

Combined in Situ QXAFS and FTIR Observation of a Ni Phosphide Catalyst - Determination of Active Species for a Hydrodesulfurization Reaction -

Supported Ni₂P catalysts have been studied as a new class of catalysts for hydrodesulfurization (HDS) of petroleum feedstocks. In order to determine the reaction mechanism of thiophene HDS over Ni₂P/MCM-41, we have developed a new technique, which conducts simultaneous time-resolved analysis of in situ X-ray absorption fine structure (XAFS) spectroscopy and Fourier transform infrared (FTIR) spectroscopy together with product analysis. The formation of a nickel phosphosulfide phase (NiPS) was observed by XAFS prior to the emergence of tetrahydrothiophene (THT) in FTIR, which was accompanied by the HDS product. It is concluded that NiPS acted as the active phase and THT as a reaction intermediate for the HDS reaction.

Over the past decade, nickel phosphide has attracted much attention as a promising catalyst for hydrodesulfurization (HDS) of petroleum feedstocks. Preliminary characterization of the active phase revealed that it had a Ni₂P composition and that Ni₂P showed a high performance due to its high resistance to sulfur [1]. However, in situ X-ray absorption fine structure (XAFS) spectroscopy under reaction conditions indicated the presence of sulfur on Ni₂P during the HDS reaction, which seemed to work as a promoter rather than as a poison [2].

In order to determine the role of this sulfur in the HDS reaction, a new simultaneous time-resolved (STR) analysis technique was developed and applied to the study of a supported Ni₂P catalyst under thiophene

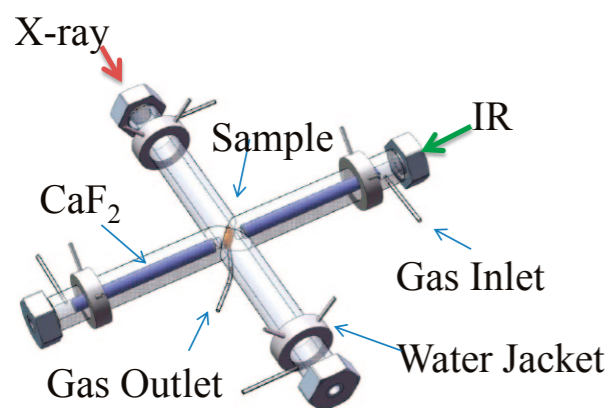


Figure 1
Diagram of a cell for the STR analysis.

HDS conditions [3]. In this STR analysis, in situ quick X-ray absorption fine structure (QXAFS) spectra were obtained simultaneously with in situ Fourier transform infrared (FTIR, JASCO VIR-9500) spectra, using a cross-shaped cell as shown in Fig. 1. The catalyst was pressed into a self-supporting pellet and set in the center of the cell positioned at 45° to both the X-ray and IR beams, and both spectra were obtained in a transmittance mode. On-line HDS product analysis was also conducted with a quadrupole mass spectrometer (QMS, Hyden Analytical HAL301). The experiments were conducted at BL-9C. The QXAFS of Ni K-edge from 8080 eV to 8900 eV was collected every 20 s with a scan time of 10 s, while the IR data were obtained with an accumulation time of 60 s. The XAFS data were analyzed by the software program REX2000 (Rigaku Co.). Curve-fitting analysis was carried out with parameters obtained with FEFF8 (Univ. of Washington).

The supported Ni₂P catalyst was prepared with a siliceous mesoporous material, MCM-41, as a support. Prior to the HDS reaction, the catalyst was pretreated under hydrogen at 723 K or 803 K to complete the formation of the active Ni₂P phase [4]. Then, a reactant mixture composed of thiophene (0.1 vol.%) and He (1.8 vol.%) and H₂ (98 vol.%) was introduced at a total flow rate of 102 cm³ (NTP)/min under atmospheric pressure. As mentioned above, due to its high tolerance to sulfur, the bulk structure of Ni₂P was retained during HDS as shown in Fig. 2 (a). However, a close examination of the X-ray absorption near-edge structure (XANES) in-

