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EXAFS study on the dispersion of molybdenum sulfide catalysts on γ-Al_2O_3

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The dispersion of molybdenum sulfide catalysts was characterized based on the lateral dimensions of MoS_2 crystallites estimated by EXAFS. A new index of $N(\mathrm{Mo})/N(\mathrm{S})$, instead of $N(\mathrm{Mo})$, was used to estimate the average MoS_2 size to minimize the contribution of the coexisting oxide or oxisulfide phase in the catalysts. EXAFS showed some advantages over other techniques, such as TEM or XPS.

Keywords: EXAFS; molybdenum sulfide; catalyst dispersion

1. Introduction

Molybdenum sulfide based catalysts supported on γ-Al_2O_3 have been used extensively for hydroprocessing petroleum fractions. A number of investigations have been devoted to the elucidation of the catalyst properties and structures to develop a better industrial catalyst. However, no conventional method has been established by which the dispersion of molybdenum sulfided catalysts can be well characterized. In the present paper, the extended X-ray absorption fine structure (EXAFS) method has been applied to the estimation of the size of molybdenum sulfide particles on catalysts with different loadings on γ-Al_2O_3. A comparison of the EXAFS results with the results obtained by other methods is made and the advantages of the present EXAFS method are discussed.

2. Experimental

The catalyst support used in the present study was an γ-Al_2O_3 extrudate with a 1/22 inch diameter. The surface area and pore volume of the support were 246

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m^2 g^{-1} and 0.62 cm^3 g^{-1}, respectively. Seven kinds of MoO_3/Al_2O_3 catalysts with different loadings of molybdenum (2.8–25.4 wt% as MoO_3) were prepared by impregnating the Al_2O_3 support with an ammonium hydroxide solution of $(NH_4)_6Mo_7O_{24}$. The catalysts were subsequently dried at 250°C for 1 h and calcined at 550°C for 1 h, followed by sulfiding in a stream of 5% H_2S/H_2 for 4 h at 400°C. After the catalyst bed was cooled below 100°C, the H_2S/H_2 gas was replaced by nitrogen.

Each sample was powdered and pressed into a pellet with a proper thickness for transmission measurements in a nitrogen atmosphere. The pellet was then placed into a plastic bag with tight seal. Thus, the samples were kept under an inert atmosphere during the following EXAFS measurements. The Mo K-edge EXAFS measurements were carried out at room temperature using a channel-cut Si(311) double crystal monochromator at the Photon Factory (BL-10B) of the National Laboratory for High Energy Physics. Fourier transformation of the $k/f(k)$ weighted EXAFS data for $\Delta k = 9.0$ $(3.9<k<12.9)$ was performed to obtain the radial distribution function around Mo. The phase shift and back-scattering amplitude $(f(k))$ were corrected by using the theoretical values for Mo as an absorber and S as a scatterer [1]. Detailed analytical procedures of EXAFS were described elsewhere [2].

3. Results and discussion

Fig. 1 shows the Fourier transforms of the Mo EXAFS for the catalysts with Mo loadings of 2.8 and 10.3% and for a powdered MoS_2 crystal (Nacaraitesque Co. Ltd., GR grade). All the spectra exhibit two notable peaks corresponding to

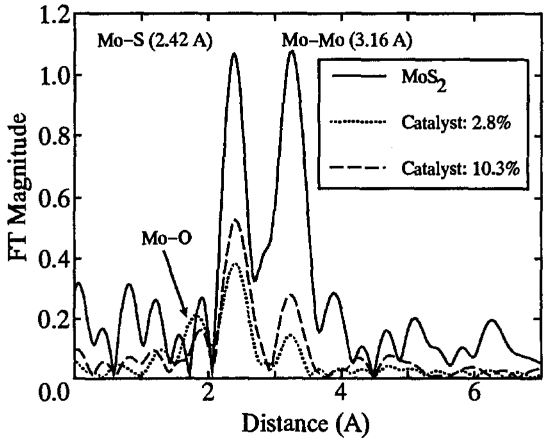

Fig. 1. Fourier transforms of Mo K-edge EXAFS of molybdenum sulfide catalysts and crystalline MoS_2.

Mo–S (at 2.42 Å) and Mo–Mo (at 3.16 Å) scattering. The weak Mo–S peaks in the catalyst spectra are most probably due to the presence of Mo–O bonding that has not been replaced by Mo–S bonding during sulfiding. In addition, the weak peak below 2.0 Å observed in the spectrum of the 2.8% Mo catalyst is assigned to Mo–O scattering. These results indicate that sulfided catalysts contain molybdenum oxide or oxisulfide species that are not completely sulfided during sulfiding. The presence of the partially oxidized species is inevitable on γ-Al_2O_3 because of the strong bonding between the catalyst and the support.

