Introduction

Increase in global energy consumption leads to a significant rise in CO₂ concentration in the atmosphere due to the burning of fossil fuels (coal, oil and natural gas), affecting Earth’s ecosystems and causing human and environmental health problems. The chemical conversion of carbon dioxide and green H₂ into value-added fuel provides a promising solution to mitigate CO₂ emission and generate renewable energy.

Recent advances in CO₂ conversion

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO₂ conversion (%)</th>
<th>Benchmarks</th>
<th>Reaction conditions</th>
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</thead>
<tbody>
<tr>
<td>Na-Fe₂O₃/HZSM-5</td>
<td>22%</td>
<td>78% hydrocarbons (3% CH₄)</td>
<td>H₂/CO₂ = 3, 320°C, 3 MPa</td>
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<tr>
<td>In₂O₃/HZSM-5</td>
<td>13.1%</td>
<td>78.6% C₆₅ selectivity</td>
<td>H₂/CO₂ = 3, 340 °C, 3.0 MPa</td>
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<tr>
<td>Co/SiO₂</td>
<td>8.6 wt%</td>
<td>70.5% methanol</td>
<td>H₂/CO₂ = 3, 320 °C, 2.0 MPa</td>
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<tr>
<td>Cu-ZrO₂-Al₂O₃-ZrO₂/LTA</td>
<td>36.1 wt%</td>
<td>100% methanol</td>
<td>H₂/CO₂=3, 260 °C, 3.0 MPa</td>
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</tbody>
</table>

The challenges

- CO₂ is fully oxidized, thermodynamically and chemically inert molecule;
- Low heat of CO₂ adsorption on catalyst, low C/H ratio, fast hydrogenation of surface adsorbed intermediates, high CO and CH₄ selectivity;
- High C-C coupling barrier;
- Thermodynamic equilibrium limitation;
- Catalyst deactivation by water.

The advantages of using zeolite X and LTA

- Zeolite X exhibits a higher CO₂ adsorption activity;
- The source of synthetic zeolites (X, LTA) is derived from natural ore, making it environment friendly and cost-effective;
- The zeolite X has a low Si/Al ratio and small pore diameter, which can promote the formation of high value short-chain hydrocarbons (≤C₁₂);
- LTA is a hydrophilic zeolite, breaking the thermodynamic equilibrium limitation, increasing CO₂ conversion and methanol selectivity.

Methods

Catalyst:
- Preparation method: incipient wetness impregnation method; ion exchange-deposition-precipitation; deposition-precipitation,
- Materials: LTA, X, SiO₂, Al₂O₃, ZrO₂ zeolites
- Metals: Na, K, Fe, Ni, Cu, Zn, Mo, In

Characterisation:
- HRTEM, SEM, XRD, XPS, Chemisorption, ICP, XRF
- H₂-TPR, NH₃-TPD, H₂-TPD, NMR, in situ FTIR, XAS

Products analysis:
- Liquid products: GC-MS and GC-FID
- Gas products: online GC-FID

Conclusions

- The cheap materials (LTA and X) have the potential to be applied in hydrogenation of CO₂ to fuels;
- The product selectivity can be modified by using different metal species;
- Cu-based catalysts promote the formation of methanol from CO₂;
- Fe-based catalysts facilitate the conversion of CO₂ to long-chain hydrocarbons;
- The acid and pore properties of zeolites play an important role in the CH₃OH to C₅ hydrocarbons.

Reference: