Highly Efficient Oxidative Coupling of Methane over LiCl-B_2O_3/MnO_2 and Li_2SO_4-Mn_xO_y/TiO_2 Catalysts

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Abstract: Because of the ever-increasing consumption of crude oil, the role played by the natural gas as a raw material has become more and more important in chemical industry and the potential of methane used as a source for the production of ethylene has attracted much attention. In this paper, the LiCl-B_2O_3/MnO_2 and Li_2SO_4-Mn_xO_y/TiO_2 catalysts for Oxidative Coupling of Methane (OCM) have been studied, and the results show that the catalysts exhibit high activity and selectivity. Furthermore, the influence of the components in the catalyst and the reaction conditions on OCM performance has been studied and a possible active new component, cubic Li_4B_7O_12Cl, has been found.

Key words: methane, ethane, ethylene, oxidative coupling, methane, lithium chloride, manganese dioxide

1. Introduction

Natural gas plays an increasingly important role in chemical industry as the result of excessive consumption of crude oil. Methane, a primary component of natural gas, is one of the prominent raw materials for the synthesis of organic compounds. Manufacture of chemical products from natural gas as a substitute for petroleum has become a natural trend.

Of all the technologies, Oxidation Coupling of Methane (OCM) [1–6] is the only one that can transform methane to C_2 hydrocarbons in one step, so this technology is attractive and has already been intensively studied. Thousands of catalysts involving many elements have been investigated for OCM, and Mn/Na_2WO_4/SiO_2, Li-Mg-Nd, Li-Mn-Ti [7] were found to exhibit comparatively high catalytic activity.

In this paper, effects of the components in catalyst, the composition of feed gas, the reaction temperature, the structures of LiCl-B_2O_3/MnO_2 and Li_2SO_4-Mn_xO_y/TiO_2 catalysts on OCM were studied. Meanwhile, the stability test of catalyst during OCM was also investigated.

2. Experimental

2.1. Catalyst preparation

LiCl-B_2O_3/MnO_2 catalyst was prepared by impregnating MnO_2 powder with LiCl and H_3BO_3 (n(Mn)/n(B)=2.9) solution for 24 h at room temperature. The precursor was dried at 120 °C with magnetic stirring, and then calcined at 400 °C for 2 h and 700 °C for 2 h. Finally, the sample was crushed and sieved to form grains of 40-60 mesh.

Li_2SO_4-Mn_xO_y/TiO_2 catalyst was prepared by the following procedure. Li_2SO_4, Mn(NO_3)_2 (50%aq) and distilled water (30 ml) were first mixed in a beaker. then TiO_2 was added to this solution, stirred at room temperature for 24 h, dried at ca 100 °C, and then calcined at 540 °C for 1 h and 810 °C for 2 h, and finally crushed and sieved to form grains of 40-60 mesh size.

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2.2. Catalytic activity test

Catalytic activity measurements for OCM were carried out in a stainless fixed-bed reactor, which has been treated with sodium pyrophosphate aqueous solution. The catalysts were pretreated in-situ in a flow of oxygen (at a space velocity of 500 ml/(g·h)) until it was heated to the reaction temperature. Next, the catalyst was switched to nitrogen for 10 minutes, and then the feed gas consisted of methane and oxygen was introduced. The feed gas and product gas were analyzed by GC (Agilent 6850, Plot-C2000 Column, TCD Detector) after removal of water at room temperature with anhydrous CaCl$_2$.

Methane conversion ($X\%$), the yield ($Y\%$) and selectivity ($S\%$) of the products were calculated by the following equations:

$$X\% = \frac{1 - \sum A_i C_i}{A_{CH_4}} \times 100\%$$

$$Y\% = \frac{A_i C_i}{\sum A_i C_i} \times 100\%$$

$$S\% = \frac{Y\%}{X\%} \times 100\%$$

$i$: CO, CO$_2$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$

$A_i$: correction factor of product $i$ [8]

$C_i$: percentage of peak area of product $i$

2.3. Catalyst characterizations

The catalysts were characterized by XRD (D8 Advance, Bruker) and TG-DTA (Mettler). XRD patterns were recorded on a Bruker AXS D8 Advance diffractometer equipped with Ni-filtered Cu K$_\alpha$ radiation. The scan speed was 0.1 degree/second (40 mA × 40 KV). TG-DTA patterns were recorded under N$_2$ protection (30 ml/min) and the temperature ascending speed was 10 °C/min.

