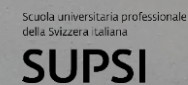
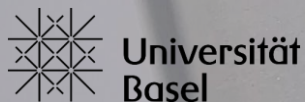
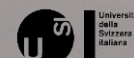
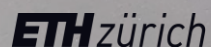


Renewable Fuels and Chemicals for Switzerland*

WP7: Methanol to Sustainable Fuels and Chemicals Subtask oligomerization

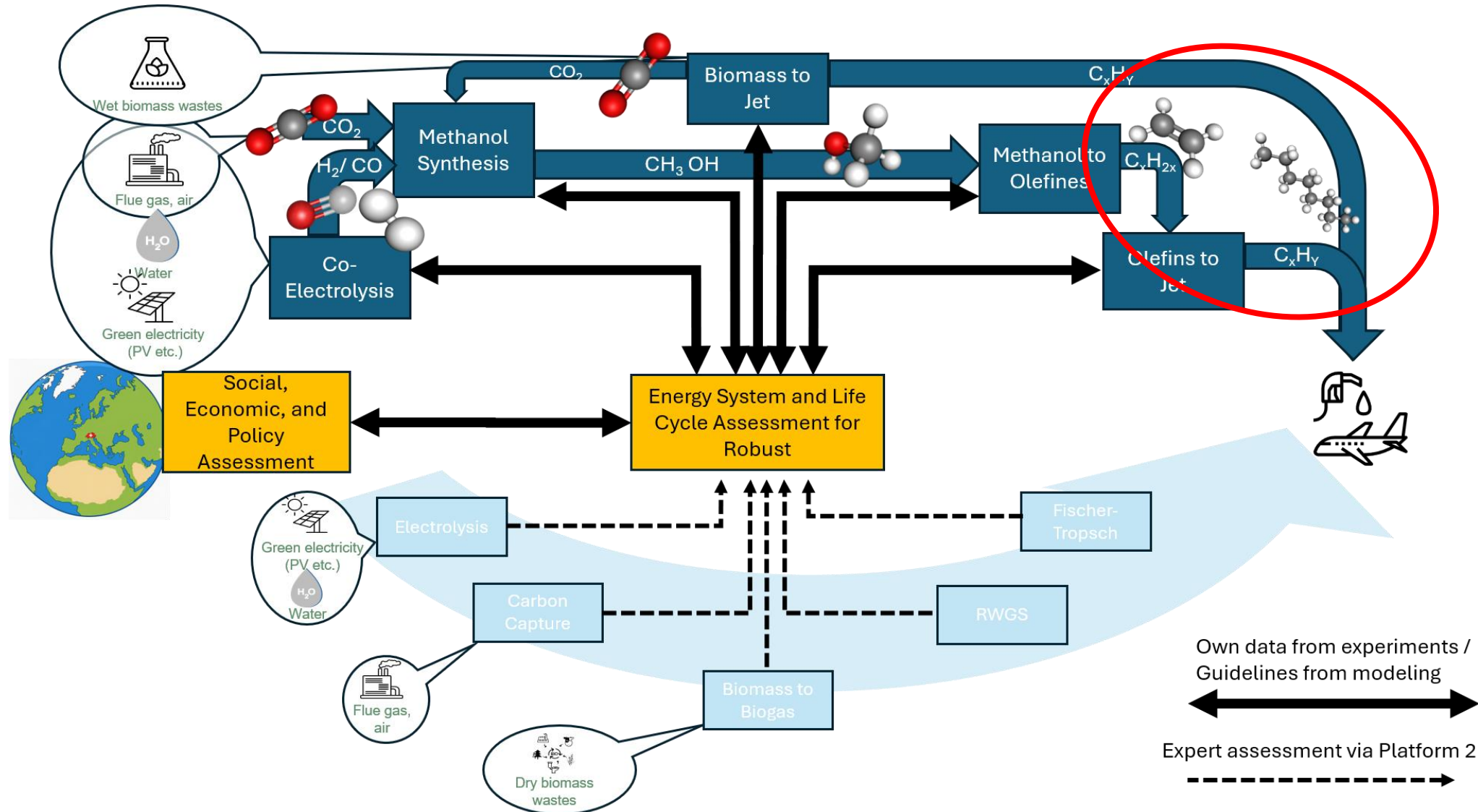


Presenter:
Andreas Borgschulte

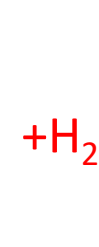
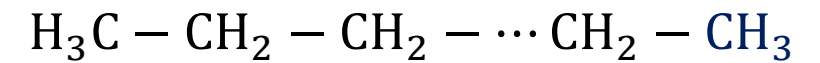
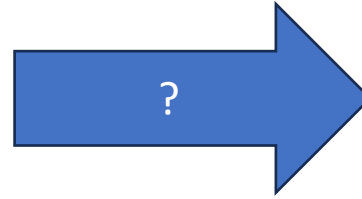


Connection to the consortium's goals

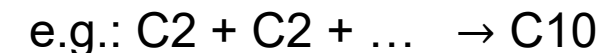
Development of long lasting oligomerization catalysts



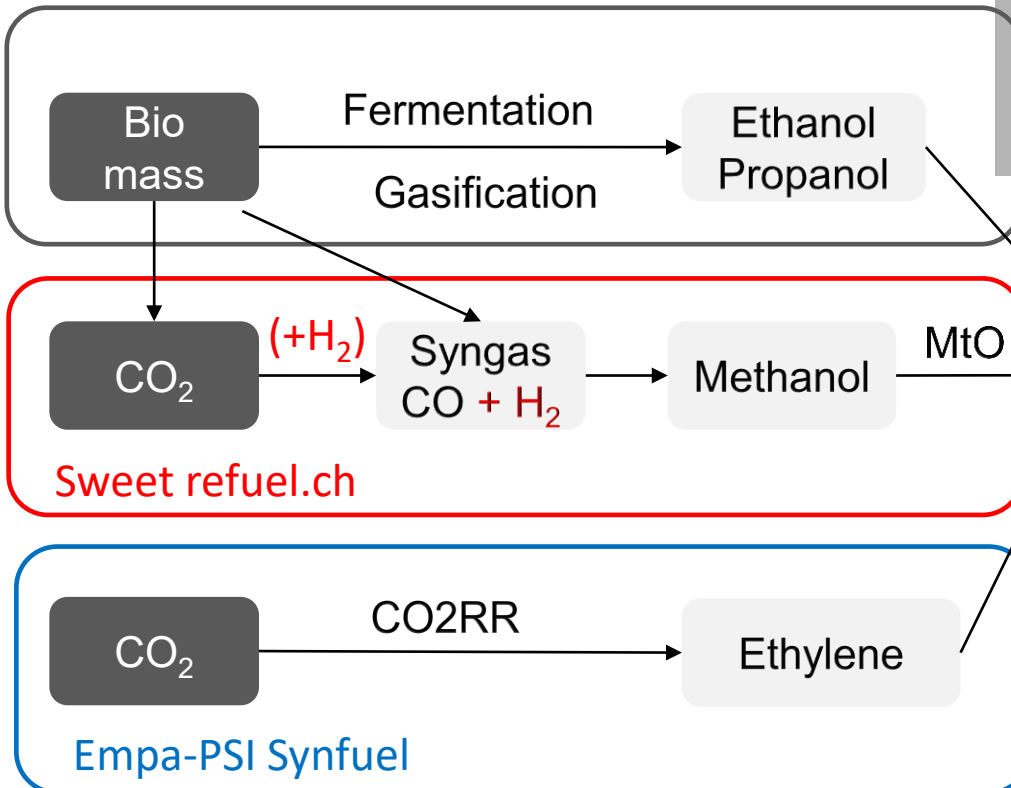
WP7 subtask *Oligomerization* is important step in Sustainable Aviation Fuel



Oligomerization to a **distinct** chain length

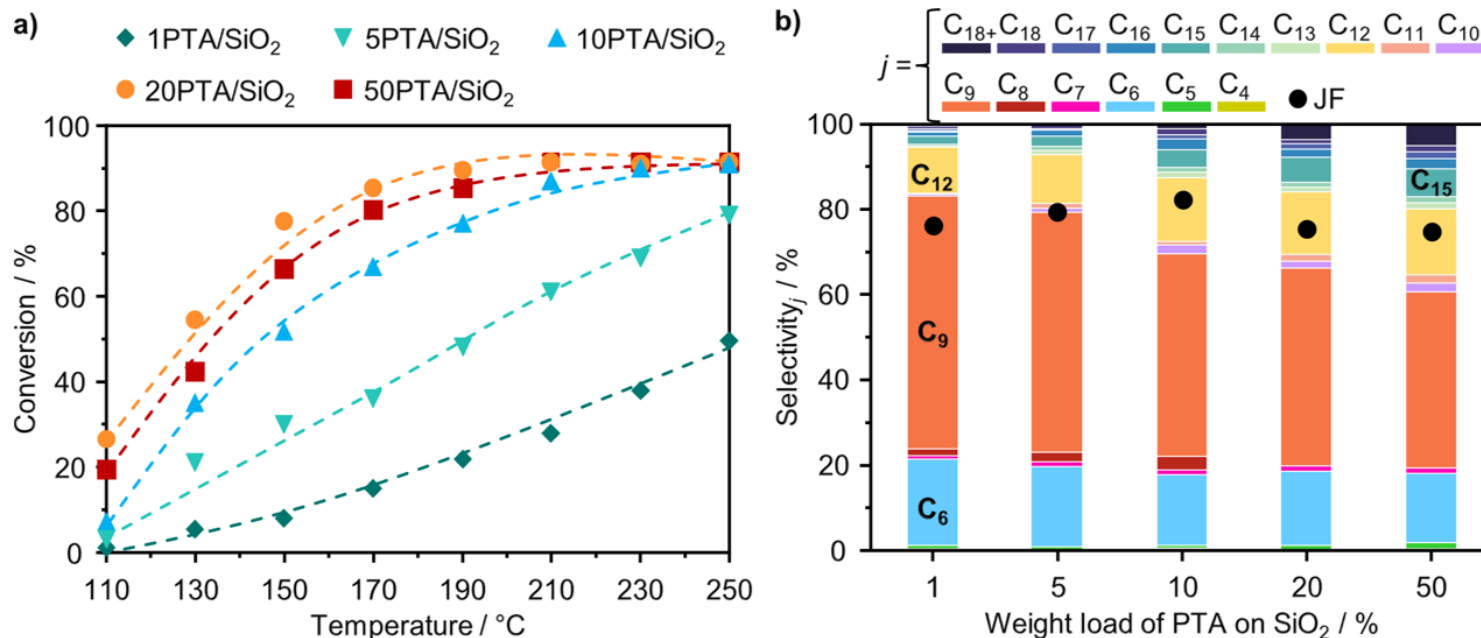
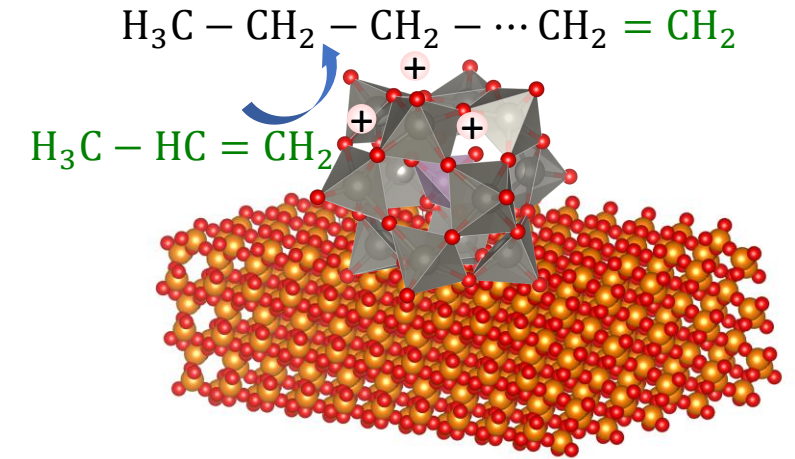


