BL9A/2001G297

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

Toshihide Kawai[1], Shinsuke.Sato[1], Wang-Jae.Chun[1], Kiyotaka Asakura[1]*, Kyoko K.Bando[2]**, Takashi Matsui[2], Yuji Yoshimura[2], Takeshi Kubota[3], Yasuaki Okamoto[3], Y-K. Chen[4], Yong-Kul Lee[4], S.Ted Oyama[4]***

[1]CRC Hokkaido University, Sapporo 060-0811, Japan. [2]AIST, Tsukuba 305-8562 Japan. [3]Shimane University, Matsue 690-8504 Japan.[4]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 by means of in-situ x-ray absorption fine structure (XAFS).

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 water-cooled acrylic plate x-ray windows (3 mm thick) .[2] 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 + thiophene (H_2 flow rate = 42 ml/min, thiophene flow rate = 1.3 ml/min). 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

Fig. 1 shows the XAFS oscillations for the passivated and reduced samples, together with those for a Ni_2P bulk reference material. The passivated catalyst had XAFS oscillations (Fig.1a) that were quite different from those of the Ni_2P bulk (Fig.1c) (almost π radian phase difference and longer wavelength). Curve fitting analysis indicated the presence of Ni-O bonds at 0.21 nm. On the other hand, NiP_x/USY and Ni_2P bulk had very similar XAFS oscillations, indicating that the Ni_2P structure was recovered after reduction with H_2. Ni-P and Ni-Ni bond distances were found at 0.224 and 0.259 nm, respectively. Thus, the sample, which was oxidized after the passivation, was reduced to Ni_2P by the reduction.[1]

Fig.2 shows the XAFS oscillations before and during the reaction. Little change was observed between the spectra. We found desulfurized hydrocarbons in the effluent by gas chromatography. Thus the active structure was Ni_2P and its structure was maintained during the reaction. Such stability of the Ni_2P structure under reaction conditions could be related to its lack of deactivation in hydrodesulfrization reactions.

Reference

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

2. K. K. Bando, T. Saito, K. Kato, T. Tanaka, F. Dumeignil, M. Imamura, N. Matsubayashi and H. Shimada, *J.Synchrotron Rad.,* **8,**581(2001).

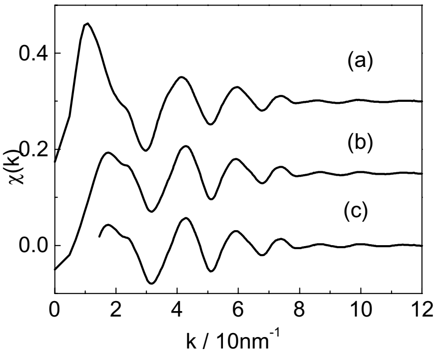

Fig.1 XAFS oscillations of (a) passivated NiP /USY,(b) NiP/USY after reduction (c) XAFS of Ni_2P bulk.

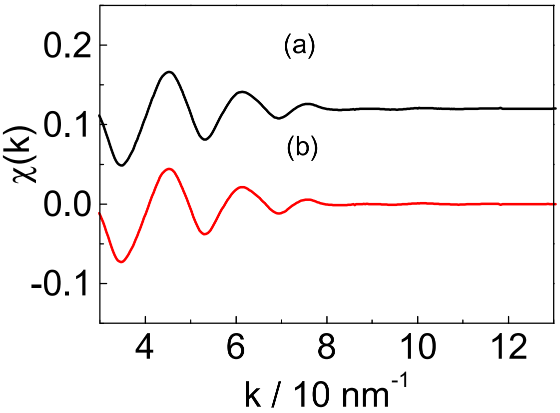

Fig.2 XAFS oscillations of (a) NiPx /USY before reaction (b) after reaction with thiophene

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