

# X-RAY ABSORPTION SPECTROSCOPY STUDY ON HYDROGEN RECOMBINATION CATALYSTS OF PALLADIUM NANOPARTICLES ON TITANIUM OXIDE UNDER WET CONDITION

Matsumura, D.<sup>1,\*</sup>, Aida, T.<sup>2</sup>, Aotani, T.<sup>2</sup>, Yamamoto, T.<sup>2</sup>, Nakamura, K.<sup>2</sup>, Inagawa, K.<sup>2</sup>, Tsuji, T.<sup>1</sup> and Tanaka, H.<sup>2</sup>

<sup>1</sup> Materials Sciences Research Center, Japan Atomic Energy Agency, 1-1-1 Koto, Sayo, Hyogo 679-5148, Japan, \*daiju@spring8.or.jp

<sup>2</sup> Graduate School of Science and Technology, Kwansai Gakuin University, 1 Gakuen Uegahara, Sanda, Hyogo 669-1330, Japan

## ABSTRACT

Hydrogen recombination catalyst is useful tool for reducing hydrogen in closed area. The catalyst is known to be poisoned under wet condition in long time use. The study is focused on the behavior of pre-oxidized Pd nanoparticle as the hard-used catalyst in high humidity environment by comparison of alumina and titanium oxide supports using in situ X-ray absorption spectroscopy technique. The reduction of surface oxide layer of Pd/TiO<sub>2</sub> was promoted by water during hydrogen recombination, although the reduction reaction of Pd/Al<sub>2</sub>O<sub>3</sub> was inhibited by water.

## 1. INTRODUCTION

Hydrogen gas management in nuclear power plants is important issue for keeping safe operation of the plant. A large amount of hydrogen gas can be released when the power plant has suffered severe accidents. Some paths of hydrogen gas formation have been considered such as radiolytic decomposition of water molecules, reduction reaction of water on a surface of zirconium alloy cladding of a fuel rod, and high-temperature reaction between molten corium and concrete [1]. In case of the severe accident at Fukushima nuclear power plant, hydrogen management system which needs external electric power did not work because all outside electric supplies had been shut down. An alternative hydrogen management system which does not rely upon external electric power should be required.

Hydrogen recombination reaction between emerged hydrogen gas and oxygen gas in the air is a promising candidate for decrease of hydrogen gas from the reactor vessel and the containment building of the nuclear power plant. The hydrogen recombination reaction is the same with a simple water formation reaction. Some hydrogen management systems in nuclear power plants use precious metal nanoparticles as catalysts for the hydrogen recombination reaction [2]. Hydrogen molecules react on the surface of precious metal nanoparticles with oxygen molecules and are converted to water molecules. This reaction is exothermic and passive one, so that it does not need external power supply, and negative enthalpy change of the reaction brings about acceleration of the surface catalytic reaction, which denotes autocatalysis. From such merits, the hydrogen management system using catalysts, called as passive autocatalytic recombiner (PAR), is greatly hoped to be developed.

The reaction system in PARs is similar with that of automotive catalysts. Some flammable and harmful gases including hydrogen are discharged from the exhaust of automobiles. Reductive gases such as hydrocarbons and carbon monoxide are converted into water vapor and carbon dioxide gases via the automotive catalytic reaction with oxygen gas. We have been studying a new PAR system based on a concept that the automotive catalyst can be used for hydrogen recombination reaction [3-7]. Automotive catalysts have been very widely researched from both fundamental and practical aspects for a long time [8]. The long development process of the automotive catalyst enables us to apply the useful catalyst to PARs in the nuclear power plant. The features of compact volume and light weight for automotive catalyst will be a good character of the new PARs because of the simplicity of assessment and inspection.