By highly active and selective catalysts
Developed via an **experimental approach**



Oxide supported *Heteropoly acids* oligomerization catalysts do the job very well

- Oxide supported HPAs show excellent conversion and selectivity for **olefin oligomerization** to SAF-chain length at low temperatures
- Support-HPA interaction depends on the coverage changing catalytic activity
- Moderate degradation, regeneration relatively simple
- Patent filed includes various (even better) catalyst systems («design»)
- We understand aspects of the mechanism



A. Cesarini, et al., ACS Catal.
2026, 16, 3, 2135–2148

A. Cesarini, et al., *Fuel* 429,
140882 (2027)

Research team



Catalysis: Alessia, Ali, Florent, Jonathan, Jeroen



Photoemission: Filippo, Connor



NMR: Daniel



E-Microscopy: Rolf, Walid



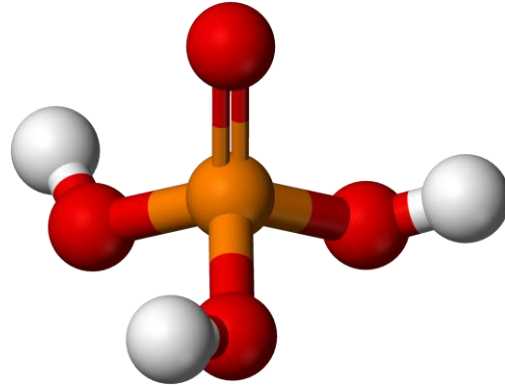
Vibrational Spec: Jong-Min, Svemir, Timmy

Hetero Poly Acids - what is a (solid) acid?

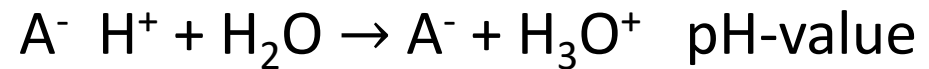


Phosphoric acid is an oligomerization catalyst

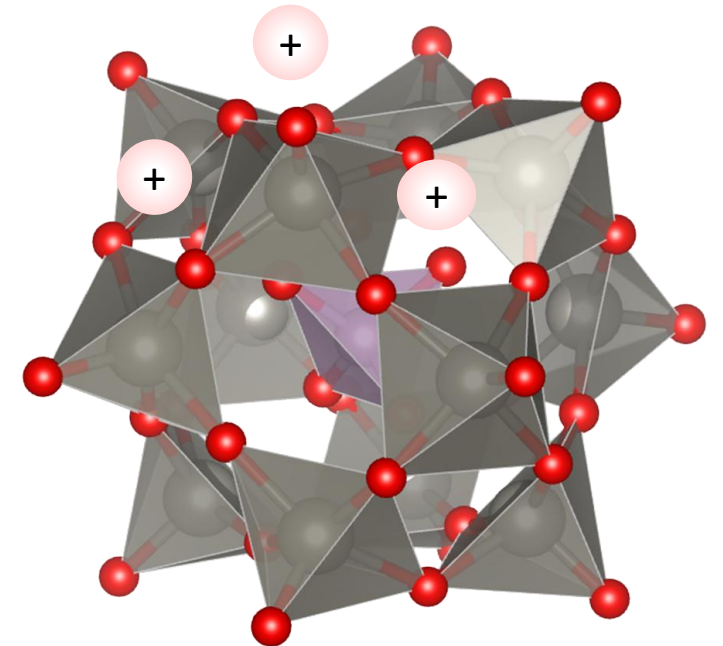
R. Bekker and N. M. Prinsloo, Ind. Eng. Chem. Res. 48 (2009) 10156



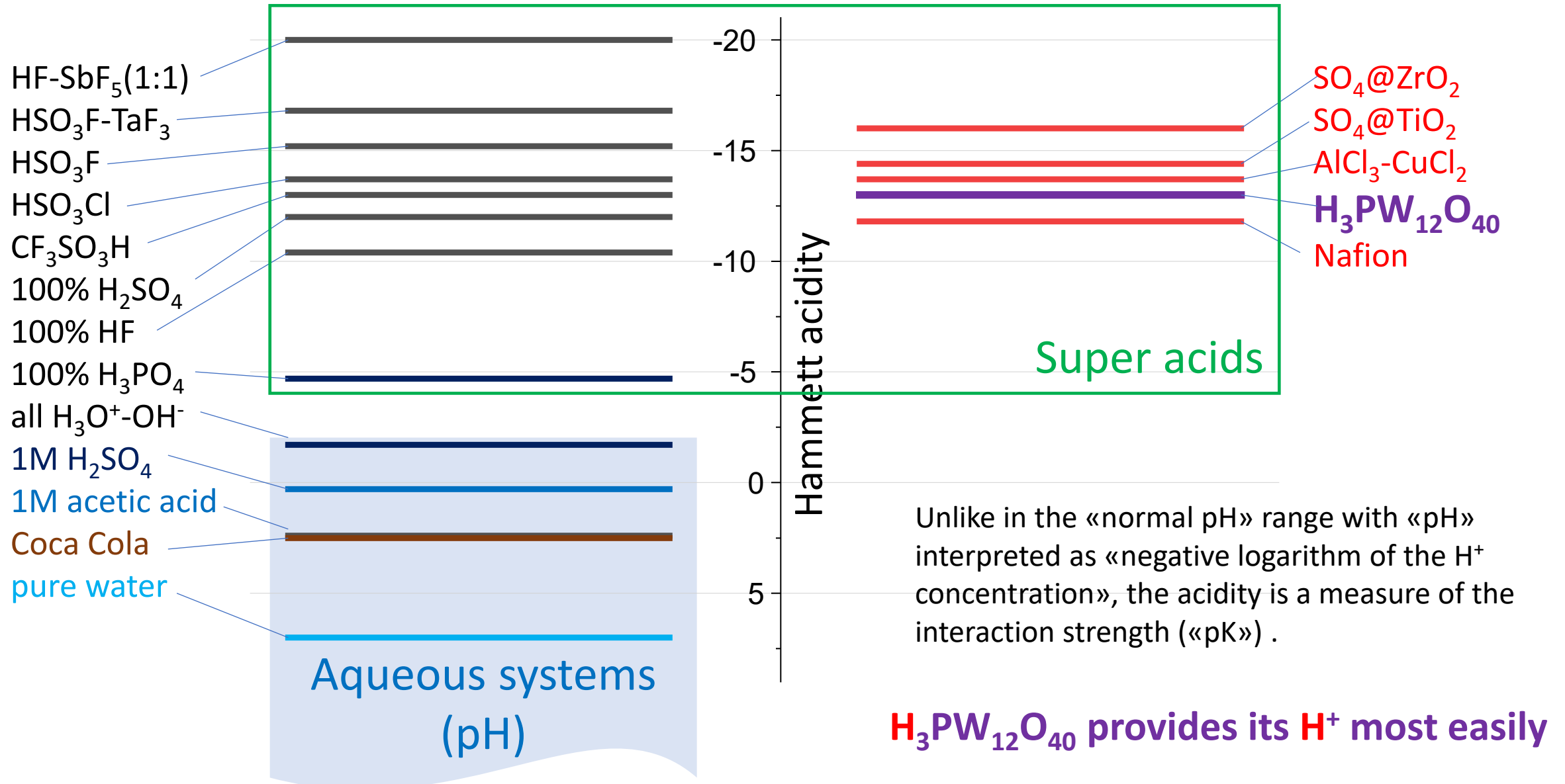
The easier an acid is to lose its protons, the stronger it is.



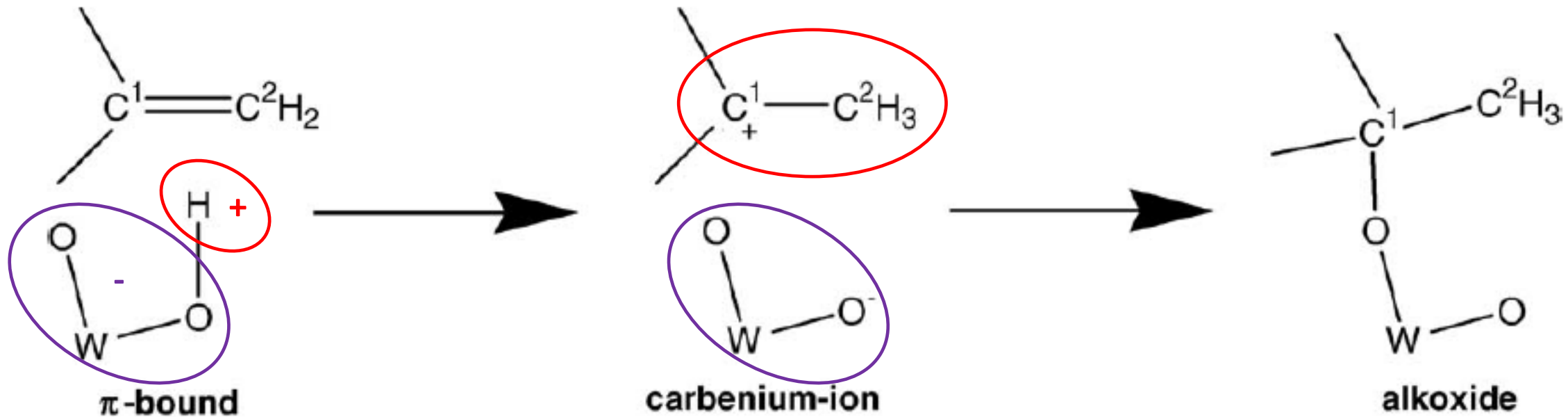
Phosphotungstic acid



Acidity – strength of liquid and solid acids (Hammett)



