Designing Bifunctional Catalysts for the One-pot Conversion of CO_2 to Sustainable Marine Transportation Fuels

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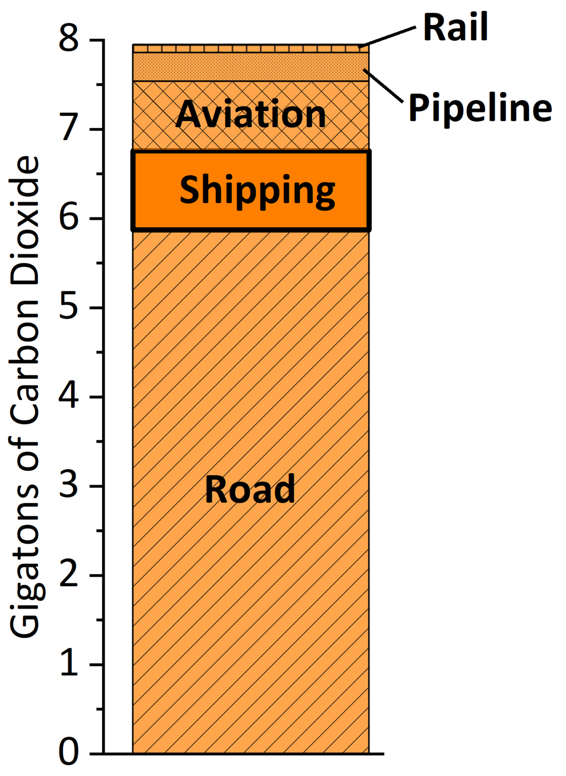
1 Decarbonising Marine Shipping



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

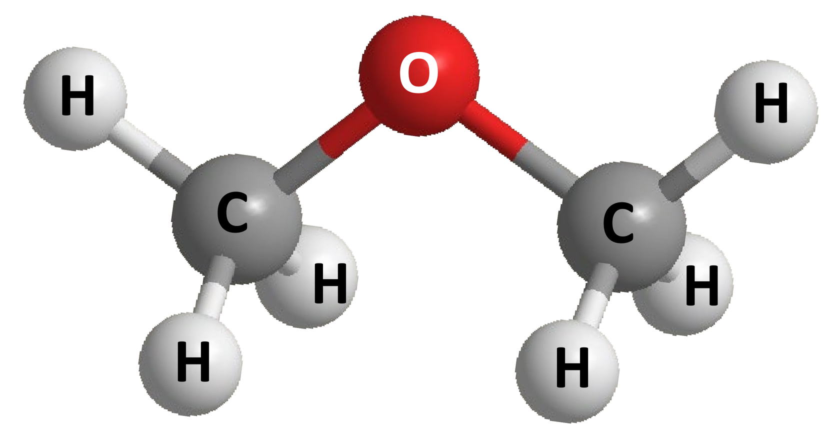
Vehicle compatibility with different energy sources[2]

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

- Shipping responsible for ***3% of global CO_2*** emissions
- ***Challenging to electrify*** long haul maritime shipping
- Require synthetic, ***sustainable fuels***