To discuss the EXAFS results quantitatively, the average coordination numbers of sulfur (N(S)) and molybdenum (N(Mo)) around molybdenum have been calculated from the Fourier transform intensities ($I(r)$). The calculations were done using the relation $N(j) = B(j)I(r(j))r(j)^2$ [3] with the assumption that the thermal and static disorder is constant, where $r(j)$ is the distance of sulfur or molybdenum from molybdenum and $B(j)$ is the proportionality constant for Mo–S or Mo–Mo bonding obtained from the MoS_2 powder standard. The changes in N(S) and N(Mo) with Mo loading are plotted in fig. 2. Because of the above assumption, the present $N(j)$ values are influenced by the static disorder of Mo–S or Mo–Mo bonding. However, curve fitting analyses were avoided in the present study, because curve fitting analyses result in ambiguous separation of the coordination number and the static disorder.

The small N(Mo) values observed for the catalysts indicate that the majority of the molybdenum sulfide in the catalysts is present as a MoS_2-like layered structure with small crystalline sizes as reported in previous papers [4,5]. In these studies, the average size of the MoS_2-like crystallite in the lateral direction was estimated from the N(Mo) values. However, it would be better to correct the index by

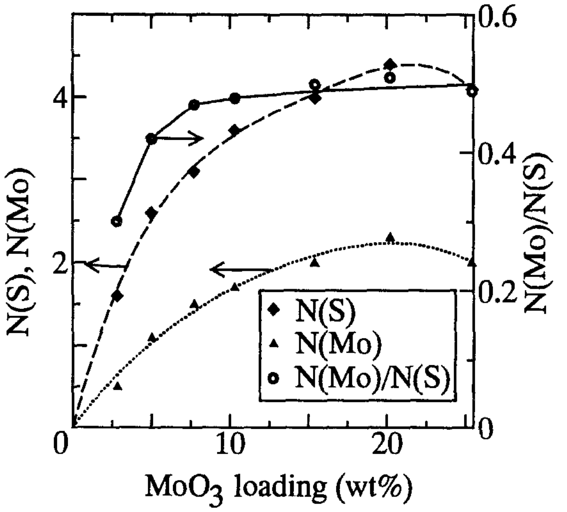

Fig. 2. Changes in N(S), N(Mo) and N(Mo)/N(S) with Mo loading.

dividing by $N(\mathrm{S})$, because the contribution of the partially oxidized phase to the $N(\mathrm{Mo})$ values can be compensated for in this way. The index derived by dividing by $N(\mathrm{S})$ increases with an increase in the lateral dimensions of the MoS_2 crystallites and becomes one for the crystal powder because $N(\mathrm{Mo}) = N(\mathrm{S}) = 6$. Fluctuation of $N(\mathrm{Mo})/N(\mathrm{S})$ is expected to be relatively small compared to that of $N(\mathrm{Mo})$ because experimental errors in $N(\mathrm{Mo})$ are partly canceled by the division. Fig. 2 shows the change in $N(\mathrm{Mo})/N(\mathrm{S})$ with Mo loading together with the changes in $N(\mathrm{Mo})$ and $N(\mathrm{S})$.

Fig. 2 demonstrates that the $N(\mathrm{Mo})/N(\mathrm{S})$ index increases steeply with Mo loading up to 7.7%. In contrast, almost constant $N(\mathrm{Mo})/N(\mathrm{S})$ values of 0.50 ± 0.01 are obtained for the catalysts with Mo loadings between 15.4 and 25.4%. This suggests that the average lateral dimensions of MoS_2 crystallites increase with Mo loading for low Mo-loading catalysts, while stacking of MoS_2 slabs mainly takes place for high Mo-loading catalysts.

Catalyst dispersion has often been estimated by X-ray photoelectron spectroscopy (XPS), which gives the surface concentrations of supported catalysts. For Mo sulfide catalysts with a layered structure, however, the information given by XPS is not sufficient to characterize the catalyst dispersion, as shown in fig. 3. XPS gives different surface Mo concentrations between (A) and (B) in fig. 3 but cannot distinguish the dispersion between (B) and (C). In contrast, EXAFS can differentiate (B) from (C) but cannot distinguish (A) and (B). If one simply assumes that the catalytically active sites of the MoS_2 slabs are located at the edge sites, the difference between (B) and (C) must be clearly characterized before one can discuss the relationship between the catalyst dispersion and catalytic activity. In this case, EXAFS gives dispersions that more accurately reflect the catalytic activities than those given by XPS.

