Combined in situ analysis of Ni$_2$P/MCM-41 under hydrodesulfurization conditions - Simultaneous observation of QXAFS and FTIR -

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Abstract. Supported Ni$_2$P catalysts are efficient for the hydrodesulfurization (HDS) of liquid fuels. In situ extended x-ray absorption fine-structure (EXAFS) analysis of the Ni$_2$P catalyst under realistic HDS conditions revealed the formation of Ni-S bonds in the catalyst system. In order to identify the origin of these bonds, a quick x-ray absorption fine structure (QXAFS) system was set up, which enabled measurement of one Ni K-edge EXAFS spectrum in 10 sec. In addition, a Fourier transform infrared (FTIR) unit was incorporated to the QXAFS system, which allowed simultaneous measurements of XAFS and IR spectra on the same sample. The catalyst (12.2 wt% Ni$_2$P/MCM-41) was activated under H$_2$ at 723 K to regenerate an active phosphide phase. After activation, a reaction gas mixture (thiophene/He/H$_2$ = 0.1 / 1.9 / 98, at a total flow rate of 102 ml/min) was introduced. Under the reaction conditions, there was a change in the pre-edge area of XANES, which corresponded to the evolution of Ni-S bonds in EXAFS. The simultaneous measurements of XANES and IR revealed that this Ni-S could be attributed to the formation of a Ni phosphosulfide species rather than bonding between Ni and S of adsorbed thiophene. The combined in situ techniques proved to be an effective tool for the characterization of working catalysts.

1. Introduction
Development of deep desulfurization catalysts is currently attracting great attention, because of strict regulations limiting the sulfur content of liquid fuels which have given rise to an urgent need for more effective catalysts. For years, Mo and W sulfides promoted by Co and Ni have been widely used in industrial processes, and their performance has made remarkable progress [1]. Recently, transition-

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metal phosphides have been recognized to have unique catalytic properties and to be promising alternative catalysts to the Mo and W sulfides [2]. Among them, supported Ni₃P catalysts have shown the best performance in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) with activity higher than commercially available Mo and W sulfide catalysts [3] based on sites counted by chemisorption. Characterization studies have shown that the Ni₃P phase has high tolerance to sulfur, and that the Ni₃P bulk structure is maintained after HDS catalytic tests [4]. However, a precise analysis of in situ extended x-ray absorption fine-structure (EXAFS) data before and after reaction revealed the formation of Ni-S bonds during HDS [5]. The origin of these Ni-S bonds has not yet been clarified. It has been speculated that the Ni-S was due to a Ni phosphosulfide (NiPS) species on the surface of Ni₃P particles, and that this NiPS phase provided the active sites, however the possibility was raised that the S signal could also be due to an adsorbed sulfur-containing intermediate [6]. In order to elucidate the reaction mechanism and to confirm the presence of the NiPS phase, we conducted time resolved in situ QXAFS (Quick X-ray absorption fine-structure) analysis combined with in situ FTIR (Fourier transform infrared) analysis under thiophene HDS conditions. The simultaneous measurement of XAFS and IR shows structural changes of the catalyst and the adsorbed species with a precise time coincidence, which enables discrimination between the NiPS phase and adsorbed sulfur compounds. Online gas analysis was also employed to monitor the HDS products and to measure catalytic activity. An active nickel phosphide phase was proposed based on the results of the structural analysis and the HDS activity.

2. Experimental

2.1. Synthesis of the catalyst
The catalyst studied in this work was Ni₃P/MCM-41. The mesoporous silicious MCM-41 support was synthesized following a literature procedure [6]. The supported Ni₃P catalyst was prepared with excess phosphorus (Ni/P = 1/2) and a metal loading of 1.15 mmol Ni g⁻¹ support (12.2 wt.% Ni₃P/support) [7]. In a first step, a supported nickel phosphate was prepared by incipient wetness impregnation of nickel and phosphorus precursors, followed by drying and calcination in static air. In a second step, the phosphate was reduced to phosphide in flowing H₂ by temperature-programmed reduction (TPR). After TPR, the sample was cooled to room temperature in flowing He and passivated in a flow of 0.5 % O₂/He for 4 h to prevent bulk oxidation of the freshly reduced phosphide.

