INNOVATIVE USES OF $CO_2$ CAPTURE FOR THE INDUSTRY WORKSHOP

# $CO_2$ Utilisation via 3D printed reactor technologies

CO2FOKUS
ADVANCING $CO_2$ CONVERSION

**Vesna Middelkoop**

**18 May 2021**

$CO_2$ utilisation focused on market relevant dimethyl ether production, via 3D printed reactor and solid oxide cell based technologies

vito · Consiglio Nazionale delle Ricerche · Hybrid Catalysis · FeyeCon · LCE · SOLID POWER · Petkim · tecnalia Inspiring Business · ATAE · HTF HIGH TECHNOLOGY FILTERS SA · ECODESIGN company · LGi sustainable innovation · ICI CALDAIE



The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

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# Outline

Introduction, background to 3D printing for chemical reactors

- Why do 3D printing of catalytic systems?
- Examples of studies on 3D printed reactors for $CO_2$ utilisation reactions

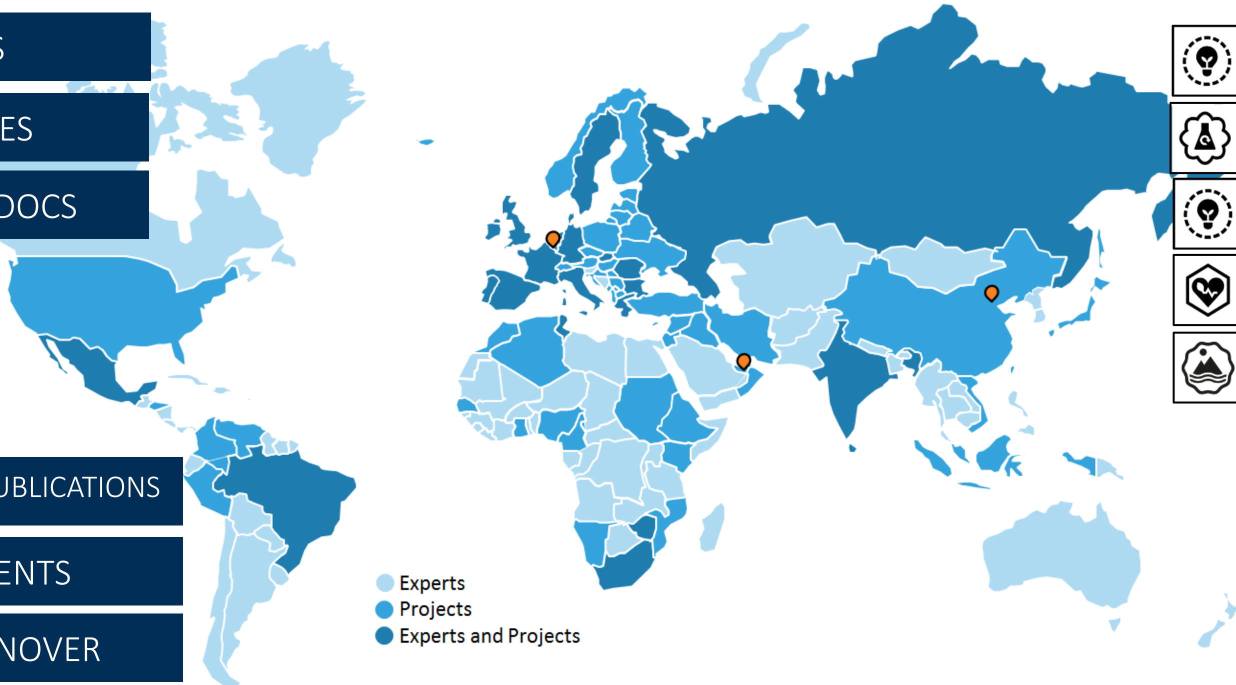
CO2Fokus project

- $CO_2$ conversion to dimethyl ether production
- 3D printed catalysts for DME conversion

Conclusions

# VITO: WHO WE ARE AND WHAT WE DO?
# FACTS and FIGURES

- 900 EMPLOYEES
- 34 NATIONALITIES
- 91 PHDS&POSTDOCS
- >250 SCIENTIFIC PUBLICATIONS
- > THAN 400 PATENTS
- >€190 MIL. TURNOVER




- ENERGY
- CHEMISTRY
- MATERIALS
- HEALTH
- LAND USE

**Some of our granted related projects on materials for chemistry and energy applications**

CARMOF
$CO_2$FOKUS ADVANCING $CO_2$ CONVERSION
ZEOCAT-3D
KEROGREEN
GLAMOUR
ORACLE 三人寄れば文殊の知恵

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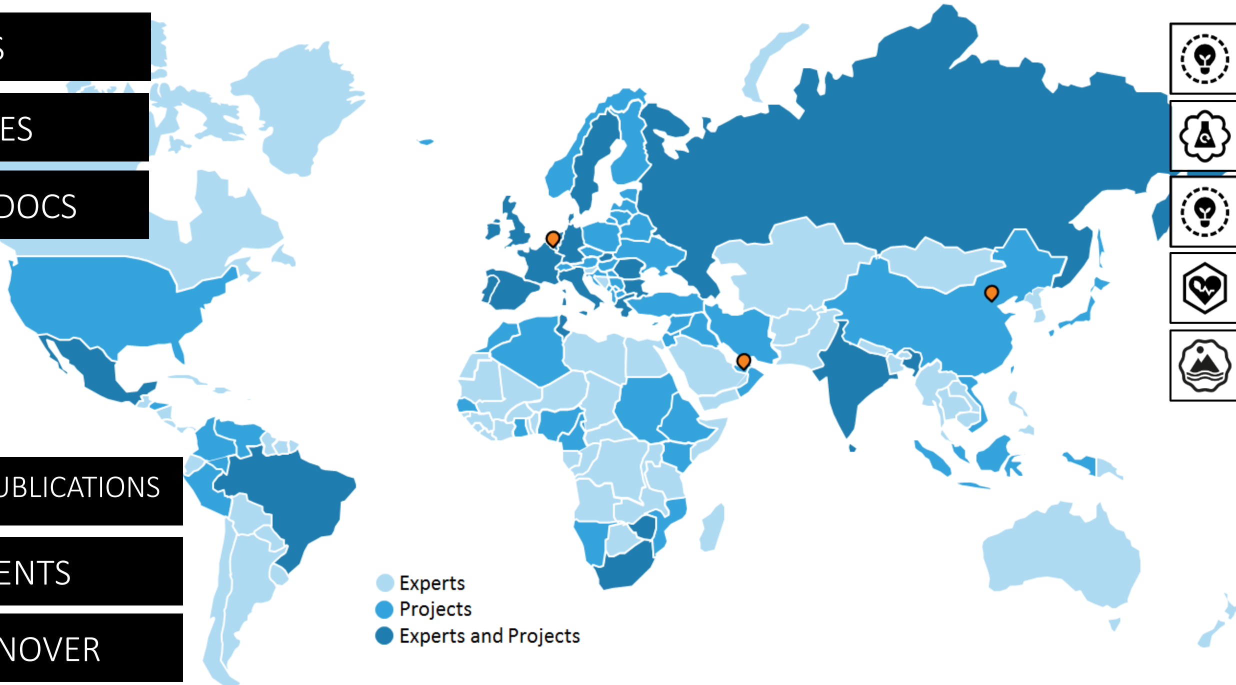


