In Situ and Simultaneous Observation of Palladium Redox and Oxygen Storage/Release in Pd/Sr–Fe–O Perovskite Catalysts Using Dispersive XAFS

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We have succeeded in in situ and simultaneously observing the redox reaction of palladium and the oxygen storage/release process in a newly developed palladium-promoted Sr–Fe–O (Pd/Sr–Fe–O) catalyst during redox-gas cycles using dispersive X-ray absorption fine structure (XAFS) analysis at 673 K with a time resolution of less than 20 ms. The Pd/Sr–Fe–O catalyst, which exhibits high performance for automotive emission control, has a unique “multi-phase-domain” structure, where a single grain is composed of nano-sized domains of three phases: SrFeO3–x, SrFeO1.1–x and SrFe2O19. In situ observation has shown a strong correlation between the redox of the palladium and the oxygen storage/release in the Pd/Sr–Fe–O catalyst, and the correlation factors differ between the reduction and oxidation reactions. The oxide phases exhibit a type of “oxygen buffer” effect in the oxidation cycle and delay the formation of PdO, resulting in the high performance of the catalyst.

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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 TWCs, precious metals are added to oxide supports with a high oxygen storage capacity (OSC), such as CeO2–ZrO2 or perovskite-type oxides. Thus, the change in the structure and chemical state of the precious metals during the redox cycles, and the relationship of that change with the oxygen storage/release properties of the supporting oxides in TWCs, are pivotal for revealing the reaction mechanisms of these catalysts, which have been investigated using various approaches.

In situ X-ray absorption fine structure (XAFS) analysis is a powerful technique for characterizing catalysts in a reactive atmosphere. A combination of XAFS and X-ray anomalous diffraction techniques has shown that the palladium in Pd/La(Fe,Co)O3 changes reversibly between a perovskite oxide and the metal during redox cycles, reducing the degradation through self-regeneration of the precious metal. In situ XAFS analysis with a shorter time resolution (less than a second) was conducted using a reaction cell with an energy-dispersive XAFS (DXAFS) technique. The dynamics and roles of the Ce and Zr ions in Pt-promoted CeO2–ZrO2 catalysts were observed by DXAFS; a fast valence change of the Ce ions and moderate structural changes around Zr were suggested to be responsible for the high OSC. Mechanistic models were also proposed for the Pt sintering/redispersion processes in Pt/CeZrY mixed oxide catalysis based on XAFS and transmission electron microscopy. These results strongly suggest that the dynamics of the structural changes of the metal ions are closely related to the oxygen storage/release process in TWCs, although little direct experimental observation has been reported.

Previously, we investigated the change in the chemical state of palladium during the redox-gas cycles in a newly developed palladium-promoted Sr–Fe–O (referred to as Pd/Sr–Fe–O) catalyst, and showed that the palladium atoms change their states between Pd0 and Pd0 reversibly according to the gas atmosphere. In this study, we propose a new analytical technique that enables the simultaneous observation of the redox reaction of palladium and the oxygen storage/release process in the Pd/Sr–Fe–O catalyst. Furthermore, the atomic structure and microstructure of the catalyst are extensively investigated. Based on these results, we propose reaction mechanisms in terms of the correlation between the redox of palladium and the oxygen storage/release during redox-gas cycles, which is crucial information for understanding the mechanism of the high performance of not only the Pd/Sr–Fe–O catalyst but also other TWCs.

2. Experimental

2.1 Sample preparation and evaluation of catalytic performance

Powder specimens of the Pd/Sr–Fe–O catalysts were prepared via a solid-state reaction of SrCO3 and Fe2O3. Starting powders of SrCO3 (>99.99%, grain size ca. 3 μm) and Fe2O3 (>99.99%, grain size ca. 3 μm) were mixed using a ball-mill for 5 h, and then calcined in air at 1273 K for 5 h. Next, the oxide powder was loaded with palladium using an aqueous solution of palladium nitrate, and the catalyst was...
calcined again in air at 1273 K for 5 h. A catalyst with the chemical composition SrFe2Pd0.08O was used for the in situ observations.

The evaluation of the catalytic performance was conducted in a purification unit with the Pd/Sr–Fe–O catalyst powder (loaded with 1.2 mass% palladium) on a metal honeycomb (Table 1). An Al2O3 slurry containing the palladium-loaded Sr–Fe–O powder was wash-coated onto metal honeycombs at a rate of 500 g/m2·h. A conventional catalysts (Pt/Sr–Fe–O loaded with 1.2 mass% palladium) served as references; these catalysts are used for commercial two-wheeled vehicles equipped with 125 and 250 cc carburetor-type engines, respectively (Table 1). The evaluation of the catalytic performance was conducted by measuring the amounts of CO, THC and NOx contained in the emission gas from commercial two-wheeled vehicles equipped with 125 or 250 cc carburetor-type engines driven according to a driving pattern described in the Euro3 regulations, in which a cycle of acceleration, constant driving, and deceleration with a time duration of 195 s was repeated six times. The evaluation was conducted at the public organization JATA (Japan Automobile Transport Association).

