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X-Ray and Ultraviolet-Photoelectron Spectra of Bismuth Molybdate Catalysts

B. GRZYBOWSKA, J. HABER, W. MARCZEWSKI, AND L. UNGIER

Research Laboratories of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland

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Changes of the surface structure of bismuth molybdate catalysts Bi_2MoO_6, $Bi_2Mo_2O_9$, and $Bi_2(MoO_4)_3$ after outgassing, after interaction with hydrogen and after interaction with propylene–oxygen mixture have been studied by XPS and UPS. Outgassing of MoO_3 and Bi_2MiO_6 results in surface reduction of Mo^{6+} to Mo^{4+} ions, Mo^{4+} constituting two kinds of donor center above the valence band. This process is enhanced on interaction with H_2, but it is only in later stages of the reduction that Bi^{3+} ions become reduced.

In the conditions of the catalytic oxidation of propylene the surface composition of the three bismuth molybdate phases reflects that of the bulk, whereas after vacuum or reducing treatment the three compounds show similar values of the Bi/Mo ratio.

INTRODUCTION

Experimental evidence collected in recent years indicates that selective oxidation of olefins on oxide catalysts proceeds by a series of consecutive steps, the first of which is the formation of an allylic intermediate. Examination of various properties of molybdate catalysts enabled two of the present authors to formulate a mechanism postulating that each of these steps requires a different kind of active center to be present at the catalyst surface (*1–3*), the product obtained depending thus on the type and mutual proportions of the various active centers at the surface of the catalyst. According to this mechanism, in case of catalysts such as bismuth molybdates, the centers responsible for the first hydrogen abstraction involve Bi^{3+} cations, whereas insertion of oxygen proceeds with the participation of oxygen polyhedra of molybdenum.

In the Bi_2O_3–MoO_3 system three different phases, namely Bi_2MoO_6, $Bi_2Mo_2O_9$ and $Bi_2(MoO_4)_3$, are known to be active and selective catalysts for the partial oxidation of olefins, but considerable differences of opinion exist as to the sequence of activities of these molybdates. Batist *et al.* (*4, 5*) assign the highest activity in butene oxidative dehydrogenation to the koechlinite phase Bi_2MoO_6, whereas Kolchin *et al.* (*6*) have found $Bi_2Mo_2O_9$ to be the most active in propylene oxidation. In our experiments carried out with flow and pulse methods (*3, 7*) also this latter molybdate was the most active in propylene oxidation, whereas in the case of butene-1 oxidative dehydrogenation the difference in activity of the three phases was very small.

A question may be raised at this point as to whether it is appropriate to discuss the differences in catalytic properties of these three phases in terms of different bulk composition, which may not reflect the true composition of their surfaces. It should also be borne in mind that the

reduction–oxidation cycles taking place in the course of the catalytic reaction may considerably alter the surface structure and composition of the catalyst in comparison with the surface of a sample which has been degassed in high vacuum at elevated temperatures, the usual procedure in such experiments as measurements of the work function (*10*), sorption of reactants (*11*, *12*), or reducibility in hydrogen (*8*, *9*). One may ask whether such surfaces are comparable with those operating in the catalytic system and to what extent their physicochemical properties may be correlated with the properties of the catalyst.

In order to answer these questions photoelectron spectroscopy appeared to offer many advantages. In recent years this technique has been exploited in several studies of the structure of molybdenum oxides and molybdates (*13–19*). In the present work studies of X-ray photoelectron spectra (XPS) and uv photoelectron spectra (UPS) of bismuth molybdate catalysts have been carried out and the changes occurring on vacuum heat treatment as well as on contacting the catalyst with hydrogen and reactants of the reaction of hydrocarbon oxidation have been followed.

EXPERIMENTAL METHODS

Bismuth molybdates Bi_2MoO_6, $Bi_2Mo_2O_9$, and $Bi_2(MoO_4)_3$ were obtained by coprecipitation from bismuth nitrate and ammonium paramolybdate solutions followed by calcination at 500°C. The details of the preparation methods and of identification of the three compounds have been reported elsewhere (*20*). Bismuth oxide was obtained *in situ* in the preparation chamber of the spectrometer by oxidizing evaporated metallic bismuth in oxygen at 150°C. Molybdenum oxide was prepared by decomposition of ammonium paramolybdate at 470°C.

