Gas-phase Hydroformylation of 1-Butene using Monolithic Supported Liquid-Phase (SLP) Catalyst

Mahtab Madani[1], Leonhard Schill[1], Nanette Zahrtmann[2], Raquel Portela[3], Linda Arsenjuk[4], Robert Franke[4], Rasmus Fehrmann[1], Anders Riisager[1]

[1]Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical, University of Denmark, Lyngby, Denmark
[2]LiqTech Ceramics A/S, Ballerup, Denmark, [3]Institute of Catalysis and Petrochemistry (ICP-CSIC), Spectroscopy and Industrial Catalysis Group. Madrid, Spain, [4]Evonik Operations GmbH, Marl, Germany

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Outline

- MACBETH project
- Hydroformylation (HyFo) of olefins
- SLP system
- SLP HyFo catalytic testing
- Summary & outlook

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

MACBETH project

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

MACBETH

Acronym:

Membrane **A**nd **C**atalysts **B**eyond **E**conomic and **T**echnological **H**urdles

Goals:

- Development of new supported liquid-phase catalysts
- Reactor systems development for large-scale chemicals production

Impacts:

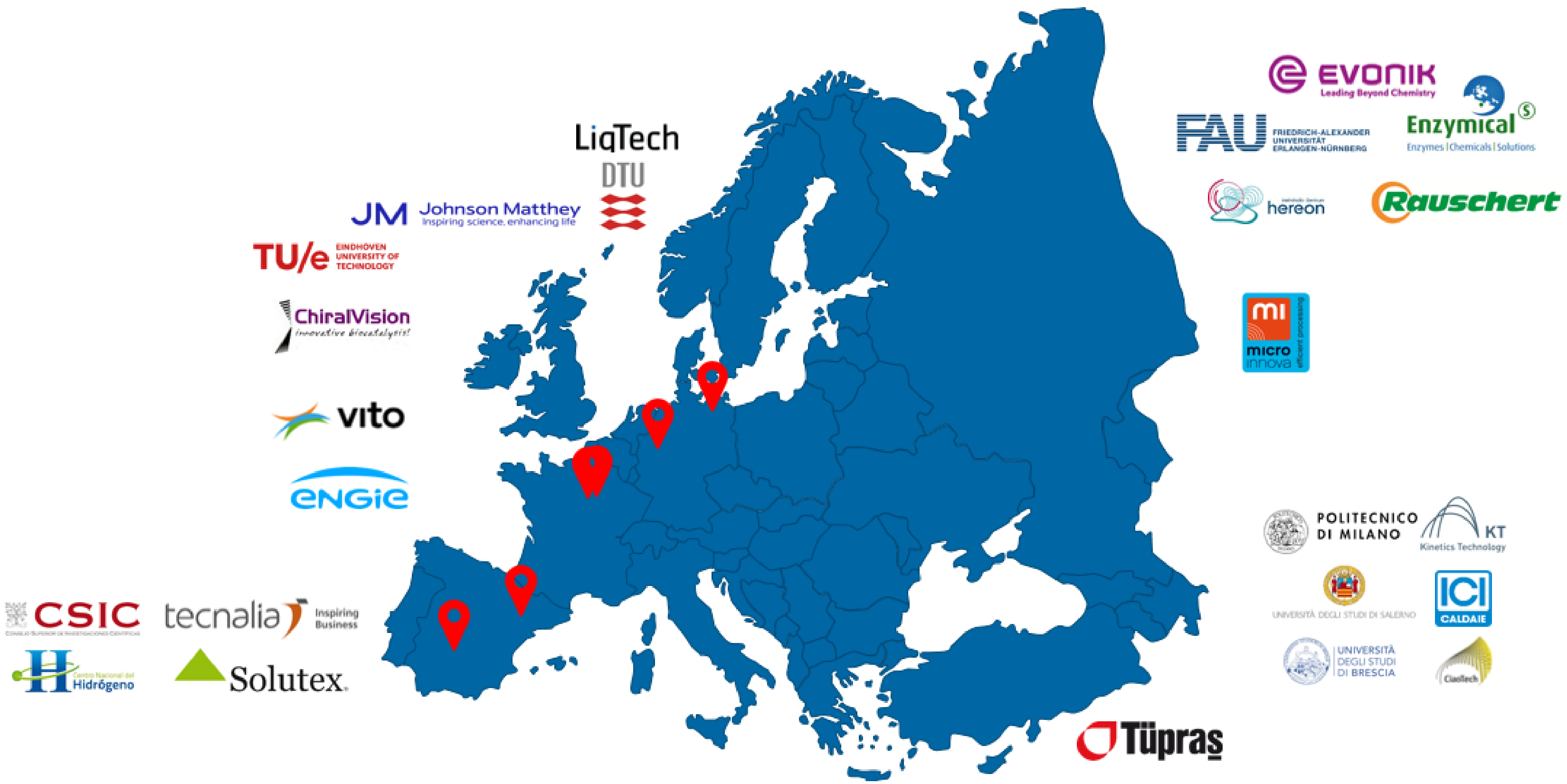
- Reduction of GHGs
- Increase of resources & energy efficiency
- Reduce operational & investment costs