The oxygen storage capacity (OSC) was measured using thermogravimetric analysis (TGA). A given amount of powder specimen was heated in air and then in 4 vol% H2–Ar until an equilibrium was obtained at a certain temperature in the range T = 373 to 1173 K. The OSC was determined from the change in the weight. The surface area of the specimens was also measured by N2 chemisorption at 77 K.

### 2.2 Characterization of atomic structure and microstructure and in situ dispersive XAFS

The structures of the powder catalysts were investigated by X-ray diffraction and transmission electron microscopy analysis. The X-ray diffraction patterns were obtained by a θ–2θ diffractometer using Cu-Kα radiation with a graphite monochromator. The crystal structures were determined using Rietveld analysis. The samples for the transmission electron microscope measurements were prepared by placing a drop of powder specimen suspended in methanol onto transmission electron microscope grids bearing an ultrathin porous-carbon film. High-resolution transmission electron microscope (HREM) images were then obtained using a field-emission HF-2000 (Hitachi Co.) operated at 200 kV with a point resolution of ca. 0.1 nm. HREM image simulation was performed using the “WinHREM™” software.

The change in the structure and chemical state of the catalyst was investigated using an in situ dispersive XAFS characterization technique for simultaneously monitoring the X-ray intensities over the entire energy range at a sub-second order time resolution. Time-resolved wavelength dispersive XAFS spectra at the palladium K-edge over the energy range (23.8–25.3 keV) were measured on the NW2A station of the Photon Factory Advanced Ring (PF-AR) at the High Energy Accelerator Research Organization (KEK) in Japan. A Si(511) bent-crystal polychromator (Laue-type) was utilized to prepare the cylindrical optics for focusing the incident X-rays at the sample. A self-scanning photodiode array (PDA: 1024 sensing elements: 25 µm width and 2.5 mm height for each element) manufactured by HAMAMATSU Photonics (S3904-1024FX) was used as a position-sensitive linear detector. The energy calibration at each sensing element of the PDA was performed by comparison with the typical XAFS spectra of palladium foil taken at the NW10A station of the PF-AR in transmission mode. The X-ray absorption spectra were calculated as ln(I(E)/I0(E)), where I0(E) and I(E) are the X-ray intensity with and without the specimens, respectively, as a function of the X-ray energy (E).

The Pd/Sr–Fe–O powder specimen (70 mg) was pressed into a disk (7 mm) and placed in a holder in an in situ cell (240 mL). The specimen was heated in a vacuum up to 673 K at a heating rate of 10 K/min, and then a constant amount of gas was introduced at t = 2.0 s in order to attain a specific pressure within 0.2 s for the reduction (H2 with P = 18.5 kPa) and oxidation (O2 with P = 47.2 kPa) cycles. After in situ observation, the in situ cell was evacuated, and the other type of gas was introduced.

The starting and ending states of the catalyst were measured in situ using a conventional XAFS technique with a longer measuring time (several hundreds of s) in order to obtain more quantitative structural information. Extended XAFS (EXAFS) spectra at the palladium K-edge over a wider energy range (23.8–25.4 keV) were measured on the NW10A station in the PF-AR in transmission mode with ionization chambers as the detectors. The obtained palladium XAFS spectra were analyzed using the REX software package. After subtraction of the background by the program, Fourier transformation of the kľ-weighted EXAFS oscillation.

### Table 1 Composition of the catalysts and the results of the performance test.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Design of catalyst</th>
<th>Amounts of precious metal analyzed (×10−3 kg/honeycomb-L)</th>
<th>Emission gas (×10−3 kg/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Sr–Fe–O TWC1 (for 125 cc)</td>
<td>SrFeO3/SrFeO13/SrFe2O19</td>
<td>Pt: 1.2</td>
<td>CO: 1.77, THC: 0.13, NOx: 0.17</td>
</tr>
<tr>
<td>TWC2 (for 250 cc)</td>
<td>CeO2/ ZrO2</td>
<td>Pt, Pd, Rh: NA</td>
<td>CO: 2.27, THC: 0.17, NOx: 0.16</td>
</tr>
</tbody>
</table>

*EURO3 Regulation
was performed over the \( k \)-range from 30 to 140 nm\(^{-1}\). The structural parameters were determined with the FEFFIT program using a curve fitting procedure in the \( R \) space, and involving multiple scattering effects. The overall amplitude reduction factors \( S_k^2 \) for all of the contributions were fixed at the values estimated from the XAFS spectra of the reference specimens, which included palladium foil and PdO powder measured at the same temperature, in order to reduce the number of free parameters in the fitting procedure.

