JOURNAL OF CATALYSIS 37, 174–178 (1975)

NOTES

X-Ray Photoelectron Spectroscopy Study of Some Bismuth Molybdates and Multicomponent Molybdates

This article reports ESCA experiments on some multicomponent molybdates discussed in a previous paper by Wolfs and Batist (*1*). The catalysts are of the following composition:

$$Me^{II}_a Me^{III}_b BiMo_{12}O_x,$$

in which Me^{II} is Ni, Co, Mg or Mn and Me^{III} is Fe, Cr or Al. It was proposed that their activity and selectivity in oxidation catalysis were connected with Bi_2MoO_6 and $Bi_2Mo_3O_{12}$, present as an outer shell on a core formed by $Me^{II}MoO_4$ and $Me^{III}_2(MoO_4)_3$. The bismuth molybdate shell was estimated to be about 100 Å thick, the core possessing a diameter of about 2600 Å. Because photoelectron spectroscopy (*2*) can be used for the nondestructive and quantitative surface ($\leq$100 Å depth) study (*3*) of solids, it appeared to us to be preeminently suitable to check whether the model given earlier for the multicomponent catalyst is indeed correct.

Bismuth molybdates, Bi_2MoO_6, $Bi_2Mo_2O_9$ and $Bi_2Mo_3O_{12}$, were prepared according to Batist *et al.* (*4*). The multicomponent catalysts were prepared according to Wolfs and Batist (*1*). They were of the following composition:

$Co_8Fe_3BiMo_{12}O_x$, $Mn_8Fe_3BiMo_{12}O_x$ and $Mg_{8.5}Fe_{2.5}BiMo_{12}O_x$.

X-Ray photoelectron spectra were measured on a Varian electron spectrometer. The aluminum $K\alpha$-line (1486.6 eV) was used for excitation and the X-ray power supply was run at 10 kV and 100 mA. Powdered samples were mounted using adhesive tape. The C 1*s* peak arising from pump oil contamination was used as the reference, the binding energies being corrected with reference to a C 1*s* binding energy of 285.0 eV. Spectra were also measured of samples from which layers of surface atoms had been removed by a bombardment with Ar^+ ions (*5*).

Figure 1 shows the Mo 3*d* and Bi 4*f* spectra for Bi_2MoO_6. The values of the binding energies correspond with the literature values (*6–8*) for Mo^{6+} and Bi^{3+}. Similar values were found for the other bismuth molybdates, $Bi_2Mo_2O_9$ and $Bi_2Mo_3O_{12}$. However, the relative intensities of bismuth, molybdenum and oxygen signals for the three bismuth molybdates are different (see Table 1). As expected, the intensity of the bismuth signal increased with an increasing concentration of bismuth in the catalysts. It is noteworthy that the intensity of the oxygen signals strongly depends on the concentration of bismuth in the catalysts, decreasing with decreasing Bi/Mo ratio, whilst the molybdenum signal is nearly constant. In the sequence Bi_2MoO_6, $BiMoO_{4.5}$ and $Bi_{2/3}MoO_4$ one might have expected a lowering of the intensity of the oxygen signal. This effect can be ascribed to the strong scattering power of the heavy Bi^{3+} ions: in Bi_2MoO_6 the concentration of bismuth is high and therefore the oxygen signal becomes weak.

Figure 2 shows the spectra of the $Co_8Fe_3BiMo_{12}O_x$ catalyst. It is evident that only oxygen, bismuth and molybde-

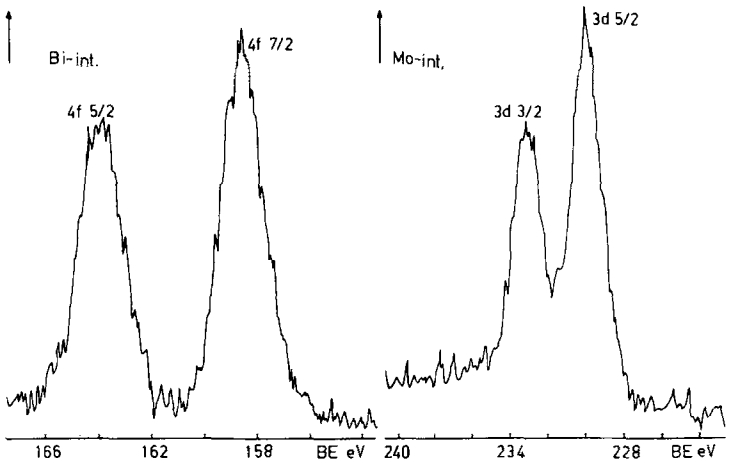

FIG. 1. Photoelectron spectrum of Bi 4*f* and Mo 3*d* in Bi_2MoO_6.

num are observable. The binding energies for oxygen, bismuth and molybdenum are equal to those of the pure bismuth molybdenum compounds. After a single sputtering with Ar^+ ions the intensity of the signals of both Bi^{3+} and Mo^{6+} decrease markedly but the Fe 2*p* signals now become observable. The binding energies for Fe^{3+} 2*p* 1/2 and 2*p* 3/2, 723 and 709 eV, are in good agreement with these given by Armour *et al.* (*7*) for $Fe_2(MoO_4)_3$. After a second sputtering the signal of bismuth disappears completely, while the Mo^{6+}-signal further decreases and the Fe^{3+}-signal increases strongly. No signals ascribed to Co 2*p* [785 eV (*7,8*)] were observed.

