JOURNAL OF CATALYSIS 36, 11-22 (1975)

The Application of X-Ray Photoelectron Spectroscopy to the Study of Molybdenum Oxides and Supported Molybdenum Oxide Catalysts

A. CIMINO

Istituto di Chimica Generale e Inorganica, Università di Roma, Rome, Italy

AND

B. A. DE ANGELIS

Laboratori Ricerche di Base, SNAM PROGETTI S.P.A. 00015 Monterotondo, Rome, Italy

Received December 21, 1973; revised May 17, 1974

X-Ray photoelectron spectroscopy (XPS or ESCA) was applied to the study of molybdenum oxides and supported molybdenum oxide catalysts. It was shown that the reduction behavior of supported oxide is substantially different from that of unsupported MoO_3. Reduction of pure MoO_3 at 400°C, in a stream of hydrogen, for 2 hr, gave a nearly metallic species, while $MoO_3/\gamma\text{-}Al_2O_3$ was not reduced below Mo^{4+}. The greater extent of reduction of MoO_3/SiO_2 compared to $MoO_3/\gamma\text{-}Al_2O_3$ indicated a considerably weaker interaction between MoO_3 and SiO_2 than between MoO_3 and $\gamma\text{-}Al_2O_3$. Both $\alpha\text{-}CoMoO_4$ (green) and $\beta\text{-}CoMoO_4$ (violet), upon treatment at 400°C in flowing hydrogen, gave nearly metallic Mo and some metallic Co. On the basis of this behavior the presence of a cobalt molybdate phase similar to bulk $CoMoO_4$ on the surface of cobalt-molybdenum-alumina catalysts was excluded. The importance of a suitable reference level when considering chemical shifts of insulating samples was pointed out.

INTRODUCTION

The potentiality of X-ray photoelectron spectroscopy (XPS, or ESCA) for the investigation of surfaces renders this technique a promising tool in catalysis. Illustrations of applications to catalytic problems were given by Delgass *et al.* (*1*). Currently several other reports appear in the literature dealing with similar applications (*2-6*). There are, however, some problems in the assignment of a precise physical meaning to the measured quantities. This is particularly true for nonmetallic systems, where charging up of the specimen can simulate chemical shifts, the latter being a fundamental quantity for deriving information on the state of the surface. Also, the transfer of the deductions arising from the observations made in the particular conditions prevailing during the XPS measurements to the case where the catalyst works as such, poses problems not dissimilar from those in Auger spectroscopy, LEED, and FIM. The difference of conditions requires a stringent examination of the physical meaning of the experimental measurements. Thus one can inquire whether the vacuum conditions, which tend at the same time to deplete the surface of some of the normal and volatile components (such as oxygen in oxide catalysts) and to deposit some impurities (carbonaceous materials), can disguise the true situation occurring in a chemical reactor. There could be the danger, therefore, of deriving information which does not apply to the catalyst, and which would erroneously be correlated to catalytic properties.

With the purpose of tackling some of these problems, we have made a study of molybdenum oxide, supported and unsupported, and of hydrodesulfurization catalysts (cobalt–molybdenum–alumina). These systems have already been studied by various physical techniques, so it is also useful to look for correlations with previous findings. Thus the results will be discussed firstly in the context of the application of XPS to oxide surfaces, and then with a view to making deductions about the specific systems.

EXPERIMENTAL

An AEI ES 100 spectrometer has been used, with X-ray excitation from Mg (1253.6 eV) or Al (1486.6 eV).

The specimen, if in polycrystalline powder form, was pressed in a trough present in the sample holder, which can be 1–2 mm deep, and 6×15 mm^2 in area. The area roughly corresponds to the surface exposed to the X-ray beam. If the specimen was a metallic foil it was held on the holder with a platinum wire. The sample holders were made of copper or of stainless steel. Gold plated holders have been used on some occasions. The specimen holder allowed a voltage to be applied from an external source.

The spectrometer does not provide a pretreatment chamber, and therefore all operations described later (reductions, oxidations) have been carried out in a separate apparatus. The sample holder was placed in a pyrex tube and the oxidation or reduction treatment was carried out in a flow of the appropriate gas. After cooling, the specimen was rapidly inserted into the spectrometer. In some cases, a further temperature treatment in vacuum was given inside the spectrometer.

Reagent grade products were used. MoO_3, MoO_2, and metallic molybdenum (3 *N*) were Alfa-Ventron products. The supports were Cabosil (Cabot Corp.), boehmite (Laporte Industries Ltd.), η-Al_2O_3 (Davison Chemical), γ-Al_2O_3 (Laporte Industries Ltd.), or laboratory aluminas prepared according to MacIver *et al.* (*7*).

Supported samples were prepared by conventional impregnation techniques, using a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ (Merck, p.a.), followed by drying at 120°C and firing at 400, 500, or 600°C. Cobalt–molybdenum–alumina catalysts were prepared in three different ways: (a) impregnation with ammonium heptamolybdate first; (b) impregnation with Co nitrate first; (c) impregnation with a solution containing both Co and Mo.

Na_2MoO_4 was obtained by dehydrating $Na_2NoO_4 \cdot 2H_2O$ (C. Erba) at 130°C. Violet β-$CoMoO_4$ was prepared by heating $CoMoO_4 \cdot H_2O$ (Alfa-Ventron) at 600°C and cooling it to room temperature. Green α-$CoMoO_4$ was obtained by grinding the violet form.

EXPERIMENTAL PROBLEMS IN THE XPS TECHNIQUE

Charging up of the Sample and Reference Levels

In oxide systems, particularly when supported on an insulating oxide such as alumina, the problem of the charging of the sample can be very serious. Ascarelli and Missoni (*8*) have shown that this problem arises from the secondary emission of electrons from both sample and enclosing chamber. Even a geometrical variation of the relative position of specimen and window or chamber can affect the charging of the sample (*9*).

