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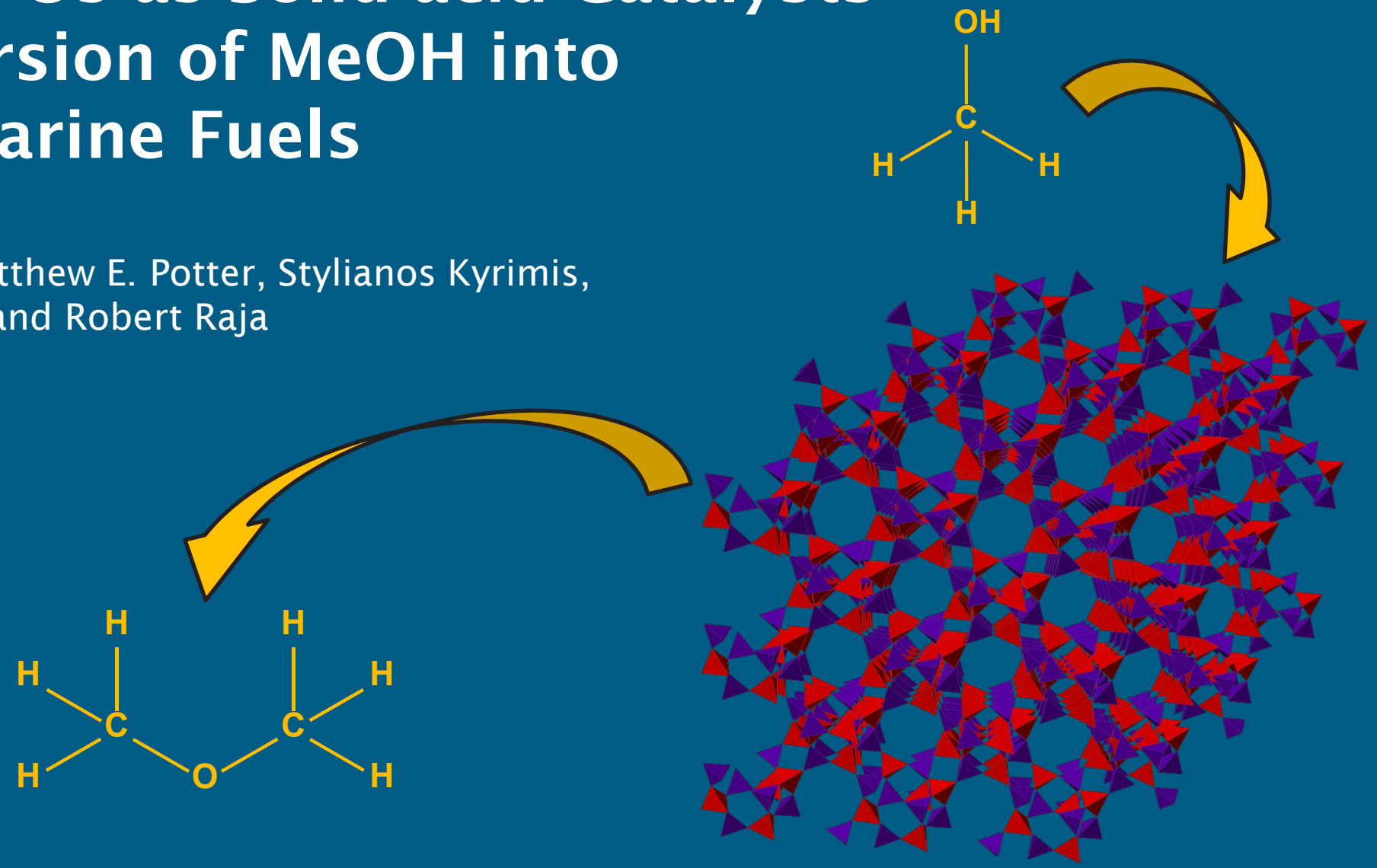
AlPOs and SAPOs as Solid-acid Catalysts for the Conversion of MeOH into Sustainable Marine Fuels

Maciej G. Walerowski,* Matthew E. Potter, Stylianos Kyrimis, Lindsay-Marie Armstrong and Robert Raja



Outline

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- Dimethyl ether as a marine fuel
- SAPOs as solid-acid catalysts
- Structure–property correlations
- Kinetic & computational models

The Need for Alternative Marine Fuels

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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

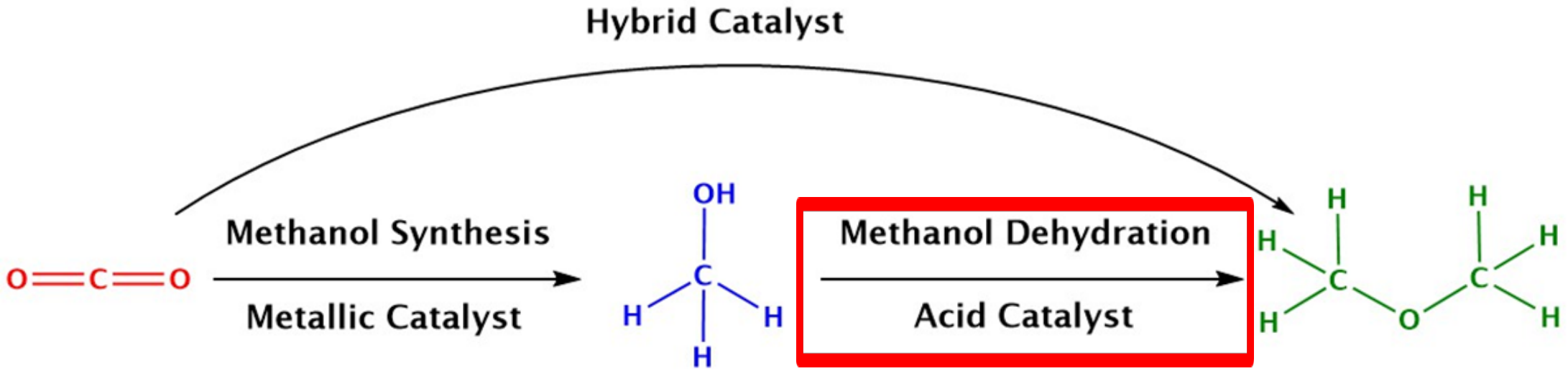
Distribution infrastructure challenge

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

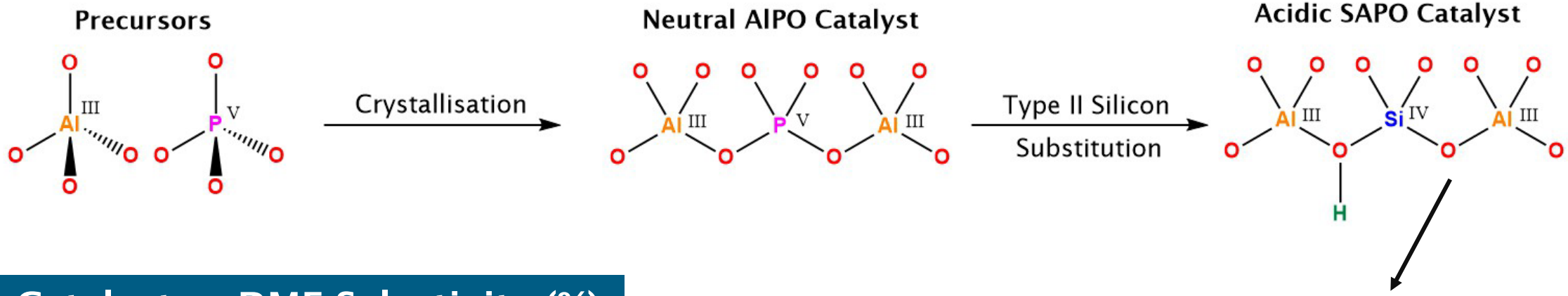
- Non-toxic, non-carcinogenic, similar to LPG[1]
- Obtain from MeOH using acid catalyst or from CO_2 using hybrid catalyst[1]
- Need to optimise acid functionality & MeOH dehydration reaction



[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

AlPOs & SAPOs as Solid-acid Catalysts



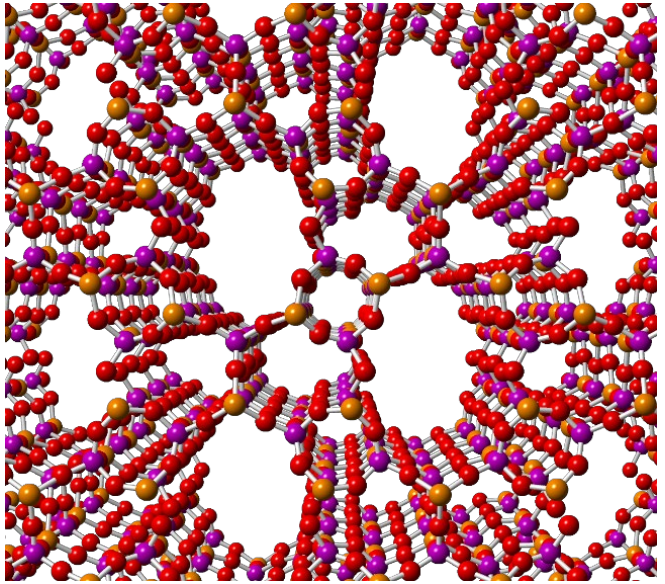
Catalyst	DME Selectivity (%)
AlPO-5	100[1]
SAPO-11	**100[1]**
MOR	94[2]
H-ZSM-5	95[2]

SAPOs

Weaker acid sites

Higher DME selectivity

Various topologies



[1] Dai *et al.*, Catalysis Communications, 2011, 12, 535– 538.
[2] Catizzone *et al.*, Microporous and Mesoporous Materials, 2017, 243, 102–111.

