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Thermal Decomposition of the 1 : 1 Bismuth Molybdate and Its Implications for Catalytic Oxidation

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To study the stability of the 1 : 1 bismuth molybdate, thin films (300–500 Å) have been prepared by thermal evaporation of the powder samples followed by heating in air or oxygen. Electron diffraction revealed that in an oxidizing atmosphere and at temperatures higher than 400°C or in vacuum and at temperatures higher than about 350°C the 1 : 1 compound decomposes into the 2 : 1 bismuth molybdate and MoO_2. These results suggest that during catalytic oxidation and (at least) for temperatures greater than 400°C the 2 : 1 compound forms near the surface of the 1 : 1 phase, being responsible for the selective catalytic oxidation.

Introduction

The bismuth molydates are interesting oxidation catalysts and therefore numerous investigations have been carried out to identify the catalytic active phases of these mixed oxides. The main conclusion so far has been that only the 1 : 1 ($Bi_2Mo_2O_9$) and 2 : 1 (Bi_2MoO_6) compounds are highly active and selective for the partial oxidation of olefins (*1*). Attempts have also been made (*2*) to relate the catalytic behavior of these compounds to their crystal structure. However, recent studies (*3, 4*) have revealed that the crystal structures of the 2 : 1 and 1 : 1 bismuth molydates are quite different and that no relationship exists between them. The structure of the 2 : 1 compound is derived by stacking layers of $(MoO_2)^{2+}$, $(Bi_2O_2)^{2+}$, and O^{2-} in the following succession:

$$(MoO_2)^{2+}\,O^{2-}\,(Bi_2O_2)^{2+}\,O^{2-}\,(MoO_2)^{2+}\,O^{2-}\,(Bi_2O_2)^{2+}\,O^{2-}\,(MoO_2)^{2+}\ldots.$$

Here the Mo^{6+} ions have a slightly distorted octahedral configuration with corner sharing of octahedra. The $(Bi_2O_2)^{2+}$ layer has a structure similar to that found in BiOCl with the oxygen arranged in square patterns. A Bi^{3+} ion is placed alternately slightly above or slightly below the center of each square. On the other hand, the 1 : 1 compound has altogether a different structure which can be represented by $Bi(Bi_3O_2)(MoO_4)_4$. Here an Mo^{6+} ion is surrounded by oxygen ions in a distorted tetrahedral form and Bi^{3+} is coordinated by eight oxygen ions at various distances. This structure is not certain because it was worked out on the basis of X-ray powder diagrams only. It is, however, believed that the positions of heavy atoms (Bi and Mo) are reasonably well defined.

Because the crystal structures of the 1 : 1 and 2 : 1 compounds are very different while their catalytic behavior is similar, either altogether different mechanisms are valid for the catalytic oxidation in each case or there exists a relationship between the two. At the

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temperatures usually used during catalytic oxidation (350–500°C), the thermal stability of these compounds is also important since their decomposition products might control the catalytic behavior. The 2 : 1 compound is stable while the 1 : 1 compound is unstable and, as is suggested in Ref. (*1*), decomposes into the 2 : 1 and 2 : 3 ($Bi_2Mo_3O_{12}$) bismuth molybdates.

These changes can be detected by X-ray powder diffraction only if a sufficiently large amount of the 1 : 1 compound has been transformed. If such changes occur only in a region of, for example, 100-Å thickness near the surface of the particles, they will not be clearly seen in the powder diagrams. Sufficiently thin crystallites can, however, transform entirely in the new phases and electron diffraction can reveal such changes. We have, therefore, prepared thin films of a few hundred angstrom thickness of the 1 : 1 compound ($Bi_2Mo_2O_9$) and employed transmission electron microscopy to obtain information on both the microstructure and structural crystallography. Changes occurring in local regions or in individual crystallites can also be followed with these techniques.

Experimental

The samples of the 1 : 1 bismuth molybdate were obtained from Dr. Ph. A. Batist. X-ray diffraction patterns were used to compute values of 2θ, d, and relative intensities of various lines. The pattern could be consistently indexed on the basis of the orthorhombic unit cell with parameters $a \simeq 11.95$ Å, $b \simeq 10.80$ Å, $c \simeq 11.88$ Å as given by van den Elzen and Rieck (*3*) and Chen