Different methods have been proposed (*8, 10–15*) to account for the shift in potential of the specimen due to the accumulation of surface charge, but none of them is free from drawbacks.

The use of Scotch tape as a support for the spread sample powder is not based on a good contact between the "standard" (the Scotch tape) and the specimen holder, on the one hand, and between the standard and sample powder on the other. Indeed, it could be argued that the carbon 1s reference line is essentially contamination which is dispersed on the specimen, the Scotch tape providing a source of contamination in addition to the normal source (oil pumps).

The deposition of a layer of gold on the sample decreases the intensity of the spectrum, and, moreover, there can be some doubt about the gold particles being at the same potential as the surface of the insulating sample.

In the case of mixing with a reference substance (*14*) electrical contact between sample and standard is by no means obvious.

The reference based on the C 1s line arising from contamination is operationally much simpler, and it is as good as other methods. If the carbon line has to be taken as standard, it must belong to a single chemical species, since a difference of chemical combination can produce an observable shift. This can be checked by observing whether a single line is present. It is also necessary to prove that the line belongs to a species in electrical contact with the specimen, if the latter is nonconducting, and not with the (conducting) sample holder. To check this, the specimen holder can be connected with a voltage-supplier, and the shift of the photoelectron lines can be monitored. The situation for the C line is illustrated in Fig. 1. Curve (a) shows the C line in the absence of an applied voltage for a sample of Na_2MoO_4. The C peak shows a shoulder, which could arise either from the presence of two chemically different carbon atoms, or from carbon atoms belonging to different electrical potentials. If a voltage is applied, no shift is observed for the Mo peaks. The situation for the C peak is shown in curves (b) and (c) for an applied voltage of −5V and −10V, respectively. It is clear that the C peak in (a) was the result of a superposition of one peak belonging to a species in electrical contact with the specimen holder, and one peak not in electrical contact with the holder, and therefore due to carbon on the Na_2MoO_4 sample which can be taken as reference. Evidence of the impurity carbon being at the same potential as the surface of an insulating sample has been reported by Johansson *et al.* (*10*). Our spectra of MoO_3 under an applied voltage show that the C line is displaced by the same amount as the MoO_3 peaks. Experiments on MgO, the spectrum of which was displaced by varying the potential of a Faraday cage mounted inside the spectrometer, also demonstrated that electrical contact exists between the impurity carbon and the sample surface (*9*).

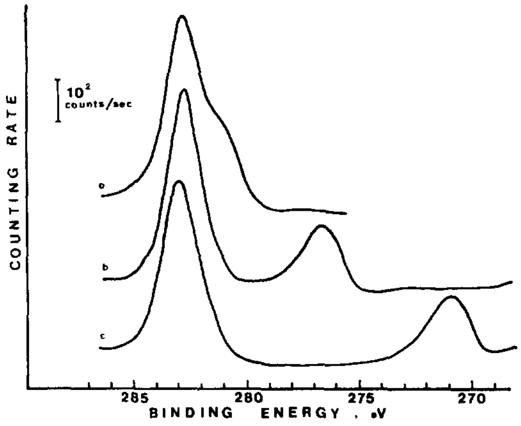

FIG. 1. The C 1s peak of a sample of Na_2MoO_4 (curve a). A voltage of −5V (curve b) and −10V (curve c) is applied to the sample holder.

Different values for the C 1s level have been reported in the literature (*10*): 283.8 eV, 284.3 eV, 285.0 eV. The binding energy values reported in our work are referred to C = 283.8 eV. A different choice would change our absolute values, but not the relative values. A difficulty in the use of contamination carbon as a reference is the fact that the chemical species to which C belongs is not known although one has reasons to assume it belongs mainly to a single species, probably elemental carbon. When the specimens are of a similar chemical nature, the carbon contamination is also likely to be similar in nature.

The use of aluminum and oxygen lines as reference has been recommended for supported catalyst samples (*15*). It has the advantage that Al and O are already present in the sample and can be used together with carbon. Analogous considerations could be made for the Si lines of silica-containing supports. These different reference lines give consistent results, as shown also in our work.

The Intensity of Peaks and Escape Depth

The XPS technique is in principle suitable for quantitative analysis. The height (or, better, the area) of the peak is a function of several parameters, some of which are difficult to control and to define. The empirical study of Wagner (*16*) shows that the sensitivity is a function of the atomic number. For the same element, however, the emitted photoelectron reflects the state of the surface, and the amount of contamination. Indeed in our work the intensity of peaks became lower as the C peak became higher.

The escape depth of electrons can be defined only in stringent vacuum conditions. It is now becoming clear that the escape depth is lower than suggested in earlier studies (*17*), the usual figures now accepted being around 10×10^{-8} cm (*18, 19*). This low value of the escape depth stresses the "surface character" of XPS and the necessity for surface cleanliness.

In addition to contamination, a factor that influences to a large extent the intensity of the peak is the sample orientation with respect to the electron collecting slit. Recently Fraser *et al.* (*20*) have shown that for the case of a flat surface, the signals coming from the outermost layers are enhanced with respect to those coming from lower layers if the electron emission is collected at a low angle to the surface plane. For a particulate specimen the geometry is not easily defined, and the effect is difficult to analyze. We have observed that the C signal intensity is reduced less than other signals when going to low collecting angles, thus pointing to the presence of carbon impurities in the outer layer. For the other component (Mo, Al) the effect of angle variation could not be obtained unambiguously. The quantitative estimate of component concentration and in particular their distribution in the outer layers is therefore an open problem, especially for catalysts whose surfaces are not in a well-defined, clean condition.

