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Oxidation of 1-Butene over Bismuth Molybdates and Bismuth Iron Molybdate

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$Bi_3(FeO_4)(MoO_4)_2$ is found to be a highly active and selective catalyst for the oxidation of 1-butene to butadiene over the temperature range of 350–450°C. Kinetic studies at 430°C indicate first-order dependence on butene partial pressure and zero-order dependence on oxygen partial pressure. These results are very similar to those obtained with Bi_2MoO_6 and $Bi_2(MoO_4)_3$. ESCA data indicate that the surface and bulk compositions are essentially the same for each catalyst studied.

INTRODUCTION

Bismuth molybdate phases are well known as highly active and selective olefin oxidation catalysts (*1*). Two recent studies (*2, 3*) claim that a phase exists in the Bi/Fe/Mo/O system that is also an excellent olefin oxidation catalyst. However, this bismuth iron molybdate phase was not prepared pure for either study. In fact, the actual composition and structure of this phase were unknown.

A bismuth iron molybdate with the formula $Bi_3FeMo_2O_{12}$ was recently reported by Sleight and Jeitschko (*4*). Our studies indicate that this is the only ternary phase in the $Bi_2O_3/Fe_2O_3/MoO_3$ system. (See Note 1 added in proof.) This phase, however, possesses a small range of stoichiometry (*5*). The structure of $Bi_3FeMo_2O_{12}$ is related to that of scheelite ($CaWO_4$), and the formula may be written as $Bi_3(FeO_4)(MoO_4)_2$ to emphasize the discrete tetrahedra. A detailed structure determination of $Bi_3FeMo_2O_{12}$, including infrared and Mössbauer studies, is being published elsewhere (*6*). Oxides with the scheelite structure generally show high activity and selectivity for olefin oxidation and ammoxidation only when they contain both bismuth and cation vacancies (*5, 7*).

EXPERIMENTAL

The preparation of $Bi_3(FeO_4)(MoO_4)_2$ by mixing a solution of bismuth and ferric nitrates with an ammonium molybdate solution has been previously described (*4*). The dried sample was crushed and sieved to collect a 40–60 mesh fraction that was calcined in air at 500° for 6.5 hr. The BET surface area was 9.66 $m^2\ g^{-1}$.

A sample of $Bi_2(MoO_4)_3$ was prepared by solid state reaction at 700° from Bi_2O_3 and MoO_3. After final calcination the sample had a surface area of 1.28 $m^2\ g^{-1}$.

A sample of Bi_2MoO_6 (Koechlinite modification) was kindly provided by Professor G. C. A. Schuit and had been prepared by the technique of Batist *et al.* (*8*). It was calcined for 4 hr at 500°. The BET surface area was 3.00 $m^2\ g^{-1}$.

Butene oxidation studies were carried out

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in a continuous flow system under differential conditions at 3 psig pressure. The catalyst was supported in a quartz U-tube reactor (5 mm i.d.) between plugs of quartz wool.

Flows of 1-butene, oxygen, and helium were metered and combined in a mixing loop of 5′ × ⅛″ s.s. tubing. The mixture then passed over a preheated section of quartz chips before contacting the catalyst. The reactor was heated by means of a fluidized sand bath controlled to ±1°. For comparison of rates at different temperatures the oxygen/olefin ratio in the feed was slightly greater than 1. Air Products helium (specified to be 99.995%) used for diluent was passed through a bed of charcoal cooled to −196°. Ultra high purity oxygen (99.95% min) and C. P. grade 1-butene (99.0% min) from Matheson were used without further purification. The 1-butene was examined by mass spectrometry and analyzed at three pressures. It contained less than 0.02% air and 0.01% butane. No other impurities were detected.

Reaction products were determined by gas chromatography using a 10′ × 0.25″ column of 20% ethyl *N*,*N*-dimethyloxamate on 60–80 mesh Gas Chrom RA at 0° with a helium flow of 50 ml/min.

Multiple samples were taken at each set of conditions. The rates given are the averages of at least three determinations.

RESULTS AND DISCUSSION

Catalytic studies. Rates of oxidation and isomerization of 1-butene over the single phase $Bi_3FeMo_2O_{12}$ at 430° as a function of the partial pressures of olefin and oxygen are given in Table 1. As in the case of bismuth molybdates (*9*), the oxidation reaction over this catalyst is essentially first order in olefin and independent of the oxygen concentration. This was found also for the iron-promoted bismuth molybdate catalyst investigated by Batist *et al.* (*2*). The ratio of isomerization/oxidation decreased very slightly with increasing 1-butene partial pressure. The isomerization reaction is therefore slightly less than, but still close to, first order in butene.

