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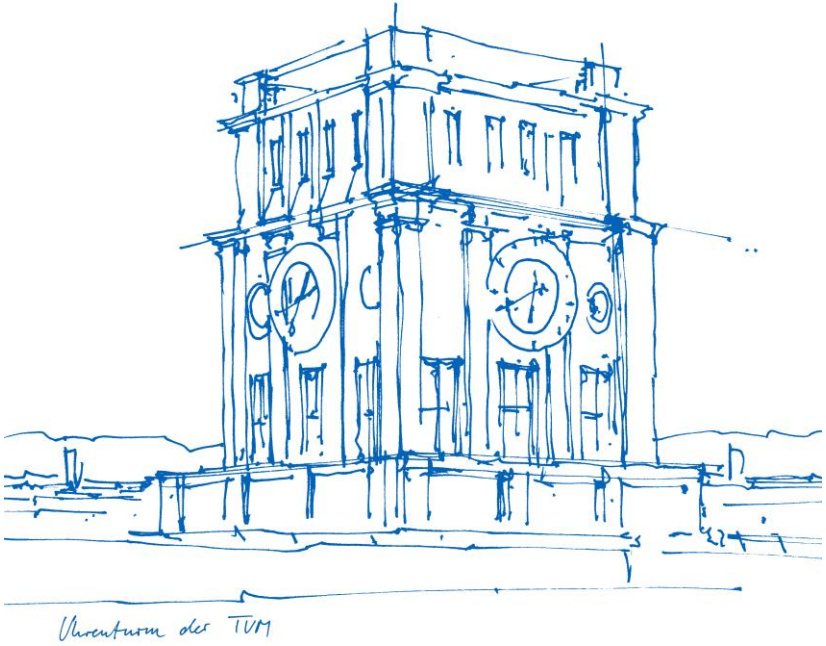
Energy transition in miniature:
Combining catalysis and reaction engineering at a particle level

Olaf Hinrichsen
Catalysis Research Center
Technische Universität München

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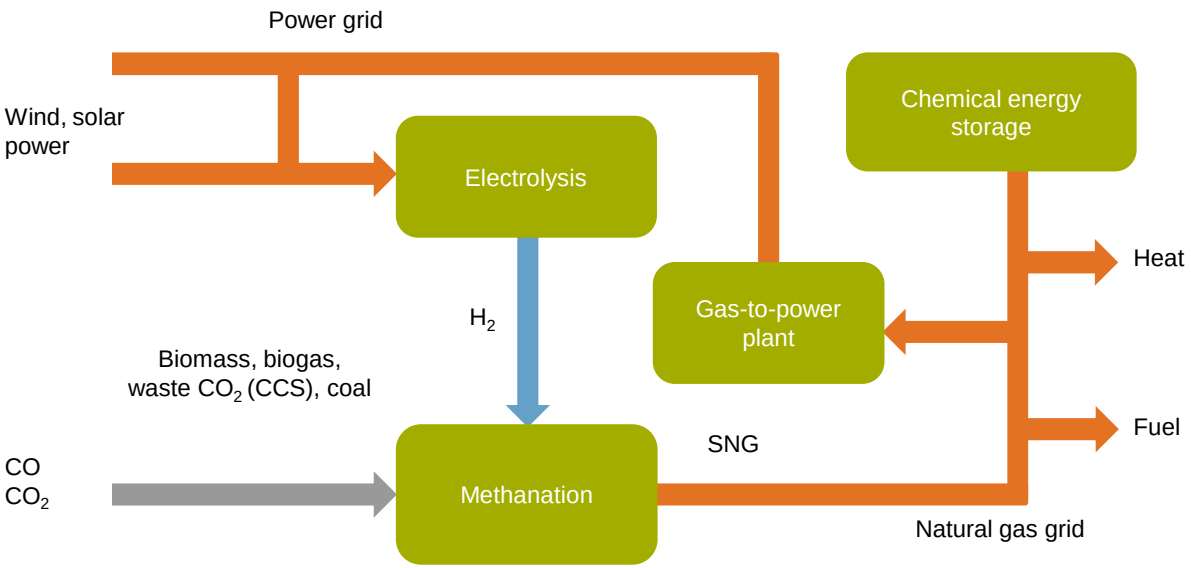
Power-to-Gas (PtG) Concept



CO methanation	$CO + 3\ H_2 \rightleftharpoons CH_4 + H_2O$	$\Delta_R H° = -206\ \text{kJ mol}^{-1}$, $\Delta_R G° = -142\ \text{kJ mol}^{-1}$
CO_2 methanation	$CO_2 + 4\ H_2 \rightleftharpoons CH_4 + 2\ H_2O$	$\Delta_R H° = -165\ \text{kJ mol}^{-1}$, $\Delta_R G° = -114\ \text{kJ mol}^{-1}$

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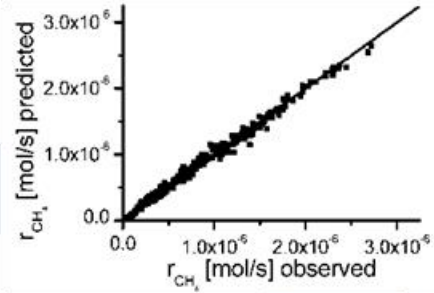
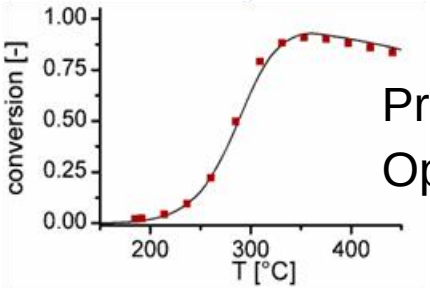
Kinetic measurements



Modeling

Catalyst synthesis



Prediction & Optimization

F. Koschany, D. Schlereth, O. Hinrichsen, *Appl. Catal. B* **2016**, *181*, 504–516.

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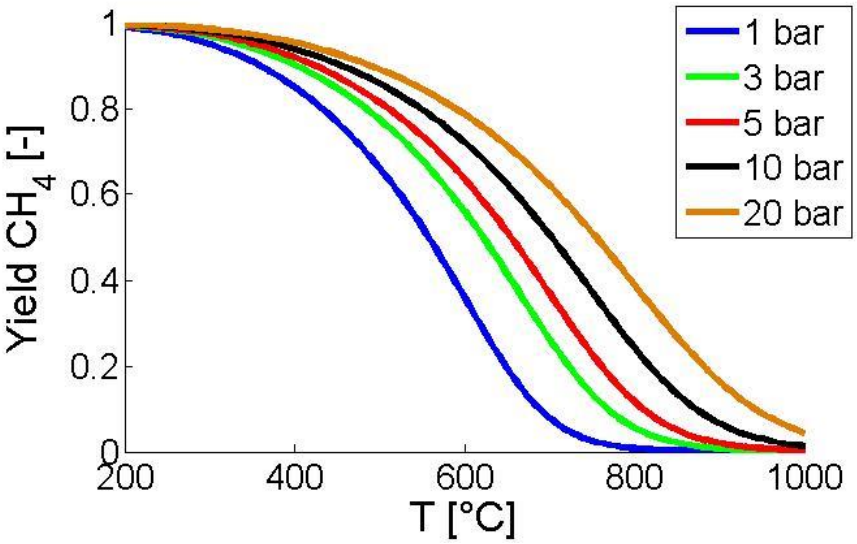
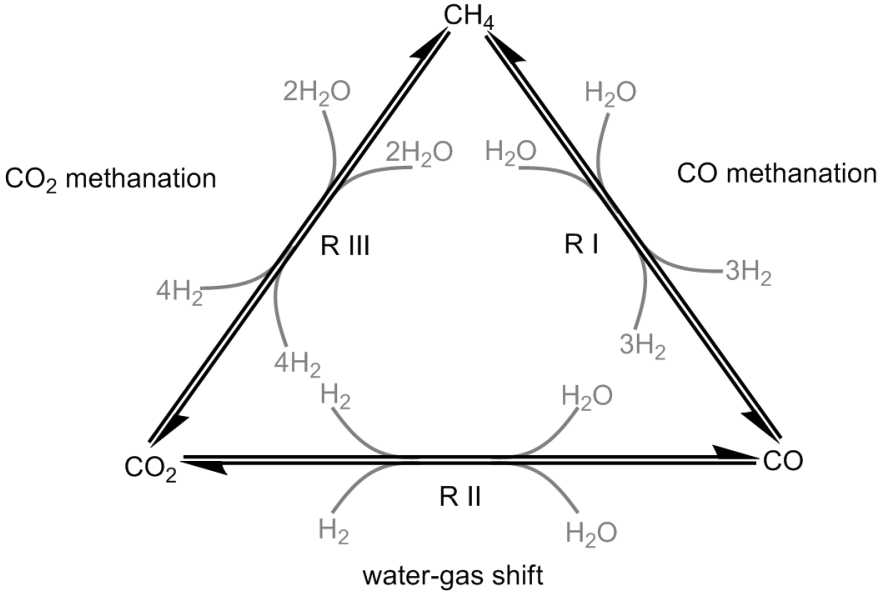
Thermodynamics of the CO_2 Methanation Reaction

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H_0 = -\,165\ \text{kJ/mol}$$





J. Xu, G.F. Froment, *AIChE J.* **1989**, *35*, 88–96.
D. Schlereth, O. Hinrichsen, *Chem. Eng. Res. Des.* **2014**, *92*, 702–712.

