"Kinetics and Mechanism of Methane Oxidative Coupling over Samarium Oxide"

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Introduction

The direct conversion of methane to higher hydrocarbons is a promising process for the chemical utilization of methane, which is a major component of natural gas. Although many metal oxides (1,2) have proven to be active and selective for the direct conversion of methane to form C₂ hydrocarbons, there has been no general agreement on the mechanism of methane coupling. Lunsford and co-workers (3) studied the oxidative coupling of methane over Li/MgO and a series of rare earth oxide catalysts. Their results suggested that methyl radicals are formed during methane activation and the coupling of methyl radicals in the gas-phase is the major route for C₂ hydrocarbons formation. On the other hand, Carreiro and Baerns (4) and Asami et al. (5) studied the oxidative coupling of methane over lead oxo-salts and PbO/MgO catalysts, respectively. Their results suggested that ethane is formed from the coupling of adsorbed methyl radicals on the catalysts surface.

In addition, the types of oxygen species used for the activation of methane or for the subsequent reactions of activated methane are not very well defined. Lunsford and co-workers (3) suggested that O⁻ is responsible for the activation of methane and O⁻ - and/or O₂(g) are used for carbon oxides formation on Li/MgO catalysts. Otsuka and Nakajima (6) suggested that adsorbed O₂ is responsible for the activation of methane and O₂(g) is responsible for the formation of carbon oxides over Sm₂O₃.

Lo et al. (7) studied the adsorption of methanol, methyl iodide and methane over Sb₂O₅/SiO₂ using NMR spectroscopy. They observed the formation of methoxy species over the catalyst surface; this intermediate is the precursor for carbon dioxide formation.

The purpose of the present study is to use samarium oxide as a model catalyst to investigate the mechanism of methane coupling at atmospheric pressure using oxygen as the oxidant.

Experimental Procedure

Catalysts preparation

Samarium oxide (Sm₂O₃) catalysts were prepared from various samarium oxides and salts. Different calcination temperatures were employed also.
(1) Hydrothermally (HT) treated samarium oxide was prepared by placing Sm₂O₃ (Aldrich 99.9%) in a beaker containing deionized water. Residues obtained after evaporation of the water were calcined at 800°C for 16 h and 800°C for 4 h.

(2) Samarium oxide was heated to 1100°C for 22 h.

(3) Samarium nitrate hexahydrate was calcined at 900°C for 1 h.

XRD was used to determine the phases present. Surface areas were determined from BET measurements using N₂ as the adsorbate at 77 K.

Reaction studies

Methane oxidation was studied using a laboratory scale fixed-bed reactor system which could be operated in either flow or pulse modes. The reactor consisted of a 7 mm ID and 19 mm length quartz tubes which act respectively as the pre-heating and catalytic zone of the reactor. The 7 mm ID tube was fused to a 6 mm OD, 1 mm ID capillary quartz tube in order to reduce the extent of post-catalytic reaction giving rise to combustion products.

Blank experiments were performed at a temperature range of 600°C to 775°C with quartz wool placed in the reactor. Catalytic tests and kinetic studies were performed using the flow mode of the reactor system at atmospheric pressure. 0.2 to 0.8 g of catalyst was used, and the flow rate ranged from 100 to 300 cc min⁻¹. Excess CH₄ was used in the reactant mixtures such that CH₄/O₂ > 3. Effluent gases were analyzed using an on-line gas chromatograph with a thermal conductivity detector. CO, O₂, and CH₄ were analyzed using a molecular sieve 5Å column and O₂(CO), CO₂, CH₄, C₂H₆, C₂H₄ and H₂O were analyzed using a Porapak Q column. Pulse experiments were performed using the pulse mode of the reactor system at a total flow rate of 25 cc min⁻¹ with or without gas-phase oxygen. Pulse experiments using CH₃I or CH₃OH as reactants involved injection of either reactant at the reactor inlet.