ENERGY

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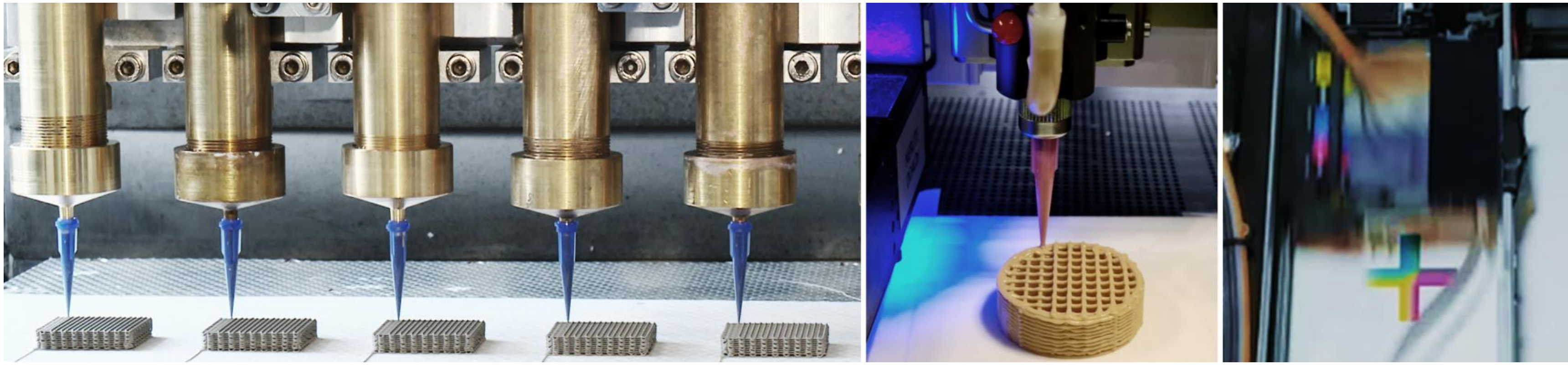
# Why do 3D printing of catalytic systems and chemical reactors?

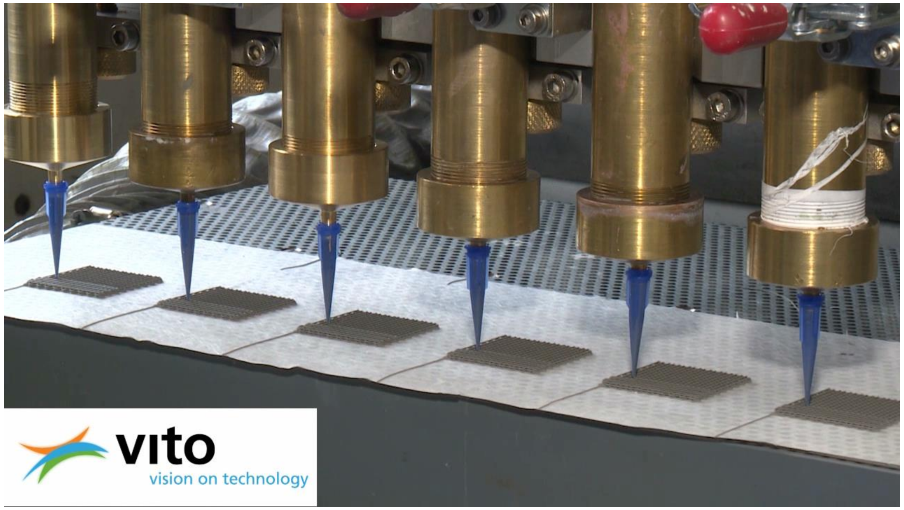


Major advantages of 'direct write' is to tailor multi-channel, multi-layer structures into multi-modal reactors that allow for:

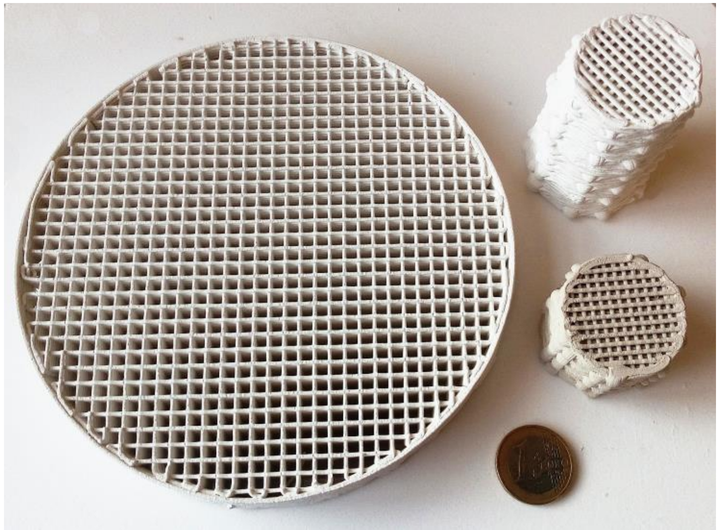
- **precise and uniform distribution of active material over a high surface area**
- **highly adaptable and well-controlled design for optimal flow pathways**
- **low pressure drop**
- **improved mass- and heat-transfer**
- **easy (in-situ) regeneration and cost-effective product removal**
- **overall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

