JOURNAL OF CATALYSIS **104**, 202–210 (1987)

Skeletal Isomerization of Hydrocarbons on Molybdenum Catalysts

I. X-ray Photoelectron Spectroscopy Study of Alumina-Supported Catalysts

Y. HOLL,[1] R. TOUROUDE, G. MAIRE, A. MULLER,* P. A. ENGELHARD,*
AND J. GROSMANGIN*

Laboratoire de Catalyse et Chimie des Surfaces, U.A. 423 du CNRS, Institut Le Bel,
*Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg, and *TOTAL,*
Centre de Recherches, BP 27, 76700 Harfleur, France

Received July 19, 1985; revised July 3, 1986

MoO_3/Al_2O_3 catalysts with 6, 12, 18, or 30 wt% MoO_3 have been studied by X-ray photoelectron spectroscopy (XPS) in their original oxide form and in a reduced state. Comparisons between bulk MoO_3 or MoO_3–alumina mechanical mixture and alumina-supported MoO_3 catalysts have shown in the latter a binding energy increase of about 0.5 eV for the molybdenum 3*d* level. This increase has been interpreted by a charge transfer from molybdenum to alumina. The supported oxide also shows a decrease in resolution of the Mo 3*d* doublet due either to the alumina surface heterogeneity from the point of view of its electron-accepting properties or to the coexistence of molybdenum ions in tetrahedral and octahedral sites. The high-temperature reduction of 6% MoO_3/Al_2O_3 has been studied at 550, 750, and 950°C under 760 Torr hydrogen. After 550°C treatment, the catalyst is close to its original oxide form. The 750°C treatment leads to an intermediate form where molybdenum atoms close to oxide and close to metal coexist. Even after reduction at 950°C, molybdenum is not perfectly reduced; it is very close to the metallic state but there remain some weakly oxidized sites at its surface. This study has shown that there is aggregation of molybdenum in large particles at the surface: after reduction under hydrogen at 950°C the amount of molybdenum contributing to the observed Mo XPS signal is divided by a factor close to 2. An oxygen treatment at 550°C not only reoxidizes, but also redisperses, all molybdenum. These XPS results are useful in the interpretation of the catalytic properties of these systems.

INTRODUCTION

The use of X-ray photoelectron spectroscopy (XPS) has made a large contribution to the study of supported and unsupported molybdenum catalysts. The fundamental questions that it may address concern the interactions of supported metals or oxides with the support (carrier) and the chemical state (oxidation state, chemical environment) of surface species after various processes (thermal, reducing, oxidizing) or various utilization conditions of the catalysts.

The interaction between supported phase and the support is able to modify greatly the properties of the supported metals or metal oxides. Various examples may be cited. The strong metal–support interaction (SMSI) between Group VIII metals and certain transition metal oxides (e.g., TiO_2) decreases the ability of these metals to chemisorb H_2 and CO (*1*). Chromium (VI) oxide supported on silica is thermally stable at temperatures at which bulk CrO_3 decomposes (*2*). Iron oxide on silica is not completely reduced under conditions at which bulk Fe_2O_3 is rapidly converted to metallic iron (*3*). Cobalt oxide–support interactions have been studied by Okamoto *et al.* (*4*). The interaction strength, measured by the reducibility of the supported oxide, decreases in the order $La_2O_3 > \gamma\text{-}Al_2O_3 > SiO_2$. Recent evidence points to a strong surface complex between WO_3 and $\gamma\text{-}Al_2O_3$ which influences the chemical and physical

---

[1] Present address: Institut Charles Sadron (CRM-EAHP) CNRS-ULP Strasbourg, 4 , rue Boussingault, 67000 Strasbourg, France.

0021-9517/87 $3.00

properties of both WO_3 and γ-Al_2O_3. The interaction inhibits both the reduction of tungsten oxide to tungsten metal (5) and the converison of γ-Al_2O_3 to α-Al_2O_3 (*6*).

