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In Situ Measurements of the Electrical Conductivity of Bismuth Molybdate Catalysts in Operation for Oxidative Dehydrogenation of Butene

D. A. G. Van Oeffelen,* J. H. C. Van Hooft,* and G. C. A. Schuit†

*Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and †Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711

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In situ measurements of electrical conductivities were performed on MoO₃, Bi₂Mo₃O₁₁, and Bi₂MoO₆ (koechlinite), the latter either as such or doped with small amounts of Mo or Bi; the reaction applied was the oxidative dehydrogenation of butene to butadiene. The reaction was performed in continuous flow or by pulsing butene over the catalyst, often followed by the addition of O₂ pulses. The catalysts were characterized by surface area, XRD, and XPS. The latter measurements showed that surface Bi/Mo ratios were often different from those in the bulk; reduction by butene at temperatures around 673 K sometimes led to considerable changes in the surface Bi/Mo ratio that ran parallel with changes in activity. Pulsing butene in a He carrier stream over the catalyst strongly increased the electrical conductivity while pulsing O₂ decreased it again; the conductivity is almost entirely located in the surface layers. The koechlinite-type catalysts, when heated in He, showed a considerably higher conductivity than the other catalysts. This is ascribed to a dissociation of O₂ presumably from the Bi₂O₃ layers. Subsequent pulsing of butene first increased the conductivity but for catalysts with Bi/Mo bulk ratios >1, the conductivities became constant while reduction continued. The first process is supposed to be connected with a stripping of the oxygen in the surface layer, the second with a migration of O²⁻ from bulk to surface and of electrons from surface to bulk. A model was presented for the surface band.

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ELECTRICAL CONDUCTIVITY OF BiMoO CATALYSTS

MoO₃, and bismuth molybdate (Bi/Mo = 0.7) in propene and air (or oxygen) at 500°C. By admitting propene to bismuth molybdate they observed a considerable increase in conductivity; this could be eliminated by subsequent admission of oxygen. They showed that the increase in conductivity was brought about by extensive reduction of the surface layers of the catalysts. Similarly, the decreases after oxygen admission had to be ascribed to reoxidation of the reduced surfaces. They were able to show that the bismuth molybdate catalyst was about 10% reduced when operating with mixtures of propene and oxygen under normal steady-state conditions. Furthermore they were able to determine the temperature dependence of the conductivity of the catalyst in oxidized and in partially reduced states. They showed that the energy gap decreased with increasing reduction. They concluded that the conductivity measurements can produce information about the reduction of the surface and perhaps a few subsurface layers, but do not furnish information about the oxidation states of the individual ions present in the surface.

Morrison (4) described the interaction of bismuth molybdates (Bi/Mo = 0.7) with oxygen and propene and the corresponding conductivity changes. At T < 275°C propene reacted only with what is assumed to be adsorbed oxygen, so that the conductivity after propene admission reaches a maximum. However, at T > 275°C propene reacted also with “irreversible oxygen,” i.e., lattice oxygen, so that in this case the conductivity did not reach a maximum and reduction was continuous.

Our conductivity measurements on the bismuth molybdates differ from those mentioned before on the following points.

The experimental arrangements were as follows. We first determined activities of the various samples as a function of the temperature in continuous-flow modes when the reactants streamed through a bed of catalyst powder.

We then repeated the experiments in a reactor where a pellet was present so that the reactants streamed around the pellet; its electrical conductivity could then be measured either in AC or DC current. These experiments were not particularly informative; electrical conductivities were low and in the order of 10⁻⁶–10⁻⁷ (Ω⁻¹ cm⁻¹) when no butene was present to increase somewhat when the olefin was added to the gas.

It was then decided to use the method whereby pulses of butene and oxygen were injected into a He stream passing the pellet. The electrical conductivities were measured when the olefin pulse passed the pellet while its degree of conversion was then measured chromatographically. To obtain an impression of how the differences in flow pattern, i.e., gas stream flowing along the pellet or through a bed of powdered catalyst, influenced the conversions, separate experiments with pulses flowing through a bed were also performed; for obvious reasons the latter experiment did not allow measurements of the conductivity.

EXPERIMENTAL

Catalytic Activity Measurements

When the butene oxidation was studied in a continuous-flow apparatus, a constant flow of a mixture of 1-butene and artificial air (ratio C₄H₈:O₂:He = 20:20:80), passed through the catalyst bed (400 mg, particle size 0.2–0.4 mm) that was placed in a microreactor made of quartz glass. The reactor was heated by means of a heating wire, mounted on an aluminum tube. The temperature inside the catalyst bed was measured by a chromel alumel thermocouple [see Batist et al. (6)].

Samples of the product stream were analyzed gas chromatographically.

We used the following definitions:

activity = \frac{(\text{butenes}_0) - (\text{butenes})_T}{(\text{butenes})_0} \times 100\%,

selectivity = \frac{\text{(dien) \text{e}}}{\text{(diene) + \frac{1}{2}(CO₂)}} \times 100\%,
FIG. 1. Experimental set up for the electrical conductivity measurements. S = sample, F = constant voltage supply, A = multimeter, V = spot galvanometer, J = junction box.

\[
\frac{1}{\rho} = \frac{L}{A} \cdot \frac{1}{R},
\]

in which

\(L\) = distance between electrodes 3 and 4 (cm),
\(A\) = cross-sectional area of pellet (cm\(^2\)),
\(R\) = resistivity (\(\Omega\)),
\(\rho\) = specific resistivity (\(\Omega \cdot \text{cm}\)),
\(\sigma\) = electrical conductivity (\(\Omega^{-1} \cdot \text{cm}^{-1}\)).