TABLE 1
BINDING ENERGIES AND RELATIVE INTENSITIES FOR BISMUTH MOLYBDATES[a]

Catalyst	Element	Level	Binding energy (eV)	Intensity
Bi_2MoO_6	Mo	3*d* 5/2	232	4,349
		3*d* 3/2	235	3,417
	Bi	4*f* 7/2	158.5	14,600
		4*f* 5/2	163.5	11,440
	O	1*s*	530	8,488
$Bi_2Mo_2O_9$	Mo	3*d* 5/2	232	4,176
		3*d* 3/2	235	3,071
	Bi	4*f* 7/2	159	11,042
		4*f* 5/2	164	8,532
	O	1*s*	530	12,480
$Bi_2Mo_3O_{12}$	Mo	3*d* 5/2	232	4,904
		3*d* 3/2	235	3,583
	Bi	4*f* 7/2	159	9,954
		4*f* 5/2	164	7,742
	O	1*s*	530	13,468

[a] Accuracy: binding energy, ±0.5 eV; intensity, ±300.

Experiments on the $Mn_8Fe_3BiMo_{12}O_x$ and $Mg_{8.5}Fe_{2.5}BiMo_{12}O_x$ catalysts gave similar results as for the $Co_8Fe_3BiMo_{12}O_x$ catalyst, the intensities of the metal-ion signals being somewhat changed. The binding energies and relative intensities for these catalysts are given in Table 2.

Wolfs and Batist (*1*) mentioned a correlation between the structure of the multicomponent catalysts and their catalytic behavior in the oxidation of olefins such as 1-butene. From activity tests, surface area and X-ray diffraction measurements and from diffuse reflectance data, they concluded that in these catalysts all the bismuth is present as a thin shell of bismuth molybdate (about 100 Å thick) on the surface of the catalyst particles. The core of the particles was supposed to be formed

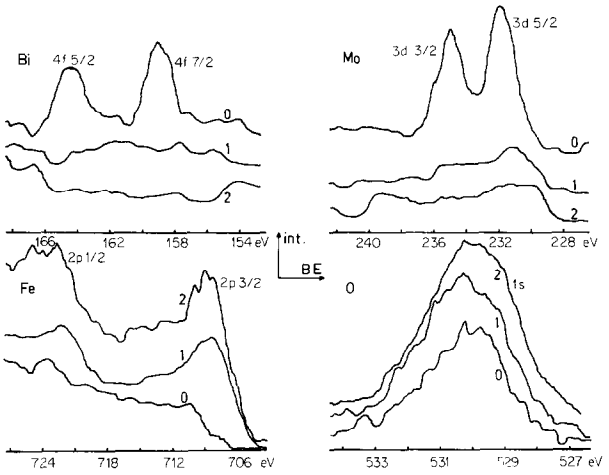

FIG. 2. Photoelectron spectrum of Bi 4*f*, Mo 3*d*, Fe 2*p* and O 1*s* in $Co_8Fe_3BiMo_{12}O_x$. (0) Spectra of the non-sputtered catalyst; (*1*,*2*) spectra after sputtering with Ar^+ ions one or two times.

TABLE 2

BINDING ENERGIES AND RELATIVE INTENSITIES FOR MULTICOMPONENT CATALYSTS

Catalyst	Element	Level	Binding energy (eV)	Intensity-0	Intensity-1	Intensity-2
CoFeBiMo	Mo	3*d* 5/2	232	2,114	1,196	780
		3*d* 3/2	235	1,880	720	418
	Bi	4*f* 7/2	159	10,960	1,048	No signal
		4*f* 5/2	164.5	6,580		
	Fe	2*p* 3/2	709	No signal	2,426	5,440
		2*p* 1/2	723		1,598	3,632
	O	1*s*	530	6,716	8,704	17,652
	Co	2*p*		No signal		
MgFeBiMo	Mo	3*d* 5/2	232	5,425	1,992	1,488
		3*d* 3/2	235	4,339	1,324	992
	Bi	4*f* 7/2	159	13,280	No signal	
		4*f* 5/2	164	12,000		
	Fe	2*p* 3/2	711	No signal	2,108	2,860
		2*p* 1/2	725		2,108	2,860
	O	1*s*	530	8,736	11,140	
MnFeBiMo	Mo	3*d* 5/2	232	3,947		815
		3*d* 3/2	235	2,821		489
	Bi	4*f* 7/2	159	12,690		No signal
		4*f* 5/2	164	9,410		
	Fe	2*p* 3/2	709			2,608
		2*p* 1/2	723	No signal		2,170
	O	1*s*	530	7,540		12,934

