

Surface Structure of CoO-MoO₃/Al₂O₃ Catalysts Studied by X-Ray Photoelectron Spectroscopy

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X-Ray photoelectron spectroscopic studies of oxidic and sulfided CoO-MoO₃/Al₂O₃ catalysts revealed the chemical species, the surface structure of the catalysts, and the promoting effect of Co. It was found from the Mo(3d)/Al(2s) and Co(2p)/Al(2s) intensity ratios that the surface structure of the oxidic catalysts was highly sensitive to the preparation method. Bilayer structures are proposed for the catalysts prepared by sequential impregnations, while a separate phase structure is suggested to be plausible for the catalysts prepared by a simultaneous impregnation. On sulfidation the surface structure of the CoO-MoO₃/Al₂O₃ catalysts was not essentially altered under atmospheric pressure, compared to that of the oxidic precursor catalysts, although Co and Mo were sulfided. The oxidic catalysts mainly consist of Co₃O₄ and pseudo-CoAl₂O₄, the fraction of Co₃O₄ increasing with Co content and depending on the preparation method. On the basis of the observation that both the extent of sintering and the sulfidation degree of Mo are depressed by Co, it is suggested that the stabilization effect of Co (most likely pseudo-CoAl₂O₄) for Mo monolayers is operative during hydrodesulfurizations, thus holding the Mo effective for the reactions.

INTRODUCTION

Physicochemical characterization of CoO-MoO₃/Al₂O₃ hydrodesulfurization (HDS) catalysts has been extensively carried out by many workers using various techniques, revealing the chemical species present in the catalyst surface. However, only a few papers (1-4) are concerned with the surface structure or morphology of the catalysts, although the information on the surface structures of the oxidic and, in particular, of the sulfided catalysts is necessary to understand the behavior of the catalysts in HDS reactions, the effect of preparation method, and finally the role of Co in the reactions.

X-Ray photoelectron spectroscopy (XPS) is one of the best techniques to study the surface structure of the catalysts (5-13). With CoO-MoO₃/Al₂O₃ catalysts, Delmon and his co-workers (4) have very recently investigated the surface structure of the catalysts by XPS and proposed a

"bilayer" structure for the oxidic catalysts, in which Co covers the Mo monolayer. They varied the Co/Co + Mo ratio, holding the loading amount of MoO₃ + Co₃O₄ constant (15 wt%). On the basis of the XPS results Ng and Hercules (12) have shown with NiO-WO₃/Al₂O₃ catalysts that Ni₂O₃ is dispersed on top of the W monolayer.

In the present paper, we examined the surface structure of CoO-MoO₃/Al₂O₃ catalysts by XPS. The catalysts with a constant MoO₃:Al₂O₃ ratio and containing various amounts of CoO were prepared by three different impregnation methods to avoid ambiguities resulting from the change in the extent of Mo dispersion with the loading amount of MoO₃ (13-15) and to examine the preparation effects on the surface structure of the catalysts. The surface structure of the sulfided catalysts were compared with that of the oxidic precursor catalysts. The stabilization effect of Co for Mo phase is proposed to understand the XPS results.

EXPERIMENTAL

Catalysts

CoO-MoO₃/Al₂O₃ catalysts were prepared by impregnating γ -Al₂O₃ (Nishio Industry Co. Ltd., Type AE-11) using aqueous solutions of ammonium paramolybdate and cobalt nitrate. The water was evaporated to dryness at 90°C under stirring, followed by drying at 100°C for 16 h. The loading amount of MoO₃ was kept constant (15 wt% with respect to the support), while the CoO content was varied up to 20 wt% with respect to the support. The catalysts prepared by sequential impregnations are denoted by Co-(Mo)/Al₂O₃ (Mo first and then Co) and Mo-(Co)/Al₂O₃ (Co first and then Mo). These catalysts were calcined twice at 550°C for 5 h after the first and second impregnations. Catalysts impregnated simultaneously with Mo and Co and calcined at 550°C for 5 h are represented by (Co-Mo)/Al₂O₃ hereafter. Supported Mo/Al₂O₃ (15 wt% MoO₃) and Co/Al₂O₃ catalysts were also examined. All the catalysts were used in fine powders as prepared. The BET surface areas of the catalysts were measured by N₂ adsorption at 77 K after the catalysts were evacuated at 300°C for 1 h.

XPS Measurements

X-Ray photoelectron spectra were measured at room temperature on a Hitachi 507 photoelectron spectrometer using AlK $\alpha_{1,2}$ radiation (10 kV, 50 mA). The performances and calibration of the spectrometer have been described elsewhere (16). The catalyst sample was mounted on double-sided adhesive tape and evacuated at room temperature to ca. 1×10^{-5} Torr (1 Torr = 133.3 N m⁻²) in the pretreatment chamber by using a sorption pump. Subsequently, the catalyst sample was transferred to the analyzer chamber for the measurements of XPS spectra (base pressure during the measurements, ca. 1×10^{-7} Torr). Binding energies were referenced to the Al(2s) level for the catalyst support, Al₂O₃ (Al(2s),

119.1 eV) as an internal standard. The accuracy in the determination of the binding-energy value was estimated to be ± 0.2 eV. The XPS spectra were analyzed in terms of relative peak area intensities and chemical shifts of the Co(2p), Mo(3d) Al(2s), S(2p), S(2s), O(1s), and C(1s) levels. The peak area intensities were measured by planimetry of the graphic displays of the spectra assuming linear baselines. The effect of carbon contamination on the relative XPS intensities was neglected here because C(1s) intensities were nearly invariant among the catalysts. Relative intensities are reported with a precision of $\pm 5\%$.