Molybdenum oxide MoO_3 also gives rise to strong interactions with carriers such as alumina or silica. XPS (*7*) and thermogravimetry (*8*) give evidence of the fact that supported MoO_3 is much more difficult to reduce than bulk MoO_3: at 500°C under hydrogen, bulk MoO_3 is reduced to the metallic state in a few hours whereas under the same conditions 12.4% MoO_3/Al_2O_3 is reduced no further than oxidation state IV (*7*). Resistance to reduction is all the more pronounced when the percentage of MoO_3 on the support is lower (*7, 8*). On silica, MoO_3 reducibility is markedly higher, although an XPS study by Gajardo *et al.* (*9*) has shown a MoO_3–SiO_2 interaction, admittedly weaker than the MoO_3–Al_2O_3 interaction, but unquestionable.

Study of the MoO_3–Al_2O_3 interaction by XPS has already been addressed widely in the literature but the principal results are still much debated (see later). This is why we have raised the problem for further study, and in particular in this work we have investigated

- supported catalysts in their original oxidized state (after air calcination) especially the MoO_3–carrier (Al_2O_3) interaction;
- high-temperature (550, 750, and 950°C) hydrogen reduction of the supported catalysts.

The reduction of alumina-supported molybdenum oxide has been widely studied with XPS but always under relatively moderate conditions, at temperatures never exceeding 500°C. Authors generally consider that under such conditions molybdenum in catalysts containing between 10 and 15% MoO_3 is not reduced beyond oxidation state IV. Kinetic studies (*10*) show that under hydrogen at 500°C a sample containing 15% MoO_3 is stabilized in 2 h and comprises only Mo^V and Mo^{IV} in equal amounts.

This work deals with more drastic reduction conditions, namely, temperatures between 550 and 950°C and a hydrogen pressure of 760 Torr (1 Torr = 133.3 N m^{-2}). The catalysts reduced under high temperature are shown to be particularly interesting from the standpoint of hydrocarbon isomerization (*11*) and this XPS study was a major factor in the interpretation of the catalytic results.

EXPERIMENTAL

Apparatus. The XPS apparatus was a Vacuum Generators ESCA-Mark III spectrometer composed of an analyzing chamber and a preparatory chamber which was used to degas and to apply different reducing treatments to the sample. The transfer from the preparatory chamber to the analyzing chamber took place without the sample passing through air. Pressure in the analyzing chamber could be reduced to under 5×10^{-11} Torr with a cryogenic pump, but during analysis the pressure rose to 10^{-8} Torr. Energy analysis of the electrons emitted by the sample was performed with a high-resolution hemispherical analyzer.

Catalysts. MoO_3/Al_2O_3 catalysts, in powder form, were pressed to obtain a pastille which could be fixed on the sample holder and analyzed either directly or after hydrogen reduction in the preparatory chamber. The reduction conditions were as close as possible to the ones which were used before all catalytic experiments. Under a static pressure of 760 Torr hydrogen, the catalyst was heated at a rate of 150°C/15 min to the chosen reduction temperature—550, 750, or 950°C—and kept 2 h at this temperature. The sample was then cooled for 30 min and the hydrogen was pumped off. The reduced catalyst was transferred to the analyzing chamber to be studied.

The catalyst nomenclature specifies the molybdenum oxide percentage on alumina and the reduction temperature. Thus, Mo6 designates a 6 wt% MoO_3/Al_2O_3 catalyst in its original form and Mo6–950 represents this catalysts after a 950°C reduction. Some details concerning the preparation techniques of the supported catalysts used can be found in Part III (*11*). The alumina used was a γ-alumina (Ketjen CK 300). The surface area was 215 m^2/g. After 2 h reduction under 760 Torr hydrogen at 550, 750, or 950°C the surface area loss was 13, 20, and 33%, respectively. The reduction at 950°C started a phase transformation from γ- to α-alumina but we did not study the extent of this transformation.

