

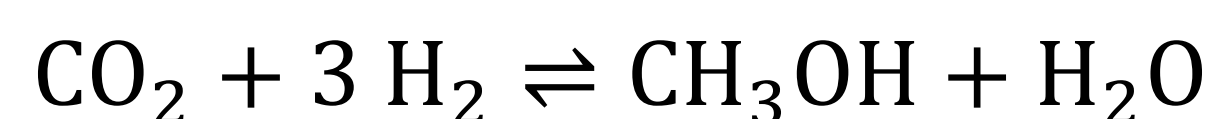
Catalytic Methanol Synthesis

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Motivation

Challenges: i) Mitigate CO₂ emissions, ii) Store excess renewable energy efficiently
Solution: CO₂ captured at industrial production facilities (cement, coal etc.) and H₂ generated by water electrolysis using excess renewable energy can react and form methanol according to:



Methanol is produced at industrial scale (~90 million tons/year¹), because it is a vital chemical feedstock and thus the distribution infrastructure for methanol is well-established. Its energy density is around half of gasoline making methanol applicable for energy storage and transportation².

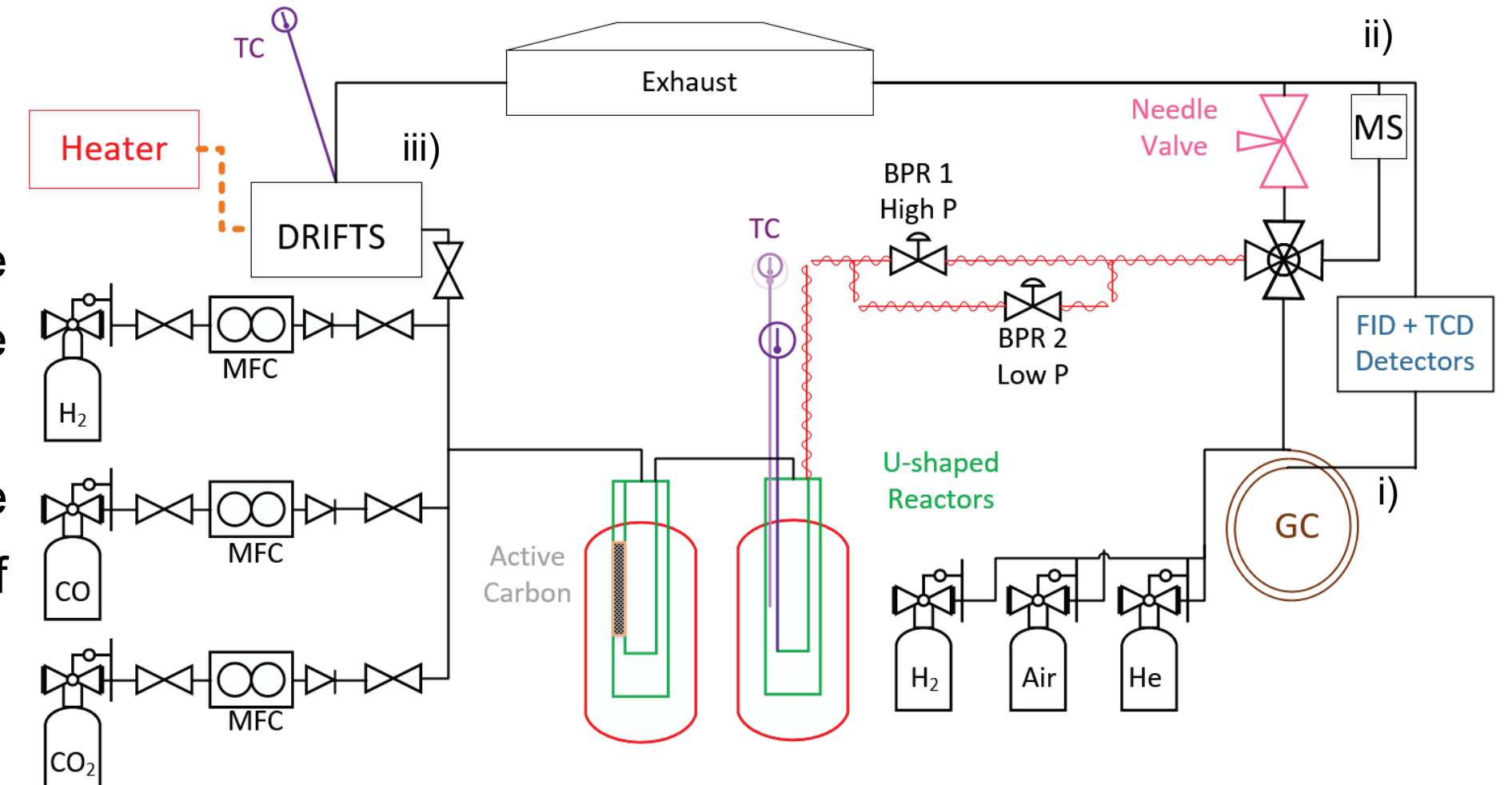
Cu/ZnO/Al₂O₃ (60/30/10) constitutes the conventional methanol catalyst (200-300°C, 50-100 atm.²) with Cu highly influencing the activity, but despite more than 50 years of research, a common agreement on the catalytic active site has not been reached. This project evaluates the Cu-oxide interaction quantitatively by comparing i) the amount of formate (HCOO) adsorbed during reaction, which is a key surface reaction intermediate³, with ii) the methanol turn-over frequency (TOF) on various Cu-oxide catalysts incl. Cu/ZnO.

