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In-situ Ni K-edge EXAFS spectroscopic study on $NiMo/Al_2O_3$ catalyst sulfided at high pressure

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Introduction

Since Topsøe and his colleagues [1] have proposed that so-called Co-Mo-S phase is formed on $Co\text{-}Mo/Al_2O_3$ catalyst by sulfiding at atmospheric pressure as hydrodesulfurization (HDS) active phase, many studies have investigated detail of the formation of such the binary sulfide clusters by means of various spectroscopic techniques. One of most important experimental evidence for the formation of Co(Ni)-Mo-S phases is that Co(Ni)-Mo coordination shells are observed in Co(Ni) K-edge EXAFS spectra of the catalysts sulfidied at atmospheric pressure [2,3]. However, these EXAFS spectra are mainly obtained with carbon-supported catalyst, not conventional Al_2O_3-supported catalyst. Carbon support was used to improve signal to noise ratio of Co and Ni K-edge EXAFS spectra, because carbon is more transparent to X-ray near Co and Ni K-edges. Furthermore, FT range of their EXAFS spectra was limited to maximum of ca. 110 nm^{-1}. This could weaken contributions from Co-Co (Ni-Ni) and/or Co-Mo (Ni-Mo) scattering pairs in their EXAFS spectra because the scattering of electrons by these atoms mainly contributes in higher *k*-range. Shorter *k*-range also means that the number of independent parameters for curve fitting analysis is also limited.

To obtain direct evidence for the formation of Ni-Mo-S phase on $NiMo/Al_2O_3$ catalyst sulfided at high-pressure, high-pressure EXAFS chamber that effectively collects transmitted X-ray to provide EXAFS spectra with high signal to noise ratio even in higher *k* range was developed, and applied to *in-situ* Ni K-edge EXAFS measurements of $NiMo/Al_2O_3$ catalyst sulfided at high-pressure.

Experimental

High-pressure EXAFS chamber was made of SUS 316 stainless steel, and designed for transmission EXAFS measurement. This high-pressure chamber was designed to have lower dead volume between X-ray windows, which minimizes X-ray absorption by high-pressure H_2S/H_2 during sulfiding pretreatment. For X-ray windows, beryllium is conventional material of choice [4]. However, commercial beryllium discs usually contain small amount of Cu impurity. This will seriously contaminate Ni K-edge EXAFS spectra above 120 nm^{-1} since Cu K-edge X-ray absorption is superimposed on Ni K-edge EXAFS spectra. This could be a main reason for limited *k* range applied for Fourier transforms of Ni K-edge EXAFS spectra of NiMo/C catalysts reported previously [3]. To extend available *k*-range for Fourier transforms, polybenzimidazole discs were chosen as X-ray windows in the present study.

A catalyst pellet (φ14, Δμt=ca. 0.7) was located between these discs. Micro ceramic heaters were located inside the cell. The temperature around the catalyst pellet was monitored by four thermocouples inserted into the chamber. After sulfiding of $NiMo/Al_2O_3$ catalyst with different Ni to Mo molar ratios in 5% H_2S/H_2 stream at 613 K and 1.1 MPa, Ni K-edge EXAFS was measured at ambient temperature. EXAFS analysis was conducted in a conventional manner using REX2000 software.

Results and discussion

Fig. displays Ni K-edge $k^3\chi(k)$ of NiMo catalyst after sulfiding pretreatment at 613 K and 1.1 MPa. EXAFS oscillation is clearly visible even in higher *k* range in this spectrum. The maximum *k* value for FT reaches to 146 nm^{-1} (indicated by k_{max} in the figure). For comparison, Ni K-edge $k^3\chi(k)$ of this catalyst measured with the same high-pressure chamber, but equipped with beryllium windows instead of PBI windows, is shown in the same figure (dash line). Even though Cu impurity level of these beryllium windows was less than 0.015%, the spectrum is seriously contaminated with Cu K-edge X-ray absorption above 110 nm^{-1}. Therefore, the use of PBI X-ray windows is effective for extending FT range. We further investigated effects of sulfiding temperature and Ni to Mo molar ratio of the catalyst (not shown here). From these results, it was concluded that Ni-Mo-S phase is formed on $NiMo/Al_2O_3$ catalyst even after sulfiding at high pressure.

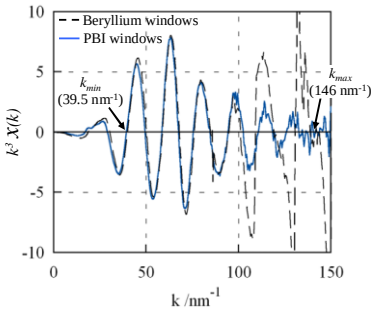

Fig. Ni K-edge $k^3\chi(k)$ of NiMo catalyst.

References

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