Results and Discussion

The XRD powder patterns for the catalysts prepared in this study are shown in Figure 1. The catalyst prepared by hydrothermally treated Sm₂O₃ shows the presence of two phases, B (monoclinic structure) and C (cubic structure) phases (8,9). The C phase was the major component of this catalyst. The catalyst prepared by calcining Sm₂O₃ at 1100°C for 22 h shows the presence of the B phase only, and the catalyst prepared by calcining Sm(NO₃)₃·6H₂O at 900°C for 1 h shows the presence of the C phase only. These results suggested that the phase composition of the catalyst is dependent on the salt used and the calcination temperature employed.
Figure 1. XRD powder patterns of samarium oxide prepared by (a) HT treatment of Sm$_2$O$_3$ (B and C phases), (b) Sm$_2$O$_3$ calcined at 1100°C for 22 h (B phase), (c) Sm(NO$_3$)$_3$·$\delta$H$_2$O calcined at 900°C for 1 h (C phase).

Figure 2. Time dependence on methane conversion over Sm$_2$O$_3$ catalysts prepared in this study at 750°C, CH$_4$/O$_2$/He = 58/12/115.
Blank experiments revealed that the conversion of methane was less than 1% with carbon oxides being the only products. This suggests that the reaction of methane over samarium oxide is surface initiated.

Table 1 shows the activity of methane coupling over untreated (used as obtained from Aldrich Chemical Co.) and hydrothermally treated Sm₂O₃ at steady state. The conversion of methane are practically the same for both catalysts. In addition, although the selectivity to CO is higher for the untreated catalyst, the total yield to carbon oxides and to C₂ hydrocarbons are constant for both catalysts. These data suggest that the two catalysts behave quite similar towards methane coupling. One possible explanation to this similarity is that the untreated catalyst has been on stream (CH₄/O₂ = 3) for several hours at 700°C. During this time period, the catalyst is continually exposed to water.

Figure 2 shows the conversion of methane over the three Sm₂O₃ catalysts prepared in the present study. Among the three catalysts tested, C-phase Sm₂O₃ is the most active and B-phase Sm₂O₃ is the least active for methane coupling. Figure 3 shows the selectivity to C₂ hydrocarbons over the three catalysts prepared. This figure shows that the HT-treated Sm₂O₃ catalyst gives the highest C₂ selectivity and B-phase Sm₂O₃ gives the lowest C₂ selectivity. In conclusion, C-phase Sm₂O₃ and HT-treated Sm₂O₃ catalysts show a similar C₂ yield for methane coupling. Since most methane coupling studies over Sm₂O₃ catalysts employ mixed phase Sm₂O₃ (B and C phases). The present study will employ HT-treated Sm₂O₃, which consists of B and C phases, as the test catalyst for kinetic and mechanism study.

Figure 4 shows the effect of CH₄/O₂ ratio on methane conversion and product distribution for methane coupling over Sm₂O₃ at 750°C. High conversions of methane and high selectivity to carbon dioxide are obtained at low CH₄/O₂ ratios. On the other hand, high CH₄/O₂ ratios favor the formation of C₂H₆ in the expense of methane conversion.

Figure 5 shows the activity of methane coupling as a function of CH₄/O₂ time on stream over HT-treated Sm₂O₃. No appreciable changes in either CH₄ conversion or product selectivities are observed after the catalyst has been used for 20 h. This suggests that the present Sm₂O₃ catalyst is much more stable than the other unpromoted low melting metal oxides (such as lead oxide) in which catalyst deactivation due to catalyst volatility is a serious problem.

