

# IN SITU X-RAY ABSORPTION SPECTROSCOPY STUDY ON WATER FORMATION REACTION OF PALLADIUM METAL NANOPARTICLE CATALYSTS

Matsumura, D.<sup>1</sup>, Taniguchi, M.<sup>2</sup>, Tanaka, H.<sup>3</sup> and Nishihata, Y.<sup>4</sup>

<sup>1</sup> Quantum Beam Science Center, Japan Atomic Energy Agency, 1-1-1 Koto, Sayo,  
Hyogo 679-5165, Japan, daiju@spring8.or.jp

<sup>2</sup> R&D Division, Daihatsu Motor Co., Ltd., 3000 Yamanoue, Ryuo, Shiga 520-2593, Japan,  
Masashi\_Taniguchi@dk.daihatsu.co.jp

<sup>3</sup> R&D Division, Daihatsu Motor Co., Ltd., 3000 Yamanoue, Ryuo, Shiga 520-2593, Japan,  
Hirohisa\_Tanaka@dk.daihatsu.co.jp

<sup>4</sup> Quantum Beam Science Center, Japan Atomic Energy Agency, 1-1-1 Koto, Sayo,  
Hyogo 679-5165, Japan, yasuon@spring8.or.jp

## ABSTRACT

Proper management of hydrogen gas is extremely important for the safety security of nuclear power plants. Hydrogen removal by the water formation reaction on a catalyst is one of the candidates for creating hydrogen safety system. We observed in situ and real-time-resolved structure change of palladium metal nanoparticles during the water formation reaction by using X-ray absorption spectroscopy technique. The effect of carbon monoxide poisoning on catalytic activity was also studied. We have found that the creation of oxidized surface layer on palladium metal nanoparticles plays an important role of the water formation reaction process.

## 1 INTRODUCTION

Hydrogen gas management is one of the biggest issues to maintain safe operation of nuclear power plants. A large amount of hydrogen gas can be released when the nuclear power plant has suffered severe accidents. Many paths of hydrogen gas generation are assumed such as radiolytic decomposition of water, reduction reaction of water molecules on a surface of zirconium alloy cladding of a fuel rod, and high-temperature reaction between molten nuclear fuel and concrete [1]. In case of the severe accident at Fukushima nuclear power plant, hydrogen management system which needs external electric power could not work because all outside electric supplies had been shut down. An alternative hydrogen management system which does not rely upon external electric power is seriously required.

Water formation reaction between emerged hydrogen and oxygen gases in the air is a promising candidate to reduce hydrogen gas from the reactor vessel and the containment building of the nuclear power plant. Precious metal nanoparticles have already been used as catalysts of the water formation reaction under the hydrogen management system in some nuclear power plants [2]. Hydrogen molecules react on the surface of precious metal nanoparticles with oxygen molecules and are converted to water molecules. This reaction itself is exothermic and passive, so that it does not need external power supply, and negative enthalpy change of the formation reaction brings about acceleration of the surface catalytic chemical reaction. From such merits of the reaction, the development of this management system called as passive autocatalytic recombiner (PAR) is greatly hoped.

The reaction system of PARs is similar with the automotive catalytic reaction. Many harmful gases including hydrogen and hydrocarbons emerge from the exhaust of automobiles. Such reductive gases are converged to water and carbon dioxide via the automotive catalytic reaction with oxygen gases. Our group is now developing a new PAR based on a new concept which connects with the automotive catalyst [3,4]. The automotive catalysts have been very widely studied from both fundamental and application aspects [5,6]. Refinement in the long-year development process makes it easy to prepare

the best-fitted catalyst for PARs in the nuclear power plants. Compact volume and light weight which are the features of the automotive catalyst can be good topics when it is applied to PARs through the simplicity of assessment and inspection.

It is important to understand the surface structure of the precious metal nanoparticles during the chemical reaction progress because some of metal nanoparticles show various structural and electronic changes stimulated by the surrounding temperature and atmosphere. X-ray absorption fine structure (XAFS) spectroscopy is a unique technique for studying element-selective atomic and electronic structures. XAFS technique has a feature of easy applicability for real-time-resolved observation. We have developed dispersive optics for the real-time-resolved XAFS observation at SPring-8 in Japan [7,8]. This system which consists of a curved crystal and a position sensitive detector enables us to take XAFS spectroscopy in second or sub-second time scale [9,10]. We have applied this observation system for the water formation reaction of precious metal nanoparticle catalysts which are used in PARs for the nuclear power plants.