The polarity could be changed to check charging effects.

For pulse experiments we used the same apparatus but the reactor was placed between sample valve and gas chromatographic column. The helium carrier gas was passing continuously over the catalyst; by means of a sample valve it was possible to pulse amounts of 1-butene over the catalyst with subsequent analysis of the reaction products. The volume of the pulse was 0.6 cm\(^3\) (25°C, 1 atm).

**Electrical Conductivity Measurements**

The electrical conductivity was measured on samples which were pressed to rectangular pellets under a pressure of 1000 kg/cm\(^2\). The dimensions were about 15 × 5 mm. The weight of the pellet was about 0.8 g.

A four-probe technique was used, in which two of the electrodes served as current leads and the other two as voltage leads. Figure 1 gives a scheme of the experimental set up.

From current and voltage measurements the resistivity could be calculated. From the sample dimensions we could get a specific resistivity and an electrical conductivity:

\[
\sigma = \frac{1}{\rho} = \frac{L}{A} \cdot \frac{1}{R},
\]

in which

\(L\) = distance between electrodes 3 and 4 (cm),
\(A\) = cross-sectional area of pellet (cm\(^2\)),
\(R\) = resistivity (\(\Omega\)),
\(\rho\) = specific resistivity (\(\Omega \cdot \text{cm}\)),
\(\sigma\) = electrical conductivity (\(\Omega^{-1} \cdot \text{cm}^{-1}\)).

The sample was spring-loaded between Pt contacts. Pt was used as electrode material; Pt leads were shielded by ceramic tubes. The electrode assembly was placed in a quartz glass tube, which could be supplied with different gases (Fig. 2). The outlet was connected with a gas chromatographic column, the same as used for the activity measurements. By means of a sample valve it was possible to carry out pulse experiments by pulsing 1-butene in a helium flow. The reactant gases were entering the tube directly below the catalyst pellet. The volume of the pulse was 0.9 cm\(^3\).

Because of the rather large volume of the tube it was not possible to get an ideal plug flow of the gases, thus preventing a good gas chromatographic analysis of the products. Freezing the reaction products for 15 min in a liquid nitrogen trap and subsequent quick heating to room temperature enabled us to get a reproducible analysis of the reaction products.
ELECTRICAL CONDUCTIVITY OF BiMoO CATALYSTS

**FIG. 2.** Electrical conductivity cell and sample holder. a = Sample, b = electrodes, c = alumina ceramic tubes, d = stainless-steel holder, e = quartz glass tube, f = springs, g = inlet gases, h = exit gases, i = electrode connections, j = thermocouple.

**XPS, XRD, and SA Measurements**

*X-Ray photo electron spectroscopy.* The apparatus used was at the Physical Chemistry Laboratory of the University of Groningen (The Netherlands). It was an AEI ES 200 spectrometer with MgKα radiation (1253.6 eV), with the power supply run at 16 kV and 15 mA. The spectra were collected using a PDP 8 computer and stored in a 32K disk. The powdered samples were either stuck onto a piece of tape or pressed into a copper gauze. Sensitivity factors used were as given by Berthou and Jørgensen (5).

*X-Ray diffraction.* We used a Philips PW 1120 spectrometer with CuKα radiation and Ni filter.

*Surface area measurements.* These were performed with an areameter of Ströhlein, which is based on the single-point BET method using nitrogen as adsorbate.

**Preparation of the Catalysts**

The preparations were carried out with the following chemicals: basic bismuth nitrate BiONO₃ (Merck), powdered molybdic acid (BHD), ammonium heptamolybdate (NH₄)₆Mo₇O₂₄ · H₂O (Merck), bismuth nitrate Bi(NO₃)₃ · 5H₂O (Merck).

Bi₂O₃ was prepared by heating basic bismuth nitrate, containing 79.94 wt% Bi₂O₃ at 520°C for 10 h to give αBi₂O₃ (Sample A).

MoO₃ was prepared by heating molybdic acid, containing 88.98 wt% MoO₃ at 500°C for 4 h (Sample B).

Bi₂MoO₆ was prepared according to the slurry method of Batist (6): 16.177 g molybdic acid (0.1 mol MoO₃) and 58.289 g basic bismuth nitrate (0.1 mol Bi₂O₃) were added to 1 liter boiling water. To the slurry was added a 4-cm³ volume of concentrated nitric acid, after which the reaction was started. The slurry was vigorously stirred. After 12 h of reaction the yellow colored mass was filtered off, dried at 120°C for 16 h, and calcined at 500°C for 2 h. The reaction could be carried out quantitatively as was shown by examining the obtained weight (Sample C).

Bi₂Mo₁.₈₂O₆.₉₆: The same method was used as for Bi₂MoO₆, except that we used...
16.500 g molybdic acid (0.102 mol MoO₃). Here again the reaction was quantitative (Sample D).

Bi₂₀₄MoO₁₀₆₀₆: Again a slurry method was used, starting with 16.177 g molybdic acid (0.1 mol MoO₃) and 59.204 g basic bismuth nitrate (0.102 mol Bi₂O₃). The molybdic acid was first dissolved in aqueous ammonia. After 18 h of stirring and boiling the mass was filtered off, dried at 120°C for 16 h, and calcined at 500°C for 2 h (Sample E). This preparation also yielded stoichiometric amounts as could be shown by weight analysis.