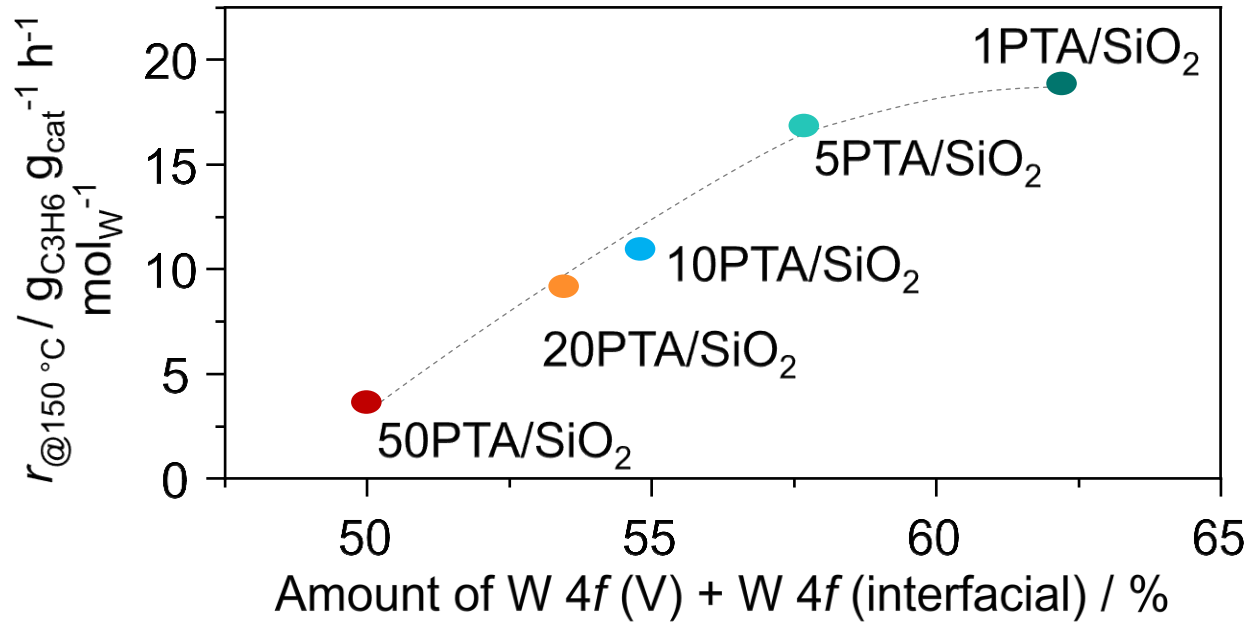
Activation of olefins via carbenium – alkoxide on HPAs



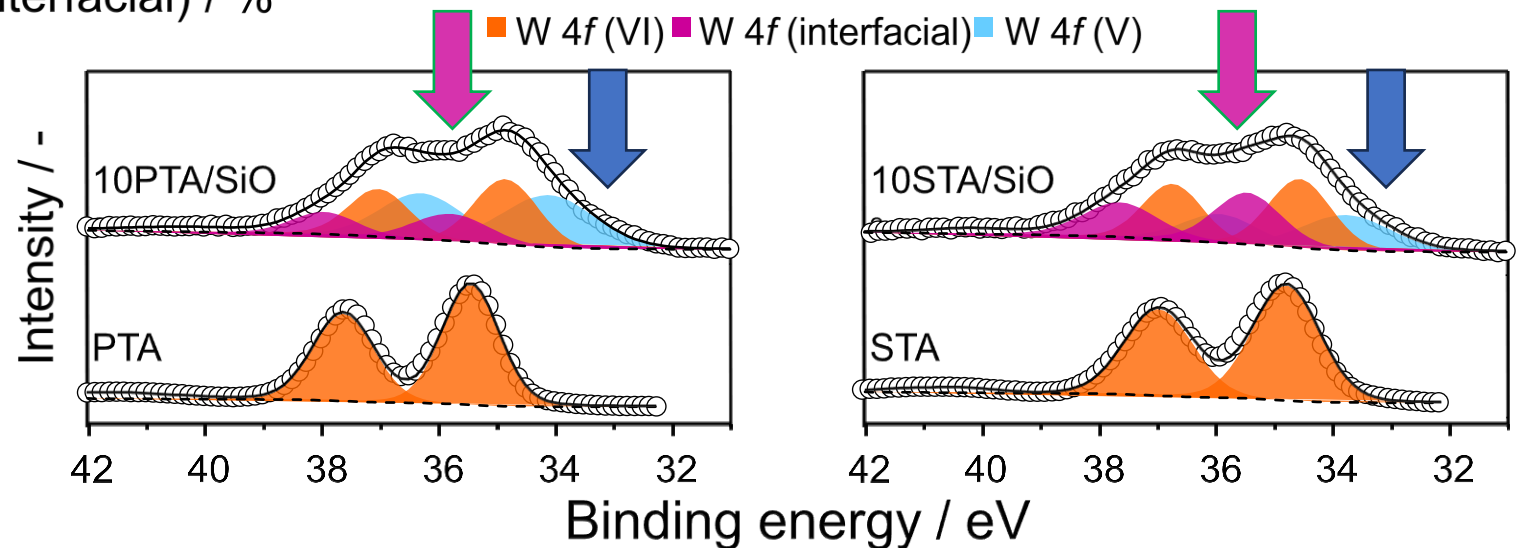
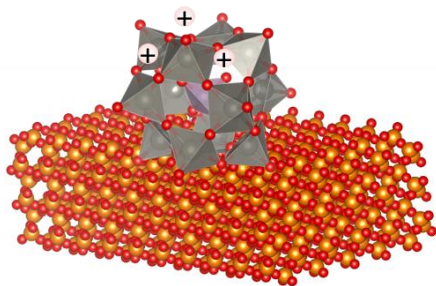
Caveat: DFT on tungsten is challenging
(E. Billeter, et al. PRB 103 (2021) 205304)

- Solid acid – olefin reaction
- Despite high acidity, activation is **highly endotherm**
- Controversial results on dependence of size of olefin (carbon number dependence)
- Many details as known for zeolites such as coverage dependence and coupling reactions (e.g., dimerization) unknown
- Charges play an important role!

Activity of *oxide supported* HPA oligomerization catalysts have depends on electronic structure

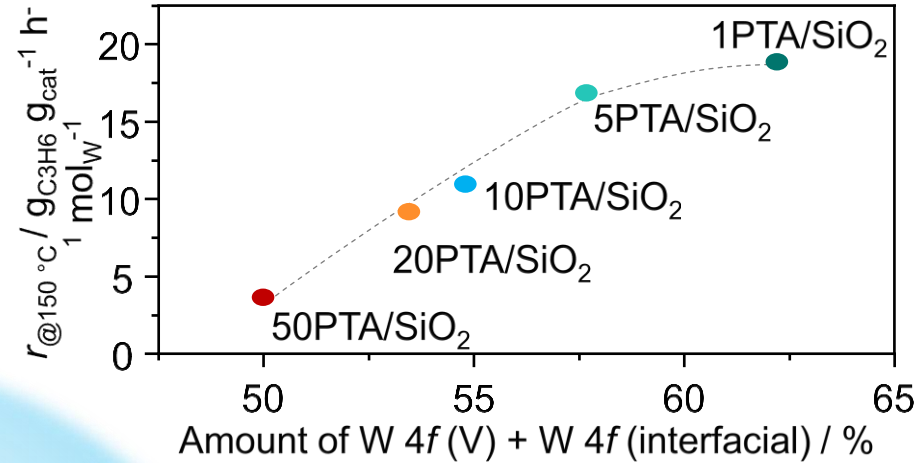
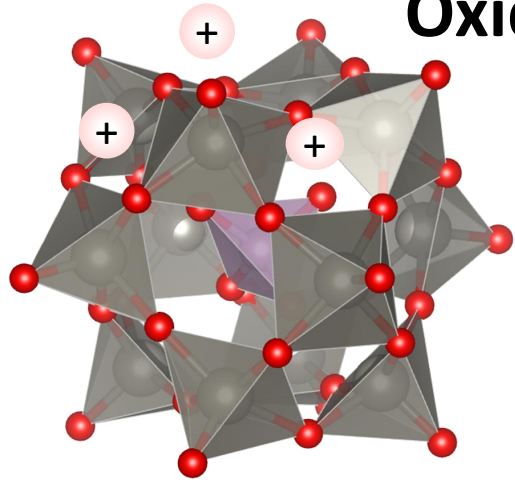


- Interaction of HPA with support leads to **reduction** and **new states**
- The new («**interfacial**») states are less trivial, but their amount scales with activity

