TPR-XAFS STUDY FOR HYDROGEN REOMBINATION REACTION OF PLATINUM METAL NANOPARTICLE CATALYSTS

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ABSTRACT

Proper management of hydrogen gas is very important for safety of nuclear power plants. Hydrogen removal system by hydrogen recombination reaction (water formation reaction) on a catalyst is one of the candidates for avoiding hydrogen explosion. We have observed *in situ* and time-resolved structure change of platinum metal nanoparticle catalyst during hydrogen recombination reaction by using simultaneous measurement of temperature-programmed reaction and X-ray absorption fine structure (TPR-XAFS). A poisoning effect by carbon monoxide on catalytic activity was focused. It was found that the start of hydrogen recombination reaction is closely connected with the occurrence of the decomposition of adsorbed carbon monoxide molecules and creation of surface oxide layer on platinum metal nanoparticles.

1. INTRODUCTION

Hydrogen gas management in nuclear power plants is very important for keeping safe operation. A large amount of hydrogen gas can be released when the power plant has suffered severe accidents. Some paths of hydrogen gas formation exist such as radiolytic decomposition of water molecules, reduction reaction of water molecules 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 (water formation reaction) between emerged hydrogen gas and oxygen gas in the air is a promising candidate for reduction of hydrogen gas from the reactor vessel and the containment building of the nuclear power plant. Some hydrogen management systems in nuclear power plants use precious metal nanoparticles as catalysts for 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 itself 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. 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 and hydrocarbons are discharged from the exhaust of automobiles. Such reductive gases are converted into water vapor and carbon dioxide gases via the automotive catalytic reaction with oxygen gas. We are now developing a new PAR based on a concept that the automotive catalyst can be used for hydrogen recombination reaction [3, 4, 5, 6].

Automotive catalysts have been very widely studied from both fundamental and practical aspects for a long time [7]. The great development processes of the automotive catalyst enable us to apply the useful catalyst to PARs in the nuclear power plants. Compact volume and light weight will be the features 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) is a unique technique for studying atomic and electronic structures 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 studying *in situ* and time-resolved XAFS by using dispersive optics at SPring-8 in Japan [8, 9]. This optics system consists of a curved crystal and a position sensitive detector. One XAFS spectroscopy can be taken in second or sub-second time scale [10, 11]. 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.

Reaction manners including 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, the hydrogen recombination reaction on platinum metal nanoparticles was examined and the deterioration by the presence of carbon monoxide was mainly focused. Simultaneous observation of temperature-programmed reaction and XAFS (TPR-XAFS) can continuously detect both of reaction product and structure of catalysts. This reveals a structure change of platinum metal nanoparticles at the time of the occurrence of reaction. The mechanism of poisoning effect of carbon monoxide and surface structure change of platinum metal nanoparticles during hydrogen recombination reaction are discussed.

2. EXPERIMENTS

All Pt L_3-edge XAFS spectra were measured with a dispersive mode at the bending magnet beamline BL14B1 of SPring-8 [12]. 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(111) reflection plane with the Bragg configuration. The polychromator was bent horizontally by grabbing both sides and was cooled by dipping in an In-Ga pool. From the curvature with a radius of about 2000 mm, X-rays with an energy range of about 600
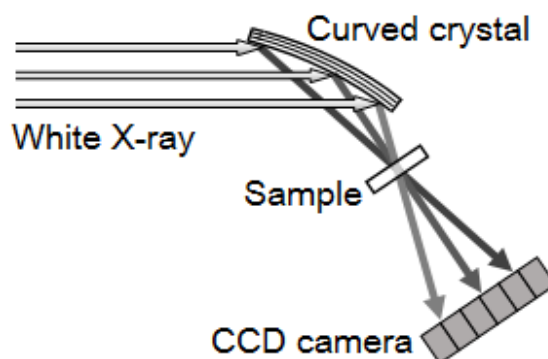

Figure 1. Schematic picture of XAFS observation system using dispersive optics with Bragg configuration (top view).

eV were generated. Samples were set to the focal point of X-rays. $Gd_2O_2S(Tb)$ 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.