Sulfidation of the Catalysts

The CoO-MoO₃/Al₂O₃ catalysts were treated with thiophene/H₂ (1/18 mol/mol, H₂; 50 ml/min) after prereduction with H₂ (50 ml/min) for 1 h or after presulfidation with CS₂/H₂ (1/9 mol/mol, H₂; 27 ml/min) for 1 h. The thiophene/H₂ treatment was continued until the catalyst reached steady-state conversion of thiophene (ca. 3 h for prereduced catalysts and ca. 2 h for presulfided ones). All the treatments were undertaken at 400°C and atmospheric pressure of thiophene/H₂, CS₂/H₂, or H₂ using a continuous-flow reactor (catalyst weight, 0.154 g). More detailed procedures have been shown elsewhere (13, 17). After the sulfidation of the catalyst, thiophene/H₂ was replaced with purified N₂. Stripping period at 400°C in flowing N₂ (50 ml/min) was about 10 min. Then the catalyst was cooled down to room temperature. The procedure took about 1 h on the whole. Subsequently, both ends of the reactor were shut off by stopcocks. This allowed isolation of the reactor containing the catalyst, to avoid any contact of the catalyst with air or moisture. The reactor was transferred to a N₂-filled glove box which was directly connected with a pretreatment chamber attached to the XPS spectrometer. The reactor with the catalyst inside was opened in the glove box and then the catalyst was rapidly mounted on double-sided

adhesive tape. In the procedure, no oxidized sulfur species such as SO_4^{2-} was observed with XPS.

RESULTS

1. Oxidic Catalysts

Shown in Fig. 1 are the X-ray photoelectron spectra of the Mo(3d) level for the catalysts. With the Mo/Al₂O₃ (15 wt% MoO₃) catalyst, a slight broadening of the Mo(3d) level (FWHM, 5.6 eV) was observed compared to unsupported MoO₃ (5.2 eV), while the binding energy of the Mo(3d_{5/2}) level was invariant, as shown in Table 1. This is in good agreement with other workers (18–20). These findings would be ascribable to charging effects and/or to nonequivalent sites for Mo in the Al₂O₃ surface. The extent of dispersion of Mo over Al₂O₃ has been discussed in a previous paper (13) based on the Mo(3d)/Al(2s) intensity ratio, indicating the formation of Mo monolayer in the Mo(3d)/Al(2s) intensity ratio, indicating the formation of Mo monolayer in the Mo/Al₂O₃ catalyst with 15 wt% MoO₃. The addition of Co induced no significant

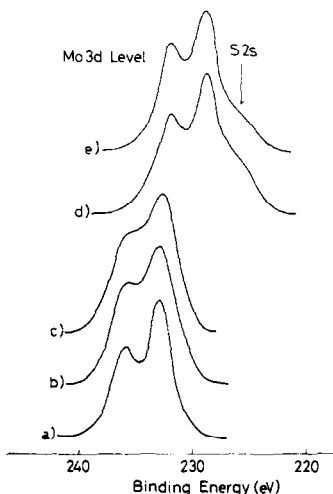


FIG. 1. X-Ray photoelectron spectra of the Mo(3d) level for the catalysts. (a) MoO₃; (b) MoO₃/Al₂O₃ (15 wt% MoO₃), oxidic; (c) Co-(Mo)/Al₂O₃ (3 wt% CoO, 15 wt% MoO₃), oxidic; (d) catalyst (b) treated with thiophene/H₂ at 400°C for 2 h after presulfided with CS₂/H₂ at 400°C for 1 h; (e) catalyst (c) treated with thiophene/H₂ after presulfided.

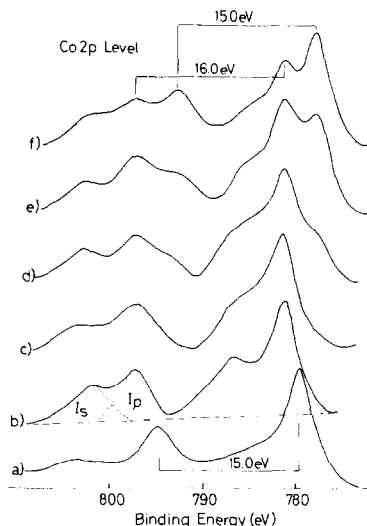


FIG. 2. X-Ray photoelectron spectra of the Co(2p) level for the catalysts. (a) Co₃O₄; (b) Co-(Mo)/Al₂O₃ (3 wt% CoO, 15 wt% MoO₃), oxidic; (c) Co-(Mo)/Al₂O₃ (10 wt% CoO, 15 wt% MoO₃), oxidic; (d) Co-(Mo)/Al₂O₃ (5 wt% CoO, 15 wt% MoO₃) treated with thiophene/H₂ at 400°C for 3 h after pre-reduced with H₂ at 400°C for 1 h; (e) catalyst (d) treated with thiophene/H₂ after presulfided; (f) Co-(Mo)/Al₂O₃ (5 wt% CoO, 15 wt% MoO₃) treated with thiophene/H₂ at 400°C for 2 h after presulfided.

change in the FWHM of the Mo(3d) level, contrary to Gajardo *et al.* (20).

