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EXAFS measurements of a working catalyst in the liquid phase: An in situ study of a Ni_2P hydrodesulfurization catalyst

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Abstract

Strict environmental regulations and declining quality of petroleum feedstocks have made sulfur removal one of the most important current problems in refining. A novel, high-activity Ni_2P/SiO_2 catalyst with exceptional activity in deep hydrodesulfurization (HDS) was studied by in situ extended X-ray absorption fine structure (EXAFS). The measurements were conducted at realistic conditions of high pressure (3 MPa) and high temperature (613 K) and were made possible by the use of a low-volume cell with cubic boron nitride windows. The spectra thus obtained reveal that the bulk Ni_2P structure is stable at reaction conditions, but that the active surface has Ni–S bonds.

Keywords: Ni_2P/SiO_2; Deep hydrodesulfurization; In situ EXAFS; High pressure; High temperature; Liquid phase; Boron nitride

1. Introduction

The study of heterogeneous catalysts at reaction conditions provides important information about surface active phases and reaction mechanisms and allows the design of improved compositions. Studies of working catalysts with methods capable of atomic-level resolution have been mostly restricted to gas-phase reactions at mild conditions, because of the strong interference of the fluid phase. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a powerful technique that can provide structural information about catalysts under operating conditions. Considerable progress has been made in the design of experimental cells for EXAFS measurements since the first reports of high-pressure [1,2] and liquid-phase [3] cells. The first cell that could be used with a liquid feed at high pressure (73 bar) and high temperature (523 K) used a downward trickle flow to wet a catalyst wafer, with the main atmosphere being gaseous [1,2].

A recent paper summarized previous research and described a cell that can be used for liquid-phase batch reactions up to 250 bar and 493 K [4]. The cell described in the present study can be operated at 50 bar and 723 K and is usable in batch or flow mode. It uses flat windows held close to the sample and a mixed flow of liquid and gas.

Recently, hydrodesulfurization (HDS), an industrial process used to remove sulfur from petroleum feedstocks, has come to prominence because of worldwide legislation limiting the amount of sulfur in transportation fuels. EXAFS has been applied to the investigation of hydrotreating catalysts, but to date little work has been done on structural analysis in the liquid phase, particularly under elevated temperature and pressure conditions [1,2]. This is because of the strong absorption of X-rays by liquids and the severe stresses on the window material at realistic reaction conditions. Nonetheless, the use of liquid-phase conditions for HDS is important, because it is well known that gas-phase conditions do not reproduce the results obtained with liquids [5,6].

A key development for the work described in this report was the construction of a low-volume cell with flat windows transparent to X-rays that were chemically, structurally, and thermally stable. Earlier cells could not handle both high tempera-

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tures (>600 K) and pressures (>20 bar) for liquids [4,7]. Candidate materials that were considered included beryllium and diamond, but these had the drawback of being susceptible to oxidation by surrounding air at the high temperatures required for reaction. In addition, diamond is expensive and gives diffraction peaks, and beryllium is dangerous because it is highly toxic and its oxide readily forms flakes. The substance finally chosen was high-purity cubic boron nitride (c-BN), a material that has become available only recently. c-BN is ideal for the cell windows because it is transparent to X-rays and is chemically stable at high temperatures. Moreover, it is the hardest substance next to diamond, with a tensile strength of 1079 MPa (compared with 2000 MPa for diamond), and has no tendency to form cracks even at 1473 K.

This paper reports measurements of a liquid-phase HDS catalytic reaction at high pressure (3 MPa) and temperature (613 K) using X-ray absorption spectroscopy. The catalyst is a novel material, Ni_2P/SiO_2. Transition metal phosphides are a new class of catalyst with extremely high activity for HDS and hydrodenitrogenation reactions, with better performance than commercial sulfide catalysts [8–10]. Among the phosphides, nickel phosphide has been found to be particularly active [10,11]. An earlier study found that the catalyst consisted of small Ni_2P clusters dispersed on the support [12], and that these clusters were stable at reaction conditions with gas-phase reactants [13]. In the present work, the state of the catalyst was probed at reaction conditions in the liquid phase. The findings reveal the presence of Ni–S bonding in the active catalyst and implicate a phosphosulfide as the active phase.

