The Partial Oxidation of Methane to Methanol with Nitrite and Nitrate Melts

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The effect of reduced oxygen species on the partial oxidation of methane to methanol was examined with nitrite melts. The experimental results support the suggestion that the formation of methanol or C₂ compounds depends on different reduced oxygen species, as observed in our previous work using nitrate melts. It has been suggested that the partial oxidation of methane proceeds to CH₃OH or C₂ compounds via parallel pathways. This suggestion was verified by increasing the oxygen concentration to carry out the partial oxidation of methane in 25 mol% NaNO₃ - 75 mol% KNO₃ melts. A methanol selectivity of 8.2% and a methanol yield of 0.43% were observed with CH₄/O₂ = 15/1 at 575 °C, whereas with CH₄/O₂ = 7/1 methanol selectivity and yield increased to 23.7% and 1.1%, respectively. The results further confirm the contribution of the superoxide ion O₂⁻ on methanol formation.

Introduction

The potential of molten salts as media for chemical reactions is well known [1, 2]. The use of molten carbonates [3, 4], hydroxides [5] and chlorides [6] as reaction media for the oxidative coupling of methane to hydrocarbons has been investigated. In these studies, the authors suggested that reduced oxygen species played an important role in the formation of C₂ compounds [3-5]. Thermodynamic and electrochemical studies in molten barium hydroxide [5, 7] and alkali carbonates [4, 8, 9] have shown that peroxide ion was the stable form of reduced oxygen species in basic media, and may increase the selectivity of formation of C₂ compounds [4, 5].

In our previous work [10], we used (Na, K)NO₃ melts as reaction media for the partial oxidation of methane to methanol, and tried to estimate the amounts of reduced oxygen species by thermochromical calculation according to eqs (1) - (7).

\[ \text{NO}_3^- \rightleftharpoons \text{NO}_2^- + \frac{1}{2}\text{O}_2 \] (1)
\[ 2\text{NO}_2^- = \text{O}_2^- + \text{N}_2 + \frac{3}{2}\text{O}_2 \] (2)
\[ 2\text{NO}_2^- = \text{O}_2^- + 2\text{NO} + \frac{1}{2}\text{O}_2 \] (3)
\[ \text{O}_2^- + \text{NO}_3^- = \text{NO}_2^- + \text{O}_2^- \] (4)
\[ \text{O}_2^- + 2\text{NO}_3^- = 2\text{NO}_2^- + 2\text{O}_2^- \] (5)

Our results indicated that there are two reduced oxygen anions (O₂⁻ and O₂²⁻) in nitrate melts, O₂⁻ being the dominant species the concentration of which is much larger than that of O₂²⁻. It was also shown that the variation of the amount of O₂⁻ followed the trend of the methanol selectivity. Furthermore, a comparison of the results with those of other studies [4, 5] which suggested that O₂²⁻ plays an important role in the C₂ compound formation indicated that O₂⁻ should lead to methanol formation [10] while O₂²⁻ should lead to C₂ compound formation [4, 5], and nitrate ions were considered to promote the oxidation of O₂⁻ and O₂²⁻ to O₂⁻ according to eqs (4) and (5).

In order to further confirm the role of O₂⁻ in methanol formation, in the present work we used molten (Na, K)NO₃ as medium to perform the partial oxidation of methane to methanol. Theoretical calculations indicate that the major reduced oxygen species in nitrite melts is O₂⁻, whereas O₂²⁻ is the major active oxygen species in nitrate melts. The analysis of eqs. (1) - (7) suggests that the increase of oxygen pressure should increase the amount of O₂⁻. Also, we tried to increase the amount of O₂⁻ in the (Na, K)NO₃ system by increasing the oxygen concentration in the feed in order to improve the selectivity and the yield of methanol.

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Table I. Experimental results of the partial oxidation of methane in the 25 mol % NaNO₂ - 75 mol% KNO₃ melts.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Conv. (mol%)</th>
<th>CH₃OH</th>
<th>CO</th>
<th>CO₂</th>
<th>NO (10⁻⁴ mol)</th>
<th>N₂ (10⁻⁴ mol)</th>
<th>O₂⁻ (10⁻³ mol)</th>
<th>O₂₂⁻ (10⁻³ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>525</td>
<td>2.7(1.8)</td>
<td>0.15(14.1)</td>
<td>73.9(24.2)</td>
<td>25.9(61.7)</td>
<td>1.25(0.10)</td>
<td>6.19(0.13)</td>
<td>113.2(0.91)</td>
<td>15.9 (50.8)</td>
</tr>
<tr>
<td>550</td>
<td>4.9(3.6)</td>
<td>0.08(13.1)</td>
<td>25.1(31.5)</td>
<td>74.8(55.4)</td>
<td>1.72(0.19)</td>
<td>9.00 (0.27)</td>
<td>187.1 (1.07)</td>
<td>26.5 (74.6)</td>
</tr>
<tr>
<td>575</td>
<td>8.5(5.2)</td>
<td>0.05(8.2)</td>
<td>0.5(38.6)</td>
<td>99.5(53.2)</td>
<td>2.92(0.64)</td>
<td>16.3(0.46)</td>
<td>237.2(1.86)</td>
<td>34.0(93.0)</td>
</tr>
<tr>
<td>600</td>
<td>10.3(7.7)</td>
<td>0.02(2.4)</td>
<td>0.2(45.0)</td>
<td>99.8(52.6)</td>
<td>3.93(1.52)</td>
<td>25.9(0.59)</td>
<td>352.5(2.26)</td>
<td>51.0(134.0)</td>
</tr>
</tbody>
</table>

