Catalytic oxidative coupling of methane on metal oxides

I. Effect of oxidation state of bismuth and reversibility of lattice oxygen on activity in barium–lanthanum–bismuth oxides

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Abstract

Oxidation of methane was studied for a number of oxides containing bismuth viz. Ba$_3$LaBi$_2$O$_6$, Ba$_{1-x}$La$_x$BiO$_3$ (0 $\leq x \leq 0.7$), Y$_{0.5}$Bi$_{1.6}$O$_3$ and Bi$_2$O$_3$. These oxides were selected in order to determine the influence of (a) oxidation state and structural environment of bismuth in an oxide lattice and (b) reversibility of lattice oxygen on catalytic activity. C$_2$H$_6$, C$_2$H$_4$, CO, and H$_2$O were the only products detected for these oxides in the temperature range of 723–1023 K at a gas hourly space velocity of 10 000 h$^{-1}$ (1 atm and 298 K) using a feed composition of 20% CH$_4$, 5% O$_2$ and 75% of Ar. The percentage methane conversion per unit area and selectivities of some of the oxides were found to be higher than those of La$_2$O$_3$ and 1% Li/MgO. No correlation was found to exist between the oxidation state of bismuth in these oxides and their catalytic activity. However, a correlation exists between the reversibility of lattice oxygen and catalytic activity for the series Ba$_{1-x}$La$_x$BiO$_3$ (0 $\leq x \leq 0.7$).

Keywords: bismuth, methane oxidative coupling, oxidation state.

INTRODUCTION

The development of a direct catalytic process for the conversion of methane to higher hydrocarbons is of considerable industrial importance. The energy requirements of any such process can easily be met by the combustion of methane itself. Methane is available in abundance and a part of this vast amount of natural gas, in the absence of an economical route for its conversion to useful products, is now simply burnt.

Partial oxidation of methane by oxygen can produce oxygenates such as
methanol and formaldehyde or higher hydrocarbons such as ethene and ethane. Though the production of oxygenates and hydrocarbonates follow two different reaction pathways, both these processes involve the intermediate formation of a surface-CH$_3$ species [1].

Thermodynamic calculations show that the formation of water instead of dihydrogen provides the necessary driving force for the oxidative coupling of methane to higher hydrocarbons. Furthermore, the formation of CO$_2$ + H$_2$O ($\Delta G^0 = -828$ kJ/mol) is thermodynamically more favourable than that of C$_2$H$_4$ + H$_2$O ($\Delta G^0 = -146$ kJ/mol) and C$_2$H$_6$ + H$_2$O ($\Delta G^0 = -74$ kJ/mol).

To prevent the complete oxidation of methane to carbon dioxide is therefore a major challenge. In order for an economically viable catalyst to be developed it is essential to gain further understanding on the relationship between solid-state parameters of a catalyst and its activity and selectivity.

Oxides of Pb, Bi, Sn and Sb [2,3] have been found to catalyse the partial oxidation of methane to hydrocarbons under both cyclic feed and co-feed conditions with high activity. These metals are known to have two stable valence states, differing from one another by two units. Further studies on multicomponent oxides of lead suggested that the variations in the selectivities of these oxides are in part due to the mobilities of lattice oxygen in these oxides [4]. Bi$_{5+}$ in conjunction with Mo$_{6+}$ has been found to play a significant role in some selective oxidation reactions [5].

The present investigation deals primarily with the study of the effect of oxidation state and structural surrounding of bismuth within an oxide lattice as well as the effect of labile lattice oxygen in these bismuth compounds on the catalytic activity. Consequently, a number of oxides of bismuth was selected in the present investigation. These oxides can broadly be classified into the following three categories.

(i) Ba$_2$LaBiO$_6$ which contains only Bi$_{5+}$.

(ii) The series Ba$_{1-x}$La$_x$BiO$_3$. Stoichiometric BaBiO$_3$ has a molecular formula of 1/2 [Ba$_2$]$_A$ [Bi$_{3+}$Bi$_{5+}$]$_B$O$_6$ [6,7]. This compound is generally found to be oxygen deficient with the degrees of anion vacancy that depends on the history of sample preparation [8]. The oxide has a monoclinic structure which transforms to rhombohedral at 450 K and finally to cubic at 750 K. There should be a consequent reduction in Bi$_{3+}$/Bi$_{5+}$ ratio when Ba$_{2+}$ is replaced by La$_{3+}$. Thus, the series Ba$_{1-x}$La$_x$BiO$_3$ provides a series of isostructural oxides containing a varying proportion of Bi$_{3+}$ and Bi$_{5+}$.