2. Experimental

2.1. Catalysis

Hydrotreating activities of the Ni_2P/SiO_2 catalyst and a sulfided $Ni–Mo–S/Al_2O_3$ reference (Criterion 434) were tested in a three-phase, packed-bed reactor operated at 3.1 MPa and 613 K with a model feed liquid containing 3000 ppm of sulfur as dibenzothiophene (DBT), 200 ppm of nitrogen as quinoline, 1 wt% tetralin, 0.5 wt% *n*-octane as an internal standard, and balance *n*-tridecane. The reactors were 19 mm o.d./16 mm i.d. 316 stainless steel tubes with central thermocouples for temperature monitoring. The catalysts were in the form of pellets (16/20 mesh). The hydrogen flow rate was set to 100 μmol/s (150 cm^3/min, NTP) with a mass flow controller (Brooks, model 5850E), and the feed liquid was injected by a high-pressure liquid pump (LDC Analytical, model NCI 11D5) at a flow rate of 5 cm^3/h, to give a liquid hourly space velocity (LHSV) of 6.1 h^{-1}. Quantities of catalysts loaded in the reactors corresponded to the same amount of CO uptake for the phosphide and O_2 uptake for the sulfide (240 μmol). Before the reactivity testing, the catalysts were pretreated in H_2 for the phosphide and in 10% H_2S/H_2 for the sulfide at 723 K for 3 h. Hydrotreating products were collected every few hours in sealed septum vials and analyzed with a gas chromatograph (Hewlett–Packard, model 5890A) equipped with a 0.32 mm i.d. × 50 m fused silica capillary column (Chrompack, CPSIL-5CB) and a flame ionization detector.

2.2. In situ EXAFS

The high-pressure cell for EXAFS studies comprised 0.8-mm c-BN windows fixed to a central block by two stainless steel end pieces sealed with Cu sheets. The c-BN was prepared in high-purity form without binders by sintering hexagonal boron nitride at high temperature and high pressure (2400 K and 7.7 GPa). Fig. 1 shows a diagram of the in situ EXAFS cell. The distance between the windows and the sample was decreased to 3 mm, to minimize the absorption of X-rays by the reaction liquid. (Importantly, the windows are thermally resistant and inert, and thus do not require external cooling.) The cell was heated by six cartridge heaters (200 V, 1200 W in total), and temperature was monitored by a thermocouple. The sample was in the form of a wafer and positioned 3 mm from the windows. According to the Roark formula,

$$\sigma_{\max} = \frac{3}{8} P(3+\nu)\left(\frac{r}{d}\right)^2, \tag{1}$$

where $\sigma_{\max}$ is maximum tensile strength, P is pressure, ν is the Poisson ratio, r is radius, and d is thickness, the 0.8-mm c-BN can bear 240 MPa of hydrostatic pressure.

The in situ EXAFS measurements were carried out at BL7C and BL9C in the Photon Factory, Institute for Material Structure Science, High-Energy Accelerator Organization (KEK-IMSS-PF) with a ring energy of 2.5 GeV and a current of 450 mA. The X-rays were passed through a Si(111) double-crystal monochromator and focused onto the sample. The EXAFS data were

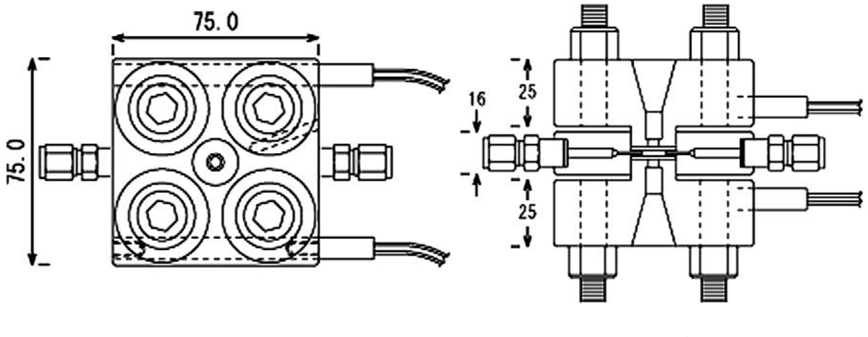

Fig. 1. Top and side views of in situ EXAFS cell. 1—end piece, 2—central block, 3—gas entry, 4—gas exit, 5—cartridge heater, 6—M12 screw, 7—sample port. Distances in mm.

collected in transmission mode using I_0 and I ionization chambers filled with 100% N_2 and 15% Ar in N_2, respectively. Reaction gases were supplied by a gas-handling system [14]. The fresh sample was ramped at a rate of 1.4 K/min to 723 K in 50 cm^3/min of H_2 for 3 h. Subsequently, the cell was cooled slowly to room temperature, and then pressurized to 3 MPa with pure H_2 and heated to the reaction temperature of 613 K in a flow of hydrogen at 80 cm^3/min. The feed of model oil was started at a rate of 2 g/h; this model oil was composed of 20 wt% tetralin, 77 wt% tetradecane, and 3 wt% DBT, corresponding to a sulfur content of 5900 ppm. EXAFS spectra were recorded after steady-state conditions were established.

