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Deactivation of Co–Mo/Al_2O_3 hydrodesulfurization catalysts during a one-year commercial run

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Abstract

A series of Co–Mo catalysts with different Co and Mo loadings were prepared and exposed to a commercial HDS run for a year. From the activity tests using model compounds, the HDS activity of the fresh catalyst was found to increase up to 4.0 Mo atoms nm^{-2} with increasing Co–Mo loading. However, no significant difference in the activity was observed in the used catalysts. TEM and EXAFS analyses revealed that the MoS_2 stacks aggregated in the lateral direction but did not grow in the normal direction to the layers during the run.

Keywords: Co–Mo catalysts; Hydrodesulfurization

1. Introduction

To meet an increasing demand for low-sulfur petroleum products, there have been lots of studies [1–3] aimed at the improvement of the hydrodesulfurization (HDS) catalysts. From a practical point of view, another important issue lies in the suppression of catalyst deactivation during hydrotreating. Many papers [4,5] have been dedicated to the clarification of the catalyst deactivation mechanisms through the analyses of the used catalysts. These studies have provided fruitful information, which has lead to great improvements of the catalyst lives. However, many of these studies have dealt with commercially available catalysts with several unknown factors. This has hindered detailed discussions on the relationship between the catalyst properties and deactivation behaviors.

Recently, the authors have started a project in which all catalysts are prepared with a common method using common supports. In the present study a series of Co–Mo catalysts with different loadings have been exposed to a commercial HDS run for a year. The fresh and used catalysts have been characterized to discuss the catalytically active sites before and after the run. The focus is on the structural analyses of

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the catalysts by means of extended X-ray absorption fine structure (EXAFS) and transmission electron microscopy (TEM).

2. Experimental

Four kinds of Co–Mo/Al_2O_3 catalysts were prepared by coimpregnation of γ-Al_2O_3 extrudates (surface area, 214 m^2 g^{-1}; pore volume, 0.80 cm^3 g^{-1}) with organic acid solution of MoO_3 and $CoCO_3$, followed by calcination at 773 K for 3 h in air. The Mo loadings were 9.3, 14.7, 20.7 and 34.7 wt.-% as MoO_3 by defining the weight of the support as 100% with a constant Co/Mo molar ratio of 0.5. The catalysts are denoted as Mo(1.8), Mo(2.9), Mo(4.0) and Mo(6.8) using the Mo loadings by a unit of atoms nm^{-2}. Each catalyst (190 ml) was charged in a cylindrical basket made of twenty mesh stainless-steel nets. The basket was located in the upper side, after the demetallation bed, of a commercial HDS unit for vacuum gas oil (543–923 K) with a capacity of 15000 BPD. The HDS unit was operated for a year at H_2 partial pressure of 5.9 MPa. The reaction temperature was raised from 633 K at the beginning of run to 673 K at the end to maintain the product sulfur level at 0.09 wt.-%. As a reference to the used catalyst, each fresh catalyst was sulfided in a stream of 5% H_2S/H_2 at 673 K for 2 h.

The HDS activities of the freshly sulfided and used catalysts were evaluated by performing HDS of dibenzothiophene (DBT) in an autoclave. The 50 ml autoclave, containing 10 ml of 1 wt.-% S DBT/n-hexadecane solution, 0.3 g of catalyst and hydrogen with an initial pressure of 6.9 MPa, was heated up to 613 K and then kept at the temperature for 1 h. The HDS rate constant was calculated from the S content in the reaction products assuming a first-order reaction.

The Mo and Co K-edge EXAFS measurements were carried out in the transmission mode at BL-10B and 7C of the Photon Factory with Si (311) and Si (111) monochromators. Phase shifts and backscattering amplitudes were corrected using the theoretical values for Mo–O and Co–O [6] in the Fourier transformation of the EXAFS data.