3. Results and discussion

3.1. Catalytic activity

3.1.1. Effect of Li$^+$ content on OCM performance

The effect of different Li/Mn (mol) ratio on OCM performance is presented in Table 1. It seems that the yield of C$_2$ hydrocarbons and the ratio of C$_2$H$_4$/C$_2$H$_6$ were enhanced with the content of Li$^+$ in the catalyst, which might be due to that more oxygen vacancies on the catalyst surface were formed when Li$^+$ content was increased. The oxygen vacancies reacted with dioxygen molecules at the high temperature and produced O$_2^-$ ions and holes [8]. Some of the O$_2^-$ ions were trapped by the holes and reacted with the adjacent Li$^+$ ions and produce [Li$^+$O$^-$]$_n$.[9], CH$_4$ reacted with [Li$^+$O$^-$]$_n$ centers and generated CH$_3$ and then two CH$_3$ radicals coupled and formed C$_2$H$_6$[10].

Table 1. Effect of Li/Mn ratio on OCM performance

<table>
<thead>
<tr>
<th>$n$(Li)/$n$(Mn)</th>
<th>$X%$</th>
<th>$S$(C$_2$)%</th>
<th>$Y$(C$_2$)%</th>
<th>$Y$(C$_2$H$_4$)%</th>
<th>$n$(C$_2$H$_4$)/$n$(C$_2$H$_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl-B$_2$O$_3$/MnO$_2^a$</td>
<td>0.33</td>
<td>38.80</td>
<td>46.10</td>
<td>17.94</td>
<td>16.33</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>40.11</td>
<td>47.24</td>
<td>18.95</td>
<td>17.24</td>
</tr>
<tr>
<td></td>
<td>1.33</td>
<td>46.31</td>
<td>41.20</td>
<td>19.08</td>
<td>17.62</td>
</tr>
<tr>
<td></td>
<td>2.67</td>
<td>40.26</td>
<td>48.06</td>
<td>19.35</td>
<td>18.10</td>
</tr>
<tr>
<td>Li$_2$SO$_4$-Mn$_x$O$_y$/TiO$_2^b$</td>
<td>0.37</td>
<td>36.70</td>
<td>22.00</td>
<td>8.09</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td>38.10</td>
<td>35.12</td>
<td>13.38</td>
<td>7.48</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>55.75</td>
<td>21.55</td>
<td>12.01</td>
<td>9.05</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>42.36</td>
<td>27.81</td>
<td>11.78</td>
<td>3.83</td>
</tr>
</tbody>
</table>

Reaction conditions: $t$=740 °C

$^a$ 2.0 g, $n$(Mn)/$n$(B)=2.9, SV=1500 ml/(g·h), $V$(CH$_4$):$V$(O$_2$)=2

$^b$ 1.0 g, $n$(Mn)/$n$(Ti)=0.044, SV=2400 ml/(g·h), $V$(CH$_4$):$V$(O$_2$)=2.8

Both the yield of C$_2$ hydrocarbons and the selectivity for ethylene were enhanced with the content of Li$^+$ at first, while the conversion of methane decreased when the Li/Mn ratio exceeded 1.33 for LiCl-B$_2$O$_3$/MnO$_2$ and 0.79 for Li$_2$SO$_4$-Mn$_x$O$_y$/TiO$_2$ because the Mn concentration in the catalyst became low. The above results seemed to suggest that lithium salts should be the catalyst promoter, which favored the formation of C$_2$ hydrocarbons but had no effect on methane conversion.
3.1.2. Effect of anions on OCM performance

A lot of catalysts have been investigated for OCM. It has been shown that Li⁺ could significantly enhance the catalytic activity. Meanwhile OCM was found to be greatly influenced by the anions in the catalyst precursors, among which Cl⁻ and SO₄²⁻ were proven to be the most active [11–15]. In this work, the influence of LiCl and Li₂SO₄ on the activity was studied.

As shown in Table 2, Figure 1 and Figure 2, LiCl exhibited more significant effect on the catalytic activity of Li⁺-B₂O₃/MnO₂ than Li₂SO₄. The selectivity and yield of C₂ hydrocarbons and C₂H₄/C₂H₆ ratio were high in the presence of LiCl. LiCl played a similar role in Li⁺-MnₓO₉/TiO₂. It seemed that the existence of Cl⁻ promote the conversion to C₂ hydrocarbons and inhibited the deep oxidation to carbon dioxide of methane effectively.

As illustrated in Figure 1 and Figure 2, the catalysts contained LiCl were more active than that contained Li₂SO₄. And moreover, LiCl-B₂O₃/MnO₂ presented very high catalytic activity and stability for OCM.