AlPOs & SAPOs can show quantitative DME selectivity

AlPOs & SAPOs Investigated

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AlPO-5/SAPO-5

AFI, 12T, 7.3 Å

AlPO-11/SAPO-11

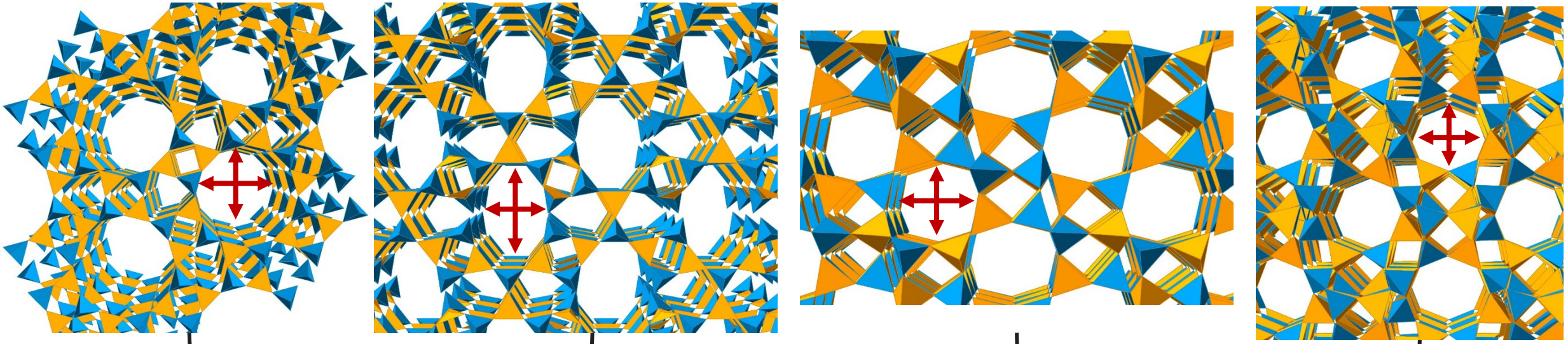
AEL, 10T, 4.0 x 6.5 Å

AlPO-18/SAPO-18

AEI, 8T, 3.8 Å

SAPO-34

CHA, 8T, 3.8 Å



1D Channels

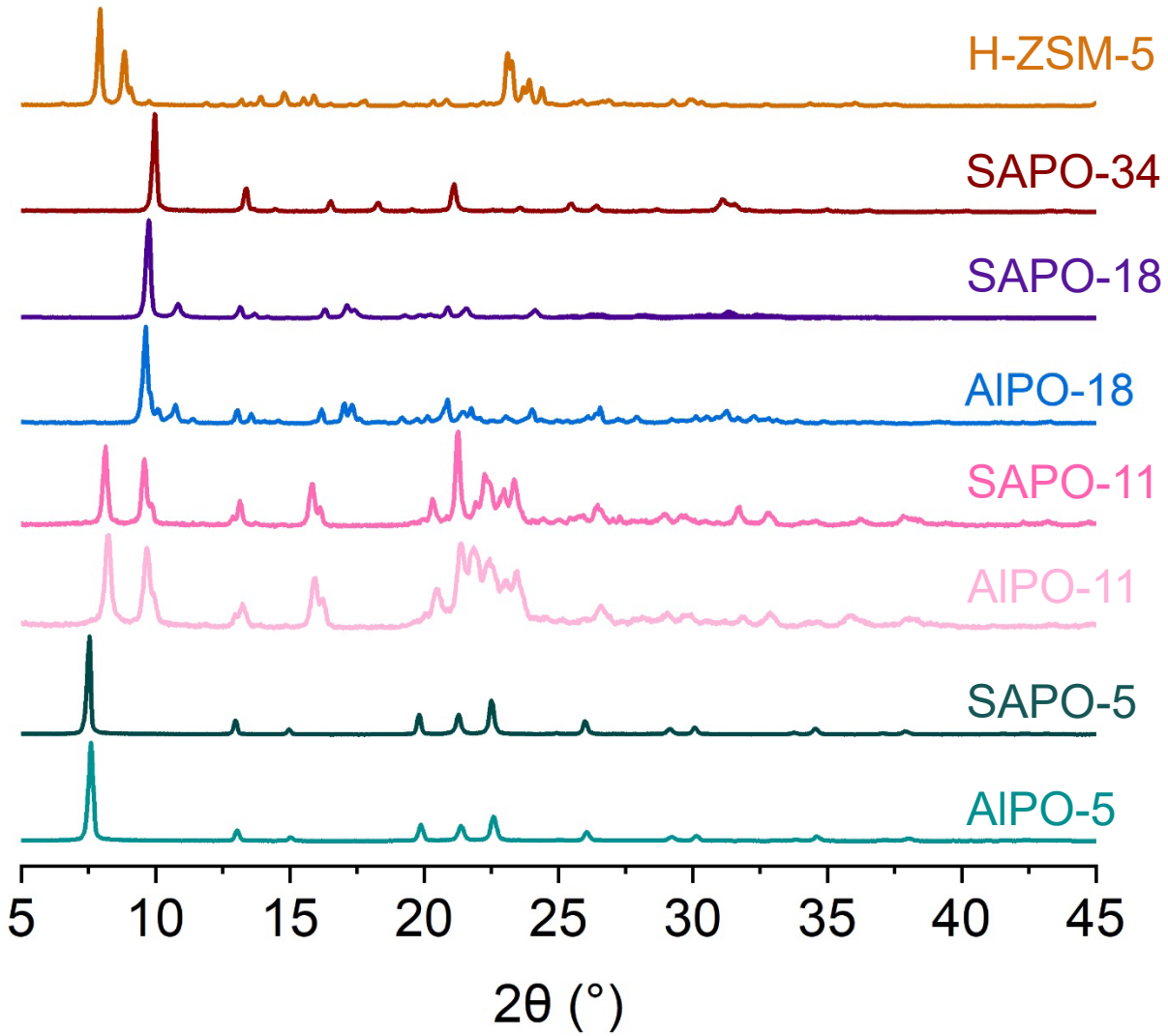
Weaker Acidity

3D Cages

Stronger Acidity

Various topologies & acid sites investigated

Powder X-Ray Diffraction

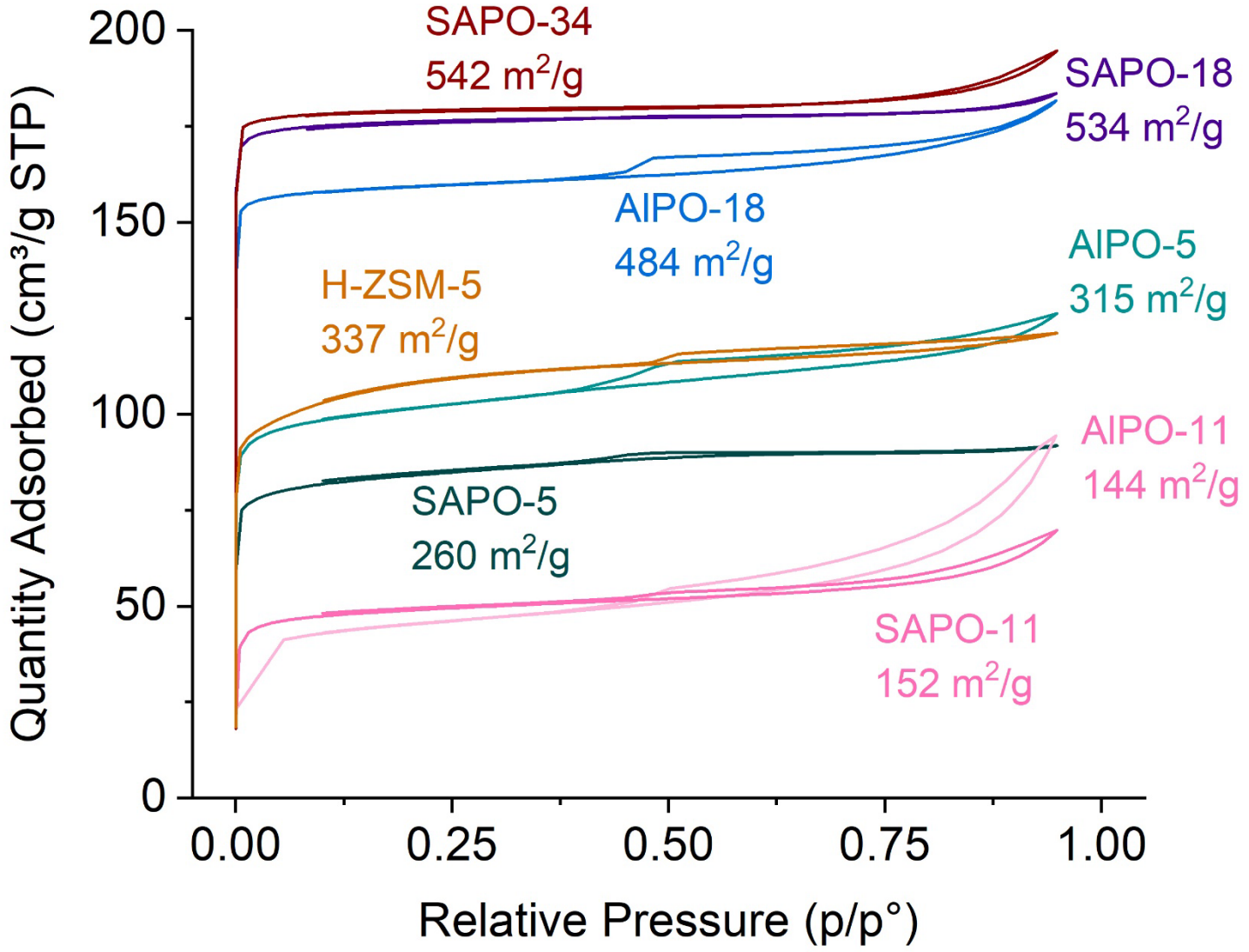


- AlPOs & SAPOs identical patterns
- Phase pure with respect to simulated pattern
- AlPO-5, SAPO-5, SAPO-18, SAPO-34 & H-ZSM-5 highly crystalline

All synthesised catalysts were phase pure

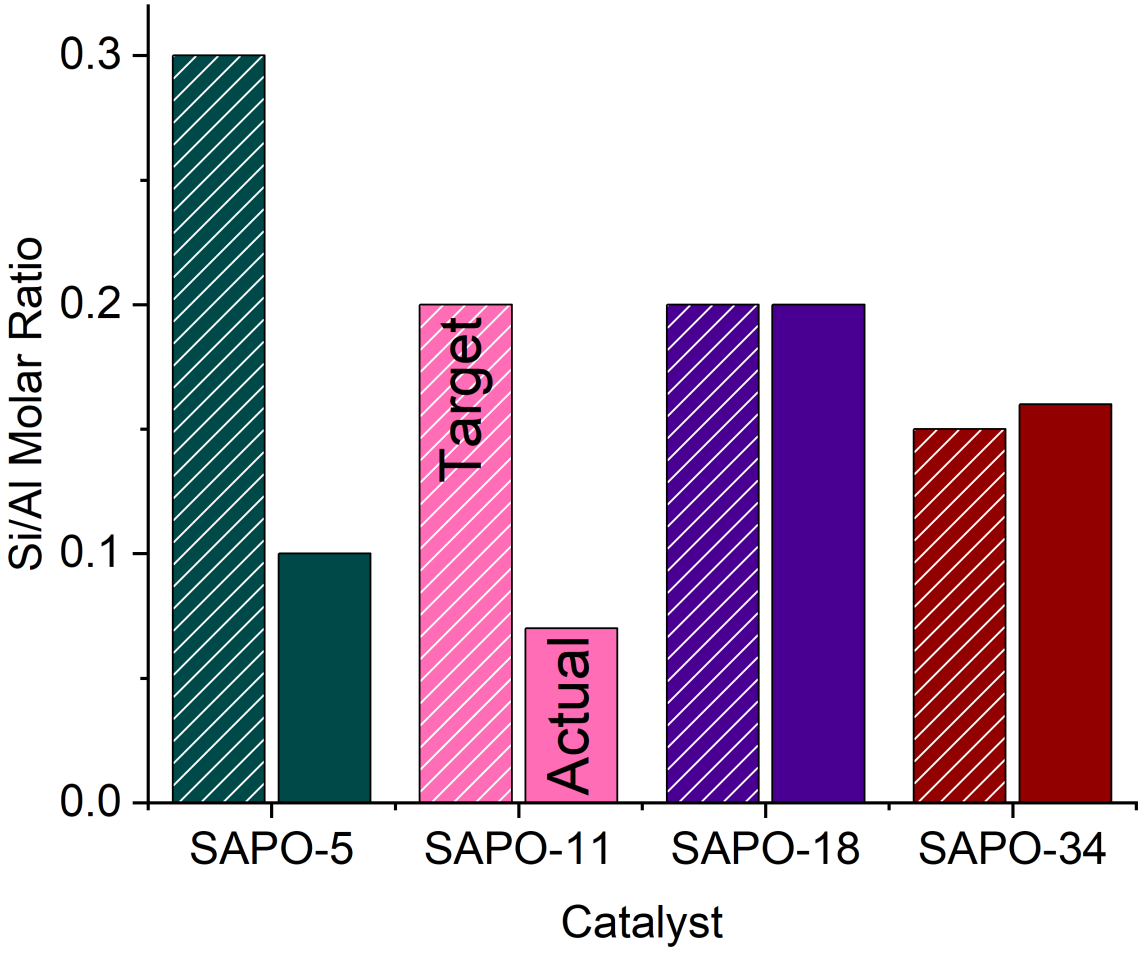
Surface area & porosity

- Type I: SAPO-5, SAPO-18, SAPO-34
- Type IV: AlPO-5, AlPO-11, SAPO-11 AlPO-18, H-ZSM-5
- H4 hysteresis loop