GHG	↓	≤ 35%
	↑	≤ 70%
	↓	≤ 50%
	↓	≤ 80%

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

MACBETH

- 24 partners
- 10 countries
- 6 plant/testing sites (📍)



www.macbeth-project.eu

@MACBETH_H2020

MACBETH

macbeth.h2020@gmail.com

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

MACBETH cases

HyFo - Hydroformylation

Conversion of olefins & syngas

to aldehydes

Production of specialty chemicals

H_2 – Hydrogen Production

Natural gas methane conversion to hydrogen

Production of pure H_2

PDH – Propane Dehydrogenation

Conversion of propane to propylene

Production of petrochemicals

BOC – Bio Catalytical Oil Cleavage

Conversion of vegetable oils to fatty acids or their alkyl ester derivates

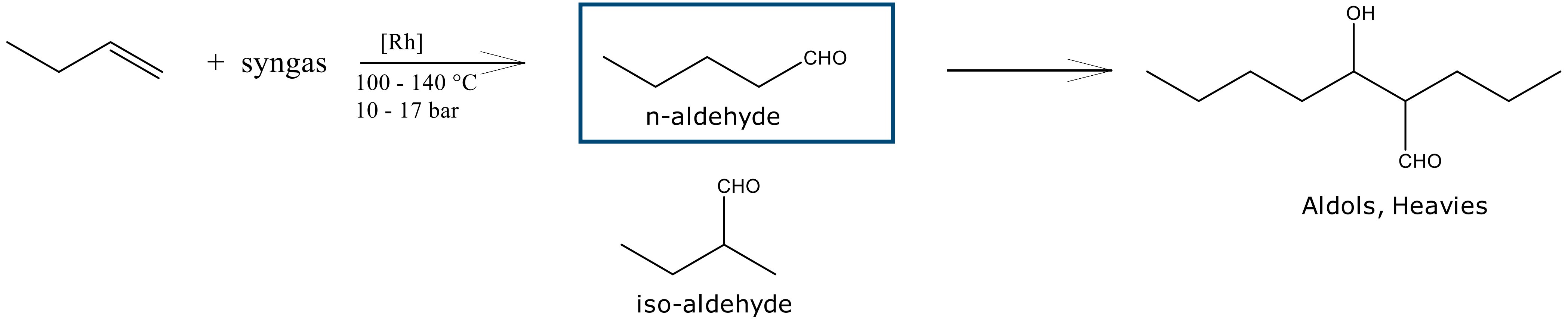
Food industry and biofuels

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

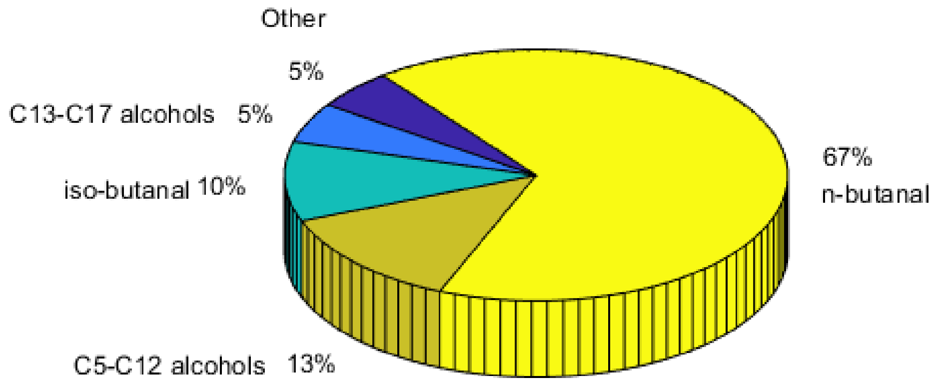
Hydroformylation of olefins

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Hydroformylation (HyFo) reaction



- > 10 mio. t per year
- Homogeneously catalyzed process
- Huge incentive for heterogenization



Chem. Rev. 2012, 112, 11, 5675

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Supported Liquid-Phase (SLP) System

A bridge between heterogeneous & homogeneous catalysis

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Catalysis classifications

Heterogeneous Catalysis

Advantages:

- Straightforward catalyst/product separation
- Simple reactor design

Drawbacks:

- Low selectivity
- Low mechanistic understanding

Homogeneous Catalysis

Advantages:

- High selectivity
- High activity
- Deep mechanistic understanding

Drawbacks:

