Local structure analysis of supported Co-Mo binary sulfide catalysts prepared by a CVD method by means of X-ray absorption spectroscopy

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Introduction

Currently, Co-Mo sulfide catalysts are used for HDS treatment. It is well known that catalytic synergy generates between Co and Mo sulfides in the catalyst system. As a result of numerous studies to clarify the cause of the synergy effects by means of a variety of physicochemical techniques, it has been proposed that a "Co-Mo-S" phase is responsible for HDS activity. But conventional catalyst preparation methods cause the formation of other Co species besides "Co-Mo-S" phase. Thus a new preparation method is desired to effective formation of Co-Mo-S phase. It is expected that a selective decoration of metal sulfide catalysts and synthesis of atomically controlled metal sulfide cluster are realized by a CVD method using metal carbonyl clusters. In this study, we investigated the structure of supported Co-Mo sulfides prepared by a CVD method by means of XAFS.

Experimental

CoS_x-MoS_2/support (support: SiO_2, Al_2O_3, TiO_2, ZrO_2) catalysts were prepared by a CVD method using $Co(CO)_3(NO)$. CoS_x-MoS_x/zeolite (zeolite: NaY, USY) catalysts were prepared by a CVD method using $Mo(CO)_6$ and $Co(CO)_3(NO)$. The sample was sulfided at 673 K. The sulfided sample was evacuated at 673 K and transferred to an EXAFS cell with two Kapton windows without exposing to air. Mo K-edge XAFS spectra were measured at BL-10B (Si(311)) in a transmission mode. Co K-edge XAFS spectra were measured at BL-12C (Si(111)) in a fluorescence mode.

Results and Discussion

Fig.1 shows Fourie transforms of the EXAFS oscillation of Co K-edge EXAFS for Co-Mo sulfide catalysts. Co atoms in the CVD method form highly dispersed sulfide clusters. In the catalyst prepared by an impregnation mehtod, Co-O shell is observed, being different from CVD-prepared catalysts. This result indicates selective formation of Co-Mo-S phase by the CVD method. Fig.2 shows Fourie transform of EXAFS oscillation of Mo K-edge EXAFS of Mo and Co-Mo sulfide catalysts prepared by a CVD method. The strucure of Mo sulfide clusters in NaY zeolite is affected by the Si/Al ratio. Namely, by using high Si/Al ratio (2.8) NaY as a support, Mo-Mo shell is shifted to a shorter bond distance. However, the cluster structure becomes identical by complexing Co and Mo. It is considered that cuban-type Co-Mo binary cluster is synthesized in zeolite super cages.

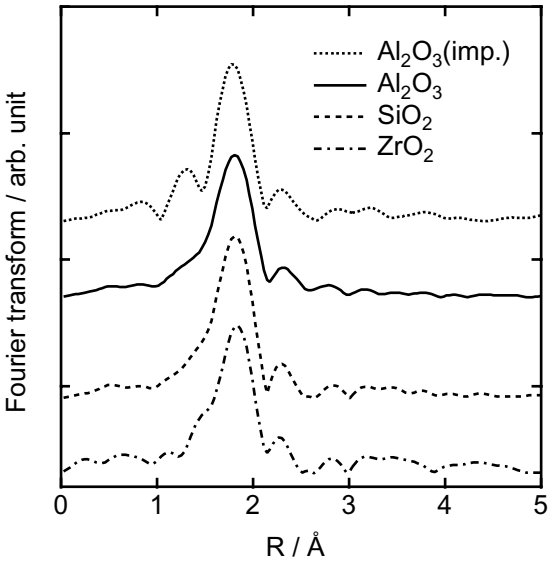

Fig.1 Fourie transform for EXAFS oscillation of Co K-edge EXAFS of Co-Mo sulfide catalysts prepared by a CVD method and an impregnation method.

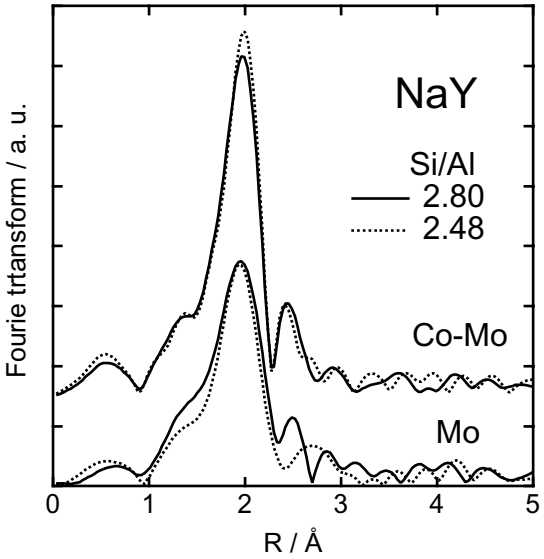

Fig.2 Fourie transform for EXAFS oscillation of Mo K-edge EXAFS of Mo and Co-Mo sulfide catalysts prepared by a CVD method. Catalysts supports (NaY zeolite) are different in Si/Al ratio.

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