Catalytic Methane Conversion to Methanol on Cu-SSZ-13

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Abstract: Direct methane conversion to methanol is achieved catalytically using N\textsubscript{2}O as oxidant at temperatures as low as 270 °C. The methanol production rates on Cu-SSZ-13 on a per gram basis was found to be more than twice the rate on Cu-mordenite and more than four times the rate on Cu-ZSM-5, reaching 33 µmol g\textsuperscript{-1} h\textsuperscript{-1} on Cu-SSZ-13 with a methanol selectivity of 40%.

Keywords: Cu-SSZ-13, methane activation, methane.

1. Introduction

Direct conversion of methane to chemicals and fuels has been a long-standing challenge for the field of catalysis. The large energy barrier for homolytic cleavage of the C-H bond of methane in contrast to the lower energy of the C-H bonds in the desired products—methanol and formaldehyde—renders the selective conversion of methane very difficult; facile over-oxidation of the products is unavoidable at the conditions where methane activation is possible. Copper exchanged zeolites (Cu-ZSM-5 [1] and Cu-mordenite [2,3]) were found to convert methane to methanol selectively following a 3-step cyclic process: (i) oxidation of the Cu-zeolite with O\textsubscript{2} at relatively higher temperatures (450 °C) to create reactive copper-oxo species, (ii) methane activation at moderate temperatures (120–200 °C) and (iii) admission of a solvent to extract methanol from the surface.

The ultimate goal for methane activation is to catalytically (at one step) and selectively convert methane into methanol. The temperature differences between the oxidation of Cu-zeolites and methane activation render the catalytic process difficult. In this study, we report successful activation of Cu-zeolites at temperatures lower than 300 °C using N\textsubscript{2}O (thus preventing over-oxidation reactions to some point) and catalytic methanol production at ambient pressure using methane, N\textsubscript{2}O and water vapor.

2. Experimental

SSZ-13 (Si/Al = 12) was synthesized using a protocol reported elsewhere [4]. Na-mordenite (Si/Al = 5) was purchased from Tricat (TZM 1011). NH\textsubscript{4}-ZSM-5 (Si/Al = 11.5) was purchased from Zeolyst (CBV 2314). Copper (II) ion-exchange was performed by exchanging H- or Na-form of the zeolites in copper (II) acetate (Aldrich, 98% purity) aqueous solution at 25 °C for 12 h. The amount of copper (II) acetate in the solutions varied depending on the mass of the zeolite and targeted Cu/Al ratio [5]. The hydrated samples (0.300 ±0.005 g and particle size between 250 – 425µm) were tested for CH\textsubscript{3}OH formation using a reactor system described elsewhere (ID = 7 mm).[6] CH\textsubscript{3}OH was analyzed using a gas chromatograph (GC) (Agilent 7890A) with a flame ionization detector and a HP-PLOT Q column (Agilent19091P-Q04, 30 m x 0.32 mm x 0.02 mm). CO and CO\textsubscript{2} were analyzed using a thermal conductivity detector of Agilent 7890A with a HayeSep Q column (Agilent G3591-81121, 12 ft 1/8" 2 mm). Hydrated Cu- zeolites were saturated at 20 °C by 120 cm\textsuperscript{3} min\textsuperscript{-1} CH\textsubscript{4}/N\textsubscript{2}O/He flow with designated compositions for 15 min. The feed mixture containing CH\textsubscript{4}/N\textsubscript{2}O/He was diverted through a water-containing saturator kept at 25 °C. Temperature of the samples was increased to reaction temperatures with a heating rate of 5 °C min\textsuperscript{-1}.

3. Results and discussion

Catalytic experiments were conducted in the temperature range of 250–300 °C using a gas composition consisting of 30% CH\textsubscript{4}, 30% N\textsubscript{2}O and 3% H\textsubscript{2}O (balance He). Steady state CH\textsubscript{3}OH production rates were observed over Cu-SSZ-13 approximately 50 minutes after the desired reaction temperature was
reached, no deactivation was observed for the duration of the measurements (up to 23 hours). CH₃OH, CO and CO₂ were observed as the main products of the catalytic CH₄ oxidation with CH₃OH selectivity between 16% and 24% for temperatures between 250 °C and 270 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu Concentration (g⁻¹)</th>
<th>Temperature (°C)</th>
<th>CH₄ Conversion (%)</th>
<th>CH₃OH Rate (µmol CH₃OH g⁻¹ h⁻¹)</th>
<th>CH₃OH Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-SSZ-13</td>
<td>0.50</td>
<td>250</td>
<td>0.016</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>Cu-SSZ-13</td>
<td>0.50</td>
<td>270</td>
<td>0.055</td>
<td>28</td>
<td>16</td>
</tr>
<tr>
<td>Cu-SSZ-13</td>
<td>0.50</td>
<td>300</td>
<td>0.75</td>
<td>55</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu-SSZ-13</td>
<td>0.22</td>
<td>270</td>
<td>0.022</td>
<td>33</td>
<td>40</td>
</tr>
<tr>
<td>Cu-mordenite</td>
<td>0.17</td>
<td>270</td>
<td>0.013</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Cu-mordenite</td>
<td>0.83</td>
<td>270</td>
<td>0.063</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Cu-ZSM-5</td>
<td>0.54</td>
<td>270</td>
<td>0.67</td>
<td>6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Standard reaction conditions: 0.300–0.005 g catalyst weight; feed 30% CH₄, 30% N₂O, 3% H₂O balance helium (30.4 kPa CH₄, 30.4 kPa N₂O, 3.2 kPa H₂O, 37.3 kPa He); flow rate: 120 cm³ min⁻¹, WHSV = 19 650 g feed g⁻¹ cat⁻¹ h⁻¹.

In addition to the observed higher methanol selectivity values, methanol production rate on Cu-SSZ-13 was observed to be more than four times than the rate on Cu-ZSM-5 at 270 °C. For Cu-SSZ-13, a decreasing trend in methanol selectivity was observed with increasing reaction temperatures. In addition to the decreased temperatures, increased H₂O pressure, increased methane pressure and decreased N₂O pressure were observed to result in increased methanol selectivity values [5]. Increasing N₂O pressures resulted in increased CH₄ conversion but decreased methanol selectivity indicating a larger rate order of N₂O for over-oxidation of methanol.

4. Conclusions

Catalytic methanol production from methane at low temperatures and ambient pressure on Cu-SSZ-13 was demonstrated here. Catalytic methanol production yields reaching 55 µmol g⁻¹ h⁻¹ are promising for ambient pressure. Observed higher methanol selectivity values for higher methane and H₂O pressures and lower N₂O pressures imply possibility of achieving higher methanol selectivity values with parameter optimization studies. For Cu-SSZ-13 and Cu-mordenite, lower Cu concentrations resulted in both higher methanol production rates and higher methanol selectivity values, indicating the importance of the design of the catalysts to prevent unwanted over-oxidation reactions.

References