ADVANCES IN CATALYSIS FOR HYDROCARBONS

RESULTS FROM ZEOCAT-3D, C123 & BIZEOLCAT EU RESEARCH PROJECTS

ZEOCAT-3D

C123 VALORISING METHANE RESOURCES

BiZeolCat

Funded by the European Union

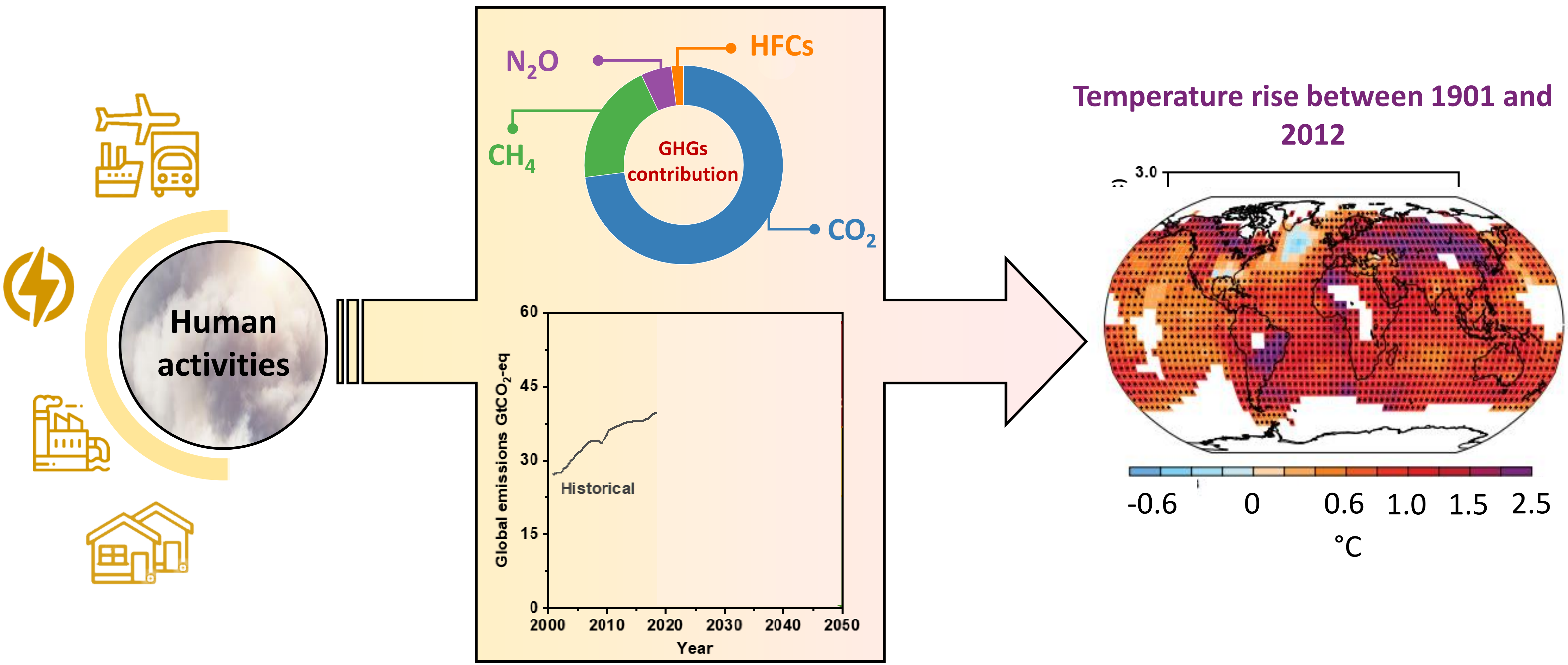
These projects have received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement Nos. 814548, 814671 & 814557

From biogas dehydroaromatization reaction to a tandem catalysis process for the production and regeneration *of* a liquid organic hydrogen carrier