3. Results and Discussion

3.1 Atomic structure and microstructure of the Pd/\( \text{Sr–Fe–O} \) catalyst

The structures of the powder catalysts were investigated by X-ray diffraction and transmission electron microscopy analysis. The crystal structures were determined using Rietveld analysis (Fig. 1), and it was found that the oxide support is a mixture of three co-existing oxides: \( \text{SrFeO}_3 \), \( \text{Sr}_4\text{Fe}_6\text{O}_{13} \) (molar fraction: 0.70), \( \text{Sr}_4\text{Fe}_6\text{O}_{13} \) (0.19) and \( \text{SrFe}_2\text{O}_{19} \) (0.11). Some of the fitted parameters in the crystal structures are listed in Table 2. The atomic structures of each phase are depicted in Fig. 2 based on the fitted parameters. The \( \text{SrFe}_2\text{O}_{19} \) phase is similar to the perovskite phase of \( \text{SrFeO}_3 \), but differs in the stacking sequence of the Fe–O and Sr–Fe–O layers, as indicated by the IL (iron layer) and PL (perovskite layer) in the figure, respectively.

Transmission electron microscope observation indicated that the catalyst is composed of 0.1–1 \( \mu \)m grains, and that each grain is composed of nano-sized oxide domains of \( \text{SrFeO}_3 \), \( \text{Sr}_4\text{Fe}_6\text{O}_{13} \) and \( \text{SrFe}_2\text{O}_{19} \) with a size of less than a few tens of nanometers. Figure 3(a) shows the typical HREM images of the domains of \( \text{SrFeO}_3 \) and \( \text{Sr}_4\text{Fe}_6\text{O}_{13} \); the magnified HREM images (Figs. 3(b) and 3(c)) are consistent with the transmission electron microscope image simulation based on the atomic structures determined by X-ray diffraction. Both domains are mixed with coherent boundaries. This mixing is possible because of the crystallographic similarity of the two phases; their atomic structures only differ in the stacking sequence of the perovskite Sr–Fe–O (PL) and Fe–O (IL) layers, as shown in Figs. 2(a) and 2(b).

X-ray diffraction and transmission electron microscope observations have shown that the oxide support has a “multi-phase-domain” structure, where a single grain is composed of nano-sized oxide domains of \( \text{SrFeO}_3 \), \( \text{Sr}_4\text{Fe}_6\text{O}_{13} \) and \( \text{SrFe}_2\text{O}_{19} \). These phases are mixed into a mosaic of domains (a few nm) within a single grain (0.1–1 \( \mu \)m). Based on the SrO–\( \text{Fe}_2\text{O}_3 \) phase equilibrium,\(^{16}\) the unique nanostructure is assumed to form through decomposition during the heat treatments used in the catalyst preparation: (1) \( 21/6\text{SrO}\text{Fe}_2\text{O}_3 \rightarrow 5/6\text{Sr}_4\text{Fe}_6\text{O}_{13} \rightarrow 1/6\text{SrFe}_2\text{O}_{19} \) when heating at \( T = 1273 \text{ K} \) for calcining, and (2) \( 1/2\text{SrFe}_2\text{O}_{19} \rightarrow 2/11\text{SrFe}_2\text{O}_{19} \) on cooling to around \( T = 1048 \) K. The domains formed by the decomposition process are connected to each other with coherent boundaries due to the crystallographic similarity; meanwhile, the atomic structures of these phases only differ in the stacking sequence of the perovskite Sr–Fe–O (PL) and Fe–O (IL) layers, as can be seen in Fig. 2(b).

