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Development of Kinetic and Computational Models for Improved Understanding and Prediction of MeOH Dehydration over Solid-acid Catalysts

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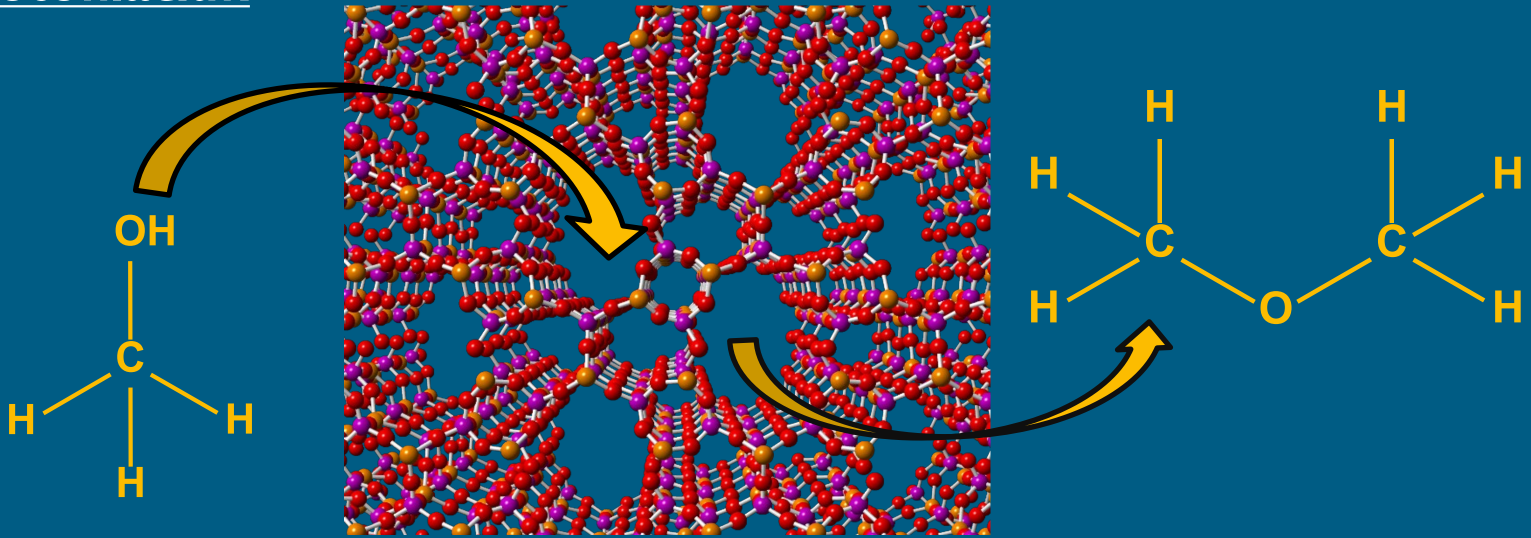

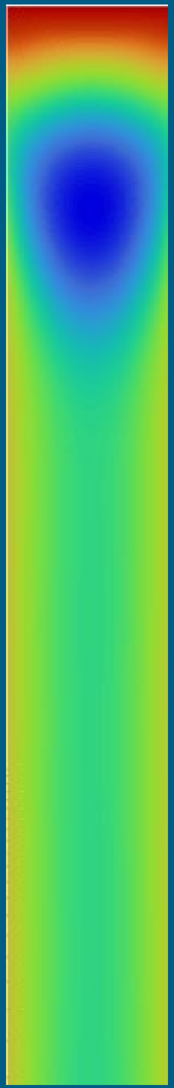

Outline

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- Dimethyl ether as a marine fuel
- SAPO-11 solid-acid catalyst
- Reaction parameters
- Kinetic & computational model

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The Need for Alternative Marine Fuels

Vehicle and duty cycle compatibility		Synthetic fuels	Electricity
City car			
Long distance car			
Urban van			
Heavy-duty truck			
Aviation	Short haul		
	Long haul		
Marine	Short journey		
	Long journey		
Distribution and refuelling challenge			

Refuelling infrastructure challenge

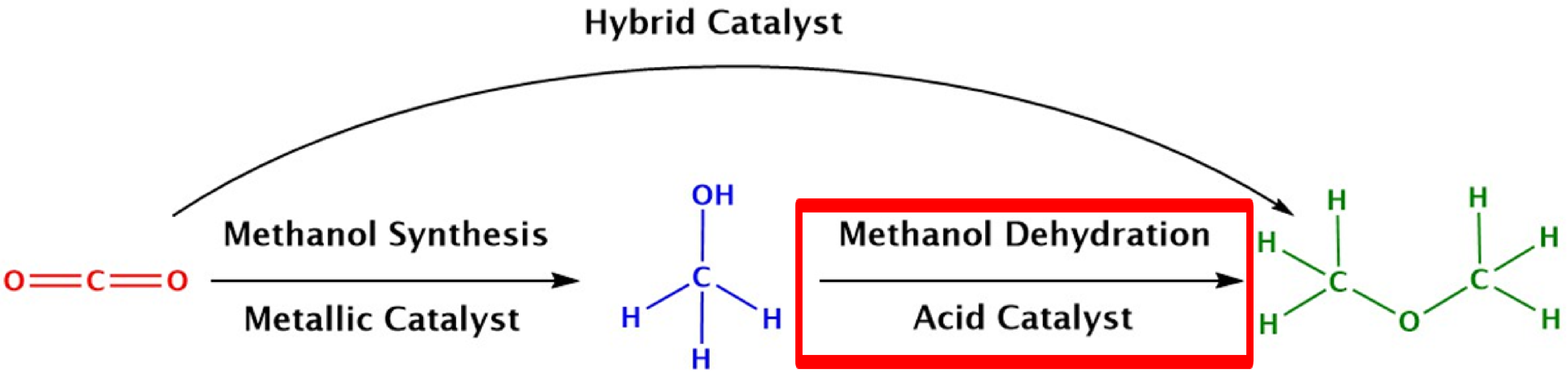
Distribution infrastructure challenge

Adapted from: The Royal Society, Sustainable synthetic carbon based fuels for transport: Policy briefing, 2019.

Challenging to electrify long haul marine transport

Dimethyl Ether as a Sustainable Alternative

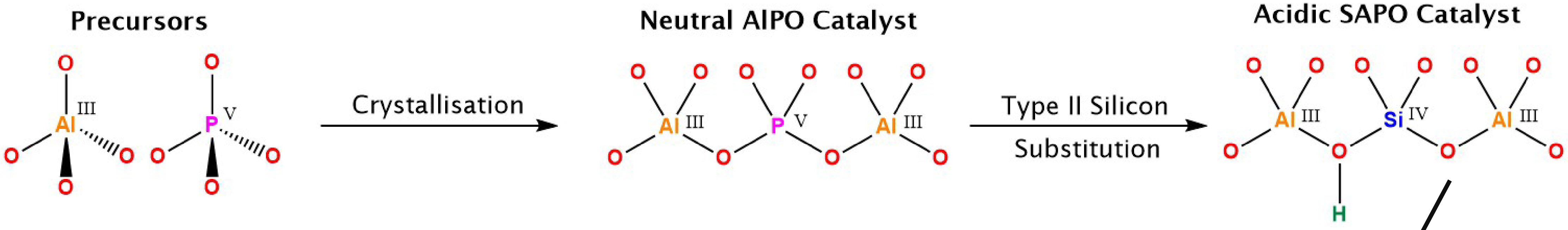
- Non-toxic, non-carcinogenic, similar to LPG[1]
- Obtain from MeOH using acid catalyst or from CO_2 using hybrid catalyst[1]
- Need to optimise acid functionality & MeOH dehydration reaction