Dilute aqueous diamminedinitro platinum, $Pt(NO_2)_2(NH_3)_2$, and powdered γ-Al_2O_3 were used for preparing a platinum metal nanoparticle catalyst by the impregnation method. Following drying and calcination at 500 °C, Pt(4 wt%)/Al_2O_3 samples were obtained. 40 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 H_2 (>99.9999 %) gas flow at 400 °C in 5 min before XAFS observation. After that, remained hydrogen gas were purged by He (>99.9999 %) flow at 400 °C in 10 min. And then the temperature was decreased until room temperature with the He flow. Observation temperature was raised for TPR-XAFS measurement at a constant ramp of 10 K/min. Mixture of gases was controlled by a gas mixture system with mass flow controllers of He, H_2 and O_2 (>99.9999 %) gases. The concentrations of H_2 and O_2 to He were set to H_2(4 %) and O_2(10 %) which insures that the mixture gas keeps below the hydrogen explosion limit. Carbon monoxide was added to the mixture gas for the poisoning experiment by a concentration of 1 %. Total flow rate was set to 100 cm^3/min and safety systems are considered. 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 components in the optics. Here we show the typical results of time-resolved XAFS spectra at Pt L_3-edge by dispersive optics in Fig. 2. Mixture of H_2(4 %) and O_2(10 %) gases were flowed for Pt(4 wt%)/Al_2O_3 at room temperature. Exposure time of one spectroscopy was 0.5 s. All spectra were taken under stable observation conditions owing to the advantage of dispersive optics. Neither spikes nor distortions are recognized in the spectra even in the case of 2 Hz observation mode, which suggests the reliability of XAFS spectra in the experimental setup.
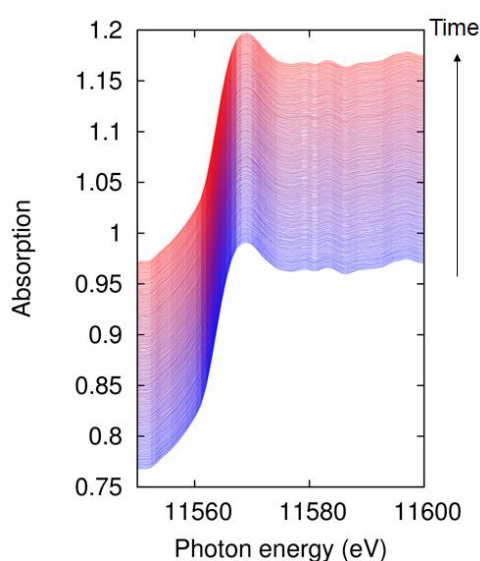

Figure 2. Typical results of time-resolved XAFS spectra for Pt(4 wt%)/Al_2O_3 at Pt L_3-edge under flow of mixture of H_2(4 %) and O_2(10 %) gases at room temperature. The sampling rate is 2 Hz.