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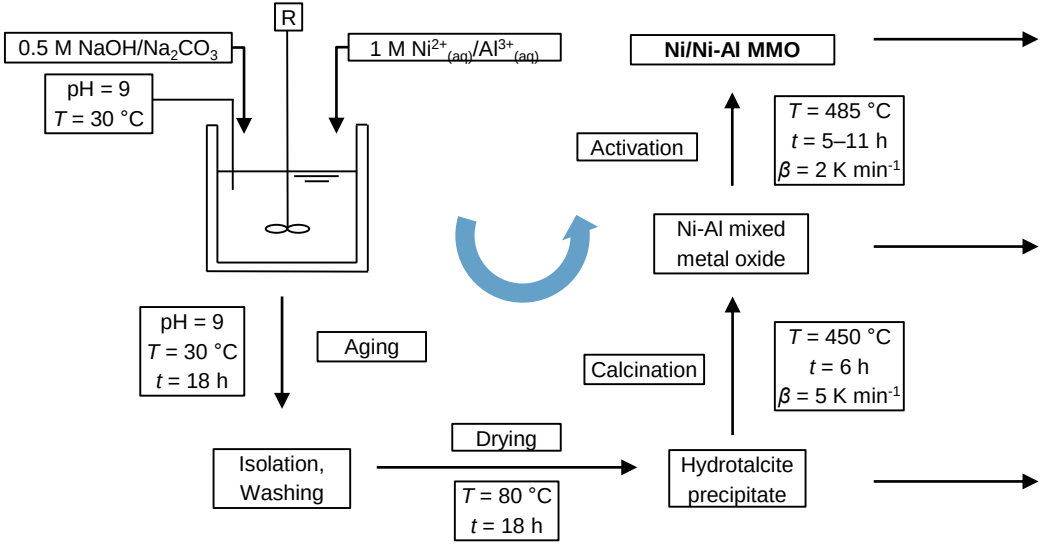
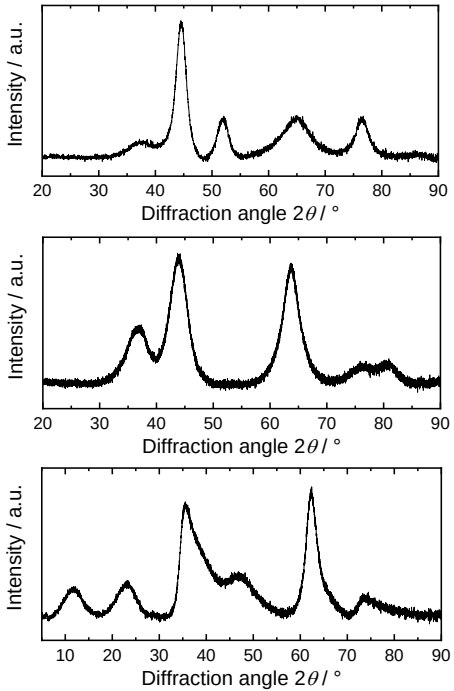
Catalyst Synthesis: Ni-Al mixed metal oxide catalysts

State-of-the-art / base catalyst: Ni-Al mixed metal oxide





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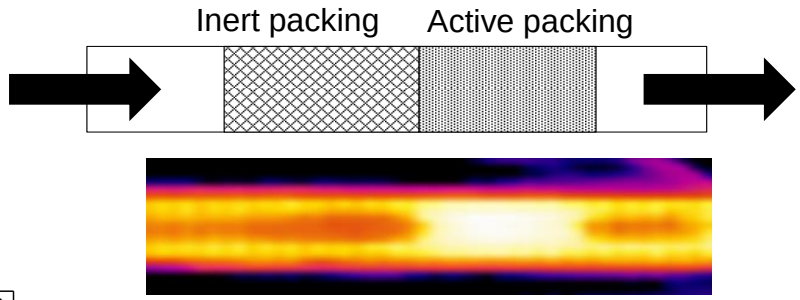
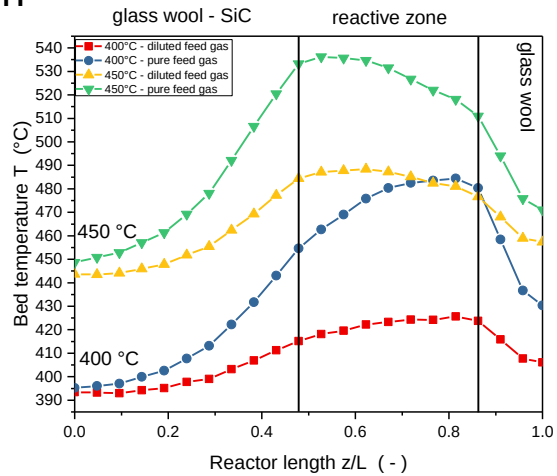
Contactless Temperature Measurements

Spatial resolved temperature measurements:



- Observation of temperature profile and hotspot formation



C. Schüler et al., *Journal of CO_2 Utilization*, **2018**, *25*, 158–169.

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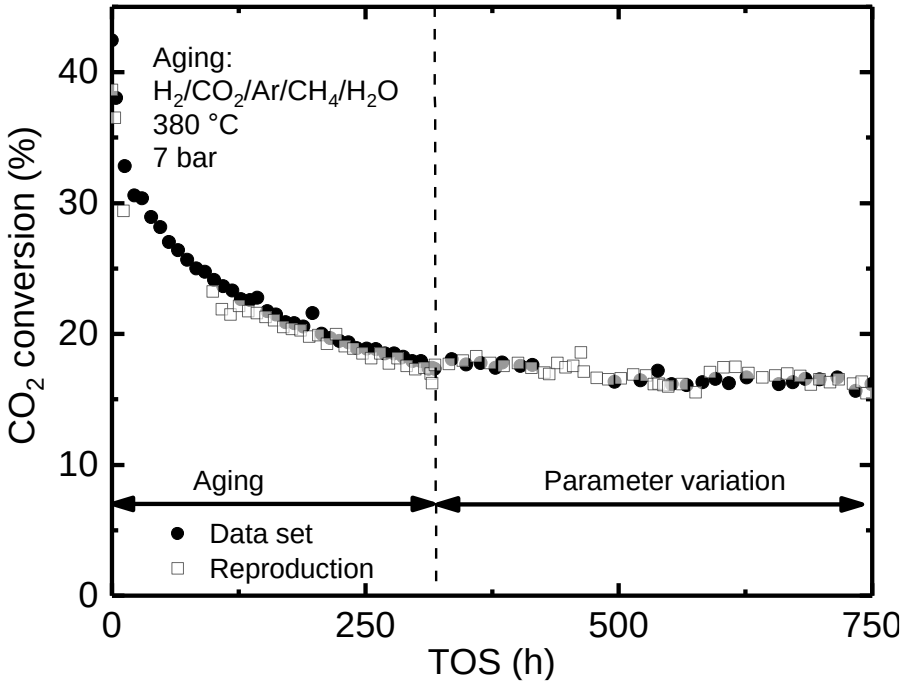
Kinetic Measurements – Long-term Experiments



Kinetic data pool

T:	180–340 °C
p:	1–15 bar
H_2/CO_2:	0.25–8
H_2O/CH_4:	0/0, 0.25/0.125
m_{cat}:	25 mg, 75 mg

$$r = \frac{k \cdot p_{H_2}^{0.5} p_{CO_2}^{0.5} \left(1 - \frac{p_{CH_4} p_{H_2O}^2}{p_{CO_2} p_{H_2}^4 K_{eq}}\right)}{\left(1 + K_{OH} \frac{p_{H_2O}}{p_{H_2}^{1/2}} + K_{H_2} p_{H_2}^{0.5} + K_{mix} p_{CO_2}^{0.5}\right)^2}$$

F. Koschany, D. Schlereth, O. Hinrichsen, *Appl. Catal. B* **2016**, *181*, 504–516.

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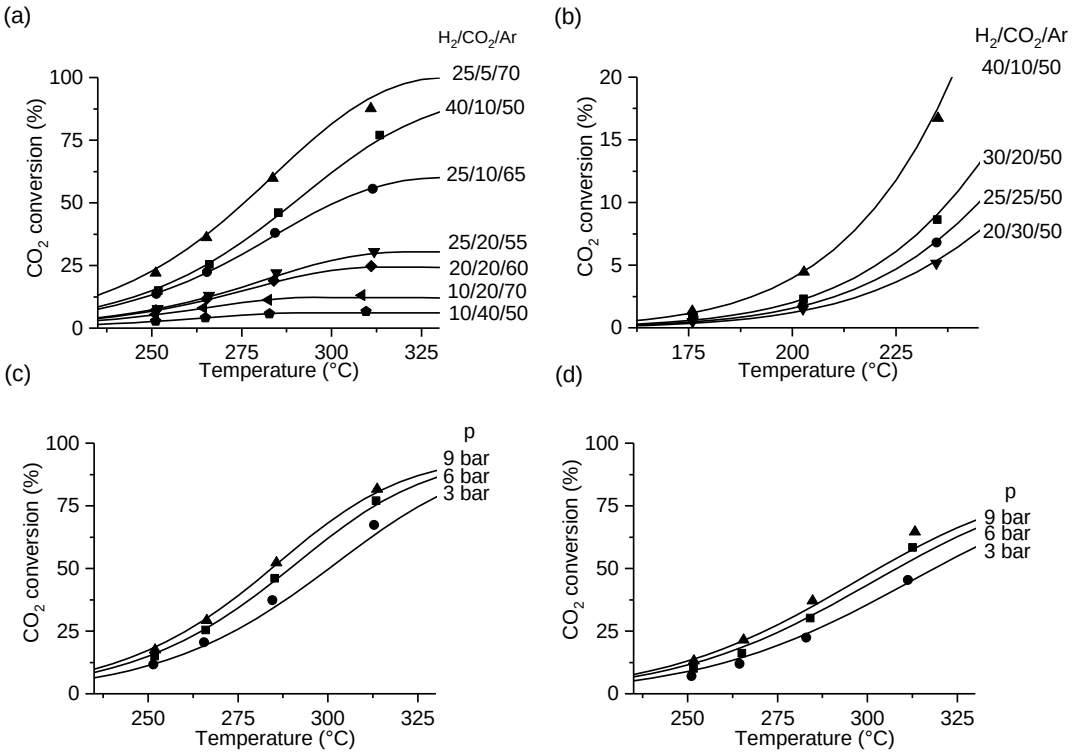
Kinetic Measurements – Variation of Reaction Conditions



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F. Koschany, D. Schlereth, O. Hinrichsen, *Appl. Catal. B* **2016**, *181*, 504–516.

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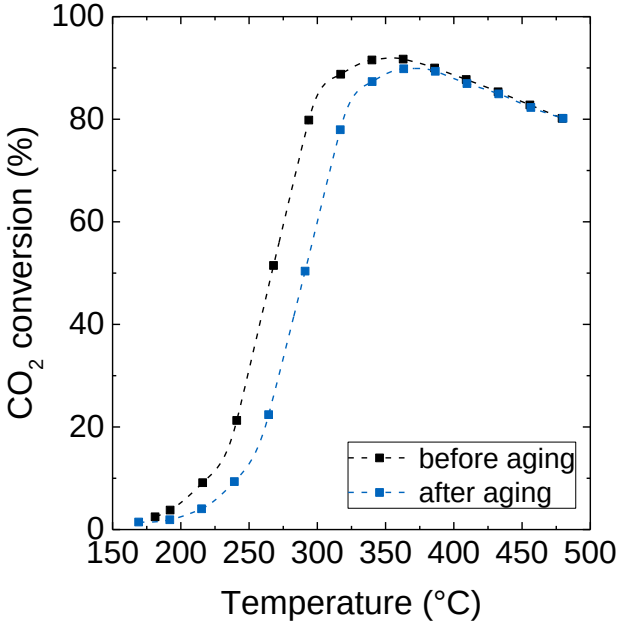
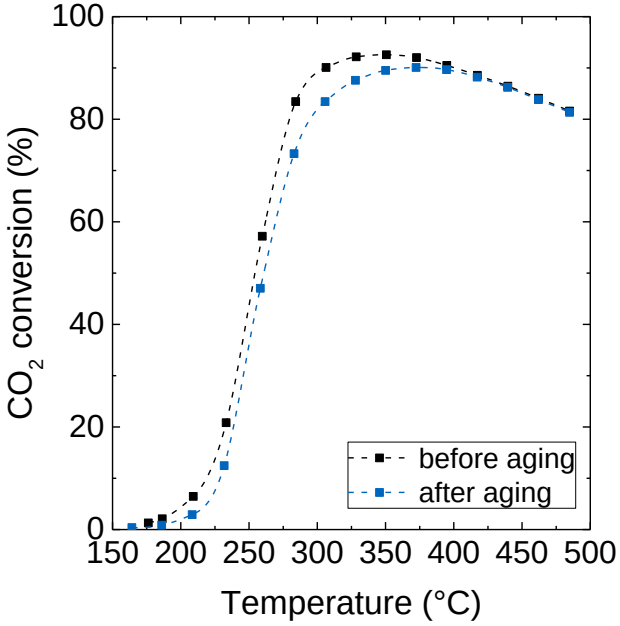
Catalyst Stability





- „rapid aging test“: simulation by aging treatment (500 °C, 32 h, 8 bar)

T. Burger, F. Koschany, O. Thomys, K. Köhler, O. Hinrichsen *Appl. Catal. A*, **2018**, *558*, 44-55.

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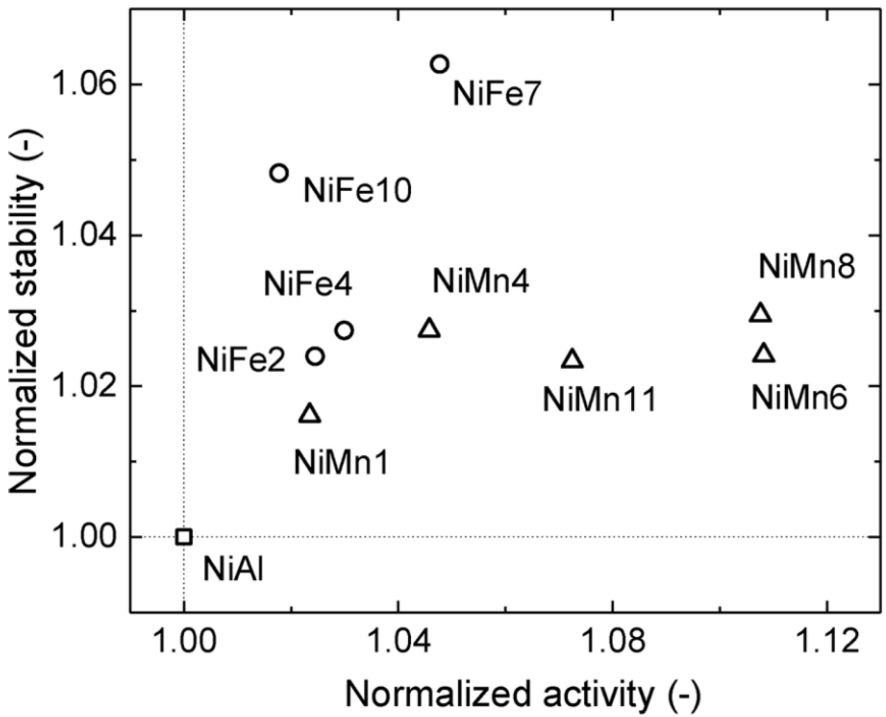
Catalyst Activity vs. Stability – Influence of Metal Doping



- Highly active and thermostable catalysts can be synthesized
- Synthesis of multimetal-promoted catalysts
  - effects on catalyst activity and stability
  - interactions between promoters
  - alternative synthesis procedures

T. Burger, F. Koschany, O. Thomys, K. Köhler, O. Hinrichsen *Appl. Catal. A*, **2018**, *558*, 44-55.

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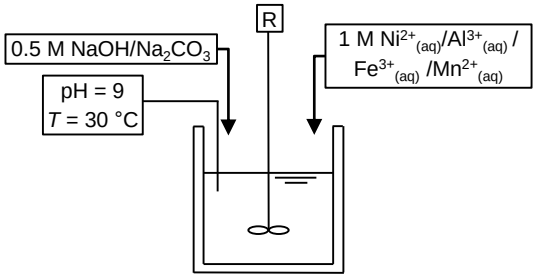
Different Synthesis Strategies for bi-promoted Ni-based Catalysts

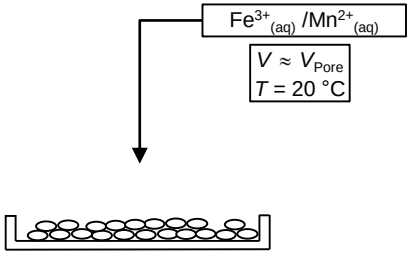
Doping of co-precipitated NiAl catalyst *via*…

… co-precipitation



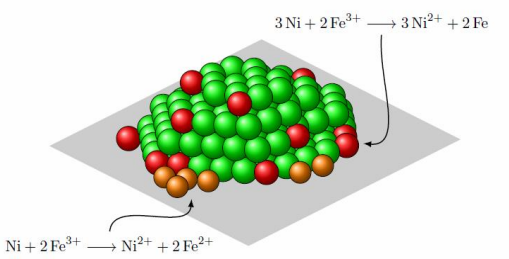
… Ni/Al/Fe/mixed metal oxide

… incipient wetness impregnation



… Fe/Mn deposition on the NiAl mixed metal oxide surface

…surface redox reaction



… Fe and Fe^{2+} deposition on the surface in vicinity to active Ni sites

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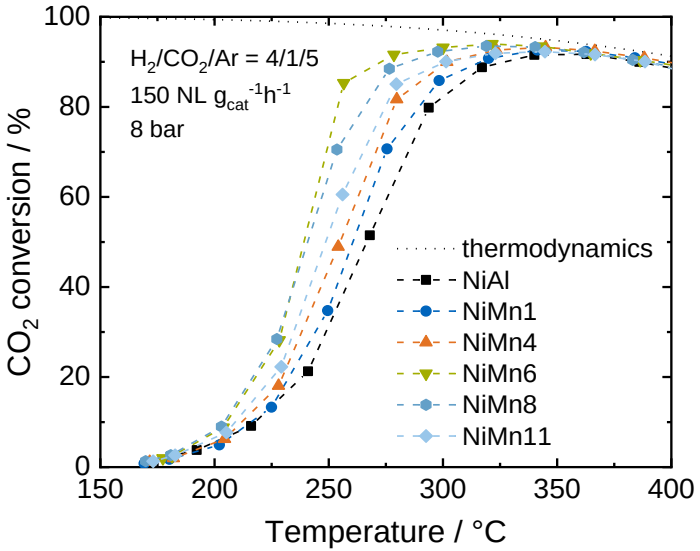
Dopant Effect of Mn on Co-Precipitated Ni-Al in CO_2 Methanation



Technique	Effect
H_2-TPR	reduction signals of Mn^{4+} to Mn^{2+}
XRD	interaction of Mn^{2+} with mixed metal oxide
IR spectroscopy (CO_2), CO_2 chemisorption	increase of basic site density
H_2-TPD	identification of Ni sites
CO_2-TPD	increase of (esp. medium) basic site density
H_2 chemisorption	enhancement of Ni particle dispersion

→ Increase of catalytic activity

T. Burger, F. Koschany, O. Thomys, K. Köhler, O. Hinrichsen, *Appl. Catal. A* **2018**, *558*, 44–54.

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Dopant Effect of Fe on Co-Precipitated Ni-Al in CO_2 Methanation

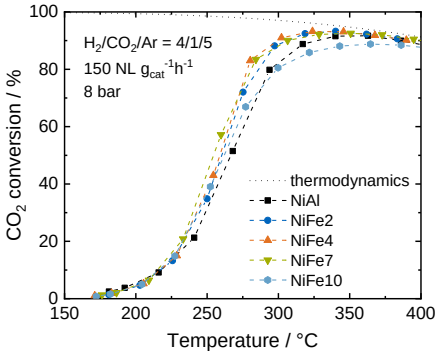
Doping *via* Co-Precipitation: Fe

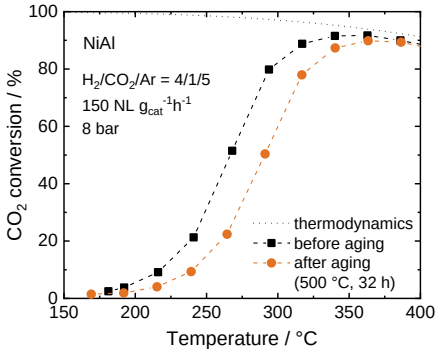
Technique	Effect
H_2-TPR	Reduction signals of Fe^{3+}
XRD	Lattice expansion, γFe,Ni formation
FMR	Increase of magnetization, anisotropy
Mössbauer spectroscopy	Formation of γFe,Ni particles
H_2 chemisorption	Decrease of Ni surface area
H_2-TPD	identification of Ni sites
IR spectroscopy (CO_2 probe)	Change of carbonyl bands

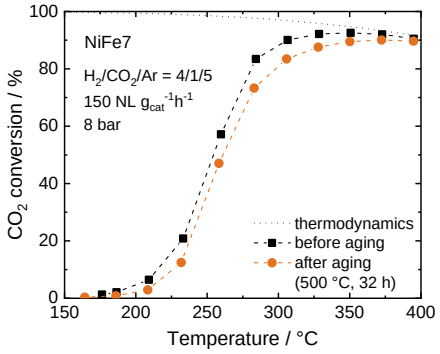
Formation of Ni-Fe alloy particles, electronic modification of the active Ni sites

Increase of

- initial catalytic activity
- apparent thermal stability under CO_2 methanation reaction conditions







T. Burger, F. Koschany, O. Thomys, K. Köhler, O. Hinrichsen, *Appl. Catal. A* **2018**, *558*, 44–54.

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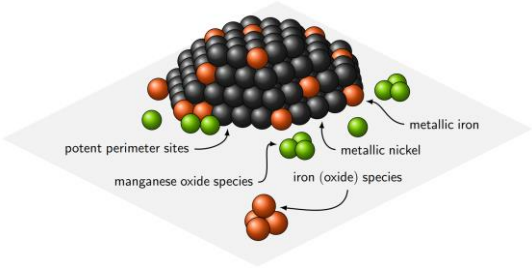
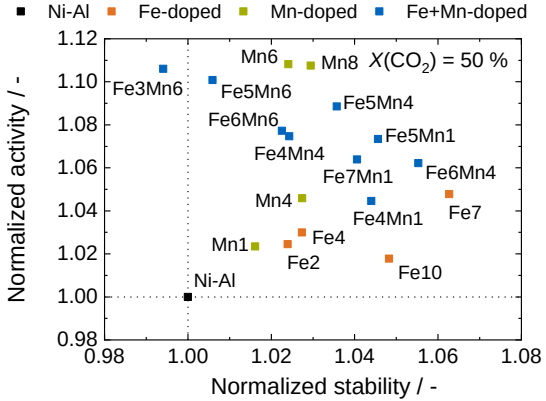
Simultaneous Dopant Effects of Fe and Mn on Co-Precipitated Ni-Al in CO_2 Methanation

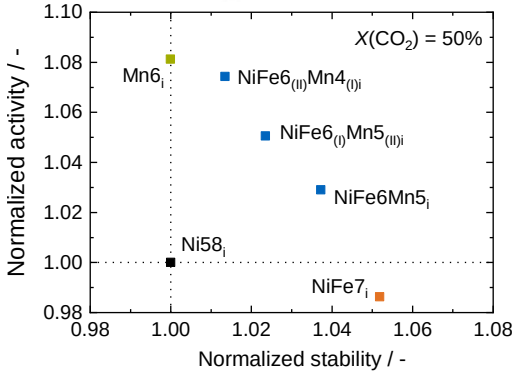
Co-Doping of Fe and Mn *via* Co-Precipitation and Impregnation



- Improved activity and apparent stability compared to Ni-Al
- Working mechanisms of Fe and Mn similar as in mono-doped catalysts
- Activity-stability behavior of impregnated catalysts depends on doping order and can be tailored

Activity-stability relationship suggests a mechanism involving active perimeter sites





T. Burger, F. Koschany, A. Wenng, O. Thomys, K. Köhler, O. Hinrichsen, *Catal. Sci. Technol.* **2018**, *8*, 5920–5932.

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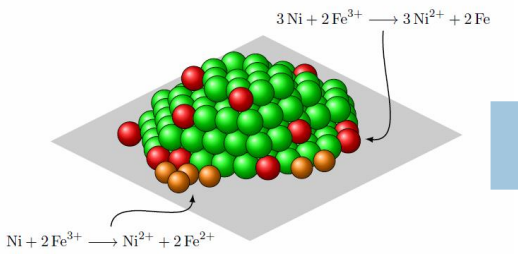
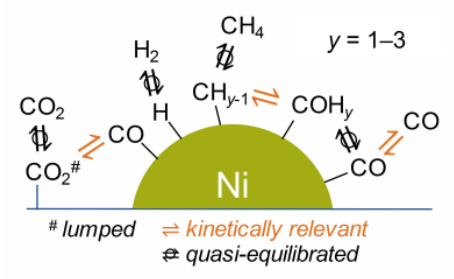
Kinetic Modeling of CO_x Methanation: Reaction Network



