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EXAFS study on Pd–Pt catalyst supported on USY zeolite

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Abstract

Local structure around Pd and Pt in the bimetallic Pd–Pt catalysts supported on ultra stable Y (USY) zeolite (SiO_2/Al_2O_3=680) was investigated by an extended X-ray absorption fine structure (EXAFS) method during oxidation, reduction, and sulfidation. The Pt L III-edge EXAFS spectra showed that a new bond that was significantly different from Pt–Pt to Pt–Pd metallic bonds was formed in the bimetallic Pd–Pt (4:1) reduced catalysts supported on USY zeolite. This new bond may reflect the ionic properties of Pt through the Pt–Pd interaction. Furthermore this new bond survived sulfidation indicating that the bond has a cationic property and sulfur-tolerance property. The Pt–Pd ionic interaction in these catalysts allows some of the Pd metal to survive as metallic phase. The existence of this metallic phase under sulfidation condition may result in high activity of Pd–Pt (4:1) catalyst supported on USY zeolite in the aromatics hydrogenation. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

For environmental protection, removal of aromatic compounds in diesel fuel is urgently required because aromatic compounds become precursors of particulates in the diesel-engine exhaust. Conventional hydrotreating catalysts, such as sulfided Ni–Mo and Ni–W on Al_2O_3, have high tolerance to sulfur in the feedstock, but their hydrogenation activity is not sufficient for removal of aromatic compounds under the mild conditions of low temperature and low pressure. Noble metal catalysts are well-known for their high activity in hydrogenating aromatics, though they are quite sensitive to the inhibitory effect of sulfur. Recently, much attention has been paid to the high sulfur tolerance of bimetallic Pd–Pt catalysts supported on Al_2O_3, TiO_2, and acidic zeolites [1–6]. We previously reported that the activity and the sulfur tolerance of Pd–Pt/USY catalysts for the hydrogenation of tetralin in the presence of dibenzothiophene (DBT) strongly depended on the Pd/Pt ratio and reached a maximum at a Pd:Pt mole ratio of 4:1 [7]. Furthermore, the hydrogenation selectivity of tetralin reaches 100% when USY zeolite is used as a support for Pd–Pt [7]. However, little is known about the structural change and sulfur tolerance of noble metals supported on USY zeolite under hydrogenation reaction conditions. Because extended X-ray absorption fine structure (EXAFS) analysis is one of the most powerful tools for investigating atomic local structure around noble metals in catalysts, we used it in this study to investigate the local structure of Pd and Pt in detail for bimetallic Pd–Pt catalysts supported on USY zeolite.

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2. Experimental

USY zeolite (SiO_2/Al_2O_3=680, hereafter called HY-680) was prepared by treating USY zeolite (Tosoh, SiO_2/Al_2O_3=15.0) with hydrochloric acid (2.0 mol dm^{-3}) at 373 K for 2 h. The crystallinity of HY-680 was calculated to 76% from the average area of 533 and 642 reflections using parent NaY (Tosoh, HSZ-320NAA) as a reference.

Monometallic Pd, monometallic Pt, and bimetallic Pd–Pt (mole ratio of 4:1, hereafter abbreviated as Pd-Pt (4:1)) catalysts supported on HY-680 were prepared by incipient wetness impregnation with either an aqueous solution or a mixed aqueous solution containing appropriate amounts of $[Pd(NH_3)_4]Cl_2$ and $[Pt(NH_3)_4]Cl_2$ [7]. The total metal content of each of these three catalysts was 1.2, 3.2, and 5 wt%, respectively.

The impregnated samples were dried in vacuum at 333 K for 6 h, pressed into a wafer, crushed into 22/48 mesh chips, and then calcined in an oxygen stream (2 dm^3 min^{-1} g^{-1}) at 573 K for 3 h at a heating rate of 0.5 K min^{-1}. In in situ cells for XAFS measurements, the precalcined samples were reduced in a hydrogen stream (100 cm^3 min^{-1}) at 573 K for 3 h and then sulfided in a stream (100 cm^3 min^{-1}) of 1000 vol ppm H_2S-2 vol% H_2 balanced with N_2 at 573 K for 0.5 h.

