Design Principles for the Synthesis of Self-Pillared ZSM-5 Zeolite Nanosheets

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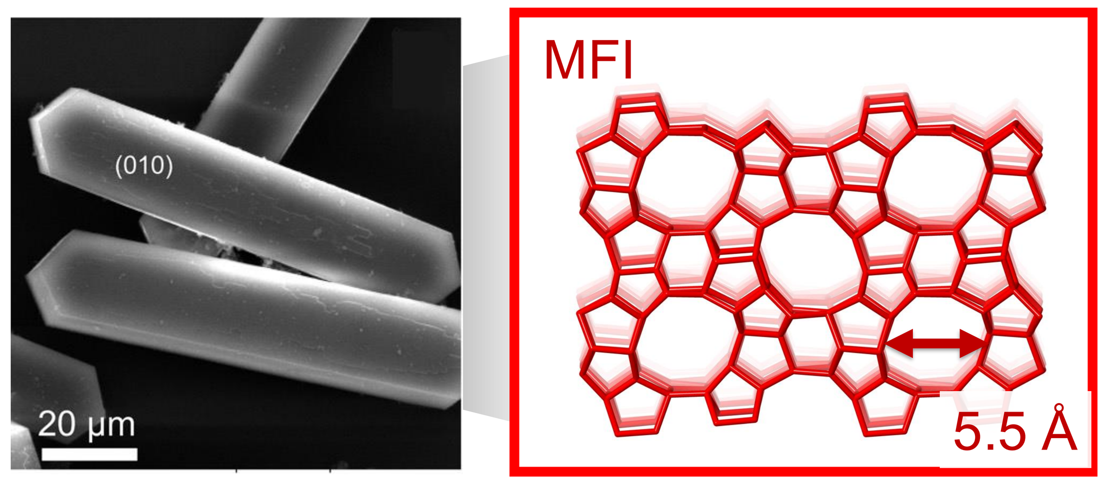
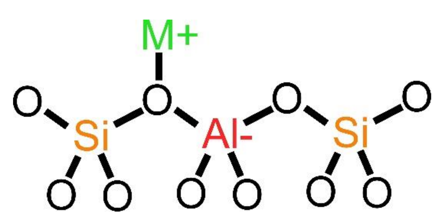
Zeolite Catalysts



> 250 framework types

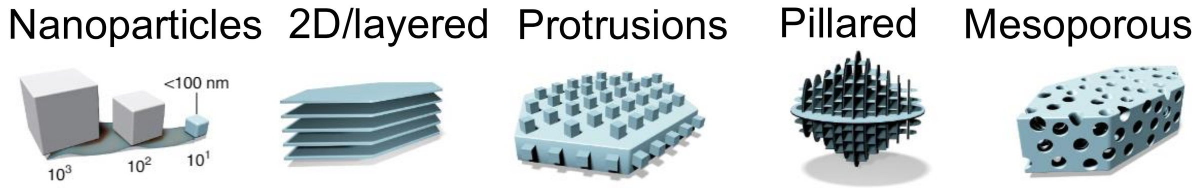


❑ H^+ Brønsted Acid
❑ M^+ Lewis Acid

- Zeolites are shape-selective catalysts with tunable physicochemical properties (e.g., acidity and pore networks).
- Catalytic applications: hydrocarbon cracking, benzene alkylation, hydrocarbon upgrading, carbon capture, etc..