Photoelectron spectra were measured with a Vacuum Generators ESCA-3 spectrometer. The aluminum K-line (1486.6 eV) was used for excitation of XPS, and uv radiation from a helium I source for excitation of UPS. For binding energy (BE) calibration a small amount of gold powder was mixed with the sample and the Au $4f_{7/2}$ peak (84.0 eV) was used as reference. The estimated accuracy in determining the BE values was ±0.2 eV. The samples were deposited as a thin layer on the sample holder from an acetone suspension and could be heated to 600°C.

The samples were outgassed in the preparation chamber of the spectrometer at 120°C for 3 hr at 10^{-8} Torr and the spectra were then recorded. In this way the BE values of initial samples were obtained. The samples were then subjected to various heat and vacuum pretreatment procedures. Preliminary experiments have shown that prolonged heating of the samples in a vacuum at 300°C for periods as long as 12 hr did not produce any visible changes either in the positions of the peaks or in their intensities. This indicates that the procedure employed for standardization provides an appropriate initial state of the surface for further investigations of its changes in the course of reduction and catalytic reaction.

RESULTS AND DISCUSSION

A. Electron Binding Energies

The electron binding energies in Bi_2O_3, MoO_3, and the three bismuth molybdates are summarized in Table 1. They are in good agreement with those published recently by Matsuura and Wolfs (*19*). The energy levels of bismuth ions in bismuth molybdates are identical with those observed in Bi_2O_3 as might be expected in view of similar coordination. It is noteworthy that also molybdenum ions are characterized by similar energy levels although their coordination is octahedral in MoO_3 and Bi_2MoO_6, whereas it is tetrahedral in $Bi_2(MoO_4)_3$. Apparently coordi-

nation has a very small influence on the core electron binding energies in molybdenum, in agreement with the observations of Armour *et al.* (*15*) for other Mo(VI) compounds.

B. Effect of Outgassing

When samples of MoO_3 or molybdates were outgassed in the preparation chamber of the spectrometer at 470°C for 10 hr, reduction of the samples was observed. This is illustrated in Fig. 1, which shows the electron spectra in the range of the Mo 3*d* energy levels registered in the case of MoO_3 and Bi_2MoO_6 after oxidizing in oxygen at 1 atm for 1 hr at 470°C (curves A) and after outgassing at 10^{-8} Torr for 10 hr at the same temperatures (curves B).

The spectra of an oxidized sample of MoO_3 reveal only the presence of hexavalent Mo ions with BE values of 231.5 and 234.7 eV for 3*d* electrons in very good agreement with those observed by Cimino and De Angelis (*18*). After outgassing a new peak appears in the lower BE range at 228.2 eV. This value is identical with the BE value of the Mo $3d_{5/2}$ peak of the doublet (228.2 and 231.4 eV) which develops in the course of the reduction of MoO_3 in hydrogen (*21*). The same doublet is characteristic for molybdenum ions in MoO_2. Detailed studies of the XPS spectra of molybdenum oxides and the products of their reduction led us to the conclusion

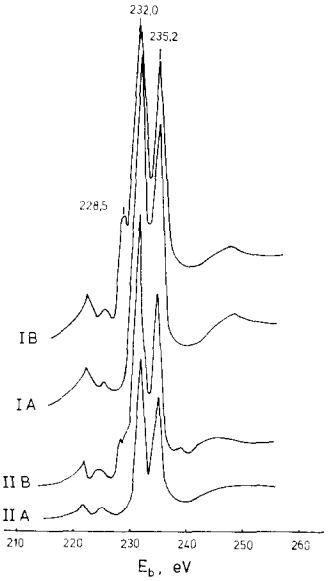

FIG. 1. Mo 3*d* signals of MoO_3 (I) and Bi_2MoO_6 (II): (A) oxidized at 470°C for 1 hr at 1 atm of oxygen; (B) outgassed at 470°C for 10 hr at 10^{-8} Torr.