Rate laws of the form:

\[
\frac{d[\text{product}]}{dt} = k[\text{CH}_4]^m[O_2]^n
\]

were determined for the formation of the principal products (CO, CO₂, and C₂H₆) in kinetic studies. Nonintegral reaction orders in both methane and oxygen were obtained for the formation of CO and C₂H₆. These results suggest that the rate-determining step for C₂H₆ formation is the reaction between methane and adsorbed oxygen (0.9 order in CH₄ and 0.6 order in O₂.
Table I. Activity of methane coupling over untreated and hydrothermally treated \( \text{Sm}_2\text{O}_3 \) at 700°C, \( \text{CH}_4/\text{O}_2 = 3 \).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>% CH(_4) Conversion</th>
<th>% Selectivity ( \text{CO} )</th>
<th>% Selectivity ( \text{CO}_2 )</th>
<th>% Selectivity ( \text{C}_2\text{H}_4 )</th>
<th>% Selectivity ( \text{C}_2\text{H}_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated ( \text{Sm}_2\text{O}_3 )</td>
<td>21.9</td>
<td>17.1</td>
<td>38.0</td>
<td>20.9</td>
<td>24.0</td>
</tr>
<tr>
<td>HT treated ( \text{Sm}_2\text{O}_3 )</td>
<td>21.2</td>
<td>11.7</td>
<td>46.2</td>
<td>19.9</td>
<td>22.2</td>
</tr>
</tbody>
</table>

Table II. Product distribution of methane coupling over \( \text{Sm}_2\text{O}_3 \) as a function of the \# of the pulse at 800°C, \( \text{O}_2/\text{CH}_4/\text{He} = 2-0/5-7/130 \) with 0.4 g of catalyst.

<table>
<thead>
<tr>
<th># of pulse</th>
<th>Rate of product formation (\text{umole/min g})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\text{CO}</td>
</tr>
<tr>
<td>1</td>
<td>17.2</td>
</tr>
<tr>
<td>2</td>
<td>19.7</td>
</tr>
<tr>
<td>3</td>
<td>17.2</td>
</tr>
<tr>
<td>4</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>10.7</td>
</tr>
<tr>
<td>6</td>
<td>9.8</td>
</tr>
<tr>
<td>7</td>
<td>13.5</td>
</tr>
<tr>
<td>8</td>
<td>23.2</td>
</tr>
<tr>
<td>9</td>
<td>24.9</td>
</tr>
<tr>
<td>10</td>
<td>21.4</td>
</tr>
<tr>
<td>reoxidation, 11 (20 cc)(^b)</td>
<td>22.2</td>
</tr>
<tr>
<td>reoxidation, 12 (10 cc)</td>
<td>21.5</td>
</tr>
<tr>
<td>reoxidation, 13 (5 cc)</td>
<td>20.9</td>
</tr>
</tbody>
</table>

\(^a\) Molecular sieve 5A column was used to analyze the products formed from this pulse experiment to determine whether all \( \text{O}_2 \) are consumed during this pulse. It was found that all \( \text{O}_2 \) are consumed during all pulse experiments.

\(^b\) Reoxidation was done by passing \( \text{O}_2 \) pulses through the catalyst until no \( \text{O}_2 \) uptake has taken place, the value in the parenthesis reflects the flow rate of oxygen used during pulse exit.
Figure 3. Time dependence on C₂ hydrocarbons selectivity over Sm₂O₃ catalysts prepared in this study at 750°C, CH₄/O₂/He = 58/12/115.

Figure 4. Effect of CH₄/O₂ ratio on methane coupling over HT treated Sm₂O₃ (B + C phases) at 750°C, total flow = 174 cc min⁻¹.

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Figure 5. Time dependence on methane coupling over HT treated Sm$_2$O$_3$ (B + C phases) at 750°C, CH$_4$/O$_2$/He = 58/12/115.

Figure 6. Product distribution in pulsed conversion of methane over HT treated Sm$_2$O$_3$ at 800°C in the absence of oxygen. Pulse size = 0.5 mL, CH$_4$/He = 57/130.
for a CH$_4$/O$_2$ ration ranging from 4.5 to 18). Rate dependences for CO$_2$ formation were first order in oxygen and a negative order in methane. This suggests that gas-phase oxygen or adsorbed molecular oxygen (or both) are used for CO$_2$ formation. In addition, the inhibition effect of CH$_4$, as indicated by the negative order, may be one reason why a 93% selectivity to C$_2$ hydrocarbons is obtained at very high CH$_4$/O$_2$ ratios, i.e., CH$_4$/O$_2$ = 45 (2).