Choice of XPS reference. Due to the fact that all the catalysts studied are insulating, there is the problem of a choice of binding energy reference. The most usually cited reference is the contaminating carbon brought back to 284 eV (1*s* level). However, the carbon peak can be weak and broad, and its top poorly defined. Furthermore, it can exist in different chemical and electrical forms. Thus the C 1*s* peak shift due to charging effects may be different from the displacement of the other peaks, which can give rise to incoherent results. Patterson *et al.* (*12*), taking gold as a reference, measured binding energies between 283.5 and 285.0 eV for C 1*s* depending on the samples.

Another possibility is to evaporate a thin gold film on the sample to render it conducting. This method not only weakens and broadens the peaks (*13*) but also makes the experimental processes more difficult. We chose the Al 2*s* level of the carrier as a satisfactory reference. The corresponding XPS peak is always strong enough in supported samples. Furthermore there is no reason to believe that alumina could carry a different charge than molybdenum oxide even in the MoO_3–Al_2O_3 mechanical mixture. This seems reasonable as the mechanical mixture was homogeneous: charging is a collective effect because when a flood gun was applied to the sample to eliminate the charges the same energy shift was observed for any element.

Several authors choose aluminum (2*s* or 2*p*) as a reference [for example see Ref. (*13*)]. Aluminum was retained as a reference in high-temperature reduction experiments (950°C) because it seems unlikely that alumina is reduced even under such conditions (*14*). Soled *et al.* (*15*) also used aluminum as reference for reduction experiments of WO_3/Al_2O_3 under hydrogen at 3 atm pressure and 900°C for several hours.

The reference value was fixed at 120.4 eV, corresponding to 118.0 eV for metallic aluminum (*16*) plus a chemical shift of 2.4 eV due to oxidation to alumina according to Barrie (*17*).

RESULTS AND DISCUSSION

I. MoO_3/Al_2O_3 CATALYSTS IN OXIDE FORM: MoO_3–Al_2O_3 INTERACTION

The binding energies of the Mo 3*d* 5/2, Al 2*s*, and O 1*s* levels were measured by XPS for

- pure MoO_3
- MoO_3–Al_2O_3 mechanical mixture,
- Al_2O_3-supported MoO_3 with 6, 12, 18, and 30 wt% MoO_3.

The values of the experimental binding energies are corrected for any charging effects by reference to the Al 2*s* level. For Mo6, Mo12, and Mo18 the experimental values result from an average over three experiments (Table 1).

Taking into account all possible errors, particularly charging effects, the uncertainty of the binding energies is ±0.2 eV. However, the values in Table 1 show a clear difference in binding energies of about 0.5 eV for supported MoO_3 over unsupported MoO_3. This difference can best be seen in Fig. 1.

On the other hand, variations in the binding energies between different supported catalysts are not significant, except perhaps in Mo30 where there is a tendency to approach that of pure MoO_3. The O 1*s* binding energies are constant at 532.3 eV.

If one considers the full width at half-height of the Mo 3*d* doublet one can observe a greater width for Mo6, Mo12, and Mo18 in comparison with unsupported molybdenum oxide. This broadening tends to

TABLE 1

XPS Study of Supported MoO_3 (Reference: Al 2*s* at 120.4 eV)

	Binding energy (eV)					
	Pure MoO_3	MoO_3–Al_2O_3 mechanical mixture	Mo6	Mo12	Mo18	Mo30
Mo 3*d* 5/2[a]	[c] (4.9)	233.2 (4.5)	234.0 (5.6)	233.8 (5.5)	234.0 (5.3)	233.6 (4.9)
Al 2*s* before correction for charging effects		125.2	125.6	125.0	125.0	125.0
O 1*s*[b]	[c]	532.2 (2.7)	532.3 (3.1)	532.3 (2.9)	532.2 (2.6)	532.3 (2.7)

[a] Full width at half-height (3*d* doublet) in parentheses.
[b] Full width at half-height in parentheses.
[c] The values are not given because Al Ref. cannot be used.

disappear with the increasing MoO_3 percentages; for Mo30, there is no broadening.