**Table 2** Some of the fitted parameters for the crystal structures based on the diffraction pattern of the Pd/\( \text{Sr–Fe–O} \) catalyst.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Volume fraction (%)</th>
<th>Lattice constants/( a )</th>
<th>Lattice constants/( b )</th>
<th>Lattice constants/( c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SrFeO}_3 )</td>
<td>( \text{Fm}-3c )</td>
<td>30 (3)</td>
<td>0.7729 (1)</td>
<td>0.7729 (1)</td>
<td>0.7729 (1)</td>
</tr>
<tr>
<td>( \text{Sr}_4\text{Fe}<em>6\text{O}</em>{13} )</td>
<td>( \text{Iba2} )</td>
<td>38 (3)</td>
<td>1.1072 (3)</td>
<td>1.9057 (5)</td>
<td>0.5558 (1)</td>
</tr>
<tr>
<td>( \text{SrFe}<em>2\text{O}</em>{19} )</td>
<td>( \text{F63/mmc} )</td>
<td>32 (2)</td>
<td>0.58815 (7)</td>
<td>0.58815 (7)</td>
<td>2.3046 (3)</td>
</tr>
</tbody>
</table>

Fitting indexes: \( R_{wp} = 13.0 \%\), \( S = 1.6 \).

**Table 3** Results of the EXAFS analysis of the Pd/\( \text{Sr–Fe–O} \) catalyst after the reduction and oxidation reactions at \( T = 673 \) K.

<table>
<thead>
<tr>
<th>States</th>
<th>Coordination</th>
<th>( N )</th>
<th>( R/\text{pm} )</th>
<th>( \sigma^2/\text{pm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>After Reduction</td>
<td>( \text{Pd–O} ) (NN)</td>
<td>0.7 ± 0.5</td>
<td>202 ± 1</td>
<td>13 ± 4</td>
</tr>
<tr>
<td>( \text{Pd–Pd} ) (2(^{nd})NN)</td>
<td>5.6 ± 0.5</td>
<td>270 ± 1</td>
<td>99 ± 2</td>
<td></td>
</tr>
<tr>
<td>After Oxidation</td>
<td>( \text{Pd–O} ) (NN)</td>
<td>2.1 ± 0.3</td>
<td>205 ± 1</td>
<td>35 ± 1</td>
</tr>
<tr>
<td>( \text{Pd–Pd} ) (2(^{nd})NN)</td>
<td>1.1 ± 0.5</td>
<td>287 ± 2</td>
<td>43 ± 2</td>
<td></td>
</tr>
<tr>
<td>( \text{Pd–Pd} ) (3(^{rd})NN)</td>
<td>2.2 ± 0.6</td>
<td>337 ± 3</td>
<td>87 ± 3</td>
<td></td>
</tr>
</tbody>
</table>

EXAFS analysis of the Pd/\( \text{Sr–Fe–O} \) catalyst after the reduction and the oxidation reactions at \( T = 673 \) K showed the change in palladium states. The magnitude of the Fourier transform (IFT) of the EXAFS around the palladium K-edge for the specimens (circles) and as calculated (red curve) can be seen in Fig. 4: (a) in a vacuum at \( T = 673 \) K after the reduction, and (b) in \( \text{O}_2 \) gas with \( P = 47.2 \text{ kPa} \) at \( T = 673 \) K after the oxidation. The EXAFS around the palladium K-edge of the virgin Pd/\( \text{Sr–Fe–O} \) catalyst is identical to Fig. 4(b). Table 3 shows the results of the analysis: the coordination number (\( N \)), distance (\( R \)), and Debye-Waller factor (\( \sigma^2 \)) for the nearest neighboring (NN) and the 2nd nearest neighboring (2NN) coordinations. The radial distribution around the palladium atoms in the Pd/\( \text{Sr–Fe–O} \) catalyst after the oxidation cycle is similar to that of a reference PdO powder, although the distances for the Pd–Pd (2NN) are smaller than that in the PdO reference. These results of the EXAFS analysis indicate that the palladium in the Pd/\( \text{Sr–Fe–O} \) catalyst exists as Pd\(^{II} \) ions, and that the coordination structure around the palladium is similar to that of PdO. The transmission electron microscope observation showed that the palladium is localized near the grain surface at a depth of ca. 20–50 nm and a concentration of ca. 7–9 mass\%, but no large grains, such as of Pd\(^{0} \) and Pd\(^{II} \)O, were observed. Thus, these observations suggest that the palladium in the Pd/\( \text{Sr–Fe–O} \) catalyst after the oxidation cycle, including the virgin specimen, is located near the surface of the oxide grains in the form of small clusters with a structure similar to that of Pd\(^{0} \). After the reduction cycle, the palladium of the Pd/\( \text{Sr–Fe–O} \) catalyst forms Pd\(^{0} \) metal clusters, where the Pd–Pd coordination number is 5.6 and much smaller than the value (12) for bulk palladium (Fig. 4(a)). This result suggests that palladium forms clusters of 1–2 nm in size, which was confirmed by transmission electron microscope observation. In situ XAFS measurements showed that the palladium state changes reversibly between small Pd\(^{II} \)O clusters and Pd\(^{0} \) metal clusters during the redox cycles.
3.2 Performance of the catalyst

