ZEOCAT-3D and beyond: 3D printed catalysts for chemical conversion

Vesna Middelkoop

CE-NMBP-24-2018 - Catalytic transformation of hydrocarbons (RIA)
Joint webinar, 13 April 2021

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814548

Outline

Introduction, background to 3D printing for chemical reactors

- Why do 3D printing of catalytic systems?
- Examples of studies on 3D printed reactors

ZEOCAT-3D project

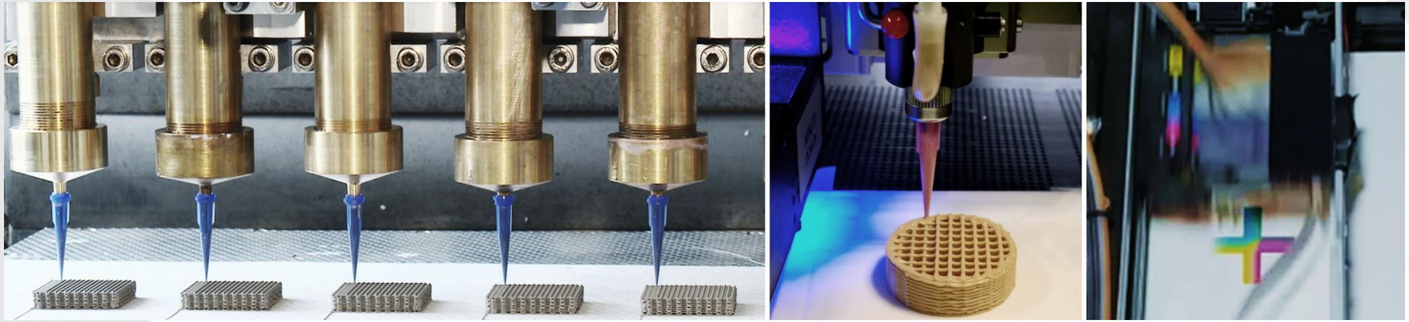
- Approaches to designing ZEOCAT-3D catalyst
- 3D printing approaches, DIW vs DLP
- Examples

Consulsions

3D Printing of monolithic catalyst
Introduction, background

Why do 3D printing of catalytic systems and chemical reactors?

ZEOCAT-3D



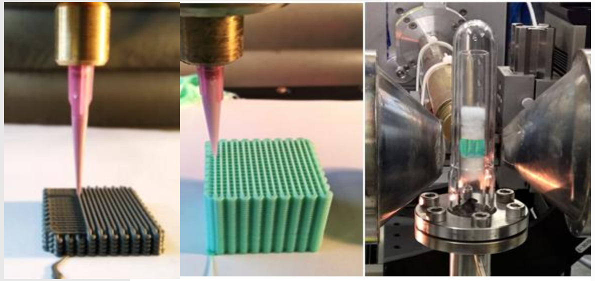
Major advantages of ‘direct write’ is to tailor multi-channel, multi-layer structures into multi-modal reactors that allow for:

- precise and uniform distribution of active material over a high surface area
- highly adaptable and well-controlled design for optimal flow pathways
- low pressure drop
- improved mass- and heat-transfer
- easy (in-situ) regeneration and cost-effective product removal
- overall greatly improved productivity per cubic meter of reactor volume