[1] G. A. Olah, A. Goeppert and G. K. S. Prakash, Journal of Organic Chemistry, 2008, 74, 487– 498

DME can be a sustainable marine fuel

SAPO-11 as a Solid-acid Catalyst



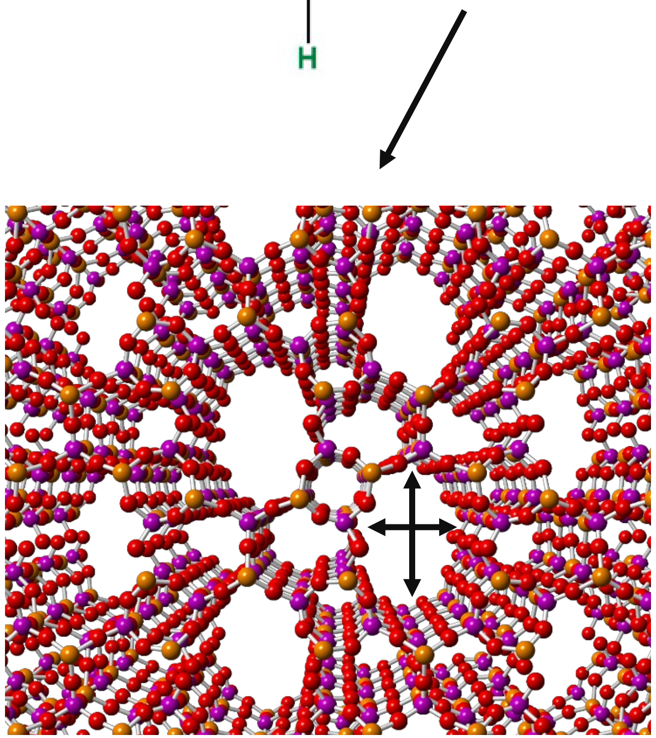
Catalyst	DME Selectivity (%)
SAPO-5	68[1]
SAPO-11	**100[1]**
SAPO-34	93[2]
H-ZSM-5	95[2]

AEL

1D elliptical channels (4.0 x 6.5 Å)

Medium pore

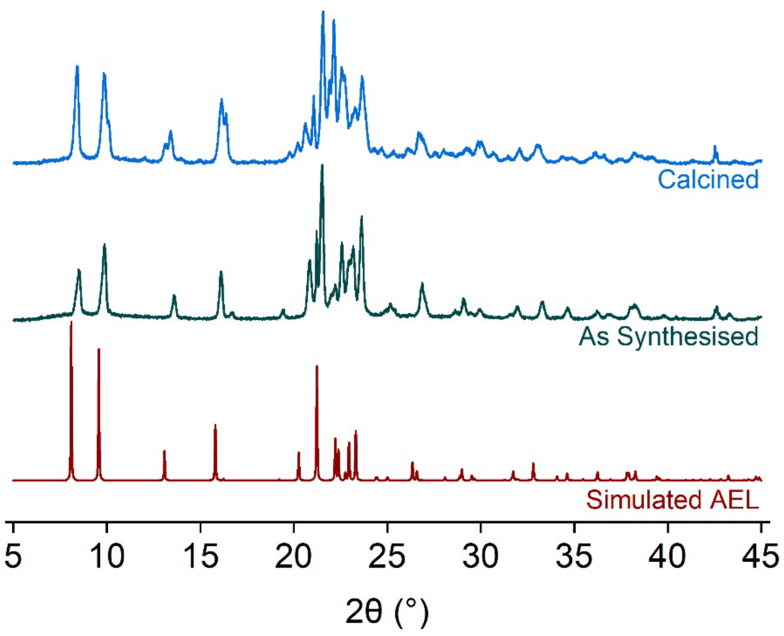
Weak to medium acid sites[1]

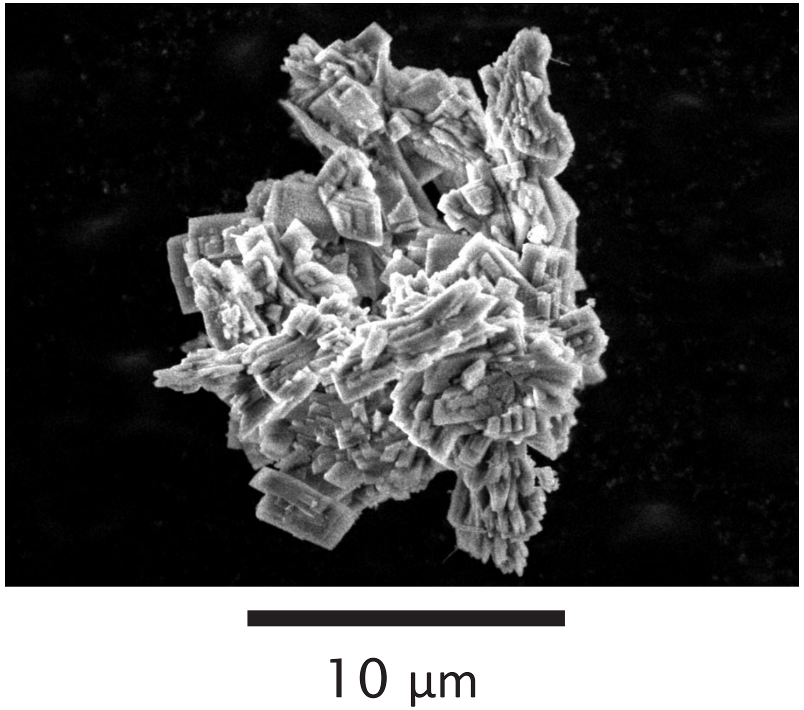


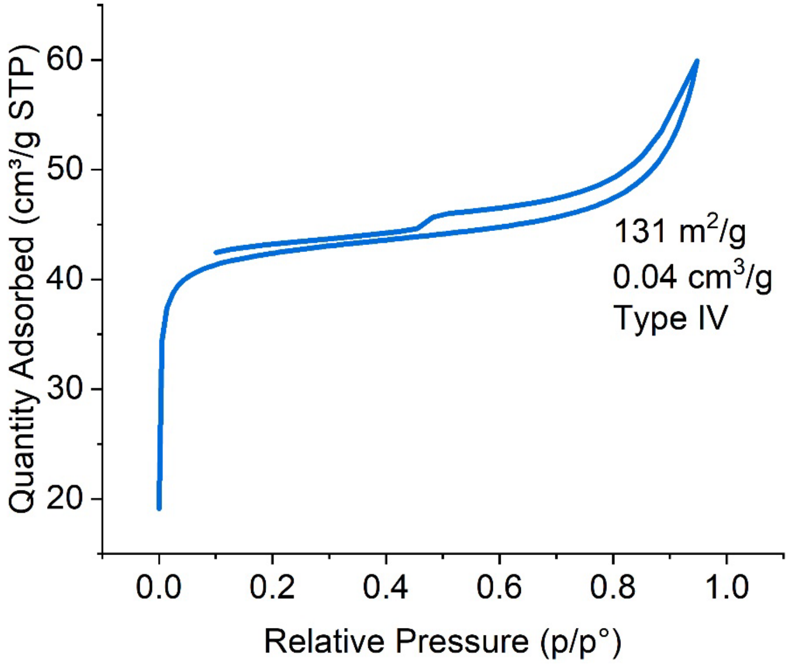
[1] W. Dai, W. Kong, G. Wu, N. Li, L. Li and N. Guan, Catalysis Communications, 2011, 12, 535– 538
[2] E. Catizzone, A. Aloise, M. Migliori and G. Giordano, Microporous and Mesoporous Materials, 2017, 243, 102–111.