L. Pinard, A. Beuque, S. Santiago, N. Bathalha, A. Sasche

Climate change challenges

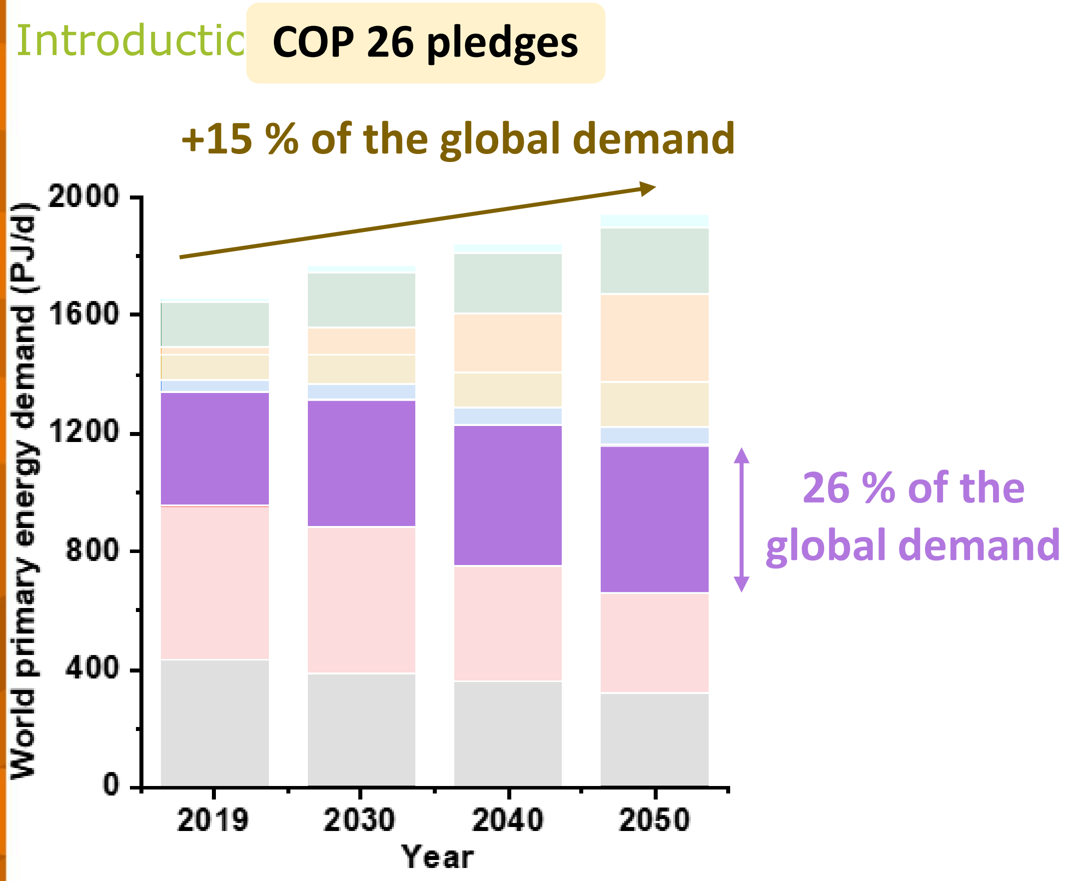
Introduction

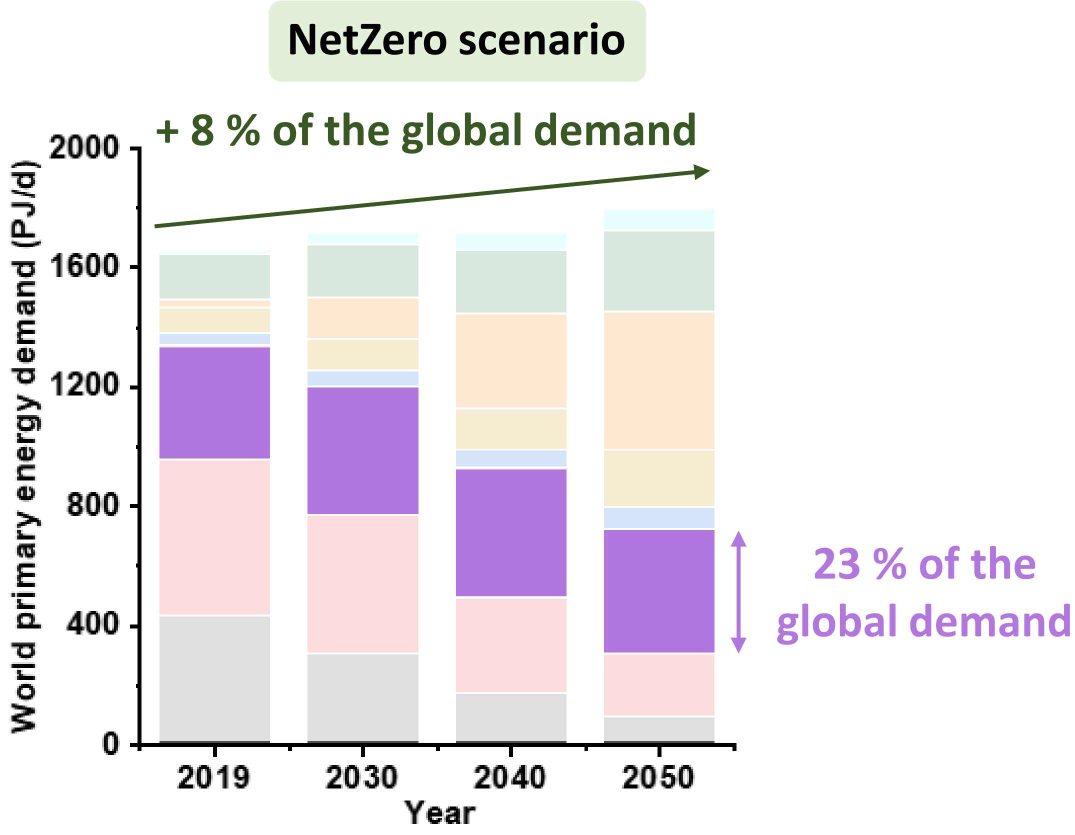


GIEC Changement climatique, 2013.

Forecast primary energy mix

Introduction



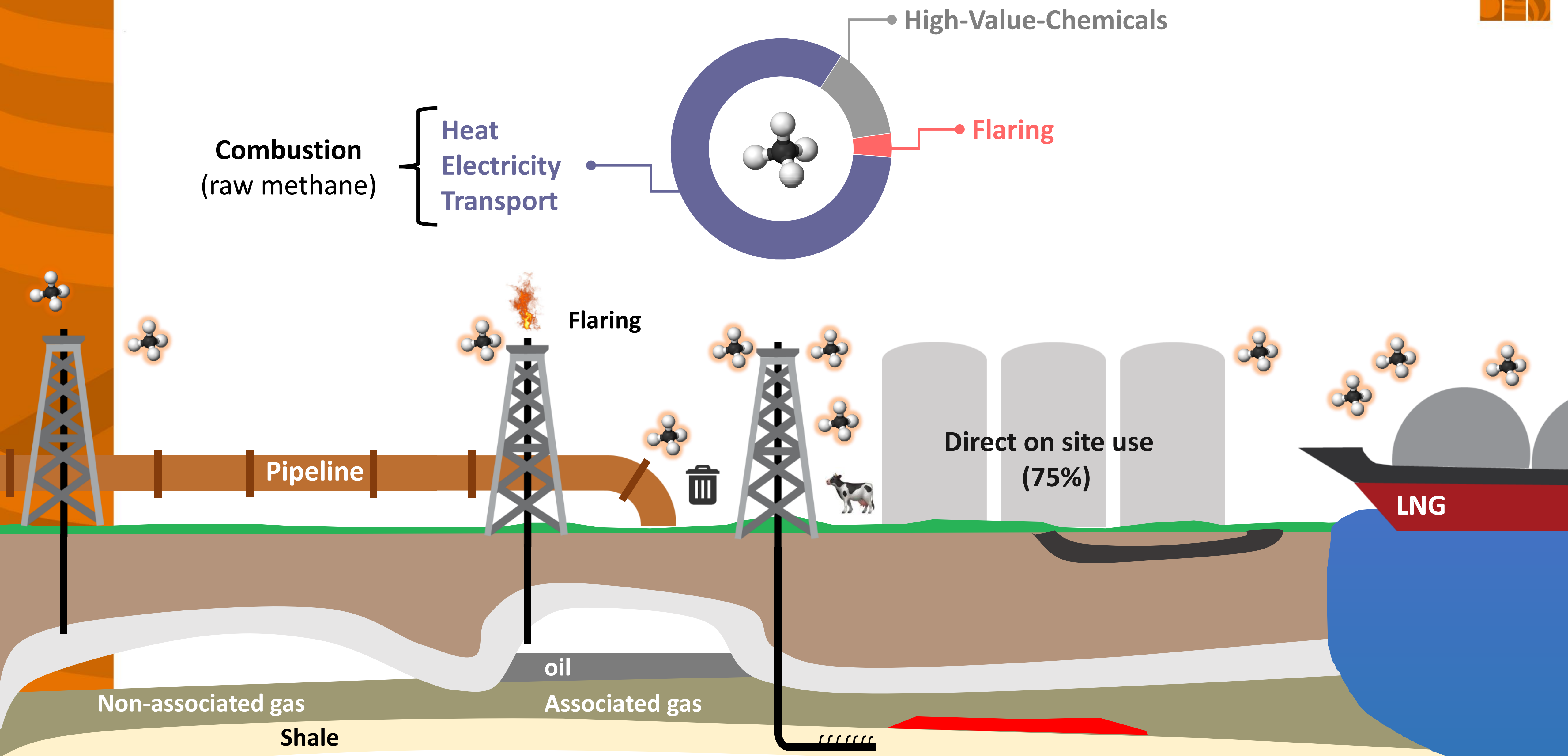


Natural gas

Natural gas is a keystone of energy transition (blue hydrogen, power, industry, …)

Energy Outlook 2021; Total Energies; pp 1–42.

Natural gas panorama

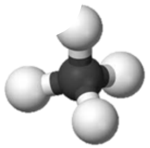


Zichittella, G.; Pérez-Ramírez, J. Status and Prospects of the Decentralised Valorisation of Natural Gas into Energy and Energy Carriers. *Chemical Society Reviews* **2021**, *50* (5), 2984–3012.

Çağlayan, M.; et al. Illuminating the Intrinsic Effect of Water Co-Feeding on Methane Dehydroaromatization: A Comprehensive Study. *ACS Catal.* **2021**, 11671–11684.

Methane catalytic upgrading

Indirect route



Steam reforming of methane (Eq. I-1)

$CH_4 + H_2O \rightleftarrows CO + 3\ H_2$

$\Delta H_{298} = +207\ kJ\ mol^{-1}$

Ni-based catalysts

700 - 1000°C

15-30 atm

Partial oxydation of methane (Eq. I-2)

$CH_4 + \frac{1}{2}O_2 \rightleftarrows CO + H_2$

$\Delta H_{298} = -36\ kJ\ mol^{-1}$

Ni-based catalysts

700 - 900 °C, 1 atm

Dry reforming of methane (Eq. I-3)