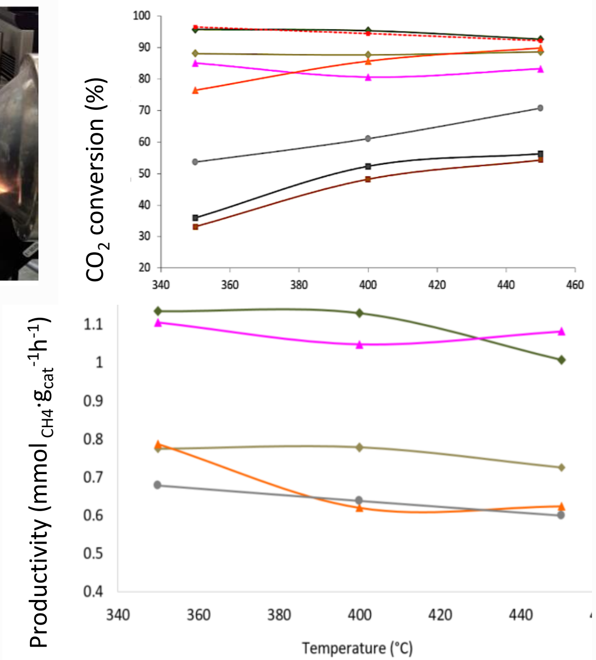
vito

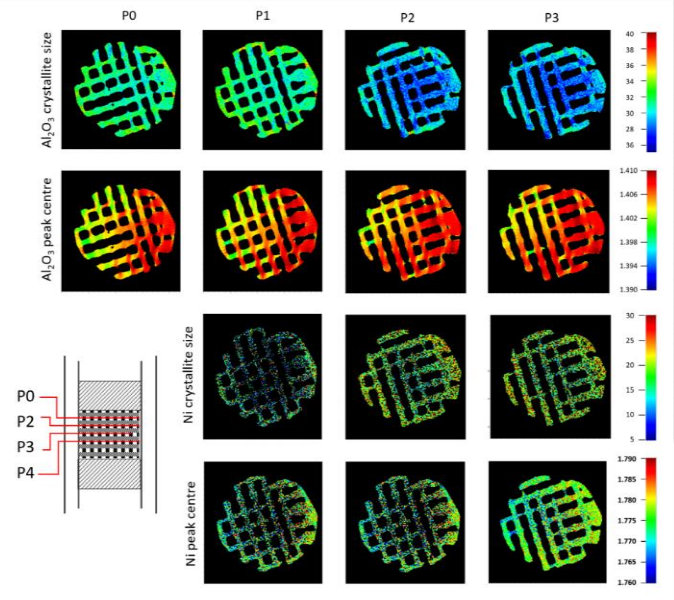
3D printed catalyst, adsorbents and reactor components at a glance

Example: 3D printed Ni/Al_2O_3 based catalysts for CO_2 methanation



Sample	SSA (m²/g)
Puralox powder as received	135-165
Calcined Ni impregnated alumina powder	109
3D printed (calcined) Ni-alumina structure	157
3D printed Ni-alumina structure after reaction	106
Ni-alumina pellets after reaction	116
Octolyst as-received powder	246
3D printed (calcined) Octolyst structure µm)	177
3D printed Octolyst structure after reaction	152
Alumina 1.0 mm spheres as received	150-170
Ni impreg. 1.0 mm spheres before reaction	156
Ni impreg. 1.0 mm spheres after reaction	129





400°C under methanation operating conditions

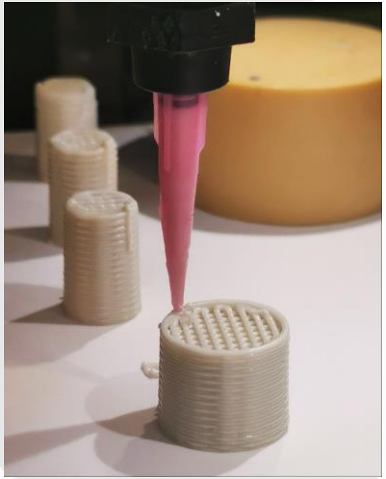
- crystalline Ni species seem to be less homogeneously distributed
- Ni species are less crystalline with smaller crystallite size

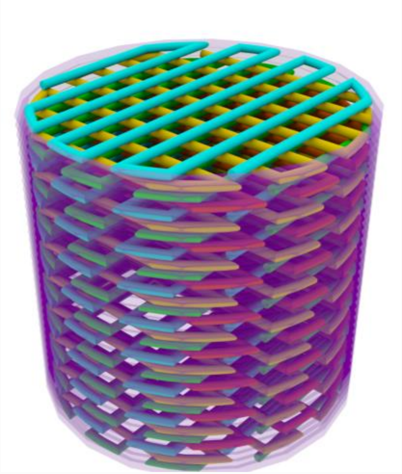
V. Middelkoop, A. Vamvakeros, D. de Wit, S.D.M, Jacques, S. Danaci, C. Jacquot, Y. de Vos, D. Matras, D., S.W.T. Price, S. W. A. Beale, 2019, *Journal of CO2 Utilization*, 33, 478–487

