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Local Structure Analysis of Unsupported MoS_2 Based Catalysts

Koichi SATO*[1,2], Yasuhiro ARAKI[3], Nobuyuki MATSUBAYASHI[1], Motoyasu IMAMURA[1],
Kyoko K. BANDO[1], Hiromichi SHIMADA[1]
[1]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan
[2]Japan Science and Technology Corporation, Kawaguchi, Saitama 332-0012, Japan
[3]Advanced Catalyst Research Laboratory, Petroleum Energy Center, Tsukuba, Ibaraki 305-8565, Japan

Introduction

For the upgrading of heavy oils, much attention has been paid to the slurry phase hydrotreating system. Unsupported MoS_2 based catalysts are essential for this system and more improvements of catalytic activity of hydrogenation are required. In the present study, we prepared two kinds of unsupported MoS_2 catalysts by the different methods and surveyed the local structure by EXAFS for the investigation of the structure-activity relationship. In addition, the effect of Ni promoter for those catalysts was discussed.

Experimental

Two kinds of MoS_2 unsupported catalysts were prepared by the thermal decomposition of ammonium tetrathiomolybdate at 673 K. One was treated under a flow of 10% H_2S/H_2 (MS-H), and the other was prepared under 8 MPa of H_2 with vapor (MS-W). Ni promoted catalysts were prepared by the impregnation of ammonium nickel sulfate to MS-H by changing the Ni/(Ni+Mo) ratio from 0.1 to 0.9 (N-MS-H).

The catalytic activity was measured by the hydrogenation of 1-methylnaphthalene (1-MN) at 603 K. The characterization of catalysts was performed by N_2 adsorption, XRD, XPS, TEM, and Mo K-edge EFAFS. The spectrum of EXAFS was collected in the transmission mode at PF BL-10B. The catalyst was pressed into a self-supporting wafer and settled in a glass cell with Kapton windows without exposing to air.

Results and Discussion

Table 1 summarizes the hydrogenation activity and surface area of the catalysts. The rate of 1-MN for MS-W was five times higher than that for MS-H. In addition, the surface area extremely differed between two unsupported MoS_2. Fig. 1 represents the Fourier transform EXAFS of MS-H and MS-W. Both of the curves exhibited two main peaks corresponding to Mo-S (2.4 Å) and Mo-Mo scattering (3.2 Å). The local structure around Mo atom was the same as that of MoS_2 for both of the catalysts. Note that the peak of Mo-O scattering was not observed. These results were corresponded to the results of surface analysis by XPS. Therefore, two catalysts had quite similar local MoS_2 structure.

On the other hand, XRD patterns reflected the different structure of particles. Although XRD patterns of both two catalysts suggested the highly distorted MoS_2 layers, the (002) reflection of MS-W was much smaller than that of MS-H. It indicated that the lower stacking layers of MoS_2 in MS-W. The previous researches suggested that the curvature of the basal planes and low stacking layers of MoS_2 crystallites were effective for the hydrogenation activities [1, 2]. That is, the low stacking layers with high distortion of MS-W affected the high catalytic activity and high surface area.

The effects of Ni addition to MS-H catalysts did not appeared in the hydrogenation activity (Table 1). The peak of Mo-Mo scattering in Fourier transformed EXAFS increased by the addition of Ni (Fig. 2). It suggested the change of MoS_2 crystal size. In fact, TEM images exhibited the linear MoS_2 layers. The Ni addition reduced the curvature and resulted in the decrease in the activity. Above results suggested the improvement of preparation method for Ni promoted MoS_2 catalyst must be needed.

References

[1] Y. Iwata et. al., Catal. Today, 45, 353 (1998).
[2] Y. Yokoyama et. al., Am. Chem. Soc. Div. Pet. Chem., 42, 353 (1998).

Table 1 Catalytic activity and surface area

catalyst	rate constant of 1-MN (10^{-5} mol/mol-metal/s)	surface area (m^2/g)
MS-W	43	251
MS-H	7.8	9
N-MS-H *[1]	7.0	

*[1] Ni/(Ni+Mo) = 0.7

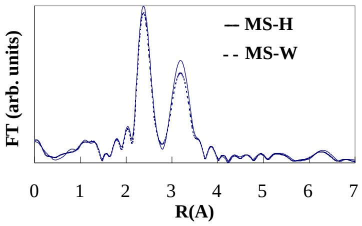

Fig. 1 Fourier transformed EXAFS of unsupported MoS_2

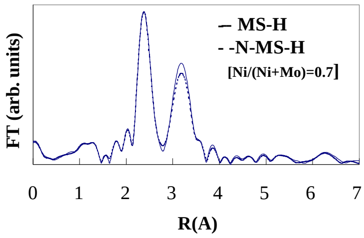

Fig. 2 Fourier transformed EXAFS of Ni promoted MoS_2

* koichi.sato@aist.go.jp