Bi₂Mo₂O₉: To 24.253 g Bi(NO₃)₃ · 5H₂O (0.025 mol Bi₂O₃) was added 13 cm³ concentrated HNO₃ and dissolved in 100 ml water; 8.827 g (NH₄)₆Mo₁₇O₄₄·4H₂O (0.05 mol MoO₃) dissolved in 100 ml water was added to the first solution with stirring. By adding aqueous ammonia the final pH was adjusted to 4. Meanwhile the solutions were cooled in ice baths. The white precipitate was filtered off, dried at 120°C for 16 h, and calcined at 500°C for 2 h. This procedure yielded a stoichiometric sample as checked by weight analysis (Sample F).

Bi₂Mo₃O₁₂: 14.577 g basic bismuth nitrate (0.015 mol Bi₂O₃) and molybdic acid (0.075 mol MoO₃) were brought into 1 liter water. The slurry was heated and stirred for 30 h, during which time the color remained white. After filtration, drying at 120°C for 16 h, and calcining for 2 h at 480°C, the resultant material contained the stoichiometric amounts of bismuth and molybdenum as was checked by weight analysis (Sample G).

The sample Bi₂₀₄MoO₁₀₆₀₆ was totally inactive over the sample temperature range investigated (380–440°C).

The sample Bi₂Mo₁₀₂O₆₀₆ showed a very high activity at temperatures higher than 420°C, whereas the sample Bi₂MoO₆ had already a high activity at 380°C, but this latter catalyst showed a considerably lower selectivity.

The catalyst Bi₂Mo₂O₉ showed fairly high activity and a very high selectivity. The sample Bi₂Mo₃O₁₂ prepared had low activity and high selectivity.

At 440°C the order of activity per unit of weight was: Bi₂Mo₁₀₂O₆₀₆ > Bi₂MoO₆ > Bi₂Mo₃O₁₀ > Bi₂Mo₃O₁₂ > Bi₂₀₄MoO₁₀₆₀₆. The order of selectivity at 440°C was: Bi₂Mo₂O₉ = Bi₂Mo₃O₁₂ = Bi₂Mo₁₀₂O₆₀₆ > Bi₂MoO₆.

The inactive Bi₂₀₄MoO₁₀₆₀₆ became reactivated after adding MoO₃. This was accomplished by taking 375 mg Bi₂₀₄MoO₁₀₆₀₆ and adding 25 mg MoO₃, corresponding to about 25 mol% Mo extra. After 30 min at T = 440°C in the reactor, this mixture exhibited an activity of 59% and a selectivity of 89.5%. At the end of this reaction time we could observe an appreciable amount of Bi₂Mo₃O₁₂ to be present, as shown by the infrared spectrum [bands at 950, 930, and 900 cm⁻¹, which are attributed to the 2/3 compound (6)].

It was also possible to activate the Bi₂₀₄MoO₁₀₆₀₆ sample by addition of an amount of a Bi₂Mo₃O₁₂ sample with low activity.

The mixing of 300 mg Bi₂₀₄MoO₁₀₆₀₆ and 100 mg Bi₂Mo₃O₁₂ after 30 min in the reactor gave a catalyst with an activity of 47% and a selectivity of 89% at 440°C.

**RESULTS**

**Activities and Selectivities**

All the catalysts except A and B were tested for their activity and selectivity in the oxidative dehydrogenation of 1-butene under continuous flow. Conditions used were 400 mg catalyst, total gas flow 120 cm³/min, C₄H₁₀:O₂ : He = 20:20:80 (the results are given in Table 1).

We used the values of Berthou and Jørgensen (5) for the elemental sensitivities of Bi(4f) = 4.3, Mo(3d) = 1.6, O(1s) = 0.6, and as reference C(1s) = 2.85 eV. Table 2 lists the binding energies (standardized) and intensities for the catalysts given before. Table 3 compares the bismuth–molybdenum ratios for bulk compound with the ob-
TABLE 1
Comparison of Conversions for Various Bi Molybdate Catalysts in Different Flow Situations

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst composition (Bi/Mo ratio)</th>
<th>Reaction temp. (°C)</th>
<th>Butene conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Surface</td>
<td>Continuous flow</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pulse 1</td>
</tr>
<tr>
<td>E, 10.7</td>
<td>2.04</td>
<td>2.27</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>C, 7.9</td>
<td>2.00</td>
<td>2.11</td>
<td>350</td>
</tr>
<tr>
<td>D, 7.3</td>
<td>1.96</td>
<td>1.78</td>
<td>350</td>
</tr>
<tr>
<td>F, 4.3</td>
<td>1.00</td>
<td>0.93</td>
<td>350</td>
</tr>
<tr>
<td>G, 2.3</td>
<td>0.67</td>
<td>0.70</td>
<td>350</td>
</tr>
</tbody>
</table>

- Symbol and surface area (in m²/g).
- Pulse (n) = highest conversion at pulse n.
- Selectivity = 84%, all others ≥95%.

observed XPS values for its surface. Figure 3 shows bismuth and molybdenum signals for Bi₂MoO₆ and Fig. 4 gives oxygen signals for some powdered samples on tape. A shoulder can be observed at higher binding energies; the low BE belongs to lattice oxygen.

