



Membrane-assisted Ethylene Synthesis over
Nanostructured Tandem Catalysts

Shaping SSZ-13 zeolite–metal oxide architectures for efficient tandem CO₂ conversion to light olefins

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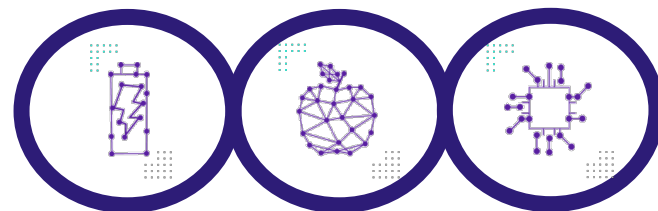
July 1st, 2026
Naples, IT



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KOLEN'KO RESEARCH GROUP

Unconventional nanomaterials for sustainable chemistry

- Heterogeneous catalysis
 - Electrolysis
 - Coatings



Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts

Why Ethylene?

1.2 tons
of CO₂
per ton of produced ethylene!

Mackenzie, 09 April 2024.

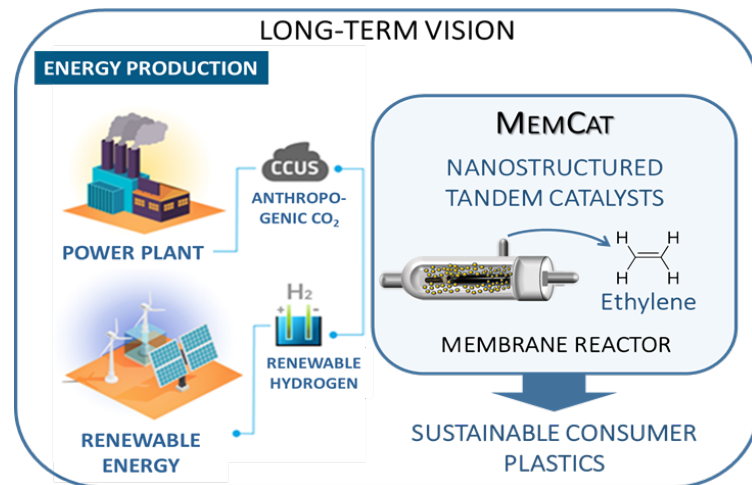


Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts

The goal of MemCat:

Deliver a proof-of-concept for carbon dioxide (CO₂) direct conversion to ethylene (ET)

using tandem catalysts within a membrane reactor



❖ CO₂ hydrogenation to Ethylene with $X \geq 80\%$ and $S \geq 95\%$



MemCat Project



Long-term Impact



Sustainable carbon negative production of ethylene using **captured CO₂** as feedstock.



Addressing the growing global demand for ethylene, expected to reach a market value of **€110 billion by 2027**, with MemCat offering a greener alternative to high CO₂-emission processes.



Supporting the **EU in green chemical production**, creating employment and contributing to a sustainable solution for plastics production.



MemCat technology could **reduce ethylene production costs** by 35%, improving yields and reducing downstream separation costs.