Information of surface structure of precious metal nanoparticles during reaction is important because metal nanoparticles often change their atomic and electronic structures by the fluctuation of surrounding temperature and atmosphere. X-ray absorption fine structure (XAFS) spectroscopy is a unique technique for studying local structure and average valence value of the target element. It is comparatively easy to employ XAFS technique for *in situ* and time-resolved observation in real-time mode because of high sensitivity and long attenuation length of X-rays. We have been developing *in situ* and time-resolved XAFS by using dispersive optics at SPring-8 in Japan [9, 10]. This optics system consists of a curved crystal and a position sensitive detector. XAFS spectra can be taken in second or sub-second time scale [11, 12]. We have adopted this observation system as the study of hydrogen recombination reaction of precious metal nanoparticle catalysts which are used in PARs for the nuclear power plants.

The mechanism of degradation of catalysts are very significant for reliable assessment and inspection. Some surrounding conditions in a containment building, such as high humidity, increase of temperature, released iodine and carbon monoxide produced by the molten corium concrete interaction, are considered as impediments for the safety management of PARs. In this study, we have focused on the influence of high humidity on the catalysis of palladium metal nanoparticle for the hydrogen recombination reaction. Some catalysts are known to be poisoned under wet condition in long-time usage. We have assumed pre-oxidized palladium nanoparticle catalysts as the model of long-time used catalysts. The catalytic reaction on palladium nanoparticles was examined by using *in situ* and time-resolved XAFS technique under dry and wet conditions. Alumina and titanium oxide were compared for understanding the effect of the support against high humidity condition. XAFS spectra have revealed the precise mechanism of the catalytic reaction and the effect of prior existence of water molecules on the water formation reaction. The mechanism of poisoning effect of water molecules and the surface structures of palladium nanoparticles and supports during hydrogen recombination reaction are 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 [13]. The schematic picture of optics is displayed in Fig. 1. A curved silicon crystal called as polychromator was exposed to white X-rays to emerge energy-dispersed X-rays. Dispersed X-rays were obtained by Si(422) reflection plane with Laue configuration. The polychromator was bent horizontally by attaching the crystal to a bent crystal holder made by copper. From the curvature with a radius of about 2000 mm, X-rays with an energy range of about 600 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 complementary metal-oxide semiconductor (CMOS) camera (2048 × 2048 channels, 16 bits). The intensities in the vertical direction (~500 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.

Palladium metal nanoparticle catalysts were prepared by impregnation method using dilute aqueous palladium nitrate, Pd(NO<sub>3</sub>)<sub>2</sub>, and powdered γ-Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Titanium oxide shows the anatase structure. Following drying and calcination at 400 °C, Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> and Pd(0.5 wt%)/TiO<sub>2</sub> samples were obtained. About 100 mg of the sample was pressed by hand to make a pellet (φ = 7 mm) and attached in an *in situ* XAFS cell. All XAFS spectra were collected under *in situ* observation and time-resolved mode in real-time measurement. The sample was set to completely reduced phase by 10 % H<sub>2</sub> gas flow at 400 °C in 10 min. Pre-oxidized catalysts were realized by following 10 % O<sub>2</sub> gas flow at 400 °C in 10 min. And then the temperature was decreased until room temperature with the He flow. XAFS observation temperatures for all samples and conditions were room temperature. Mixture of gases was controlled by a gas mixture system with mass flow controllers of He, H<sub>2</sub> and O<sub>2</sub> gases. The concentrations of H<sub>2</sub> and O<sub>2</sub> to He were set to H<sub>2</sub>(5 %) and O<sub>2</sub>(5 %) which insures that the mixture gas keeps outside the hydrogen explosion limit. High humidity condition was realized with a

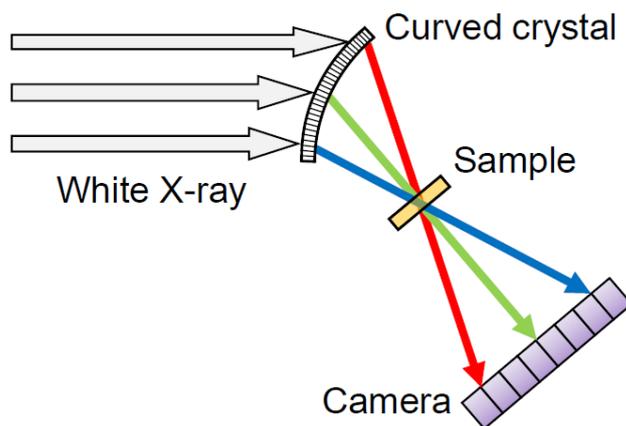


Figure 1. Schematic picture of XAFS observation system using dispersive optics with Laue configuration (top view).