The X-ray photoelectron spectra of the Co(2p) level for the catalysts are shown in Fig. 2. Since the information on the binding-energy value is not enough to characterize the chemical state of Co (21), I_s/I_p intensity ratios (I_s , intensity of satellite peak; I_p , intensity of parent peak) for the Co(2p_{1/2}) level (22) were also examined. The XPS data are summarized in Table 1, together with the BET surface areas of the catalysts. The Co(2p_{3/2}) binding energy and I_s/I_p ratio decreased with increasing the CoO content for all the catalyst series, whereas the Mo(3d_{5/2}) binding energies were unchanged (232.7 ± 0.2 eV). These results would indicate the increase of the fraction of Co₃O₄ with increasing the CoO content with respect to the fraction of "CoAl₂O₄" (pseudo-CoAl₂O₄ where Co²⁺ is dispersed in the Al₂O₃ matrix) rather than the increase in the fraction of CoMoO₄,

TABLE 1
XPS Data for the CoO/Al₂O₃, MoO₃/Al₂O₃, and CoO-MoO₃/Al₂O₃ Catalysts

Catalyst ^a	CoO wt%	Surface area (m ² /g)	Binding energy ^b (eV)					I _s /I _p ^c
			Mo(3d _{5/2})	Co(2p _{1/2})	Co(2p _{3/2})	O(1s)	C(1s)	
Al ₂ O ₃		156				531.2	285.0	
MoO ₃ /Al ₂ O ₃		168	232.9			531.1	285.0	
CoO/Al ₂ O ₃	1.5	215		797.2	781.2	531.1	285.0	0.65
	3.0	165		797.1	781.1	531.1	284.6	0.79
	3.0 ^d			797.3	781.3	531.2	285.0	0.90
	5.0	141		797.0	781.1	531.1	284.5	0.69
	10	143		796.6	781.0	531.4	285.2	0.72
Co-(Mo)/Al ₂ O ₃	20			797.1	781.2	531.1	285.2	0.73
	1.5	166	232.7	797.3	781.4	530.9	284.9	0.79
	3.0	162	232.6	797.3	781.4	531.0	284.9	0.88
	5.0	154	232.9	796.9	781.5	531.1	285.0	0.79
	10	146	232.7	797.3	781.5	531.1	285.0	0.68
(Co-Mo)/Al ₂ O ₃	20			796.2	780.6	530.9	284.6	0.42
	1.5	166	232.9	797.5	781.6	531.0	284.9	0.85
	3.0	176	232.5	796.2	780.7	530.9	284.7	0.74
	5.0	177	232.8	796.2	780.9	531.0	285.0	0.66
	10	148	232.6	796.9	780.9	531.2	285.1	0.52
Mo-(Co)/Al ₂ O ₃	20			795.8	780.2	530.7	284.7	0.44
	1.5	140	232.6	797.0	781.5	531.0	284.9	0.66
	3.0	138	232.7	797.6	781.5	531.0	284.8	0.76
	5.0	131	232.6	797.4	781.1	531.1	284.7	0.61
	10	114	232.7	796.8	781.2	531.0	284.9	0.70
Co ₃ O ₄				796.9	781.1	531.0	285.0	0.63
CoO				794.6	779.6		285.0	0.35
CoMoO ₄ ^e			231.8	796.7	780.7		285.0	0.88
CoAl ₂ O ₄				797.3	781.3	531.2	285.0	0.90
Al ₂ (MoO ₄) ₃ ^e			232.7			531.2	285.0	
MoO ₃			232.9			531.1	285.0	

^a Calcined at 550°C for 5 h; MoO₃ content 15 wt% with respect to the support; Co-(Mo)/Al₂O₃, sequential impregnation (Mo first and then Co); (Co-Mo)/Al₂O₃, simultaneous impregnation; Mo-(Co)/Al₂O₃, sequential impregnation (Co first and then Mo).

^b Referenced to the Al(2s) (119.1 eV) or Al(2p) (74.3 eV) level for the support.

^c I_s/I_p for Co(2p_{1/2}) level; I_s, area intensity of satellite peak; I_p, area intensity of parent peak.

^d Calcined at 700°C.

^e From Patterson *et al.* (26).

taking into consideration the Co(2p_{3/2}) binding energies and I_s/I_p ratios for Co₃O₄, CoAl₂O₄, and CoMoO₄ in Table 1.¹ With the preparation effect of the catalyst, the Co(2p_{3/2}) binding energy is inclined to decrease in the order Co-(Mo)/Al₂O₃ ≥ Mo-(Co)/Al₂O₃ > (Co-Mo)/Al₂O₃.

¹ Although I_s/I_p values for CoMoO₄ are not given in Table 1, the I_s/I_p ratio is estimated to be ca. 0.9 based on the fact that CoMoO₄ contains octahedral Co²⁺ similar to CoO.

In Fig. 3, the diffuse reflectance spectra of the CoO-MoO₃/Al₂O₃ catalysts are shown. The relative intensity of triplet bands (540, 580, and 630 nm) attributable to "CoAl₂O₄" (23) decreased with increasing the CoO content with respect to a ligand field band around 710 nm and a broad charge transfer band starting around 600 nm due to Co₃O₄ (23). However, no apparent bands ascribable to CoMoO₄ (530 and 580 nm) were observed in all the catalysts.

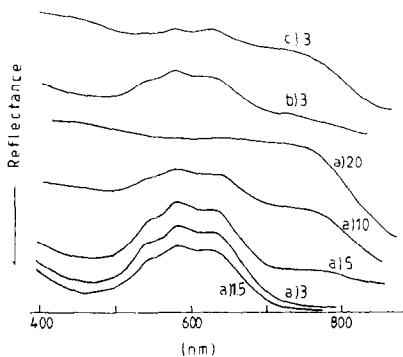


FIG. 3. Diffuse reflectance spectra of CoO-MoO₃/Al₂O₃ catalysts. (a) Co-(Mo)/Al₂O₃; (b) (Co-Mo)/Al₂O₃; (c) Mo-(Co)/Al₂O₃. Numbers refer to CoO content (wt%).

Concerning the preparation effects, the fraction of "CoAl₂O₄" decreased in the order Co-(Mo)/Al₂O₃ > (Co-Mo)/Al₂O₃ \approx Mo-(Co)/Al₂O₃. This coincides approximately with the decreasing order for the binding energy of the Co(2p_{3/2}) level. The difference between XPS and DRS data would result from the differences in the sampling depth and in the extent of dispersion of Co₃O₄ as discussed below.

