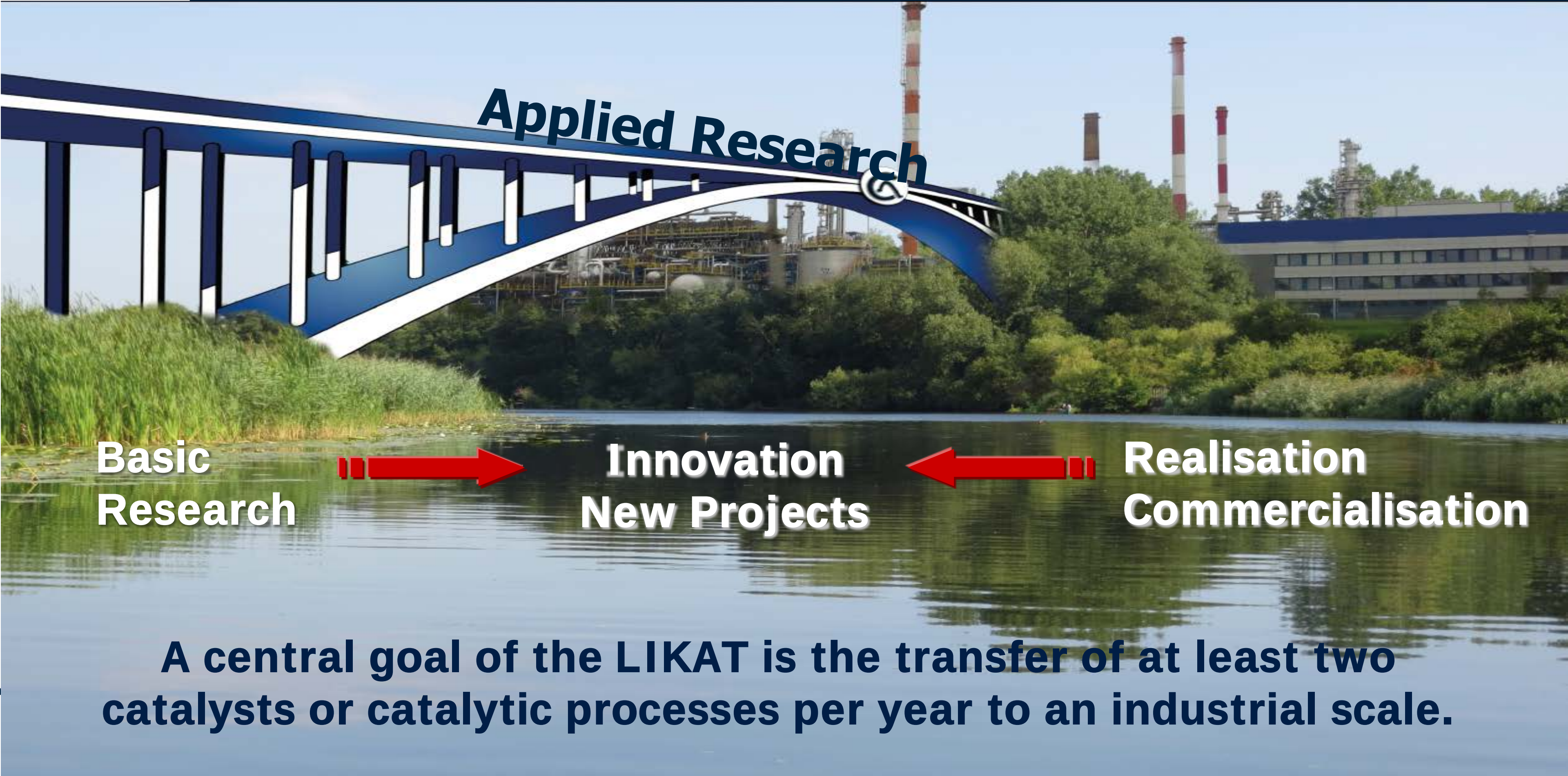
Overview of catalytic purification and conversion of biogas: Approaches to overcome utilization problems

