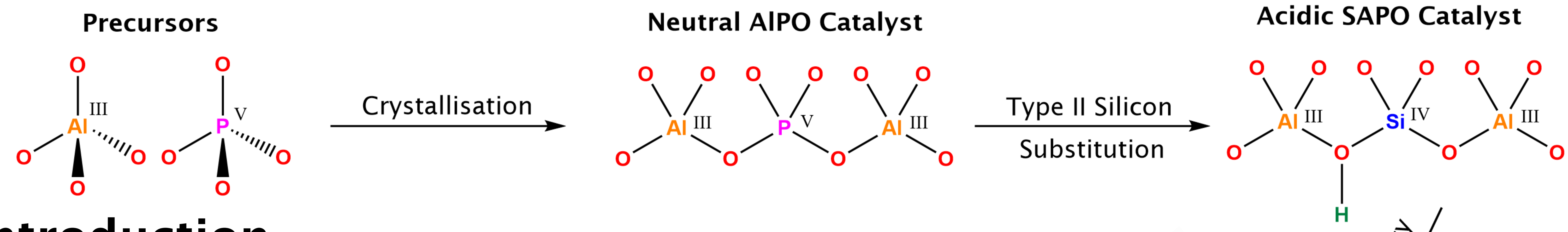
Development of Hybrid Catalysts for the Conversion of CO_2 into Sustainable Marine Fuels

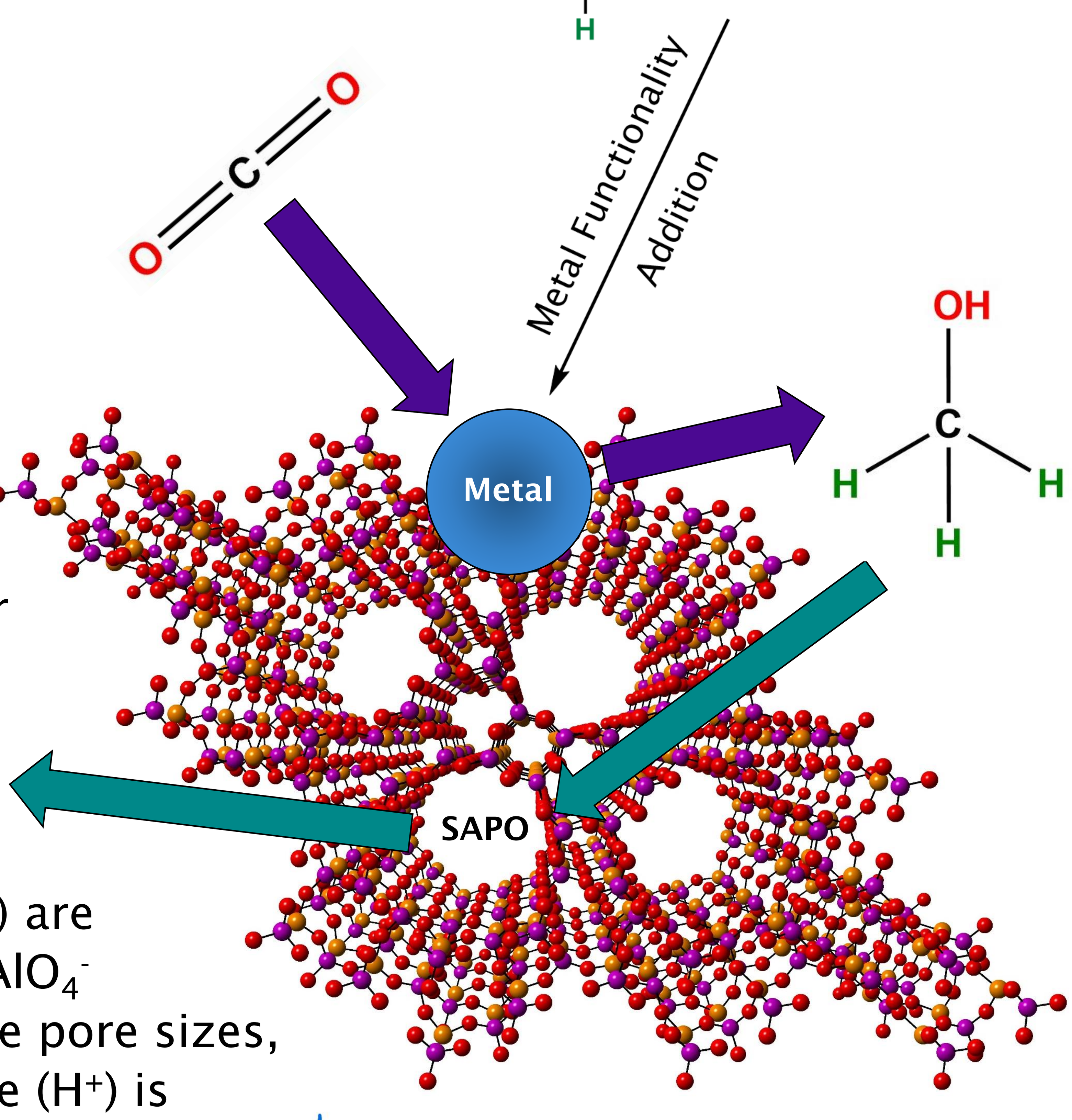
Maciej G. Walerowski[a], Matthew E. Potter[c], Stylianos Kyrimis[a,b], Lindsay-Marie Armstrong[b], Robert Raja[a]