3. Results and discussion

3.1. Catalytic tests

It was found that the activity of Ni_2P/SiO_2 (dibenzothiophene conversion, 74%) was higher than that of a commercial Ni–Mo–S/Al_2O_3 catalyst (69%) (Fig. S1) in the HDS of dibenzothiophene. The data were collected in the presence of 200 ppm N (a strong inhibitor of HDS) at a relatively high LHSV, 6.1 h^{-1}. Steady state was reached quickly (in 6 h) with both catalysts. The stability of the Ni_2P catalyst suggests that it reached a steady-state surface composition early in the reaction run. The conversions were based on equal sites (240 µmol) loaded in the reactor based on CO chemisorption for the phosphide and low-temperature O_2 chemisorption for the sulfide, and so are directly comparable.

3.2. XRD

XRD data of the samples (Fig. S2) fit the main lines of a Ni_2P reference at $2\theta = 40.7°, 44.6°, 47.4°, 54.2°$, and 55.0°. The lines are broadened and indicate the presence of particles ∼6 nm in diameter. There is no change before and after reaction, indicating that the particles are stable.

3.3. XAFS

EXAFS spectra of the bulk (Figs. 2a–2c) and supported Ni_2P samples before (Figs. 2d–2f) and after (Figs. 2g–2i) reaction were measured at room temperature. In addition, in situ EXAFS spectra were measured at 613 K just before the initiation of the reaction (Figs. 2j–2l) and again 10 h after the introduction of reactants under steady-state conditions (Figs. 2m–2o). The Fourier transform of the SiO_2-supported catalyst before and after the reaction (Figs. 2f and 2i) measured at room temperature shows the characteristic double-peak profile of Ni_2P [15] (Fig. 2c) due to Ni–P and Ni–Ni distances, consistent with the XRD data. The Fourier transforms for the in situ EXAFS spectra (Figs. 2l and 2o) show a single peak with a shoulder, due to the large Debye–Waller factors that attenuate the EXAFS oscillations, particularly in the high-k region.

Due to the correlation effects in multishell fitting, only a two-shell fitting of Ni–P and Ni–Ni bonds was carried out, producing distances of 0.222 and 0.261 nm, respectively (Table S1). The curve fitting results for Ni_2P supported on SiO_2 agree with those for Ni_2P bulk [16] within measurement error. After the reaction, the double-peak profile is maintained, and little change is seen in the curve fitting results.

Because a 6-nm cluster has only about 15% Ni atoms in the surface region, analyzing this region requires removing the contribution of the core. One way to do this is to take difference spectra between samples before and after the reaction; but this approach is not generally applicable because of sample movement due to thermal expansion and contraction in heating to reaction temperature. In contrast, in situ EXAFS spectra of the catalyst before and during reaction can be directly compared because the measurement temperature is kept constant and the position changes due to thermal expansion are negligibly small.

Such an analysis was carried out; the results show a small but distinctive oscillation (Fig. 3). The lack of any systematic distortion in the background indicates that the subtraction was successful. Curve fitting simulations assuming different bonds, including Ni–P, Ni–S, Ni–C, and Ni–Ni, were carried out; the calculated curve for a Ni–S bond gave a good fit, as shown in Fig. 3 by the dotted curve. The calculated distance of 0.228 ± 0.004 nm is longer than that of the Ni–P bond (0.222 nm) found in Ni_2P. In general, Ni–S bonds are longer than Ni–P bonds. In typical Ni_xS_y compounds, Ni–S bonds are found in the range of 0.225–0.240 nm (0.238 nm for NiS [17], 0.236 nm for NiS_2 [18], and 0.225 and 0.229 nm for Ni_3S_2 [19]), whereas in Ni_xP_y, Ni–P bonds are in the range of 0.218–0.231 nm (0.223 nm for Ni_2P [16], 0.223–0.231 nm for NiP [16], 0.221 nm for NiP_2 [16], and 0.218–0.224 nm for Ni_8P_3 [20]). Therefore, the newly found bond corresponds to a Ni–S bond formed during the reaction on the surface. It was previously suggested [10,11] that a surface phosphosulfide phase was formed in the HDS reaction; the Ni–S bond found here provides direct evidence of its formation. The difference spectra between the in situ EXAFS measurements can be used to elucidate the nature of the active surface, because the experimental conditions just before and at steady state are the same except for the presence of the reactant. The newly built in situ cell permits such measurements at reaction conditions.