## SCALING UP

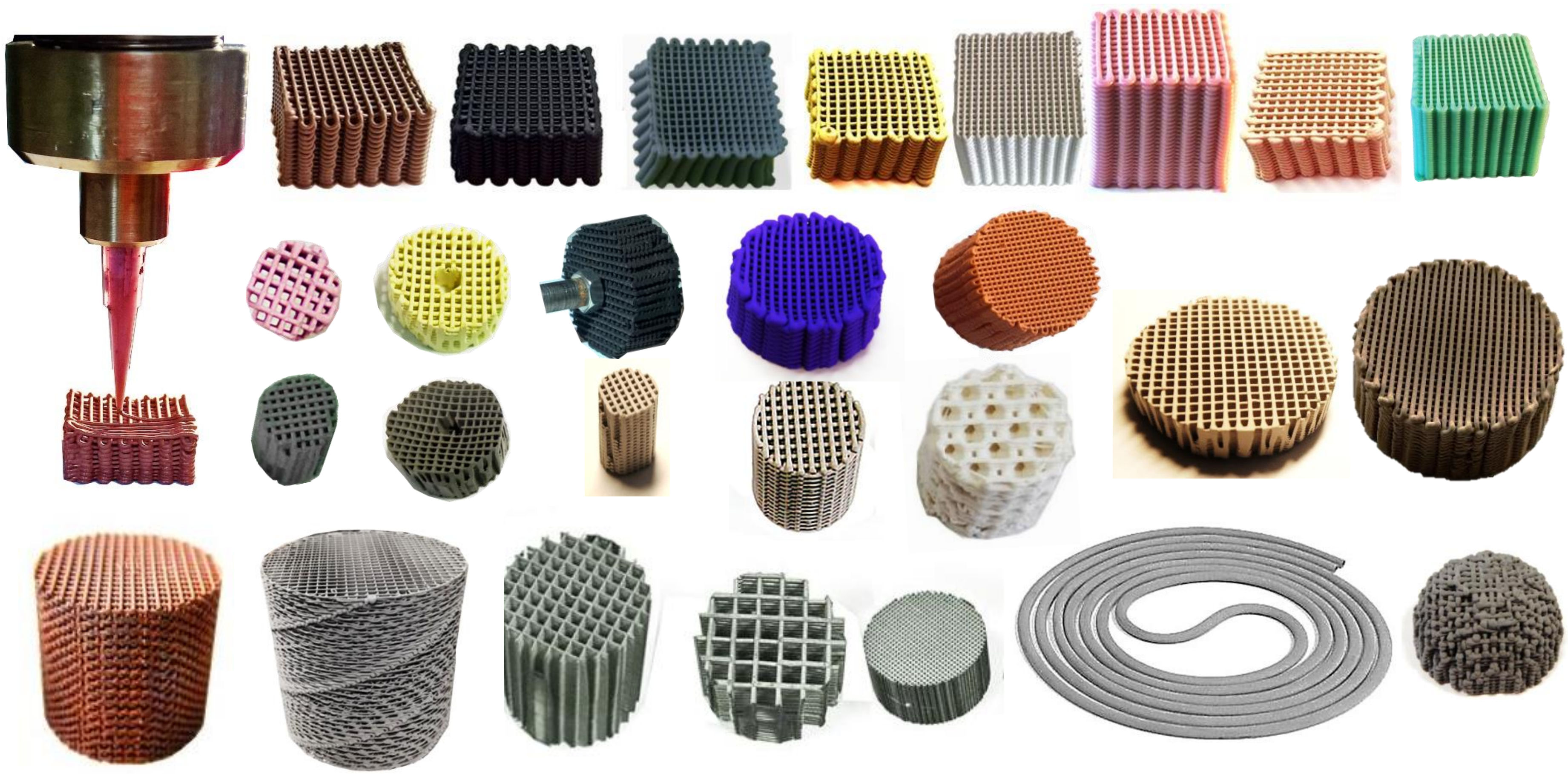
in numbers




in size

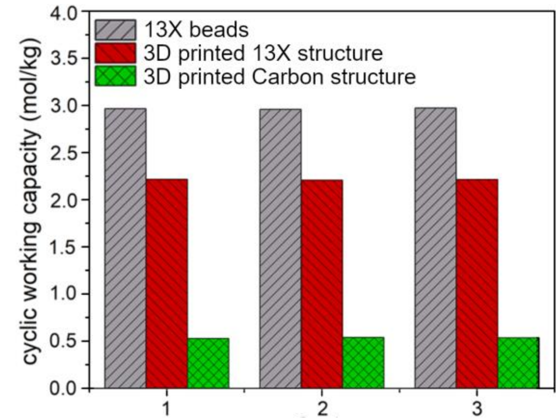


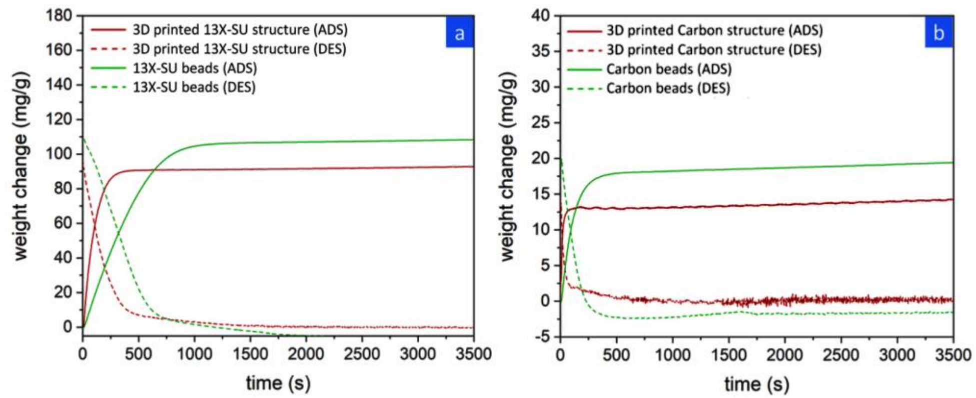
# 3D printed catalyst, adsorbents and reactor components at a glance



# 3D PRINTED ADSORBENTS 13X AND CARBON

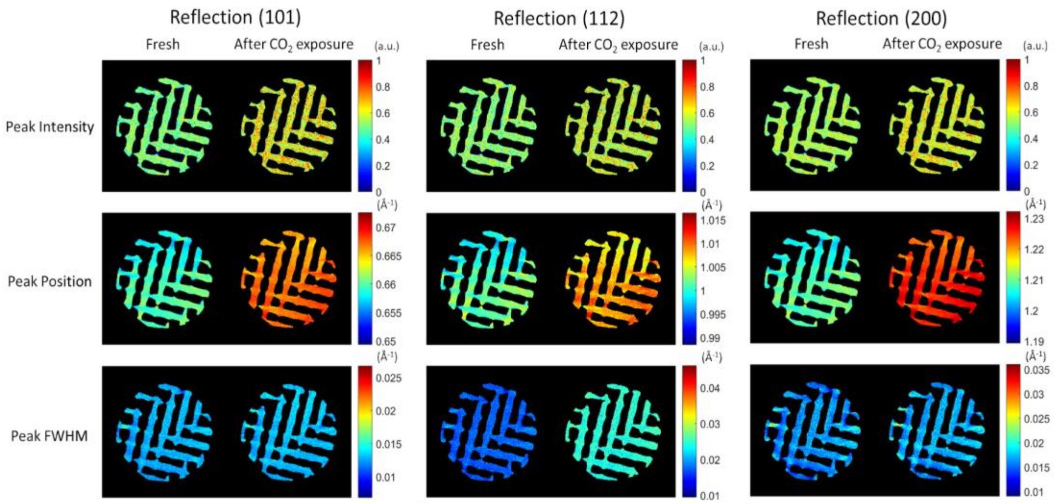
Monoliths stacked onto 6mm thermocouple used for experiments in PBR
Adsorption & desorption rates of monoliths are markedly faster than those for beads.