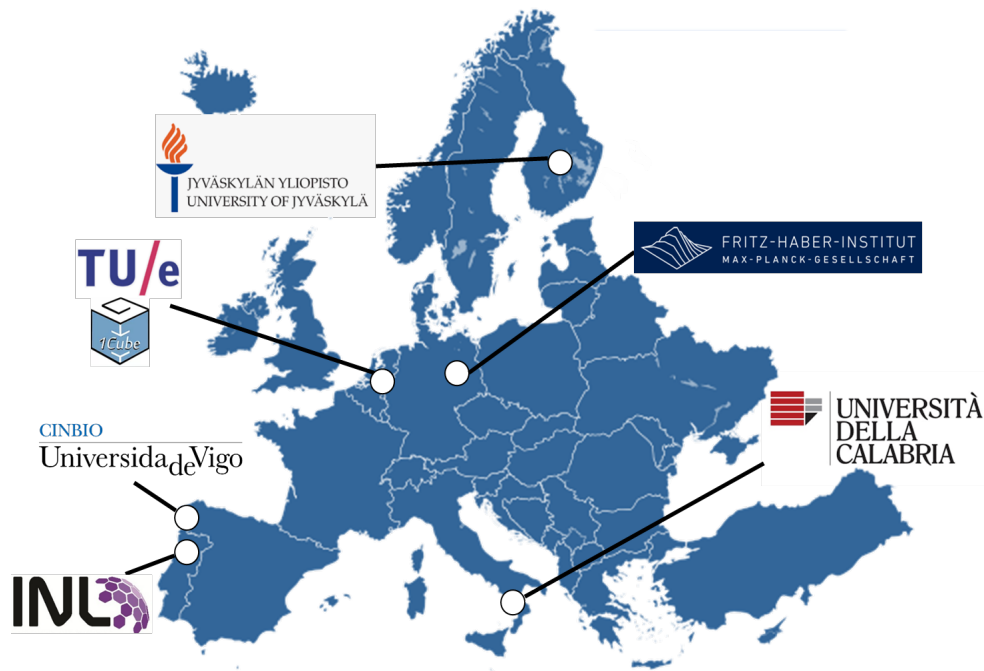
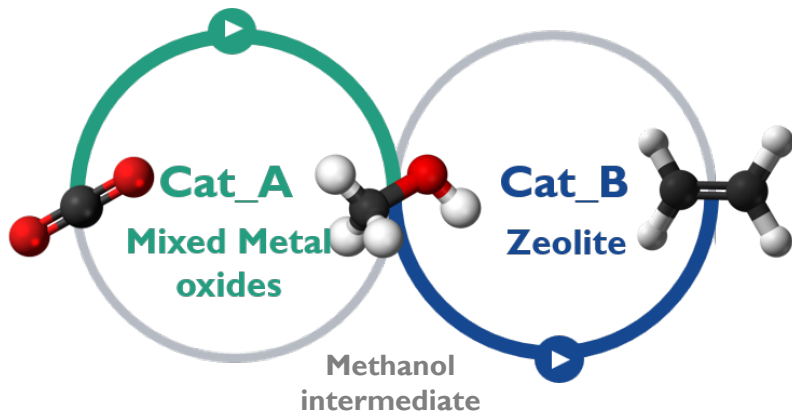




MemCat Project



Our role



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Four matching rules for constructing high-performance bifunctional MCs-zeolites-based catalysts

Catalysis Reviews, 2024, 1-76

1

Methanol catalyst:

High CO₂-to-methanol selectivity under high temperatures

2

Zeolite:

Appropriated topology, moderate acidity, and pore-structure to high selectivity

3

Efficient matching in conversion rate:

MeOH formation higher than its conversion rate: unconverted MeOH can be decomposed to CO;

MeOH formation lower: zeolite-efficiency cannot be fully utilized, and the over-hydrogenation will form paraffin

4

Unique spatial distributions:

Too far, diffusion distance of MeOH prolonged: concentration gradient and decreases the catalytic activity;

Too close, active sites can poison each other: loss of catalytic activity.

