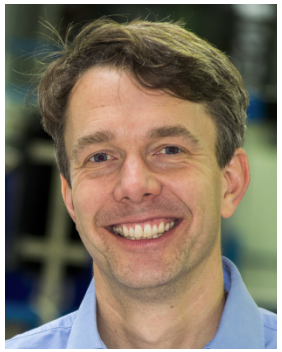
Long-term stable, Co-based catalysts for Sabatier reaction with changing loads

SPP 2080
DynaKat

Marcus Bäumer

Lutz Mädler



Jorg Thöming

Jan Ilsemann

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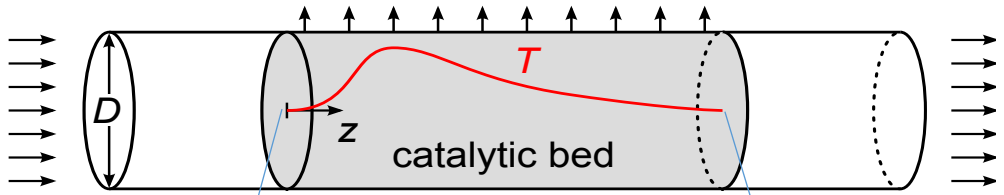
Christoph Sinn

Georg Pesch

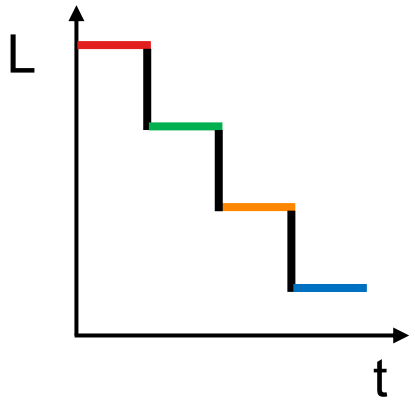
Problem

Sabatier reaction ΔH_r= -165 kJ/mol

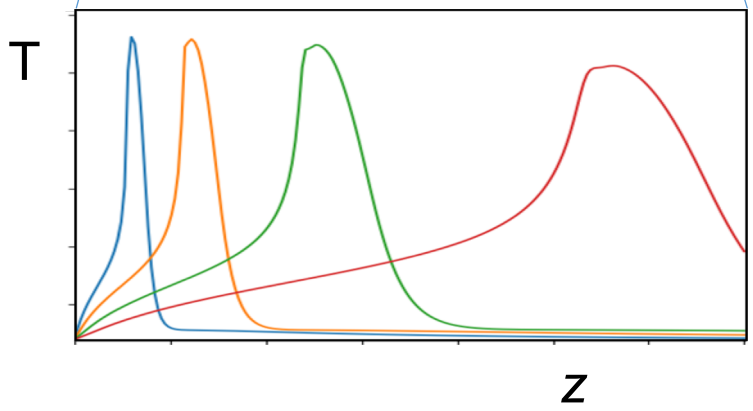
Gas load **L** $CO_2 + 4\ H_2$



$CH_4 + 2\ H_2O$



Temperature profiles



Deactivation phenoma depend on temperature:

- Cobald sintering
- Coking
- Carbonate formation
- Reoxidation

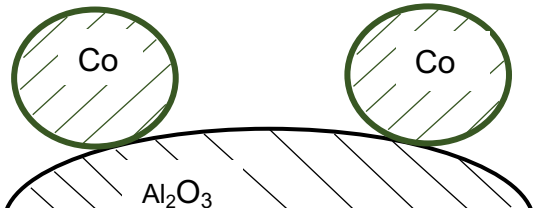
Methods

Flame spray pyrolysis (FSP)

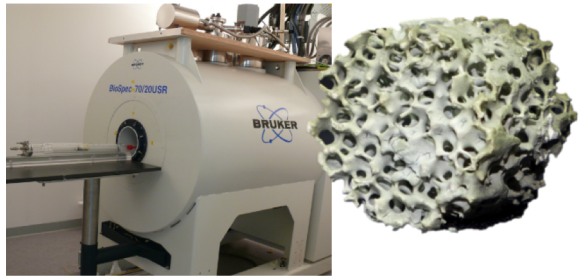
Nuclear magnetic resonance (NMR)

