Elucidating Synthesis-Structure-Property Correlations for Design of Improved Bifunctional Catalysts

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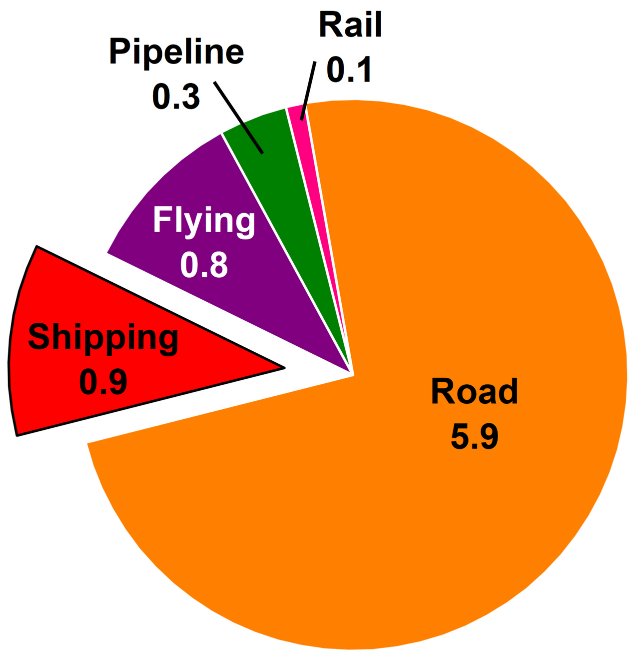
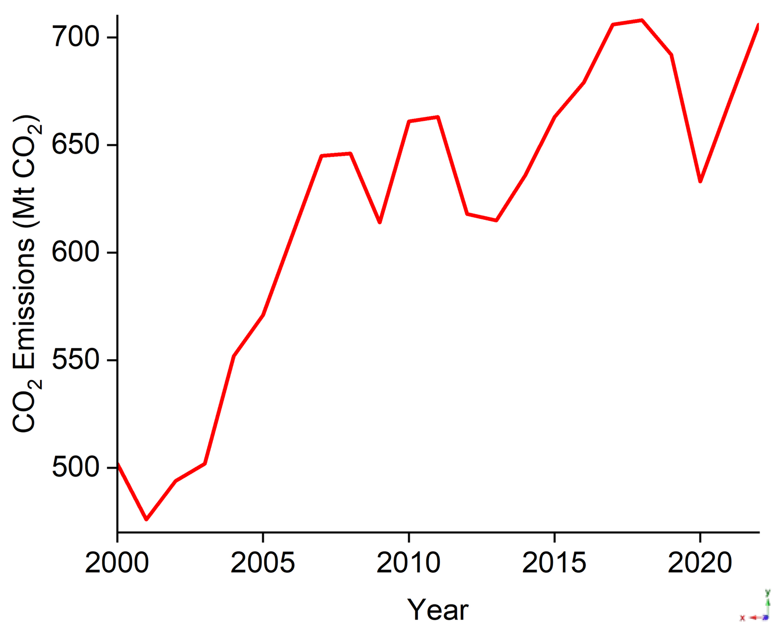
1 Need for Sustainable Marine Fuels

- Shipping responsible for ***2-3% of global CO_2*** emissions[1]
- ***Challenging to electrify*** long haul maritime shipping

