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

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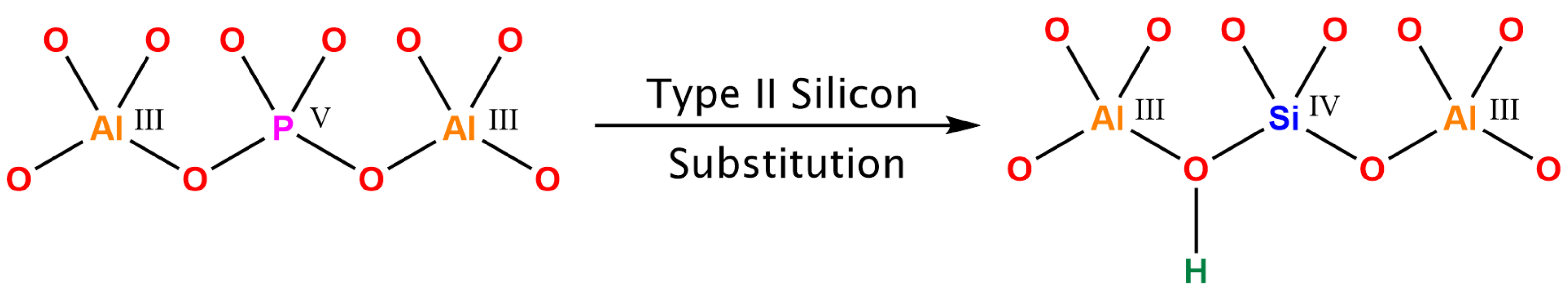
1. Introduction

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 (e.g. $Cu/ZnO/Al_2O_3$) firstly convert CO_2 and H_2 to MeOH, which is then dehydrated using a solid-acid catalyst (e.g. zeolite) 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. The effect of temperature and MeOH weight hourly space velocity (WHSV) was also explored.

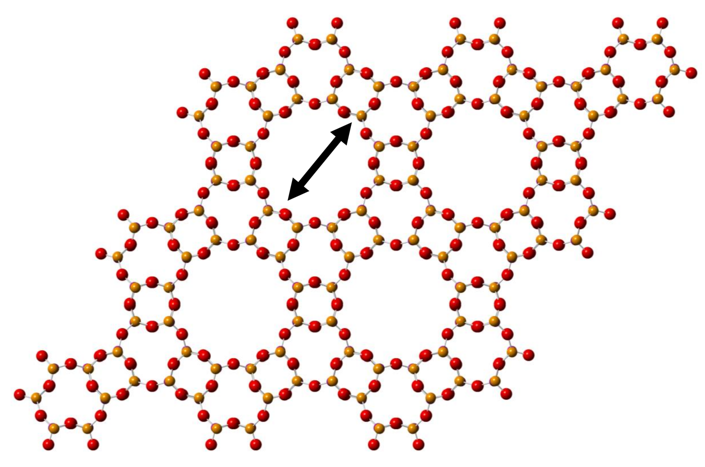
2. Aluminophosphates



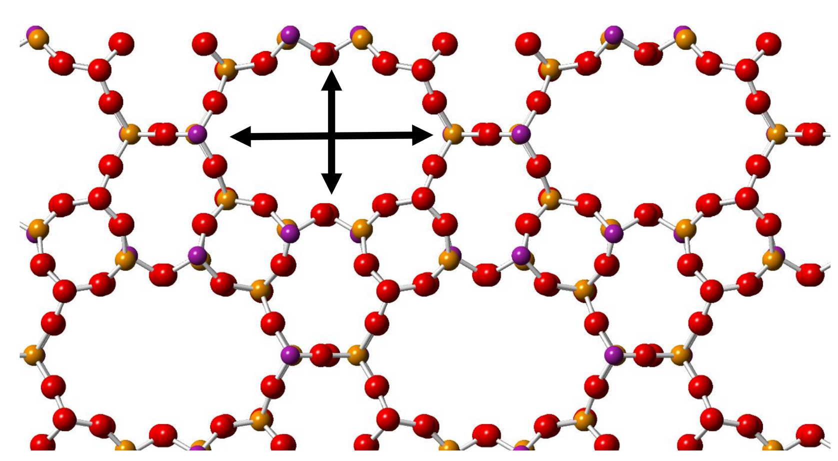
Aluminophosphates (AlPOs) and silicoaluminophosphates (SAPOs) are microporous, solid-acid catalysts with weak to moderate strength acid active sites. AlPOs are built from PO^{4+} and AlO^{4-} tetrahedra, which link via oxygen to form frameworks with diverse pore sizes (Å), channel dimensionalities (1D or 3D) and cage structures. A Brønsted acid site (H^+) is created as a result of charge imbalance generated when Si^{4+} substitutes P^{5+} during SAPO framework formation.[2]

AlPOs and SAPOs are more selective towards DME than zeolites during MeOH dehydration as they have weaker acid sites which only partially dehydrate MeOH to DME.[2,3] Stronger acid sites in zeolites, such as H-ZSM-5, can fully dehydrate MeOH to olefins.

