

In-situ XAFS measurement of Pd-Pt/SiO₂ under HDS reaction conditions

Kyoko K. BANDO^{1*}, Toshihide KAWAI², Kiyotaka ASAKURA³, Atsushi TAKAHASHI¹,
Noriyasu HAMAKAWA¹, Juan Jose BRAVO SUAREZ¹, Yuji YOSHIMURA¹, and
S. Ted OYAMA⁴

¹National Institute of Advanced Industrial Science and Technology, Tsukuba, 305-8569, Japan

²Spring-8, JASRI, Koto, Mikazuki, Hyogo 679-5198, Japan

³Catalysis Research Center, Hokkaido Univ., Sapporo, Hokkaido 001-0021, Japan

⁴Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0211, USA

Introduction

Supported Pd-Pt catalysts are efficient catalysts for hydrodesulfurization (HDS) and hydrodearomatization (HDA) of diesel fuel. But their catalytic performance is closely dependent on the support [1]. In our previous work, in-situ XAFS (X-ray Absorption Fine Structure) measurements under HDS conditions were carried out for an Al₂O₃ supported Pd-Pt (Pd-Pt/Al₂O₃) catalyst [2]. It was found that the structure of the active phase was not identical to that obtained after gas phase sulfidation, and that sulfidation of Pd atoms proceeded more deeply under HDS conditions. In this work, in-situ XAFS analysis of a SiO₂ supported Pd-Pt (Pd-Pt/SiO₂) catalyst was conducted and the results are discussed in connection with the catalytic activity.

Experimental

A SiO₂ supported Pd-Pt catalyst was prepared by the incipient wetness impregnation method. The total metal content was 2 wt% and the atomic ratio of Pd/Pt was 4. The impregnated sample was calcined under O₂ at 573 K for 3 h. A round disk of calcined catalyst (60 mg, 8 mm in diameter) was placed in an in-situ XAFS cell [3]. Reduction of the sample was carried out under a flow of 100 % H₂ gas at a flow rate of 50 ml/min at 573 K for 3 h. After pretreatment, the HDS reaction was conducted at 553 K under 4 MPa of total pressure. Hydrogen gas was supplied at 40 ml/min and a model oil composed of dibenzothiophene (500 ppm in sulfur), tetraline (30 wt %) and n-hexadecane (as solvent) was fed at a rate of 4 g/h. The reaction was carried out for 24 h. XAFS measurements were carried out at BL10B for Pd K-edge and at BL7C, 9A and 9C for Pt L_{III}-edge. All the spectra were obtained by a step-scanning mode with a data accumulation time of 0.5 – 1 s for each step. Analysis of the data was conducted with commercially available software (REX, Rigaku Co.). Parameters for the curve-fitting analysis were extracted from spectra obtained for standard substances at reaction temperature.

Results and Discussion

Fig.1 shows Fourier transformed EXAFS ($k^3\chi(k)$) spectra for (a) the Pd K-edge and (b) the Pt L_{III}-edge observed during the HDS reaction. After reduction at 573 K, an intense peak due to metal-metal scattering appeared

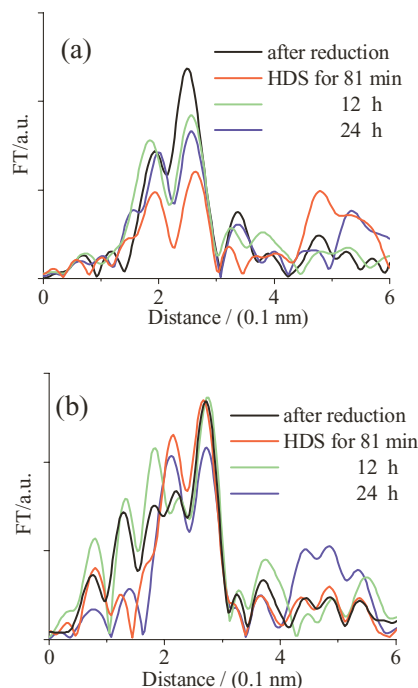


Fig.1 Fourier transform of (a) Pd K-edge and (b) Pt L_{III}-edge EXAFS spectra during HDS.

in the region from 0.16 to 0.3 nm. For the Pd K-edge the intensity of the metal-metal scattering peaks decreased during the reaction, but no distinct peak appeared at 0.2 nm, which could be assigned to the Pd-S scattering. No evidence of Pd-S was found in the XANES (not shown), either. In the Pt L_{III}-edge, there was also no evidence of Pt-S observed, that is, the Pt-S scattering peak did not appear at 0.2 nm in Fig.1 (b), and Pt L_{III}-edge XANES spectra did not show any notable change during HDS. Taking into account the fact that the HDA activity of Pd-Pt/SiO₂ is much lower than that of Pd-Pt/Al₂O₃, it was suggested that the surface of the metal particles of Pd-Pt/SiO₂ was covered with a rigid thin sulfide layer.

References

- [1] H. Yasuda, et al., Appl. Catal. A: General 185, L199 (1999).
- [2] K. K. Bando, et al., PF Activity Report, 21, 75 (2004).
- [3] T. Kawai, et al., Chem.Lett., in preparation.

* kk.bando@aist.go.jp