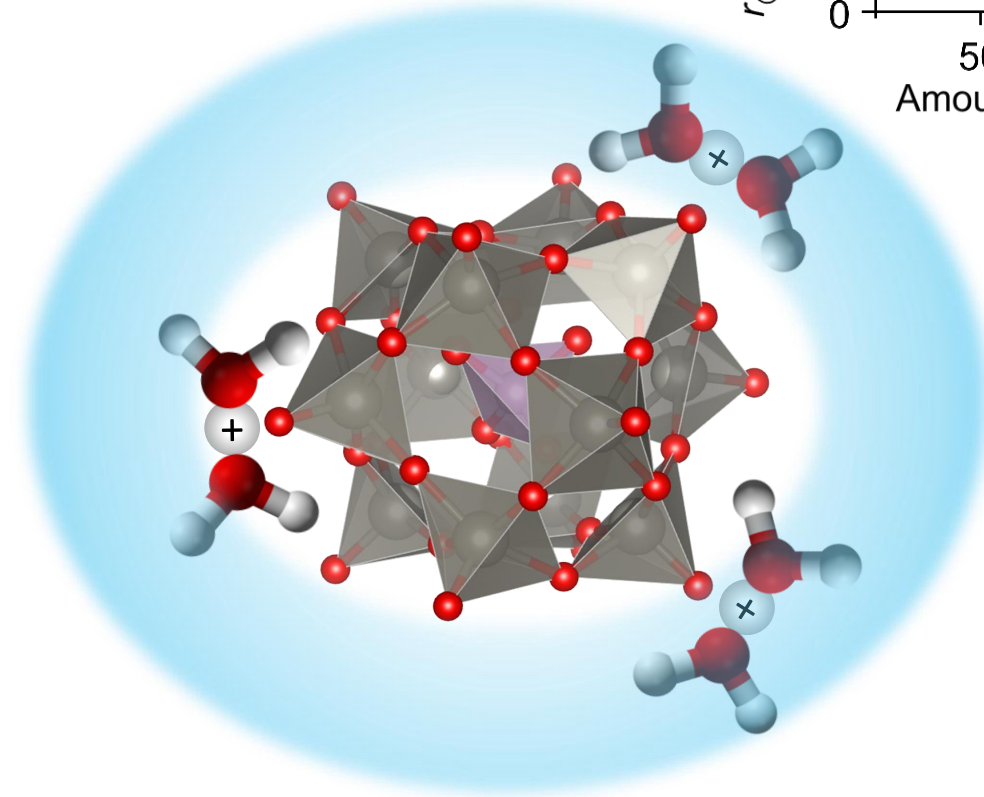


Oxide supported HP*Acid* oligomerization catalysts

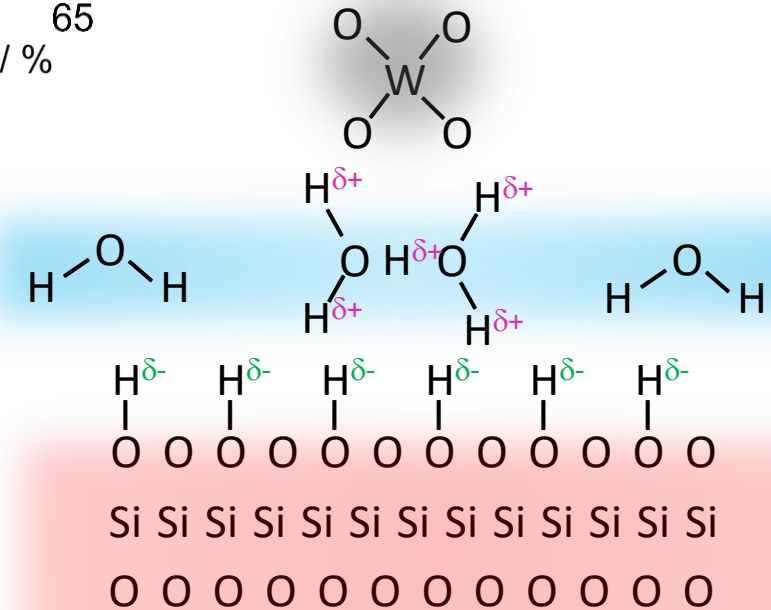
Where is the proton?



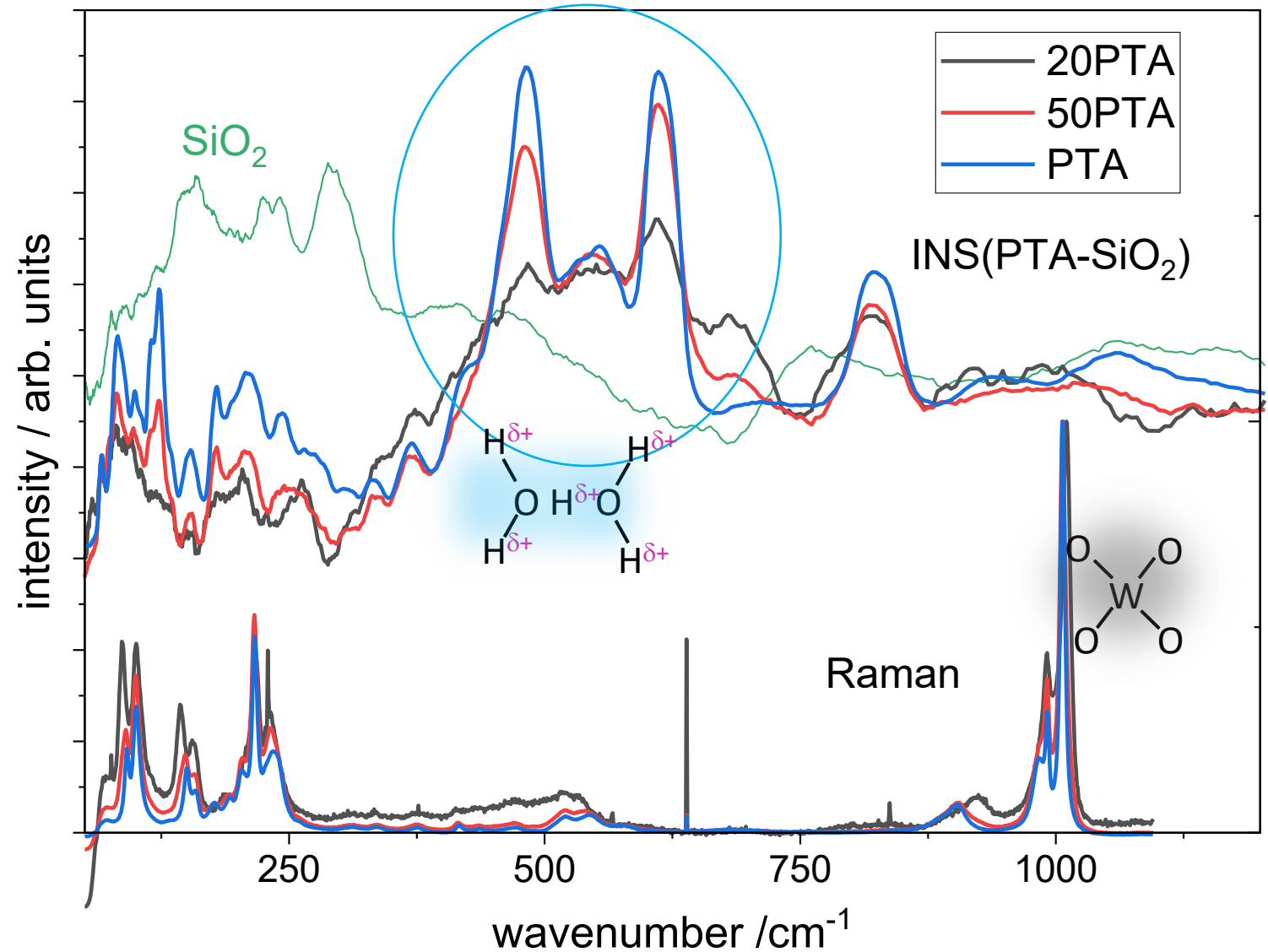
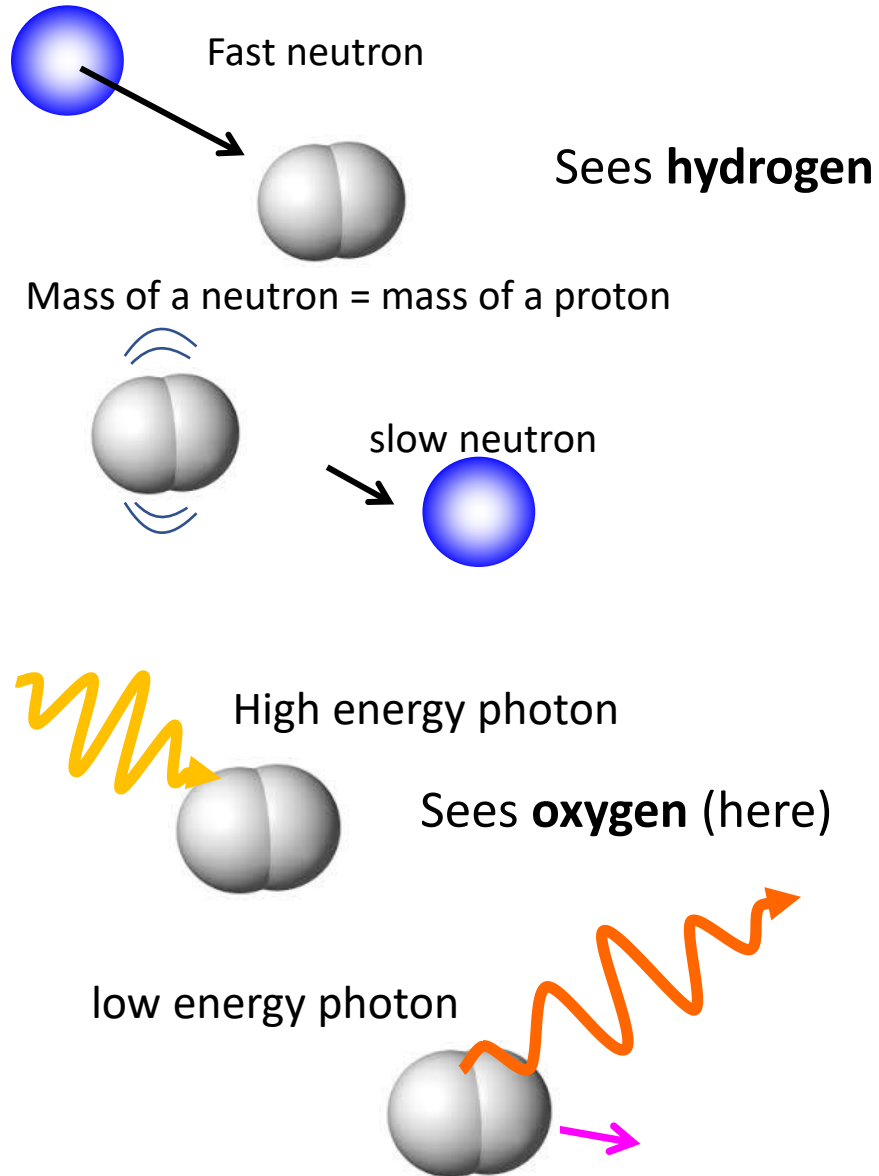
And can we tailor by
interaction with support?