TABLE 1

OXIDATION AND ISOMERIZATION OF 1-BUTENE OVER $Bi_3FeMo_2O_{12}$ AT 430°[a]

A. Partial pressure O_2 = 0.17 atm[b]

Partial pressure, 1-butene (atm)	Rate of oxidation (moles $\mathrm{hr}^{-1}\,\mathrm{g}^{-1}$)	Rate of isomerization (moles $\mathrm{hr}^{-1}\,\mathrm{g}^{-1}$)
0.09	9.9×10^{-2}	3.2×10^{-2}
0.11	1.2×10^{-1}	4.1×10^{-2}
0.16	1.7×10^{-1}	5.2×10^{-2}
0.22	2.6×10^{-1}	7.8×10^{-2}
0.32	3.6×10^{-1}	1.0×10^{-1}

B. Partial pressure 1-butene = 0.16 atm

Partial pressure, O_2 (atm)	Rate of oxidation (moles $\mathrm{hr}^{-1}\,\mathrm{g}^{-1}$)	Rate of isomerization (moles $\mathrm{hr}^{-1}\,\mathrm{g}^{-1}$)
0.08	2.0×10^{-1}	6.6×10^{-2}
0.12	2.1×10^{-1}	6.9×10^{-2}
0.17	2.2×10^{-1}	7.0×10^{-2}
0.23	2.2×10^{-1}	7.0×10^{-2}

[a] 0.0200 g catalyst and 0.1068 g 60–80 mesh silica. Total gas flow: 250 ml/min.

[b] 1 atm = 1.013×10^5 Pa.

Similar kinetics over these catalysts makes possible a comparison of their activities by measurement of rates under the same set of conditions and normalization to unit surface area. The rates of oxidation of 1-butene to butadiene over $Bi_3FeMo_2O_{12}$ from 350 to 450° are given in Table 2. An Arrhenius plot from these data (Fig. 1) can be roughly divided into two regions. From the 400–450° plots an apparent activation energy of −75 kJ mole^{-1} is derived, whereas at lower temperature the measured apparent activation energy is much higher (−209 kJ mole^{-1}). This behavior of our single phase scheelite catalyst is similar to that found for Bi_2MoO_6 (*10*) and for iron

TABLE 2

Rates of Oxidation of 1-Butene over $Bi_3FeMo_2O_{12}$[a]

Temp. (°C)	Rate (moles hr^{-1} m^{-2} × 10^3)	Isomerization/oxidation	Selectivity[b]
350	0.65	0.65	0.95
370	2.03	0.57	0.95
390	7.84	0.5	0.97
410	12.6	0.4	0.97
430	16.7	0.33	0.97
450	24.7	0.26	0.97

[a] Partial pressure of O_2 = 0.163 atm, and of 1-butene = 0.156 atm. Total flow = 250 ml/min: 0.0203 g 40–60 mesh catalyst blended with 0.1005 g 60–80 mesh silica.

[b] The selectivity is expressed as the butadiene fraction of total oxidation product.

TABLE 3

Oxidation of 1-Butene over $Bi_2(MoO_4)_3$

Temp. (°C)	Rate (mole hr^{-1} m^{-2} × 10^3)	Isomerization/oxidation	Selectivity
325[a]	0.17	$\sim$4[b]	0.95
350	0.69	$\sim$2	0.98
375	2.04	1.2	0.99
390	2.97	0.9	0.99
390	3.16	0.8	0.99
410	4.25	0.7	0.99
430	5.46	0.6	0.99
450	7.53	0.5	0.99

[a] Gas flow was 100 ml/min with partial pressure of O_2 = 0.100 atm and of 1-butene = 0.098 atm. First set of runs at 325–390° used 0.2501 g catalyst; second set of runs at 390–450° used 0.1250 g of catalyst.

[b] The amount of isomerization falls as the catalyst is used.

modified bismuth molybdate (*2*). In the case of these two catalysts, this phenomenon has been shown to be due to inhibition by product butadiene below 400°. Although we have not demonstrated this for $Bi_3FeMo_2O_{12}$, it is probably the same for this catalyst. Batist *et al.* found only a slight inhibition for $Bi_2(MoO_4)_3$ and no marked change in the slope of the Arrhenius curve (*8*). For purposes of a comparison of the two catalysts under the same conditions we measured the rate of oxidation of 1-butene over our sample of single phase $Bi_2(MoO_4)_3$ The results are given in Table 3. This catalyst did show a definite break in the plot of log rate versus reciprocal temperature and Arrhenius apparent activation energies of −159 and −59 kJ mole^{-1} at 325–390° and 390–450° respectively (Fig. 2). A comparison of the rates of oxidation per unit surface area over the two catalysts $Bi_3FeMo_2O_{12}$ and $Bi_2(MoO_4)_3$ in the temperature range 400–450° shows the rates over the iron-substituted scheelite to be around three times as great.