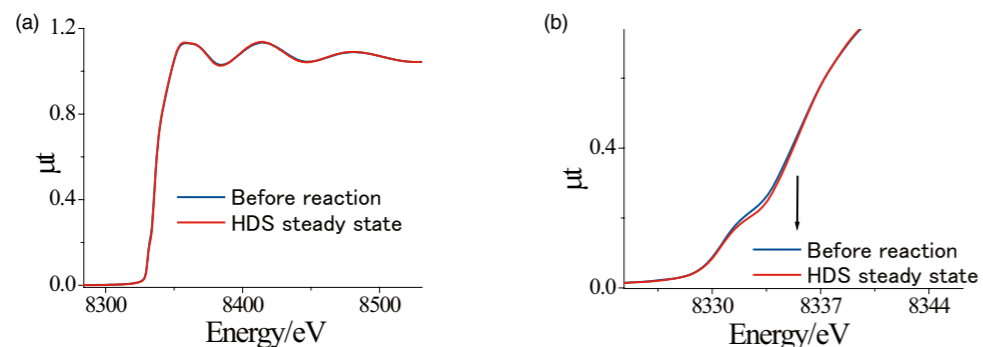


Figure 2
XAFS spectra before and during the HDS reaction. (a) All area, (b) XANES area.

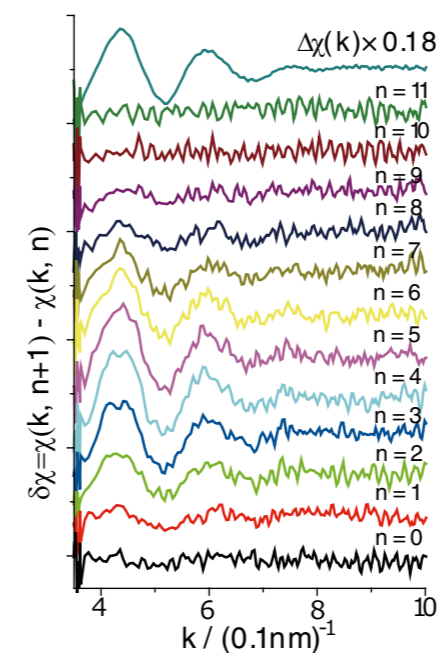


Figure 3
Difference spectra between consecutive scans. The difference spectrum between the ones before the reaction and under the steady state ($\Delta\chi(k) = \chi(k, n) - \chi(k, 0)$) is given at the top.

dicated a decrease in intensity at 8333.3 eV as shown in Fig. 2 (b), which was assigned to the formation of a nickel phosphosulfide phase, since the presence of a Ni-S bond was also confirmed by the extended X-ray absorption fine structure (EXAFS) under the steady state condition [2]. Further investigation of EXAFS spectra in the transient process to the steady state was carried out with difference spectra between consecutive scans as depicted in Fig. 3 [5]. The transient difference spectra were found to consist of one component that was proportional to the EXAFS difference spectrum obtained for the steady state, in other words, the species that evolved during the transient process was the Ni-S bond in the NiPS phase. In addition, it was confirmed that the change in XANES properly corresponded to the evolution of the NiPS phase in EXAFS.

The STR study was applied to the structural analysis of Ni₂P during the HDS reaction. As shown in Fig. 4 [3], immediately after the reaction started, a rapid decrease in XANES was observed, which was assigned to the formation of NiPS, as mentioned above. After the NiPS formation was saturated, adsorbed tetrahydrothiophene

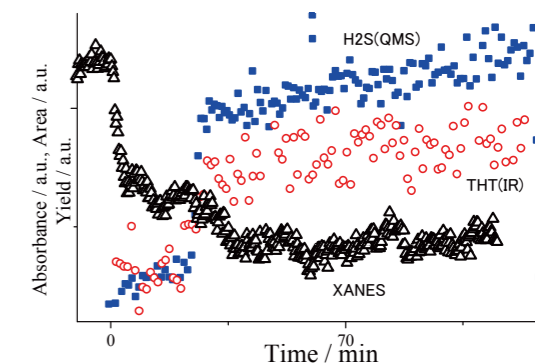


Figure 4
Change in XANES at 8333.3 eV (triangles) compared with that of IR band in the aliphatic $\nu(\text{CH})$ region (open circles) and the formation of H₂S detected by QMS ($m/z = 34$) (squares) during HDS at 513 K.

(THT) started developing in FTIR, which coincided with the detection of HDS products by QMS. All these experimental data indicated that NiPS acted as the active phase and identified THT as a reaction intermediate for the HDS reaction. The STR study proved to be a powerful tool for the precise study of reaction intermediates.

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K.K. Bando¹, T. Wada², T. Miyamoto², K. Miyazaki², S. Takakusagi², Y. Koike³, Y. Inada⁴, M. Nomura³, A. Yamaguchi¹, T. Gott⁵, S.T. Oyama^{5, 6} and K. Asakura² (¹AIST, ²Hokkaido Univ., ³KEK-PF, ⁴Ritsumeikan Univ., ⁵Virginia Polytechnic Inst. State Univ., ⁶The Univ. of Tokyo)