- Difficult catalyst/product separation

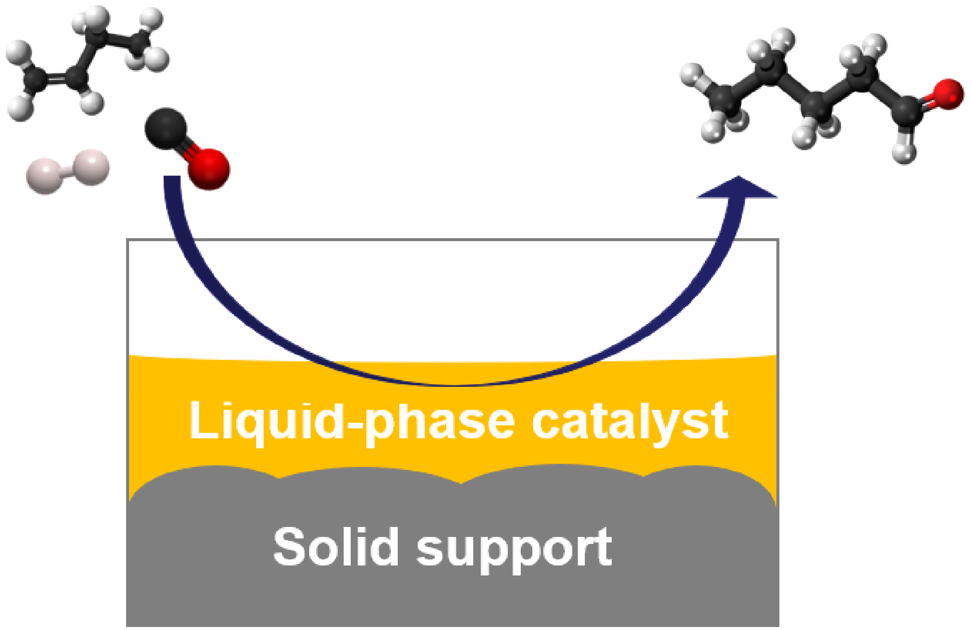
Heterogenized homogeneous Catalysis

- Secure the advantages of both homogeneous & heterogeneous catalysis
- An example → SLP system

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

SLP system

- SLP system → one example of heterogenized homogeneous catalysis
- Immobilization of a homogeneous catalyst solution on a solid support
- Secure the advantages of both homogeneous & heterogeneous catalysis

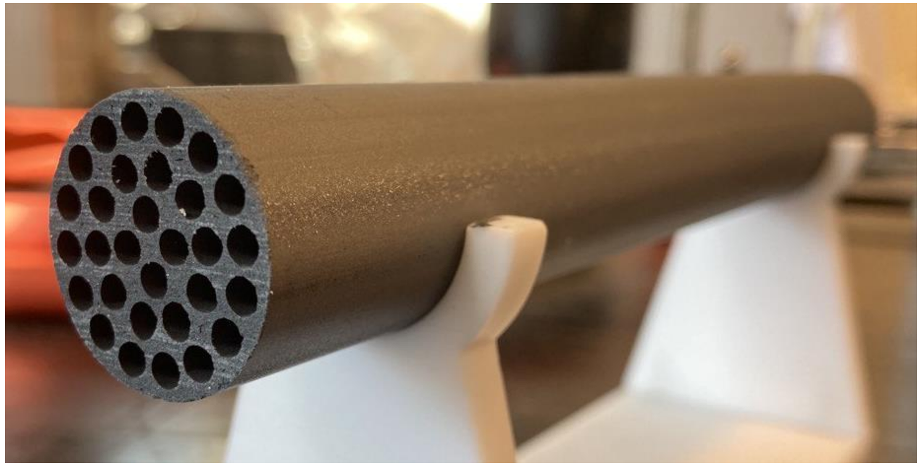


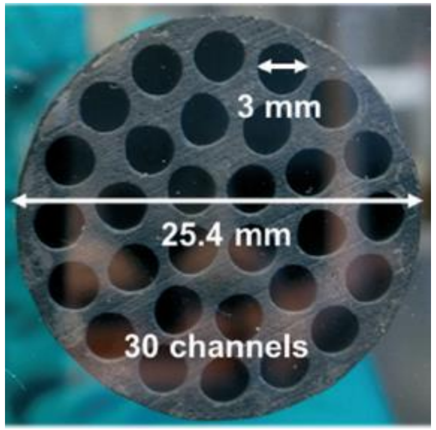
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Monolithic SiC support

Monolithic SiC support:

- Chemically inert
- Efficient thermal conductivity
- Reduced pressure drop
- Simple up-scaling by modular design





This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Monolithic SiC support – leaching issue

Large macropores in the SiC monolith

Too weak capillary forces

Catalyst system leaching

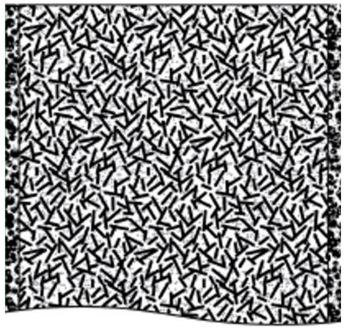
New porous monoliths have to be developed