The EXAFS of Pt L III-edge (11.6 keV) and Pd K-edge (24.3 keV) were measured for samples of each catalyst at three different conditions (e.g., calcined, reduced, and sulfided) using a Si (3 1 1) double-crystal monochromator at the Photon Factory (BL-10B) of the Institute of Materials Structure Science (KEK-PF in Tsukuba, Japan). All measurements were done at room temperature.

EXAFS spectra were extracted from X-ray absorption spectra using cubic spline function [8]. Fourier transformation of the k^3-weighted EXAFS data was done in the Δk range of 13 $Å^{-1}$ for Pt L III-edge and in the 14 $Å^{-1}$ for Pd K-edge with a square window dumping at 5% of either side of the range by Hamming function.

3. Results and discussion

Fourier transforms of Pt L III-edge EXAFS spectra for $PtCl_2$, PtO, and Pt metal as standards in Fig. 1 show that the radial distance R from an absorbing atom obtained by EXAFS is shifted from the real bond distance due to phase shift by potentials of absorbing atoms and scattering atoms. The spectra of $PtCl_2$ and PtO were simulated by the FEFF [9] calculation using crystal structure of $PtCl_2$ and PtO, respectively, reported in [10,11]. Peaks at R=1.64, 2.02, and 2.64 Å were assigned to the Pt–O (2.02 Å) bond in PtO, the Pt–Cl (2.389, 2.416 Å) bond in $PtCl_2$, and the Pt–Pt (2.775 Å) bond in Pt metal, respectively.

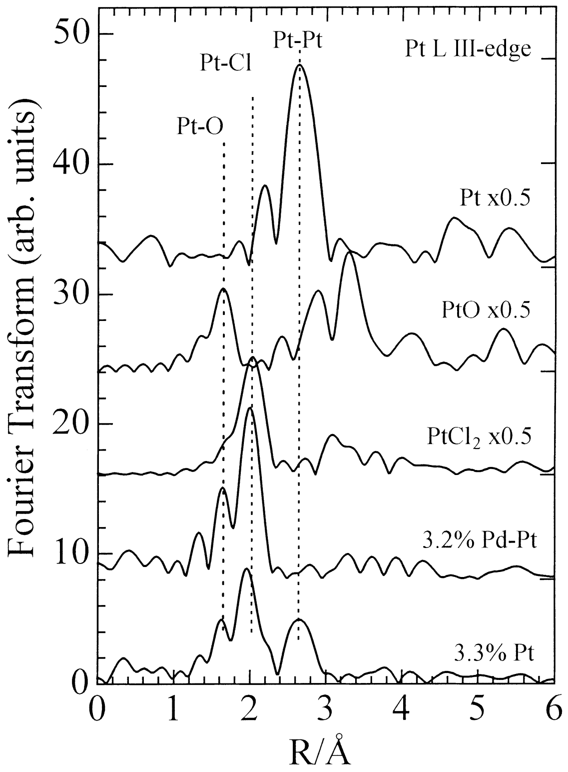

Fig. 1. Fourier transforms of Pt L III-edge EXAFS spectra for Pt and Pd–Pt (4:1) catalysts supported on HY-680 and calcined at 573 K. Spectra of $PtCl_2$, PtO, and Pt metal are included as standards.

Fourier transforms of Pt L III-edge EXAFS spectra for Pt and Pd–Pt (4:1) catalysts supported on HY-680 and calcined at 573 K in Fig. 1 show that most of Pt was supported as chloride on the USY zeolite after calcination. For the monometallic Pt catalyst, the Pt L III-edge spectrum show that Pt existed not only as oxide and chloride but also as metal, whereas, Pt in the bimetallic Pd–Pt catalyst existed only as chloride and oxide. This indicates that the presence of Pd inhibits reduction of Pt chloride to Pt metal.