In order to secure a reliable assessment and inspection, the information about the precise reaction path including the mechanism of degradation of a catalyst is very important. Some products and conditions in a nuclear containment, such as humidity, increase of temperature, released iodine and carbon monoxide produced from the molten corium concrete interaction, are considered as impediments for the safety management of PARs. In this study, the reaction mechanism of the water formation reaction between hydrogen and oxygen gases on palladium metal nanoparticles was examined. Besides, the mechanism of deterioration by the presence of carbon monoxide was also studied. In situ and real-time-resolved observation by continuous XAFS spectra can reveal a subtle change of surface of palladium metal nanoparticles due to the surface catalytic chemical reaction. Importance of the surface structure of palladium metal nanoparticles for the water formation reaction is discussed.

## 2 EXPERIMENTS

All Pd *K*-edge XAFS spectra were measured with a dispersive mode at the bending magnet beamlines BL14B1 and BL28B2 of SPring-8 [7,8]. Both beamlines are equipped with similar apparatus. The schematic picture of optics is displayed in Fig. 1. A curved silicon crystal called as a polychromator was exposed to white X rays to emerge energy-dispersed X rays. Dispersed X rays were obtained by Si(422) reflection plane with the Laue configuration. The polychromator was bent horizontally by setting it in a curved copper block cooled by water. From the curvature with a radius of about 2000 mm, X rays with an energy range of about 1000 eV were generated. Samples were set to the focal point of X rays. Gd<sub>2</sub>O<sub>2</sub>S(Tb) of 100 μm thickness was exposed to re-dispersed X rays from the sample position and emitted lights were collected using a charge coupled device (CCD) camera (640 × 480 channels, 12 bits). The intensities in the vertical direction (~200 channels) were summed up to produce a one-dimensional spectroscopy. The horizontal focal size of X ray was measured to be 0.05 mm in full width at half maximum (FWHM) and the vertical size is widened to about 3 mm height for accumulating the intensity of transmitted X rays.

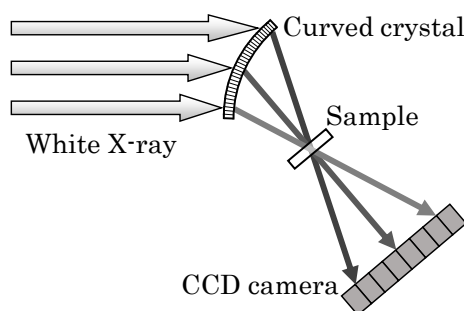


Figure 1. Schematic picture of dispersive optics (top view).

Dilute aqueous palladium nitric acid,  $\text{Pd}(\text{NO}_3)_2$ , and powdered  $\gamma\text{-Al}_2\text{O}_3$  were used for preparing a palladium metal nanoparticle catalyst by the impregnation method. Following drying and calcination at  $500\text{ }^\circ\text{C}$ ,  $\text{Pd}(2, 1, 0.5\text{ wt\%})/\text{Al}_2\text{O}_3$  samples were obtained.

All XAFS spectra were collected under in situ and real-time-resolved mode. Before the observation under a reactive gas flow, the sample was set to completely reduced phase by hydrogen gas flow at  $400\text{ }^\circ\text{C}$  in 5 min. Remained gases were removed by the pure He flow at  $400\text{ }^\circ\text{C}$  in 10 min. Observation temperature was set to between room temperature and  $200\text{ }^\circ\text{C}$ . Carbon monoxide gas was used as reaction obstruction gas. Gas concentration was controlled by a gas flowmeter and a mixture system with He gas and set to  $\text{H}_2(2\text{-}10\text{ \%})$  and  $\text{O}_2(2\text{-}4\text{ \%})$  which were kept below the hydrogen explosion limit. Total flow rate was set to  $100\text{ cc/min}$ . In the case of cyclic gas flow experiment,  $\text{H}_2$  and  $\text{O}_2$  were flowed alternately by 10 s.