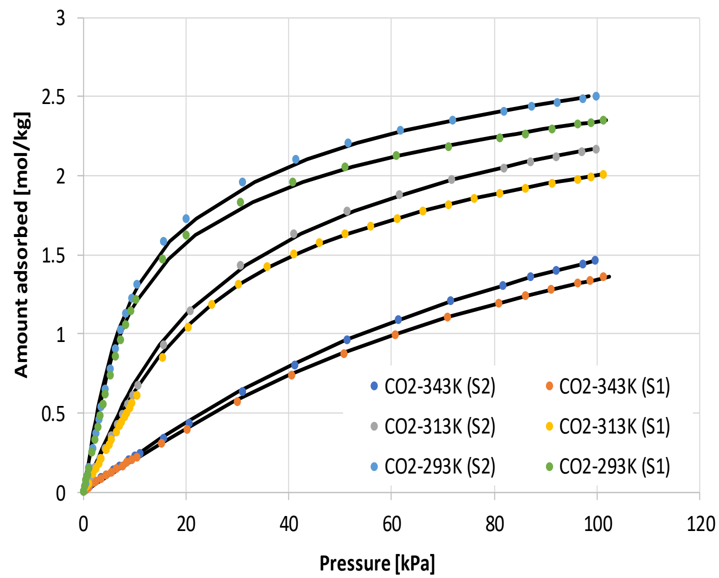




V. Middelkoop, K. Coenen, J. Schalck, M. Van Sint Annaland, F. Gallucci, 3D printed versus spherical adsorbents for gas sweetening, Chemical Engineering Journal, 2019, 357, 309-319

# 3D PRINTED ADSORBENTS 13X AND CARBON




Operando XRD-CT



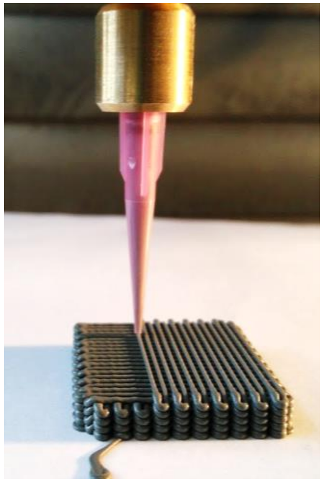

Adsorption equilibrium isotherms.

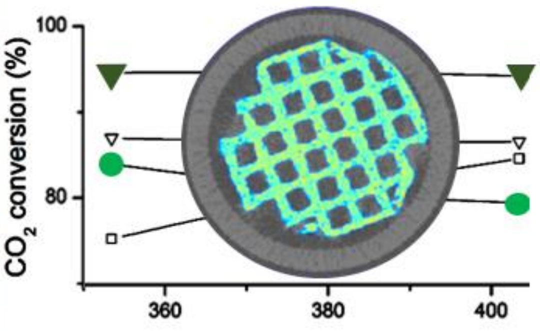
Solid lines are fitting of the Virial model.

C. A. Grande, R. Blom, V. Middelkoop, D. Matras, A. Vamvakeros, S.D.M. Jacques, A. M. Beale, M.Di Michiel, K.A. Andreassen, A.M.Bouzga, Multiscale investigation of adsorption properties of novel 3D printed UTSA-16 structures, Chemical Engineering Journal, 2020, 402, 126166

## 3D printed $Ni/Al_2O_3$ based catalysts for $CO_2$ methanation

$CO_2 + 4 H_2 \rightarrow CH_4 + H_2O$

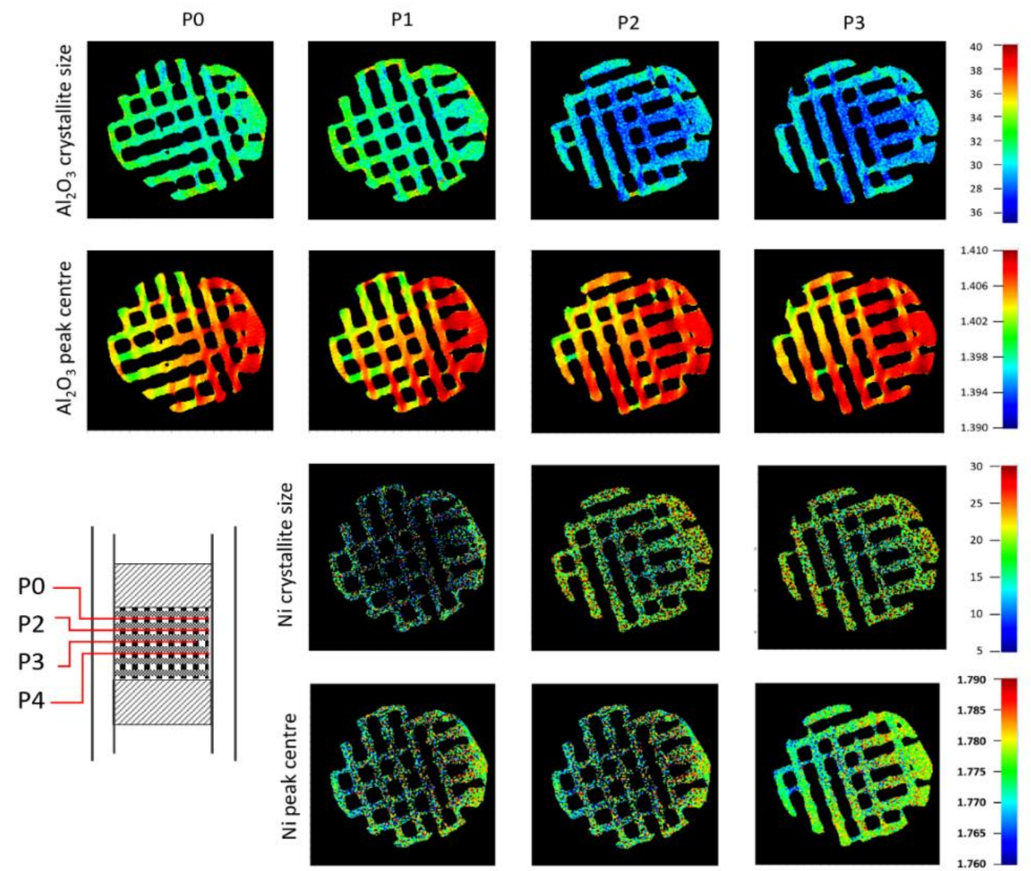





XRD-CT scans, 78.5 keV focused to a spot size of 30 µm x 30 µm, 10 ms per step covering 0 to 180 ° in steps of 1 ° translated over 11 mm in steps of 50 µm (220 steps). Each scan comprised 39 600 diffraction patterns.