Reaction conditions: 1 atm, 525 - 600 °C, CH₄/O₂/He = 15:1:4, 50 ml/min. The selectivity of C₂ compounds was below 0.1% in each run above 575 °C. ( ) The data obtained with (Na, K)NO₃ [10]. The amounts of NO and N₂ are measured values.

Experimental

The experimental device and analysis methods were the same as previously described [8]. Experiments were carried out under atmospheric pressure and at temperatures in the range of 525 - 600 °C. NaNO₂, KNO₂, NaNO₃, and KNO₃, used were of reagent grade. 100 g of the salts of the chosen ratio (Na/K = 25 mol%/75 mol%) were dried at 150 °C for 12 h in a vacuum and melted under helium atmosphere, then heated up to the reaction temperature. A reactant gas mixture of CH₄/O₂/He = 15/1/4, 11/1/3 or 7/1/2 was bubbled through the molten phase at a constant flow rate of 50 ml/min. All products were analyzed by conventional GC techniques with thermal conductivity and flame ionization detectors. The conversion of CH₄, the selectivity and the yields of products were calculated from the GC analysis, while CO₂ was estimated from the carbon balance between products and reacted methane. NO₃ products emitted by the thermal decomposition of molten nitrates were quantified by the Saltzman absorptiometry method [11].

Results and Discussion

The experimental results obtained in 25 mol% NaNO₂ - 75 mol% KNO₂ melts at 525 - 600°C are given in Table I together with the amounts of reduced oxygen species. The data of our previous work are also shown for comparison. The amounts of reduced oxygen species in molten nitrates were calculated according to eqs (1) - (7) using thermochemical data as in previous work [10]. Methane conversion is larger than that obtained with nitrate melts, but the methanol selectivity is very low. Methane was almost completely oxidized to CO₂ and H₂O above 575 °C. The variation of the amounts of O₂⁻ and O₂₂⁻ in nitrate and nitrite melts is shown in Fig. 1 and 2, respectively. The amount of O₂⁻ is much larger than that of O₂₂⁻ in nitrate melts (Fig. 1), but in nitrite melts (Fig. 2) the amount of O₂₂⁻ is larger. This may account for the low methanol selectivity obtained in nitrite melts, where O₂⁻ competes with O₂₂⁻ to react with methane thus reducing the reaction of O₂⁻ with methane. O₂₂⁻ is apparently too active and promotes methane oxidation to CO₂ and H₂O in nitrate melts.
Table II. The results of the partial oxidation of methane to methanol in the 25 mol% NaNO₂ - 75 mol% KNO₂ melts under various oxygen concentrations.

<table>
<thead>
<tr>
<th>CH₄/O₂</th>
<th>Temp. (°C)</th>
<th>Conv. (mol%)</th>
<th>CH₃OH select. (mol%)</th>
<th>yield (mol%)</th>
<th>NO (× 10⁻⁴ mol)</th>
<th>N₂ (× 10⁻⁴ mol)</th>
<th>O₂²⁻ (× 10⁻⁴ mol)</th>
<th>O₂⁻ (× 10⁻⁴ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:1</td>
<td>525 [10]</td>
<td>1.8</td>
<td>14.1</td>
<td>0.25</td>
<td>0.10</td>
<td>0.13</td>
<td>0.91</td>
<td>50.8</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>3.6</td>
<td>13.1</td>
<td>0.47</td>
<td>0.19</td>
<td>0.27</td>
<td>1.07</td>
<td>74.6</td>
</tr>
<tr>
<td></td>
<td>575</td>
<td>5.2</td>
<td>8.2</td>
<td>0.43</td>
<td>0.64</td>
<td>0.46</td>
<td>1.86</td>
<td>93.0</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>7.7</td>
<td>2.4</td>
<td>0.18</td>
<td>1.52</td>
<td>0.59</td>
<td>2.26</td>
<td>134.0</td>
</tr>
<tr>
<td>11:1</td>
<td>525</td>
<td>1.4</td>
<td>21.0</td>
<td>0.29</td>
<td>0.07</td>
<td>0.09</td>
<td>0.62</td>
<td>62.1</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>2.9</td>
<td>18.7</td>
<td>0.54</td>
<td>0.14</td>
<td>0.21</td>
<td>0.82</td>
<td>87.8</td>
</tr>
<tr>
<td></td>
<td>575</td>
<td>4.8</td>
<td>13.9</td>
<td>0.67</td>
<td>0.36</td>
<td>0.31</td>
<td>1.59</td>
<td>125.2</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>7.6</td>
<td>2.8</td>
<td>0.21</td>
<td>1.40</td>
<td>0.50</td>
<td>1.89</td>
<td>142.8</td>
</tr>
<tr>
<td>7:1</td>
<td>525</td>
<td>1.1</td>
<td>29.7</td>
<td>0.33</td>
<td>0.05</td>
<td>0.06</td>
<td>0.35</td>
<td>72.4</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>2.6</td>
<td>26.5</td>
<td>0.69</td>
<td>0.11</td>
<td>0.18</td>
<td>0.52</td>
<td>100.3</td>
</tr>
<tr>
<td></td>
<td>575</td>
<td>4.6</td>
<td>23.7</td>
<td>1.10</td>
<td>0.26</td>
<td>0.25</td>
<td>1.06</td>
<td>145.6</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>7.7</td>
<td>4.2</td>
<td>0.32</td>
<td>1.23</td>
<td>0.44</td>
<td>1.78</td>
<td>154.8</td>
</tr>
</tbody>
</table>