2 Dimethyl Ether: a Sustainable Marine Fuel

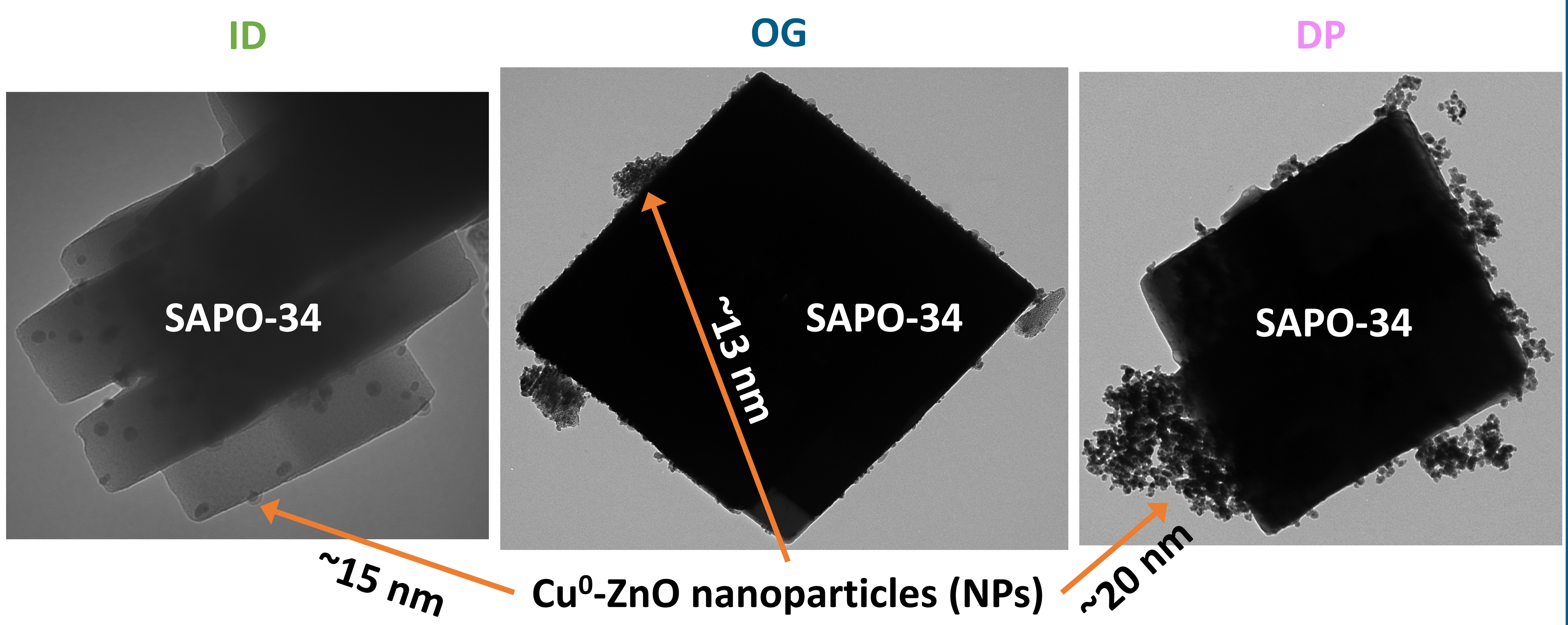
- Producible via a ***circular carbon economy*** ^{12}C
- non-carcinogenic, non-corrosive, ***non-toxic***



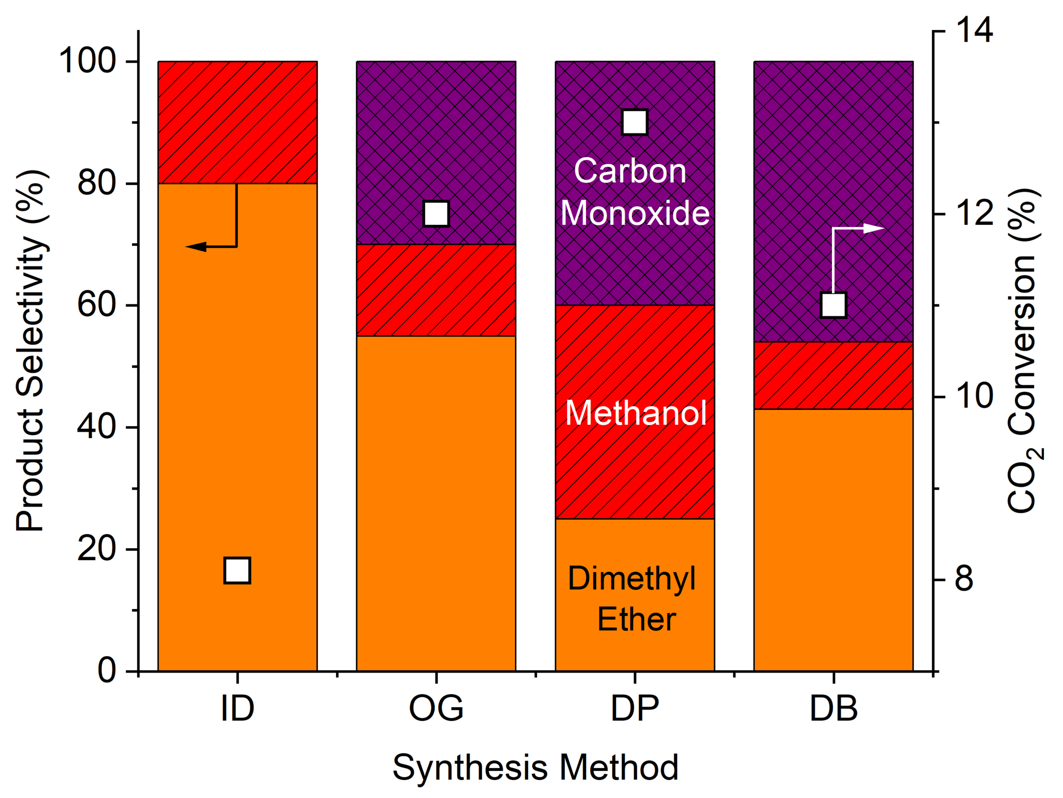
- Burns ***more effectively*** in an engine than diesel
- Compatible with existing ***LPG infrastructure[3]***