Electronic transfer from oxide to Cu⁴ together with HCOO's "electron-withdrawing" nature⁵ indicate, that electron transfer under reaction conditions regulates the HCOO surface coverage (θ_{HCOO}) on Cu and thereby the catalytic activity (TOF). Enhanced understanding of Cu-oxide interactions can be beneficial both for the industry and for basic research applications as the principles may be general, and apply to other similar metal-oxide catalysts.

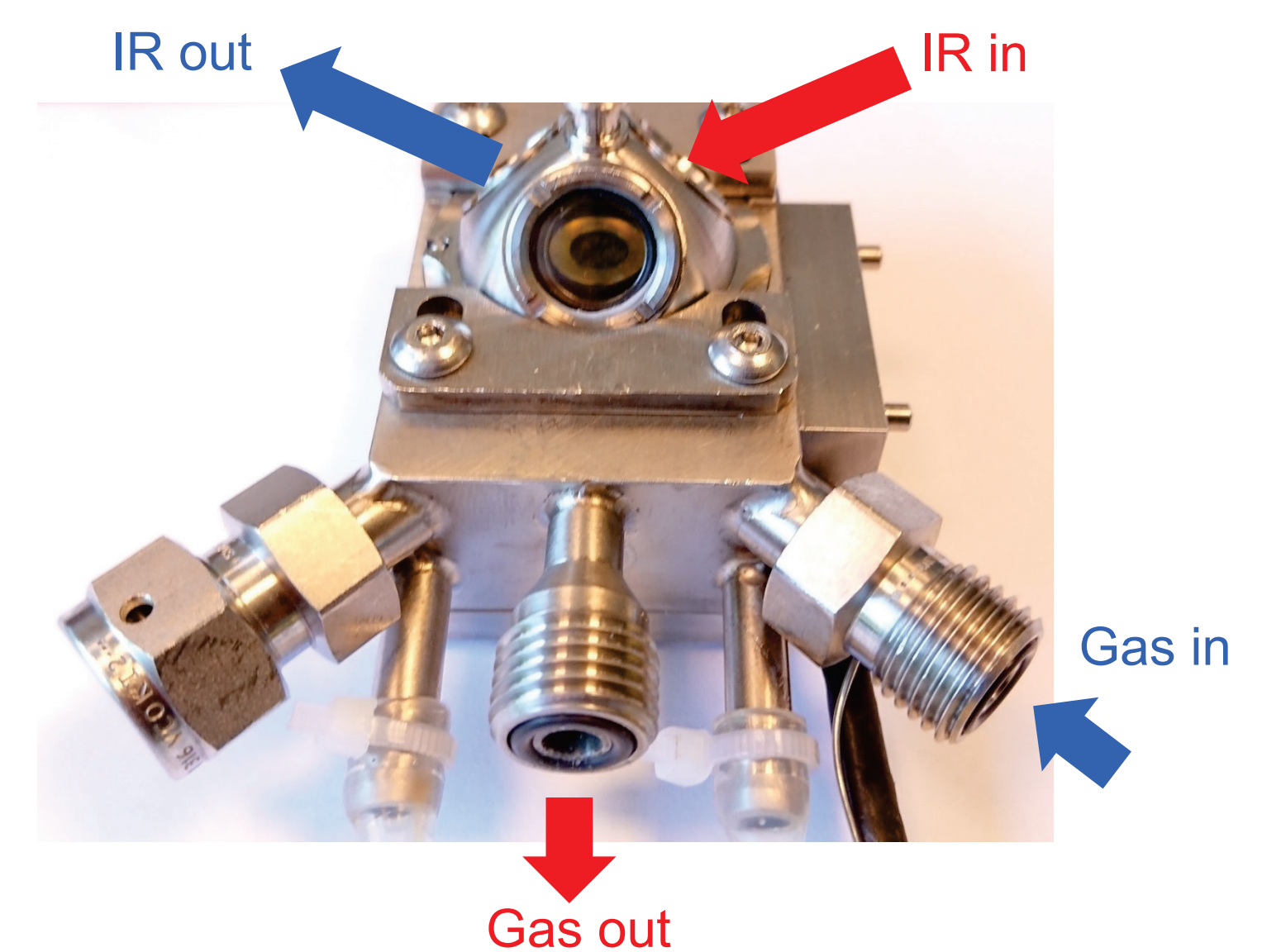
Experimental Setups