(iii) Bi$_2$O$_3$ and cubic Y$_{0.5}$Bi$_{1.5}$O$_3$, both of which should contain only Bi$_{3+}$ ions.

EXPERIMENTAL

Sample preparation

The multicomponent oxide samples were all prepared from Speccpure (Johnson-Matthey) Ba(NO$_3$)$_2$, Bi$_2$O$_3$, La$_2$O$_3$ and Y$_2$O$_3$ by a standard ceramic method.
Appropriate quantities of the constituents were mixed thoroughly by grinding under Analar grade cyclohexane for 30 min. The mixture was then oven-dried in air at 348 K, pelletised and heated at 873 K for 24 h. The samples were quenched in air, further ground and pelletised followed by a final heating at 1123 K for an additional period of 2 h. For comparison of catalytic activity, a standard sample of 1% Li₂O/MgO was prepared. Specpure (Johnson-Matthey) MgO and LiNO₃ were thoroughly mixed, pelletised and calcined at 823 K for 6 h.

**X-ray powder diffraction measurement**

X-ray powder diffraction patterns of the samples were recorded on a Philips diffractometer (Model PW1700) with Cu Kα radiation using a nickel filter. The lattice parameters were calculated from the diffraction angles, obtained in the region of 2θ = 20°–80° with a scanning speed 1°/min and using silicon as an internal standard. Cell parameter calculations and structural determination were further refined using linear regression procedures applied to the measured positions of all major reflections up to 2θ = 70°.

**X-ray photoelectron emission spectra measurement**

The X-ray photoelectron emission spectra were recorded using Cu Kα radiation in a Kratos XSAM800 spectrometer. The spectrometer resolution was 1 eV.

**Surface area measurement**

The surface area of all samples, both before and after catalytic reaction, was determined by the single point BET method using a Micromeritics pulse chemisorb apparatus (Model 2700).

**Catalytic activity measurement**

Catalytic studies were carried out in a Labcon microreactor coupled with a Hewlett Packard gas chromatograph (series 5890) fitted with a 25 m × 3.2 mm Poraplot Q column and a Hewlett Packard multichannel mass spectrometer (series 5970).

Catalyst particles (100–200 μm) were packed up to a length of 25 mm inside a 20 cm long quartz reactor tube which had an internal diameter of 1.6–1.8 mm. The reactor tube was singly placed inside a bore cut out from a cylindrical SS block heated by cartridge heaters. All the gases (99.99% purity) used in the present investigation were obtained from G&E. A feed consisting of 20% CH₄, 5% O₂ and Ar, making up the balance, was passed through the catalyst at a gas
hourly space velocity (GHSV) of 10 000 h\(^{-1}\) (298 K and 1 atm). The product gases were vented through a 6-port auto-gas sampling valve. A fixed volume of the product gas, when required, was injected into the GC-MS for analysis.

RESULTS AND DISCUSSION

The X-ray powder diffraction patterns of \(\text{Ba}_2\text{LaBiO}_6\) and \(\text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3\) and selected samples of \(\text{Ba}_{1-x}\text{La}_x\text{BiO}_3\) \((0 \leq x \leq 0.7)\) preceding catalytic reaction are shown in Fig. 1. The lattice parameters of these oxides are given in Table 1.