Dr. Sebastian Wohlrab

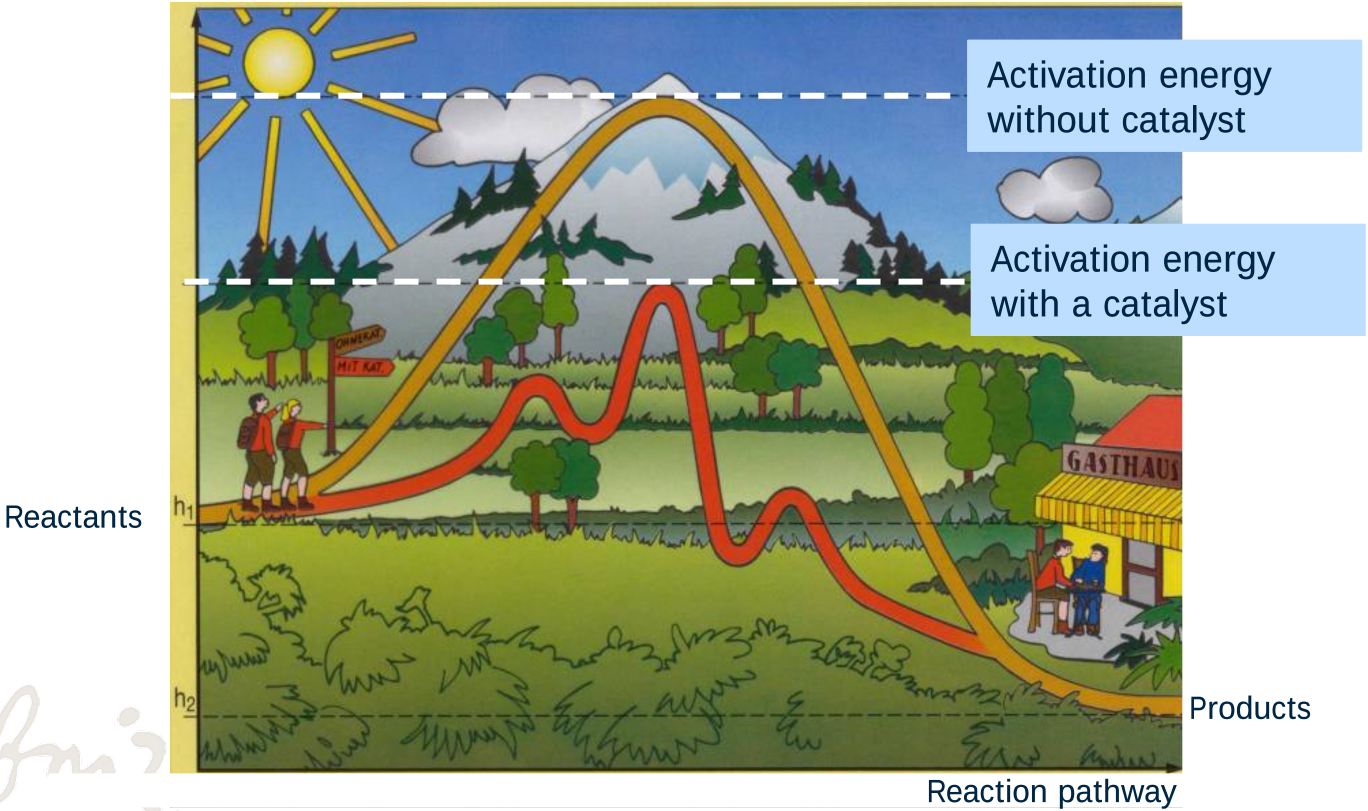
Leibniz-Institut für Katalyse e.V.
LIKAT Rostock