The Pd/Sr-Fe-O catalyst shows low emissions of CO, THC and NOₓ in the exhaust gas from a two-wheeled vehicle, as shown in Table 1. Table 4 lists the estimated surface area and turnover frequencies. To calculate these values, the total amount of emissions was averaged over the time of the test according to Euro3 regulations. Because the structure of the catalyst changes during the cycles (see discussion below), it was difficult to determine the number of active sites. Thus, the turnover frequency was estimated based on the two models that correspond to the extreme cases: Model A, in which the surface of the perovskite structure is active and iron or palladium atoms in the oxide are active sites; and Model B, where palladium atoms on the surface of palladium clusters are the active sites. The clusters...
are assumed to be in spherical in shape with a radius of 1 nm based on the results of in situ EXAFS observations (Fig. 4).

Figure 5 shows: (a) the OSC of the oxide supports of the new Pd/Sr–Fe–O catalyst and the conventional one, and (b) the OSC of the three types of oxides that comprise the oxide supports of the Pd/Sr–Fe–O catalyst: SrFeO$_3$–δ, Sr$_4$Fe$_6$O$_{13}$–δ and SrFe$_2$O$_3$–δ. The Pd/Sr–Fe–O catalyst exhibited a high OSC compared with the conventional CeO$_2$–ZrO$_2$ catalyst over a wide temperature range (600 < T < 1200 K), because each phase in the Pd/Sr–Fe–O catalyst showed a high OSC at the different temperatures. Furthermore, the Pd/Sr–Fe–O catalyst was found to provide higher OSC and catalytic activity than the simple mixture of the three phases; additional effects other than simple mixing of the three oxides may come from the unique microstructure: the “multi-phase-domain” structure.

The catalytic performance of the Pd/Sr–Fe–O catalyst is not degraded compared with that of the conventional TWCs, even though the amount of loaded precious metals is cut from 3.18 or 1.85 to 0.51 × 10$^{-3}$ kg/honeycomb-L, which corresponds to a reduction of the precious metals by 84 and 72%, respectively. The estimated turnover frequency of the Pd/Sr–Fe–O catalysts is on the same order as the palladium catalysts supported on α-alumina, although the difference in the derivation of the values makes direct comparison difficult. Thus, the performance of the Pd/Sr–Fe–O catalyst cannot be explained only by the morphological factor, i.e., the distribution of small-sized palladium clusters results in a high surface area. Other factors contributing to the performance may include the interaction between the palladium atoms and the oxide support, and the high value of the OSC of the oxides. These possibilities have been investigated by in situ observation and are discussed in the following sections.

### 3.3 In situ observation of the change in the palladium states and oxygen deficiency during redox cycles

Figure 6 shows a series of time-resolved Pd K-edge absorption near edge structure (XANES) spectra of the Pd/Sr–Fe–O catalyst obtained by in situ DXAFS at 673 K during the redox cycles. The virgin Pd/Sr–Fe–O specimen gave a typical singlet white line that is characteristic of Pd$^0$ ions, and is similar to that of Pd$^0$O. In the reduction cycle, the edge position shifted to a lower energy, and the singlet changed into the doublet of Pd$^0$ metal at t > 10 s. In the oxidation cycle, the doublet transformed into a singlet, and the edge position shifted to a higher energy. This change proceeded quickly (within 12.0 s), and the spectrum was identical to that of the virgin specimen after 60 s. The identical change and reversion of the spectra were observed for more than 10 redox cycles, indicating that the palladium states change reversibly between small Pd$^0$O clusters and Pd$^0$ metal clusters. This behavior is similar to that reported for Pd/LaFe$_2$O$_4$, where the palladium states change reversibly between Pd$^0$ in the B-site of the perovskite structure and Pd$^0$ metal.

Another slight, but significant, change in the spectrum was observed for the background absorbance at energies lower than the absorption edge. The absorbance, corresponding to the specimen density, decreased and increased reversibly during the redox cycles. The same sequence of changes was observed for 5 different runs using different sample tablets. Furthermore, the background absorbance remained the same during the redox cycles in the case of Pd/Al$_2$O$_3$, the analysis of which was conducted under the same conditions for comparison. Thus, the reversible change in the background absorbance is intrinsic to the Pd/Sr–Fe–O catalyst.