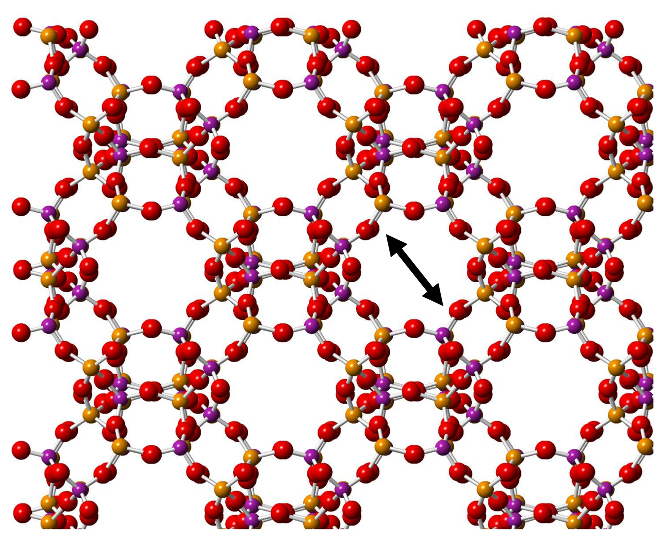
AlPO-5, 7.3Å, 1D



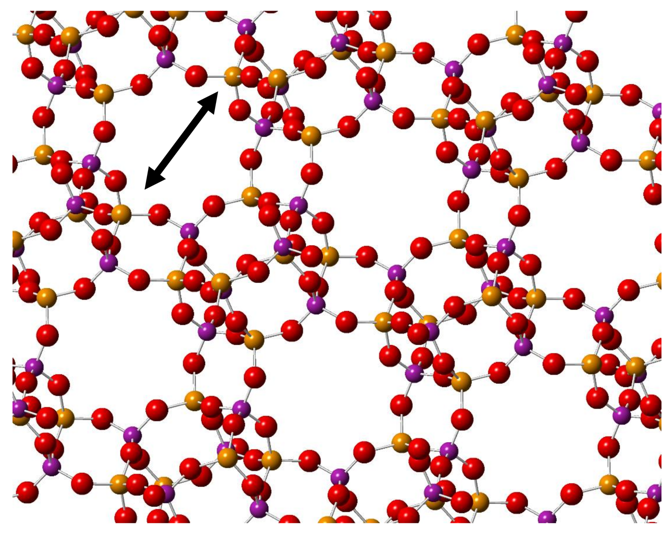
AlPO-11, 4.0 x 6.5Å, 1D



AlPO-18, 3.8Å, 3D

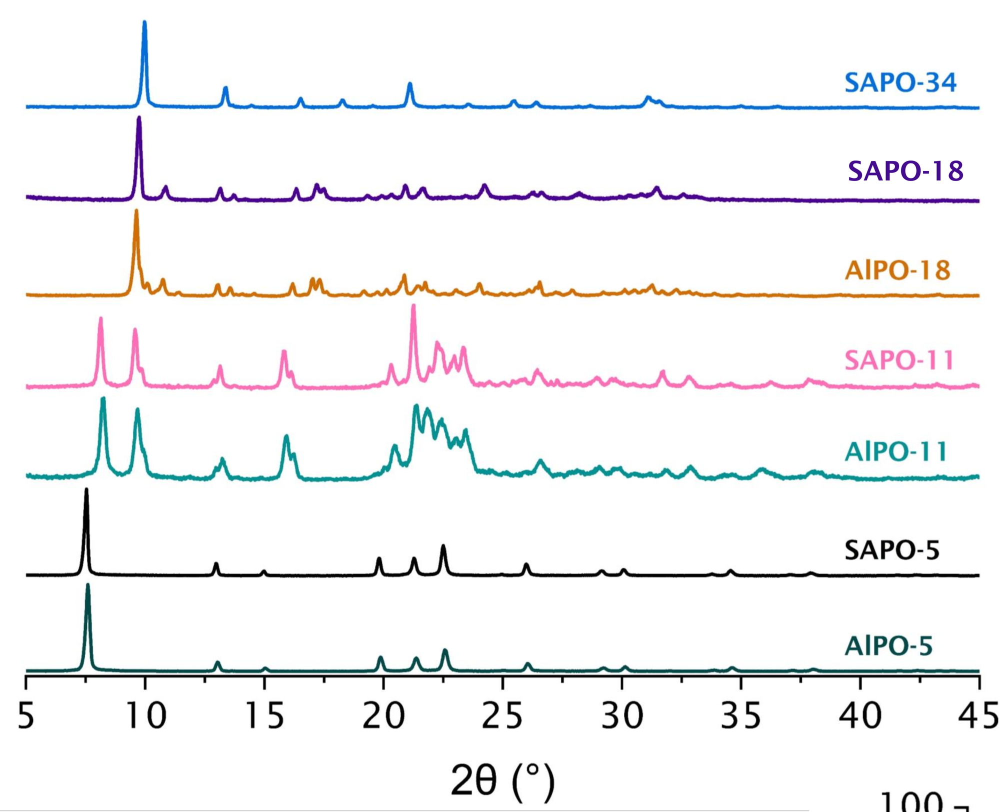


AlPO-34, 3.8Å, 3D