In summary, the XPS results give evidence of manifest differences between pure molybdenum oxide and alumina-supported molybdenum oxide, and we may note, in particular,

- a shift toward higher binding energies of about 0.5 eV for supported oxide in comparison with bulk oxide;
- for supported oxide, a diminished resolution of the Mo 3*d* doublet at low concentration (the broadening, equal to 0.5 eV for Mo6, decreases progressively with increasing molybdenum oxide content and vanishes for Mo30).

Let us now discuss the above results.

The binding energy shift of the Mo 3*d* level between bulk and supported MoO_3 is controversial. Some authors do not measure any shift (*7, 10, 18, 19*). Some observe a binding energy decrease of 0.5 eV but give no interpretation (*20*) and, as in the present study, others note a binding energy increase of about 0.5 eV (*21–24*).

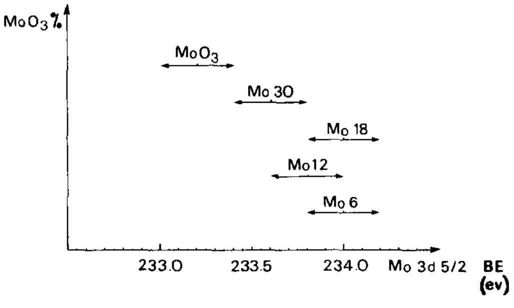

FIG. 1. Mo 3*d* 5/2 peak binding energy (BE) in Mo6, Mo12, Mo18, Mo30, and pure MoO_3. Reference: Al 2*s* at 120.4 eV.

The binding energy increase is interpreted as a charge transfer from molybdenum to alumina, the charge-accepting properties of which are emphasized (*25*). Under such conditions molybdenum becomes a site highly sensitive to electron donors. Moreover, Declerck-Grimee *et al.* (*23*) indicate a more important binding energy shift, thus a charge transfer, for $CoMo/Al_2O_3$ catalysts. These inconsistencies can be explained by the differences in catalyst preparation techniques and by the different alumina used.

On the other hand, the decreased resolution of Mo 3*d* doublet from bulk MoO_3 to supported MoO_3 is unanimously accepted. Various views have been advanced:

(i) Those authors who speak of charge transfer to alumina (*21–24*) explain that the alumina surface is heterogeneous from the point of view of its electron-accepting properties, and that different molybdenum ions which are more or less electron deficient can coexist.

(ii) Ratnasamy (*19*) interprets the broadening of the 3*d* doublet as being due to the existence of three types of molybdenum:

- one type which is strongly bound to the carrier, not reducible even under hydrogen at high temperatures;
- one type which is weakly bound and easily reducible;
- one type which is partially reducible in the presence of a promoter like cobalt or nickel, which seems to contradict the results of Declerck-Grimee *et al.* (*23*).

(iii) Grimblot *et al.* (*20*) attribute the broadening to the existence of molybdenum in both tetrahedral [Mo(T)] and octahedral [Mo(O)] sites. This kind of interpretation is contested by Cimino and De Angelis (*7*) and by Armour *et al.* (*26*), who consider that differences between tetrahedral and octahedral molybdenum are not revealed by XPS.

(iv) More recently, Zingg *et al.* (*10*) attributed the decreased resolution to charging effects only. They showed that the Mo 3*d* broadening correlates with the Al 2*s* broadening and with the shift due to charging effects. The slightly different molybdenum ions responsible for broadening are localized in surface sites with slightly different charges. However, although the correlation is unquestionable in their case, it does not rule out other possible causes of the broadening. Table 1 shows the values of the charging effects and illustrates that there is no correlation between charging effects and peak width. Therefore the interpretation of Zingg *et al.* is not valid in our case.

We have no experimental evidence that Mo(O) and Mo(T) have slightly different binding energies. Broadening, in our case, can be due either to Mo(O) and Mo(T) coexistence or to surface heterogeneity from the charge transfer point of view.

II. Reduction of Alumina-Supported MoO_3

Preliminary Study of the Binding Energy Shift of the Mo 3d Level between Mo^0 and Mo^{VI}

The binding energy shift between metallic molybdenum and molybdenum in oxidation state VI needed to be measured with great precision in order to determine if the high-temperature reduction of supported oxides can lead to metallic molybdenum. The chosen process consisted of oxidizing a high-purity metallic molybdenum sample (Goodfellow Metals) progressively to oxidation state VI while measuring at each stage the 3*d* level binding energy (Table 2).

