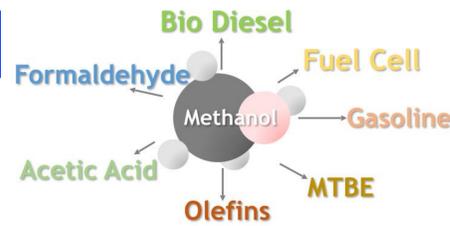
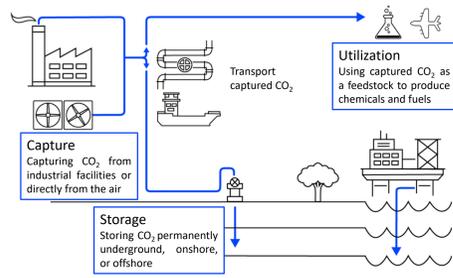


Background and Motivation

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 legislated its commitment 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.

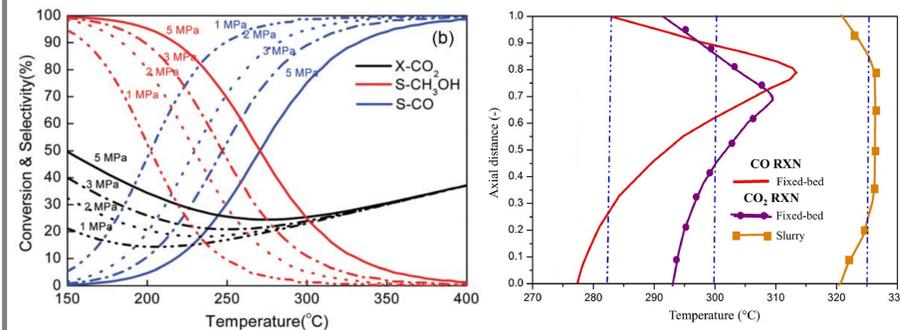


Converting captured CO₂ to Methanol

- 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 100 Mt/year releasing 300 Mt CO₂ emissions and predicted to reach 500 Mt by 2050 with 1.5 Gt CO₂ emissions [2].
- 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:** $\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ $\Delta H_{298\text{K}} = -49.5 \text{ kJ/mol}$
- Reversible water gas shift (RWGS):** $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$ $\Delta H_{298\text{K}} = 41.2 \text{ kJ/mol}$
- CO hydrogenation:** $\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$ $\Delta H_{298\text{K}} = -90.6 \text{ kJ/mol}$



- 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 [3].
- Fixed-bed reactor:** local high-temperature spots and catalyst thermal decomposition issues [4].
- Gas-liquid-solid slurry reactor:** better heat removal and temperature control [3, 4].

Objectives

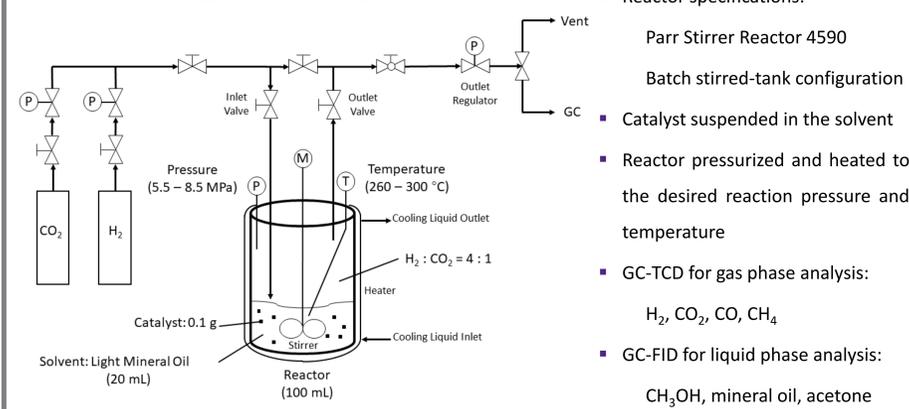
- Formulate In₂O₃-based catalysts for methanol synthesis via CO₂ hydrogenation in a gas-liquid-solid slurry reactor.
- Identify the support effects of ZrO₂ and ZnO for the In₂O₃ catalysts.
- Identify the loading effect of In₂O₃ and compare with the CuO catalysts.
- Improve the catalytic performance of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

Materials and Methods

Catalyst preparation methods

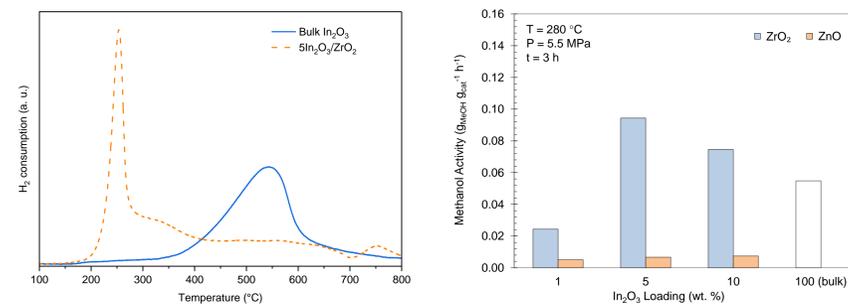
- Precipitation:**
 - Solution of In(NO₃)₃ + NH₃(OH) → Mixed at 80 °C → Aged for 20 min → Filtered → Dried at 65 °C for 12 h → In(OH)₃ precipitates → Calcination at 300 °C for 3 h → In₂O₃
- Wet impregnation:**
 - Solution of In(NO₃)₃ and Cu(NO₃)₂ + ZrO₂ support → Mixed at 25 °C → Aged for 12 h → Evaporate the solvent → Dried at 65 °C for 12 h → In(NO₃)₃-Cu(NO₃)₂/ZrO₂ → Calcination at 450 °C for 3 h → In₂O₃-CuO/ZrO₂