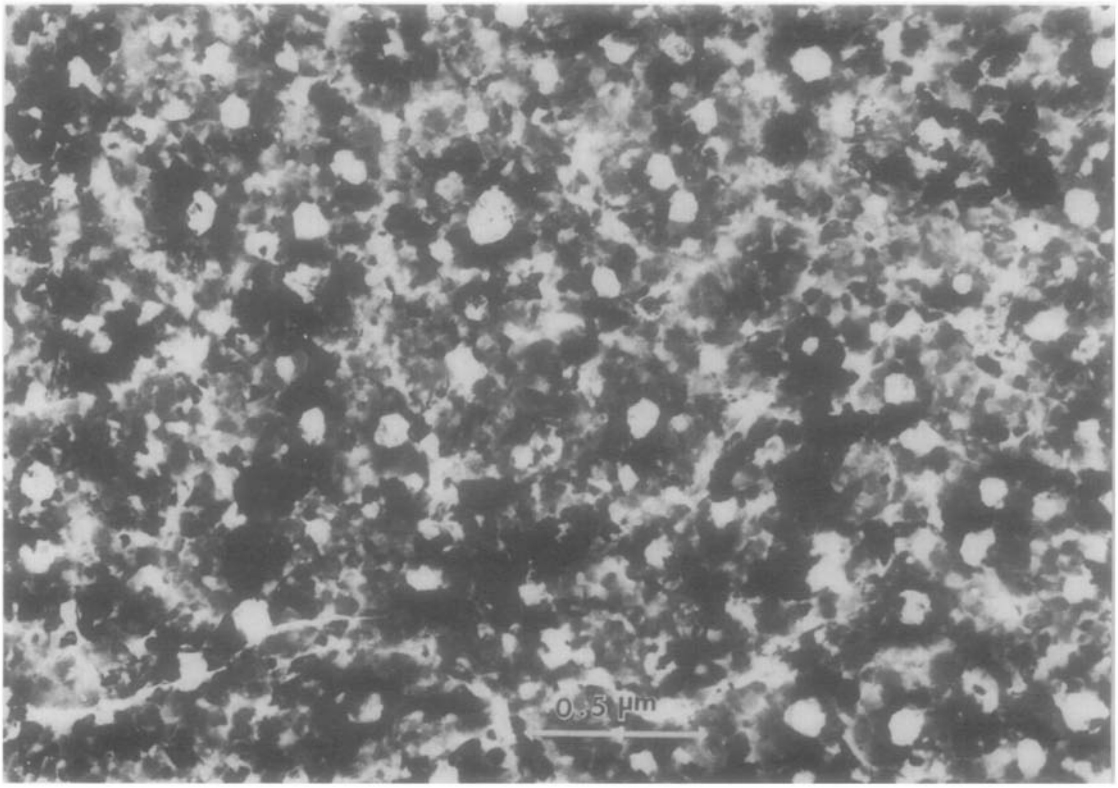

FIG. 1. Crystallized region of $Bi_2Mo_2O_9$ obtained after heating 1 hr in air at 350°C the initially deposited thin film.

and Smith (*4*). This assured us that we had a genuine 1 : 1 compound.

Thin films (300–500 Å) were then prepared by thermal evaporation of the powder samples at low pressures ($\sim 10^{-6}$ Torr) in a precleaned molybdenum boat. The resulting bismuth molybdate vapor was collected either onto a Formvar film spread over a glass slide or on thoroughly cleaned quartz plates held at room temperature at a distance above the source. To obtain homogeneous films the temperature of the boat was raised slowly to the stage of sublimation. As the temperature was raised, the color of the compound changed to gray. This change was thought to be caused by oxygen depletion. The films formed were therefore heated in air or oxygen for reoxidation. The pale yellow color that is characteristic of bismuth molybdates was thus recovered.

The initial film produced was fairly continuous and composed of very small particles. Electron diffraction patterns contained the diffuse haloes characteristic of amorphous phases. Sometimes however, in addition to haloes, faint lines of a fcc phase appeared. Samples heat treated in air showed some minor changes in their microstructure but electron diffraction patterns continued to have haloes until the temperature was raised to a sufficiently high level. The temperature required appears to depend on the film thickness, being higher for greater film thicknesses. The film crystallized above this required temperature. Figure 1 shows a crystallized thin film of $Bi_2Mo_2O_9$. The size of the crystallites increased with the heating time and with an increase in the temperature of calcination. the electron diffraction pattern of another sample is depicted in Fig. 2. This pattern can be consistently indexed with the orthorhombic unit cell noted above for the 1 : 1 bismuth molybdate (Table I). This implies that with the procedure described here, it is possible to prepare thin films of 1 : 1 bismuth molybdate.

