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Surface Chemistry of Activated Hydrodesulfurization Catalysts by X-Ray Photoelectron Spectroscopy

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The surface chemical composition has been monitored by X-ray photoelectron spectroscopy (ESCA) for a series of hydrodesulfurization catalysts (Co–Mo–Al_2O_3) as a function of bulk cobalt concentration and fixed molbydenum concentration, with respect to sulfiding with a mixture of $H_2S:H_2$ at elevated temperatures. The chemical species present on the surface of the alumina-based catalysts are compared with those present on a carbon-based Co–Mo catalyst. It is concluded that in addition to a sulfided molybdenum species, the catalyst surface is rich in a reduced, but not sulfided, cobalt species. For alumina supports, the fraction of surface cobalt available for reduction is found to be tied directly to catalyst fabrication.

I. INTRODUCTION

Hydrodesulfurization (HDS) catalysts are used to eliminate sulfur contaminants from petroleum feedstocks, an important aspect in reducing atmospheric pollution. The starting catalyst is composed of oxides of cobalt and molybdenum on an alumina support. It is activated during the process of sulfur removal. The nature of this active state has been the subject of numerous classical catalytic studies and has recently been reviewed by Schuit and Gates (*1*).

Commercial HDS catalysts are composed of cobalt oxide in the concentration range of 3 to 5% CoO and molybdenum oxide in the range of 12 to 15% MoO_3. The concentration ranges make this system very attractive for study by X-ray photoelectron spectroscopy (XPS) and indeed it is the most widely studied catalyst system by this technique (*2–7*). The features of XPS which make it suited for catalyst studies revolve about the surface sensitivity of the technique, its ability to detect changes in relative concentration of surface atoms as well as changes in the chemistry of these surface atoms upon reaction (*9, 10*).

In contrast to most of the published XPS work which has concentrated on the nature of the Mo species present on HDS catalysts, the primary focus of our study is concerned with the nature of cobalt in the sulfided or activated catalyst. Since it is known that these metal ions can interact with the alumina support under certain conditions, catalysts prepared on a carbon-based support were also investigated.

II. CATALYST PREPARATION

The catalyst base, $\frac{1}{16}$-in. γ-alumina extrudates, was fabricated from spray-dried, precipitated alumina powder and was calcined at 650°C. Molybdenum was introduced by impregnating calcined alumina extrudates to pore volume saturation with ammonium heptamolybdate, drying at 120°C, and calcining at 650°C. This catalyst, with 12% MoO_3 on alumina, served as a base for succeeding catalysts in which cobalt was introduced at levels of 2, 4, and

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6% (as CoO) by a second pore volume saturation impregnation step. These Co–Mo catalysts were then dried at 120°C and calcined at 650°C.

To provide samples which were generally more suitable for ESCA examination, the catalysts were ground into fine powders. For sulfiding, the catalysts were held between two glass wool plugs in 8-mm diameter Pyrex glass reactor tubes which were mounted in a temperature-controlled oven and connected to a gas manifold. In this configuration a variety of gases could be made to flow over the catalyst bed while it was mounted in the oven. The samples were heated to 400°C in a stream of dry nitrogen. At 400°C, the nitrogen flow was stopped, and a mixture of 10% hydrogen sulfide and 90% hydrogen was passed over the catalyst. Flow rates varied due to differences in pressure drop between samples but were typically 30 ml/min.

The sulfiding reaction appeared to go to completion very rapidly as judged by the evolution of water vapor which is a reaction product. Nevertheless, the $H_2S:H_2$ gas flow was maintained for 45 to 60 min in every case to insure as complete a sulfiding as possible. The catalysts were cooled to room temperature while still in the reactor oven. The $H_2S:H_2$ mixture continued to flow through the reactor tubes during the cooling process.

The sulfided catalysts were transferred under nitrogen to a nitrogen filled dessicator and were placed in a large glove bag attached to the probe end of the ESCA spectrometer. After purging several times with nitrogen, the glove bas was filled, and the samples were placed on the sample mounts covered with double-sided tape, inserted onto the sample probe, and introduced into the spectrometer for measurement. Generally, the sulfided catalysts were ready for examination within 1 hr after being removed from the reactor. For some measurements pressed wafers were sulfided and handled in the same manner.