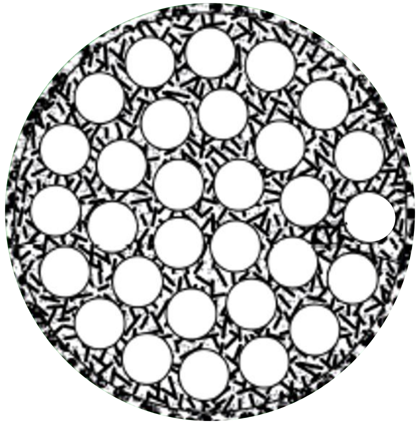
Infiltration by metal oxide (SiO_2) nanoparticles

Portela et al., Reaction Chemistry & Engineering, 2021, **6**, 2114

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Monolithic support structure





SiC core support

- Macropores (~ 10 µm)

SiO_2 washcoat

- Mesopores (~ 3-30 nm)
- Provides high surface area
- Better liquid catalyst dispersion

SiC skin

- Smooth surface for membrane application

J. M. Marinkovic, Technical University of Denmark, 2019

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Support variations

Variable parameters:

- Number of SiO_2 washcoat layers
- Size of the SiO_2 washcoat particles

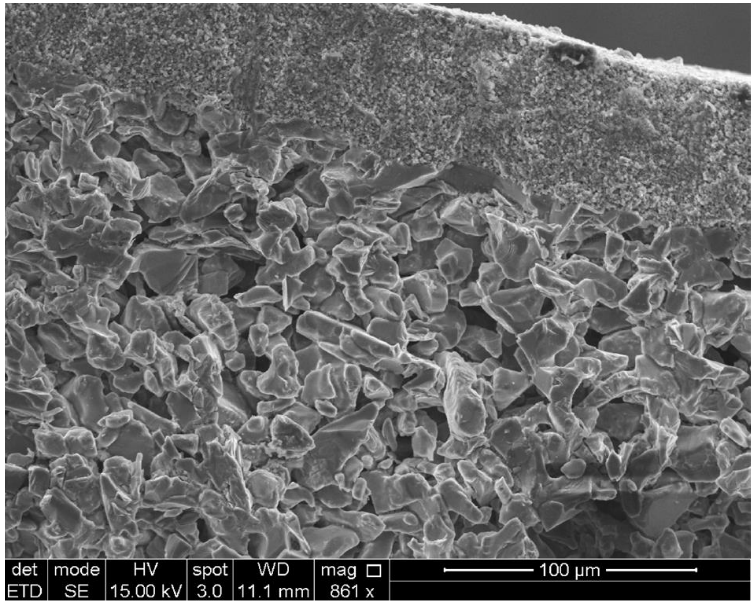
Support name	SiO_2 particle size (nm)	# of washcoat layer	Intermediate washcoat calcination	Theo. Size of mesopores (nm)
1×Si 7	7	1	-	2.8
1×Si 70	70	1	-	28
2×Si 70	70	2	-	28
2×Si 70-calc.	70	2	✓	28

Portela et al., Catalysis Today. 2022, 383, p 44-54

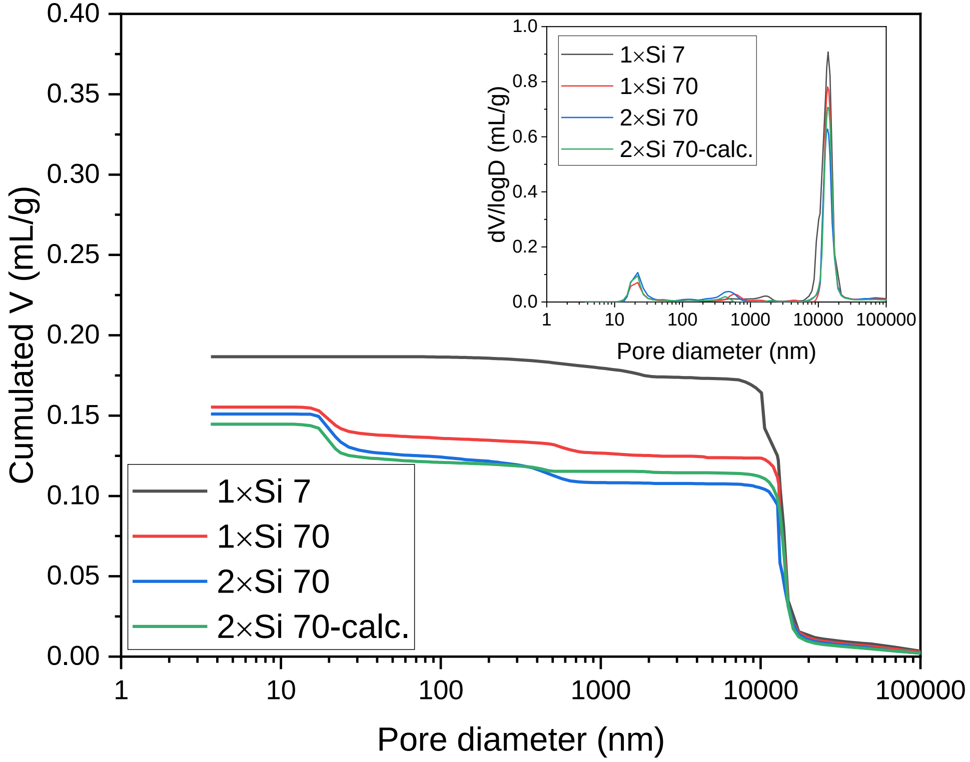
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Support structure