BET surface areas in expected ranges

EDS Elemental Composition



- Each SAPO has an optimum Si/Al ratio
- Only 33% Si incorporated in SAPO-5 & SAPO-11
- Challenging to control Si loading

Si loading is framework dependent to an extent

SEM Imaging

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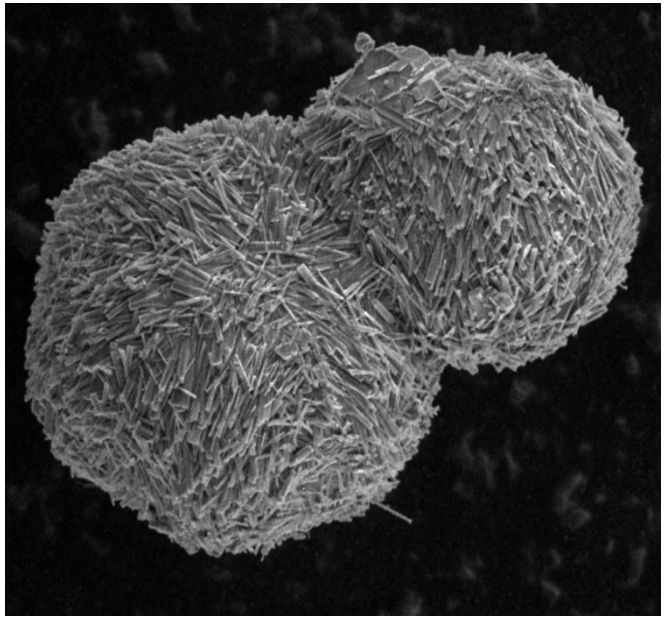
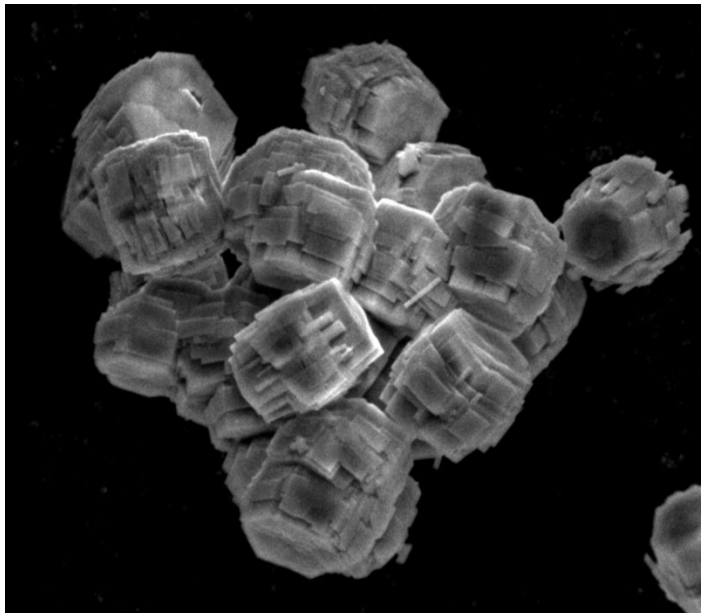


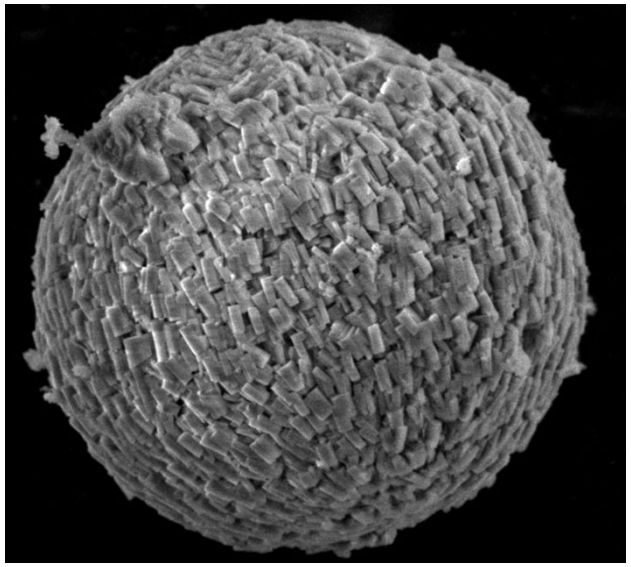
AlPO-5

~29 µm



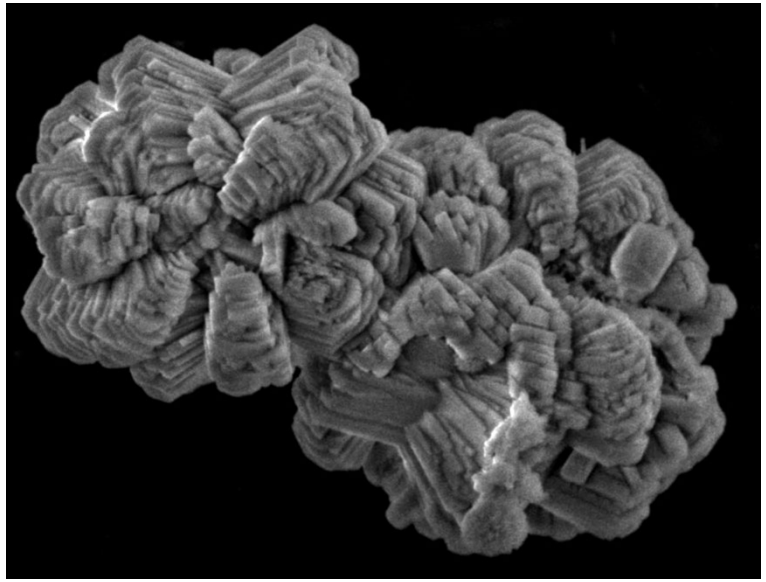
SAPO-5

~3 µm



AlPO-11

~18 µm



SAPO-11

~9 µm

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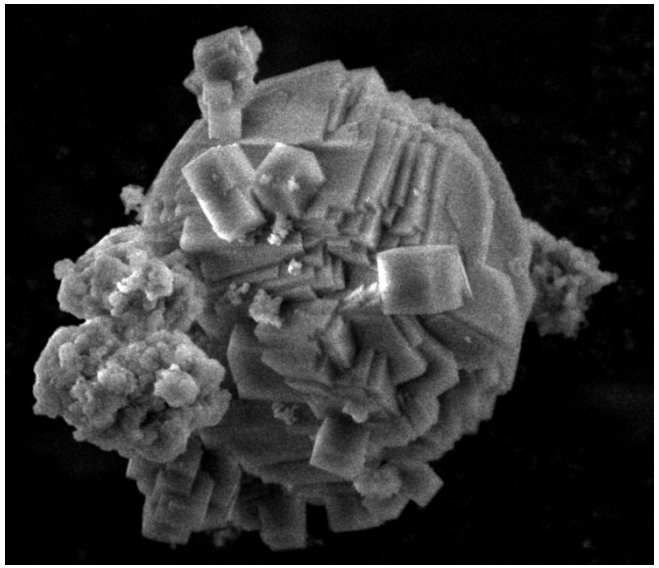
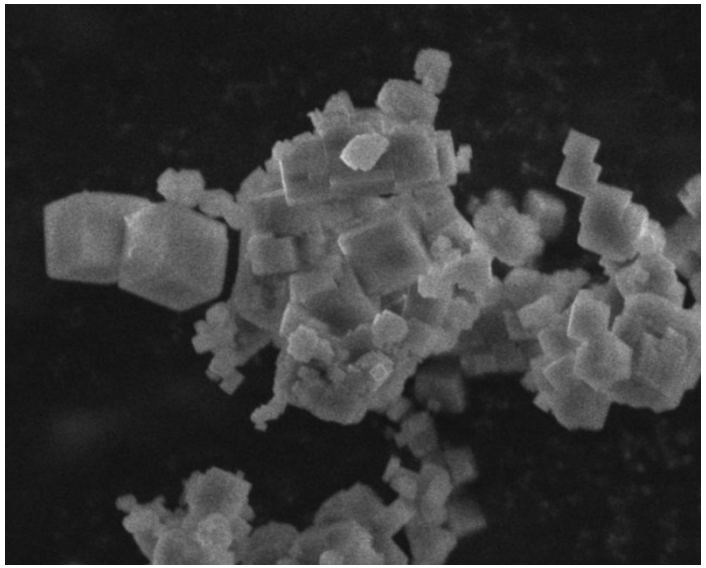


