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Rationalising Catalytic Performance using a Unique Correlation Matrix

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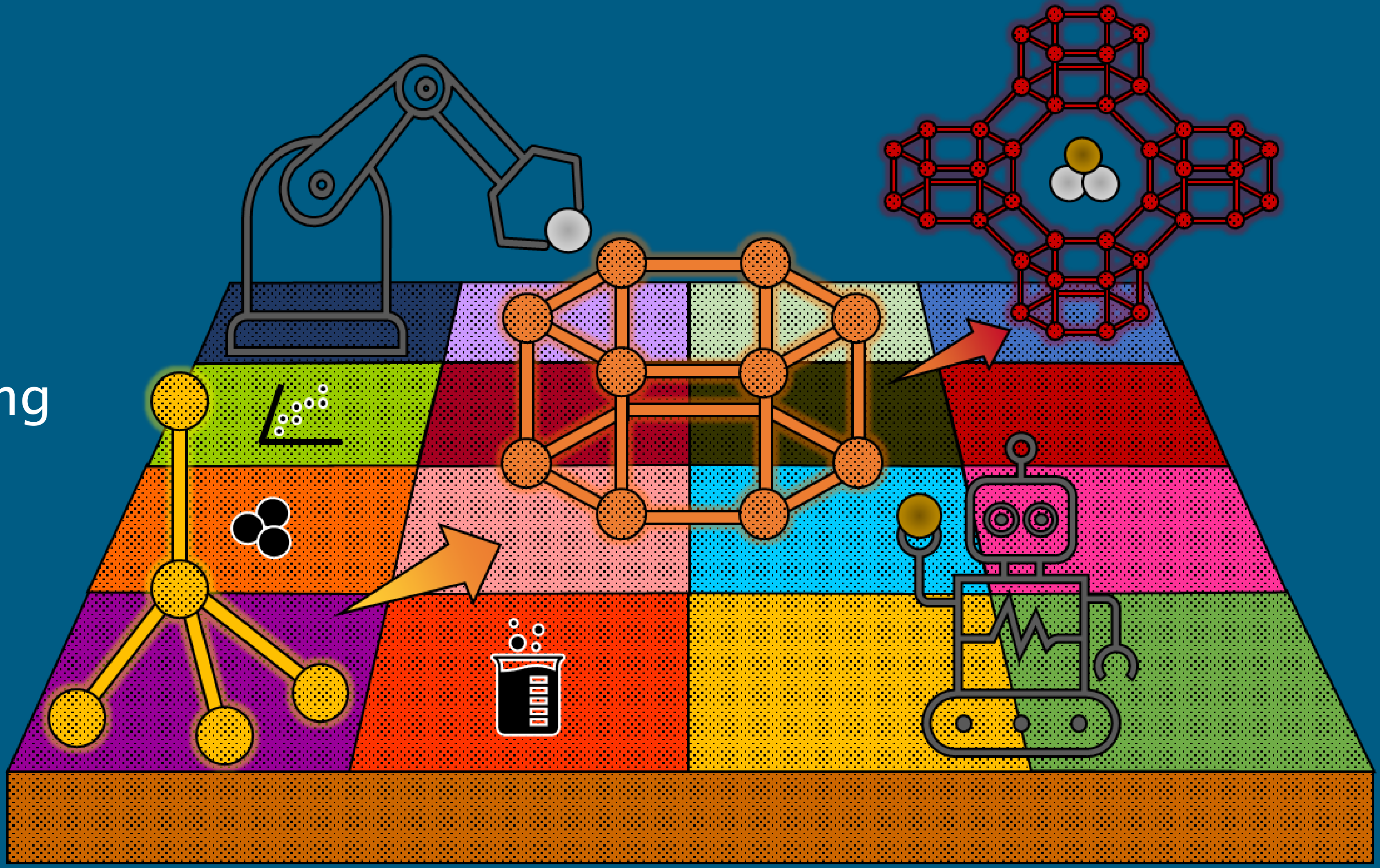

1st EPoMM Conference
19th September 2024

Outline

- Dimethyl ether as a marine fuel
- Cu^0-ZnO/SiAlPO-34 cascade nanoreactors
- Controlling Cu^0-ZnO nanoparticle size
- Structure-property-performance correlation matrices

The Need for Alternative Marine Fuels

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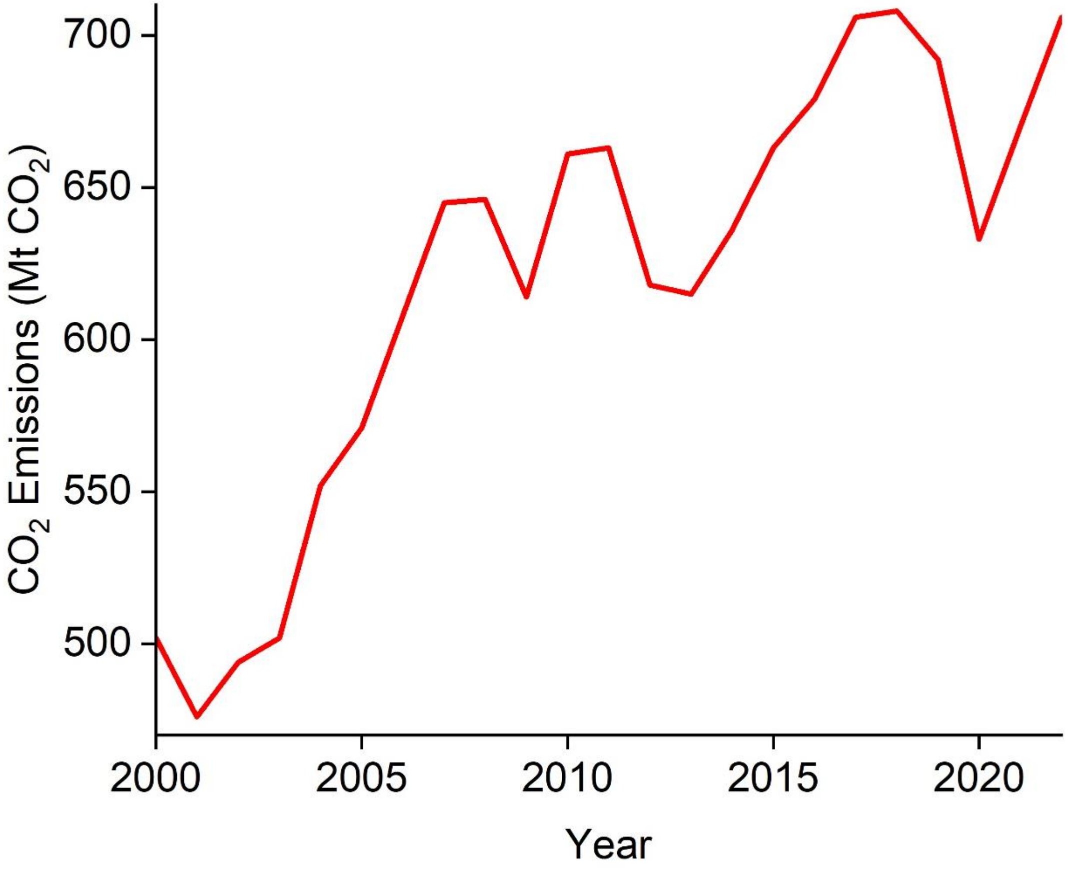
International shipping emissions