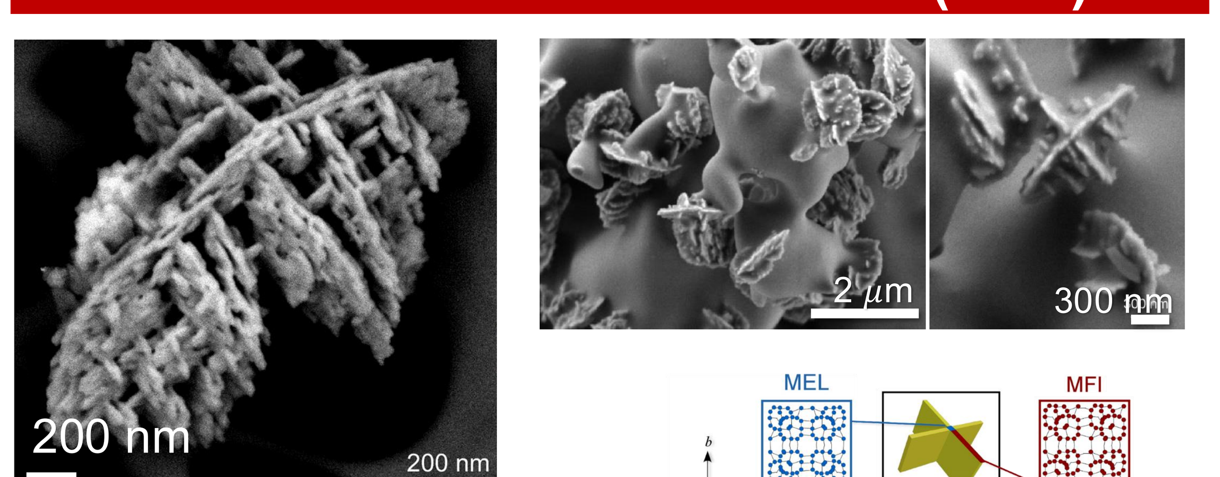
Improving Mass Transport

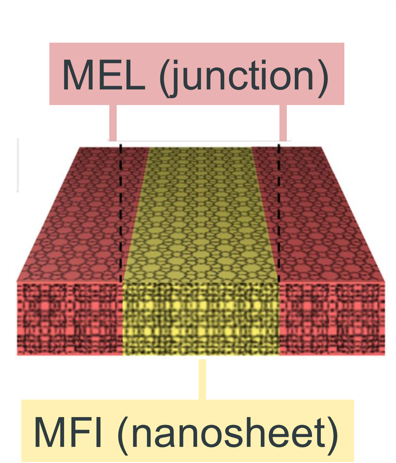
Nanosized			Hierarchical	
Nanoparticles	2D/layered	Protrusions	Pillared	Mesoporous

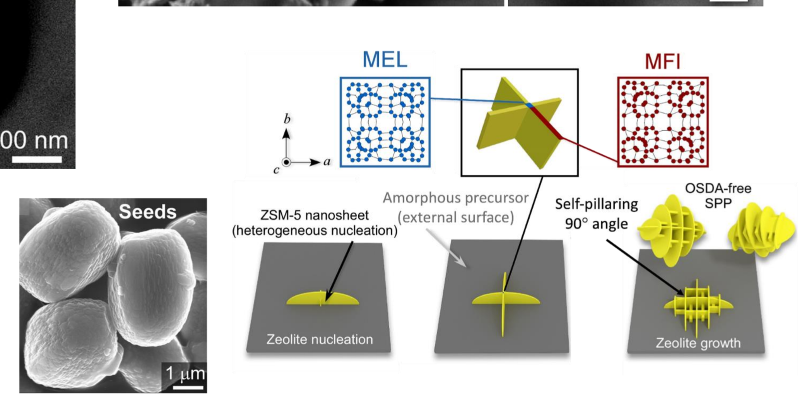


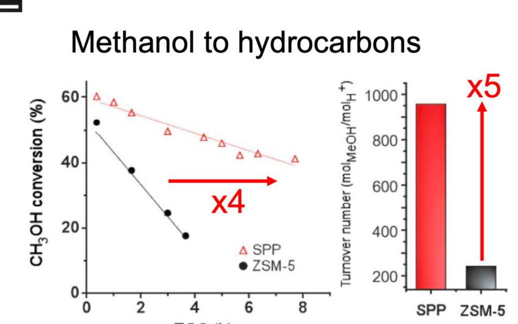
- Synthesizing nanosized and hierarchical zeolites can reduce diffusion limitations in confined zeolite pores.
- Syntheses of these state-of-the-art materials typically require complex procedures and/or costly organics.