The picture emerging from the XRD and EXAFS data is that the particles are composed of core domains of Ni_2P, with substantial proportions of surface atoms. In the course of the HDS reaction, the surface is partially sulfided, and a Ni–S distance appears in the difference EXAFS spectra. The surface phosphosulfide has high activity, although it is well known that Ni sulfide itself has low reactivity in HDS [21]. Particles of Ni_2P with a layer of nickel sulfide are also expected to have low activity because the surface chemistry will be dominated by the exterior composition.

In this work, the in situ EXAFS measurements were applied to Ni_2P catalysts, but the same apparatus can be used to study other systems, including hydrotreating catalysts such as NiMoS, CoMoS, and PtPd. The high-pressure and high-temperature EXAFS cell will allow the study of severe reaction conditions.

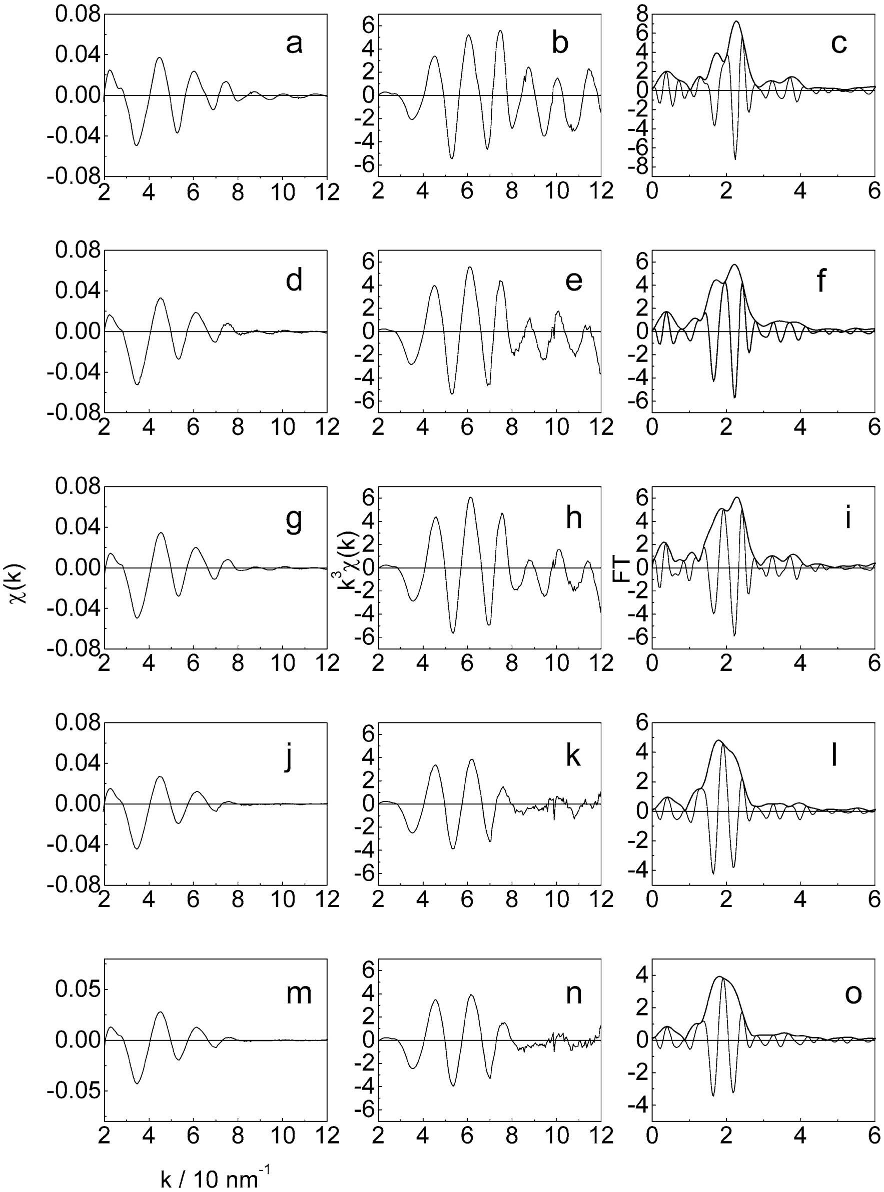

Fig. 2. EXAFS oscillations $\chi(k)$ (a, d, g, j, m), $k^3\chi(k)$ (b, e, h, k, n) and their Fourier transforms (c, f, i, l, o) for Ni_2P bulk (a, b, c), SiO_2-supported Ni_2P before reaction (d, e, f) and after reaction (g, h, i), just before the feed flow (j, k, l) and 10 h after the reaction initiation (m, n, o) under steady state conditions (613 K, 3 MPa).