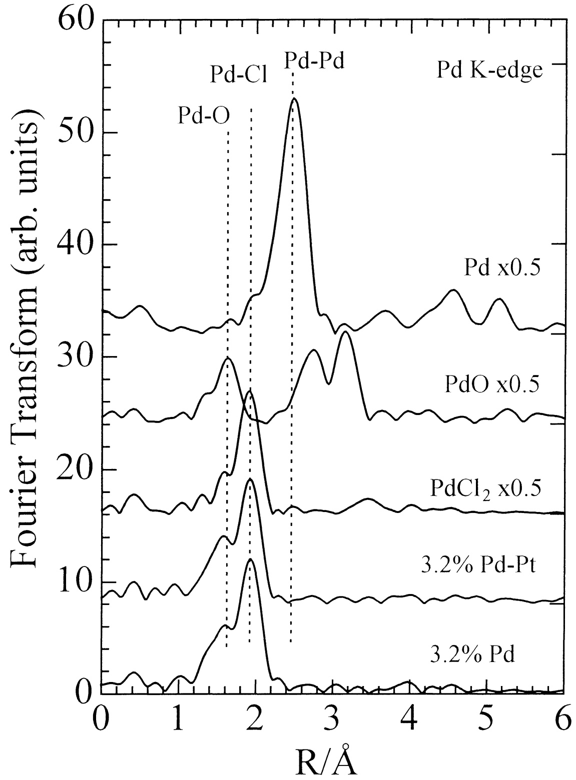

Fig. 2. Fourier transforms of Pd K-edge EXAFS spectra for Pd and Pd–Pt (4:1) catalysts supported on HY-680 and calcined at 573 K. Spectra of $PdCl_2$, PdO and Pd metal are included as standards.

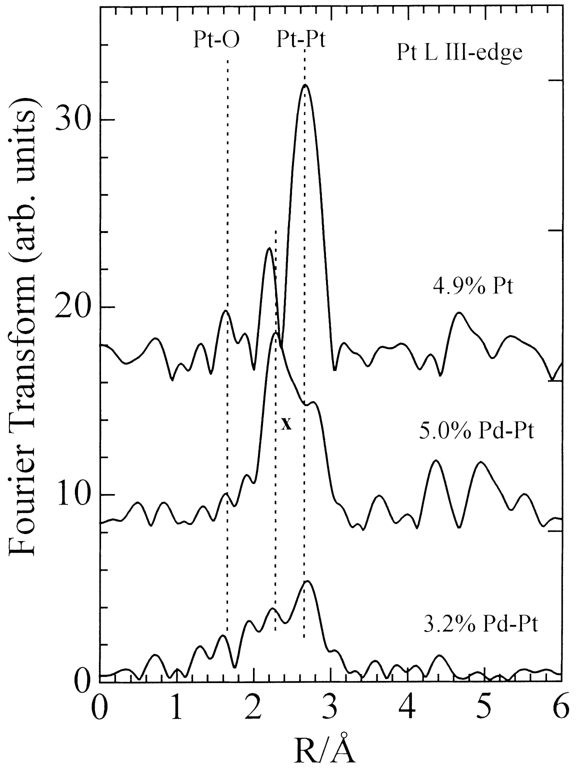

Fig. 3. Fourier transforms of Pt L III-edge EXAFS spectra for Pt and Pd–Pt (4:1) catalysts supported on HY-680 and reduced at 573 K.

In the Fourier transforms of Pd K-edge EXAFS spectra for Pd and Pd–Pt (4:1) catalysts and calcined at 573 K (Fig. 2), peaks at R=1.58, 1.91, and 2.48 Å were assigned to the Pd–O (2.018 Å) bond in PdO, the Pd–Cl (2.309 Å) bond in $PdCl_2$, and the Pd–Pd (2.751 Å) bond in Pd metal, respectively. The Pd K-edge spectra show that the Pd–Cl bond remained after calcination in both the monometallic and bimetallic catalysts, however, there was no Pd metal in those catalysts.