Tandem Catalyst Materials selection

Cat_A_{MeOH}: Metal oxides

Co-precipitation procedure



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MAX-PLANCK-GESELLSCHAFT

CZA

CuZnO/Al₂O₃

ZZ

Zn/ZrO₂

Mixed Metal oxides

500 mL of nitrates

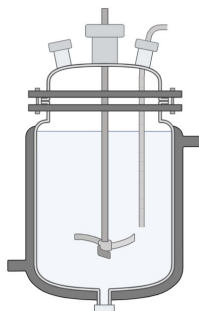


+

Base (pH control) or
precipitation agent



Dropwise

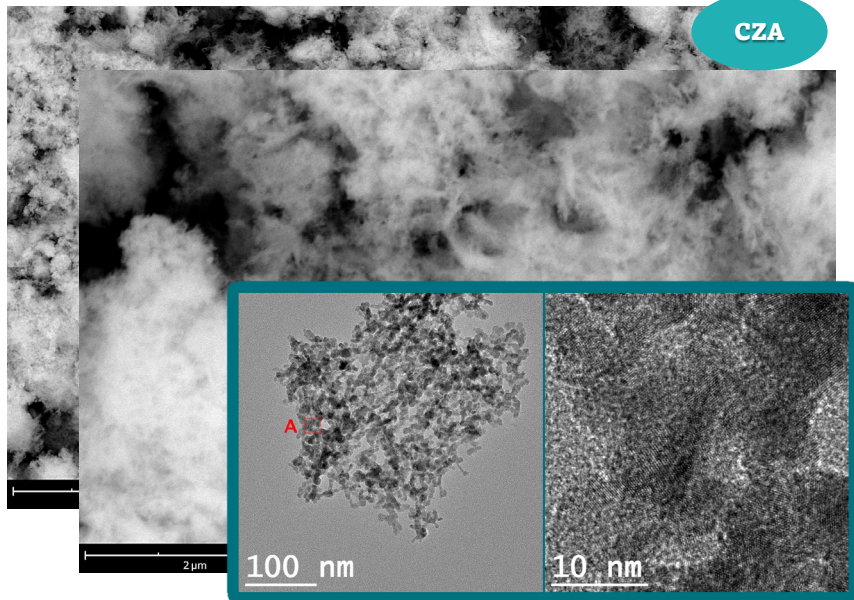


MQ water

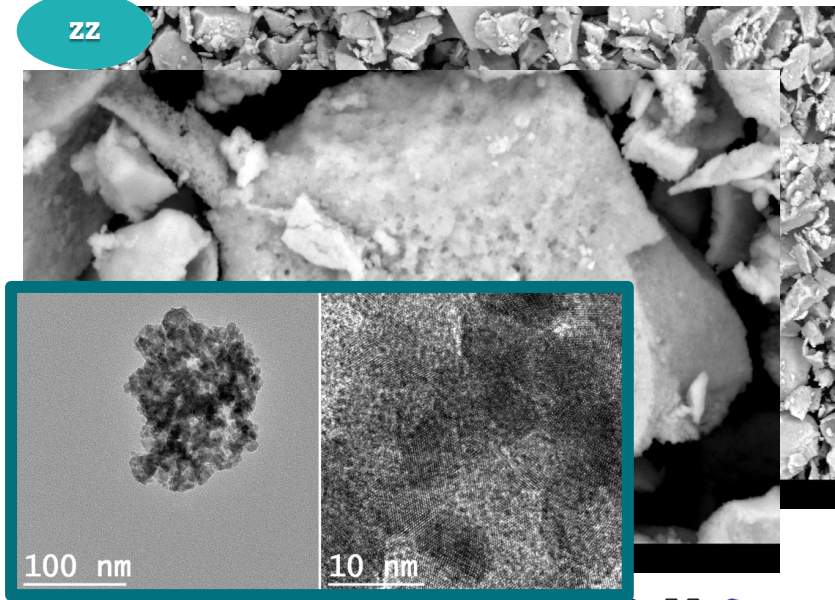


Tandem Catalyst Materials selection

Morphology



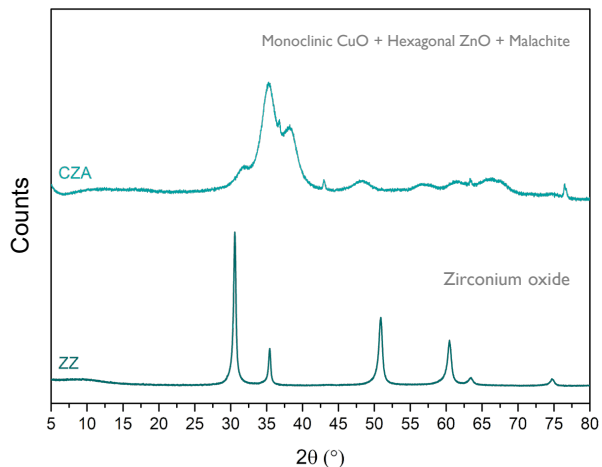
Crystallite size: $9 \text{ nm} \pm 1 \text{ nm}$



Crystallite size: $7 \text{ nm} \pm 1 \text{ nm}$

Tandem Catalyst Materials selection

Crystalline structure, porosity and elemental composition



CZA

$S_{\text{BET}} = 90.93 \text{ m}^2/\text{g}$
 $V_{\text{pore}} = 0.524 \text{ cm}^3/\text{g}$
 $D_p = 8.1 \text{ nm}$

	Cu (%)	Zn (%)	Al (%)	O (%)	Cu	Zn	Al
XRF data	31.7	12.5	0.8	55.0	42.5	16.8	1.0

ZZ

$S_{\text{BET}} = 46.51 \text{ m}^2/\text{g}$
 $V_{\text{pore}} = 0.082 \text{ cm}^3/\text{g}$
 $D_p = 4.2 \text{ nm}$

