

Observation of structure changes of active sites for hydrodesulfurization catalysts with probe molecule adsorption by means of XAFS

Takeshi KUBOTA*¹, Masataka ITO¹, Yasuaki OKAMOTO¹

¹Department of Material Science, Shimane-Univ.,
Matsue, Nishikawatsu, Shimane 690-8504, Japan

Introduction

Co(Ni)-Mo(W) binary sulfide catalysts have been used in industry for hydrodesulfurization (HDS) reaction. These catalyst systems have received extensive attention of many chemists, because it has been known that very strong synergy effects appear between Co(Ni) and Mo(W) in these catalysts. It has been accepted that so-called "Co(Ni)-Mo-S" phase is catalytically active in HDS reaction in these catalyst systems. NO and O₂ have been used as probe molecules for the characterization of active sites of the Co-Mo sulfide catalysts because these molecules adsorb on the Co-Mo-S sites, which is active sites of the catalysts [1]. However, the influence of adsorption of these probe molecules to adsorption sites, such as Co(Ni) is still uncertain. We investigated the changes of the active sites of the Co-Mo sulfide catalysts by means of XAFS and FT-IR techniques.

Experimental

Catalysts Preparation

An alumina-supported Mo oxide catalyst (MoO₃/Al₂O₃) was prepared by a conventional impregnation method using (NH₄)₆Mo₇O₂₄·4H₂O as a precursor. MoO₃/Al₂O₃ was sulfided at 673 K in a flow of H₂/H₂S=90/10 for 1.5 h (MoS₂/Al₂O₃). A model catalyst, CVD-Co/MoS₂/Al₂O₃, was prepared by a CVD method using Co(CO)₃(NO). Detailed preparation procedures have been reported previously [2].

XAFS measurements

The Co K-edge XAFS spectra for Co-Mo catalysts were measured in a fluorescence mode at BL-7C of the Photon Factory. The synchrotron radiation was monochromatized by a Si(111) double-crystal monochromator. The storage ring was operated in 2.5 or 3.0 GeV. The fluorescence detection was carried out by using a Lytle type detector with flowing Ar. The incidence X-ray was monitored by an ion chamber with flowing N₂.

The catalyst was evacuated at room temperature after sulfidation, then transferred to a XAFS cell with Kapton windows without exposure to air. After the XAFS measurement of the sample in vacuum, 6.7 kPa of NO or O₂ was introduced to the cell and XAFS spectra for the catalysts exposed to probe molecules were recorded again.

Results and Discussion

Figure presents the Co K-edge XANES spectra of CVD-Co/MoS₂/Al₂O₃ before and after adsorption of probe molecules. On the NO adsorption, a shift of absorption

edge was immediately observed (ca. 0.5 eV), indicating the changes of electronic state of the Co atoms by the adsorption. It is considered from a comparison of XANES that dissociation of NO and concomitant oxidation of the Co sites does not take place even after 3h, since no changes were observed characteristic of oxidation of Co atoms (appearance of white line at 7726 eV or large shift of absorption edge). On the other hand, O₂ adsorption caused a shift of absorption edge (ca. 1.0 eV), accompanying an evolution of a peak at 7727 eV, characteristic of the oxidized Co atoms (Co²⁺ in CoAl₂O₄). The intensity of this peak increased with time, indicating a gradual oxidation of Co atoms by O₂ adsorption. These results clearly indicate that NO is superior to O₂ as a probe molecule for the characterization of Co-Mo HDS catalysts [3].

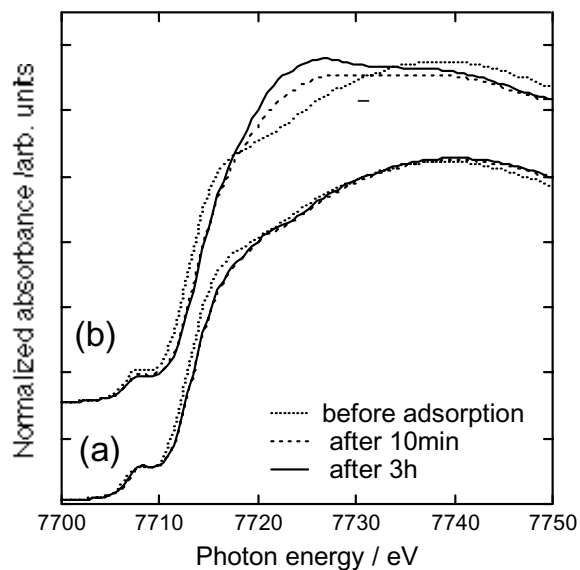


Figure Co K-edge XANES spectra of CVD-Co/MoS₂/Al₂O₃ catalysts before and after NO (a), or O₂ (b) adsorption.

References

- [1] T. Kubota et al., *Applied Catal. A*, 290, 17 (2005).
- [2] Y. Okamoto et al., *J. Catal.*, 222, 143 (2004).
- [3] T. Kubota et al., *Physica Scripta.*, T115, 667 (2005).

* kubitake@riko.shimane-u.ac.jp