Tailoring catalytic nano materials

Characterisation and testing of catalyst



Visualization and validation using NMR



→ Long-term stable Co-based catalysts under changing loads

Functional catalysts synthesis from the gas phase

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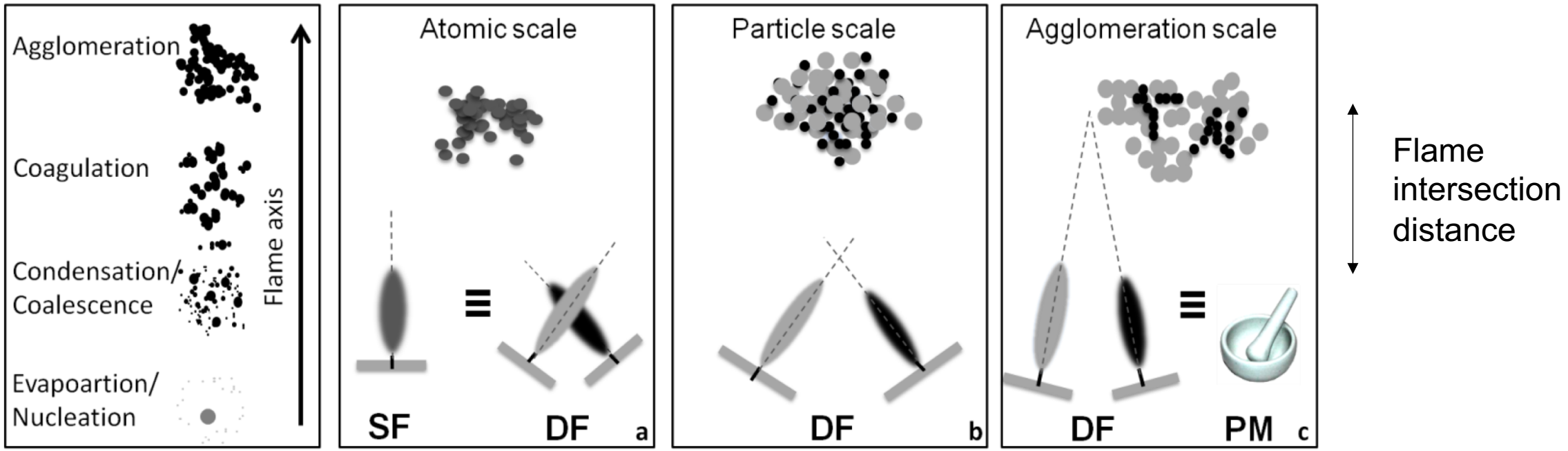
Design of doped / mixed catalyst systems using double spray flames



Hypothesis: Design of specific intermittent phase between components
a) is possible and
b) leads to higher thermal stability

Functional catalysts synthesis from the gas phase

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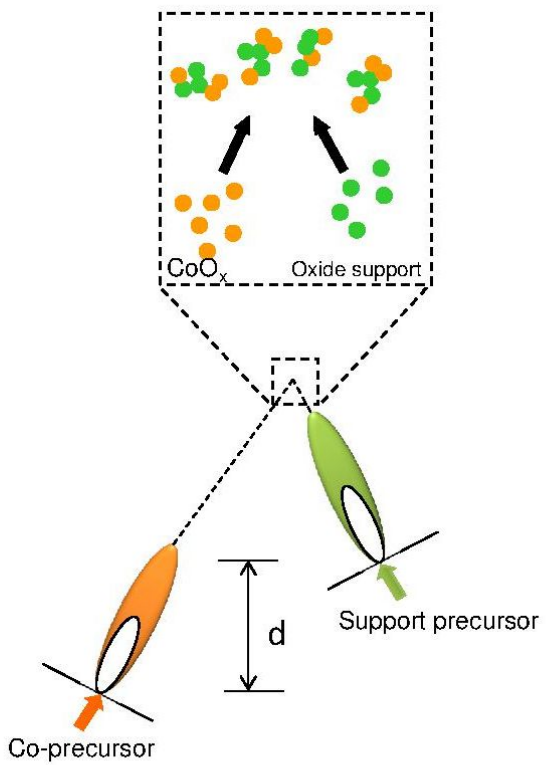
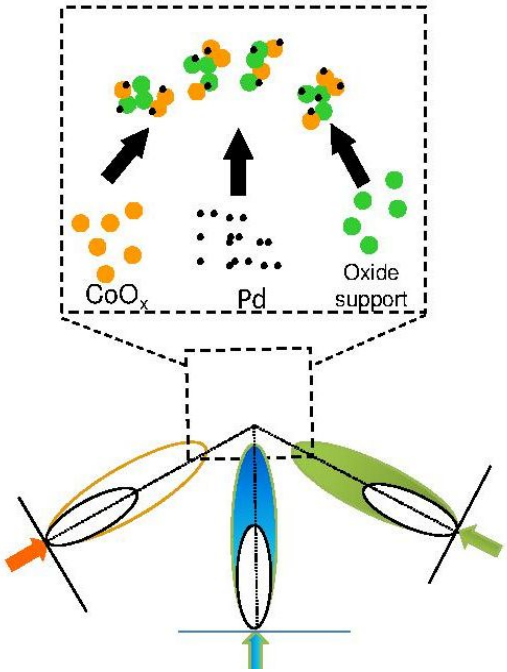
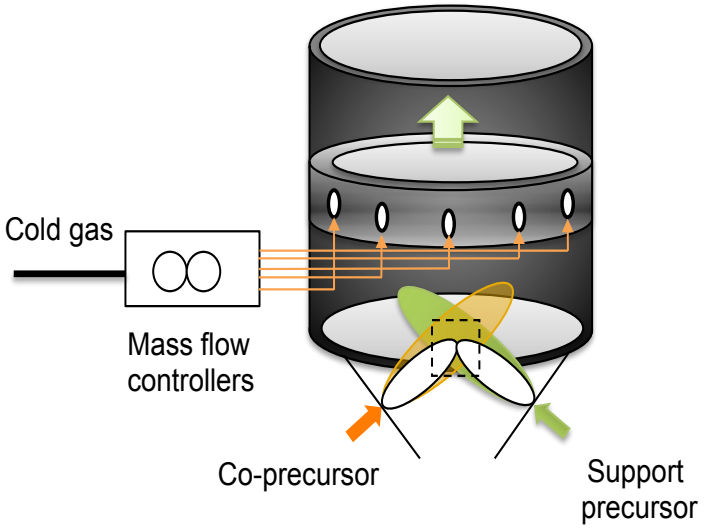
Asymmetric mixing:
Design individual particles before hetero-contact