The changes of XAFS spectra by gaseous adsorption on the surface of Pt nanoparticles are summarized in Fig. 3. This figure indicates the spectra change of Pt metal nanoparticles between clean surface and oxygen or carbon monoxide adsorbed surfaces. It is recognized that Fig. 3(a) shows the slight increase of the peak intensity which is located at around the absorption edge. The peak intensity around the absorption edge is well known to relate to the oxidation state of platinum element [13]. The increase of the peak intensity by oxygen flow is understood to be originated in surface platinum oxidation or surface oxygen adsorption. On the other hand, in the case of carbon monoxide flow, the peak position is slightly shifted to the higher energy side (Fig. 3(b)). It was reported that chemisorption of carbon monoxide on platinum surface results the higher energy shift of the absorption peak of Pt L_3-edge [14]. The surface of Pt metal nanoparticle is covered by carbon monoxide molecules in the case of carbon monoxide flow. We want to note that the style of spectra change by oxygen flow is different with that by carbon monoxide flow. This means that we can distinguish the surface adsorption species of Pt metal nanoparticles by monitoring the peak intensity and the peak position of Pt L_3-edge XAFS spectra. In this study, we focused on X-ray absorption near edge structure (XANES) region. The changes in the peak intensity and the peak position in XANES spectra were determined by fitting the spectra with the Gaussian peak and the error function.
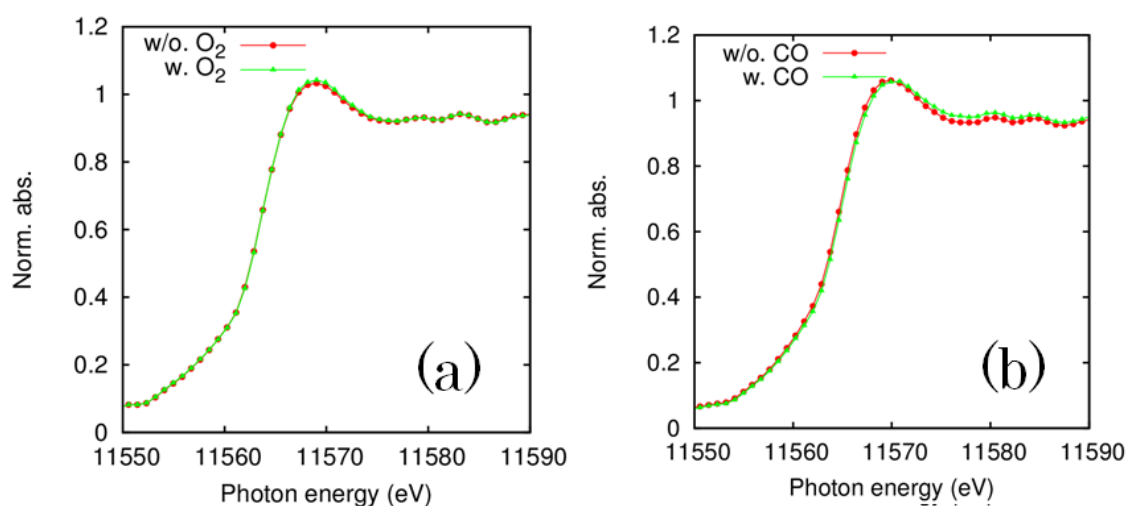

Figure 3. Pt L_3-edge XAFS spectra for Pt(4 wt%)/Al$_2$O$_3$ with and without (a) oxygen and (b) carbon monoxide flow at room temperature.

