Investigation of Hydrogen -activation Sites on Metal Sulfide Catalysts under in-situ Conditions by Mean of X-ray Absorption Spectroscopy

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Introduction

Recently, regulation of sulfur content in gasoline has become severer to reduce for particulate materials and SO_x in exhaust. For these reasons, development of new catalysts for ultra-deep-HDS treatment is strongly needed now. Currently, Co-Mo sulfide catalysts are used for HDS treatment. But the information about hydrogen activation site of the Co-Mo catalysts is not enough. To clarify hydrogen activation site is necessary to improve activity of catalysts. In our previous papers, we found the peak appeared in the XANES difference spectra of Pt $L_{2,3}$-edge before and after H adsorption, had definite photon energy independent of amount of adsorbed hydrogen, cluster size, coadsorbates and supports. It is interesting if this method can be extended to other metal elements or metal sulfides/oxides to characterize the adsorbed hydrogen quantitatively. In this study, we investigated the structure of Mo sulfides supported in zeolite supercages by a CVD method with adsorbed hydrogen by means of XAFS.

Experiments

MoSx/NaY catalysts were prepared by a CVD method using $Mo(CO)_6$. The sample was sulfided at 673 K. The sulfided Mo/NaY was reduced in a 13.3 kPa of D_2 at 673 K. Mo K-edge EXAFS spectra for MoS_x/NaY 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 Fourier transform of the EXAFS oscillation of Mo K-edge EXAFS for Mo sulfide catalysts after D_2 adsorption. While almost no changes were shown by D_2 adsorption between 423 K and 623 K, D_2 adsorption at 673 K induced the increase of intensity of Mo-Mo peaks (ca. 0.25 nm) and the decrease of that of Mo-S peak. From the results of XPS and NO adsorption, these changes were attributed to reduction of Mo sulfide clusters. Fig.2 shows Mo K-edge XANES spectra for Mo sulfide catalysts after D_2 adsorption at indicated temperature. By D_2 adsorption, the absorption edge was shifted to a lower energy side and the intensity of first peak was slightly decreased. These changes may be attributed to D_2 adsorption, but the extent of change is smaller than Pt particles. It is considered that the spectra are influenced by the difference of transition (s->p at K-edge and p->d at $L_{2,3}$-edge).

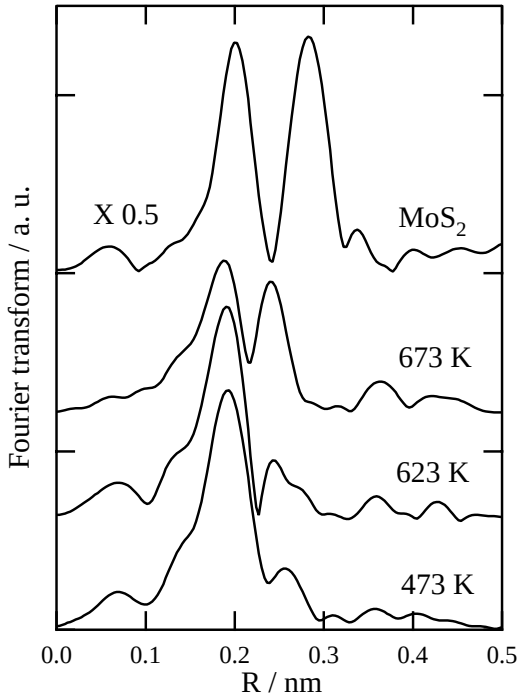

Fig.1 Fourier transform for EXAFS oscillation of Mo K-edge EXAFS of Mo sulfide catalysts after D_2 adsorption.

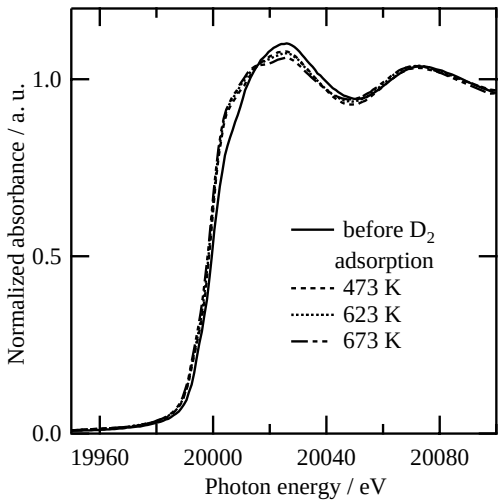

Fig.2 Mo K-edge XANES spectra for Mo sulfide catalysts after D_2 adsorption at indicated temperature.

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