![Fig. 1. Powder X-ray diffractograms before catalytic reaction of \(\text{Ba}_2\text{LaBiO}_6\) and \(\text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3\) and selected members of the series of general formula \(\text{Ba}_{1-x}\text{La}_x\text{BiO}_3\) \((0 \leq x \leq 0.7)\); (a) \(\text{Ba}_2\text{LaBiO}_6\) (b) \(\text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3\) (c) \(x=0\) (d) \(x=0.075\) (e) \(x=0.1\) and (f) \(x=0.7\).](image)

**TABLE 1**

Lattice parameters of \(\text{Ba}_2\text{LaBiO}_6\), \(\text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3\) and \(\text{Ba}_{1-x}\text{La}_x\text{BiO}_3\) \((0 \leq x \leq 0.7)\)

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Nature of crystalline phase</th>
<th>(a) (nm)</th>
<th>(b) (nm)</th>
<th>(c) (nm)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba}_2\text{LaBiO}_6)</td>
<td>Cubic</td>
<td>0.61850</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Y}<em>{0.5}\text{Bi}</em>{1.5}\text{O}_3)</td>
<td>Cubic</td>
<td>0.54915</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{BaBiO}_3)</td>
<td>Pseudo-moniclinic</td>
<td>0.6185</td>
<td>0.61375</td>
<td>0.86663</td>
<td>90.158</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.93}\text{La}</em>{0.07}\text{BiO}_3)</td>
<td>Pseudo-moniclinic</td>
<td>0.61848</td>
<td>0.61427</td>
<td>0.86671</td>
<td>90.123</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.92}\text{La}</em>{0.07}\text{BiO}_3)</td>
<td>Pseudo-moniclinic</td>
<td>0.61847</td>
<td>0.61421</td>
<td>0.86667</td>
<td>90.115</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.9}\text{La}</em>{0.1}\text{BiO}_3)</td>
<td>Pseudo-moniclinic</td>
<td>0.61901</td>
<td>0.61445</td>
<td>0.86764</td>
<td>89.883</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.3}\text{La}</em>{0.7}\text{BiO}_3)</td>
<td>Pseudo-moniclinic</td>
<td>0.62308</td>
<td>0.61487</td>
<td>0.86257</td>
<td>88.386</td>
</tr>
</tbody>
</table>
1. In agreement with previously published data [9,10] both Ba$_2$LaBiO$_6$ and Y$_{0.5}$Bi$_{1.5}$O$_3$ were found to have a cubic structure (Figs. 1a and b). BaBiO$_3$ ($x=0$) was found to have a monoclinic structure (Fig. 1c) as reported earlier [6,7]. This monoclinic structure is retained until 7.5% ($0 \leq x \leq 0.075$) of Ba$^{2+}$ in BaBiO$_3$ is replaced by La$^{3+}$ (Fig. 1d). The sample with $x=0.1$ is almost monophasic with a trace of La$_2$O$_3$, estimated to be no more than 2%. Attempts to prepare samples with $x>0.075$ resulted in the formation of multiphase products (Figs. 1e and f) containing Ba$_{0.975}$La$_{0.025}$BiO$_3$ ($x=0.075$) and an increasing amount of unreacted La$_2$O$_3$ and Bi$_2$O$_3$ with increasing $x$.

The Bi 4f X-ray photoelectron spectra of Bi$_2$O$_3$, Ba$_2$LaBiO$_6$ and BaBiO$_3$ are shown in Figs. 2a–c. The binding energies of the Bi 4f levels of all the oxides
TABLE 2

Binding energies of Bi 4f core levels

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Binding energy (eV)</th>
<th>Bi 4f(\gamma/2)</th>
<th>Bi 4f(\delta/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(_2)O(_3)</td>
<td>158.4</td>
<td>163.8</td>
<td></td>
</tr>
<tr>
<td>BaBiO(_3)(^a)</td>
<td>158.0</td>
<td>163.3</td>
<td></td>
</tr>
<tr>
<td>BaBiO(_3)(^b)</td>
<td>158.0</td>
<td>163.4</td>
<td></td>
</tr>
<tr>
<td>BaBiO(_3)(^c)</td>
<td>157.9</td>
<td>163.3</td>
<td></td>
</tr>
<tr>
<td>Ba(_0.5)LaBiO(_6)</td>
<td>158.3</td>
<td>163.3</td>
<td></td>
</tr>
<tr>
<td>Ba(_0.5)La(_0.5)BiO(_3)</td>
<td>158.0</td>
<td>163.3</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Sample heated in air at a temperature of 1023 K for 2 h.
\(^b\)Sample heated in air at a temperature of 1023 K for 24 h.
\(^c\)From \(^b\) after annealing in pure oxygen at 723 K for 15 h.

