

Hydrodesulfurization Reaction Mechanism of Ni₂P/MCM-41 by Operando Analysis

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Introduction

Supported Ni₂P catalysts show a very high activity for hydrodesulfurization reaction (HDS) of petroleum feed stocks [1]. In our previous work we have revealed that a new Ni phosphosulfide (NiPS) phase is formed from the Ni₂P during the HDS reaction [1]. But we have not understood the role of this NiPS phase. In order to elucidate the role of NiPS and the reaction mechanism of the Ni₂P, operando analysis has been applied to the Ni₂P catalyst. We have measured QXAFS, FTIR and QMS of Ni₂P catalyst during the HDS reaction.

Experimental

The catalyst was 12.2 wt% Ni₂P/MCM-41. It was synthesized according to the literature [3]. 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. The catalyst was activated *in situ* under H₂ 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 H₂ (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

Figure 1 shows Operando analysis results of Ni₂P/MCM-41 under HDS at 513 K. The amount of Ni-S is estimated by the intensity of XANES at 8333.3 eV. Adsorption of tetrahydrothiophene (THT) is measured by FTIR. The amount of NiPS phase rapidly increased in the initial period for 10 min, while the IR band intensity stayed at a low level. But after 20 min passed and the

change in XANES slowed down, the IR band suddenly started to increase. In addition to this, the H₂S production showed the same profile as IR, that is, the H₂S signal showed a drastic increase at about 20 min. These results mean that when the NiPS phase formation was almost completed, the catalytic HDS reaction of thiophene started and THT species appeared on the catalyst as a reaction intermediate. We concluded that NiPS is the active phase and THT is a reaction intermediate.

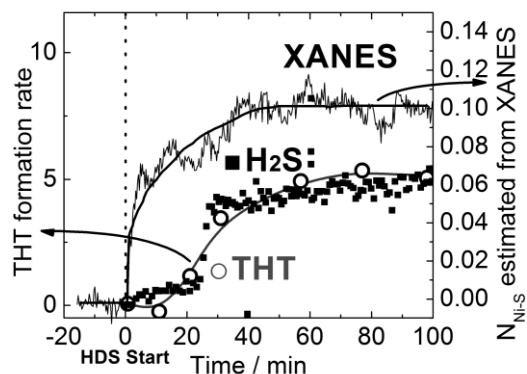


Figure 1. The amounts of Ni-S bond estimated from change of XANES at 8333.3 eV (solid line) compared with that of IR band in the aliphatic ν (CH) region (circles) and the formation of H₂S detected by QMS ($m/z=32$) (dots) during HDS at 513 K.

References

- 1) S. Ted Oyama, *Journal of Catalysis* **216**, 343 (2003).
- 2) K.K Bando *et al.*, *Journal of Physics : Conferenced Series* **190**, 012158. (2009).
- 3) S. Ted Oyama, *Journal of Catalysis* **216**, 343 (2003).