SAPO-11 is 100% selective for DME

SAPO-11 Characterisation







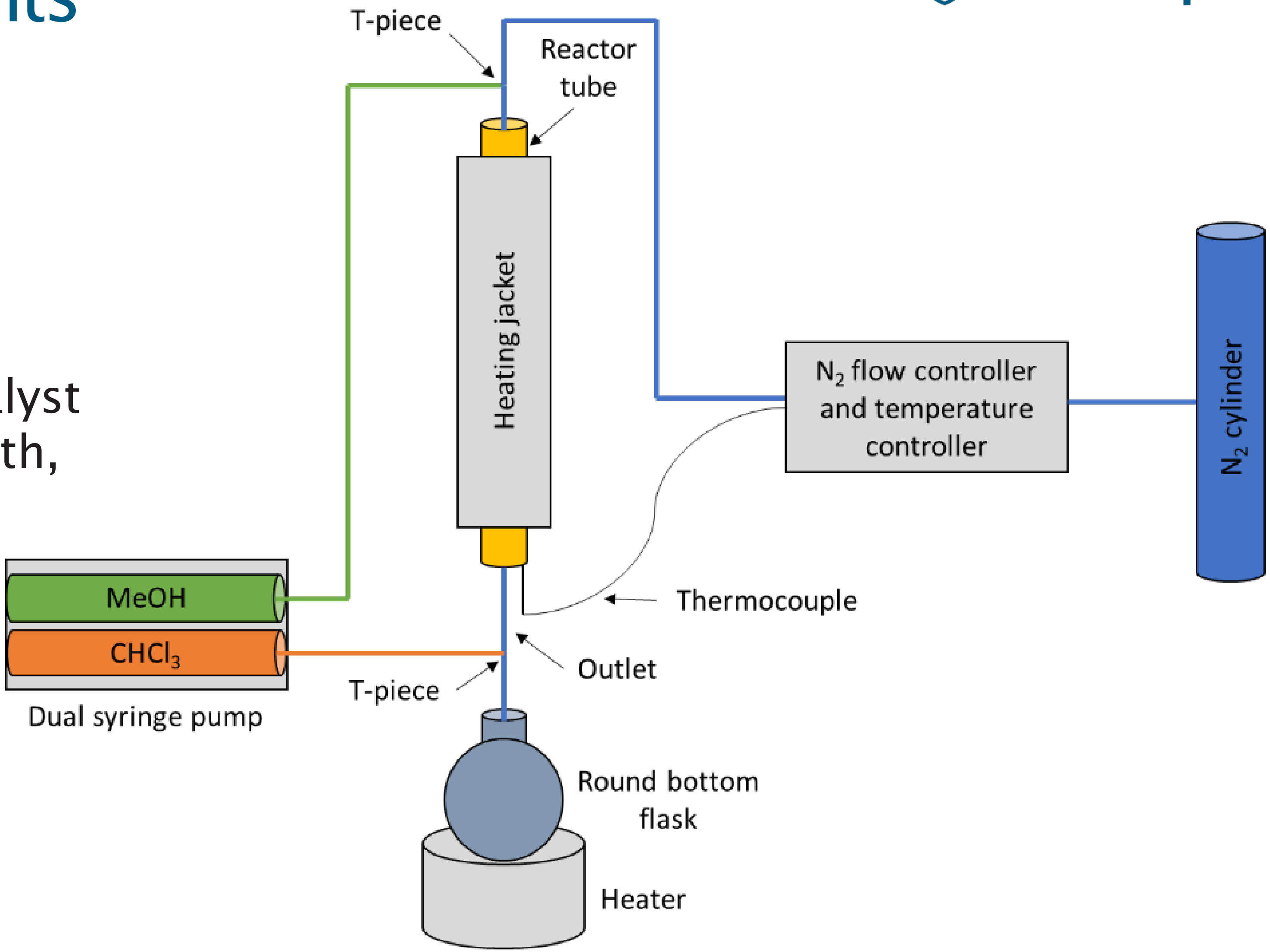
EDS: 21.4 P, 20.9 Al, 2.5 wt% Si

ICP: 21.4 P, 19.4 Al, 2.7 wt% Si

Weak acid site SAPO-11 successfully synthesised

Reactor and Experiments

- Fixed bed reactor
- MeOH (7-31 mol%) in N_2
- $CHCl_3$ external standard
- Investigated temperature, catalyst particle size, catalyst bed length, MeOH WHSV, MeOH concentration & stability

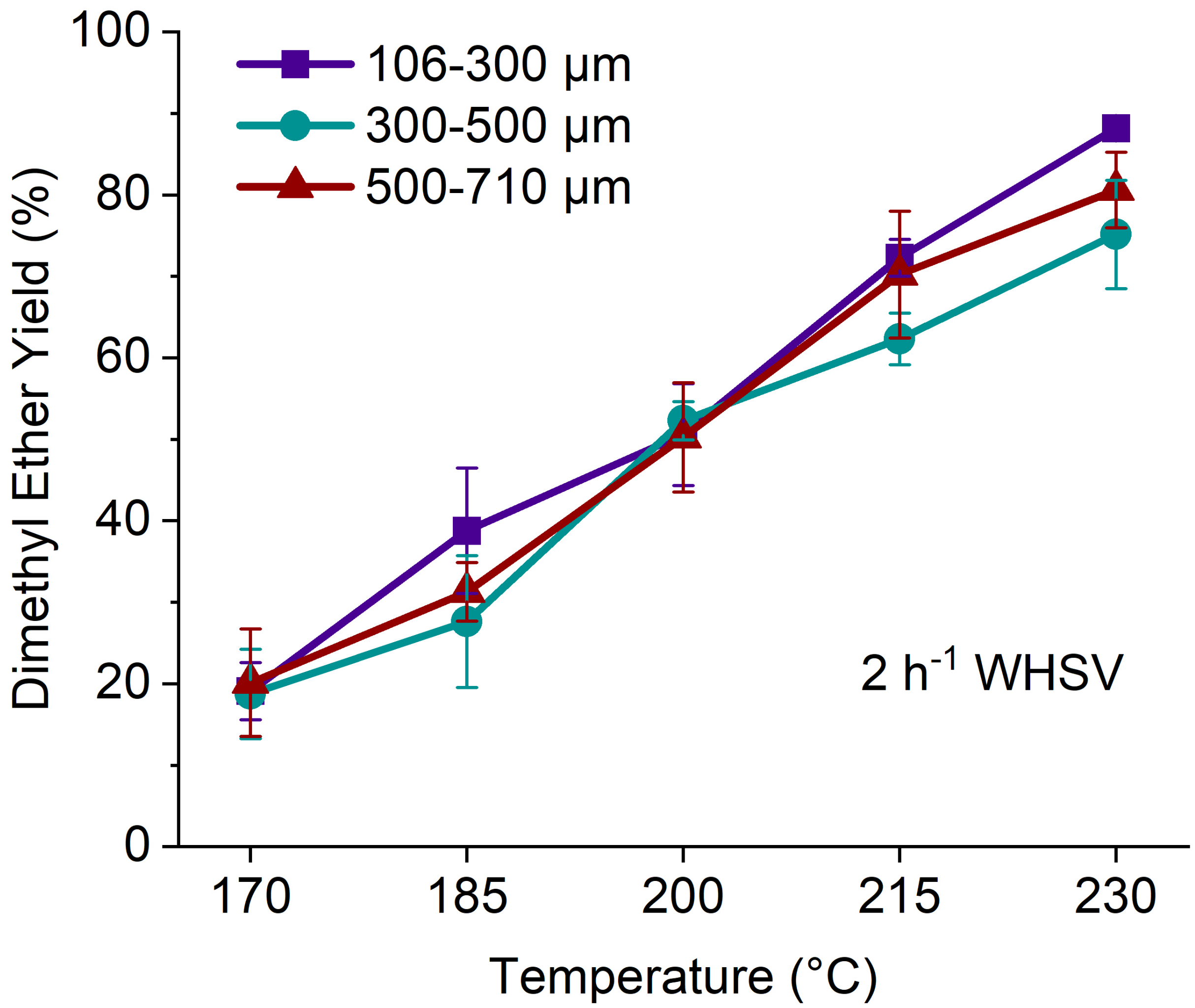


All experiments performed in triplicate

Particle Size Effect on DME Yields

- Particle sizes tested: **106-300**, **300-500** and **500-710** μm
- Sieved 5x
- Limited effect