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 printed $Ni/Al_2O_3$ based catalysts for $CO_2$ methanation - operando XRD-CT



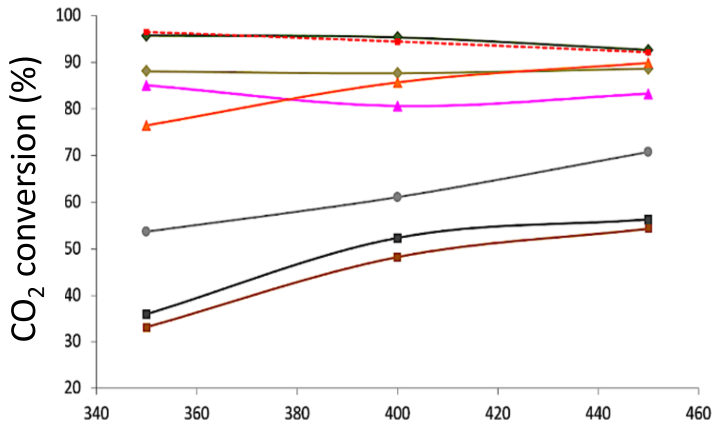

400°C under methanation operating conditions

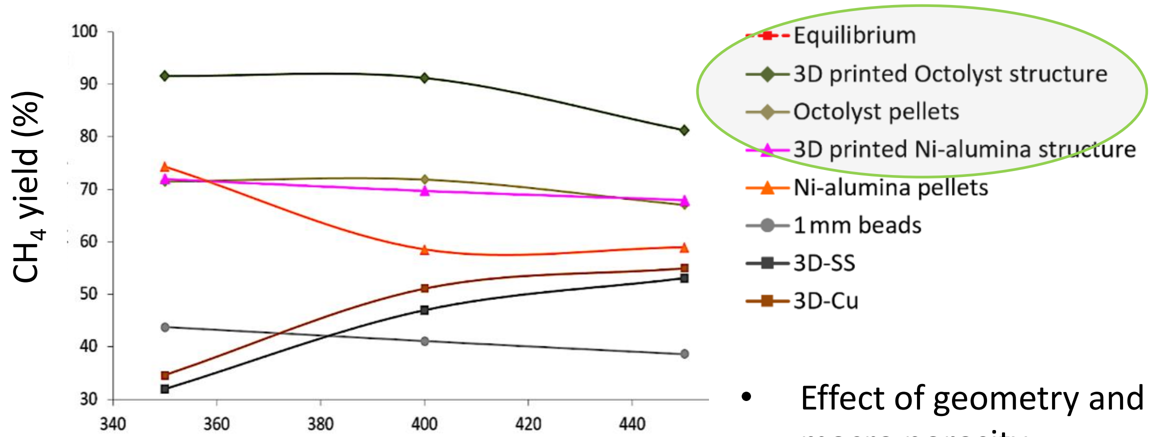
| Sample | SSA ($m^2/g$) |
|---|---|
| Puralox powder as received | 135-165 |
| Calcined Ni impregnated alumina powder | 109 |
| 3D printed (calcined) Ni-alumina structure | 157 |
| 3D printed Ni-alumina structure after reaction | 106 |
| Ni-alumina pellets after reaction | 116 |
| Octolyst as-received 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 |

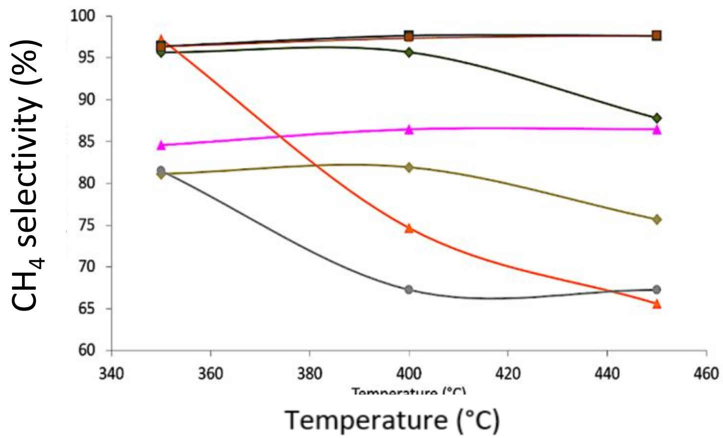
- crystalline Ni species seem to be less homogeneously distributed
- Ni species are less crystalline with smaller crystallite size

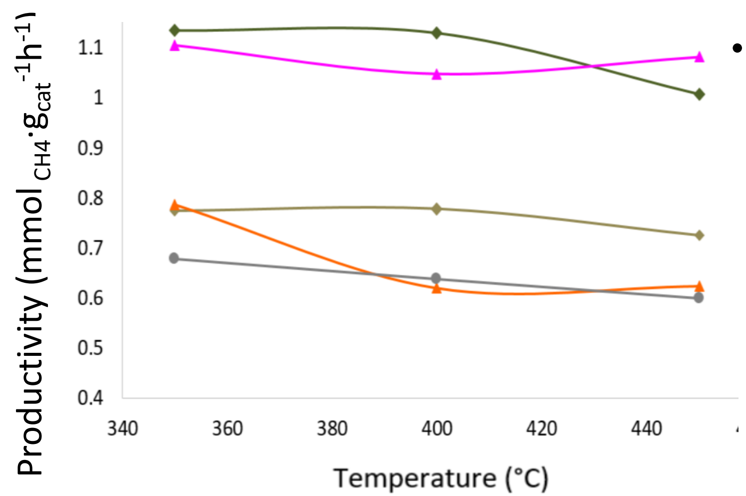
V. Middelkoop, A. Vamvakeros, D. de Wit, S.D.M, Jacques, S. Danaci, C. Jacquot, Y. de Vos, D. Matras, D., S.W.T. Price, S. W. A. Beale, 2019, *Journal of CO2 Utilization*, 33, 478–487