TABLE 2
XPS Data: Binding Energy Values (eV) and Intensities (Int.) of Bi, Mo, and O Signals for the Various Catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bi 4f</th>
<th>Mo 3d</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b.e. (eV)</td>
<td>Int.</td>
<td>b.e. (eV)</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>159.3</td>
<td>8.38</td>
<td>232.6</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>164.6</td>
<td></td>
<td>235.7</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>159.5</td>
<td>10.65</td>
<td>232.7</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>164.9</td>
<td></td>
<td>235.9</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>159.8</td>
<td>131.7</td>
<td>233.0</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>160.0</td>
<td>28.46</td>
<td>233.0</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>165.5</td>
<td></td>
<td>236.0</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>159.9</td>
<td>3.169</td>
<td>233.2</td>
</tr>
</tbody>
</table>
TABLE 3
Comparison of the Calculated Bismuth–Molybdenum
Bulk Ratios with the Observed Values
from XPS Experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calc.</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>2$Mo$</em>{1.02}$O$_{6.66}$</td>
<td>1.96</td>
<td>1.767</td>
</tr>
<tr>
<td>Bi$<em>{2.04}$MoO$</em>{6.06}$</td>
<td>2.04</td>
<td>2.245</td>
</tr>
<tr>
<td>Bi$_2$MoO$_6$</td>
<td>2.00</td>
<td>2.11</td>
</tr>
<tr>
<td>Bi$_3$Mo$_2$O$_6$</td>
<td>1.00</td>
<td>0.928</td>
</tr>
<tr>
<td>Bi$_2$Mo$<em>3$O$</em>{13}$</td>
<td>0.67</td>
<td>0.695</td>
</tr>
<tr>
<td>Bi$<em>{2.04}$MoO$</em>{6.06}$ (after activation)</td>
<td></td>
<td>1.10</td>
</tr>
</tbody>
</table>

Pressing in Cu gauze showed the high BE signal only as broadening.

**Pulse Experiments**

We performed pulse experiments by pulsing 0.6 cm$^3$ of 1-butene over the powdered sample at different temperatures. Figure 5 shows the result for the catalyst Bi$_2$Mo$_{1.02}$O$_{6.66}$. The conversion of butene per pulse decreased after the first pulse. At 450°C a small increase was observed for the second pulse, but subsequently there again was a decrease in conversion. A completely different behavior was shown by the catalyst Bi$_{2.04}$MoO$_{6.06}$ (Fig. 6). At 400°C there was no conversion during the first three pulses, but subsequently the activity increased, to reach a maximum whereafter it decreased again, as observed for the first catalyst. After an intermediate reoxidation, the conversion at 450°C started again at a low level, but rose very quickly; it reached its maximum value at the fourth pulse.

During this activation process not only did the conversion increase, but the selectivity also became higher. After activation by reduction at 450°C the sample Bi$_{2.04}$Mo...
Electrical Conductivity Measurements

The measurements performed can be divided into three groups:

(a) Measurement of the temperature dependence of the conductivity in the oxidized state. From these measurements an overall activation energy for conduction can be calculated.

(b) Measurement of conduction after admission of pulses of 1-butene (reduction) at different temperatures, together with the amount of butene converted at the same temperature (simultaneous measurement of conduction and conversion).

(c) Measurement of conduction and conversion after a reoxidation.

Temperature Dependence of the Conductivity under Air and He

For this purpose we examined two of our samples, i.e., Bi$_2$Mo$_{1.02}$O$_{6.06}$ and Bi$_2$Mo$_{0.6}$O$_{6.06}$, the active and the inactive sample, in the temperature range 350-500°C. The measurements were carried out in air. The measured values of conductivity can be analyzed using the formula

\[
\sigma(T) = \sigma_0 \cdot \exp \left( \frac{E}{kT} \right). \tag{1a}
\]

Plotting log \(\sigma\) vs \(\frac{1}{T}\) gave results as plotted in Fig. 7, for the active and the inactive sample. The active sample had much lower activation energy (0.8 eV) than the inactive sample (1.97 eV).

When we carried out the temperature dependence measurements in a helium atmosphere instead of air, we obtained different results. The initial activation energy for both active and inactive samples were much lower than under air, viz. 0.45 and
TABLE 4
The Activation Energy \( E \) (in eV) of the Electrical Conductivity for Samples D and E after Repeated Heating and Cooling in a Helium Stream

<table>
<thead>
<tr>
<th>Heating–cooling cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Bi}_2\text{MoO}_6 )</td>
<td>0.45</td>
<td>0.46</td>
<td>0.67</td>
<td>0.81</td>
</tr>
<tr>
<td>( \text{Bi},\text{MoO}_6 )</td>
<td>1.02</td>
<td>1.10</td>
<td>0.87</td>
<td>0.79</td>
</tr>
</tbody>
</table>

1.02 eV. After several heating–cooling periods the activation energies for active and inactive sample appeared to reach the same value (Table 4).

The time dependence of the conductivity under reducing conditions (propene 5 cm\(^3\)/min) at \( T = 400^\circ\text{C} \) again demonstrated a marked difference between the two samples. The active sample gave an immediate rise in conductivity, while the inactive sample had a much slower increase.

After several minutes of reduction with propene the conductivity appeared to approach the conductivity of the active sample.

**Electrical Conductivity after Pulsing 1-Butene**

Conductivity and conversion were now measured simultaneously. The time between the successive pulses of butene was fixed at 25 min because of time requirements for analyzing the reaction products.

