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In-situ X-ray Absorption Fine Structure Studies of the Structure of Ni_2P in USY Zeolite

Toshihide Kawai[1], Wang-Jae.Chun[1], Kiyotaka Asakura[1*], Kyoko K.Bando[2**], Takashi Matsui[2], Yuji Yoshimura[2], Yong-Kul Lee[3] S.Ted Oyama[3***]
[1]CRC Hokkaido University, Sapporo 060-0811, Japan. [2]AIST, Tsukuba 305-8562 Japan.
[3]Virginia Tech. VA24061 USA.

Introduction

Metal phosphides constitute a new class of catalysts showing very high activity towards hydrodesulfurization, with better performance than conventional sulfide catalysts like CoMoS. NiP_x supported on USY zeolite is one of the most active catalysts. We have studied the structure of the catalyst under reaction conditions- high pressure and high temperature conditions by means of in-situ x-ray absorption fine structure (XAFS). In the hydrosuflrization reaction, in-situ work is not so easy because of the presence of liquid phase oil which absorbs the X-rays so much that the x-ray windows and samples are placed closely, which prevents the effective cooling of the windows. Thus we have to construct the windows which are tolerable against both high temperature and high pressure.

Experimental

The preparation of NiP_x on USY zeolite was similar to that of NiP_x/SiO_2.[1] XAFS measurements were carried out at beamlines BL9A and BL7C of the Photon Factory (KEK-PF) in Tsukuba, Japan using an in-situ cell with PBI windows. The passivated catalysts were first treated in H_2 flow at a temperature of 673 K. After the XAFS measurements at reaction temperature (593 K), the gas flow was switched to a mixture of H_2 + dibenzothiophene (1.73 % w/w) in n-tetradecane (H_2 flow rate = 40 ml/min, n-tetradecane flow rate = 2 g ./hour). The changes in the catalyst during the reaction were monitored by XANES (x-ray absorption near-edge structure) and the structure under steady-state conditions was determined by EXAFS (extended x-ray absorption fine structure).

Results and Discussion

In a previous work, we have two XAFS results which are contradicted with each other. This is because the difference of the experimental conditions. One was in-situ and under atmospheric pressure while the other was ex-situ and under high pressure. Thus we conducted the new experiment with in-situ and under high pressure conditions. Figure 1 shows the in-situ EXAFS oscillations before and under the steady state conditions. We could not find any difference between the two spectra. To confirm this point we took the difference spectrum of the two as shown in figure 1. The difference spectrum lies at a zero line, indicating that the two spectra are identical. High-pressure in-situ EXAFS demonstrated that the Ni_2P structure in KUSY is quite stable under the reaction conditions. It is a surprising result because the latter spectrum is measured in the presence of oil and the absolute absorbance is larger than that of the former. But we can compare two spectra directly by removing the background from the raw data. This means the quality of the spectra is very high in the point that the homogeneous sample thickness and little contamination of the higher harmonics. Otherwise we should have the glitches and/or the smooth deviation from the zero line in the difference spectrum. The flat windows we adopted enable us to carry out such a high quality XAFS measurement. In conclusions we Ni_2P structure was stable enough even under the high-pressure reaction conditions. Further studies are now going on to carry out the in-situ experiment under the other reaction conditions.

Reference

1. S. T. Oyama, X. Wang, F. G. Requejo, T. Sato and Y. Yoshimura,*J.Catal*, **209,**1(2002).

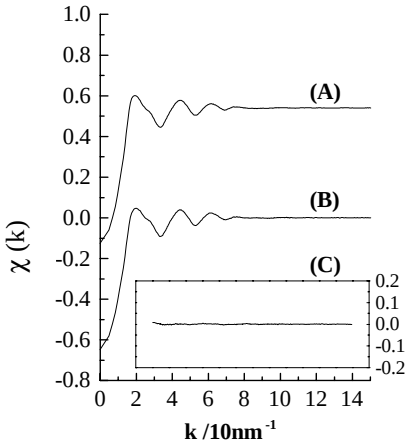

Fig.1 (A) and (B) In situ XAFS oscillations of Ni_2P/KUSY; (C) differences of EXAFS oscillations of the two spectra.

*askr@cat.hokudai.ac.jp
**kk.bando@aist.go.jp
***oyama@vt.edu