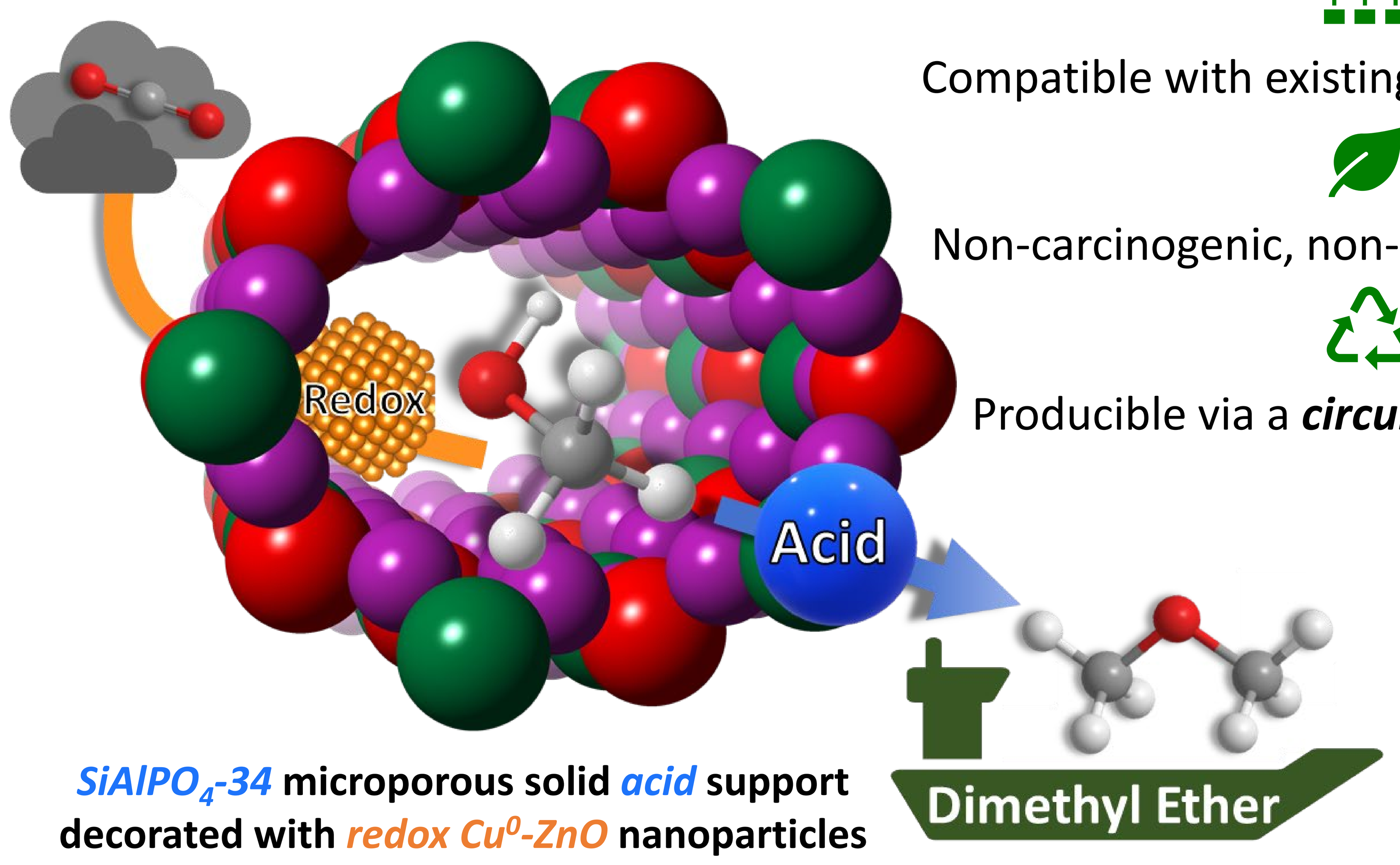


Global transport CO_2 emissions (Gt) in 2022 by sector[1]



International shipping emissions between 2000 and 2022[1]

2 Dimethyl Ether as a Sustainable Fuel



SiAlPO$_4$-34 **microporous solid *acid* support decorated with *redox Cu^0-ZnO* nanoparticles**