3D Printing of monolithic catalyst in ZEOCAT-3D

Monolithic catalysts development by both DIW and DLP

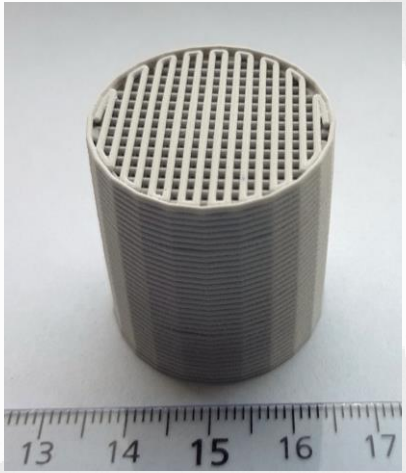
Highly viscous paste → Computer controlled deposition in x,y,z → Drying → Thermal treatment





Printing model

DIW (extrusion)
30 min printing time



vs DLP
11 hours printing time

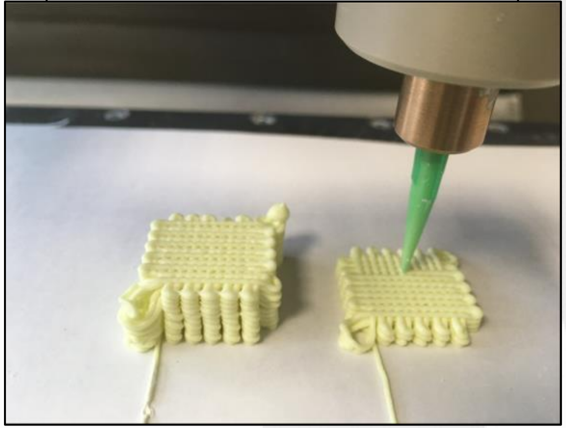
3D-Printing of monolithic catalysts by DIW

