$$\sigma = \sigma_h + \frac{\Sigma_\omega}{L}. \quad (7)$$

With $(E_f - E_\omega)$ large enough, adsorption will result in an increase of QT that varies inversely with particle size. Furthermore, an increase in σ is possible according to (6) if the surface conductance is large enough to overcome the decrease in conductivity of Ni^{3+} holes.

This model qualitatively accounts for the observations. Similar effects should be detected with films produced by other condensible vapors such as acetone and alcohols. However, further analysis of these parameters is complicated by the many processes involved. It is clear that the over-all electrical properties of a semiconducting catalyst, prepared in the particle size range of interest in practice, are functions of the charged adsorbed species and the particle size. Theories of catalysis that attempt to reconcile surface electrical properties and catalytic mechanisms with measured quantities must take the above factors into account.

REFERENCES

1. VOLKENSTEIN, T., *Advan. Catalysis* **12** (1960).
2. RICHARDSON, J. T., AND MILLIGAN, W. O., *Phys. Rev.* **102**, 1289 (1956).
3. DEREN, J., HABER, J., AND STOCZYNSKI, J., *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **9**, 245 (1961).
4. KUTSEVA, L. N., *Dokl. Akad. Nauk SSSR* **138**, 409 (1961).
5. YOSHIO, I., SHIMADO, K., AND OZAKI, S., *J. Chem. Soc. Japan* **33**, 1372 (1960).
6. MITOFF, S. P., *J. Chem. Phys.* **35**, 882 (1961).
7. DE BOER, J. H., AND VERWEY, E. J. W., *Proc. Phys. Soc. London* **49**, 59 (1937).
8. MORIN, F. J., *Bell. Syst. Tech. J.* **37**, 1047 (1958).
9. VAN HOUTEN, S., *J. Phys. Chem. Solids* **17**, 7 (1960).
10. RAO, K. V., AND SMAKULA, A., *J. Appl. Phys.* **36**, 2031 (1965).
11. PARRAVANO, G., AND DOMENICALLI, C. A., *J. Chem. Phys.* **26**, 359 (1957).
12. DOWDEN, D. A., AND WELLS, D., *Actes du Deuxieme Congrès International de Catalyse*, p. 1499, Editions Technip, Paris (1961).
13. JÄNTSCH, O., *J. Phys. Chem. Solids* **26**, 1233 (1965).
14. ERIKSEN, W. T., STATZ, H., AND DE MARS, G. A., *J. Appl. Phys.* **28**, 133 (1957).

JAMES T. RICHARDSON

Esso Research and Engineering Company
Baytown Research and Development Division
Baytown, Texas

Received July 16, 1965;
revised June 17, 1966

X-Ray Studies of a Bismuth Molybdate Catalyst under Reaction Conditions

Studies designed to correlate activity and selectivity with catalyst composition or structure represent an attempt to elucidate the way in which the catalyst functions. Central to these studies is a determination of the structure of the catalytically active phase. In the past, the great majority of catalyst structure studies have been performed under conditions substantially removed from reaction conditions. A question immediately arises as to the resemblance, if any, between the structure existing under these conditions convenient for physical measurements and the structure existing under actual catalytic reaction conditions. This question, while asked before by others, rarely has been subjected to systematic study. An X-ray study by Isaev and Kushnerev (*1*) on a copper oxide catalyst is one of the few performed under reaction conditions.

The purpose of this note is to present XRD data obtained on an active bismuth molybdate catalyst in the conventional manner and under catalytic reaction conditions. This work represents our initial and preliminary attempt to answer the question posed above.