Kinetics and characterization



T. Burger, P. Donaubauer, O. Hinrichsen, *Appl. Catal. B* **2021**, *282*, 119408.

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Kinetic Modeling of CO_x Methanation: Kinetic Expressions

$$\frac{d\theta_{CO}}{dt} = 0 = r_{ads,CO} - r_{des,CO} + r_{ads,CO_2} - r_{des,CO_2} - r_{Met} + r_{SR} =$$

$$= \underbrace{k_{ads,CO}\, p_{CO}\, \theta^* - \frac{k_{ads,CO}}{K_{CO}} \theta_{CO}}_{R_{CO}} + \underbrace{k_{ads,CO_2}\, p_{CO_2}\, \theta_H\, \theta^* - \frac{k_{ads,CO_2}}{K_{CO_2}}\, \theta_{CO}\, \theta_{OH}}_{R_{CO_2}} - \underbrace{k_{Met}\, K_{COH_y}\, \frac{\theta_{CO}\theta_H{}^y}{\theta^{*y}}\, \theta^* + \frac{k_{Met}}{K_{Met}}\, \theta_{CH_{y-1}}\, \theta_{OH}}_{R_{CH_4}}$$

- Methanation reaction mechanism may involve decomposition of different COH_y species
- Minimum sum of squared residuals for a discrete value of $y = 2$
- Kinetic expression for $y = 2$ gives an average on kinetics

Number of parameters: 14
Number of species: 3
Number of responses: 1626

Thermodynamic consistency
Strong Boudart criteria
Model significance
Statistic relevance

	reparametrized	
	value / -	95 % CI / -
A_{Met} / mol (g_{cat} s)$^{-1}$	9.39E+07	-2.58E+07 +3.55E+07
$E_{A,Met}$ / kJ/mol^{-1}	130.87	±1.41
A_{ads,CO_2} / mol (g_{cat} s)$^{-1}$	6.23E+02	-4.80E+02 +6.03E+02
E_{A,ads,CO_2} / kJ mol^{-1}	56.94	±0.98
$A_{ads,CO}$ / mol (g_{cat} s)$^{-1}$	2.35E+03	-1.29E+02 +1.63E+02
$E_{A,ads,CO}$ / kJ mol^{-1}	56.47	±0.99
$\Delta_{ads}S_{H_2}$ / J (mol K)$^{-1}$	-67.51	±1.92
$\Delta_{ads}H_{H_2}$ / kJ mol^{-1}	-58.38	±1.02
$\Delta_{ads}S_{CH_4}$ / J (mol K)$^{-1}$	-217.02	±9.26
$\Delta_{ads}H_{CH_4}$ / kJ mol^{-1}	-156.45	±5.65
$\Delta_{ads}S_{H_2O}$ / J (mol K)$^{-1}$	-135.09	±4.75
$\Delta_{ads}H_{H_2O}$ / kJ mol^{-1}	-89.85	±2.86
$\Delta_{ads}S_{CO}$ / J (mol K)$^{-1}$	-17.56	±1.95
$\Delta_{ads}H_{CO}$ / kJ mol^{-1}	-44.68	±0.78

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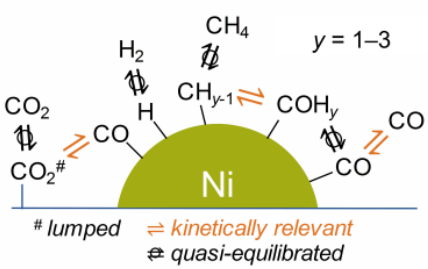
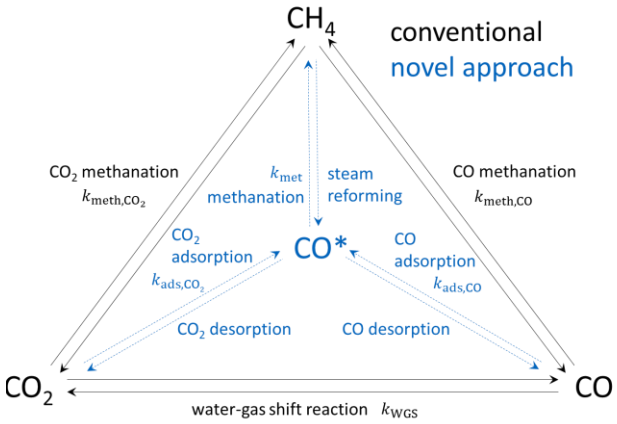
Kinetic Modeling of CO_x Methanation: Reaction Network

Intrinsic kinetic measurements

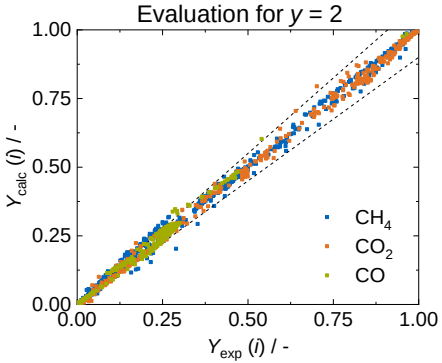
Isotope studies



Model discrimination



Parameter Fitting
Sensitivity analysis



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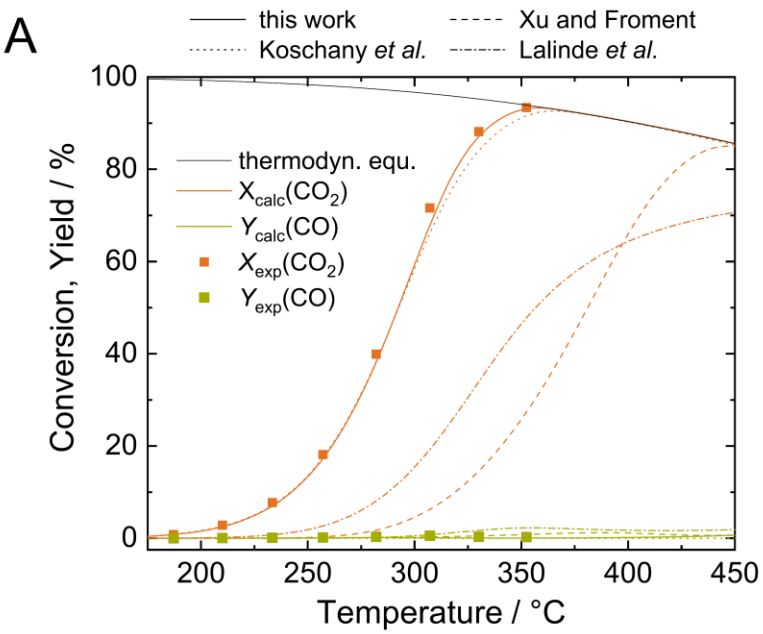
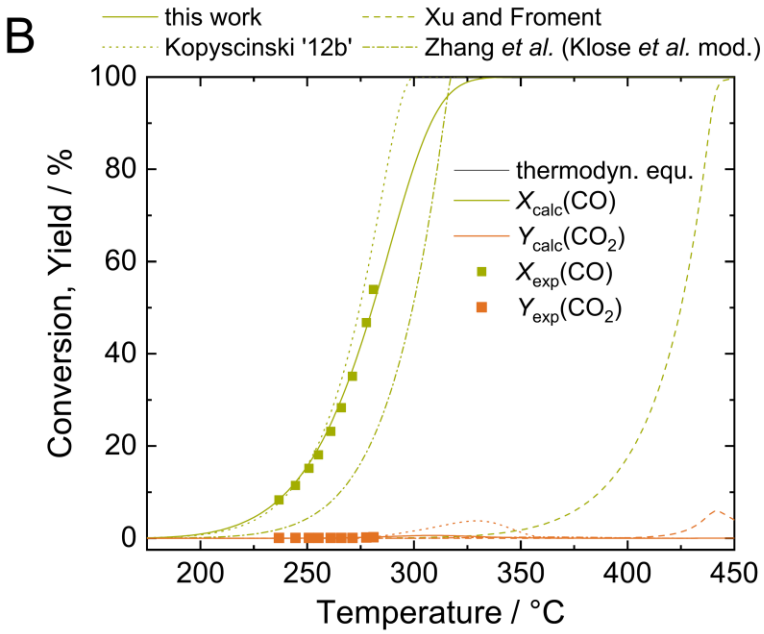
Kinetic Modeling of CO_x Methanation: Results





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Microkinetic Model of CO_x Methanation

→ 13 surface species
→ 42 elementary steps (forward and reverse reactions)