Sieving/Milling

	Not sieved	Sieved
D10 [µm]	1,53	1,25
D50 [µm]	12,60	13,93
D90 [µm]	45,30	40,21

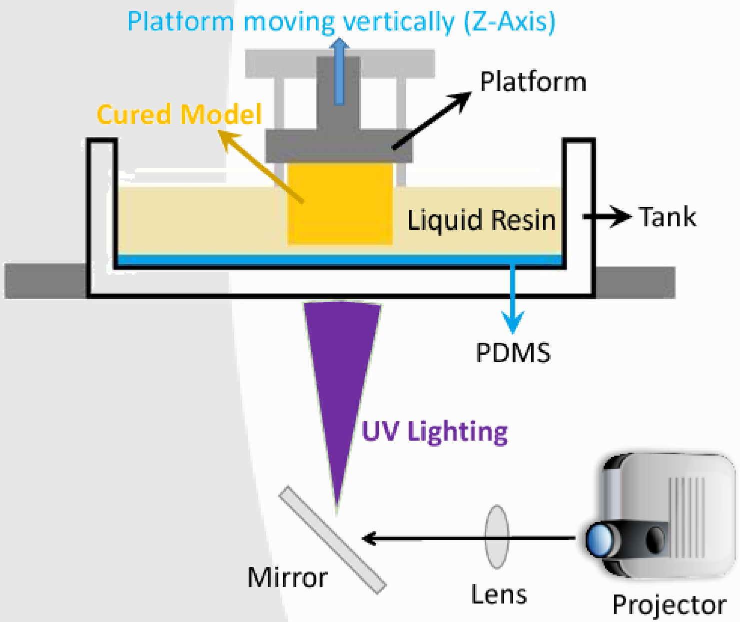
Paste preparation

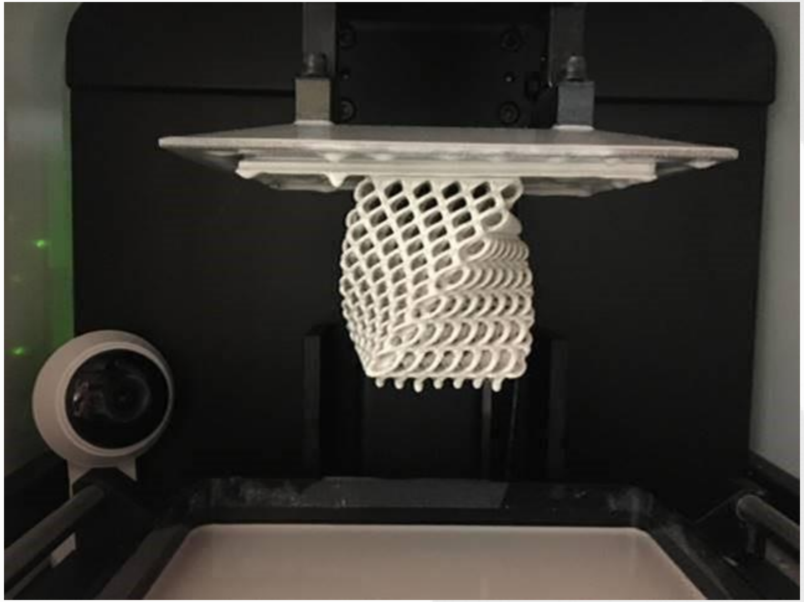
DIW 3D micro-extrusion



→ Post printing treatment (calcination) prior to catalytic testing

3D-Printing of monolithic catalysts by DLP





Wu et al, 2016, DOI:[10.1109/IROS.2016.7759338](https://doi.org/10.1109/IROS.2016.7759338)

3D-Printing of monolithic catalysts by DLP

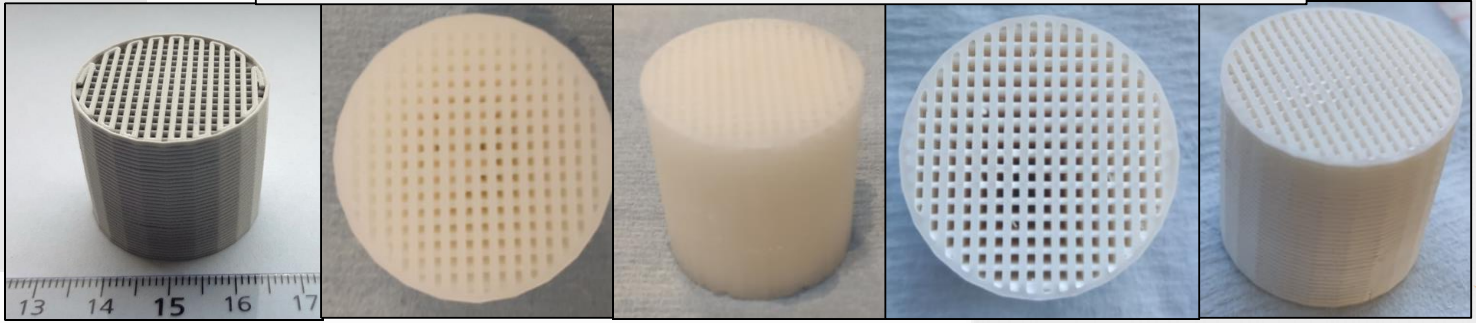
Tuning printing parameters

- Initial exposure time
- Basic exposure time
- Layer waiting time
- Brightness
- Motor moving speed
- Motor moving distance
- Temperature

Insufficient exposure times causes structures to break during printing

Too high exposure times causes 'bleeding' of cured fibers

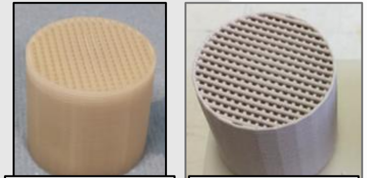
Examples of successfully printed monoliths



3D-Printing of monolithic catalyst

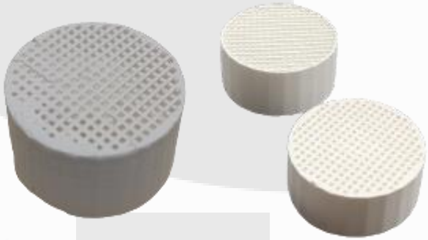
DLP Printing of Mo-ZSM5 (TUe/HYBRID) + binders

