Preparation of Finely Dispersed-Palladium Metal in Zeolite by High Frequency-Ultrasonic Irradiation

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New technique to prepare finely dispersed metallic species in a zeolitic framework has been developed by a high frequency-ultrasonic (HFUS) irradiation. The parent Pd ions in the zeolite were reduced with isopropyl alcohol into carbon containing Pd metal during the irradiation. These species was observed by EXAFS analysis to be highly dispersed into small clusters consisted of less than several atoms in zeolitic crystal.

The particle size of metallic species is one of the most important factors in the evaluation of supported metal catalysts. During the last five years, we have examined to prepare finely dispersed metallic particles in Y-zeolite framework by a reduction-reoxidation treatment. Microclusters of Cu[1,2] and Pd[3] consisted of 15-25 atoms have already been obtained in zeolitic pores by this treatment. These small clusters showed excellent activities and selectivity in catalysis such as reduction of nitrogen monoxide into nitrogen and oxygen[4,5] and partial oxidation of methane into hydrogen and carbon monoxide.[6,7] In the present report, technique of a HFUS irradiation has been applied to prepare microclusters of Pd metal in zeolitic crystal. The structure changes of Pd ions in Y-zeolite during the HFUS reduction process, furthermore, were investigated by means of X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), and temperature-programmed oxidation (TPO) techniques.

Pd-Y Zeolite (7 wt%) was prepared from Linde LZY-52 molecular sieves and $Pd(NH_3)_4Cl_2 \cdot H_2O$ by traditional ion-exchange method. Ultrasonic irradiation was carried out using a multi-wave ultrasonic generator (200 kHz, 6.0 $W \cdot cm^{-2}$) and a barium titanate oscillator (o.d. = 65 mmϕ) in a cylindrical glass vessel (55 mmϕ), which had a silicon rubber septum for gas bubbling or sample extracting without exposing the sample to the air. The bottom of the vessel was planar and 1 mm in thickness. The glass vessel was placed on just above the oscillator in a water bath ($\lambda/2$ = 3.75 mm) at room temperature. The Pd-Y (1 g) sample was suspended in 60 cm^3 of water in the vessel, and then the system was purged with argon. 10 $mMol \cdot dm^{-3}$ of isopropyl alcohol was added as the reductant in the slurry. The ultrasonic irradiation was carried out for 6 h, and the purge with argon and the addition with isopropyl alcohol have been done every 1 h during the irradiation. The resulted sample was filtered, washed, and dried in an oven at 380 K for one day. For simplicity in this report, ultrasonically treated sample is expressed as Pd-Y(HFUS), for examples. In the EXAFS (Rigaku) measurement of Pd-Y X-ray source was operated at 40 kV, 360 mA. The details of measurement and data analysis have already been given elsewhere.[8]

White sample gradually turned to black and the formation of acetone was recognized according to the reduction of Pd ions into metal during the HFUS irradiation, indicating that Pd ions in the zeolitic crystal are reduced with isopropyl alcohol into Pd metal. In the X-ray diffraction pattern of zeolitic crystal, however, no appreciable change was observed between the samples before and after the HFUS treatment.

In order to understand the local structures around Pd atoms, EXAFS spectra were measured for the Pd-Y samples before and after the HFUS treatment. Fourier transforms of these spectra are shown in Figure 1, where the peaks are slightly displaced from true interatomic distances because of the phase shift and the filtered ranges of transformation are 30-110 nm^{-1} for (a), (b), and (c), and 29-125 nm^{-1} for (d). The Fourier transforms of the original Pd-Y zeolite (a) shows a predominant peak at 0.204 nm corresponding to the Pd-O distance in PdO crystals (c). After the HFUS irradiation for 6 h (b), however, only one peak is observed at 0.204 nm due to

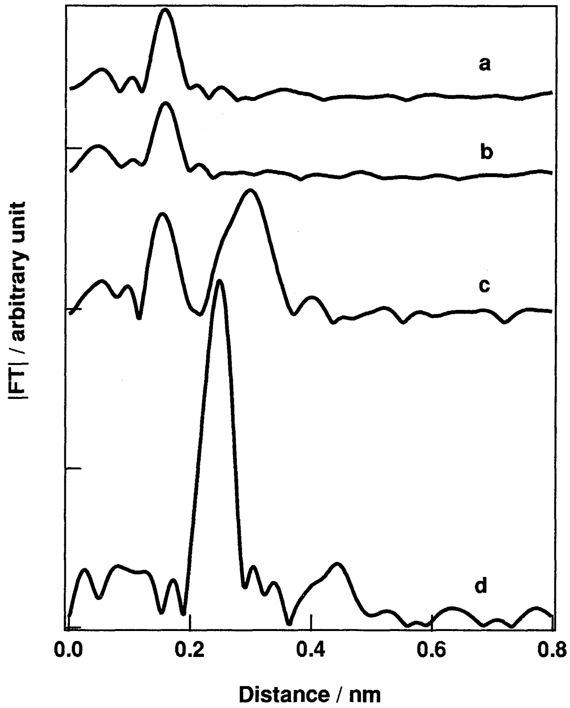

Figure 1. Radial distribution functions of (a) the original Pd-Y, (b) Pd-Y(HFUS), (c) PdO powder, and (d) Pd foil as references material.