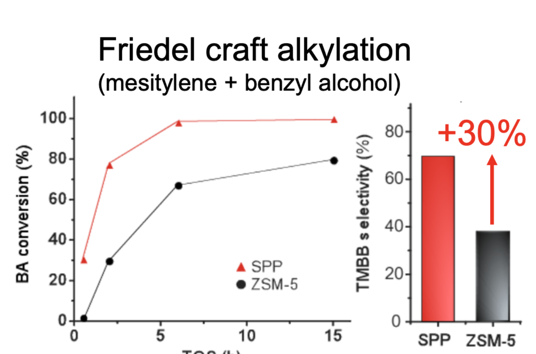
Self-Pillared ZSM-5 Zeolites (SPP)











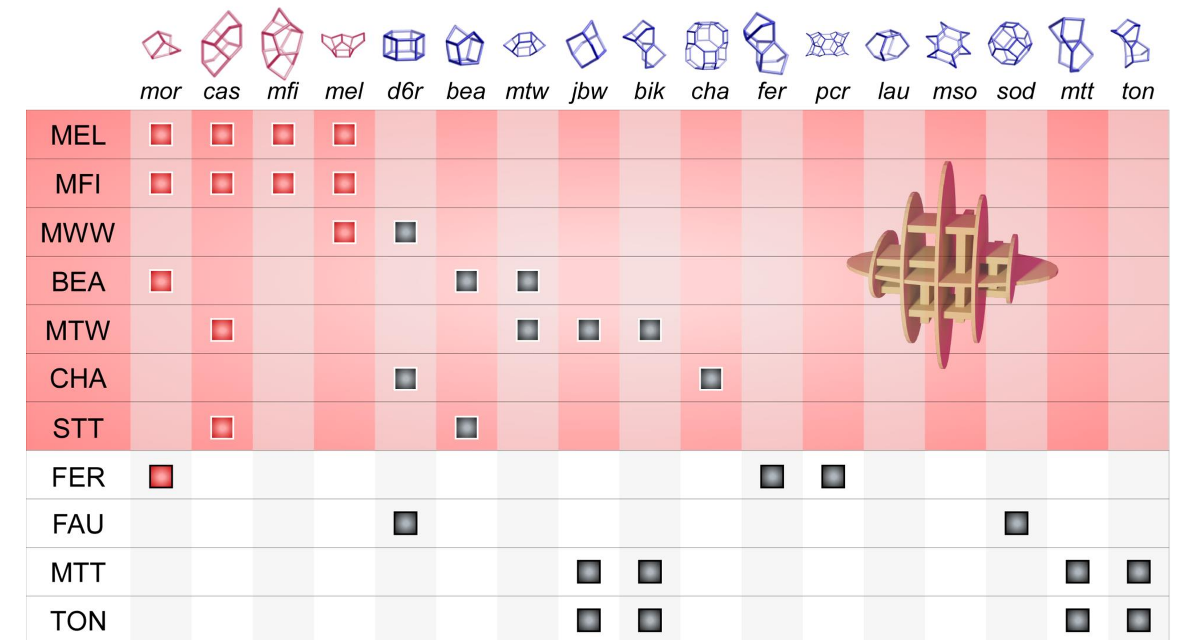
Key Features

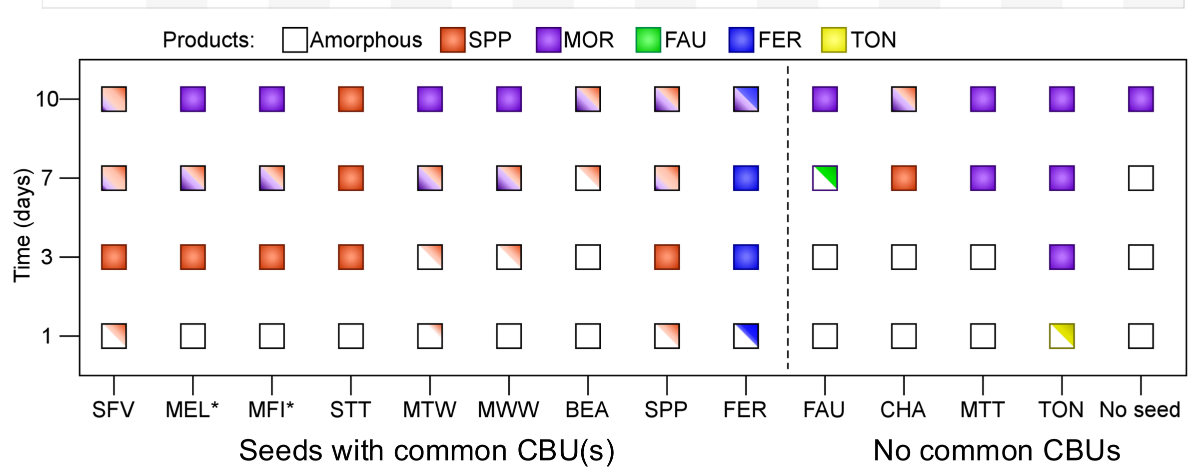
- ✓ Organic-free synthesis
- ✓ High yield synthesis
- ✓ Control over Si/Al ratio
- ✓ Enhanced catalytic performance and lifetime