Burch et al [16] presented a view on the function of Cl⁻ in OCM. They suggested that ethylene was produced by CH₃ collide collisions, in which CH₃ formation was the rate-limiting step. When Cl⁻ was added into the catalyst, it interacted with other ingredients and formed Cl⁻, which might react with CH₄ to produce CH₂⁻ and enhanced the formation rate of CH₂⁻. Hence the selectivity and yield of C₂ hydrocarbons and ethylene increased. Some comparatively stable molecules, such as HClO, were formed because some kinds of free radicals (-O, -OH, -OH₂) collided with Cl⁻, and the deep oxidation of methane was effectively inhibited. Thus the selectivity for C₂ hydrocarbons and the C₂H₄/C₂H₆ ratio were increased consequently [17].

3.1.3. Effect of CH₄/O₂ ratio on OCM performance

The effect of CH₄/O₂ ratio on OCM is illustrated in Figure 3. Methane conversion declined when the oxygen concentration in the feed gas was lowered, while the selectivity for C₂ hydrocarbons increased sharply and attained ca. 53% when CH₄/O₂ ratio exceeded 3. The yield of C₂ hydrocarbons improved at first, reached a maximum when CH₄/O₂ ratio was

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### Table 2. Effect of different anions on OCM performance

<table>
<thead>
<tr>
<th>Anion</th>
<th>X/%</th>
<th>Selectivity (%)</th>
<th>Y(C₂)/%</th>
<th>n(C₂H₄)/n(C₂H₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺-B₂O₃/MnO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>40.02</td>
<td>14.9</td>
<td>2.9</td>
<td>17.8</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>44.01</td>
<td>44.5</td>
<td>3.4</td>
<td>48.0</td>
</tr>
<tr>
<td>Li⁺-MnₓO₉/TiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>30.53</td>
<td>39.2</td>
<td>16.3</td>
<td>55.4</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>36.23</td>
<td>39.3</td>
<td>13.4</td>
<td>52.7</td>
</tr>
</tbody>
</table>

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a 2.0 g, n(Li):n(Mn):n(B)=1.33:1:2.9, SV=1500 ml/(g.h), V(CH₄):V(O₂)=2, t=750 °C

b 1.0 g, n(Li):n(Mn):n(Ti)=0.53:1:0.044, SV=2400 ml/(g.h), V(CH₄):V(O₂)=2.8, t=750 °C
2.8, and then dropped. It is suggested [18] that as the ethane formation rate is limited by the reaction of methane with the lattice oxygen and C\textsubscript{2} hydrocarbons are formed through the coupling of methyl radicals either in the gas phase or on the solid surface at a very rapid rate, thus the yield of C\textsubscript{2} hydrocarbons will increase with increasing the methane partial pressure.

![Figure 3. Effect of CH\textsubscript{4}/O\textsubscript{2} ratio on OCM performance](image)

Reaction conditions: 

- Li\textsubscript{2}SO\textsubscript{4}-Mn\textsubscript{x}O\textsubscript{y}/TiO\textsubscript{2} catalyst 1.0 g, n(Li):n(Mn):n(Ti)=0.53:1:0.044, t=730 °C, SV=2400 ml/(g-h)  
- (1) X(CH\textsubscript{4}), (2) S(C\textsubscript{2} hydrocarbons), (3) Y(C\textsubscript{2} hydrocarbons)

**3.1.4. Effect of reaction temperature on OCM performance**

The effect of reaction temperature on OCM performance catalyzed by LiCl-B\textsubscript{2}O\textsubscript{3}/MnO\textsubscript{2} and Li\textsubscript{2}SO\textsubscript{4}-Mn\textsubscript{x}O\textsubscript{y}/TiO\textsubscript{2} are presented in Figure 4 and Figure 5 respectively. Methane conversion, the yield of C\textsubscript{2} hydrocarbons and the selectivity for ethylene increased with temperature at first and then they decreased when the temperature exceeded 750 °C, while the ratio of C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} was high in the high temperature zone. It is generally accepted [1,19,20] that ethylene is generated from ethane via dehydrogenation reactions, and C-H bond fractures more easily at high temperature with the operation of surface O\textsuperscript{-} ions. Therefore, high temperature favored the formation of ethylene and the ratio of C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} went up to 17.7 at 800 °C over LiCl-B\textsubscript{2}O\textsubscript{3}/MnO\textsubscript{2}.