	Zr (%)	Zn (%)	O (%)	Zr	Zn
XRF data	14.55	1.92	83.30	7.6	1.0

Tandem Catalyst Materials selection

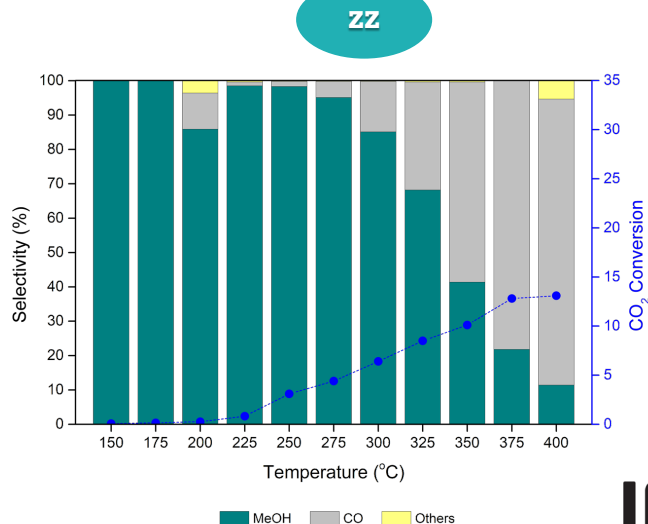
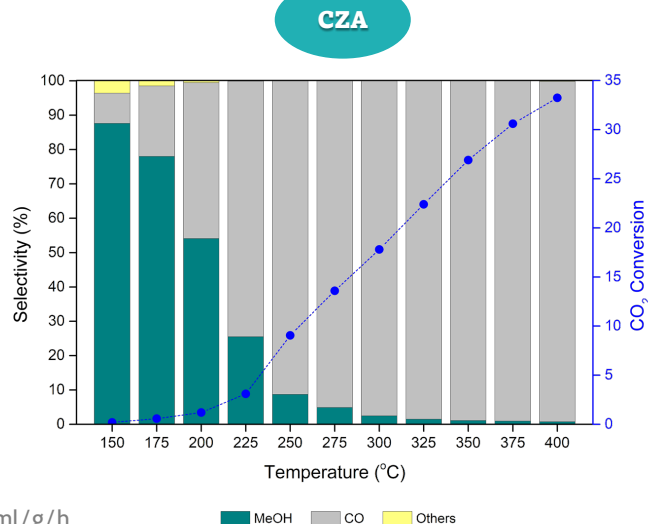
Catalytic activity



FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

K. Kappis, M. Borrelli, A. Trunschke

Route to ethylene!



WHSV: 16800 ml/g/h

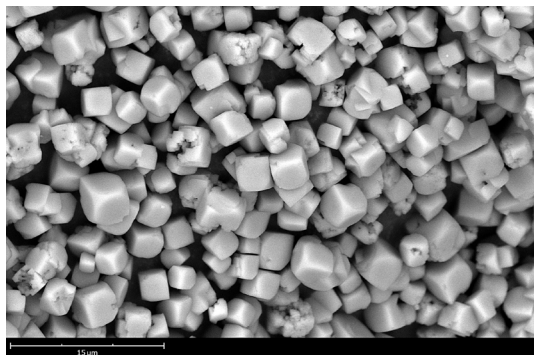
CO₂ : H₂ → 1:3

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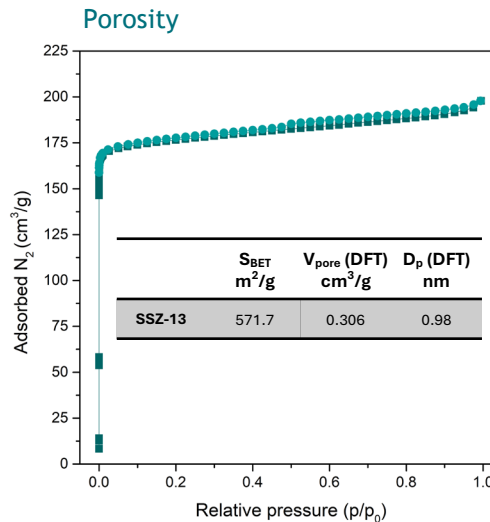
Tandem Catalyst Materials selection