LIKAT: From Basic Science to Applications

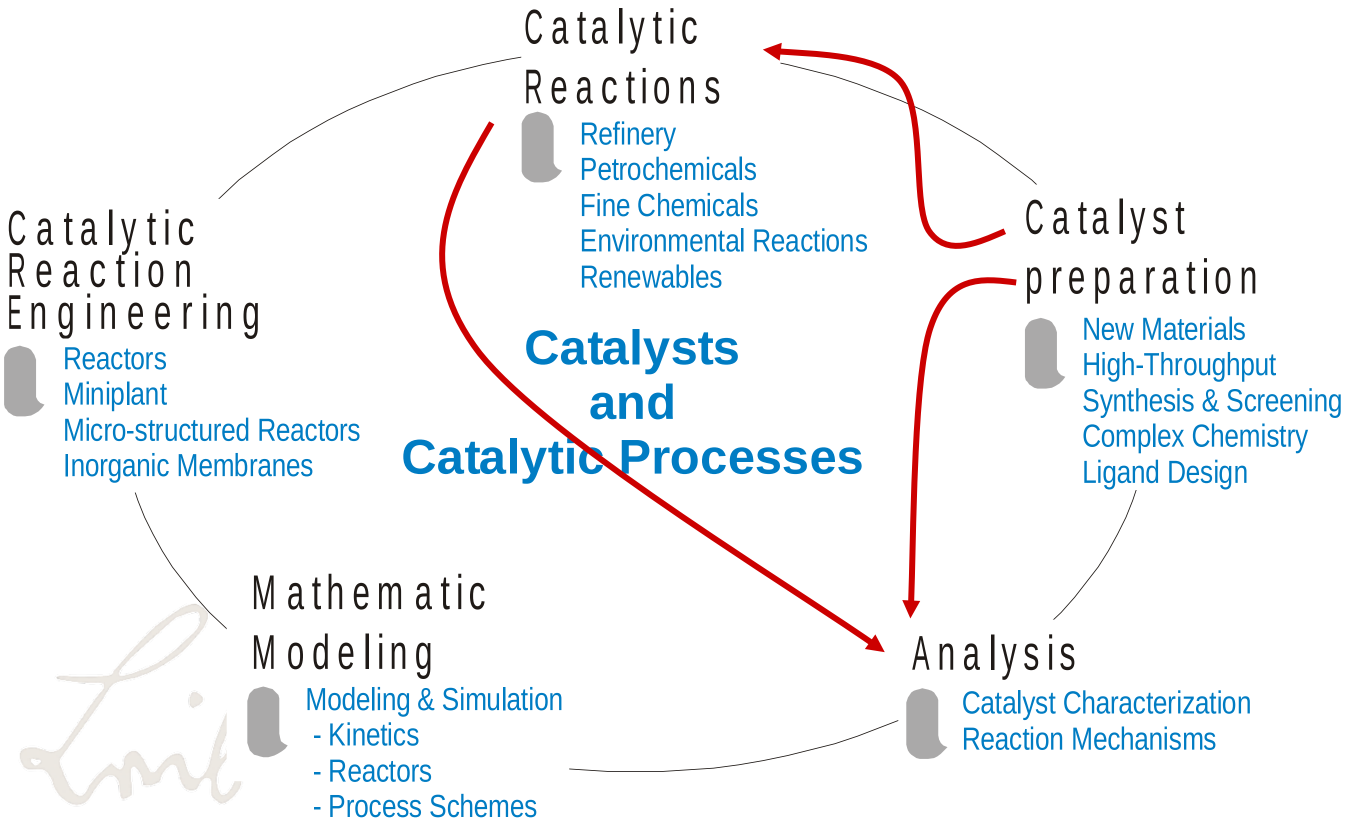


A central goal of the LIKAT is the transfer of at least two catalysts or catalytic processes per year to an industrial scale.

What is catalysis?