- Successfully printed several cylinders (diameter = ~3cm)
- Slow calcination up to 700°C
- Sufficient mechanical strength for transport/testing
- Catalytic tests and BET measurements

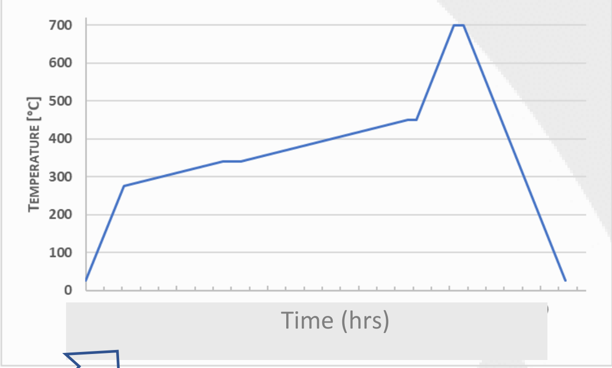


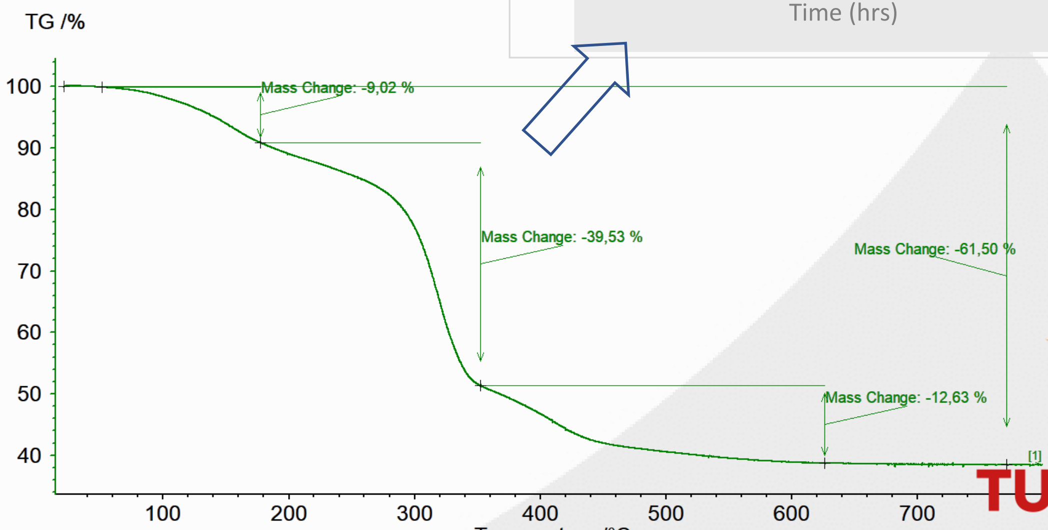
Before calcination

After calcination



Calcination



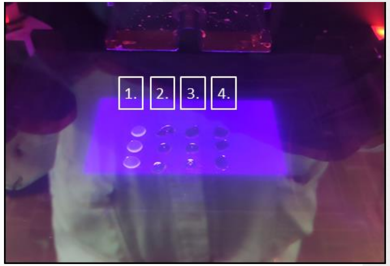


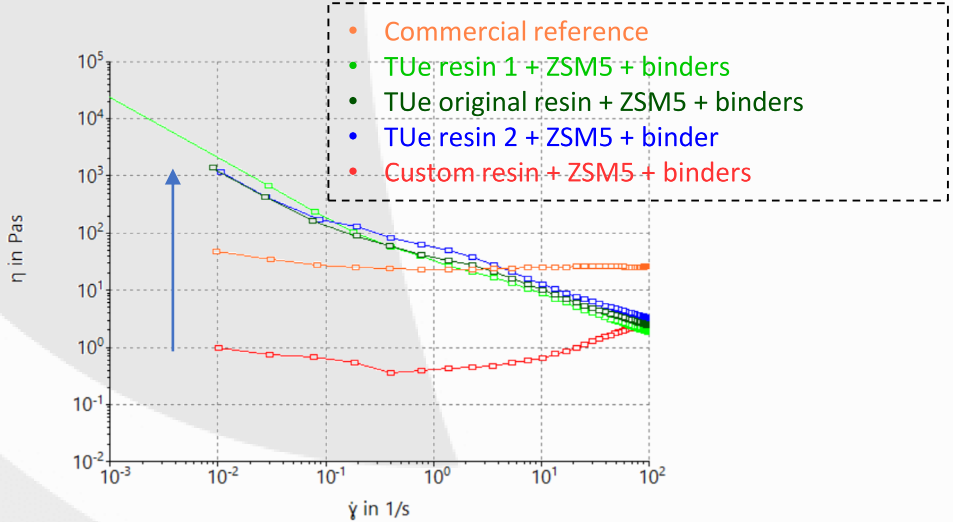
3D-Printing of monolithic catalysts by DLP

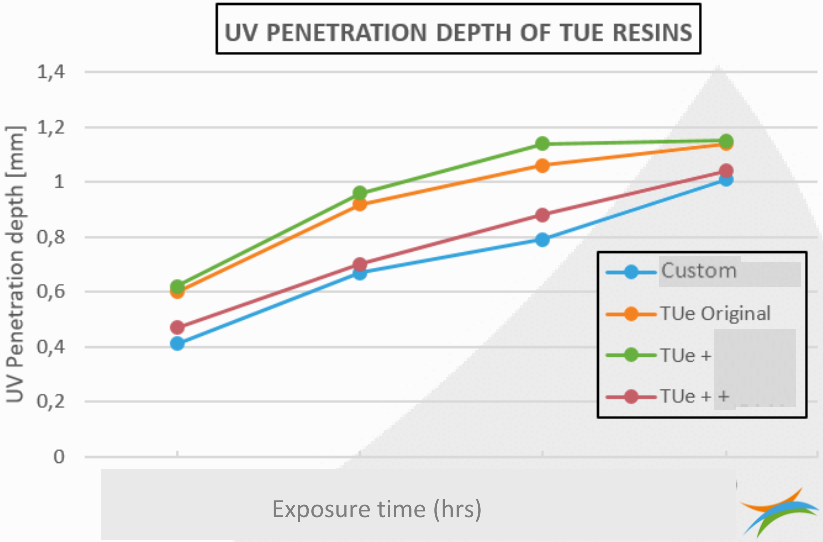
ZEOCAT-3D

