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To cite this article: D Matsumura et al 2009 J. Phys.: Conf. Ser. 190 012154

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Dynamic structural change of Pd particles on LaFeO$_3$ under redox atmosphere and CO/NO catalytic reaction studied by dispersive XAFS

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Abstract.

The local structure of Pd metal fine particles on LaFeO$_3$ which has a high catalytic activity was observed by dispersive XAFS optics from the viewpoint of dynamical structure change of Pd during oxide-metal change and CO/NO catalytic reaction. The oxide-metal change of Pd nanoparticles on LaFeO$_3$ and Al$_2$O$_3$ was investigated by 20-50 Hz rate. It was recognized that, under the reductive atmosphere, Pd atoms show similar speed of movement from oxide to metal state both on the two supports. However, under the oxidative atmosphere, Pd atoms on LaFeO$_3$ show faster movement from metal to oxide state than those on Al$_2$O$_3$. CO/NO catalytic reaction on Pd metal nanoparticles was also observed by 0.2 Hz rate. Slow observation mode made the four EXAFS parameters: coordination number, interatomic distance, Debye-Waller factor and edge shift, precisely determined during catalytic reaction. There are two particular differences between Pd particles on LaFeO$_3$ and Al$_2$O$_3$. Large enhancement of interatomic distance of Pd particle was only observed on Al$_2$O$_3$. Stable surface oxide layer of Pd particle is created on LaFeO$_3$.

1. Introduction

Pd metal particles are used for automotive exhaust catalysts for removal of CO, NO$_x$ and hydrocarbons. Because of the high temperature of exhaust gases, the prevention of the growth of metal particles is the key point for the long time use of automotive exhaust catalysts. Pd/LaFeO$_3$ is known to keep its particle size small even in long time use and is attracted much attention for high property catalysts [1, 2, 3]. It was revealed that the Pd atoms make solid solution and reside in B sites of LaFeO$_3$ perovskite-type crystal under oxidative atmosphere [1]. Different mechanism of preventing the aggregation of metal fine particles, which is making the interface oxide between metal and the support, was also pointed out [4]. These studies for the elucidation of preventing the aggregation were achieved by using x-ray absorption fine structure (XAFS) technique, which means that the XAFS technique is very useful for the study of supported fine particle which is only a few wt% component in total amount.

Dispersive XAFS mode adopting the curved crystal enables us to observe XAFS spectra without mechanical movement at all [5, 6]. Dispersive mode has been mainly applied for the
real-time-resolved observation of chemical reaction [7, 8, 9]. However, precise observation of XAFS parameters has also accomplished in recent years because of the same reason that no mechanical movement is operated during spectra take [10, 11].

In this study, we have utilized the advantage of dispersive XAFS mode, that is fast and stable observation, and applied to the structure and shape changes of Pd metal fine particles. First, oxide-metal structural transformation was studied by high speed observation (20-50 Hz). Next, CO/NO catalytic reaction on the Pd metal particle was studied by slow (0.2 Hz) and highly stable observation. Through these studies, by comparison with supported metal particles Pd/Al$_2$O$_3$, a feature of Pd metal fine particles on LaFeO$_3$ will be recognized.

2. Experiments

Pd(4 wt%)/LaFeO$_3$ was prepared by the alkoxide method. A solution of metal ethoxyethylates [M$^{3+}$-(OC$_2$H$_4$OC$_2$H$_5$)$_3$ (M = La$^{3+}$ and Fe$^{3+}$)] and palladium acetylacetonate [Pd$^{2+}$-(CH$_3$COCHCOCH$_3$)$_2$] in toluene was hydrolyzed with deionized water to give a Pd-containing precipitate [3]. This precursor was dried and then calcined at 800 °C for 2 h in air to give a perovskite powder catalyst containing homogeneously distributed Pd.

Powdered γ-Al$_2$O$_3$ was used as the conventional catalyst by the impregnation method with dilute aqueous palladium nitric acid, Pd(NO$_3$)$_2$. Following drying and calcination at 500 °C, Pd(4 wt%)/Al$_2$O$_3$ whose wt% is similar with the Pd/LaFeO$_3$ sample was prepared.

The Pd K-edge XAFS spectra were measured at the bending magnet beamline BL14B1 of SPring-8 [12]. Some of the spectra were also measured at the BL28B2. The main systems of optics equipment at both beamlines are same. Dispersed x-rays were obtained from the curved crystal of the Si(422) reflection plane with the Laue configuration. From the curvature with a radius of 2000 mm, x-rays with an energy range of 800 eV were obtained. 40 mm thickness of Gd$_2$O$_2$S(Tb) was exposed to dispersed x-rays from the sample and emitted lights were collected using a charge coupled device (CCD) camera (640 × 480 channels, 12 bits). The intensities in the vertical direction (about 200 channels) were summed to get a one-dimensional spectroscopy. The horizontal focus size of the x-rays at the sample position was measured to be 0.1 mm in full width at half maximum (FWHM) and the vertical size is equal to the sample pellet height for accumulating the intensity of transmitted x-rays. Neither vertical focusing nor removal of higher-order reflection using a mirror was adopted.