TPR-XAFS technique is very useful for monitoring structure change of catalysts and relating the changes to catalysis [15]. Continuous observation of XAFS spectra by using dispersive optics is powerful tool for the determination of the effects of time and/or temperature on the change of structure of catalyst. Fig. 4 summarizes the TPR-XAFS results for Pt(4 wt%)/Al$_2$O$_3$ catalyst during hydrogen recombination reaction. Top graphs in Fig. 4 indicate the changes of reaction gas component obtained by the quadrupole mass spectrometer. Middle and bottom graphs show the shifts of the peak intensity and the peak position obtained from XAFS spectra, respectively. Mixture gas of H$_2$(4%) and O$_2$(10%) was flowed at 0 s of the graphs under room temperature condition. For the case of only hydrogen and oxygen flow (Fig. 4(a)), water molecules are formed via hydrogen recombination reaction right after the reaction gas flowed even at room temperature. About 200 s after the start of reaction gas flow, temperature was increased at constant ramp of 10 K/min. As temperature increases, the amount of water molecule gradually increases and hydrogen gas decreases. This suggests the reaction rate of hydrogen recombination reaction grows in higher temperature region. For the XAFS spectra change, it is seen that only the gradual increase in both the peak intensity and the peak position is observed. Oxidation of platinum element is known to cause not only the increase of peak intensity but also the higher energy shift of peak position [13]. These changes of XAFS spectra are understood that the surface of Pt metal nanoparticle is gradually oxidized by the increase of temperature and the surface oxidation of Pt metal nanoparticle is important for hydrogen recombination reaction.
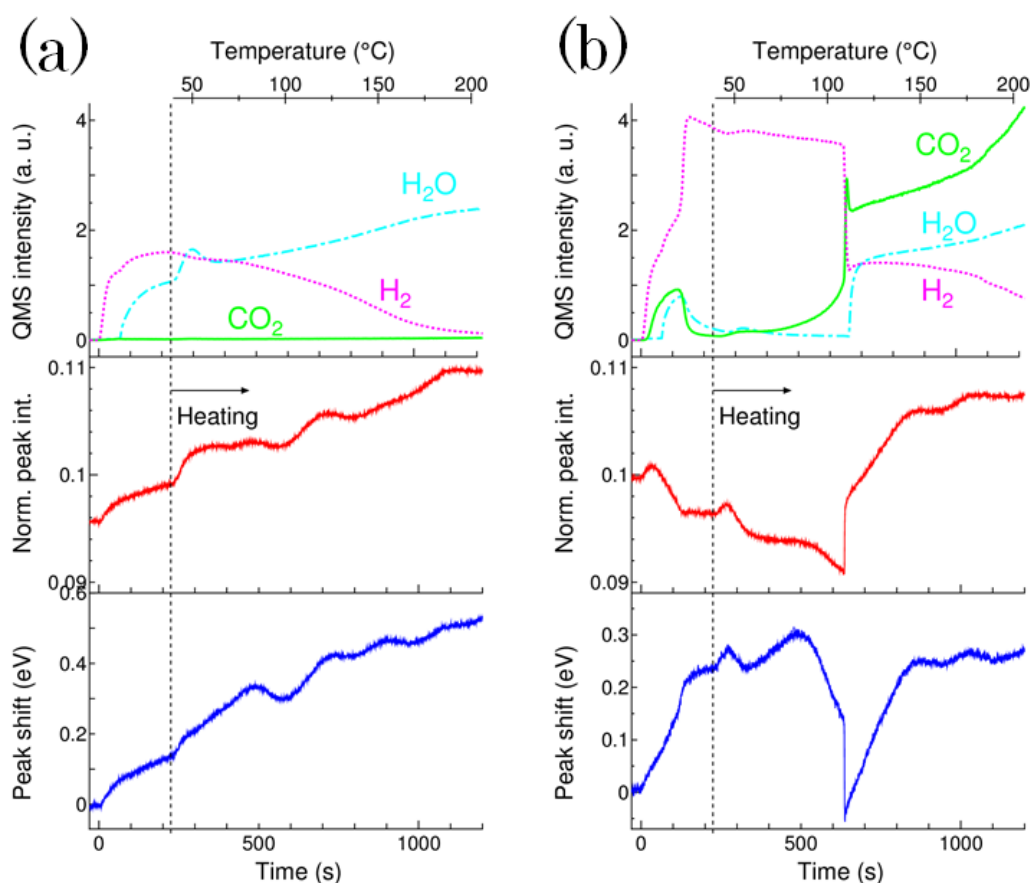
Figure 4. TPR-XAFS results for Pt(4 wt%)/Al$_2$O$_3$ during hydrogen recombination reaction. Top graphs indicate the flowed gas intensity after passage the sample obtained from the quadrupole mass spectrometer. Middle and bottom graphs are the peak intensity and the shift of the peak position obtained from XAFS spectra, respectively. Reaction gases of (a) H$_2$(4%) + O$_2$(10%) and (b) H$_2$(4%) + O$_2$(10%) + CO(1%) were started to flow at 0 s. Temperature was increased from room temperature at constant ramp of 10 K/min from vertical dashed line position.

Adding carbon monoxide in reaction gas should influence largely on hydrogen recombination reaction because carbon monoxide is well known to have poisoning effect on catalytic reaction. Fig. 4(b) is the TPR-XAFS results for the case of CO addition. The hydrogen gas elimination style is completely different with the case of only hydrogen and oxygen gas flow. Although water molecules are formed right after mixed reaction gas flow, the intensity of water molecules rapidly decreases and water formation reaction stopped. We can see the similar change of carbon dioxide intensity right after mixed gas flow. The peak intensity of XAFS spectra shows small peak right after the mixed reaction gas flow, and then decreases beyond the initial position. The peak position shows gradual positive shift by the mixed reaction gas flow, indicating that the surface of Pt metal nanoparticle first adsorbs oxygen molecules and then hydrogen and carbon monoxide oxidation reactions proceeds in short time, but after several tens of seconds, the surface of Pt metal nanoparticles gradually adsorbs carbon monoxide molecules, and finally the surface is completely covered by carbon monoxide molecules and hydrogen and carbon monoxide oxidation reactions stops at about 150 s. Temperature increase changes such situation. Sudden increase of carbon dioxide and water molecules, and sudden decrease of hydrogen is observed at around 110 °C. And at the same time and temperature, sweep increase of the peak intensity and negative shift of the peak position is shown. It is considered that the changes of gas component and XAFS spectra occur at the same time at least in the limit of time scale of simultaneous measurement of TPR-XAFS (0.5 s). The sharp increase of the peak intensity indicates the surface of Pt metal nanoparticles is quickly covered by oxide. The sharp negative shift of the peak position is related to the fast decomposition of adsorbed carbon monoxide. For carbon monoxide

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oxidation reaction in the lower temperature region, it is observed that the adsorbed carbon monoxide is gradually decomposed and oxidized to carbon dioxide from the results that the carbon dioxide intensity shows gradual growth and the peak position shows gentle negative shift in 80-110 °C.