Evaluation of custom-made in-house TU/e polymeric resin compositions

- Optimisation of rheology by evaluating various ratios of resin/Mo-ZSM5 powder
- Viscosity increases with higher powder loading
- Evaluation of effect of binders and additives
- Tuning subsequent mechanical strength after calcination
- Preserving/maximising specific surface area



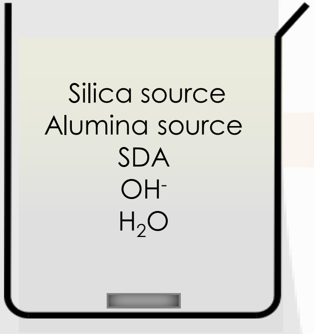




vito

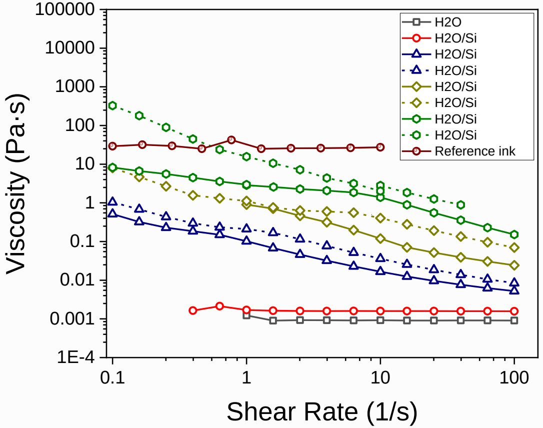
Production of zeolitic materials by an in-situ templating approach

