

In-situ XAFS observation of USY supported Pd-Pt catalysts during sulfidation process

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Introduction

Ultra stable Y-type zeolite supported Pd-Pt catalysts show higher activity for hydrogenation of aromatic compounds in the presence of sulfur, compared with monometallic supported Pd or Pt catalysts. However, either the real structure of active metal species under the reaction conditions, or the reason for promotion in sulfur tolerance as observed in hydrotreating conditions is not yet clear for the bimetallic Pd-Pt species. In order to clarify this point, we carried out an *in-situ* X-ray absorption fine structure (XAFS) spectroscopy analysis of the Pd-Pt catalysts and elucidated structural change of surface species during reduction and sulfidation process.

Experimental

Supported Pd-Pt (molar ratio of Pd/Pt was 4) bimetallic catalysts (Pd-Pt/USY for short) were prepared using ultra stable Y-type zeolite (USY, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13.9$) by impregnation method. The precursors were $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ (41.21 wt% Pd) and $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ (55.6 wt% Pt). The total metal content was 1.2 wt%. The impregnated samples were dried in vacuum at 333 K for 6 h, then calcined at 573 K under oxygen flow for 3 h. Pd K-edge and Pt L_{III}-edge XAFS measurements were made in a transmission mode at BL10B and 9A. The sample was pressed into a round disc and set in an *in-situ* cell designed for measurements under a flow of a reactant gas. Figure 1 shows a schematic diagram of XAFS observation system designed for measurement under sulfidation conditions. Exhausted H_2S was absorbed in a 20 % NaOH aqueous solution and H_2 was burned and converted into water by a burner set at the end of the system. After all the toxic and flammable gases were removed, the effluent gas was led to a duct. XAFS spectra were observed by step scanning mode with a data accumulation time of 0.5 – 1 sec for each step. XAFS analysis of the obtained data was conducted with commercially available software (REX, Rigaku Co.).

Results and discussion

After reduction at 573 K, the catalysts were sulfided at 553 K under a flow of H_2S (100ppm) / H_2 (20%) / Ar (balance). Figure 2 shows Fourier transform of Pt L_{III}-edge EXAFS spectra observed for Pd-Pt/USY during sulfidation. The peak at 0.20 nm is assigned to Pt-S scattering and it already appeared at 20 min and became dominant at 100 min. Sulfidation of Pt proceeded much faster than that of Pd, where the Pd-S peak became dominant at 140 min. This fact suggests that Pt species located on a sulfur-accessible position. Possible

structures expected for reduced Pd-Pt active metal species on the surface are: (1) fine Pt metal particles were located on the surface of large Pd metal particles, or (2) primary monometallic (Pd or Pt) particles gathered randomly and formed larger bimetallic metal particles. To clarify this point, precise analysis of EXAFS spectra is now in progress.

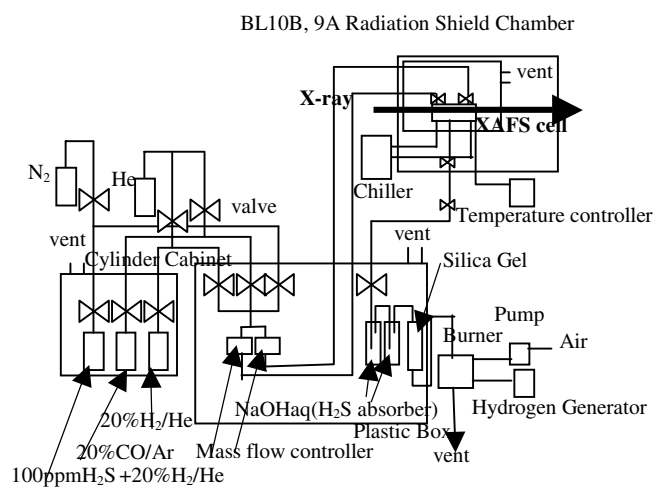


Fig.1 Schematic diagram of an in-situ XAFS system designed for measurements under reaction conditions.

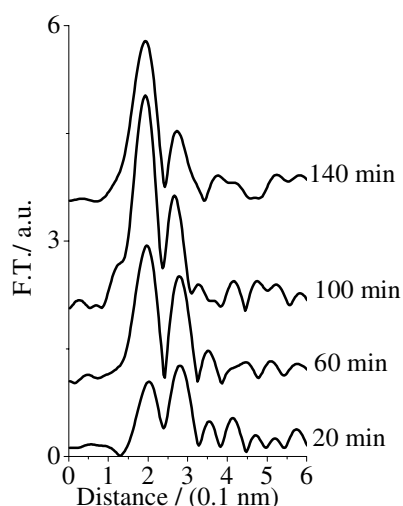


Fig.2 Change in Fourier transform of Pt L_{III}-edge EXAFS spectra with elapsed time observed during sulfidation in a flow of H_2S (100 ppm)/ H_2 (20%)/Ar for Pd-Pt/USY.

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