



Liquid-phase alcohol promoted methanol synthesis from CO₂ and H₂

M.Sc. Theses:

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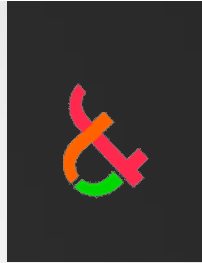
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13.12.2017

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Background



- **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
 - CO₂ 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

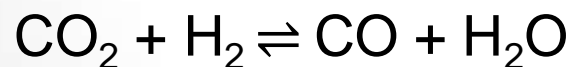
■ Conventional synthesis

- Based on fossil-derived synthesis gas consisting of $\text{CO} + \text{H}_2$ + minor amounts ($\sim 2\text{-}5\%$) of CO_2
- Gas-phase reaction catalyzed by Cu/ZnO-based catalysts
- Reaction temperature $\sim 220\text{-}280^\circ\text{C}$ a compromise between thermodynamics and kinetics
- Control of reaction heat critical for catalyst life
- Reaction pressure 50-100 bar

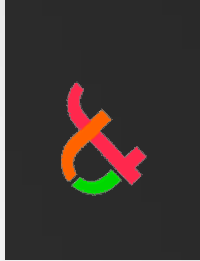


CO₂ hydrogenation to methanol

- **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



Alcohol-promoted methanol synthesis^{3,4}

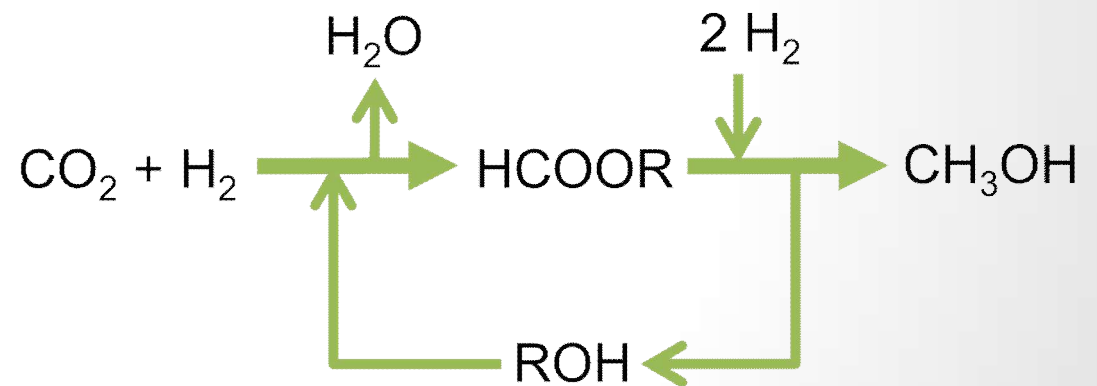


- **Alternative, liquid-phase method for CO₂ hydrogenation to methanol**
 - Conventional Cu/ZnO catalyst combined with alcohol solvent as co-catalyst
 - The presence of the alcohol alters the reaction mechanism
 - Lower reaction temperatures are feasible
 - Lowered temperature allows higher equilibrium 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



