Development of Cascade Nanoreactors for the Direct Conversion of CO_2 to Sustainable Marine Transportation Fuels

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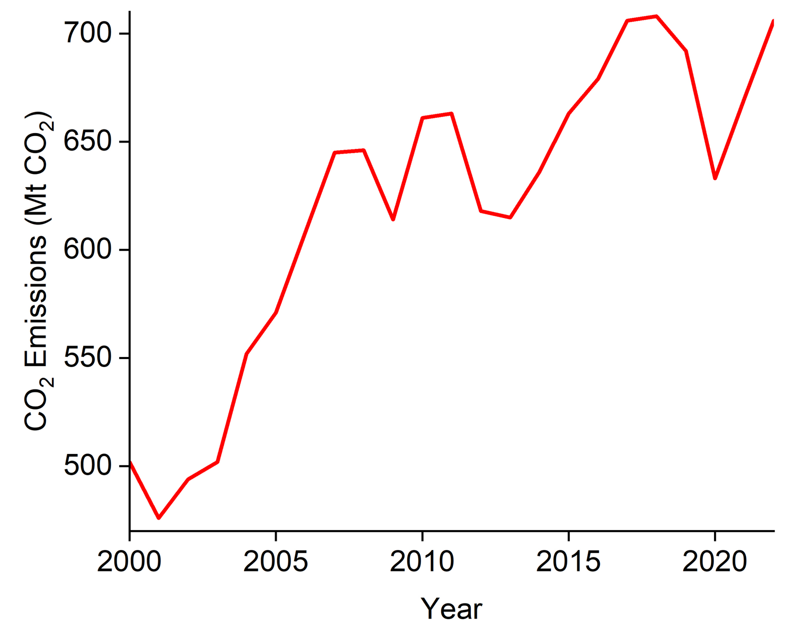
1 Need for Sustainable Marine Fuels

Shipping responsible for ***2-3% of global CO_2*** emissions[1]



International shipping emissions between 2000 and 2022[1]

Vehicle compatibility with different energy sources[2]

Vehicle and duty cycle compatibility		Synthetic fuels		Electricity	
Aviation	Short haul				
	Long haul				
Marine	Short journey				
	Long journey				
Refuelling and distribution challenge					

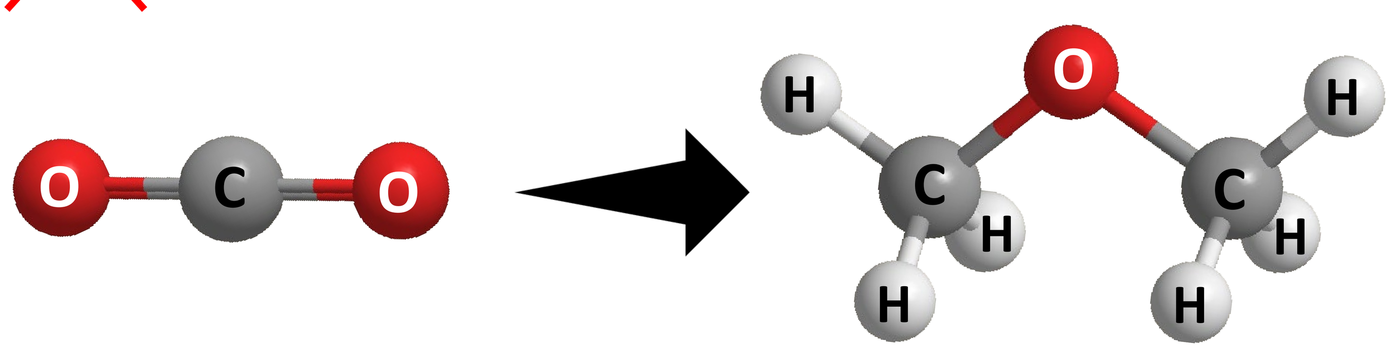
Challenging to electrify long haul shipping