## 3D printed Ni/$Al_2O_3$ based catalysts for $CO_2$ methanation – catalytic testing



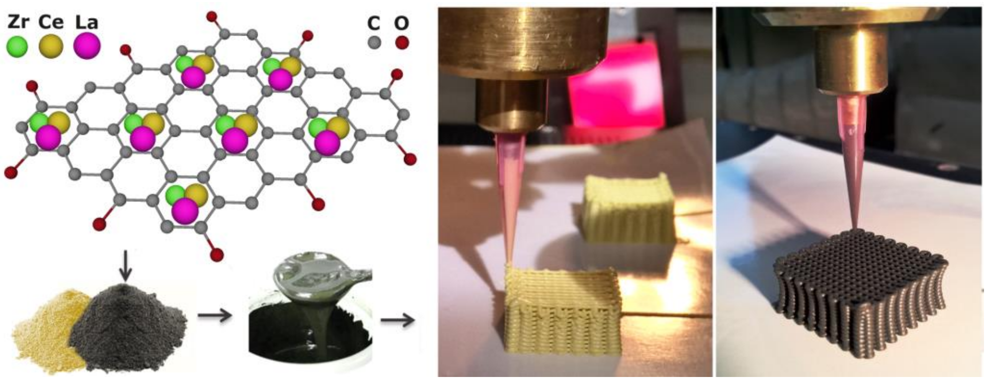



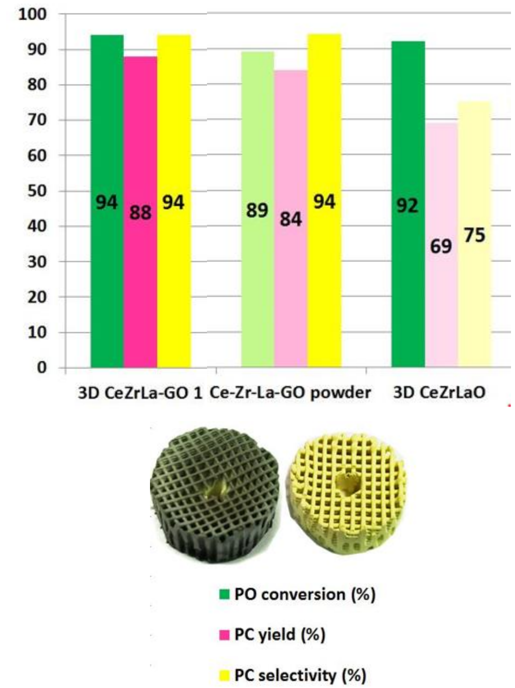

- Effect of geometry and macro porosity
- productivity ↓ $CO_2$ consumption attributed to the simultaneous occurrence of reverse water gas shift (unreacted $CO_2$ and $H_2$ forming undesired product, CO)

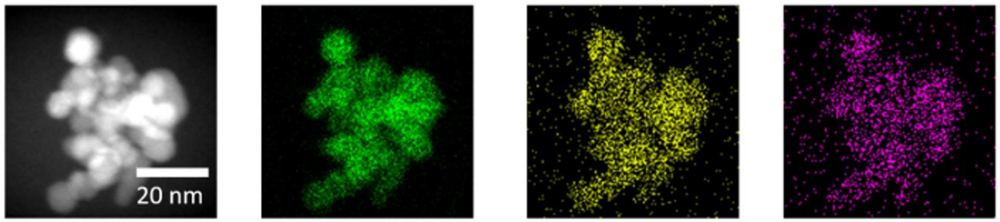
V. Middelkoop, A. Vamvakeros, D. de Wit, S.D.M, Jacques, S. Danaci, C. Jacquot, Y. de Vos, D. Matras, D., S.W.T. Price, S. W. A. Beale, 2019, *Journal of CO2 Utilization*, 33, 478–487

# 3D printed graphene oxide nano-composite catalyst for $CO_2$ utilisation

CeZrLa-graphene oxide nano-catalyst for conversion of $CO_2$ and propylene oxide to propylene carbonate



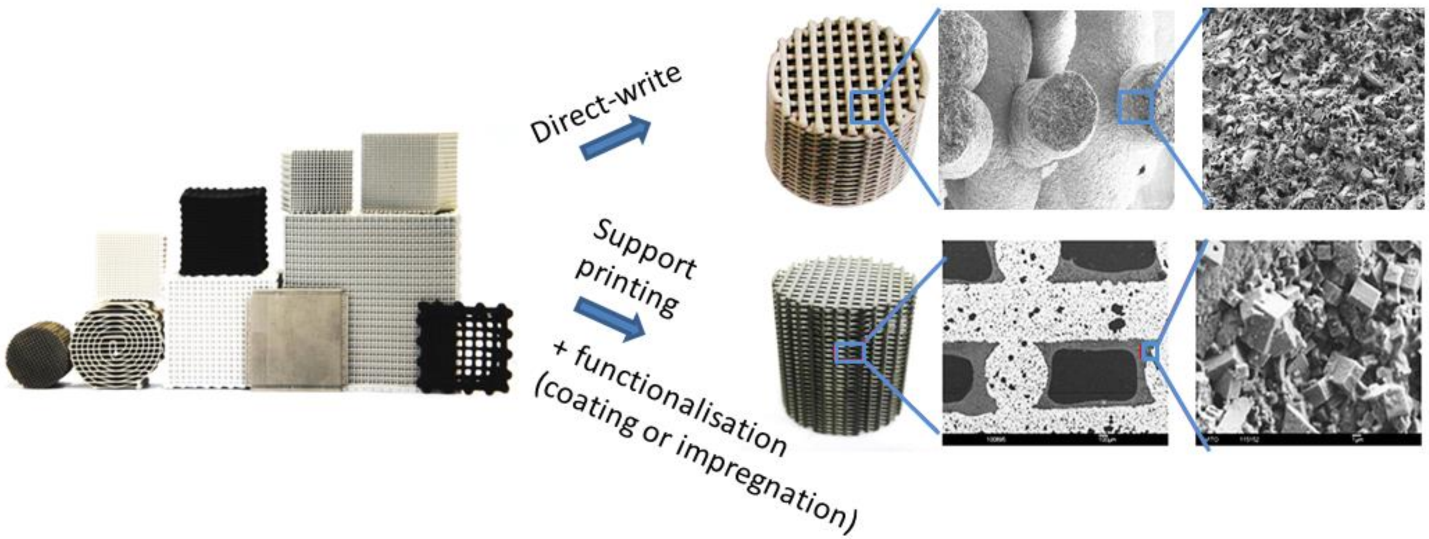




V. Middelkoop, T. Slater, M. Florea, F. Neațu, S. Danaci, V. Onyenkeadi, K. Boonen, B. Saha, I-A. Baragau, S. Kellici, Next frontiers in cleaner synthesis: 3D printed graphene-supported CeZrLa mixed-oxide nanocatalyst for CO2 utilisation and direct propylene carbonate production, *Journal of Cleaner Production*, 2019, 214, 606-614

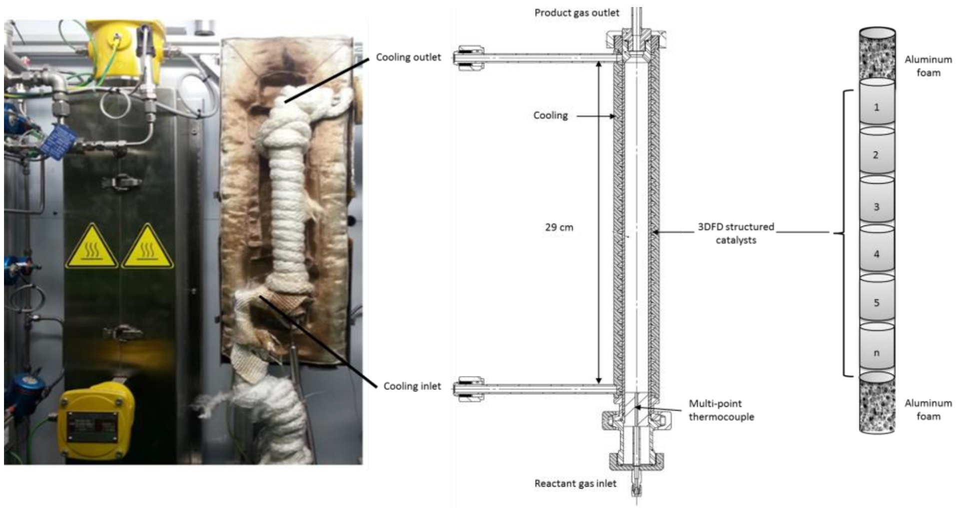
MANCHESTER 1824
The University of Manchester