Figure 8 gives an example (\( \text{Bi}_2\text{MoO}_6 \)) of the changes in conductivity with increasing number of butene pulses for three different temperatures. In general the conductivity increased with the number of pulses passed over the catalyst. It is noteworthy, however, that between pulses a decrease of the conductivity could be observed. This decrease was typical for all measurements.

In order to avoid complicated drawings, the following figures will show only the maxima in conductivity after each pulse (compare Fig. 8b with a).

Figures 9–14 show conductivity and conversion values at 350, 400, and 450°C for,
respectively, Bi$_2$Mo$_{1.02}$O$_{6.06}$, Bi$_2$MoO$_{6.06}$, Bi$_2$Mo$_2$O$_9$, Bi$_2$Mo$_3$O$_{12}$, MoO$_3$, and Bi$_2$O$_3$. Figure 9 shows that Bi$_2$Mo$_{1.02}$O$_{6.06}$ already had a fairly high conductivity and a high conversion at 350°C (log $\sigma = -2.8$ resp. $\eta = 0.23$ after the first pulse with $\eta$ the fractional conversion). During further reduction the conductivity increased somewhat, but already after a few pulses a maximum value was reached. At 450°C there was hardly any change both in conductivity and conversion. This sample Bi$_2$Mo$_{1.02}$O$_{6.06}$ showed the highest level of conduction of all our catalysts (highest value log $\sigma = -2.4$). Figure 8b shows that Bi$_2$MoO$_6$ had a similar behavior as the former. The conductivity values were at a slightly lower level (maximum log $\sigma = -2.45$ at 450°C), but the conversion values were even a little higher.

Figure 10 shows some remarkable features. The sample Bi$_2$MoO$_6$ had a very low level of conversion at 350°C; also the conductivity was relatively low compared to the former koechlinite samples (log $\sigma = -4$). At 400°C after two pulses of butene the conversion increased considerably and at the same time the conductivity arrived at a much higher level. At 450°C the conversion reached almost the same level as for the active catalysts; again the conductivity followed this trend and became as high as the value of the conductivity for the sample Bi$_2$Mo$_{1.02}$O$_{6.06}$. After the runs at 450°C, the temperature was lowered to 400°C and again butene pulses were given; there was now no initial period and from the first pulse on, the sample showed a high conversion.

The samples Bi$_2$Mo$_2$O$_9$ and Bi$_2$Mo$_3$O$_{12}$ showed in principle the same behavior as the Bi$_2$Mo$_{1.02}$O$_{6.06}$ sample although the conductivity level was lower (maximum log $\sigma = -4$ for Bi$_2$Mo$_2$O$_9$ and log $\sigma = -4.5$ for Bi$_2$Mo$_3$O$_{12}$) (Figs. 11 and 12). Figure 13 shows the situation for MoO$_3$ which had a very low conversion and a low conductivity level (log $\sigma = -6$).

No conductivity could be measured for bismuth oxide at temperatures below...
500°C. Reduction lowered the conductivity at 500°C (Fig. 14) and reoxidation increased it again. This is completely opposite to the behavior of the bismuth molybdates. The difference can be explained by assuming that Bi₂O₃ is a p-type semiconductor while the molybdates are n-type semiconductors.

**Intermittent Reoxidation**

The foregoing experiments showed that the conductivity increased by reduction while simultaneously the fractional conversion decreased. The question is now how do conductivity and conversion behave after an intermittent oxidation pulse?

The method chosen was to dose an oxygen pulse at a certain moment after passage of a butene pulse and subsequently apply a new butene pulse. The time between oxygen pulse and second butene pulse was to

**Fig. 11.** Conversion of 1-butene (○) and electrical conductivity (△) during pulse reduction and oxidation of Bi₂M₀₂₀₉ at 350, 400, and 450°C. The numbers indicate the time intervals (in minutes) between an oxygen pulse and the next butene pulse.

**Fig. 12.** Conversion of 1-butene (○) and electrical conductivity (△) during pulse reduction of Bi₂M₀₂₀₁₂ at 350, 400, and 450°C.

**Fig. 13.** Conversion of 1-butene (○) and electrical conductivity (△) during pulse reduction and oxidation of M₀₂₀₃ at 350, 400, and 450°C. The numbers indicate the time intervals (in minutes) between an oxygen pulse and the next butene pulse.
be varied. During the series of pulses there always remained a helium flow over the catalyst.

The scenario of the experiments was as follows.

(a) A series of butene pulses was fed to the reactor similarly as before (time intervals of 25 min),
(b) an oxygen pulse was given,
(c) after $t = t_1$ a new butene pulse followed,
(d) a new series of butene pulses were added to arrive at the same situation as after the first series,
(e) again an oxygen pulse was added, and
(f) after $t = t_2$ a new butene pulse followed; the time differences $t_1$ and $t_2$ were varied.

Figure 15 shows the conductivity and conversion values during these experiments for the Bi$_2$Mo$_{0.9}$O$_{0.1}$ sample. After reoxidation the conductivity became much lower. Most remarkable is the fact that conversion after reoxidation was dependent on the time between the oxygen pulse and the next butene pulse, i.e., the time during which the oxygen can do its reoxidizing work.

A short time results in a high conversion, while a long time gives a lower conversion, although this is still higher than the conversion with the first butene pulse. Reoxidation experiments were also carried out with the Bi$_2$Mo$_5$O$_9$ (Fig. 11) and Bi$_2$Mo$_3$O$_{12}$ (Fig. 12) with similar results as given above.