### 3 RESULTS AND DISCUSSION

Dispersive optics are expected to bring about high-precision data set of real-time-resolved XAFS spectra because there are no mechanical motion components. We show the typical results of real-time-resolved XAFS spectra at Pd  $K$ -edge by dispersive optics in Fig. 2. Mixture of hydrogen (10 %) and oxygen (2 %) gases were dosed for palladium (2 wt%) metal nanoparticles on aluminum oxide at room temperature. Exposure time of one spectroscopy was 0.5 s. All spectra were taken under high stable observation conditions owing to the advantage of dispersive optics. We can distinguish the slight change of spectra by the increase of the white line which is located at just above the absorption edge. Small increase of white line and subtle high energy shift of the absorption edge induced by the oxidative reaction under  $\text{H}_2$  and  $\text{O}_2$  flow are recognized owing to the increase of average valence value of palladium, which is considered to be derived from the creation of surface oxide layers. In this study, we mainly focused on X-ray absorption near edge structure (XANES) region and the change of the absorption edge energy which is sensitive for the oxidation and reduction reaction of surface of Pd metal nanoparticles. The absorption edge position was evaluated by fitting spectra with a simple step function and was determined to be a middle point of the step function.

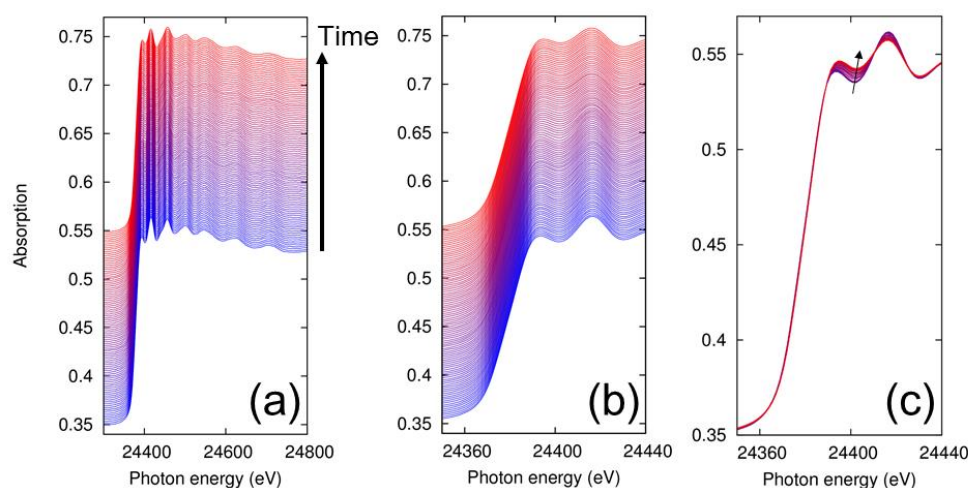


Figure 2. Typical change of XAFS spectra of  $\text{Pd}(2\text{ wt\%})/\text{Al}_2\text{O}_3$  just after the injection of the mixture gas containing  $\text{H}_2(10\text{ \%})$  and  $\text{O}_2(2\text{ \%})$  at room temperature. 100 spectra are displayed and exposure time of one spectroscopy is 0.5 s. The spectra are shifted toward vertical direction in the case of extended energy region (a) and XANES region (b). (c) is same energy region with (b) and the spectra are not vertically shifted.

Figure 3 shows the variations of the absorption edge position during a flow of mixture of  $\text{H}_2$  and  $\text{O}_2$  gases for the  $\text{Pd}(2\text{ wt\%})/\text{Al}_2\text{O}_3$  with a frame rate of 2 Hz. Before the flow of reaction gases, the sample was set to complete metal state by  $400\text{ }^\circ\text{C}$  reduction reaction and following He flow. The injection of

the reaction gas was started at 0 s. An abrupt increase of the absorption edge position is observed just after the reaction gas flow. Fast creation of surface oxide layer is clearly indicated. As the gas flow proceeds, the absorption edge position slightly increases. For the case of only oxygen gas flow, similar change of the absorption edge position is recognized. Because hydrogen gas is a reductive one, if hydrogen gas is effective for the creation of the surface oxide layer of palladium nanoparticles, the absorption edge energy should be increased compared with the case of mixture of hydrogen and oxygen gas flow. It is shown that the surface layer is oxidized irrespective of the existence of hydrogen gas. A precise determination of the oxidation states of metal nanoparticles is realized because the relative precision of the absorption edge position is only about 0.05 eV even in the case of 2 Hz observation and no fluctuation of base line is observed in this time scale. We can also evaluate the reaction rate of surface oxidation from the real-time-resolved data.