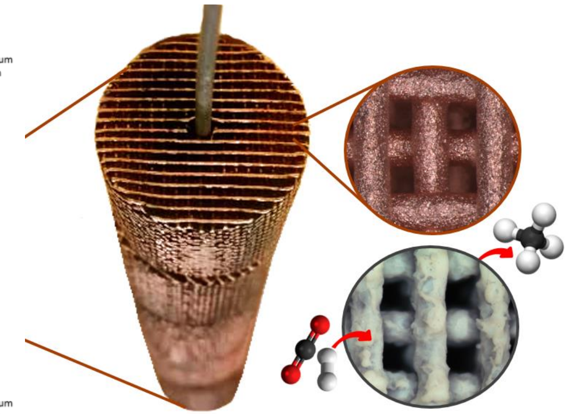
# PRO'S AND CON'S WHEN DESIGNING CATALYST MONOLITHS

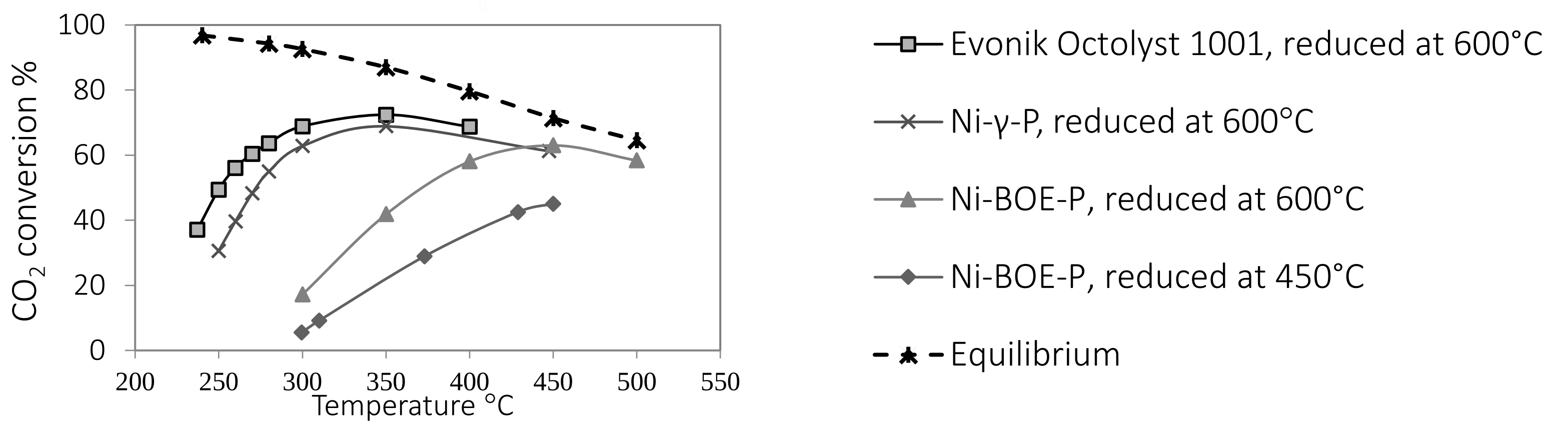



| Conventional coating | Support impregnation | Direct 3D printing |
| --- | --- | --- |
| ✓ Support is mechanically strong<br>✗ Adhesion could be an issue (use of inorganic binder) | ✓ More catalyst per reactor volume<br>✗(Lack of) control of distribution and homogeneity of active material | ✓Catalyst and support can be co-printed<br>✓ More catalyst per reactor volume<br>✗ Mechanical strength |

# 3D PRINTED AND $Ni/Al_2O_3$-COATED REACTORS FOR $CO_2$ METHANATION






S. Danaci, L. Protasova, V. Middelkoop,.. React. Chem. Eng., 2019, 4, 1318

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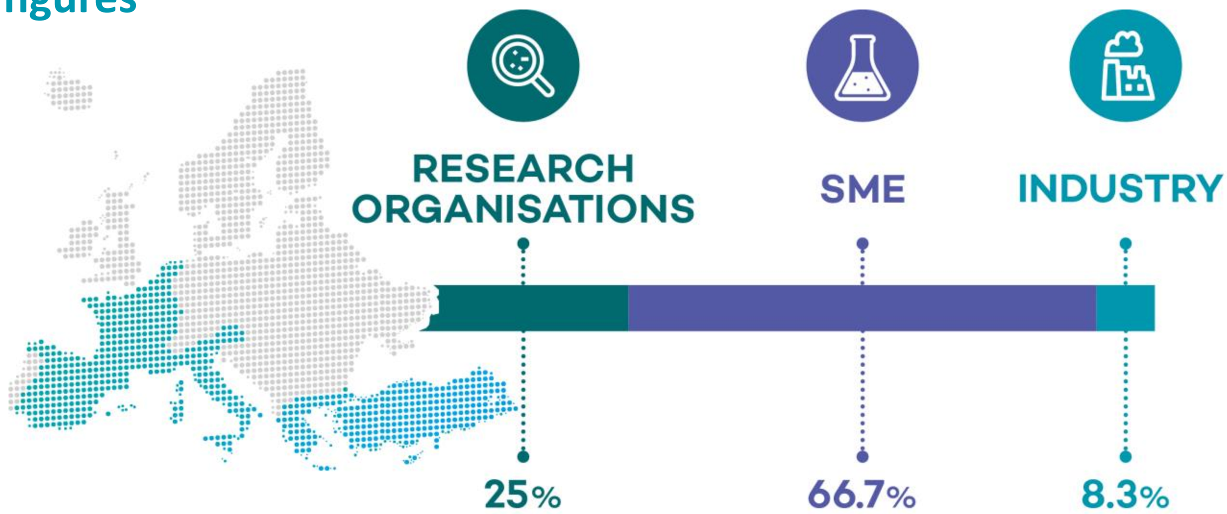
## $CO_2$Fokus facts and figures

12
PARTNERS




42
MONTHS

2019/07/01
STARTING DATE

8
COUNTRIES

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## $CO_2$Fokus at a glance

The project will develop a cutting-edge technology to directly convert industrial $CO_2$ into DME (Dimethyl Ether), by:

- employing innovative 3D printed multichannel catalytic reactors and solid oxide electrolyser cells
- integrating and testing them in industrial environment with $CO_2$ point source at end-user facilities

