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Stabilization Effect of Co for Mo Phase in Co–Mo/Al_2O_3 Hydrodesulfurization Catalysts Studied with X-Ray Photoelectron Spectroscopy

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The promotional effects of Co in Co–Mo/Al_2O_3 hydrodesulfurization (HDS) catalysts were studied by means of X-ray photoelectron spectroscopy. The higher MoO_3-content Mo/Al_2O_3 catalysts (10 and 20 wt% MoO_3) contain mobile Mo, which migrates from the pores to the outermost surface layers of the catalysts and segregates to form less active crystalline MoS_2 during the HDS reaction, while in the case of Mo/Al_2O_3 (5 wt% MoO_3) catalyst no migration of Mo was observed. It is revealed that the Co in Co–Mo/Al_2O_3 catalyst inhibits the migration and segregation of Mo and that it keeps Mo effective for the HDS reaction, since no surface enrichment of Mo was observed. It is concluded that stabilization of the Mo monomolecular layer is the main role of Co. The active species of Mo is suggested to have the composition of S/Mo(IV) = 1 on the basis of the sulfur contents of the catalysts under the mild HDS reaction conditions.

INTRODUCTION

A great amount of research has been carried out to determine the role played by the promoter Co in Co–Mo/Al_2O_3 carried out to determine the role played by the promoter Co in Co–Mo/Al_2O_3 hydrodesulfurization (HDS) catalysts. However, no clear-cut explanation has been presented.

Richardson (*1*) has suggested that an unknown Co–Mo complex is responsible for HDS reactions based on magnetic susceptibility measurements. Phillips and Fote (*2*) have presented, assuming the surface enrichment of Co on the Mo phase, a surface complex model in which the complexes of Co and Mo are active species and a boundary model in which the grain boundaries of Co and Mo phases are active, in order to explain the activity dependence on the Co/Mo ratio observed by DeBeer *et al.* (*3*). On the other hand, Co compounds such as $CoMo_2S_4$, Co_9S_8, $CoMoO_4$, CoO, $CoAl_2O_4$, and $Co_2Mo_3O_8$ have been ruled out as being the primary catalytic species (*1, 4–7*). In addition, $CoMoO_4$ was found to be absent in industrial catalysts (*8*) and laboratory-prepared Co–Mo/Al_2O_3 catalysts (*5, 9*). DeBeer *et al.* (*10*) have presented an intercalation model in which the Co–Mo/Al_2O_3 catalyst starts as a monomolecular system, but is converted into an intercalated structure (small MoS_2 crystallites intercalated by Co^{2+}) by the migration of Co from the bulk to the surface in a few hours during the presulfiding treatment.

A synergistic effect of Co has been claimed by some workers (*11–13*) on the basis of results on the unsupported Co–Mo sulfide system, where the synergy between MoS_2 and Co_9S_8 is supposed to promote the catalyst.

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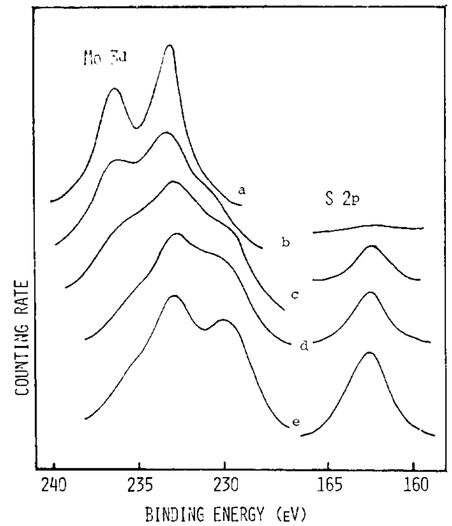

FIG. 1. XPS spectra of Mo 3d and S 2p levels for the Mo(10)/Al_2O_3 catalyst during the HDS reaction at 400°C: (a) calcined; (b) 400°C, 1-hr evacuation; and (c) 10, (d) 40, and (e) 100 min of reaction.

Finally, an explanation for the promotional effect of Co has been suggested by Schuit and Gates (*14*) based on the monolayer model. They have supposed the stabilization of the Mo monomolecular layer by Co which is located in the tetrahedral sites of the alumina surface.

However, no decisive evidence has been presented even for the above-mentioned explanations to elucidate the role played by Co in Co–Mo/Al_2O_3 catalysts.