There might be some reasons for the decline of the methane conversion and the yield of C\textsubscript{2} hydrocarbons when the temperature was above 750 °C. For LiCl-B\textsubscript{2}O\textsubscript{3}/MnO\textsubscript{2}, LiCl and the probable active component Li\textsubscript{4}B\textsubscript{7}O\textsubscript{12}Cl, generated after the catalyst was calcined at 700 °C, might be lost at high temperatures. Meanwhile, lithium in both LiCl-B\textsubscript{2}O\textsubscript{3}/MnO\textsubscript{2} and Li\textsubscript{2}SO\textsubscript{4}-Mn\textsubscript{x}O\textsubscript{y}/TiO\textsubscript{2} could react with CO\textsubscript{2} and form Li\textsubscript{2}CO\textsubscript{3}, which was less active for OCM. Methane and C\textsubscript{2} hydrocarbons were deeply oxidized to CO\textsubscript{2} and more Li\textsubscript{2}CO\textsubscript{3} was formed in high temperatures, thus the catalysts would deactivate quickly.

![Figure 4. Effect of reaction temperature on OCM performance over LiCl-B\textsubscript{2}O\textsubscript{3}/MnO\textsubscript{2}](image)

Reaction conditions: catalyst 2.0 g, n(Li):n(Mn):n(B)=1.33:1:2.9, SV=770 ml/(g-h), V(CH\textsubscript{4}):V(O\textsubscript{2})=2
3.2. Stability test of catalyst in OCM

Figure 6 gives the stability of LiCl-B$_2$O$_3$/MnO$_2$ in OCM. The catalyst was stable and exhibited high activity at 720 °C initially, while the catalytic activity dropped slowly after 5.5 h reaction. This might be due to the loss of LiCl and Li$_4$B$_7$O$_{12}$Cl which occurred gradually after a period of reaction at high temperatures.
As shown in Figure 7, Li₂SO₄-MnₓOᵧ/TiO₂ was very stable at 750 °C. Methane conversion, the yield and selectivity of C₂ hydrocarbons and ethylene, the ratio of C₂H₄/C₂H₆ remained unchanged in the reaction for 12.5 h. Li₂SO₄-MnₓOᵧ/TiO₂ displayed comparatively high stability at high temperatures although its catalytic activity was a bit lower than that of LiCl-B₂O₃/MnO₂.

### 3.3. Result of the catalyst characterizations

Figure 8 illustrated the XRD patterns of fresh LiCl-B₂O₃/MnO₂ catalyst and used LiCl-B₂O₃/MnO₂ catalyst that had no catalytic activity. The characteristic peaks attributed to LiCl (2θ=32.9° and 23.2°) and to a new phase, cubic Li₄B₇O₁₂Cl (2θ=25.4°, 32.9°, 36.2°, 44.1° and 53.3°), were observed only in the fresh catalyst. MnO₂ was observed in both the fresh and the used catalysts. The cubic Li₄B₇O₁₂Cl and cubic MnO₂ were generated after the catalyst was calcined at 700 °C.

As shown in Figure 9, two endothermic DTA peaks at 610 and 750 °C appeared in the fresh catalyst accompanied by a major weight loss in the TG curve. The peak at 610 °C could be ascribed to the loss of LiCl, and the one at 750 °C might be attributed to the loss of the new phase, Li₄B₇O₁₂Cl. There was no detectable peak in the TG and DTA curves in the used catalyst. The above results suggest that the loss of LiCl and Li₄B₇O₁₂Cl, which probably was the active component in catalyst, led to the deactivation of the catalyst.
As presented in Figure 10, anatase, Mn$_2$O$_3$ and Li$_2$SO$_4$ were the main components in Li$_2$SO$_4$-Mn$_x$O$_y$/TiO$_2$ and they stayed unchanged after OCM. That is to say the Li$_2$SO$_4$-Mn$_x$O$_y$/TiO$_2$ catalysts were very stable at high temperatures.

4. Conclusions

The effects of different components of LiCl-B$_2$O$_3$/MnO$_2$ and Li$_2$SO$_4$-Mn$_x$O$_y$/TiO$_2$ catalysts, the reaction temperature, the ratio of CH$_4$/O$_2$ on OCM and the stability test of the catalyst during OCM have been studied. For both catalysts, high yield of C$_2$ hydrocarbons was obtained. They were 22% and 20% respectively. LiCl-B$_2$O$_3$/MnO$_2$ exhibited high catalytic activity, while Li$_2$SO$_4$-Mn$_x$O$_y$/TiO$_2$ was more stable than LiCl-B$_2$O$_3$/MnO$_2$ during OCM. Meanwhile, It appears possible that cubic Li$_4$B$_7$O$_{12}$Cl might be the active component, which may have potential value in application and for further research.

References