TABLE 1

Supported Catalysts Studied

Catalyst	CoO (wt%)	MoO_3 (wt%)
Alumina-supported catalysts		
A	0	12
B	2	12
C	4	12
D	6	12
A–S	0	12
B–S	2	12
C–S	4	12
D–S	6	12
C′ (790°C)	4	12
C′–S (790°C)	4	12
Carbon-supported catalysts		
AC	0	15
BC	6	30
AC–S	0	15
BC–S	6	30

The carbon-supported catalyst was prepared on a 12 × 20-mesh Darco carbon by pore volume saturation with an aqueous solution of ammonium molybdate followed by mild calcination at 230°C in air for 30 min to prevent extensive Mo redistribution during the subsequent cobalt deposition. The cobalt was then deposited from an aqueous solution of cobalt nitrate, and the catalyst was then dried at 110°C prior to use. Samples containing Mo on Darco and Co on Darco were also prepared for comparison. The Darco-supported catalysts were sulfided under conditions similar to those described above.

Table 1 lists the catalysts prepared for use in the sulfiding experiments.

III. SPECTRAL MEASUREMENTS

XPS spectra were obtained with a Hewlett–Packard 5950 A ESCA spectrometer using monochromatic Al$K\alpha$ radiation. Charging effects were minimized by use of an electron flood gun. For the Co 2*p* lines a 50-eV scan was used, and data were ac-

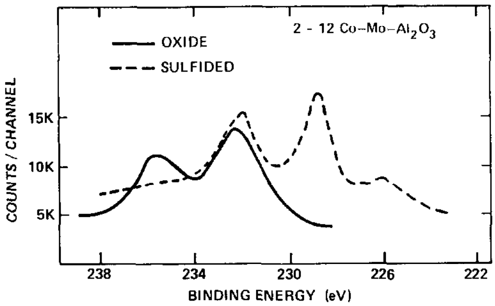

FIG. 1. Mo 3*d* lines for catalysts B (before) and B–S (after) presulfiding. This catalyst is a 2–12 Co–Mo catalyst.

cumulated for up to 10 hr. For the Mo 3*d*, S 2*p*, and Al 2*p* lines, 20-eV scans were used. Wherever possible, spectral accumulation times were kept constant to facilitate direct comparisons of the data. Spectra were analyzed in terms of relative intensities (peak areas), relative changes in binding energies and, particularly in the case of cobalt, peak separations and satellite structure.

IV. SURFACE CHEMISTRY OF ALUMINA-BASED CATALYSTS

Figure 1 shows the Mo 3*d* spectra for catalysts B and BS. The lines are considerably broader than those for (bulk) MoO_3 and MoS_2 as shown in Fig. 2. This broadening, particularly in the case of the oxide, has been attributed both to interactions of Mo with the support (*4*, *11*) as well as charging effects due to the insulating property of the aluminum oxide, Al_2O_3. For the sulfided catalyst (*2*, *3*, *6*, *7*, *12*) the Mo 3*d* lines have shifted to lower binding energy by ~4 eV indicating the presence of Mo in a more highly reduced state, probably Mo^{IV}. ESR spectra obtained from the activated catalyst indicates that Mo^{V} species are present, at levels on the order of 1%.[1] The high binding energy tail in the XPS spectrum also shows that some Mo^{VI} is still present, less than 10%. It is not known whether this represents unreacted MoO_3 or reoxidized reduced Mo^{IV}. The S 2*s* line appears on the low binding energy side of the spectrum. Examination of the S 2*p* spectrum clearly shows little if any oxidized sulfur species (SO_4^{2-}) present, suggesting the residual Mo^{VI} is due primarily to unreacted starting MoO_3. The S 2*p* spectra from Catalyst A–S and sulfided MoO_3 (bulk) are shown in Fig. 3. The broadened S 2*p* lines reflect charging effects, the presence of different Mo oxidation states, and possibly S other than in the form of S^{2-}. The binding energy of S in SO_4^{2-} would however be ~7 eV higher in binding energy.

The Mo 3*d* spectra observed for catalyst pairs C and C–S, D and D–S, C′ and C′–S are virtually identical with the spectra shown in Fig. 1 and discussed above.

As implied above, much less attention has been focused on the changes which occur in the spectrum of cobalt upon sulfiding of the catalyst. In general, whenever cobalt was examined attention was focused solely on the $2p_{\frac{3}{2}}$ line (and accompanying satellites). In this work, both Co 2*p* spin orbit components (and satellites) have been examined. Figure 4 shows the spectrum of the Co 2*p* lines obtained from a sputtered film of Co metal on glass. The solid curve from the air-exposed film shows the presence of two Co species with spin orbit splittings of 15 and 16 eV, respectively. After Ar ion etching, the surface oxide is removed, and a film of metallic Co remains. This spectrum is characterized (dashed curve) by a spin orbit splitting of 15 eV, with no discernible satellite structure.