(*21*) that the doublet at 228.2 and 231.4 eV corresponds to Mo^{4+} ions forming pairs with metal–metal bonds between the two paired Mo^{4+} ions of edge-sharing octahedra, the phenomenon known to occur in the MoO_2 lattice (*22*). We have advanced a hypothesis that the formation of paired Mo^{4+} ions in the course of the reduction of MoO_3 may be related to the transformation of the MoO_3 layers from the array of corner-linked zigzag strings of edge-sharing MoO_6 octahedra into units of these strings linked by edge-sharing of the last three octahedra in each unit along the shear plane (*21*). Crystallographic shear results thus in the formation of clusters of edge-sharing octahedra, in which pairing of Mo^{4+} ions occurs. Apparently similar domains of edge-sharing octahedra are formed on outgassing in the surface layers of Bi_2MiO_6. The crystal structure of Bi_2MoO_6 is composed of layers of $[Bi_2O_2]$ and $[MoO_2]$, linked together by layers of oxygen ions. The formation of shear structures in this case may be visu-

TABLE 1

Bismuth, Molybdenum and Oxygen Binding Energies (eV), in Bismuth Molybdates and Component Oxides

	Bi_2O_3	MoO_3	Bi_2MoO_6	$Bi_2Mo_2O_9$	$Bi_2(MoO_4)_3$
O 1*s*	529.8	529.8	529.8	529.7	529.8
Mo $3d_{3/2}$		235.0	235.0	235.0	235.0
$3d_{5/2}$		231.8	231.8	231.8	232.0
Bi $4f_{5/2}$	164.4		164.4	164.4	164.4
$4f_{7/2}$	158.8		158.8	159.0	159.0
$5d_{3/2}$	28.5		28.8	28.4	28.8
$5d_{5/2}$	25.6		25.6	25.6	25.6

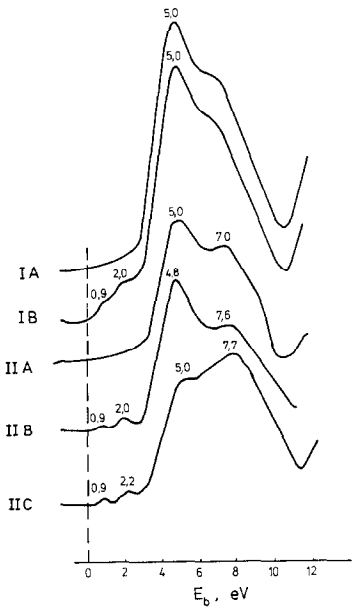

FIG. 2. Ultraviolet photoelectron spectra of MoO_3 (I) and Bi_2MoO_6 (II): (A) oxidized at 470°C for 1 hr at 1 atm of oxygen; (B) outgassed for 10 hr at 470°C; (C) contracted with propylene at 440°C.

alized as resulting from the rearrangement of the Mo–O octahedra in the $[MoO_2]$ layers, which transform from the corner-sharing into edge-sharing structure without much affecting the structure of $[Bi_2O_2]$ layers.

The tetravalent molybdenum ions appearing as the result of the formation of shear planes constitute surface energy levels situated in the forbidden energy gap of the solid, as revealed by the uv photoelectron spectra shown in Fig. 2. MoO_3 which has been oxidized at 470°C shows the valence band with two maxima at 5.0 and 7.6 eV. The valence band boundary is observable at a binding energy of about 2.8 eV. After outgassing, local energy levels appear at ~0.9 and ~2.0 eV. Similar levels are also formed on outgassing the Bi_2MoO_6 as indicated by curve IIB. These levels should have a donor character, as the substitution of higher valent ions in the lattice sites of an oxide by lower valent ions results in the appearance of *n*-type conductivity. In fact, measurements of the electrical conductivity of MoO_3 and its dependence on oxygen pressure showed that this oxide has *n*-type conductivity (*23*).

C. Reduction in Hydrogen

The conclusion that on reduction of Bi_2MoO_6 the $[MoO_2]$ layers are first reconstructed without change of the structure of $[Bi_2O_2]$ layers is further substantiated by the results of electron spectra of Bi_2MoO_6 samples contacted with hydrogen for various times. Figure 3 illustrates the Bi 4*f*, Mo 3*d* and O 1*s* signals of such samples.