The present catalysts were analyzed by transmission electron microscopy

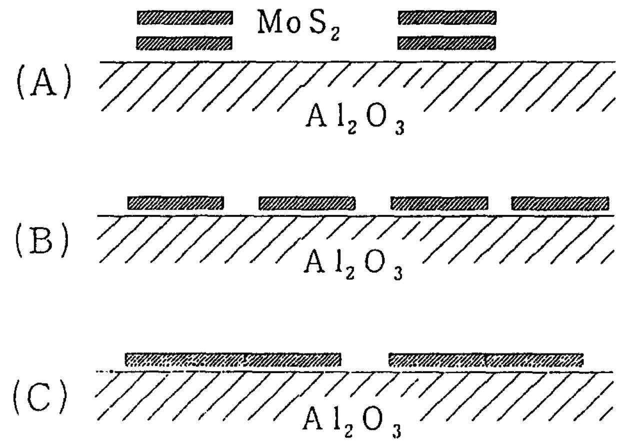

Fig. 3. Schematic diagrams of molybdenum sulfide catalyst dispersion on γ-Al_2O_3.

(TEM) in a previous study [8]. Few MoS_2-like slabs were observed for the catalysts with Mo loadings lower than 10%. For catalysts with moderate Mo loadings (10–15%), most of the MoS_2-like crystallites were present as single slabs with lateral dimensions of 30–40 Å. Multi-layered MoS_2 slabs, some of which were as large as 100 Å, were observed for high Mo loaded catalysts. The present EXAFS results are basically consistent with the TEM observations; single and small slabs are primarily formed at low Mo loadings, while large slabs with stacking are formed at high Mo loadings. EXAFS has an advantage over TEM observations in giving numerically averaged information. In addition, the result shows that EXAFS is applicable to the estimation of the sizes of small MoS_2 slabs, which are difficult to observe by TEM. On the other hand, the present index given by EXAFS is at a disadvantage when used to estimate the size of large MoS_2 slabs, because the change of the index with MoS_2 size is relatively small for large MoS_2 slabs.

It should be noted that EXAFS does not give MoS_2 crystallite sizes that are consistent with TEM observations. Bouwens et al. [4] suggested 10–13 Å as an average size of the locally ordered MoS_2 structure from a N(Mo) value of 2.7 obtained by curve fitting of the EXAFS for a Mo(7.0%)/C catalyst. Topsøe and Clausen [5] also assumed a very small MoS_2 crystallite site ($\sim$ 10 Å) for a Mo(8.6%)/Al_2O_3 catalyst from a N(Mo) value given by curve fitting of the EXAFS spectrum. Thus, the sizes obtained by EXAFS were quite small compared with 30–100 Å obtained by TEM observations [6–8].

Careful observation of TEM photographs shows that most of the MoS_2 slabs, which appear as black lines in TEM photographs, are not straight but curved, as typically seen in the literature [9]. The curved structure results in a large static disorder of the Mo–Mo distances, which may not be properly estimated in the Debye–Waller term of EXAFS analyses, as has been pointed out by Clausen et al. [10]. Thus, EXAFS, even when curve fitting analyses are employed, gives smaller sizes for MoS_2 crystallites than TEM observations. However, this leads to the question of whether or not highly curved sites in the MoS_2-like crystallites, which may cause vacant sulfur sites, are catalytically active. Also, it cannot be excluded that TEM misses very small Mo sulfide crystallites, which results in the small average size of MoS_2 crystallites by EXAFS. Further studies are needed to conclude which tool gives sizes for the MoS_2-like crystallites that are more relevant to the catalytic activities.

4. Conclusion

As has been discussed, EXAFS is a powerful tool for characterizing molybdenum sulfide catalyst dispersion. EXAFS has shown advantages over other techniques in the estimation of the lateral dimensions of MoS_2 slabs, especially for catalysts with low loadings. For catalysts with high Mo loadings, however, EXAFS might overestimate the catalyst dispersion. Also, it should be noted that EXAFS does not give information on the stacking of MoS_2 slabs. The EXAFS method combined with other methods may be the best to accurately characterize the dispersion of molybdenum sulfide catalysts with high loadings.

Acknowledgement

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