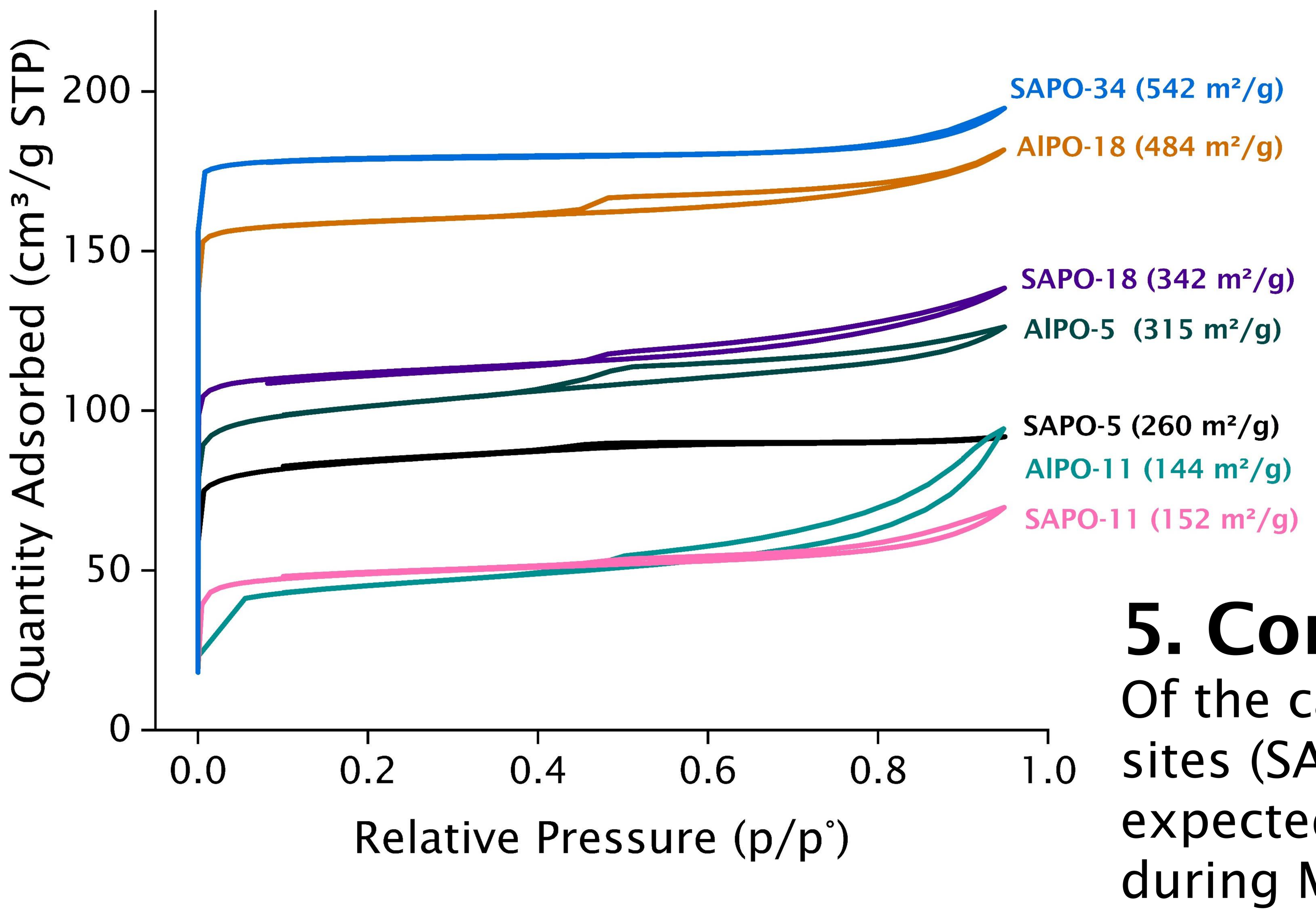


3. Structural and Textural Properties

Powder X-ray diffraction patterns show that all synthesised catalysts were phase pure with respect to the intended framework.