Require synthetic & ***sustainable fuels***

2 Dimethyl Ether (DME): a Marine Fuel

Producible via a ***circular carbon economy*** ^{12}C

non-carcinogenic, non-corrosive, ***non-toxic***

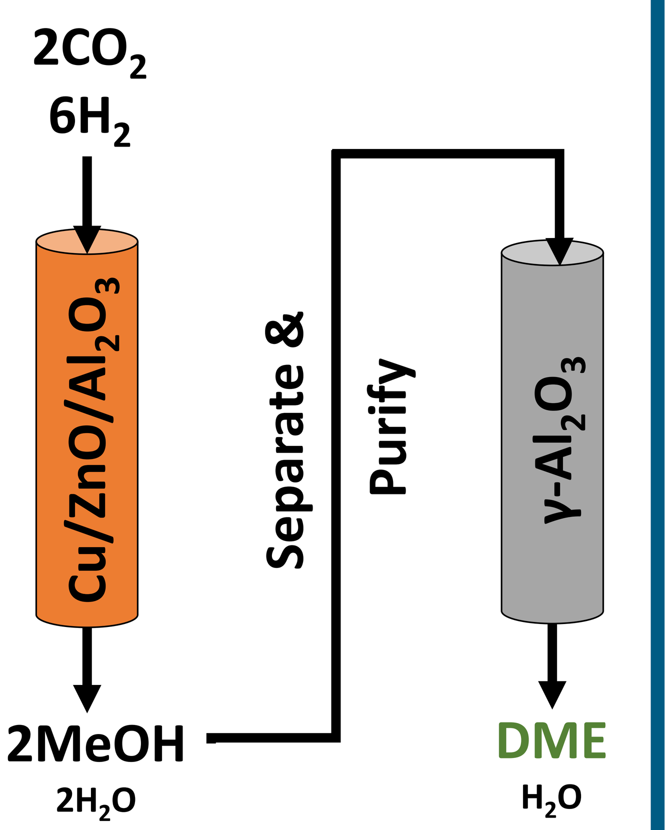


Burns ***more effectively*** in an engine than diesel

Compatible with existing ***LPG infrastructure***[3]

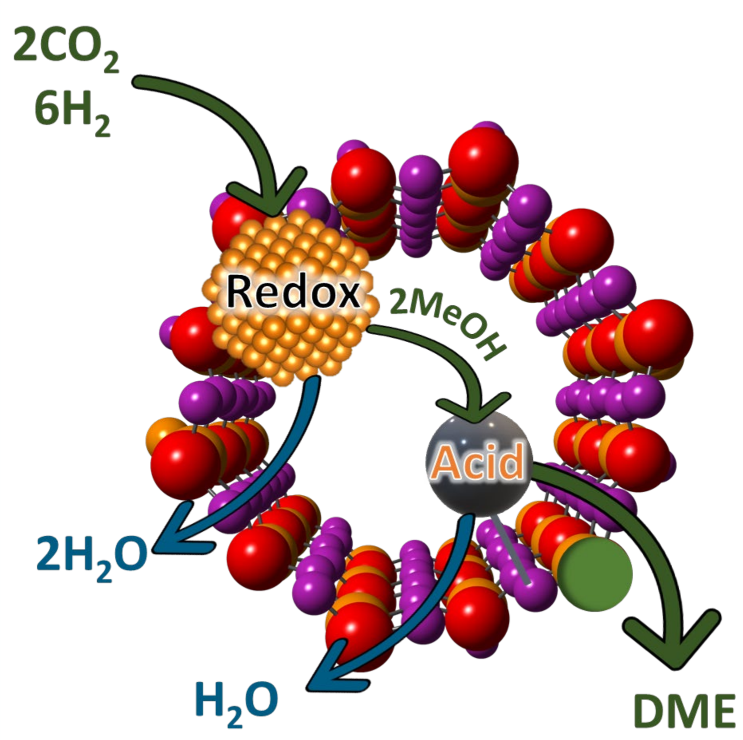
3 One-pot DME Synthesis

Traditional two-pot



- Easier to optimise & reactivate catalysts
- Mature technology & catalysts
- Two reactors: more expensive & complex
- Need to treat intermediates