However, the amount of palladium-doping is small (3.0 mass%), and the change in the density cannot be explained only by the change between Pd$^0$ and Pd$^0$O through the reaction: Pd$^0$O = Pd + 1/2O$_2$ or Sr$_4$Fe$_6$O$_{13}$–δ(PdO)$_{0.08}$ = Sr$_4$Fe$_6$O$_{13}$–δPd$_{0.08}$ + 0.04O$_2$. The absorbance caused by the change in the oxygen concentration is less than 1 × 10$^{-3}$ for a 70 mg sample in the form of a tablet with a diameter of 7 mm, and does not explain the reverse in the absorbance (ca. 8 × 10$^{-5}$) observed in situ. Thus, the change in the density cannot be explained only by the change between Pd$^0$ and Pd$^0$O.

Therefore, the reversible change in the density can be attributed to the change in the density of the Sr–Fe–O oxides, which is not observed in Pd/Al$_2$O$_3$. It is reasonable to consider that the density change during the redox cycles is caused by chemical expansion and contraction of the perovskite-type SrFeO$_3$–δ and Sr$_4$Fe$_6$O$_{13}$–δ phases in response to changes in the oxygen deficiency (δ), which is typically found in oxides with perovskite-type structures, such as La$_{1−x}$Sr$_x$MnO$_{3+δ}$, SrCo$_{0.9}$Nb$_{0.1}$O$_{3−δ}$, Nd$_{2−x}$Sr$_x$NiO$_{4+δ}$.
and Ca$_{0.5}$Sr$_{0.5}$Mn$_{1-x}$Fe$_x$O$_3$. The observed change in the density can be concluded to indicate the change in the oxygen deficiency $\delta$ that is located in the perovskite-type SrFeO$_3$ or SrFe$_2$O$_3$. Thus, it can also be concluded that we succeeded in 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, when we measured the change during redox-gas cycles using dispersive XAFS with a time resolution of less than 20 ms, when we measured the change in the density of SrFeO$_3$, SrFe$_2$O$_3$, and SrFe$_2$O$_{13-\delta}$. The maximum change in the density measured during the redox cycles was ca. 0.9%. Assuming that the volume change of the Pd/Sr–Fe–O catalyst is determined by the average contributions of each co-existing phase (SrFeO$_{3-\delta}$, SrFe$_2$O$_{13-\delta}$, and SrFe$_2$O$_{19-\delta}$), the maximum change in the density of SrFeO$_{3-\delta}$ is estimated to be ca. 2%, corresponding to $\Delta \delta = 0.07$ as estimated from the measured OSC. These values are consistent with the reported value of a similar system (4% volume change and $\delta = 0.16$ for SrCo$_{0.8}$Fe$_{0.2}$O$_3$). Thus, it can be concluded that Fig. 7 clearly shows that the change in the density and oxygen deficiency at the same time (Fig. 8(a)).

In the Red-I period, the decrease in $x_{\text{val}}$ and the decrease in $\rho_{\text{norm}}$ (or the increase in $\delta$ in SrFeO$_{3-\delta}$ and SrFe$_2$O$_{13-\delta}$) progressed simultaneously with a linear dependence on $t$ (Fig. 7(a)). This behavior shows that the reduction of the Pd$^{II}$-O clusters into Pd$^0$ metal clusters accompanies the change in oxygen deficiency in the oxide phases in the different reaction periods: Red-I, II, and Ox-I, II, III.

Fig. 7 Time evolution of the atomic fraction ratio ($x_{\text{val}}$) and the normalized density ($\rho_{\text{norm}}$) during redox reactions for the Pd/Sr–Fe–O catalyst with 3.0 mass% Pd. The redox reaction periods are classified as Red-I, Red-II, Ox-I, Ox-II and Ox-III according to the characteristics of the time dependence of $x_{\text{val}}$ and $\rho_{\text{norm}}$. The arrows in the figures show the time evolution of the spectra.
oxygen) suggests that the reduction of PdII is not the rate-determining step in the Red-I period. Possible rate-determining processes include: (1) the adsorption or decomposition of hydrogen gas and (2) the diffusion of reacting hydrogen atoms.

In the following Red-II period ($t > 4$), the recovery of $\rho_{\text{norm}}$ (or the decrease in $\delta$) started at the moment when the reduction of PdII finished. The density increased by 0.4% over the period $t = 4$ to 12 s, whereas there was no change in the palladium valence. A clear exponential dependence on $t$ indicates that the reaction was proportional to the first order of $\rho_{\text{norm}}$ or $\delta$ (Table 5, see Appendix). A possible explanation is the ordering of the oxygen and defects$^{18}$ in the catalyst, resulting in chemical contraction of the perovskite-type SrFeO$_{3-\delta}$ and Sr$_4$Fe$_6$O$_{13-\delta}$ (Fig. 8(a)).