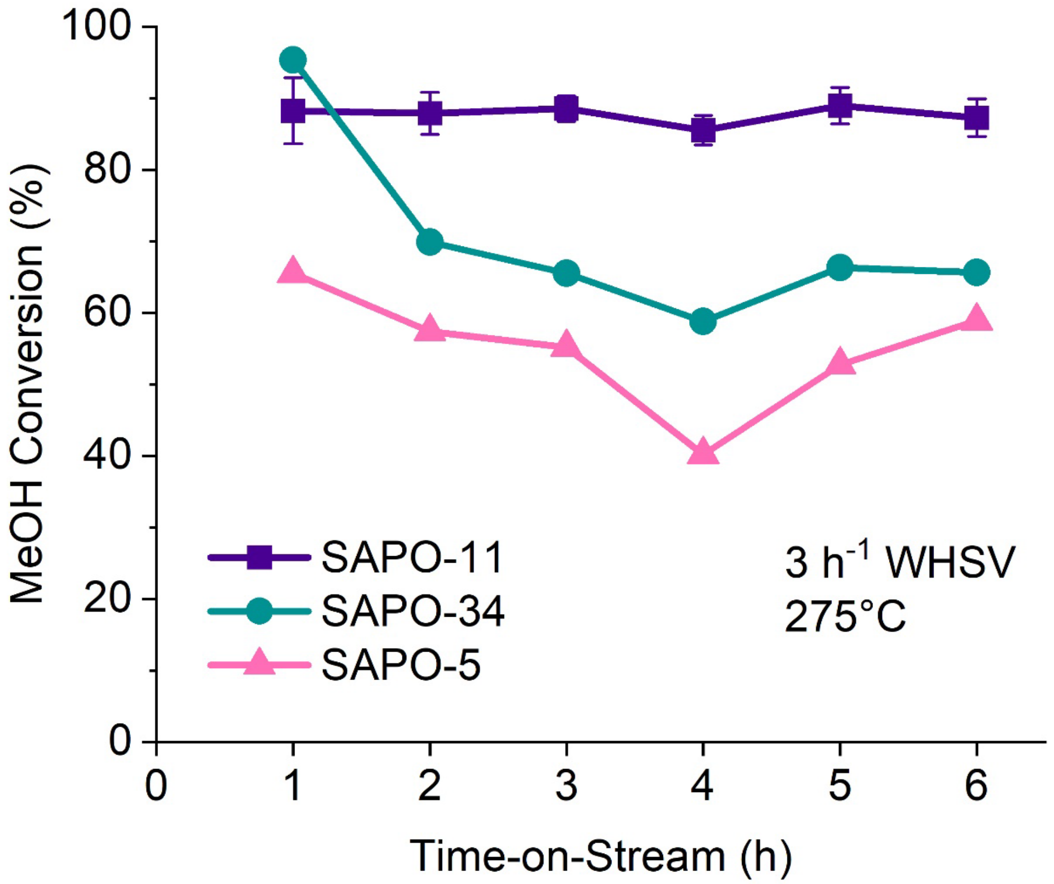
- **106-300** μm selected for subsequent experiments



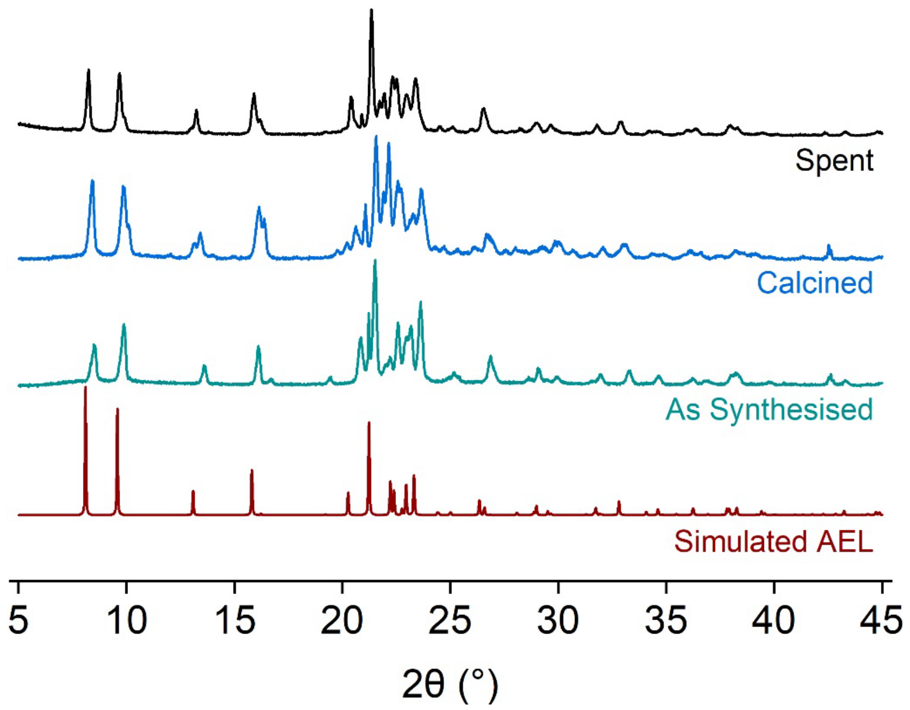
Operating in kinetic limited regime

SAPO-11 Time-on-Stream Stability

- CHN: 1.35 wt% C



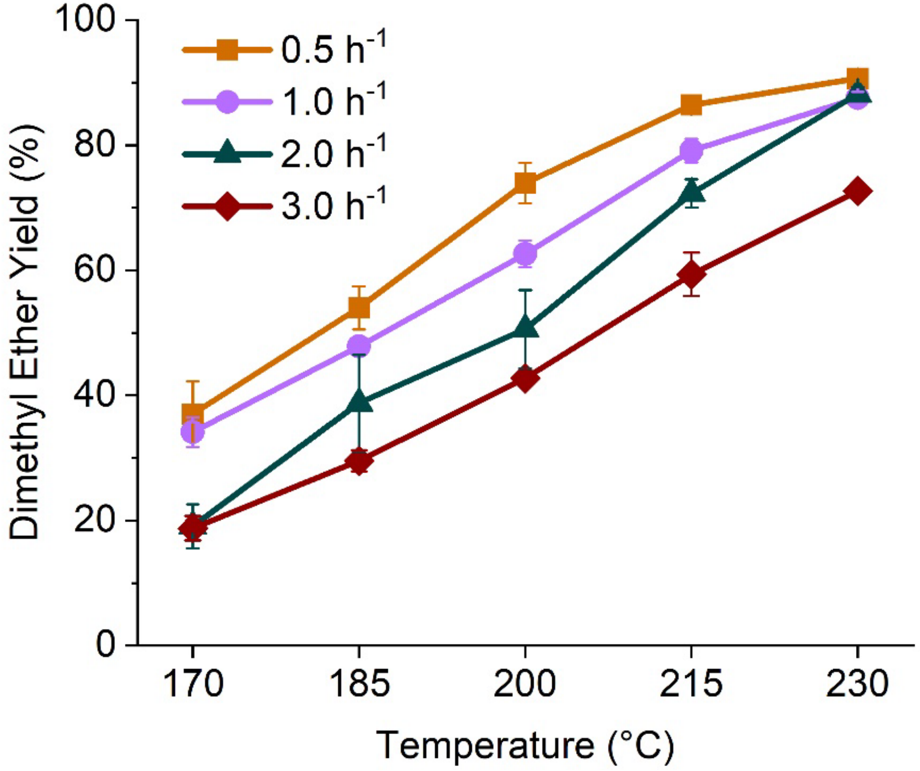
Catalyst	TGA Mass Loss (wt%)
SAPO-5	7
SAPO-11	**2**
SAPO-34	19