Although the X-ray photoelectron spectroscopy technique has been applied to the investigation of Co–Mo/Al_2O_3 catalysts, the promotional effect of Co is still ambiguous. Mo(VI) is reduced to form Mo(V) and Mo(IV) and is sulfided by reduction, sulfiding treatment, and HDS reaction (*9, 15–17*). With regard to Co, some Co is reduced to metal after the HDS reaction or after sulfiding of the catalysts, and the unreduced Co remains as $CoAl_2O_4$ (*16, 17*). In addition, no discrete phase such as CoS, CoS_2, or Co_9S_8 was found, although Co was partially sulfided (*17*). Cimino and DeAngelis (*9*) have reported that cobalt molybdate similar to bulk $CoMoO_4$ is excluded on the surface of the catalysts. As for the role played by Co, Friedman *et al.* (*16*) suggested the stabilization of surface active phase by $CoAl_2O_4$ based on the relationship between the intensity ratios of $CoAl_2O_4$/Mo and the HDS reaction activities. Recently, Grimblot and Bonnelle (*18*) have claimed the appearance of a phase with the composition of Mo/Co = 4 in which Mo occupies an octahedral site and Co occupies a tetrahedral site on the alumina surface.

In this paper, we present XPS results which support clearly the stabilization of Mo phase by Co in the course of the HDS reaction. The migration of Mo on the Mo/Al_2O_3 catalysts was investigated. Moreover, the active species of Mo is suggested based on the sulfur contents of the catalysts.

EXPERIMENTAL METHODS

Material. Mo/Al_2O_3 catalysts were prepared by a conventional impregnation technique using ammonium paramolybdate. After drying at 100°C, catalysts were calcined at 500°C for 5 hr in air. The supported amounts of MoO_3 were 5, 10, and 20 wt%, and these catalysts are denoted as Mo(5), Mo(10), and Mo(20)/Al_2O_3. The surface area of the γ-alumina was 160 m^2/g. The Co–Mo/Al_2O_3 catalyst (CoO: 3.5 wt%; MoO_3: 10 wt%) was prepared by impregnating cobaltous nitrate on the Mo(10)/Al_2O_3 catalyst and calcining at 500°C for 5 hr in air after drying.

Procedure. The photoelectron spectra were measured on a Hitachi 507 photoelectron spectrometer using Al$K\alpha_{1,2}$ radiation. The samples were mounted on a sample holder made of stainless steel. The samples were treated in the sample pretreatment chamber. All binding energy values were referenced to C 1s of contaminant carbon (285.0 eV). The intensities of the spectra were obtained by measuring the peak areas of the Al 2s level for aluminum, Mo 3d level for molybdenum, S 2p level for sulfur, and Co $2p_{\frac{3}{2}}$ level (including the associated satellite peaks) for cobalt.

HDS reactions were carried out at 400°C for 10 min by introducing 10 Torr of reaction gas (thiophene: H_2 = 1:15) in the sample pretreatment chamber. The XPS spectra during the reaction were recorded after evacuating the reaction gas and cooling down the sample to room temperature. The same procedure was repeated for the prolonged reaction time.

The reaction rates of the catalysts used in this study were measured with a usual flow reactor. The catalytic activities reached the steady state after about 2 hr. The amount of catalyst used was 50 mg. Atmospheric hydrogen was saturated with thiophene (H_2 flow rate; 1 ml/sec) at room temperature. The reaction temperature was 400°C. The products were analyzed with a gas chromatograph.

RESULTS

The Mo 3d/Al 2s intensity ratios of the calcined Mo/Al_2O_3 catalysts were 1.87, 2.27, and 2.70 for the Mo(5), Mo(10), and Mo(20)/Al_2O_3 catalysts, respectively, and they were not proportional to the amount of supported MoO_3. This fact implies that the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts include some small crystalline MoO_3. X-Ray diffraction analysis actually showed the presence of crystalline MoO_3 in the Mo(20)/Al_2O_3 catalyst.