We have shown that the surface structure of Pt metal nanoparticle strongly influences the catalytic activity of hydrogen recombination reaction. The change of surface structure of Pt metal nanoparticle is displayed in Fig. 5. Pt oxide layers are created on the surface of Pt metal nanoparticles after hydrogen and oxygen gas flow, which accelerates hydrogen recombination reaction. This reaction mechanism is the same with the case of Pd metal nanoparticles [6]. The hydrogen recombination reaction stopped when the surface of Pt metal nanoparticle is covered by CO molecules. At around 110 °C, decomposition of adsorbed CO molecule and oxidation of surface of Pt metal nanoparticles happens simultaneously in a short time. Thus, hydrogen recombination reaction proceeds via the surface Pt oxide with carbon monoxide oxidation reaction. For making a new PAR which works even at the room temperature and the existence of CO gas, it is important to cover the surface of Pt metal nanoparticle by oxide. Supports with oxygen storage capacity will be the candidate for overcoming the CO poisoning effect below 110 °C. We are now developing new PAR systems with other several supports for Pt metal nanoparticles. These results will be reported soon.
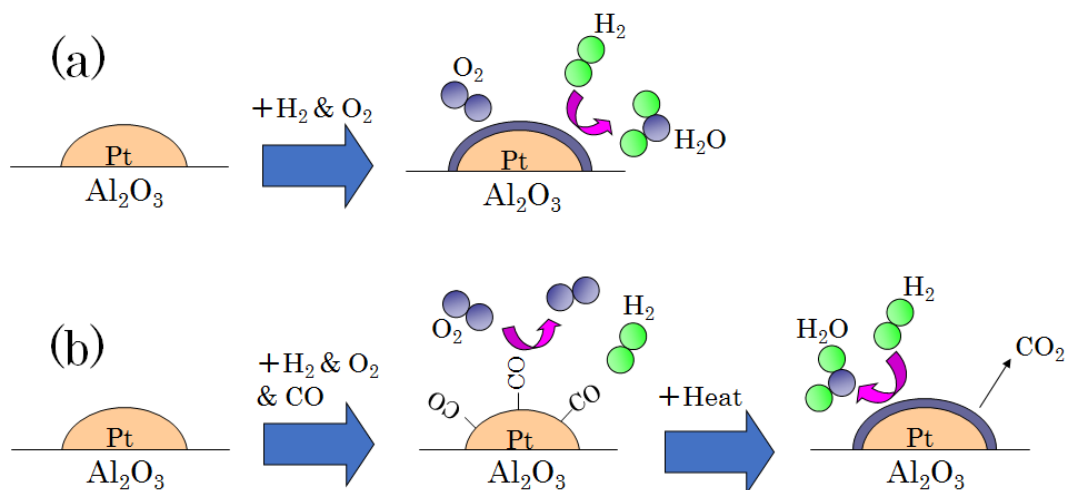

Figure 5. The images of hydrogen recombination reaction on Pt metal nanoparticle catalysts with the cases of (a) $H_2 + O_2$ and (b) $H_2 + O_2 + CO$ mixed reaction gas flow.

4. CONCLUSIONS

We have shown the experimental results of TPR-XAFS technique with the time-resolved XAFS spectra for hydrogen recombination reaction of Pt metal nanoparticles which can be used in the PARs. The hydrogen recombination reaction progresses on the surface of Pt oxide layer. It is found that the hydrogen recombination reaction does not occur as far as CO is molecularly adsorbed on the metallic surface of Pt nanoparticles. We have shown that the creation of oxidized surface layer on Pt nanoparticles and the decomposition of adsorbed CO molecular happens simultaneously in a short time. Surface oxide species are important for hydrogen recombination reaction process.

5. ACKNOWLEDGEMENTS

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