It is imperative that the following three

TABLE 2

Oxygen Treatments on Bulk Molybdenum

Treatment			No.	Mo 3*d* 5/2		O 1*s*		I
				BE (eV)	FWHH[a]	BE (eV)	FWHH[a]	I_O/I_{MO}
Starting form after ion bombardment (Ar)			0	228.3	1.1	—	—	—
10^{-1} Torr O_2	15 min	20°C	1	228.7	1.75	530.8	1.8	31
10^{-1} Torr O_2	15 min	140°C	2	228.7	1.9	530.7	1.95	37
10^{-1} Torr O_2	15 min	250°C	3	228.7		530.9	1.9	39
10^{-1} Torr O_2	15 min	350°C	4	228.7		530.9	1.9	63
10^{-1} Torr O_2	15 min	450°C	5	229.8		530.5	1.85	74
10^{-1} Torr O_2	45 min	450°C	6	229.8		530.5	1.85	78
760 Torr O_2	60 min	450°C	7	233.2	1.3	531.1	1.55	100

[a] Full width at half-height.

conditions be met in order to obtain an accurate value.

(1) The sample surface must be perfectly decontaminated in order to ensure starting at oxidation state zero.

(2) The molybdenum at the surface must be totally oxidized to state VI at the end of the process.

(3) The MoO_3 layer must be thin enough to avoid the appearance of a charging effect which would lead to an energy shift overvalue.

Disregard of conditions 1 and 2 will result in an underestimate of the measured shift.

The principal contaminant of the molybdenum sample was oxygen. Hydrogen treatments and ionic bombardments with argon and hydrogen at room or high temperature led to an acceptably oxygen-free surface.

The binding energy and the full width at half-height of the Mo 3*d* 5/2 level are listed in Table 2 and the Mo 3*d* doublet shape is shown in Fig. 2 (Treatment 0).

The sample is then treated with oxygen under more and more severe conditions (Table 2). Treatments are performed successively on the same sample. Oxygen is introduced at the chosen pressure, the temperature is adjusted, and the treatment itself is performed under the conditions described in Table 2. The sample is then cooled under oxygen for 5 min before pumping. The Mo 3*d* doublet shifts progressively to higher binding energies (Table 2). Its shape evolves into the MoO_3 oxide shape; some examples of intermediate shapes are shown in Fig. 2. The intensity ratio $I_{O\,1s}/I_{Mo\,3d}$ also increases progressively. The value of interest to us (Table 2) is the difference between the binding energy of fully oxidized molybdenum (233.2 eV) and the binding energy of metallic molybdenum (228.3 eV), and that is 4.9 eV. The margin of error on the two limits is 0.1 eV, and therefore the difference is defined with an error of ±0.2 eV.

Several authors have published binding energy shift values between Mo^0 and Mo^{VI}. Values range from 4.2 (*27*) to 6.4 (*28*) eV; examples include 4.5 (*29*), 4.7 (30), 4.8 (*7*, *20*), 4.95 (*31*), 5.0 (*10*) and 5.05 (*18*) eV. If extremes are eliminated, our value is in relatively good agreement with the literature values.

