Hydrogenation of Carbon Dioxide to Methanol in a Slurry Reactor: Catalytic Performance of Cu-In-Zr Oxide Catalysts

Jingyuan Guan, Dominic Pjontek

Reduction of CO₂ emissions
- **CO₂ emissions**: main contributor to global warming and primarily released from fossil fuels for energy and industrial production. The Paris Agreement requires to limit global warming by 1.5 to 2 °C by reducing carbon dioxide (CO₂) and other greenhouse gas emissions.
- **Net-zero emissions**: zero carbon emissions or all emissions are offset by capturing emitted carbon. The Canadian government has legislatively committed to achieve net-zero emissions by 2050.
- **Carbon capture and utilization (CCU)**: converts captured CO₂ to fuels and chemical commodities using renewable energy and helps achieve net-zero emissions.

Converting captured CO₂ to Methanol
- **Methanol (MeOH)**: a stable and transportable feedstock for chemicals and fuels as well as an energy resource for transportation and electricity production.
- **High demand with high emissions**: currently produced 300 Mt/year releasing 300 Mt CO₂ emissions and predicted to reach 500 Mt by 2050 with 1.5 Gt CO₂ emissions \(^1\).
- **Production**: mainly by syngas-based CO and H₂ conversion using fossil carbons, such as natural gas and coal. Renewable methanol only <0.2 Mt/year \(^2\).
- **Potential**: converting captured CO₂ to MeOH not only provides a renewable MeOH feedstock, but also helps achieve net-zero emissions.

CO₂ hydrogenation to MeOH
- **Direct CO₂ hydrogenation**: \( \text{CO}_2 + 3 \text{H}_2 \rightarrow \text{CH}_3 \text{OH} + \text{H}_2 \text{O} \)
  - \( \Delta H_{\text{rxn}} = -49.5 \text{ kJ/mol} \)
- **Reversible water gas shift (RWGS)**: \( \text{CO} + \text{H}_2 = \text{H}_2 \text{O} + \text{CO}_2 \)
  - \( \Delta H_{\text{rxn}} = +41.2 \text{ kJ/mol} \)
- **CO hydrogenation**: \( \text{CO} + \text{H}_2 \rightarrow \text{CH}_3 \text{OH} \)
  - \( \Delta H_{\text{rxn}} = -60.6 \text{ kJ/mol} \)
- **MeOH formation**: more favorable at lower temperatures and higher pressures \(^3\).
- **Stability of CO₂**: high temperatures to overcome the activation energy.
- **RWGS reaction**: more favorable at higher temperatures to form CO and reduce MeOH selectivity, waste the H₂ feed, and produce more water \(^4\).
- **Catalysts**: mostly developed for syngas-based MeOH synthesis in gas-phase reactors, could suffer from water sintering and thermal deactivation \(^5\).
- **Fixed-bed reactor**: local high-temperature spots and catalyst thermal deactivation issues \(^6\).
- **Gas-liquid-solid slurry reactor**: better heat removal and temperature control \(^7,8\).

Objectives
- Formulate In₂O₃-based catalysts for methanol synthesis via CO₂ hydrogenation in a gas-liquid-solid slurry reactor.
- Identify the support effects of ZrO₂ and ZnO for the In₂O₃ catalysts.
- Identify the loading effect of In₂O₃ and compare with the CuO catalysts.
- Improve the catalytic performance of In₂O₃-based catalysts.

Materials and Methods
- **Catalyst preparation methods**
  - **Precipitation**: \( \text{NH}_4 \text{OH} \)
  - Mixed at \(T = 280 \degree C\) and aged for \(20 \text{ min}\).
  - Filtered, dried at \(65 \degree C\) for \(12 \text{ h}\).
  - In\(_2\)O\(_3\) precipitates.
- **Calcination**: at \(300 \degree C\) for \(3 \text{ h}\).

Schematic of the experimental setup
- **ZrO₂ support**: \( \text{ZrO}_2 \)
- Mixed at \(25 \degree C\) and aged for \(24 \text{ h}\).
- Evaporate the solvent at \(110 \degree C\) for \(3 \text{ h}\).
- In\(_2\)O\(_3\) solution.
- **Calcination**: at \(450 \degree C\) for \(3 \text{ h}\).

Results and Discussion
- **H₂ Temperature programmed reduction and support effect of ZrO₂ and ZnO on In₂O₃**
- **CO₂ Conversion** (%)
- **Methanol Activity (gMeOH gcat⁻¹ h⁻¹)**
- **CO₂ Conversion** (%)

**Notes**
- **The interactions between In-Zr can create more oxygen vacancies, which can improve methanol formation** \(^8\).
- A higher In₂O₃ loading could lead to the formation of larger clusters and reduce the conversion.
- CO formation is more favored on Cu, which leads to higher conversions but lower MeOH selectivities.

**Promotion effect of CuO on In₂O₃ supported by ZrO₂**
- The presence of Cu with In₂O₃ improved conversion and selectivity as more CO₂ was converted to CO by the RWGS reaction, while more MeOH was formed by CO hydrogenation.
- The competition between the CO₂ adsorption on In and Cu surfaces led to an optimized activity on Swt.% In₂O₃ Swt.% CuO/ZrO₂.

**Comparison with previous studies for the slurry system**
- Conclusions
  - Cu showed promotion effects on methanol selectivity and CO₂ conversion of In₂O₃ catalysts for CO₂ hydrogenation to methanol in the slurry reactor.
  - Compared to the previously developed catalysts in the slurry systems, Swt.% In₂O₃ Swt.% CuO/ZrO₂ reached the highest MeOH activity of 0.165 \(\text{gMeOH gcat}^{-1} \text{h}^{-1}\), relatively higher CO₂ conversion of 20%, but lower selectivity of 38%, which still needs improvement.

**References**