EXPERIMENTAL RESULTS

(*a*) *Pure Compounds*

Table 1 reports the binding energy (B.E.) values of the Mo 3d doublet in the various compounds and oxidation states relevant to this work, as measured in our laboratory. These values are referred to C = 283.8 eV.

The $3d_{3/2}$–$3d_{5/2}$ doublet gives the most intense peaks in the X-ray photoelectron spectrum of Mo. Its position is dependent mainly upon the oxidation state. It is therefore possible to study the oxidation–reduction behavior of Mo and of its oxides by following the displacements of the 3d doublet. In several instances one obtains composite spectra resulting from the superposition of more than one peak, and this must be kept in mind in the examination of the spectra. In what follows the results will be illustrated by showing representative examples. Figures 1–8 have been obtained by drawing, on transparent paper, over the actual spectrum. Errors in the estimate of the B.E. vary with the type of specimen, ranging from ± 0.1 eV for sharp symmetric peaks to a few tenths of an electron-volt for broad and/or asymmetric peaks. The signal to noise ratio was in the range 50–100.

TABLE 1

BINDING ENERGY VALUES OF THE Mo 3d DOUBLET IN DIFFERENT COMPOUNDS AND OXIDATION STATES (C = 283.8 eV)

	$3d_{3/2}$	$3d_{5/2}$
MoO_3	234.8	231.6
MoO_2	231.5	228.3
MoO_x[a]	230.4	227.2
Mo metal	230.0	226.8
Mo^{5+}	233.8–233.3	230.6–230.1
Na_2MoO_4	234.0	230.9
$CoMoO_4$	234.5	231.4

[a] Oxygen containing "metallic" form of Mo, obtained by reduction of the oxides (see text).

Molybdenum foil. Molybdenum metal has been studied in the form of a foil, which was mounted in such a way as to cover completely the area of specimen holder exposed to X-rays. The foil was peeled before mounting inside the spectrometer so that a fresh surface was examined. Fig. 2, curve a shows the Mo doublet and the oxygen 1s peak. One can see the presence of Mo metal (230.0 eV and 226.8 eV) and a small amount of MoO_3 (234.8 eV and 231.6 eV). The spectrum of oxygen (1s peak) clearly consists of at least two components at 530.0 and 531.8 eV. Different treatments were then applied. A 2-hr heating at 300°C inside the spectrometer and a subsequent exposure to the air causes the disappearance of Mo^{6+} (B.E. 234.8 eV) and the appearance of a shoulder at about 233.8 eV. The oxygen peak shows a decrease of the high B.E. component. Reduction in a stream of H_2 at 450°C, for 2 hr, eliminates most of the oxide (curve b). The oxygen peak shows a strong decrease of the low B.E. component. Heating the sample inside the spectrometer at 300°C for 15 hr produces only a small increase in the low B.E. component in the oxygen peak and no significant change of the Mo doublet. MoO_3 can be formed again by heating the sample at 250°C in oxygen for 1 hr (curve c). Concurrently, the low B.E. component of the O peak strongly increases (notice reduced scale). Reduction at 300°C in a stream of H_2 eliminates most of the MoO_3, as shown by the diminution of the 234.8 and 231.6 eV Mo components.

Molybdenum oxides. The spectra of MoO_3 and of the products of its reduction in a stream of H_2 are reported in Fig. 3. Curve (a) refers to pure MoO_3 and shows the 3d doublet at 234.8 eV and 231.6 eV. Two-hour heating at 300°C produces only a beginning of the reduction (small shoulders marked by arrows in curve b). One hour heating at 400°C (curve c) gives a reduced

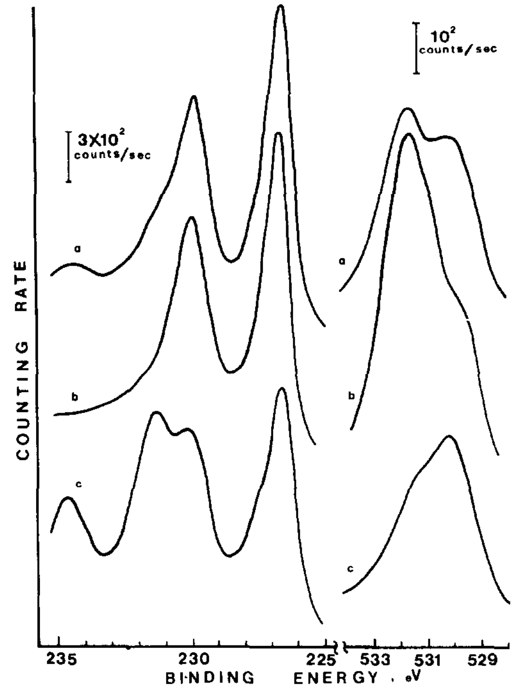

FIG. 2. Molybdenum 3d doublet (left) and oxygen 1s peak (right) from a metallic Mo sheet (curve a), after reduction at 450°C, for 2 hr in a stream of hydrogen (curve b) and subsequent oxidation at 250°C in oxygen (curve c). Curve c of oxygen is on the same scale as the Mo peaks.

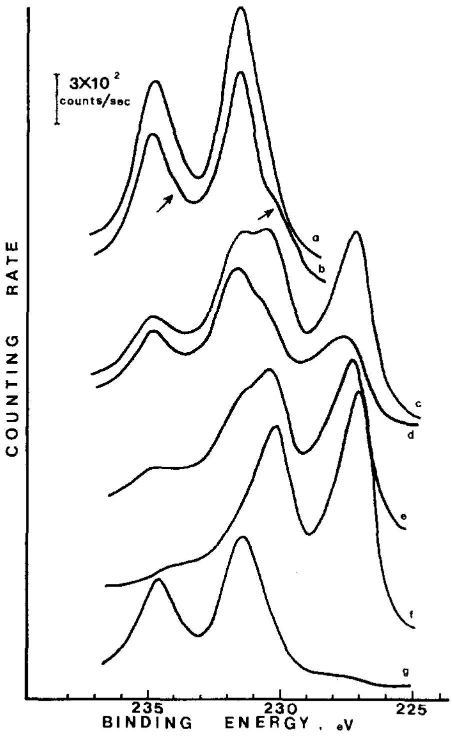

FIG. 3. XPS spectra of pure MoO_3 and its reduction products (see text).