https://www.iea.org/energy-system/transport

Vehicle compatibility with energy sources

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

Sustainable synthetic carbon based fuels for transport: Policy briefing, 2019

Challenging to electrify long haul marine transport

Dimethyl Ether as a Sustainable Alternative

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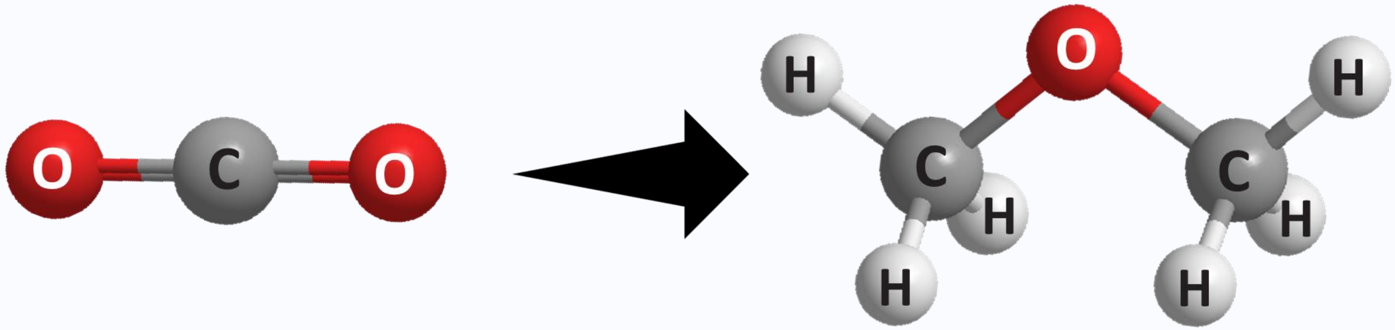
Producible via a ***circular carbon economy*** ^{12}C

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



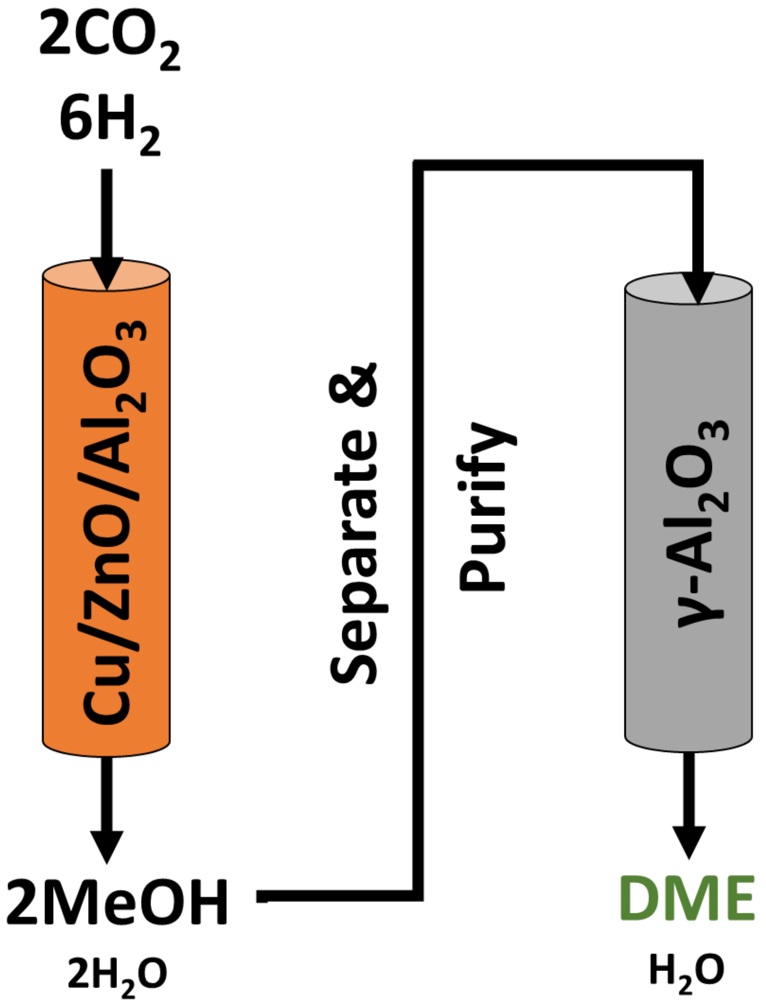
Burns ***more effectively*** in an engine than diesel