Compatible with existing ***LPG infrastructure[2]***

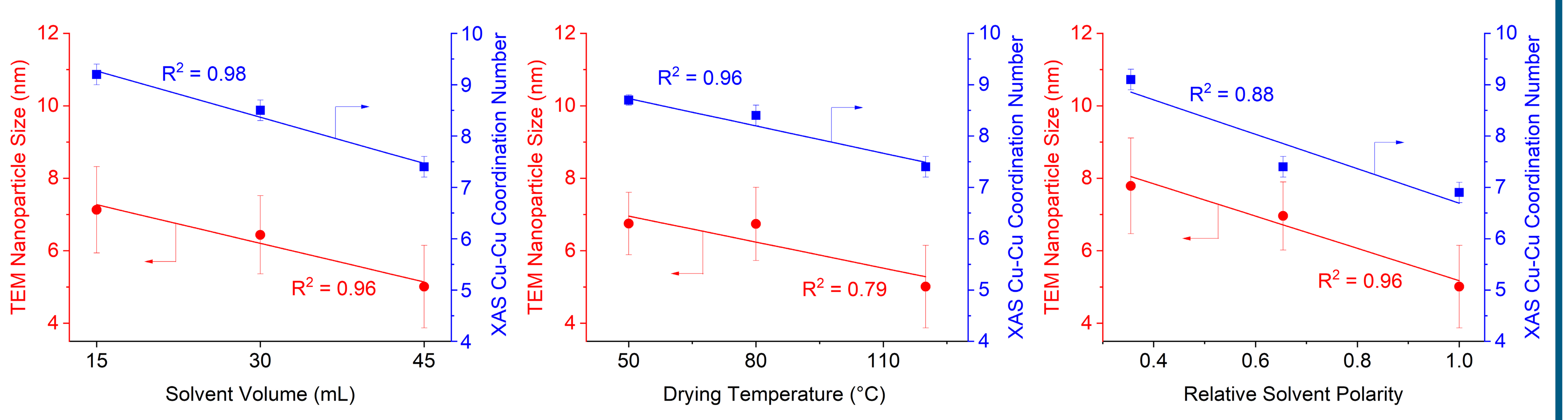
Non-carcinogenic, non-corrosive, ***non-toxic***

Producible via a ***circular carbon economy***

Convert CO_2 to dimethyl ether (DME) via MeOH in ***one-pot*** using a Cu^0-ZnO/SiAlPO$_4$-34 bifunctional catalyst[3]

3 Controlling Cu^0-ZnO Nanoparticle Size

- Initial formation of MeOH intermediate is the rate limiting step of the cascade reaction
- DME yields thus limited by the redox site activity
- Decrease Cu^0-ZnO nanoparticle size to increase redox site availability and DME yields

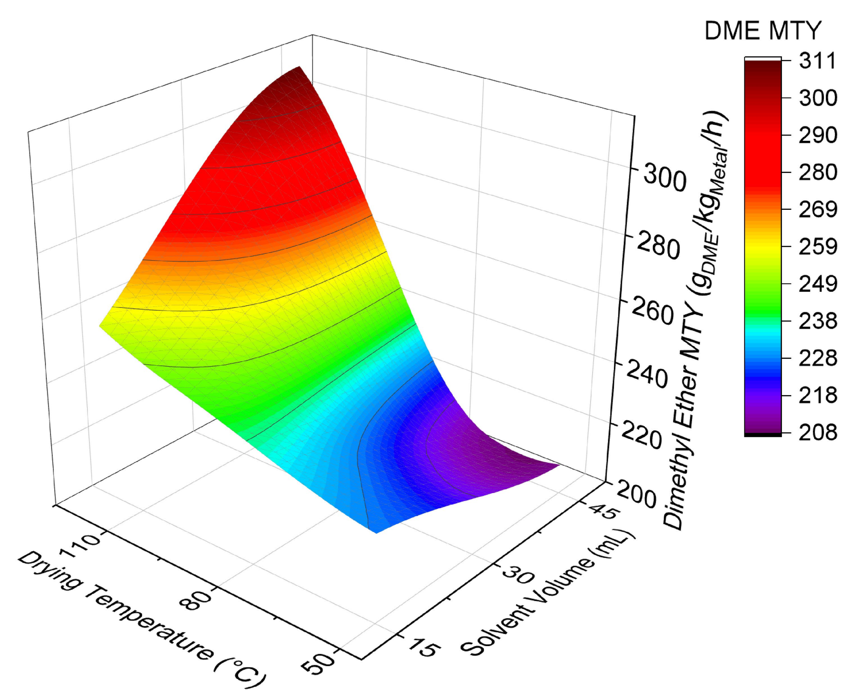


- Can obtain smaller Cu^0-ZnO nanoparticles by increasing solvent volume, drying temperature and solvent polarity during impregnation onto SiAlPO$_4$-34
- Green, facile & precise nanoparticle size control

4 Impact of Synthesis on DME Yields

- Use a 3D response surface to study the impact of modifying catalyst preparation on catalyst activity

DME Metal Time Yield (MTY)