4 Bifunctional Cu^0-ZnO/SiAlPO$_4$ Catalysts

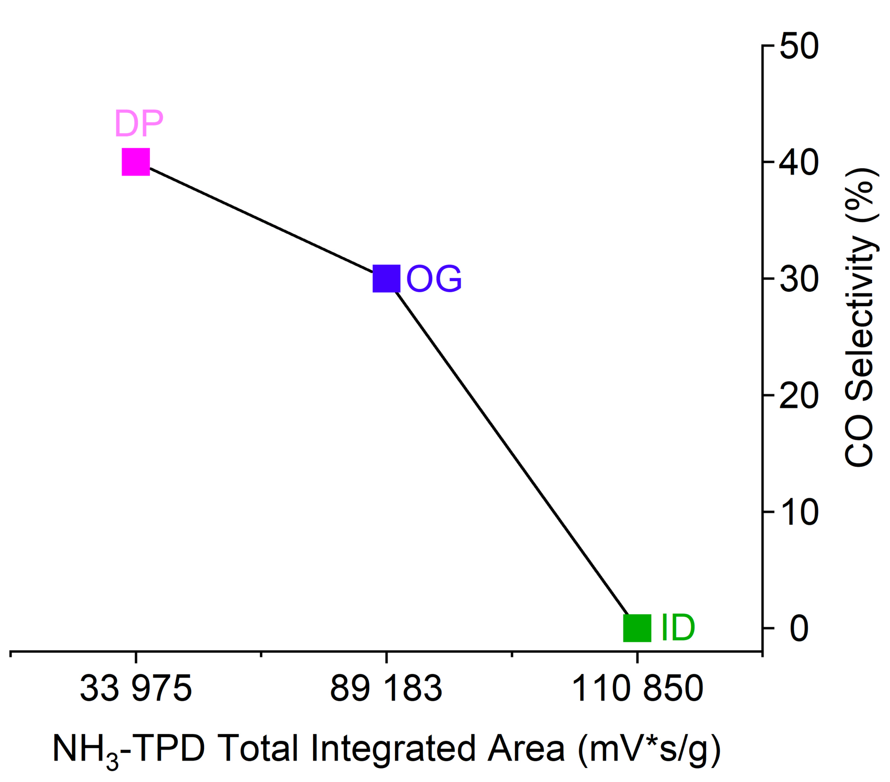
- Develop bifunctional catalysts for CO_2 to DME conversion by ***combining Cu^0-ZnO (redox sites) with SiAlPO$_4$-11 or SiAlPO$_4$-34*** microporous supports (acid sites).[4]
- Tested three synthesis methods: impregnation & drying **(ID)**, oxalate gel deposition precipitation **(OG)** & deposition precipitation **(DP)**.



- **ID** synthesis method yields only supported Cu^0-ZnO NPs, **OG** & **DP** give supported NPs & unsupported NP agglomerates.
- Acid site strength & abundance: **ID** > **OG** > **DP** with **ID** synthesis approach creating a range of new acid sites with varying strengths.