There have been several reports in the literature where satellite structure and spin orbit splitting have been used for determining the oxidation state of cobalt in both unsupported and supported systems. XPS spectra of paramagnetic Co^{2+} species are characterized by a spin orbit splitting of

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[1] ESR estimates of Mo^{V} concentrations were made by comparing the number of spins of the $g = 1.96$ resonance (Mo^{V}) with that of standard phosphomolybdate glasses of known Mo^{V} concentrations (unpublished work).

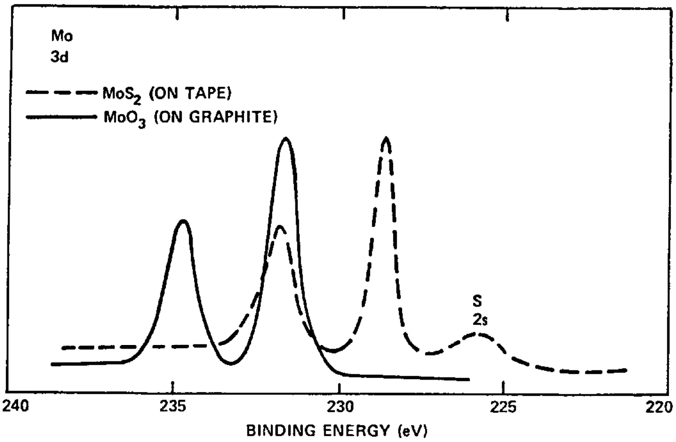

FIG. 2. Mo 3*d* lines for unsupported MoO_3 and MoS_2.

16 eV for the Co 2*p* lines and are generally accompanied with pronounced satellite structure. A spin orbit separation of 15 eV is generally seen for diamagnetic Co^{3+} compounds and metallic cobalt with little or no satellite structure (*13*, *14*, *15*).

Figure 5 shows the cobalt 2*p* lines obtained from Catalyst B (2–12 Co–Mo) in both oxide and activated states. Substantial changes have occurred as a result of treatment with H_2:H_2S (90:10) at 400°C. The spectrum obtained from the catalyst in the oxide form is typical of a Co^{2+} species: spin orbit splitting of 16 eV between the $2p_{3/2}$ and $2p_{1/2}$ lines as well as strong satellite peaks separated by ~6 eV from the primary photoline (*14*). The Co 2*p* lines from the activated catalyst have changed both in binding energy and structure in comparison with the starting catalyst. A shift of 2.6 eV to lower binding energy is observed for the Co 2*p* lines upon activation. Even more significant is the reduction in the intensity of the satellite peaks and the sharpening of the spectral lines and the reduction in spin orbit separation to 15.1 eV.

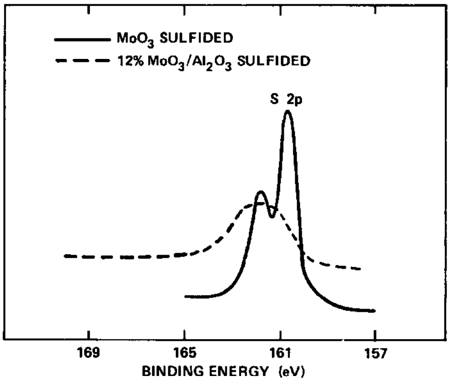

FIG. 3. The S 2*p* lines from sulfided MoO_3 (unsupported) and from Catalyst A-S (12% MoO_3/Al_2O_3 sulfided).

By graphical reconstruction, the cobalt spectrum of the activated catalyst appears to be composed of two distinct cobalt species. Approximately 30% of the signal can be attributed to the cobalt originally present on the catalyst surface while the remainder comes from a species resulting from the activation process.

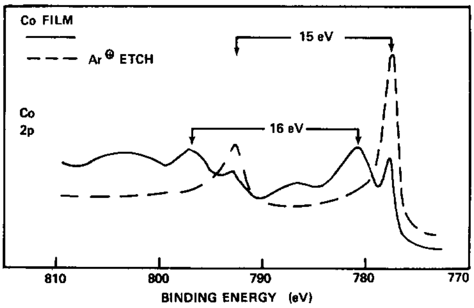

FIG. 4. Co 2*p* lines from a thin film of cobalt on a glass substrate before and after Ar^+ ion etching which removes the thin film of surface oxide.

