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Study of the changes of local structure of the active sites of Co-Mo hydrodesulfurization catalysts by sulfidation condition

Takeshi KUBOTA, Kazuya HIOKA, Kenichi ARAKAWA, Yasuaki OKAMOTO *
Shimane University, Matsue, Shimane 690-8504, Japan

Introduction

It is predicted from STM, TEM and DFT studies that the morphology of the active phase of Co-Mo hydrodesulfidation catalysts is changed by sulfidation atmosphere of the catalysts. For example, it is reported that with MoS_2/TiO_2 sulfided in H_2S/N_2, MoS_2 particles are edge-bonded to the surface of TiO_2 support [1]. This is very interesting from the viewpoint of the control of the MoS_2 structure and, accordingly, of HDS activity. In the present study, we examined the effect of sulfidation conditions (H_2S/H_2, H_2S/He) on the local structure of the active sites of the Co-Mo catalysts.

Experimental

MoO_3/Al_2O_3(8.6wt%) and MoO_3/SiO_2(6.7wt%) were prepared by an impregnation technique. These catalysts thus prepared were presulfided at 673, 773K, or 873K in a 10% H_2S/H_2 or H_2S/He flow at an atmospheric pressure for 2h. Cobalt was introduce to the presulfided Mo catalysts by means of a chemical vapor deposition (CVD) technique using $Co(CO)_3NO$ as a precursor [2]. The sample was sulfided again at 673K for 1.5h. Co K-edge XAFS spectra for the Co-Mo sulfide catalysts were measured in a fluorescence mode at room temperature at BL-9C.

Results and Discussion

The activity of the H_2S/He-sulfided catalyst was increased by 1.1-2 times compared with that of the H_2S/H_2-sulfided catalyst. Mo K-edge EXAFS results revealed that the coordination number (CN) of Mo-S and Mo-Mo were not changed by the presulfidation using H_2S/He. Thus the increased HDS activity is not attributed to the increase of the number of the active sites.

Fig.1 shows the Fourier transforms of the Co K-edge EXAFS oscillation for the Co-Mo catalysts sulfided under various conditions. The intensity of a peak assigned to Co-S shell was increased by the sulfidation with H_2S/He flow compared to the sulfidation by H_2S/H_2 for SiO_2-supported catalysts. However, this change was not observed in the case of Al_2O_3-supported catalysts in agreement with the activity of thiophene HDS. Fig.2 shows relationship between the TOF of Co-Mo sulfide catalysts for thiophene HDS and the CN of Co-S shell. A good linear correlation was observed between the TOF and CN number. From these results, it is suggested that coordinatively saturated sites with a higher HDS activity are formed on the edge sites of MoS_2 by the sulfidation treatment using a H_2S/He flow, as predicted from the result of DFT calculation [3].

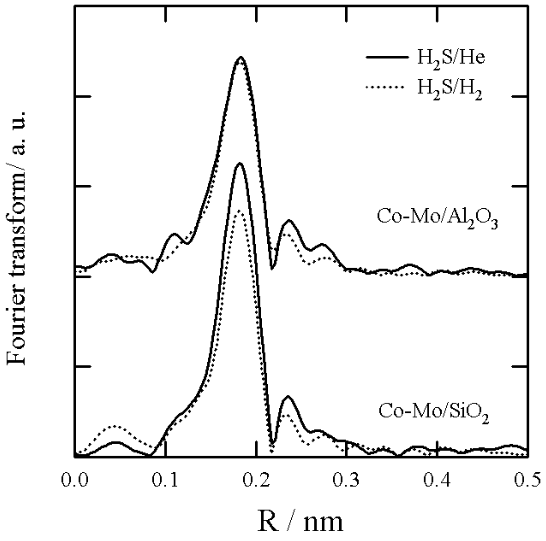

Fig.1 Fourier transforms of the Co K-edge EXAFS oscillation for the Co-Mo catalysts sulfided with H_2S/H_2 or H_2S/He.

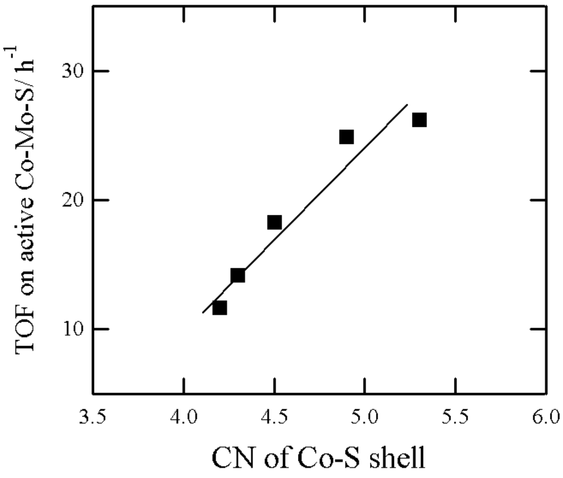

Fig.2 Relationship between the CN of Co-S shell derived from EXAFS analysis and the HDS activity per number of active sites of the catalysts (TOF).

References

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* yokamoto@riko.shimane-u.ac.jp