$CH_4 + CO_2 \rightleftarrows 2\ CO + 2\ H_2$

$\Delta H_{298} = +248\ kJ\ mol^{-1}$

Ni-based catalysts

~ 900 °C, 1 atm

Syngas

Via methanol synthesis

Olefins

500 - 600 °C, 1 atm

Sapo-34

Gasoline

400 - 500 °C, 1 atm

HZSM-5

FTS route

Wax/ diesel fuels

200 - 240°C, 20 - 40 atm

Co-based catalysts

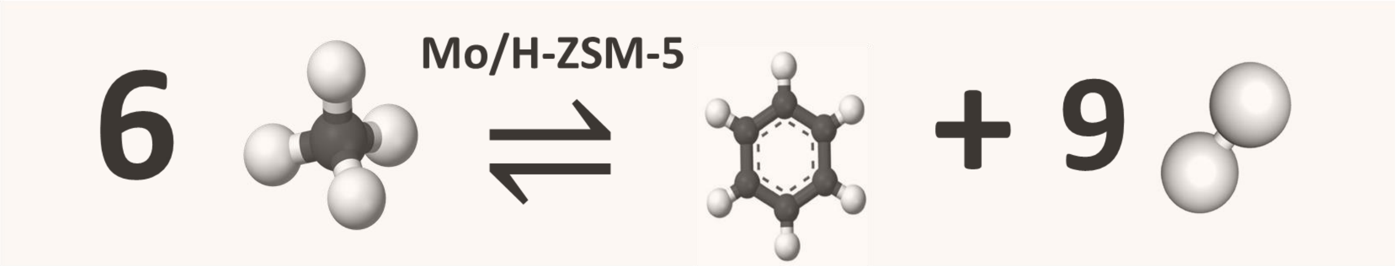
Olefins/liquid fuels/ oxygenates

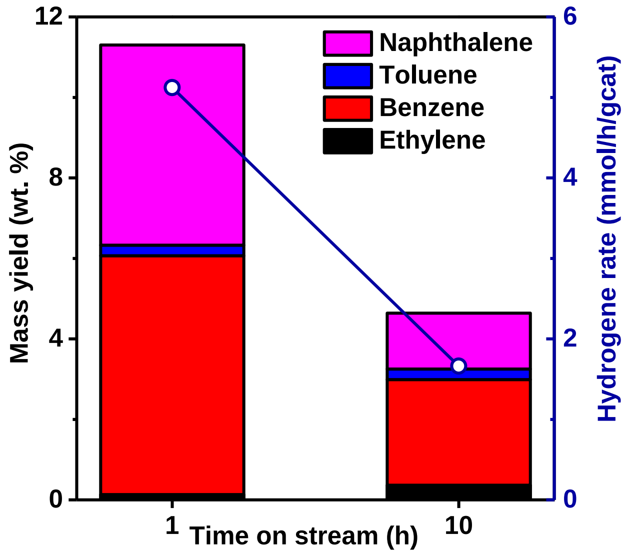
300 - 350 °C, 20 - 40 atm

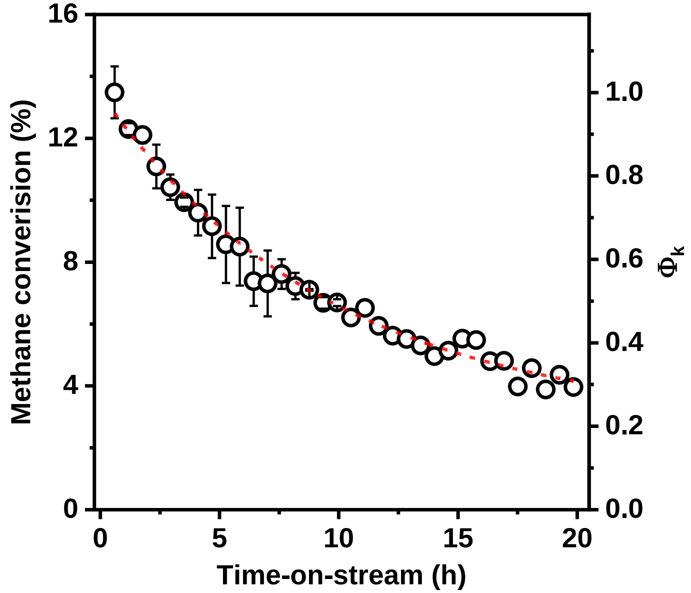
Fe-based catalysts

Antoine Beuque's Thesis (2022)

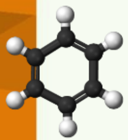
Methane dehydroaromatization under non oxydative conditions







Products valorization



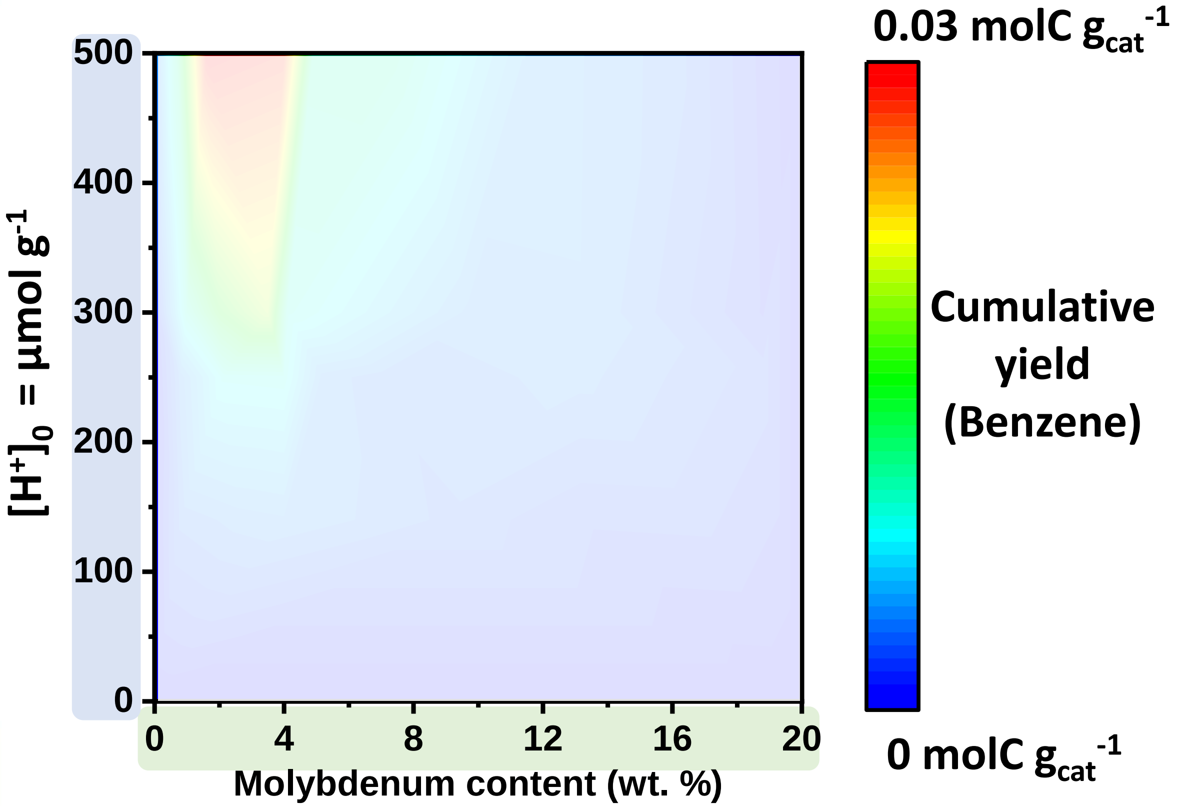
Highly selective towards benzene ~70%

Energy vector

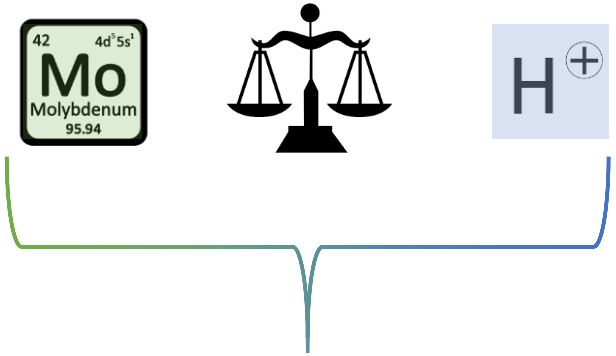
3 Majors hurdles

- Thermodynamic conversion ~12.5% at 700 °C
- Rapid catalyst deactivation : ~ 10 hours
- Selectivity in Naphthalene : 30 %