Powdered samples were pressed with minimum weight keeping safe for sample treatment in order to make a square pellet (∼5 × 5 × 0.3 mm$^3$). For avoiding the hindrance of gas penetration, no dilution materials were used [13]. The absorption coefficient (µt) and edge jump (∆µt) were 2.9 and 0.3 for Pd/LaFeO$_3$, and 1.4 and 0.3 for Pd/Al$_2$O$_3$, respectively.

H$_2$(50%)/He and O$_2$(50%)/He were used for the oxide-metal structural transformation study as the reducing and oxidizing gases, respectively. The gases were supplied at a flow rate of 100 cc/min. A trigger signal from a thermal conductivity detector was used to start the measurement. Spectra were measured at 20-50 Hz as high speed mode. After measurement in an oxidative atmosphere, temperature was increased to 700 °C in the same oxidative atmosphere for 30 s to completely restore the Pd to its oxidation state. Cycle measurements in a reducing-oxidizing treatment were operated. XAFS spectra were accumulated 10 times in order to improve counting statistics.

For the CO/NO catalytic reaction study, CO(9%)/He and NO(9%)/He were used for reaction gases. The gases were supplied at a flow rate of 50 cc/min. Spectra were measured at 0.2 Hz as low speed mode, but high precision results were obtained. No cycle experiments were operated for CO/NO catalytic reaction study.
3. Results and Discussion

3.1. Oxide-metal structural change observed by fast mode (20-50 Hz)

Figure 1 shows the XAFS spectra and the Fourier transform intensities of $k^2$-weighted extended x-ray absorption fine structure (EXAFS) function ($\Delta k = 2.5 \sim 10.5 \text{ Å}^{-1}$) for Pd/LaFeO$_3$ before and after H$_2$ dosing. Pd atoms create metal particles by reduction reaction. Under oxidative atmosphere, Pd atoms are considered to occupy B sites of LaFeO$_3$ perovskite-type structure [1]. For the Fourier transform intensities of EXAFS function, almost all Pd atoms show oxide state under oxidative atmosphere and most of Pd atoms show metallic state under reductive atmosphere.

Dynamic structural transformation induced by surrounding gas change was observed at high speed mode (20-50 Hz). Obtained EXAFS functions were analyzed under assumption that the sample was constructed by simple mixture of Pd oxides and Pd metal particles [14, 15]. Only the nearest-neighbors were considered. The fitting parameters employed were coordination number (CN) and interatomic distance ($R$). Edge energy shift and mean square relative displacement ($C_2$) were fixed through the fitting of time-resolved data set. The absolute values of the edge energy shift and $C_2$ were determined with comparing the simulated spectra using the FEFF 8.4 code [16, 17].

The time-resolved CN of Pd-O and Pd-Pd shells during reductive and oxidative atmospheres at 300 °C are displayed in Fig 2. The zero point of time axis was set by the trigger action. Before the observation of spectra, samples were completely oxidized. Just after H$_2$ dosing, Pd-O shell rapidly decreases and Pd-Pd shell increases. The formation of Pd metal particles on LaFeO$_3$ is accomplished in 1.5 s, though some Pd-O bondings remain unchanged. Pd particles on Al$_2$O$_3$ are also created by 2 s. Both samples show linear shift of change which supports that in this case adsorption or diffusion process governs the structural change rate.

After O$_2$ dosing, striking difference is seen between Pd particles on LaFeO$_3$ and Al$_2$O$_3$. Pd particles on LaFeO$_3$ change their structure from metal to oxide in 2 s. On the other hand, Pd particles on Al$_2$O$_3$ show fast decrease of Pd-Pd shell and increase of Pd-O shell at the start of the oxidation, and then slow changes of both shells are observed. Even at 5 s, most of Pd-Pd bondings remain their chemical bondings.

Past results of transmission electron microscope (TEM) and XAFS observation indicated that the Pd particles on LaFeO$_3$ have 1-2 nm mean diameter [2, 3]. Many surface analysis techniques have revealed that small Pd particles are more easily oxidized than larger ones [18, 19, 20]. In this study, it is considered that the feature of small Pd metal particles appeared. We want to note that the interface oxidation can be realized in Pd metal particles on LaFeO$_3$ [20, 21]. Because Pd atoms make solid-solution with LaFeO$_3$ under oxidative atmosphere, the path of interface oxidation exists. Such components create the faster oxidation mechanism of Pd particles on LaFeO$_3$. 

![Figure 1](image-url)
3.2. CO/NO catalytic reaction on Pd metal nanoparticle observed by slow mode (0.2 Hz)

Most of catalytic chemical reaction take place on the surface of the metal particles. CO/NO catalytic reaction on Pd metal fine particles is widely studied and the reaction model has been recognized. Dissociative adsorption of NO reacts with the molecularly adsorbed CO, then CO$_2$ is generated from atomic O and molecular CO, and also N$_2$ is generated left two atomic N [22].