SEM on SiC monolith



Mercury Intrusion porosimetry (MIP)



Silica NPs infiltration shows trimodal pore size distribution comprising meso, small & large macropores

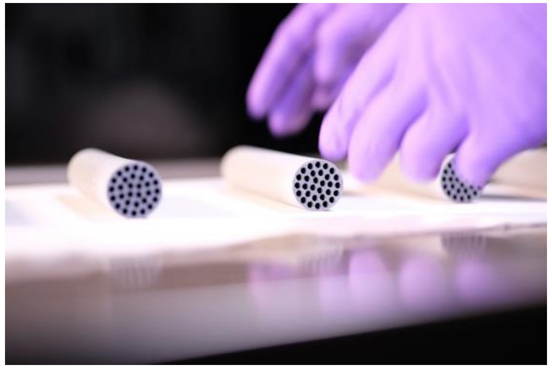
J. M. Marinkovic, Technical University of Denmark, 2019

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

SLP catalyst system

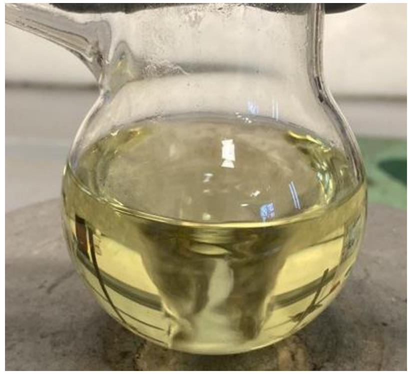
- Impregnation of a porous solid material with the homogeneous catalyst solution

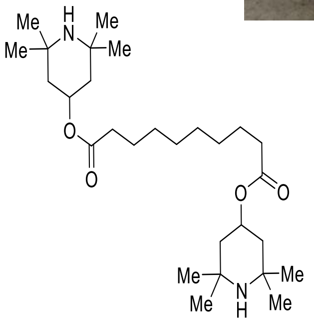
Monolithic support



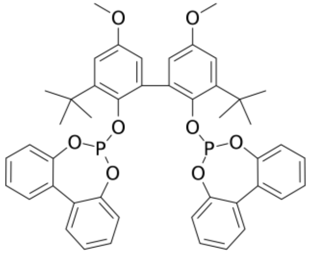
Sebacate melts at the reaction temperature & forms the liquid-phase