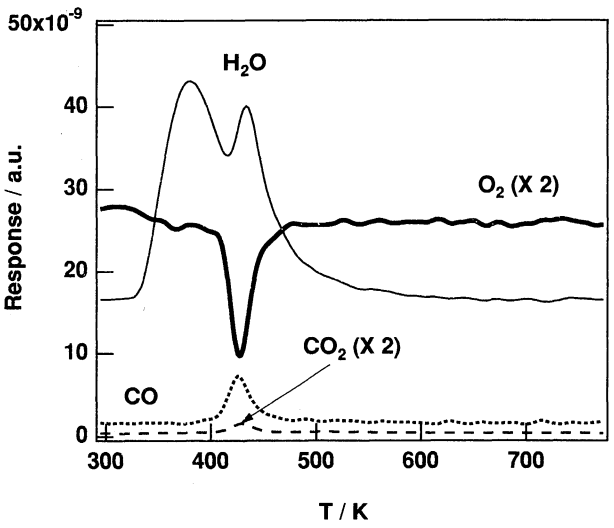

Figure 2. Profile of mass spectra during TPO process of Pd-Y(HFUS) zeolite. The amplitude of curves for O_2 and CO_2 is twice in order to compare directly with that of curves for CO and H_2O.

the Pd-O bond. It should be noted that in the Pd-Y(HFUS), as shown in Figure 1(b), no substantial peak is observed at 0.275 nm for the Pd-Pd bond in metal (d), indicating lack of Pd atoms in the first shell of a certain central atom.

As a highlight of the results obtained by XRD and EXAFS measurements, where no characteristic peaks of Pd metal crystals are virtually observed in the diffraction pattern and the radial distribution function [Figure 1(b)] of the HFUS-reduced samples, respectively. No significant difference is recognized between the Fourier transforms of original Pd-Y [Figure 1(a)] and HFUS-reduced Pd-Y [Figure 1(b)] samples, i. e., in the latter figure no appreciable peak corresponding to the Pd-Pd bond in metallic crystal can be observed upon the reduction. It might be speculated, therefore, that the reduced Pd species in the Pd-Y(HFUS) are present atomically or as very small particles because of virtually lack of adjacent metal atoms which can be identified by EXAFS measurement.

In order to obtain further information about Pd species in the zeolitic pores reduced by the HFUS irradiation, two kinds of TPO experiments were carried out, *i. e.*, by a circulation system for a quantitative determination of oxygen consumption according to the reduction of Pd ions into Pd metal and by a flow system for the qualitative analysis of the oxidation products with a mass spectrometry.

The Pd-Y(HFUS) sample consumed 710 μmol•g^{-1} of oxygen around at 490 K. This value is much larger than the theoretical value of 329 μmol•g^{-1}, assuming that metallic Pd^0 on the 7 wt% Pd-Y zeolite is oxidized into Pd^{2+} ions or PdO species.

The second TPO experiment by the mass spectroscopy was carried out to explain the discrepancy between the oxygen consumption and the Pd ion content. The result is shown in Figure 2. The predominant gaseous products during the TPO process consisted of water and carbon monoxide. The water evolution at 390 K is attributed to the desorption of physically adsorbed water in zeolitic crystal, because it is not accompanied by the oxygen uptake. The following evolution of water and the formation of carbon monoxide simultaneously take place at the same temperature of 430 K, where the maximum consumption of oxygen is also observed.

Although the discrepancy between experimental and theoretical values of oxygen consumption is still obscure at present, it is presumably attributed to the existence of carbonaceous materials on the Pd surface (CHx, proposed by Solymosi *et al.*[9]), which are produced by the decomposition of isopropyl alcohol during the HFUS reduction. In Figure 2, the ratio of water and carbon monoxide formation at 430 K is almost unity (H_2O : CO = 1:1). Furthermore, a traditional hydrogen-reduced Pd-Y zeolite evolved appreciable amount of water at same temperature of 430 K in the similar TPO process, indicating that the Brönsted acid sites convert into Lewis acid sites with formation of water. From these points of view, we speculate that the reduction of one Pd site of the parent Pd-Y zeolite with isopropyl alcohol under the HFUS irradiation gives one PdC and two protonic sites on the surface.

In the present paper, we could show a possibility for the preparation of a finely dispersed metal in the zeolite crystal by using HFUS irradiation, i.e., the most significant characteristics of the HFUS technique is that the reduction of Pd^{2+} ions into Pd^0 could take place without appreciable agglomeration. Further detailed investigations are, of course, required to explain details of mechanism under the HFUS irradiation.

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