Photocatalytic Methane Coupling and Methane Dry Reforming over Gallium Oxide

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Abstract: Methane coupling to produce mainly ethane and hydrogen proceeded at room temperature under UV irradiation over gallium oxide. In the presence of carbon dioxide, not only methane dry reforming but also methane dry reforming to produce carbon monoxide and hydrogen proceeded photocatalytically at mild temperatures such as 473 K. The increase in the reaction temperature gave a positive effect for dry reforming but not in the case of coupling reactions. This led to a higher selectivity for CO production at higher reaction temperature as a result from a synergic effect between photoenergy and thermal energy.

Keywords: methane, carbon dioxide, Ga₂O₃ photocatalyst, methane coupling, dry reforming

1. INTRODUCTION

The conversion of methane has been an important topic for many years. Even though many improvements have been developed, so far, steam reforming of methane to produce syngas, CH₄ + H₂O → CO + 3H₂, is still the major pathway to utilize methane. Besides from steam reforming of methane, syngas, which is important for industrial sector, can also be obtained via dry reforming of methane (DRM) with carbon dioxide, CH₄ + CO₂ → 2CO + 2H₂. This is attractive since carbon dioxide, which is a greenhouse gas, can also be consumed at one time. Therefore, successful developments of this DRM reaction will give a positive contribution for our environmental preservation.

Since methane and carbon dioxide are stable molecules, their conversions to other useful molecules are thermodynamically difficult. DRM reaction has a large ΔG (∆G₂⁹₈K = 170 kJ mol⁻¹), thus, high temperature is usually necessary for the conversion. It has been proposed that the use of photoenergy and photocatalyst can be an alternative way to make thermodynamically difficult reactions proceed easier at lower temperature such as around room temperature. We have developed some photocatalytic methane conversion reactions, such as photocatalytic steam reforming of methane to produce hydrogen [1] and photocatalytic non-oxidative coupling of methane (NOCM) to produce mainly ethane and hydrogen [2-8]. Various photocatalysts have been reported to be active for photocatalytic NOCM, such as silica-based photocatalysts [2-5], ceria-based photocatalysts [6], zeolites [7], and mesoporous silica materials [8].

On the other hand, Ga₂O₃, which is a wide band-gap semiconductor, has been reported to show activity for water splitting [9,10] and benzene decomposition [11], referring its potential as a good photocatalyst. In the present study, photocatalytic NOCM and photocatalytic methane conversion in the presence of carbon dioxide were investigated at various temperatures over Ga₂O₃. We found that besides methane coupling, photocatalytic dry reforming of methane (DRM) could also proceed in the presence of carbon dioxide when the reaction was carried out under UV irradiation at mild temperatures, such as 473 K.

2. EXPERIMENTAL

Ga₂O₃ was obtained commercially (Kishida). BET specific surface area was measured by a Yuansa Ionic monosorb. Powder X-ray diffraction (XRD) pattern was recorded on a Rigaku diffractometer RINT 2500 using Cu-Kα radiation (50 kV, 100 mA). Diffuse reflectance (DR) UV-vis spectrum was recorded at room temperature on a JASCO V-550 equipped with an integrating sphere covered with BaSO₄. Ga K-edge XANES spectrum was recorded at AR-NW10A station of Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization in Tsukuba (KEK-PF, Japan).

Photocatalytic reactions were carried out in the similar way to the previous studies [2-8]. The Ga₂O₃ sample (0.2 g) was spread on a flat bottom of a closed quartz reactor. Prior to the reaction, the sample was treated in the oxygen atmosphere at 1073 K for 1 h, then evacuated at 1073 K for 1 h. Methane or a mixture of methane and carbon dioxide was introduced to the reactor. Then, the sample was irradiated by a Xe lamp for 3 h at various temperatures. For the sake of comparison, thermal reactions without UV irradiation were also carried out at various temperatures. The products were analyzed by gas chromatography.

3. RESULTS AND DISCUSSION

3.1. Characterization

BET specific surface area of the sample was around 2 m² g⁻¹. From XRD pattern, the employed sample could be assigned to β-Ga₂O₃. In DR UV-visible spectrum, a strong absorption band in the wavelength shorter than 290 nm was observed. The K-edge XANES spectrum of Ga₂O₃ showed two distinguishable peaks which has been assigned to gallium in tetrahedral coordination, Ga(Td), and gallium in octahedral coordination, Ga(Oh), respectively. From deconvolution of the spectrum by curve-fitting method, it was confirmed that the ratio of Ga(Td) to Ga(Oh) was close to unity, in good agreement.
with previously reported literature [12].

3.2. Non-oxidative coupling of methane (NOCM)

The results of photocatalytic NOCM are shown in Table 1. Coupling products were obtained around room temperature under UV irradiation (Table 1, Entry 1). Ethane was the main product (78%), followed by ethene (9%), and propane (9%). No oxygenated compound was detected. The amount of H₂ obtained from the experiment was closed to the amount of H₂ calculated from the stoichiometric ratio of the total hydrocarbons products. Moreover, it was confirmed that the reaction did not occur either in the dark or without photocatalyst, suggesting that the NOCM proceeded photocatalytically over Ga₂O₃ as follows:

\[ 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2. \Delta G_{298 \text{K}} = 68.6 \text{ kJ mol}^{-1}. \] (1)

Among the reported photocatalysts for NOCM under the same reaction condition, Ga₂O₃ showed comparable activity to the silica-titania [2] which to date showed the highest activity for NOCM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light</th>
<th>Reaction temp./K</th>
<th>Products/µmol</th>
<th>H₂ exp./H₂ calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>on</td>
<td>RT</td>
<td>C₂H₆ 0.58</td>
<td>0.74</td>
</tr>
<tr>
<td>2</td>
<td>on</td>
<td>473</td>
<td>1.29</td>
<td>2.41</td>
</tr>
<tr>
<td>3</td>
<td>on</td>
<td>573</td>
<td>2.29</td>
<td>5.08</td>
</tr>
<tr>
<td>4</td>
<td>on</td>
<td>773</td>
<td>0.49</td>
<td>4.03</td>
</tr>
<tr>
<td>5</td>
<td>off</td>
<td>773</td>
<td>tr.</td>
<td>0.07</td>
</tr>
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</table>

Table 1. Reaction results over Ga₂O₃.