Process integration:
Design specific multicomponent particle

Process adaption:
Preserve meta-stable materials

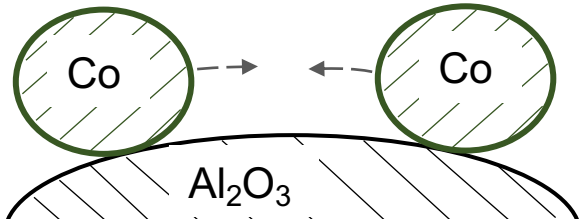




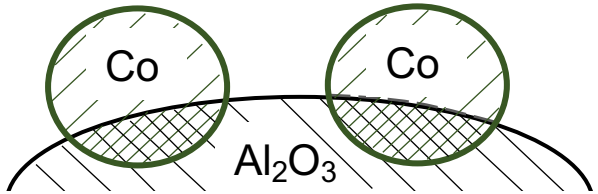


Catalyst characterisation

Propensity for sintering due to weak metal support interaction



vs.

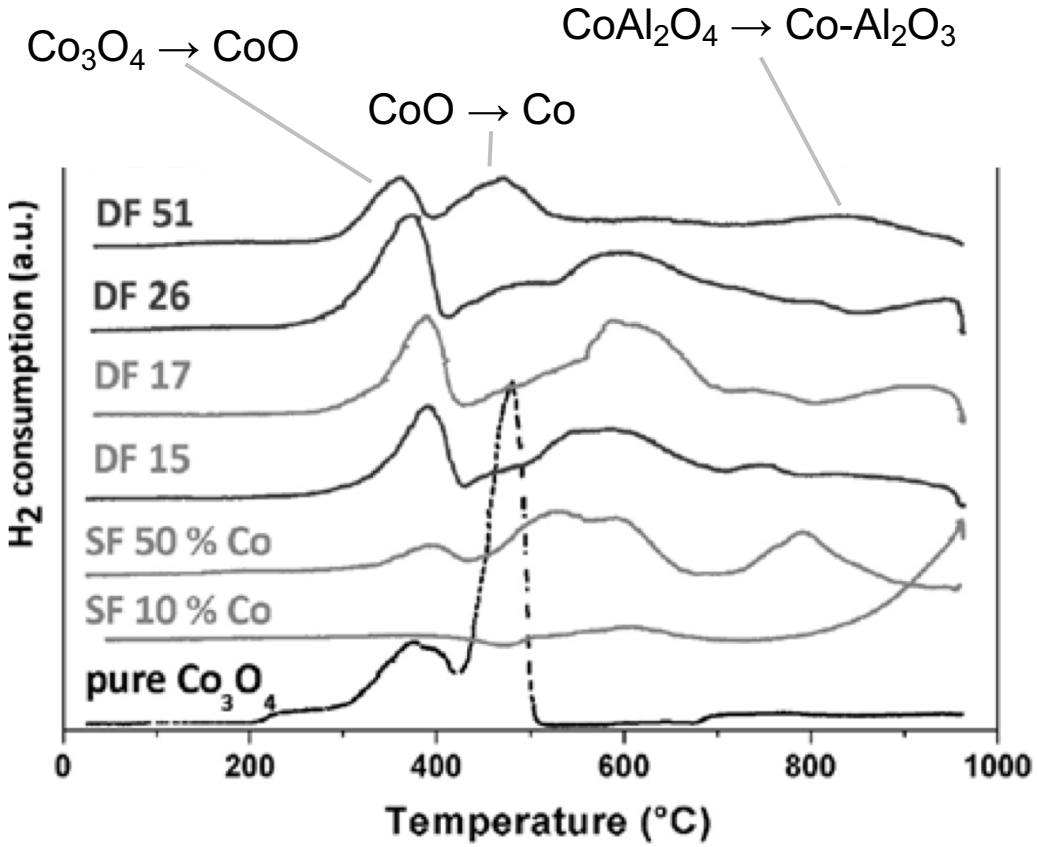


$CoAl_2O_4$ spinel

Increased sinter stability by

- tailored spinel formation at the metal-support interface
- using different FSP conditions