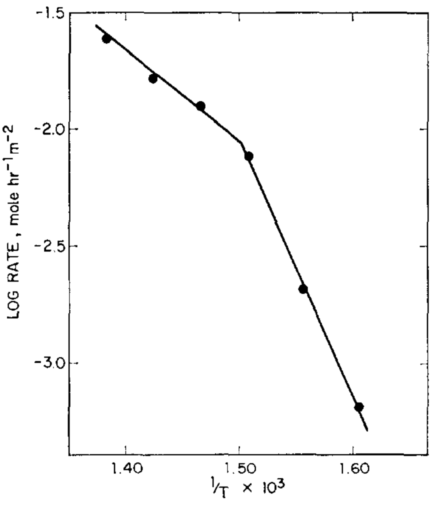

Fig. 1. Arrhenius plot for the oxidation of 1-butene over $Bi_3FeMo_2O_{12}$.

Using the same conditions, the rates of oxidation of 1-butene over the Bi_2MoO_6 catalyst furnished by Professor Schuit were measured over the range 370–430° (Table 4). Comparison of the data in Tables 2 and 4 shows that the ratio of rates of oxidation over $Bi_3FeMo_2O_{12}$ to those over Bi_2MoO_6 is in the range of 0.7–1., i.e. they are essentially the same. This is in spite of the fact that the bulk structures of the catalysts are decidedly different; e.g., the Mo atoms are octahedrally coordinated in Bi_2MoO_6

and tetrahedral in both $Bi_3FeMo_2O_{12}$ and $Bi_2(MoO_4)_3$.

There is a marked difference in isomerization over the two types of catalysts. Over Bi_2MoO_6, as has been noted before, the amount of isomerization to 2-butenes is uniformly low. We found the ratio of isomerization/oxidation to be slightly greater than 0.1 over the range 370–430°. In contrast, the $Bi_2(MoO_4)_3$ catalyst gives appreciable isomerization. The isomerization/oxidation ratio is smaller at higher temperatures, but is somewhat less in all cases over $Bi_3FeMo_2O_{12}$. Although we have not made an exhaustive study of the change in this ratio with time of use, it appeared to be relatively constant at any given temperature over $Bi_3FeMo_2O_{12}$ and Bi_2MoO_6. However, with $Bi_2(MoO_4)_3$ there is initially a rapid change of the catalyst insofar as isomerization is concerned. When the oxidation reaction was started at 325°, and the first sample taken at 20 min. the amount of isomerization was 4.5 times that of oxidation. About 1 hr later the ratio had dropped to 3.8, with little change in the rate of oxidation. We did not wait until the ratio was stabilized at the lower temperature, but in the higher temperature range the ratio was essentially unchanged with time.

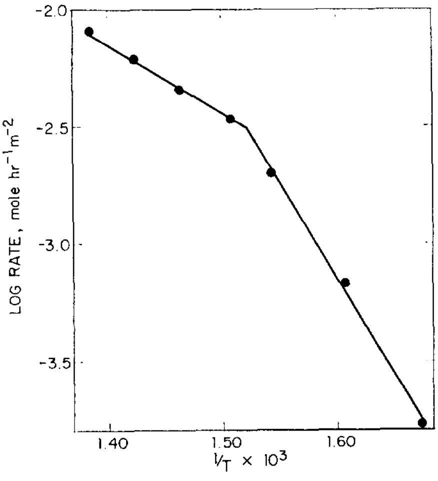

FIG. 2. Arrhenius plot for the oxidation of 1-butene over $Bi_2(MoO_4)_3$.

TABLE 4

OXIDATION OF 1-BUTENE OVER Bi_2MoO_6[a]

Temp. (°C)	Rate (mole hr^{-1} m^{-2} × 10^3)	Isomerization/oxidation	Selectivity
370	2.53	0.13	0.99
390	7.83	0.13	0.99
410	16.7	0.15	0.99
430	24.8	0.15	0.99

[a] 0.100 g catalyst with total gas flow of 180 ml/min, where partial pressure of O_2 = 0.169 atm and of 1 butene = 0.156 atm.