The catalyst was prepared at Bi/Mo = 1 by a double impregnation technique: 82 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was dissolved in 300 ml of hot distilled water to impregnate, with vigorous stirring, 450 ml of Carborundum alumina SAHT 99 (⅛ × ⅛ inch cylindrical pellets). After air-drying the impregnate for 10 hr at 120°C, it was impregnated again with 300 ml of concentrated nitric acid solution containing 226 g of bismuth nitrate, $Bi(NO_3)_3\cdot 5H_2O$. It was finally air dried for 10 hr at 100°C. The thermal behavior of this catalyst was determined with a Robert L. Stone differential thermal analyzer, Model 12BC2. On the basis of this DTA data, three catalysts were prepared differing only in calcination temperature: 450°, 600°, 750°C (the batches were calcined in air for between 2–6 hr).

The catalysts were subjected to reactor studies to determine the activity and selectivity levels for butene-1 and propylene oxidation. The system consisted of a conventional stainless steel fixed-bed reactor with a heated stainless steel sample bomb for periodic effluent analysis. Total product composition was determined by VPC analysis using chromatographs having flame ionization (organic product) and thermal conductivity (fixed gases) detection. Some of the data obtained are listed in Table 1. In this note conversion means percentage of hydrocarbon material fed which is converted to another material; and selectivity (%) to a given product means percentage of hydrocarbon reactant converted which goes to that product. The reactor results for butene-1 can be summarized as follows: The catalyst exhibits high activity for butene-1 oxidation (e.g., 77% conversion at 515°C) and gives essentially the same kind of product distribution as obtained by Shell workers (*2*) on an unsupported bismuth molybdate catalyst (butadiene is the major product, there are roughly equal amounts of the *cis* and *trans* isomers and furan is the major oxygenated hydrocarbon).

TABLE 1

OXIDATION OF PROPYLENE OVER SUPPORTED BISMUTH MOLYBDATE[a] CATALYST: BM-SAHT 99(1)–120–600 (CALCINED AT 600°C)

Temp. (°C)	463	600
Conversion (%)		
C_3H_6	17	37
O_2	29	46
Selectivity (%)		
Acrolein	89	26
CO_2	0	52
CO	~0	19
Other	11	3

[a] Oxygen fed as air, $C_3H_6/O_2 = 0.94$. GHSV (Gas Hourly Space Velocity) = 7814.

The X-ray powder patterns were obtained using copper radiation on a General Electric XRD-5 diffractometer equipped with a Materials Research Corp. high-temperature diffractometer attachment, Model X-86G. This attachment allows one to mount the sample vertically in a parafocusing geometry and to control the sample temperature to within ±0.5°C in the temperature range 25° to 1000°C. In addition, ports on the top and side of the high-temperature cell allowed us to circulate a reactive propylene-air mixture, similar to that used in the reactor studies, over the sample during the XRD determinations.

The results of the XRD determinations can be summarized as follows: With the aid of previously published data obtained on pure oxide systems, we were able to identify four compounds present in our supported catalyst: $Bi_2O_3\cdot 3MoO_3$ (*3*, *4*), $Bi_2O_3\cdot MoO_3$ (*3*, *4*), $2Bi_2O_3\cdot MoO_3$ (*5*), $3Bi_2O_3\cdot MoO_3$ (*3*). Table 2 shows that for all the calcined catalysts studied in air, the crystalline compound phases determined at room temperature are drastically different from those determined at the calcination temperature. In addition, we see that catalysts (a) and (b) and (c) and (d) have different compositions and catalysts (e) and (f) have the same. This shows the importance of attaining equilibrium conditions during the X-ray determination. Catalysts (b), (d), and (f) have been precalcined at the indicated temperature from 2–6 hr and are therefore at or very close to equilibrium

