

Heterogeneous Electrochemical CO₂ reduction

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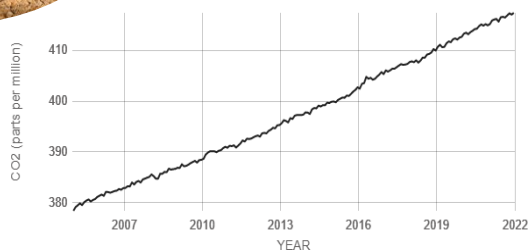
Spectroscopy and catalysis, IMM

Motivation



- Green house effect
- Global warming
- Climate change

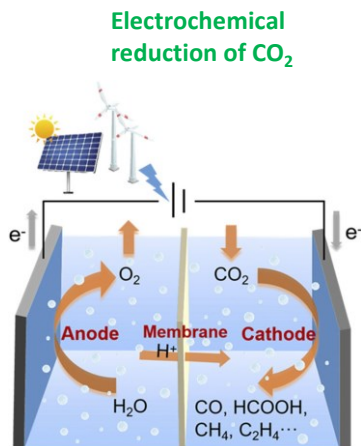
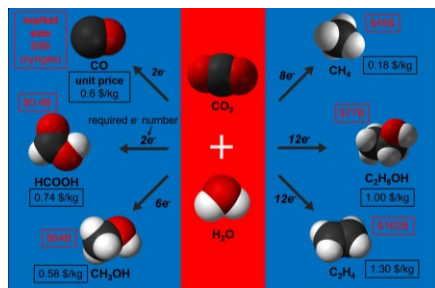
Utilization of emitted CO₂



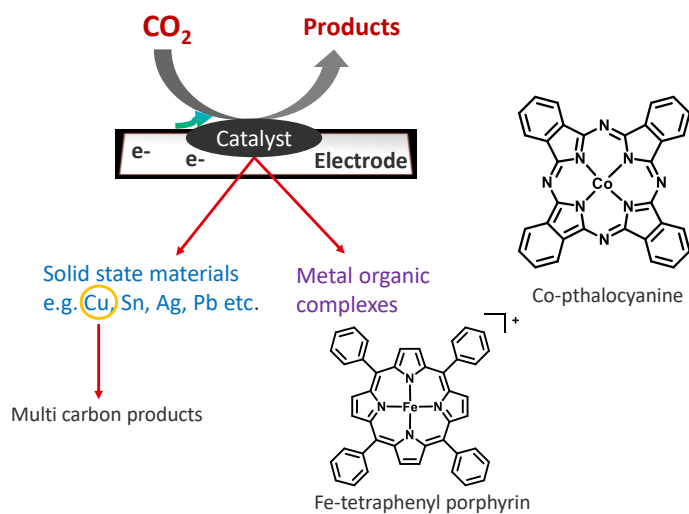
Source: climate.nasa.gov

CO₂ level in the atmosphere

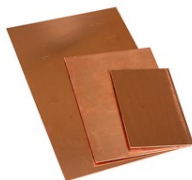
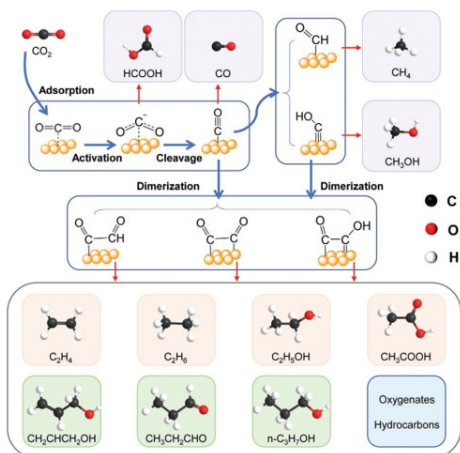
CO₂ as a synthetic feed stock



Activation of CO₂



“Cu” – A promising catalyst



What is the bottle neck for industrialization?

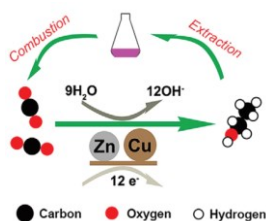
- Poor selectivity for targeted Products
- Does not yet meet required industrial activity

Modification of the catalyst

How could we modulate the CO₂RR activity of a Cu Catalyst?

Composition

- Alloying- CuAg, CuZn
 - ¹Pure Ag produces 'CO', CuAg - carbonyls
 - ²Cu_xZn - selective towards ethanol



- Introducing non metals-B, N, O

³Cu₃N – selective for ethylene

1. ACS Energy Lett. 2018, 3, 12, 2947–2955
 2. ACS Catal. 2016, 6, 12, 8239–8247
 3. Nano Lett. 2019, 19, 12, 8658–8663

Modification of the catalyst

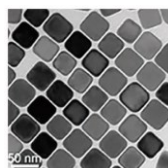
Crystal phase

- Crystalline/amorphous nature

Crystal facet

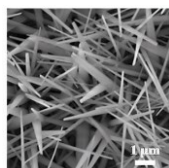
- Cu -111 facets - favours C_1 products (e.g. CH_4 , $HCOOH$)
- Cu -100 facets - favours C_2 products (e.g. C_2H_4)

Morphology of the Nano-structured catalysts



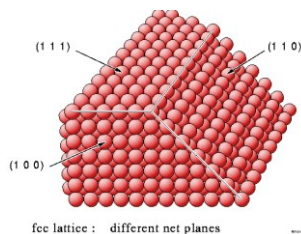
Cu Nano cubes

ACS Catal. 2019, 9, 6, 5217–5222



Cu wires

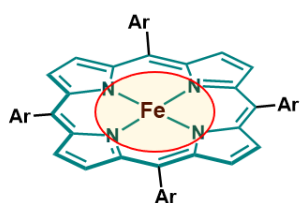
Nanoscale, 2019,11, 12075-12079



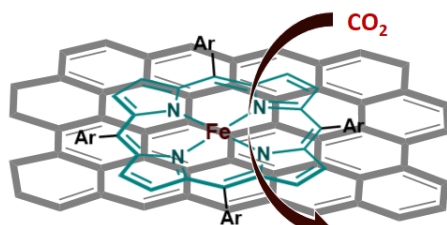
fcc lattice : different net planes

<http://www.fhi-berlin.mpg.de/~hermann/Balsac/BalsacPictures/fccnet.gif>

Molecular catalysts



- ✓ Easily tuneable active centres
- ✓ excellent selectivity (eg. Highly selective for c_1 products)
- ✓ Mechanisms can be understand easily by homogenous catalysis studies



➔ Heterogeneous catalyst

Conducting carbon supports
Eg. Carbon black, carbon nanotubes,
Graphene

Thank you

References

- (1) Wang, J.; Dou, S.; Wang, X. Structural Tuning of Heterogeneous Molecular Catalysts for Electrochemical Energy Conversion. *Sci. Adv.* **2021**, *7* (13), 1–14. <https://doi.org/10.1126/sciadv.abf3989>.
- (2) Adv Funct Materials - 2021 - Yu - Recent Progresses in Electrochemical Carbon Dioxide Reduction on Copper-Based Catalysts.