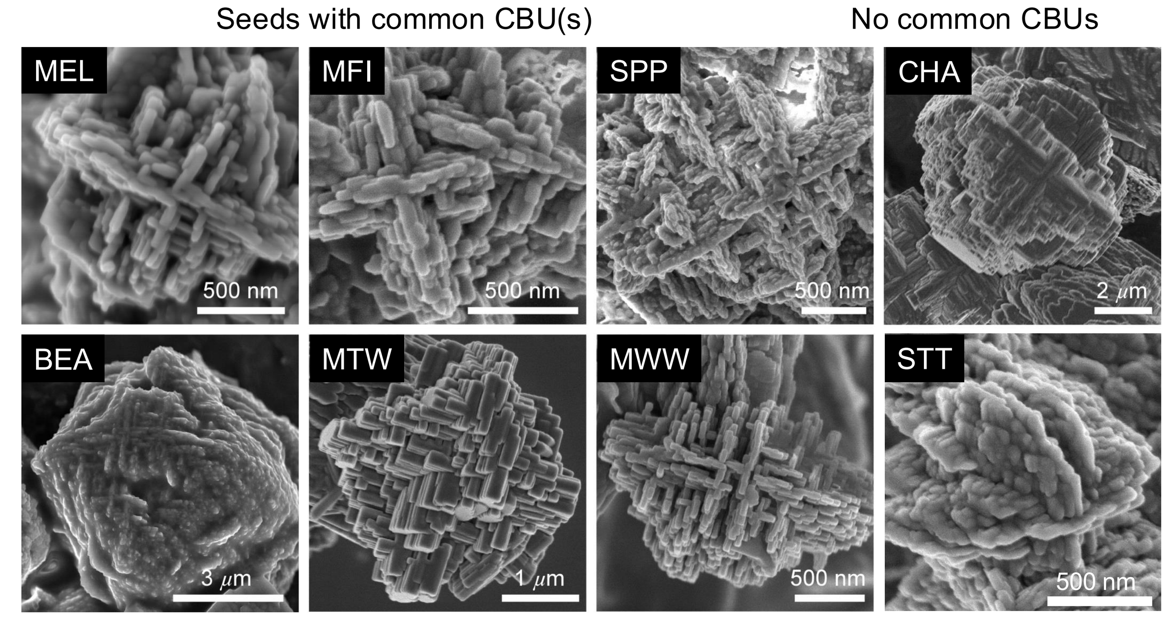
Research objectives: (1) elucidate the mechanism of seed-assisted synthesis of SPP zeolites; (2) synthesis optimization; and (3) explore scale-up feasibility