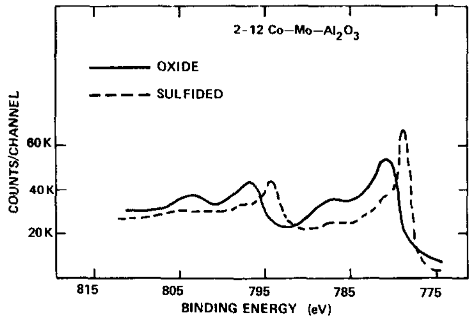

FIG. 5. Co 2*p* lines from Catalysts B and B–S (2–12 Co–Mo/Al_2O_3) showing the effects produced by presulfiding.

Cobalt spectra obtained for catalysts C and D as well as C–S and D–S were essentially the same as those obtained for B and B–S. Small differences in the fraction of unreacted Co were, however, observed. To gain further insight into the nature of the newly generated cobalt species, the spectra were analyzed in terms of the (S/Mo) intensity ratio, using Mo 3*d* and S 2*p* and S 2*s* lines, as a function of cobalt concentration. The results of this analysis are given in Table 2. It is quite clear that the (S/Mo) intensity ratio, and therefore atom ratio, is independent of the total cobalt concentration for these catalysts. For the catalyst containing 6% CoO, the stoichiometry is such that the number of cobalt atoms is approximately equal to the number of molybdenum atoms. To verify that bulk and surface stoichiometries are related, the (Co/Al) intensity ratio obtained from the XPS spectra were plotted as a function of bulk CoO concentration. A linear relationship was obtained to ~5% CoO. At that point observed intensity ratios were lower than expected. These results therefore suggest that the cobalt in the activated state is *not* sulfided. A substantial increase in the (S/Mo) intensity ratio would be expected if cobalt were sulfided, particularly at the 6% CoO level.

TABLE 2

Observed XPS Intensity Ratios for Activated Catalysts[a]

Catalyst	CoO–MoO_3	(S 2*p*/Mo 3*d*)	(S 2*s*/Mo 3*d*)
Alumina base			
A–S	0–12	0.37	~0.21
B–S	2–12	0.35	~0.21
C–S	4–12	0.35	~0.23
C′–S[b]	4–12	0.35	~0.20
D–S	6–12	0.39	~0.23
D–S	6–12		~0.26[c]
Carbon base			
AC–S	0–15	0.37	~0.21
BC–S	6–30	0.36	~0.20

[a] Intensity ratios were obtained by measurement of areas under sulfur and molybdenum lines.

[b] Catalyst C which had been calcined to 790°C to maximize $CoAl_2O_4$ formation.

[c] *In situ* sulfiding of extrudates of catalyst D, see text. Only ~60% of Mo on the surface had reacted.

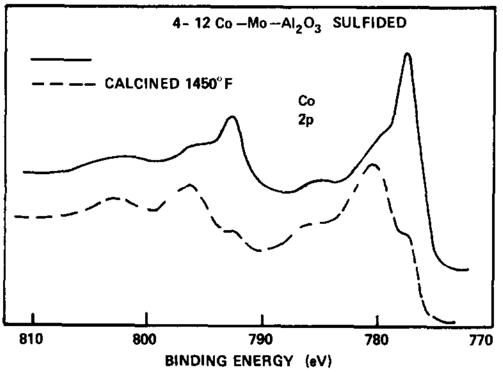

FIG. 6. Co 2*p* lines for Catalyst C–S (4–12 Co–Mo/Al_2O_3) (calcined at 790°C) and Catalyst C′–S (calcined at 650°C). Note the effects of calcination temperature on formation of Co metal.

The spectrum of the cobalt species formed upon activation is characterized by a spin orbit splitting of 15.1 eV and little or no satellite structure, characteristic of diamagnetic Co^{3+} compounds and metallic or zerovalent cobalt. The most likely assignment is to the latter, since the reaction is performed in a reducing environment.