humidifier with 30 °C of the dew point. In the case of dry gas condition, gas line for the humidifier was skipped. Total flow rate was set to 100 cm<sup>3</sup>/min. Flowed gas from the sample was monitored by a quadrupole mass spectrometer (OmniStar, Pfeiffer Vacuum GmbH).

### 3. RESULTS AND DISCUSSION

Dispersive optics are expected to bring about high-precision data set of time-resolved XAFS spectra in real-time measurement because there are no mechanical motion process during observation of spectra. Here we show the typical results of time-resolved XAFS spectra at Pd *K*-edge by dispersive optics in Fig. 2. O<sub>2</sub>(5 %) gases was flowed for pre-oxidized Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> at room temperature. Exposure

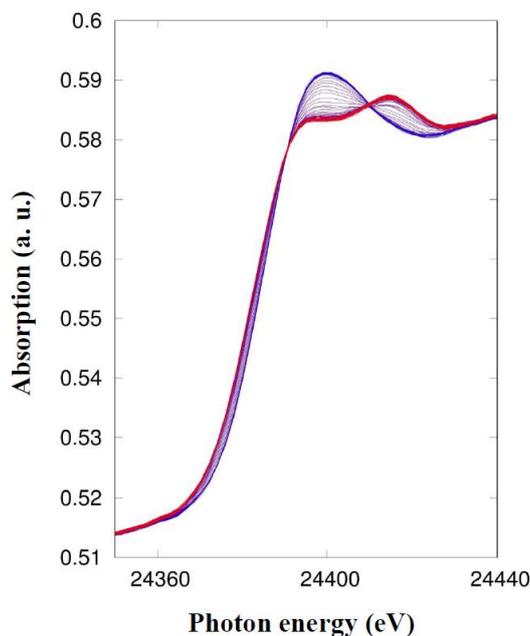


Figure 2. Typical results of time-resolved XAFS spectra for pre-oxidized Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> at Pd *K*-edge during reduction reaction with H<sub>2</sub>(5 %) gas flow at room temperature. The sampling rate is about 0.8 Hz. Blue lines indicate the pre-oxidized Pd nanoparticles and red lines indicate reduced Pd nanoparticles.

time of one spectrum was 1.2 s. All spectra were taken under stable observation conditions owing to the advantage of dispersive optics. Although small distortions are observed in the spectra with dispersive mode, we can recognize the spectra show the smooth change during the reduction reaction even in the case of about 0.8 Hz observation mode. This suggests the reliability of XAFS spectra in this experimental setup. Main spectroscopic change is found at the edge position and the peak intensity which is located just after the edge jump. We evaluated the average valence value of Pd element by the photon energy of edge position. The edge position was determined by fitting the spectra with error function including asymmetric factor. This study was focused on only X-ray absorption near edge structure region and the change of the absorption edge energy which is sensitive for the redox state of surface of palladium nanoparticles.