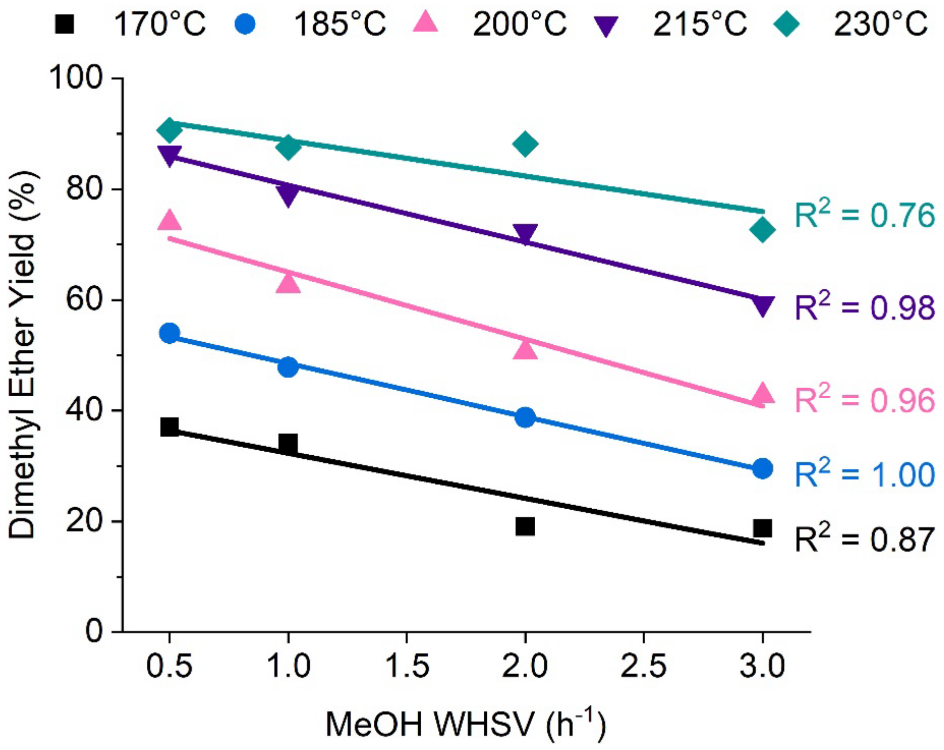


SAPO-11 remains stable during MeOH dehydration

MeOH Weight Hourly Space Velocity Effect on DME Yields

- **High WHSV** → low residence time & high MeOH concentration
- Active site saturation or short residence time?

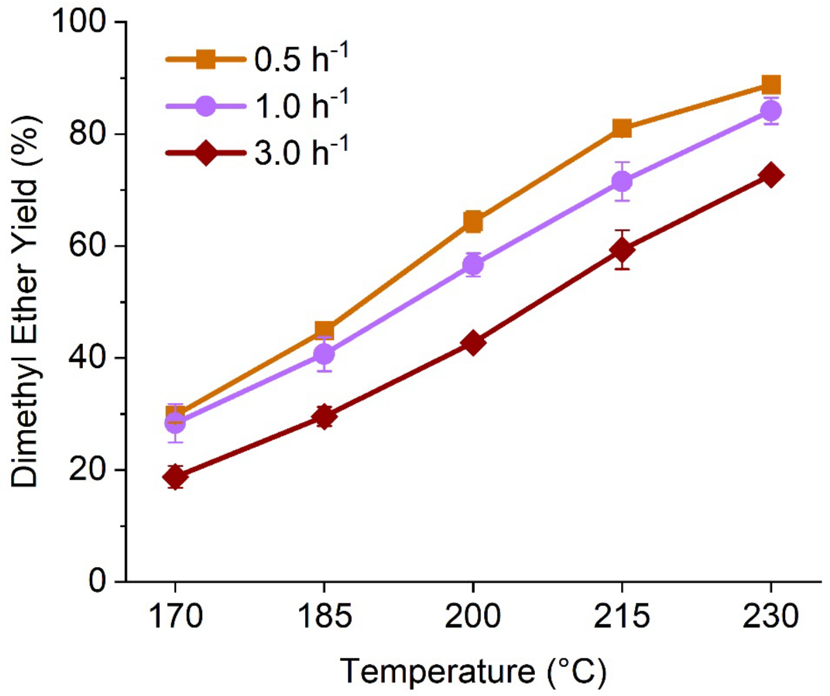


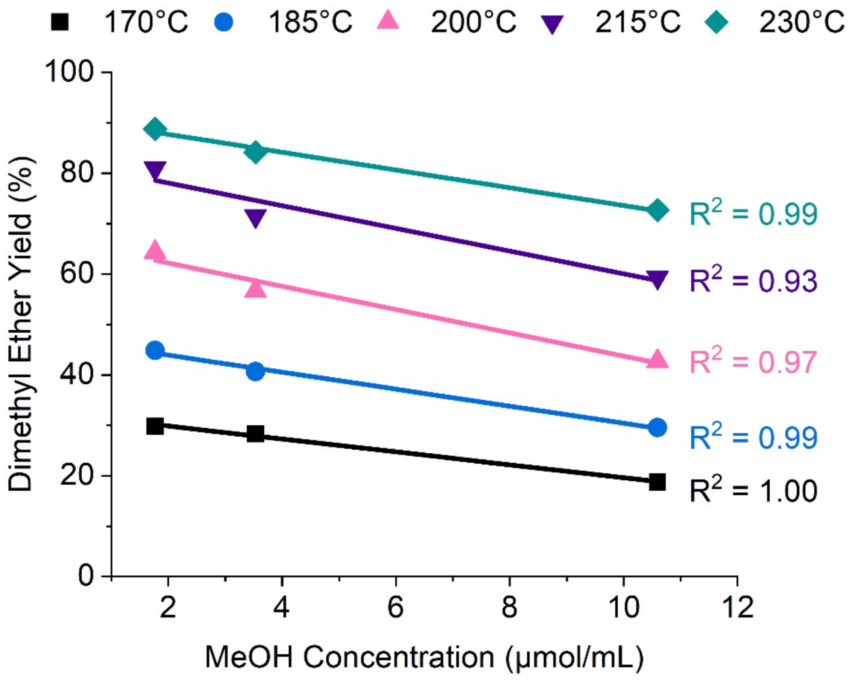


Inverse relationship between DME yields and MeOH WHSV

MeOH Concentration Effect on DME Yields

- N_2 carrier gas flow varied
- Lower residence time → lower DME yields
- Linear dependence of DME yields on MeOH concentration