In this subsection, CO and NO were successively dosed on bare Pd metal particles and structure and shape changes of Pd particles were observed by dispersive XAFS mode.

Figure 3 shows variations in the XAFS parameters determined from dispersive XAFS spectra during CO/NO successive dosing for Pd metal particles on Al$_2$O$_3$. In this subsection, Pd-Pd shell of metal state was analyzed and CN, $R$ and $C_2$ were used as unknown EXAFS parameters. The values of edge shift were obtained from x-ray absorption near edge structure (XANES). It is understood that all obtained XAFS parameters show high relative statistics, that is, 0.02 eV for edge shift, 0.05 for CN and 0.002 Å for $R$.

For CO first dosing, huge enlargement of the interatomic distance (∼0.07 Å) is observed for Pd/Al$_2$O$_3$. This may be considered to be induced by the effect that some of adsorbed CO dissociate on the Pd surface and fcc crystal lattice is expanded by atomic C which is absorbed into the interstitial position. Besides, the CN of Pd-Pd shell gradually decreases with the same time scale of the interatomic distance enlargement. This means that CO dissociative adsorption can induce the dispersion of Pd metal fine particles.

After NO dosing, adsorbed CO is removed and expanded fcc lattice rapidly contracts. At the same time, the edge shift is returned to its original value as well as the CN. This means that NO dissociative adsorption removes the adsorbed CO and absorbed C, and then bare Pd metal surface is revived.

The edge shift shows gradual increase after CO removal by NO flow, which indicates that Pd metal surface is gradually oxidized by the dissociative adsorption of NO. This surface oxidized layer is smoothly removed by the next CO dosing (at ∼2200 s), which is confirmed by the abrupt changes of the edge shift and CN. As for the edge shift, slight positive shift is also observed just after second CO dosing. CO adsorption on the Pd oxidized layer may induce the charge transfer from Pd to CO. After the removal of the surface oxidized layer, gradual increase of the Pd-Pd
interatomic distance is observed again. Different variations of XAFS parameters in the case of Pd/LaFeO$_3$ are displayed in Fig. 4. Scales of all axes of Fig. 4 are the same as those of Fig. 3. It is recognized that all parameters of Pd/LaFeO$_3$ do not show large change during CO/NO successive dosing. Particularly, the interatomic distance of Pd-Pd shell does not altered by the dosing of both of CO and NO at least 0.005 Å, which is quite difference with the case of Pd/Al$_2$O$_3$. After the removal of CO induced by NO dosing, it is implied by the change of the edge shift that saturated surface oxide layer is realized in Pd/LaFeO$_3$. The surface oxide layer is slowly removed by CO dosing, which means that relatively stable surface oxide layer is created.

Gas-solid interaction in the metal fine particles has been widely studied from the viewpoint of the dependence of the mean particle size [23, 24, 25]. The small metal fine particles have many steps, edges and kinks, which induces the dissociative adsorption at the surface of particle. However, in this study, the expansion of the Pd fcc lattice is only observed in the case of Pd/Al$_2$O$_3$ which is considered to have larger particles. We have to consider the particle-support interaction as another explanation of the differences between Pd/LaFeO$_3$ and Pd/Al$_2$O$_3$. As for the oxidation mechanism, Pd/LaFeO$_3$ creates the stable surface oxide layer by NO, whereas the oxidation of the total particles by O$_2$ is easily achieved in Pd/LaFeO$_3$. Because the creation of the oxide layer prevents the dissociative adsorption of NO, the feature of stable surface oxide layer in Pd/LaFeO$_3$ connects to the low power of NO removal reaction. However, preventing inner oxidation during NO dosing for Pd/LaFeO$_3$ may promote the catalysis via Pd metal component.
4. Conclusion
The local structural change of a Pd/LaFeO$_3$ catalyst was compared with that of a Pd/Al$_2$O$_3$ catalyst by using dispersive XAFS mode. 20-50 Hz observation has been revealed that Pd metal particles on LaFeO$_3$ show faster change to oxide state at 300 °C than Pd/Al$_2$O$_3$. For CO/NO catalytic reaction, precise changes of XAFS parameters were indicated by 0.2 Hz observation. Different particle-support interaction induces the different lattice expansion and surface oxidation. From the analysis of real-time-resolved XAFS spectra by dispersive mode, we have clearly demonstrated contraction-expansion, aggregation-dispersion and oxidation-reduction changes in metal fine particles.

Acknowledgments
We are grateful to Dr. A. Suzuki and Professors Y. Inada and M. Nomura of Institute of Materials Structure Science for stimulating discussions. We also thank Mr. K. Kato, Dr. T. Uruga and Dr. H. Tanida for constructing the dispersive XAFS system. This work was supported by the Elements Science and Technology Project.

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