How to increase the benzene yield? *Catalyst optimization*



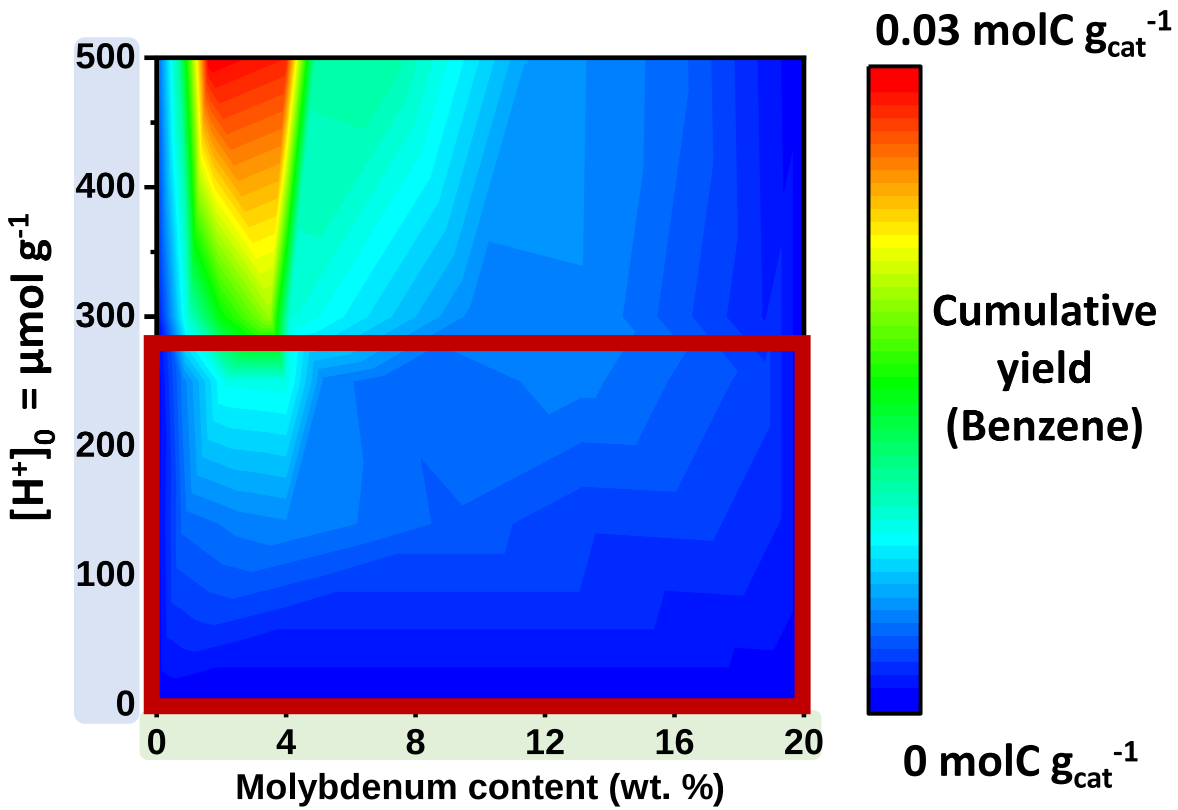
Optimisation of the Balance Mo/H^+

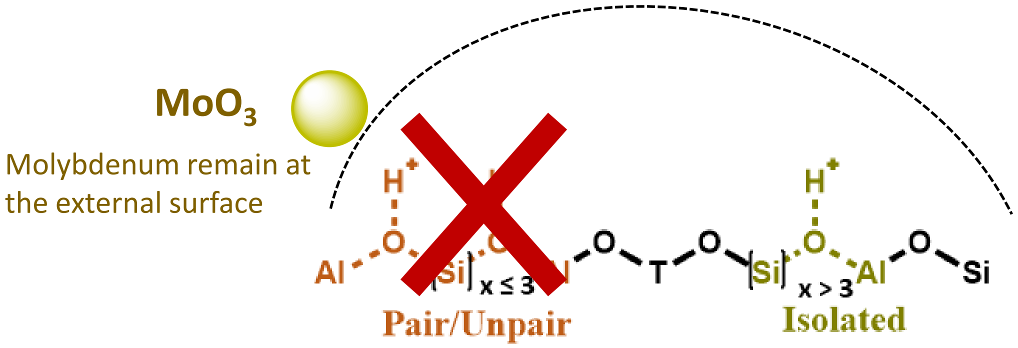


Impact of the balance of the two functions (metallic and acidic)

Beuque, A et al. How Does the Balance of Metal and Acid Functions on the Benchmark Mo/ZSM-5 Catalyst Drive the Methane Dehydroaromatization Reaction? *Catalysis Today* **2022**.

How to increase the benzene yield? *Catalyst optimization*





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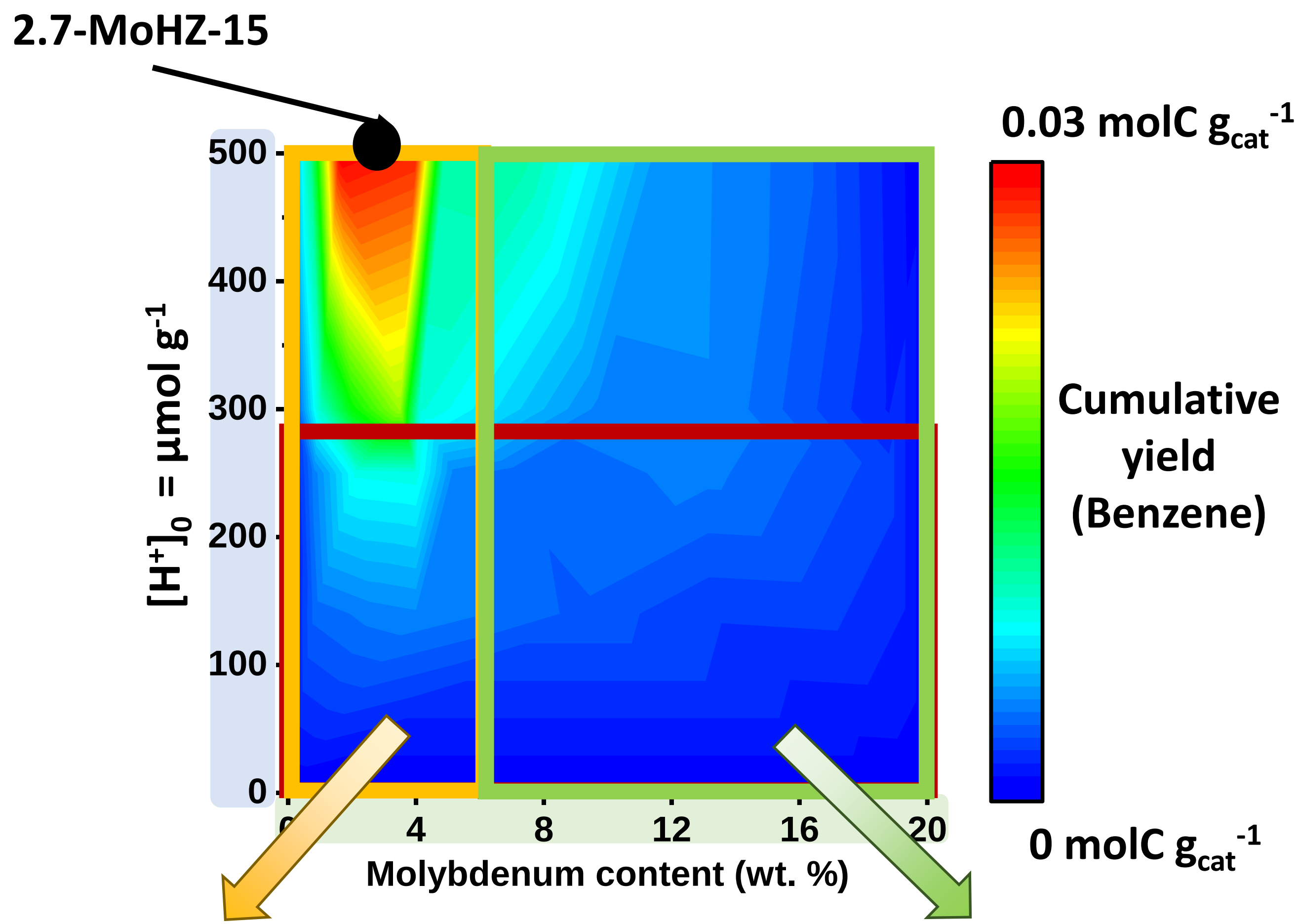

Benzene yield is still too low

Reversible deactivation by pore blocking

Irreversible deactivation by zeolite amorphization

Selection of the well-balanced catalyst (2.7-MoHZ-15)

Beuque, A et al. How Does the Balance of Metal and Acid Functions on the Benchmark Mo/ZSM-5 Catalyst Drive the Methane Dehydroaromatization Reaction? *Catalysis Today* **2022**.