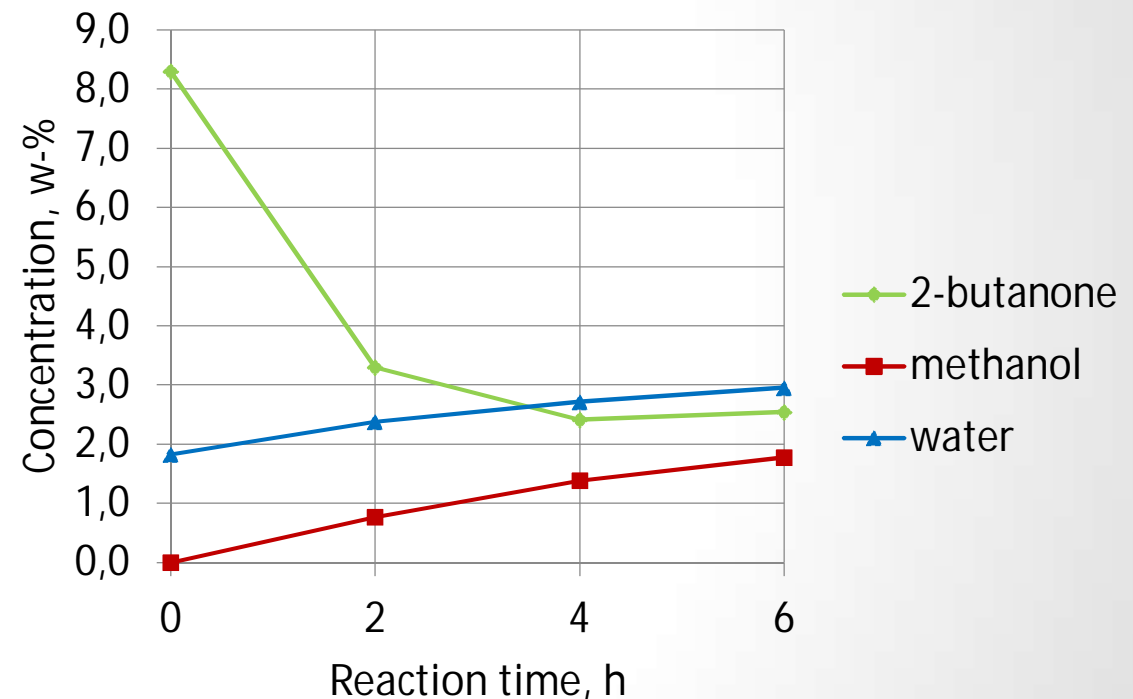


Experimental methods

- Autoclave reactor with 450 ml of volume (200 ml of solvent)
- Commercial Cu/ZnO/Al₂O₃, and 3Å zeolite molecular sieve ground to 150-500 μm, copper chromite powder used as supplied
- Catalyst(s) reduced prior to experiments using 5% H₂ in nitrogen
- Feed gas: 75% H₂, 25% CO₂ (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**