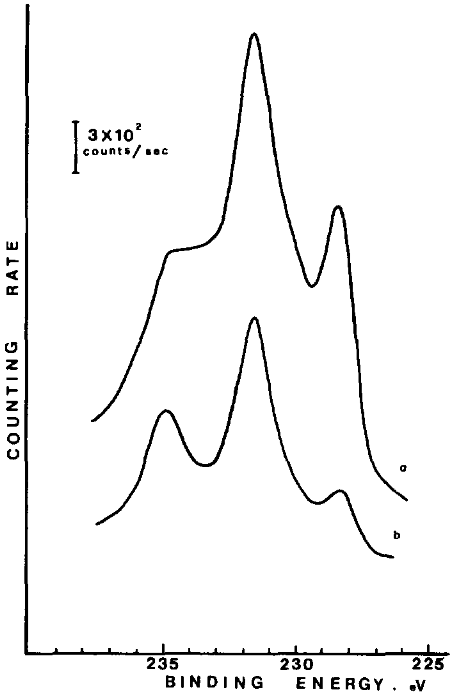

FIG. 4. XPS spectrum of MoO_2 as taken from the bottle (curve a) showing the oxidation on the surface. Curve b: spectrum of MoO_3 slightly reduced (1 hr at 400°C, 500 Torr H_2).

product (230.4 eV, 227.2 eV) in addition to the starting MoO_3. The reduced product tends to reoxidize in air: after standing for 3 days outside the spectrometer curve d is obtained, which shows, by comparison with curve c, a definite trend toward the state described by curve a. Subsequent reduction at 400 and 500°C gives mainly the reduced product (curves e and f). One should notice the shoulder in the range 233–234.5 eV. The reduced product can be easily oxidized in oxygen at 200°C (curve g).

MoO_2, as taken from the bottle (Fig. 4, curve a), is actually oxidized on the surface. The $3d_{5/2}$ peak of MoO_3 is almost coincident with the $3d_{3/2}$ peak of MoO_2, thus leading to the characteristic three-peak shape. The flatness of the curve in the region 233.5–234.5 eV might indicate the presence of oxidation states less than 6+ (probably in the range 6+ to 5+).

MoO_3 partially reduced (1 hr at 400°C, 500-Torr static H_2) shows again the three-peak shape characteristic of MoO_3–MoO_2 mixture, without the flat region (Fig. 4b). A spectrum very similar to curve b is obtained by a mechanical mixture MoO_2–MoO_3 in the ratio 5:1 by weight.

From the spectrum of Fig. 4 the B.E. of molybdenum in MoO_2 can be obtained: 231.5 eV and 228.3 eV.

Sodium molybdate. Na_2MoO_4 gives a B.E. of 234.0 eV and 230.9 eV for Mo.

(b) *Effect of an Applied Voltage*

The application of a voltage (e.g., −10V) to the sample holder has no effect on the spectrum of MoO_3: neither the Mo nor the C peak is displaced. With a higher applied voltage (e.g., −40V) the peaks are broadened, but not substantially displaced. If the spectra are recorded at different times after the insertion of the sample into the spectrometer, MoO_3 being continuously exposed to the X-ray irradiation, the peaks are displaced by an amount smaller than the applied voltage. A deformation of the peaks also takes place. However after irradiation for 8 hr even a small voltage (e.g., −5V) displaced the spectrum by the same amount as the applied voltage, thus indicating that the sample has become a conductor. The spectrum with no applied voltage, taken after 8 hr, is identical to the starting one. The sample when extracted from the spectrometer is bluish, which indicates a loss of oxygen.

Partially reduced MoO_3 (Fig. 4, curve b) is displaced by an amount exactly equal to the applied voltage. The same behaviour is shown by MoO_2 in accordance with the conducting properties of this compound. Mechanical mixtures $MoO_2 + MoO_3$ behave like MoO_3 when the trioxide is present in high percentages (e.g., 50%, by weight), while at low percentages (e.g., 20% by weight and less) the applied voltage is only partially followed. By X-ray irradiation the mixtures gradually became conducting, and this happened more quickly at low percentages of MoO_3.

In all the spectra recorded with the application of a voltage, the C peak behaves exactly like the Mo peaks: it is displaced by the same amount, so that the relative distance is unchanged. Moreover, when the applied voltage produces a deformation of the shape of the Mo peaks, the same effects are observed on the C peak.

(c) *Supported Oxides*

Several samples of MoO_3 supported on γ-Al_2O_3, η-Al_2O_3 and SiO_2 (Cabosil) have been examined. The Mo 3d peaks are less intense and broader than in pure MoO_3 (full width at half maximum, FWHM, ~2.5 eV vs ~1.5 eV). The signal to noise ratio was typically around 20. Binding energy values of Mo in the oxidized state are in agreement with those of MoO_3.

Figure 5a shows the spectrum of the oxidized state of a sample of MoO_3 (5% atomic, meaning 5 Mo atoms/100 Al atoms, equivalent to 12.4% MoO_3 by weight) supported on γ-Al_2O_3. Figure 5b shows the reduced sample (2 hr at 400°C, in a stream of H_2).

Figure 6 reports a representative spectrum of a cobalt–molybdenum–alumina catalyst in the oxidized state (curve a), after a 2-hr reduction in a stream of H_2 at 380°C (curve b), and at 500°C (curve c).

