200 Hz observation of hydrogenation reaction of Pd nanoparticles by using dispersive XAFS optics

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Abstract. Observation of X-ray absorption fine structure (XAFS) spectroscopy with dispersive optics is attractive application for the study of chemical reaction from a viewpoint of real-time-resolved structural change. We have constructed dispersive optics for XAFS spectroscopy measurement at SPring-8 BL14B1 and succeeded to detect real-time-resolved structural transformation of Pd nanoparticles under hydrogenation reaction with high reaction rate at room temperature. 200 Hz observation of the hydrogenation reaction of Pd nanoparticles reveals the expansion of Pd-Pd interatomic distance with a time step of 5 ms by analysing extended X-ray absorption fine structure (EXAFS) region.

1. Introduction

Palladium is one of the classical materials for the hydrogen storage system and well known to show high performance for hydrogenation reaction because of the small activation barrier for the surface adsorption and the exothermal reaction for the inner absorption [1]. Hydrogen atoms are known to be absorbed into the octahedral interstitials of Pd face-centered-cubic (fcc) structure and hydrogenation reaction is realized in the wide ranges of the hydrogen pressure and the sample temperature. The low-concentrate phase of Pd-H system creates the solid-solution with high solubility (α phase). Some types of Pd-H chemical bondings are generated in the high-concentrate phase and metal hydride phase with largely expanded lattice is established (β phase).

Although there is a significant phase boundary between the α phase and the β phase in the bulk Pd, the Pd metal fine particles show smooth change between two phases [2]. Surface effect [3] and size effect [4] were suggested for the explanation of the peculiar properties of hydrogenation in the Pd metal fine particles. It is necessary to observe the structure of the Pd nanoparticles during hydrogen absorption reaction in order to judge the formation of hydride phase over the whole of particles.

There are also open questions about the dynamic absorption process because most of dynamic studies were carried out from the viewpoint of pressure change of surrounding hydrogen gases. Direct observation of the dynamical structural and electronic changes of Pd metal nanoparticles during...
hydrogenation reaction, which consists of surface adsorption and following inner penetration processes, has been achieved by our group using X-ray absorption fine structure (XAFS) with dispersive optics system [5,6]. The continuous structural change of Pd nanoparticles under hydrogenation reaction in millisecond order was revealed by the real-time-resolved XAFS spectra. Surface dissociative adsorption process of hydrogen molecular gases was found to be the limiting-rate process of hydrogenation reaction of Pd nanoparticles.

In this study, we report 200 Hz observation of hydrogenation reaction of Pd nanoparticles by using dispersive XAFS system. As far as we know, 200 Hz observation is the fastest operation in the meaningful real-time-resolved XAFS observation including extended X-ray absorption fine structure (EXAFS) region. We will here show the details of the observed spectra and structural parameters.

2. Experiments

A powdered γ-Al$_2$O$_3$ was used for 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$_3$ sample was prepared. Evaluated mean diameter of Pd nanoparticles by the CO pulse adsorption method is 5.1 nm.

XAFS spectra were taken at the beamlines of BL14B1 and BL28B2 at SPring-8 with transmission and dispersive modes [7,8]. Both beamlines are used for white X-ray study and have similar optics for dispersive XAFS system [5,6,9,12]. Main results were obtained at BL14B1. Dispersed X rays were generated by a curved polychromator with Si(422) reflection plane and Laue configuration. Samples were set at the position of 2000 mm distance from the polychromator. Transmitted X rays were converted to visible light by a P43 phosphor screen and detected by a charge coupled device (CCD) camera (640 × 480 pixels, 12 bits, 120 Hz for full region detection). 200 Hz detection is realized in the CCD camera by using 2 × 2 binning mode. Neither vertical focusing nor cutting higher-order harmonics by a mirror was adopted.