In Fig. 1, the XPS spectra of Mo and S for the Mo(10)/Al_2O_3 catalyst are shown during the HDS reaction in the sample pretreatment chamber. Mo was in the Mo(VI) state (Mo $3d_{\frac{5}{2}}$; 233.3 eV) after calcination, but some Mo(VI) was reduced by evacuation at 400°C (ca. 1×10^{-5} Torr). Mo(VI) was gradually reduced to forms Mo(V) and Mo(IV) and sulfided in the course of the HDS reaction. After 100 min of reaction (10 times the 10-min reaction over the same sample), deconvolution of the Mo 3d spectrum revealed that Mo(VI), Mo(V), and Mo(IV) contents were 17, 30, and 53% by assuming that the binding energy values of the Mo $3d_{\frac{5}{2}}$ level for Mo(VI), Mo(V), and Mo(IV) were 233.2, 231.7, and 230.2 eV, respectively. These binding energies gave the best fits and are consistent with those reported by Patterson *et al.* (*17*). The amount of Mo(V) had a maximum value of about 35% after 20 min of reaction, then gradually decreased and reached a plateau of 30% after 60 or 70 min. Mo(IV) increased and Mo(VI) decreased as the reaction proceeded; they reached constant values after 60 or 70 min of reaction. These tendencies for the reduction of Mo agree with those obtained by Patterson and co-workers (*17*). In the cases of Mo(5)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts, similar behavior of the Mo reduction was observed. Forty and fifty-five percent Mo(IV) were produced after 80 min for the Mo(5)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts, respectively. The higher the content of MoO_3 on the catalyst, the higher the extent of reduction observed.

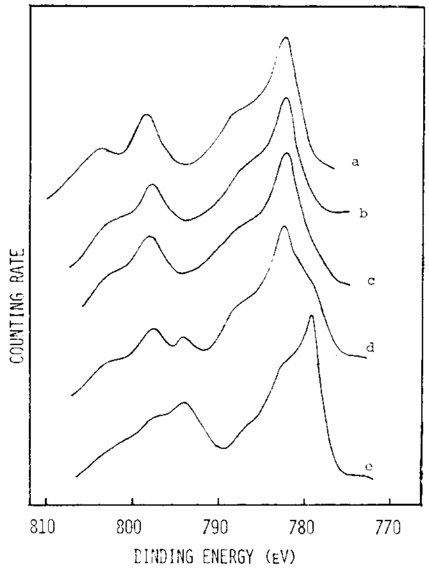

FIG. 2. XPS spectra of Co 2p level for the Co–Mo/Al_2O_3 catalyst during the HDS reaction at 400°C: (a) calcined, (b) 400°C, 1 hr evacuation; and (c) 10, (d) 30, and (e) 80 min of reaction.

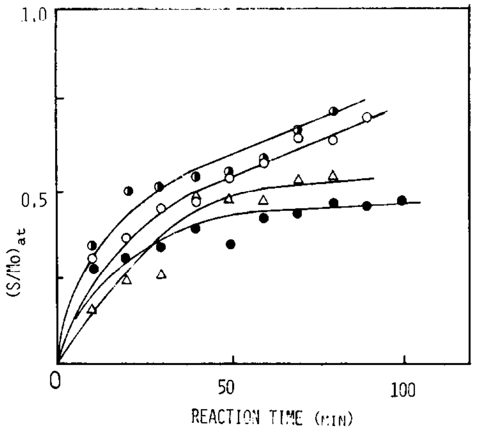

FIG. 3. Sulfur content of the catalyst in the course of the HDS reaction at 400°C: (●) Mo(5)/Al_3O_3; (○) Mo(10)/Al_2O_3; (◑) Mo(20)/Al_2O_3; (△) Co-Mo/Al_2O_3.

The amounts of Mo(V) observed in our study (30–35%) were much higher than those reported by Seshadri and Petrakis (*19*) who have revealed the concentration of Mo(V) to be 5–10% in Mo, depending on the reduction conditions, by means of ESR. These facts may indicate the enrichment of Mo(V) in the surface.

The Mo 3d spectra for the Co–Mo/Al_2O_3 catalyst were similar to those for the Mo(10)/Al_2O_3 catalyst in Fig. 1, but only subtle changes in the respective contents of Mo oxidation states were observed after 100 min of HDS reaction [Mo(VI), 18%; Mo(V), 32%; and Mo(IV), 50%). In Fig. 2, the changes in Co 2p spectra with reaction are shown. Some Co was found to be reduced. A new peak with the Co $2p_{\frac{3}{2}}$ binding energy of 777.8 eV can be ascribed to metal, since the spin–orbit splitting of Co 2p level was 15.0 eV, which is same for the metal (*20*). The reduction of Co during HDS reactions has been reported by some workers (*16, 17*). The unreduced Co is considered to be $CoAl_2O_4$ (*16, 17, 20*). Contrary to the results reported by Patterson *et al.* (*17*), we could not observe the sulfidation of Co under our experimental conditions, because no new peak except the peak due to Co metal appeared.