V. EFFECTS OF SUPPORT INTERACTIONS ON SURFACE CHEMISTRY

Previously, it was shown that the alumina support affected the observed ESCA spectra when these were compared with spectra obtained for unsupported materials. Some of these differences can be ascribed to specific interactions of the metal ions with the support. It is also known that under certain conditions a discrete chemical species, $CoAl_2O_4$, can be formed. To fully examine the nature of the support interactions, Catalyst C was calcined to 790°C (to form C′) and then sulfided. Heating the catalyst to this temperature favors the formation of $CoAl_2O_4$. A comparison of the Co spectra of sulfided catalysts C–S and C′–S is shown in Fig. 6. Exposure of the catalyst to high calcination temperatures results in a drastic decrease in the concentration of metallic Co on the surface of the activated catalyst. The major fraction of surface Co is present as $CoAl_2O_4$ which does not undergo any significant reaction (reduction or sulfiding) under the conditions employed in these experiments. The S/Mo ratio, however, is found to be the same as that measured for Catalyst C–S.

Experiments were also performed on carbon-supported catalysts (Catalysts AC, BC, AC–S, BC–S) where alumina interactions are completely removed. Figure 7 shows the Mo 3d spectrum of Catalysts BC and BCS. In addition, a spectrum of Catalyst D–S is included for contrast. The carbon-supported catalyst spectra are considerably sharper than those observed for standard alumina catalysts. Sulfiding produces a shift to lower binding energy of ~3 eV producing little or no broadening of the spectral lines. These narrow lines reflect a difference in the nature of the interaction of the Mo species with the support as well as a difference in the conductivity of the support. In spite of this, the S/Mo intensity ratio on the carbon-supported catalyst is found to be identical with that obtained for alumina-supported catalysts, again demonstrating that, with respect to the catalyst surface, only Mo is being sulfided.

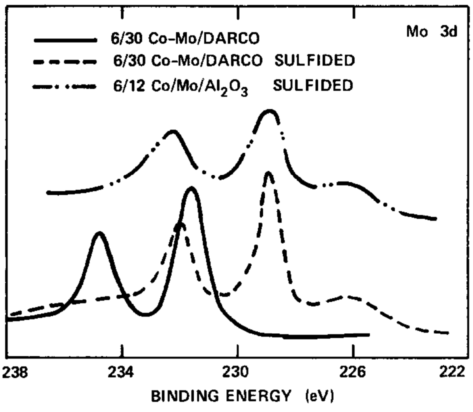

FIG. 7. A comparison of the Mo 3*d* lines for Catalysts AC and AC–S (6–30 Co–Mo/Darco) with Catalyst D–S (6–12 Co–Mo/Al_2O_3).

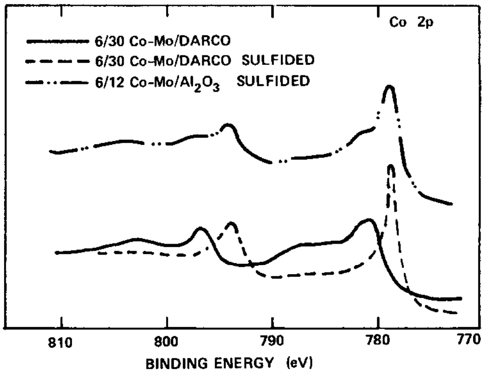

FIG. 8. A comparison of the Co 2*p* lines for Catalysts AC and AC–S (6–30 Co–Mo/Darco) with Catalyst D–S (6–12 Co–Mo/Al_2O_3).

The Co spectra corresponding to the catalysts described in the preceding paragraph are shown in Fig. 8. In the oxide form, the cobalt spectra from D and BC are nearly identical. The Co 2*p* splitting, ΔE, is found to be ~16 eV with fairly pronounced satellite structure, characteristics of paramagnetic Co^{2+} ions. (It should be mentioned that the spectrum of CoO on Al_2O_3, calcined to ~790°C to insure the formation of $CoAl_2O_4$, is the same as observed for these catalyst samples.) Sulfiding in a stream of $H_2:H_2S$ at 400°C results in nearly complete reaction of Co to form the species characterized by $\Delta E \cong 15$ eV