How to increase the benzene yield? *Catalyst structuring*

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Granules

- d = 1–20 mm
- Fixed bed / Moving bed
- Lower … d… co…
- Carreful… monitoring the packing

Pellets

- d = 3–15 mm
  l = 3–15 mm
- Fixed bed
- …
- Disruption of the pore system

Extrudates

- d = 1–50 mm
  l = 3–30 mm
- Fixed bed
- …rface to …xibility …al …orosity
- Tune pressure drop

Regeneration issue

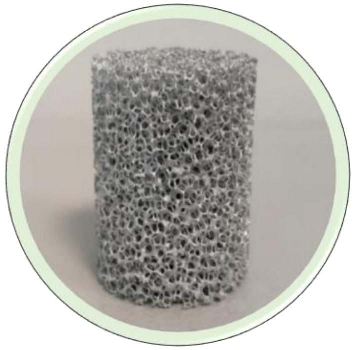
- Difficulty for proper heat management and acceptable pressure drop

Dense packed beds ➔ Randomly packing

Honeycomb monoliths

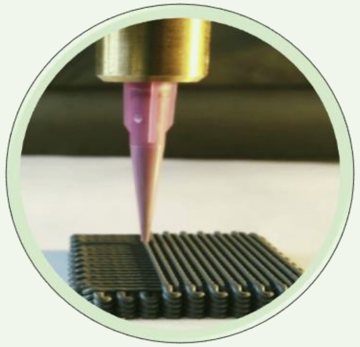
- 2D channels
- Low pressure drop
- Efficient heat …
- …
- … geometry

Foam



- 3D channels, interconnected pore system
- …t heat

3D printing monoliths



- 3D channels, interconnected pore system
- Efficient heat removal
- Low mechanical strength
- Ultrahigh variety of geometry

Reaction issue

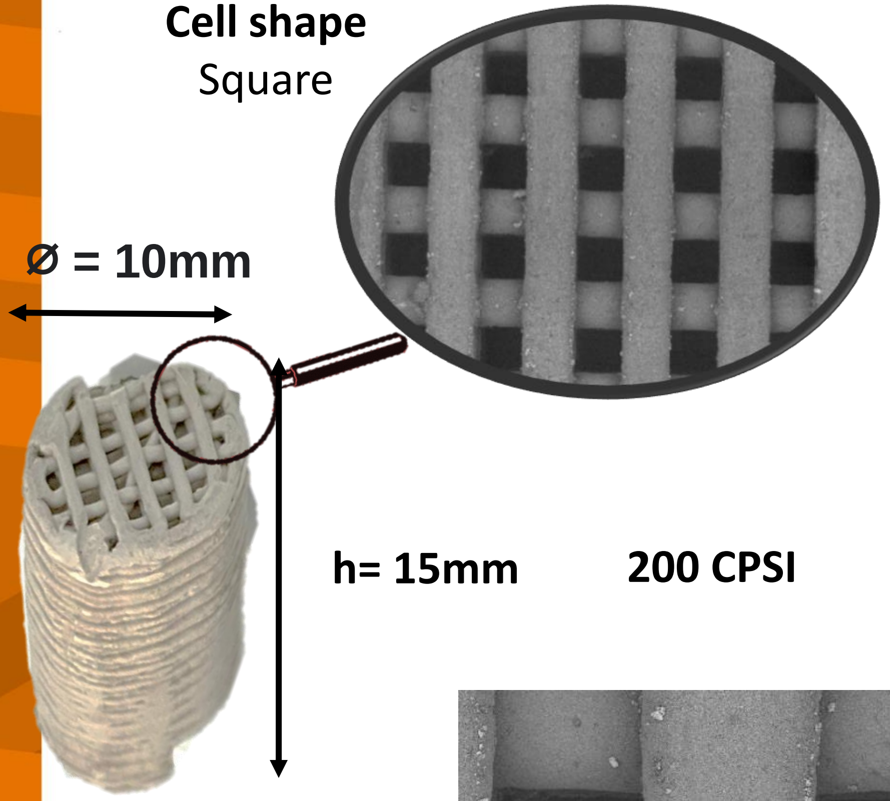
- Low weight of catalyst per unit volume
  ➔ short contact time

Cellular structures ➔ Standalone reactors

Rosseau, L. R. S et al. (2022) Front. Chem. Eng. 4. DOI:10.3389/fceng.2022.834547

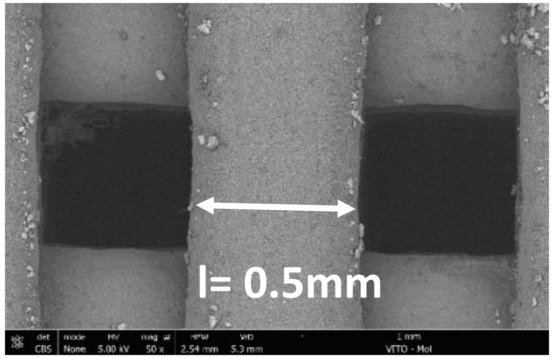
Influence of design (TRL 4)