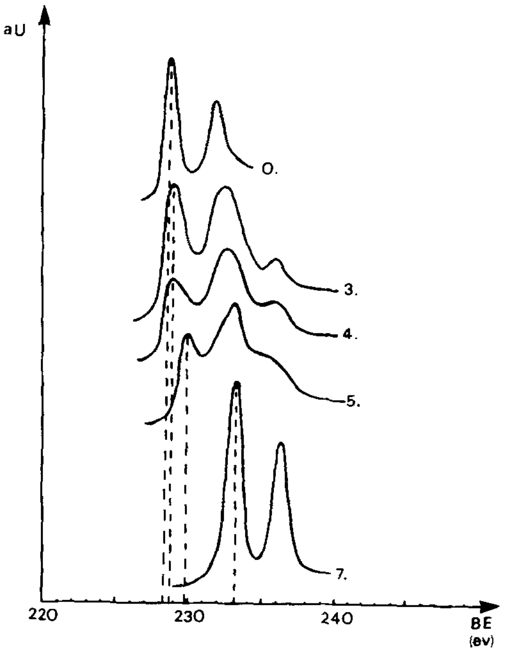

FIG. 2. Bulk molybdenum. Mo 3*d* doublet after various oxygen treatments. (0) Starting form. (3) 10^{-1} Torr O_2, 15 min, 250°C. (4) 10^{-1} Torr O_2, 15 min, 350°C. (5) 10^{-1} Torr O_2, 15 min, 450°C. (7) 760 Torr O_2, 60 min, 450°C.

Detailed Study of Reduction of 6% MoO_3/Al_2O_3

The Mo6 samples were studied by XPS after hydrogen treatment at 550, 750, or 950°C. Each experiment was performed with a new sample in oxidized form. The XPS results—binding energy, peak width, and intensity ratios—are listed in Table 3. The 3*d* doublet assumes four different shapes, which fall into the following groups: the oxidized form and the forms which result from treatment at 550, 750, and 950°C (Fig. 3).

It can be seen that after 550°C treatment, the catalyst is close to its original form.

TABLE 3

Study of Reduction of 6 wt% MoO_3/AL_2O_3 (Conditions: 760 Torr H_2; 550, 750, or 950°C; Reference: Al 2*s* at 120.4 eV)

Sample	Mo 3d 5/2		Al 2*s* FWHH[a] (ev)	O 1*s*		Mo/Al[b]
	BE (eV)	F.W.H.H. 3d doublet		BE (eV)	FWHH	
Oxide form	234.1	5.6	3	532.7	3.1	100
Mo6—550	233.6	5.7	3	?	?	?
Mo6—750	230.7	8.2	2.9	532.4	2.9	78
Mo6—950	230.0	6.5	3	531.5	3.1	59

[a] Full width at half-height.

[b] Mo/Al = Mo 3*d*/Al 2*s* peak surface area ratios.

The 750°C treatment leads to an intermediate form where molybdenum atoms coexist close to the oxide and close to the metal.

The 950°C treatment result is highly important in the interpretation of catalytic results (*11*). We saw in the preceding section that for Mo 3*d* 5/2, the binding energy difference between Mo metal and Mo(VI) oxide was 4.9 eV. In the case of supported oxide reduced at 950°C, the difference between its binding energy and that of the original form is 4.1 eV (Table 3). Here the supported oxide shows a binding energy shift toward higher values in comparison with unsupported oxide. Moreover, the doublet of the reduced form is broader than that of the oxidized form (6.5 eV as compared to 5.6 eV). Thus it is obvious that molybdenum on Mo6–950 is different from metallic molybdenum. These results will be discussed in the next section.

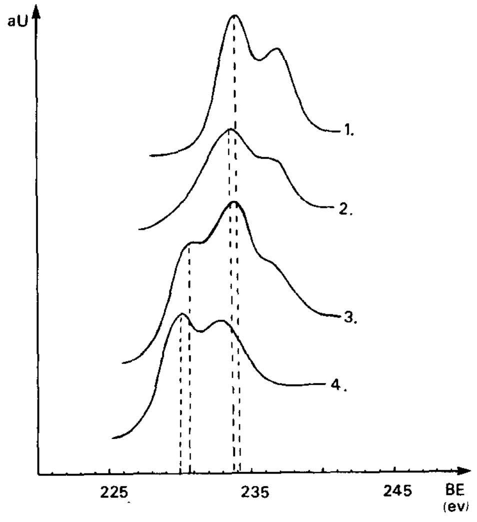

FIG. 3. Mo6. Mo 3*d* doublet after various hydrogen treatments. (1) Starting form. (2) 760 Torr H_2, 2 h, 550°C. (3) 760 Torr H_2, 2 h, 750°C. (4) 760 Torr H_2, 2 h, 950°C.

