In Situ EXAFS Studies on Ni₂P Hydrodesulfurization Catalysts in the Presence of High Pressure and High Temperature Oil

Toshihide Kawai*, Kyoko K. Bando¶, Yong-Kul Lee†, S. Ted. Oyama†, Wang-Jae Chun‡ and Kiyotaka Asakura*

*Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan
¶National Institute of Advanced Industrial Science and Technology, 16-1, Onogawa, Tsukuba, 305-8569, Japan
†Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA
‡JST-CREST

Abstract. A Ni₂P/SiO₂ catalyst that is highly active for hydrodesulfurization (HDS) reaction was studied by in situ extended x-ray absorption fine structure (EXAFS) under the real reaction conditions. The measurements were conducted at realistic conditions of high pressure (3 MPa) and high temperature (613 K) in the presence of model oil. We used a low-volume cell with cubic boron nitride windows. The obtained spectra revealed that the bulk Ni₂P structure was stable at reaction conditions and that the active surface had Ni-S bonds under reaction conditions, which played an important role for HDS reactions.

Keywords: Ni₂P, hydrodesulfurization, cubic BN, in situ EXAFS, liquid phase, high pressure

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INTRODUCTION

Sulfur in transportation fuel causes serious environmental problems and its removal from petroleum feedstocks is currently important to the refining industry. Research to improve catalysts has been carried out intensively. Transition metal phosphides have recently been reported as a new class of catalysts with high activity for both hydrodesulfurization (HDS) and hydrodenitrogenation reactions (HDN).[1] Ni₂P supported on SiO₂ showed higher activity than commercially available CoMoS or NiMoS catalysts.[2]

In situ spectroscopy investigation to obtain the catalyst structure under real working conditions is important to understand the reaction mechanisms.[3] In situ EXAFS is a powerful tool for this purpose because the hard X-ray can penetrate through the reactants and we can obtain the structure even in the presence of high pressure gas.[4-7] In case of the catalytic reaction involving a liquid phase, X-ray absorption of the liquid is not negligible and the windows must be put close to the sample except in case of the utilization of the liquid film method.[8] The X-ray windows must withstand high pressure and high temperature while keeping good transparency for X-rays. Using Be windows may be a good choice but the Be is toxic.[9]

Another choice is to use a plastic window but in this case the highest temperature is limited.[10] Sometimes the plastic windows show radiation damage. The third way is to use a capillary cell, [11,12] with no dead space between the sample and windows. It can minimize the absorption of reactants and allows the measurements of XRD and EXAFS in the same set up. However, the cell has a curved window, which could have an inhomogeneous thickness effect on the EXAFS oscillation.[13] In this study we used high purity cubic boron nitride (cBN) as an X-ray window which has a high x-ray transparency and is tolerable against high temperature and high pressure. We applied this window to the measurement of the Ni₂P on SiO₂ under hydrodesulfurization reaction conditions.

EXPERIMENTAL

c-BN has a ZnS structure (diamond type). Its hardness is next to diamond. The cell is shown in Figs. 1 and 2. The high pressure cell for EXAFS studies had 0.8 mm c-BN windows fixed to a center block by two stainless steel end pieces. The cell was heated by 6 cartridge heaters (200 V 1200 W in total) and the
temperature was monitored by a thermocouple. The path length was 2 mm and sample was loaded in the form of a disk. According to the Roark formula [14], the 0.8 mm cBN can bear 240 MPa hydrostatic pressure. The in situ EXAFS measurements were carried out at BL7C at the Photon Factory, Institute for Material Structure Science, High Energy Accelerator Organization (KEK-IMSS-PF; Proposal No. 2003G247) with a ring energy of 2.5 GeV and a current of 450 mA. The X-rays were monochromatized by a Si (111) double crystal and were focused onto the sample by sagital focusing. Higher harmonics were rejected by the detuning of the monochromator. The EXAFS data were collected in transmission mode using I0 and I ionization chambers filled with 100% N2 and 15% Ar balanced with N2, respectively. Reaction gases were supplied by a gas handling system. [15] The fresh sample was reduced by the temperature programmed reduction (TPR, ramping rate of temperature =1.4 K/min, final temperature =723 K, H2 flow= 50 cm3/min). The HDS reaction was carried out at 613 K in the 3 MPa H2 flow at 80 cm3/min. The feed rate of a model oil was 2 g/hour. The model oil was composed of 20 wt% tetralin and 77 wt% tetradeane with 3 wt% dibenzothiophene(DBT). The preparation of Ni2P/SiO2 was reported previously [16] and the loading of Ni was 12 wt %. The EXAFS data were analyzed by using REX2000 [17] and the phase shift and amplitude functions were derived from FEFF.[18] Fitting range was usually 3 - 12 Å⁻¹.

RESULTS AND DISCUSSION

Figure 3 shows a series of XANES spectra during the reduction process of Ni2P catalyst which was partially oxidized during the storage. The reduction started to occur around 363 K and was completed at 723 K. Then we cooled down the sample and measured the EXAFS spectra at room temperature to obtain the catalyst structure. Curve fitting analyses showed the Ni-P and Ni-Ni distances at 0.223 and 0.261 nm, respectively, confirming the formation of Ni2P cluster. Then we pressurized the sample with H2 up to 3 MPa and heated it at 613 K under the flow of H2. We measured EXAFS just before the introduction of the model oil as shown in Fig.4a. We started to flow the oil and again measured the EXAFS after the steady state conditions were established as shown in Fig. 4b. Basically the EXAFS spectra before and during the reaction were very similar. In order to derive the subtle change during the reaction, we took difference spectrum between them. Note that the temperature and the x-ray hitting place were exactly the same so that the EXAFS had to be the same unless a structural change occurred during the reaction. We found a small but distinctive oscillation in the difference spectra as shown in Fig. 5. This oscillation could be fitted with Ni-S and Ni-P with the distance of 0.228 ± 0.004 nm which was longer than the Ni-P distance (0.223 nm). The phase shift and amplitude functions of Ni-S and Ni-P are indistinguishable. However, the Ni-S bonds are generally found in the range of 0.225 -0.238 nm while those for Ni-P are in the range of 0.218-0.225 nm.[19] Therefore, the newly observed oscillation may correspond to a Ni-S bond, which is formed during the reaction of DBT and the surface. Compared to P, S has a larger electron density that can eliminate α hydrogen from the DBT to induce the C-S bond cleavage reaction due to E2 mechanism, which is the key elementary reaction step of the hydrodesulfurization reaction. In this work the in situ EXAFS measurements were applied to Ni2P catalysts but the same apparatus can be used to study other systems, including hydrotreating catalysts such as NiMoS, CoMoS and PtPd where the high-pressure and high-temperature liquid phase reactions were carried out.
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