Schematic of the experimental setup



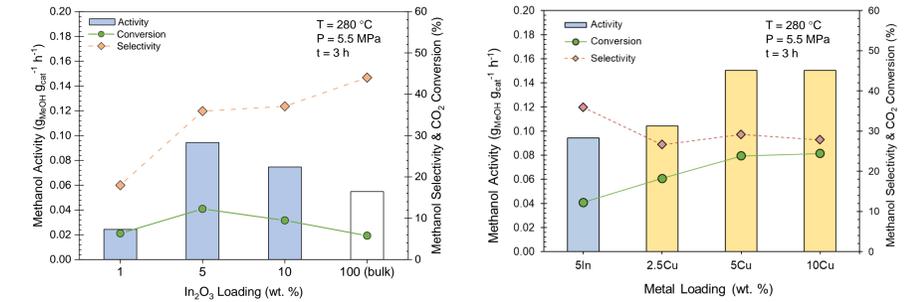
Results and Discussion

H₂-Temperature programmed reduction and support effect of ZrO₂ and ZnO on In₂O₃

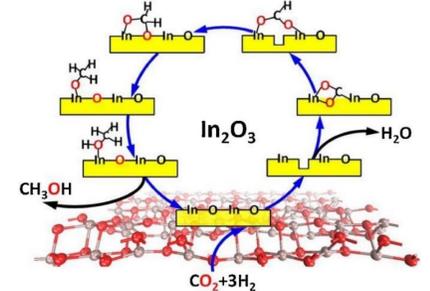


- The 5wt.% In₂O₃/ZrO₂ showed a sharp H₂ consumption peak at 260 °C.
- The ZrO₂ support shows significantly higher methanol activity than the ZnO support since ZrO₂ can decrease the H₂ reduction temperature of In₂O₃ to below the reaction temperature, which could promote MeOH formation on In-Zr surface.

Loading effects of In₂O₃ and CuO supported by ZrO₂

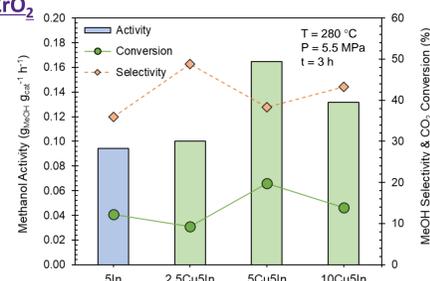


- The interactions between In-Zr can create more oxygen vacancies, which can improve methanol formation [5].
- A higher In₂O₃ loading could lead to the formation of larger clusters and reduce the conversion.
- CO formation is more favored on Cu, which leads to higher conversions but lower MeOH selectivities.

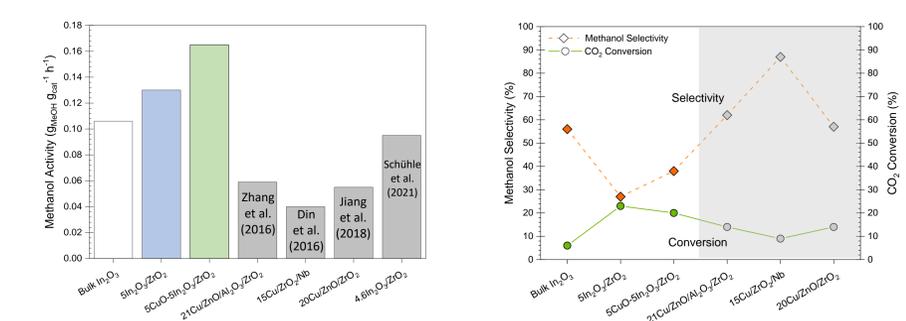


Promotion effect of CuO on In₂O₃ supported by ZrO₂

- 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 5wt.% In₂O₃-5wt.% 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, 5wt.% In₂O₃-5wt.% CuO/ZrO₂ reached:
- The highest MeOH activity of 0.165 g_{MeOH} g_{cat}⁻¹ h⁻¹, relatively higher CO₂ conversion of 20%, but lower selectivity of 38%, which still needs improvement.

References

- IEA, World Energy Outlook 2021, IEA, Paris 2021.
- IRENA, MI, Innovation Outlook: Renewable Methanol, International Renewable Energy Agency and Methanol Institute, Abu Dhabi 2021.
- S. Saiedi, S. Najari, V. Hessel, K. Wilson, F. J. Keil, P. Concepción, S. L. Suib, A. E. Rodrigues, *Progress in Energy and Combustion Science* **2016**, 85, 100905.
- S. Kanuri, S. Roy, C. Chakraborty, S. P. Datta, S. A. Singh, S. Dinda, *International Journal of Energy Research* **2022**, 46, 5503.
- J. Ye, C. Liu, D. Mei, Q. Ge, *ACS Catalysis* **2013**, 3, 1296.
- Y. Zhang, L. Zhong, H. Wang, P. Gao, X. Li, S. Xiao, G. Ding, W. Wei, Y. Sun, *Journal of CO₂ Utilization* **2016**, 15, 72.
- U. Din, M. S. Shaharun, D. Subbarao, A. Naeem, F. Hussain, *Catalysis Today* **2016**, 259, 303.
- Y. Jiang, H. Yang, P. Gao, X. Li, J. Zhang, H. Liu, H. Wang, W. Wei, Y. Sun, *Journal of CO₂ Utilization* **2018**, 26, 642.
- P. Schühle, S. Reichenberger, G. Marzun, J. Albert, *Chemie-Ingenieur-Technik* **2021**, 93, 585.