TABLE 3

Percentage conversion and selectivity on different catalysts at 1073 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methane oxidised ((%))</th>
<th>Surface area ((m^2 \cdot g^{-1}))</th>
<th>Selectivity ((%))</th>
<th>CO(_2)</th>
<th>CO</th>
<th>C(_2)H(_6)</th>
<th>C(_2)H(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(_2)LaBiO(_6)</td>
<td>25.0</td>
<td>0.31</td>
<td>50.1</td>
<td>35.3</td>
<td>14.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y(<em>{0.5})Bi(</em>{1.5})O(_3)</td>
<td>27.27</td>
<td>0.29</td>
<td>52.7</td>
<td>26.9</td>
<td>20.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(_2)O(_3)</td>
<td>6.56</td>
<td>0.17</td>
<td>41.2</td>
<td>49.9</td>
<td>8.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(_2)O(_3)</td>
<td>27.0</td>
<td>6.87</td>
<td>32.3</td>
<td>17.3</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Li/MgO</td>
<td>26.8</td>
<td>10.83</td>
<td>38.3</td>
<td>33.0</td>
<td>13.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(_{1-x})La(_x)BiO(_3)(x=0)</td>
<td>20.41</td>
<td>0.09</td>
<td>59.3</td>
<td>30.4</td>
<td>10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>5.77</td>
<td>0.06</td>
<td>66.0</td>
<td>30.1</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>6.19</td>
<td>0.15</td>
<td>54.7</td>
<td>39.2</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>17.24</td>
<td>0.13</td>
<td>48.1</td>
<td>39.1</td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>16.02</td>
<td>0.07</td>
<td>54.5</td>
<td>40.7</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>20.16</td>
<td>0.15</td>
<td>49.3</td>
<td>38.6</td>
<td>12.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>23.23</td>
<td>0.49</td>
<td>62.2</td>
<td>28.7</td>
<td>9.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.70</td>
<td>23.05</td>
<td>0.58</td>
<td>56.7</td>
<td>32.5</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

studied in the present investigation are given in Table 2. It is seen that the binding energies of the Bi 4f levels of the oxides containing Bi\(^{3+}\) and Bi\(^{5+}\) are identical. These results are in agreement with those reported earlier by Morgan et al. [11] who found that the binding energies of Bi 4f\(\gamma/2\) levels in Bi\(_2\)O\(_3\) and NaBiO\(_3\) were identical. Stoichiometric BaBiO\(_3\) contains equal proportions of Bi\(^{3+}\) and Bi\(^{5+}\) ions with Bi\(^{3+}\)-O and Bi\(^{5+}\)-O bond distances of 0.227 and 0.215 nm, respectively [8]. These two ions, therefore, have significantly different
Fig. 3. Powder X-ray diffractograms after catalytic reaction of \( \text{Ba}_2\text{LaBiO}_6 \) and \( \text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3 \) and selected members of the series of general formula \( \text{Ba}_{1-x}\text{La}_x\text{BiO}_3 \) \( (0 \leq x \leq 0.7) \); (a) \( \text{Ba}_2\text{LaBiO}_6 \) (b) \( \text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3 \) (c) \( x=0 \) (d) \( x=0.075 \) (e) \( x=0.1 \) and (f) \( x=0.7 \).

Fig. 4. Percentage reversibility of lattice oxygen of the series of general formula \( \text{Ba}_{1-x}\text{La}_x\text{BiO}_3 \) \( (0 \leq x \leq 0.7) \).

Site potential energies in \( \text{BaBiO}_3 \). These should have resulted in different chemical shifts in the core levels of these two ions. However, contrary to expectations the binding energies of the 4f level of \( \text{Bi}^{5+} \) and \( \text{Bi}^{6+} \) in \( \text{BaBiO}_3 \) appear to be identical within the resolution of the instrument. \( \text{BaBiO}_3 \) is known
to lose oxygen above 623 K [8]. A sample of BaBiO₃ was, therefore, heated for 24 h at 1023 K and its X-ray photoelectron spectrum was recorded (Fig. 2d). The sample was subsequently annealed in pure oxygen at 723 K for 15 h and again its X-ray photoelectron spectrum was recorded, as shown in Fig. 2e. Neither of these spectra appear to be different from that of BaBiO₃ (Fig. 2c). On the basis of the photoemission studies on some metal oxides, Holm and Storp [12] has suggested that the changes in the chemical shifts with the changes in oxidation states can not be observed where transition from ionic to covalent bonding occurs. Bi³⁺–O and Bi⁵⁺–O bonds may be partly ionic and partly covalent and the ionicity of Bi–O may not change appreciably with a change of the oxidation state of bismuth. This may explain the observed invariance of the binding energies of the Bi 4f levels in Ba₁₋ₓLaₓBiO₃ (0 < x < 0.1) Bi₂O₅ and Ba₀LaBiO₆.