Fourier transforms of Pt L III-edge EXAFS spectra for Pt and Pd–Pt (4:1) catalysts supported on HY-680 and reduced at 573 K in Fig. 3 show that the peaks of Pt–Cl that appeared in the calcined catalysts disappeared after the reduction. This indicates that chlorine was removed after the reduction with hydrogen. Except for intensity, the spectrum of the 4.9% Pt catalyst is similar to that of Pt metal (foil) shown in Fig. 1: one main peak at 2.64 Å and a small peak at 2.20 Å. This similarity indicates that Pt precursors (Fig. 1) were completely converted into Pt metal particles. The peak at 2.20 Å observed in the 4.9% Pt catalyst was not assigned to any bond in the metal structure of Pt. Because this peak appeared even in the FEFF simulation of the spectra, we regarded it as a side peak that accompanied the main peak at 2.64 Å due to the phase shift by potential of absorbing and scattering atoms and to the terminal effect in Fourier transformation.

For the bimetallic catalysts, two peaks appeared at 2.24 Å (indicated by **x** in Fig. 3) and at 2.76 Å. The mean size of Pd–Pt bimetallic particles on HY-680 evaluated by the preliminary measurement of TEM was in the range from 30 to 40 Å. Thus, most of the Pd–Pt bimetallic particles would be existed on the external surface of HY-680. In addition, no peak was observed at 2.24 Å for the monometallic Pt on HY-680. Therefore, the peak at 2.24 Å is probably due to the Pt–Pd bond of Pd–Pt particles, and not due to the bond between Pt and lattice oxygen in zeolite structure.

The *R* of these two peaks was slightly longer than that of the side peak at 2.20 Å in the spectra for Pt metal and that of the peak at 2.64 Å for the Pt–Pt bond in Pt metal, respectively. The shift in *R* of the two peaks suggests a strong interaction between Pt and Pd because the shift occurred only in the bimetallic Pd–Pt catalysts. The peak of 2.24 Å in the spectra of the 5.0% Pd–Pt and 3.2% Pd–Pt catalysts is not a side peak because its intensity in the 5.0% Pd–Pt catalyst was stronger than that of the 2.76 Å peak. This *R* (2.24 Å) is too short to be a typical *R* of a metal (2.64 Å), thereby making it difficult to assign a *R* to any atomic distances in crystals of platinum chloride and oxide of platinum. The peak was not assigned to Pt–Pt shortened by structural change in Pt metal because Pt metal has face-centered cubic structure, which is the closest packing structure. The peak was not assigned to Pt–Pd bonds formed by physical mixing of a Pt metal and a Pd metal shortened because Pd metal also has face-centered cubic structure and its lattice constants are similar to that of Pt metal. Therefore, shortening of the bond distance may be caused by the formation of an ionic bond of $Pt^{x\delta+}$–$xPd^{\delta-}$. In the infrared spectra study of the adsorption of CO on Pd–Pt catalysts supported on γ-Al_2O_3, Lin et al. [5] showed that Pt has cationic property. According to the model of ionic bonding, the shift in the *R* in Fig. 3 can be explained as (a) Coulombic attraction between $Pt^{x\delta+}$–$xPd^{\delta-}$, which results in a decrease in the *R* (from 2.64 to 2.24 Å), and (b) Coulombic repulsion between $Pt^{\delta+}$–$Pt^{\delta+}$, which results in an increase in the *R* (from 2.64 to 2.76 Å). An average coordination number of a Pd atom around a Pt atom will affect the degree of shortening and lengthening of the bond distances.

In the Fourier transforms of Pd K-edge EXAFS spectra for the Pd and Pd–Pt (4:1) catalysts supported on HY-680 and reduced at 573 K (Fig. 4), Pd–Pt may contribute to the main peak at 2.48 Å because the bond distance for Pd (2.751 Å) and for Pt (2.775 Å) metals are very similar. In the bimetallic catalysts, the shoulder peaks at a *R* slightly shorter than 2.48 Å may be related to the peak **x** observed in Fig. 3. Small Pd–O peaks at 1.58 Å appeared for the monometallic and bimetallic catalysts, suggesting that Pd is more oxygen sensitive than Pt.