Concept of Applied Research in Catalysis



Leibniz-Institute for Catalysis covers completely all aspects of heterogeneous and homogeneous catalysis from synthesis of catalytic material to catalytic reaction engineering

Department “Heterogeneous Catalytic Processes“

Dr. Sebastian Wohlrab
(sebastian.wohlrab@catalysis.de)

36 scientists, technicians, postdocs & PhD students

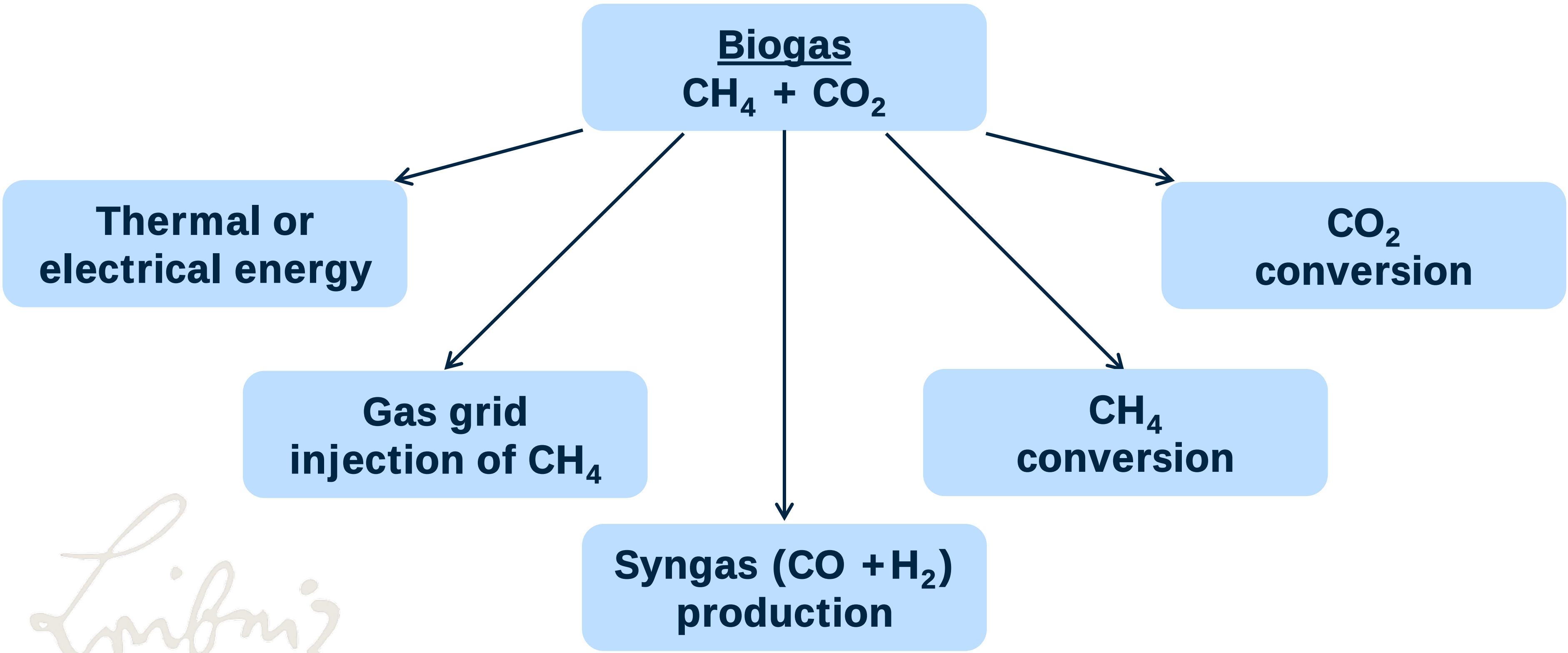
plug flow reactors, membrane reactors, autoclaves (up to 800 °C and 400 bar, 25 ml to 5 l)
GC, GC/MS (on line), online-IR

Biomass to chemicals or energy (biogas, bio crude oil, glycerol to chemicals)

Catalytic processes in fine chemical synthesis (batch and continuous processing)

Environmental catalysis (automotive catalysts, CO_2 utilization, hydrogen generation)
Efficient use of resources