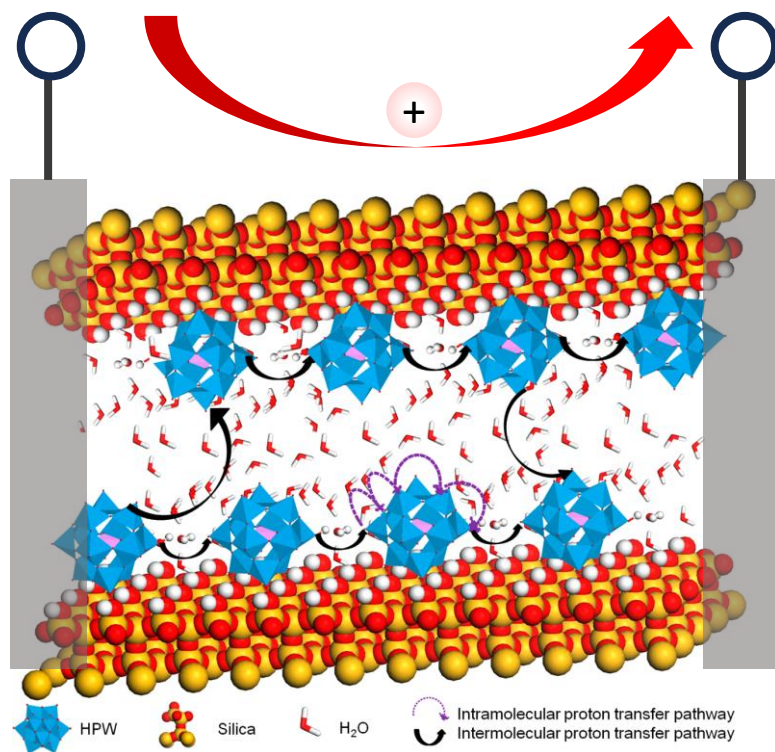
**Pseudo-liquid
proton/water
layer**



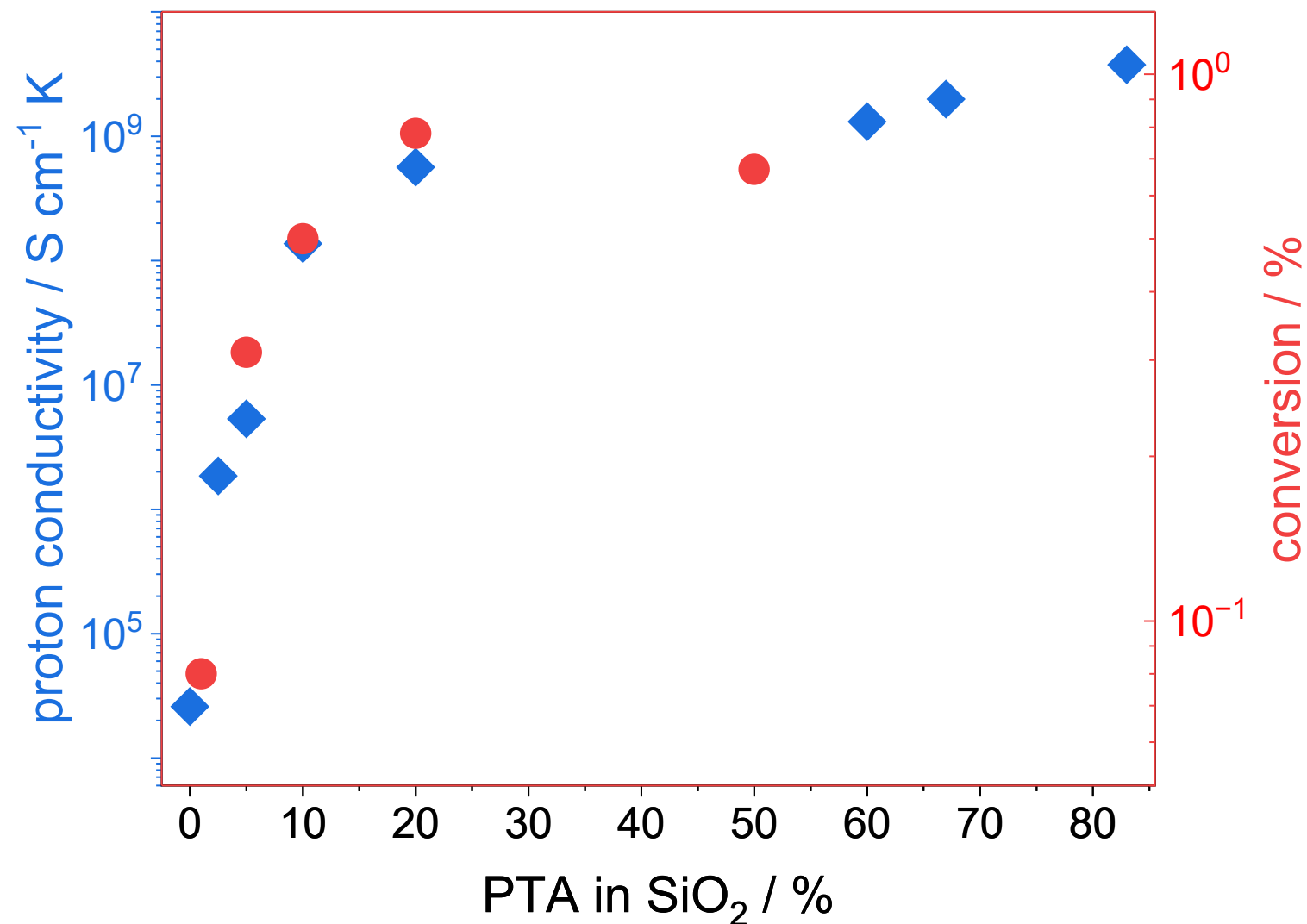
Neutrons measure the «Pseudo-liquid proton/water layer»



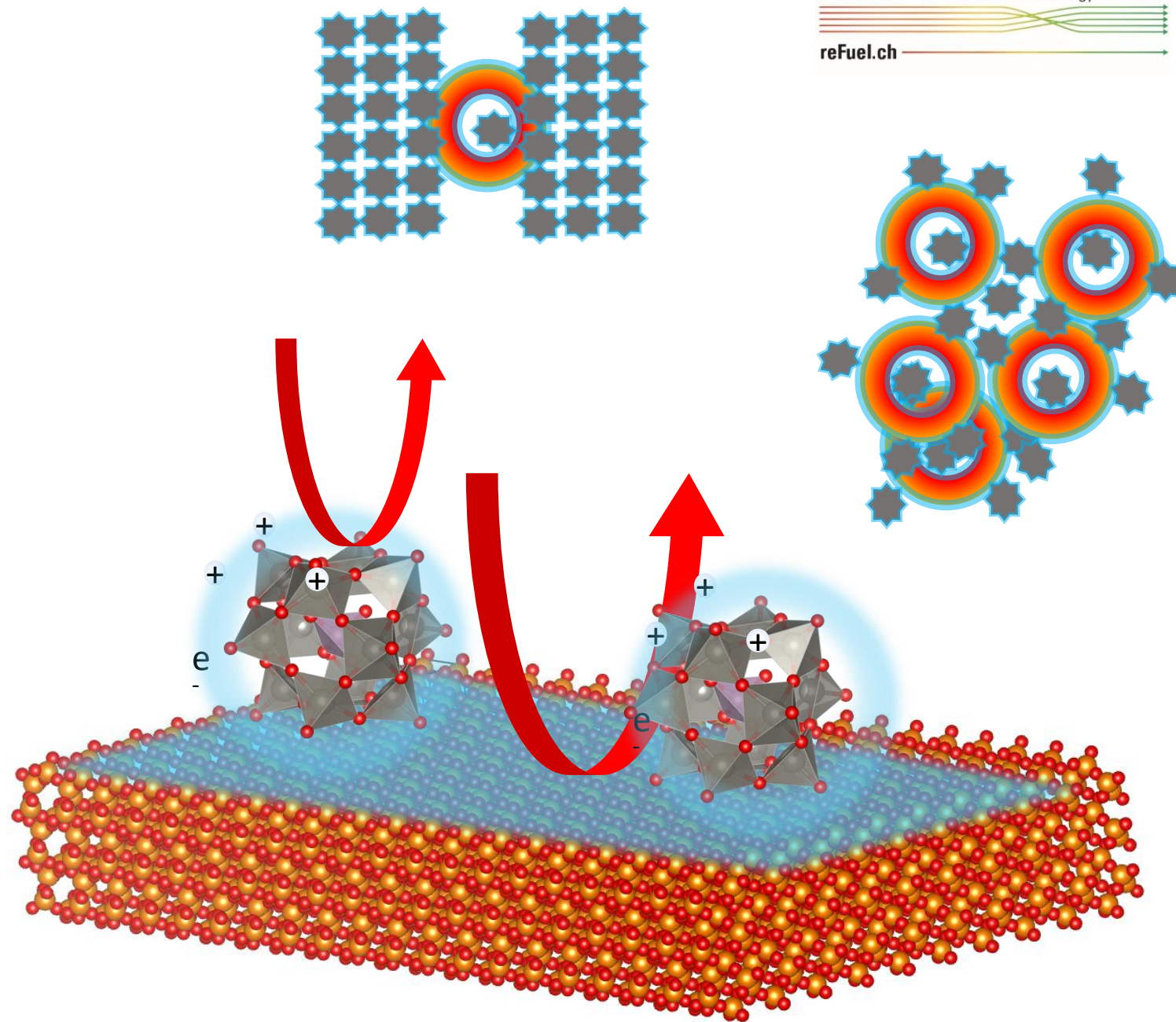
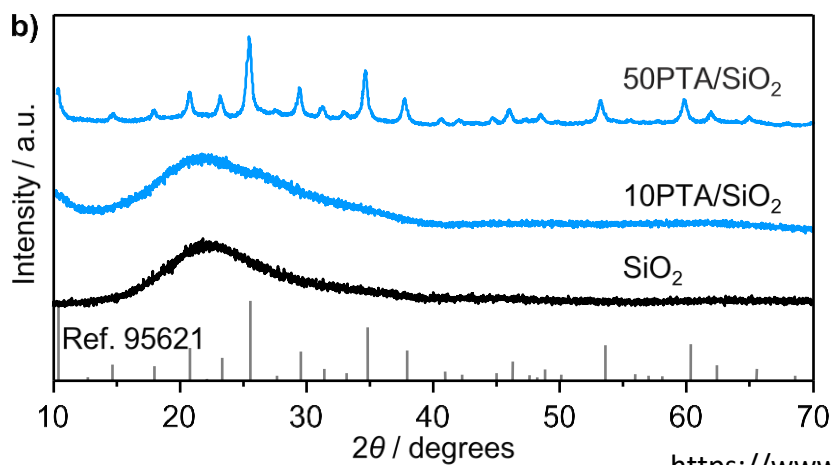
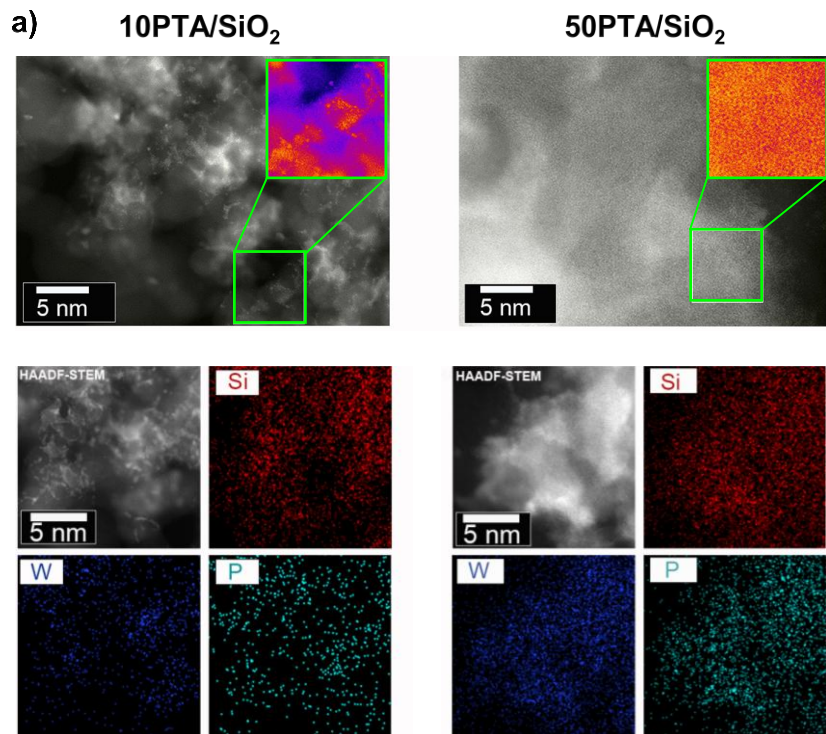
A Pseudo-liquid proton/water layer is a proton conductor!