3. Results

3.1. Catalytic activities

Fig. 1 shows the HDS rate constants for the catalysts. For the freshly sulfided catalysts, the HDS activity increases with Mo loading up to 4.0 atoms nm^{-2} and then significantly drops with further loading. In contrast, no distinct difference in the activity is observed among the used catalysts. The largest deactivation during the run is observed for the catalyst Mo(4.0) having the highest initial activity.

3.2. Structural analyses of the catalysts

Fig. 2 shows the coordination numbers of sulfur (N(S)) and molybdenum (N(Mo)) around molybdenum obtained from the magnitudes of Fourier transformed Mo K EXAFS spectra. For the fresh catalysts, the N(Mo) increases with increasing Mo loading, indicative of the MoS_2 crystallite growth in the lateral direction. The N(S) and N(Mo) for each used catalyst are significantly larger than those for the fresh catalyst. These changes are attributed to deep sulfid-

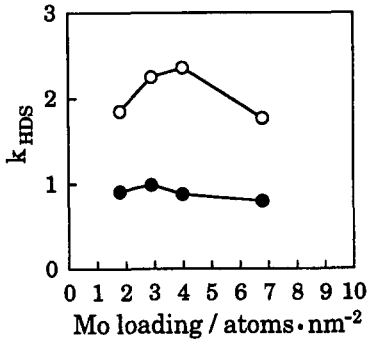

Fig. 1. HDS rate constants of the fresh (○) and used (●) catalysts.

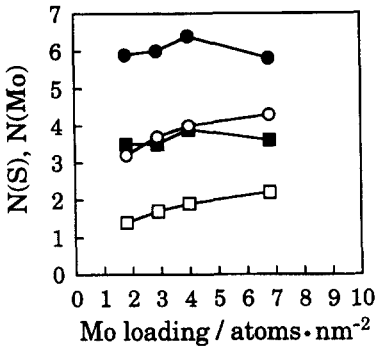

Fig. 2. The N(S) (○) and N(Mo) (□) values of the catalysts obtained from Mo K EXAFS (open: fresh, filled: used).

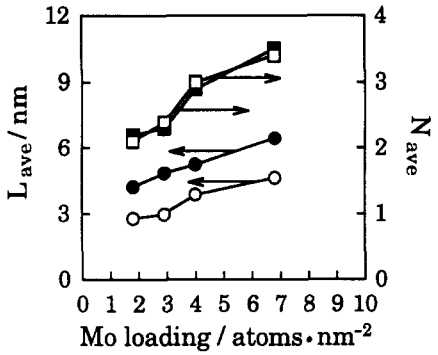

Fig. 4. The L_{ave} (○) and N_{ave} (□) values of the catalysts observed in TEM photographs (open: fresh, filled: used).

ing of molybdenum species and more aggregated MoS_2 crystallites in the used catalysts [7–9].

Fig. 3 shows the TEM photographs of the fresh and used Mo(6.8) catalysts, in which the MoS_2 stack sizes of the used catalysts are much larger than those of the fresh catalysts. For further discussion on TEM results [10], average number of layers per a stack (N_{ave}), average stack size in the lateral direction (L_{ave}) and the MoS_2 stack density (σ: number of stacks per 10000 nm^2) were obtained from the photographs with three different fields (102 nm × 76 nm) for each sample (Figs. 4 and 5). As shown in Fig. 4, L_{ave} increases with increasing Mo loading both for the fresh and used catalysts. For each catalyst, L_{ave} of the used catalyst is much larger than that of the corresponding fresh catalyst. These are consistent with the EXAFS results. Small discrepancy between TEM and EXAFS results is observed in the comparison of the stack size between the used catalysts Mo(4.0) and Mo(6.8). This is due to the underestimation