As mentioned above, outgassing at 470°C results already in the reduction of Mo^{6+} to Mo^{4+} ions, which is manifested by the appearance of the $3d_{5/2}$ peak of paired Mo^{4+} at 228.3 eV (spectrum II). No changes of the Bi peaks could be observed, as illustrated by the 4*f* doublet. On exposing the sample to hydrogen at 470°C for 10 min, the intensity of the peak at 228.3 eV increases indicating further reduc-

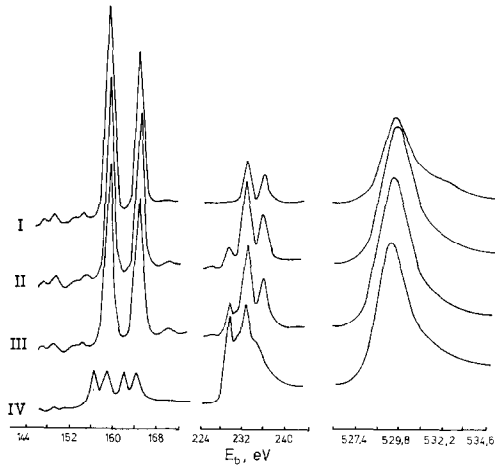

FIG. 3. Bi 4*f*, Mo 3*d* and O 1*s* signals of Bi_2MoO_6 samples reduced in hydrogen: (I) initial sample, outgassed at 120°C; (II) after outgassing at 470°C for 15 hr; (III) after exposing to hydrogen at 470°C for 10 min; (IV) after again exposing to hydrogen at 470°C for 1 hr.

tion of Mo^{6+} ions to Mo^{4+}, whereas the Bi peaks still remain unchanged. Only after reduction in hydrogen at 470°C for 2 hr, when the Mo $3d_{3/2}$ peak at 235 eV remained only as a shoulder indicating that the majority of Mo^{6+} ions have already been reduced, did the doublet appear at the binding energy of 156.2 and 161.8 eV, characteristic for the 4*f* peaks of metallic bismuth. An identical position of the doublet was obtained after deposition of a thin layer of metallic bismuth onto the gold support.

It may therefore be concluded that the interaction of hydrogen with Bi_2MoO_6 results first in a rearrangement of the $[MoO_2]$ layers to form shear structures with the reduction of Mo^{6+} to Mo^{4+} ions, and only in the later stages of this process does the reduction of Bi^{3+} take place. It is interesting that throughout the whole process of reduction and rearrangement the position of the oxygen 1*s* peak is constant, indicating that the charge distribution around oxygen ions remains practically unchanged.

D. Surface Composition

The reduction–oxidation processes have a pronounced influence on the composition of the surface layer of bismuth molybdate grains. Figure 4 shows the relative intensities of the Bi $4f_{7/2}$ and Mo $3d_{5/2}$ peaks with respect to the O 1*s* peak as function of the Bi/Mo atomic ratio in the molybdates for fresh samples, outgassed at 120°C for 3 hr at 10^{-8} Torr (curves IA and IIA), samples which were heated at 470°C in vacuum for 10 hr (curves IB and IIB) and samples treated at 440°C for 5 hr in a flow reactor with the reacting mixture ($C_3H_6:O_2:N_2 = 24:21:55$ vol%). Annealing in vacuum at high temperature leads to a considerable decrease in Bi intensity (curve IB) and to increase in Mo intensity (curve IIB). This effect is most pronounced in the case of the Bi-rich phase

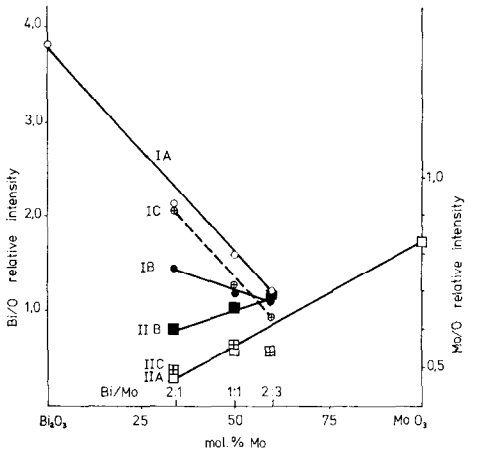

FIG. 4. Relative intensities of Bi $4f_{7/2}$ peak (I) and Mo $3d_{5/2}$ peak (II) with respect to the O 1*s* peak for bismuth molybdates: (A) initial samples; (B) after heating in vacuum at 470°C; (C) after treatment with reaction mixture ($C_3H_6 + O_2 + N_2$) at 440°C.