Basic characterization

Cat_{B_{MTO}}: SSZ-13 Zeolite
(commercially available)
Morphology



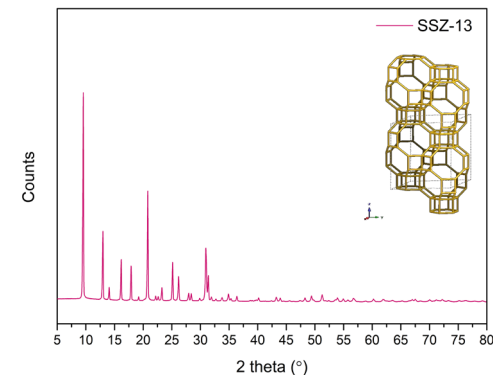
Particle size:
2.7 μm ± 0.4



Elemental composition

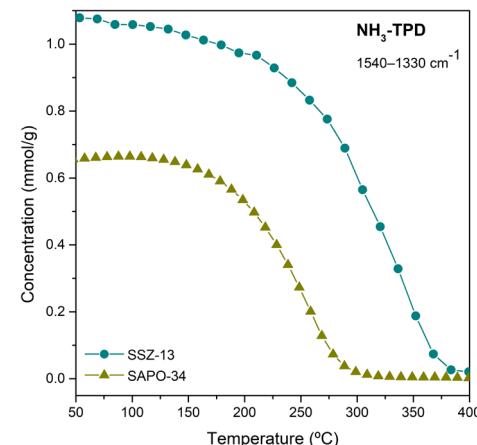
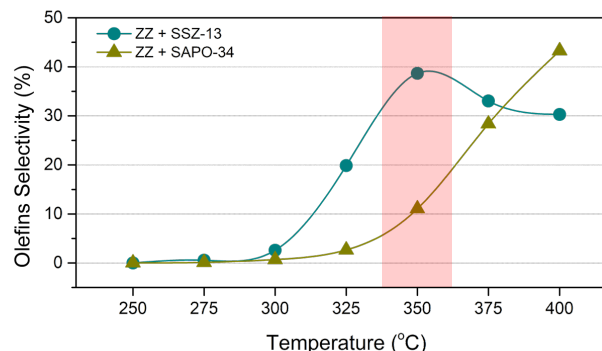
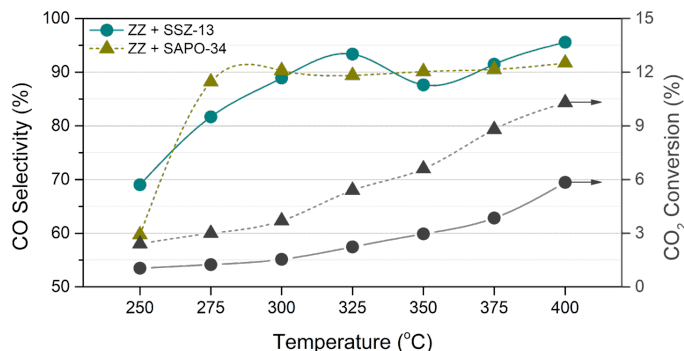
XRF data	Si (%)	Al (%)	O (%)	Si/Al ratio
SSZ-13	39.20	2.69	58.10	14.6

Crystallinity



Tandem Catalyst Materials selection: why not SAPO-34?

❖ Samples prepared by co-precipitation



At 400 °C, SAPO-34 wins on paper:

- X_{CO_2} is 10.3% vs 5.8%
- S_{CO} is lower
- O/P 3.3 vs 1.3

Olefins at 50 °C cooler

- SSZ-13 peaks ~39% at 350 °C
- SAPO-34 needs 400 °C to match

Headroom on O/P

- Our SSZ-13 is low Si/Al
- Paraffins are tunable via Si/Al ratio
- SAPO-34 acidity is fixed

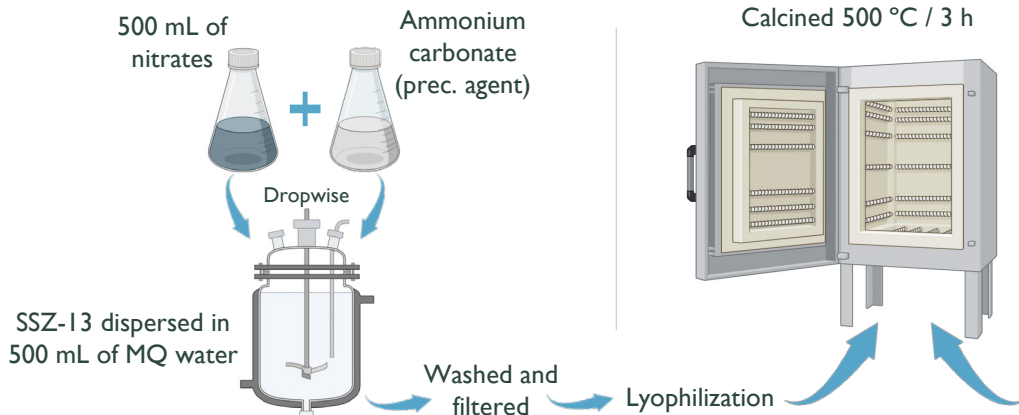
Catalyst synthesis



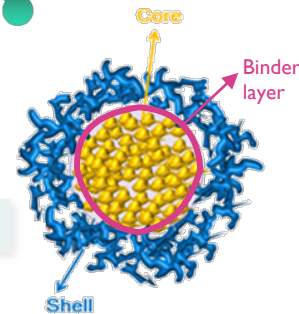
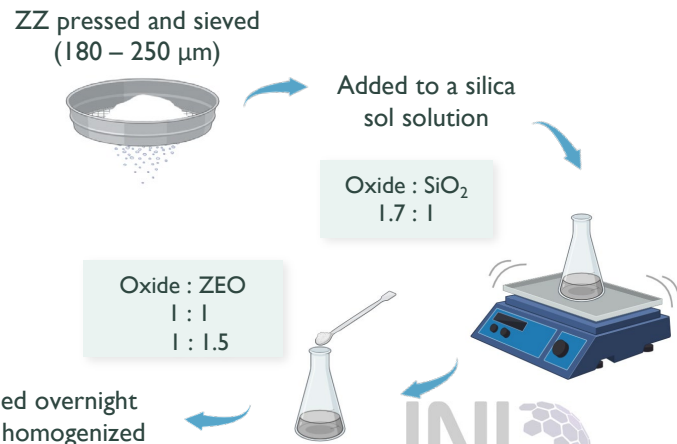
Tandem Catalyst Synthesis