Impact of Composite Building Units

Hypothesis: seeds sharing common CBUs with MFI and MEL lead to pillared zeolites



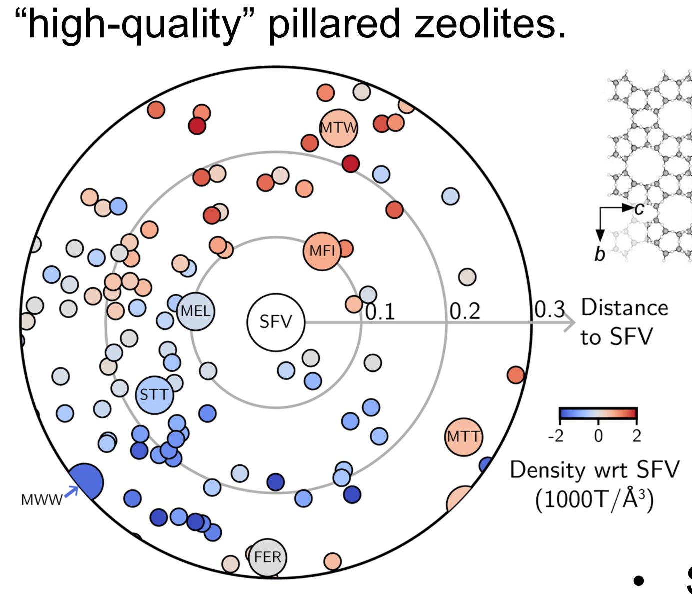


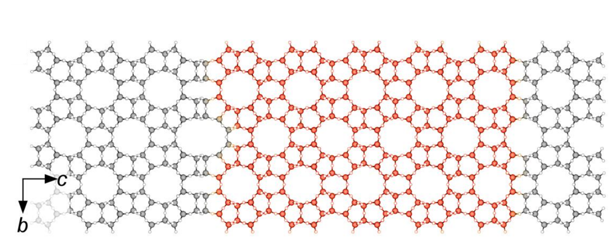


- Our study found seeds with common CBUs can lead to (partial) pillaring but not a universal trend (e.g. CHA).

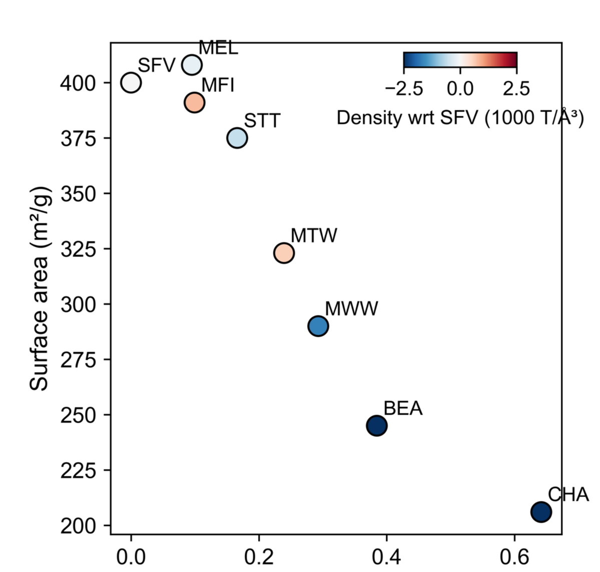
Distance Matrix as a Descriptor for Seed Selection

Hypothesis: seeds with structural similarity (i.e. low distance) with SFV (SPP hybrid) increase the likelihood formation of "high-quality" pillared zeolites.





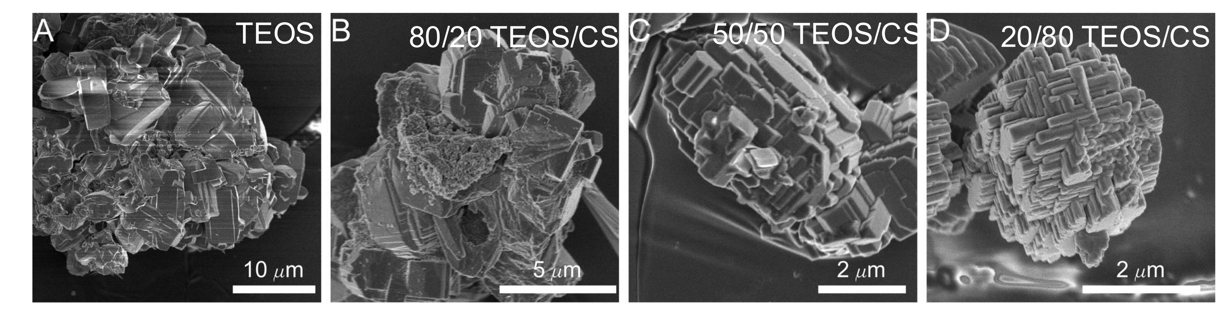
SFV: reference structure to maximize the similarity with the target framework.



- Structural similarity of zeolite seeds and products offers predictive power for final products.
- A remarkable correlation exists between seed distance to SFV and surface area.
- The distance matrix and density might explain why some seeds (e.g., FER) do not lead to SPP.