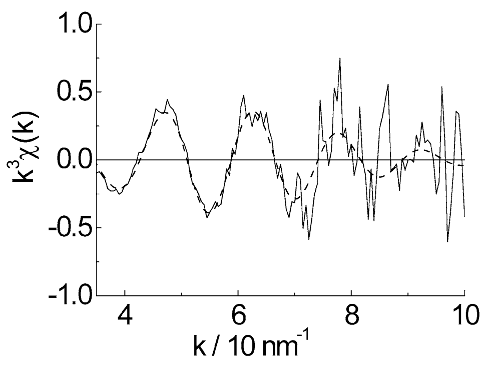

Fig. 3. Difference between the spectra before reaction and under steady state conditions measured at 613 K. Solid curve corresponds to the observed difference spectrum and the dotted line corresponds to that calculated for a Ni–S bond using FEFF.

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Supplementary material

The online version of this article contains additional supplementary material.

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References

[1] M. Boudart, R.A. Dalla Betta, K. Foger, D.G. Loffler, M.G. Samant, Science 228 (1985) 717.

[2] M. Boudart, R. Dalla Betta, K. Foger, D.G. Löffler, in: K.O. Hodgson, B. Hedman, J.E. Penner-Hahn (Eds.), EXAFS and Near Edge Structure III, Proceedings of an International Conference, Springer-Verlag, Berlin, 1984, pp. 187–189.

[3] G. Sankar, J.M. Thomas, Top. Catal. 8 (1999) 1.

[4] J.-D. Grunwaldt, M. Ramin, M. Rohr, A. Michailovski, G.R. Patzke, A. Baiker, Rev. Sci. Inst. 76 (2005) 054104.

[5] J.P. van den Berg, J.P. Lucien, G. Germaine, G.L.B. Thielemans, Fuel Process. Technol. 35 (1993) 119.

[6] F.E. Massoth, S.C. Kim, Catal. Lett. 57 (1999) 129.

[7] N. Weiher, E. Bus, B. Gorzolnik, M. Möller, R. Prins, J.A. van Bokhoven, J. Synchrotron Rad. 12 (2005) 675.

[8] C. Stinner, R. Prins, T. Weber, J. Catal. 191 (2000) 438.

[9] D.C. Phillips, S.J. Sawhill, R. Self, M.E. Bussell, J. Catal. 207 (2002) 266.

[10] S.T. Oyama, J. Catal. 216 (2003) 343.

[11] S.T. Oyama, X. Wang, Y.-K. Lee, W.-J. Chun, J. Catal. 221 (2004) 263.

[12] T. Kawai, S. Sato, W.J. Chun, K. Asakura, K.K. Bando, T. Matsui, Y. Yoshimura, T. Kubota, Y. Okamoto, Y.K. Lee, S.T. Oyama, Chem. Lett. 32 (2003) 956.

[13] T. Kawai, S. Sato, W.J. Chun, K. Asakura, K.K. Bando, T. Matsui, Y. Yoshimura, T. Kubota, Y. Okamoto, Y.K. Lee, S.T. Oyama, Phys. Scr. (2004) T115.

[14] K.K. Bando, T. Saito, K. Sato, T. Tanaka, F. Dumeignil, M. Imamura, N. Matsubayashi, H. Shimada, Top. Catal. 18 (2002) 59.

[15] X. Wang, Y. Lee, S.T. Oyama, K. Bando, F.G. Requejo, J. Catal. 210 (2002) 207.

[16] E. Larson, Arkiv. Kemi. 23 (1965) 335.

[17] J. Trahan, R.G. Goodrich, S.F. Watkins, Phys. Rev. B 2 (1970) 2859.

[18] T. Fujii, K. Tanaka, F. Marumo, Y. Noda, Miner. J. 13 (1987) 448.

[19] J.B. Parise, Acta Crystallogr. B 36 (1980) 1179.

[20] O.N. Il’nitskaya, L.G. Aksel’rud, S.L. Mikhalenko, Yu.B. Kuz’ma, Kristallografiya 32 (1987) 50.

[21] T.A. Pecoraro, R.R. Chianelli, J. Catal. 67 (1981) 430.