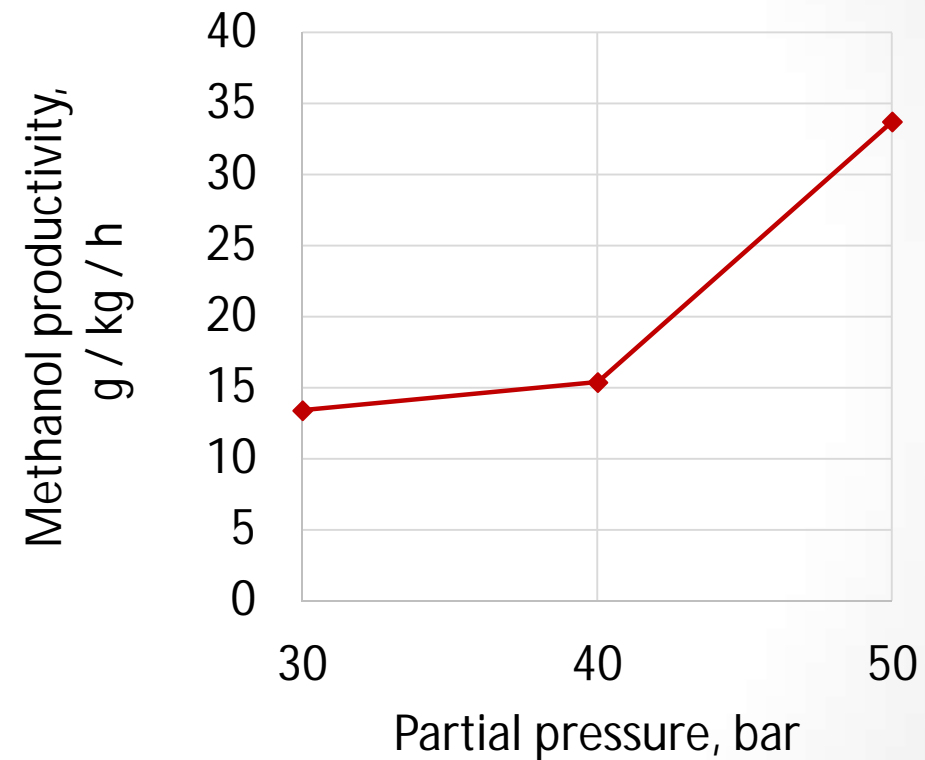
Concentration profile

- Example: 2-butanol, 20 g
Cu/ZnO, 180 °C, 60 bar
- Alcohol dehydrogenation
also catalyzed by Cu/ZnO:
 $C_4H_9OH \rightarrow C_4H_8O + H_2$
- Increasing methanol
concentration over 6 hours
(equilibrium not limiting)



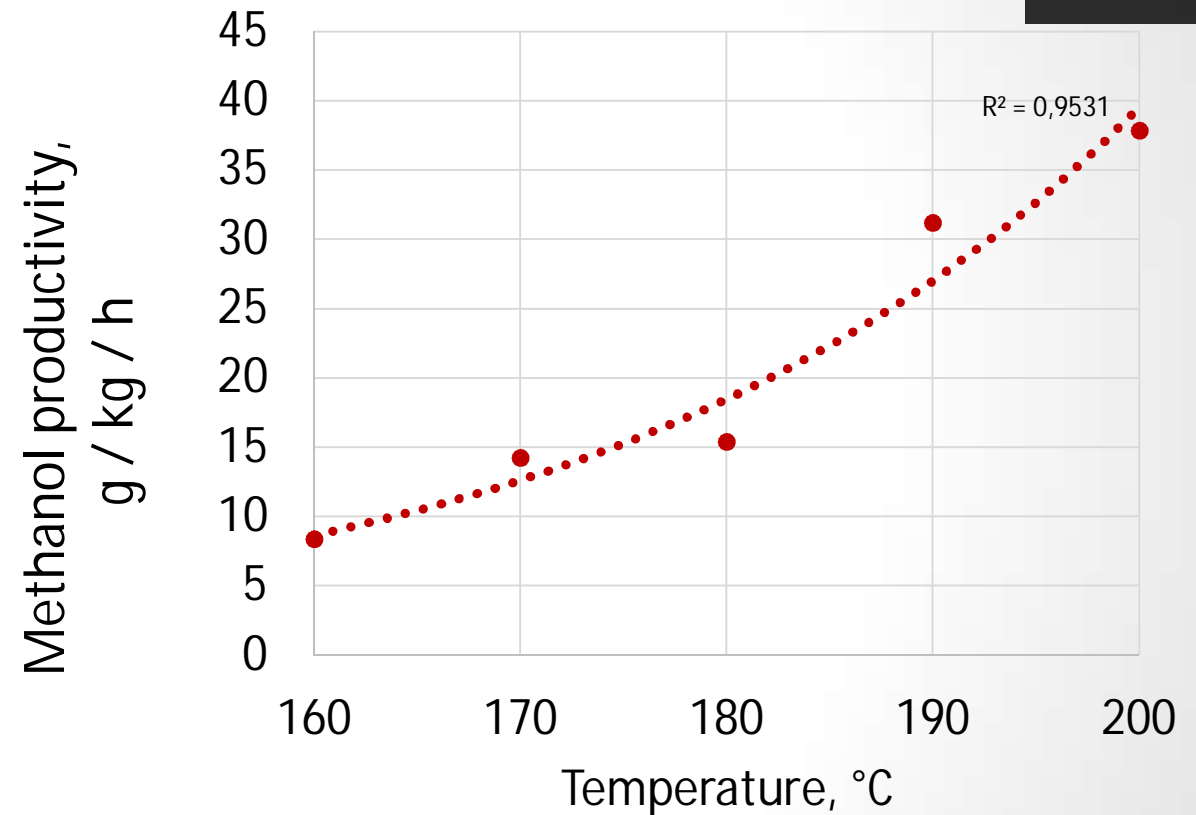
Effect of pressure

- 10 g of Cu/ZnO in 2-butanol
- Partial pressure of the feed gas ($\text{CO}_2 + 3 \text{H}_2$) = total pressure – solvent vapor pressure



