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In situ XAFS and FT-IR Analysis of Ni_2P/MCM-41 Under HDS Conditions

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Introduction

We have been studying the catalysis of Ni_2P during hydrodesulfurization (HDS) using in situ XAFS techniques. It is found that the bulk Ni_2P structure was stable under HDS conditions, but we also confirmed formation of a Ni phosphosulfide phase on the very surface of the Ni_2P nanoparticles. In order to elucidate the role of this Ni phosphosulfide phase in the reaction, we employed a new in situ technique which enables simultaneous measurements of XAFS and IR for the same sample under the same conditions.

Experimental

The catalyst was 12.2wt%Ni_2P/MCM-41. It was synthesized according to the literature [1]. About 35 mg of the catalyst was pressed into a pellet and set in the in situ cell designed for a simultaneous measurement of XAFS and IR (Fig.1). The catalyst was activated in situ under H_2 at 723 K for 2 h. The HDS reaction was conducted under a flow of reactant gas composed of thiophene (0.1 vol%), He (1.8 vol%), and H_2 (98 vol%). The experiment was carried out at BL9C with a Si(111) monochromator. Ni K-edge XAFS was measured continuously every 20 sec in a transmittance QXAFS mode. At the same time, FT-IR was observed every 1 min during the reaction by JASCO VIR-9500. The reaction products were monitored by an online QMAS (Hyden Analytical HAL301).

Results and Discussion

Fig.2 shows the change of Ni K-edge shoulder band intensity (μt) at 8333.3 eV and the IR band area from 2817 to 3000 cm^{-1} during the HDS reaction at 513 K. The decrease in μt corresponds to formation of Ni-S bonding. And the emergence of IR band at 2817 - 3000 cm^{-1} indicates production of adsorbed hydrothiophene species. At the beginning of the reaction, a rapid decrease in the μt at 8333.3 eV was observed, indicating the evolution of Ni-S bonding, while the IR band gradually increased after the initial μt change slowed down. This result suggests that the active Ni phosphosulfide phase was formed at the beginning of the reaction and subsequently the reaction proceeded on these active sites.

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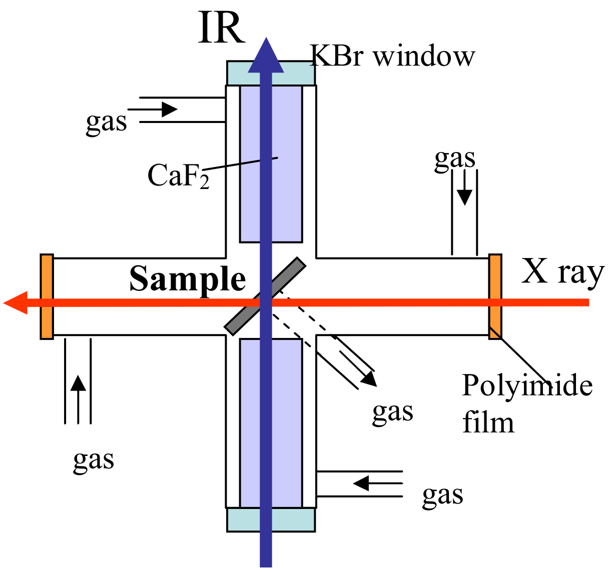

Figure 1 In situ XAFS and FT-IR cell

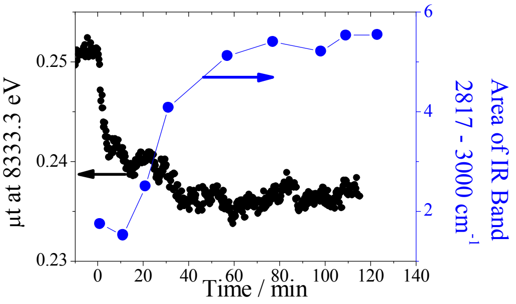

Figure 2 Change of the intensity of Ni K-edge at 8333.3 eV comapred to that of the area of IR band, ranging from 2817 to 3000 cm^{-1} during HDS at 513 K.

References

[1] S. T. Oyama, et al., J. Catal., 258,393 (2008).

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