Reducibility of Co/Al_2O_3 catalysts (temperature programmed reduction)



Minnermann et al., Catalysis Today, 214, 2013

Experimental study of dynamic reaction conditions

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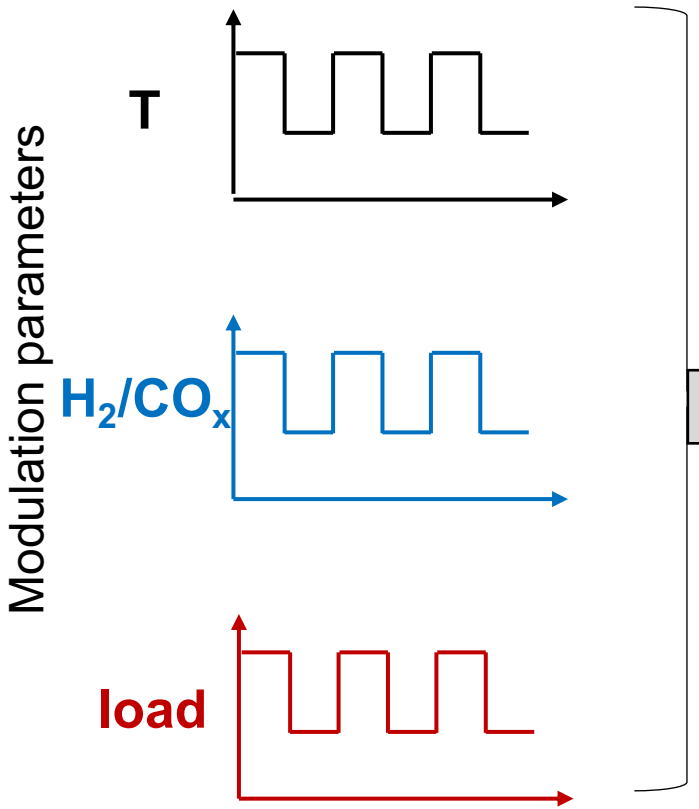
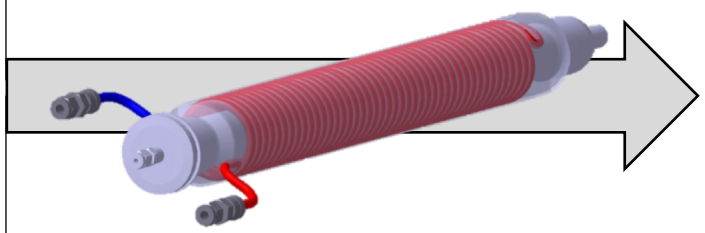
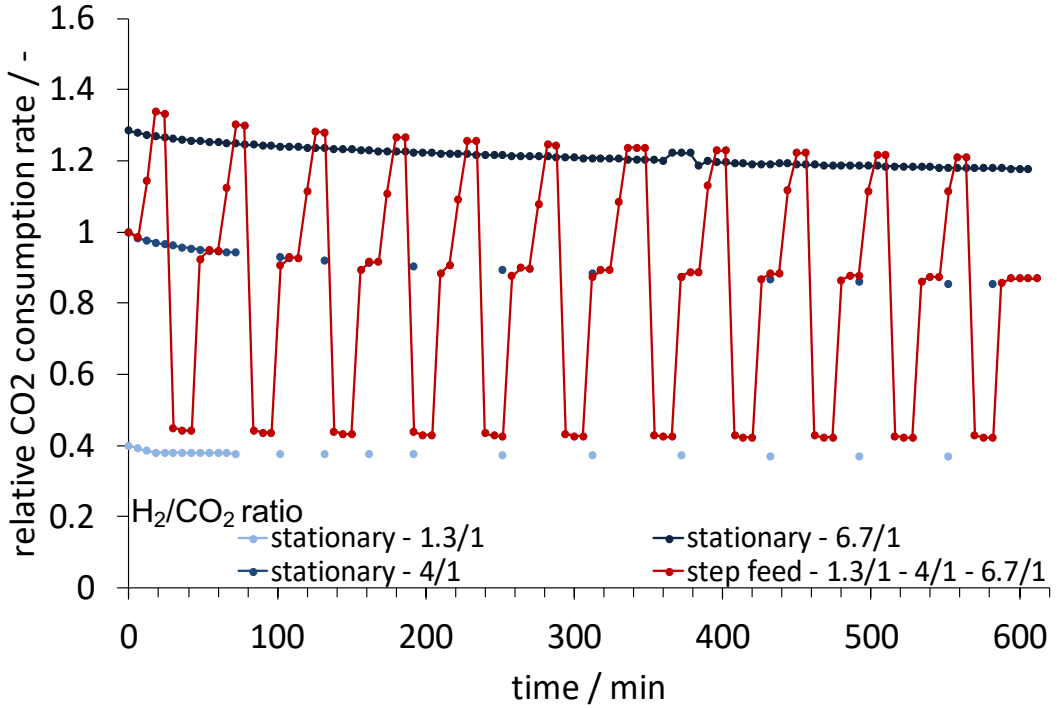
Periodical variation of…