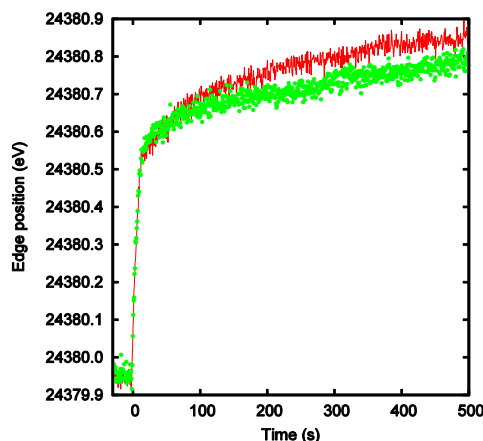


Figure 3. The change of the absorption edge position for Pd(2 wt%)/Al<sub>2</sub>O<sub>3</sub> by flow of H<sub>2</sub>(10 %) and O<sub>2</sub>(2 %) (red line), and O<sub>2</sub>(2 %) (green point) at room temperature.

Some palladium metal nanoparticles are compared in order to assess the creation of the surface oxide layer. Samples of Pd loading of 2, 1, 0.5 wt% are summarized in Fig. 4. In this loading range, the mean diameter of palladium nanoparticles show a positive correlation with the loading amount. The mean diameter of palladium nanoparticles determined by a CO pulse adsorption method is 4.2, 3.2 and 2.0 nm for 2, 1 and 0.5 wt% of Pd loading, respectively. This figure indicates that, as the mean diameter decreases, the positive shift of the absorption edge position increases. This is a reasonable change if the only surface region is oxidized by the mixture of hydrogen and oxygen gas flow. Pd nanoparticles show a thin surface oxide layer and the inner region keeps a metallic state in this reaction condition.

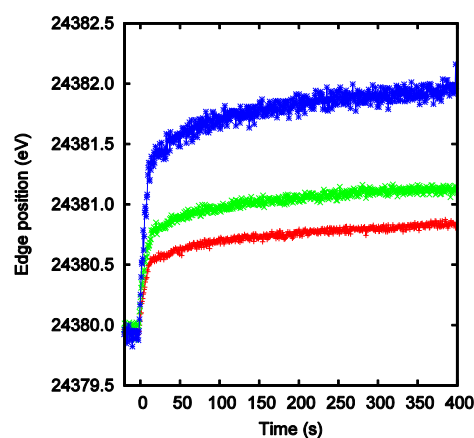


Figure 4. The change of the absorption edge position for Pd/Al<sub>2</sub>O<sub>3</sub> with a loading of 2 (red), 1 (green) and 0.5 wt% (blue) by flow of H<sub>2</sub>(10 %) and O<sub>2</sub>(2 %) at room temperature.

Cyclic flow of hydrogen and oxygen gases provides information that is different from the case of the mixture of hydrogen and oxygen gas flow. Results of some concentrations of the cyclic gas are displayed in Fig. 5. In this figure, the first flowed gas is hydrogen and only the first gas is supplied for 20 s following 10 s cycle of H<sub>2</sub>/O<sub>2</sub> flow. The negative shift of the absorption edge position indicates that palladium hydride is created via the hydrogenation reaction of palladium nanoparticles. Just after the first oxygen gas flow, the absorption edge position shows steady positive shift, which means that the fast dehydrogenation and oxidation reactions occur. In the case of hydrogen-rich condition such as H<sub>2</sub>(10 %)/O<sub>2</sub>(2 %) and H<sub>2</sub>(10 %)/O<sub>2</sub>(4 %), the excess negative shift beyond the value of the pure metal state is observed under the reductive condition. This shows that the hydrogenation reaction progresses continuously after the disappearance of the surface oxide layer. Two types of hydrogen molecular elimination mechanisms, that is, surface catalytic reaction and palladium hydrogenation reaction, may indicate the positive character of PAR developed by the palladium base system.