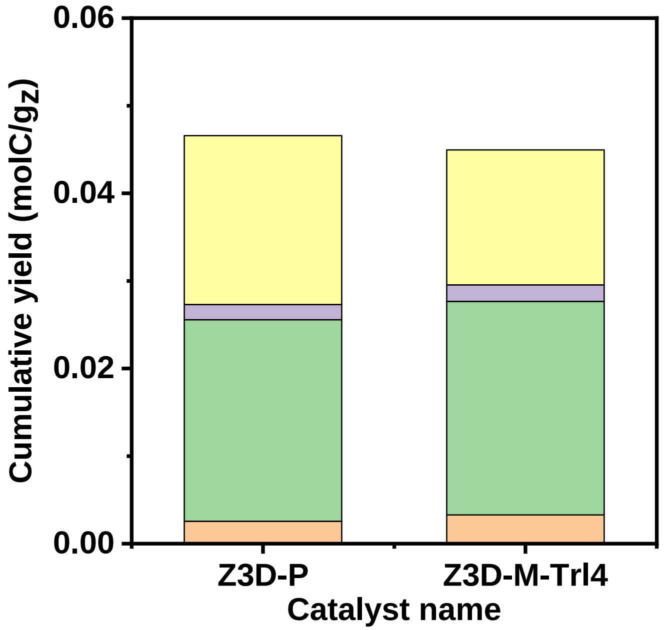
Cell shape
Square



200 CPSI

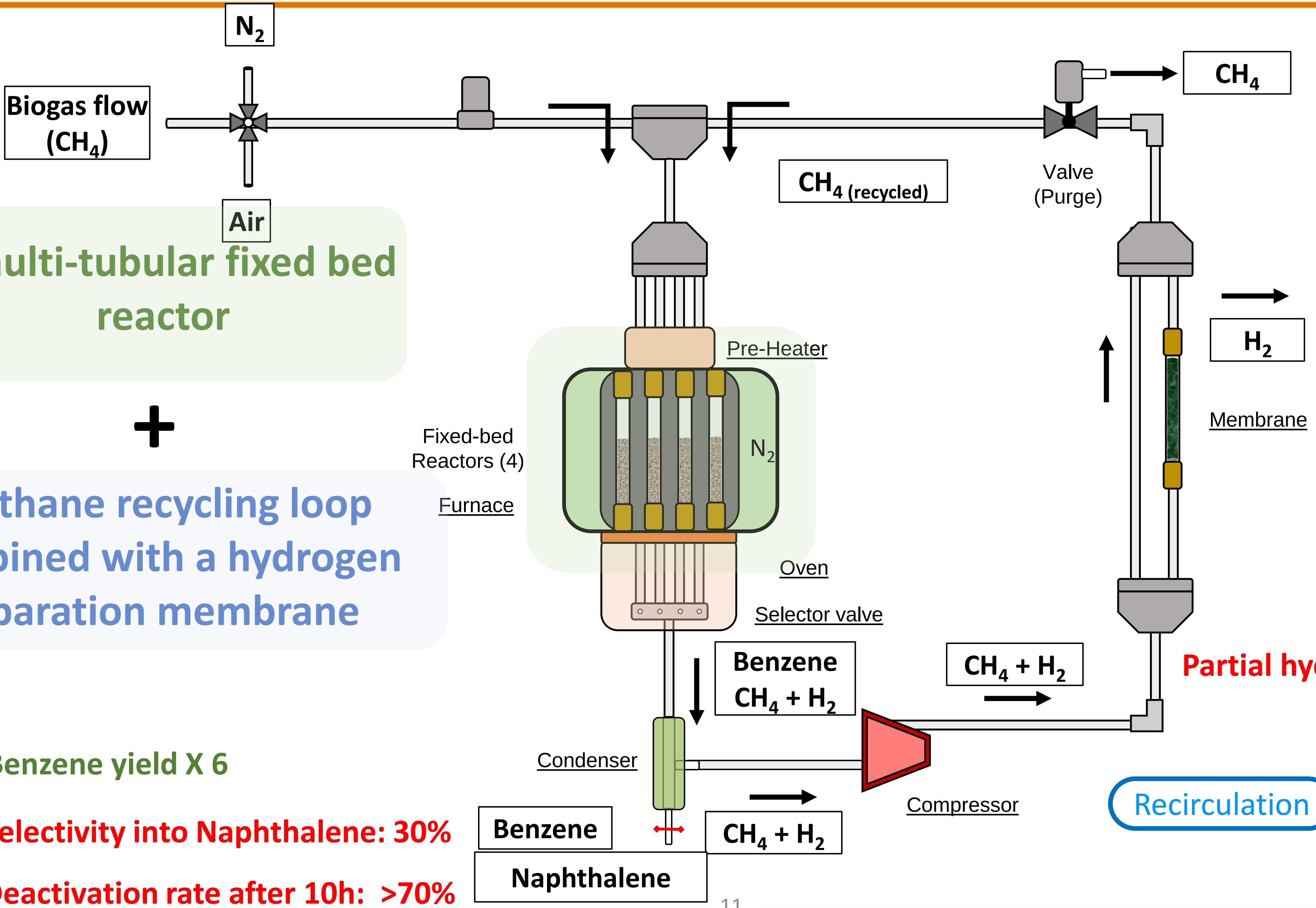
Z3D-M





No influence of the design at the lab scale
➔ possibility to preserve the catalytic properties during the scale-up

How to increase the benzene yield? *Process optimisation*



A multi-tubular fixed bed reactor

+

Methane recycling loop combined with a hydrogen separation membrane

Partial hydrogen separation (80%)

Benzene yield X 6

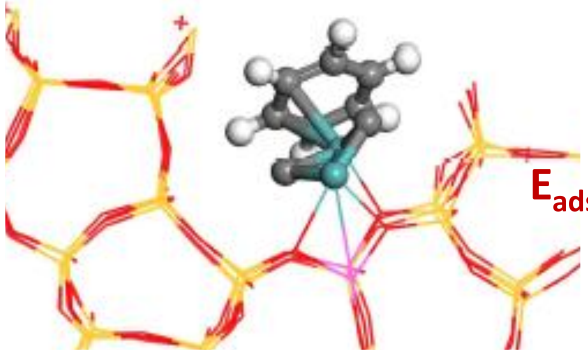
Selectivity into Naphthalene: 30%

Deactivation rate after 10h: >70%

Why the deactivation mitigation is limited ?

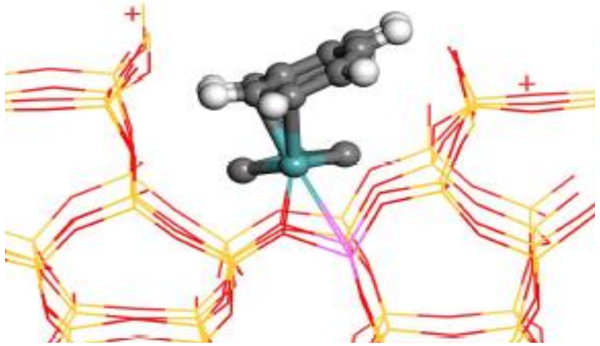
Inhibition of the active sites by the reaction products