Flow reactor setup applications:

- Methanol activity by GC
- Catalyst cooling before quantification of surface species with MS by TPD
- Estimate qualitatively the desorption temperatures of surface species by DRIFTS

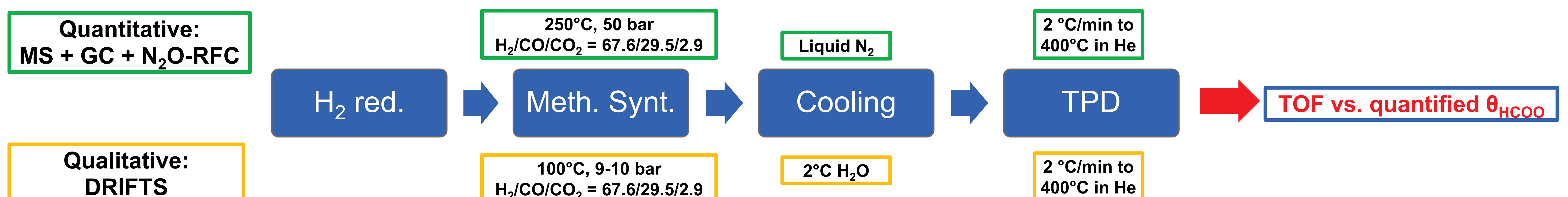


DRIFTS cell consisting of a 3-window dome on a combined heating and gas-delivery metal block. Catalysts loaded in the dome are investigated using infrared (IR) spectroscopy to measure qualitatively the desorption temperature of species adsorbed on the surface.