It is evident (5-13) that the Mo(3d)/Al(2s) and Co(2p)/Al(2s) intensity ratios reflect the surface structure of the catalysts, the extent of dispersion of Mo or Co, and the morphology of Co-Mo oxide phases, since the XPS intensities depend on the dispersion degree of each component as well as on the composition of the topmost surface layers in the catalysts. To examine the surface structure of the catalysts, the Mo(3d)/Al(2s) and Co(2p)/Al(2s) ratios are plotted in Fig. 4 as a function of the CoO content. With the Co-(Mo)/Al₂O₃ catalysts, the Mo(3d)/Al(2s) ratio decreased with increasing CoO content up to 15 wt%, followed by a significant increase with further addition of CoO. The Co(2p)/Al(2s) ratios were higher than those for the corresponding Co/Al₂O₃ catalysts. In contrast, as for the (Co-Mo)/Al₂O₃ catalysts, the Mo(3d)/Al(2s) ratios increased with increasing CoO content and the Co(2p)/Al(2s) ratios were significantly higher than those for the Co/Al₂O₃ cata-

lysts. On the other hand, the Mo-(Co)/Al₂O₃ catalysts showed nearly invariant Mo(3d)/Al(2s) ratios and lower Co(2p)/Al(2s) ratios than those for the Co/Al₂O₃ catalysts. These findings in Fig. 4 would imply that the surface structure of the CoO-MoO₃/Al₂O₃ catalysts is highly sensitive to the preparation method of the catalysts.

2. Sulfided Catalysts

Typical XPS spectra of the Mo(3d) and Co(2p) levels for the sulfided catalysts are shown in Figs. 1 and 2. With the Co(2p) level, a new peak appeared at the Co(2p_{3/2}) binding energy = 777.9 eV (spin-orbit splitting, 15.0 eV) on sulfidation of the catalysts. The Co(2p) peak remaining intact (Co(2p_{3/2}), 781.3 eV) is ascribable to "CoAl₂O₄" (21, 22, 24-28). With the Mo(3d) spectra, the binding energy of the Mo(3d_{5/2}) band was shifted to 228.8 eV, indicating the formation of sulfided Mo(IV) species (13, 26). X-Ray diffraction analyses showed the presence of Co₉S₈ (ASTM 19-364) in the catalysts containing more than 20 wt% CoO under the sulfidation conditions employed here.

The Mo(3d)/Al(2s) and Co(2p)/Al(2s) ratios are shown in Fig. 5 as a function of CoO content for the catalysts sulfided with thiophene/H₂ after prereluction. The intensity patterns are more or less similar to those for the corresponding oxidic precursors.

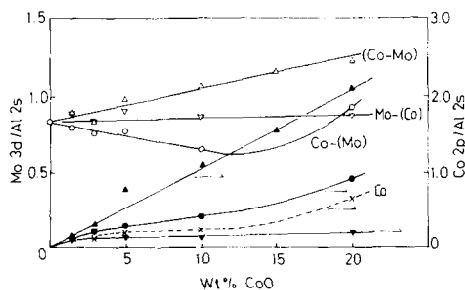


FIG. 4. Dependences of the Mo(3d)/Al(2s) and Co(2p)/Al(2s) XPS intensity ratios on the CoO content for the oxidic CoO-MoO₃/Al₂O₃ catalysts. (O) Co-(Mo)/Al₂O₃; (Δ) (Co-Mo)/Al₂O₃; (∇) Mo-(Co)/Al₂O₃; (X) Co/Al₂O₃. Open symbols, Mo(3d)/Al(2s); closed symbols, Co(2p)/Al(2s).

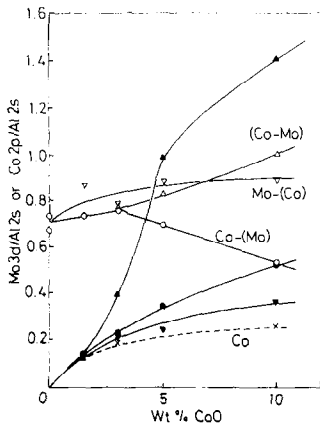


FIG. 5. Dependences of the Mo(3d)/Al(2s) and Co(2p)/Al(2s) XPS intensity ratios on the CoO content for the CoO-MoO₃/Al₂O₃ catalysts treated with thiophene/H₂ at 400°C for 3 h after prerduced with H₂ at 400°C for 1 h. Same symbols are used as in Fig. 4.

or catalysts except for the decrease in the Co(2p)/Al(2s) ratios. However, a slight decrease in the Mo(3d)/Al(2s) ratio was observed for the Mo/Al₂O₃ catalyst (CoO content = 0 in Fig. 5) compared to the oxidic catalyst. As for the catalysts treated with thiophene/H₂ after presulfidation (Fig. 6), the decrease of the Mo(3d)/Al(2s) ratio was prominent for the Mo/Al₂O₃ catalyst, whereas the Mo(3d)/Al(2s) ratios did not change so much for the Co-containing catalysts. It is evident that the decreases in the

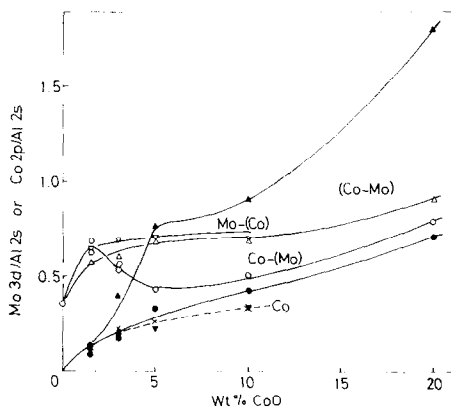


FIG. 6. Dependences of the Mo(3d)/Al(2s) and Co(2p)/Al(2s) XPS intensity ratios on the CoO content for the CoO-MoO₃/Al₂O₃ catalysts treated with thiophene/H₂ at 400°C for 2 h after presulfidated with CS₂/H₂ at 400°C for 1 h. Same symbols are used as in Fig. 4.