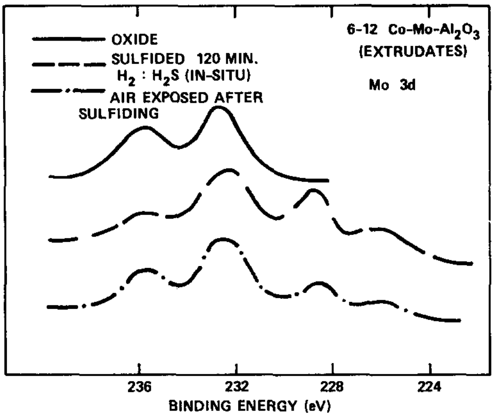

FIG. 9. Mo 3*a* lines for extrudated of Catalyst D (6–12 Co–Mo/Al_2O_3) before and after *in situ* presulfiding. The bottom spectrum shows the resulting spectrum obtained after air exposure.

and little satellite structure, namely, metallic or zero-valent cobalt. For this sample, BC–S, $\geq 90\%$ of the surface Co species have undergone reduction. The superposition of cobalt spectra from BC and BC–S resembles that obtained from D–S.

The difference in the extent of Co conversion on alumina-based catalysts may be attributable to the formation of some surface $CoAl_2O_4$ even though they were prepared at temperatures not expected to enhance the existence of this phase. Spectra obtained for $CoAl_2O_4$ before and after presulfiding under the same conditions used here show that this species is not altered upon treatment. Thus, it suggests that the unreacted Co could be attributed to the presence of such a phase whereas this species ($CoAl_2O_4$) cannot be present on Darco.

A commercial sample of $CoMoO_4$ was presulfided, and the observed XPS spectrum was found to be virtually identical with that obtained for catalyst BC–S, with one major difference: The S/Mo intensity ratio was nearly twice that observed from the sulfided catalyst samples, ~0.65. X-ray diffraction, a bulk measurement, showed the presence of Co_9S_8, with no other Co or any Mo species observed. The ESCA spectrum clearly showed strong Mo^{IV} spectra. These results suggest that, although XRD is not looking at the same part of the sample that the ESCA is, the increased S/Mo ratio can be attributed to a sulfided Co species which does not form when Co and Mo are dispersed on a support.

VI. *IN SITU* ACTIVATION

To verify that the activated catalysts discussed above were not subjected or affected by unintentional exposure to oxygen, several experiments were performed which precluded this possibility. Extrudates of Catalyst D (6% CoO–12% MoO_3) were mounted on a modified sample holder, and XPS spectra were obtained. The sample was then retracted to the sample preparation chamber of the spectrometer and heated to 300°C (the high temperature limit of our probe) in an atmosphere of H_2:H_2S for 2 hr. After cooling and pumping out the preparation chamber, the activated catalyst was returned to the normal position for obtaining spectra. Although 300°C is not the optimum temperature for sulfiding, partial activation has occurred as may be seen in Figs. 9 and 10.

From Fig. 9, using the known relative intensities of the spin orbit components of the Mo 3d doublet, it may be shown that

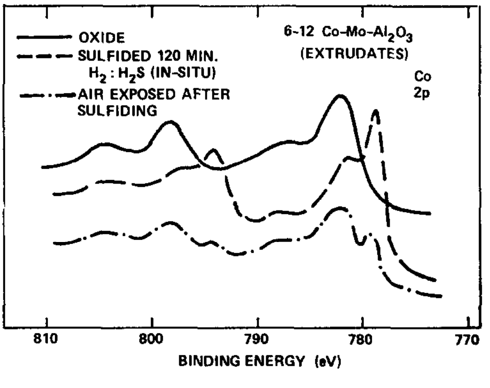

FIG. 10. Co 2*p* lines for extrudates of Catalyst D (6–12 Co–Mo/Al_2O_3) before and after *in situ* presulfiding. The bottom spectrum shows the resulting spectrum obtained after air exposure.

~60% of the observed Mo has been reduced to Mo^{IV}. Approximately 50% of the surface cobalt has also been reduced. The (S/Mo) intensity ratio, using the S 2s line and the reduced Mo species is ~0.26, very close to the values obtained from the non-*in-situ* experiments. This result lends substantial credence to the claim that little or no exposure had occurred in the experiments performed using the glove bag technique and that the surface cobalt atoms are not sulfided.

Figures 9 and 10 also demonstrate the sensitivity of the activated catalyst to air exposure. Both reduced Mo and Co species decrease in intensity with respect to the higher oxidized species present on the activated catalyst, with Co being much more sensitive. A weak SO_4^{2-} peak is also observed in the S 2p spectrum.