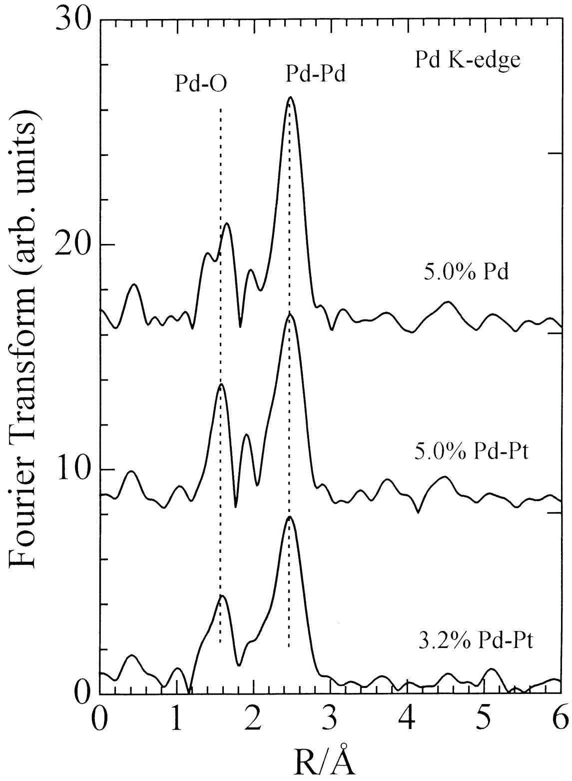

Fig. 4. Fourier transforms of Pd K-edge EXAFS spectra for Pd and Pd–Pt (4:1) catalysts supported on HY-680 and reduced at 573 K.

The reason why the peak at 2.24 corresponding to Pd–Pt is not observed from Pd edge in Fig. 4 would be a Pt atom is surrounded by some Pd atoms but a Pd is surrounded by only one Pt atom due to the molar ratio (Pt:Pd=1:4).

In the Fourier transforms of Pt L III-edge EXAFS spectra for Pt and Pd–Pt (4:1) catalysts supported on HY-680 sulfided at 573 K (Fig. 5), the *R* of the Pt–S bond (dotted line at R=1.94 Å) was assigned using spectra simulation from FEFF [9] calculation for PtS structure take from (Pt–S, 2.31 Å) [12].

The Pt L III-edge spectra for the monometallic catalysts (Fig. 5) show that in the 1.2% Pt catalyst the Pt was almost completely sulfided, whereas in the 4.9% Pt catalyst a portion of Pt remained as Pt metal. This difference in the extent of sulfidation may be due to the non-equilibrium sulfidation for the 4.9% Pt catalyst. For the bimetallic catalysts, the peak at 2.24 Å (indicated by **x** in Fig. 5), which was observed

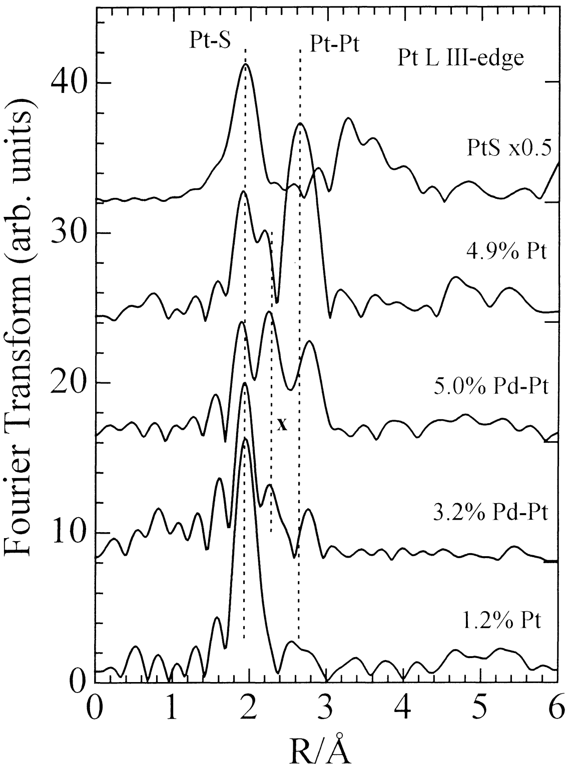

Fig. 5. Fourier transforms of Pt L III-edge EXAFS spectra for the Pt and Pd–Pt (4:1) catalysts supported on HY-680 and sulfided at 573 K. A spectrum of PtS is included as a standard.