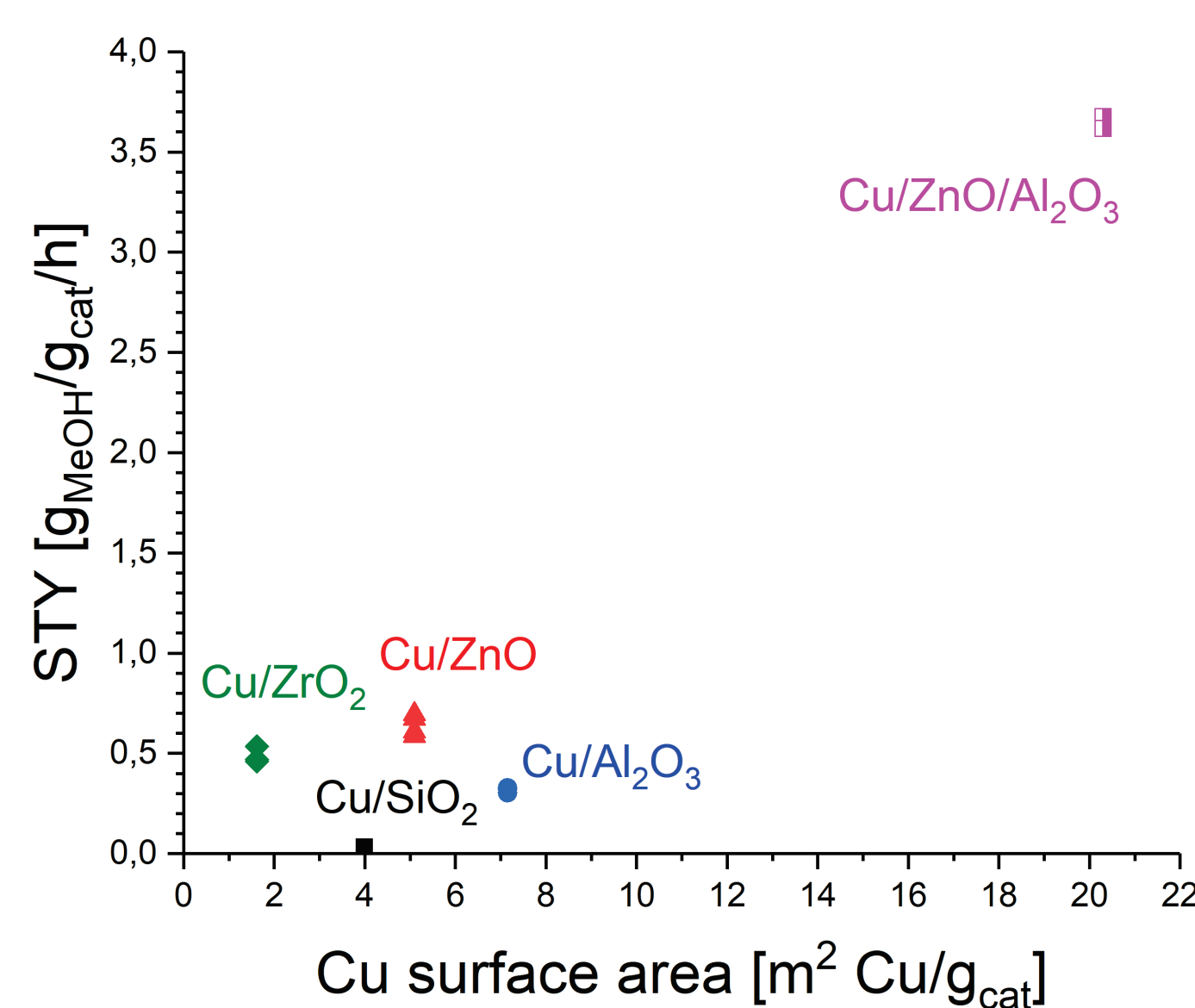
Methods

Cu-oxide catalysts are synthesized by impregnation and co-precipitation. Technical abbreviations: DRIFTS = Diffuse Reflectance Infrared Fourier Transform Spectroscopy, GC = Gas Chromatography, MS = Mass Spectrometry, TPD = Temperature Programmed Desorption, N₂O-RFC = N₂O Reactive Frontal Chromatography.

