Liquid-phase alcohol promoted methanol synthesis from CO$_2$ and H$_2$

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Efficient utilization of renewable electricity requires storage of energy
- Solar and wind possess significant periodic and day-to-day fluctuation
- Storage of excess electricity produced during peak production

Chemical energy carriers
- Conversion of electricity into chemical energy by production of chemical compounds
- Advantages: high energy density, simple handling and transportation
- Methanol provides a versatile option in convenient liquid form
Background

- **Power-to-Methanol**
  - Hydrogen for methanol synthesis is produced by water electrolysis powered by renewable electricity
  - CO$_2$ is captured from point emission sources (utility plants, industry) and potentially directly from the atmosphere

- **”Methanol economy”¹**
  - Methanol replaces current fossil fuels in transportation, heating and electricity generation
  - Methanol and derived materials replace fossil raw materials in (petro)chemical industry
Methanol synthesis

- Reactions
  - \( \text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \) (CO hydrogenation, exothermic)
  - \( \text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \) (CO\(_2\) hydrogenation, exothermic)
  - \( \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \) (Water-gas shift, endothermic)
  - The water-gas shift is also activated on methanol synthesis catalysts
  - Reaction equilibrium is favorable for methanol synthesis at low temperatures and high pressures
Methanol synthesis

- **Conventional synthesis**
  - Based on fossil-derived synthesis gas consisting of CO + H₂ + minor amounts (~2-5%) of CO₂
  - Gas-phase reaction catalyzed by Cu/ZnO-based catalysts
  - Reaction temperature ~220-280°C a compromise between thermodynamics and kinetics
  - Control of reaction heat critical for catalyst life
  - Reaction pressure 50-100 bar
**CO₂ hydrogenation to methanol**

- Methanol synthesis from CO₂ + H₂ is feasible on Cu/ZnO catalysts
- Disadvantages:
  - Lower activity (production rate)²
  - Lower conversion levels due to less favorable equilibrium compared to CO-containing feeds
  - More hydrogen consumed
  - Increased formation of water due to reverse water-gas shift (RWGS) -> catalyst inhibition/deactivation

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}
\]
Alcohol-promoted methanol synthesis\textsuperscript{3,4}

- **Alternative, liquid-phase method for CO\textsubscript{2} hydrogenation to methanol**
  - Conventional Cu/ZnO catalyst combined with alcohol solvent as co-catalyst
  - The presence of the alcohol alters the reaction mechanism
  - Lower reaction temperatures are feasible
  - Lowered temperature allows higher equilibrium conversion
  - Effective heat control provided by the liquid solvent
Alcohol-promoted methanol synthesis

- The reaction proceeds through the formate ester (HCOOR) of the alcohol solvent (ROH)
- The solvent is not consumed in the overall reaction

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\text{CO}_2 + \text{H}_2 \xrightarrow{\text{H}_2\text{O}} \text{HCOOR} \xrightarrow{2 \text{H}_2} \text{CH}_3\text{OH}
\]
Experimental methods

- Autoclave reactor with 450 ml of volume (200 ml of solvent)
- Commercial Cu/ZnO/Al$_2$O$_3$, and 3Å zeolite molecular sieve ground to 150-500 µm, copper chromite powder used as supplied
- Catalyst(s) reduced prior to experiments using 5% H$_2$ in nitrogen
- Feed gas: 75% H$_2$, 25% CO$_2$ (constant feed in semi-batch mode), reaction time 6 hours
- Liquid samples taken every 2 hours, analyzed by GC

Performance measured by methanol productivity: g of methanol produced / kg of catalyst / hour
Concentration profile

- Example: 2-butanol, 20 g, Cu/ZnO, 180 °C, 60 bar
- Alcohol dehydrogenation also catalyzed by Cu/ZnO: $\text{C}_4\text{H}_9\text{OH} \rightarrow \text{C}_4\text{H}_8\text{O} + \text{H}_2$
- Increasing methanol concentration over 6 hours (equilibrium not limiting)
Effect of pressure

- 10 g of Cu/ZnO in 2-butanol
- Partial pressure of the feed gas (CO$_2$ + 3 H$_2$) = total pressure − solvent vapor pressure
Effect of temperature

- 10 g of Cu/ZnO in 2-butanol
- Activation energy 63.5 kJ/mol based on Arrhenius fit

Methanol productivity, g/kg/h

Temperature, °C

R² = 0.9531

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Solvents

- Tested at 180°C, 60 bar, with 20 g Cu/ZnO
- Similar performance found with each alcohol tested
- Effect of alcohols confirmed by a blank experiment in hexane (no methanol formed)
Effects of water

- Water was identified as a key component
- The molar amount of water formed always exceeded that of methanol
  - Excess water presumably from RWGS
  - Estimated methanol selectivity as low as 20%
- 3 w-% water was added to 2-butanol -> methanol productivity decreased by 75%

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\begin{align*}
\text{CO}_2 + 3 \text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2 & \rightleftharpoons \text{CO} + \text{H}_2\text{O}
\end{align*}
\]
Water adsorption

- 3Å molecular sieve (MS) was tested for in-situ adsorption of water
- Experiments at 180 °C, 60 bar
- 30 g of MS added to 20 g Cu/ZnO -> productivity up by over 300%
- Peak methanol concentration 0.6 mol/dm³
The overall reaction consists of two steps:

- Combination of catalysts optimized for each step would seem interesting.
- Copper chromite (CuCr) was tested with Cu/ZnO based on performance in the second step (ester hydrogenolysis)\(^5\).
Dual catalysts

- 10 g of CuCr added to 20 g Cu/ZnO -> productivity per total catalyst mass increased
- Productivity further increased with 20 g CuCr and 10 Cu/ZnO
- A synergistic effect was found, however the explanation is currently unknown
Conclusions

- Alcohol co-catalysts allow CO₂ hydrogenation to methanol at lowered temperatures
- Water by-product has a significant negative effect on methanol production
- Water can be removed by molecular sieve absorption, significantly improving methanol productivity
- Combining separate catalysts, each optimized for separate reaction steps, appears promising
Needs for further research

- **Catalyst development**
  - Activity is still low compared to gas-phase CO$_2$ hydrogenation to methanol (~50 g/kg/h vs. several hundred g/kg/h$^6$)
  - Selectivity needs to be improved by suppression of RWGS
  - Long-term stability is unknown

- **Water adsorption**
  - Demonstrated only in principle, feasibility of practical implementation has not been explored

- **From (semi)batch to continuous?**
References


