Development of New Catalysts for Ultra Deep HDS Using TiO₂-Al₂O₃ Composite Supports

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Introduction
Because of the new environmental regulations regarding the sulfur content of diesel, the ultra-deep hydrosulfurization (HDS) of gas oil is currently demanded. To improve catalytic HDS activity, we have studied a new preparation method of NiMo catalysts using the citric acid as a chelate agent. We found that addition of citric acid into the NiMo impregnation step is effective in improving HDS activity of 4,6-dimethyl-dibenzothiophene. We assumed that the higher activity of HDS was correlated with the increase of the number of catalytic active sites on NiMo catalysts from our HDS reaction data, but no detailed structural study was available. In this research, we have studied both NiMo/Al₂O₃ and NiMo/TiO₂-Al₂O₃ with citric acid catalysts by using XAFS measurements.

Experimental
The two different supports investigated in this study are as follows: γ-Al₂O₃ and TiO₂-coated alumina supports prepared by CVD. The supported Ni and NiMo catalysts were prepared by successive impregnation with citric acid at 1.16 mol ratio of citric acid per Ni. These catalysts were sulfided with a mixture of H₂S (5%) and H₂ at 673 K without calcination. Both before and after sulfided catalysts were characterized with XAFS. Spectra at Mo K-edge and Ni K-edge were measured in a transmission mode at room temperature at the BL-10B using Si (311) as a crystal monochromator. XPS spectra of Mo 3d, S 2p and Al 2p were also measured by using the excitation energy-variable XPS at the BL-13C.

Result and discussions
We started from an XAFS study for clarification of the effects of both Ni and citric acid addition into Mo catalysts by using alumina supports. Figure 1 shows the fourier transforms of Mo K-edge XAFS of Ni/Al₂O₃ and NiMo/Al₂O₃ catalysts with citric acid. The phase shift and back scattering amplitude were corrected as Mo-O bond using FEFF8. The peak around 0.17 nm was assigned to Mo-O bonds of MoO₄²⁻ with tetrahedral structure considering the intensity and the width of the peak. This indicates that Mo was impregnated on Al₂O₃ as MoO₄²⁻ before sulfidation. The peaks assigned to Mo-S (0.24 nm) and Mo-(S)-Mo (0.32 nm) of the spectra of after sulfidation in the Fig. 1 show that Mo mostly changed to MoS₂ by sulfidation.

Fourier transforms of Ni K-edge XAFS of NiMo catalysts with and without citric acid addition are shown in Fig. 2. The peak at 0.30 nm was assigned to Ni-(O)-Ni of nickel alminate with spinel structure and the peak at 0.32 nm to Ni-(O)-Ni of Ni₂O₃. The results show that addition of citric acid inhibited the formation of nickel alminate and nickel oxide. The existence of Mo also suppressed the formation of nickel alminate. Nickel alminate was so stable that it remained after sulfidation. NiMo catalysts are activated by sulfidation, therefore, nickel alminate decreases the catalytic active sites. This result was well aligned with our reaction result, which indicated an increase of catalytic acidic sites for NiMo catalysts with citric acid.

The depth profile of Mo/Al ratios in XPS spectra of NiMo/Al₂O₃ with and without citric acid catalysts before and after sulfidation.

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