Catalyst stock solution



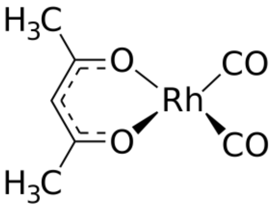


Sebacate



Solvent drying

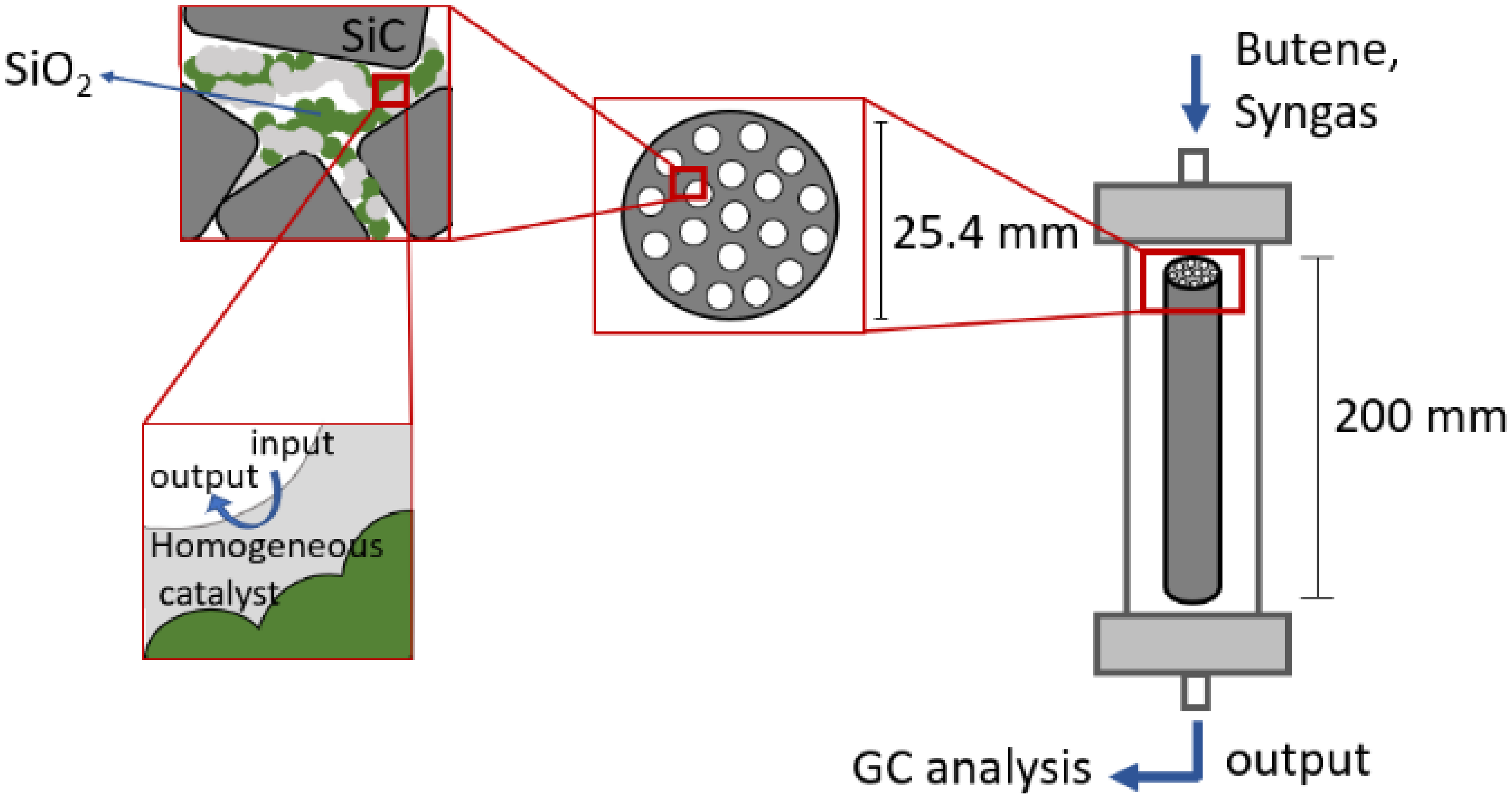
Ar flow



SLP catalyst

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

The overall SLP system



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

SLP HyFo catalytic testing

Monolithic supported Rh-catalysts in gas-phase HyFo of 1-butene

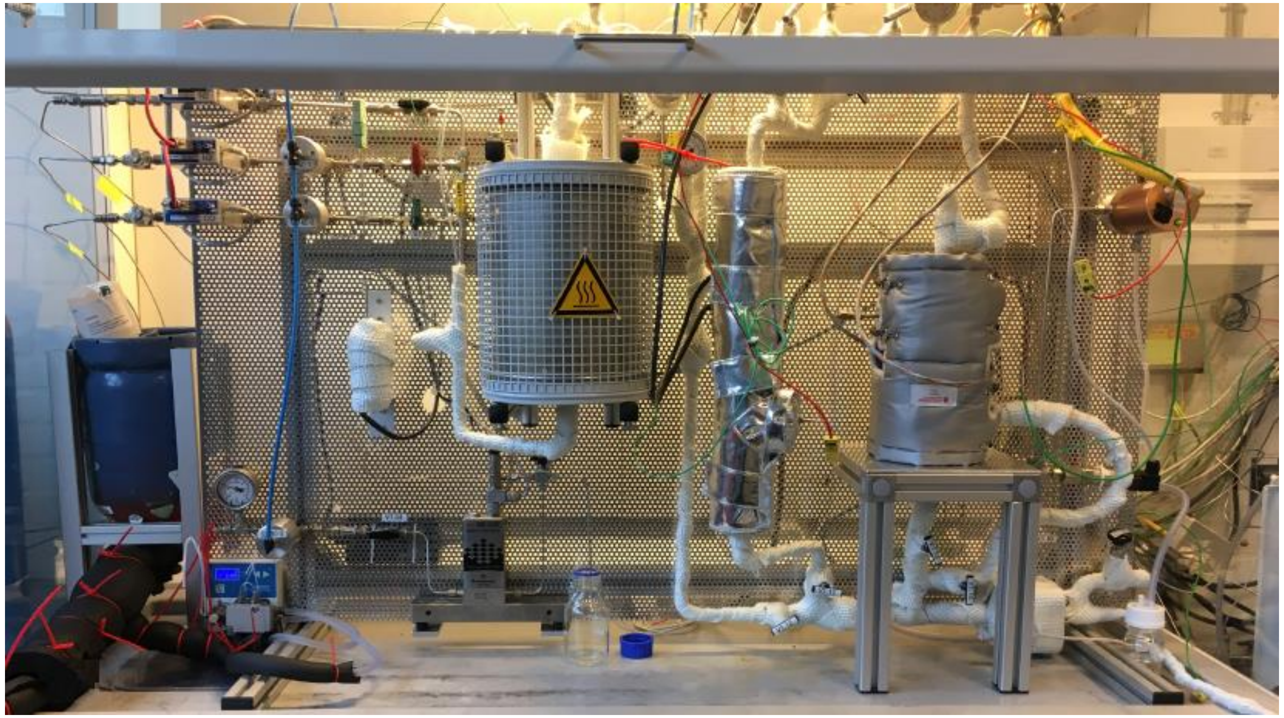
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