Ways of biogas utilization

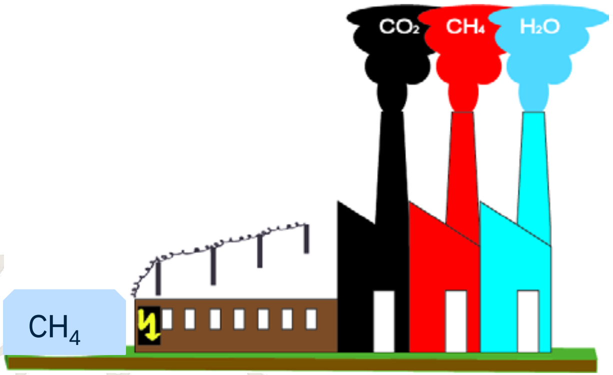


Methane – As energy carrier

as resource

- 90-95% CH_4 used for energy production
- fuel for combustion engines
- chemical for industrial processes

A. Holmen, *Catal. Today*, **2009**, 142, 2-8.

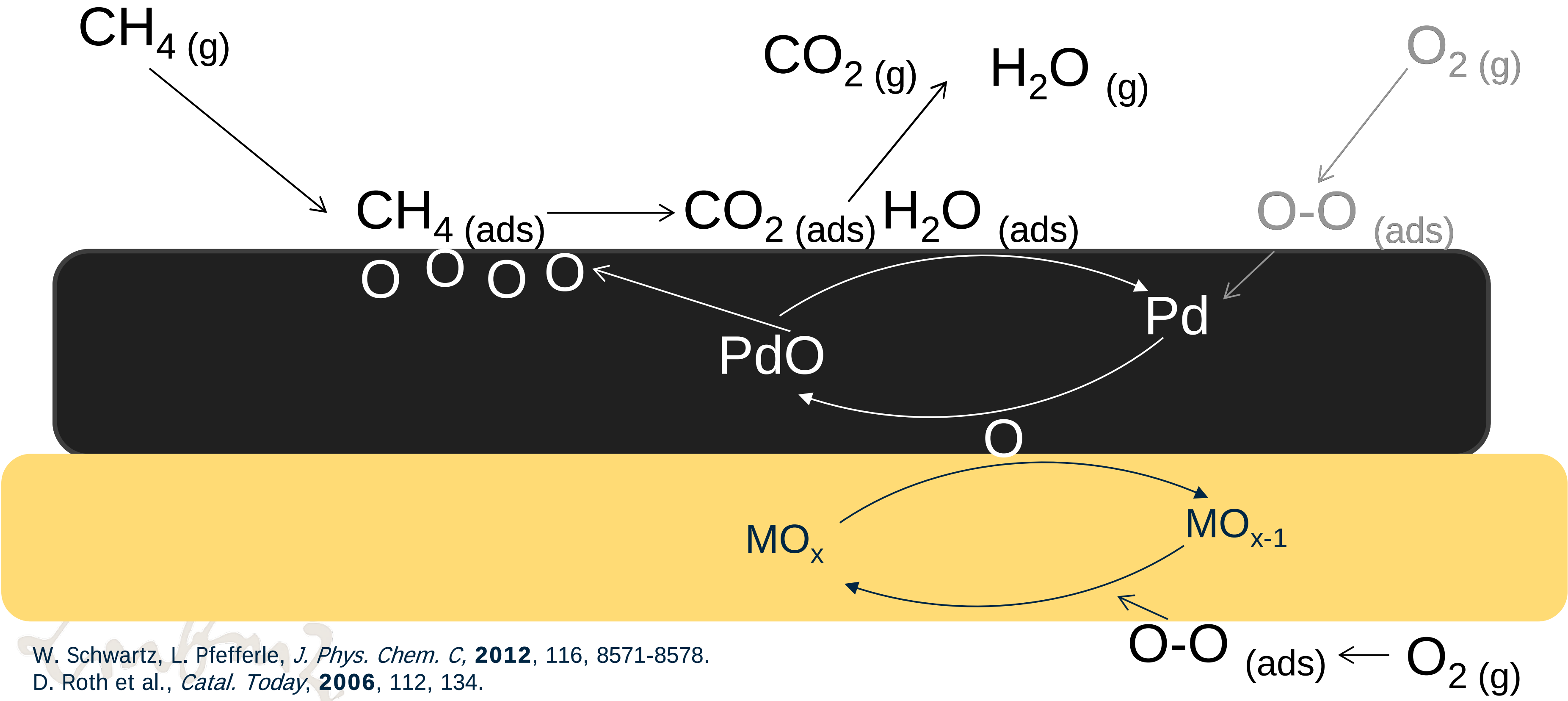


as greenhouse gas

- 25 times higher global warming potential than CO_2
- unburnt CH_4 from natural gas combustion engines (NGV, Gas-fired power plant, bio gas plant...)