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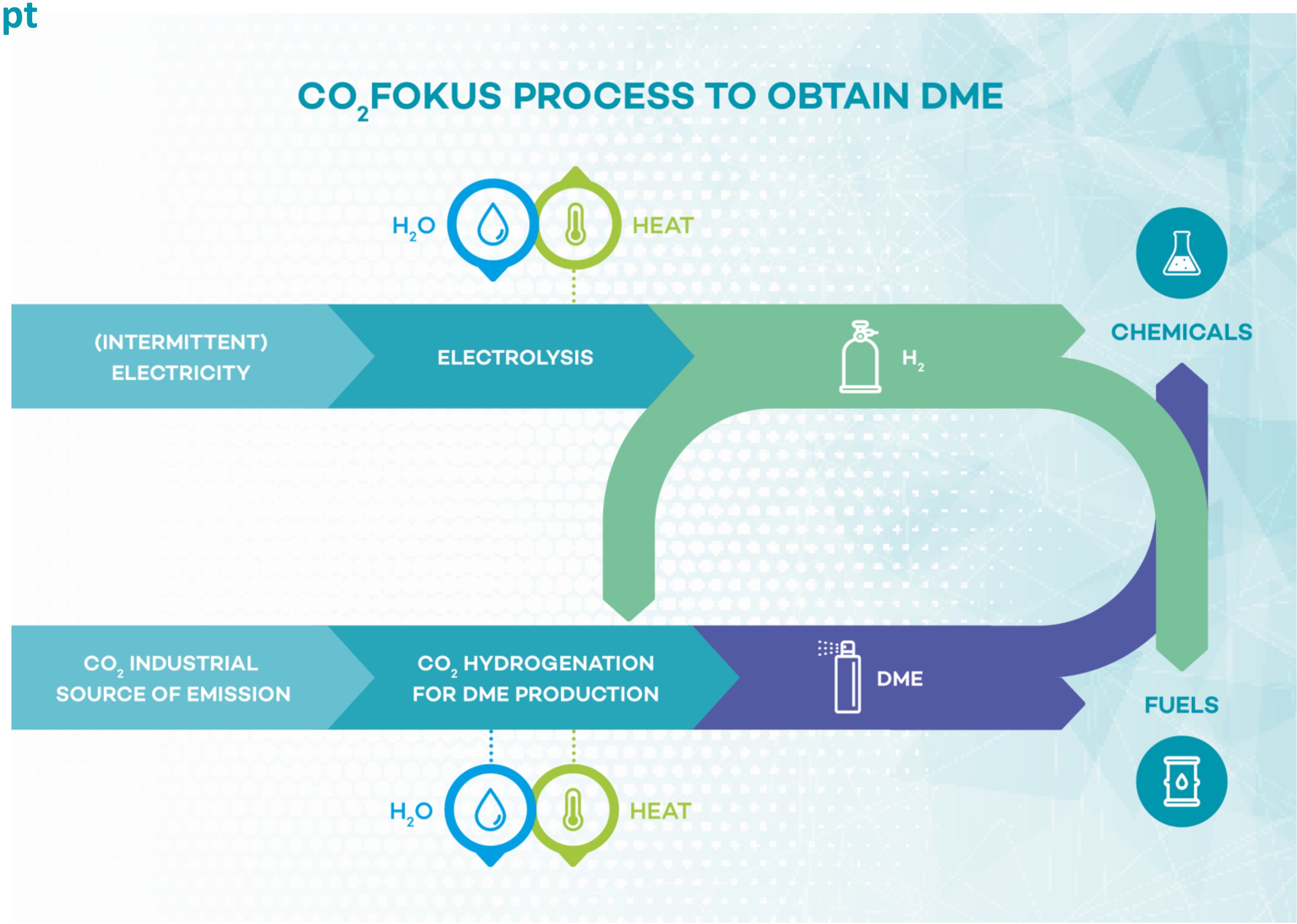
# Concept



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# 3D printed catalyst for DME production in CO2Fokus

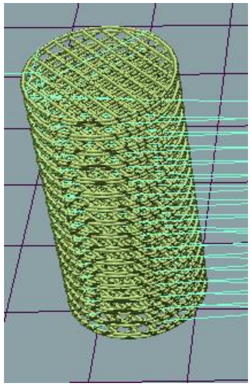

as-prepared


mixing


printing


calcination


calcined


optimising
the printing model


varying design and size


integration
into the reactor

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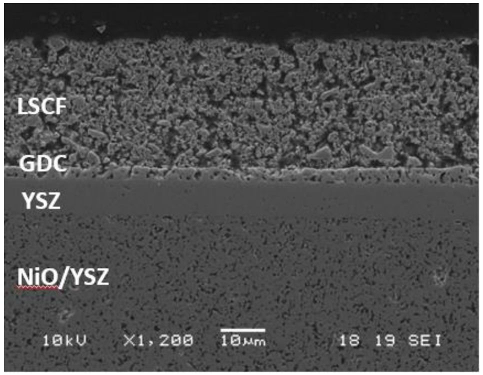
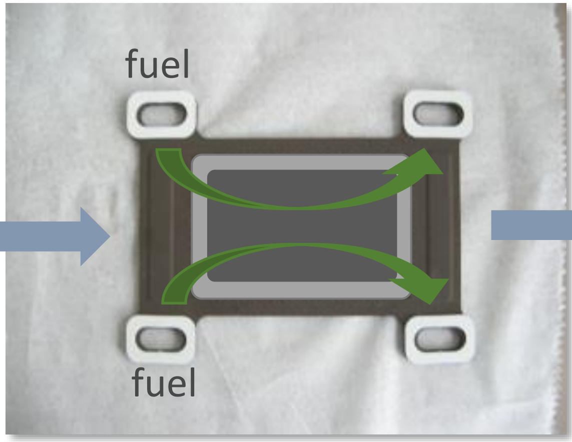
# Solid oxide electrolyser cell and design, development and build up for H2 production

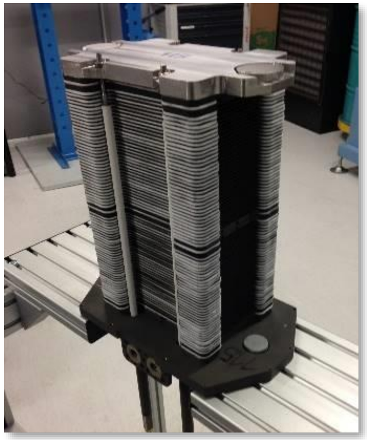
cell design




air




air



- Thin (ca. 250 μm) anode support with GDC/LSCF cathode
- Low cost state-of-the-art materials
- High mechanical strength and reliability

| performances | unit | nominal |
|---|---|---|
| Conversion | % | 60 |
| $H_2$ Production | Nl | 0.30-0.32 |
| Stack power DC | kW | 4.5 |
| Thermal cycling | - | 100-200 |

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## Conclusions

## Advance beyond the state-of-the-art

- 3D printing used for effective controlled deposition of active catalyst particles
- tuning of catalyst composition and morphology (shape/geometry/porosity)
- choice of architecture has effect on pressure drop, mixing, mass and heat transfer
- scale-up/increasing throughput in size: milli to centi reactors; in number: stacking up monoliths and numbering-up tubes
- Reactor design: large surface to volume ratio and controlled shape, geometry and macrostructure; millichannel reactors offer enhanced mass and heat transfer and 10-20% increase in reaction performance
- CO2Fokus integration and operation at Petkim's facilities - industrial $CO_2$ point source to demonstrate direct conversion of $CO_2$ and $H_2$ to DME

## Thank you for watching!

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