CO adsorption and decomposition on Pd/Al₂O₃ studied by time-resolved XAFS using dispersive optics

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Abstract.

We have studied surface structural change of supported Pd metal nanoparticles caused by CO adsorption and following temperature increase by using in situ and time-resolved X-ray absorption fine structure technique with dispersive optics. CO adsorption on Pd metal nanoparticles at room temperature shows two types of adsorption behavior and the less stable CO which brings about surface expansion of Pd metal nanoparticles is desorbed just after temperature increase. Pd carbide layer is created at around 350 °C by CO decomposition, which was clearly detected by the elongation of Pd-Pd interatomic distance and the increase of Debye-Waller factor and third cumulant.

1. Introduction

Supported Pd metal nanoparticles have been widely used as practical catalytic reactions such as hydrogenation reaction, cross-coupling reaction, and redox reaction of exhaust gas. Catalysis at surface often accompanies changes of surface structure of Pd metal nanoparticles [1, 2]. Because the surface structural change due to adsorption is relatively small against the bulk structural change, it is needed to build up high-stable observation system for obtaining information of change of surface structure when we adopt useful bulk-sensitive approach such as X-ray absorption fine structure (XAFS).

XAFS spectroscopy with dispersive optics enables us to observe XAFS spectra without mechanical movement at all [3, 4], which means that this technique has a potential of high-stable XAFS observation especially in the high energy region due to the low X-ray band width. We have applied dispersive XAFS system to the structure and shape changes of supported Pd metal nanoparticles [5, 6, 7]. Continuous observation with high sampling rate brings about large data sets, therefore the precise change of structural parameters such as interatomic distance, Debye-Waller factor (C₂) and third cumulant (C₃) can be revealed by the consistent analysis of large XAFS data sets [8].

In this study, we employed the in situ and time-resolved XAFS technique with dispersive optics for understandings of CO surface adsorption on Pd nanoparticles at room temperature and following temperature raising. Time-resolved XAFS observation by dispersive optics were performed for estimation of surface structural change of Pd metal nanoparticles. We have
succeeded to reveal the CO surface adsorption and decomposition mechanism on Pd metal nanoparticles.

2. Experiments
Pd K-edge XAFS spectra were measured by the dispersive mode with Laue configuration at the bending magnet beamline BL14B1 and BL28B2 of SPring-8, Japan [5, 6]. The optics of both beamlines are similar. Dispersed X rays were obtained by Si(422) reflection plane. From the curvature with a radius of 2000 mm, X rays with an energy range of 1000 eV were generated. Samples were set to the focal point of X rays. Gd₂O₂S(Tb) was exposed to re-dispersed X-ray and emitted lights were collected using a charge coupled device (CCD) camera. The intensities in the vertical direction were summed up to produce a one-dimensional spectroscopy. All XAFS spectra were collected under in situ and time-resolved mode with a sampling rate of 2 Hz.

Supported Pd metal nanoparticles were prepared by the impregnation method with powdered γ-Al₂O₃ and dilute aqueous solution of palladium nitrate, Pd(NO₃)₂. Following drying and calcination at 500 °C, Pd(4 wt%)/Al₂O₃ sample was obtained.

100 mg of powdered Pd sample was set into a cylindrical sample holder (φ10 × φ7 × 10 mm³) and pressed by hand in order to make a disk pellet (φ = 7 mm). The sample holder with the pellet was placed in an in situ flow type XAFS cell [9]. Gas flow was checked by a quadrupole mass spectrometer whose capillary was directly attached to the in situ XAFS cell. Samples were reduced to complete metal state by H₂(10 %)/He of 50 cc/min flow at 400 °C for 10 min. After cooling to room temperature under He flow at 50 cc/min, CO(5 %)/He gas was flowed at 50 cc/min as an adsorption gas.

3. Results and Discussion
We show the result of time-resolved extended X-ray absorption fine structure (EXAFS) spectra as Fig. 1. 100 spectra of Pd(4 wt%)/Al₂O₃ taken in 50 s at room temperature are displayed. It is understood that there are no distinct distortions and scatters in the spectra set and all spectra were recorded under high precision with clear fine structures. Pd metal nanoparticles were kept metal state before flow of CO(5 %)/He gas. After CO flow, slight change in EXAFS functions is observed in the difference spectra (Fig. 1 (b)). Structure change of Pd metal nanoparticles is brought about by CO surface adsorption on Pd surface.