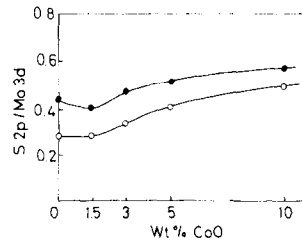


FIG. 7. Dependences of the S(2p)/Mo(3d) ratios on the CoO content for the (Co-Mo)/Al₂O₃ catalysts treated with thiophene/H₂ at 400°C after prerduction (O) or presulfidation (●).

Mo(3d)/Al(2s) ratio for the Mo/Al₂O₃ catalyst on sulfidation bring about the apparent maxima or steep increases of the Mo(3d)/Al(2s) ratio in Fig. 5 and particularly in Fig. 6 for the CoO-MoO₃/Al₂O₃ catalysts in the low-CoO-content region.

Figure 7 shows the sulfidation degree of the catalysts expressed by the S(2p)/Mo(3d) ratio (S(2p), 162.0 eV). Although adsorbed H₂S would contribute to the S(2p) intensity (29, 30) in our experimental conditions (short stripping period at 400°C), it is estimated that the degree of the H₂S contribution to the S(2p) XPS intensity is similar for the Mo/Al₂O₃ and CoO-MoO₃/Al₂O₃ catalysts due to the identical treatments. The Mo/Al₂O₃ catalyst was sulfided to S/Mo = 2.00 (atomic ratio) for the presulfided catalyst and to S/Mo = 1.27 for the prerduced one as judged from the S(2p)/Mo(3d) intensity ratios (13, 17). It is noteworthy that the S(2p)/Mo(3d) ratio decreased by the addition of a small amount of CoO especially with the presulfided catalysts, followed by gradual increase with increasing CoO content. With other CoO-MoO₃/Al₂O₃ catalysts, similar results were confirmed too. The decrease in the sulfur content of the catalyst is readily seen in the Mo(3d) spectra in Fig. 1. The relative intensity of the S(2s) level to the Mo(3d) level is apparently decreased by the addition of Co (Figs. 1d and e). In contrast, such a decrease in the S(2p)/Mo(3d) ratio by the addition of Co was not observed with CoO-MoO₃/SiO₂ catalysts and the S(2p)/Mo(3d) ratio increased monotonously with increasing CoO content (17).

DISCUSSION

1. Surface Species on CoO–MoO₃/Al₂O₃ Catalysts

It is apparent from Table 1 that the chemical state of Mo in the CoO–MoO₃/Al₂O₃ catalysts is similar to that in the Mo/Al₂O₃ catalyst and that Co is present mainly as “CoAl₂O₄” and Co₃O₄, the latter being predominant in the high-CoO-content catalysts. However, the formation of CoMoO₄ is surmised to be very little from XPS, X-ray diffraction analysis, and diffuse reflectance spectra even for the catalysts prepared by simultaneous impregnation. This is consistent with other workers (4, 19, 24, 28) and is due presumably to a solid-state reaction like (31) $3\text{CoMoO}_4 + 4\text{Al}_2\text{O}_3 \rightarrow 3\text{CoAl}_2\text{O}_4 + \text{Al}_2(\text{MoO}_4)_3$. On the other hand, some workers (15, 32, 33) reported the formation of CoMoO₄ over Al₂O₃-supported catalysts. The discrepancy among workers would be due to catalyst preparation methods, particularly to calcination temperature. Richardson (32) showed from magnetic susceptibility measurements that CoMoO₄ was formed when CoO–MoO₃/Al₂O₃ catalysts were calcined at temperatures higher than 650°C, whereas it was not formed at lower calcination temperatures. LoJacono *et al.* (33) and Medema *et al.* (15) found CoMoO₄ formation in the catalysts calcined at 600°C using ESR or Raman spectroscopy. It can be conjectured from these results that a high calcination temperature (probably > 600°C) facilitates CoMoO₄ formation in CoO–MoO₃/Al₂O₃ catalysts. Accordingly, it would be reasonable that CoMoO₄ formation is very small under our preparation methods (calcination temperature, 550°C). In the case of CoO–MoO₃/SiO₂ catalysts, the formation of CoMoO₄ is clearly detected by diffuse reflectance and Raman spectroscopies, X-ray diffraction analysis, and XPS (15, 17, 34–36). The discrepancies between Al₂O₃- and SiO₂-supported catalysts result from the differences in the support–active-phase interactions, that is, Al₂O₃ has much

stronger interactions with Mo and Co, while SiO₂ does not, compared to Co–Mo interactions (35, 36).

The apparent binding-energy values and I_s/I_p ratios of the Co(2p) level depend both on the concentration of each species in the topmost surface layers and on the dispersion degree of each component. In other words, the contribution to XPS spectra is greater for the component present in greater amount and better dispersed in the catalyst surface. Accordingly, it is difficult to evaluate the respective fractions of the chemical species on the basis of the XPS data in Table 1. To estimate the approximate fraction of Co₃O₄ in the CoO–MoO₃/Al₂O₃ catalysts, the Co(2p) spectra obtained after the prereduction followed by the thiophene/H₂ treatment were deconvoluted into two species (“CoAl₂O₄,” Co(2p_{3/2}) = 781.3 eV, and reduced or sulfided Co, 777.9 eV). The latter Co species (Co₉S₈ as discussed below) is undoubtedly produced from Co₃O₄ and CoMoO₄, if present, since “CoAl₂O₄” is hardly reduced or sulfided. Table 2 shows the fraction of Co₃O₄ thus estimated in the CoO–MoO₃/Al₂O₃ catalysts. The proportion of Co₃O₄ increased with CoO content, this being qualitatively consistent with the XPS data in Table 1 and with the diffuse reflectance spectra in Fig. 3. This finding is in agreement with that reported by LoJacono *et al.* (37). With the preparation method, the proportion of Co₃O₄ increased in the order Co–(Mo)/Al₂O₃ < Mo–(Co)/Al₂O₃ < (Co–Mo)/Al₂O₃. These results are in good agreement with those in Table 1 and Fig. 3. Consequently, it is apparent that the fraction of Co₃O₄ depends on the CoO content and on the preparation method of the catalyst.