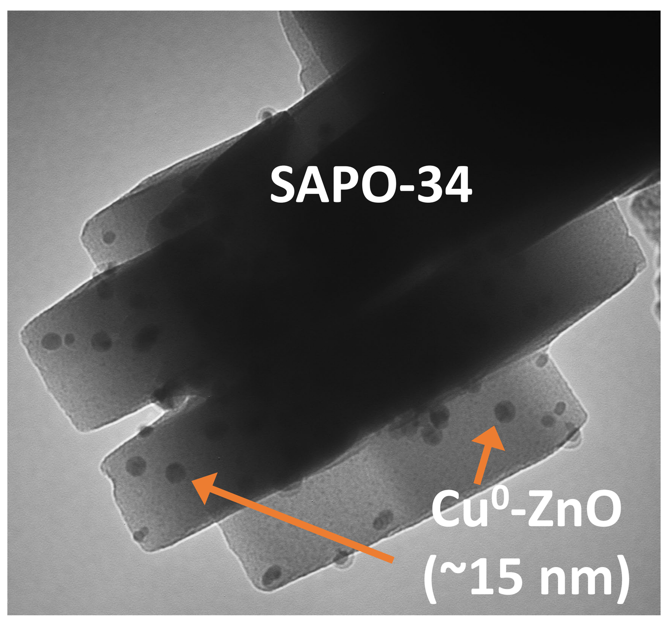
Newer one-pot



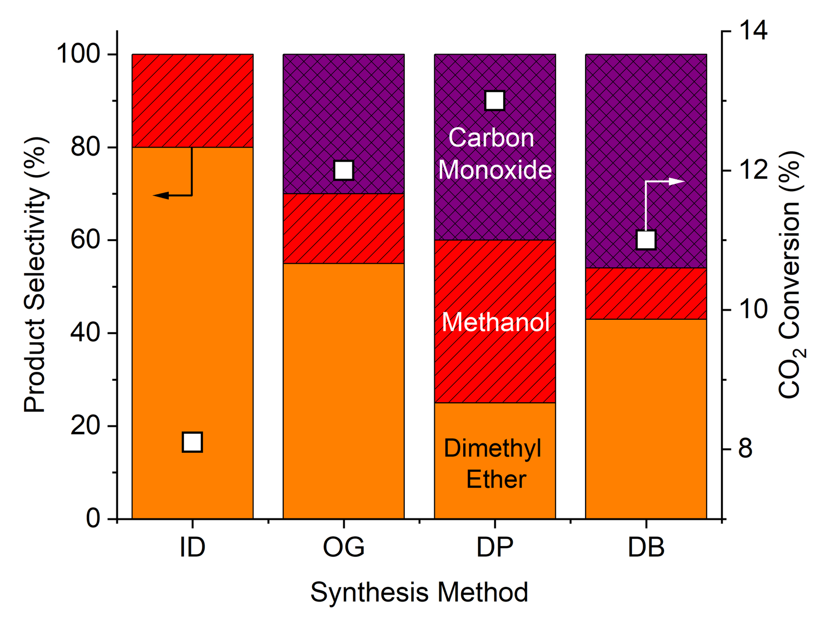
- Singular reactor: cheaper & simpler
- *In situ* dehydration can increase CO_2 conversions
- Need new bifunctional catalysts
- Catalysts difficult to design and can deactivate rapidly