Placing the sample reduced at 950°C under 760 Torr oxygen at 550°C for 1 h returns it to oxidized molybdenum with oxidation state VI.

An examination of I_{Mo}/I_{Al} ratios (Table 3) shows that hydrogen treatments at increasing temperatures remove molybdenum from the surface are contributing to the XPS spectrum, probably by agglomeration in large particles. However, treatment with oxygen redisperses molybdenum again.

We now turn to a discussion of these results.

It appears that resistance to reduction is considerable for Mo6. Actually this result was announced several years ago by Cimino and DeAngelis (*7*) and Massoth (*8*).

A similar study concerning WO_3/Al_2O_3 (15) gave analogous results. For a 6% WO_3/Al_2O_3 sample, a reduction for 2 h at 900°C produced 2.5% metallic tungsten, as compared to 85% for 25% WO_3/Al_2O_3. According to that study (*15*), supported tungsten is reduced directly from oxidation state VI to

0, whereas reduction of bulk WO_3 proceeds through oxidation states V, IV, and II.

We consider now the interpretation of the XPS results concerning the reduction of Mo6 at 950°C.

A first hypothesis could be that metallic molybdenum particles are present which are very small (less than 20 Å). It is an acknowledged fact that very small metallic particles present XPS shifts and peak broadenings [see Ref. (*32*) for palladium and Ref. (*33*) for osmium and iridium]. However, it is virtually unacceptable that a 950°C treatment could produce such small particles and the signal decrease allows us to dismiss this hypothesis.

The most likely interpretation is that some rare, weakly oxidized sites exist at the surfaces of the alumina-supported metallic molybdenum particles, which are responsible for the Mo 3*d* doublet shift and the broadening of the peaks. These sites could be localized at the edges of the particles, close to the support. It would be surprising if molybdenum atoms were insensitive to such close proximity of oxygen atoms.

CONCLUSIONS

Comparisons between bulk MoO_3 or MoO_3–alumina mechanical mixture and alumina-supported MoO_3 catalysts have shown that in the latter there is a binding energy increase of about 0.5 eV for the Mo 3*d* level. This increase has been interpreted by a charge transfer from molybdenum to alumina. The supported oxide also shows a decrease in resolution of the Mo 3*d* doublet due either to the alumina surface heterogeneity from the point of view of its electron-accepting properties or to the coexistence of molybdenum ions in tetrahedral and octahedral sites.

Until now, no one has studied the high-temperature reduction (between 550 and 950°C) of alumina-supported MoO_3 catalysts. We have made such a study because this kind of treatment leads to particularly interesting catalytic properties from the perspective of hydrocarbon skeletal isomerization. The binding energy shift of the Mo 3*d* level between Mo^0 and Mo^{VI} was measured to be 4.9 eV. Reduction of the Mo6 catalyst has been studied under conditions as close as possible to the catalytic conditions (*11*). This study has shown the agglomeration of molybdenum in large particles at the surface: after reduction under hydrogen at 950°C, the amount of molybdenum contributing to the XPS signal is divided by a factor close to 2. An oxygen treatment at 550°C for 1 h not only reoxidizes, but also redisperses, all molybdenum. Between the oxidized form Mo6 and the reduced form at 950°C under hydrogen at 760 Torr for 2 h, the Mo 3*d* binding energy shift is only 4.1 eV and the doublet shape is not a simple one. These results can be interpreted by the existence at the surface of the metallic particles of rare, weakly oxidized sites.

ACKNOWLEDGMENTS

The authors thank the Compagnie Française de Raffinage (TOTAL) for financial support and Dr. L. Hilaire for helpful discussions.