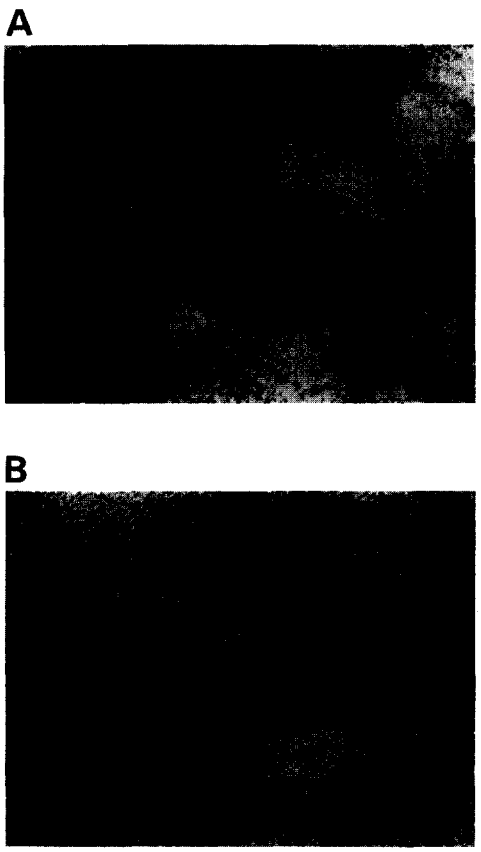

Fig. 3. TEM photographs of Mo(6.8) catalyst at a total magnification of 1 800000 (A: fresh, B: used).

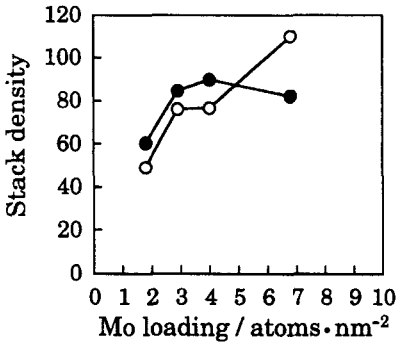

Fig. 5. The σ values of the catalysts observed in TEM photographs (○: fresh, ●: used).

of N(Mo) by EXAFS because of the curved structure of large MoS_2 crystallites [9].

As reported in many papers, the stack sizes deduced from the EXAFS spectra are much smaller than those observed in TEM, which was first attributed to the underestimate of N(Mo) in EXAFS analysis [11,12]. The invisibility of very small MoS_2 clusters by TEM was also pointed out [10]. In the present results, TEM and EXAFS give same tendency for the stack size estimation. Thus, we assume the TEM results to represent the averaged structural information.

The N_{ave} increases with increasing Mo loading both for the fresh and used catalysts (Fig. 4), indicative of the MoS_2 growth in the normal direction to the MoS_2 layer. In contrast to L_{ave}, however, no difference in the N_{ave} is observed between each fresh and used catalysts. This indicates that MoS_2 crystallites do not grow in the normal direction to the layer during the HDS run.

Fourier transforms of the Co K EXAFS of the fresh and used Mo(6.8) catalysts are shown in Fig. 6, together with that of Co_9S_8 which is thermodynamically the most stable species under the reaction conditions. The Co_9S_8 spectrum exhibited a broad peak at 0.230 nm assigned to an overlap of Co–S (0.213, 0.221, 0.239 nm) and Co–Co (0.250 nm) scattering together with a peak corresponding to the second nearest Co–Co scattering (0.348, 0.354 nm). An intense peak at 0.209 nm observed in the fresh catalyst spectrum is assigned to Co–S scattering, which is partly affected by Co–O scattering. After the HDS run, the peak is shifted at 0.217 nm. Considering the XANES results (not shown here), the oxide species in the fresh catalyst was converted into sulfide during the run.

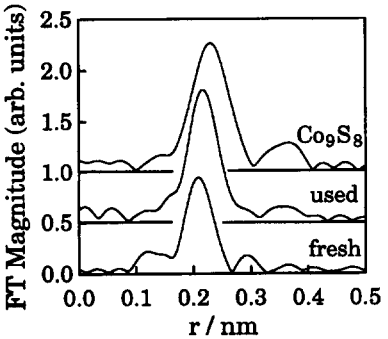

Fig. 6. Fourier transforms of the Co K EXAFS of the fresh and used Mo(6.8) catalysts and Co_9S_8.