Compatible with existing ***LPG infrastructure***

G. A. Olah *et al.*, *Journal of Organic Chemistry*, 2009, 74, 487– 498

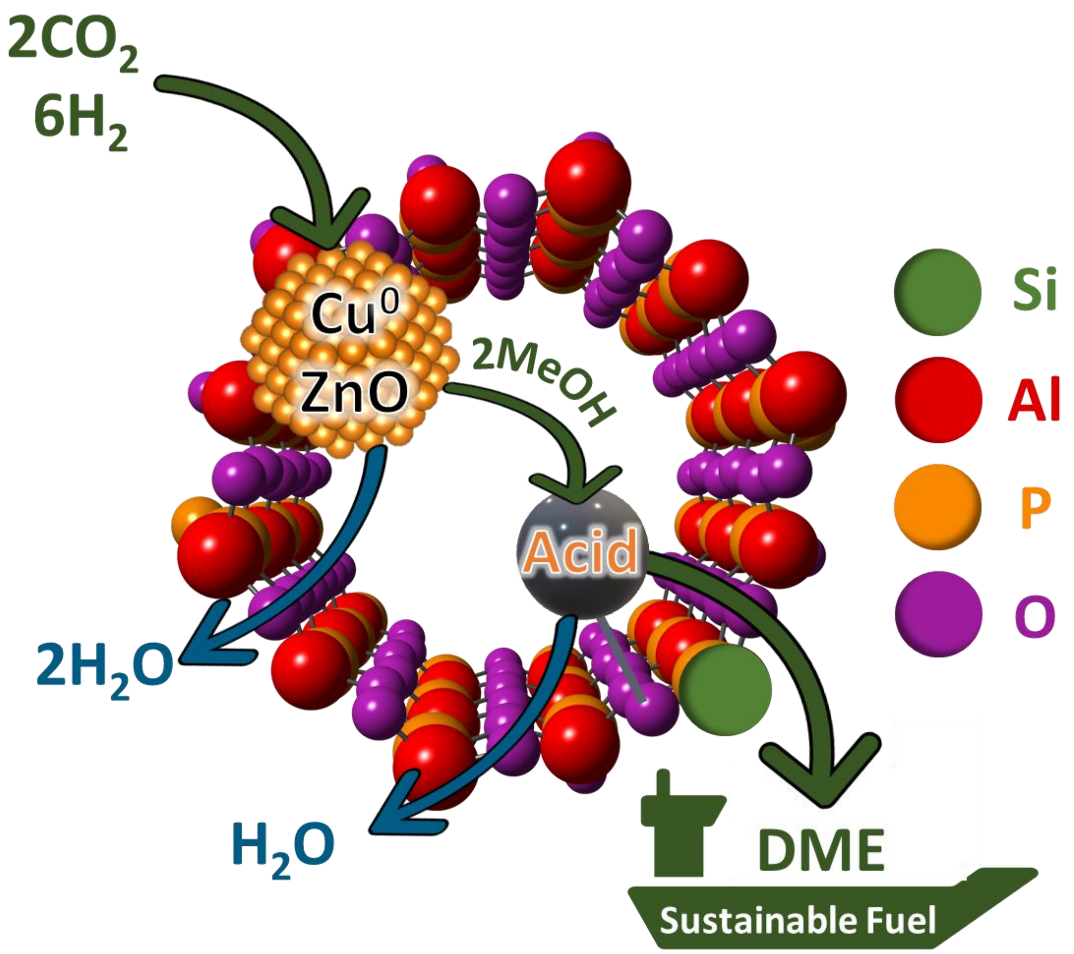
DME can be a sustainable marine fuel

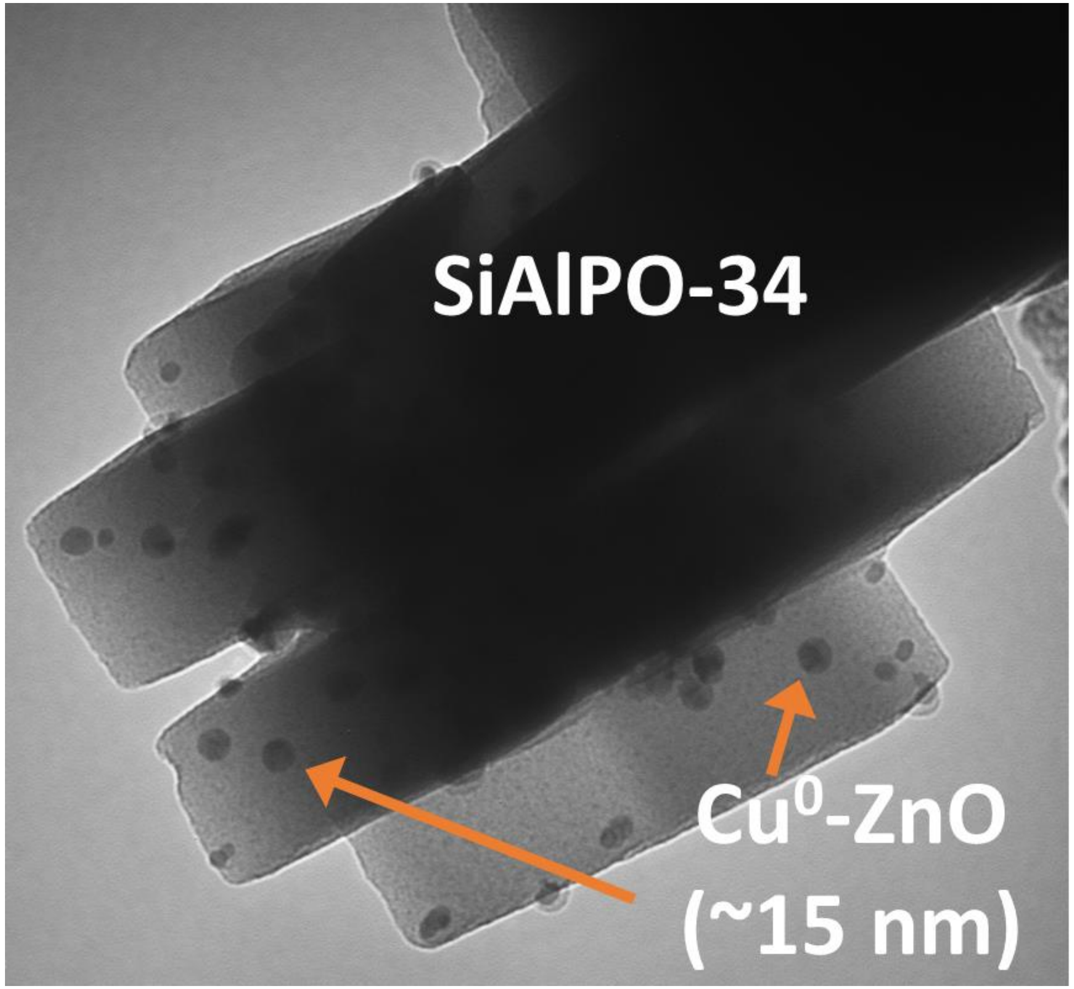
Two-pot DME Synthesis



Dimethyl ether was traditionally made in two reactors

Cu^0-ZnO/SiAlPO$_4$-34 Cascade Nanoreactor





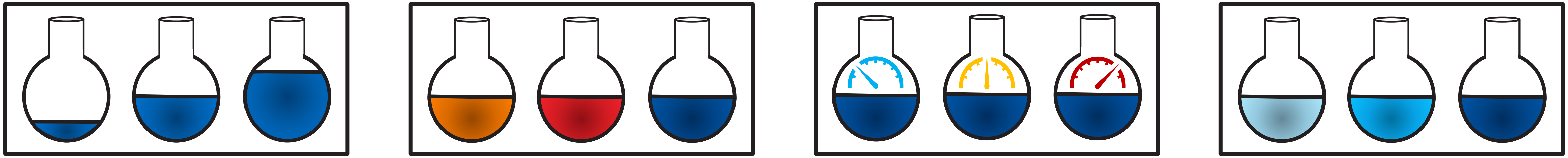
M.G Walerowski *et al.*, *Catalysis Science & Technology*, 2024, **14**, 3853 - 3863

Convert CO_2 to DME using a Cu^0-ZnO/SiAlPO$_4$-34 catalyst

Controlling Cu^0-ZnO Nanoparticle Size

- Cu^0-ZnO/SiAlPO-34 synthesised via impregnation and drying method
