petrol 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 (NOx) – into carbon dioxide (CO2), water (H2O), and nitrogen (N2) [1]. In a real engine, the time lag of the gas-control system results in a fluctuation of exhaust emission between a reduction and an oxidation condition. In these catalysts, thus, structural changes in precious metals and oxygen deficiency in reduction and oxidation (RedOx) reactions are of great importance in understanding the mechanism.

X-ray absorption spectroscopy is one of powerful technique to characterize catalysts in reactive atmosphere, and various approaches have been carried out [2]. We developed an in situ technique to observe structural changes in precious metals and oxygen concentration simultaneously. We applied this technique to a new type of Pd on Sr-Fe-O catalyst for exhaust emission in order to understand the change of palladium in the catalyst during RedOx reactions.

Experimental
The catalyst of Sr-Fe-O system was prepared by a solid-state reaction method. Starting powders were mixed by using a ball-mill, followed by calcining them in air at 1273 K for 5 hrs. Pd was loaded on the calcined powder using an aqueous solution of Pd nitrate.

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The catalytic performance was evaluated using the exhaust gas from a two-wheeled vehicle. The slurry containing the Pd-loaded Sr-Fe-O powder was wash-coated onto metal honeycombs with 500 g/m³ of precious metal. A conventional three-way catalyst (TWC), Pt/Pd/Rh-loaded CeO₂ and/or ZrO₂ oxides was used as reference; it is used for a commercial two-wheeled vehicle equipped with carburettor-type engines of 125 cc. The test conditions followed the Euro3 emission program at Japan Automobile Transport Association (JATA).

In situ XAFS measurements[2-4] were carried out using a reaction cell with the energy-dispersive XAFS (DXAFS) technique [5-8]. Figure 1 shows a reaction cell used for in situ XAFS that was developed based on previous reports[2-4]. The cell is made of stainless steel with Kapton®-film windows which an X-ray beam can pass through. A specimen powder was mixed with a powder of hexagonal boron nitride (BN) for 40 min. and the mixture was pressed into a shape of tablet by a pressure of ca. few tenths MPa. A typical size of the tablet was 7 mm in diameter and 2-3mm in thickness. This kind of preparation of the specimen is expected to affect measurements of reaction rates, because the speed of the pore diffusion of gas may be comparable with that of the reaction (“mass transfer problems”) [4]. Therefore we waited for an enough time after switching gases until the change of Pd state seemed to be saturated in order to make sure that the whole part of catalyst reacted with gas. This was checked by a pre-experiment: the specimen tablet of PdO and BN was reduced in the in situ cell. SEM observation of the reduced specimen showed that all parts of the tablet contains Pb metal. An X-ray beam in a size of 1 X 1 mm² was irradiated into the centre of the specimen with a diameter of 7 mm.

The specimen can be heated up to ca. 1073 K by rod heaters located above the specimen in a flow of gas. The temperature of the specimen was monitored with a thermo-couple located above the specimen holder (“TC” in Fig. 1). The temperature difference between the thermo-couple and the specimen was corrected by preparatory experiments where the temperature of the specimen was measured by another thermo-couple inserted into the specimen and the temperature difference from TC was checked under the same heating conditions as real in situ measurements. In situ measurements were carried out in gas of 4 vol.%H₂-He or 20 vol.%O₂-He with a flow rate of 2×10⁵ mm³/min. The dead volume of the reaction cell is about 500 mm³ and the response time is estimated to be ca. 1 sec.

XAFS measurements around the Pd K-edge were carried out by using a synchrotron radiation source at the undulator beam line NW2A station of PF-AR, Photon Factory, KEK, Japan. In situ and time-resolved observation was performed with DXAFS technique with a time resolution of 100 msec [9].

Figure 1. The main part of the developed reaction cell.
The atomic fraction $x_{\text{val}} = \frac{\text{Pd(II*)}}{\text{Pd(II*)} + \text{Pd(0)}}$ was obtained by the X-ray absorbance at 24,363 eV (See Section 3.1 for Pd(II*)). The change of averaged density of the specimen was obtained by fitting linear-combination of the spectrum of as-prepared (fully oxidized) specimen and that of fully reduced specimen. The latter was similar to that of Pd metal.

Results and discussion

1.1. Performance and characterization of catalyst

The new catalyst showed low emissions of CO, THC, and NOx in the exhaust gas from a two-wheeled vehicle as shown in Table 1. The catalytic performance of the new catalyst is the same as or better than conventional TWC even though the amount of loaded precious metals is cut by 70%.

Table 1. Compositions of catalysts and results of the performance test.

| Specimen       | Compositions        | Performance test |
|----------------|---------------------|------------------|
|                | Oxide support       | Emission gas    | Amounts of precious metal |
|                |                     | (g/Km)           | (g/honeycomb-kL)         |
| New catalyst   | Sr-Fe-O Pd1.2       | 1.74 0.15 0.17   | 0 0 0.51                 |
| TWC (for 125cc)| CeO/CoO             | 2.27 0.17 0.16   | 2.61 0.57 <0.05          |

Microstructure and atomic structure of the catalyst were investigated by X-ray diffraction (XRD) and transmission electron microscope (TEM). The new catalyst is composed of grains with a size in a range of 0.1-1μm, and each grain contains different types of Sr-Fe-O oxides in a size of ca. 10 nm: mainly SrFeO$_{3-\delta}$. Palladium is not simply loaded on the oxide surfaces, but it is embedded only in the surface region of the oxide grains with ca. 20–50 nm in depth. XANES spectra around the Pd K-edge were measured for the new catalyst and PdO powder. The edge energy of the catalyst showed a slightly higher energy than PdO, and their states are hereafter referred as Pd(II*). These results suggest that palladium atoms locate in Sr-Fe-O oxide and possibly occupy iron sites.