Screening in isothermal mini reactor



Preliminary experiments:
stationary vs. step feed operation



Load changes: deactivation rates showed a linear combination of those in stationary runs

Conditions:
T = 400 °C, flow = 50 sccm, x/1 H_2/CO_2 and Ar for balancing;
catalyst: 20 mg of Ni-Sm_2O_3; step size: 18 min

Profiles of composition and temperature

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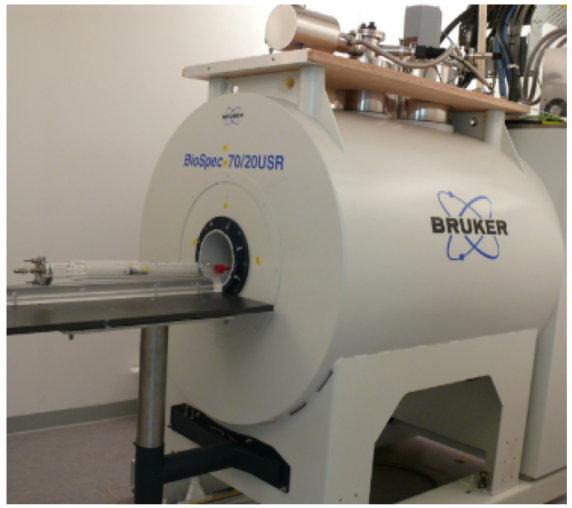
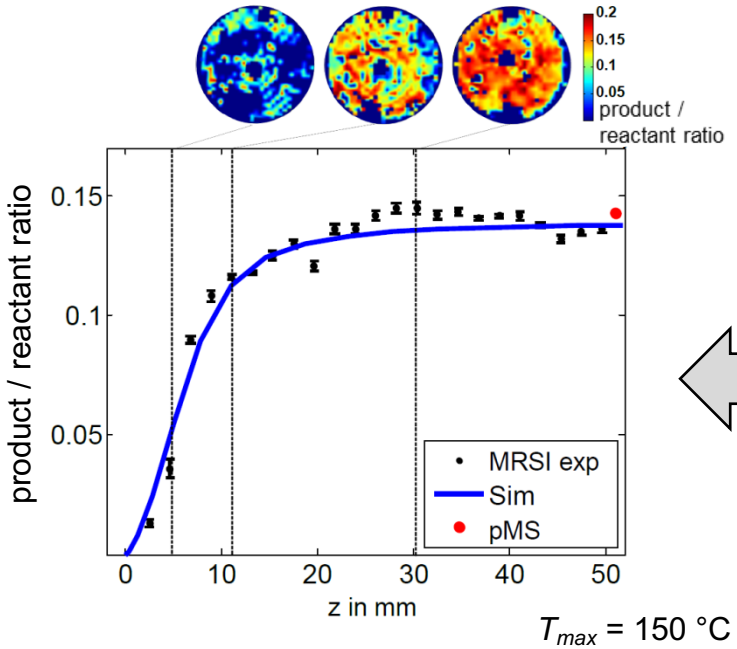
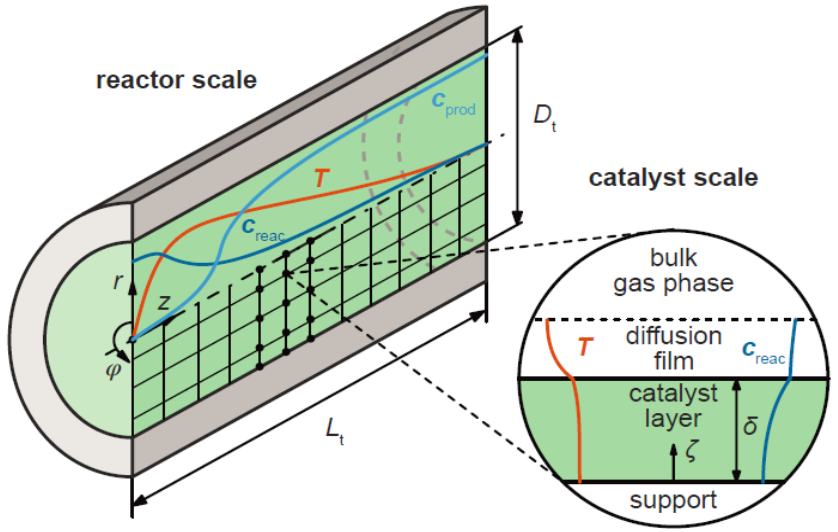
Operando NMR-imaging (MRI) for *gas phase* reactions