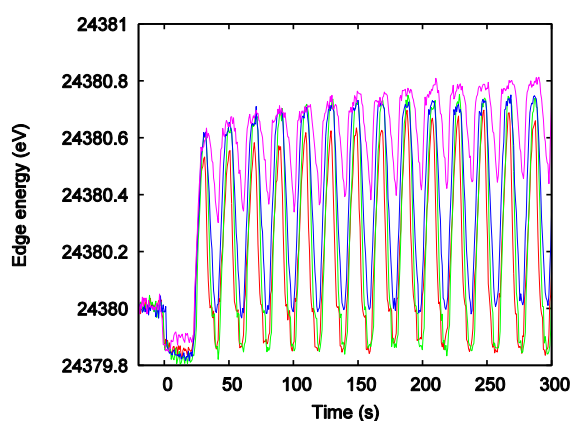


Figure 5. The change of the absorption edge position for Pd(2 wt%)/Al<sub>2</sub>O<sub>3</sub> by cyclic flow of H<sub>2</sub>(10 %)/O<sub>2</sub>(2 %) (red), H<sub>2</sub>(10 %)/O<sub>2</sub>(4 %) (green), H<sub>2</sub>(5 %)/O<sub>2</sub>(4 %) (blue) and H<sub>2</sub>(2 %)/O<sub>2</sub>(4 %) (violet) at room temperature.

Figure 6 also shows the result of cyclic flow of H<sub>2</sub>/O<sub>2</sub>, but in this case the first supplied gas is oxygen. Positive shift of the absorption edge position is related to the creation of the surface oxide layer of Pd nanoparticles and the oscillation of the absorption edge position indicates growth and decline of the oxidized surface of Pd, because it corresponds to the atmosphere switching. These results show that the thickness of the oxidized surface layer increases as temperature increases, which implies that the creation of the surface oxide layer correlates with the effectiveness of the surface catalytic reaction because a faster reaction rate is usually observed at higher temperature.

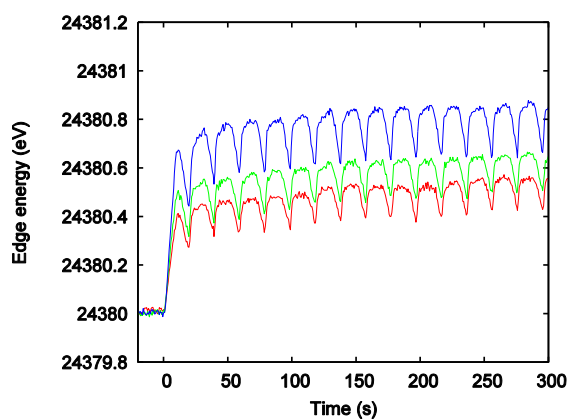


Figure 6. The change of the absorption edge position for Pd(2 wt%)/Al<sub>2</sub>O<sub>3</sub> by cyclic flow of H<sub>2</sub>(2 %)/O<sub>2</sub>(4 %) at room temperature (red), 100 °C (green) and 200 °C (blue).

Deterioration of catalytic activity by CO is a severe problem not only for PARs but also for several catalytic systems using Pd or Pt metal nanoparticles [11]. When CO is combined with the cyclic flow of hydrogen and oxygen gases, the absorption edge shift of Pd nanoparticles completely disappears (Fig. 7). This indicates that the surface of Pd nanoparticles is completely covered with CO molecules and oxygen gas does not reach the surface of nanoparticles. Besides, hydrogen conversion was not observed under the CO existence condition. Oxide layer creation should be the key of the water formation reaction. However, at a temperature of 200 °C, some variations of the absorption edge position are observed although the oscillation style is completely different from the case without CO gas. Hydrogen removal process was also recovered in this situation of the elevated temperature. That is to say, the change of the absorption edge energy, which means the occurrence of creation and removal of the surface oxide layer, is closely related to the activity of Pd metal nanoparticle as the water formation catalysts used for the hydrogen elimination in PARs. CO oxidation reaction is known to start from around 200 °C [12]. The observed complicated oscillation of the absorption edge position may be due to the combination of the CO oxidation reaction and hydrogen oxidation reaction. The selectivity of the oxidation reaction of CO and hydrogen is the big issue for the property of PARs because CO gas is considered to hinder the hydrogen removal process of PARs. The improvement of the selectivity is another subject in the future study [13].