- Modify synthesis variables to reduce Cu^0-ZnO nanoparticle size

Solvent Volume **Solvent Polarity** **Drying Temperature** **Metal Loading**



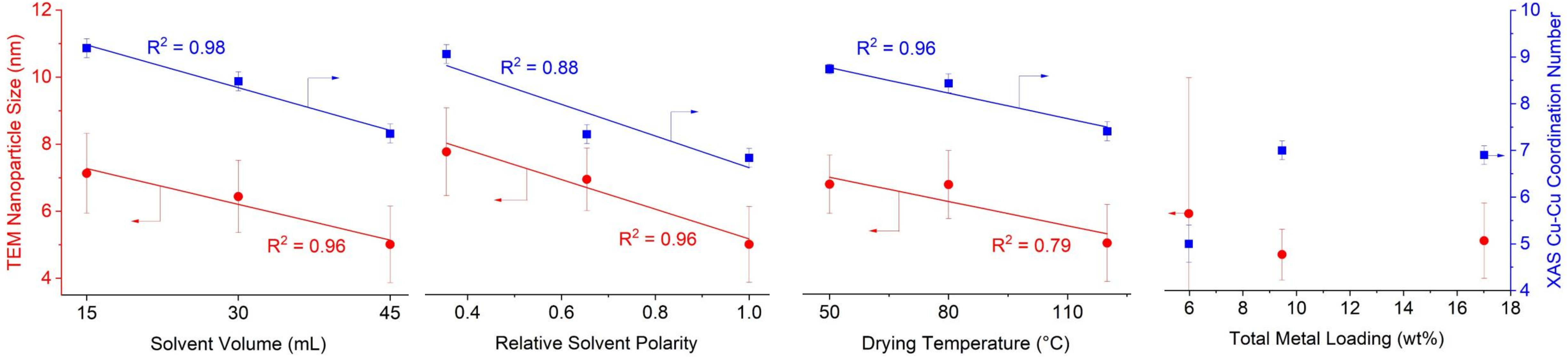
- Characterised using **TEM (nanoparticle size), XAS (Cu-Cu coordination number),** XRD, BET & ICP-OES

Varied four synthesis variables

Controlling Cu^0-ZnO Nanoparticle Size

- Precise nanoparticle size possible by tailoring volume, polarity & temperature
- Varying metal loading gives poor size control

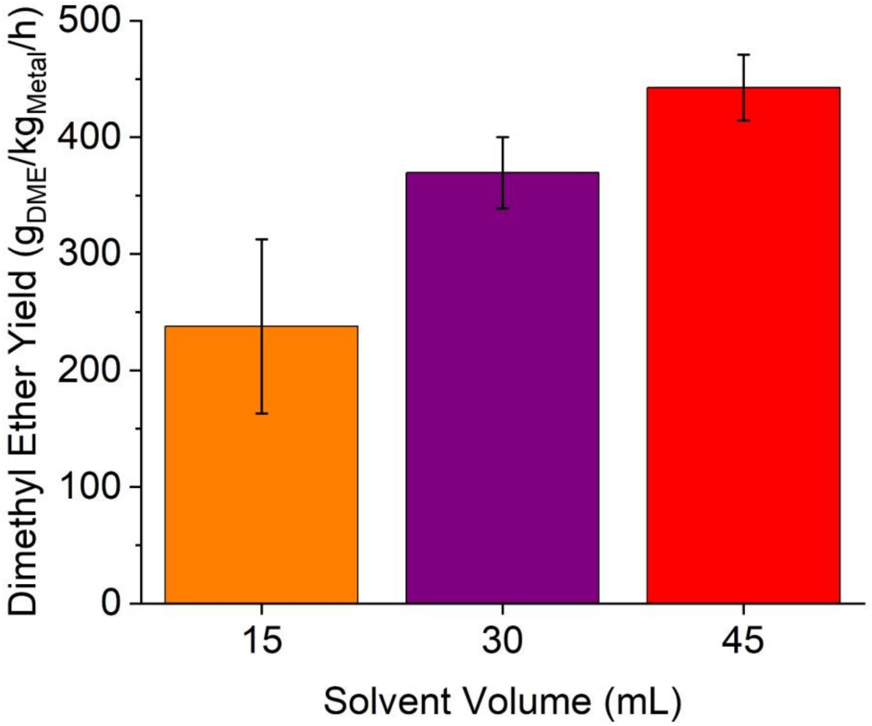
Solvent Volume **Solvent Polarity** **Drying Temperature** **Metal Loading**

