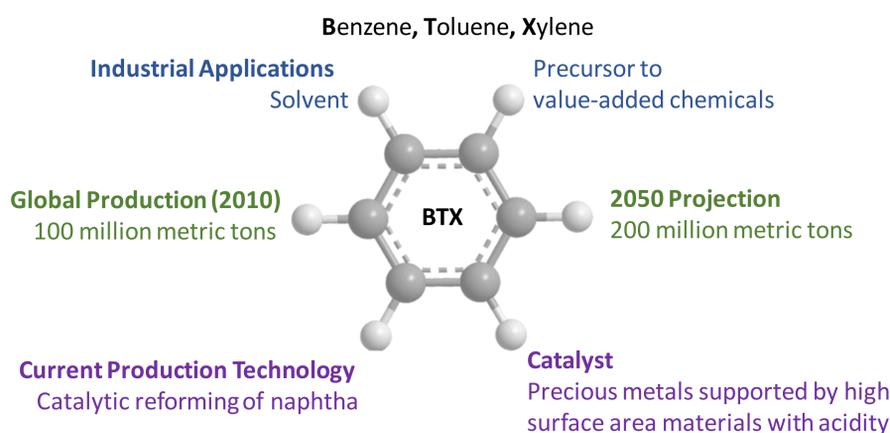


Design of Transition-Metal/Zeolite Catalysts for Direct Conversion of Coal-Derived Carbon Dioxide to Aromatics (FE0031719)

The objective of this project is to develop a technology for the conversion of coal-derived CO₂ directly into mixed aromatic chemicals that are currently sourced from petroleum. Aromatic chemicals such as benzene, toluene, and xylenes (BTX) face growing demand due to their expanding use in plastics and packaging, chiefly in poly(ethylene terephthalate) (PET). BTX is normally produced from oil in a petroleum refinery via multiple steps, involving several different reactions and separations. In this project we will explore a process intensification effort that begins the development of a new technology for the conversion of coal-derived CO₂ directly into BTX in a single reactor. This approach involves hydrogenation of CO₂ into methanol or short chain alkanes and related olefins, which subsequently encounter a second catalyst that converts the intermediate species to BTX in the same reactor. A BTX production technology based on this reaction scheme would significantly deviate from the state-of-the-art, allowing the use of CO₂ as a feedstock, reducing the number of process steps and unit operations, and allowing smaller, more modular installations, which is commensurate with siting near large coal-fired power plants, minimizing costs of CO₂ storage and transportation.

Motivation



Carbon Dioxide (CO₂)

- Domestic CO₂ emission from coal combustion: 1500 million metric tons in 2017
- Could fully support the BTX global market

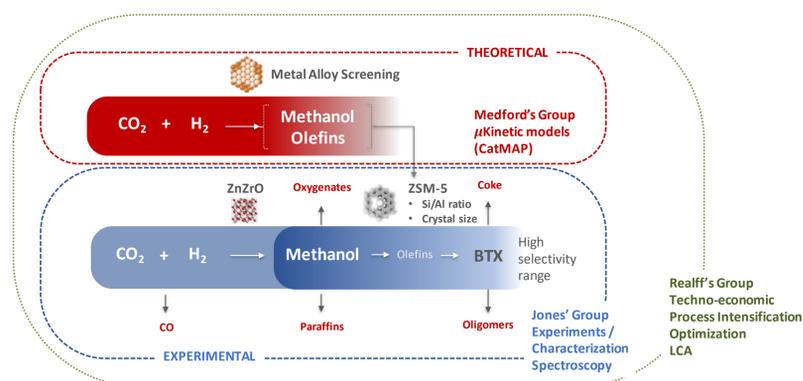
CO₂ to BTX (CO₂ → Intermediate → BTX)

Two steps in a single reactor (CO₂ from flue gas, some H₂ source)

CO₂ to Intermediates (MOH/DME): Metal Oxides (ZnZrO_x)

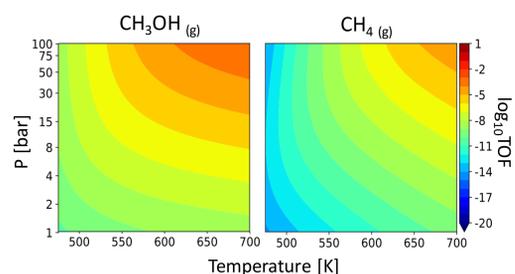
Oligomerization + Aromatization: MFI (H-ZSM-5)