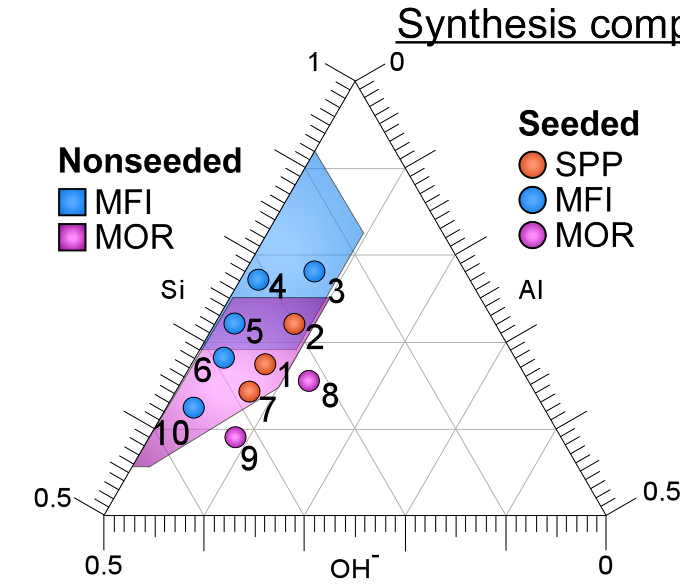
Effect of Amorphous Precursors

Source of silica (synthesis reagents)

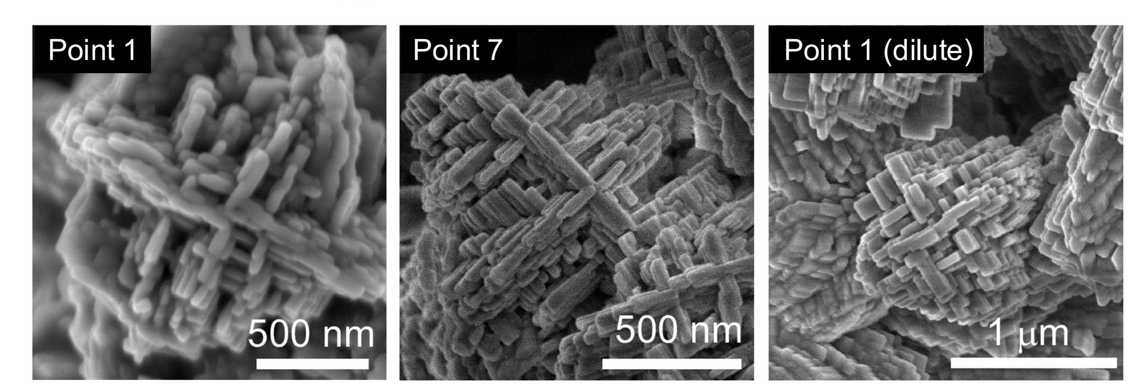


- Changes in the silicon source (TEOS and colloidal silica) and order of reagent addition alters speciation and impacts the trajectory of SPP synthesis.

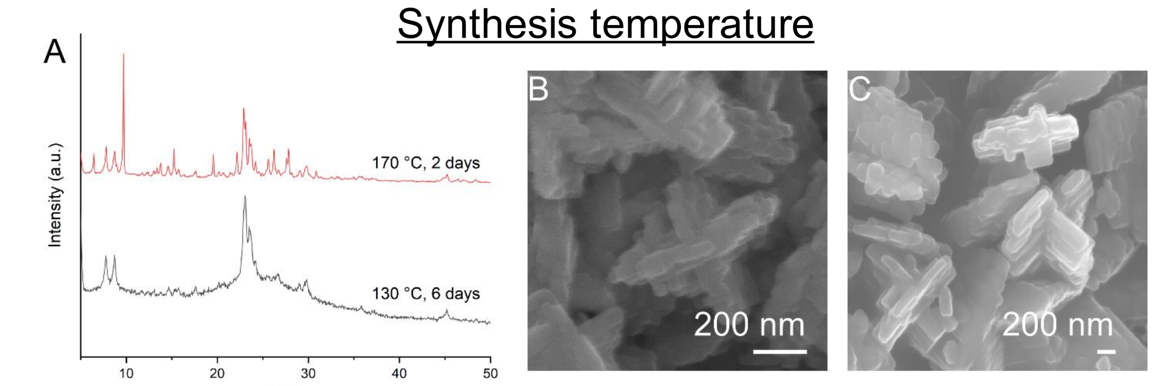
Synthesis composition



- Limited synthesis window to form pillared zeolites (confirmed by kinetic phase diagram).
- Water content influences degree of pillaring and crystal size.