In Fig. 7 the spectra of MoO_3 on SiO_2 (5% atomic, i.e., 5 Mo atoms/100 Si atoms) in the oxidized state (curve a) and after reduction in a stream of H_2 for 2 hr at 400°C (curve b), and 500°C (curve c) are reported. For comparison, the spectrum of MoO_3 on γ-Al_2O_3 reduced at 400°C is also given (curve d). The reduction treatment of the supported samples is analogous to that performed on pure MoO_3, but the reduction occurs to a much smaller extent. One should note the displacement of the peaks and the appearance of a low B.E. shoulder which is more pronounced after reduction at 500°C (2 hr), or after longer reduction times (15 hr) at 400°C.

The displacement is due to the diminution of the amount of Mo^{6+} and to the formation of a less oxidized state, possibly Mo^{5+}. The low B.E. shoulder is due to the formation of Mo^{4+}, which is the lowest oxidation state that can be obtained in alumina-supported Mo catalysts.

Silica-supported MoO_3 is considerably more reducible (Fig. 7). Reduction at 500°C gives a certain amount of the nearly "metallic" MoO_x, which was obtained from pure MoO_3.

The spectrum of cobalt was examined in

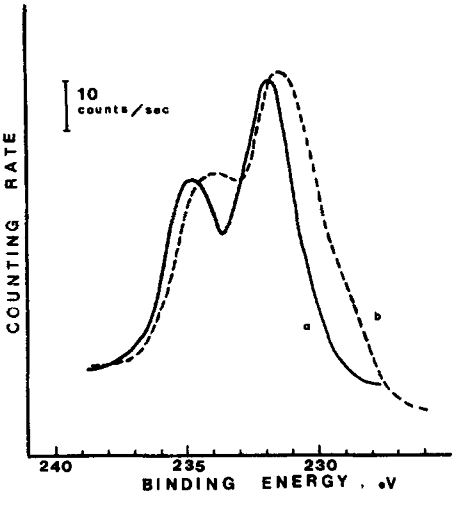

FIG. 5. XPS spectrum of the Mo 3d doublet in a sample of MoO_3 (5% atomic) supported on γ-Al_2O_3, in the oxidized (curve a) and reduced (curve b) state. Reduction conditions: 2 hr at 400°C in a stream of H_2.

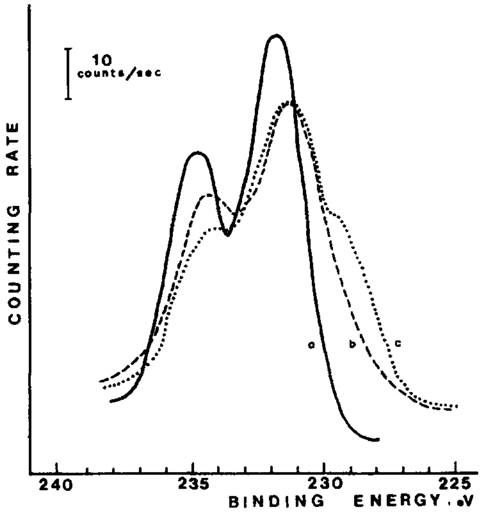

FIG. 6. XPS of the Mo 3d doublet in a cobalt–molybdenum–alumina catalyst in the oxidized state (curve a) and after 2-hr reduction in a stream of H_2 at 380°C (curve b), and at 500°C (curve c).

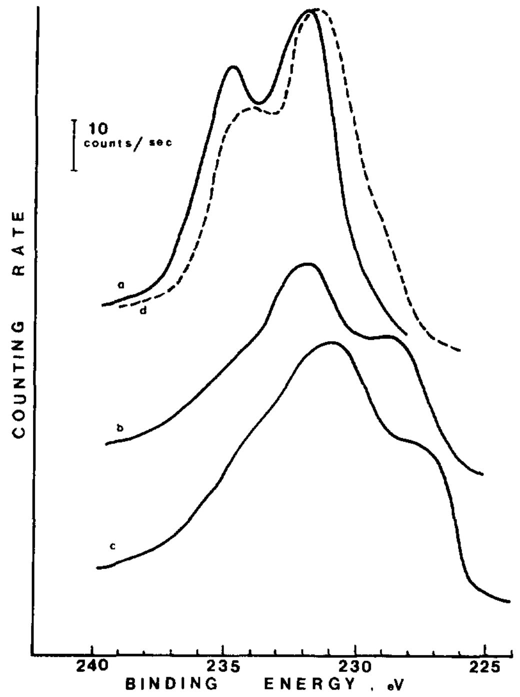

FIG. 7. XPS spectrum of the Mo 3d doublet in a sample of MoO_3 (5% atomic) supported on SiO_2 in the oxidized state (curve a), after reduction for 2 hr at 400°C (curve b), and at 500°C (curve c) in a stream of hydrogen. For comparison the spectrum of MoO_3 on γ-Al_2O_3 reduced at 400°C is also given (curve d).

several samples containing from 4% at. to 1.5% at. cobalt on γ-Al_2O_3 and in all the Co–Mo–alumina catalysts, which contained 2.5% at. cobalt. The $2p_{3/2}$ peak, the most intense of all Co peaks, was rather weak and broad (FWHM ~4 eV).

Samples containing 1.5% at. Co give peaks that are barely above the noise level. A 2-hr reduction at 400°C, in a stream of H_2, did not affect the Co peak. Impregnation with Co first or with Mo first gave no difference in the spectra, both for the oxidized and the reduced samples. Also, samples fired at different temperatures (400 or 600°C) failed to show any difference, even though a difference in colour could be seen. The Co $2p_{3/2}$ peak intensities (measured as peak heights from the horizontal baseline at the low B.E. side) were on the average some 20% higher in samples containing only supported cobalt than in Co–Mo–alumina catalysts, a possible indication that cobalt tends to be sited below the molybdenum.

