Role of Excess MoO$_3$ in Iron-Molybdate Methanol Oxidation Catalysts

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Introduction
It has been recognized for sometime that the presence of excess crystalline MoO$_3$ in bulk mixed metal oxide catalysts enhances the resulting catalytic performance during selective oxidation reactions [1, 2]. To account for this interesting catalytic phenomenon several different hypotheses have been put forth: contact potential [1], remote control or oxygen spillover [2], etc. In spite of the numerous studies on this interesting and important observation, its origin has not been resolved because none of the studies examined the intrinsic surface characteristics of the catalysts. This catalytic enhancement phenomenon is most widely employed in commercial bulk mixed MoO$_3$-Fe$_2$(MoO$_4$)$_3$ oxide catalyst for CH$_3$OH oxidation to HCHO [3]. Although the active phase is generally considered to be the crystalline bulk Fe$_2$(MoO$_4$)$_3$ phase, the highest catalytic performance is obtained in the presence of excess crystalline MoO$_3$ (Mo/Fe > 1.5) [4].

In order to investigate this interesting catalytic phenomenon, CH$_3$OH oxidation to HCHO was undertaken with both CH$_3$OH-temperature programmed surface reaction (TPSR) spectroscopy and steady-state methanol reactivity studies. The CH$_3$OH oxidation reaction was selected since methanol is also a 'smart' chemical probe molecule that can discriminate between different types of surface sites (redox, acid or base) [5], determine the number of exposed sites [6], and the surface reaction mechanism is well understood [7]. This is especially true of the kinetics and mechanism of the bulk Fe$_2$(MoO$_4$)$_3$ catalyst that is commercially employed for methanol oxidation to formaldehyde. Consequently, the mixed bulk MoO$_3$-Fe$_2$(MoO$_4$)$_3$ oxide catalyst system was chosen to investigate this interesting catalytic phenomenon for the selective oxidation of CH$_3$OH to HCHO.

Experimental
The bulk Fe$_2$(MoO$_4$)$_3$ catalyst was synthesized by co-precipitation of aqueous Fe(NO$_3$)$_3$•9H$_2$O and (NH$_4$)$_2$MoO$_4$•4H$_2$O. The thermal treatment and other details about the synthesis of the bulk Fe$_2$(MoO$_4$)$_3$ catalyst have been previously presented [6]. The crystalline MoO$_3$ phase was prepared by thermal decomposition of (NH$_4$)$_2$MoO$_4$•4H$_2$O at 500°C. Physical mixtures of MoO$_3$ and Fe$_2$(MoO$_4$)$_3$ were ground to increase the Mo/Fe ratio from 1.5, the stoichiometric ratio for Fe$_2$(MoO$_4$)$_3$, to 3.7 and 5.5. It was previously demonstrated that the same catalytic enhancement is obtained independent of the specific preparation method [8]. The experimental procedure followed for the CH$_3$OH-TPSR as well as the mathematical expression used for kinetic parameter estimation have previously been discussed [9].

Results and Discussion

CH$_3$OH-TPSR The results from CH$_3$OH-TPSR experiments of Fe$_2$(MoO$_4$)$_3$ and the MoO$_3$ enriched Mo/Fe= 3.7 and 5.5 catalysts are presented in Table 1. During the reaction the exclusive formation of HCHO as the reaction product, no DME or CO/CO$_2$ formation, reflects the redox nature of the catalytic active sites in this series of iron-molybdate catalysts. The addition of excess MoO$_3$ shifts the HCHO Tp value from 178 to 189°C, which corresponds to slightly less active catalytic sites (see Table 1). This temperature shift corresponds to a slight decrease in the specific first-order $k_{obs}$, by as much as a factor of ~2, and reflects the lower catalytic activity of crystalline MoO$_3$ (Tp=220°C) compared to Fe$_2$(MoO$_4$)$_3$ for methanol oxidation. Table 1: Influence of excess MoO$_3$ on iron-molybdate catalyst parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tp for HCHO (°C)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>Exposed Ns redox sites/gm</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(MoO$_4$)$_3$</td>
<td>178</td>
<td>26</td>
<td>3.9 x 10$^{-7}$</td>
<td>74</td>
</tr>
<tr>
<td>Mo/Fe= 3.7</td>
<td>185</td>
<td>16</td>
<td>4.6 x 10$^{-7}$</td>
<td>96</td>
</tr>
<tr>
<td>Mo/Fe=5.5</td>
<td>189</td>
<td>12</td>
<td>4.7 x 10$^{-7}$</td>
<td>95</td>
</tr>
</tbody>
</table>

The number of exposed redox catalytic active sites/gm, Ns, is proportional to the area under the CH$_3$OH-TPSR curve for HCHO formation. The Ns redox sites of the iron-molybdate catalysts normalized per gram of catalyst are presented along with their corresponding $k_{obs}$ values in Table 1. The Ns values reveal that the number of exposed sites in the bulk iron-molybdate catalysts just slightly increases with increasing excess MoO$_3$ in the catalyst. Table 1 also shows that with addition of MoO$_3$, the HCHO selectivity increases from 74 to 96% while the DME selectivity decreases from 26 to 5%. This HCHO selectivity enhances is related to the covering of the exposed unselective Fe sites in Fe$_2$(MoO$_4$)$_3$, by the excess MoO$_3$.

Significance
The excess MoO$_3$ in MoO$_3$-Fe$_2$(MoO$_4$)$_3$, catalysts serves to slightly decrease $k_{obs}$, slightly increases the Ns redox sites, and significantly increases HCHO selectivity by suppressing the DME formation. The enhanced selectivity performance of excess MoO$_3$ is, thus, primarily related to surface MoOx species covering exposed unselective Fe sites from Fe$_2$(MoO$_4$)$_3$. References