The temporal change of the absorption edge position of pre-oxidized Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> during the switching gas flow of H<sub>2</sub>(5 %) and O<sub>2</sub>(5 %) is shown in Fig. 3. Hydrogen and oxygen gases were alternately flowed in 100 s in order to understand precise structural change of palladium nanoparticles. The cyclic gas flow of H<sub>2</sub> and O<sub>2</sub> was started at 100 s in Fig. 3. Before the cyclic gas flow, the sample was kept under He gas flow. The comparison between dry and wet conditions are included in Fig. 3. Under the dry condition, an abrupt decrease of the absorption edge position was observed right after the first hydrogen gas flow. This corresponds to the reduction of palladium oxide to form metal phase. Similar abrupt increase of the absorption edge position was observed right after the oxygen gas flow. This corresponds to the re-oxidation of the Pd nanoparticle. Reduction and oxidation reactions of Pd nanoparticles are intense in the case of dry condition through all observation time. On the other hand, under the wet condition, the magnitude of reduction and oxidation reaction observed in the change of absorption edge position was smaller than that under the dry condition. In particular, the first reduction reaction at the beginning of the cyclic gas flow under the wet condition is the slowest reaction in the process. The magnitude of redox reaction of palladium nanoparticles grows as the cyclic reaction proceeds. This suggests that the prior water molecule covers the surface of the pre-oxidized palladium nanoparticles, which hindered the reduction reaction of palladium oxide by the hydrogen flow. The poisoning effect of high humidity connects with the low catalytic activity on the hydrogen recombination reaction.

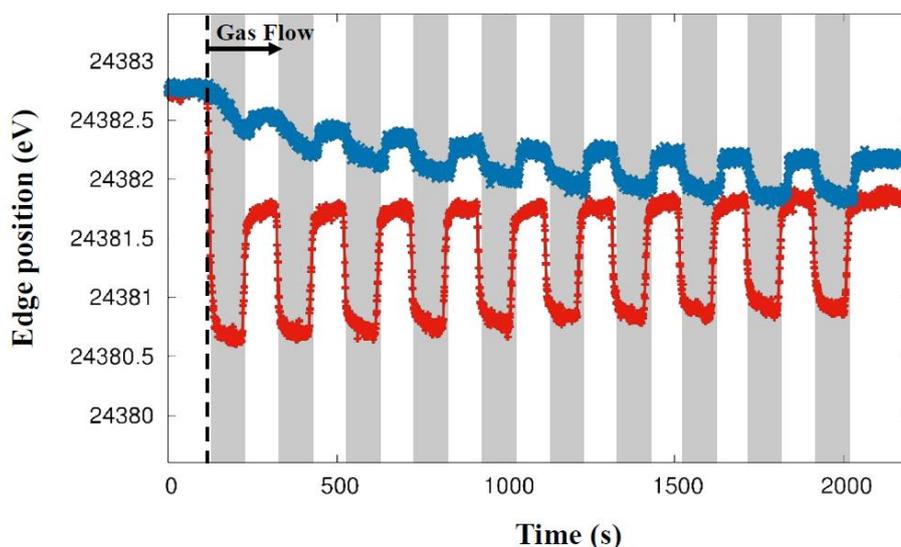


Figure 3. The temporal change of the absorption edge position for pre-oxidized Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> during cyclic gas flow of hydrogen (grey area) and oxygen (white area) gases at room temperature under the dry (red) and wet (blue) conditions.

In order to overcome the poisoning effect of water molecules observed in the wet condition for pre-oxidized Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts, titanium oxide was used as the supports of the catalyst. The temporal change of the absorption edge position of pre-oxidized Pd(0.5 wt%)/TiO<sub>2</sub> catalyst during the cyclic gas flow of hydrogen and oxidation gases are displayed in Fig. 4. Because X-rays are absorbed much for the TiO<sub>2</sub> support than Al<sub>2</sub>O<sub>3</sub> support, the exposure time for one XAFS spectrum was set to 3.8 s. The change of the absorption edge position during cyclic gas flow for pre-oxidized Pd(0.5 wt%)/TiO<sub>2</sub> indicates sharp contrast with the case of pre-oxidized Pd(0.5 wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts shown in Fig. 3. Pre-oxidized Pd(0.5 wt%)/TiO<sub>2</sub> performs active change both under the dry and wet conditions. Furthermore, the magnitude of redox reaction of palladium nanoparticles under the wet condition is larger than that under the dry condition for pre-oxidized Pd(0.5 wt%)/TiO<sub>2</sub>. This trend is clearly recognized especially in the first region of the cyclic gas flow. The TiO<sub>2</sub> support is known to form interfacial oxides with Pd metal nanoparticles [14]. It has also been reported that oxygen vacancies are likely to be generated around the interface, and then water molecule is adsorbed on the vacancies to form hydroxyl groups [15-17]. Therefore, the formation of hydroxyl groups makes a difference in the oxidation and reduction reaction under dry and wet conditions between TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> support. This mechanism can relate with the high performance of Pd/TiO<sub>2</sub> for the hydrogen recombination catalyst under wet condition in long time use. We have proved the availability of palladium nanoparticle catalysts on TiO<sub>2</sub> support for the PAR system in the nuclear power plant.