On sulfidation a new Co phase appeared as shown in Fig. 2. From the binding energy of the new peak (Co(2p_{3/2}), 777.9 eV), it would be attributable to Co₉S₈ or Co metal. It is rather difficult to distinguish between them on the basis of the binding energy, spin–orbit splitting, and satellite structure,

TABLE 2

Fraction of Co₃O₄ in the CoO-MoO₃/Al₂O₃ Catalysts

Catalyst ^a	wt% CoO	Fraction of Co ₃ O ₄ ^b (%)
CoO/Al ₂ O ₃	3.0	16
	5.0	29
	10	29
Co-(Mo)/Al ₂ O ₃	1.5	11
	3.0	13
	5.0	20
	10	31
(Co-Mo)/Al ₂ O ₃	1.5	22
	3.0	57
	5.0	56
	10	51
Mo-(Co)/Al ₂ O ₃	1.5	17
	3.0	32
	5.0	48
	10	44

^a See Table 1.^b Estimated from the amount of Co₉S₈ produced by the treatment with thiophene/H₂ at 400°C and atmospheric pressure for 3 h after prerduced with H₂ at 400°C for 1 h.

since the binding energy of the Co(2p_{3/2}) level for Co metal is only a few electron volts lower than that for Co₉S₈ (38) and the spin-orbit splitting for Co metal (21) and Co₉S₈ (calculated from stoichiometric Co₉S₈ in Ref. (38)) are 15.0 eV and moreover both species show no characteristic satellite structures (21, 38, 39). Therefore, the only decisive distinction between them should be based on stoichiometric considerations as described in our previous paper (38). From the relationships among the S(2p), Mo(3d), and reduced or sulfided Co(2p) XPS intensities similar to those found for unsupported CoO-MoO₃ catalysts sulfided *in situ* (38), it was substantiated (17) that the new peak at 777.9 eV was attributable to Co₉S₈ (26, 39) rather than to Co metal (40) under our sulfidation conditions. This conforms to the X-ray diffraction study showing the presence of Co₉S₈ in the catalysts containing more than 20 wt% CoO and also to the thermodynamic considerations (41). The sulfidation of Co is

readily seen in the S(2p)/Mo(3d) ratios for the presulfided catalysts in Fig. 7. The S(2p)/Mo(3d) ratios for the catalysts containing more than ca. 3 wt% CoO are higher than that corresponding to MoS₂ (S(2p)/Mo(3d) = 0.44), indicating apparently the sulfidation of Co.

As for the state of Mo in the sulfided catalysts, it is evident that Mo is reduced and sulfided on the basis of the Mo(3d_{5/2}) binding energy (228.8 eV). The sulfidation degree of Mo (expressed by S/Mo, atomic ratio) was calculated from the S(2p)/Mo(3d) intensity ratios to be 2.00 for the presulfided Mo/Al₂O₃ catalysts and 1.27 for the prerduced one. The decrease in the S(2p)/Mo(3d) ratio in Fig. 7 by the addition of a small amount of Co must be a consequence of the decrease in the sulfidation degree of Mo by the stabilization effect of Co for the Mo monolayer (1, 17, 27). This is discussed below in more detail in connection with the surface structure of the sulfided catalysts.

2. Surface Structure of the Oxidic Catalysts

In order to estimate the surface structure or morphology of the catalyst based on the XPS results in Fig. 4, it is necessary to discuss XPS intensity patterns characteristic to various surface structures. We consider here the simple surface structures presented schematically in Figs. 8 and 9, where stippling denote subsurface "CoAl₂O₄." However, the surface structure of actual CoO-MoO₃/Al₂O₃ catalysts is not so simple and is simultaneously comprised of structures I-III. We discuss here the surface structure simply on the basis of the XPS intensity patterns characteristic of the special structures in Figs. 8 and 9. Accordingly, the surface structures suggested here would represent only a major one and, of course, we cannot rule out the presence of the other less important structures. Although the information from XPS on the surface structure is thus restricted, it would be useful to estimate a major struc-

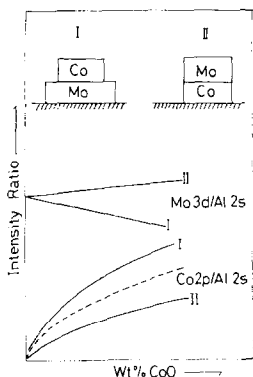


FIG. 8. Schematic diagram showing the relationships between the Mo(3d)/Al(2s) or Co(2p)/Al(2s) XPS intensity ratio and the CoO content in CoO-MoO₃/Al₂O₃ catalysts with constant MoO₃ content for the surface structures I and II.

ture in the catalyst surface and to suggest the changes in the surface structure with preparation method and with sulfidation.

