In Situ X-ray Absorption Fine Structure Studies on the Structure of Nickel Phosphide Catalyst Supported on K-USY

Toshihide Kawai,[†1] Shinsuke Sato,[†1] Shushi Suzuki,[†1] Wang-Jae Chun,[†1,†2] Kiyotaka Asakura,*[†1] Kyoko K. Bando,[†3]
Takashi Matsui,[†3] Yuji Yoshimura,[†3] Takeshi Kubota,[†4] Yasuaki Okamoto,[†4] Yong-Kul Lee,[†5] and Shigeo Ted Oyama[†5]
[†1]*Catalysis Research Center, Hokkaido University, Sapporo, 060-0811*
[†2]*Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation*
[†3]*National Institute of Advanced Industrial Science and Technology, Tsukuba 305-856*
[†4]*Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue 690-8504*
[†5]*Environmental Catalysis and Materials Laboratory, Departments of Chemical Engineering and Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0211, U. S. A.*

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Local structure around Ni in a nickel phosphide catalyst supported on K-USY was investigated by an in situ X-ray absorption fine structure (XAFS) method during the reduction process of the catalyst and the hydrodesulfurization (HDS) reaction of thiophene. In the passivated sample, Ni phosphide was partially oxidized but after the reduction, 1.1 nm diameter Ni_2P particles were formed with Ni–P and Ni–Ni distances at 0.218 and 0.261 nm, respectively, corresponding to those of bulk Ni_2P. In situ XAFS clearly revealed that the Ni_2P structure was stable under reaction conditions and was an active structure for the HDS process.

Removal of sulfur from petroleum feedstocks is currently of great concern to the refining industry because environment regulations to limit sulfur levels in transportation fuels have steadily been tightened internationally.[1] Recognition of this problem has led to a worldwide search for better catalysts[2] of high performance.

Transition metal phosphides have recently been reported as a new class of catalysts with extremely high activity for both hydrodesulfurization (HDS) and hydrodenitrogenation reactions (HDN).[3–6] Several kinds of metal phosphide catalysts have been developed and the catalytic activities of a series of phosphides for HDN and HDS have been compared.[7–10] Ni_2P showed the highest activity among the iron-group phosphides though samples with low P content deactivated with time on stream. Supporting the Ni_2P on SiO_2 improved its activity and stability. XRD and adsorption studies indicated the presence of about 10 nm Ni_2P crystalline particles on the SiO_2. More recently nickel phosphide catalysts supported on USY or K-USY have been found to be much more active than on SiO_2. TEM observations revealed that the particle size was as small as 1–3 nm. XAFS (X-ray absorption fine structure) is a powerful structure analysis tool for nano particles which cannot give diffraction signals due to their small sizes.[11–13] Thus XAFS can provide useful information about the active structure of nanometer sized nickel phosphides on the USY or K-USY supports. Moreover, in situ XAFS spectra of the catalysts under reaction conditions can be measured because of the large penetration power of X-rays. In this paper we describe the active structures of nickel phosphides on K-USY which were determined by in situ XAFS under reaction conditions.

XAFS measurements were carried out in a transmission mode at BL7C of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The ring energy and the ring current were 2.5 GeV and 300 mA, respectively. The X-ray was monochromatized with a Si(111) double crystal monochromator and detected by I_0 and I ionization chambers filled with N_2 gas and Ar/N_2 mixed gas (ratio = 15/85), respectively. The catalyst was prepared in the same way as reported in the previous literature.[10] It was then passivated and stored in an Ar-filled ampule. 60 mg of the sample was pressed into a disk with a diameter of 10 mm and set in the stainless-steel cell[14] in a N_2-filled glovebox. 3-mm acrylic plastic plates were used for X-ray windows because the acrylic plastic windows have no toxicity and much lower metallic impurities than Be windows that are usually used in high-pressure in situ XAFS cells.[15] Since the sample might be oxidized during the passivation process, the sample was activated by heating to 723 K with a ramping rate of 5 K/min in H_2 flow (50 mL/min) and by treatment at that temperature for 2 h. The reaction was carried out at 593 K under a mixture of H_2 and thiophene (H_2 flow rate = 42 mL/min, thiophene flow rate = 1.3 mL/min). The reacted gas was analyzed by a gas chromatography and conversions of thiophene were observed under the conditions. XAFS data thus obtained were analyzed by REX2000 (Rigaku Co.) software.[16]

Figure 1 shows the X-ray absorption near edge structure (XANES) spectra of the sample together with those of reference compounds. In the passivated sample, a strong first peak was found just above the edge similar to that observed with $Ni(H_2O)_6$, indicating the oxidation of Ni phosphides. The k^3-weighted EXAFS (Extended X-ray Absorption Fine Structure) oscillations for the passivated catalyst (Figure 2a(3)) had larger amplitude in the low k-region, consistent with the presence of Ni–O bonds. There were two peaks found in its Fourier transform as shown in Figure 2b(3). A curve fitting analysis using Ni–P and Ni–Ni bonds failed but a fit succeeded when Ni–O, Ni–P, and Ni–Ni distances were assumed to be at 0.204, 0.229 and 0.262 nm, respectively. The presence of Ni–O bonds indicated that the passivated catalyst was partially oxidized. Figure 1a(4) shows that the XANES spectrum after reduction and cooling down to 323 K was similar to that of the Ni_2P standard compound, indicating the generation of the Ni_2P structure.