2D reactor model



For pellets and sponges

First goals:

- NMR thermometer for measuring a wider T range
- MRI spectroscopy of methanation at 250°C ($T_{inlet = wall}$)

Ulpts et al., Catal. Today, 310, 2018
Kiewidt and Thöming, *Chem. Eng. J., 359,* 2019

NMR Reactor for elevated temperature and pressure

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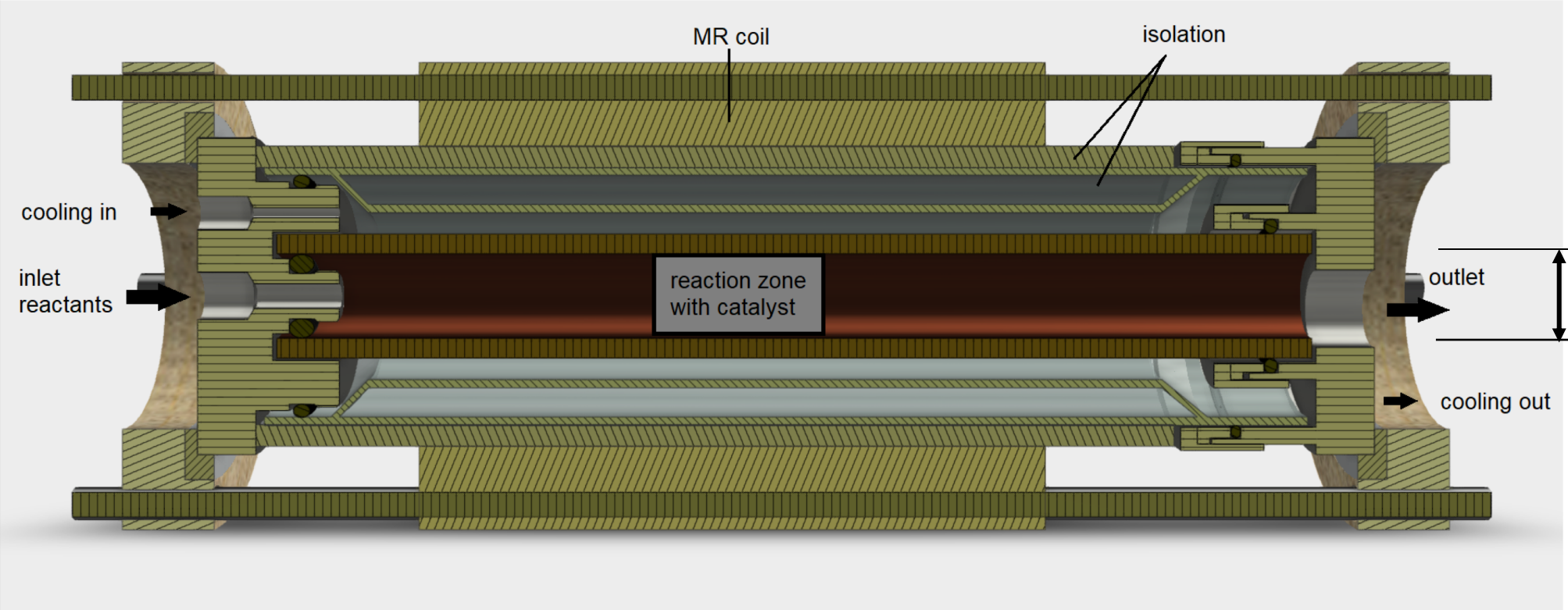
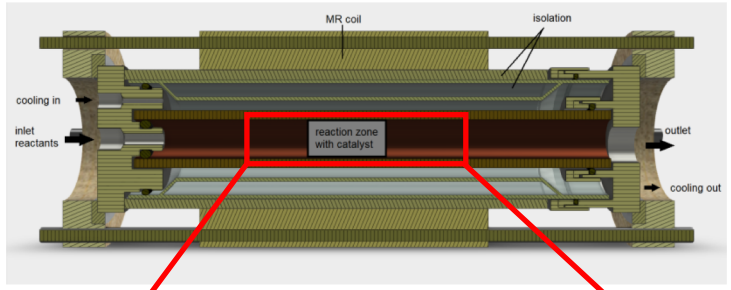
p = 3 - 30 bar