\( ^{a} \) Sample was 0.2 g, methane was 200 µmol, irradiation/reaction time was 3 h. \( ^{b} \) Ratio of hydrogen obtained experimentally to the one calculated from the total hydrocarbons products. RT = room temperature around 314 K, tr. = trace.

When the reactions were carried out at higher temperatures up to 573 K under UV irradiation, the amounts of coupling products as well as hydrogen product also increased (Table 1, Entries 1-3). The increase in the activity might be contributed from a mild thermal activation, such as a thermal desorption of products. However, the amount of coupling products decreased at 773 K, even though hydrogen product still increased (Table 1, Entry 4). For all cases, when the reaction temperature was higher than room temperature, the stoichiometric ratio of H₂ obtained from experiment to the expected one calculated from the stoichiometric of total hydrocarbons product was higher than unity. These results suggest that consecutive coupling reactions, such as coupling of products to higher hydrocarbons, and/or dehydrogenation of hydrocarbons to form carbonaceous species might proceed, resulting in producing hydrogen but with a lower amount of detectable hydrocarbons products. These side reactions would proceed easier at higher reaction temperature, i.e., 773 K.

In the case of thermal NOCM at 773 K in the dark, only a very trace amount of ethane and a small amount of hydrogen were obtained (Table 1, Entry 5), which were much smaller than the amounts of products obtained in the reaction which employed photoenergy around room temperature (Table 1, Entry 1). This suggests that, compared to photoenergy, thermal energy from a high temperature of 773 K was not good enough to convert methane to higher hydrocarbons. In other words, photoenergy would play an important role to activate methane molecules in the coupling reactions. The amount of hydrogen was much higher than the amount of detected hydrocarbon products, suggesting that the formation of hydrogen should come from side reactions such as the dehydrogenation of methane to form carbon species, which would thermodynamically proceed at 773 K easier than the NOCM reaction to produce higher hydrocarbons.

3.3. Methane conversion in the presence of CO₂

The reaction results of methane conversion in the presence of CO₂ are shown in Table 2. In the presence of CO₂ around room temperature, coupling products were detected in a similar amount to that obtained in the reaction without CO₂ (Table 2, Entry 1). However, a trace amount of CO was also obtained, suggesting that a small amount of CO₂ would be reduced during the reaction.

When the reaction temperature was raised to 473 K under UV irradiation, besides coupling products, an obvious amount of CO was obtained (Table 2, Entry 2). Hydrogen was also obtained, which amount was much higher than the calculated one from stoichiometric ratio of the total coupling products. This suggests that the hydrogen would not only obtained from the NOCM reaction. When another reaction was assumed to occur according to eq. 2, a good mass balance was obtained from eqs. 1 and 2, suggesting that these two reactions, NOCM and DRM, were the major reactions occurred at 473 K under UV irradiation. It was confirmed that DRM could not proceed without UV irradiation and/or photocatalyst, suggesting that DRM proceeded photocatalytically over Ga₂O₃, as follows:

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2. \Delta G_{298 \text{K}} = 170 \text{ kJ mol}^{-1}. \] (2)

<table>
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<tr>
<th>Entry</th>
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<th>Reaction temp./K</th>
<th>Products/µmol</th>
<th>H₂ exp./H₂ calc.</th>
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<tbody>
<tr>
<td>1</td>
<td>on</td>
<td>RT</td>
<td>C₇H₈ 0.51</td>
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</tr>
<tr>
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<td>8</td>
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<td>773</td>
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<td>1.54</td>
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<tr>
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<td>873</td>
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<td>5.93</td>
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</tbody>
</table>

\( ^{a} \) Sample was 0.2 g, methane was 200 µmol, carbon dioxide was 200 µmol, irradiation/reaction time was 3 h. \( ^{b} \) Ratio of hydrogen obtained experimentally to the one calculated from the total hydrocarbons and CO products. \( ^{c} \) The hydrogen ratio could not be determined since no hydrogen or only a trace amount of hydrogen was detected. RT = room temperature around 314 K, tr. = trace.

Under UV irradiation, the coupling products decreased gradually while CO product increased distinctly as the reaction temperatures increased (Table 2, Entries 3-6). The selectivity (S%) to CO among detected carbonaceous compounds could be calculated as follows, \( S\% = \frac{\text{amount of CO}}{\text{amount of CO} + \text{amount of detected}} \times 100\% \).
was confirmed that dry reforming of ethane proceeded additionally; in a separated experiment, it might also undergo dry reforming reaction with CO suggesting that some coupling products, such as ethane, could be activated via thermal energy at high temperature such as 773 K. As expected, the amount of CO product increased when the reaction was carried out at higher temperatures, such as 873 K. In dry reforming of methane, a synergic effect between photo-and thermal energy was observed at mild temperatures.

**ACKNOWLEDGEMENTS**

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