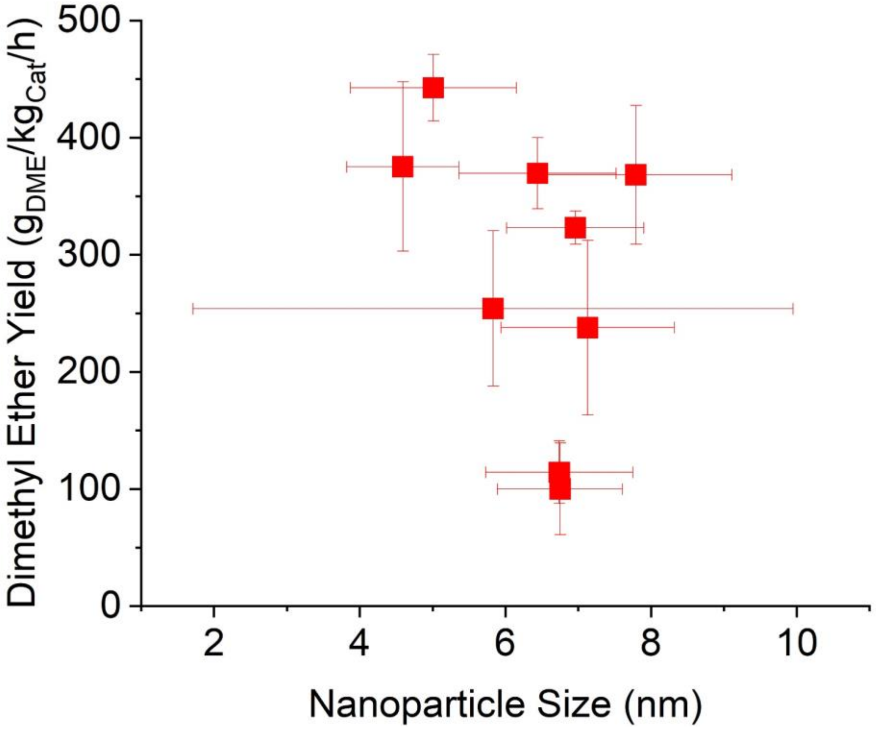


Facile, green & precise nanoparticle size control

Correlating Yield with Nanoparticle Size

- Changing solvent volume impacts DME yield directly, nanoparticle size influence?
- Plotting nanoparticle size vs DME yield gives no correlation….