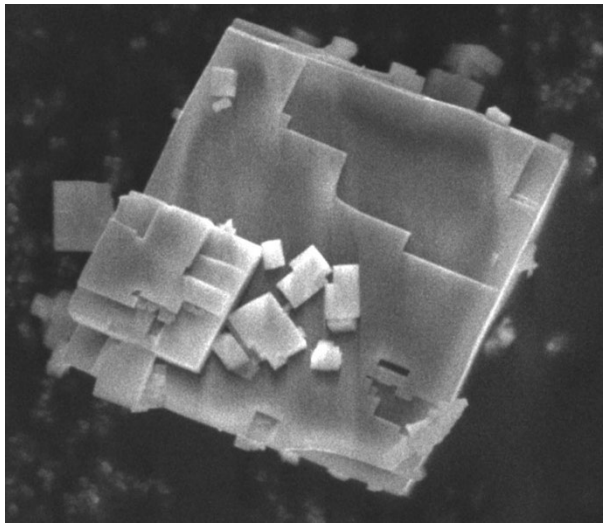
AlPO-18

~18 μm



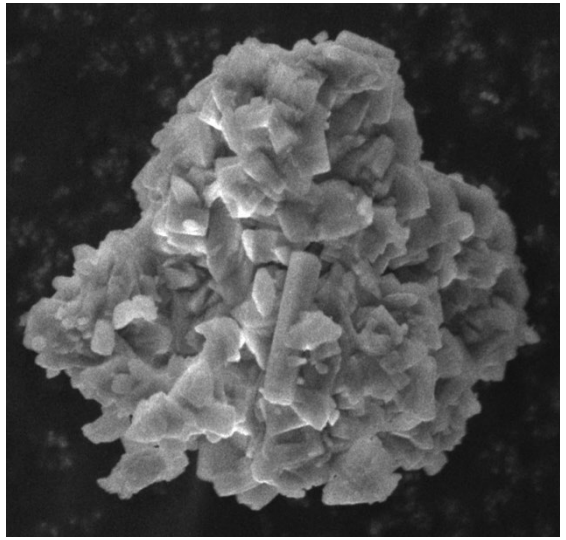
SAPO-18

<1 μm



SAPO-34

~2 μm

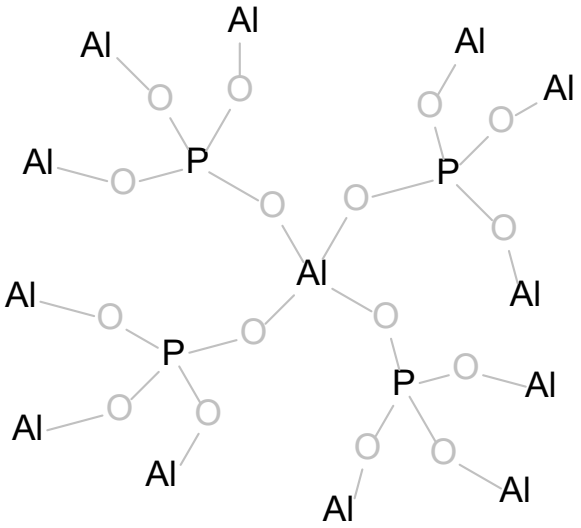


H-ZSM-5

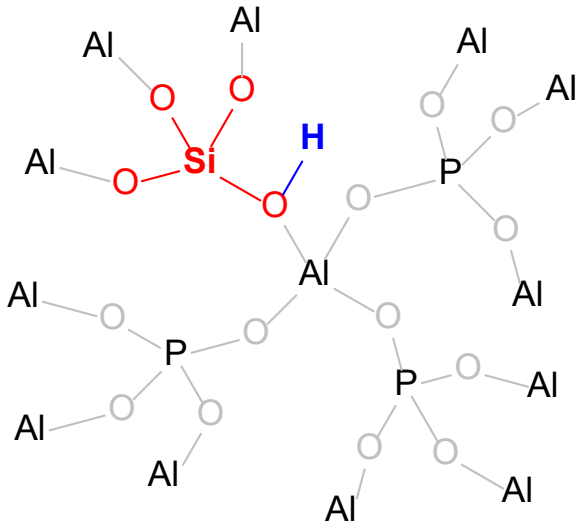
~6 μm

Higher Si loading gives smaller particles

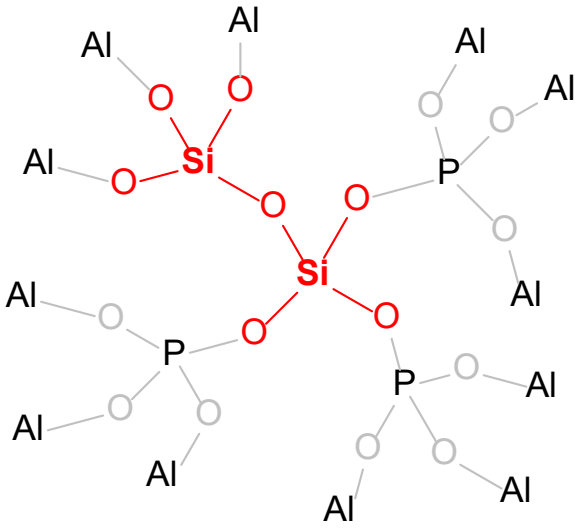
Types of Si substitution in SAPOs



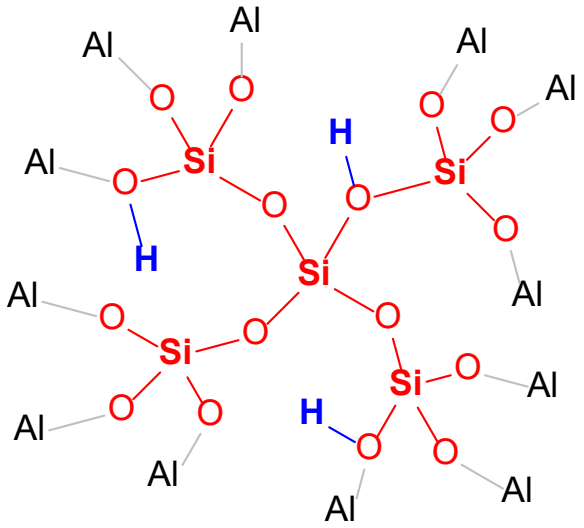
Bare Framework (Neutral)



Type II Substitution (Strong)



Type III Substitution



Silicon Islanding (Weak)

Multiple silicon sites possible in SAPOs

NH_3-TPD Acid Site Characterisation

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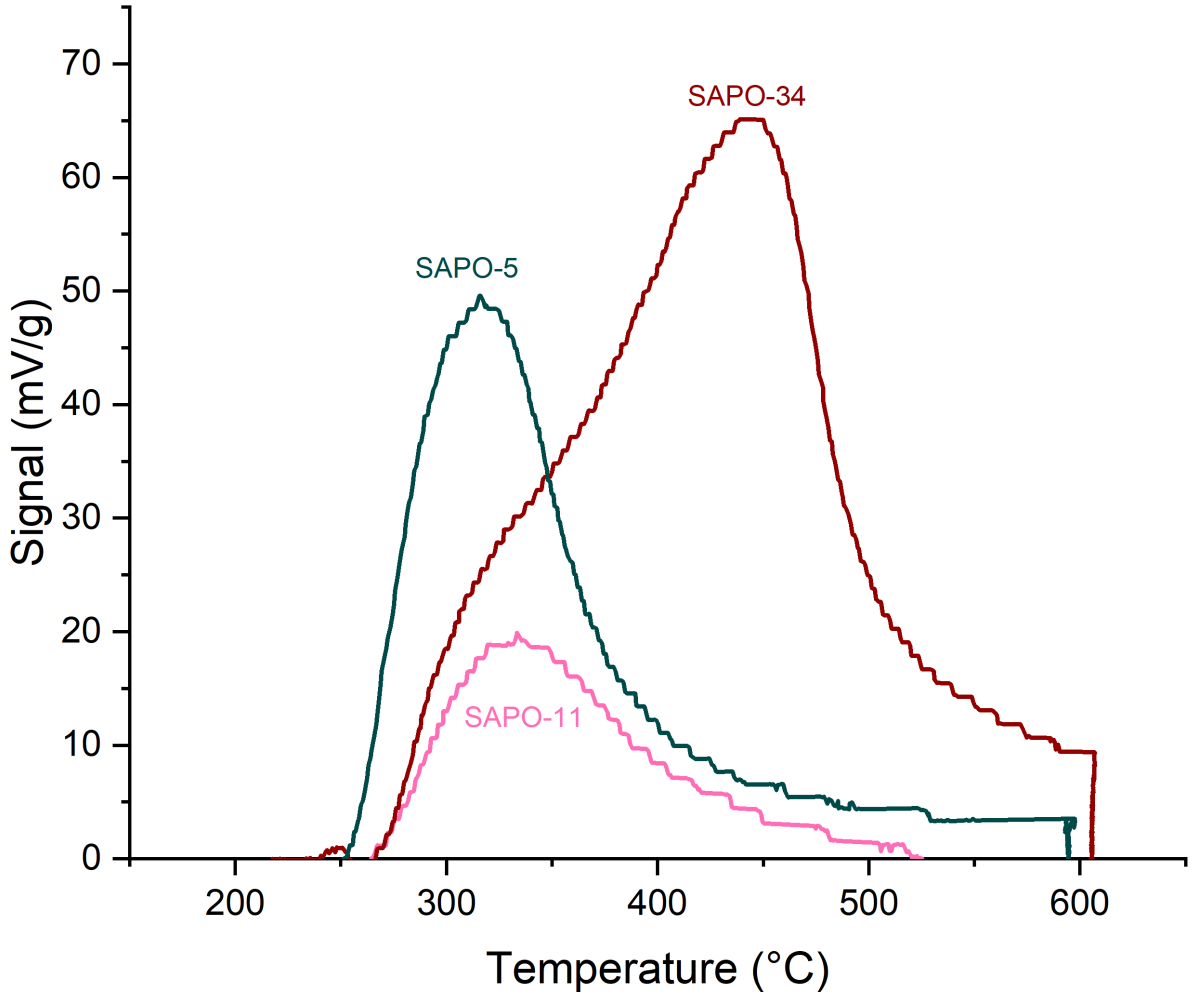
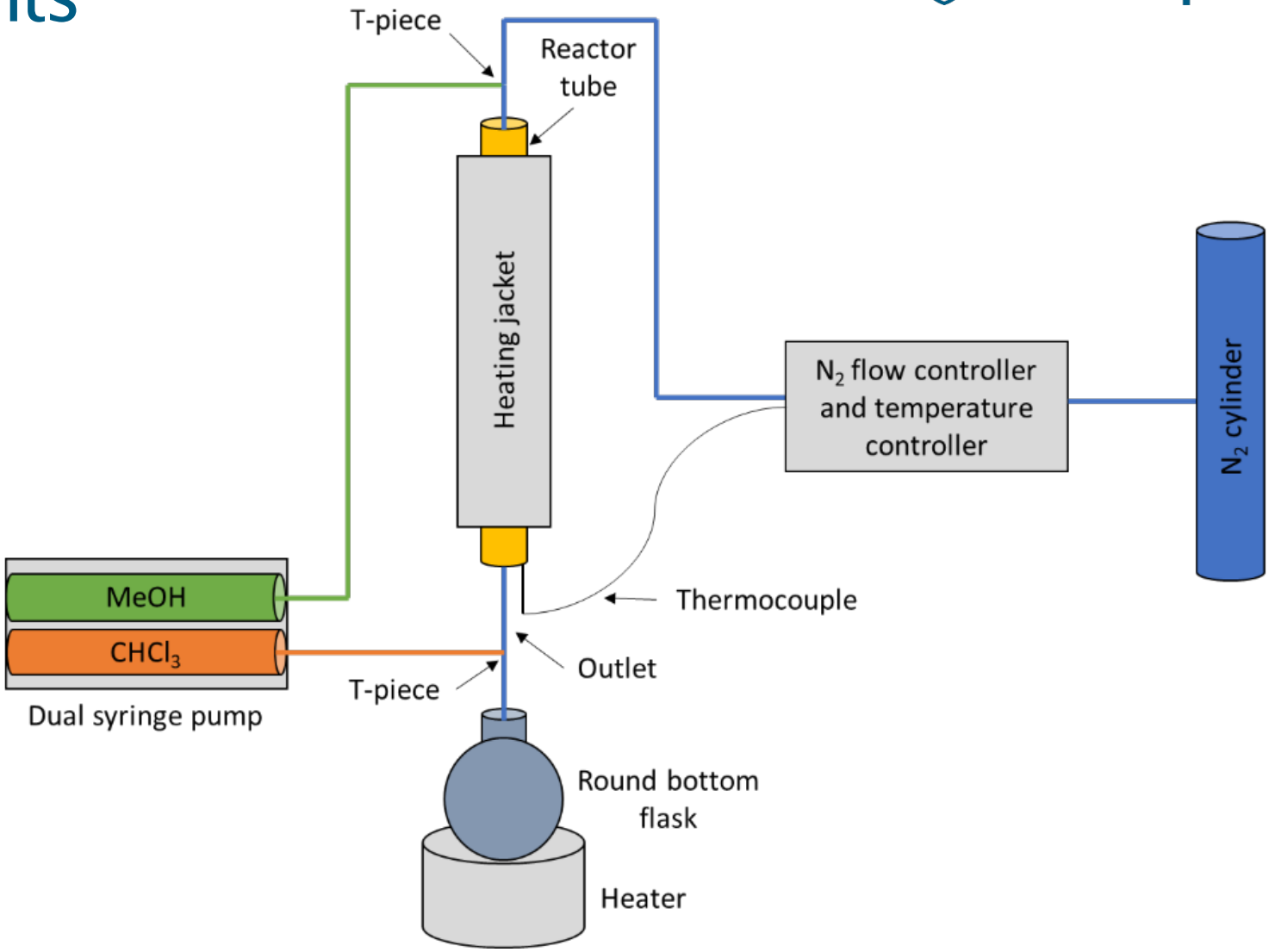
- Type III: SAPO-5, SAPO-11
- Type II: SAPO-34, (SAPO-18)
- Si loading affects acid site quantity*