Figures 2a(4) and 2b(4) show the EXAFS oscillation of the reduced sample and its k^3-weighted Fourier transform. The curve fitting analyses gave Ni–P and Ni–Ni distances at 0.218

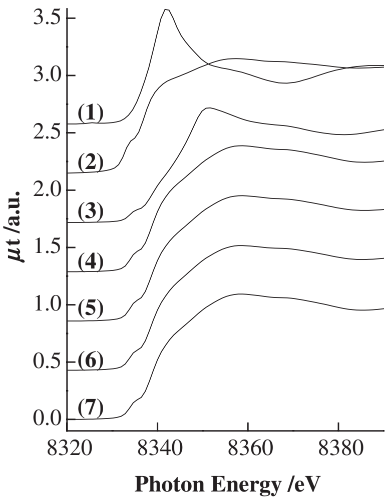

Figure 1. In situ XANES spectra of NiP/K-USY and references. (1) $Ni(H_2O)_6^{2+}$(reference), (2) Ni_2P bulk(reference), (3) passivated, (4) after reduction (323 K), (5) before HDS (593 K), (6) during HDS (593 K), (7) after HDS (323 K). Parentheses indicate the measurement temperature. Otherwise the sample was measured at room temperature.

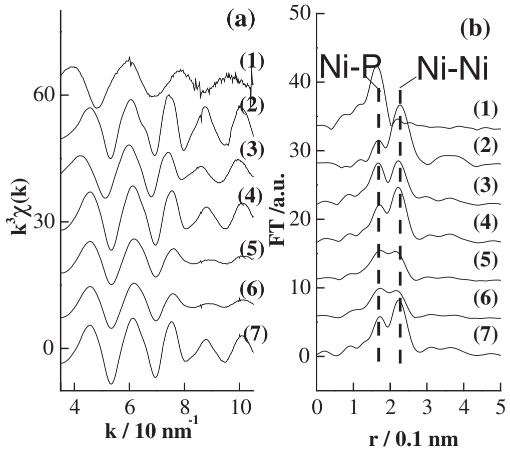

Figure 2. (a) EXAFS oscillations of NiP/K-USY and references. (b) k^3-weight Fourier transforms over 30–100 nm^{-1}. (1) $Ni(H_2O)_6^{2+}$, (2) Ni_2P bulk, (3) passivated, (4) after reduction (323 K), (5) before HDS (593 K), (6) during HDS (593 K), (7) after HDS (323 K). Parentheses indicate the measurement temperature. Otherwise the sample was measured at room temperature.

and 0.261 nm, respectively, which were almost equal to the corresponding bond lengths found in the Ni_2P standard compound. After the reduction, the Ni–O bonds were eliminated and the sample was converted to the Ni_2P structure. However, the second Fourier peak decreased in intensity compared to that of the Ni_2P bulk. Curve fitting analyses showed that the coordination number of Ni–Ni decreased to 70% of that in Ni_2P bulk, indicating the presence of small Ni_2P particles. Comparing the coordination numbers determined by XAFS with the calculated one assuming a spherical particle shape, the particle size of Ni_2P was estimated to be around 1.1 nm.[17] Considering the particle size and the pore size of USY, the Ni_2P particles may be located in the supercages of USY.

Figures 1(5) and (6) show the XANES spectra just before the reaction and under steady state reaction conditions at 573 K, respectively. Both XANES spectra were almost the same, indicating the Ni_2P structure was stable under the hydrodesulfurization reaction conditions. Figures 2a(5), (6) and 2b(5), (6) show XAFS oscillations and their transforms just before and during the steady state conditions measured at 573 K, respectively. Although the data at 573 K show considerable decrease in amplitude compared to that measured at 323 K because of thermal disorder, these EXAFS oscillations and Fourier transforms were completely identical. Thus the Ni_2P structure was stable and was the active structure under the steady state conditions.

The present in situ XAFS work clearly indicates that the Ni phosphide catalyst in K-USY, which showed high performance for the HDS reaction, has a Ni_2P structure with a particle size about 1.1 nm. The Ni_2P structure is stable under the reaction conditions.

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