Available in Chemkin-Format
→ This Format is read by catalyticFOAM

The rate coefficient of each reaction is:

$$k_j = A_j T^{\beta_j} \exp\left(\frac{-E_{a,j}}{RT}\right)\exp\left(\frac{\epsilon_{ij}\theta_{ij}}{RT}\right)$$

The production rate of each species is then calculated by:

$$\dot{s}_i = \sum_j \nu_{ji} k_j \prod_i c_i^{\nu_{ji}}$$

Table 2. Detailed, Thermodynamically Consistent Reaction Mechanism for the Methanation of CO and CO_2 over Ni[a]

reaction	A_j (cm, mol, s) or S_0 (*)	β_j	$E_{a,j}$ (kJ mol^{-1})	ϵ_{ij} (kJ mol^{-1})
$H_2 + 2(s) \rightarrow 2H(s)$ (R1)	1.46×10^{-2}*	0	0	
$2H(s) \rightarrow H_2 + 2(s)$ (R2)	4.54×10^{22}	−0.138	96.1	
$CH_4 + (s) \rightarrow CH_4(s)$ (R3)	1.06×10^{-2}*	0	0	
$CH_4(s) \rightarrow CH_4 + (s)$ (R4)	2.79×10^{15}	0.085	37.0	
$H_2O + (s) \rightarrow H_2O(s)$ (R5)	1.16×10^{-1}*	0	0	
$H_2O(s) \rightarrow H_2O + (s)$ (R6)	2.04×10^{12}	−0.031	61.0	
$CO_2 + (s) \rightarrow CO_2(s)$ (R7)	6.29×10^{-4}*	0	0	
$CO_2(s) \rightarrow CO_2 + (s)$ (R8)	4.99×10^{7}	0.018	25.8	
$CO + (s) \rightarrow CO(s)$ (R9)	3.74×10^{-1}*	0	0	
$CO(s) \rightarrow CO + (s)$ (R10)	1.14×10^{12}	−0.103	112.0	50.0[f]
$CO_2(s) + (s) \rightarrow CO(s) + O(s)$ (R11)	1.60×10^{20}	−1.001	89.3	
$CO(s) + O(s) \rightarrow CO_2(s) + (s)$ (R12)	5.81×10^{19}	0	123.6	50.0[f]
$CO(s) + (s) \rightarrow C(s) + O(s)$ (R13)	2.36×10^{18}	0	116.2	50.0[f]
$C(s) + O(s) \rightarrow CO(s) + (s)$ (R14)	2.54×10^{20}	0	148.1	105.0[g]
$CO(s) + H(s) \rightarrow C(s) + OH(s)$ (R15)	3.05×10^{18}	−0.223	105.3	50.0[f]
$C(s) + OH(s) \rightarrow CO(s) + H(s)$ (R16)	2.18×10^{20}	0.128	62.8	105.0[g]
$CO(s) + H(s) \rightarrow HCO(s) + (s)$ (R17)	6.82×10^{22}	−0.979	132.1	
$HCO(s) + (s) \rightarrow CO(s) + H(s)$ (R18)	2.18×10^{20}	−0.021	0.2	−50.0[f]
$HCO(s) + (s) \rightarrow CH(s) + O(s)$ (R19)	5.10×10^{15}	0.023	81.7	
$CH(s) + O(s) \rightarrow HCO(s) + (s)$ (R20)	3.42×10^{19}	−0.023	110.2	
$H(s) + C(s) \rightarrow CH(s) + (s)$ (R21)	1.33×10^{24}	−0.456	157.7	105.0[g]
$CH(s) + (s) \rightarrow C(s) + H(s)$ (R22)	2.63×10^{22}	0.456	22.3	
$CH(s) + H(s) \rightarrow CH_2(s) + (s)$ (R23)	3.21×10^{20}	−0.084	81.1	
$CH_2(s) + (s) \rightarrow CH(s) + H(s)$ (R24)	6.16×10^{24}	0.084	95.2	
$CH_2(s) + H(s) \rightarrow CH_3(s) + (s)$ (R25)	7.78×10^{22}	−0.048	59.5	
$CH_3(s) + (s) \rightarrow CH_2(s) + H(s)$ (R26)	6.16×10^{24}	0.048	95.9	
$CH_3(s) + H(s) \rightarrow CH_4(s) + (s)$ (R27)	3.63×10^{22}	−0.048	65.7	
$CH_4(s) + (s) \rightarrow CH_3(s) + H(s)$ (R28)	6.16×10^{22}	0.048	53.6	
$H(s) + O(s) \rightarrow OH(s) + (s)$ (R29)	1.16×10^{24}	−0.176	104.2	
$OH(s) + (s) \rightarrow H(s) + O(s)$ (R30)	7.70×10^{19}	0.176	29.8	
$H(s) + OH(s) \rightarrow H_2O(s) + (s)$ (R31)	2.34×10^{20}	0.075	44.1	
$H_2O(s) + (s) \rightarrow OH(s) + H(s)$ (R32)	2.91×10^{22}	−0.075	90.4	
$2OH(s) \rightarrow H_2O(s) + O(s)$ (R33)	1.01×10^{20}	0.251	95.1	
$H_2O(s) + O(s) \rightarrow 2OH(s)$ (R34)	1.89×10^{25}	−0.251	215.8	
$H(s) + CO_2(s) \rightarrow COOH(s) + (s)$ (R35)	1.29×10^{22}	−0.46	117.2	
$COOH(s) + (s) \rightarrow CO_2(s) + H(s)$ (R36)	1.29×10^{20}	0.46	33.8	
$COOH(s) + (s) \rightarrow CO(s) + OH(s)$ (R37)	6.03×10^{22}	−0.216	54.4	
$CO(s) + OH(s) \rightarrow COOH(s) + (s)$ (R38)	1.45×10^{22}	0.216	97.6	50.0[f]
$COOH(s) + H(s) \rightarrow HCO(s) + OH(s)$ (R39)	4.22×10^{22}	−1.145	104.7	
$HCO(s) + OH(s) \rightarrow COOH(s) + H(s)$ (R40)	3.25×10^{19}	0.245	16.1	
$2CO(s) \rightarrow CO_2(s) + C(s)$ (R41)	6.31×10^{23}	0.5	241.7	100.0[f]
$C(s) + CO_2(s) \rightarrow 2CO(s)$ (R42)	1.88×10^{20}	−0.5	239.3	105.0[g]

D. Schmider, L. Maier, O. Deutschmann, *Ind. Eng. Chem. Res.* **2021**, *60*, 5792−5805.

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Microkin

→ 13 surface s
→ 42 elementa

Available in Chem
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The rate coefficie