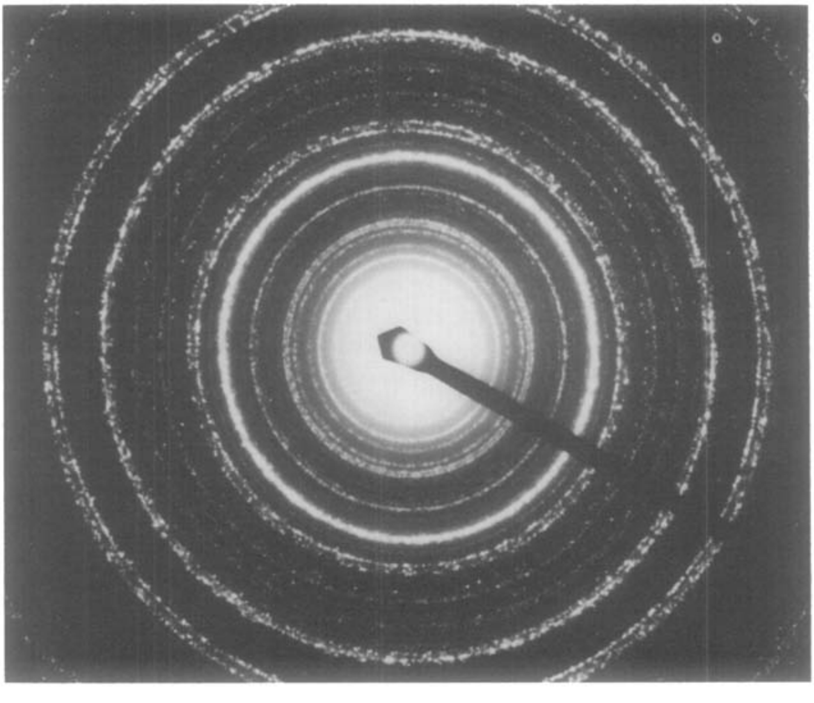

FIG. 2. Electron diffraction pattern of a sample heated in air at 400°C for 1.5 hr and at 475°C for 15 min. The *d* values and indices are given in Table I and correspond to the 1 : 1 bismuth molybdate.

When these films were heated further in air at higher temperatures (425–500°C), decomposition of the 1 : 1 compound into the 2 : 1 compound and MoO_2 took place in local regions after times as short as 30 min. By heating for longer times, sufficiently large areas containing the 2 : 1 compound and MoO_2 could be developed.

TABLE I

d VALUES COMPUTED FROM THE ELECTRON DIFFRACTION PATTERN OF THE 1 : 1 BISMUTH MOLYBDATE THIN FILM AND THEIR ASSIGNED INDICES (*hkl*)

Ring No.	Interplanar spacing *d* (Å)	*hkl*
1.	8.414	101
2.	7.994	110, 011
3.	6.630	111
4.	5.951	200, 002
5.	5.191	012
6.	4.919	120, 021
7.	4.765	211,112
8.	4.518	121
9.	4.206	202
10.	4.039	220, 022
11.	3.922	212
12.	3.777	301
13.	3.567	311
14.	3.437	031
15.	3.297	131
16.	3.194 (double)	320, 023, 312, 213
17.	3.080	230, 032
18.	2.975	231, 132, 004
19.	2.804	322, 223, 303, 411, 114
20.	2.735	232
21.	2.699	040

A spot pattern obtained from a single crystallite in the transformed region is presented in Fig. 3. This pattern can be indexed with the orthorhombic unit cell with dimensions $a = 4.587$ Å, $b = 16.226$ Å, $c = 5.506$ Å as reported by van den Elzen and Rieck (*3*) for the 2 : 1 bismuth molybdate. If heated for much longer times, the MoO_2 rings were no longer seen in the diffraction patterns. Their disappearance was probably due to the oxidation of MoO_2 to MoO_3 which sublimates easily.

Subjecting the 1 : 1 bismuth molybdate films to heat treatment at low pressures ($\sim 10^{-5}$ Torr) led to decomposition at even lower temperatures (~350–400°C), yielding the 2 : 1 compound and MoO_2. Figure 4 shows the diffraction pattern of a specimen heated at 350°C in vacuum for 30 min. The diffraction ring corresponding to MoO_2 for the interplanar spacing 3.41 Å is indicated by an arrow. Obviously, under high vacuum the oxygen is lost more easily than in the presence of O_2 or air. When samples previously reduced through annealing under vacuum were heated again in air above 400°C, the MoO_2 lines disappeared in the electron diffraction pattern. This indicates that sublimation of MoO_2 occurs, probably after its oxidation to MoO_3. Note that bulk MoO_3 sublimates at 750°C. The decomposition of the 1 : 1 bismuth molybdate thin films seems to follow the equation

$$2Bi_2Mo_2O_9 \rightarrow 2Bi_2MoO_6 + 2MoO_2 + O_2.$$

Discussion

It was shown above that thin films of 1 : 1 bismuth molybdate decompose completely into the 2 : 1 compound and MoO_2 at the temperatures prevailing during catalytic reactions. This occurs during both heating in oxygen and heating under vacuum. Using X-ray analysis, Haber (*5*) and Batist (*6*) have detected the same decomposition during heating in a reducing atmosphere. Because the transformation occurs under both oxidizing and reducing conditions it has a thermal origin.