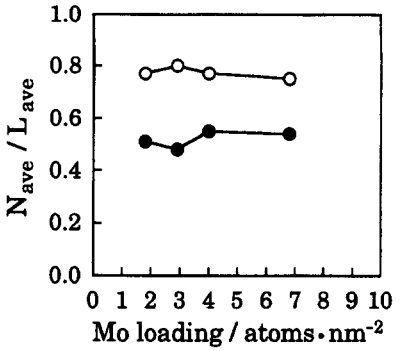

Fig. 7. The stacking indices (N_{ave}/L_{ave}) of the catalysts (○: fresh, ●: used).

4. Discussion

4.1. Active sites of fresh Co–Mo catalysts

It is widely believed that the active sites of Co–Mo binary sulfide are located at the edges of MoS_2 layer decorated with Co [13]. Recently, further discussion on the active sites of MoS_2 structure has been proposed, either multi-layer or single-layer structure is more active [14,15]. To characterize the MoS_2 stacking structure, we introduce an index of N_{ave}/L_{ave}, shown in Fig. 7. All the fresh catalysts give almost the same indices, about 0.75–0.80, indicative of isotropic growth of the stacking structure with increasing Mo loading. This is consistent with the activity profile in Fig. 1, which is monotonously increasing but not proportional to the Mo loading, up to 4.0 atoms nm^{-2}. Low loading catalysts rich in the very small clusters give higher activities than expected from the TEM results. The notable decrease in the activity from Mo(4.0) to Mo(6.8)

is presumably due to the decrease in the number of these clusters.

4.2. Structural change and catalyst deactivation during HDS run

The MoS_2 stacks grow in the lateral direction but do not grow in the normal direction to the layers during the HDS run. It is most likely that very small MoS_2 clusters aggregate each other or are bound to the edge sites of the Co–Mo–S stacks. The former aggregation results in the increase in σ (Fig. 5), the latter leading to the increase in L_{ave} (Fig. 4). For the high Mo loading catalysts, it is also plausible that the Co–Mo–S stacks move along the support surface and aggregate each other, which is most clearly observed for Mo(6.8) as the decrease in σ during the run (Fig. 5). The aggregation reduces the number of very small MoS_2 clusters which are invisible by TEM. On the assumption that these clusters are highly active, the catalytic activity significantly decreases by the aggregation.

The formation of Co_9S_8 is not clear in the EXAFS spectra, indicating that in the used catalysts the major part of Co atoms are not released from the edge of MoS_2 stacks in spite of the aggregation.

Table 1 summarizes the amounts of C, Ni and V deposited on the used catalysts. More amounts of the foulants are found to be deposited on more active catalysts. Since the deposition takes place on the catalytically active sites, it is unavoidable for high activity catalysts to have large amounts of the depositions. Indeed, the carbonaceous and metallic depositions, which poison the active sites and lower the pore diffusion, have long been claimed to be the major cause of the catalyst deactivation [4,5]. Quite recently, however, the aggregation of MoS_2 stacks was claimed to be the main cause of the catalyst deactivation when the feed was almost free of the resid [10]. The present results suggest that both causes are important in the catalyst deactivation during the hydrotreating of vacuum gas oil.

Table 1
C, Ni and V depositions on the catalysts

Catalysts	C /wt.-%	NiO /wt.-%	V_2O_5 /wt.-%
Mo(1.8)	6.5	0.2	1.2
Mo(2.9)	7.2	0.3	1.4
Mo(4.0)	8.0	0.4	2.3
Mo(6.8)	7.6	0.3	1.9

5. Conclusion

By the analysis of the Co–Mo catalysts used in a commercial HDS run, it was found that the MoS_2 stacks grew in the lateral direction but did not grow in the normal direction to the layers. This structural change significantly decreases the number of the catalytically active edge sites. Further study is needed to conclude to what extent the structural change contributes to the catalyst deactivation.

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