The percentage methane conversion and product selectivities at 1073 K on the catalysts and their surface areas before catalytic reaction are given in Table 3. It is to be noted that no discernible difference was observed between the surface area of the fresh and that of the spent bismuth containing catalysts. However, Li/MgO oxide catalysts are known to undergo sintering following catalytic reaction. The X-ray powder diffractograms of Ba₂LaBiO₆, Y₀.⁵Bi₁.₅O₃ and selected samples of Ba₁₋ₓLaₓBiO₃ (0 ≤ x ≤ 0.7) following catalytic reaction are shown in Fig. 3. All monophasic multicomponent oxide samples containing barium showed traces of BaCO₃, estimated to be no greater than 2.5%. However, the powder diffraction patterns of the spent catalysts did not show any
trace of La$_2$O$_3$, Bi$_2$O$_3$ or Y$_2$O$_3$. These results suggest that only a small amount, not exceeding 2.5% of the compounds studied in the present investigation decomposed during the course of catalytic reaction. The Bi$_2$O$_3$ formed probably evaporates at higher temperatures during reaction and consequently does not appear in the XRD pattern. The La$_2$O$_3$ formed is below the detectable limit of the XRD. Although the XRD pattern of the spent Y$_{0.5}$Bi$_{1.5}$O$_3$ did not show any trace of either Y$_2$O$_3$ or Bi$_2$O$_3$, this does not exclude the possibility that a small amount of decomposition does occur. The Bi$_2$O$_3$ evaporates at higher temperatures as mentioned earlier and the remaining Y$_2$O$_3$ could not be detected as this is attributed to the known wide solubility limit of Y$_2$O$_3$ in Bi$_2$O$_3$. These results suggest that a small amount, no greater than 2.5% of the bismuth compound, is decomposed during the reaction even at high temperatures and the original structure of the compound is essentially retained. The observed catalytic activities therefore reflect the behaviour of the monophasic compounds. It can be seen from Table 3 that:

(i) CO$_2$, C$_2$H$_6$, C$_2$H$_4$ and H$_2$O were the only products detected up to 1073 K. It is significant to note that no carbon monoxide was formed on any of these catalysts at the temperatures investigated. A similar absence of carbon monoxide in the reaction products was also observed during the catalytic oxidation of methane on several compounds such as BaPbO$_3$, Ba$_2$PbO$_4$, BaSnO$_3$ and Ba$_2$SnO$_4$ [13]. These catalysts are thus seen to behave quite differently from other oxide catalysts such as La$_2$O$_3$, 1% Li/MgO, where a significant amount of carbon monoxide is also observed as shown in Table 3. This is in agreement with previously reported data [14,15]. In contrast, oxidation of methane on a number of metals such as palladium dispersed on a variety of oxide supports resulted in the formation of carbon dioxide at lower temperatures and only carbon monoxide and hydrogen at 1073 K [16]. It thus appears that carbon dioxide and carbon monoxide are probably formed via two separate mechanisms — the former being formed through gas phase and the latter involving surface reaction.

(ii) There is a very marked difference in the catalytic behaviour of Y$_{0.5}$Bi$_{1.5}$O$_3$ and Bi$_2$O$_3$ though both these oxides contain Bi$^{3+}$ ions. The former oxide showed a much higher percentage methane conversion.

(iii) The concentration of Bi$^{3+}$ increases while that of Bi$^{5+}$ decreases linearly with increasing replacement ($x$) of Ba$^{2+}$ by La$^{3+}$ in the iso-structural series Ba$_{1-x}$La$_x$BiO$_3$ (0 ≤ $x$ ≤ 0.075). The percentage methane conversion on this series of oxides, however, does not show a linear variation with $x$; but starting with BaBiO$_3$ ($x = 0$) the catalytic activity decreases sharply, passes through a minimum at $x = 0.05$ and then gradually increases up to $x = 0.075$.