Schematic correlations between the Mo(3d)/Al(2s) and Co(2p)/Al(2s) intensity ratios and the specific surface structures are shown in Figs. 8 and 9. If Co phase covers the Mo phase ("bilayer" structure I), the Mo(3d)/Al(2s) ratio is expected to decrease with increasing CoO content, since the Mo(3d) photoelectrons are attenuated by Co by a factor of $1 - \theta_{Co} (1 - \exp(-d_{Co}/\lambda_{Mo}))$, where θ_{Co} is the coverage of Co phase over the Mo phase, d_{Co} the thickness of Co layer, and λ_{Mo} the escape depth of the Mo(3d) photoelectrons (7, 8, 11, 13, 42). On the other hand, the Co(2p)/Al(2s) ratio would be larger than those for the corresponding Co/Al₂O₃ catalysts because of the attenuation of the Al(2s) photoelectrons by the thicker Co-Mo double layers and presumably because of better dispersion of Co induced by the well-dispersed Mo monolayer. Another "bilayer" structure (II) to be considered is shown in Fig. 8, where Mo covers Co phase. Assuming that the Co phase is fully covered by Mo, the Co(2p) photoelectrons are attenuated by a factor of $\exp(-d_{Mo}/\lambda_{Co})$, where d_{Mo} is the thickness of the Mo layer and λ_{Co} the escape depth of the Co(2p)

photoelectrons. The Mo(3d) intensity would be almost invariant and the Al(2s) photoelectrons slightly attenuated by the addition of Co due to the Co-Mo double layers. If Co and Mo are distributed over the support constituting a "separate phase" (structure III) in Fig. 9, both the Mo(3d)/Al(2s) and the Co(2p)/Al(2s) ratios increase with the CoO content compared to those for the Mo/Al₂O₃ and Co/Al₂O₃ catalysts, since only the Al(2s) photoelectrons are effectively attenuated by the Mo and Co phases, the latter of which is presumably dispersed well by the presence of the well-dispersed Mo phase.

With the Co-(Mo)/Al₂O₃ catalysts, it is apparent by comparing Figs. 4 and 8 that part of Co covers the Mo monolayer, forming a "bilayer" structure as suggested by Delmon *et al.* (4). Moné (2) proposed a similar "bilayer" structure in which Co adsorbed on Mo sites, reducing the Brønsted acidity on the catalysts. However, with the catalysts containing more than 10–15 wt% CoO, a large part of Co₃O₄ seems to constitute separate phases (structure III), since both the Mo(3d)/Al(2s) and the Co(2p)/Al(2s) intensity ratios begin to increase from there. This is probably due to the limiting capacity of the Mo phase for Co adsorption. With the Mo-(Co)/Al₂O₃ cata-

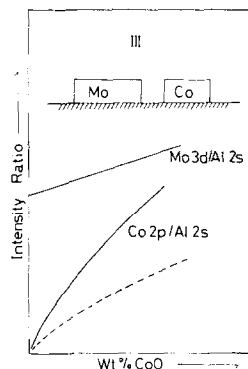


FIG. 9. Schematic diagram showing the relationships between the Mo(3d)/Al(2s) or Co(2p)/Al(2s) XPS intensity ratio and the CoO content in CoO-MoO₃/Al₂O₃ catalysts with constant MoO₃ content for the surface structure III.

lysts, it is considered that Mo covers the preexisting Co phase as expected from the preparation method, forming a reversed "bilayer" structure. These assignments would become more convincing when it is taken into account that the fraction of Co₃O₄ (Table 2) decreases in the order Mo-(Co)/Al₂O₃ > Co/Al₂O₃ > Co-(Mo)/Al₂O₃.

With the (Co-Mo)/Al₂O₃ catalysts, the intensity patterns coincide with those in Fig. 9. This seems to indicate that Mo and Co phases are dispersed well over the Al₂O₃ surface, constituting mainly a "separate-phase" structure (III). From the enormously larger Co(2p)/Al(2s) ratios compared to those for the Co/Al₂O₃ catalysts, it is very plausible that Co is dispersed very well and that the Co and Mo phases are well contacted or in close proximity due to Co-Mo interactions. However, there is a possibility that structure I or II contributes considerably to the surface structure of the (Co-Mo)/Al₂O₃ catalysts as well as structure III, since the fraction of Co₃O₄ in these catalysts is significantly higher than that in the other Co-containing catalysts.

As for the dispersion degree of Co₃O₄, which is sulfided to Co₉S₈ during HDS reactions, it is considered that Co₃O₄ in the Co-(Mo)/Al₂O₃ and (Co-Mo)/Al₂O₃ catalysts is dispersed much better than that in the Mo-(Co)/Al₂O₃ and Co/Al₂O₃ catalysts, this suggesting better contacts between Co and Mo phases in the former catalysts than in the latter ones. This idea could explain higher HDS activities of the Co-(Mo)/Al₂O₃ and (Co-Mo)/Al₂O₃ catalysts compared to those of the Mo-(Co)/Al₂O₃ catalysts (17, 39).

Nevertheless, as mentioned above, these surface structures are major ones in the catalysts and the minor contributions of the other structures should not be ignored. More detailed and qualitative information would be obtained by the use of scanning Auger electron spectroscopy in connection with depth profiling by means of noble gas ion sputtering. Although we have discussed the surface structure of the CoO-MoO₃/

Al₂O₃ catalysts on the basis of the simple surface models, it is noteworthy that the surface structure of the catalysts is very sensitive to the preparation method.