Shaping SSZ-13 zeolite-metal oxide architectures

I Co-precipitation Composites



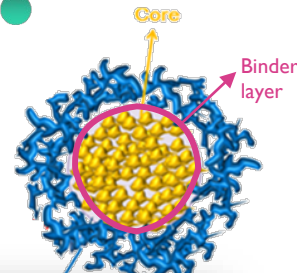
II Physical coating Colloidal silica assisted



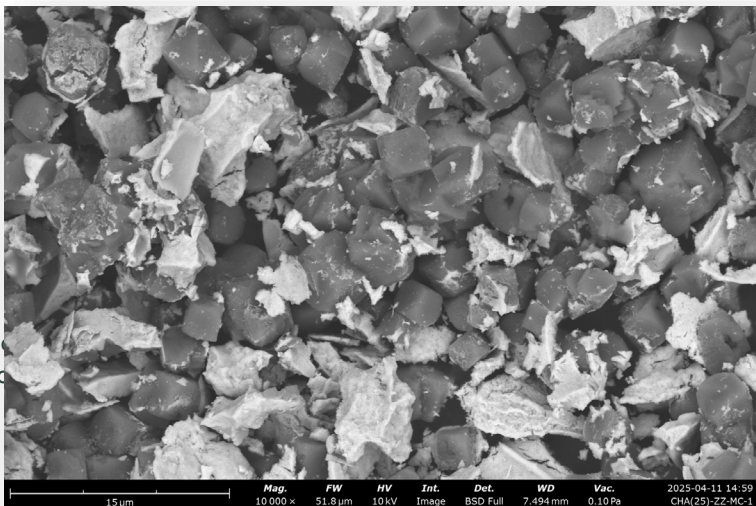
Oxide CORE@zeolite SHELL

Tandem Catalyst Synthesis

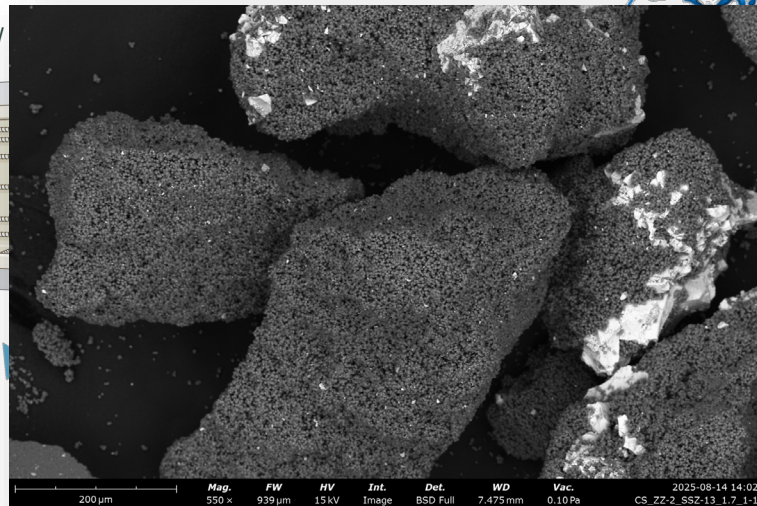
Shaping SSZ-13 zeolite-metal oxide architectures