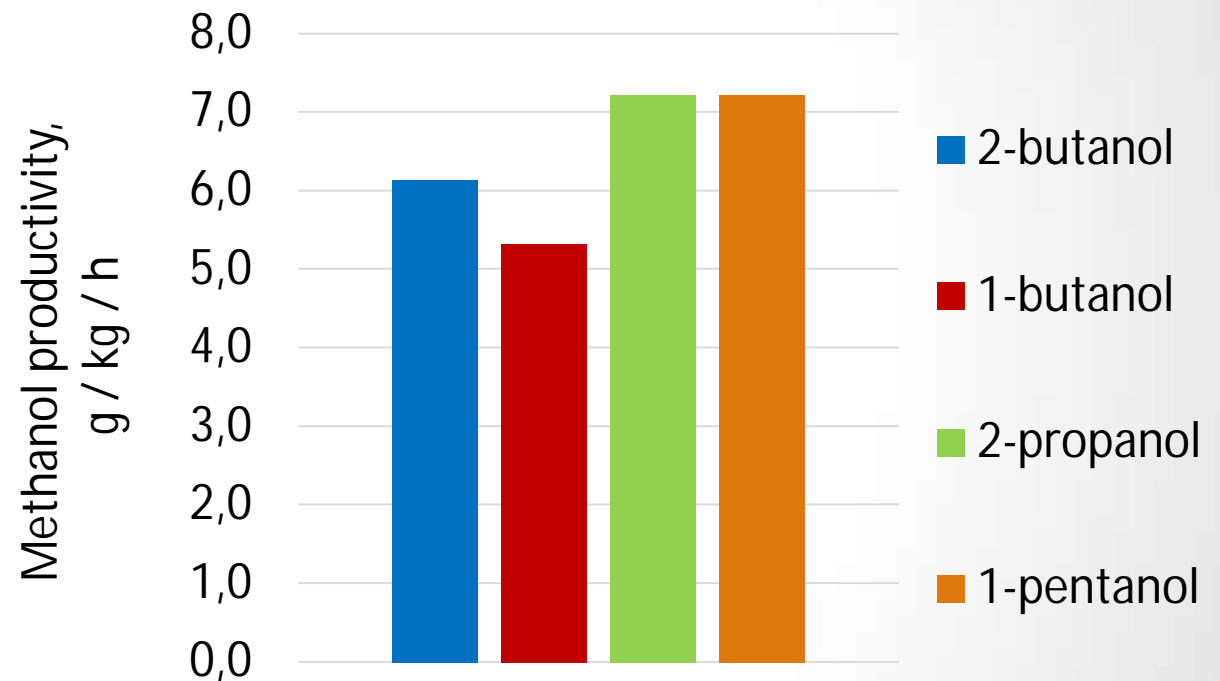
Effect of temperature

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



Solvents

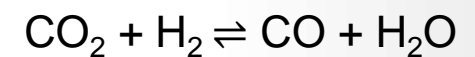
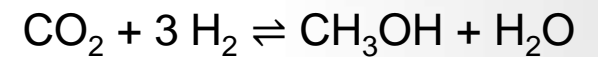
- Tested at 180°C, 60 bar, with 20 g Cu/ZnO
- Similar performance found with each alcohol tested
- Effect of alcohols confirmed by a blank experiment in hexane (no methanol formed)