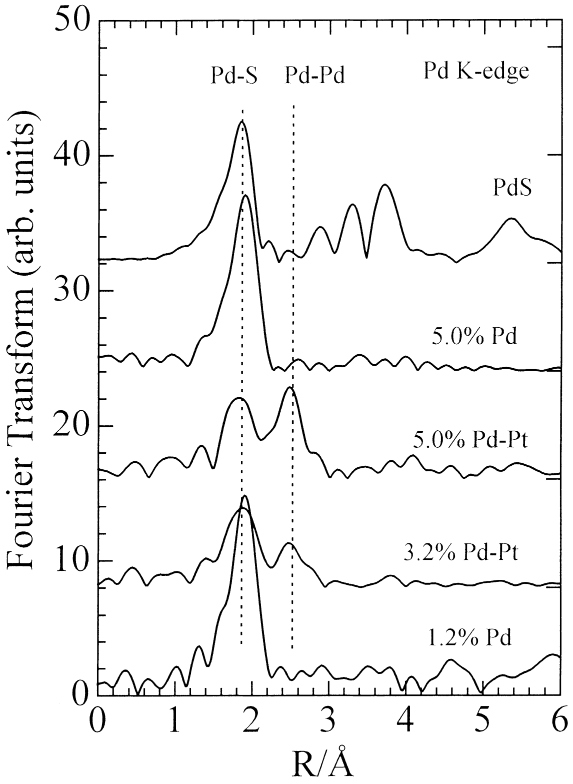

Fig. 6. Fourier transforms of Pd K-edge EXAFS spectra for the Pd and Pd–Pt (4:1) catalysts supported on HY-680 and sulfided at 573 K. A spectrum of PdS is included as a standard.

after the reduction, remained after sulfidation. The peak at 2.76 Å also survived sulfidation. This survival indicates that once Pt has cationic properties through Pt–Pd interactions, those Pt phases will become sulfur tolerant. Sulfur tolerance of the bimetallic catalysts is at a maximum at the Pd/Pt molar ratio of 4/1 in tetralin hydrogenation in the presence of dibenzothiophene [7]. Therefore, the cationic properties of Pt will also be maximum at this molar ratio.

In the Fourier transforms of Pd K-edge EXAFS spectra for the Pd and Pd–Pt (4:1) catalysts supported on HY-680 and sulfided at 573 K (Fig. 6), the *R* of Pd–S (indicated by dotted line at 1.86 Å was assigned using simulation by the FEFF [2] calculations for PdS structure (Pd–S, 2.3 Å) reported in the literature [13]. For the monometallic Pd catalysts (1.2% Pd and 5.0% Pd), Pd was almost completely sulfided. On the contrary, for the bimetallic catalysts, metallic Pd phase remained due to the presence of Pt. The peak at 2.48 Å in the spectra of the Pd–Pt (4:1) bimetallic catalysts has small shoulder peaks in the low-*R* range (2.40 Å). These shoulder peaks may be related to the peak **x** seen in Fig. 5. In the Pd–Pt (4:1) bimetallic catalysts, although Pd has an ionic property through Pt–Pd bonds, no shift in the Pd–Pd distance occurred (i.e., Pd–Pd distance and Pd metal (foil) distance were similar). These results indicate that both metals in Pd–Pt (4:1) bimetallic catalysts are much more protected from sulfidation than the individual metals in monometallic catalysts due to the Pd–Pt interaction. The detailed structure of the sulfur-tolerant Pd–Pt (4:1) phase will be clarified in future work.

4. Conclusion

The Pt L III-edge EXAFS spectra showed that a new bond which is significantly different from Pt–Pt and

Pt–Pd metallic bonds was formed in bimetallic Pd–Pt (4:1) reduced catalysts supported on HY-680. This new bond may reflect the ionic properties of Pt through the Pt–Pd interaction. This new bond survives sulfidation, indicating that the bond has cationic and sulfur-tolerance properties. The Pt–Pd ionic interaction in these catalysts allows some of the Pd metal to remain as metallic phase, which in turn may result in high activity of Pd–Pt (4:1) catalyst supported on USY zeolite in aromatics hydrogenation under sulfidation conditions.

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