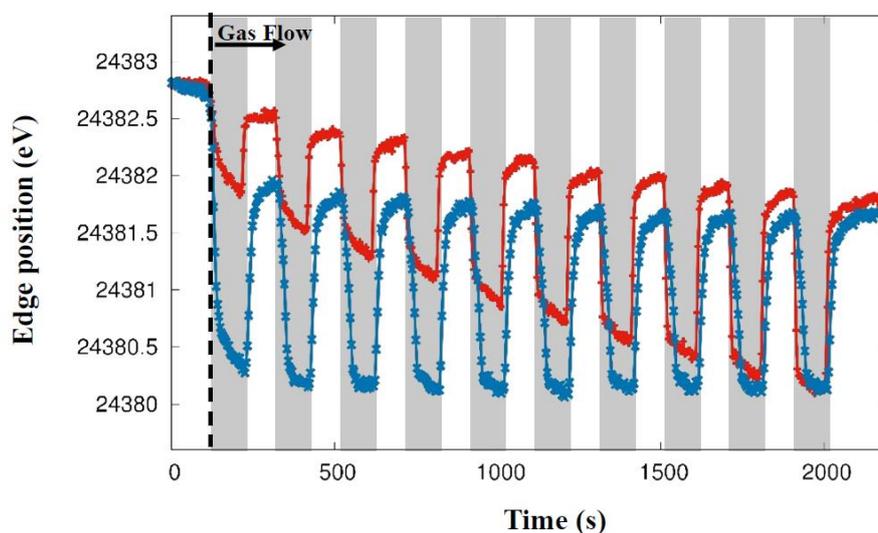


Figure 4. The temporal change of the absorption edge position for pre-oxidized Pd(0.5 wt%)/TiO<sub>2</sub> during cyclic gas flow of hydrogen (grey area) and oxygen (white area) gases at room temperature under the dry (red) and wet (blue) conditions.

#### 4. CONCLUSIONS

*In situ* and time-resolved XAFS observation for hydrogen recombination reaction of pre-oxidized palladium nanoparticles with alumina and titanium oxide supports under wet condition was employed. The surface redox reaction of palladium nanoparticle is hindered under the wet condition in the case of alumina support. On the other hand, high humidity assists the reduction reaction of surface palladium oxide layer in the case of titanium oxide support catalyst. The palladium nanoparticle catalyst on titanium oxide support will be a good candidate for the hydrogen recombination catalyst.

## ACKNOWLEDGEMENTS

We would like to thank Ms. Y. Okajima of SPring-8 Service Co. Ltd. and Mr. K. Kato of Japan Synchrotron Radiation Research Institute for their helpful discussion about dispersive optics. Part of this work was supported by the Advanced Nuclear Hydrogen Safety Research Program funded by Agency for Natural Resources and Energy of Ministry of Economy, Trade and Industry. The present experiment was performed under the approval of Japan Synchrotron Radiation Research Institute (Proposal Nos. 2015B1443, 2018A1453, 2020A3609, 2021A3609, 2021B3609, 2022A3609, 2022B3609 and 2022B3630). The SPring-8 experiment was also supported by the Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM Japan) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Grant No. JPMXP1222AE0023) and the Shared-Use Program of JAEA Facilities (Proposal No. 2022B-E05). A part of this work was the results of the international joint project “Towards Safe Storage and Transportation of Cryogenic Hydrogen (STACY)” supported by Strategic International Collaborative Research Program of Japan Science and Technology Agency (JST SICORP), Grant No. JPMJSC21C3, Japan.

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