Active site saturation & residence time affect DME yields

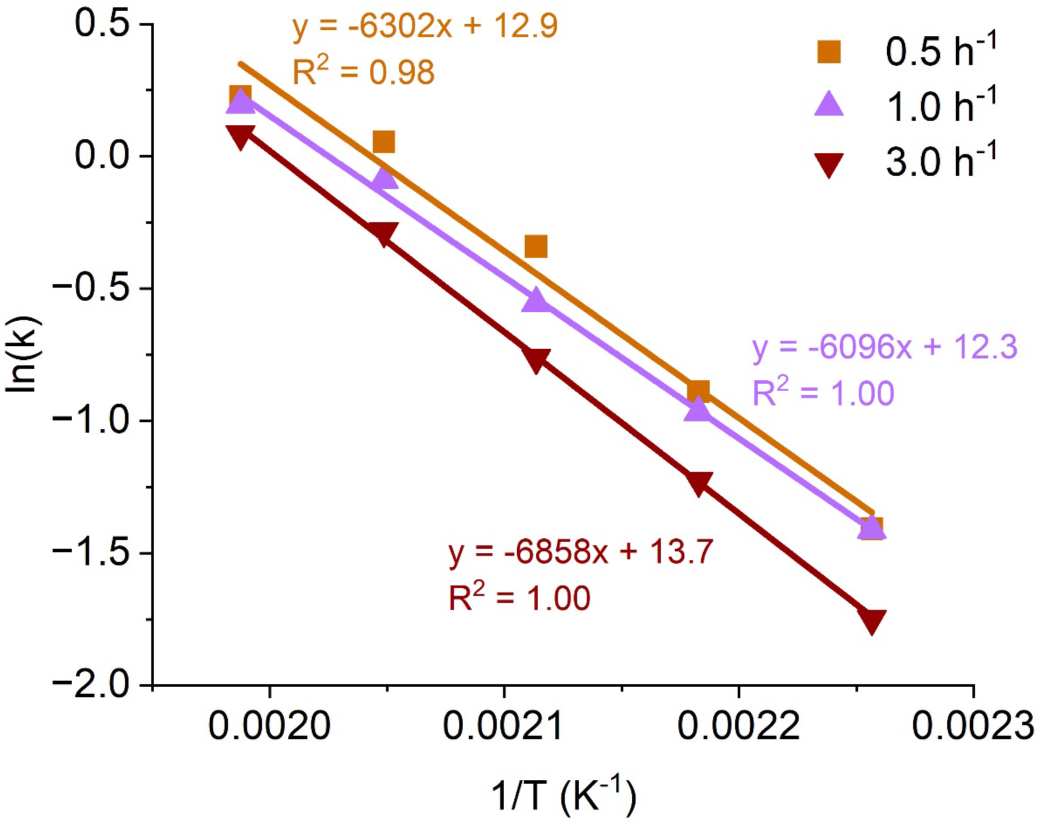
Kinetic and Computational Fluid Dynamics Model

Copasi - Kinetics

- 1st Order Arrhenius
- Average: $A = 5.1 \times 10^5\ s^{-1}$, $E_a = 53.4\ kJ\ mol^{-1}$
- Kinetic results similar to those obtained by Catizzone *et al.* for various zeolites[1]

Ansys Fluent - CFD

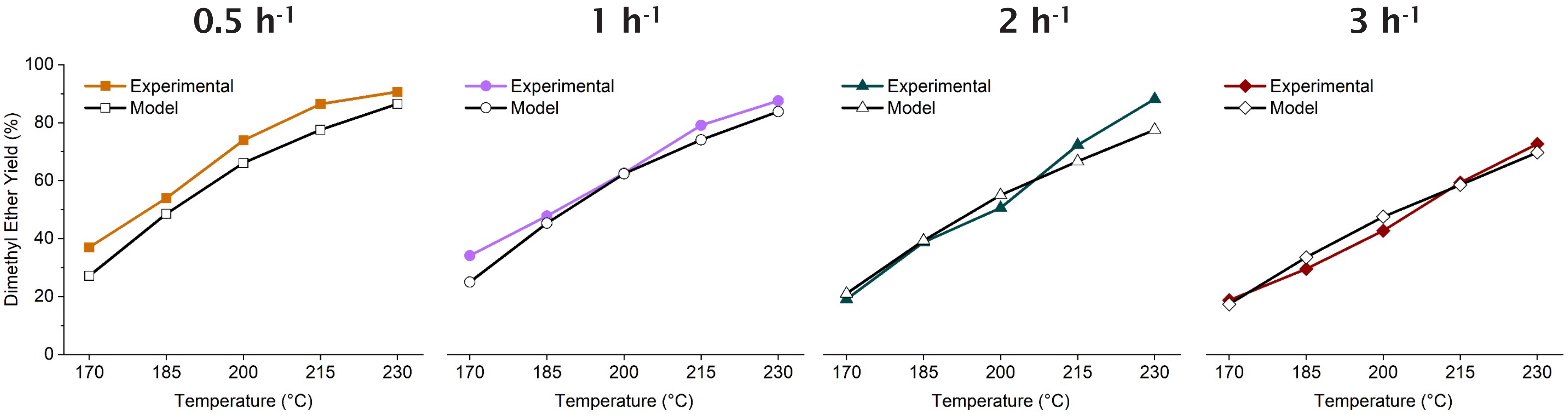
- Custom code to describe reactor & reaction
- Cylindrical geometry – porous medium
- Employ kinetics obtained via Arrhenius plot



[1] E. Catizzone, E. Giglio, M. Migliori, P. C. Cozzucoli and G. Giordano, *Materials*, 2020, **13**, 5577

Simple kinetic & CFD model built using Copasi & Ansys Fluent

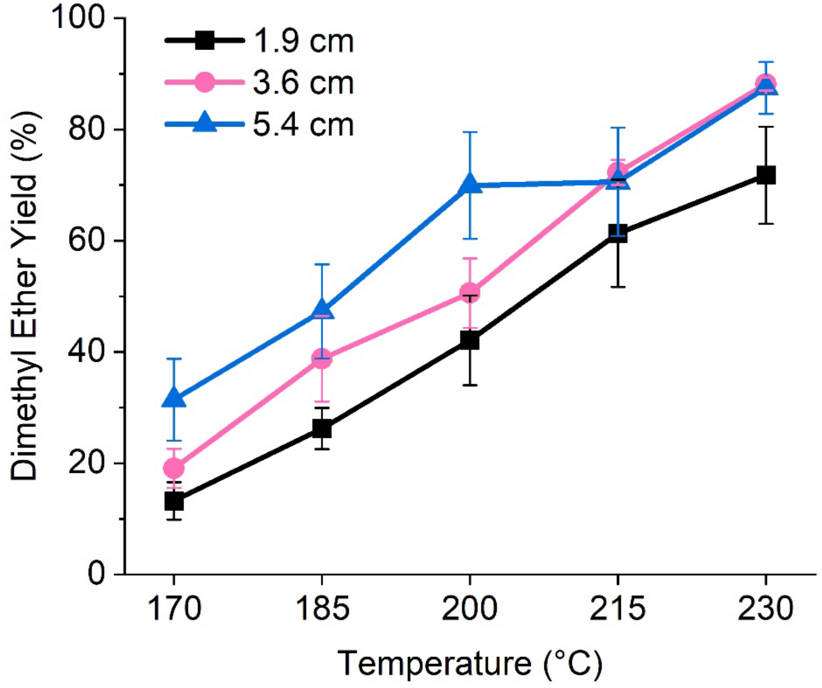
Experiment vs Model at Different MeOH Weight Hourly Space Velocity