REFERENCES

1. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211**, 1121 (1981).
2. Hogan, J. P., *J. Polym. Sci.* **8**, 2637 (1970).
3. Garten, R. L., *J. Catal.* **43**, 18 (1970).
4. Okamoto, Y., Nakano, H., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Japan* **48**, 1163 (1975).
5. Thomas, R., De Beer, V. H. J., and Moulijn, J. A., *Bull. Soc. Chim. Belg.* **90**, 1349 (1981).
6. Tittarelli, P., Iannibello, A., and Villa, P. L., *J. Solid State Chem.* **37**, 95 (1981).
7. Cimino, A., and De Angelis, B. A., *J. Catal.* **36**, 11 (1975).
8. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
9. Gajardo, P., Pirotte, D., Defosse, C., Grange, P., and Delmon, B., *J. Electron. Spectrosc.* **17**, 121 (1979).
10. Zingg, D. S., Makovsky, L. E., Tischer, R. E., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **84**, 2898 (1980).
11. Holl, Y., Garin, F., Maire, G., Muller, A., Engelhard, P. A., and Grosmangin, J., *J. Catal.* **104**, 225–232 (1987).

12. Patterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., *J. Phys. Chem.* **80,** 1700 (1976).
13. Gajardo, P., Grange, P., and Delmon, B., *J. Catal.* **63,** 201 (1980).
14. Fripiat, J. J., and Bonnelle, J. P., personal communication.
15. Soled, S., Murrell, L., Wachs, I., and McVicker, G., *Prepr. Amer. Chem. Soc. Div. Pet. Chem.* **28,** 1310 (1983).
16. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S., Lindgren, I., and Lindberg, B., "ESCA, Atomic, Molecular and Solid-State Structure Studies by Means of Electron Spectrocopy," Almquist and Wiksells Boktnyckeri AB, Uppsala, 1967.
17. Barrie, A., *Chem. Phys. Lett.* **19,** 109 (1973).
18. Aptekar', E. L., Chudinov, M. G., Alekseev, A. M., and Krylov, O. V., *React. Kinet. Catal. Lett.* **1,** 493 (1974).
19. Ratnasamy, P., *J. Catal.* **40,** 137 (1975).
20. Grimblot, J., Bonnelle, J. P., and Beaufils, J. P., *J. Electron. Spectrosc.* **8,** 437 (1976).
21. Miller, A. W., Atkinson, W., Barber, M., and Swift, P., *J. Catal.* **22,** 140 (1971).
22. Friedman, R. M., Declerck-Grimee, R. I., and Fripiat, J. J., *J. Electron. Spectrosc.* **5,** 437 (1974).
23. Declerck-Grimee, R. I., Canesson, P., Friedman, R. M., and Fripiat, J. J., *J. Phys. Chem.* **82,** 885 (1978).
24. Edmonds, T., and Mitchell, P. C. H., *J. Catal.* **64,** 491 (1980).
25. Flockhart, B. D., Scott, J. A. N., and Pink, R. C., *Trans. Faraday Soc.* **62,** 730 (1966); Wolberg, A., Ogilvie, J. L., and Roth, J. F., *J. Catal.* **19,** 85 (1970).
26. Armour, A. W., Mitchell, P. C. H., Folkesson, B., and Larsson, R., *J. Less-Common Met.* **36,** 361 (1974).
27. Kim, K. S., Baittinger, W. E., Amy, J. W., and Winograd, N., *J. Electron Spectrosc.* **5,** 351 (1974).
28. Swartz, W. E., and Hercules, D. M., *Anal. Chem.* **43,** 1774 (1971).
29. Holm, R., and Storp, S., *Appl. Phys.* **9,** 217 (1976).
30. Haber, J., Marczewski, W., Stoch, J., and Ungier, L., *Ber. Bunsen Ges.* **79,** 970 (1975).
31. Wagner, C. D., Riggs, W. M. Davis, L. E. and Moulden, J. F., *in* "Handbook of X-Ray Photoelectron Spectroscopy," (G. E. Muilenberg, Ed.), Perkin Elmer Corporation, Physical Electronics Division, Eden Prairie, Minnesota 1978.
32. Takasu, Y., Akimaru, T., Kasahara, K., and Matsuda, Y., *J. Amer. Chem. Soc.* **104,** 5249 (1982).
33. Legare, P., Rhodin, T. N., and Brucker, C. F., *J. Vac. Sci. Technol. A* **1,** 1228 (1983).