Another type of experiment was performed with Bi$_2$Mo$_5$O$_{12}$. We examined the influence of the reoxidation during longer periods under helium. At 450°C after the fourth butene pulse we kept the catalyst for 1 h in a helium atmosphere. The next butene pulse showed a high conversion, while the conductivity during the intermediate period had decreased somewhat.

With MoO$_3$ (Fig. 13) little changes were observed during reoxidation apart from a considerable decline in selectivity. This decrease in selectivity after a reoxidation pulse was also observed for the samples Bi$_2$Mo$_{1.02}$O$_{6.01}$ and Bi$_2$Mo$_3$O$_{12}$ although to a lesser degree.

Some Additional Pulse Experiments

The catalyst Bi$_2$Mo$_{1.02}$O$_{6.06}$ was used to study the conductivity under reaction conditions by giving pulses of mixtures of oxygen and butene at $T = 400°C$.

Figure 16 gives the influence of the ratio $r = (\text{butene})/(\text{butene} + \text{oxygen})$ on conductivity and conversion. It shows that the conductivity is lower the more oxygen is present in the pulse while the fractional conversion is higher for greater oxygen contents. The selectivity of the reaction increases with higher butene ratios.

The variation of the amount of butene...
Fig. 16. Electrical conductivity (Λ), conversion of 1-butene (O), and selectivity (+) during pulses of butene-oxygen mixtures with variable composition on Bi₂Mo₁.₀₂O₆.₀₆ at 400°C.

added per single pulse was studied for Bi₂Mo₂O₉ at 450°C (Fig. 17), i.e., a situation in which the use of one pulse of the habitually applied size, i.e., 0.9 cm³ immediately gave a maximum conductivity that did not vary further with additional pulses. By varying the amount of butene delivered per first pulse after complete reoxidation it was tried to determine how much butene was necessary to arrive at the maximum level. Two loops were used for this purpose while moreover the butene content could be varied still further by dilution with helium. It is seen that amounts in the order of half those normally added sufficed to obtain maximal conductivity. It should be stressed that this could not be due to complete reduction of the catalyst as seen by the amount of butene converted that was still rising.

DISCUSSION

The reduction of an oxidic catalyst starts at its surface and will proceed to the interior by diffusion of oxygen anions from the bulk to the exterior. As a measure of the amount reduced per unit of surface we introduce the variable Σηₚ/S where ηₚ is the fractional conversion of pulse p, Σηₚ the sum of the conversions of p pulses and S is the surface of the sample. Further on we shall abbreviate this to Σ/S, the definition of the degree of reduction.

It is helpful to estimate the maximal Σ/S value for the reduction of a surface layer. Consider a layer comparable to the (Bi₂O₃)O or the (MoO₂)O layers in the bulk of γ-Bi₂MoO₆ (koechlinite). Such a layer has about $2 \times 10^{19}$ oxygens/m²; if we assume that Mo⁴⁺ and zero valent Bi represent the ultimate degree of reduction for (MoO₂)O and (Bi₂O₃)O, the maximal degree of reduction shall be between 33 and 100%, and the number of oxygens removed between 0.6 and $2 \times 10^{19}$/m². For pulses of 0.9 cm³ (containing $2.25 \times 10^{19}$ butene molecules), the maximal Σ/S should be between 0.27 and 0.9. Because in our experiments Σ/S never surpassed a value of 0.5, our results appear typically relevant for an incipient reduction of the catalyst's outer layers.

The experiments shown in Figs. 8a to 13 become more relevant when electrical conductivities are plotted as a function of Σ/S instead of the pulse number. For all catalysts we found σ to be linearly dependent on Σ/S provided the degree of reduction remained below 0.1.

$$σ = α + β \cdot Σ/S.$$  (2)

For some catalysts, such as MoO₃ and Bi₂Mo₃O₁₂, Eq. (2) could account for all data points. However, for Bi₂Mo₂O₉, the electrical conductivity became constant above Σ/S around 0.2 although reduction

Fig. 17. Relation between the electrical conductivity of the first pulse of butene and the volume of the pulse (in cm³) at $T = 450°C$ for Bi₂Mo₂O₉.
still persisted at an approximately constant level. Similar results were also obtained for the koechlinite samples (see Figs. 8–10). Equation (2) was useful as an interpolation formula for the calculation of the activation energy $E$ at a fixed value of $\Sigma/S$ and different temperatures. After insertion in Eq. (1b),

$$\log \sigma = \log \sigma_0 - 5\epsilon \times 1000/T \quad (1b)$$

where $\sigma$ is expressed in $\Omega^{-1} \text{cm}^{-1}$, and $\epsilon$ in eV we find $\epsilon$ as a function of $\Sigma/S$.

Proceeding in this manner, we arrived at Fig. 18. The figure shows four curved lines for five catalysts, viz., MoO$_3$, Bi$_2$Mo$_2$O$_{12}$, Bi$_2$Mo$_2$O$_9$, and the overlapping koechlinite (C) and Mo-doped koechlinite (D). The inactive Bi-doped koechlinite E could be represented by a single point $\epsilon(0) = 0.98$ at $\Sigma/S = 0$ [values of $\epsilon$ at $\Sigma/S = 0$ will be further indicated as $\epsilon(0)$].