The monoclinic structure of BaBiO$_3$ is not maintained when more than 7.5% ($x > 0.075$) of Ba$^{2+}$ is replaced by La$^{3+}$ and a mixed phase consisting of varying proportions of La$_2$O$_3$, BaBiO$_3$ and Ba$_{1-x}$La$_x$BiO$_3$ ($x ≈ 0.075$) is produced. The catalytic activities of the mixed phases for 0.075 < $x$ < 0.7 do not vary much and
the activities of the mixed phases obtained for \( x = 0.5 - 0.7 \) are similar to that of \( \text{Ba}_2\text{LaBiO}_6 \). The values of surface area of the samples of \( \text{La}_2\text{O}_3 \) and \( 1\% \text{ Li/MgO} \) used in the present study were found to be 6.87 and 10.83 m\(^2\)/g, respectively while those of bismuth oxides were in the region of 0.1-0.7 m\(^2\)/g. It can, therefore, be seen from Table 3 that the catalytic activities per unit area of \( \text{Ba}_2\text{LaBiO}_6, \text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3, \text{BaBiO}_3 \) and \( \text{Ba}_{1-x}\text{La}_x\text{BiO}_3 (0.3 \leq x \leq 0.7) \) are higher than those of \( \text{La}_2\text{O}_3 \) and \( 1\% \text{ Li/MgO} \).

(iv) The percentage methane conversion on \( \text{Ba}_2/\text{LaBiO}_6 \) containing \( \text{Bi}^{5+} \) ions and that of \( \text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3 \) which contains \( \text{Bi}^{3+} \) ions are nearly equal.

It thus appears that there is no correlation between the oxidation state of bismuth in an oxide and the catalytic activity and selectivity for the partial oxidation of methane of that oxide. Although the reported high activity of \( \text{Bi}_2\text{O}_3 \) \([2,3]\) may be attributed to the existence of \( \text{Bi}^{3+} \) and \( \text{Bi}^{5+} \) as two stable oxidation states of bismuth, the observed variation of activity does not depend alone on the presence of one or the other oxidation state. It is therefore suggested that other solid state parameters must also play a prominent role in determining the variation of catalytic activity.

Studies on the catalytic oxidation of methane on different oxides indicate \([17,18]\) that \( \text{O}^- \) ions may be the active centres for this reaction. An ionic mechanism for methane oxidation has also been suggested by Lee and Oyama \([17]\) for the reducible metal oxides. From their study on the catalytic oxidation of methane on \( \text{Sm}_2\text{O}_3 \), Ekstrom and Lapszewicz \([19]\) concluded that the rate of methane conversion on oxides depended greatly on the rate of exchange of lattice oxygen with molecular oxygen in the gas phase. It was shown by Winter \([20]\) that the formation of \([\text{O}^-]\), i.e. an oxygen atom trapped in an anion vacancy, is initiated by such an exchange reaction between the catalyst surface and the gas phase. In order to estimate the reversibility of the lattice oxygen in \( \text{Ba}_{1-x}\text{La}_x\text{BiO}_3 \) \( (0 \leq x \leq 0.7) \) a small quantity of sample of appropriate composition was heated in a quartz tube at 1073 K in a flow of argon \((50 \text{ ml/min})\) for 15 h. The tube was cooled quickly and weighed. The sample was then heated in a flow of oxygen \((50 \text{ ml/min})\) at 1073 K for 15 h and weighed after cooling. The ratio of the weight loss during argon treatment to the weight gain during oxygen treatment was taken as a measure of the reversibility of lattice oxygen. Fig. 4 shows variation of percentage reversibility of lattice oxygen for the samples belonging to the series \( \text{Ba}_{1-x}\text{La}_x\text{BiO}_3 \). The rate of methane oxidation on these oxides at various temperatures is shown in Fig. 5. It is seen that a correlation exists between percentage reversibility of lattice oxygen and rate of methane oxidation in both the monoplastic and multiphasic regions. It may therefore be concluded that the activity of these oxides depends at least, in part, on the number density of loosely bound lattice oxygen.
REFERENCES