4 Bifunctional Catalysts for One-Pot DME Synthesis

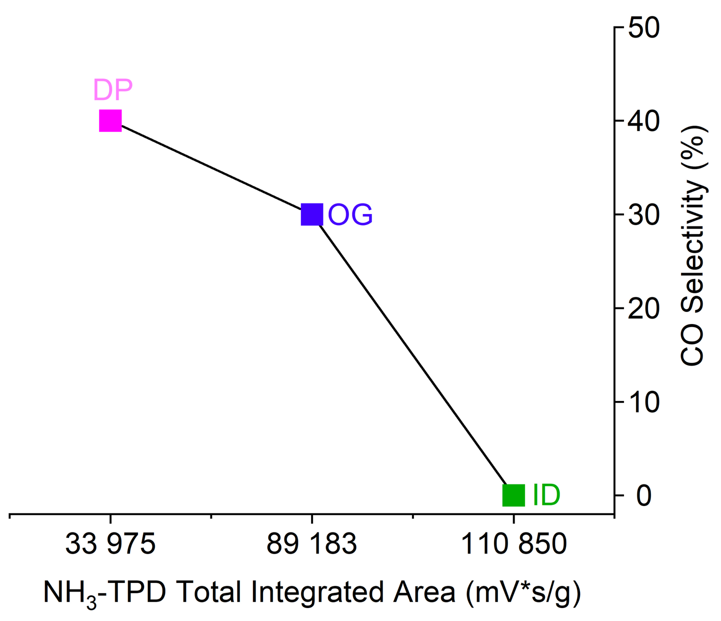
- Develop bifunctional catalysts by ***combining Cu^0-ZnO (redox sites) with $SiAlPO_4$-11 or $SiAlPO_4$-34*** microporous supports (acid sites)[4]
- Tested 3 synthesis methods: impregnation & drying **(ID)**, oxalate gel deposition precipitation **(OG)** & deposition precipitation **(DP)**
- Different synthesis methods give Cu^0-ZnO/$SiAlPO_4$ catalysts ***with varied acid properties***



$SiAlPO_4$-34 microporous solid acid support decorated with redox Cu^0-ZnO nanoparticles



Impact of synthesis method choice on catalytic performance of Cu^0-ZnO/$SiAlPO_4$-34