Si substitution mechanism impacts acidity

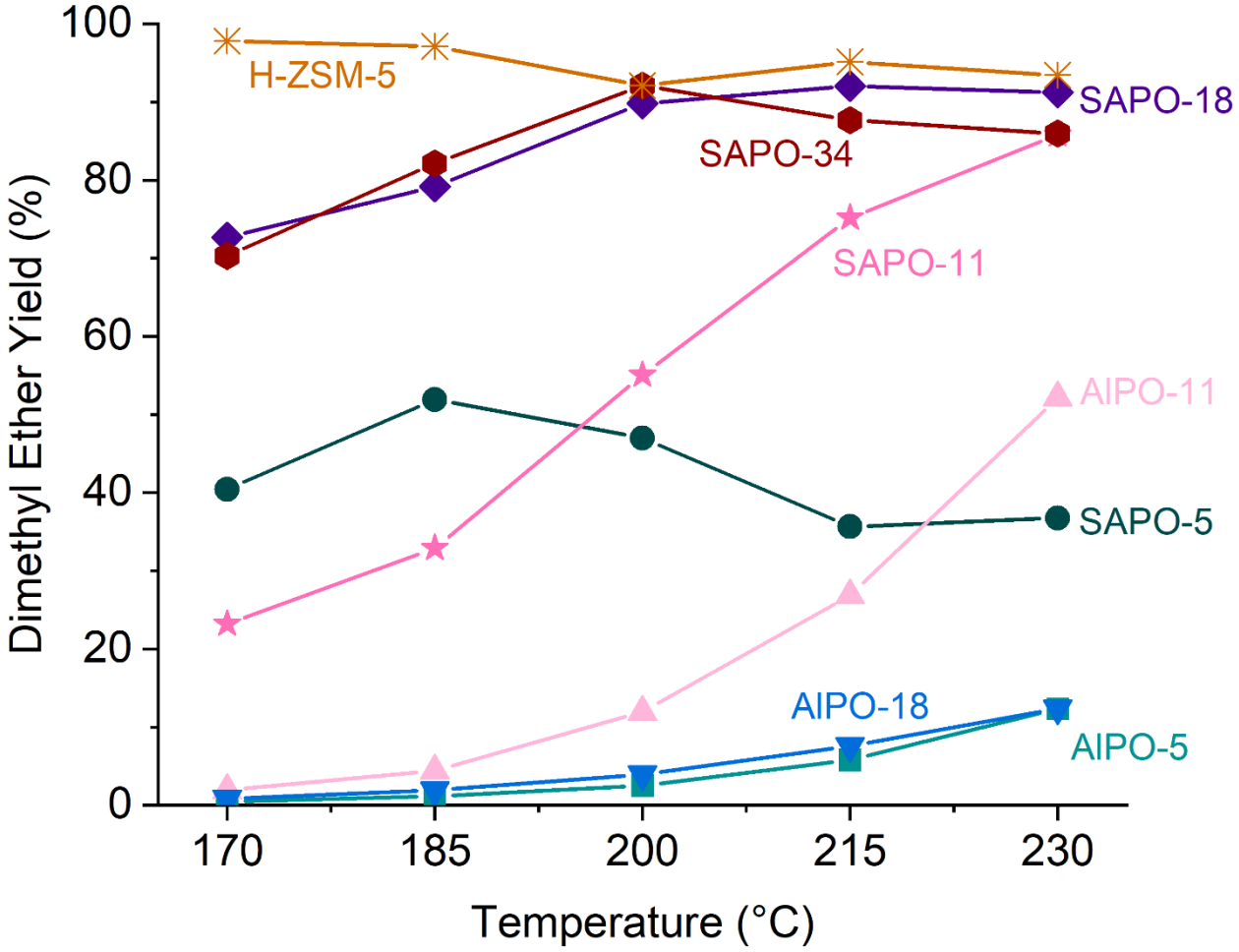
Reactor and Experiments

- 300-500 μm catalyst particles
- MeOH (13-31 mol%) in N_2
- $CHCl_3$ external standard
- Investigated temperature & MeOH WHSV



Catalysts tested in a fixed bed reactor

MeOH Dehydration over AlPOs & SAPOs

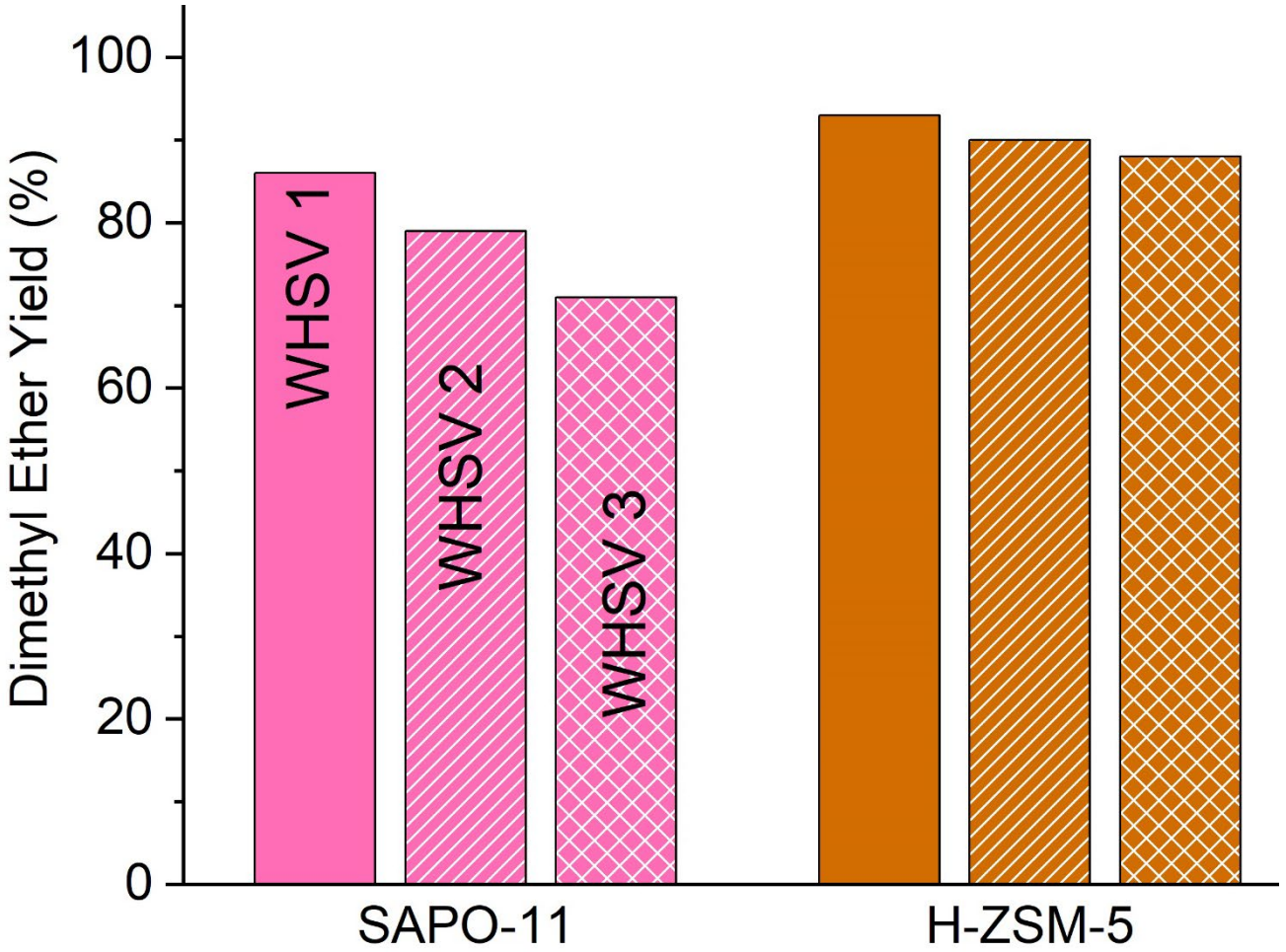


- Higher temperature → higher activity
- Higher acid site strength and quantity (**SAPO-34**) → higher activity

WHSV 1

Acidity impacts MeOH conversion

MeOH Dehydration over AlPOs & SAPOs

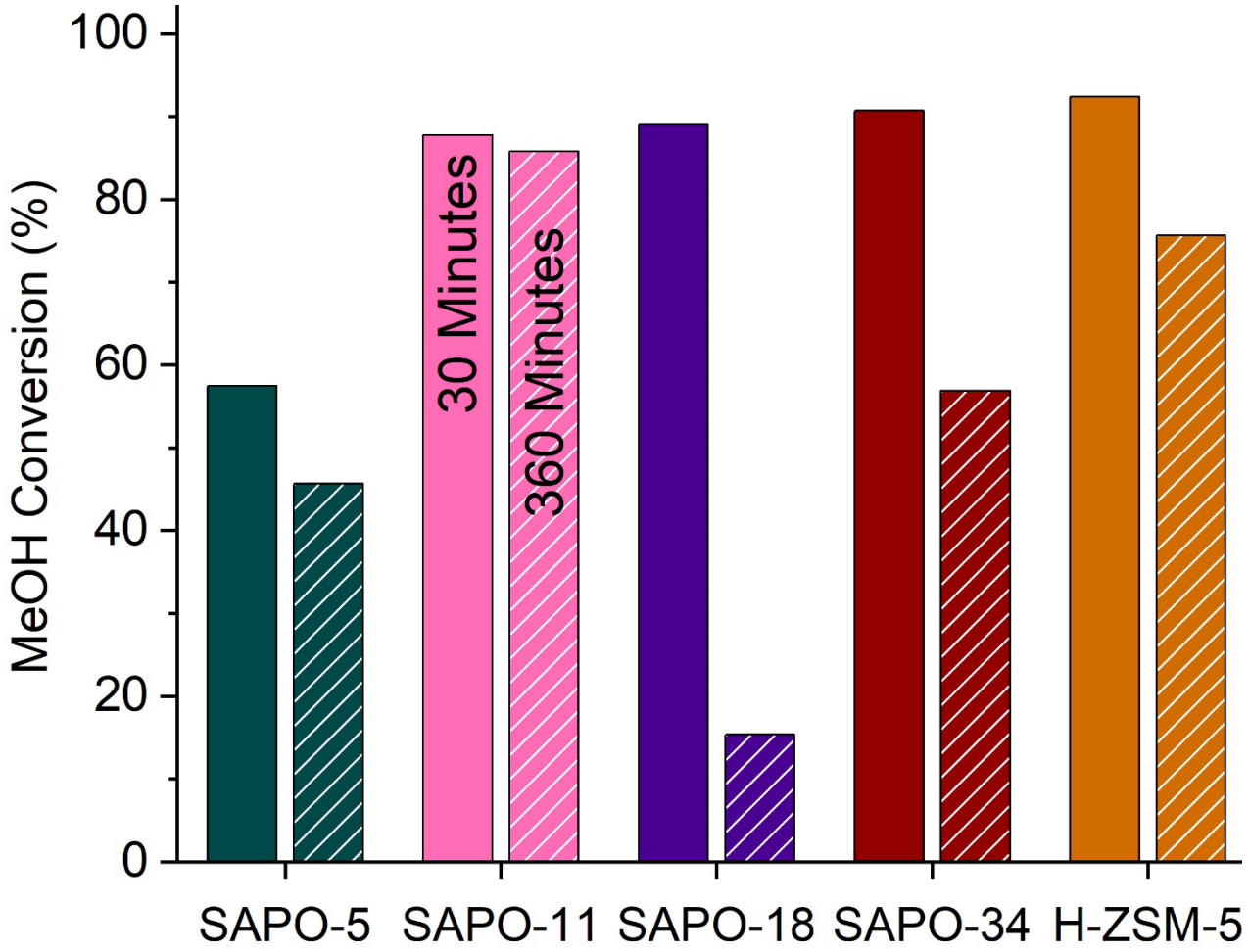


- MeOH weight hourly space velocity impacts DME Yields
- Active site saturation?