Approach



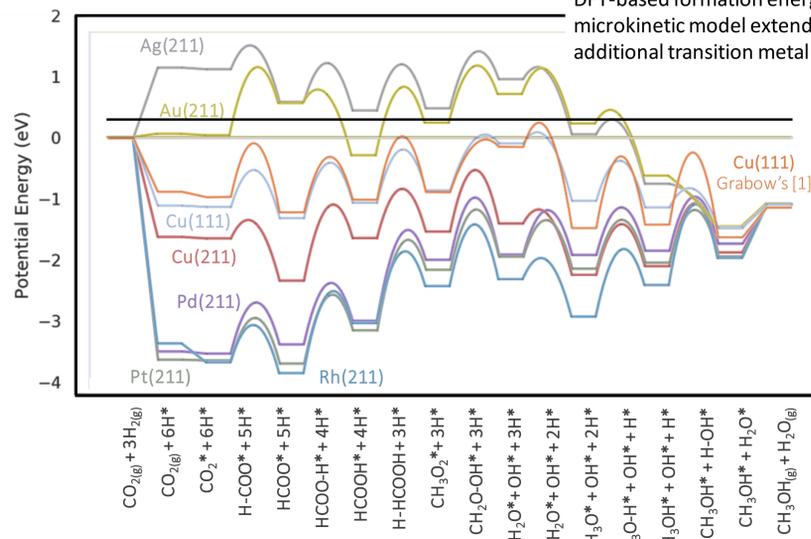
Computational Catalysis Progress

- Comprehensive DFT-based mean-field microkinetic catalytic model on Cu(111) encompassing 28 adsorbate- and 13 gas-species in 42 elementary reactions.
- Forward and reverse water-gas shift from [1] Grabow, L.C. and M. Mavrikakis, *ACS Catal.* 2011. Oxygenates formation: ethanol, formic acid, formaldehyde from [1], ethanol, acetic acid and acetaldehyde from Schumann, J. et al., *ACS Catal.* 2018. Hydrocarbons formation: methane [1] and ethane from Martin Hangaar, H. et al., *J. Catal.* 2019. Oxygen dissociation from Falsig, H., et al., *Top. Catal.* 2014.



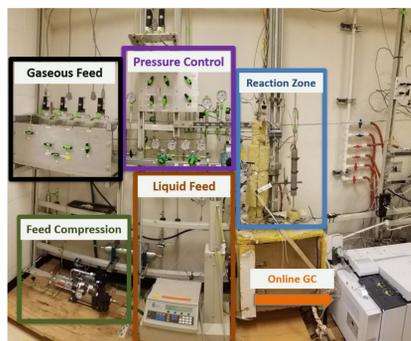
Turn-over frequencies (log₁₀TOF) for methanol and methane on Cu(111) at static gas phase concentration 0.90:0.05:0.05 H₂:CO₂:CO

Potential Energy Diagram CO₂ to Methanol
DFT-based formation energies for microkinetic model extended to additional transition metal catalysts



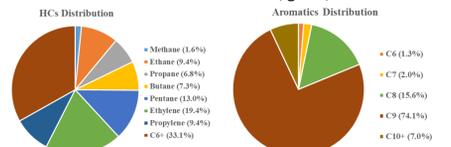
Experimental Progress

Process Setup:



Typical Products Distribution:

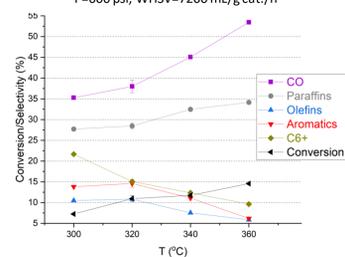
Zn/Zr=1/6, ZnZrO_x/H-ZSM-5=1/2, Si/Al=80, H₂/CO₂=3 P=600 psi, T=320 °C WHSV=7200 mL/g cat./h



- Only olefins present are ethylene and propylene → Not following the typical ASF distribution
- Aromatics are mainly C9 perhaps due to the small ZSM5 particle size (excess external surface area)

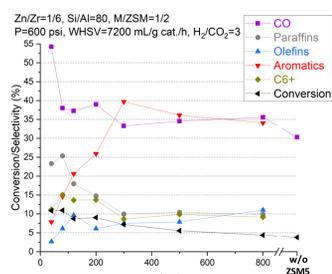
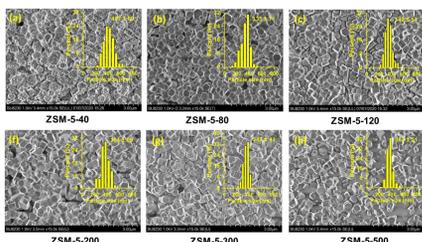
Catalyst Temperature Dependence:

Zn/Zr=1/6, ZnZrO_x/H-ZSM-5=1/2, Si/Al=80, H₂/CO₂=3 P=600 psi, WHSV=7200 mL/g cat./h



- Aromatics selectivity is maximized at 320 °C
- Olefin hydrogenation to paraffins becomes dominant at high temperatures
- RWGS reaction is endothermic → Increasing CO selectivity with temperature

Catalyst Acid Density Dependence:



- Very low acid density is desired. Max aromatics selectivity at Si/Al=300
- CO selectivity is minimum at Si/Al ratio of 300-600
 - High acid density promotes the RWGS reaction
 - Low acid density reduces H-transfer rate for olefins synthesis → Reduced CO selectivity

Current Status

- Maximum aromatics selectivity is obtained at T=320 °C, WHSV=7200 mL/g cat./h, Si/Al=300: 39.7% (STY= 1.04 mmol CO₂/g cat/h)
- DFT-based rates have been calculated for the main intermediate species for the CO₂ hydrogenation on Cu(111). DFT-energies have been extended to the 211 facet of Ag, Au, Pd, Pt, Rh and Cu.

Next steps

- Studying the effect of diffusion path length on catalytic activity.
- DFT-based identification of target alloy catalysts for methanol production.

Acknowledgments

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