2.2. QXAFS measurements
In situ Quick XAFS[8] was carried out at the bending magnet beam line 9C of Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK). The ring energy and current were 2.5 GeV and 430 mA, respectively. An incident X-ray beam was focused on the sample with a bent-cylindrical mirror. The intensity of the incident beam (I₀) and the transmitted X-ray (I) was monitored by ionization chambers filled with 100% N₂ and 25% Ar balanced with N₂, respectively. A Si(111) double crystal monochromator was rotated by a stepping motor with a speed which enables QXAFS measurements at 10 sec per spectrum in the Ni K-edge region from 8080 to 8900 eV. It took another 10 sec to save the collected data in a computer. As a result, measurement of a spectrum was done every 20 sec. The data were processed by REX2000 (Rigaku Co.). Parameters for curve fitting analysis were extracted by FEFF8 (Univ. of Washington).

2.3. FTIR measurements
For combined measurements of QXAFS and FTIR, a cross-shaped in situ cell was built as shown in figure 1. The cell has two pairs of windows for the X-ray and IR beams which intersect at the center, where a sample disk was positioned at an angle of 45 ° to both beams. Polymide films with 125 μm thickness were used as windows for the X-rays, and KBr crystal disks (3 mm in thickness) were used for the IR beam. CaF₂ crystal rods were placed in the IR optical path to minimize the dead volume and suppress absorption of the IR radiation by gas phase species. In situ FTIR spectra were collected
every 1 min by a JASCO VIR-9500 instrument equipped with an MCT detector and an optical fiber (ZnSe). The IR light source and the detector were connected with the optical fiber so that it could be fitted to any XAFS beam line as shown in figure 2.

![Diagram of the in situ cell for simultaneous measurement of XAFS and IR.](image1)

**Figure 1.** Diagram of the in situ cell for simultaneous measurement of XAFS and IR.

**Figure 2.** Photo during an experiment at KEK.

2.4. In situ measurements
About 35 mg of the catalyst was pressed into a disk and set in the in situ cell. The catalyst was activated in situ under H$_2$ at 723 K for 2 h. The HDS reaction was conducted at 1 bar under a flow of reactant gas composed of thiophene (0.1 vol%), He (1.9 vol%), and H$_2$ (98 vol%) at a total flow rate of 102 ml/min. The reaction products were monitored by an online quadrupole mass spectrometer (QMAS, Hyden Analytical HAL301).

3. Results

3.1. Activation
Since the catalyst underwent passivation, activation of the Ni$_2$P was conducted by temperature-programmed reduction (TPR) under a flow of H$_2$ (100 ml/min). The temperature was raised at 5 K/min to 723 K and kept at 723 K for 2 h. Figure 3 shows the change of (a) XANES (X-ray absorption near-edge structure) during TPR and (b) Fourier transform (FT) of the EXAFS data before and after activation. A strong white line was found at 8347 eV in the initial XANES spectrum, which indicated most of the Ni was in an oxidized state (figure 3(a)). The FT of the catalyst before activation showed two intense peaks which were assigned to Ni-O (0.162 nm) and Ni-Ni (0.282 nm) of a Ni(OH)$_2$ structure (figure 3 (b)).

![Change of (a) XANES during TPR and (b) FT of EXAFS (k$^3$χ(k)) before and after TPR.](image2)

**Figure 3.** Change of (a) XANES during TPR and (b) FT of EXAFS (k$^3$χ(k)) before and after TPR.
When the temperature reached 723 K, the white line diminished drastically (figure 3 (a)), which indicated reduction of the Ni. The FT for the activated catalyst showed one broad band (figure 3 (b)) and was assigned to Ni-P bonds (coordination number (N) = 3.4, distance (R) = 0.222 nm) and Ni-Ni bonds (N = 2.6, R = 0.254 nm) of Ni2P. Judging from the coordination numbers, the particle size of Ni2P on MCM-41 was less than 1 nm.

3.2. XANES change during HDS

Figure 4. XANES spectra before and during HDS at 573 K for 2 h. The inset shows a magnified portion of the pre-edge region.

The HDS reaction was conducted at 453K, 513 K and 573 K. Figure 4 shows the XANES data observed after 2 h of the reaction at 573 K, compared with that of the catalyst just before the reaction. Owing to the high sulfur tolerance of the bulk Ni2P, there was little change between the two spectra. However, by careful examination of the signal at 8333.3 eV (inset), a clear (and reproducible) decrease in intensity could be discerned under HDS conditions. As will be discussed, this decrease in intensity can be ascribed to an increase in Ni coordination by the formation of Ni-S bonds.

Figure 5 shows the difference EXAFS spectrum obtained by subtracting the spectra before and during the reaction. A curve fitting analysis of the oscillation in the difference spectrum identified the signal as consistent with Ni-S bonds (N = 0.3, R = 0.233 nm). The emergence of a Ni-S signal was also found in an in situ observation under dibenzothiophene HDS reaction conditions [5]. Taking all these results into account, we have concluded that the decrease in XANES intensity at 8333.3 eV can be attributed to the formation of Ni-S bonds.