The sulfur contents of the catalysts during the HDS reaction are shown in Fig. 3. The atomic ratios of sulfur and molybdenum $(S/Mo)_{at}$ were evaluated by comparing the intensity ratios (S 2p/Mo 3d) of the catalysts and that of MoS_2. The extent of sulfidation diminished with decreasing MoO_3-content from 20 to 5 wt% for the Mo/Al_2O_3 catalysts. The Co–Mo/Al_2O_3 catalyst was less sulfided compared to the Mo(10)/Al_2O_3 catalyst under the same reaction conditions. The amounts of sulfur on the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts continued to increase considerably even after 80 or 90 min of reaction, while the sulfur contents of the Mo(5)/Al_2O_3 and the Co–Mo/Al_2O_3 catalysts reached their equilibrium values.

In Fig. 4, the peak intensity ratios of Mo 3d/Al 2s are plotted against the HDS reaction time. These values are normalized for their initial values. The intensity of the contaminant or deposited carbon peak was not changed during the reaction. The Mo(5)/Al_2O_3 catalyst gave no change in the intensity ratio, while the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts showed con-

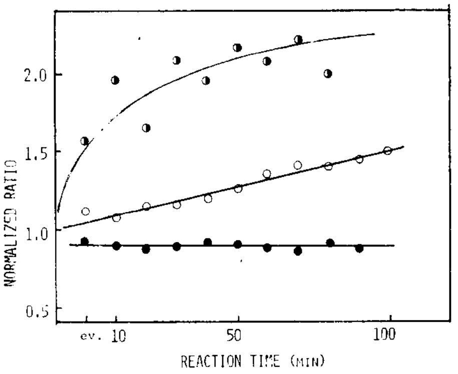

FIG. 4. Change in the normalized (Mo 3d/Al 2s) intensity ratio for the Mo/Al_2O_3 catalyst during the HDS reaction at 400°C (ev. means the evacuation at 400°C for 1 hr in the pretreatment chamber): (●) Mo(5)/Al_2O_3; (○) Mo(10)/Al_2O_3; (◑) Mo(20)/Al_2O_3.

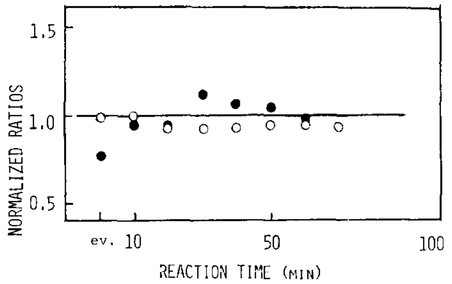

FIG. 5. Changes in the normalized (Mo 3d/Al 2s) and (Co $2p_{3/2}$/Mo 3d) intensity ratios for the Co–Mo/Al_2O_3 catalyst during the HDS reaction at 400°C (ev. means the evacuation at 400°C for 1 hr in the pretreatment chamber): (○) normalized (Mo 3d/Al 2s); (●) normalized (Co $2p_{3/2}$/Mo 3d).

siderable changes during the reaction; they increased gradually.

In Fig. 5, the Mo 3d/Al 2s and Co $2p_{3/2}$/Mo 3d ratios are shown for the Co–Mo/Al_2O_3 catalyst in the course of the reaction. Interestingly, these ratios were invariant during the reaction, although the Mo(10)/Al_2O_3 catalyst gave a considerable change as is shown in Fig. 4.

The steady-state activities of the catalysts used in the present study, which were obtained with the usual flow reactor, were 25.7, 23.1, 12.3, and 35.2%, as measured by the conversions of thiophene for 50 mg of the Mo(5)/, Mo(10)/, Mo(20)/, and Co–Mo/Al_2O_3 catalysts, respectively. The promotional effect of Co in the Co–Mo/Al_2O_3 catalyst was confirmed by comparing the activity of the promoted catalyst to that of the Mo(10)/Al_2O_3 catalyst. The conversion of thiophene per unit MoO_3 was higher for lower MoO_3-content catalysts. The product distributions of C-4 compounds were almost the same for all catalysts (1-butene, 32 ± 1%; *cis*-2-butene, 31 ± 1%; *trans*-2-butene, 23 ± 1%; and butane, 14 ± 1%).