As readily seen, the four lines followed similar patterns. The values of $\epsilon(0)$ were always highest, i.e., the conductivities were initially low. For four catalysts we found a sharp decrease in $\epsilon$ between $\Sigma/S = 0$ and 0.1 after which the $\epsilon - \Sigma/S$ lines became almost horizontal. However, the line for Bi$_2$Mo$_2$O$_{12}$ was horizontal over the whole range. Numerically, the average $\epsilon$ values of the four lines were found markedly different; the higher the Bi/(Bi + Mo) ratio, the lower $\epsilon$ and the higher the conductivity. It should be noted that this applied already from the very beginning of the run. The position of the line appeared essentially defined by what happened to the catalyst in the period preceding the introduction of butene, i.e., when the catalyst was heated in He before being exposed to butene.

The horizontal parts of the lines appear to represent a steady state where oxygen migration from bulk to surface is fast enough to replenish the oxygen depletion caused by the olefin oxidation. Evidently, to prevent the formation of electrical charge differences, oxygen migration should occur simultaneously with a countercurrent electron migration inward.

$$\text{(Surface) } \overset{2e^-}{\longrightarrow} \overset{0^2-}{\text{(Bulk)}.} \quad (3)$$

Once situated in the bulk, these electrons apparently do not contribute any more to the conductivity, an observation to which we shall return later on.

The observation, that the electrical conductivities of the various catalysts differ considerably over the entire $\Sigma/S$ range can hardly be explained otherwise than by assuming a reversible dissociation of O$_2$ from the catalyst. Indeed, data in Fig. 7 and Table 4 for catalysts E and D show higher values of $\epsilon$ and therefore lower conductivities when heated in air instead of He; the conductivity decreases with the O$_2$ pressure. It is noteworthy that there is a definite correlation between the average $\epsilon$ values and the ratios Bi/(Bi + Mo); the higher the Bi content the lower $\epsilon$ and the higher the conductivity. We therefore postulate that O$_2$ dissociation occurs more readily for surface oxygens bonded to Bi cations and in particular, will be more facile on (Bi$_2$O$_2$)O layers. We suggest that a pair of oxygen
ions donate electrons to a group of trivalent Bi cations under formation of an oxygen molecule and some Bi atoms in a stepwise reaction such as shown below:

\[(\text{Bi}^{3+}\text{O}^{2-})_2\text{O}^{2-} \rightleftharpoons (\text{Bi}^{1+}\square)_2\text{O}^{2-} + \text{O}_2, \quad (4a)\]

where \(\square\) is an oxygen vacancy, followed by a rapid disproportionation

\[3\text{Bi}^+ \rightleftharpoons \text{Bi}^{3+} + 2\text{Bi}^0. \quad (4b)\]

It is indeed well established [see, for instance, Batist et al. (8) and Grzybowska et al. (9)] that Bi deposits are formed if koechlinite is heated in vacuum or He at temperatures above 673 K. Evidently, a layer-like structure as koechlinite will be particularly favorable for this reaction although it might also occur on Bi$_2$Mo$_3$O$_{12}$. Since Bi atoms can be supposed to evaporate from the catalyst this would also explain the striking changes in the surface Bi/Mo ratio as found by XPS for catalyst E after activation (see Table 3).

It will be helpful at this place to analyze the activity and selectivity data as obtained in this study; they are summarized in Table 1. The first point of interest is given by a comparison of conversions in continuous flow and pulse operation; for the latter activities we only consider “first pulse” conversions. It is readily seen that the activities in continuous flow are much higher than those in pulse operation. There might be two entirely different explanations for this discrepancy. One of these is directly related to what has been discussed above; since catalysts were already reduced in He before the first pulse, their activity should be lower because part of the surface sites were still inactive because of previous oxygen losses to the carrier gas. Another explanation can be derived from thermal effects; reactions in continuous flow are exothermic while those in pulse in the absence of oxygen are about thermoneutral. Recent studies by Burban (16) have shown that isothermicity in continuous flow cannot be established for these reactions unless the catalysts are diluted by inert diluents such as SiC while the reactor is cooled in a fluidized sandbath.

Correct activities will therefore be intermediate between those found in continuous flow and in pulse operation. Another noteworthy observation is given by the dependency of the activity on the Bi/Mo ratio. Calculated per gram of catalyst, the conversion was virtually zero for XPS equal to Bi/Mo = 2.2, to become very high around 2. A further decrease in the bulk Bi/Mo ratio from 2 to 0.67 caused a proportional decrease of conversion. However, when calculated per unit surface area the conversions remained virtually constant in this range which indicates a constant number of similar sites per unit of surface in the Bi/Mo range 2 to 0.67. Indeed, XPS values for the surface Bi/Mo ratio remained approximately constant. Matsuura et al. (7) earlier reported similar conclusions. Since catalyst E with a Bi/Mo ratio >2, was inactive, the impression was gained that a Bi oxide surface is inactive towards olefins. However, considering the evidence presented in Figs. 15 and 16, this is not entirely correct; catalysts with a Bi/Mo ratio around 2 tend to become less selective under extreme circumstances such as high oxygen pressures or temperatures. Figure 15 shows that this may be connected with the formation of a transient Bi–oxygen species during the reoxidation of a partly reduced Bi oxide surface layer.