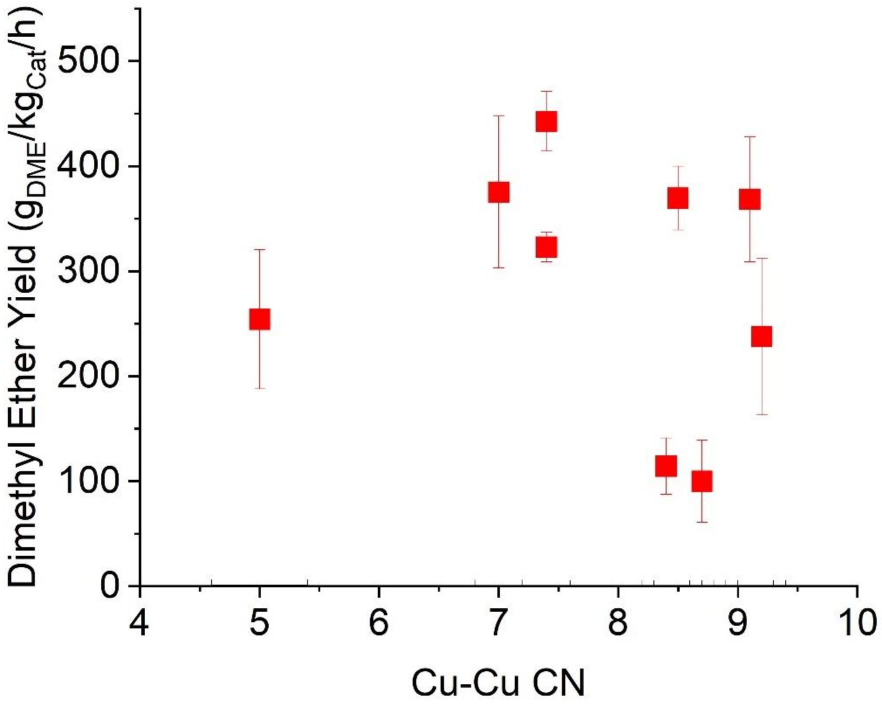


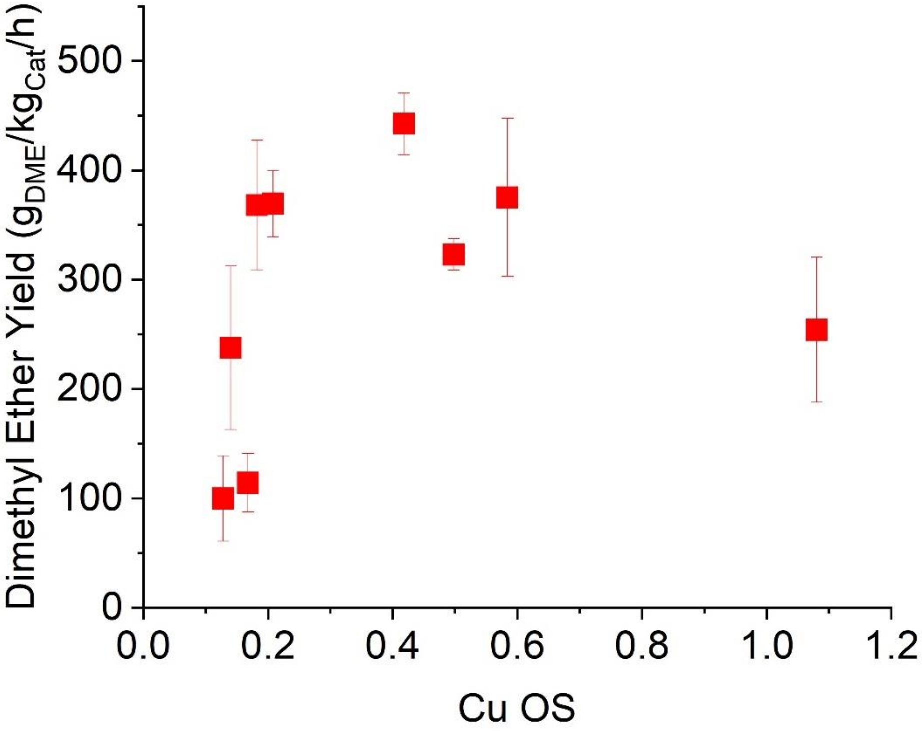


Nanoparticle size alone cannot explain activity

Correlating Yield with Cu CN & OS

- Plotting Cu-Cu CN or Cu OS vs DME yield gives no correlation….

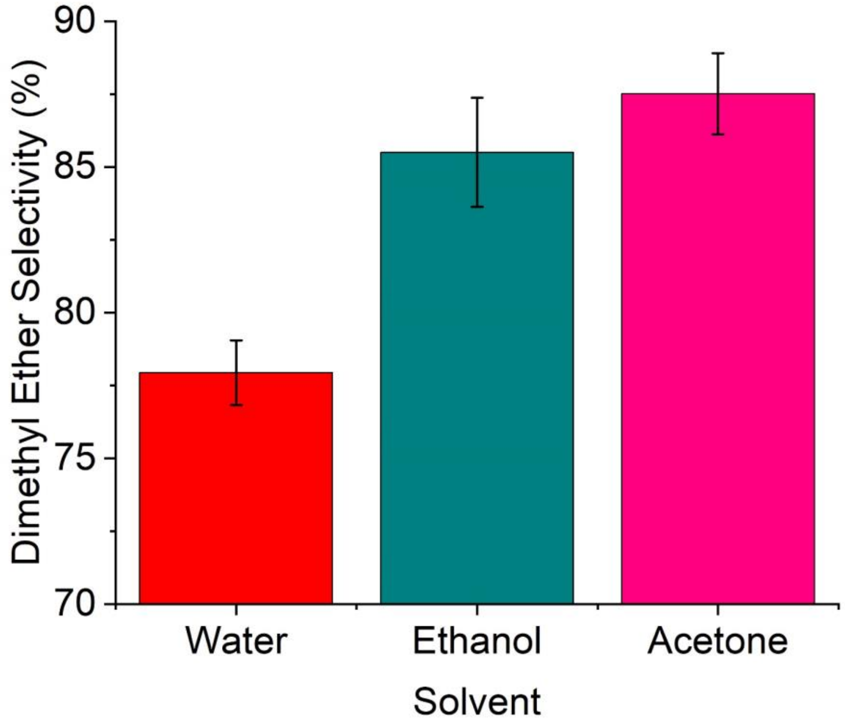




Cannot easily explain yield

Influence of Synthesis on Selectivity

- Synthesis appears to affect selectivity which unlikely due to nanoparticle size
- Changing synthesis clearly affects more than just the nanoparticle size…



Changing synthesis has a complex impact on catalysis

Three-Dimensional Response Surface

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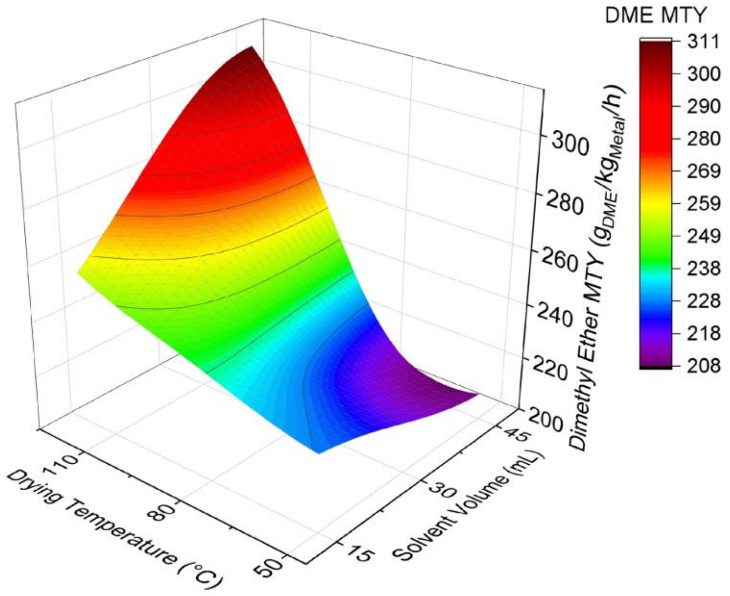
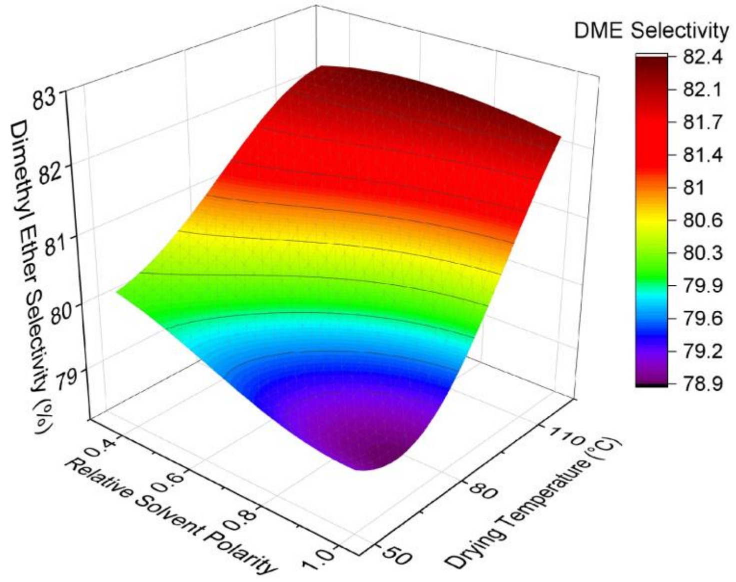
- 3D response surfaces built according to Kyrimis *et al.*
- Demonstrates influence of synthetic variables on catalytic performance