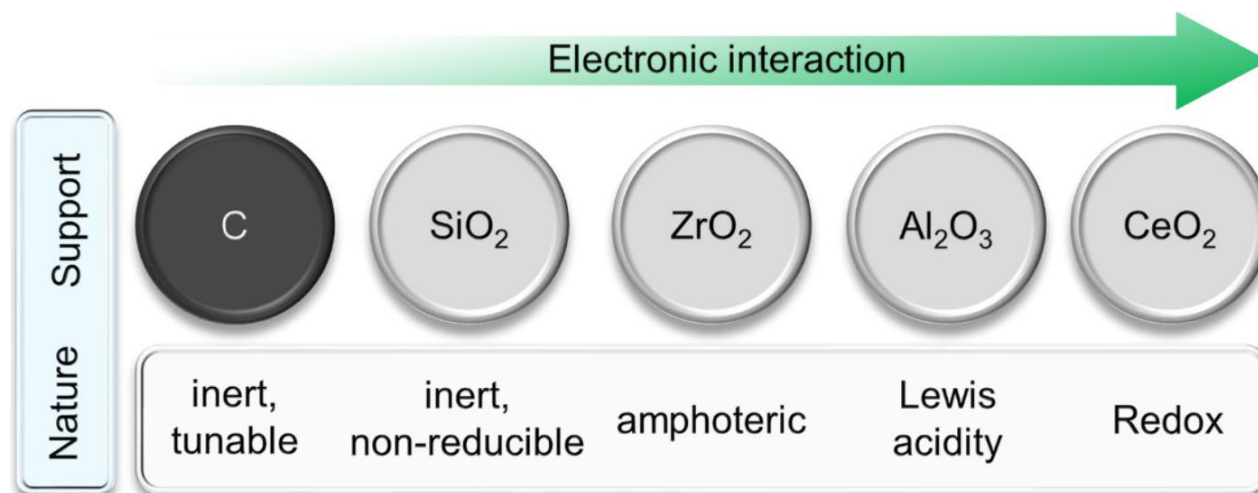
**The support (the “interface”)
is “acidified”.
(soggy sand electrolyte)**



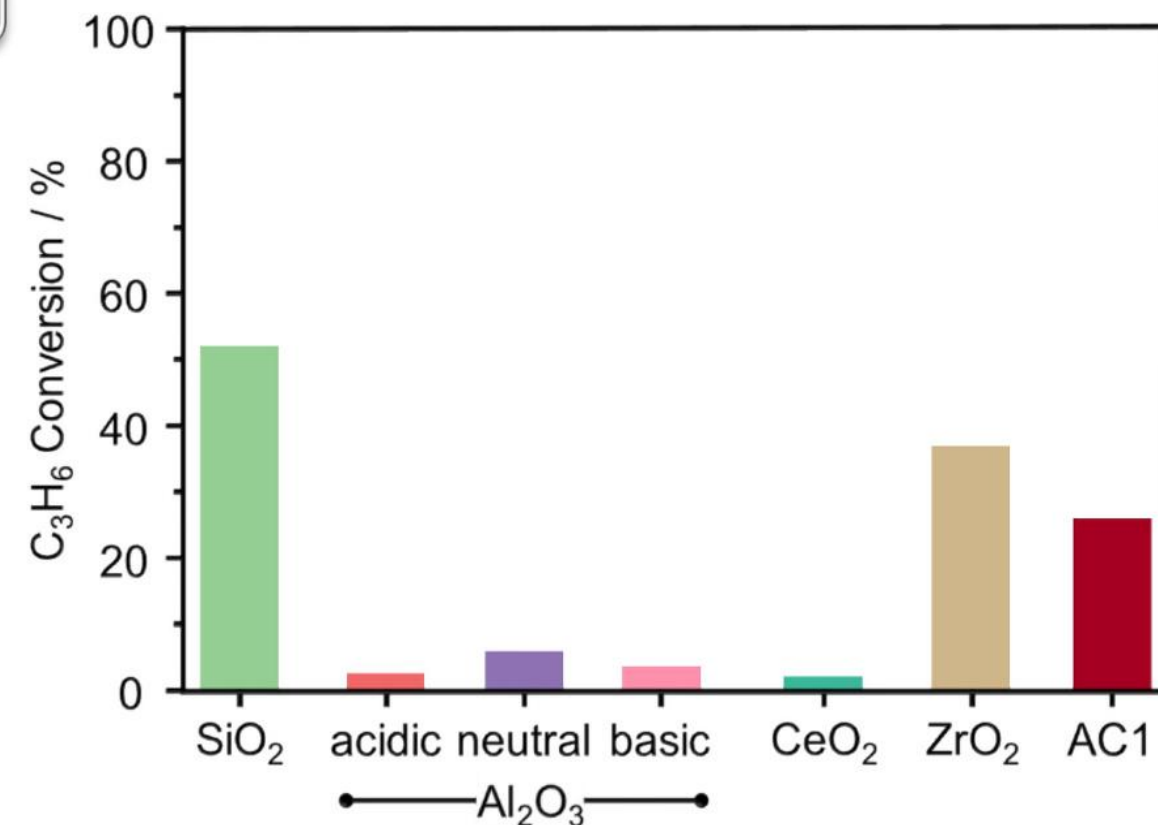
How does our catalyst looks like?



The support is active part of the catalyst



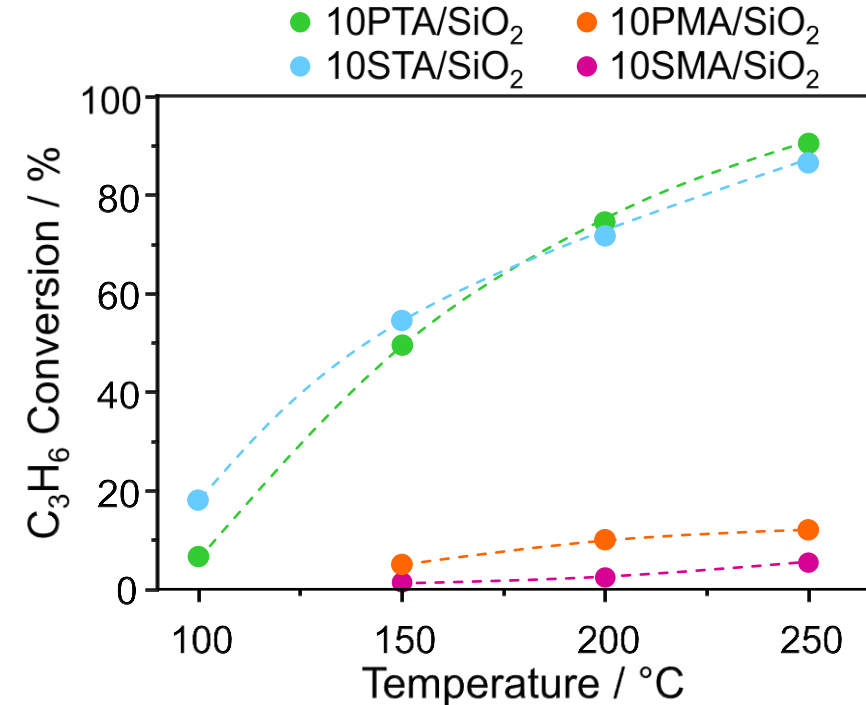
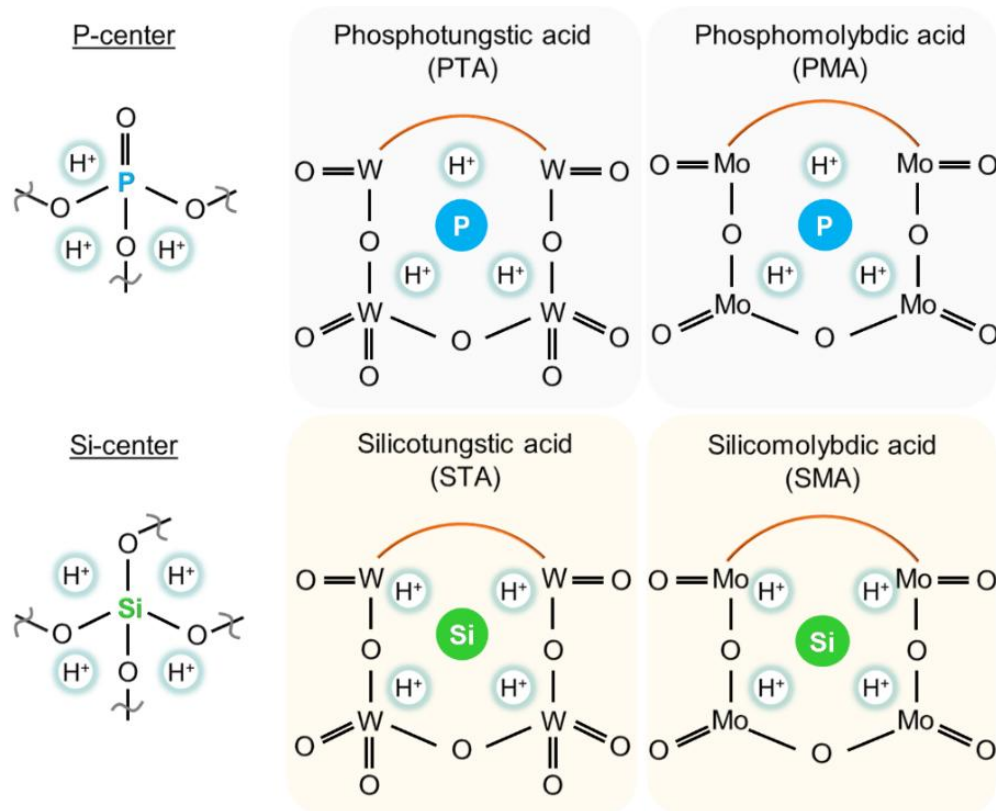
Which means it is crucial



«Even better» HPA oligomerization catalysts

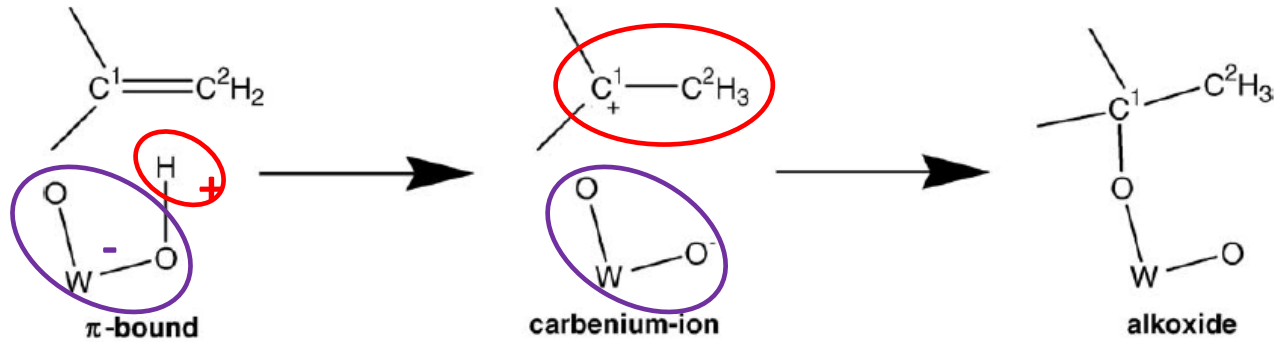
- PTA is one example of heteropoly acid (HPA) - oxide catalyst systems
- Silico-tungsten acid (STA) proved to be the best choice
- Molybdenum based systems do not work

Tungsten mining: China controls over 80% of global tungsten production and has implemented strict export controls.

