Quick XAFS Analysis of Pt Supported on Zeolites Active in the Preferential Oxidation of CO

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When hydrogen is used as a fuel cell, the total elimination of CO is an important subject to prevent the poisoning of Pt electrode caused by strong adsorption of CO. For this purpose, the preferential oxidation (PROX) of CO without consuming H2 is an effective method to reduce the concentration of CO. Recently, much effort has been devoted to develop the active and selective catalyst in the PROX reaction. Recently, we found that the Pt supported H-Mordenite catalyst exhibited high activity and selectivity in the PROX reaction. On the other hand, Pt loaded on other supports, such as zeolites and A12O3, exhibited low selectivity toward the CO oxidation. The objective of this study is to characterize the active Pt species generated on the H-Mordenite. Furthermore, the formation process of active Pt species was directly followed by means of OXAFS technique measured under in-situ conditions.

Pt was loaded on various zeolites with an ion-exchange method. The sample was pressed into wafer form prior to the XAFS measurement. The loading of Pt was 4 wt.

Ptx-edge OXAFS data was collected at BL01B1. Si(111) single crystal was continuously moved from 10.2 to 8.9 degrees. The measurement was carried out in a transmission mode. It took 1 min to collect one spectrum. The energy of X-ray was calibrated with Pt foil as a reference. A self-supported wafer form of the sample was placed in an in-situ cell. The sample was heated with a ramping rate of 5 K min⁻¹ in a He flow (45 ml min⁻¹) or 10° H2 diluted with He (50 ml min⁻¹) under atmospheric pressure. The data of Pt x-edge spectra were collected in every 10 K.

Figure 1 gives the Fourier transforms of Pt L2,3 edge EXAFS of Pt/zeolites measured after the reduction with H2. The spectra of Pt loaded on H-beta, H-Y, USY and H-ZSM-5 were similar to that of Pt foil (reference sample). However, the spectra of Pt loaded on H2, Na-Mordenite were much different from those of other zeolites, where the intensity of Pt-Pt bond was considerably small and the peak position shifted to the shorter distance. The coordination numbers (CNs) and bond distance (R) of the nearest-neighbor Pt-Pt bond were calculated based on the curve-fitting analysis based on the Pt foil measured at room temperature, and the data were summarized in Table 1. The Pt-Pt bond distance of Pt/Mordenite was determined to be 0.268 nm, which was significantly shorter than that loaded on other zeolite. In addition, the coordination numbers were smaller than those of other zeolites. These data meant the formation of small Pt clusters over Mordenite supports. It could be expected that the small Pt clusters acted as effective catalysts for PROX reaction. The analysis of the XAFS data measured during temperature programmed reduction are under progress.

Local structure of liquid alloys between noble metals and IVb elements in the eutectic composition

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Au-Si alloy has a deep eutectic region at a composition around 19 at.% Si in the phase diagram, where the melting point falls down to 363°C although those of pure elements are 1064°C for Au and 1415°C for Si, respectively. It is well known that metallic glass was firstly obtained by quench from the liquid state with 25 at.% Si, near the eutectic composition [1]. Several alloys between noble metals and IVb elements such as Au-Ge, Ag-Si, Ag-Ge, Pt-Si, Pt-Ge and so on exhibit similar eutectic type phase diagram and some of them form metallic glass. In contrast with Pt systems, any reliable structure factors of Au systems have not obtained. It is mainly because Au atom is strong absorber both for X-rays and neutrons. The purpose of this research project is as follows: (1) to obtain the static structures of eutectic liquids and metallic glasses in this category by XAFS and high-energy X-ray diffraction measurements with a transmission geometry which is the best way to measure bulk properties, (2) to observe the crystallization from the amorphous state and discuss the mechanism to stabilize non-equilibrium structure.

Parallel to the diffraction measurements which we have already started using BL04B2 and BL08W high-energy beamlines[2], XAFS measurements for Au-Si, Au-Ge, Pt-Ge alloys were carried on the Au L3-absorption edge, Ge and Pt K-absorption edges using the XAFS spectrometer with a Si(111) double-crystal monochromator installed at BL01B1 beamline.

The alloys of Au-Si and Au-Ge were prepared by the direct reaction of pure elements. The Pt-Ge sample was supplied by Dr. K. Shibuta. The liquid samples were put into the quartz cell with the windows of the thickness 0.2mm.

Fig. 1 XAFS signals, $\chi(k)$ of quenched Au34Ge50 which is located at the deep eutectic composition with the melting point of 350°C. Although this material is still crystal colored silver, the powder diffraction pattern is completely different from that of the annealed sample with gold color.

Fig. 2 Fourier transformed, $F(r)$, of the XAFS signals. In the $F(r)$ at Ge edge, the main peaks coincide between the magnitude and imaginary functions, which suggests that the randomness in the circumstance around a central Ge atom is not large. The second and third neighbors have been also observed which might be different from those of the annealed sample. Precise curve fitting analysis is now on progress.

Fig. 1 Fourier transformed, $F(r)$ of the XAFS signals for quenched Au34Ge50 on the Au L3-edge and K-absorption edges.

Fig. 2 Fourier transformed, $F(r)$ of the XAFS signals for quenched Au34Ge50 on the Au L3-edge and K-absorption edges.