$$k_j = A_j T^{\beta_j} \exp\left(\frac{-E_{a,j}}{RT}\right)$$

The production ra

$$\dot{s}_i = \sum_j \nu_{ji} k_j \prod_i c_i^{\nu_{ji}}$$

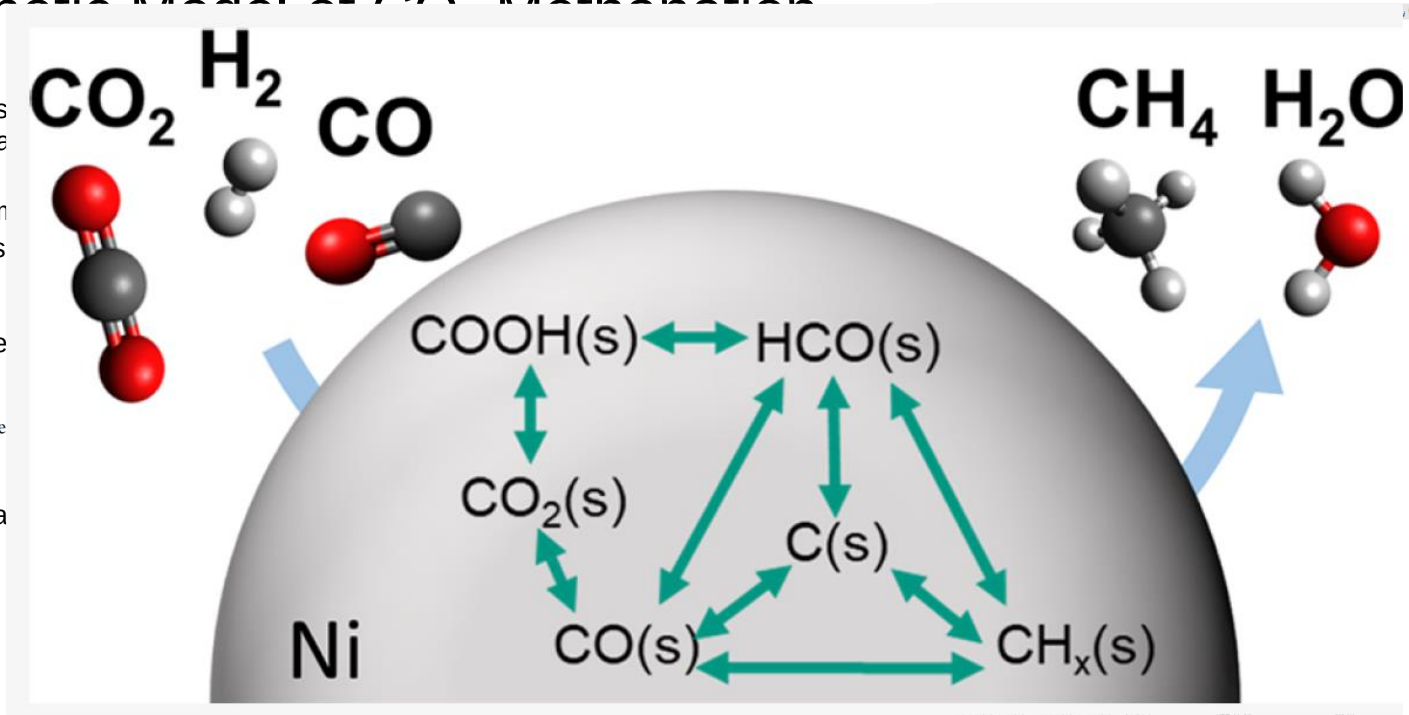

Table 2. Detailed, Thermodynamically Consistent Reaction Mechanism for the Methanation of CO and CO_2 over Ni[a]

			ϵ_{ij} (kJ mol^{-1})	$E_{a,j}$ (kJ mol^{-1})
$H_2(g) + Ni(s) \rightleftharpoons H(s) + H(s)$	(R1)	1.00×10^{-2}	0	96.1
$H(s) + Ni(s) \rightleftharpoons OH(s) + H(s)$	(R2)	1.00×10^{-2}	0	37.0
$OH(s) + Ni(s) \rightleftharpoons O(s) + H(s)$	(R3)	1.00×10^{-2}	0	61.0
$CO(g) + Ni(s) \rightleftharpoons CO(s)$	(R4)	1.00×10^{-2}	0	25.8
$CO(s) + Ni(s) \rightleftharpoons C(s) + O(s)$	(R5)	1.00×10^{-2}	0	112.0
$CO(s) + Ni(s) \rightleftharpoons HCO(s) + H(s)$	(R6)	1.00×10^{-2}	89.3	50.0[f]
$HCO(s) + Ni(s) \rightleftharpoons COOH(s) + H(s)$	(R7)	1.00×10^{-2}	123.6	50.0[f]
$COOH(s) + Ni(s) \rightleftharpoons CO_2(s) + H(s)$	(R8)	1.00×10^{-2}	116.2	50.0[f]
$CO_2(g) + Ni(s) \rightleftharpoons CO_2(s)$	(R9)	1.00×10^{-2}	148.1	105.0[f]
$CO_2(s) + Ni(s) \rightleftharpoons CO(s) + O(s)$	(R10)	1.00×10^{-2}	105.3	50.0[f]
$C(s) + Ni(s) \rightleftharpoons CH(s) + H(s)$	(R11)	1.00×10^{-2}	62.8	105.0[f]
$CH(s) + Ni(s) \rightleftharpoons CH_2(s) + H(s)$	(R12)	1.00×10^{-2}	132.1	0.2
$CH_2(s) + Ni(s) \rightleftharpoons CH_3(s) + H(s)$	(R13)	1.00×10^{-2}	0.2	−50.0[f]
$CH_3(s) + Ni(s) \rightleftharpoons CH_4(g) + Ni(s)$	(R14)	1.00×10^{-2}	81.7	110.2
$CH_3(s) + Ni(s) \rightleftharpoons CH_2(s) + H(s)$	(R15)	1.00×10^{-2}	157.7	105.0[f]
$CH_2(s) + Ni(s) \rightleftharpoons CH(s) + H(s)$	(R16)	1.00×10^{-2}	22.3	81.1
$CH(s) + Ni(s) \rightleftharpoons C(s) + H(s)$	(R17)	1.00×10^{-2}	95.2	59.5
$CH(s) + Ni(s) \rightleftharpoons CH_x(s) + Ni(s)$	(R18)	1.00×10^{-2}	95.9	65.7
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + H(s)$	(R19)	1.00×10^{-2}	53.6	104.2
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + C(s)$	(R20)	1.00×10^{-2}	29.8	44.1
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + O(s)$	(R21)	1.00×10^{-2}	90.4	95.1
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + OH(s)$	(R22)	1.00×10^{-2}	215.8	117.2
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + COOH(s)$	(R23)	1.00×10^{-2}	33.8	54.4
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + HCO(s)$	(R24)	1.00×10^{-2}	97.6	50.0[f]
$CH_x(s) + Ni(s) \rightleftharpoons CH_{x-1}(s) + CO(s)$	(R25)	1.00×10^{-2}	104.7	16.1
$HCO(s) + OH(s) \rightarrow COOH(s) + H(s)$	(R40)	3.25×10^{19}	0.245	241.7
$2CO(s) \rightarrow CO_2(s) + C(s)$	(R41)	6.31×10^{23}	0.5	100.0[f]
$C(s) + CO_2(s) \rightarrow 2CO(s)$	(R42)	1.88×10^{20}	−0.5	239.3
				105.0[f]

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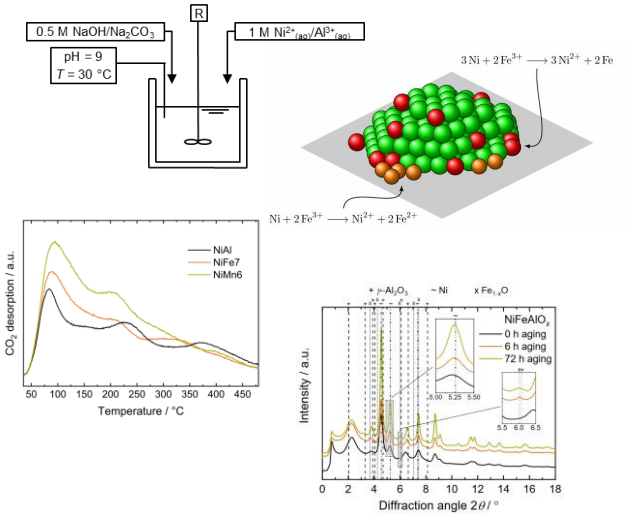
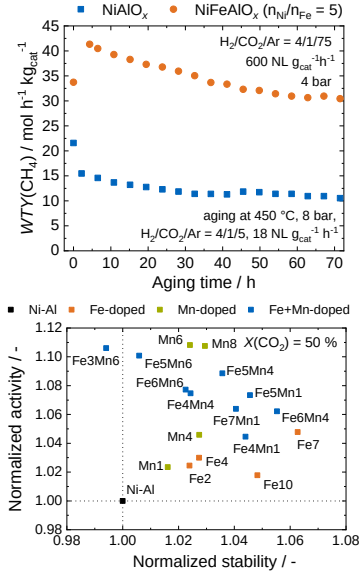
Summary

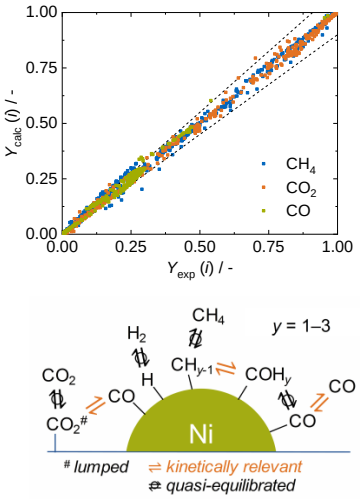
Catalyst Synthesis and Characterization



Structure - Activity Analysis



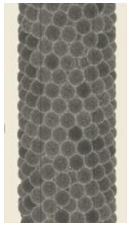
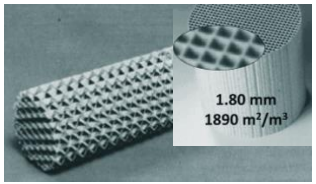
Kinetic Measurements and Kinetic Modeling



CO_2 Methanation

CO_x Methanation

Types of fixed beds

powder bed	random (pellet) bed	structured bed [2]	foams [1]	periodic open cellular structures (POCS) [1]
				