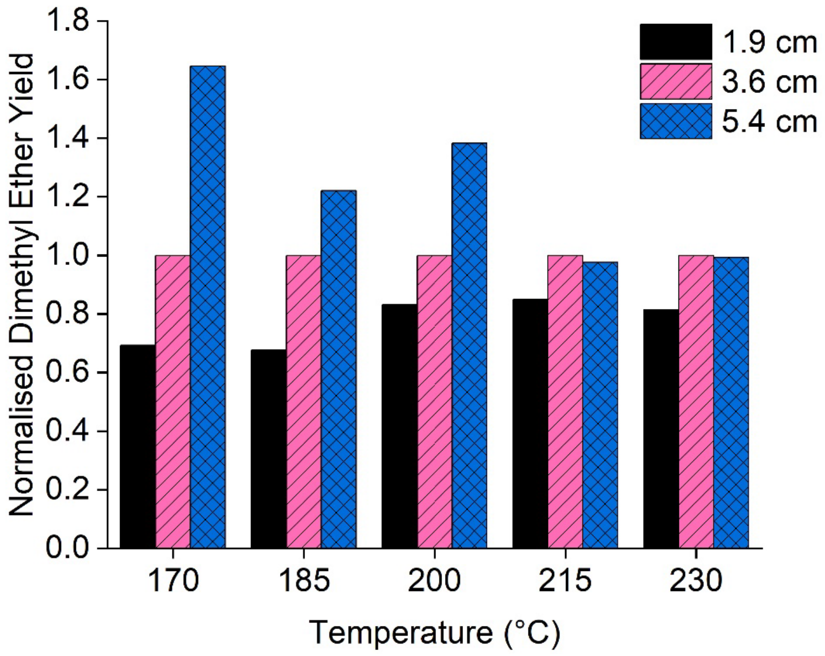


CFD model is able to replicate experimental DME Yields

Catalyst Bed Length Effect on DME Yields

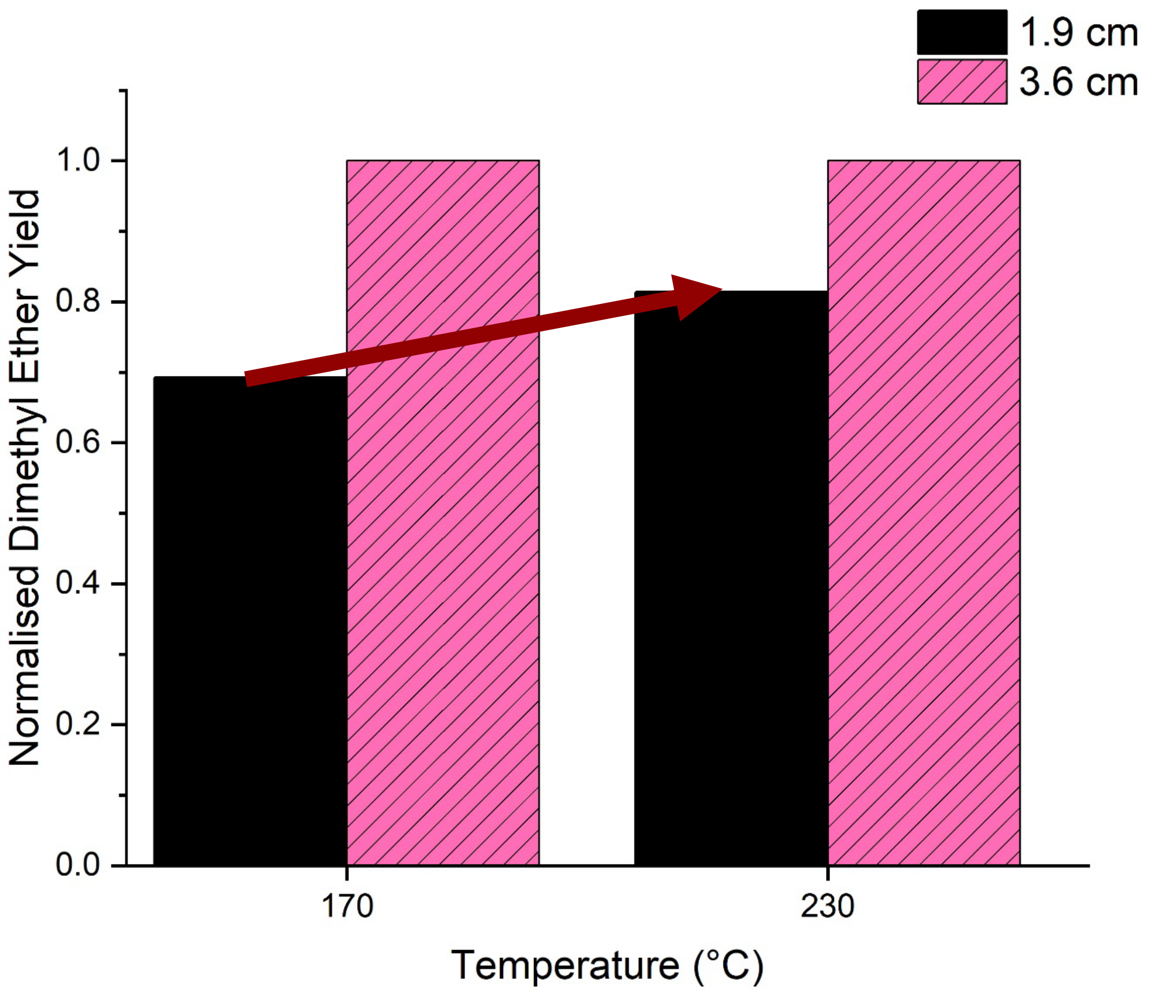
- Bed lengths tested: **1.9**, **3.6** and **5.4** cm
- **Longer** catalyst bed length → higher yield*
- **Half** of catalyst bed can give up to 80% of DME yield compared to **full** catalyst bed