230˚C

Lower MeOH concentrations give higher DME yields

Time-on-Stream Stability - **Activity**



- Higher acidity (**SAPO-18**) → faster deactivation
- Topology plays a role

275˚C, WHSV 3

SAPO-11 is very stable

Time-on-Stream Stability - **Selectivity**

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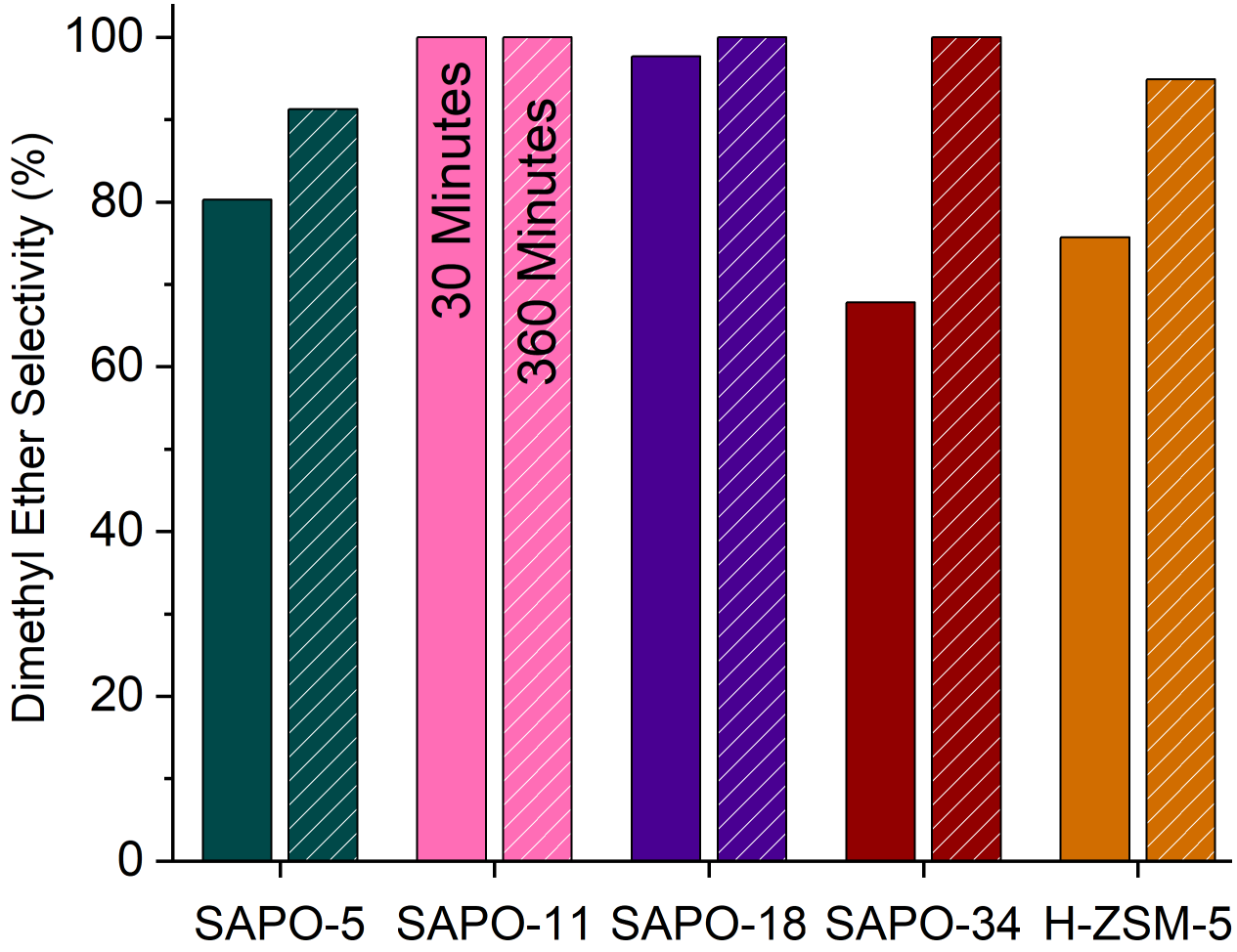
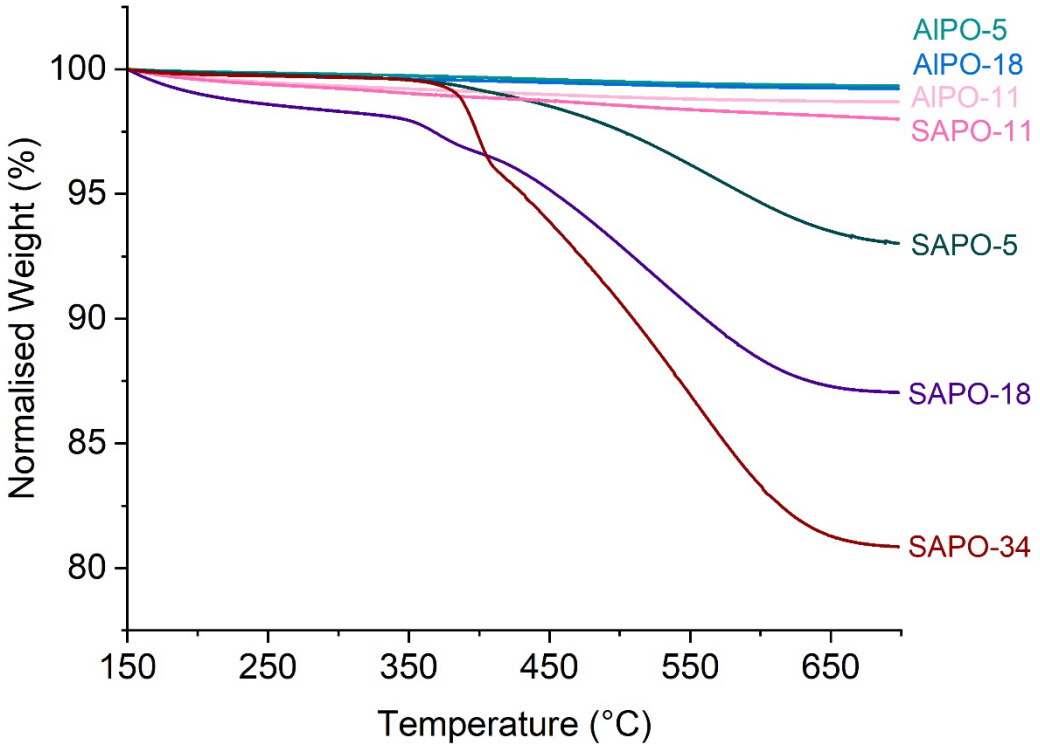
- Strong acids (**H-ZSM-5**): MeOH to olefin at start
- Strongly acidic sites deactivate rapidly
- SAPO-11 is 100% selective

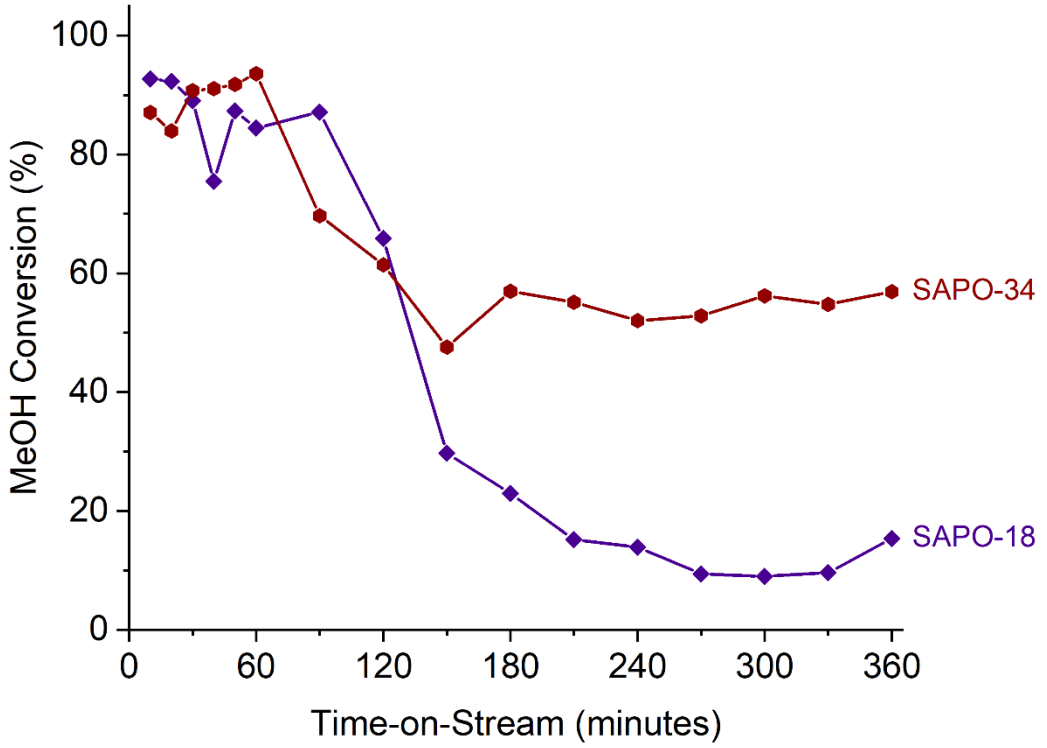
275˚C, WHSV 3



SAPO-11 highly selective and stable

Coke Content of Spent AlPOs & SAPOs





- Higher acidity (**SAPO-34**) → higher coke content
- More coke does not always cause faster deactivation

Acid strength & topology impact AlPO & SAPO stability

Kinetic Model of MeOH Dehydration

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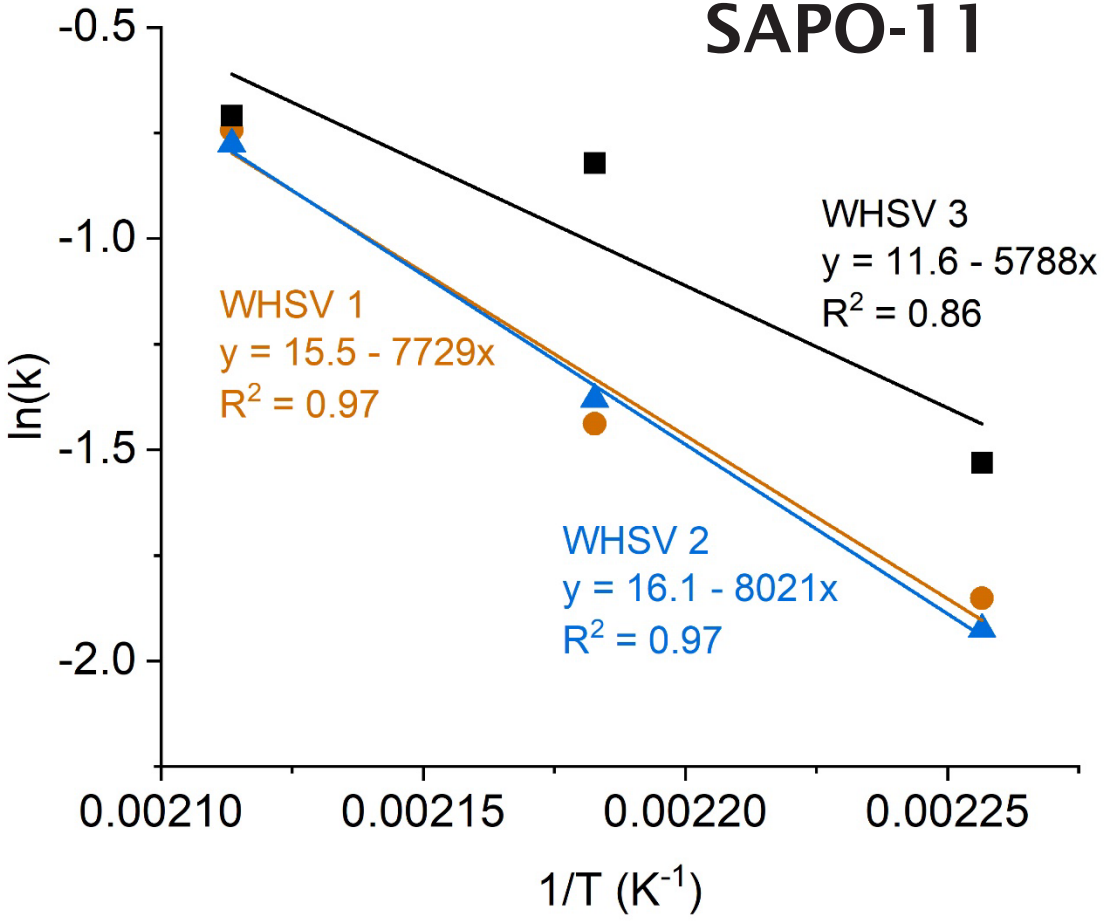
Copasi – Kinetics