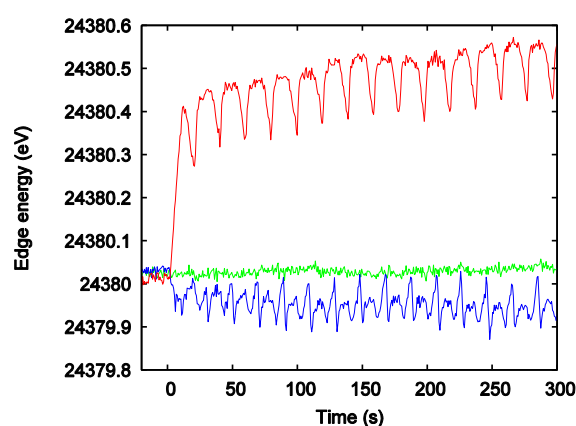


Figure 7. The change of the absorption edge position for Pd(2 wt%)/Al<sub>2</sub>O<sub>3</sub> by cyclic flow of H<sub>2</sub>(2 %)/O<sub>2</sub>(4 %) at room temperature (red), H<sub>2</sub>(2 %)/O<sub>2</sub>(4 %) with CO(5 %) at room temperature (green), and H<sub>2</sub>(2 %)/O<sub>2</sub>(4 %) with CO(5 %) at 200 °C (blue).

The water formation reaction and CO poisoning processes are summarized in Fig. 8. Hydrogen is not directly reacted with oxygen on the clean surface of Pd nanoparticles but is reacted on the oxide layer of Pd nanoparticles. Hydrogen gas does not show the dissociative adsorption and does not create Pd hydride. CO molecule is adsorbed on the surface of Pd nanoparticles around at room temperature. Strong adsorption energy hinders the creation of the oxide layer and water molecule formation. The start of CO oxidation catalytic reaction is a trigger of the start of the water formation reaction and hydrogen elimination system. The competition of the oxidation reaction of hydrogen and carbon monoxide molecules should be studied in order to reveal the complete reaction process of the ternary mixture of hydrogen/oxygen/carbon monoxide system used in PARs for the nuclear power plant aiming at safety against severe accidents.



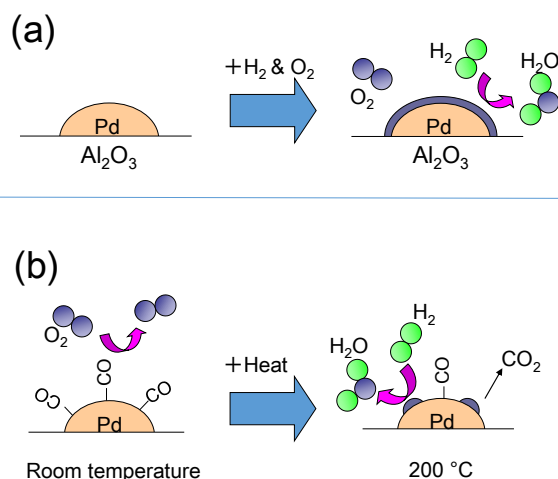


Figure 8. The images of (a) a surface catalytic reaction between hydrogen and oxygen gases, and (b) a CO poisoning effect for Pd nanoparticles.

#### 4 CONCLUSIONS

We have shown the experimental results of the real-time-resolved XAFS spectra for Pd metal nanoparticles which will be used in the new PARs under the condition of water formation reaction. The water formation reaction progresses on the surface of Pd oxide layer and hydrogen gas does not create Pd hydride. CO poisoning effect was also studied and it is revealed that the water formation reaction will not occur as far as CO is molecularly adsorbed on the metallic surface of Pd nanoparticles. We have found that the creation of an oxidized surface layer on Pd nanoparticles plays an important role in the water formation reaction process.

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