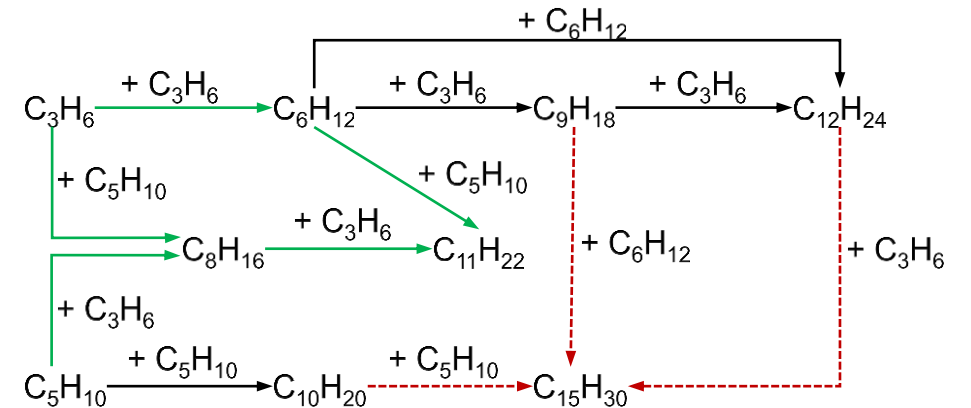
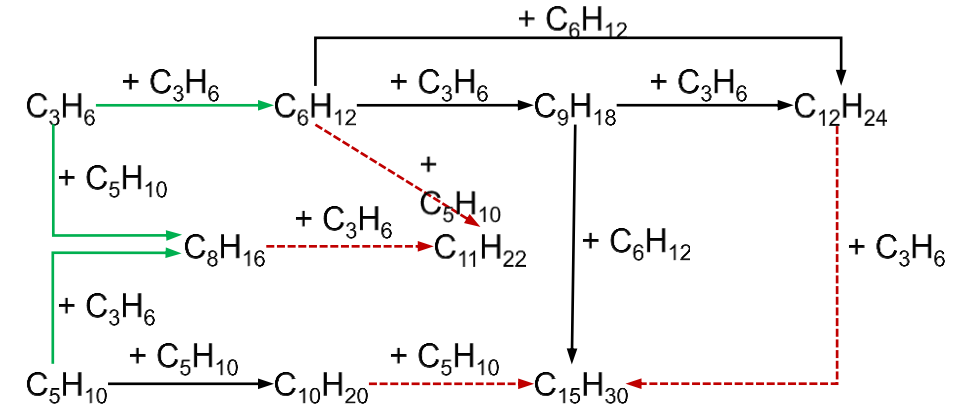
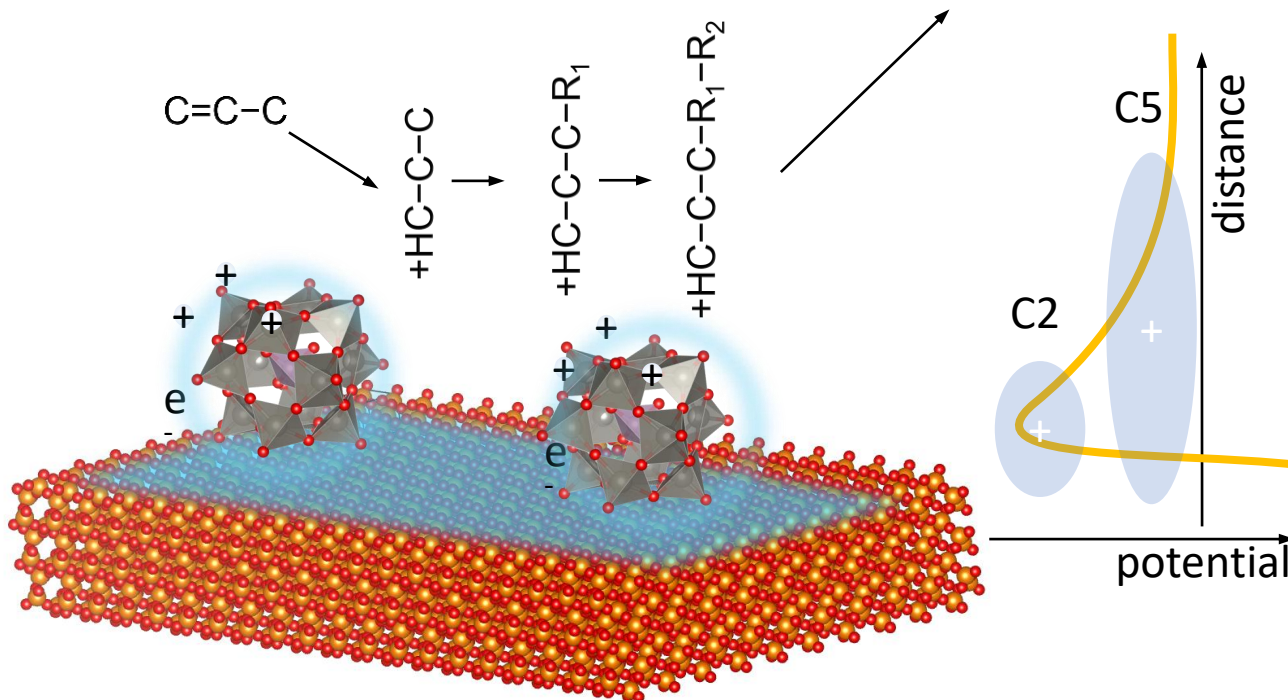


A. Cesarini, et al., to be submitted (2026)

Olefin oligomerization – selectivity

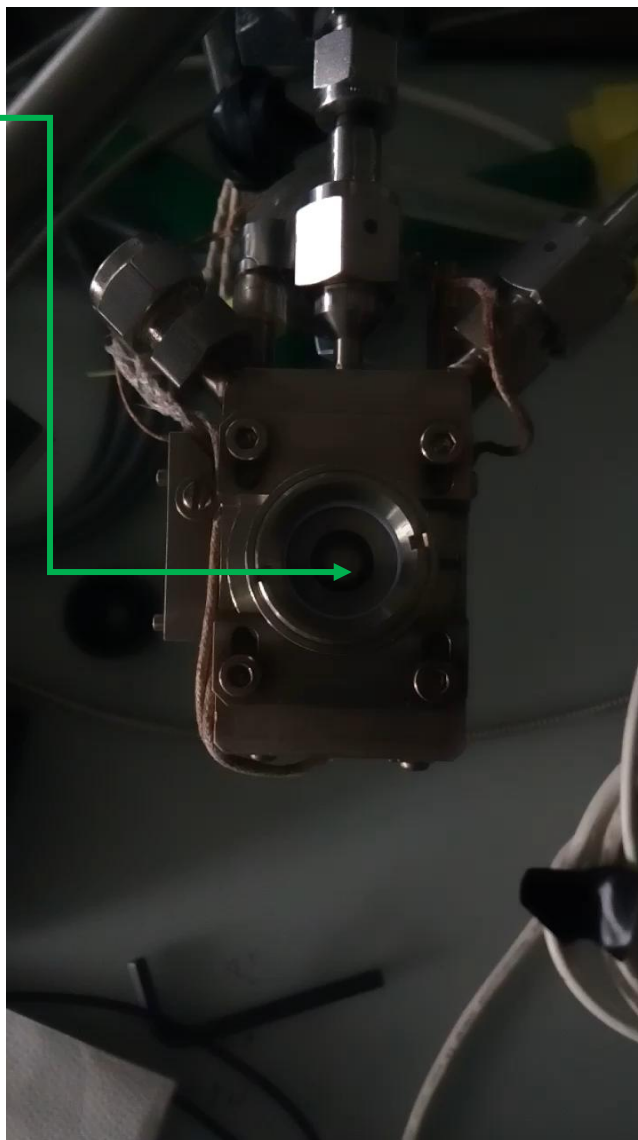


M.J. Janik et al. Catalysis Today 116 (2006) 90

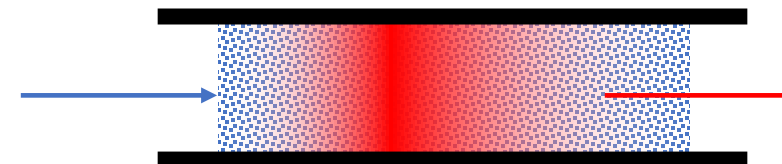


A. Cesarine, PhD 2026 (to be published)

The importance of the reactor



- Catalytic oxidation of methanol
- $CH_3OH + \frac{3}{2} O_2 \rightarrow CO_2 + 2H_2O$;
 - $\Delta H = 726 \text{ kJ/mol}$
- DRIFTS-cell kept at 400°C
- **BUT this is not the temperature of the catalyst**
- **Oligomerization: 100 kJ/mol**
- **Gas reactors have a severe temperature problem**

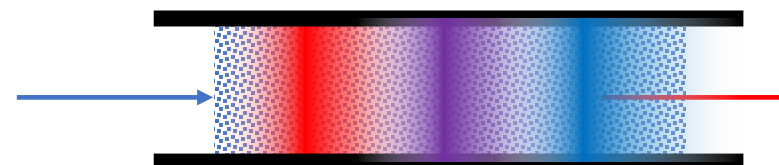


Alessia's solution:

- Liquid reaction: olefin is dissolved in hexane (mixture is kept liquid due to high pressure)
- Better heat transport
- Intrinsic temperature control
- Low coking

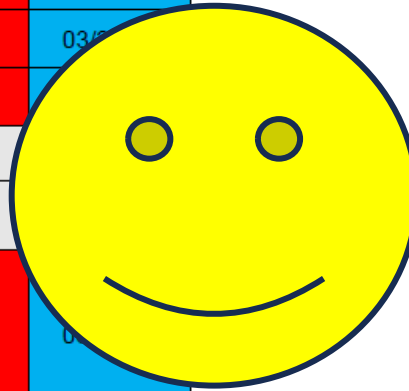
Connor's follow up project:

- Reactor length $\Leftrightarrow$ selectivity



Milestone and deliverable status (no limit)