3. Surface Structure of Sulfided Catalysts

As for the catalysts sulfided with thiophene/H₂ after prereluction with H₂, the Mo(3d)/Al(2s) and Co(2p)/Al(2s) ratios depended on the CoO content in a more or less similar manner to those for the corresponding oxidic catalysts, except for the catalysts in the low-CoO-content region. The Mo(3d)/Al(2s) ratio for the Mo/Al₂O₃ catalyst decreased from 0.83 to 0.70 on sulfidation, while the ratios for the catalysts containing Co did not change as much. With the CoO-MoO₃/Al₂O₃ catalysts used for thiophene HDS after presulfidation with CS₂/H₂, the anomalies in the Mo(3d)/Al(2s) ratio observed in the low-CoO content region were much more prominent than those for the prereluced catalysts. The Mo(3d)/Al(2s) ratio for the Mo/Al₂O₃ catalyst diminished greatly from 0.83 to 0.36 under presulfidation conditions. Although small decreases in the Mo(3d)/Al(2s) ratio are noted on sulfidation, the CoO-MoO₃/Al₂O₃ catalysts show enormous stabilities against a decrease in the Mo(3d)/Al(2s) ratio compared to the Mo/Al₂O₃ catalyst. Consequently, it is considered that the apparent maxima or steep increases in the Mo(3d)/Al(2s) ratio in Fig. 5 and particularly in Fig. 6 are induced simply by the great decreases in the Mo(3d)/Al(2s) ratio for the Mo/Al₂O₃ catalyst rather than by special reconstructions of the surface structure of the Co-containing catalysts. From the results of the water extractions of Mo in fresh MoO₃/Al₂O₃ and reoxidized catalysts after sulfidation, it has been shown (13) that the decrease in the Mo(3d)/Al(2s) ratio for the MoO₃/Al₂O₃ catalysts results from a shrinkage and/or sintering of Mo phase to form MoS₂ at the expense of Mo monolayer and that the extent of Mo sintering increases with the sulfidation degree of Mo. The selectivity to

butane formation during the HDS of thiophene over $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts was found to be reasonably explained in terms of the sintering of Mo phase (43).

Taking into consideration the above points and comparing Figs. 4, 5, and 6, we are inclined to believe that the surface structure or morphology of the $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts is not essentially altered by sulfidation, that is, a "bilayer" structure produces a sulfided "bilayer" structure and a "separate-phase" structure forms a sulfided "separate-phase" structure when sulfided under our conditions. However, it is noteworthy that the sintering of Mo or Co phase is considerably depressed by the addition of Co into the $\text{Mo}/\text{Al}_2\text{O}_3$ or by the introduction of Mo into the $\text{Co}/\text{Al}_2\text{O}_3$, although some sinterings of Mo and Co phases occur on sulfidation.

In the previous paper (38) on unsupported $\text{CoO}-\text{MoO}_3$ catalysts, surface segregation of Co or Mo was reported to occur when $\text{CoO}-\text{MoO}_3$ catalysts were contacted with reactive gases such as H_2 , thiophene/ H_2 , and $\text{H}_2\text{S}/\text{H}_2$. However, these phenomena were completely obscured in the supported $\text{CoO}-\text{MoO}_3$ catalysts due to sintering of Co and Mo and could not be detected, although they may have occurred.

4. Stabilization of Mo Phase by Co

As discussed above, the $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts show great resistivity against the sintering of the Mo phase. This is supported further by the results in Fig. 7. In our previous paper (13) on various $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts, it has been shown that the sulfidation of Mo accompanies the sintering of Mo phase, producing MoS_2 at the expense of Mo monolayer, and that the degree of sintering increases with the degree of sulfidation of Mo. As shown in Fig. 7, the sulfidation degree of the catalyst expressed by the $\text{S}(2p)/\text{Mo}(3d)$ ratio decreased by the addition of a small amount of Co, although the sulfur attached to Co contributes to the $\text{S}(2p)$ XPS inten-

sity, this indicating the decrease in the sulfidation degree of Mo by the presence of Co and the concurrent decrease in the extent of Mo sintering. This fact conforms to the stabilization of Mo phase by Co. Contrary to the Al_2O_3 -supported catalysts, no such effect of Co was observed with $\text{CoO}-\text{MoO}_3/\text{SiO}_2$ catalysts (17). Therefore, it is concluded that Mo monolayer is stabilized by Co (most likely by " CoAl_2O_4 ") as pointed out previously (17, 27), thus holding the Mo more effective for HDS reactions. This is evidently one of the promoting effects of Co in $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$ HDS catalysts. The stabilization effect of Co seems to conform to the monolayer model (1, 29b, 44). However, the occurrence of some extent of Mo sintering would support the surface model proposed by DeBeer *et al.* (45) that oxidic $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts are correctly described by the monolayer model (1, 29b, 44), but that during sulfidation or by actual operation the catalysts are converted to a state that is similar either to the intercalation model (46) or the synergetic model (47).

CONCLUSIONS

The XPS studies of the oxidic and sulfided $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts revealed the chemical species, the surface structure of the catalysts, and the promoting effect of Co. The salient findings of this study are as follows:

(1) Co exists mainly as Co_3O_4 and " CoAl_2O_4 ," the fraction of Co_3O_4 increasing with increasing CoO content.

(2) With the preparation method, the fraction of Co_3O_4 increases in the order $\text{Co}-(\text{Mo})/\text{Al}_2\text{O}_3 < \text{Mo}-(\text{Co})/\text{Al}_2\text{O}_3 < (\text{Co}-\text{Mo})/\text{Al}_2\text{O}_3$.

(3) With the surface structure of the oxidic catalysts, the sequential impregnation of Co over $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts results in a "bilayer" structure where Co covers part of Mo phase. In the reverse impregnation order, Mo covers part of Co.

(4) In the case of simultaneous impregnation, Mo and Co seem to form a "sepa-

rate-phase" structure on the Al₂O₃ surface.

(5) The surface structure of the sulfided catalysts is essentially similar to that of the oxidic precursor catalysts, although Co and Mo are sulfided and sintered.

(6) The stabilization of Mo phase by Co, most likely by "CoAl₂O₄," is substantiated, the dispersion of Mo phase being held better and the sulfidation degree of Mo being held lower.

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