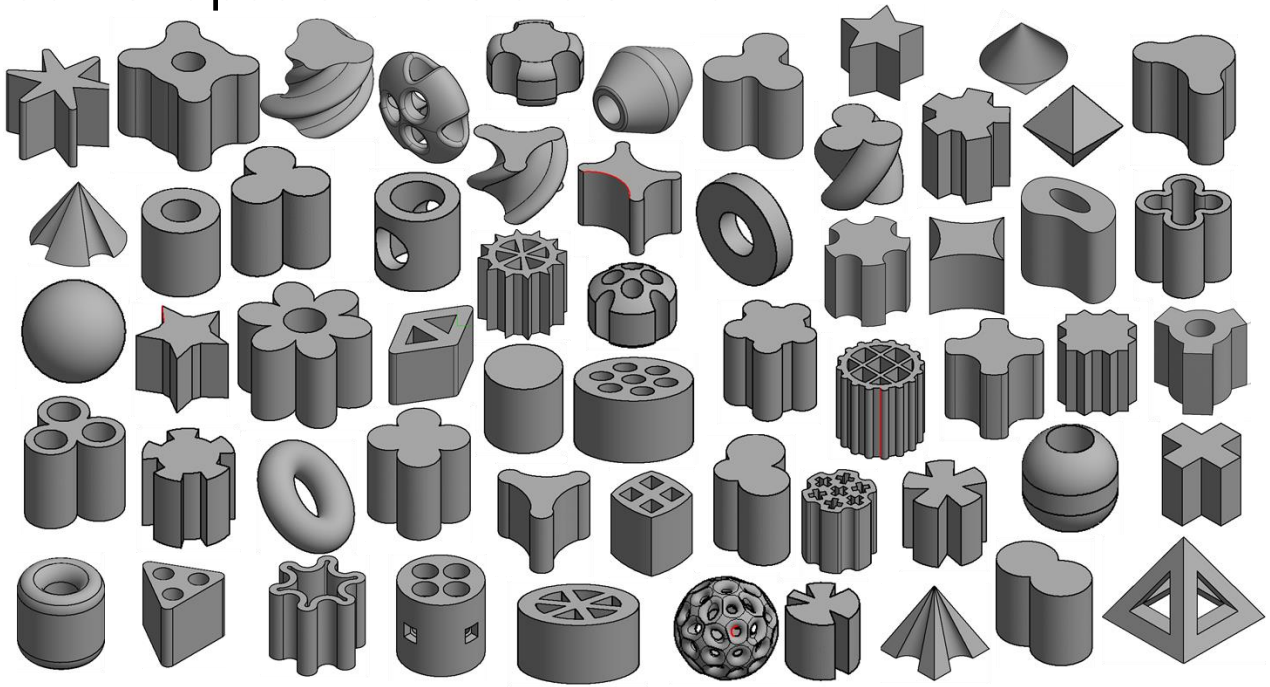
development – decrease of pressure drop

+ direct use of catalyst powder - very high pressure drop	+ maintanance + catalyst synthesis + shaping - pressure drop - broad residence time distribution (turbulences)	+ radial dispersion + narrow residence time distribution - wall contact (channeling and heat transport) - sensitive to roundness of tube - adhesion of catalyst	+ even flow profile + high specific suface area	+ lowest pressure drop + good heat transport + wall contact - low residence time - adhesion of catalyst

[1] A. Inayat et al. Chem. Eng. Sci. 2011, 66, 2758.

[2] A. Gascon et al. Catal. Sci. Technol. 2015, 5, 807.

Pellet Beds - Shapes of the State of the Art?



J. von Seckendorff, PhD Thesis, Technical University of Munich, **2021**.
P. Donaubauer, O. Hinrichsen, *IEC Research* **2019**, *58*, 110-119.
J. von Seckendorff, P. Scheck, M. Tonigold, R. Fischer, O. Hinrichsen *Chem. Eng. J.* **2021**, *404*, 126468.

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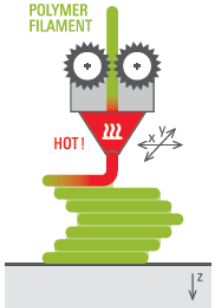
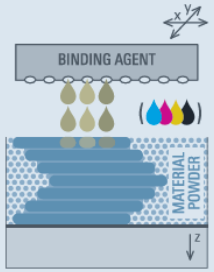
Classification of AM processes for ceramics

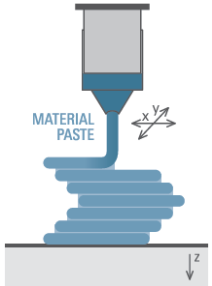
Based on DIN 8580 and Formnext AM Field Guide Compact (2019)

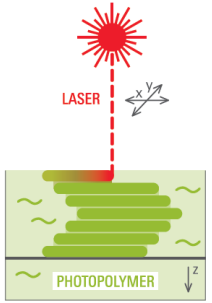
For **all** processes: 3D structures are created by a selective layer-by-layer process

- Solid
  - Filament
    - Melting and solidifying
    - **Fused Layer Modeling (FDM)**
  - Powder
    - Joined with bonding agent
    - **Binder Jetting (BJ)**
- Liquid
  - Paste
    - Fluid-solid transition
    - **Direct Ink Writing (DIW)**
  - Liquid
    - Polymerization
    - **Stereolithography (SLA)**









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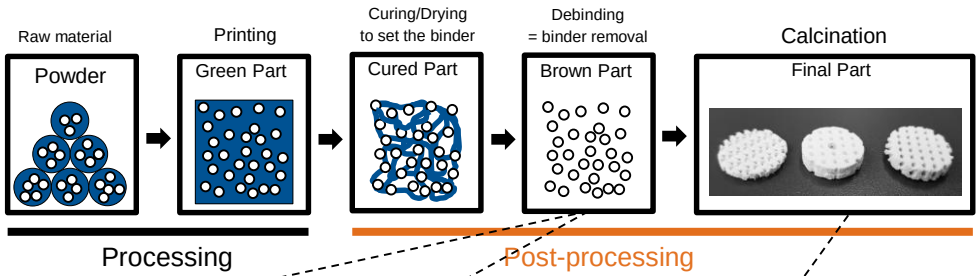
Binder Jetting (BJ) Fabrication Steps



Shapes still embedded in powder

Removing loose powder

ΔT

Calcined 3D-printed parts

H_2

ΔT

Reduced catalysts

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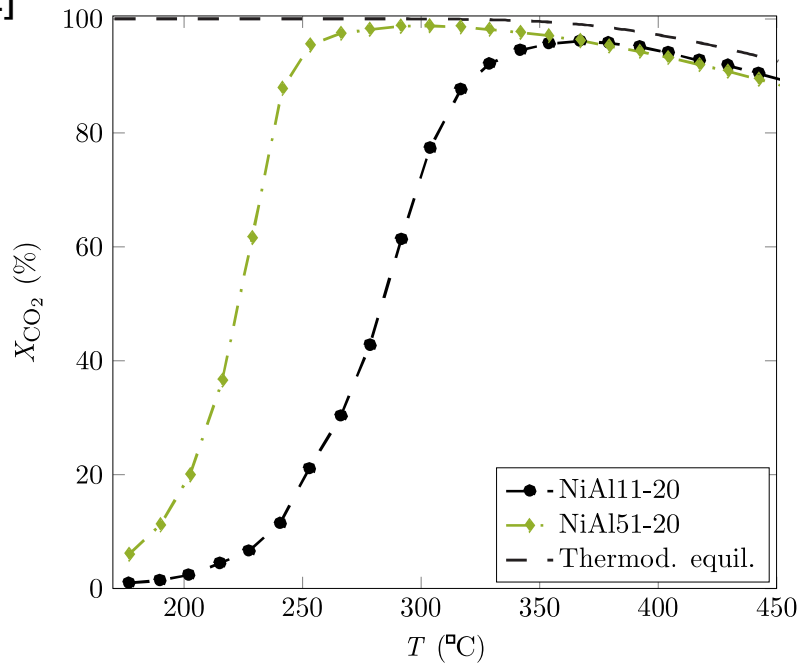
Preliminary Results for CO_2 Methanation over BJ printed catalysts

[2]



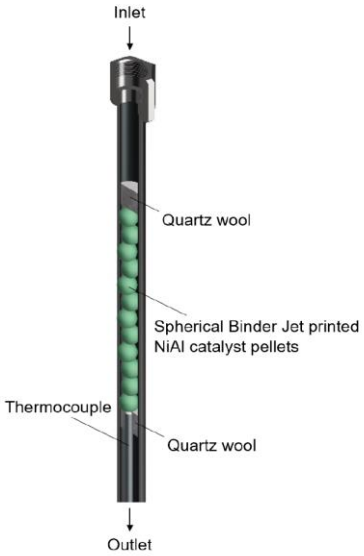
CO_2 methanation

10 cm catalyst packing

p = 9 bar

Feed ratio H_2/CO_2 = 4

[1]



[1] J. Fernengel, L. Bolton, O. Hinrichsen, *CET* **2020**, *43*, 172−178.
[2] confidential results

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