- 1st Order Arrhenius
- Approach similar to Catizzone *et al.* for various zeolites[1]
- 170-200˚C, average of all WHSV



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

MeOH dehydration modelled using 1st order Arrhenius

Kinetic Parameters of AlPOs & SAPOs

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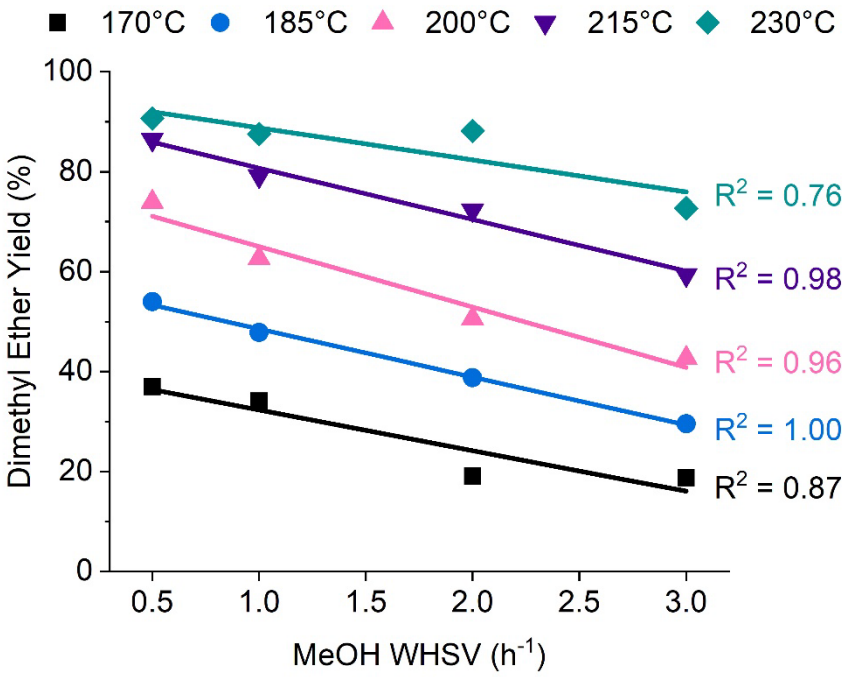
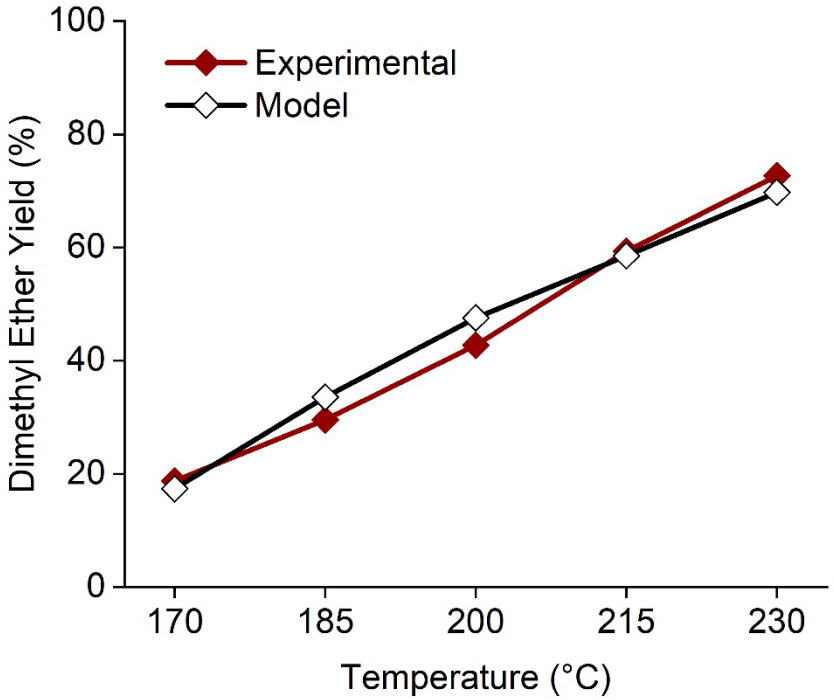
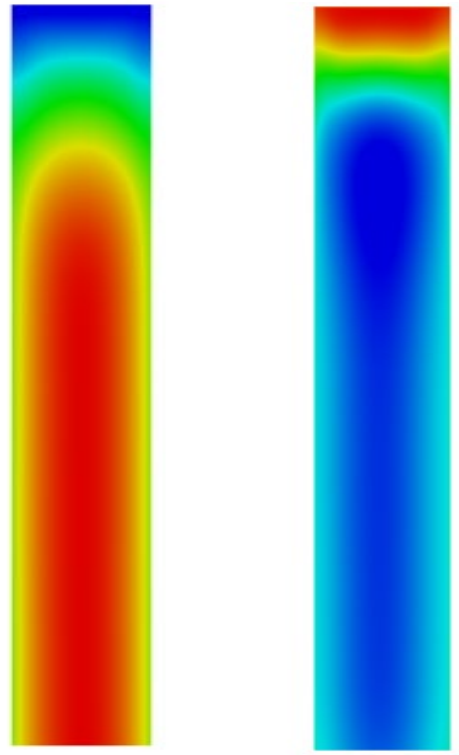
Catalyst	A (s^{-1})	E_a (kJ mol^{-1})
SAPO-5	5.6×10^4	43
SAPO-11	5.4×10^6	60
SAPO-18	8.0×10^3	34
SAPO-34	4.0×10^4	34
AlPO-5	1.1×10^9	92
AlPO-11	3.9×10^{11}	111
AlPO-18	1.3×10^8	80

Stronger acid sites less sensitive to temperature change

SAPO-11: Computational Fluid Dynamics







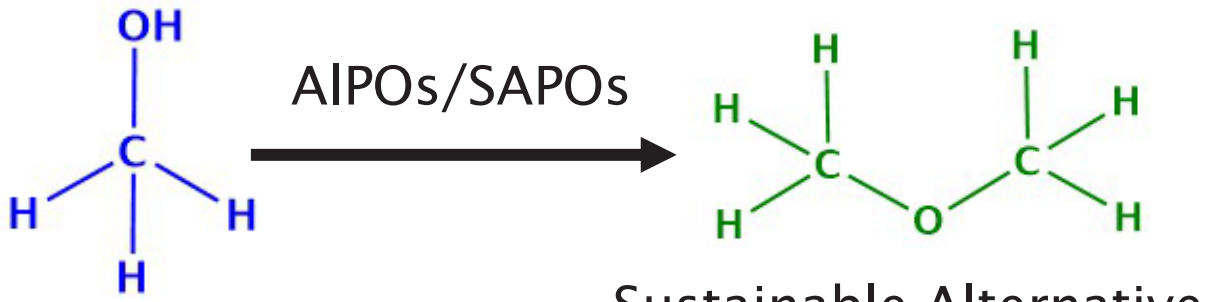
Distribution inside catalyst bed

Explored MeOH dehydration over SAPO-11 in depth

Conclusions & Future Work

- ✓ Stronger & more abundant acid sites → high activity
- ✓ Weaker acid sites & medium 1D channel structure → high selectivity & stability
- ✓ SAPO-11 highly active, selective & stable so promising for use in bifunctional catalysts for one-pot CO_2 to DME conversion

This Work

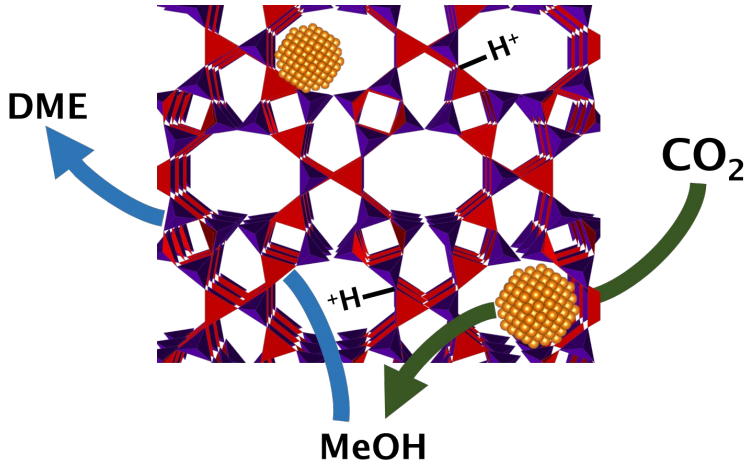


Future

12% CO_2 Conversion

80% DME Selectivity

4.1 g_{DME} g_{Cat}^{-1} h^{-1}



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- Matthew Potter – UK Catalysis Hub & UCL
- ViridiCO_2 - University of Southampton

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Thank you for your attention. Any questions?

