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Catalytic Oxidation of 1-Butene over Bismuth Molybdate Catalysts

I. The System Bi_2O_3–MoO_3

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In the system $Bi_2O_3-MoO_3$ the following compounds were identified:

(1) $Bi_2O_3 \cdot 3MoO_3 = Bi_2(MoO_4)_3$ m.p. 676°C
(2) $Bi_2O_3 \cdot MoO_3 = Bi_2MoO_6 = (BiO)_2MoO_4$ m.p. 938°C
(3) $3Bi_2O_3 \cdot MoO_3 = Bi_6MoO_{12}$ m.p. 995°C

These compounds were found by investigation of the phase diagram of the $Bi_2O_3-MoO_3$ binary system by means of thermal analysis. X-ray studies of sintered mixtures in this system confirmed the existence of the three compounds. A compound $Bi_2O_3 \cdot 2MoO_3$ could not be detected.

INTRODUCTION

Oxides of vanadium, molybdenum, and related elements find frequent use as oxidation catalysts. The application of V_2O_5 for the oxidation of aromatics has been known for a considerable time: the oxidation of naphthalene and *o*-xylene to phthalic anhydride and of benzene to maleic anhydride have been applied in the industry for some decades. Somewhat more recent is the discovery of the selective oxidation of olefins.

Veatch, Callahan, Milberger, and Forman (*1*) reported on the oxidation of propylene to acrolein over a bismuth phosphomolybdate/silica catalyst while Hearne and Furman (*2*) showed that butylene was converted in good yields to butadiene. It is the latter reaction that forms the subject of Paper II.

Thanks to the work of Adams and Jennings (*3*); Sachtler (*4*); Adams (*5*); and Adams, Voge, Morgan, and Armstrong (*6*) considerable information became available regarding the reaction mechanism of the oxidation of various olefins and in particular of propylene and butylene. Using D- and C^{14}-tagged olefins they showed that as an intermediate state an allyl radical or ion must be formed, presumably on the surface of the oxidation catalyst. When this allyl radical has a structure such that by dissociation of another H atom a conjugated diene can be formed, this reaction appears more favored than the oxidation of the radical to an unsaturated aldehyde. Consequently 1-butene is converted almost exclusively to butadiene.

The organic chemistry of the oxidation therefore appears relatively well understood. The inorganic chemistry seems far less clear. It has often been observed that binary catalysts, such as, for instance, $SnO_2-V_2O_5$, appear to be more active and selective than the single components. For the olefin oxidation this is also true: neither MoO_3 nor Bi_2O_3 are particularly selective. The general impression is that the ratio Bi/Mo = 1 presents the best catalyst composition available but the evidence seems somewhat meager (*1*). It has not been investigated whether or not this ratio corresponds to the existence of a binary compound. The dependency of conversion and yield has not been studied in detail as far as we know.

The experiments reported in this paper are concerned with the binary system $Bi_2O_3-MoO_3$. It will be followed by a second paper in which the relation between activity and selectivity on the one hand and catalyst composition on the other hand is discussed. Subsequent experiments have been performed to study the interaction of hydrocarbon and inorganic catalyst systems without air being present. They will be reported in the third paper. Similar experiments will be reported on nonstoichiometric Mo oxides.

From literature data it appears that in the system $Bi_2O_3-MoO_3$ the existence of only one of the compounds described is beyond doubt, viz. the compound $Bi_2O_3 \cdot MoO_3$, which occurs in nature as the mineral koechlinite. Gattow (*7*) prepared the mixed oxide $2Bi_2O_3 \cdot MoO_3$ by precipitation from aqueous solution. Zambonini (*8*) obtained tetragonal $Bi_2(MoO_4)_3$ by melting together Bi_2O_3 and MoO_3 (m.p. 643°C). Sillèn and Lundberg (*9*) could not affirm the existence of this last compound. They found a number of phases of the type $Bi_{1-x}Mo_xO_{1.5(1+x)}$ with x between 0.05 and 0.15. Belyaev and Smolyaninov (*10*) studied the ternary system $Bi_2O_3-MoO_3-PbO$. In the $Bi_2O_3-MoO_3$ range they found the following compounds: $Bi_2(MoO_4)_3$, m.p. 648°C; Bi_2MoO_6, m.p. 970°C; and Bi_6MoO_{12}, m.p. 990°C.