Bi_2MoO_6. It may therefore be concluded that on annealing the surface layer of the grains becomes enriched in molybdenum. This may be related to three effects, namely formation of shear structures, surface migration of molybdenum oxide and evaporation of bismuth ions from the surface. As shown above, on heat treatment in a vacuum a surface reduction takes place resulting in the formation of domains of edge-sharing Mo octahedra. The number of molybdenum ions per unit volume in such domains is twice that in the layer of corner-sharing octahedra which would easily account for the increase in the Mo peak intensity. On the other hand, molybdenum polyhedra are known to migrate readily over oxide surfaces (*25*) and heating in a vacuum may cause reconstruction of the exposed crystal planes, resulting in the decrease of the intensity of the Bi peaks. Evaporation of some of the bismuth ions from the surface may also take place resulting in similar reconstruction of the surface. It is noteworthy that samples treated in the propylene + oxygen mixture show Bi/O and Mo/O ratios similar to

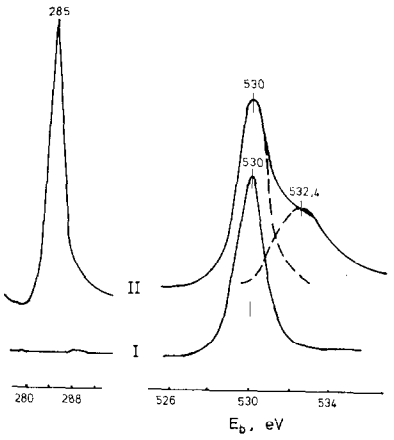

Fig. 5. C 1*s* and O 1*s* signals of Bi_2MoO_6: (I) sample oxidized at 470°C for 1 hr at 1 atm of oxygen; (II) after treatment in the reaction mixture (C_3H_6: O_2: N_2 = 24:21:55 vol%) at 440°C for 1 hr.

those of fresh samples. This may be taken as an indication that in the conditions of the catalytic oxidation of propylene the surface of the bismuth molybdate catalyst remains totally oxidized and the surface composition of the three bismuth molybdate phases reflects that of the bulk. In contrast, in the reducing atmosphere due either to the action of high vacuum or to the presence of reducing agents, a reconstruction of the surface occurs, resulting in a similar composition for the surfaces of all three molybdates. This fact should be taken into account when correlations are sought between the catalytic activity and physicochemical properties of these catalysts.

It is interesting to mention that after the samples had been treated with the reacting mixture in the flow reactor, their spectrum reveals the appearance of the second kind of oxygen species. This is illustrated in Fig. 5, which shows the O 1*s* signals of the fresh oxidized Bi_2MoO_6 sample and the same sample after reaction in $C_3H_6 + O_2$ mixture.

The appearance of the peak at 532.4 eV was also observed when the Bi_2MoO_6 sample was exposed to propylene at 500°C *in situ* in the spectrometer. This peak is accompanied by the appearance of the C 1*s* peak at 284.5 eV. As we have observed a similar value of the 1*s* electron binding energy for oxygen in adsorbed propionic acid we suggest that the 532.4 eV peak may be assigned to oxygen in oxygenated hydrocarbon species strongly bonded to the surface of the catalyst. It must be remembered that a similar position of the O 1*s* peak is also observed for surface OH groups. However, as the appearance of this peak was not observed on reduction of the sample in hydrogen (cf. Fig. 3), the first assignment seems to be more plausible. This would indicate that in the course of the catalytic reaction the bismuth molybdate catalyst becomes covered with strongly bonded oxygenated hydrocarbon species which persist at the surface even after outgassing at 430°C for 12 hr.

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