TABLE 2
Structure Study in Air

Sample	XRD Temp. (°C)	Composition (%)[a]	
		$Bi_2O_3 \cdot 3MoO_3$	$Bi_2O_3 \cdot MoO_3$
BM-SAHT 99(1)-120-450	24	80	20
BM-SAHT 99(1)-120 (a)	450	40	60
BM-SAHT 99(1)-120-450 (b)	450	10	90
BM-SAHT 99(1)-120-600	24	20	80
BM-SAHT 99(1)-120 (c)	600	~100	—
BM-SAHT 99(1)-120-600 (d)	600	80 $2Bi_2O_3 \cdot MoO_3$	20
BM-SAHT 99(1)-120-750	24	50 $3Bi_2O_3 \cdot MoO_3$	50
BM-SAHT 99(1)-120 (e)	750	100 $3Bi_2O_3 \cdot MoO_3$	—
BM-SAHT 99(1)-120-750 (f)	750	100 $3Bi_2O_3 \cdot MoO_3$ (Higher Crystallinity)	—

[a] Must be regarded as semiquantitative. The same is true for Table 3 and 4.

composition. Catalysts (a) and (c) have not been precalcined, and it appears that the length of time in the heated XRD cell was insufficient for attainment of equilibrium composition. Catalysts (e) and (f) have the same composition because having the highest calcination temperature (750° C) the rate of equilibrium attainment is highest for catalyst (e) as compared to (a) and (c).

We also note from Table 2 that as the catalyst calcination temperature is increased, MoO_3 is lost from the crystalline phase with the remaining crystalline compounds becoming Bi_2O_3-rich. Thus while our catalyst was made with Bi/Mo = 1, we note that catalyst (f) of Table 2 has Bi/Mo = 6. This apparent loss of MoO_3 from the crystalline lattice into a probable amorphous phase is in accordance with reported observations (*6*) for other mixed oxides containing MoO_3 such as the V_2O_5–MoO_3 system.

Table 3 shows the compositions determined in a propylene-air mixture. The temperatures and mole ratio are close to those used in our reactor studies of propylene oxidation. The data show an abrupt change in composition between 500° and 600°C and another composition change between 600° and 660°C. By comparing the data of Table 3 with the data for the same catalyst in Table 2, we note the fact that use of the conventional technique (room temperature in air) alone would have caused us to miss entirely the compound $2Bi_2O_3 \cdot MoO_3$ which we know to be present in the catalyst under reaction conditions (Table 3). This fact suggests the inadequacy of conventional structure studies in determining the structure of the catalytically active phase.

Table 4 shows that under identical conditions, one observes the appearance of a new structure with the air-propylene atmosphere that is not present with air atmos-

TABLE 3
Structure Study in Propylene-Air Mixture[a,b] Catalyst: BM-SAHT 99(1)-120-600

XRD Temp. (°C)	Composition (%)
408	20 $Bi_2O_3 \cdot 3MoO_3$ + 80($Bi_2O_3 \cdot MoO_3$ + $2Bi_2O_3 \cdot MoO_3$)
462	20 $Bi_2O_3 \cdot 3MoO_3$ + 80($Bi_2O_3 \cdot MoO_3$ + $2Bi_2O_3 \cdot MoO_3$)
500	20 $Bi_2O_3 \cdot 3MoO_3$ + 80($Bi_2O_3 \cdot MoO_3$ + $2Bi_2O_3 \cdot MoO_3$)
600	16 $Bi_2O_3 \cdot MoO_3$ + 64 $2Bi_2O_3 \cdot MoO_3$ + 20 Unknown
660	15 $Bi_2O_3 \cdot MoO_3$ + 50 $2Bi_2O_3 \cdot MoO_3$ + 20 $3Bi_2O_3 \cdot MoO_3$ + 15 Unknown

[a] Analysis (mole %): C_3H_6—9.8; O_2—9.6; N_2—80.5. Molar ratio: (C_3H_6/O_2)—1.02.

[b] Flowing through cell at 30 ml/min.