In the oxidation process, different reaction mechanisms were observed compared to those seen during the reduction (Fig. 7(b)). A clear incubation period (Ox-I, $t = 2.2$–3.8 s) was found in advance, then the oxidation of Pd$^0$ started. The $\rho_{\text{norm}}$ sharp drop of 0.4% was observed just after the introduction of O$_2$/He gas ($t = 2.0$–2.1 s). Because the value of the sharp drop is the same as the increase in $\rho_{\text{norm}}$ observed in the Red-II period of the previous reduction cycle, this process may be related to the ordering of the oxygen and

![Diagram](image)

**Fig. 8** Schematic illustration of the reaction mechanisms that provides a clear understanding of the difference in the reaction mechanisms for the different reaction periods: Red-I, II, and Ox-I, II, and III. For simplicity, the Fe–O structure is symbolized by a square of oxygen atoms with an iron atom at its center. Pink broken circles show oxygen vacancies. The illustration is drawn in 2D, and does not indicate the exact atomic configuration.

**Table 5** Reaction rates for changes in density ($k_{\rho_{\text{norm}}}$) and valence states ($k_{x_{\text{val}}}$) for each step during redox cycles; they were determined on the assumption of the linear or exponential dependence on the time, as shown “Linear” or “Exp.” respectively in the table.
defects.\(^{18}\) The introduced oxygen may react with the hydrogen stored in the palladium, which has been reported for Pd/Al\(_2\)O\(_3\).\(^{22,24}\) The \(\rho_{\text{norm}}\) then began to increase with a linear dependence on \(t\) without the accompanying oxidation of Pd\(^0\), suggesting that the recovery of the oxygen deficiency progresses in advance before the electron transfer process in the Ox-I period, and that it is not the rate-determining step. A possible rate-determining process is the adsorption or the Ox-I period, and that it is not the rate-determining step.

In the following Ox-II period (\(t = 3.8-12\) s), the oxidation of Pd\(^0\) to Pd\(^{II}\) began, accompanied by an increase in \(\rho_{\text{norm}}\) and with an exponential dependence on \(t\) (Table 5). The increase in \(\rho_{\text{norm}}\) continued at the same rate constant in the following Ox-III period (\(t > 12\) s), even after the oxidation of Pd\(^0\) into Pd\(^{II}\) was nearly completed. The exponential dependence of \(x_{\text{val}}\) and \(\rho_{\text{norm}}\) on \(t\) indicates that the reaction is proportional to the first order of the concentration of Pd and \(\rho_{\text{norm}}\) (or \(\delta\)). Possible rate-determining steps include the diffusion of Pd\(^0\) to form Pd\(^{II}\)O, or oxygen diffusion into the deficient sites of the perovskite oxides (Fig. 8(b)).

3.4 Reaction mechanisms and the high performance of the Pd/Sr–Fe–O catalysts

First, the high performance of the Pd/Sr–Fe–O can be attributed to the high OSC, as the OSC is generally considered to be one of the indexes for high performance.\(^{25}\) The high OSC results because the Pd/Sr–Fe–O catalyst is composed of different oxides (SrFeO\(_3\)\(_{fi}\), SrFe\(_6\)O\(_{13}\)\(_{fi}\) and SrFe\(_2\)O\(_{19}\)\(_{fi}\)) that show a high OSC at different temperatures. Furthermore, oxygen atoms possibly diffuse easily among multiple phase domains that are as small as several nm in size and surrounded by coherent domain boundaries in the Pd/Sr–Fe–O catalyst with the “multi-phase-domains” structure, where palladium is loaded only near the surface of grains, which may enhance the mobility of oxygen and activate redox reactions in spite of the small amount of palladium.

Second, the strong correlation between the redox of Pd and the oxygen storage/release in the Pd/Sr–Fe–O catalyst, which has been revealed by \textit{in situ} observation, may contribute to the high performance (Fig. 8). In the Red-I period (\(2 s < t < 4 s\)), Pd\(^{II}\)O clusters are reduced into Pd\(^0\) metal clusters with a simultaneous increase in the oxygen deficiency. Reduction from Pd\(^{II}\) to Pd\(^0\) begins just after the introduction of H\(_2\)/He gas without an incubation period, and the reduction of Pd\(^{II}\) is rapid and not the rate-determining step. In the following Red-II period (\(t > 4\)), the recovery of \(\rho_{\text{norm}}\) (or the decrease in \(\delta\)) begins as soon as the reduction of Pd\(^{II}\) is completed.