Benzene adsorption



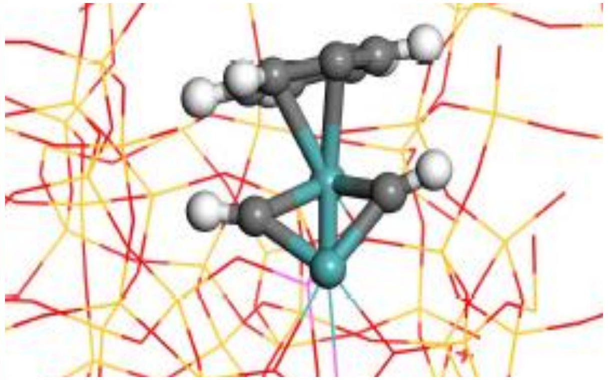
E_{ads} (C_6H_6) = -0.78eV

Naphthalene adsorption



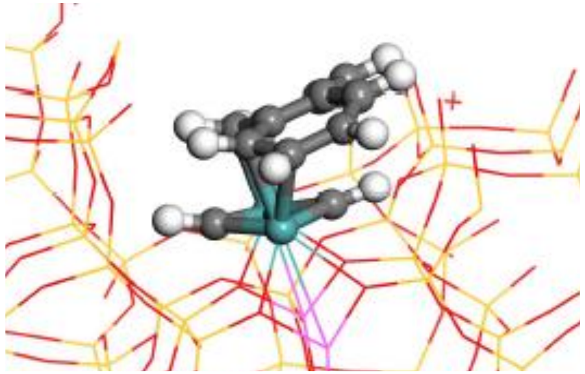
Eads ($C_{10}H_8$) = -0.65eV

CO-hydrogen/benzene adsorption



E_{ads} ($C_6H_6 + H_2$) = + 0.16eV

CO-hydrogen/napthalene adsorption

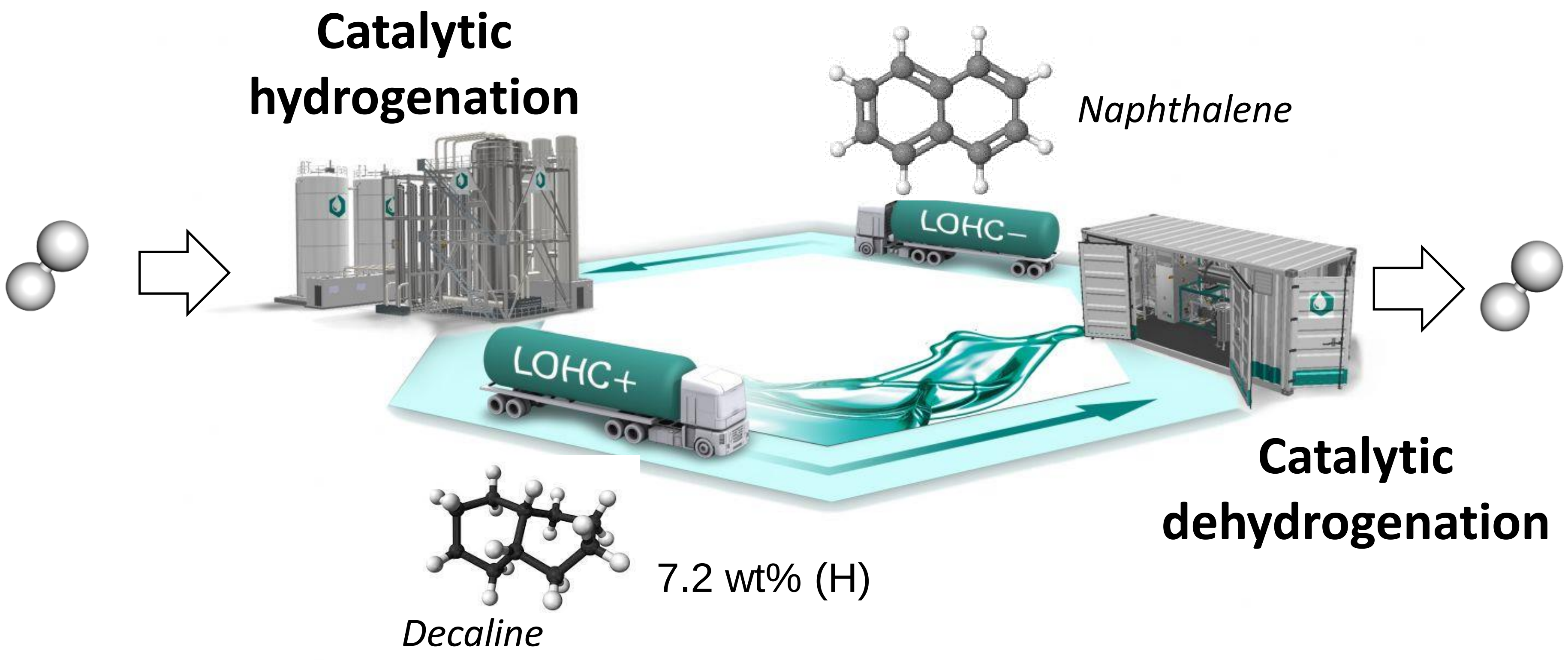


Eads ($C_{10}H_8 + H_2$) = +0.68

Presence of hydrogen reduces strength of the benzene adsorption on active sites

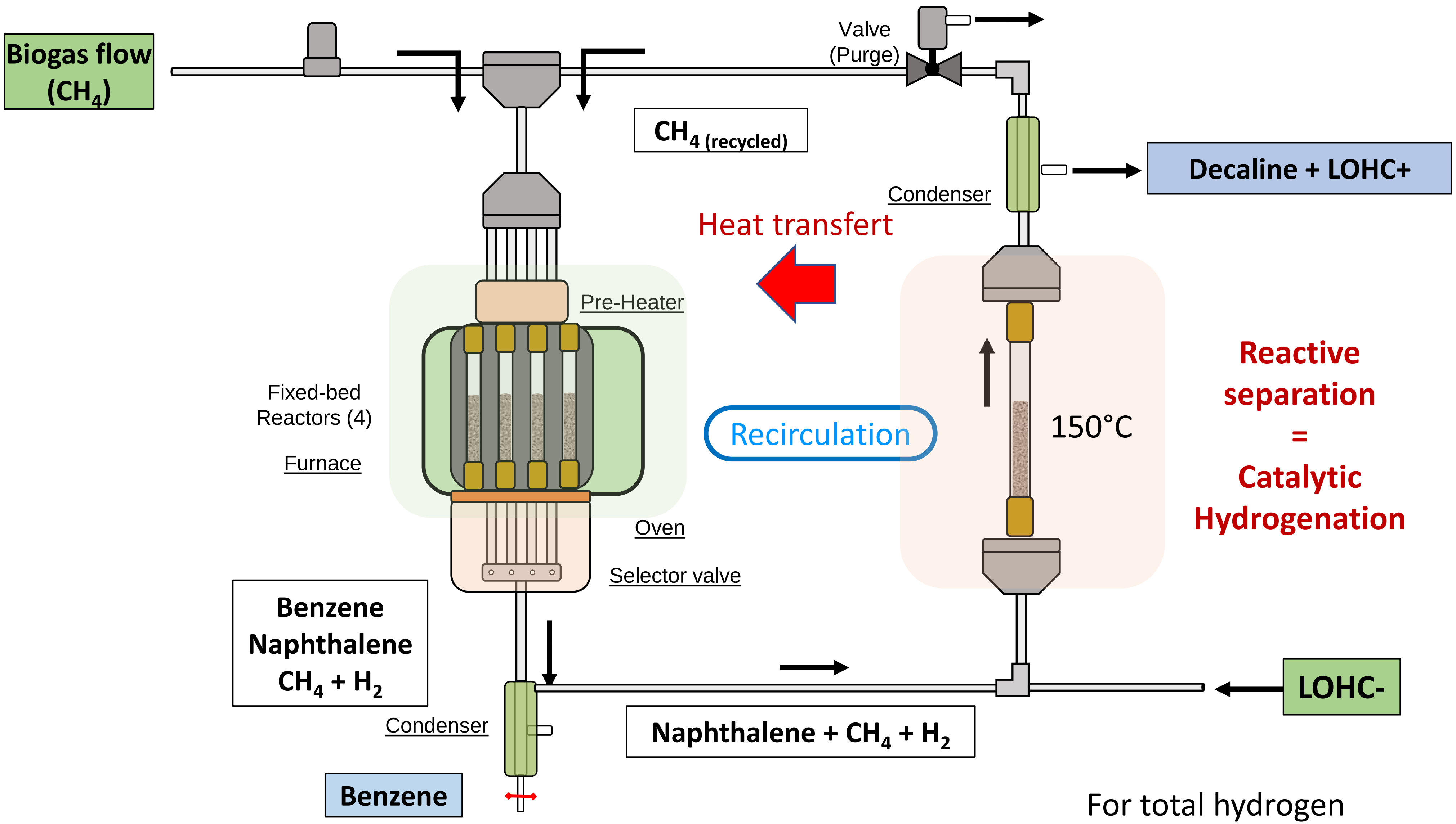
Beuque, A et al. How Do the Products in Methane Dehydroaromatization Impact the Distinct Stages of the Reaction? *Applied Catalysis B: Environmental* **2022**, *309*, 121274

How to valorize naphthalene?



Naphthalene a possible Liquid Organic Hydrogen Carrier (LOHC-)

Tandem catalysis for biogas to Liquid Organic Hydrogen Carrier

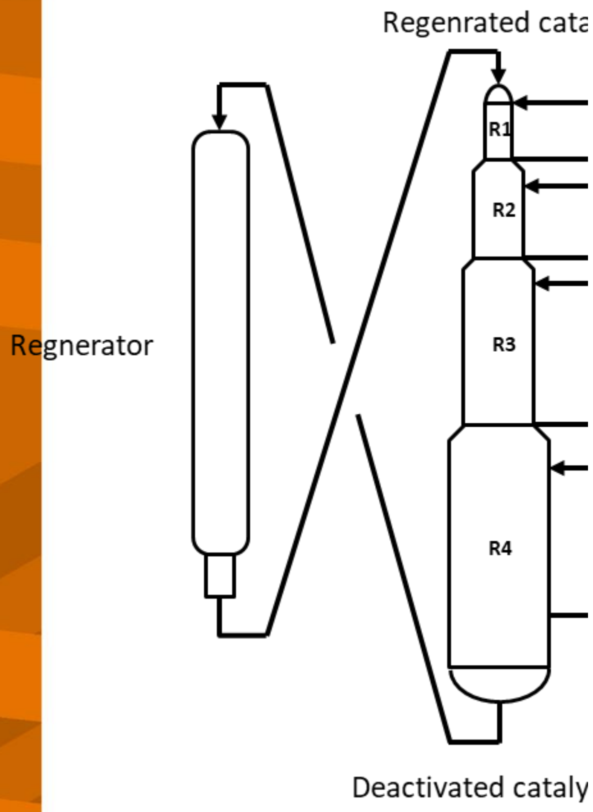


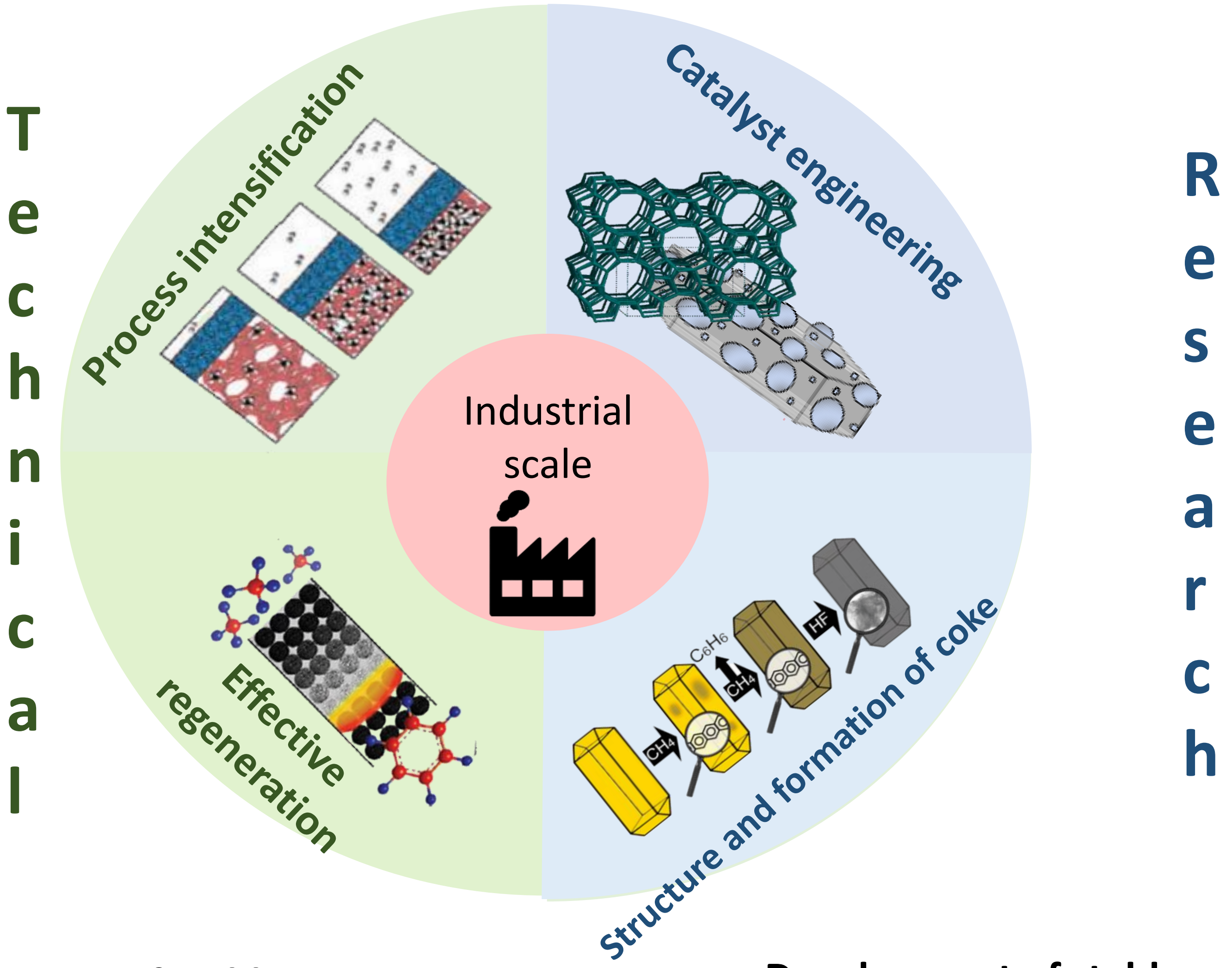
Reactive separation = Catalytic Hydrogenation