Yield



Selectivity



S. Kyrimis *et al.*, *Fuel*, 2024, 368 , 131511

Model synthetic variable impact on performance

Synthesis-Property Correlation Matrix

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- Understand how changing one synthesis variable impacts multiple structural features at once

Parameter	**Solvent Volume**	**Solvent Polarity**	**Drying Temperature**	**Cu Intended Loading**	**Zn Intended Loading**	Surface Area	Pore Volume	Nanoparticle Size	Cu-Cu CN	Cu-O CN	Cu Actual Loading	Zn Actual Loading
Solvent Volume	1.0	0.0	0.0	0.0	0.0	0.1	0.3	-0.4	-0.5	0.4	-0.2	-0.2
Solvent Polarity	0.0	1.0	0.0	0.0	0.0	0.3	0.3	-0.7	-0.5	0.4	-0.1	-0.5
Drying Temperature	0.0	0.0	1.0	0.0	0.0	0.1	0.1	-0.2	-0.3	0.5	-0.3	-0.1
Cu Intended Loading	0.0	0.0	0.0	1.0	0.0	-0.2	-0.5	0.3	0.4	-0.4	0.4	0.5
Zn Intended Loading	0.0	0.0	0.0	0.0	1.0	-0.6	-0.6	0.2	0.4	-0.4	0.5	0.6
Surface Area	0.1	0.3	0.1	-0.2	-0.6	1.0	0.4	-0.2	-0.3	0.3	-0.2	-0.3
Pore Volume	0.3	0.3	0.1	-0.5	-0.6	0.4	1.0	-0.3	-0.4	0.4	-0.2	-0.4
Nanoparticle Size	-0.4	-0.7	-0.2	0.3	0.2	-0.2	-0.3	1.0	0.4	-0.4	0.2	0.4
Cu-Cu CN	-0.5	-0.5	-0.3	0.4	0.4	-0.3	-0.4	0.4	1.0	-0.5	0.3	0.4
Cu-O CN	0.4	0.4	0.5	-0.4	-0.4	0.3	0.4	-0.4	-0.5	1.0	-0.3	-0.4
Cu Actual Loading	-0.2	-0.1	-0.3	0.4	0.5	-0.2	-0.2	0.2	0.3	-0.3	1.0	0.3
Zn Actual Loading	-0.2	-0.5	-0.1	0.5	0.6	-0.3	-0.4	0.4	0.4	-0.4	0.3	1.0

A unique insight into catalytic design

Synthesis-Property Correlation Matrix

- Number shows the strength of correlation
- Increasing solvent polarity increases surface area (red) but reduces nanoparticle size (blue)
- Increasing loading reduces surface area (blue) but increases nanoparticle size (red)

Parameter	Surface Area	Pore Volume	Nanoparticle Size	Cu-Cu CN	Cu-O CN
Solvent Volume	0.1	0.3	-0.4	-0.5	0.4
Solvent Polarity	0.3	0.3	-0.7	-0.5	0.4
Drying Temperature	0.1	0.1	-0.2	-0.3	0.5
Cu Intended Loading	-0.2	-0.5	0.3	0.4	-0.4
Zn Intended Loading	-0.6	-0.6	0.2	0.4	-0.4

Changing variables impacts more than NP size

Property-Performance Correlation Matrix

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- Increasing surface area increases DME selectivity (red) but decreases MeOH selectivity (blue)
- Increasing nanoparticle size decreases DME and MeOH yield (blue) but increases DME selectivity (red)

Name	DME MTY	MeOH MTY	DME Selectivity	MeOH Selectivity
Surface area	0.0	-0.2	0.2	-0.2
Pore volume	0.1	-0.2	0.1	-0.1
Nanoparticle Size	-0.3	-0.2	0.2	-0.2
Cu-Cu CN	-0.2	-0.2	-0.1	0.1
Cu-O CN	0.0	0.1	0.0	0.0
Cu Actual Loading	0.1	0.4	-0.1	0.1
Zinc Actual Loading	0.0	0.0	-0.1	0.1