DISCUSSION

As is shown in Fig. 4, the Mo 3d/Al 2s ratios for the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts increased as the reduction and sulfidation of the catalysts proceeded during the HDS reaction. However, in the case of the Mo(5)/Al_2O_3 catalyst, no change was observed. Namely, the enrichment of Mo on the outermost surfaces of the catalysts took place in the high MoO_3-content catalysts. Therefore, it is considered that in the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts migration of Mo occurs from the pores to the topmost surfaces of the catalysts and segregates there. According to Defaux *et al.* (*21*), a surface interaction complex arising from an acid–base reaction during the calcination was suggested. On the other hand, it is well known (*22*) that the alumina has an acid strength distribution. Then, it is considered that the strength of the interaction between Mo and alumina is heterogeneous. Actually, Massoth (*23*) has reported that the reducibility of supported MoO_3 on alumina depends on the amount of MoO_3 and that the lower MoO_3-content catalysts are more difficult to reduce than are the higher MoO_3-content catalysts under the same conditions. Therefore, the stability of supported Mo is supposed to be heterogeneous on the alumina surface, although it is generally accepted that MoO_3 is extremely well dispersed over the alumina surface of a Mo/Al_2O_3 catalyst to form a monomolecular layer when MoO_3 content does not exceed about 10 wt% (*8, 10, 23*).

There is some controversy as to the nature and structure of the Mo phase. Richardson (*1*) and Lipsch and Schuit (*8*) have proposed a monolayer of MoO_3 on alumina, the MoO_3 having bulk properties. Ashley and Mitchell (*6*) and Massoth (*24*) have suggested a surface interaction between MoO_3 and alumina. A combined model has been presented by LoJacono *et al.* (*25*). On the basis of our results, we support the third model (*25*). In the cases of the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts, the Mo which has a weak interaction with alumina and/or which exists as a MoO_3 small crystallite migrates from the pores to the outermost surfaces during the HDS reaction. However, with regard to the $Mo(5)/Al_2O_3$ catalyst, the interaction between MoO_3 and alumina is considered to be strong enough for the Mo to be stabilized on the support in the course of the reaction, since no migration takes place.

In the presence of Co, no migration of Mo or Co was observed. The role played by Co in the $Co-Mo/Al_2O_3$ catalyst can be immediately understood by comparing the results on the Mo/Al_2O_3 catalysts to those on the promoted catalyst. Namely, the Co inhibits the migration of Mo and, therefore, the segregation of Mo to form crystalline MoO_3 and/or MoS_2 on the surface during the HDS reaction, although the actual nature of the inhibiting effect for the Mo diffusion is still ambiguous. It is well known that Co occupies a tetrahedral site to form $CoAl_2O_4$ and Mo occupies an octahedral site on the alumina surface (*1, 8, 18, 25*). Then, it might be reasonable to assume that the surface diffusion of Mo occurs through a process whereby Mo in an octahedral site jumps to an adjacent tetrahedral site and then to another octahedral site and segregates there with former occupants. If that is the case, occupation of tetrahedral sites by Co will retard Mo diffusion. Another explanation may be possible, in which some interaction between Co and an adjacent Mo will stabilize the Mo phase. Although the nature of the interaction is not clear, it may relate to the synergistic effect of Co (*11–13*). In both cases, however, Co in $CoAl_2O_4$ is considered to act as a promoter, because catalysts with higher $CoAl_2O_4/Mo$ ratios have higher activities for HDS reaction (*16*).

Before discussing the sulfur contents of the catalysts, we must mention some difficulties in obtaining quantitative information from the XPS peak intensities. Contaminating impurities such as deposited or adsorbed carbon on the surface change the XPS intensities and even the peak intensity ratios. A second difficulty arises from differences in the depth distribution of the atoms concerned in the sample and in the standard specimen. Both difficulties arise from the differences of the escape depths of the electrons ejected by X-ray radiation. Other problems such as the surface roughness and the surface geometry of the sample were ignored here. However, fortunately, the kinetic energies of the S 2p (ca. 1320 eV) and Mo 3d levels (ca. 1250 eV) are very close to each other, and, consequently, the escape depths of the electrons are about 15 Å for both levels (*26*). Therefore, in our measurement of sulfur content we can neglect these problems associated with the XPS technique and we can obtain reasonable atomic ratios; $(S/Mo)_{at}$ without any correction for the escape depths. $(S/Mo)_{at}$ values were calculated by dividing the observed S 2p/Mo 3d ratios for the catalysts by the 0.5 (S 2p/Mo 3d) ratio obtained from MoS_2.