For total hydrogen consumption

Conclusion

Tandem catalysis for biogas to Liquid Organic Hydrogen Carrier





Development of stable bifunctional MDA catalysts

Development of stable zeolite-based hydrogenation catalysts

N. Kosinov, E.J. Hensen Advanced Materials, 2020, DOI: (10.1002/adma.202002565)

Acknowledgments

cnrs

IC2MP
Institut de Chimie des Milieux et Matériaux de Poitiers

ZEOCAT-3D

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ΒΙΟΕΝΕΡΓΕΙΑ ΝΙΓΡΙΤΑΣ Ο.Ε.

ΔΗΜΟΚΡΙΤΟΣ

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HELLENIC PETROLEUM

THANK YOU FOR YOUR ATTENTION

THANK YOU

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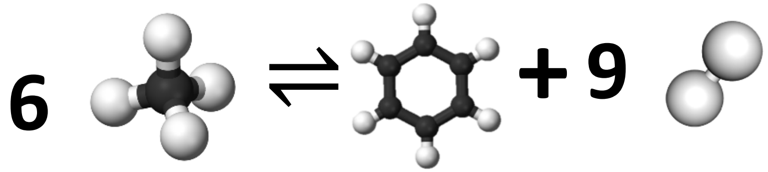
Importance of the regeneration step

Reaction



Extremely endothermic

$\Delta H_r^0 = 532\ kJ\ mol^{-1}$

Thermodynamically limited

~ 12% at 700 °C

Long contact time

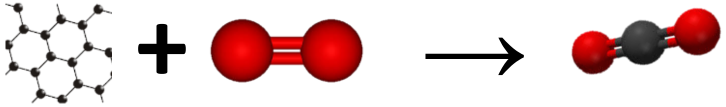
Deactivation few hours

3wt. %Mo/H-ZSM-5

Spent catalyst

~ 8%wt. of carbon

Regeneration



Highly exothermic

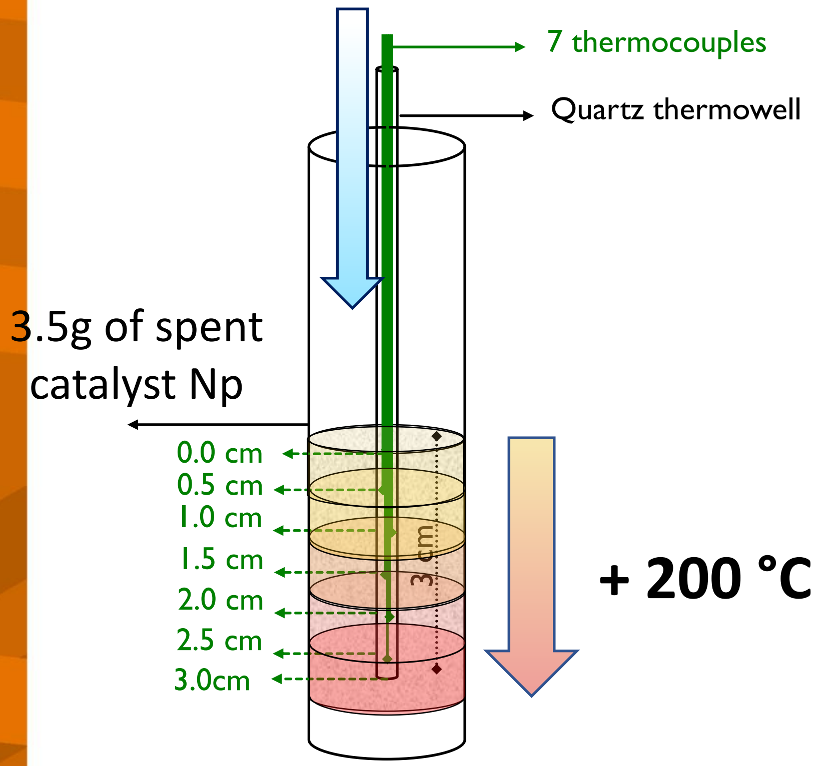
$\Delta H_r^0 = -283\ kJ\ mol^{-1}$

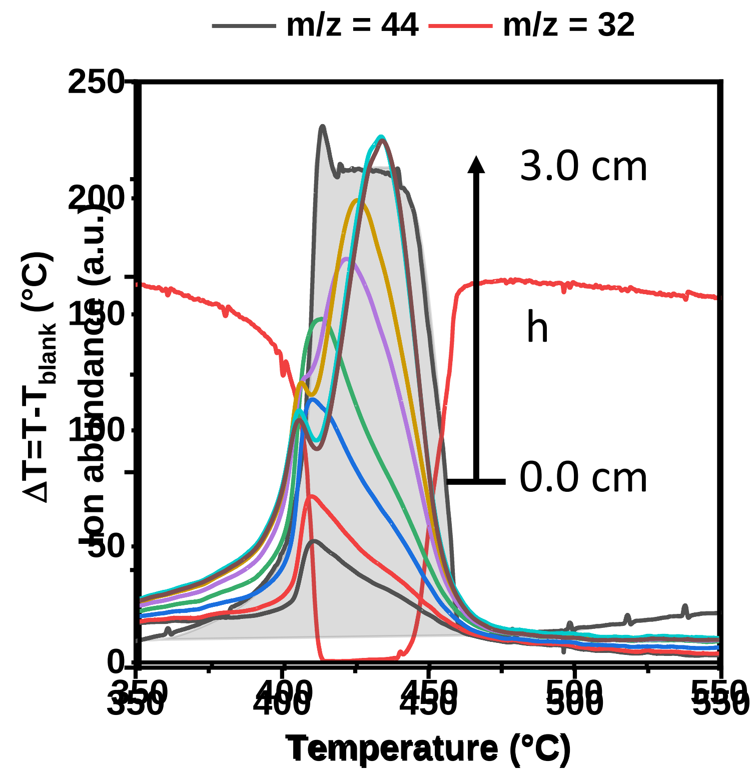
Short contact time

Risk of thermal runaway

Management of the regeneration step

Regeneration
Air 140 mL min^{-1}





Reach 700°C in the reactor

Formation of extraframework species $Al_2(MoO_4)_3$
➔ collapse of the internal zeolite structure

Coke combustion ➔ oxygen comsommation

$$C_s + O_2 \rightarrow CO_2$$

Highly exothermic

$$\Delta H_r^0 = -283\ kJ\ mol^{-1}$$

Irreversible deactivation

Key point to manage heat temperature