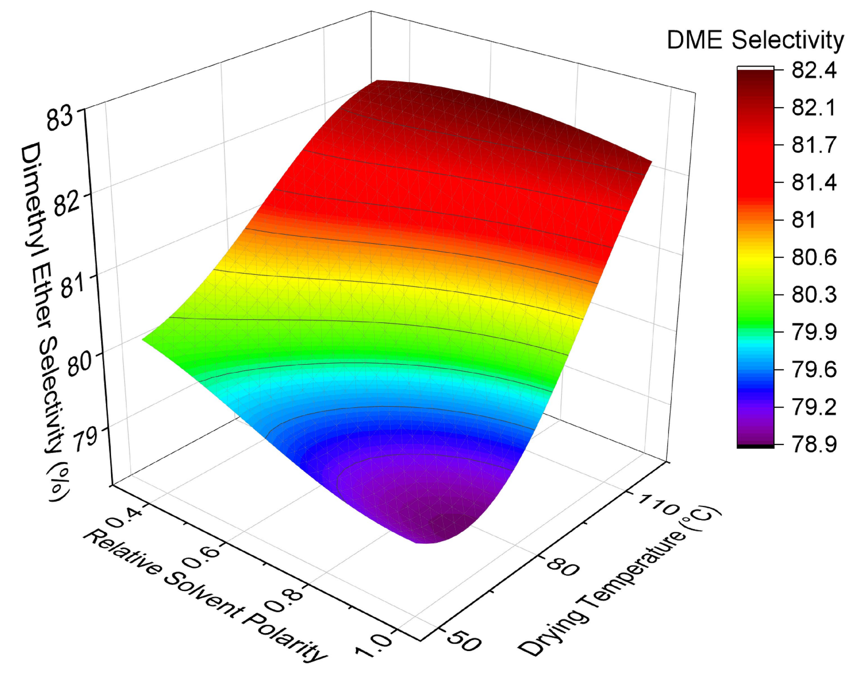


Catalysts prepared using:

- Higher solvent volumes
- Higher drying temperatures
- Higher polarity solvent

Yield higher DME MTY

DME Selectivity



Catalysts prepared using:

- Higher solvent volumes
- Higher drying temperatures
- Lower polarity solvent

Yield higher DME selectivity

5 Synthesis-Structure-Property Correlations

- Differences in nanoparticle size alone could not rationalise differences in DME yields
- Modification of Cu^0-ZnO nanoparticle size by tailoring solvent volume, drying temperature and solvent polarity must also impact other structural characteristics
- We developed correlation matrices to fully understand catalyst structural features which influence DME yields and selectivity and how strongly[4]

Structure-Performance Correlation Matrix

Parameter	Pore volume	Nanoparticle Size	Cu-Cu C.N	Cu Loading	**DME Yields**	**DME Selectivity**
Pore volume	1.0	-0.3	-0.4	-0.2	0.1	0.1
Nanoparticle Size	-0.3	1.0	0.4	0.2	-0.3	0.2
Cu-Cu CN	-0.4	0.4	1.0	0.3	-0.2	-0.1
Cu Actual Loading	-0.2	0.2	0.3	1.0	0.1	-0.1
DME MTY	0.1	-0.3	-0.2	0.1	1.0	0.3
DME Selectivity	0.1	0.2	-0.1	-0.1	0.3	1.0

- Positive number indicates that as an input (structure) parameter increases so does the output (performance), whereas negative number indicates the output decreases
- Increasing pore volume and Cu loading and decreasing nanoparticle size and Cu-Cu coordination number gives catalysts with higher DME yields and selectivity

6 Conclusions

- Bifunctional Cu^0-ZnO/SiAlPO$_4$-34 catalysts can convert CO_2 to the sustainable marine fuel, DME, ***in one-pot***
- Possible to ***control Cu^0-ZnO nanoparticle size*** by tailoring solvent volume, drying temperature and solvent polarity
- Higher solvent volumes, drying temperature and solvent polarity creates more active Cu^0-ZnO/SiAlPO$_4$-34 catalysts
- ***Synthesis-structure-property correlation*** matrices can be used to fully rationalise and optimise catalyst performance

References
[1] International Energy Agency, https://www.iea.org/energy-system/transport, accessed June 2024
[2] 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.
[4] M.G Walerowski *et al.*, *ChemComm*, manuscript in preparation.

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