T_{coil} < 40 °C

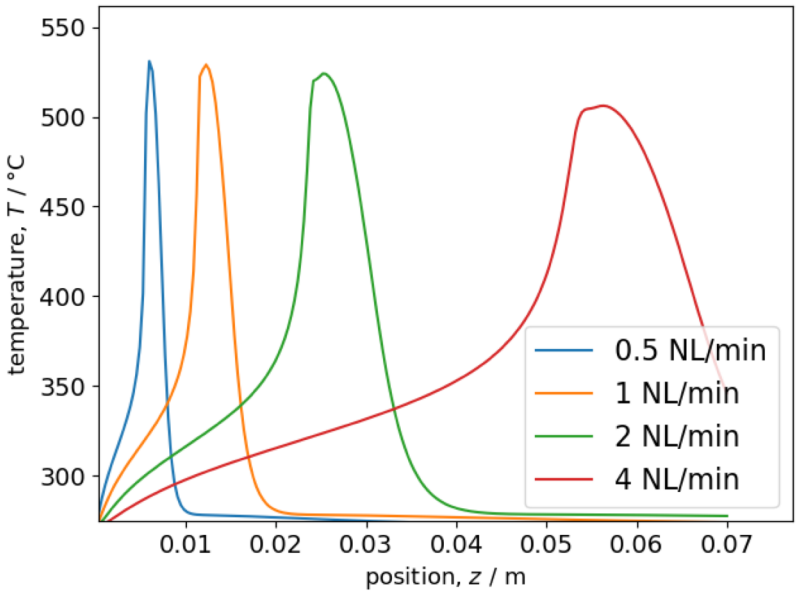
T_{wall} = 250 °C



Deactivation and re-activation zones under changing loads



Temperature profiles



Conditions
1 bar; $T_{wall} = T_{in}$
Ni on open-cell foam

Hypothesis 2:

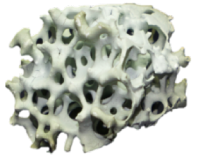
Observation of reaction zone shifting

- is possible via *operando* MRI
- allows for taking samples at deactivated spots

Sample analysis enables to tailor catalysts

Hypothesis 3:

Reaction zone shifting can be controlled using

- structured supports 
- longitudinal gradients of catalyst loading

SPP cooperations

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- Supply of FSP catalysts
- Test deactivation behavior of other SPP catalysts
- Interested in: micro-kinetic studies
- Simulation (with Deutschmann‘s group)

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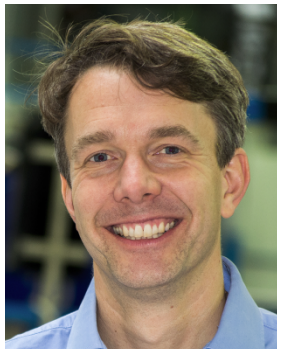