Development, optimisation and scale-up of proto-zeolitic inks based on silica, alumina precursors organic templates, additives for DLP printing



Initial gel

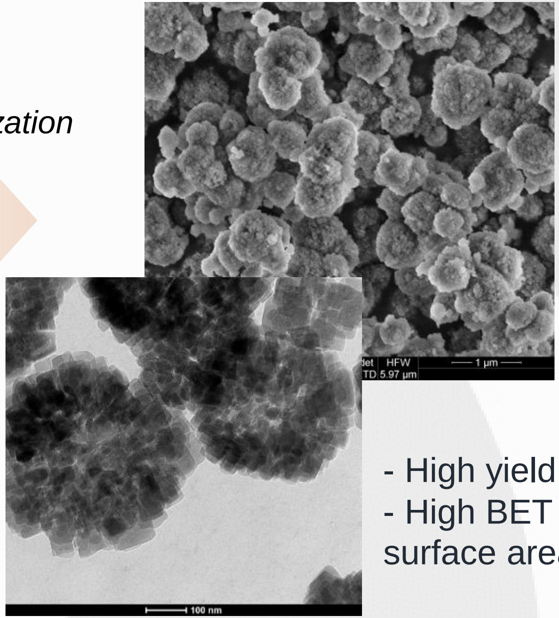
Tuning H_2O/Si ratio



No phase separation

Crystallization

nano-ZSM-5 samples

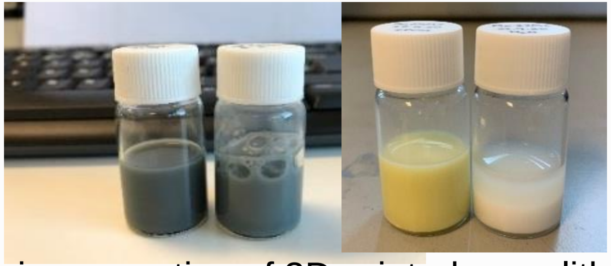


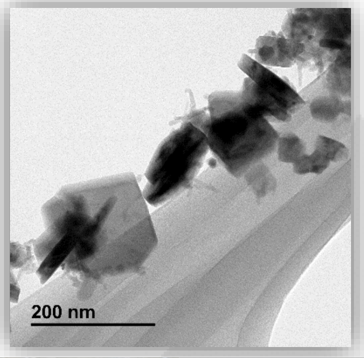
- High yield
- High BET surface areas

Production of metallic nano-oxides by FSP

Synthesis of doped tailored multi-metal nano-oxides by Flame Spray Pyrolysis (FSP)

- Tuning nanoparticles production conditions for pre and post printing deposition
- Control of particle size, SSA, morphology and degree of agglomeration, dispersion.
- Ion doping will increase the efficiency and catalytic activity.
- FSP parameters control: flame, temperature, pressure control