The following phenomena may occur during the process involving selective catalytic oxidation with the 1 : 1 bismuth molybdate. (1) The 2 : 1 phase forms through thermal decomposition near the surface of the 1 : 1

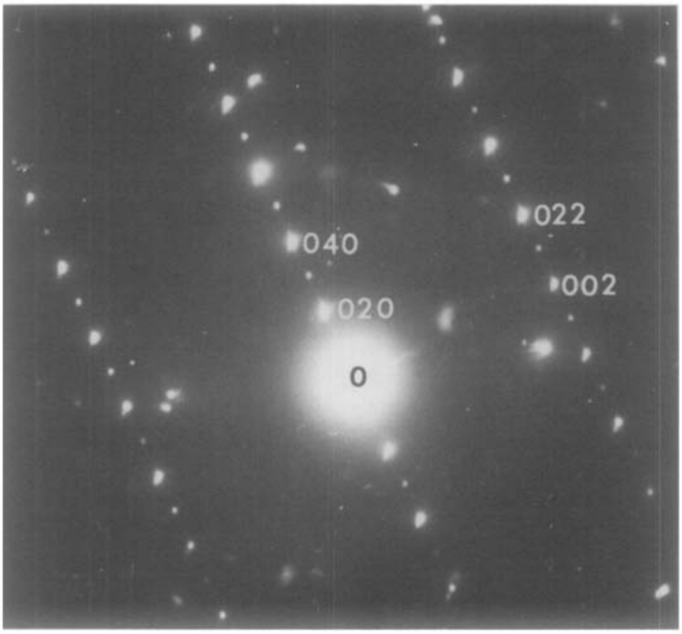

FIG. 3. Spot pattern of a single crystallite of the transformed region; it corresponds to the 2 : 1 bismuth molybdate.

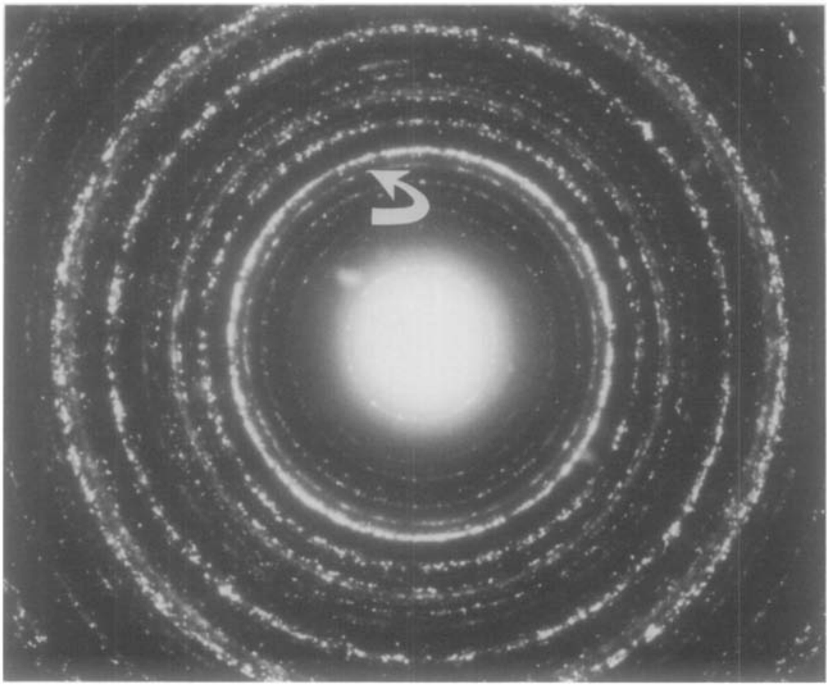

FIG. 4. Electron diffraction pattern after the film of 1 : 1 bismuth molybdate was vacuum heated at 350°C for 30 min. It reveals the presence of the 2 : 1 compound and MoO_2. The ring corresponding to MoO_2 for the interplanar spacing 3.41 Å is indicated by an arrow.

phase. (2) The highly stable 2 : 1 phase provides catalytic activity and selectivity and simultaneously protects the 1 : 1 compound from the core of the particles.

Conclusions

(1) Thin films (300–500 Å thick) of 1 : 1 bismuth molybdate can be prepared by thermal evaporation of bulk material and subsequent heat treatment in air or oxygen. Electron diffraction reveals that they transform during heating in oxygen or heating under high vacuum into the 2 : 1 compound and MoO_2.

(2) Because this decomposition occurs both in oxidizing and reducing atmospheres the oxidizing catalytic behavior of the 1 : 1 bismuth molybdate is probably due (at least at temperatures higher than about 400°C) to the presence of the 2 : 1 compound near the surface of the particles.

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