1.2. In situ XAFS Measurements

The temperature of reduction was compared between the catalyst and PdO. Specimens were heated from RT up to $T = 500$ K with a rate of 10 K/min. in 4 vol.%H$_2$-He with a flow rate of $2 \times 10^5$ mm$^3$/min. Pd(II*) atoms in the catalyst were reduced at $T > ca. 403$ K in 4% H$_2$/He gas, whereas PdO was reduced even at $T = 300$ K. This shows that Pd(II*) atoms in the catalyst are expected to bind to the Sr-Fe-O oxides stronger than those simply loaded on oxides, and may occupy iron sites.

The change of palladium states in the catalyst during RedOx reactions was investigated by switching the flow gas between 4 vol.%H$_2$-He and 20 vol.%O$_2$-He. Typical XANES spectra are shown in Fig. 2. Figure 3 shows a part of change of XANES spectra from the state A to B in Fig. 3 with a time interval of 80 msec. Figure 4 shows the atomic fraction $x_{\text{val}} = \frac{\text{Pd(II*)}}{\text{Pd(II*)} + \text{Pd(0)}}$. In H$_2$-He gas, almost
all Pd(II*) atoms in the catalyst were reduced into Pd(0) in a short time of less than 10 s. In O2-He gas, the reduced Pd(0) atoms were oxidized into Pd(II*) in a longer time of ca. 1,000 s, and returned to Pd(II*) in the catalyst. The reverse change between Pd(0) and Pd(II*) was confirmed during more than five RedOx cycles. However, in PdO, most of the palladium remained in the Pd(0) state that formed in the reduction cycle, even the specimen was kept in 20 vol.%O2-He at T = 673 K for more than a few hours. These results show that palladium in the Pd(0) state in the catalyst forms a very small cluster and they are strongly correlated with the Sr-Fe-O oxides, which may prevent palladium atoms from easily growing into large particles during operation at elevated temperatures. This complete reverse reaction suppresses the large growth of Pd particles and maintains Pd clusters as small as ca. 1–1.5 nm during the cycles as shown by in situ XAFS measurements; hence explaining the high performance with less precious metal. The reversible change between Pd(II*) and Pd(0) found in the new catalyst of Sr-Fe-O is similar to that of reported in Pd-doped perovskite oxides [10-12]. DXAFS measurements have shown that the change in structure of Pd in LaCoO3 is ca. 1 s and ca. 1.5 s in reduction and oxidation processes, respectively[11,12]. In the case of the new catalyst of Sr-Fe-O, it takes longer time for the change between Pd(0) and Pd(II) (or Pd(II*)), especially in the oxidation process, compared with the Pd doped LaCoO3 catalyst. The difference in structures of oxides and the mass transfer problems described in Sec.2 may cause these differences. Further experiments using specimens free of BN are now going and details are shown elsewhere.

In this study, the change of oxygen content as well as the change of Pd valence could be monitored simultaneously by monitoring the change of averaged density of the specimen. It was found that the change of base line at an energy lower than the edge energy also showed reversible changes, showing that the averaged density of the specimen change reversibly. The averaged density obtained by monitoring absorbance at 24,300 eV showed at a ca. 0.8 % lower value in 4 vol.%H2-He than in 20 vol.%O2-He at T = 673 K. The difference can be explained by considering that all oxygen atoms combined with palladium are removed in the reduction cycle and that all palladium atoms changed into oxide in the oxidation cycle. This kind of change of density was not observed by in situ observation of a Pd/Al2O3 catalyst which was performed as reference. Oxygen atoms are expected to get in and out from perovskite-typed oxide. For high-performance of Pd-doped perovskite oxides, the movement of oxygen atoms may be as important as that of metal atoms, though most of previous XAFS study[10-12] focus on the latter.

Figure 2. Typical XANES spectra obtained by in situ measurements at T = 673 K in 4 vol.%H2-He and 20 vol.%O2-He. Spectra A, B, and C correspond to the states in Fig. 3.
Figure 3. A part of change of XANES spectra from the state A to B in Fig.3 with a time interval of 80 msec.

Figure 4. Time-evolution of the atomic fraction by in situ XAFS measurements during RedOx reactions.

It is noted that the change of density is almost synchronized with the change of Pd valence in the reduction cycle but that there is a time lag of ca. 1 sec. between them in the oxidation cycles. This suggests that there is a difference in the process of oxygen movement and the electron transfer.
between the reduction and the oxidation cycles. Further experiments are now going and details are shown elsewhere.

These results explain why the new catalyst exhibited the high catalytic activity. Palladium atoms form metal clusters quickly in reduced atmosphere and return into the oxide state in oxidative gas. The reverse reaction between Pd(II*) and Pd(0) is deeply associated with the diffusion of oxygen atoms, which may be enhanced in the new catalyst of Sr-Fe-O oxides. TEM observation showed that each grain of the new catalyst is composed of multi-phase Sr-Fe-O oxides and that the size of each crystal domain is less than ca. 10 nm. This unique morphology may enhance the diffusion of oxygen atoms.

**Conclusion**

*In situ* DXAFS techniques have shown changes in palladium states and oxygen concentration in the new Pd/Sr-Fe-O catalyst simultaneously during reduction and oxidization 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.

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