SLP HyFo-rig and reaction conditions

Aim:

Structure-catalytic performance correlation in different supports

- T = 120 °C
- P_{feed} = 10 bar
- Rh/bpp/sebacate molar ratio = 1/4/16
- Rh loading = ca. 0.01 wt.%
- TOS = 0-44 h → start-up conditions
- TOS = 44-140 h → standard conditions (syngas = 4.46, 1-butene = 1.045, N_2 = 5.67 $mmol.min^{-1}$)

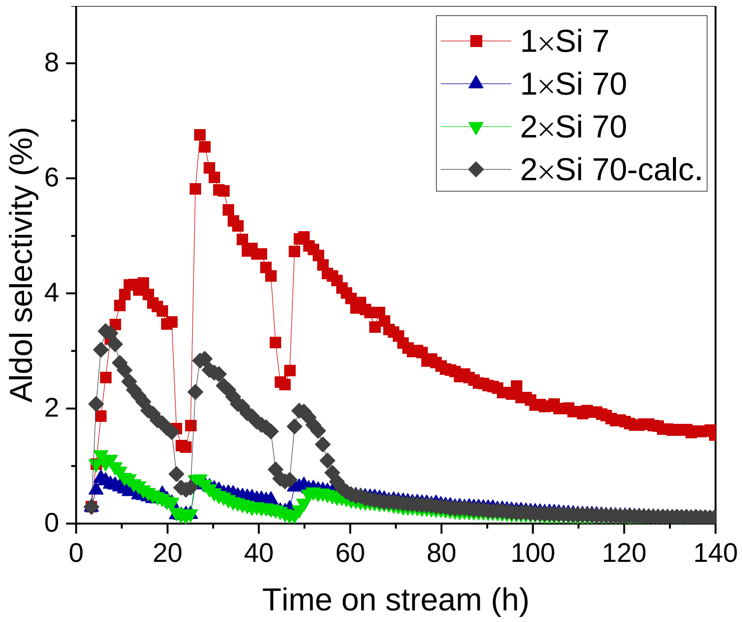


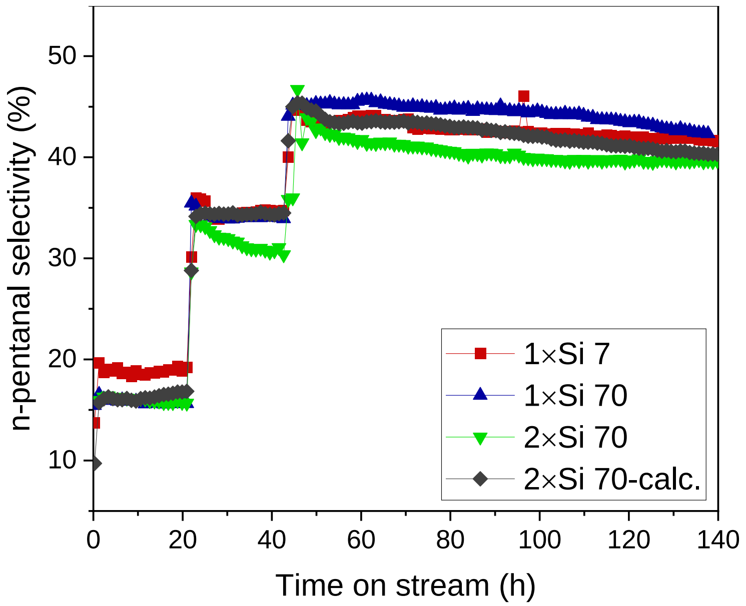
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

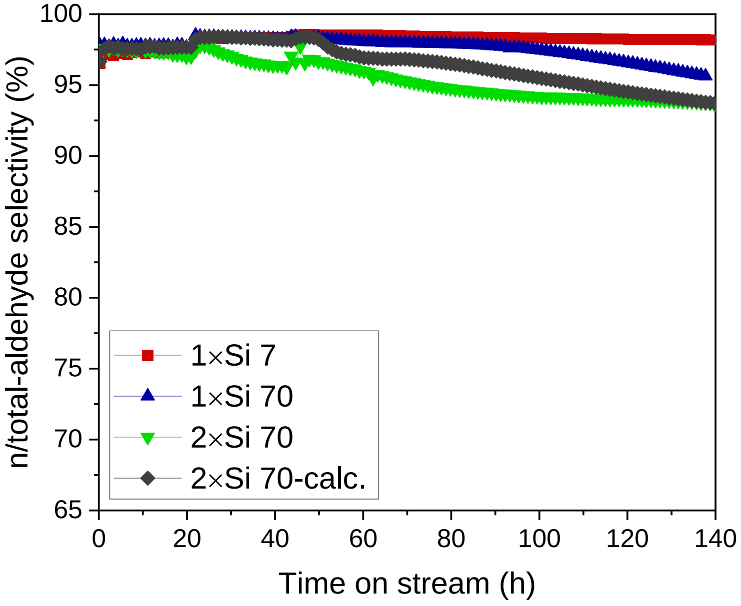
Catalytic performance results

Catalyst selectivity

- Higher aldol accumulation in **7** nm SiO_2 washcoat containing support due to smaller pore size in the washcoat (2.8 vs. 28 nm)
- Steady decrease of n/iso-aldehyde due to autocatalytic decomposition of bpp ligand