Contrary to this mechanism, an incubation period (Ox-I, \(t = 2.2-3.8\) s) was observed before the oxidation of Pd\(^0\) began. In the Ox-I period, \(\rho_{\text{norm}}\) showed a sharp drop of 0.4% in less than 0.1 s, and began to increase with a linear dependence on \(t\) without the accompanying oxidation of Pd\(^0\), suggesting that the recovery of the oxygen deficiency proceeds before the electron transfer process. In the following Ox-II period (\(t = 3.8-12\) s), the oxidation of Pd\(^0\) to Pd\(^{II}\) proceeded with an increase in \(\rho_{\text{norm}}\). The increase in \(\rho_{\text{norm}}\) continued at the same rate constant in the following Ox-III period (\(t > 12\) s), even after the oxidation of Pd\(^0\) into Pd\(^{II}\) was nearly completed. Oxidation from Pd\(^0\) to Pd\(^{II}\) (the increase of \(x_{\text{val}}\)) and the decrease in the oxygen deficiency (the increase of \(\rho_{\text{norm}}\)) are the rate-determining steps and ca. 5 times slower than the reduction as shown by comparison of periods Red-I (ca. 2 s) and Ox-II (ca. 10 s). This is considered to be due to the conversion of Pd\(^0\) to form Pd\(^{II}\)O and/or oxygen diffusion into the deficient sites of the perovskite oxides.

In other words, the responses of change in the palladium states and the oxygen deficiency (\(\delta\)) of oxide supports: SrFeO\(_{3-\delta}\) and Sr\(_4\)Fe\(_6\)O\(_{13-\delta}\) are different between reduction and oxidation during redox-gas cycles; the oxidation requires a longer reaction period than the reduction. This is because the oxygen gas is used for the decrease of deficiency (\(\delta\)) as well as the formation of oxidation Pd\(^{II}\)O clusters. Thus, the oxide supports play a role of “buffer” for oxygen before the Pd\(^{II}\)O clusters start to form, when the oxidative gas is introduced.

This type of strong correlation between the precious metals and the supporting oxides in TWCs has been proposed for Pt on CeO\(_2\) using Raman spectroscopy\(^{26}\) and EXAFS,\(^{27}\) where the strong correlation is attributed to a sintering inhibition mechanism of the Pt particles. In this study, the strong correlation was revealed in a new Pd/Sr–Fe–O catalyst for the first time using \textit{in situ} and simultaneous observation of the redox of Pd and the oxygen storage/release.

4. Conclusion

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 SrFeO\(_3\)\(_{fi}\), Sr\(_4\)Fe\(_6\)O\(_{13}\)\(_{fi}\) and SrFe\(_2\)O\(_{19}\)\(_{fi}\), and small clusters with Pd\(^{II}\)O-like structures are located near the surface region of the oxide grains.

In addition, 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 Pd\(^{II}\) to Pd\(^0\) begins just after the introduction of H\(_2\)/He gas, with a simultaneous increase in the oxygen deficiency (\(\delta\)) in perovskite-type SrFeO\(_3\)\(_{fi}\) and Sr\(_4\)Fe\(_6\)O\(_{13}\)\(_{fi}\). After the completion of the Pd reduction, the recovery (decrease) of \(\delta\) follows. Contrary to this sequence, oxidation from Pd\(^0\) to Pd\(^{II}\) begins after an incubation period, after which the change in \(\delta\) precedes. The palladium oxidation and the increase of \(\delta\) then progress simultaneously.

The palladium-oxidation step accompanying the increase of \(\delta\) is the rate-determining step and is slow, whereas the palladium-reduction step is not rate-determining and ca. 5 times faster than the oxidation. In other words, the oxide phases exhibit a type of “oxygen buffer” effect in the oxidation cycle and delay the formation of Pd–O. The strong correlation between palladium and the supporting oxides causes these phenomena, and the growth of Pd\(^0\) clusters is suppressed in the Pd/Sr–Fe–O catalyst, resulting in its good performance, despite the small amount of loaded precious metal.
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Appendix

Calculation of the reaction rate. When the rate of the reaction $A \rightarrow B$ is given as:

$$v = -d[A]/dt = k[A],$$

the rate constant $k$ is given by:

$$\ln \left( 1 - \frac{[B]_t - [B]_0}{[B]_\infty - [B]_0} \right) = -kt, \quad (A-1)$$

or

$$\frac{[B]_t - [B]_0}{[B]_\infty - [B]_0} = 1 - \exp(-kt), \quad (A-2)$$

where $[B]_t$ represents the concentration of $B$ at time $t$. Here, the left side of eq. (A-2) shows the exponential dependence on $t$.

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