Direct Dehydrogenative Conversion of Methane into Higher Hydrocarbons through Liquid-Metal Indium Catalyst

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Abstract: Dehydrogenative conversion of methane (DCM) is an attractive reaction. We already reported that liquid-metal indium supported on silica (In/SiO2) was an effective catalyst for DCM. Characterization studies and kinetic studies indicated that liquid-metal indium catalyzed cleavage of a C-H bond of methane and coupling methane to ethane selectively. In addition, conversion of ethane and temperature-programmed reaction in ethane (TPR-C2H6) suggested that indium did not activate both a C-H bond and a C-C bond of ethane. Indium has the unique catalysis to activate only a C-H bond of methane, therefore, selectivity to hydrocarbons was still high despite high temperature.

Keywords: Methane conversion, Liquid metal catalysis, Indium catalysis.

1. Introduction

Methane (CH4) is the main component of natural gas, which is an abundant energy sources in the earth. Most of CH4 is currently used to generate electric power and heat because it is difficult to convert CH4 to valuable compounds. Steam reforming of CH4 to syngas (CO + H2) and following catalytic reactions are only realized as industrial processes for utilization of CH4. These processes need large amount of energy and costs because of multi-step reaction. Therefore, direct conversion of methane to chemicals and liquid fuels is a promising way to utilize natural gas.

In dehydrogenative conversion of CH4, molybdenum/zeolite (Mo/zeolite) catalysts have been extensively studied and tested to overcome coke deposition[1,2]. Recently, a few new DCM catalysts were reported. For example, Guo et al. reported the Fe/SiO2 catalyst (single Fe sites in a silica matrix) to convert CH4 to ethylene, benzene and naphthalene at >1223 K[3]. We also reported the In/SiO2 catalyst to convert CH4 to ethylene, propylene and benzene[4]. CH4 conversion was 4.8% and selectivity to hydrocarbons was 75 % by the In/SiO2 catalyst at 1173 K. In this work, we study detailed reaction mechanisms for the DCM reaction on the In/SiO2 catalyst.

2. Experimental

The In/SiO2 catalyst was prepared by a conventional impregnation method. Indium nitrate hydrate was dissolved in deionized water and CARiACT Q-3 (SiO2 support) was added to the solution. The mixture was dried up at 393 K. This catalyst precursor was calcined at 773 K in air and was reduced with H2 at 873 K. The DCM reaction tests were conducted using a fixed-bed quartz reactor (I.D. 12 mm) with In/SiO2 (100 mg) and CH4 (1 atm, 10 mL min-1) was flowed. Hydrocarbons and H2 were analyzed by gas chromatographs or an online mass spectrometer. In the cases of conversion of C2H6, 5% C2H6/Ar (1 atm, 30 mL min-1) or 0.5% C2H6/H2 (1 atm, 20 mL min-1) was flowed. A Ni/SiO2 catalyst as a reference one was prepared from nickel nitrate hexahydrate using the same method.

3. Results and discussion
Figure 1 (a)-(d) show the profiles of temperature-programmed reaction (TPR) from 323 K to 1173 K with 4 K min\(^{-1}\) monitored by a mass spectrometer. In the TPR using CH\(_4\) on In/SiO\(_2\) (a), formation of C\(_2\)H\(_6\) (m/z = 30) was observed from 800 K. On the other hand, no formation of C\(_2\)H\(_6\) on SiO\(_2\) (b). It was clear that indium catalyzed CH\(_4\) activation and propylene and benzene were successively produced following the C\(_2\)H\(_6\) formation. In the TPR using C\(_2\)H\(_6\) on In/SiO\(_2\) (c), significant products were not detected at 800 K. Formations of H\(_2\) (m/z = 2) and CH\(_4\) (m/z = 16) were observed over 950 K, corresponding to conversion of C\(_2\)H\(_6\) (m/z = 28, 30). In the case of SiO\(_2\) (d), similar profiles were observed except for hydrogen production which was slightly suppressed by In/SiO\(_2\). Figure 1 indicated that indium could activate a C-H bond of CH\(_4\), however, a C-H bond of C\(_2\)H\(_6\) cannot.

![Figure 1](image-url)

**Figure 1.** Mass spectra of temperature-programmed reaction in CH\(_4\) over (a) SiO\(_2\) and (b) In/SiO\(_2\) and in C\(_2\)H\(_6\) by (c) SiO\(_2\) and (d) In/SiO\(_2\) with 4 K min\(^{-1}\).

To obtain more information of indium catalysis, conversion of C\(_2\)H\(_6\) in H\(_2\) was conducted. As references, results of no catalyst and Ni/SiO\(_2\) catalyst were shown in Table 1. Ni/SiO\(_2\) catalyst converted C\(_2\)H\(_6\) into CH\(_4\) and coke, therefore, a C-C bond of C\(_2\)H\(_6\) was cleaved. On the other hand, dehydrogenation of C\(_2\)H\(_6\) to C\(_2\)H\(_4\) was mainly proceeded on In/SiO\(_2\).

The selectivities on In/SiO\(_2\) were very similar to that of no catalyst. This indicated that distributions were thermodynamically decided. Indium cannot activate C-H and C-C bonds of C\(_2\)H\(_6\), therefore, carbon deposition was suppressed. In the presentation, DFT-calculation results will be discussed.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C(_2)H(_6) conv. / %</th>
<th>Selectivity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiO(_2)</td>
<td>91</td>
<td>67</td>
</tr>
<tr>
<td>In/SiO(_2)</td>
<td>61</td>
<td>21</td>
</tr>
<tr>
<td>None</td>
<td>67</td>
<td>67</td>
</tr>
</tbody>
</table>

**Table 1.** C\(_2\)H\(_6\) conversion in H\(_2\) over Ni/SiO\(_2\), In/SiO\(_2\) and no catalyst at 1073 K.

4. Conclusions

Results of TPR-CH\(_4\) and TPR-C\(_2\)H\(_6\) on In/SiO\(_2\) indicated that indium could activate only a C-H bond of CH\(_4\) but not a C-H bond of C\(_2\)H\(_6\). Additionally, indium cannot cleave a C-C bond of C\(_2\)H\(_6\) from the results of conversion of C\(_2\)H\(_6\). These unique catalysis of In/SiO\(_2\) for CH\(_4\) and C\(_2\)H\(_6\) results in higher selectivity to hydrocarbons in the DCM reaction.

References