The samples were reduced by hydrogen gases at 200-400 °C in the XAFS sample cell just before the XAFS study. The sample cell was evacuated about 15 minutes at room temperature in order to ensure the complete pure metal phase before the Pd K-edge X-ray observation. Hydrogen gas was stored in the inlet line after closing the valve connected to the sample cell. After closing the vacuum

![Figure 1. Pd K-edge XAFS spectra for the Pd(4 wt%)/Al$_2$O$_3$ during hydrogenation reaction with 660 kPa hydrogen gas at room temperature. XAFS spectra were observed by dispersive mode at a rate of 200 Hz. Hydrogen dosing signal is set to 0 ms. Wide energy region (a) and focusing on oscillation region (b) are displayed. Vertical lines are eye guides for the contraction of oscillation wavelength after hydrogen dosing.](image-url)
line, an opening signal from the valve connected to the inlet line was used to start the XAFS measurement. The XAFS measurements of Pd nanoparticles on Al₂O₃ during H₂ dosing were operated at room temperature by 200 Hz rate (sampling time for one spectrum is only 5 ms) with the real-time-resolved mode. No data accumulation by the repetition of the reaction was adopted.

3. Results

Figure 1 shows the results of the 200 Hz observation of XAFS spectra for the Pd(4 wt%)/Al₂O₃ taken with dispersive mode just after the 660 kPa hydrogen dosing at room temperature. It is recognized that the oscillations in the extended region from Pd absorption edge are clearly observed even in the case of 200 Hz observation mode. The oscillation wavelength contracts just after the hydrogen dosing, indicating that the Pd-Pd interatomic distance is elongated by the hydrogen absorption. Figure 2 shows EXAFS functions and Fourier transform intensities of the spectra depicted in figure 1. We are also convinced that the Pd-Pd interatomic distance is elongated as the hydrogenation reaction proceeds.

EXAFS curves were fitted for getting the structural parameters [13]. Free parameters were coordination number, interatomic distance, and Debye–Waller factor. Figure 3 shows the time-resolved observation of the expansion of the Pd-Pd interatomic distance for the Pd nanoparticles with the hydrogen pressure dependence at room temperature. This figure clearly demonstrates that the hydrogen absorption rate strongly depends on the surrounding hydrogen pressure. The reaction rate increases as the hydrogen pressure increases. This indicates the non-zeroth order of the chemical reaction rate. The half-life reaction time is only 5 ms at the highest hydrogen pressure of 660 kPa in the figure 3. It is noted that high-rate observation itself is easy in dispersive optics because it only depends on the frame rate of one- or two-dimensional detector. However, meaningful high-rate observation is not easy. In this study, it is revealed that the reaction time between hydrogen gases and Pd nanoparticles reaches about 5 ms. The reaction time of 5 ms can be determined by 200 Hz and above real-time-resolved observation only. We have first succeeded to observe meaningful XAFS spectra including EXAFS region with a high rate of 200 Hz in real-time-resolved mode.

The monotonic slope of the value of the interatomic distance implies that Pd undergoes smooth change from α to β phase in nanoparticles. The Pd nanoparticles directly change to β phase without

![Figure 2](image-url)

*Figure 2. k²-weighted EXAFS functions (a) and Fourier transform intensities (b) for the spectra depicted in figure 1.*
duration time for coexistence of α and β phases. Figure 3 also indicates that the saturated value of the interatomic distance also depends on the surrounding hydrogen pressure. The saturated value of the interatomic distance increases as the hydrogen pressure increases. Nanoparticle Pd shows a smooth change to β phase with a change of hydrogen pressure although a sudden change to β phase occurs in the bulk Pd. The observed two hydrogen pressure dependences which are the reaction rate and the saturated interatomic distance clearly suggest that the interatomic distance directly reflects the hydrogen absorption property of the Pd nanoparticle.

The chemical reaction order was estimated from the inverse of the half-life reaction time under the assumption that the kinetics of the absorption reaction is constructed by the one chemical reaction step [6]. The value of the reaction order was determined to $0.84 \pm 0.08$. The hydrogen absorption process normally consists of the two reaction steps: the surface dissociative adsorption and the inner diffusive penetration. If the reaction rate of hydrogenation is limited by the surface adsorption step, the chemical reaction order must be evaluated to 1 because the hydrogen in the gas phase is evaluated as $H_2$ molecules. On the other hand, if the hydrogenation reaction is limited by the inner diffusion step, the chemical reaction order must be evaluated to 2 because the diffusion is operated by $H$ atoms. The determined chemical reaction order in this study is almost one. This indicates that, even in the case of high hydrogen pressure and short reaction time, the hydrogenation reaction of the Pd nanoparticle is limited by the surface dissociative adsorption step, which is a same result with the previous work which was operated lower hydrogen pressure than this study [6].