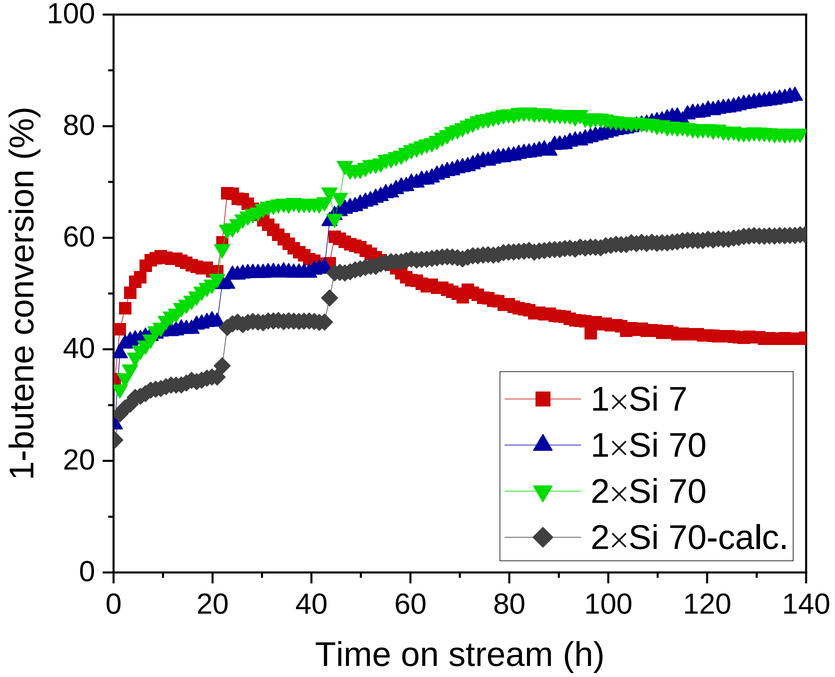


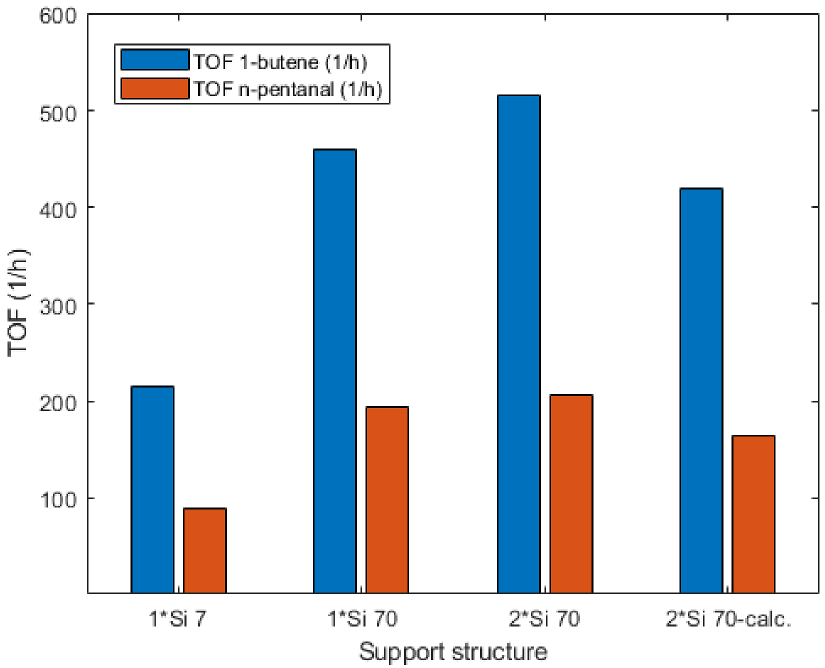
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Catalytic performance results

Catalyst activity

- Steady decrease of 1-butene conversion in **7** nm SiO_2 washcoat containing support → due to higher aldol formation





This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Summary & outlook

- Silica washcoated monolithic SiC supports with different porosity were developed for 1-butene HyFo after impregnation with a homogeneous Rh-catalyst system
- Catalytic performance showed better catalytic activity for 70 nm silica washcoated supports along with desired negligible aldol formation
- Better *n*-pentanal selectivity in 7 nm silica washcoated support
- Prominent catalytic performance in different support modifications and long-term stability
- Outlook → optimization of catalyst components → e.g. optimization of the ratio between active catalyst components, liquid loading, etc.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.

Acknowledgements

The MACBETH Hydroformylation team

(DTU, FAU, CSIC, EVONIK, HEREON, LIQTECH)

European Union’s Horizon 2020 research and innovation program for funding the MACBETH project

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869896.