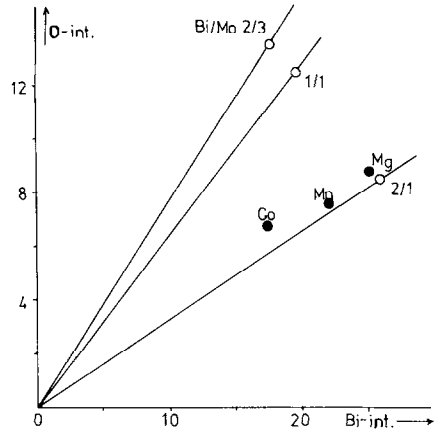

FIG. 3. Relation between the intensities of the signals of O and Bi for bismuth molybdates and multicomponent molybdates.

by a mixture of β-$Me^{II}MoO_4$ and $Me^{III}_2(MoO_4)_3$.

From the present ESCA experiments on non-sputtered catalysts it is seen that the model of a bismuth molybdate surface layer on a core of the other molybdates is indeed correct. Figure 3 gives the intensity of the oxygen signal with reference to the intensity of the bismuth signal for the three bismuth molybdates and the multicomponent catalysts. It is also clear that for the multicomponent catalysts the surface skin composition is near to that of Bi/Mo = 2/1 (Bi_2MoO_6).

From the intensities of the signals of sputtered samples it appears that the concentration of bismuth in the multicomponent catalysts decreases to zero on going from the surface to an inner layer of the particles of the catalysts. From X-ray data on the multicomponent molybdates (*1*) we know that both Bi_2MoO_6 and $Bi_2Mo_3O_{12}$ are present in these catalysts. These ESCA experiments showed that the situation on the surface of the multicomponent molybdates is like Bi_2MoO_6, so directly under the surface there has to be a situation as in $Bi_2Mo_3O_{12}$. No iron was present at the surface of the catalysts. In the second shell the intensity of the iron signal increases and the intensity of the molybdenum signal decreases on going to the interior of the catalysts. Since we know (*1*) that $Fe_2(MoO_4)_3$ is present in the catalysts, we may conclude that the second shell consists of an iron molybdate that is iron-rich as we go to interior. Either the iron is reduced or there is an excess of oxygen (Fe^{III}-oxide).

Our ESCA experiments show that all Co, Mg or Mn is in the interior of the catalysts. Moreover, from X-ray data (*1*) we observe that Co, Mg or Mn are present as $Me^{II}MoO_4$ (Me = Co, Mg or Mn), so the core of the particles of the catalysts is formed by $Me^{II}MoO_4$.

	Shell	
Core	Second	First
$Me^{II}MoO_4$	Fe-molybdate ← Fe-rich	Bi-molybdate 2/3 ← Bi/Mo → 2/1
Center	– radius →	Surface

The final model is a core of the divalent molybdates with two surface shells: one shell is directly at the surface, consisting of bismuth molybdates, and one is below that, consisting of iron molybdate that is iron-rich on going towards the core of the catalysts.

One of the authors (M. W.) acknowledges financial assistance by Texaco Oil Co. which enabled him to assist in this work. Thanks are due to Professor G. C. A. Schuit and Mr. P. A. Batist for their interest and help in this work. Thanks are especially due to Dr. Y. Niwa of the Government Chemical Industrial Research Institute, Tokyo, Japan for putting the ESCA facilities of the Research Institute at our disposal.

REFERENCES

1. Wolfs, M. W. J., and Batist, P. A., *J. Catal.* **32**, 25 (1974).
2. Siegbahn, K., *et al.*, "ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy." Almqvist and Wiksell, Uppsala, Sweden, 1967.

3. James, T. L., *J. Chem. Educ.* **48**, 11 (1971).
4. Batist, P. A., Bowens, J. F. H., and Schuit, G. C. A., *J. Catal.* **25**, 1 (1972).
5. Hüfner, S., Cohen, R. L., and Wertheim, G. K., *Phys. Scr.* **5**, 91 (1972).
6. Baker, A. D., and Betteridge, D., "Photoelectron Spectroscopy." Pergamon, Oxford, 1972.
7. Armour, A. W., Mitchell, P. C. H., Folkesson, B., and Larsson, R., *in* "International Conference on the Chemistry and Uses of Molybdenum," Reading Univ., Climax Molybdenum Co., (1973.)
8. Van Sint Fiet, T. H. M., thesis, Eindhoven, 1973.

I. MATSUURA
M. W. J. WOLFS

Department of Inorganic Chemistry and Catalysis
University of Technology
Eindhoven, The Netherlands
Received February 11, 1974