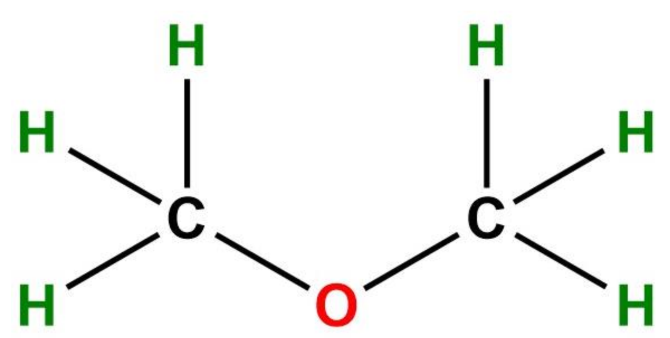
[a] School of Chemistry, University of Southampton, SO17 1BJ (UK) [b] School of Engineering, University of Southampton, SO17 1BJ (UK).
[c] Chemistry Department, University College London, UK & UK Catalysis Hub, Harwell, UK.



1. Introduction

Dimethyl ether (DME) has been identified as a sustainable diesel alternative for marine transport.[1] DME can be synthesised in two steps from CO_2 and H_2 using a hybrid catalyst which utilises both metallic and acidic functionalities. Metallic catalysts firstly convert CO_2 and H_2 to methanol, which is then dehydrated using a solid-acid catalyst to form DME. Optimisation of the hybrid catalyst's individual components is required to obtain high DME yields. Herein, we screened a range of microporous solid-acid catalysts to identify which frameworks would be most suitable for use in a hybrid catalyst.

