**In situ** and simultaneous observation of Palladium Redox and Oxygen Storage/Release Reactions in Pd/Sr-Fe-O Perovskite Catalysts using Dispersive XAFS

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1 Introduction

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 (NOx)—into carbon dioxide (CO2), water (H2O), and nitrogen (N2). 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, thus, 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 catalysts for exhaust emissions was developed [1]. The catalyst is composed of nano-sized domains of perovskite phases, such as Pd/SrFeO3, and showed low emissions of CO, THC, and NOx 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 conventional TWCs, even though the amount of loaded precious metals was cut by 70%

2 Experiment

The change of palladium states in the catalyst during RedOx reactions was investigated by switching the flow gas between 4 vol.%H2-He and 20 vol.%O2-He [1]. 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.

In situ and time-resolved observation of palladium states were carried out using a reaction cell with quick-scanning XAFS (QXAFS) and dispersive XAFS (DXAFS [2]) techniques. In situ QXAFS and DXAFS measurements around the Pd K-edge were carried out at NW2A and NW10A of KEK/PF-AR.

3 Results and Discussion

A newly developed palladium-promoted Sr-Fe-O (Pd/Sr-Fe-O) catalyst showing good performance has a unique “multi-phase-domain” structure in which a single grain is composed of nano-sized domains of the three phases SrFeO3-δ, SrFe2O13-δ, and SrFe12O19-δ, and small clusters with Pd0O-like structures are located near the surface region of the oxide grains.

We proposed and demonstrated a new analytical technique for the simultaneous observation of the redox reaction of palladium and the oxygen storage/release process during redox-gas cycles using dispersive XAFS with a time resolution of less than 20 ms. We have succeeded in revealing a strong correlation between the redox of palladium and the oxygen storage/release in the Pd/Sr-Fe-O catalyst as follows. Reduction from PdII to Pd0 begins just after the introduction of H2/He gas, with a simultaneous increase in the oxygen deficiency (δ) in perovskite-type SrFeO3-δ and SrFe2O13-δ. After the completion of the Pd reduction, the recovery (decrease) of δ follows. Contrary to this sequence, oxidation from Pd0 to PdII begins after an incubation period, after which the change in δ precedes. The palladium oxidation and the increase of δ then progress simultaneously [1].

Figure 1 Spectral changes obtained by in situ DXAFS measurements during the RedOx reactions for the new catalyst with 3.0 mass% Pd that was measured under gas-closed conditions at T = 673 K (a) in H2, P = 18.5 kPa, and (b) in O2, P = 47.2 kPa. The arrows in the figures show the time evolution of the spectra.

References


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