Special Issue for IACIS2012

doi:10.1246/cl.2012.1238

Operando Observation of Ni_2P Structural Changes during Catalytic Reaction: Effect of H_2S Pretreatment

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In situ X-ray absorption spectroscopy was used to study the effect of H_2S pretreatment on the activation of Ni_2P catalysts for the thiophene hydrodesulfurization (HDS) reaction. It was found that H_2S treatment produced Ni–S bonds that were slightly longer and that had higher coordination numbers than those formed during reaction. The longer Ni–S bonds formed by H_2S treatment were changed to the shorter Ni–S bonds by the catalytic reaction, and these shorter bonds were associated with high activity. The work provides evidence that a NiPS phase is active in the HDS reaction.

Removal of sulfur compounds from petroleum feedstocks is important for satisfying environmental regulations. Nickel phosphide (Ni_2P) catalysts have shown higher catalytic activity in hydrodesulfurization (HDS) reactions than commercially available NiMoS or CoMoS catalysts have.[1–4] Previous work with time-resolved simultaneous measurements of quick X-ray absorption fine-structure (QXAFS) and Fourier transform infrared (FTIR) spectra of Ni_2P catalysts during thiophene HDS indicated that a nickel phosphosulfide (NiPS) phase was responsible for the catalytic activity.[5–9] Recently, it was reported that pretreatment of Ni_2P by H_2S had a positive effect on the catalytic activity probably because of the formation of a surface NiPS phase.[10,11] However, no information has been presented about the structure of the active catalyst formed by the H_2S treatment. This paper reports results of in situ XAFS analysis of the Ni_2P during the H_2S pretreatment and the Ni_2P after the HDS reaction with and without H_2S treatment. The results indicate the formation of a catalytically active NiPS phase.

The MCM-41-supported Ni_2P catalysts of loading 1.15 mmol Ni $g_{support}^{-1}$ (12.2 wt % Ni_2P/support) were prepared as described in previous reports.[6,8] Briefly, the support was impregnated with a solution of nickel nitrate and ammonium phosphate, dried, calcined, and reduced (See Supporting Information (SI)).[23] For the measurements in this study, 30.0 mg of reduced and then passivated samples was pressed into a disk with a diameter of 15 mm and was re-reduced in a XAFS cell under H_2 flow (100 mL min^{-1}) at 803 K for 2 h (H_2 activated sample). The thus-reduced sample was first cooled to a set temperature (529, 559, and 583 K) to measure the in situ EXAFS and was then treated in 5.0 vol % H_2S/H_2 at 559 K for 0.3 h until in situ XAFS monitoring of a Ni–S bond showed no changes. The sample was then cooled or heated again to the HDS reaction temperatures under He flow. The sample was not moved during these steps, which allowed the measurement of accurate difference spectra. The mixed reactant gas composed of thiophene (0.1 vol %), He (1.9 vol %), and H_2 (98 vol %) was introduced at a rate of 100 mL min^{-1}.

Table 1. Relative hydrodesulfurization activities at different temperatures in the steady state

Temp /K	TOF/s^{-1} (%)[a] With H_2S treatment	TOF/s^{-1} (%)[a] Without H_2S treatment
529	$3.0 \pm 0.4 \times 10^{-3}$ (18 ± 2)	$2.0 \pm 0.4 \times 10^{-3}$ (12 ± 2)
559	$6.0 \pm 0.6 \times 10^{-3}$ (36 ± 3)	$5.4 \pm 0.5 \times 10^{-3}$ (32 ± 3)
583	$8.4 \pm 0.5 \times 10^{-3}$ (50 ± 3)	$8.2 \pm 0.5 \times 10^{-3}$ (49 ± 4)

[a]Values in parenthesis are conversions.

In situ QXAFS measurements were carried out at beam line 12C of the Photon Factory (PF) of the Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), in Tsukuba, Japan.[12] The ring energy and current were 2.5 GeV and 430 mA, respectively. The monochromator was rotated by a stepping motor at a speed at 10 s per spectrum in the Ni K-edge region from 8080 to 8900 eV. It took another 10 s to rewind the motor and save the collected data, so each measurement of a spectrum took 20 s. The incident beam intensity (I_0) and the transmitted beam intensity (I) were monitored using ionization chambers filled with 100% N_2 and 15% Ar/N_2, respectively. The data were processed using REX2000[13,14] (Rigaku Co.). Parameters for curve fitting analysis were derived from FEFF8.[15] The reaction products were monitored by an online quadrupole mass spectrometer (QMS, Hyden Analytical HAL301) and an infrared spectrometer (MKS Multigas 2030). Errors in the curve fitting analysis were estimated using the Hamilton ratio method[16] at a confidence level of 70%.