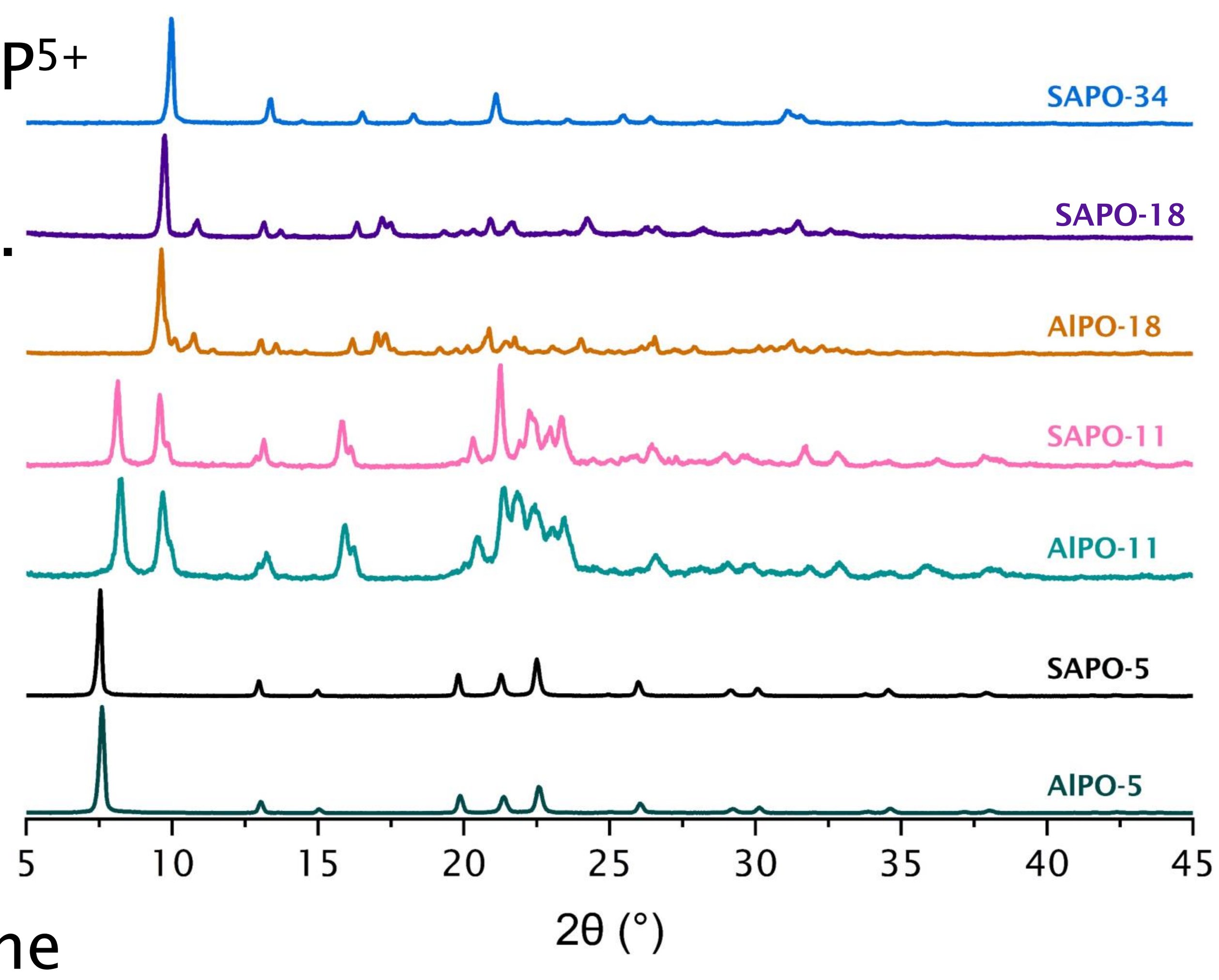




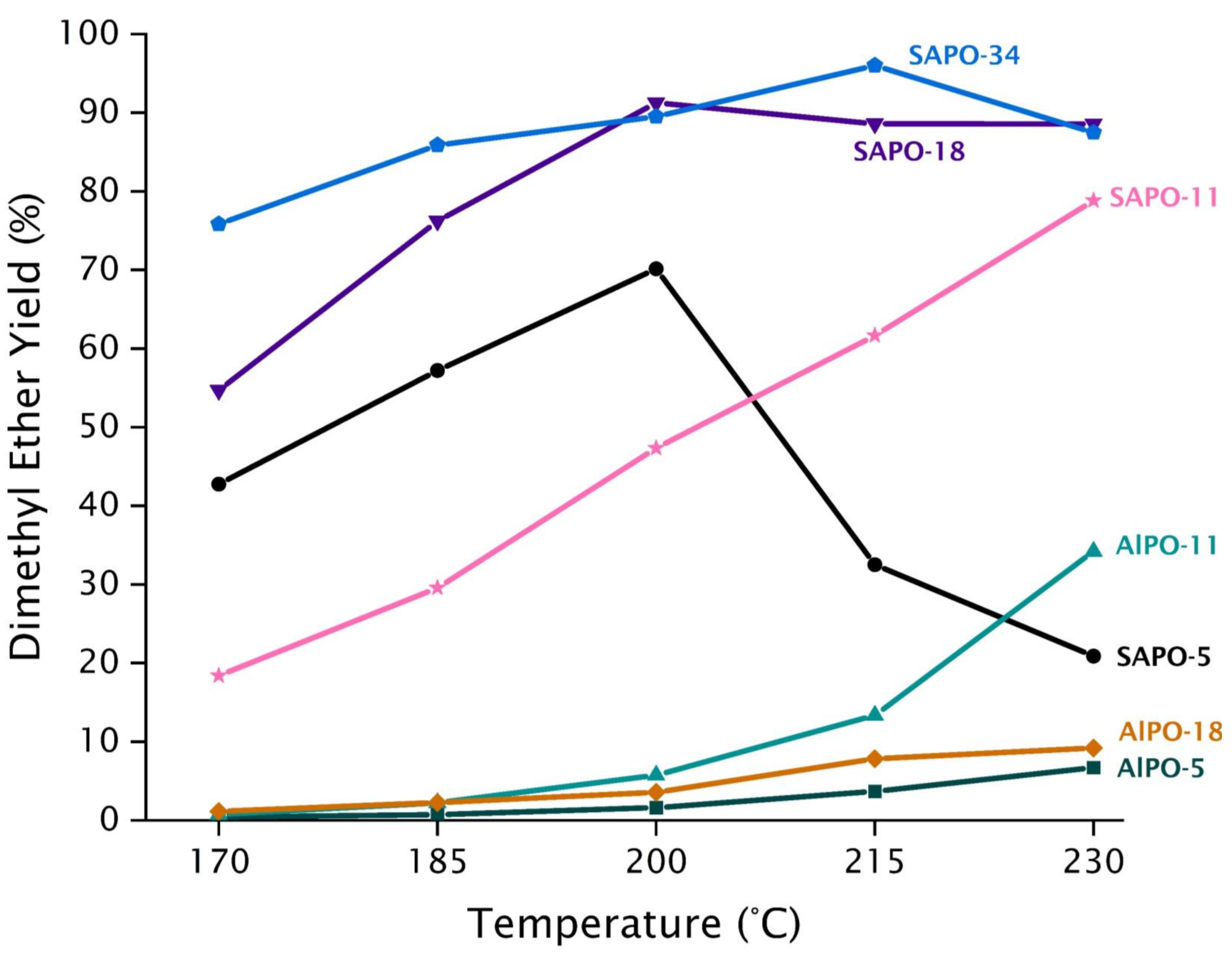
2. Aluminophosphates

Aluminophosphates (AlPOs) and silicoaluminophosphates (SAPOs) are microporous, solid-acid catalysts. AlPOs are built from PO_4^+ and AlO_4^- tetrahedra, which link via oxygen to form frameworks with diverse pore sizes, channel dimensionalities and cage structures. A Brønsted acid site (H^+) is created as a result of a charge imbalance generated when Si^{4+} substitutes P^{5+} during SAPO framework formation.[2] It is possible to create different frameworks and tailor catalytic activity by altering the synthetic procedure.

Fingerprint-like powder X-ray diffraction patterns verify that all synthesised catalysts were successfully synthesised with no impurities.