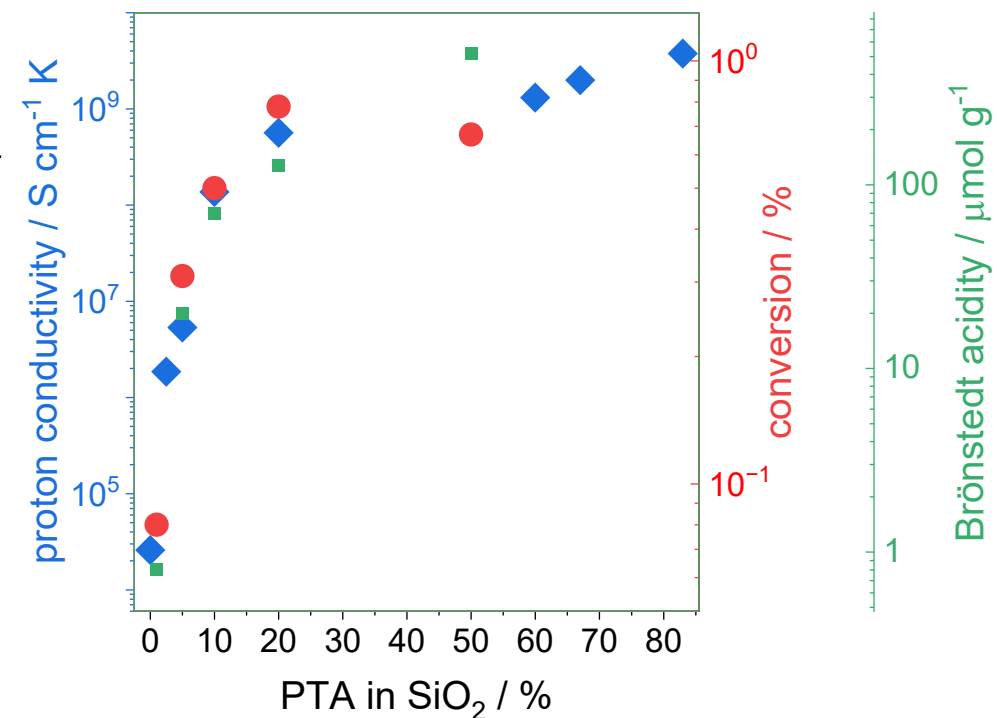
Milestones						
No.	Name	Delivery date (full proposal)	Status			New delivery date
M7.1	Synthesis of composite zeolite catalysts with improved selectivity and stability in the MtO process (R submitted Feb 19.26)	12/2024 and 09/2026	x			
M7.2	Modelling the reaction mechanism of MtO and involved energetics. (A: modeling framework has been developed and used at SUPSI)	09/2025	x			
M7.3	Development of reaction design for OtF catalysts with increased activity including regeneration strategies	12/2026	x			
M7.4	Optimization of the regeneration protocol for the most stable MtO catalyst based on understanding of the coke-formation mechanism.	03/2026		x		12/2026
M7.5	Process design feedback loop. Feedback loop between WP7 process design and WP3 systems analysis for methanol-to-X routes established	06/2027	x			
M7.6	Modelling desorption and diffusion of adsorbates on OtF catalysts	12/2025		x		03/2026
M7.7	Modelling desorption and diffusion of adsorbates on MtO catalysts	03/2027		x		
Deliverables						
No.	Name	Delivery date (full proposal)	Status			
D7.1	Improved MtO catalyst. Zeolite catalysts with optimized active site distribution and added reactive oxides. Benchtop spectroscopic reactor setup for the observation of catalyst surface by UV-vis. Novel zeolite catalysts with improved product selectivity and catalyst stability	12/2026		x		
D7.2	Model of the MtO reaction mechanism. Established model of the reaction mechanism of MtO reaction and involved energetics.	06/2026	x			12/2026 (despite on track, new date allows more useful results)
D 7.3	Model of adsorbates in MtO and OtF. Established model for dynamics and stability of adsorbates in MtO and OtF process.	12/2027		x		03/2028
D7.4	Reaction design for OtF catalysts. An optimized reaction design for OtF has been defined based on standard or innovative regeneration strategies, such as microwaves, UV light, etc.	12/2026	x			
D7.5	Optimized regeneration protocol for MtO catalysts.	12/2027	x			



- Oxide supported HPAs show excellent conversion and selectivity for **olefin oligomerization** to SAF-chain length at low temperatures
- Support-HPA interaction depends on the coverage changing catalytic activity
- Moderate degradation, regeneration relatively simple
- Patent filed includes various (even better) catalyst systems («design»)
- We understand aspects of the mechanism

Backup Acidity of catalyst

Catalyst	W content ^a / wt. %	P content ^a / wt. %	Si/Al ratio ^a / -	$S_{\text{BET}}^{\text{b}}$ / $\text{m}^2 \text{g}^{-1}$	$V_{\text{pore}}^{\text{c}}$ / $\text{cm}^3 \text{g}^{-1}$	$c_{\text{Brønsted}}^{\text{d}}$ / $\mu\text{mol g}^{-1}$	$c_{\text{Lewis}}^{\text{d}}$ / $\mu\text{mol g}^{-1}$
1PTA/SiO ₂			-	226	0.6	0.8	1.5
5PTA/SiO ₂			-	204	0.5	20	2.5
10PTA/SiO ₂			-	186	0.5	70	10
20PTA/SiO ₂			-	166	0.5	128	11
50PTA/SiO ₂			-	84	0.3	516	10
SiO ₂			-	257	1.0	-	-
Z140	-	-	140				
Z25	-	-	30				
ASA-50	-	-	60				



^aDetermined by ICP-OES.

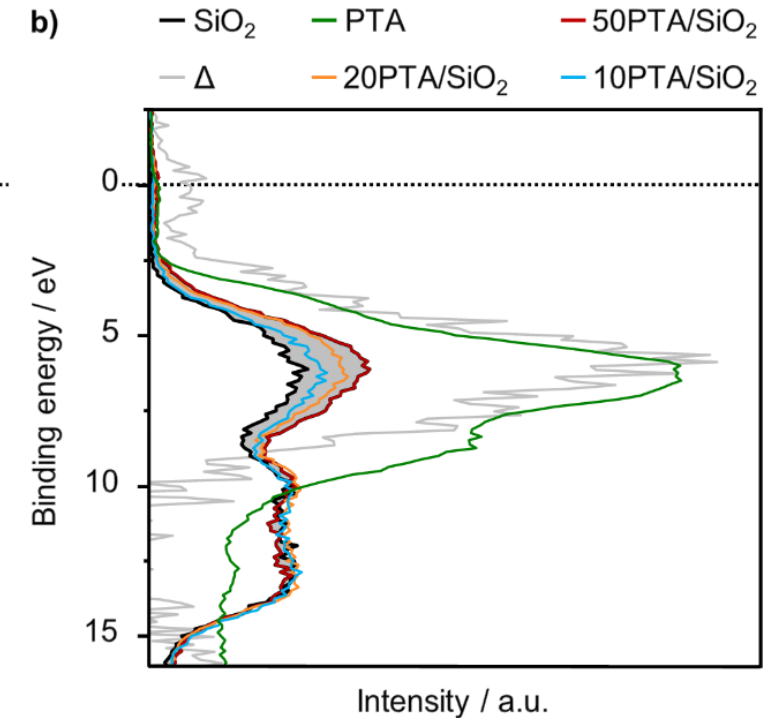
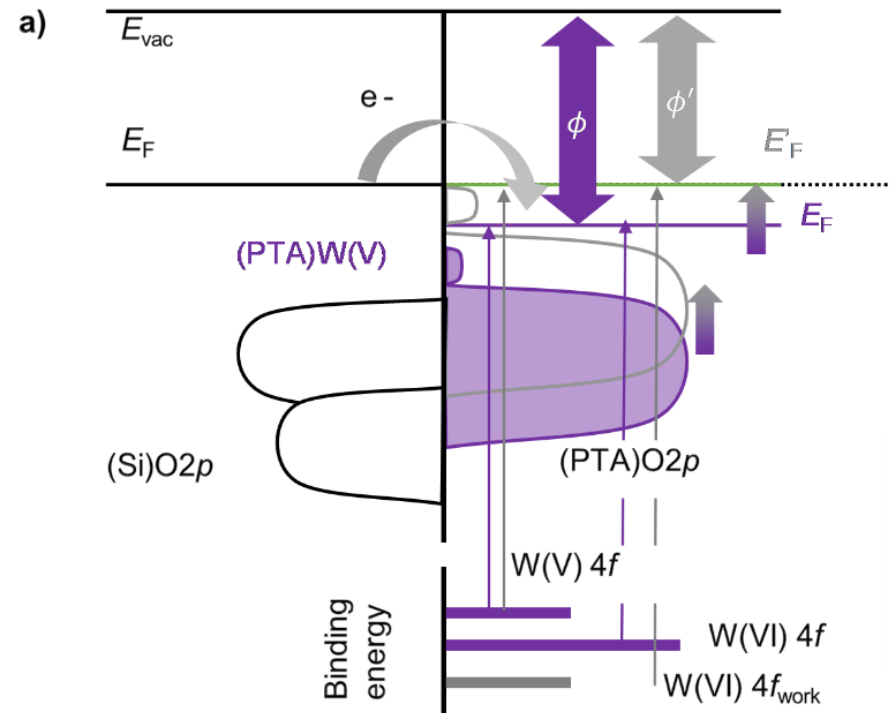
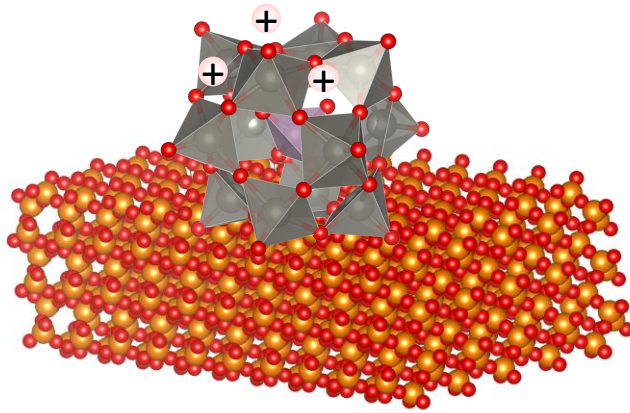
^bBET model.

^cVolume of N₂ adsorbed at p/p₀ = 0.98.

^dDetermined by IR spectroscopy of adsorbed pyridine.

Backup: Electronic structure of Interface

- Mechanistic ideas: interaction of HPA with support leads to **reduction** and new states («**interfacial**»)
 - The new states («**interfacial**») are also visible in the valence band, indicating band bending (shift of E_F) and reduction (states at E_F)



- The Idea: Electrically driven proton transfer promotes Brønsted acid catalysis (taken from Westendorff et al., Science 383, 757–763 (2024))