Table 1 summarizes the thiophene HDS activities expressed as turnover frequencies (TOF) based on surface atoms titrated by the chemisorption of CO. Treatment with H_2S gave larger activities for the Ni_2P catalysts at 529 K, but the differences became smaller with an increase in the temperature. At 559 and 583 K, almost the same activities were observed with or without H_2S treatment.

Figure 1 shows Ni K-edge EXAFS oscillations of the Ni_2P/MCM-41 at 559 K before the H_2S treatment (dotted line) and 20 min after the treatment with H_2S (solid line). The inset shows the difference spectrum. A similar sinusoidal structure in the difference spectrum was also observed during the HDS reaction.[17] Curve fitting analysis showed that the oscillation corresponded to a Ni–S bond distance. The length of the Ni–S bond was $R = 0.235 \pm 0.002$ nm and the coordination number was 0.35 ± 0.05.

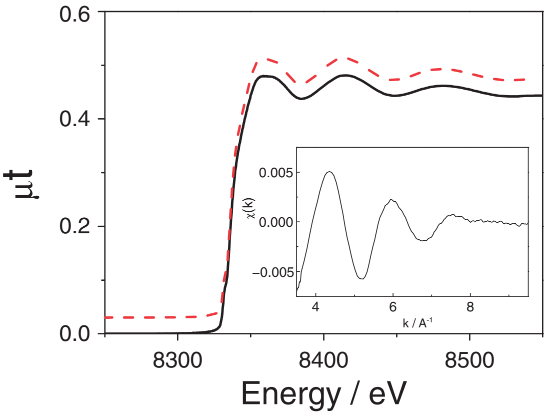

Figure 1. Ni K-edge EXAFS spectra of Ni_2P catalysts. The solid line and broken line correspond to Ni_2P before and after H_2S treatment at 559 K. The inset is the difference spectrum between the two.

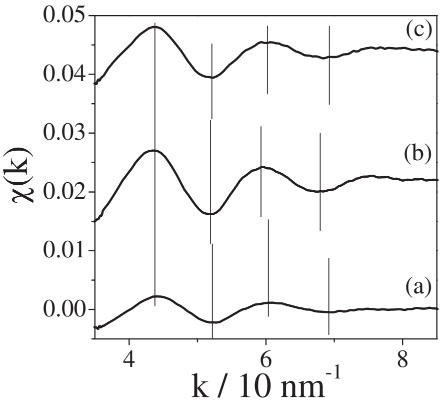

Figure 2. Ni_2P EXAFS difference spectra between (a) samples without H_2S treatment, before and during the HDS reaction at 529 K; (b) samples before and after the H_2S treatment at 559 K; (c) samples with H_2S treatment before and during the HDS reaction at 529 K.

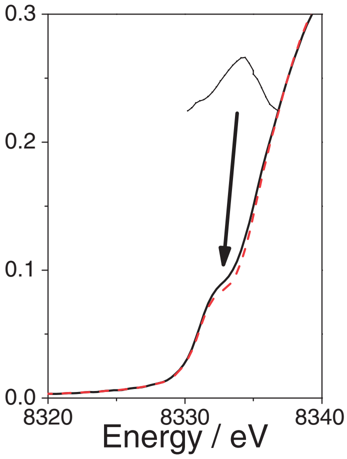

Figure 3. XANES spectra before the H_2S treatment at 559 K (solid line) and during the H_2S treatment at 559 K (broken line).

Figure 2 shows difference EXAFS oscillations for different cases. In particular, the comparison of the difference spectrum of the sample without the H_2S treatment, before and during the HDS reaction at 529 K (Figure 2a), with the difference spectrum of the sample before and after the H_2S pretreatment at 559 K (Figure 2b) reveals that the peak and valley positions are slightly different. This indicates that the lengths of the Ni–S bonds were different. For the case of HDS reaction on the Ni_2P without H_2S treatment, the length of the Ni–S bond was 0.230 ± 0.002 nm, 0.005 nm shorter than the Ni–S bond formed with H_2S treatement.[5,7–9,17,18] The Ni–S coordination number during the HDS reaction without H_2S treatment was 0.15 ± 0.05 nm smaller than that after the H_2S treatment.