EXPERIMENTAL PROCEDURE

As starting materials we used the oxides MoO_3 and Bi_2O_3, which were made by heating in air: ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, E. Merck A.G. Z.A. 1182; and bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, E. Merck A.G. 1860, at 600°C during 20 hr in platinum crucibles.

Twenty-one mixtures were made (pure Bi_2O_3 and MoO_3 included) with a difference of 5 at % Mo in compositions. These mixtures were sintered in air at 600°C in platinum crucibles during 20 hr, ground in an agate ball mill during half an hour, and sintered again under the same conditions.

The thermal analysis experiments were performed according to the D.D.K. method (*11*) with the apparatus of the Linseis Co. We used platinum crucibles, Pt–Pt10Rh thermocouples and as reference α-Al_2O_3 heated at 1250°C. The linear temperature rise of the furnace was 10°C min^{-1}.

The X-ray investigations were carried out with a Philips X-ray diffractometer with Geiger-Müller counter and Ni-filtered Cu $K\alpha$ radiation.

RESULTS

Figure 1 shows some of the thermograms. They were interpreted in the following way: (a) As the temperature at which the eutectic line was passed the temperature at the foot of the first peak was taken. (b) The temperature at the top of the last peak was regarded the final melting point. The phase diagram based on the thermogram data is presented

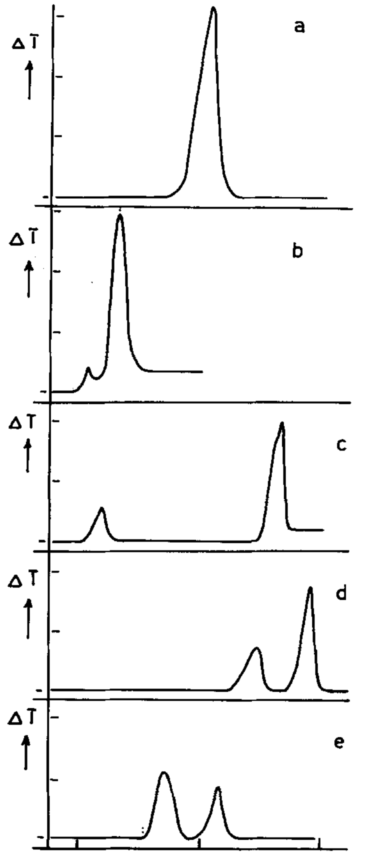

FIG. 1. Thermograms of (a) MoO_3; (b) $Bi_2O_3 \cdot 3MoO_3$; (c) $Bi_2O_3 \cdot MoO_3$; (d) $17Bi_2O_3 \cdot 6MoO_3$; (e) Bi_2O_3. ΔT is the temperature difference between sample and reference in arbitrary units.

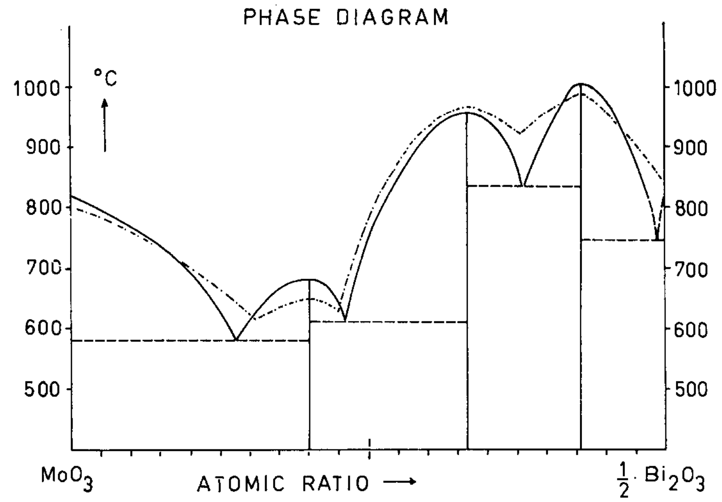

FIG. 2. Phase diagram of the system Bi_2O_3–MoO_3 (---, from ref. *10*).

in Fig. 2. As a first approximation we drew (horizontal) eutectic lines, though there are indications for the occurrence of crystalline solutions, as we will discuss later.