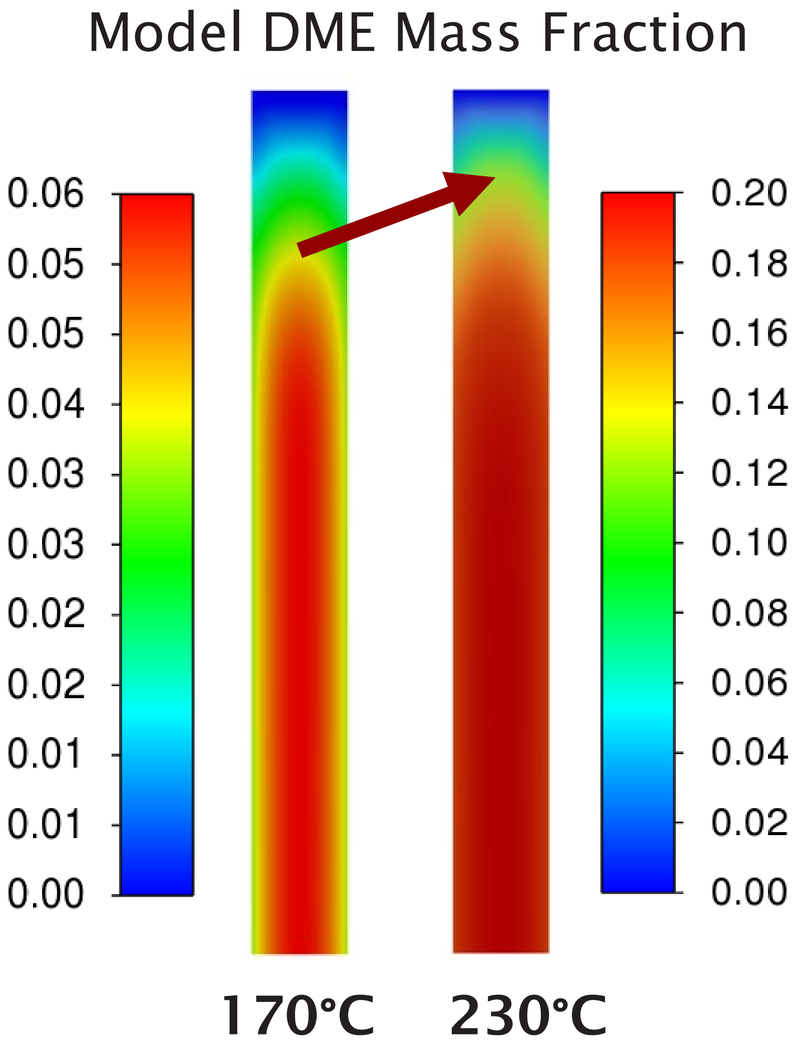




Reaction occurs predominantly early on in the catalyst bed

Location of Reaction Inside the Bed





Experiment and model predict reaction taking place early in bed

Location of Temperature Hotspot Inside the Bed

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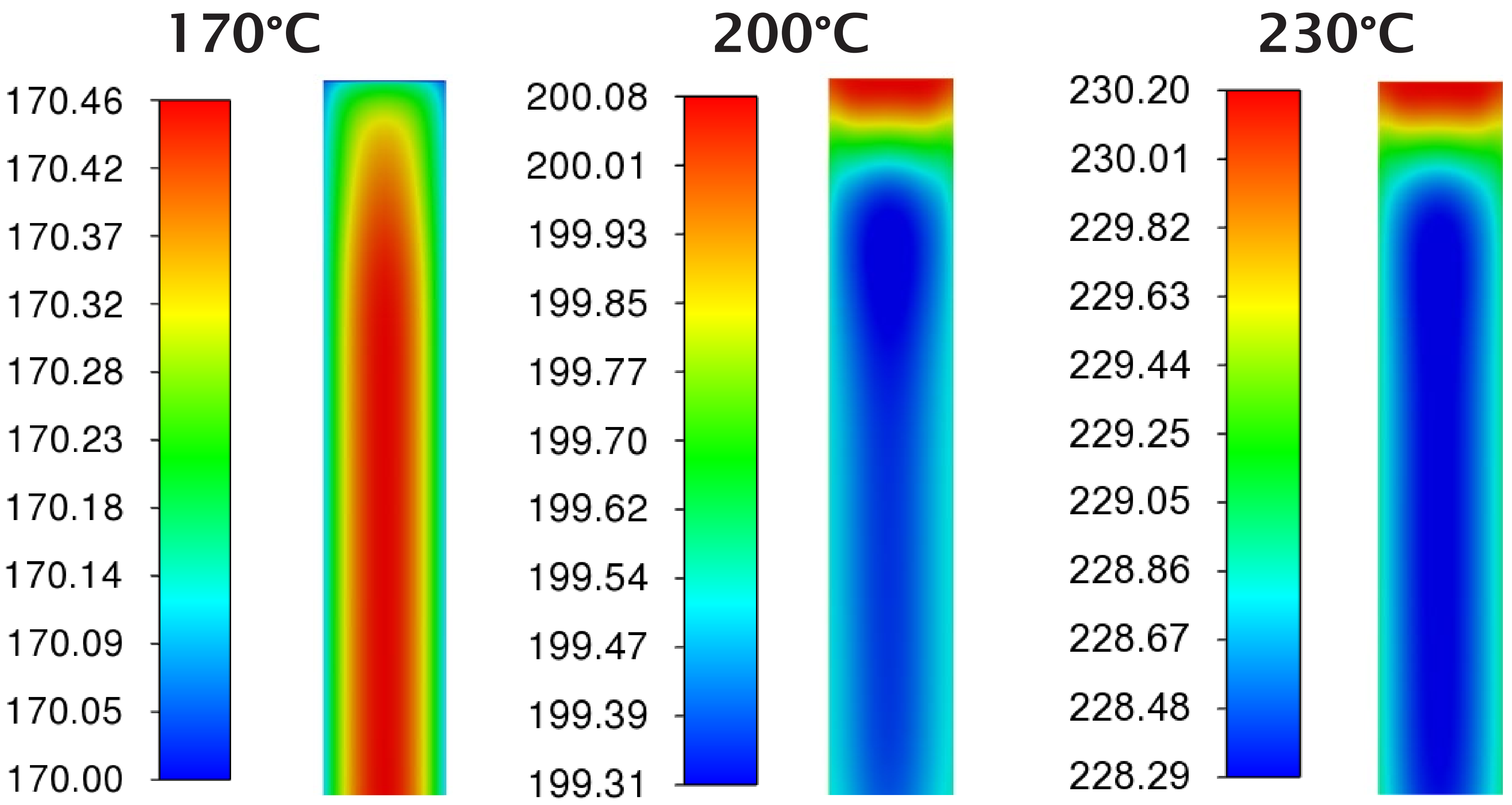
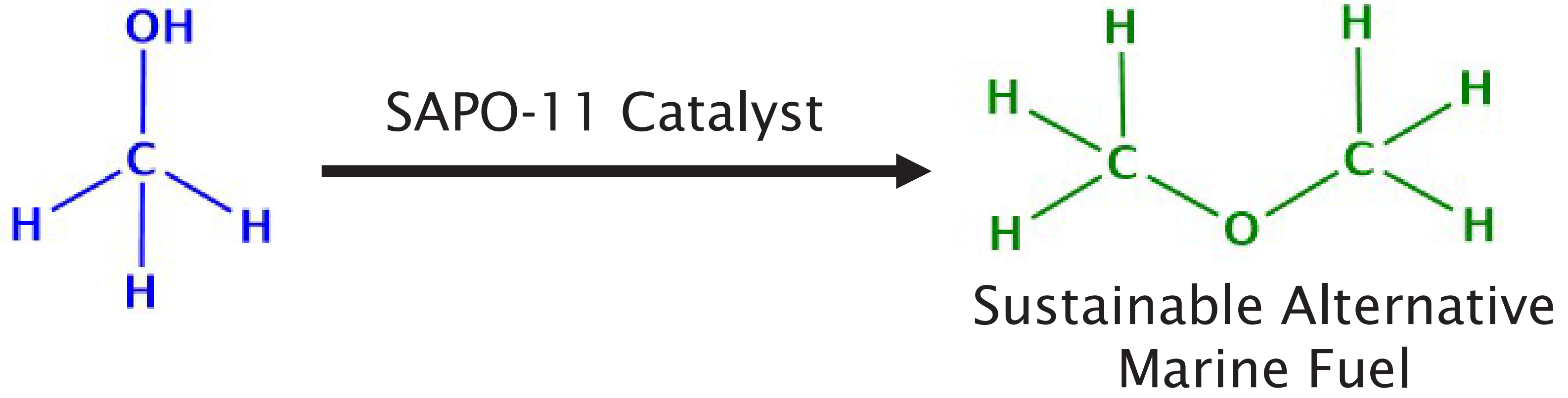


Hotspot moves towards inlet of bed at higher temperatures

Conclusions & Future Work

- ✓ Dimethyl ether is a sustainable alternative marine fuel which can be produced using highly active, selective and stable SAPO-11 catalyst
- ✓ Thorough experimentation enabled the creation of kinetic and computational models to better understand SAPO-11 catalysed methanol dehydration
- ✓ Our computational models replicate experimental results and behaviours and can be used to aid catalytic optimisation and predict outcomes

- ➢ Develop more complex, detailed kinetic and CFD models



Acknowledgements

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Southampton Marine & Maritime Institute

Thank you for your attention.
Any questions?

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