We previously reported good correlation between the change in the shoulder structure signal at 8333 ± 1 eV in Ni X-ray absorption near edge structure (XANES) spectra and the amount of Ni–S bonds.[9] Figure 3 shows the expanded spectrum of the Ni K-edge region in Figure 1. In the edge region of Ni_2P, there was a small shoulder at 8333 ± 1 eV. A definite decrease in intensity (marked by an arrow) was observed after the H_2S treatment, which was quite similar to the change found during HDS reactions.[9] However, the bond lengths were different from each other. If the change occurred owing to the electronic modification of Ni or a multiple scattering effect, the changes in the 8333 eV feature should be different for the Ni–S bonds obtained from H_2S and from thiophene during the HDS reaction. We ascribed the peak decrease as due to a decrease in the symmetry around Ni.[5] There are two types of Ni structures in Ni_2P. One has a square-pyramidal geometry, and the other has a tetrahedral arrangement. The peak here can be assigned to a 1s–3d transition based on similar positions for other Ni compounds.[19] The feature is enhanced for the tetrahedral symmetry by p–d orbital mixing. The decrease in the peak height from tetrahedral to 5- or 6-coordinated structures are often observed in 3d transition metals.[19–22] Thus, the peak intensity decrease may be due to a decrease in the number of tetrahedral Ni sites because of site-selective Ni–S bond formation.[6] This would indicate that tetrahedral Ni on the surface preferentially reacts with sulfur.

Figure 2c shows the EXAFS difference spectrum for the sample before the H_2S treatment and the same sample with the H_2S treatment during the HDS reaction. The measurement temperature for both spectra was 529 K. The oscillation was somewhat decreased in its amplitude compared to the difference spectrum between the samples before and after the H_2S treatment at 559 K (as shown in Figure 2b), though the measurement temperatures of the latter were higher (559 K) than those of the former (529 K). Moreover, the period of oscillation of the former spectrum became slightly longer than that of the latter one and was similar to that directly produced during the HDS reaction without H_2S treatment, as shown in Figure 2a.

Table 2 shows the curve fitting results for the difference spectra. The longer Ni–S bond distance obtained after the H_2S treatment always became shorter during the HDS reaction and was the same as that of the bond formed after the HDS reaction without H_2S treatment. The Ni–S coordination numbers were also the same. Thus, the NiPS phase had the same structure during the reaction with or without the H_2S pretreatment. Although it is quite difficult to identify the sulfur species on Ni_2P created by the H_2S treatment, we tentatively assign them as SH

Table 2. Curve fitting results for Ni–S bond obtained in difference spectrum

Conditions	N^a	r/nm
H_2/H_2S/559 K	0.35 ± 0.05	0.235 ± 0.002
H_2/H_2S/HDS/529 K	0.25 ± 0.05	0.230 ± 0.002
H_2/HDS/529 K	0.15 ± 0.05	0.231 ± 0.002
H_2/H_2S/HDS/559 K	0.22 ± 0.05	0.230 ± 0.002
H_2/HDS/559 K	0.24 ± 0.05	0.231 ± 0.002
H_2/H_2S/HDS/583 K	0.24 ± 0.07	0.230 ± 0.002
H_2/HDS/583 K	0.23 ± 0.06	0.231 ± 0.002

[a] Coordination number.

species directly bound to Ni, because we observed IR vibrational mode at 2450 cm^{-1} and SH species adsorbed on the surface should have a Ni–S distance that is longer than that of the S atom. Part of the –SH might be removed during the HDS. A majority of the groups were converted readily to the active NiPS.

The results presented in Tables 1 and 2, indicate that there is a relation between the activity and the number of Ni–S bonds. During the HDS reaction at 529 K, the Ni–S bond formation was incomplete, and the activity of the untreated Ni_2P sample was found to be slightly lower than that of the sample treated with H_2S where more Ni–S bond formation occurred. The ratios of activity at 529 K to Ni–S bond were $(1.2 \pm 0.3) \times 10^{-2}$ and $(1.3 \pm 0.4) \times 10^{-2}$ with and without H_2S treatment, respectively. At higher temperature, the same Ni–S coordination number was obtained and the thiophene activity was the same. Thus, the results could again confirm a correlation between the activity and the Ni–S coordination number or the degree of formation of the NiPS phase, providing further evidence that NiPS is the active-phase structure.

Finally, the XANES spectra should be considered. The changes in the XANES signal indicate a decrease in the number of Ni with tetrahedral coordination, indicating that S was interacting with the tetrahedral Ni species. This suggests that the surface square-pyramidal Ni played a role in the activation of thiophene with the assistance of sulfur-bound Ni tetrahedral sites.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, through Grant DE-FG02-963414669, a JST Grant-in-Aid for Scientific Research (Category S, No. 16106010 and Category B, No. 16360405), and the Cooperative Research Program of Catalysis Research Center, Hokkaido University (Grant #10B1001 and #10B2009). The XAFS experiments were conducted with the approval of PF-PAC (Project Nos. 2010G127, 2008G129, and 2006G109).

Paper based on a presentation made at the International Association of Colloid and Interface Scientists, Conference (IACIS2012), Sendai, Japan, May 13–18, 2012.

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