The X-ray powder patterns are rather complex. Figure 3 gives a survey of the strongest lines in the patterns of the various samples; numerous weak to very weak lines have been omitted from this figure.

Some minor observations may be of interest for the catalytic work. Firstly, there is a peculiar change in the color of the samples with increasing Bi content. Up to 25 at % Bi they are nearly white with a slight green haze, as is known for pure MoO_3; from 30 to 70 at % Bi they are increasingly yellow; above this composition the cream color of Bi_2O_3 is developed. Spectrophotometer

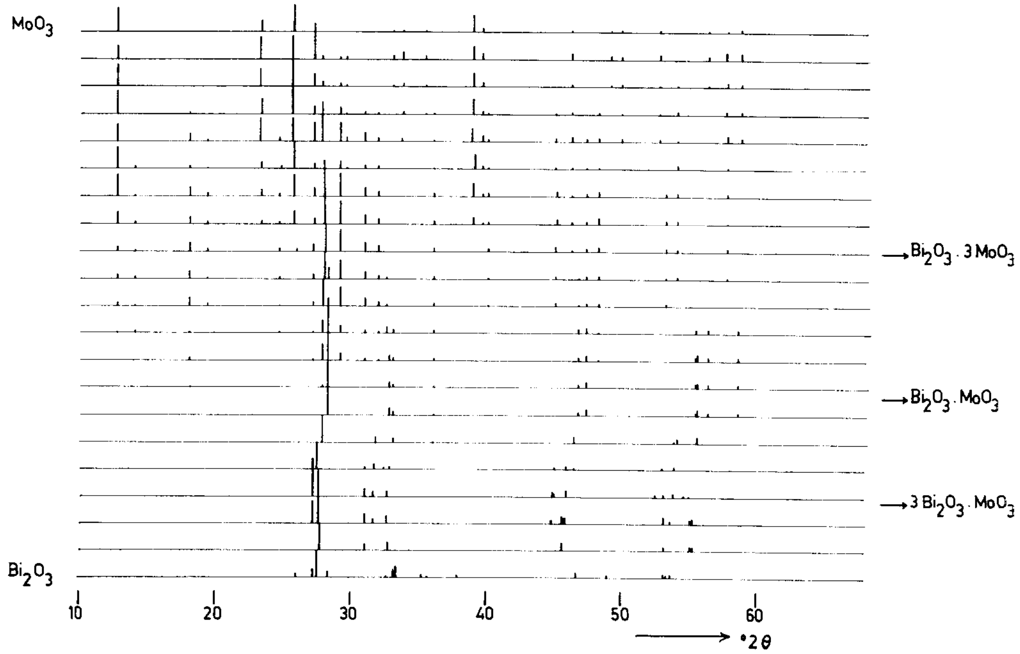

FIG. 3. Survey of X-ray diffraction patterns (weak and very weak lines omitted).

measurements show that the yellow color is caused by the flank of a very strong charge-transfer band in the far UV. Crystal field bands in the visible and near infrared region could not be detected. The absence of ESR signals of the different compositions and their diamagnetism also indicate that no Mo^V is present.

Discussion

The phase diagram (Fig. 2) shows that there are three well-defined compounds in the system $Bi_2O_3-MoO_3$:

(1) $Bi_2O_3{\cdot}3MoO_3$, m.p., 676°C
(2) $Bi_2O_3{\cdot}MoO_3$, m.p., 938°C
(3) $3Bi_2O_3{\cdot}MoO_3$, m.p., 995°C

in good agreement with the results of Belyaev and Smolyaninov (*4*). The small differences in melting temperature may be due to the different technique they used.