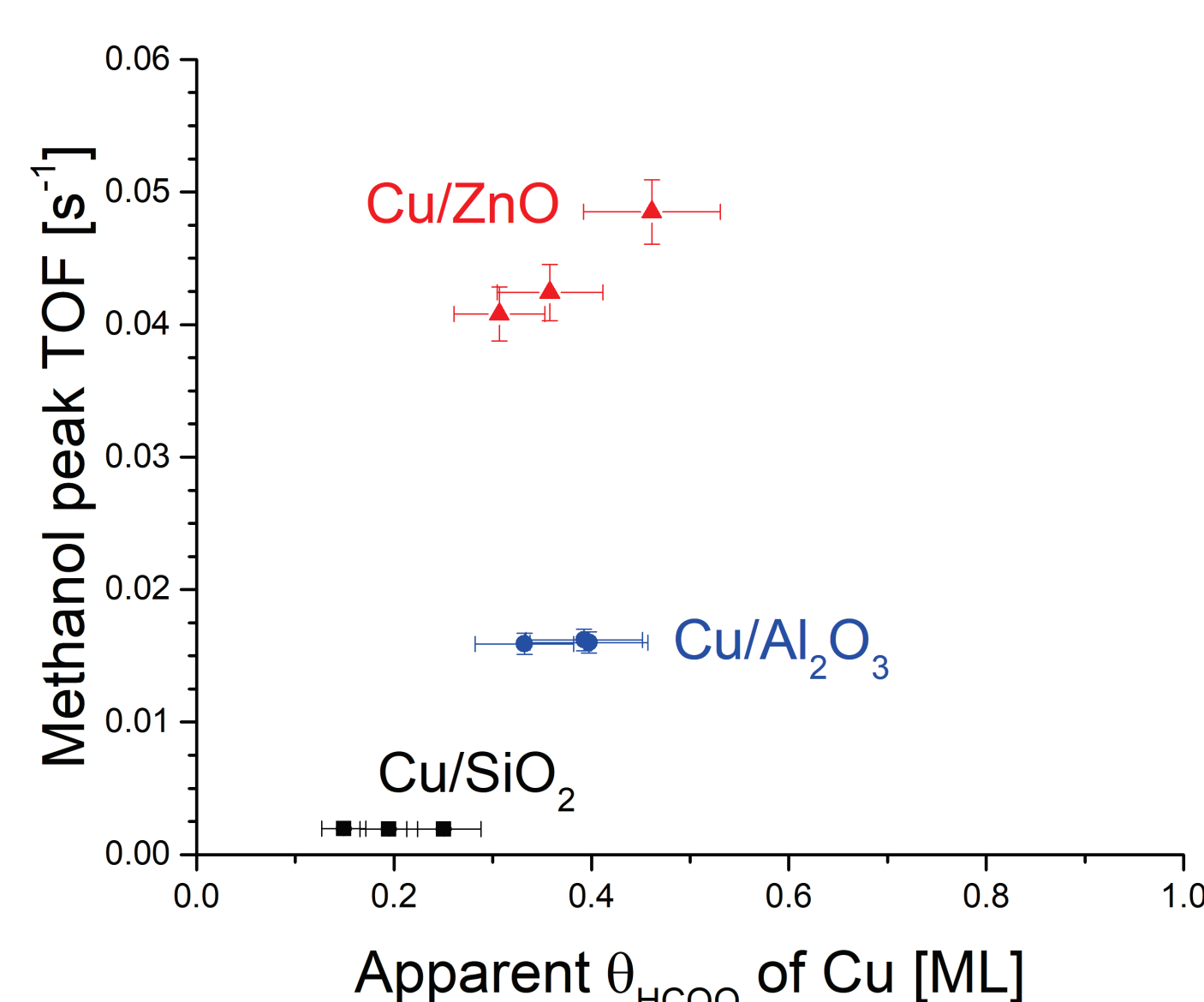


Results

Preliminary quantitative TPD experiments show simultaneous peak H₂ and CO₂ desorption at ~140-170°C, which studies have attributed to desorption of HCOO from Cu⁶. However, the desorption profiles are complicated by contributions from the oxide. The STY (space time yield) to Cu surface area relation for different catalysts indicate an electron support effect influencing the STY in addition to the Cu surface area.



Methanol STY evaluated as each catalyst obtains its peak activity as function of the Cu surface area based on N₂O-RFC.



Peak TOF as function of apparent HCOO coverage of Cu based on TPD integrated CO₂ desorption at 140-170°C.

Conclusions and Further Work

- Quantitative evaluation of surface species coverages at operational conditions can be conducted by rapid cooling with N₂
- STY vs. Cu surface area indicates a support effect potentially due to electronic transfer phenomena
- Preliminary results indicate a strong influence of θ_{HCOO} on TOF
- Future DRIFTS studies are designed to relate concurrent CO₂ and H₂ desorption at a specific temperature interval to Cu-HCOO desorption
- Blank experiments may allow subtraction of the contributions from the oxides to the CO, CO₂ and H₂ desorption profiles thus simplifying the quantitative analysis of the Cu-HCOO desorption

References

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Acknowledgements

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