

In-situ XAFS and IR Study of Supported Pd-Pt Alloy Catalysts

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Introduction

Catalysts composed of Pd-Pt alloy nano-particles supported on metal oxides are known to show high activity for deep hydrodesulfurization (HDS) and dearomatization (HDA). Their activities greatly depend on the kind of oxide support. Preliminary XAFS analysis revealed that the bulk structure of the metal particles was different for catalysts supported on different supports. But the structure on the outer surface of metal particles is more crucial for catalysis. Regarding this point, there is little information so far. In this study, we carried out simultaneous measurement of XAFS and IR. Since IR can see the change of adsorbed species on the outer surface, the metal species which show change in XAFS along with the change in IR can be regarded as the sites located on the outer surface and that react directly with reactants. Difference in outer surface structure between Al₂O₃ and SiO₂ supported catalysts is investigated.

Experimental

The Pd-Pt catalysts were prepared by an incipient wetness method, using Al₂O₃ and SiO₂ 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 an in-situ cell. The cell is designed for a simultaneous measurement of XAFS and IR. Both X-ray and IR penetrate the cell and intersect each other at the center of the cell, where the sample was placed. The XAFS and IR measurements were carried out at BL9A and NW10A. A portable FT-IR (JASCO, VIR-9500) was installed at the XAFS beam line for IR measurement. The sample 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.

Results and discussion

For the Al₂O₃ supported catalyst, a change in the shape of the first peak in the Pt L_{III}-edge XANES spectrum was observed during CO adsorption. The

first derivative of the Pd K-edge XANES also presents a change in the first peak by CO adsorption. Estimated by pattern fitting of XANES, the surface of Pd-Pt particle on Al₂O₃ was composed of 16% Pt and 84% Pd. Fig.1 shows the change of IR peak area together with the change in concentration of Pd-CO and Pt-CO during TPR. The sum of Pd-CO and Pt-CO estimated from XANES data well reproduces the change of IR area, indicating that the change in the XANES caused by CO adsorption corresponds to the formation of metal-CO. On the other hand, the SiO₂ supported catalyst showed no change in the Pt L_{III}-edge XANES, and only a small change in the Pd K-edge XANES. This fact suggests that the surface of SiO₂ supported Pd-Pt was almost 100 % covered with Pd rather than Pt. The difference in the outer surface structure of metal particles is closely related to the difference in the catalytic activity.

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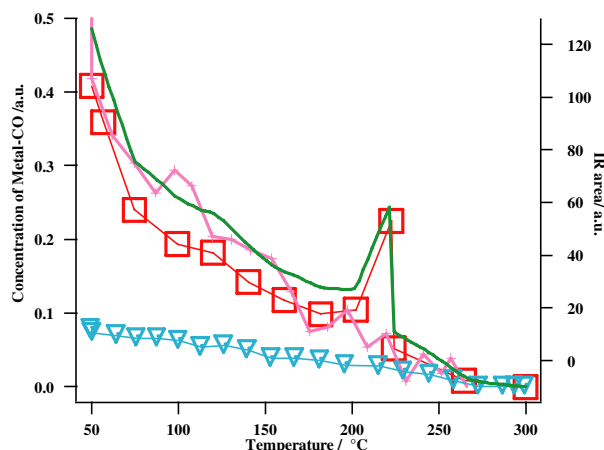


Fig.1 Change in concentration of metal-CO sites estimated by XANES, compared with the change in the area of adsorbed CO peaks observed by IR for Pd-Pt/Al₂O₃. □:Pd-CO, ▽: Pt-CO, — Pd-CO+Pt-CO, — IR area