Let us now try to qualitatively explain the conductivity data and more in particular the \(\varepsilon\) versus \(\Sigma/S\) relation. We shall therefore apply band theory with special emphasis on surface band bending (see Fig. 19). As always, the electronic band shall consist of a valence band that is filled, a conduction band that is empty and a band gap between the two. Situated in the band gap are supposed to be two sets of localized energy levels, one near the top of the valence band and the other near the bottom of the conduction band. The first set, if empty, represents Mo$^{6+}$ cations, the second set Bi$^{3+}$ cations.
The band model is also supposed to represent MoO$_3$, with only Mo levels present, or Bi$_2$O$_3$ where only Bi levels occur. The transition from molybdenum oxide to bismuth oxide via the bismuth molybdates is assumed to be continuous by gradually replacing one Mo by two Bi. This assumption is certainly not appropriate for bulk structures but might be acceptable for surfaces. The literature furnishes some quantitative information on the properties of our surface band. Grzybowska et al. (9) studied the surface band situation of MoO$_3$ by XPS. They found the top of the valence band to be at an energy around 2.8 eV. Incipient reduction revealed the presence of two levels in the band gap at 0.9 and 2.0 eV; the latter might very well be equivalent to the $\varepsilon = 1.8$ level found by us for MoO$_3$; see Fig. 18. According to them these UPS bands belong to Mo$^{4+}$. Batist et al. (10) used UV-Vis diffuse reflectance spectroscopy to study the surface band properties of MoO$_3$, Bi$_2$MoO$_5$ and Bi$_2$O$_3$. The charge transfer band for MoO$_3$ was found at 2.9 eV, hence closely similar to the results of Grzybowska et al. They also noticed a shift of the edge position for Bi$_2$MoO$_5$ to 2.58 eV. Replacement of Mo by Bi apparently caused a narrowing of the band gap, the reason why Bi molybdates are bright yellow.

Let us now consider the consequences of this qualitative surface model. Any type of reduction, whether by olefin oxidation or by oxygen dissociation, injects electrons into the surface; these electrons are placed in the localized levels of the band gap. Increasing the reduction shall cause the Fermi level to rise in the band gap thereby diminishing $\varepsilon$. The low-lying Mo levels will be filled first and Bi levels will be occupied at higher reduction. The conductivity shall increase because the electron density of electrons in the localized levels shall become higher while also the energy difference between Fermi level and conduction band shall diminish.

Consequently, $\sigma$ shall rise and $\varepsilon$ shall decrease. If the localized band system is narrow, the decrease in $\varepsilon$ might be small, but the rise in $\sigma$ remains observable because $\Sigma/S$ increases; see Eq. (2). This behavior is typical for MoO$_3$ and Bi$_2$Mo$_3$O$_{12}$. However, for the Bi-rich samples reduction persisted but both $\sigma$ and $\varepsilon$ remained constant. We postulate that this occurs when the Fermi level arrives at an energy coinciding with the lower Mo levels in the bulk. Electrons can now "spill over" from surface to bulk levels. Energetically, the bulk electrons are still far below the bulk conduction band. Since, moreover, the number of levels in the bulk is vastly greater than those in the surface band, the electron density at this particular level remains virtually constant and the surface Fermi level shall become anchored at this position. The inward migration of the electrons shall give rise to an electrical double layer with the positive charge at the surface that also contains the anion vacancies. Oxygen anions shall therefore migrate outward.

Our model provides a chemical explanation for the kinetic "inlet"—"outlet" model of Keulks et al. (11), as based on experiments with oxygen isotopes. The inlet is now identified as an ensemble of Bi atoms preferably on a partly reduced (Bi$_2$O$_2$)O layer but not restricted hereto. Similar suggestions were published earlier by Linn and Sleight (13) and by Otsubo et al. (14). As to the outlet, because of the work of Burlington and Grasselli (12), Matsuura et al.
(7), and Gai (16), there seems to be general agreement about its structure; it is a surface complex containing one Bi and one Mo, similar to configurations as encountered in Bi₂Mo₂O₉. As shown earlier, our results are in reasonable agreement herewith. As far as we know, however, it has never been explained why the inlet-outlet operation is necessary at all. The common Mars–van Krevelen model (M–vK model) assumes that reduction by the hydrocarbon (outlet) occurs at the same place as the reoxidation (inlet).

We want to propose here that the inlet–outlet operation is a necessary attribute of selective oxidation because the outlet has to be a single active oxygen in order to maintain selectivity. The inlet, however, has to contain a pair of oxygen vacancies. Inlet and outlet are therefore necessarily different both as to their composition and structural type.

When summarizing our results we conclude that most of the new information produced concerns the clarification of the function of the bismuth component. We showed above that a surface (Bi₂O₂)O plane is easily reduced in vacuum or inert gas by dissociation of molecular oxygen, a reaction that is reversible, and therefore directly related to Keulks’ inlet site. Another function is connected with the relative inactivity of bismuth oxide versus olefins; at the temperatures applied here it is almost inert in this respect. (Bi₂O₂)O layers can therefore partly cover (MoO₂)O surfaces and form small Mo–O ensembles even containing only one active oxygen. This guarantees a selective oxidation of olefins but leads to an inhibition of a local reoxidation by molecular oxygen. Note that this is equivalent to an alternative description of the outlet site. Moreover, the facile dissociation of O₂ by the (Bi₂O₂)O layers and the high mobility of oxygen ions and electrons created thereby ensure a facile oxygen diffusion through the lattice and as a consequence the possibility for the replenishment of oxygen-depleted surface sites.

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