The differences in XAFS spectra between before and after CO adsorption at room temperature on Pd metal nanoparticles are summarized in Fig. 2. In these data sets, we can see the small difference in near edge structure, EXAFS function and Fourier transform intensity. CO adsorption is thought to influence surface atomic and electronic structure for Pd metal nanoparticles. However, in normal sense for spectra comparison, it is not easy to judge that CO

![Figure 1.](image-url)
surface adsorption brings about surface structure change of Pd metal nanoparticles by taking only two spectra before and after CO adsorption into consideration because the difference in the spectra is so small that normal error value hinders the justification of the effect of CO surface adsorption. On the other hand, clear change in continuous XAFS spectra by CO surface adsorption at room temperature is recognized in Fig. 1. Continuous observation by time-resolved XAFS spectra enables us to detect small changes in metal nanoparticles.

**Figure 2.** Pd K-edge (a) X-ray absorptoin near edge structure (XANES) spectra, (b) enlarged XANES spectra just after the absorption edge, (c) EXAFS functions and (d) Fourier transform intensities for Pd(4 wt%)/Al₂O₃ metal nanoparticles before (red solid) and after (green dashed) CO adsorption at room temperature. These data correspond to the first and last spectra in Fig. 1.

**Figure 3.** Changes of interatomic distance, C₂ and C₃ for Pd metal nanoparticles during temperature increase at 20 K/min under CO(5 %) flow.

**Figure 4.** Temporal behavior of edge shift, interatomic distance and C₂ for Pd nanoparticles during CO adsorption at room temperature and following temperature increase.
In order to understand the details of CO adsorption on Pd nanoparticles, we employed time-resolved XAFS measurement with constant temperature ramp. The sample was heated at a rate of 20 K/min, and XAFS was continuously observed at 2 Hz. Interatomic distance, $C_2$ and $C_3$, for Pd-Pd nearest neighbor shell of Pd metal nanoparticles are plotted in Fig. 3. The $C_2$ and $C_3$ increase linearly by heating, indicating the increase of the thermal vibration and anharmonicity. Over 350 °C, which is shown in the hatched area of Fig. 3, small shifts are recognized in the $C_2$ and $C_3$, and at the same temperature region, the interatomic distance starts to increase. These increases of the interatomic distance, $C_2$ and $C_3$ indicate that the adsorbed CO molecules are decomposed and Pd carbide layer are created by interstitial solution of C atoms [5, 10].

Figure 4 shows the variations of XAFS parameters during CO surface adsorption and following temperature raising for the Pd metal nanoparticles with a sampling rate of 2 Hz. The relative precisions of the interatomic distance and the edge shift are about 0.001 Å and 0.02 eV, respectively. CO surface adsorption reaction at room temperature brings about elongation of interatomic distance and positive chemical shift of Pd nanoparticles. Only expanded interatomic distance recovers its original value by heating treatment. This means that there are two types of CO surface adsorption behavior at least. The less stable CO molecule causes surface expansion of Pd metal nanoparticles, which results increase of mean interatomic distance by about 0.007 Å. The CO is desorbed from surface of Pd metal nanoparticles by heating treatment.

4. Conclusions

Dispersive optics for time-resolved X-ray absorption fine structure spectroscopy are powerful tool for the observation of small structure change. The relative precisions of the interatomic distance and the edge shift are about 0.001 Å and 0.02 eV, respectively. There are at least two CO adsorption behaviors on Pd metal nanoparticles at room temperature and the less stable CO brings about surface expansion of Pd metal nanoparticles. Adsorbed CO shows decomposition and creates Pd carbide layer over 350 °C, which is clearly detected by the elongation of Pd-Pd interatomic distance and the increase of $C_2$ and $C_3$.

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References

[1] Newton M A, Belver-Colderia C, Martínez-Arias A and Fernández-García M 2007 Nature Materials 6 528
[2] Iglesias-Juez A, Kubacka A, Fernández-García M, Michiel M D and Newton M A 2011 J. Am. Chem. Soc. 133 4484
[3] Matsushita T and Phizackerley R P 1981 Jpn. J. Appl. Phys. 20 2223
[4] Kaminaga U, Matsushita T and Kohra K 1981 Jpn. J. Appl. Phys. 20 355
[5] Matsumura D, Okajima Y, Nishihata Y, Mizuki J, Taniguchi M, Uenishi M and Tanaka H 2009 J. Phys.: Conf. Ser. 190 012154
[6] Matsumura D, Nishihata Y, Mizuki J, Taniguchi M, Uenishi M and Tanaka H 2010 J. Appl. Phys. 107 124319
[7] Matsumura D, Okajima Y, Nishihata Y and Mizuki J 2011 J. Alloys Compd. 2011 S849
[8] Yokoyama T, Hamamatsu H and Ohta T 1998 EXAFS The University of Tokyo 2nd ed
[9] Suzuki A, Yamanaguchi A, Chihara T, Inada Y, Yuasa M, Abe M, Nomura M and Iwasawa Y 2004 J. Phys. Chem. B 108 5616
[10] Newton M A, Michiel M D, Kubacka A and Fernández-García M 2010 J. Am. Chem. Soc. 132 4540