Figure 6 shows the changes of the XANES signal at 8333.3 eV during reaction at various reaction temperatures. The decrease in XANES became larger with increasing temperature indicating that the amount of Ni-S bonding increased with temperature. On the other hand, the ratio of the HDS activity estimated from the H2S signal (m = 32 by QMAS) was 5.7 : 1.3 : 1 for the reactions at 573 K, 513 K and 453 K, respectively. The correlation between the amount of Ni-S and the HDS activity was positive, which meant that the catalyst was not poisoned by the formation of Ni-S.

3.3. FTIR changes during HDS

Figure 7 shows the changes of the FTIR spectra during HDS at 453 K. It took 1 min for the measurement of one spectrum. The first spectrum already showed absorption due to aliphatic ν(CH) stretches of tetrahydrothiophene (THT) species in the region from 2824 cm⁻¹ to 2975 cm⁻¹[6], indicating that the adsorption and hydrogenation of thiophene to THT occurred within 1 min. The deposition of THT on the surface was nearly saturated within the first several minutes.
On the other hand, the FTIR signal during HDS at 573 K showed completely different behaviour as shown in figure 8. During the initial 20 min no band was observed in the aliphatic $\nu$($\text{CH}$) region. After 118 min, a band was barely observed in the $\nu$($\text{CH}$) region but its intensity was weak, less than 1/10, compared to that at 453 K. It indicated that at 573 K, the amount of adsorbed tetrahydrothiophene on the catalyst was very small.

Figure 9 shows that at 513 K, at the beginning of the reaction, a weak band was observed in the $\nu$($\text{CH}$) region, which did not change for more than 10 min. After 20 min passed, the band suddenly began to increase and was almost saturated at 57 min. Figure 10 depicts the change of XANES at 8333.3 eV and the area of the $\nu$($\text{CH}$) band in the FTIR during the reaction at 513 K. During the initial Ni-S formation period indicated by the rapid decrease of the XANES signal, the IR band intensity for the THT remained at a low level. At 20 min, a rapid increase in the FTIR band occurred, whereas the change in XANES nearly settled down. The above results clearly demonstrate that the change in Ni-S signal from XANES was independent of that of adsorbed tetrahydrothiophene (THT), and that the THT was not causing the Ni-S signal.

4. Discussion
This work presents for the first time simultaneous measurements of x-ray absorption fine-structure (XAFS) and Fourier transform infrared (FTIR) spectra of working catalysts, made possible by the installation of QXAFS equipment and the use of a four-window in situ cell (figures 1 and 2). As will be shown, measurements in transient mode allow deeper understanding of catalytic phenomena through comparison of the time evolution of the signals.
Standard application of a single technique for sample characterization using methods such as x-ray absorption near-edge structure (XANES) or extended x-ray absorption fine structure (EXAFS) is now almost routine, and still provides valuable information. For example, in this study XANES was used to follow the reduction of the nickel phosphide sample in the course of its activation (figure 3a). The decrease in the white line area showed very clearly that the sample was reduced in this process. Using EXAFS analysis before and after activation (figure 3b) it was possible to show that the changes corresponded to the transformation of the sample from a Ni hydroxide-like material to a finely dispersed Ni₃P phase with characteristic Ni-P (0.222 nm) and Ni-Ni (0.254 nm) distances.

In situ measurements, even using a single technique, are particularly useful in catalysis research, where the nature of the sample changes as a consequence of reaction. In this study XANES was applied to the catalyst before and after introduction of the reactant thiophene. The gross features of the spectra show little change (figure 4), but enhancement of the pre-edge region (insert) shows a minor, but distinct, decrease in the absorbance in the pre-edge region at 8333.3 eV when the catalyst is exposed to thiophene. The simplest interpretation for the decrease in intensity is an increase in the coordination of the Ni due to bonding with sulphur. This is related to the well-known decrease in intensity for K-edge transitions as coordination increases, for example, in going from tetrahedral to octahedral Ti coordination [9]. More rigorously, for Ni₃P itself, a multiple scattering theoretical calculation of the XANES spectrum also predicts a decrease in intensity at 8333.3 eV upon formation of Ni-S, which agrees well with the present observations [10].

In situ EXAFS measurements also provide valuable information. Here they allow the calculation of the difference spectrum of the sample before and after the hydrodesulfurization (HDS) reaction (figure 5). The analysis of the oscillations by FEFF gives a distance (0.233 nm) that is characteristic of Ni-S bonds. The coordination (N = 0.3) indicates low concentrations, consistent with a surface species.