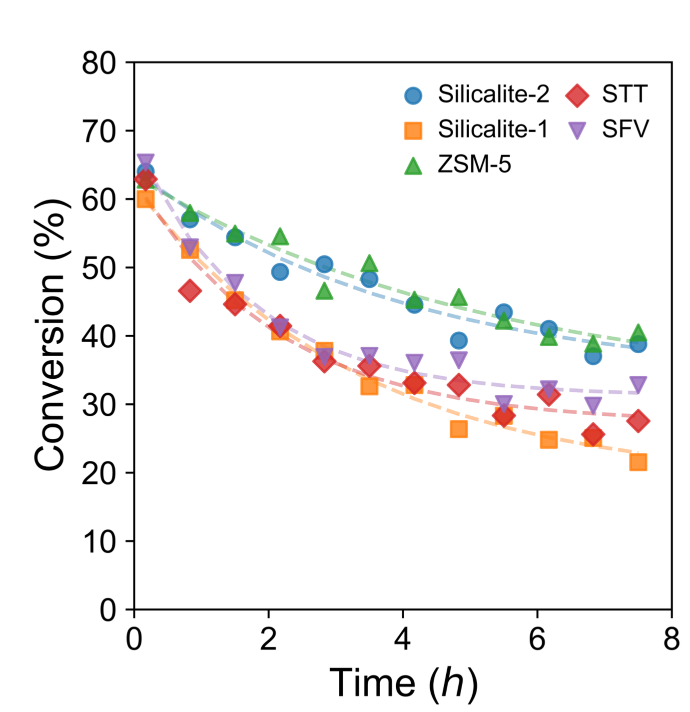
Synthesis temperature



- Synthesis temperature influences morphology and kinetic of SPP synthesis.

Impact of seed selection on catalytic performance

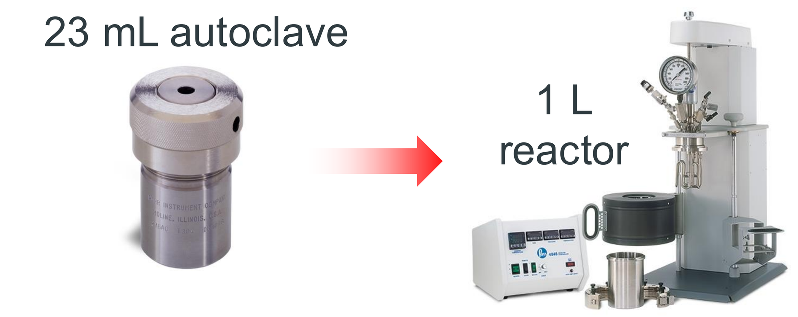
Seed [a]	BET S_A (m^2/g)	S_{ext} (m^2/g)	V_{micro} (cm^3/g)	Si/Al	C_{acid} (μmol g^{-1})
MEL	408	68	0.15	9	444
MFI (ZSM-5) [b]	391	61	0.15	9	424
MFI (silicalite-1)	374	85	0.13	10	497
STT	380	120	0.13	9	464
SFV	400	99	0.13	9	473



- Order of seed crystals from best to worst SPP catalysts: MEL (silicalite-2) ≈ MFI (ZSM-5) > STT ≈ SFV ≈ MFI (silicalite-1).
- Catalytic testing reveals a clear structure–function relationship, where the materials with highest degree of pillaring are those with the highest total surface area and MTH catalyst performance.

Scale-up and Optimization Efforts

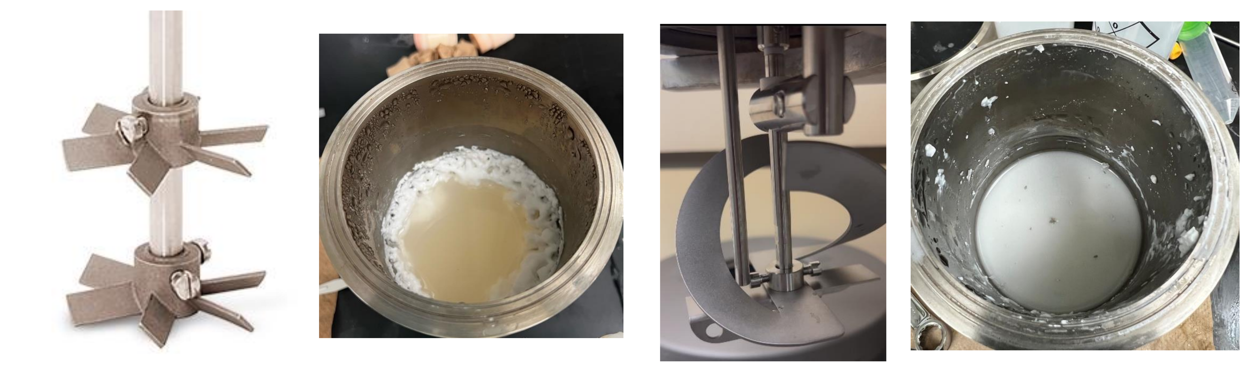
- ➢ With its superior catalytic performance compared to commercial zeolites, we are working on the scale-up of SPP materials.