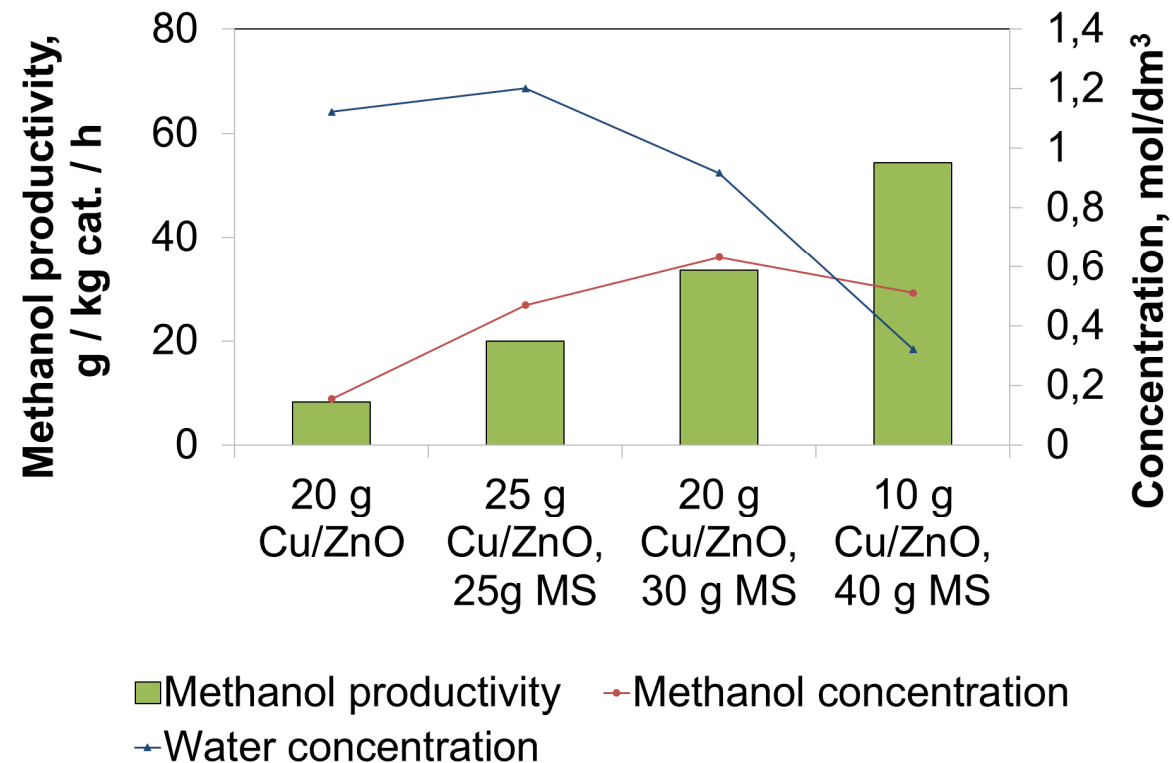
Effects of water

- 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%



Water adsorption

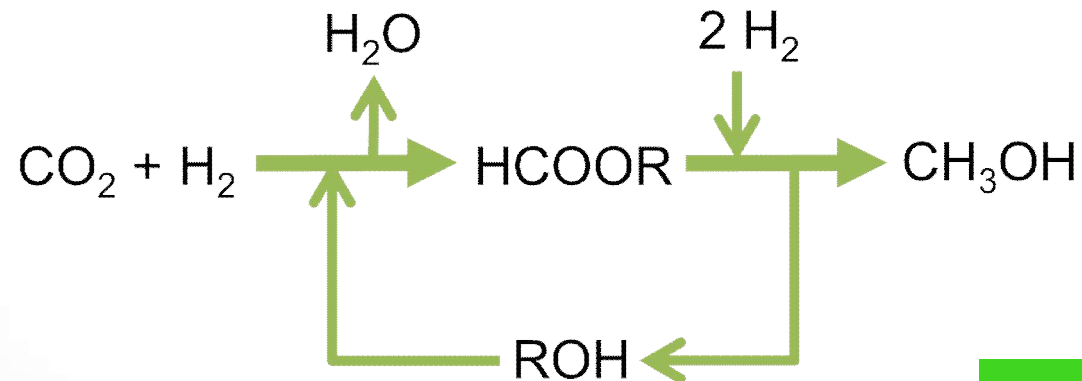
- 3Å molecular sieve (MS) was tested for in-situ adsorption of water
- Experiments at 180 °C, 60 bar
- 30 g of MS added to 20 g Cu/ZnO -> productivity up by over 300%
- Peak methanol concentration 0.6 mol/dm³