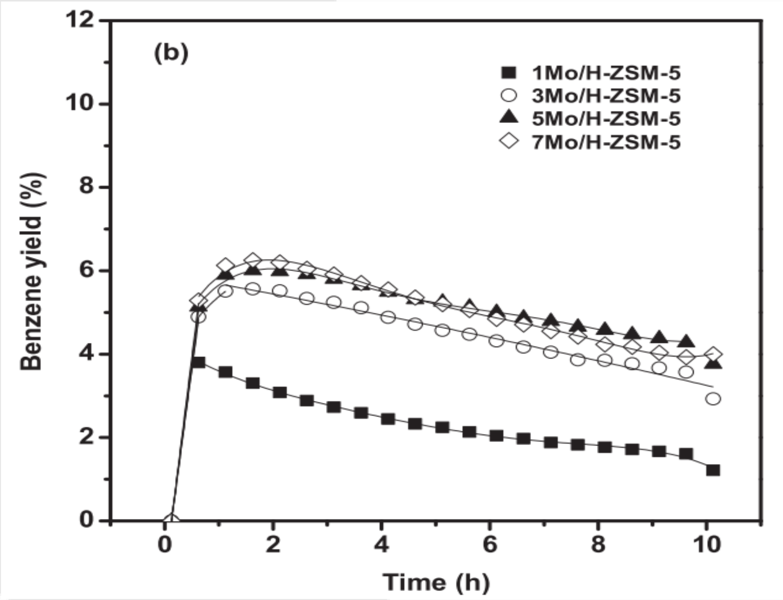




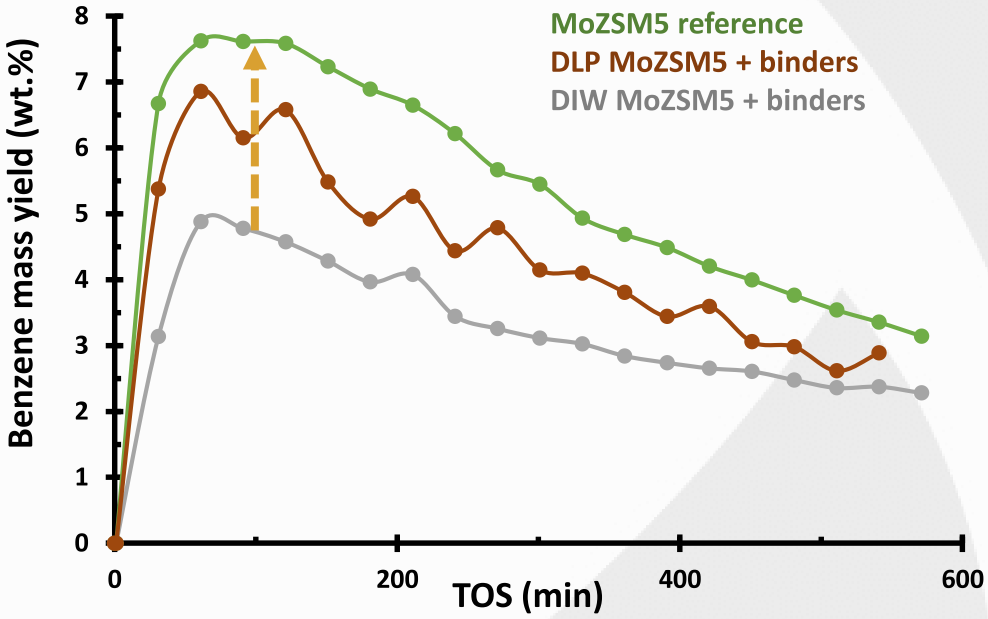
- impregnation of 3D-printed monoliths

3D-Printing of monolithic catalyst

DLP Printing of Mo-ZSM5 (TUe/HYBRID CATALYSIS) + effect of binders



State of art



Reaction conditions: CH4 / inert gas mixture, 700 °C

S.J. Han et *al*. Applied Catalysis B: Environmental 241 (2019) 305–318

3D-Printing of monolithic catalyst

DLP Printing of Mo-ZSM5 (TUe/HYBRID) + effect of binders

Conclusions

Advance beyond the state-of-the-art

- 3D printing used for effective controlled deposition and distribution of active catalyst particles
- Reactor design: large surface to volume ratio and controlled shape, geometry and macrostructure; enhanced mass and heat transfer and 10-20% increase in reaction performance
- Improve overall kinetics of the MDA process; further optimization of reaction and catalyst regeneration
- ZEOCAT-3D integration and operation at industrial partners facilities

Thank you

Any questions?

Cristina Salazar, Carmen Garijo
cristina.salazar@lurederra.es
www.lurederra.es

Fotis Katsaros, George Romanos
f.katsaros@inn.demokritos.gr
www. inn.demokritos.gr

Erik Abbenhuis, Gijsbert Gerritsen & Arjan Koekkoek
H.C.L.Abbenhuis@tue.nl
www.hybridcatalysis.com

Aleksei Bolshakov, Leon Rosseau, Martin van Sint Annaland
A.Bolshakov@tue.nl,
M.v.SintAnnaland@tue.nl
www.tue.nl

Antoine Beuque, Ludovic Pinard, Raúl Piñero
ludovic.pinard@univ-poitiers.fr
raupin@cartif.es

Ben Sutens, Vesna Middelkoop
vesna.middelkoop@vito.be
www.vito.be