SSZ-13
500 mL



Co-precipitation
Composites



Physical coating
Colloidal silica assisted

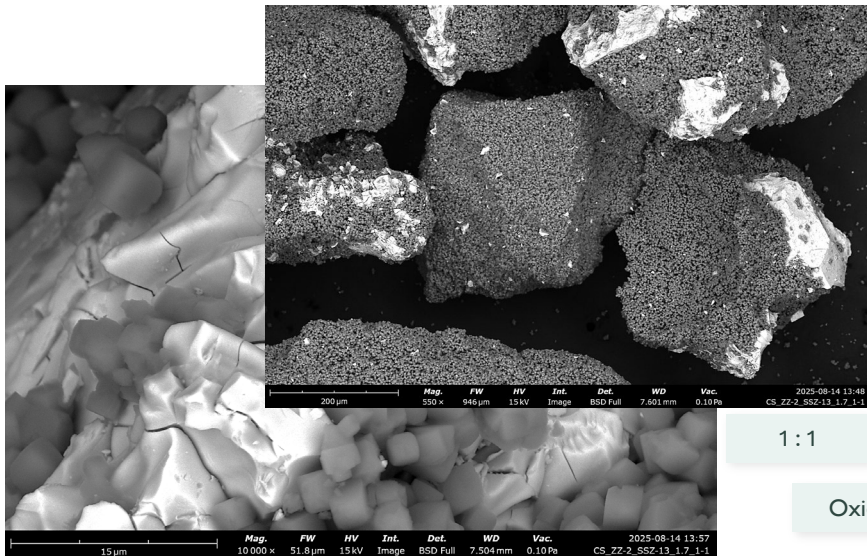
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Tandem Catalyst Synthesis

Shaping SSZ-13 zeolite-metal oxide architectures

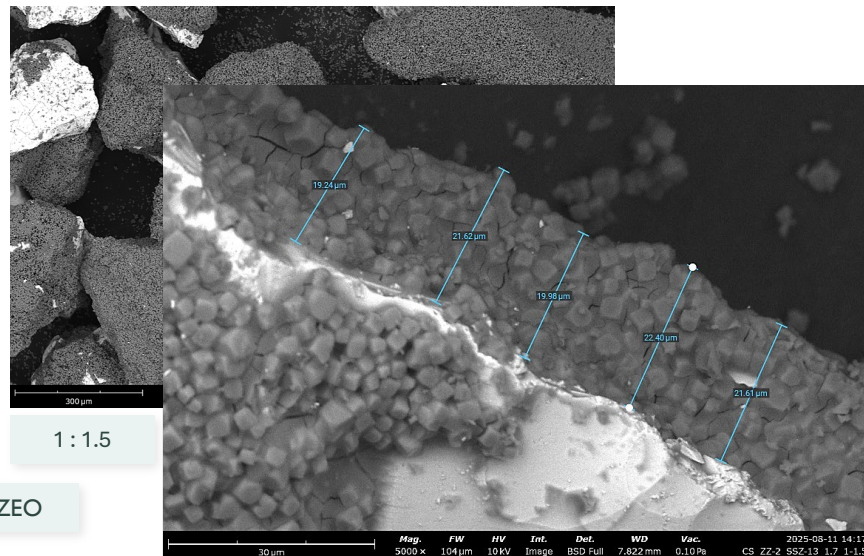
II

Physical coating
Colloidal silica assisted



1 : 1

Oxide : ZEO



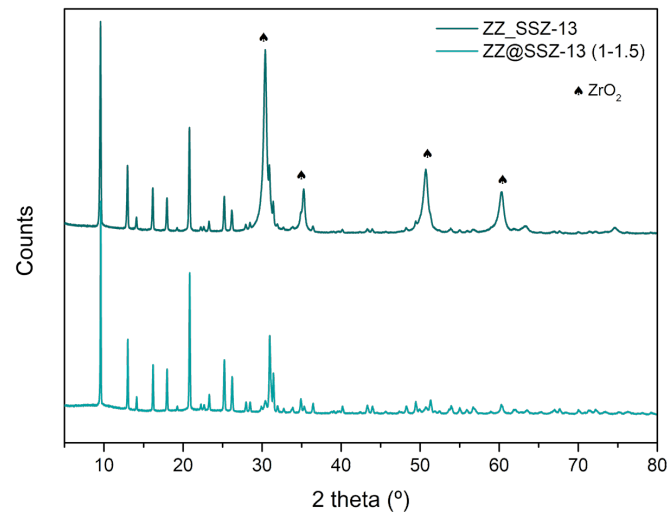
1 : 1.5

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Tandem Catalyst Characterization

Crystalline structure, and elemental composition

	Zr (%)	Zn (%)	Si (%)	Al (%)	O (%)	Zr	Zn	Si/Zr ratio
ZZ_SSZ-13(I)	14.30	2.12	14.95	1.12	67.55	6.8	1.0	1.0
ZZ@SSZ-13_1-1 (II)	7.64	1.45	28.00	1.48	61.40	5.3	1.0	3.7
ZZ@SSZ-13_1-1.5 (II)	6.13	1.15	28.85	1.50	62.35	5.4	1.0	4.7