The types of oxygen used for methane activation as well as the subsequent reactions of activated methane was investigated by using the pulse reaction studies. Figure 6 shows the product distribution obtained for the pulse reaction with CH$_4$ as the only reactant. Consecutive CH$_4$ pulses led to an immediate decrease in the formation of both C$_2$H$_6$ and C$_2$H$_4$. No C$_2$H$_4$ is observed after the second pulse and no C$_2$H$_6$ is observed after three pulses. The total amount of oxygen used for the formation of oxygenates during the first three pulses is less than one monolayer of oxygen (assuming an oxygen packing density of 1 x 10$^{15}$ atoms/m$^2$). This suggests that only surface oxygen species are used for the formation of C$_2$ hydrocarbons. This result is in good agreement with the kinetic data in which the rate-determining step for C$_2$H$_6$ formation is found to be the reaction between gaseous methane and adsorbed monoatomic oxygen. This also suggests that the mobility of bulk oxygen to the surface is slow compared with the rate of C$_2$H$_6$ formation.

Table II provides the product distribution for the pulse experiments performed by co-feeding methane and oxygen (CH$_4$/O$_2$/He = 5.7/2/13) to the reactor. Despite the fact that a high O$_2$/CH$_4$ ratio was used, the rate of products formation declined as the pulse experiment progressed. This suggests that adsorbed oxygen species is involved in the formation of products. If only gas-phase oxygen were required we would expect to observe a constant rate of product formation.

The results also show that the decrease in the rate of CO$_2$ formation is much faster than the rate of the replenishment of oxygen species on the surface of the catalyst. This result is in good agreement with the kinetic data in which the rate of CO$_2$ formation is reoxidation limited.

The rate of formation of C$_2$H$_6$ and C$_2$H$_4$ also decreased as the pulse number increased, but to a lesser extent compared to the decrease in the rate of CO$_2$ formation. However, when the catalyst is reoxidized with O$_2$ prior to CH$_4$/O$_2$ pulses, the rate of C$_2$H$_6$ formation is independent to the partial pressure of oxygen in the reactant (pulses #11 to 13). This indicates that the catalyst is partially reduced at steady state since a partial dependency on O$_2$ partial pressure is observed in kinetic studies.

In addition, since the replenishment of oxygen species for CO$_2$ formation is slow and is the rate-determining step for CO$_2$ formation, suppression in this replenishment of oxygen species may lead to an increase in C$_2$ yield. This also explains why a 93% in C$_2$ selectivity is obtained by Otsuka et al. (2) when CH$_4$/O$_2$ = 45 was used. In such experiments, replenishment of surface oxygen for CO$_2$ formation is suppressed.
It is generally accepted that the breaking of a C-H bond of methane is the rate-determining step in methane coupling. As a result, methyl radical or radical-like intermediates are formed. The details on the subsequent steps of these intermediates are not very clear yet. The use of methanol or methyl iodide as reactants, in conjunction with the pulse technique, has permitted the subsequent steps following methane activation to be probed. The major products formed from methanol and methyl iodide are methane, carbon dioxide and carbon monoxide. Less than 10% of C$_2$ hydrocarbons are formed in both reactions. These results suggest that methoxy species is a common intermediate formed from both methanol and methyl iodide, as well as methane. This methoxy species will form either carbon oxides or methane, plus ethane in cases where methane is the reactant, depending on the availability of surface oxygen. Since less than 10% of C$_2$ hydrocarbon are formed, it seems reasonable to conclude that the coupling of gas-phase methyl radical is a major pathway for ethane formation during methane coupling.

References

(3) (a) K. D. Campbell, E. Morales and J. H. Lunsford, J. Am. Chem. Soc., 109, 7900 (1987);