Use a correlation matrix to rationalise catalytic performance

Validation of Model

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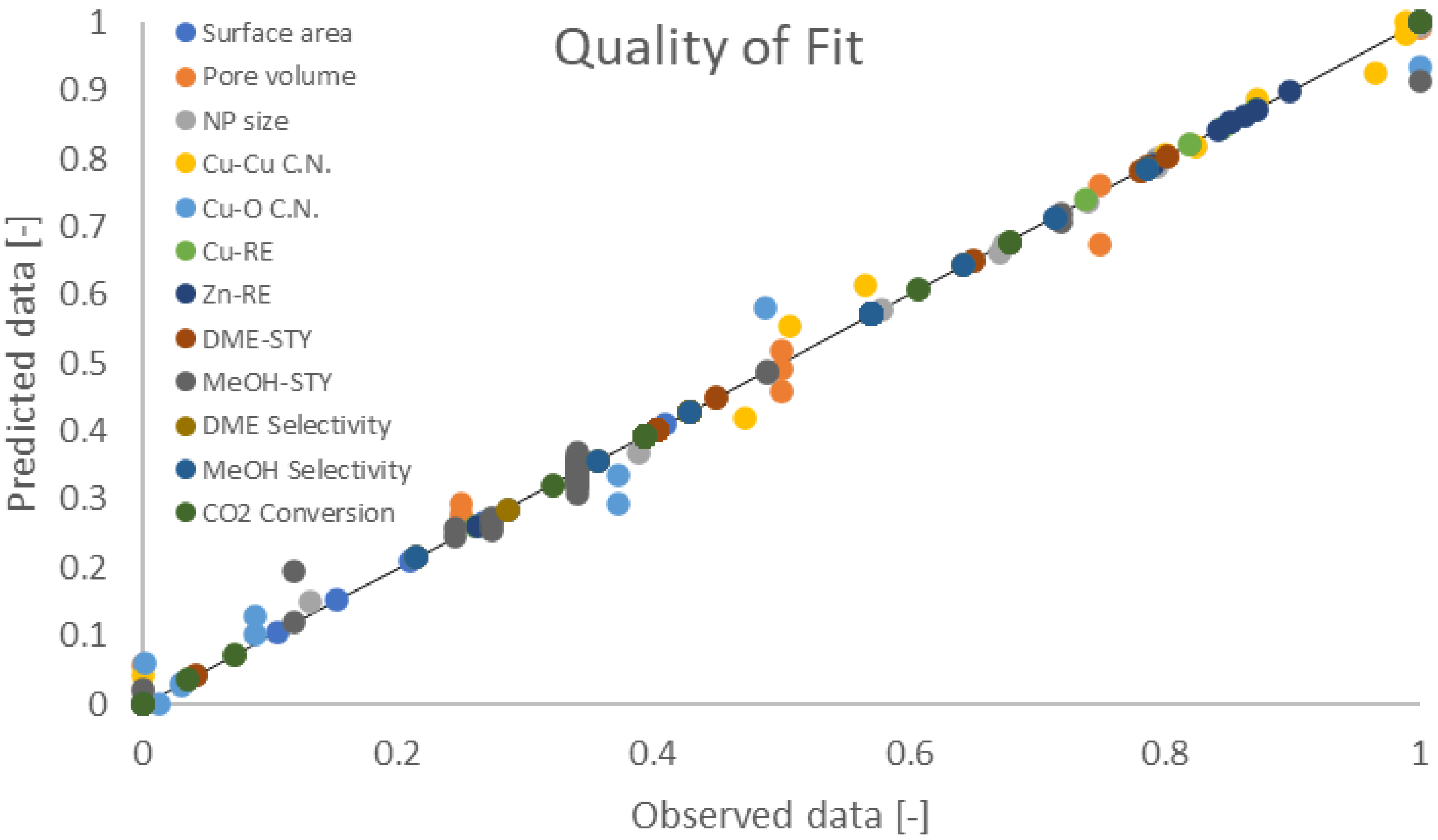
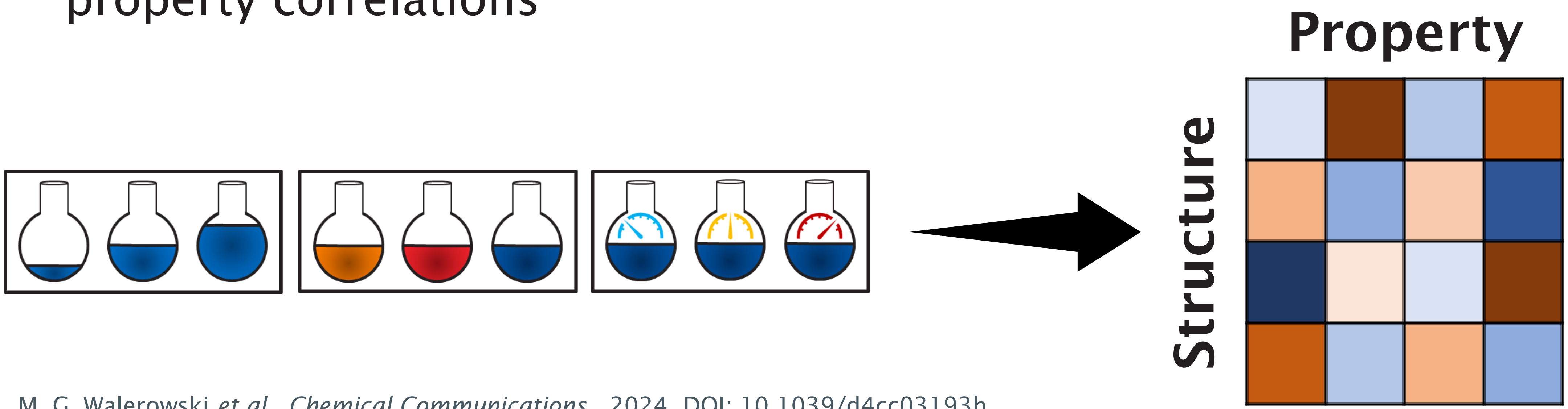


Model predicted results match experiments well

Three take home messages

- ✓ Possible to tailor nanoparticle size by changing solvent volume, solvent polarity & drying temperature
- ✓ Changing synthesis affects multiple structural features at once
- ✓ Need to use a correlation matrix to derive robust synthesis-structure-property correlations



M. G. Walerowski *et al.*, *Chemical Communications.*, 2024, DOI: 10.1039/d4cc03193h

Acknowledgements

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Link to paper

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Southampton Marine & Maritime Institute

Thank you for your attention!
Any questions?

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