VII. DISCUSSION AND SUMMARY

The experiments described above clearly demonstrate the dependence of the surface chemistry of activated HDS catalysts on catalyst fabrication. Mo, present in the starting catalyst as Mo^{VI} (MoO_3), is reduced primarily to Mo^{IV} (and to a much lesser extent to Mo^{V} as found from ESR data). The Mo 3d lines observed from the activated catalyst do not indicate any substantial surface concentration of Mo^{V}. The fraction of surface Mo atoms which are reduced is greater than 90% for all catalysts examined and is independent of the concentration of Co atoms present (for the series examined).

In the case of cobalt, the conclusion derived from the above experiments is that cobalt on the surface is reduced but not sulfided.[2] This was not expected because bulk cobalt is known to readily form the sulfide Co_9S_8 in H_2S/H_2. It has generally been assumed that the surface cobalt oxide on alumina also forms a sulfide presumed to be Co_9S_8. In our experiments when bulk $CoMoO_4$ was sulfided under the same conditions used for the catalyst activation, Co_9S_8 was formed as confirmed by X-ray diffraction and as reflected in the XPS spectrum by an increase in the S/Mo intensity from ~0.35 to ~0.65. For the catalyst containing 6% CoO and 12% MoO_3, the Co/Mo atom ratio is 0.96, approximately the same as that for $CoMoO_4$. Yet, the sulfided catalyst shows a S/Mo intensity of ~0.35. This same value of S/Mo intensity was observed for all catalysts regardless of the cobalt loading when the MoO_3 loading was constant at 12%.

Two possible ways to rationalize the constancy of the S/Mo intensity are the formation of a reduced but not sulfided species such as Co^0 or the formation of a sulfided molybdenum species with a S/Mo atom stoichiometry of 1 (with some form of sulfided cobalt species). We exclude the second of these possibilities based on the result obtained from the sulfided 0 to 12 CoO–MoO_3 catalyst. In that case, in the absence of cobalt, the S/Mo intensity was also ~0.35 just as it was for all the sulfided catalyst with CoO levels up to 6%. This, coupled with the reduction in spin orbit separation between the Co 2*p* lines from 16.0 to 15.0 eV upon H_2S/H_2 reaction, supports the assignment of the reduced surface cobalt to Co^0.

The formation of Co^0 on both alumina and carbon supports suggests that factors

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[2] The conclusion that the surface cobalt atoms are reduced and not sulfided is not in agreement with published XPS literature. In fact, Walton (*8*) has commented from this literature that if one only considers the chemical shifts of the Co 2*p* lines then it can be argued that Co is sulfided but not reduced. His statement is based partially on the work of Frost *et al.* (*13*) for which a chemical shift of −2.4 eV is observed in going from CoO to CoS. This is similar to the shift observed for Co in going from the fresh to activated catalyst. The spectrum of CoS reported by Frost *et al.* (*13*), however, contains strong satellite structure which is not the case for the Co species present on the activated catalyst. This points out the danger of using only chemical shift information in interpreting XPS spectra, particularly of transition metal ions.

other than the type of support may be responsible for this behavior. Since $CoMoO_4$ and Co_3O_4 do form Co_9S_8 upon sulfiding while our catalysts do not suggests that the role of the support is related to the dispersion of CoO and MoO_3 and the size of the crystallites ultimately formed. To confirm the degree of dispersion, the catalyst samples containing up to 6% CoO in the presence of 12% MoO_3 were analyzed by X-ray diffraction. No diffraction patterns were found for any cobalt or molybdenum species. Oxide and sulfided catalysts on carbon also did not give diffraction patterns. A 19% MoO_3 catalyst on Al_2O_3 was examined in both the oxide and sulfide form, but in each case no diffraction pattern for a molybdenum species was observed. These results are interpreted to mean that both metals are widely dispersed and, with respect to cobalt, too low in concentration to be detected by X-ray diffraction.

The S/Mo intensity ratio can be used, in conjunction with Scofield's calculations of photoionization cross sections (16) and the knowledge that the surface cobalt atoms are not sulfided, to calculate the ratio of sulfur to molybdenum atoms on the surface. Bearing in mind that >90% of the surface Mo atoms have been reduced to Mo^{IV}, the calculation results in a (S/Mo) atom ratio of 2. This, plus the magnitude of the chemical shift to lower binding energies, is consistent with, but does not unequivocally prove, the formation of MoS_2 on the surface. The stoichiometry does not rule out the possibility of the presence of the thioanion $MoO_2S_2^{2-}$ as suggested by Walton (*8*).

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