Decomposition of Isopropyl Alcohol on γ-Phase Bismuth Molybdate Catalyst

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Bismuth molybdate (Bi₂MoO₆) promotes dehydration of isopropyl alcohol in the absence of gaseous oxygen while oxidative dehydrogenation occurs in the presence of oxygen. The structural stability of the catalyst both in the presence and absence of oxygen in the feed is also considered.

The γ-phase bismuth molybdate was prepared by the slurry method and its structural identity was established by X-ray and IR techniques. The surface area (BET method) of the fresh sample was found to be 2.8 m²/g. The catalytic decomposition of isopropyl alcohol was carried out in the temperature range 220 to 280°C using a conventional flow-type fixed bed reactor working at atmospheric pressure. The liquid products were analysed by GLC and the gaseous products by Orsat analysis.

The γ-phase bismuth molybdate preferentially promoted dehydration of isopropyl alcohol to propylene with about 95% selectivity in the absence of oxygen. The selectivity of this order has been earlier observed in the dehydration of isopropyl alcohol on a Bi-Mo oxide catalyst in the presence of air and ammonia. The formation of acetone (maximum of 2.1 mol% at 280°C and at a contact time of 2.1 s) was also observed. The selectivity to propylene increases slightly with increase in temperature for a given contact time (Table 1).

From contact time-conversion plots the initial rates were evaluated and these were used in the evaluation of Arrhenius parameters. The activation energies (Ea) and frequency factors for dehydration and decomposition of isopropyl alcohol are as follows:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ea (kJ/mol)</th>
<th>Frequency factor (s⁻¹m⁻²)</th>
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</thead>
<tbody>
<tr>
<td>Dehydration</td>
<td>62.7</td>
<td>4.3 × 10⁶</td>
</tr>
<tr>
<td>Decomposition</td>
<td>57.4</td>
<td>1.4 × 10⁶</td>
</tr>
</tbody>
</table>

When isopropyl alcohol decomposition was carried out in the presence of oxygen, increased amounts of acetone were formed than those in the absence of gaseous oxygen. With increase in partial pressure of alcohol the amount of propylene formed (mol/hr) registered an increase. However, the amount of acetone formed (mol/hr) passed through a maximum (Fig. 1), the maximum corresponding to the stoichiometric ratio for the oxidative dehydrogenation of isopropyl alcohol according to the equation

2 CH₃CHOHCH₃ + O₂ → 2 CH₃COCH₃ + 2 H₂O

The yellow colour of the freshly prepared Bi₂MoO₆ turned greenish black on reacting with isopropyl alcohol in the absence of oxygen. Yellow colour could...
be restored on passing air for 5 hr at 440°C. However, when the reaction was carried out in the presence of gaseous oxygen, the catalyst did not change its colour at any stage. X-ray and IR data did not indicate any phase change in the catalyst after reacting with isopropyl alcohol in the absence of oxygen. No phase change was detected in Bi$_2$MoO$_6$ catalyst after ammoxidation of propylene by pulse technique in the absence of oxygen. However, when the reaction was carried out in the presence of gaseous oxygen, the catalyst did not change its colour at any stage. X-ray and IR data did not indicate any phase change in the catalyst after reacting with isopropyl alcohol in the absence of oxygen. No phase change was detected in Bi$_2$MoO$_6$ catalyst after ammoxidation of propylene by pulse technique in the absence of oxygen. Contrary to these observations, the formation of Bi metal and MoO$_2$ from z-phase of bismuth molybdate has been reported in the oxidation of propylene in the absence of gaseous oxygen. ESR spectra of Bi$_2$MoO$_6$ catalysts after reaction with isopropyl alcohol in the absence of gas phase oxygen for different time intervals (10, 30 and 60 min) were recorded at room temperature and no signal due to Mo$^{4+}$ could be detected, thus indicating that molybdenum was reduced to Mo$^{6+}$. Batist et al. have also reported similar results in 1-butene oxidation over Bi$_2$MoO$_6$ at 470°C.

In the present study it was observed that when isopropyl alcohol was decomposed in the absence of oxygen the mol % of propylene formed with respect to time increased and reached a steady value after some time. However, the mol % of hydrogen formed with respect to time remained unchanged at higher temperatures while at lower temperatures a decrease was noticed with increase in time of reaction (Fig.2). It is probable that the catalyst Bi$_2$MoO$_6$ in the surface layers undergoes reduction. This surface reduced catalyst can be more active for dehydration of isopropyl alcohol than the fresh catalyst itself. However, the amount of bismuth metal formed is probably less than the limit of detection by X-ray diffractometry. Similar increase in % conversion with respect to time has been noticed by Mitchell et al. in the oxidation of 1-butene in the absence of oxygen over Bi$_{2.14}$MoO$_{6.23}$, a bismuth rich γ-phase bismuth molybdate.

The effect of admitting isopropyl alcohol and oxygen mixture (1:2 mol ratio) or isopropyl alcohol alone on the electrical conductivity of the catalyst at 280°C was studied. In the presence of isopropyl alcohol + oxygen mixture the electrical conductivity of the catalyst initially increased and then remained constant for a longer time. However, in the presence of isopropyl alcohol alone there was a rapid increase in the electrical conductivity followed by steady increase with time. It is, therefore, clear that reduction of the catalyst surface alone occurs which acts as the active phase. These observations are in accord with the reports of Peacock et al.

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References