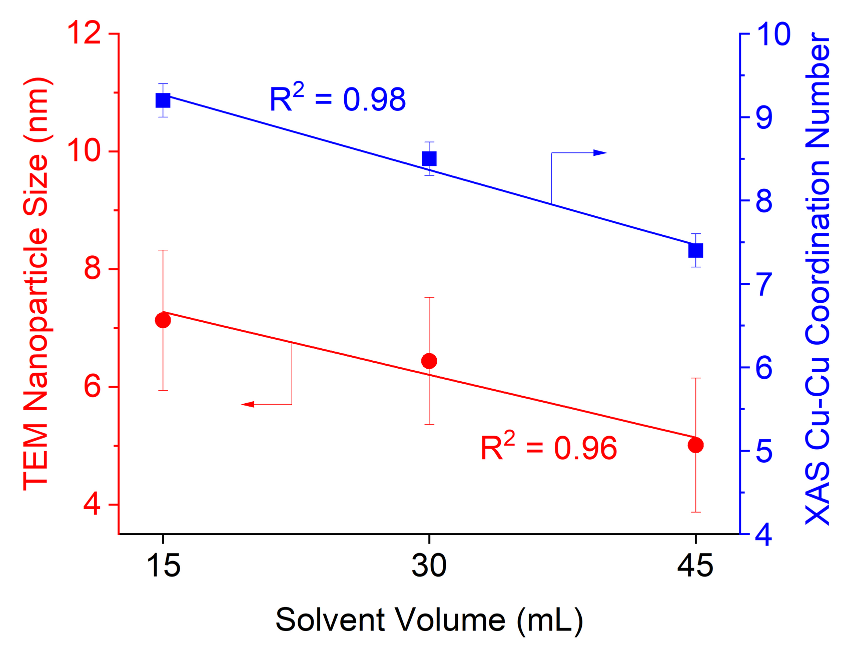


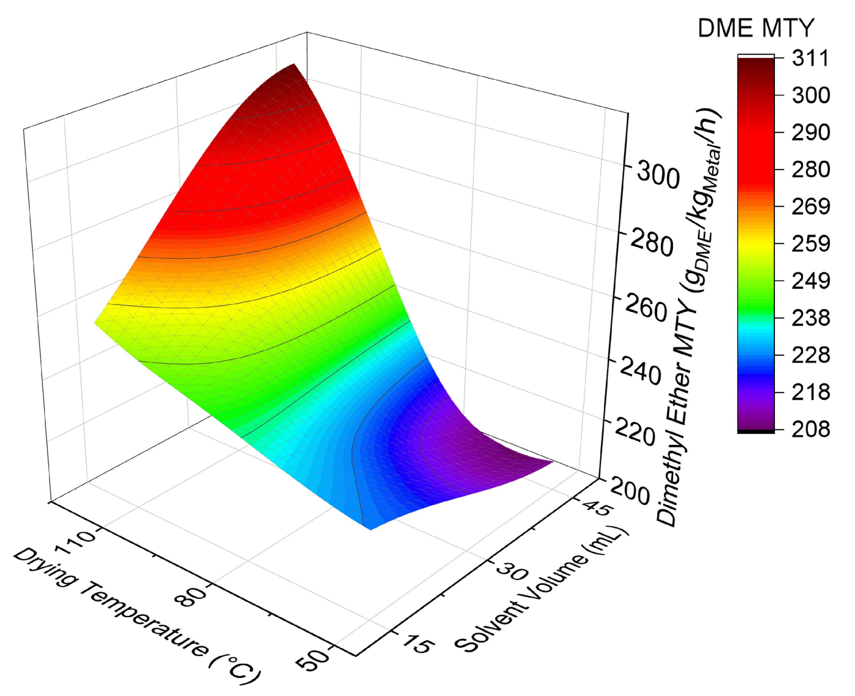
Cu^0-ZnO/$SiAlPO_4$-34 acid site abundance impact on CO selectivity

- Acid site strength & abundance: **ID** > **OG** > **DP** with **ID** creating a ***range of acid sites***
- Cu^0-ZnO/$SiAlPO_4$-34 catalyst synthesised via **ID** approach gives exceptional DME selectivity and ***no detectable CO formation.*** Superior selectivity compared to a dual bed (DB)
- Acid site abundance impacts selectivity due to theorised ***localised water inhibition effect***

5 Optimising Bifunctional Catalyst Preparation Method

- Initial formation of MeOH intermediate is rate limiting: DME yields thus ***limited by redox site***
- Decrease Cu^0-ZnO nanoparticle size by ***modifying the ID catalyst synthesis method*** to increase redox site availability and DME yields





- Smaller Cu^0-ZnO nanoparticles and more active catalysts obtained by ***increasing solvent volume, drying temperature and solvent polarity*** of **ID** method

Impact of modifying ID preparation method on nanoparticle size and catalyst activity

6 Conclusions

- Bifunctional Cu^0-ZnO/$SiAlPO_4$ catalysts can convert CO_2 to the sustainable marine fuel, DME, ***in one-pot***
- Choice of synthesis method has profound influence on ***structural and catalytic properties*** of Cu^0-ZnO/$SiAlPO_4$
- Catalysts with ***abundant acid sites yield high DME selectivity*** and supress CO formation
- Most ***active catalyst synthesised*** using high volumes of polar solvents and high drying temperatures

References

[1] International Energy Agency, https://www.iea.org/energy-system/transport, accessed June 2024.
[2] The Royal Society, Sustainable synthetic carbon based fuels for transport: Policy briefing, 2019.
[3] J. Sun *et al.*, *ACS Catal.*, **2014**, 4, 3346–3356.
[4] M.G Walerowski *et al.*, *Catal. Sci. Technol.*, https://doi.org/10.1039/D4CY00020J.

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