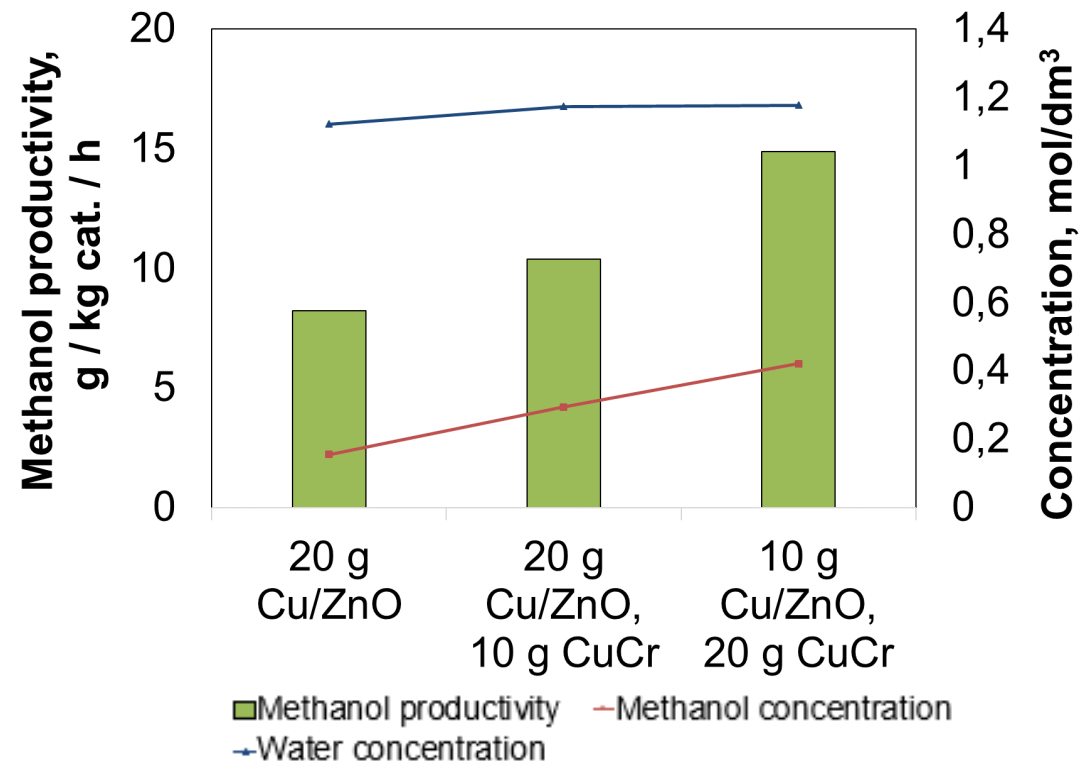
Dual catalysts

- 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 g 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 CO₂ hydrogenation to methanol (~50 g/kg/h vs. several hundred g/kg/h⁶)
 - Selectivity needs to be improved by suppression of RWGS
 - Long-term stability is unknown
- **Water adsorbtion**
 - Demonstrated only in principle, feasibility of practical implementation has not been explored
- **From (semi)batch to continuous?**

References



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