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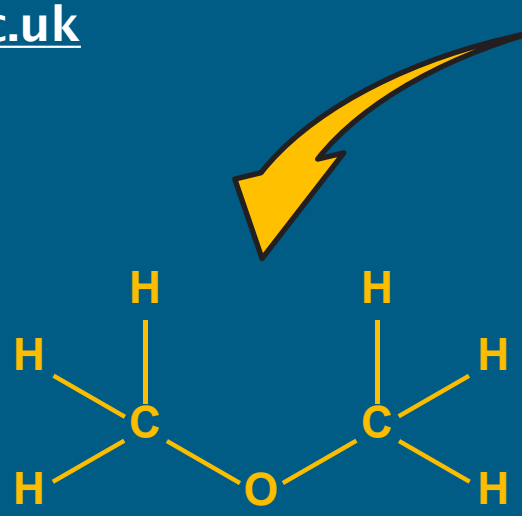
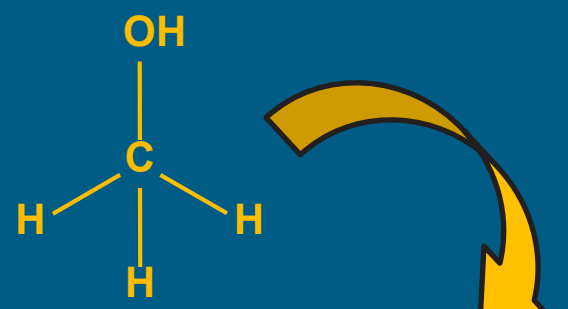
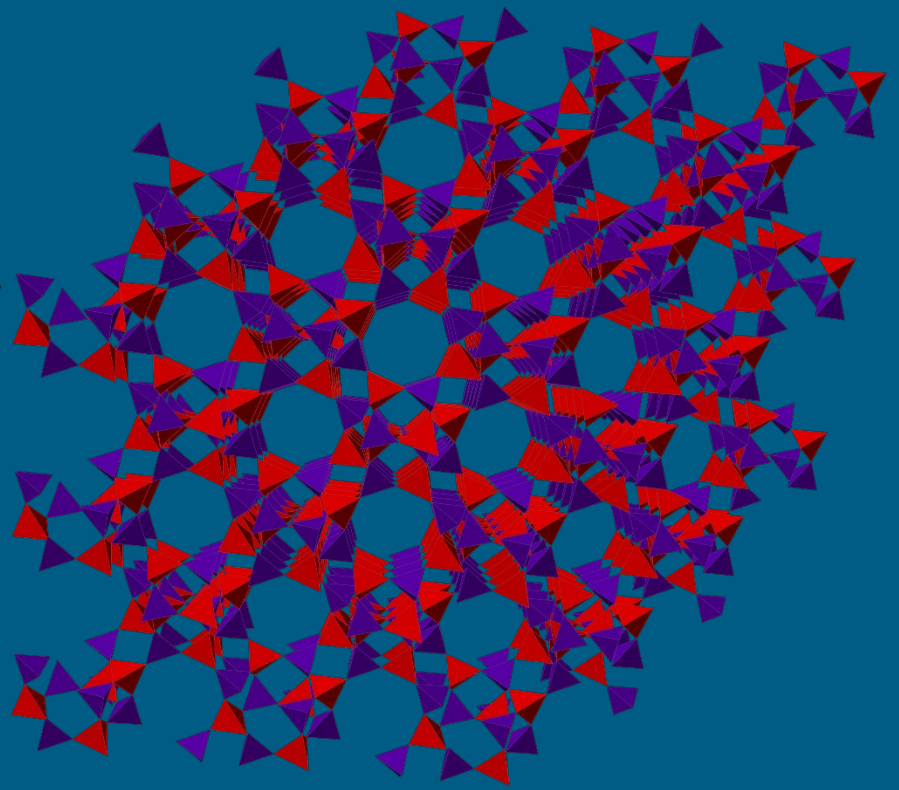
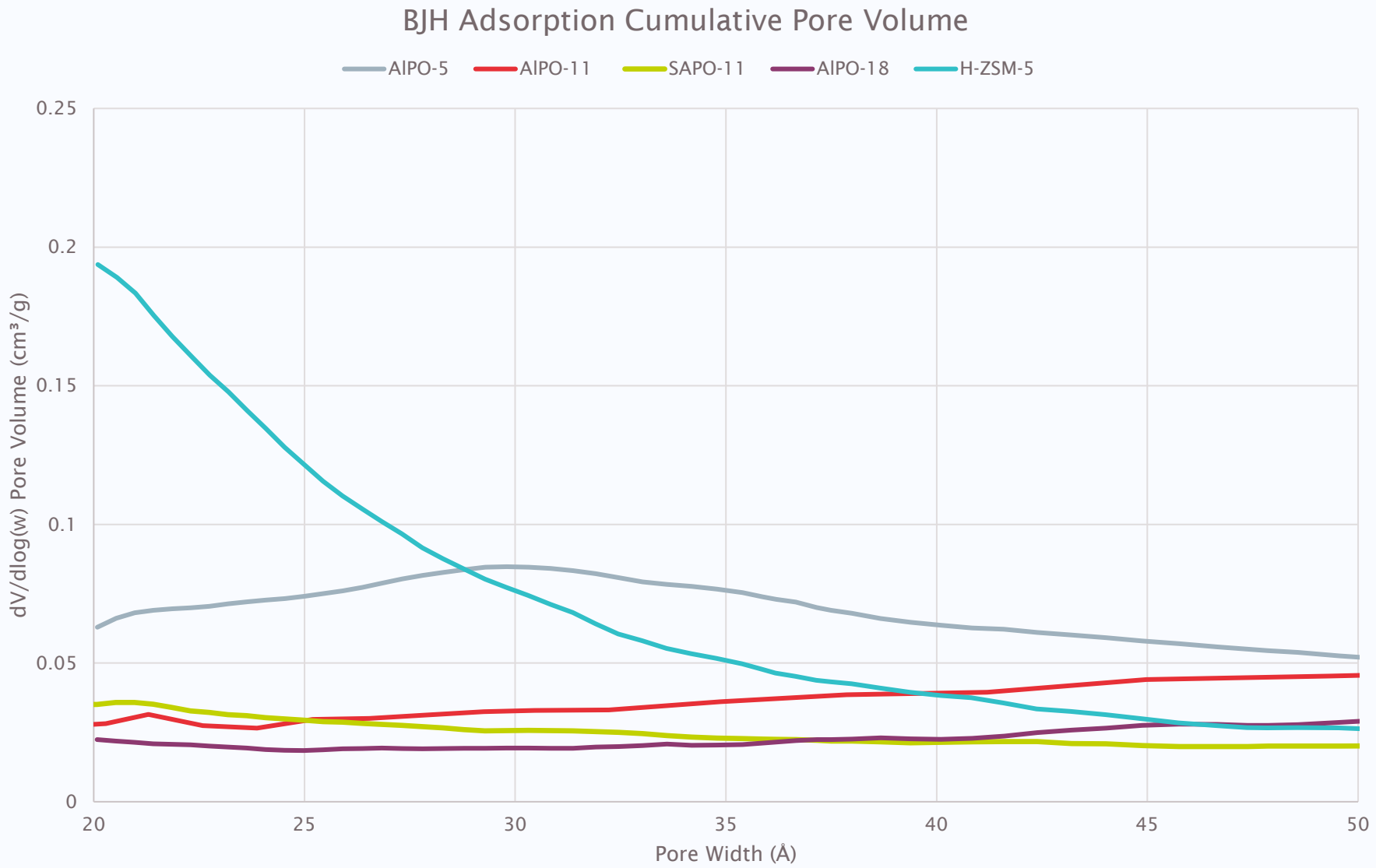






Appendix A – BJH Plots



Appendix B - Stability of AlPOs & SAPOs

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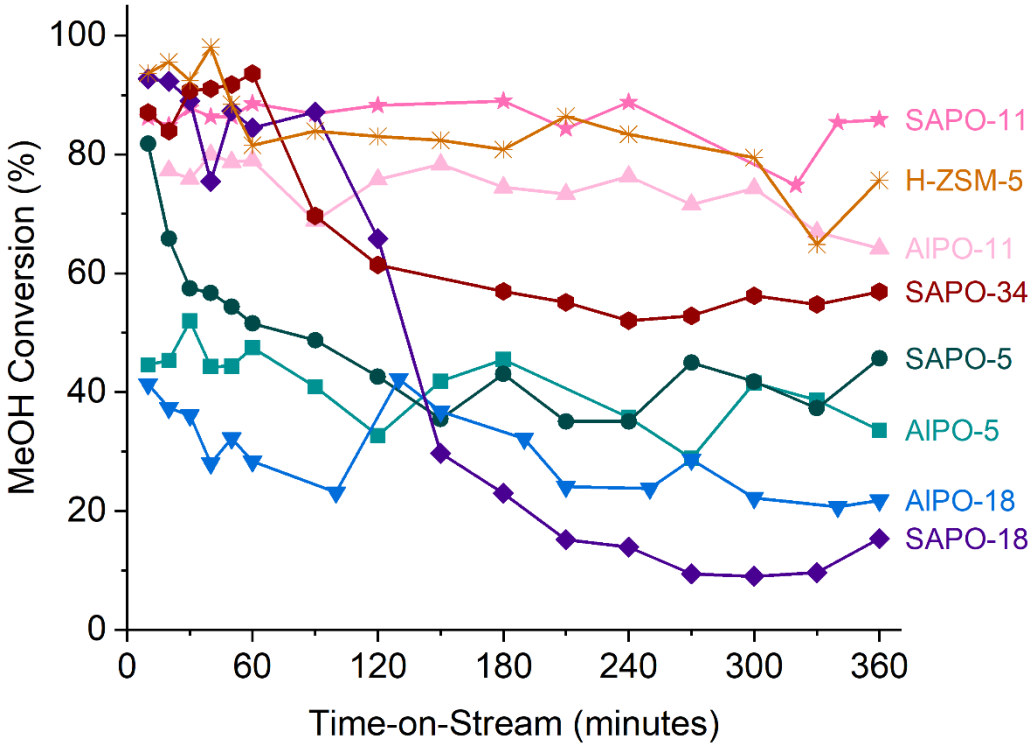
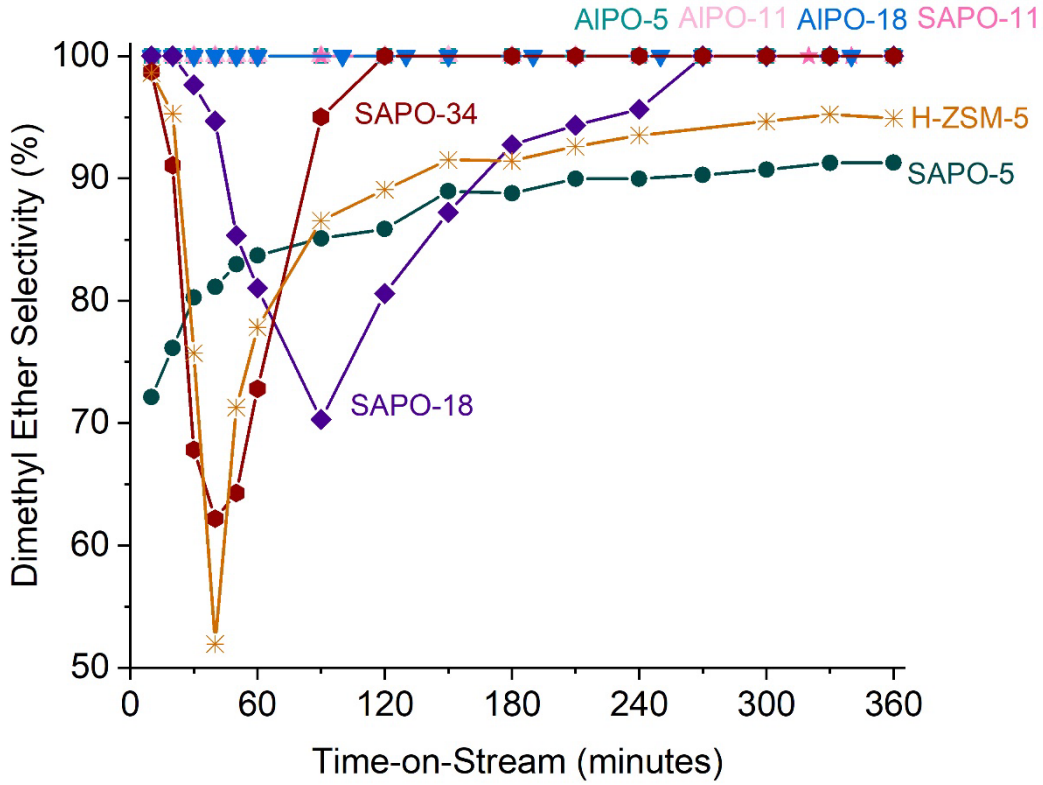
Activity



Selectivity



275˚C, WHSV 3

Appendix C - EDS Elemental Composition

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Catalyst	Elemental Composition (Al, P, [Si] wt%)	Solid Catalyst Molar Ratio (Al : P : [Si])	Initial Gel Molar Ratio (Al : P : [Si])
AlPO-5	19.5, 21.1	**1.00:0.94**	**1.00:1.50**
SAPO-5	20.7, 20.7, **2.1**	1.00:0.87:0.10	1.00:1.40:0.30
AlPO-11	21.1, 22.2	1.00:0.92	1.00:1.00
SAPO-11	20.3, 20.3, **1.4**	1.00:0.87:**0.07**	1.00:1.00:**0.20**
AlPO-18	19.8, 21.2	1.00:0.93	1.00:1.00
SAPO-18	21.6, 23.2, **4.4**	1.00:0.94:**0.20**	1.00:0.90:**0.20**
SAPO-34	20.8, 18.9, **3.4**	1.00:0.79:0.16	1.00:1.00P:0.15
H-ZSM-5	3.7, - , 45.5	1.00:0.00:11.81	1.00:0.00:11.5