(d) Cobalt Molybdate

Both α-$CoMoO_4$ (green) and β-$CoMoO_4$ (violet) were examined. In the oxidized state the binding energy of Mo was 234.5 eV and 231.4 eV for both forms, i.e., ~0.3 eV lower than in MoO_3. The structural differences between the green and the violet

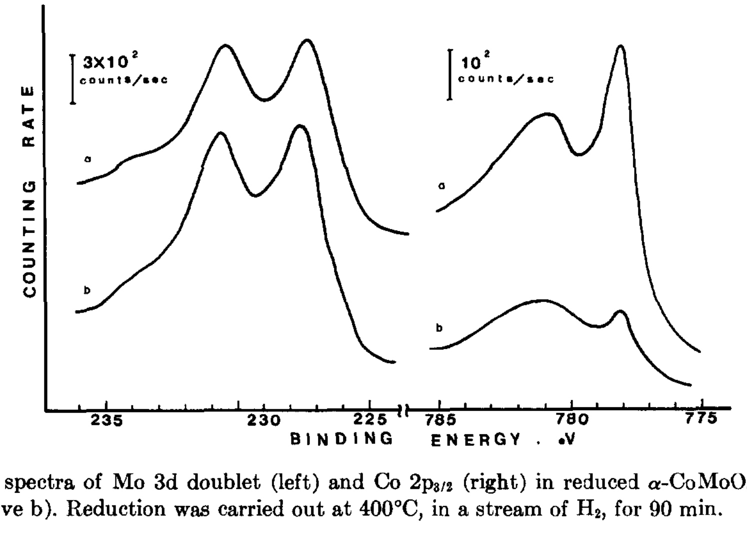

Fig. 8. XPS spectra of Mo 3d doublet (left) and Co $2p_{3/2}$ (right) in reduced α-$CoMoO_4$ (curve a) and β-$CoMoO_4$ (curve b). Reduction was carried out at 400°C, in a stream of H_2, for 90 min.

form do not therefore give rise to appreciable changes in the spectrum.

Figure 8 shows the spectra of Mo and Co in the two forms after reduction. The reduction was carried out in the same conditions for both forms of $CoMoO_4$ viz., 90 min at 400°C in a stream of hydrogen. From the spectrum of cobalt it can be seen that Co^{2+} ions are reduced, and that the amount of metallic Co formed is larger for green $CoMoO_4$. Molybdenum goes mostly to MoO_x, with some Mo^{5+} and Mo^{6+} left.

The different reducibility of the two forms of cobalt molybdate can be seen also from the Mo spectrum, when the reduction occurs to a lesser extent than in the case reported in Fig. 8: a greater intensity of the peak at 230.5 eV as compared to the one at 227.5 eV indicates a larger amount of molybdenum left in its high oxidation states (6+, or possibly 5+) for the violet form. It should be noted that thermogravimetric studies of cobalt molybdate reduction (*21*) also confirm the greater ease of reduction of the green form as compared to the violet one, e.g., 4.5% loss by weight in H_2 at 450°C for the green form, in comparison to 0.2% at the same temperature for the violet form.

Discussion

It is convenient to discuss the specimens (pure compounds, or supported oxides) prior to reduction before considering the reduced compounds or reduced supported oxides. For the "oxidized" state, the previous investigations of molybdenum oxide systems based on physico-chemical techniques provide a firm basis for correlating structural and XPS data.

Most of the information refers to the molybdenum ions, which give rise to an intense peak. When possible, comments on the evidence arising from cobalt or oxygen ions will also be made.

(*a*) *Samples in the Oxidized State*

The Mo 3d binding energy in Na_2MoO_4, after correction for surface charging, is 0.8 eV lower than in MoO_3. This is in accordance with the more covalent character of the bond in the tetrahedral molybdate ion. The B.E. of Mo^{6+} in MoO_3 was obtained from the pure oxide and from a slightly oxidized metallic sheet. The Mo^{4+} B.E. value was taken from the spectrum of commercial MoO_2, which contains MoO_3 in the outer layers, and from a partially reduced MoO_3 sample (Fig. 4), which also presents unreduced MoO_3 besides MoO_2. From both cases the position of Mo^{4+} relative to Mo^{6+} was also obtained. Our B.E. values for MoO_3 and MoO_2 agree with those of Bond, Waghorne, and Rivlin (*22*). Contrary to Swartz and Hercules (*23*), the curve B.E. vs oxidation number is not linear, the MoO_2 value being much closer to the metal than to MoO_3 (Fig. 9).

The displacement of the Mo peaks toward higher B.E. observed by Miller *et al.* (*24*) in Mo/Al_2O_3 samples was probably due to a charging effect.

The oxygen 1s spectrum (Fig. 2) on metallic molybdenum shows the presence of two main peaks. We can easily assign the peak at 530 eV to the oxide O^{2-}, while the one at 531.8 eV could be assigned to oxygen dissolved in the metal or to adsorbed oxy-

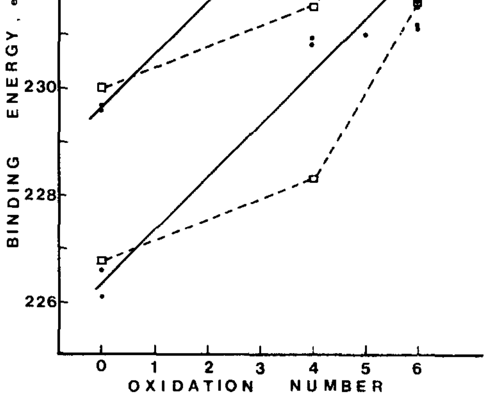

FIG. 9. Plot of the B.E. of the Mo 3d doublet versus oxidation number. The data of Swartz and Hercules (*23*) are also reported for comparison.

gen. The oxygen species on metals, as seen by XPS, have been discussed by several authors (*25–28*). There is agreement on the assignment of the O^{2-} species, while the peak at higher B.E. is assigned to strongly adsorbed oxygen (as O^-), OH^-, or H_2O. In summary, the XPS data agree well with the known existence of Mo (VI) on the surface of supported molybdenum oxide catalysts (*29*). The data, however, do not discriminate between site symmetry, as indicated by the two forms of $CoMoO_4$, one of which (β-$CoMoO_4$) contains tetrahedral Mo^{6+} ions whilst the other (α-$CoMoO_4$) contains octahedral ions (*30*).