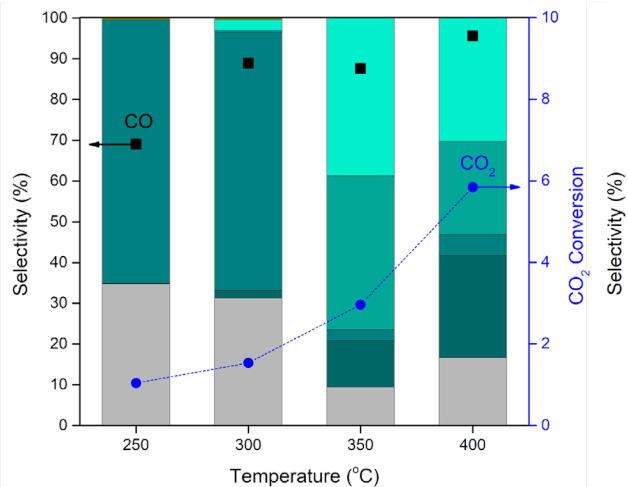
Tandem Activity

Catalytic tests

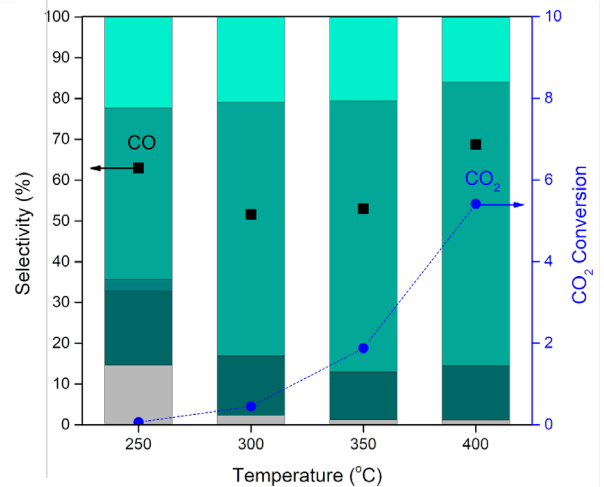


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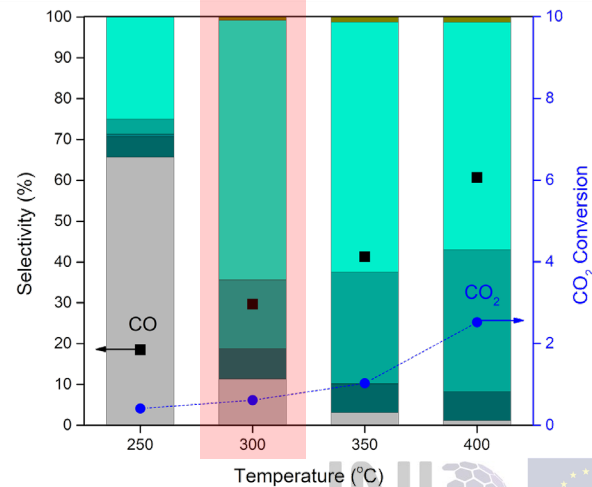
I ZZ_SSZ-13



II ZZ@SSZ-13_1-1



II ZZ@SSZ-13_1-1.5



MeOH CH4 DME Paraffins Olefins Others

Conclusions



MCs and MTO catalysts

Operating temperature range

Materials selection driven by high conversion and selectivity for both methanol and MTO conversions



Nanostructuring

Spatial distribution rule

Core-shell optimized the distance of catalytic sites to nano-level, improving olefins production



Cat_A_{MeOH} / Cat_B_{MTO} ratio

Efficient matching rule

Improved equilibrium between MeOH formation and conversion, leading to S_{olefins} 63% at 350 °C!

The Future



Tune Si/Al ratio to 50 and 100 (MTO catalyst acidity control)



Post synthesis modification by ion-exchange (final core-shell acidity)



Incorporation into membrane reactor ($X \geq 80\%$ and $S \geq 95\%$ goal)



Towards green polymer production...



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Thank you for your attention

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MemCat Project

Experimental details

Catalytic activity

- Catalytic tests



- ✓ Activation: 250 °C (5 °C/min) for 2h with 10% H₂/Ar, total flow rate: 1460 NmL/min (~209 NmL/min per reactor)
- ✓ Reaction stream, CO₂ : H₂ → 1:3 (22.5 vol.% CO₂ / 67.5 vol.% H₂ / 10% Ar as internal standard)
- ✓ Analysis via GC/MS
- ✓ T = 150-400 °C, p = 30.0 bar
- ✓ Weight of catalyst: 0.5 g
- ✓ Total flow rate: 140 NmL/min per reactor - dwell: 12h in each temperature
- ✓ Weight Hourly Space Velocity (WHSV): 16800 ml g⁻¹ h⁻¹