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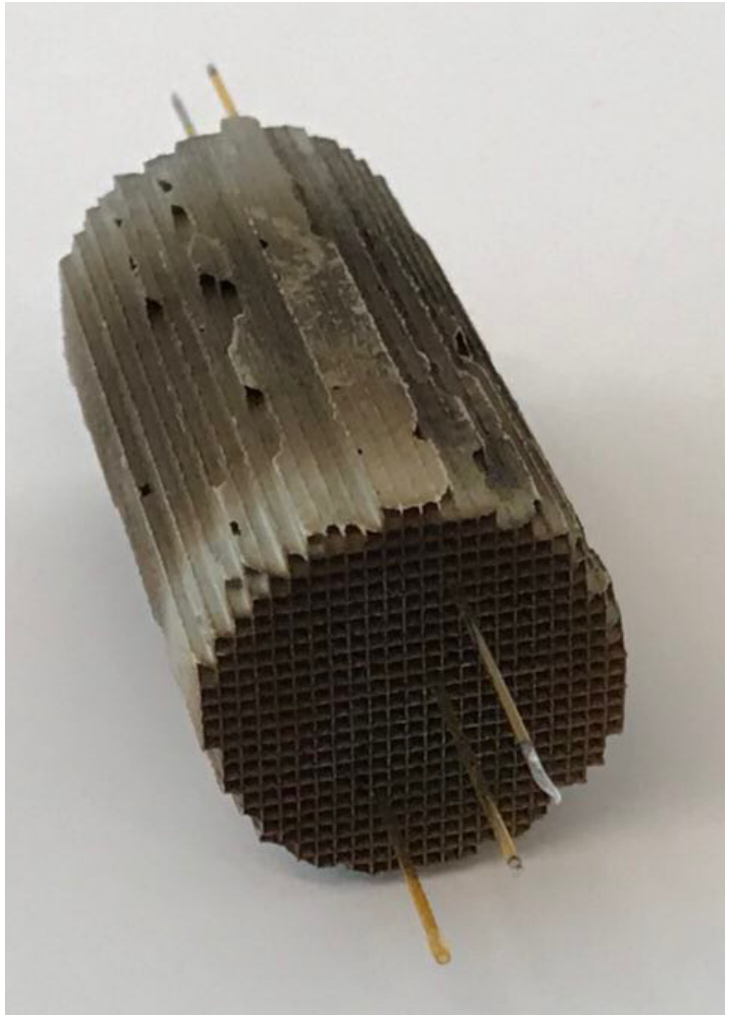
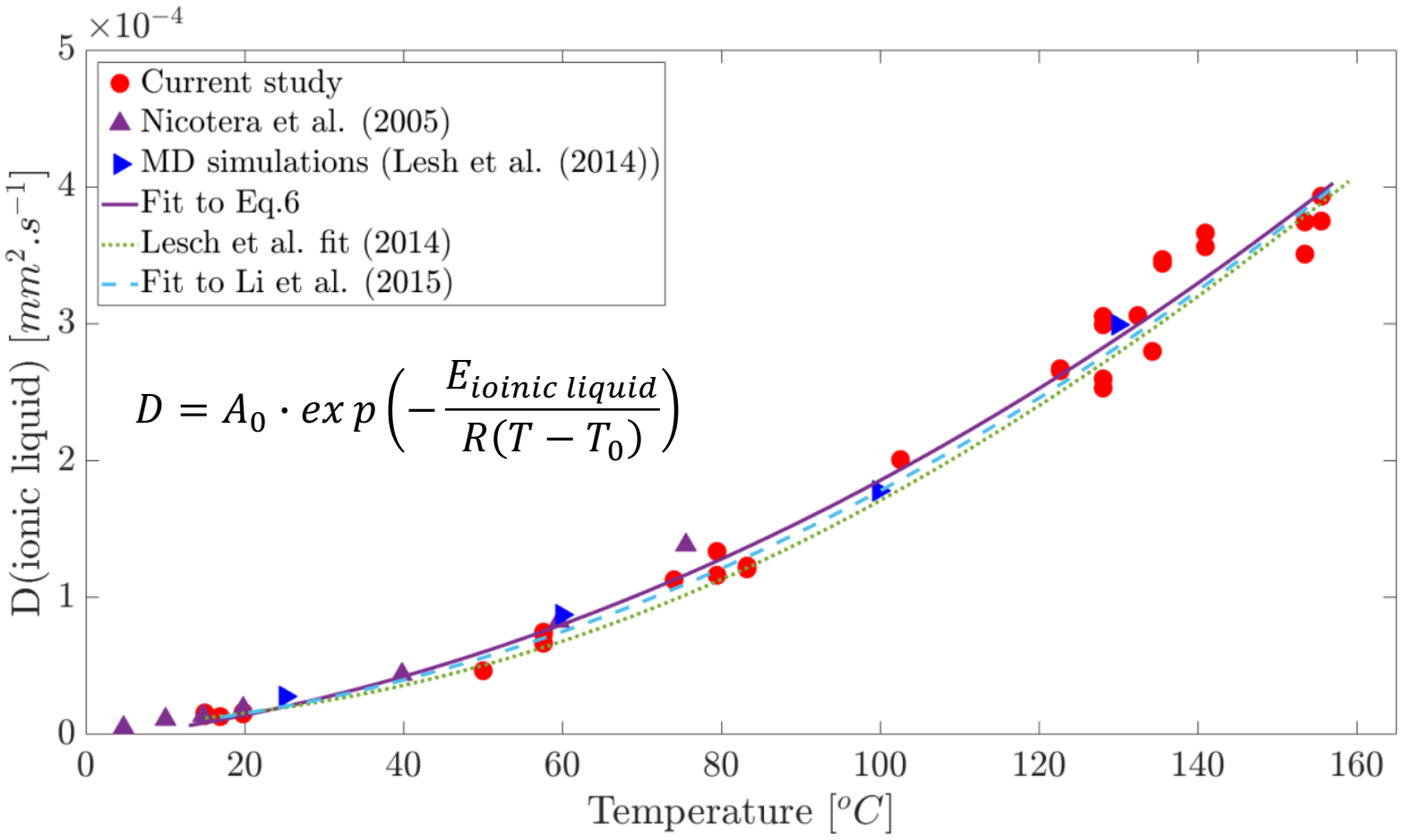
NMR thermometer for *diffusion-weighted magnetic resonance imaging*





Diffusion coefficient of Pyr_{13} [TFSI] over temperature