Impact of synthesis method on catalytic performance of Cu^0-ZnO/SiAlPO$_4$-34



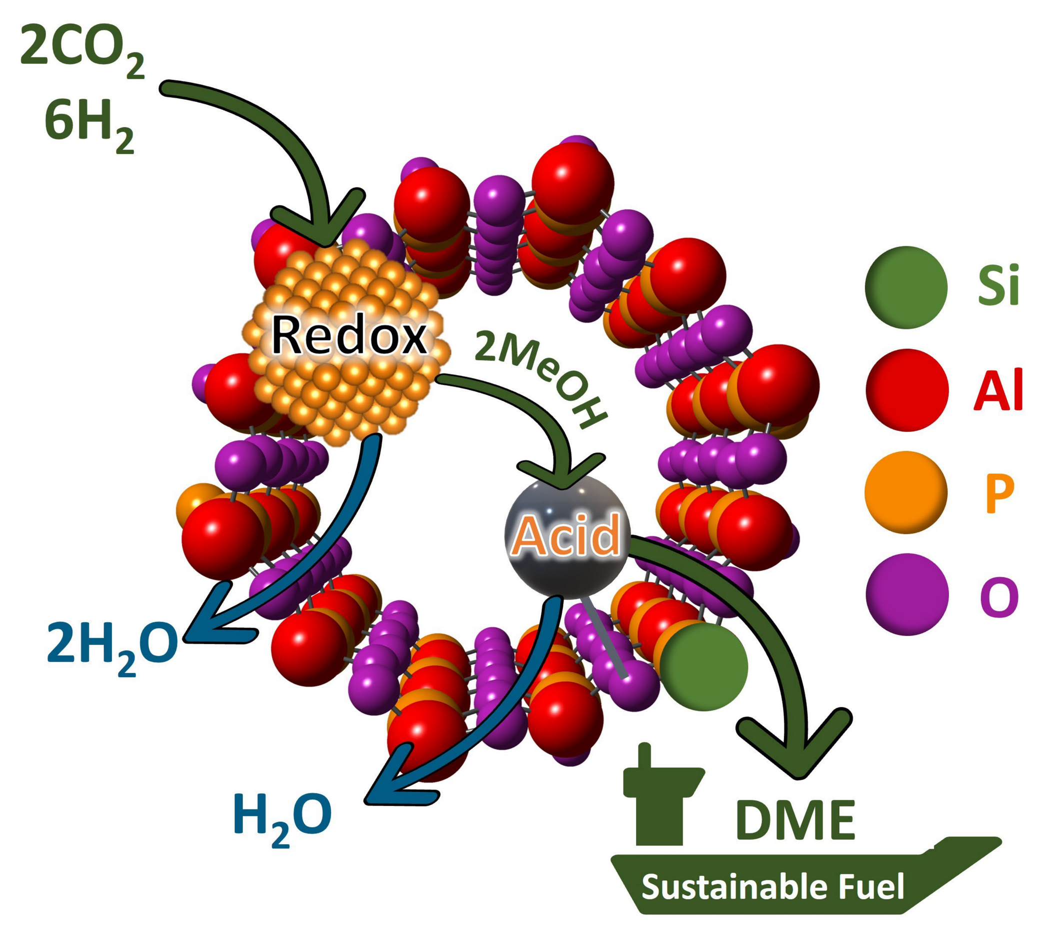
Cu^0-ZnO/SiAlPO$_4$-34 acid site abundance impact on CO selectivity

- Cu^0-ZnO/SiAlPO$_4$-34 bifunctional catalyst synthesised via **ID** approach gives exceptional DME selectivity and ***no detectable CO formation.*** Superior performance compared to a dual bed (DB) catalyst arrangement.
- Acid site abundance of bifunctional catalysts impacts product selectivity due to theorised localised water inhibition effect.

3 One-pot Dimethyl Ether Synthesis

- Two-pot: convert CO_2 to MeOH, separate & purify the intermediate MeOH and then dehydrate it to DME. ***Requires two distinct reactors & catalysts.***
- One-pot: Convert CO_2 to DME via a MeOH intermediate in one reactor. ***Require a bifunctional catalyst with two (redox & acid) active sites.***

Advantages of One-pot	Drawbacks of One-pot
Singular reactor	Need new catalysts
Cheaper and simpler	Can deactivate quicker
No separation & purification	Difficult to optimise & reactivate
In situ dehydration of MeOH can increase CO_2 conversions	Combining two active sites in one catalyst is challenging



Converting CO_2 to DME using a bifunctional catalyst

5 Conclusions

- Bifunctional Cu^0-ZnO/SiAlPO$_4$ catalysts can convert CO_2 to the sustainable fuel, DME, ***in one-pot***.
- The method used to synthesise Cu^0-ZnO/SiAlPO$_4$ catalysts has a profound influence on ***structural and catalytic properties.***
- Catalysts with ***abundant acid sites yield high DME selectivity*** and supress CO formation due to theorised localised water inhibition.

References

[1] International Energy Agency, CO_2 Emissions in 2022, Paris, 2023.
[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.*, submitted.

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