

Structural study of alkali-added supported noble metal catalysts which is active for hydrogenation of phenols

Satoru NISHIYAMA*, Rei HAMADA, and Shigeru TSURUYA

Department of Chemical Science and Engineering, Faculty of Engineering,
Kobe University, Rokkoda, Nada, Kobe 657-8501, Japan.

The Pd and Ru catalysts supported on active carbon were effective for hydrogenation of aromatic compounds. Especially, the sodium added catalysts indicated the high selectivity. The state of Pd and Ru on carbon has been studied by CO adsorption and TEM observation. It was suggested that a direct interaction of sodium and the active noble metals. XAFS measurement will be helpful for consideration of the state of Pd or Ru on active carbon.

The Pd/AC (PdA), Na-modified Pd/AC (Na-PdA), Ru-Re/AC (RuA) and Na-modified Ru-Re/AC (Na-RuA) were prepared by a conventional impregnation method. The obtained catalysts were activated in liquid phase by using a reducing agent. The samples are pressed to obtain the appropriate thickness discs, which have been calculated prior to the XAFS measurements. The absorption spectra, Pd and Ru K-edge, were measured in atmosphere without any further treatment.

The Pd K-edge XANES spectra of the Pd catalysts indicated that the electronic state of Pd was not similar to metallic Pd, whereas an oxide would be expected. Figure 1 shows Pd K-edge EXAFS Fourier transforms. The bond between Pd and oxygen was observed in the all of EXAFS of the Pd catalysts even though all of catalysts were reduced. Possibility of the peak assignment to Pd-C bond instead of Pd-O bond was not excluded completely because of the active carbon support. The minor peak was observed assignable to Pd-Pd in Pd oxide. These results suggested that Pd atoms are two-dimensionally dispersed on the active carbon, in other words, a raft like structure will be expected. In-

creasing Na content, relative intensity of Pd-O (or Pd-C) and Pd-Pd in Pd oxide seemed to be increased as shown in Fig. 1. These results suggested that sodium significantly affected the structure and electronic state of supported Pd particles on the active carbon.

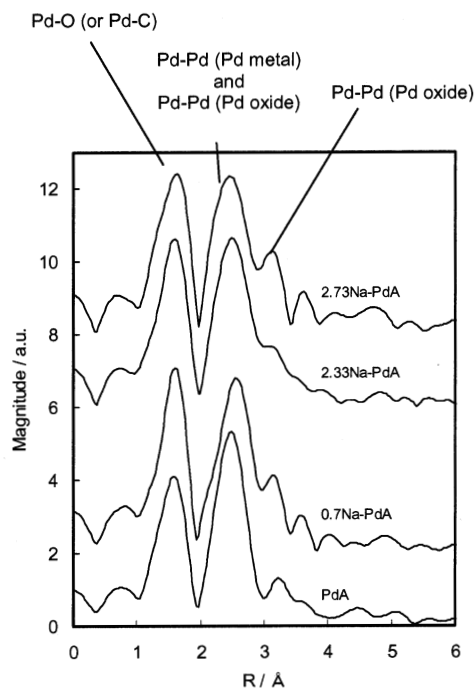


Fig. 1 Pd K-edge EXAFS Fourier transforms of the Pd catalysts supported on active carbon. The number in the catalyst names indicate the sodium content in weight percent.

Local lattice distortion in metal - insulator transition compound $\text{PrRu}_4\text{P}_{12}$

C. H. Lee¹⁾, H. Yamaguchi¹⁾, T. Honma²⁾, C. Sekine³⁾ and I. Shirota³⁾

¹⁾AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

²⁾JASRI, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan

³⁾Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan

Filled skutterudite compound $\text{PrRu}_4\text{P}_{12}$ has been studied with interest of the mechanism of a metal - insulator (M - I) transition occurred at $T_{\text{MI}} = 61$ K. According to the previous reports, there is no evidence of magnetic ordering at T_{MI} . Pr L_2 - edge XANES measurements have indicated that the Pr atoms are almost trivalent independent of temperature [1]. Recently, we have found a structural phase transition from body centered cubic (Im3) to simple cubic below T_{MI} using an electron diffraction technique [2]. This result has provided valuable information, whereas, the mechanism of the M - I transition is still controversial. In this work, we focus our attention on a possibility that local lattice distortion can be a driven force of the M - I transition.

Pr K - edge EXAFS measurements were performed in a transmission mode at BL01B1 of SPring-8. The incident and transmitted x-ray intensities were measured by ionization chambers filled with Kr (25 %) - Ar (75 %) mixed gas and Kr gas, respectively. Powder samples were synthesized by a high-pressure cell under high temperature using a wedgetype cubic - anvil high - pressure apparatus. The samples were mixed with BN powder and pressed into pellets.

Figure 1 shows temperature dependence of Pr - P and Pr - Ru bond length. The Pr -

Ru bond length decreases with cooling down, which is consistent with temperature dependence of a lattice constant. On the other hand, the Pr - P bond length shows opposite temperature dependence. At T_{MI} , both bond

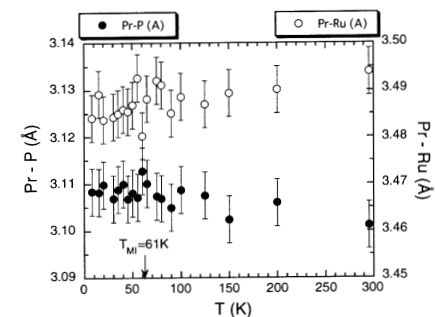


Fig. 1 Pr - P and Pr - Ru bond length for $\text{PrRu}_4\text{P}_{12}$ estimated by Pr K - edge EXAFS measurements.

length seems to show a weak kink. This result suggests that local environment around Pr atoms may change below T_{MI} . It would appear that the local structure correlates strongly with conduction electrons. To elucidate the mechanism of the M - I transition, further measurements are required.

[1] C. H. Lee et al.: Phys. Rev. B 60, 13253 (1999)

[2] C. H. Lee et al.: J. Phys.: Condens. Matter 13 (2001) L45