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In-situ XAFS measurement of Pd-Pt/Al_2O_3 under HDS reaction conditions

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Introduction

Supported Pd-Pt catalysts are efficient catalysts for hydrodesulfurization (HDS) and hydrodearomatization (HDA) of diesel fuel. But it is still not clear that what kind of phase of supported metal species is active for these reactions. In order to elucidate this point, in-situ observation of an active phase under the HDS reaction conditions is indispensable. But, it is difficult to construct an XAFS (X-ray Absorption Fine Structure) cell which can be used under high pressure high temperature liquid phase flow reaction conditions. In 2003, we succeeded in development of a cell which is available under HDS conditions [1],[2]. In this wok, in-situ XAFS measurements of an Al_2O_3 supported Pd-Pt catalyst were carried out under high temperature high pressure HDS reaction conditions.

Experimental

An Al_2O_3 supported Pd-Pt catalyst was prepared by an incipient wetness impregnation method. The metal content was 2 wt% in total and the atomic ratio of Pd/Pt was 4. The impregnated samples were dried and calcined under O_2 at 573 K for 3 hrs. A round disk of calcined catalyst (100 mg, 8 mm in diameter) was set in a newly developed in-situ XAFS cell [1]. First, the sample was pretreated under a flow of 100 % H_2 gas at a flow rate of 50 ml/min at 573 K for 3 hrs. After preparation, the temperature was set at 553 K and the pressure was increased to 4 MPa under H_2 (40 ml/min). Then a model oil was introduced to the cell at a feed rate of 4 g /h. The oil included 500 ppm sulfur as dibenzothiophene (DBT), 30 wt% tetraline and n-hexadecane as solvent. The reaction was carried out for 24 hrs. The XAFS spectra were measured every 10 min during the course of all treatments. Pd K-edge XAFS spectra were measured at BL10B. All the spectra were observed by a step-scanning mode with a data accumulation time of 0.5 – 1 sec for each step. Analysis of the data was conducted with commercially available software (REX, Rigaku Co.). Parameters for curve-fitting analysis were extracted from spectra observed of standard substances at the reaction temperature.

Results and Discussion

Prior to the in-situ XAFS measurement under the HDS conditions, we already conducted in-situ measurements under gas phase model reaction conditions. There the reaction gas was composed of 100 ppm H_2S and 20 % H_2 , which were diluted by He. The ratio of H_2S and H_2 was set at the same value as that of sulfur / H_2 in the HDS reaction. Fig.1 (a) shows Fourier transformed of Pd K-edge EXAFS ($k^3\chi(k)$) spectra observed under the gas phase reaction. After reduction at 573 K, a peak due to metal-metal scattering strongly appeared at 0.27 nm (shown in black). This peak was still dominant after sulfidation (in red). However, as shown in Fig.1 (b), the metal-metal scattering peak at 0.27 nm diminished and the Pd-S scattering peak at 0.20 nm became dominant after HDS. It is suggested that more serious sulfidation of metal sites occurred during HDS than the gas phase sulfidation.

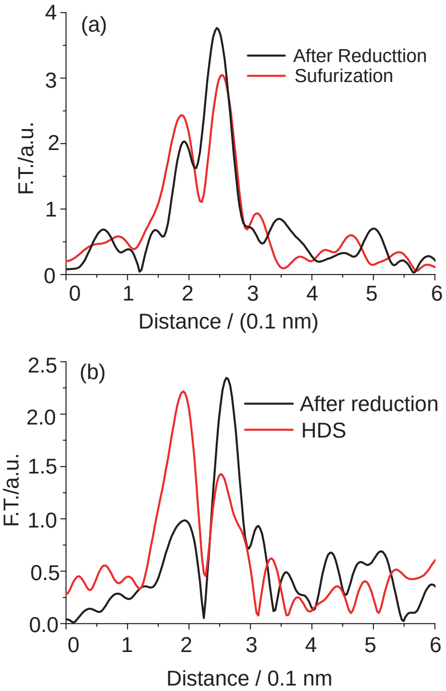

Fig.1 Fourier transform of Pd K-edge EXAFS (kχ(^{3}k))) spectra obserevd for 2wt% Pd-Pt/Al2O3. Black lines were observed after reduction at 573 K. Red lines were observed (a) after gas phase sulfidaton , and (b) after HDS reaction.

References

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