Neither in the X-ray patterns nor in the phase diagram can indications be found for the existence of a compound $Bi_2O_3{\cdot}2MoO_3$. Also during visual examination of the melting process under the microscope the presence of such a compound in the region of 45–55 at % Bi could not be ascertained. Crystalline solutions seem to be present in a great part of the system. The X-ray diagrams reveal that on the Bi-rich side of the compounds $Bi_2O_3{\cdot}3MoO_3$ and $Bi_2O_3{\cdot}MoO_3$ solid solutions occur to an appreciable extent with a strong influence on the lattice dimensions (corresponding lines are shifted to higher spacings).

From the melting phenomena observed under the microscope the conclusion has to be drawn that also on the Mo-rich side of the compound $Bi_2O_3{\cdot}MoO_3$ crystalline solutions to a limited extend will be present, in this case without noticeable influence on the lattice constants.

Only a few speculations concerning the structures of the compounds can be made in view of the complexity of the X-ray powder diagrams. Zambonini reports compound (1) to have a defect scheelite structure, so the composition should be written as $Bi_2(MoO_4)_3$. If so, each Bi ion is surrounded by eight MoO_4 ions, which are strongly deformed tetrahedra. One of the three cation sites remains vacant.

According to Sillèn and Lundberg (*9*) the structure of compound (2) will have some relation to that of $(LaO)_2MoO_4$, which consists of layers of La_2O_2 alternating with layers of MoO_4 tetrahedra. The composition of compound (2) (the mineral koechlinite) then can be written as $(BiO)_2(MoO_4)$. However, although there are certain similarities between the powder diagrams of $(LaO)_2MoO_4$ and of $(BiO)_2MoO_4$ [e.g., the $00l$ reflections of $(LaO)_2MoO_4$ correspond in intensity to lines in the $(BiO)_2MoO_4$ diagram], it is not possible to describe the $(BiO)_2MoO_4$ lattice completely with the $(LaO)_2MoO_4$ lattice.

Below 700°C bismuth oxide occurs as the monoclinic α-Bi_2O_3, which at higher temperature, is converted into cubic δ-Bi_2O_3. This δ-Bi_2O_3 has a CaF_2 structure with only three-quarters of the oxygen sites occupied (*7*). It is stabilized by building in SiO_2, MoO_3, or WO_3 molecules, which can fill up the vacant oxygen sites. Probably the compound (3) ($3Bi_2O_3{\cdot}MoO_3$) is the end member of this series of crystalline solutions.

Attempts are being made to obtain single crystals of the three compounds in order to establish their structure.

Acknowledgments

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References

1. Veatch, F., Callahan, J. L., Milberger, E. C., and Forman, R. W., *Actes Congr. Intern. Catalyse, 2e, Paris, 1960* **2,** 2647 (1961).
2. Hearne, G. W., and Furman, K. E., Shell Development Company U.S. Patent 2,995, 320, July 4, 1961 (to Shell Development Co.).
3. Adams, C. R., and Jennings, T. T., *J. Catalysis* **2,** 63 (1963).
4. Sachtler, W. M. H., *Rec. Trav. Chim.* **82,** 243 (1963); *Proc. Intern. Congr. Catalysis 3rd, Amsterdam, 1964,* p. 252.

5. ADAMS, C. R., *Proc. Intern. Congr. Catalysis 3rd, Amsterdam, 1964,* p. 240.
6. ADAMS, C. R., VOGE, H. H., MORGAN, C. Z., AND ARMSTRONG, W. E., *J. Catalysis,* to be published.
7. GATTOW, G., *Z. Anorg. Allgem. Chem.* **298,** 64, 71 (1959).
8. ZAMBONINI, F., *Z. Krist. Min. Petrog.* **58,** 226 (1923); **59,** 563 (1924).
9. SILLÈN, L. G., AND LUNDBERG, K., *Arkiv Kemi Min. Geol. Sci.* **A17** (1945).
10. BELYAEV, I. N., AND SMOLYANINOV, N. P., *Russ. J. Inorg. Chem.* (*English Transl.*) **7,** (1962), 579.
11. SCHWIETE, H. E., AND ZIEGLER, G., "Grundlage und Anwendungsgebiete der dynamische Differenzkalorimetrie," *Ber. Deutsch. Keram. Ges.* **35,** 193 (1958).