The XANES and EXAFS measurements give evidence for the formation of Ni-S bonds upon exposure of the samples to thiophene. However, the origin of this Ni-S species is not clear as several possibilities exist: the Ni-S signal could be due to an inactive sulfide rather than an active site or could be caused by the adsorption of sulfur compounds such as thiophene or tetrahydrothiophene [6]. In order to distinguish between these possibilities, measurements were carried out simultaneously with a combination of XANES and FTIR.

As shown in figures 6 and 8, in the initial period after exposure to thiophene at 573 K XAFS indicated the formation of Ni-S whereas FTIR showed negligible adsorption of thiophene. Therefore, it is concluded that the Ni-S species detected by XAFS can be assigned to a Ni phosphosulfide species rather than to a surface Ni-S bond due to a thiophene species or tetrahydrothiophene (THT). The results at 513 K and 453 K also support this conclusion. At 453 K, the FTIR band emerged immediately after the introduction of the reactants (figure 7), whereas the change in XANES was gradually progressing even after the FTIR signal reached saturation (figure 6).

At 513 K the FTIR signal for THT showed a considerable lag (20 min) before growing to a steady value (figure 9), and this contrasted with the time signature of the XANES signal (figure 6). This again indicated that the Ni-S bonding detected by XANES was not associated with the formation of the THT species. The data at 513 K are compared in figure 10. FTIR demonstrated that the accumulation of adsorbed THT species occurred after the Ni-S bond signal detected by XAFS was nearly saturated. These results give strong support to the assignment of the Ni-S species detected by XAFS to Ni phosphosulfide species but not to Ni-S bonds of adsorbed THT.

In this work XANES and FTIR were used simultaneously to study the initial processes in the HDS of thiophene on a Ni₃P/MCM-41 catalyst. Normally these measurements are conducted independently with different equipment, and comparisons are generally made at steady-state conditions. With the use of the QXAFS technique it was possible here to make simultaneous dynamic measurements with FTIR which permitted the unraveling of catalyst surface composition changes and adsorption. It was thus possible to show that a phosphosulfide phase was first formed on the catalyst surface, and this was followed by adsorption and hydrogenation of thiophene to a tetrahydrothiophene intermediate.
In addition, it was demonstrated that there was a positive correlation between the amount of Ni phosphosulfide species and the HDS activity, suggesting that the Ni phosphosulfide phase was associated with the active sites rather than deactivated sites or spectators. The intensity of the FTIR band decreased with the temperature. A possible reason is hydrogenation of THT at higher temperature, which would make the concentration of adsorbed species low under working conditions.

5. Conclusions

Combined in situ x-ray absorption near-edge spectroscopy (XANES) at the Ni K-edge and Fourier transform infrared (FTIR) spectroscopy in transient mode were applied to the surface analysis of a Ni$_2$P/MCM-41 catalyst under thiophene hydridesulfurization conditions. The intensity of the Ni pre-edge XANES signal at 8333.3 eV decreased with reaction time due to an increase in Ni coordination and this was assigned to the formation of Ni-S bonds. The adsorbed hydrothiophene emergence in the FTIR spectra did not correspond to the formation of Ni-S in the XANES measurements, so that the Ni-S observed by XAFS was assigned to a Ni phosphosulfide phase. The Ni phosphosulfide phase is associated with the active sites present on the surface of the catalyst at steady-state conditions.

Acknowledgement

This work was financially supported by JST Grant-in-Aid for Scientific Research (Category S, no. 16106010) and the US Department of Energy, Office of Basic Energy Sciences, (Grant DE-FG02-963414669), and the experiments were conducted under approval of PF-PAC (Project no.2008G129).

References

[1] Okamoto Y and Kubota T 2003 Catal. Today 86 31-43
[2] Oyama S T 2003 J. Catal. 216 343-352
[3] Oyama S T, Wang X, Requejo F G, Sato T and Yoshimura Y 2002 J. Catal. 209 1-5
[4] Kawai T et al 2003 Chem. Lett. 32 956-957
[5] Kawai T, et al 2006 J. Catal. 241 20-24
[6] Oyama S T. Gott T, Asakura K, Takakusagi S, Miyazaki K, Koike Y, Bando K K, J. Catal. Submitted
[7] Oyama S T, Wang X, Lee Y-K and Chun W-J 2004 J. Catal. 221 263-273
[8] Frahm R, 1989, Rev.Sci.Instrum, 60, 2515
[9] Farges F Brown G E, and Rehr J J 1996 Geochim. Cosmochim. Acta, 60, 3023.
[10] Nagamatsu S and Fujikawa T 2009 private communication.