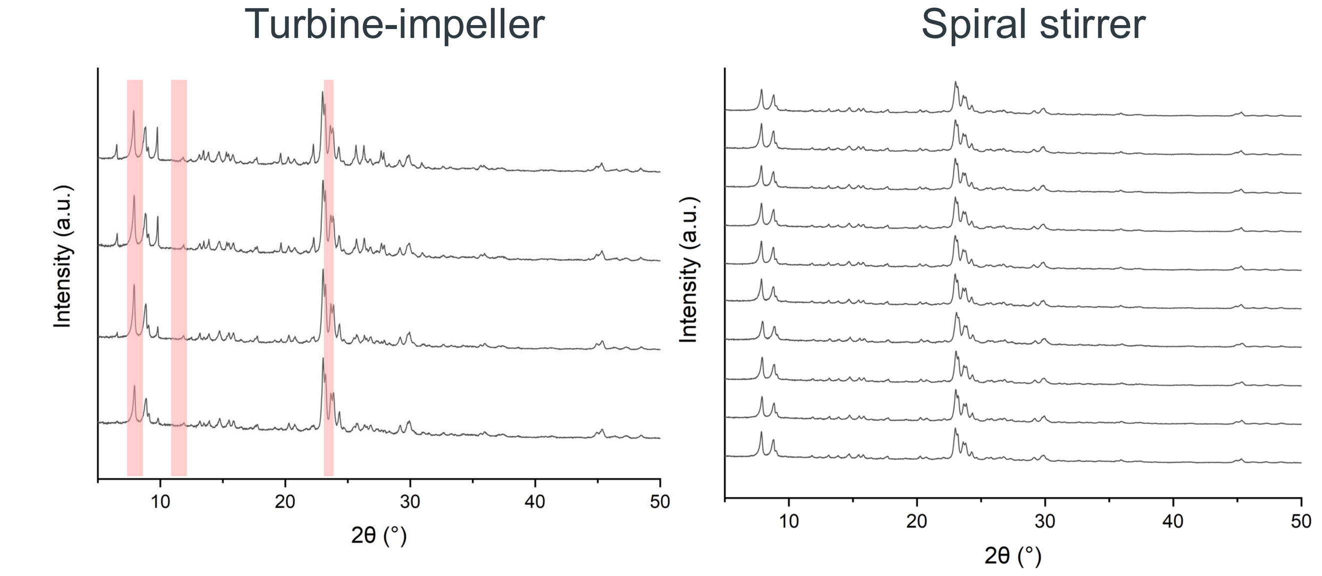
Challenges

- Temperature gradient
- Crystallinity
- Mixing
- Safety

Optimization efforts



Turbine-impeller	Spiral stirrer



Product phases (split into 4 parts)	Uniform product phases (split into 10 parts)

Sample	BET S_A (m^2/g)	Ext. S_A (m^2/g)	V_{micro} (cm^3/g)
Turbine-impeller	180 - 308	18 - 34	0.07 – 0.12
Spiral	263-302	56-65	0.1

- Synthesis conditions (e.g. reactor size, synthesis time, seed amount, stirrer speed, etc.) have been systematically studied to optimize materials scale up.
- Choice of stirrer is an important factor for large-scale synthesis of SPP zeolites.

Summary of Key Findings

- We identified an SPP synthesis that is scalable and provides a viable pathway to commercialization.
- We have elucidated factors governing the synthesis of self-pillared ZSM-5 zeolites by employing rational and data-driven hypotheses.
- We have optimized the synthesis of SPP zeolites using a variety of approaches.

References

[1] *Mallette et al., Nature Synthesis* (2022) 1–14
[2] *Jain et al., Advanced Materials* 33 (2021) 2100897
[3] *Kumar et al., Nature Materials* (2020) 443–449

Acknowledgments

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