TABLE 4
COMPOSITION VS. ATMOSPHERIC CONDITION
CATALYST: BM-SAHT 99(1)-120-600
XRD TEMPERATURE 600°C

Air	Air-propylene mixture
20% $Bi_2O_3 \cdot MoO_3$	16% $Bi_2O_3 \cdot MoO_3$
80% $2Bi_2O_3 \cdot MoO_3$	64% $2Bi_2O_3 \cdot MoO_3$
	20% Unknown

phere alone. Unfortunately, due to the small number of observed diffraction peaks (three) from this new structure, it is not possible to identify it. The three d spacings in Å (3.187—medium; 2.659—weak; 2.249—medium) do not correspond to any known compounds in the Bi_2O_3–MoO_3 system. Identification of this unknown structure will be the subject of future investigations. At this time, however, we speculate that this unknown structure, in analogy with the results of Isaev and Kushnerev (*1*), may represent some reduced compound in the Bi_2O_3–MoO_3 system. We note that our feed composition and propylene-oxygen molar ratio are quite similar to those used by Isaev and Kushnerev, and they observed reduction of their cupric oxide to both cuprous oxide and metallic copper during the XRD runs.

The compositions shown in the tables are semiquantitative (within 15–20% of the true amounts present) and were estimated by the following procedure: In Table 2 sample (c) appears to contain only $Bi_2O_3 \cdot 3MoO_3$. The height of the major peak was taken as representing 100%. Therefore, we estimated on that basis the relative amounts of $Bi_2O_3 \cdot 3MoO_3$ in the rest of the samples. Now, considering sample (b) it was assumed that since one of the two components present is equivalent to 10%, therefore, the second component should be 90%. Knowing the height of the major peak for $Bi_2O_3 \cdot MoO_3$ at 90% the relative percentages of this compound were computed for the other samples. It was found that % $Bi_2O_3 \cdot MoO_3$, for all the samples, obtained by difference checks within 3% of the calculated percentage obtained on the basis of comparison of peak heights with sample (b). For sample (d) 80% $2Bi_2O_3 \cdot MoO_3$ was assigned only on the basis of the calculated 20% for $Bi_2O_3 \cdot MoO_3$. The rest of the data were calculated in a similar fashion.

We summarize our results as follows: Both temperature and atmospheric composition significantly affect the structure of a supported bismuth molybdate catalyst. Further, we believe that our results may serve as a basis for questioning the validity of many activity–structure correlations developed in the literature which are based on structure data obtained under nonreaction conditions. For while these correlations may be "true" in their own right, since the structure they are based on may bear no resemblance to the structure actually existing under reaction conditions, these correlations may be misleading and give an incorrect idea of how the catalyst functions. These conclusions are not limited to structure studies by XRD alone but are also applicable for similar studies using IR, ESR, magnetic susceptibility, or any other analytical technique.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of Mr. M. F. Kraemer of the CRD Catalysis Group, who obtained most of the catalytic data, and Mr. Donald Parker of the Physical Sciences Center, who obtained the XRD data.

REFERENCES

1. ISAEV, O. V., AND KUSHNEREV, M. YA., *Proc. Acad. Sci. USSR, Phys. Chem. Sec.* **124**, 129 (1959).
2. ADAMS, C. R., VOGE, H. H., MORGAN, C. Z., AND ARMSTRONG, W. E., *J. Catalysis* **3**, 379 (1964).
3. BLEIJENBERG, A. C. A. M., LIPPENS, B. C., AND SCHUIT, G. C. A., *J. Catalysis* **4**, 581 (1965).
4. ERMAN, L. YA, GAL'PERIN, E. L., KOLCHIN, I. K., DOBRZHANSKII, G. F., AND CHERNYSHEV, K. S., *Russ. J. Inorg. Chem.* **9**, 1174 (1964).
5. GATTOW, G., *Z. Anorg. Allgem. Chem.* **298**, 64, 71 (1959).
6. MUNCH, R. H., AND PIERRON, E. D., *J. Catalysis* **3**, 406 (1964).

JAY A. RASHKIN
EMILE D. PIERRON*

Central Research Department
Monsanto Company
St. Louis, Missouri

Received June 14, 1966; revised July 22, 1966

---

* To whom inquiries concerning this work should be sent.