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Investigation of Dynamic Behavior of Catalysts for Hydrotreatment Using Co-Mo Binary Sulfide Cluster

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Introduction

Recently, regulation of sulfur content in gasoline has become severer to reduce particulate materials and SO_x in exhaust. For these reasons, development of new catalysts for ultra-deep-Hydrodesufurization (HDS) treatment is strongly needed now. Currently, Co-Mo sulfide catalysts are used for HDS treatment. But the reaction mechanism of HDS on the Co-Mo catalysts is not well-known. To clarify the reaction mechanism is necessary to develop new catalysts. It is helpful to investigate HDSe reaction using organo-selen compounds because Se K-edge XAFS can be used for Se-exchanged catalysts. In this study, we studied the local structure of Se on Mo sulfides catalysts after HDSe reaction by means of XAFS.

Experiments

MoS_x/NaY catalysts were prepared by a CVD method using $Mo(CO)_6$. MoS_2/Al_2O_3 catalysts were prepared by impregnation. The sample was sulfided at 673 K. The HDSe reaction of selenophene was performed using a closed circulation system at 623 K. Se and Mo K-edge EXAFS spectra for catalysts after HDSe reaction were measured at BL-10B in a transmission mode. The synchrotron radiation was monochromatized by a Si(311) monochromator.

Results and Discussion

Fig.1 shows XANES spectra for standard compounds of Se and MoS_x/NaY catalysts after HDSe reaction (5 min). It is obvious that the spectrum of MoS_x/NaY is different from that of Se metal or selenophene adsorbed on NaY zeolite, and is similar to that of $MoSe_2$. So, it is concluded that Se atoms on the catalysts after HDSe interact with Mo atoms. Fig.2 shows Fourier transform for EXAFS oscillation of Se K-edge EXAFS of Mo sulfide catalysts after HDSe reaction. A sharp peak around 2.3Å is assigned to Se-Mo bonding. The position of the peak is not shifted by HDSe reaction time. On the other hand, the intensity of the peak is increased with reaction time for MoS_x/NaY catalytsts, although the intensity of the peak is invariant with reaction time for MoS_2/Al_2O_3 catalysts. Taking into account the formation of highly dispersed Mo sulfide clusters in MoS_x/NaY, these results indicate that Se atoms move from on-top sites to bridged site during HDSe reaction in MoSx/NaY. In MoS_2/Al_2O_3, Se atoms seem to remain around edge sites of MoS_2.

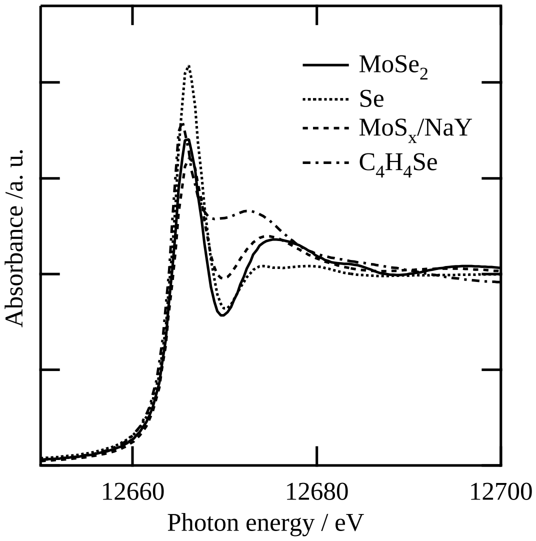

Fig.1 Se K-edge XANES spectra of standard compounds of Se and MoS_x/NaY catalysts after HDSe reaction (5 min).

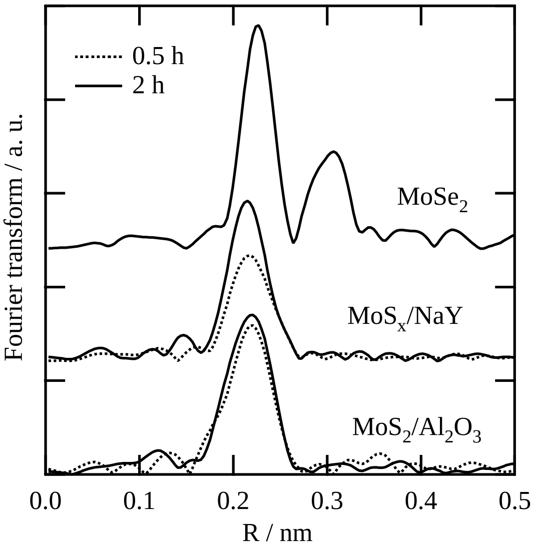

Fig.2 Fourier transform for EXAFS oscillation of Se K-edge EXAFS of Mo sulfide catalysts after HDSe reaction and $MoSe_2$.

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