Batist *et al.* have suggested that the promoter action of iron in bismuth molybdate catalysts is to increase the concentration of the Bi_2MoO_6 phase (*2*). However, because of the great similarities of all the bismuth molybdate phases insofar as olefin oxidation activity is concerned, we believe that the active sites at the surface are much the same in all of the catalysts. The rate is primarily a function of the concentration of these sites at the surface.

ESCA studies. We have made a brief study of the ESCA spectra of the catalyst samples used in this study to determine if the surface, or near-surface, layers have essentially the same composition as the bulk. Quantitative interpretation of ESCA data is fraught with difficulties. These have been discussed by Brundle (*11*). However Carter, Schweitzer and Carlson (*12*) have recently described a model for calculating relative intensities of photoelectron peaks for the elements of a homogeneous solid sample. They found satisfactory agreement between calculated and experimental values in solids. The method should give some indication of the homogeneity of these catalyst preparations. This method makes use of photoelectron cross sections that have been calculated by Scofield for both magnesium (1254 eV) and aluminium (1487 eV) radiation (*13*). If one makes the assumption that the spectrometer factor is the same for two different elements, then the atom ratio (n) for the two elements (i and j) in a sample would be

$$n_{i/j} = I_i\sigma_j\lambda_j/I_j\sigma_i\lambda_i,$$

where λ is the mean free path for inelastic scattering, I is the integrated intensity of the peak for any given core level of the atom under consideration, and σ is the photoelectron cross section for that same level. The mean free path can be approximately fitted to a square root dependence on the kinetic energy and therefore for the purpose of the ratio,

$$n_{i/j} = I_i\sigma_j(h\nu - BE_j)^{\frac{1}{2}}/I_j\sigma_i(h\nu - BE_i)^{\frac{1}{2}},$$

where BE is the binding energy of the level under investigation and $h\nu$ is 1487 or 1254 depending on the X-ray source used. This model assumes no surface contamination, a condition that certainly does not hold in most ESCA determinations. In our present experiments we can only make a qualitative estimate of the effect of surface contamination on our samples.

Table 5 gives the results of the measurements of the ESCA spectra for the three catalysts used in this study. Two different samples of $Bi_3FeMo_2O_{12}$ were run, one of the catalyst directly from the preparation and the other after having been calcined in air at 500° for 6.5 hr. Batist *et al.* (*2*) noted that their sample of $Bi_2(MoO_4)_3$ underwent change with time and suggested that this was due to phase change. We noted above that the isomerization activity changed initially in our preparation. Therefore, we exposed a sample of the catalyst to 200 mm of butene at 450° for 10 min and reexamined the spectrum of this catalyst.

Table 5 also gives atom ratios determined by the method described above. Within experimental error, the two samples of $Bi_3FeMo_2O_{12}$ are the same. Likewise, we can see no significant difference in the spectra of $Bi_2(MoO_4)_3$ before and after the brief exposure to butene. For all three of the catalysts, the Bi/Mo ratio computed from the peak intensities of the Bi 4f7/2 and Mo 3d5/2 photoelectrons using the method described above is low. A contamination layer should attenuate the less energetic Mo 3d5/2 electrons to a great extent, which would have the effect of lowering the ratio

TABLE 5

ESCA Spectra of Bismuth Molybdates and Bismuth Iron Molybdate[a]

Catalyst	Observed intensity ratios[b]				Atom ratios as obtained by method of Carter *et al.* (*12*)			
	Bi 4f7/2 / Mo 3d5/2	Bi 4f7/2 / Fe 2p3/2	Bi 4f7/2 / O 1s	Mo 3d5/2 / O 1s	Bi/Mo	Bi/Fe	Bi/O	Mo/O
$Bi_2O_3\cdot MoO_3$	3.76		1.79	0.48	1.49		0.29	0.20
$Bi_2O_3\cdot 3MoO_3$	1.24		0.74	0.60	0.49		0.12	0.25
$Bi_2O_3\cdot 3MoO_3$ (after butene treatment)	1.32		0.82	0.62	0.52		0.13	0.26
$Bi_3FeMo_2O_{12}$ (as prepared)	3.23	5.70	1.15	0.35	1.28	3.0	0.19	0.15
$Bi_3FeMo_2O_{12}$ (calcined)	2.97	5.94	1.20	0.41	1.18	3.1	0.20	0.17

[a] Spectra taken on a Varian IEE 15 using Mg radiation.