(*b*) *Reduced Samples*

Pure oxides are considered first. A temperature of 400°C, as used here, is too low for the *bulk* reduction of MoO_3 (or MoO_2) to the metallic state Mo. In fact, following Guichard (*31*), Sondag *et al.* (*32*) and Massoth (*33*) show that bulk reduction would require a temperature of about 500°C. In contrast, the *surface* reduction could occur at a lower temperature. The XPS data, which definitely indicate a shift of the Mo peaks to a state lower than Mo (IV), close to Mo (0) as far as the B.E. value is concerned, provide experimental evidence for the surface reduction, and demonstrate the sensitivity of the technique to the outer layers. A loss of oxygen from the outer two or three layers would imply a weight loss of only about 1%, which is not easily interpreted in normal thermogravimetric analyses, especially when supported oxides are examined. The low valency state of molybdenum could be a lower oxide MoO_x.

Schönberg (*34*) has reported the oxides Cr_3O and Mo_3O, but their existence has been questioned (*35*). A solid solution (Cr, Mo)$_3$O has also been reported (*36*). The existence of the so-called β-tungsten is well known, although there has been some disagreement on its stoichiometry: some consider it a well defined oxide W_3O, whilst others say it is metallic W with oxygen impurities. It is well established, however, that some oxygen is necessary for its stability (*37*). By analogy with β-tungsten, we could regard MoO_x as a metallic species whose oxygen content we cannot determine from our data. We must also consider the fact that the experimental conditions required the reduced sample to be exposed to the atmosphere prior to measurement.

The reduction behaviour of supported samples is substantially different from that of unsupported MoO_3. For supported MoO_3 the lowest oxidation state that can be attained is 4+. A part of Mo^{6+} is reduced to Mo^{4+}, but part of it is in an oxidation state intermediate between 6+ and 4+. The XPS data can be correlated with the known formation of Mo^{5+} (*38*), and with the possibility that different surface arrangements and oxygen/molybdenum ratios could introduce small B.E. shifts, thus justifying the intensity of the spectrum at B.E. values between those of Mo^{6+} and those of Mo^{4+} (see curve b in Fig. 5 and curves b and c in Fig. 6). Some Mo^{5+} is present also in reduced MoO_3/SiO_2 (Fig. 7).

The spectra of Figs. 5–7 require some further comment. The relative position of the spectra before and after the reduction has been established by taking as reference the lines of C, Al (or Si), and oxygen: all three give results which are consistent within about ±0.1 eV. About 20 samples have been studied, and the spectra of some have been examined, both in the oxidized and in the reduced state, several times. In this way a considerable level of confidence in the results was attained. This, we believe, is a case in point to show the importance of the reference in giving meaning to the experimental data. Without a careful check of the position of the curve for the reduced state one would have disregarded small differences in B.E. values which are nevertheless significant, since their value and sign are consistently reproduced.

The higher or lower reducibility of different supported samples could, in principle, be inferred, qualitatively, from the area under the low B.E. side shoulder of the spectrum of reduced samples. This would require strictly controlled experimental conditions. For our alumina supported samples a different reducibility could not be observed, in spite of the differences in the preparation procedures (impregnation with Co first or with Mo first, firing at 400 or 600°C). This conclusion, although it can be considered reasonable as far as Mo is concerned, is unexpected when we look at cobalt, because for Co differences can be seen on the same samples with other techniques, particularly with diffuse reflectance spectroscopy. The low intensity of the cobalt peak as well as the reduction conditions used in our work (not drastic enough to reduce Co^{2+}) may have prevented the observation of differences in the behavior of cobalt in differently prepared samples.

From Fig. 7, a greater extent of reduction of MoO_3/SiO_2 as compared to MoO_3/Al_2O_3 is apparent, indicating a smaller degree of interaction between MoO_3 and support than in alumina-supported samples.

Finally, a conclusion can be drawn concerning possible definite compounds present in hydrodesulfurization catalysts. $CoMoO_4$ has previously been considered as one of the possible phases present on the surface of Co–Mo–Al_2O_3. Our data on the reducibility of $CoMoO_4$ indicate that nothing similar to bulk $CoMoO_4$ is present on alumina. In pure $CoMoO_4$, most of the Mo is reduced to nearly metallic MoO_x and a part of the Co^{2+} is reduced. On Co–Mo–Al_2O_3, molybdenum is reduced to Mo^{4+} at most, and Co^{2+} is not reduced. These XPS results agree with other observations based on magnetic and U.V. spectroscopic (*39*, *40*), and Raman (*41*) techniques.

A final comment on the reduction of Co–Mo–Al_2O_3 catalysts can be made. The lack of evidence for the reduction of Mo^{6+} below Mo^{4+} does not exclude the possibility that a few molybdenum ions undergo a further reduction process. The limitations of XPS as far as sensitivity is concerned do not allow the detection of a few percent of reduced ions in the presence of a majority of Mo^{4+} ions. It can be ruled out, however, that a considerable number of ions are reduced to Mo^{3+} or below.