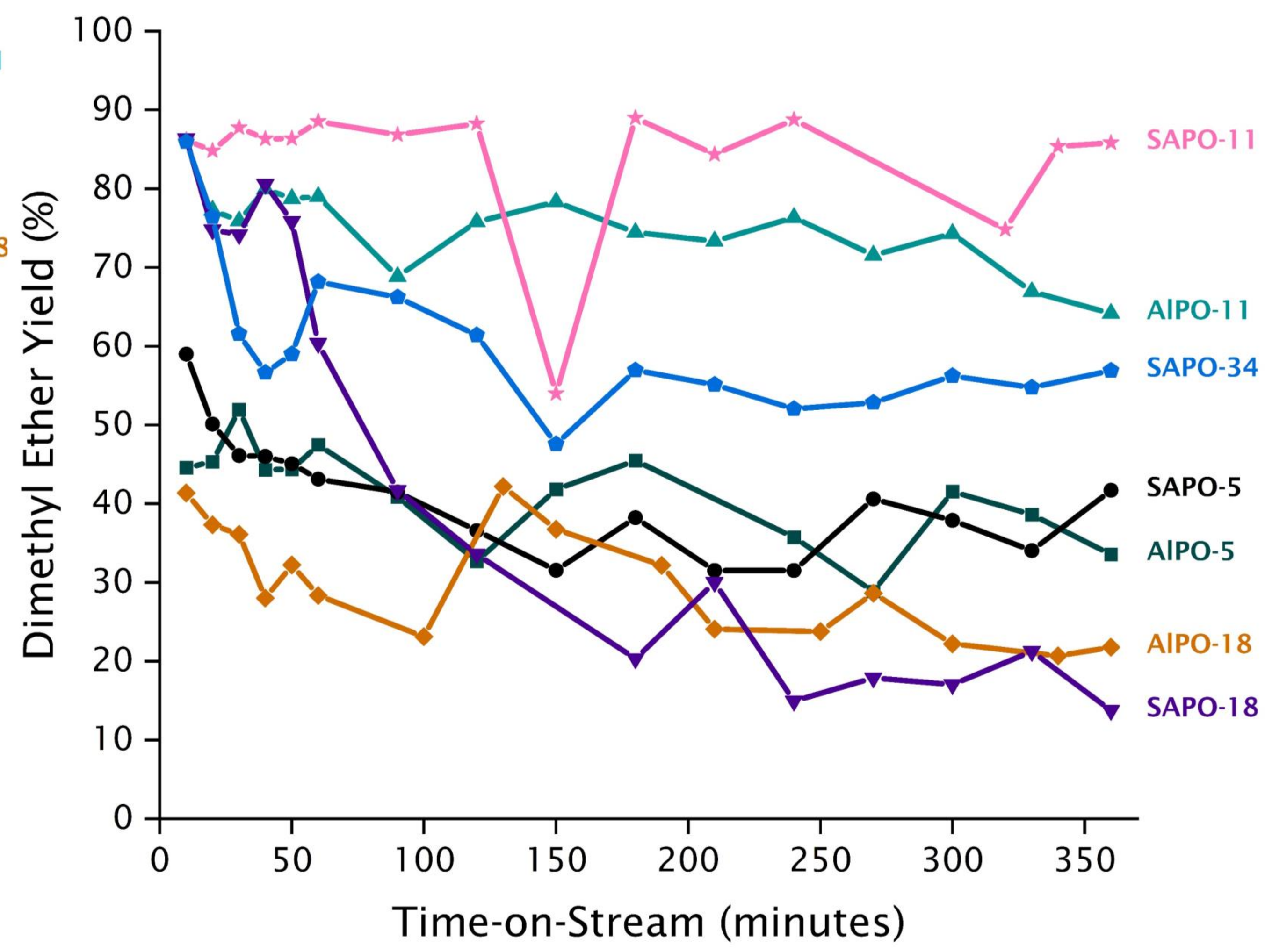


3. Methanol Dehydration Activity & Stability



Neutral AlPOs show limited methanol dehydration activity, while acidic SAPOs are highly active. DME yields increase inline with temperature up to equilibrium yields.

Small pore, 3D AlPO-18 and SAPO-18 undergo rapid deactivation due to coke formation while medium pore 1D AlPO-11 and SAPO-11 remain highly active throughout.



4. Conclusions and Future Work

Small pore 3D frameworks with predicted strongest acid sites (SAPO-18/34)[3] give the highest DME yields, but medium pore 1D frameworks with predicted weaker acid sites (SAPO-11) remain highly stable during methanol dehydration. Work is currently ongoing to develop SAPO-based hybrid catalysts for converting CO_2 to DME.

References

[1] The Royal Society, *Sustainable synthetic carbon based fuels for transport: Policy briefing*, 2019.
[2] M. E. Potter, *ACS Catalysis*, 2020, **10**, 9758–9789.
[3] K. S. Yoo, J. H. Kim, M. J. Park, S. J. Kim, O. S. Joo and K. D. Jung, *Applied Catalysis A:General*, 2007, **330**, 57–62.

Acknowledgements: I would like to thank the Southampton Marine and Maritime Institute and the Faculty of Engineering and Physical Sciences for their funding.