4. Discussion

Dispersive optics is suitable for very high-rate real-time-resolved XAFS observation. Quick motion of monochromator is also used for the high-rate real-time-resolved XAFS observation, which is now approaching 100 Hz observation [14,15]. This technique is the exact opposite of dispersive optics from the viewpoint of the motion of optics. Dispersive optics shows no mechanical motion during XAFS observation, which brings about high data stability and low sample generality. Successive XAFS spectra taken by dispersive optics are very stable without any energy correction in one dataset. However, dispersive optics is almost only used under transmission mode. It is also noted that quick motion of monochromator is difficult in high-energy region because of the narrow bandwidth of diffracted X rays.

The hydrogen absorption reaction for the metallic system is largely different from the other normal gas-solid chemical interaction from the viewpoints of the time-dependence. The hydrogen atom sometimes fast diffuses to the inner side of metal without large structural rearrangement because of the small atomic radius of the hydrogen atom. This character of the hydrogen absorption is quite unique.

Figure 3. Real-time-resolved change of the interatomic distance of the Pd(4 wt%)/Al$_2$O$_3$ during the hydrogenation reaction at room temperature. The spectra were continuously observed at 200 Hz and the sampling time of each point is 5 ms. Partial hydrogen pressures at the sample position are 160 kPa (●), 230 kPa (▲), 410 kPa (▼) and 660 kPa (♦).
when comparing with the other light-element addition reactions in the gas-solid reaction systems such as the oxidation, nitrogenation, and carbonization. It is important to adopt the method with high frame rate and high sensitivity for making a reliable analysis in order to observe fast and subtle reaction. XAFS technique is an element selective method and can be used as a time-resolved analysis by adopting dispersive optics, which is very useful for the research of the real-time-resolved atomic and electronic structure during hydrogenation reaction.

The high-pressure experiments around the atmospheric pressure such as this study are seldom conducted in the case of the bulk Pd surface. The hydrogen absorption kinetics under low pressure has been studied [16]. It was pointed out that the inner diffusion step limits the rate of the hydrogen absorption reaction for the clean surface of Pd. It is deduced that the hydrogen diffusion step is more critical than the case of the low pressure study because the absorbed hydrogen largely elongates the interatomic distance of Pd in the hydride phase. Therefore, the hydrogen diffusion step should limit the reaction rate for the hydrogen absorption reaction in the high-pressure region. However, the surface dissociative adsorption step is the key process for the hydrogen absorption reaction in this study. Two reasons are considered for the change of the limiting-rate step. One is the difference of the surface in nanoparticle and single crystal. There are many steps and kinks in the surface of nanoparticle, which may change the surface dissociative adsorption property of Pd nanoparticles [17]. Another is the change of the diffusive penetration rate of the hydrogen atoms in the nanoparticles. The penetration mechanism can be influenced by the size of the particles because the size of the particles is as small as nanometer range [18].

Although the limiting-rate process for the hydrogen absorption reaction of Pd nanoparticles was revealed by the kinetic analysis, there are open and important problems to be resolved from the viewpoint of the time-resolved observation. Pd nanoparticles are not energetically stabilized during the middle stage of the hydrogenation reaction proceeds. It is a problem whether the hydrogen atoms are thinly diffused over the whole particle or densely reside at the surface of the particle in this non-equilibrium state. The hydrogen permeation for Pd membranes with a thickness of micrometer order was discussed from the competition of inner diffusion, surface adsorption, and desorption processes [19]. The diffusion process is still unclear in the case of nanometer size and high hydrogen concentration phase. Width of the domain walls was discussed from the conception named coherent and incoherent models as for the domain boundary in the bulk Pd-H system [20]. There are stress-free surface and stressfull interface in the case of nanoparticles. It is interesting to determine the model of domain walls in nanoparticles because the interface stress can be controlled by changing support material and/or particle size. The support and/or size dependent study can enable us to understand the hydrogen absorption property of nanoparticle with more deeply interesting hydrogenation mechanism.

5. Conclusion
Hydrogenation reaction of Pd nanoparticles at room temperature was studied by using real-time-resolved XAFS spectra including EXAFS region. Dispersive XAFS optics at SPring-8 beamline enables us to observe the dynamic structural change of Pd nanoparticles with 5 ms of reaction time by 200 Hz detection mode. Surface dissociative adsorption process is the limiting-rate process even in such short time reaction.

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