For the purpose of judging how realistic are some of the models proposed for the structure of the surface of Co–Mo–Al_2O_3 catalysts, it could be very interesting to see if it is possible to determine the depth of location of Co, Mo, and Al in the surface layers. We have observed that the peak heights of Co in samples containing only supported Co were somewhat higher than in those containing Co (at the same concentration) and Mo. This can be considered as an indication that Co lies below Mo. It should be remarked, however, that quantitative estimates of intensities are rather difficult to make, because the Co peak is weak and broad.

ACKNOWLEDGMENTS

Thanks are due to Dr. P. Ascarelli and Professor G. Missoni for many valuable discussions and to Dr. M. Lo Jacono for kindly providing some specimens.

REFERENCES

1. DELGASS, W. N., HUGHES, T. R., AND FADLEY, C. S., *Catal. Rev.* **4**, 179 (1970).
2. WOLBERG, A., OGILVIE, J. L., AND ROTH, J. F., *J. Catal.* **19**, 86 (1970).
3. OGILVIE, J. L., WOLBERG, A., AND ROTH, J. F., *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* **17**, C 61 (1972).
4. BRINEN, J. S., AND MELERA, A., *J. Phys. Chem.* **76**, 2525 (1972).
5. CARBERRY, J. J., KUCZYNSKI, G. C., AND MARTINEZ, E., *J. Catal.* **26**, 247 (1972).
6. BILOEN, P., AND POTT, G. T., *J. Catal.* **30**, 169 (1973).
7. MACIVER, D. S., TOBIN, H. H., AND BARTH, R. T., *J. Catal.* **2**, 485 (1972).
8. ASCARELLI, P., AND MISSONI, G., *Discuss. Faraday Soc.* **54**, 298 (1972).
9. ASCARELLI, P., AND MISSONI, G., personal communication.
10. JOHANSSON, G., HEDMAN, J., BERNDTSSON, A., KLASSON, M., AND NILSSON, R., University of Uppsala, Institute of Physics, Report UUIP-769 (1972).
11. HNATOWICH, D. J., HUDIS, J., PERLMAN, M. L., AND RAGAINI, R. C., *J. Appl. Phys.* **42**, 4883 (1971).
12. JORGENSEN, C. K., AND BERTHOU, H., *Kong. Dan. Vid. Selsk. Mat. Fys. Medd.* **38**, 50 (1972).
13. WERTHEIM, G. K., AND ROSENCWAIG, A., *J. Chem. Phys.* **54**, 3235 (1971).
14. SWARTZ, W. E., WATTS, P. E., WATTS, J. C., BRASCH, J. W., AND LIPPINCOTT, E. R., *Anal. Chem.* **44**, 2001 (1972).

15. Ogilvie, J. L., and Wolberg, A., *Appl. Spectr.* **26**, 401 (1972).
16. Wagner, C. D., *Anal. Chem.* **44**, 1050 (1972).
17. Siegbahn, K., Nordling, C., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S.-E., Lindgren, I., and Lindberg, B., "ESCA—Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy." Almqvist and Wiksells, Uppsala, 1967.
18. Klasson, M., Hedman, J., Berndtsson, A., Nilsson, R., and Nordling, G., *Phys. Scripta* **5**, 93 (1972).
19. Brundle, C. R., and Roberts, M. W., *Chem. Phys. Lett.* **18**, 380 (1973).
20. Fraser, W. A., Florio, J. V., Delgass, W. N., and Robertson, W. S., *Surface Sci.* **36**, 661 (1973).
21. Lo Jacono, M., and Valigi, M., personal communication.
22. Bond, G. C., Waghorne, R. M., and Rivlin, V. G., personal communication.
23. Swartz, W. E., and Hercules, D. M., *Anal. Chem.* **43**, 1774 (1971).
24. Miller, A. W., Atkinson, W., Barber, M., and Swift, P., *J. Catal.* **22**, 140 (1971).
25. Schön, G., and Lundin, S. T., *J. Electron Spectrosc.* **1**, 105, (1973).
26. Novakov, T., and Prins, R., *Solid State Comm.* **9**, 1975 (1971).
27. Robert, T., Bartel, M., and Offergeld, G., *Surface Sci.* **33**, 123 (1972).
28. Kim, K. S., and Davis, R. E., *J. Electron Spectrosc.* **1**, 251 (1972).
29. Schuit, G. C. A., and Gates, B. C., *AIChE J.* **19**, 417 (1973).
30. Sleight, A. W., and Chamberland, B. L., *Inorg. Chem.* **7**, 1672 (1968).
31. Guichard, M., *C. R. Acad. Sci.* **125**, 105 (1897).
32. Sondag, P., Kim, D. Q., and Marion, F., *C. R. Acad. Sci.* **259**, 4704 (1964).
33. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
34. Schonberg, N., *Acta Chem. Scand.* **8**, 617 (1954).
35. Kihlborg, L., *Acta Chem. Scand.* **16**, 2458 (1962).
36. Den Broder, F. J. A., and Burgers, W. G., *Acta Cryst.* **21**, 1003 (1966).
37. Wells, A. F., "Structural Inorganic Chemistry." Oxford University Press, Oxford, 1962, p. 467.
38. Masson, J., and Nechtschein, J., *Bull. Soc. Chim. Fr.* 3933 (1968).
39. Ashley, J. H., and Mitchell, P. C. H., *J. Chem. Soc.* (*A*), 2821 (1968).
40. Lipsch, J. M. J. G., and Schuit, G. C. A., *J. Catal.* **15**, 174 (1969).
41. Villa, P. L., Trifirò, F., and Pasquon, I., *React. Kin. Catal. Lett.* **1**, 341 (1974).