[b] Intensity = peak maximum × FWHM.

even more. However, there is a definite difference between the three structures. Furthermore, if one develops a sensitivity factor for the Bi/Mo ratio based on an assumed homogeneity for $Bi_2O_3 \cdot MoO_3$ and applies this to the two scheelite-like structures, values very close to the theoretical are obtained. The Fe 2p3/2 peak from the spectra of $Bi_3FeMo_2O_{12}$ is rather broad on a steeply assending baseline. Therefore it is difficult to get a very reliable estimate of the peak intensity. However, the corrected values of Bi/Fe from the two samples measured were 3.0 and 3.1. The absolute agreement is probably fortuitous.

In view of the complications and assumptions involved one must be cautious in interpreting these data, but they suggest that the surface ratio of atoms is close to that of the bulk structure. (See Note 2 added in proof.)

Note 1 added in proof. After this paper had gone to press, a paper on the bismuth iron molybdate system by T. Notermann, G. W. Keulks, A. Skliarov, Yu. Maximov, L. Ya. Margolis, and O. V. Krylov appeared in this journal [**39**, 286 (1975)]. In addition to $Bi_3FeMo_2O_{12}$, which we had previously reported (*4–6*), these authors claim a compound at the composition $Bi_2O_3 \cdot Fe_2O_3 \cdot 2MoO_3$. However, we find that this composition is not a compound but rather a mixture of known phases, e.g., $Bi_3FeMo_2O_{12}$, Fe_2O_3, $Fe_2Mo_3O_{12}$, $Bi_2Fe_4O_9$, etc. The Mössbauer data given by Notermann *et al.* for the $Bi_2O_3 \cdot Fe_2O_3 \cdot 2MoO_3$ composition support our finding in that their data are best interpreted as arising primarily from a mixture of $Bi_3FeMo_2O_{12}$ and α-Fe_2O_3 (probably in a finely divided form). Both the monoclinic and the tetragonal forms of bismuth iron molybdate have compositions very close to $Bi_3FeMo_2O_{12}$ (*6*).

Note 2 added in proof. After our manuscript was submitted for publication, a paper appeared describing some ESCA data on bismuth molybdates [Matsuura, I., and Wolfs, M. W. J., *J. Catal.* **37**, 174 (1975)]. The ratios of intensities for the photoelectron peaks reported by those workers agree well with ours for $Bi_2O_3 \cdot MoO_3$ but differ significantly for $Bi_2O_3 \cdot 3MoO_3$. This suggests that $Bi_2O_3 \cdot 3MoO_3$ phases prepared by different techniques can have significantly different surface compositions.

REFERENCES

1. Veath, F., Callahan, J. L., Idol, J. D., and Milberger, E. C., *Chem. Eng. Progr.* **56**, 65 (1960).
2. Batist, Ph. A., van de Moesdijk, C. G. M., Matsuura, I., and Schuit, G. C. A., *J. Catal.* **20**, 40 (1971).
3. Daniel C., and Keulks, G. W., *J. Catal.* **29**, 475 (1973).
4. Sleight, A. W., and Jeitschko, W., *Mat. Res. Bull.* **9**, 951 (1974).
5. Aykan, K., Rogers, D. B., and Sleight, A. W., U. S. Patent 3,806,470 (1974).
6. Jeitschko, W., McClellan, W. R., Weiher, J. F., and Sleight, A. W., *Acta Cryst.*, in press.
7. Aykan, K., Sleight, A. W., and Rogers, D. B., *J. Catal.* **29**, 185 (1973); U. S. Patent Nos. 3,843,553 and 3,843,544.
8. Batist, Ph. A., der Kinderen, A. H. W. M., Leeuwenburgh, Y., Metz, F. A. M. G., and Schuit, G. C. A., *J. Catal.* **12**, 45 (1968).
9. Batist, Ph. A., Lippens, B. C., and Schuit, G. C. A., *J. Catal.* **5**, 55 (1966).
10. Batist, Ph. A., Prettre, H. J., and Schuit, G. C. A., *J. Catal.* **15**, 281 (1969).
11. Brundle, C. R., *J. Electron Spectrosc. Relat. Phenom.* **5**, 291 (1974).
12. Carter, W. J., Schweitzer, G. K., and Carlson, T. A., *J. Electron Spectrosc. Relat. Phenom.* **5**, 827 (1974).
13. Scofield, J. H., Lawrence Livermore Laboratory Report UCRL-51326 (1973).