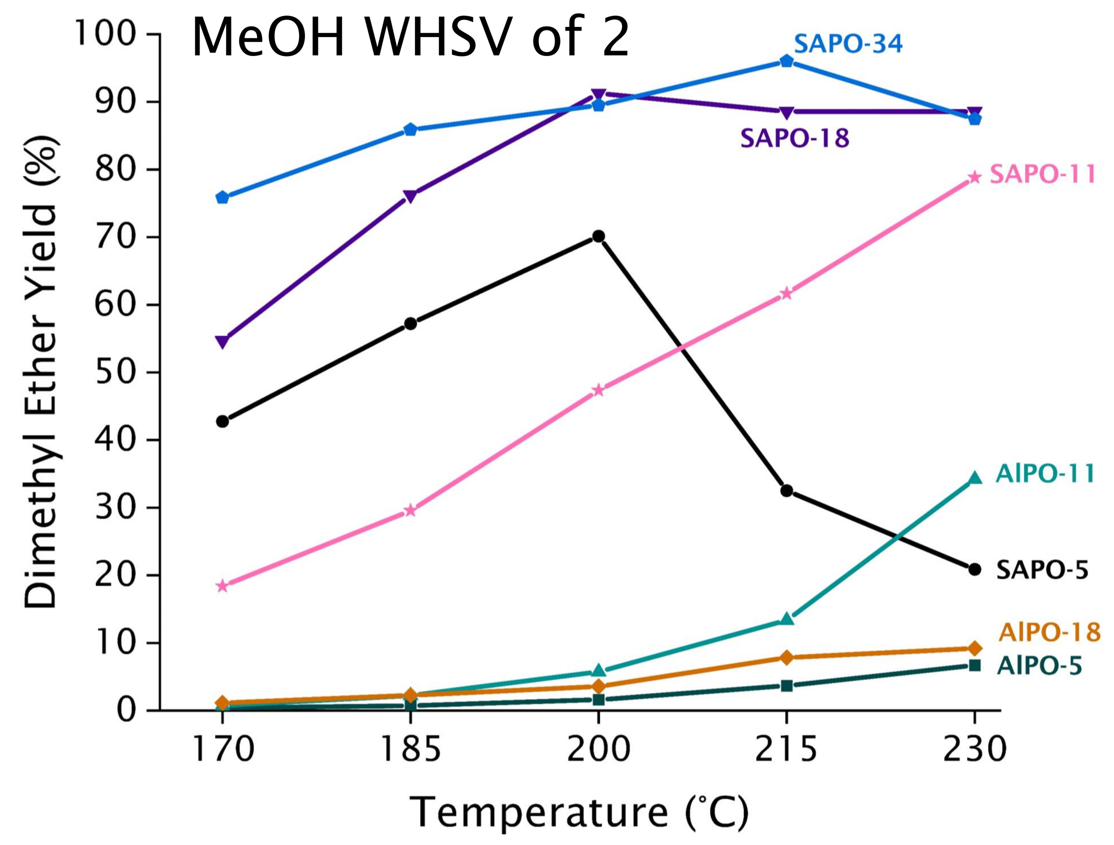


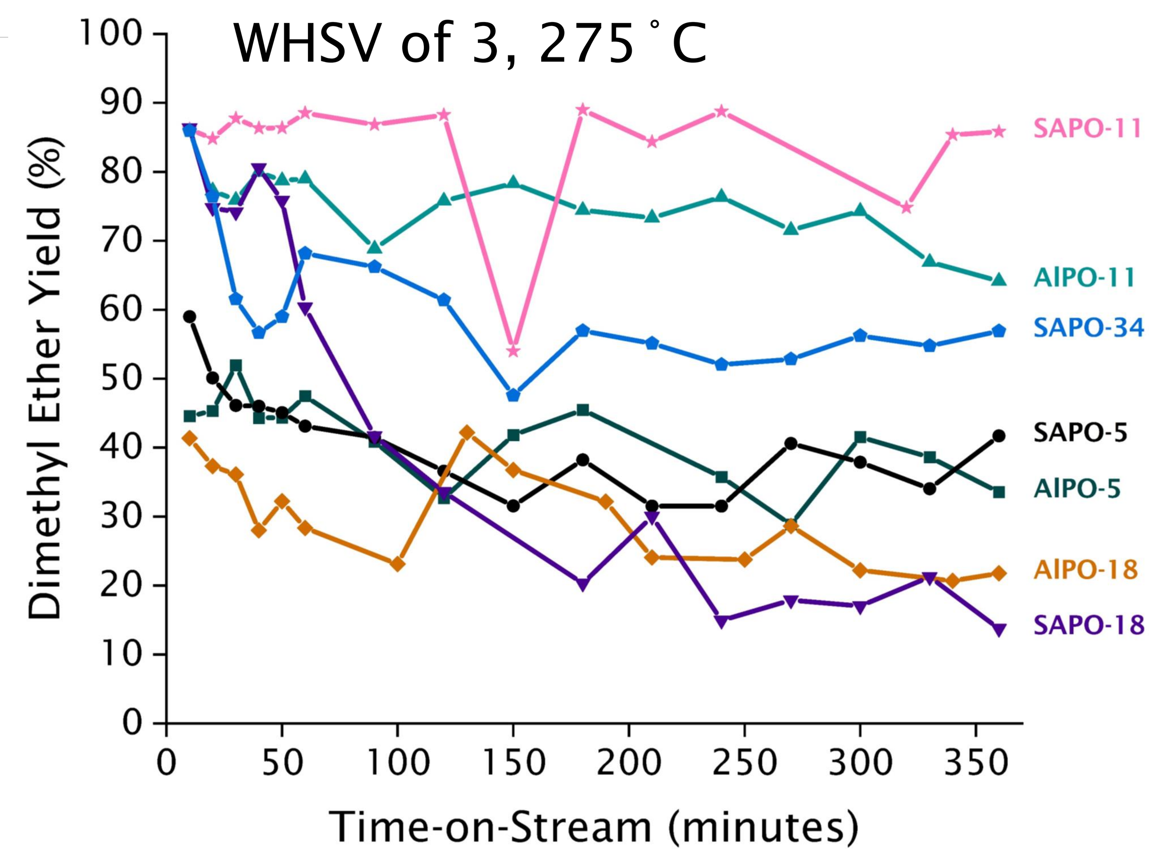
SAPO-5/34 show typical Type I N_2 physisorption isotherms expected for microporous frameworks. AlPO-5/11/18 and SAPO-11/18 show type IV isotherms indicating the presence of micro and mesopores.



4. Methanol Dehydration Activity & Stability

Neutral AlPOs show limited MeOH dehydration activity, while acidic SAPOs are highly active. DME yields increase inline with temperature up to equilibrium yields, while different MeOH WHSV have negligible effect.





Highest deactivation rates were seen in the first 100 minutes on-stream. Small pore, 3D AlPO-18 and SAPO-18 undergo the greatest deactivation due to coke formation while medium pore 1D AlPO-11 and SAPO-11 remain highly active throughout.

5. Conclusions and Future Work

Of the catalysts investigated, small pore 3D frameworks with expected strongest acid sites (SAPO-18/34)[4] give the highest DME yields, but medium pore 1D frameworks with expected weaker acid sites and structural mesoporosity (SAPO-11) remain highly stable during MeOH dehydration. Work is currently ongoing to create kinetic models for the MeOH dehydration reaction and develop novel hybrid catalysts using SAPO-11/34.

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] W. Dai, W. Kong, G. Wu, N. Li, L. Li and N. Guan, *Catalysis Communications*, 2011, **12**, 535–538.

[4] 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.

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