In our present and previous work [10] trace amounts of C₂H₂ and C₂H₄ were observed above 575 °C. This suggests that the formation of methanol or C₂ compounds may follow parallel reaction routes requiring different reduced oxygen species for their formation. The suggestion is consistent with the proposal made by Walsh et al. [12, 13] that the partial oxidation of methane to CH₃OH or C₂ compounds proceeds via parallel pathways.

Formaldehyde has not been found in nitrite and nitrate melts. CO selectivity increases as the temperature increases from 525 °C to 600 °C, whereas the methanol selectivity is greatly decreased. This suggests that CO is a secondary product of the further oxidation of methanol.

The partial oxidation of methane involves several elementary reactions, and its reaction pathways have been discussed by many authors [12 - 18]. Although it is difficult to make a direct comparison of the reaction pathways suggested for different reaction conditions, a simple classification is possible: CH₄ → CH₃ву → C₂H₆ → C₂H₄ → CO₂ for oxidative coupling, and CH₄ → CH₃ву → CH₃OO⁻ → CH₃OOH → CH₃O⁻ → CH₃OH → CO₂ for the direct conversion to methanol. The initiating step is common for both pathways and most likely best represented by:

CH₄ + O₂ → CH₃ву + HO₂⁻.

The methyl and hydroperoxy radicals then continue the reaction to form C₂ compounds or methanol. Although O₂ makes a major contribution in the above reactions, the oxygen species has not been clari-

fied. The present results suggest that superoxide O₂⁻ brings about methanol formation and peroxide O₂²⁻ brings about C₂ compound formation. Based on this suggestion, a simplified reaction route for the partial oxidation of methane with nitrate melts has been proposed as follows:

In order to verify this assumption, we tried to increase the amount of O₂⁻ in the (Na, K)NO₃ system by increasing the oxygen concentration as suggested by eqs (1) - (5). We performed the experiments with CH₄/O₂ = 11/1 and 7/1 in the melts of 25 mol% NaNO₃ - 75 mol% KNO₃, and compared the results to our previous results obtained with CH₄/O₂ = 15/1 [10]. The results are given in Table II. As expected, methanol selectivity depends significantly on the oxygen concentration in the feed gas. A methanol selectivity of 8.2% and a methanol yield of 0.43% were obtained with CH₄/O₂ = 15/1 at 575 °C, whereas with CH₄/O₂ = 7/1 methanol selectivity and yield increased to 23.7% and 1.1%, respectively. The amounts of NO and N₂ decreased as the oxygen concentration increased, indicating that the thermal decomposition of NO₃⁻ was suppressed. The amounts of NO and N₂ at 600 °C were much larger than those below 575 °C, indicating that the thermal decomposition of NO₃⁻ is violent above 600 °C, and it apparently influenced the methanol selectivity. The effect of the oxygen concentration...
Fig. 3. The influence of oxygen concentration on methanol selectivity. □: 525 °C; ○: 550 °C; ◆: 575 °C; △: 600 °C.  

on methanol selectivity is shown in Fig. 3. Methanol selectivity greatly decreases at 525 - 575 °C as the ratio of CH₄/O₂ increases, but at 600 °C this variation disappears due to complete oxidation of methane, indicating that the role of reduced oxygen species is much less significant at high temperature.

Studies [19 - 23] of the partial oxidation of methane to methanol in homogeneous and heterogeneous systems showed that methane conversion increases and methanol selectivity decreases as the oxygen concentration is increased. A maximum methanol yield is obtained with medium oxygen concentrations. The present results indicate that methane conversion decreases as the oxygen concentration is increased, while methanol selectivity and yield increase as the oxygen concentration is increased. This seems to be a very special feature for molten salt reaction systems, in which oxygen participates in the ion equilibria.