The sulfur content of the catalyst depends on the amount of MoO_3 supported on the alumina. The lower the MoO_3 content, the smaller the extent of sulfidation of the Mo as is shown in Fig. 3. A similar dependence of the sulfur content on the supported MoO_3-contents has been reported by DeBeer and co-workers (*27*). These findings will confirm the properties of the supported MoO_3 discussed above and will suggest the active state of Mo for the HDS reaction. In the $Mo(5)/Al_2O_3$ catalyst, $(S/Mo)_{at}$ was about 0.4, and the content of Mo(IV) was about 40%. Therefore, the active state of Mo would have a composition of $S/Mo(IV) = 1$, since the $[S/Mo(IV)]_{at}$ value was 1.0 under our reaction conditions, assuming that the sulfur is combined to Mo(IV). The $Mo(10)/Al_2O_3$ and $Mo(20)/Al_2O_3$ catalysts showed higher values (larger than 1.5). It suggests the formation of some

MoS_2. Accordingly, it is plausible that migrated and segregated Mo forms small crystallites of MoS_2 on the Mo(10)/Al_2O_3 and Mo(20)/Al_2O_3 catalysts and that crystalline MoS_2 is less active, taking into account the results on the activities of the catalysts. Mitchell and Trifiro (*28*) have reported, on the basis of the electronic spectra for the sulfided catalysts, that no discrete sulfides, e.g., MoS_2 and Co_9S_8, are predominant and that there probably exists a small amount of MoS_2 in the sulfided catalysts. These findings seem to support our model.

In the case of the Co–Mo/Al_2O_3 catalyst, the $[S/Mo(IV)]_{at}$ value was 1.1 under the steady state of the catalyst and its value was very close to the 1.0 found for the Mo(5)/Al_2O_3 catalyst. Consequently, it is concluded that the Co in the Co–Mo/Al_2O_3 catalyst inhibits the migration and segregation of the weakly bound Mo on alumina and that it keeps Mo as active species which would have the composition of $S/Mo(IV) = 1$. Our results on sulfur content seem to support the monolayer model (*14*) which predicts $S/Mo = 1$ for the sulfidation of the catalysts.

The binding energy value of Mo $3d_{\frac{5}{2}}$ for Mo(IV) species obtained in our study (230.2 eV) agreed with that for MoS_2 within the reproducibility of the spectrometer (±0.2 eV). Cimino and DeAngelis (*9*) have reported a 0.7 eV-lower value for MoO_2 than for MoS_2. The binding energy of the active Mo(IV) species, therefore, should fall between these values, but we could not discriminate between it and that of MoS_2 because of the small chemical shift. The binding energy of S 2p was consistent with that in MoS_2.

DeBeer *et al.* (*3*) have reported that the optimum activity of Co–Mo/Al_2O_3 catalysts for HDS reaction is observed by varying the Co/Mo ratio. In our opinion, Co is considered to act as a promoter, as is discussed above for the catalysts with low Co/Mo ratios, but in the catalysts with high Co/Mo ratios, Co accumulation on the Mo monomolecular layer, which is suggested by the XPS results reported by Brinen (*29*) and which has been assumed by Phillips and Fote (*2*), will retard the activity since Co itself has little activity for HDS reaction (*4*).

Interestingly, the Mo migration of the Mo/Al_2O_3 catalysts was observed even under our mild reaction conditions (10 Torr of the thiophene/H_2 reaction gas). Therefore, more extensive migrations of Mo and probably of Co would occur under the practical HDS reaction conditions and under the usual reaction conditions employed in many reports. In the intercalation model (*10*), they have assumed the migration of Co from the bulk to the small crystalline MoS_2 where Co^{2+} is intercalated. There is a strong possibility on the basis of our results that the intercalation model is adequate in the practical operations, although there remains some doubt whether the intercalated MoS_2 is the main active species or not. In addition, we cannot rule out the synergistic effect of Co (*11–13*) under practical reaction conditions, since Co would be sulfided to some extent and might act as a promoter. Under our mild reaction conditions, the monolayer model (*14*) is the most plausible one, although some modifications will be required.

Consequently, the stabilization of Mo phase by Co in Co–Mo/Al_2O_3 HDS catalysts was suggested on the basis of the XPS study of Mo/Al_2O_3 and Co–Mo/Al_2O_3 catalysts. The high MoO_3-content Mo/Al_2O_3 catalysts contain mobile Mo, which migrates from the pores to the outermost surfaces and segregates to form crystalline less-active MoS_2 during the HDS reaction, while the low MoO_3-content catalyst does not contain mobile Mo. The active species for HDS reaction might have the composition of $S/Mo(IV) = 1$ under our mild reaction conditions.

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