

Development of Combined in-situ Analysis Technique - Simultaneous Measurement of XAFS and IR Applied to Analysis of supported Pd-Pt Catalysts

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Introduction

Supported Pd-Pt bimetallic catalysts are active for hydrodearomatization of diesel fuel due to the high sulfur tolerance. However, it is still not clear how the Pd-Pt bimetallic system obtained high tolerance against sulfur. We have done in-situ XAFS studies of Pd-Pt catalysts and have obtained some information about the structure of active phase. But XAFS analysis gives averaged information of all the metal species contained in the catalysts. We need to know the structural information of metal species on the outer surface, which really exposed to sulfur. In this work, we combined in-situ FT-IR with XAFS. As in-situ FT-IR provides the information about the structural change of adsorbed species, we compared the results obtained by XAFS with FT-IR and tried to extract the structural information of surface species from XAFS data.

Experimental

For the development of the simultaneous measurement method of XAFS and IR, it is needed to adjust the IR spectrometer to the equipment of XAFS beam lines. For that purpose, we used a portable FT-IR (JASCO, VIR-9500), which could lead an incident IR beam from the main machine to a sample compartment unit through an optical fiber composed of ZnSe. An MCT detector was attached to the sample compartment unit and the IR beam was set to intersect the X-ray beam for XAFS measurement at an angle of 90°(fig.1). The XAFS cell had a cross shape equipped with 4 windows, which let both X-ray and IR penetrate the cell at the same time.

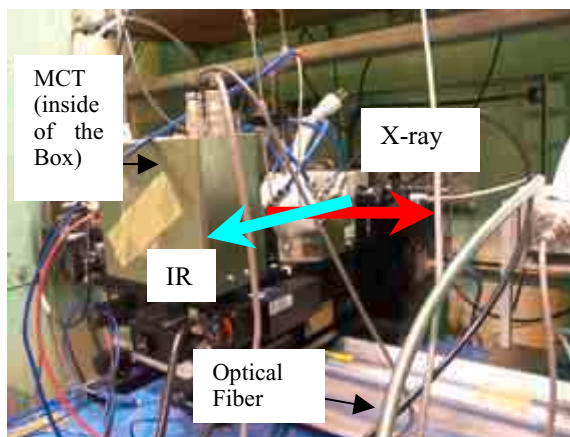


Fig.1 In-situ XAFS and IR combined analysis system set at BL10B.

The Pd-Pt catalysts were prepared using Al_2O_3 as supports. The metal loading was 2 wt% and the atomic ratio of Pd/Pt was 4. The calcined catalyst was pressed into a pellet and set in the in-situ cell. The amount required for EXAFS measurement

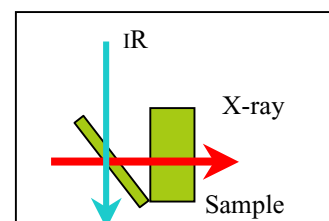


Fig.2 Diagram of the sample setting inside of the cell

was about 0.38 g/cm^2 . However, for IR measurement, a disk should be thinner than 0.038 g/cm^2 . To make both measurement possible at the same time, two disks with different thickness was set in the center of the cell as shown in fig.2. The catalyst was treated in-situ under hydrogen at 573 K, and exposed to 20% CO/He at 323 K. Then TPR (temperature programmed reduction) was carried out under a flow of hydrogen from 323 K to 573 K at the ramp of 5 K/min. During the TPR process, FT-IR and XAFS measurement was conducted continuously every two min. for IR and every 3 min. for XAFS.

Results and discussion

For Al_2O_3 supported Pd-Pt catalyst, adsorbed CO species gradually desorbed with temperature upto 523 K, no noticeable change was observed for the Pd K-edge XANES spectra during TPR. Pt L_{III} -edge XANES (observed separately) also showed corresponding gradual change. It is strongly suggested that Pt atoms were located on the outer surface of metal particles rather than in the bulk.

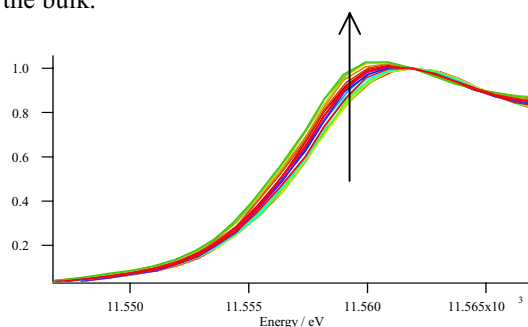


Fig.3 Change in Pt L_{III} -edge XANES observed for Pd-Pt/ Al_2O_3 during TPR.

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