- exhaust gas contains up to 5000 ppm CH_4 [2]

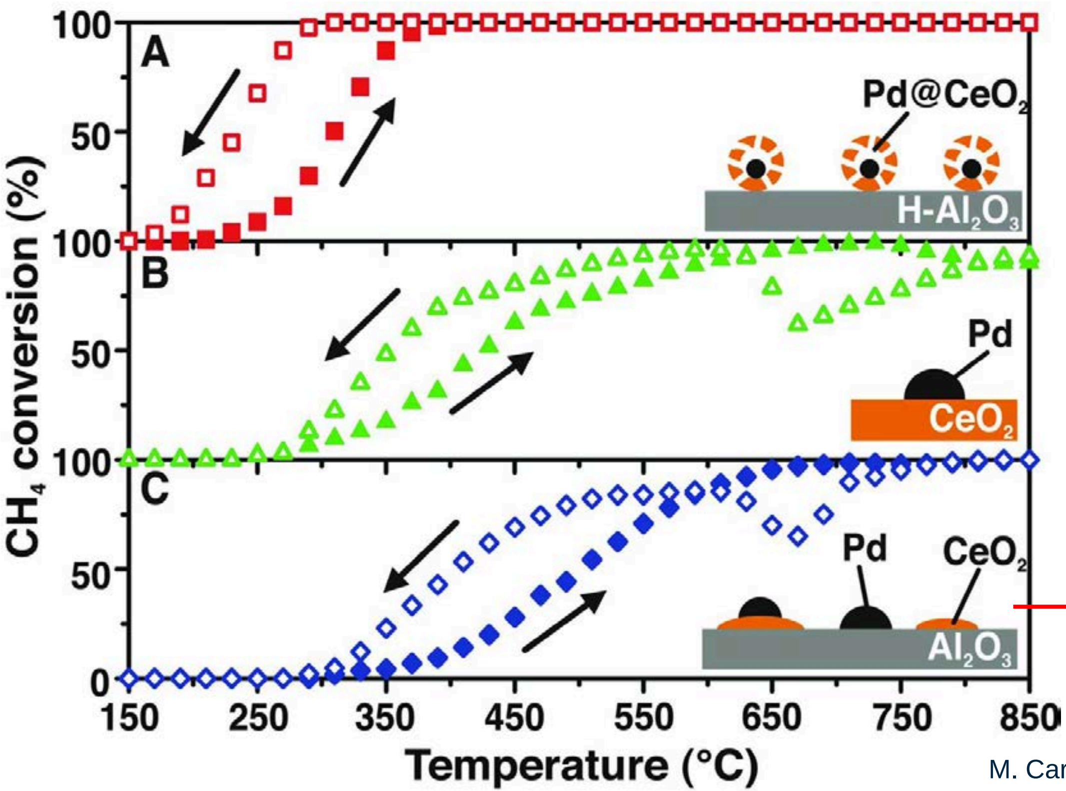
M. Zanoletti et al., *Chem. Eng. Sci.*, **2009**, 64, 945-954.

Methane lean combustion - The Mars-van-Krevelen-Mechanism



W. Schwartz, L. Pfefferle, *J. Phys. Chem. C,* **2012**, 116, 8571-8578.
D. Roth et al., *Catal. Today*, **2006**, 112, 134.

Pd – CeO_2 interactions: Catalyst design determines performance?



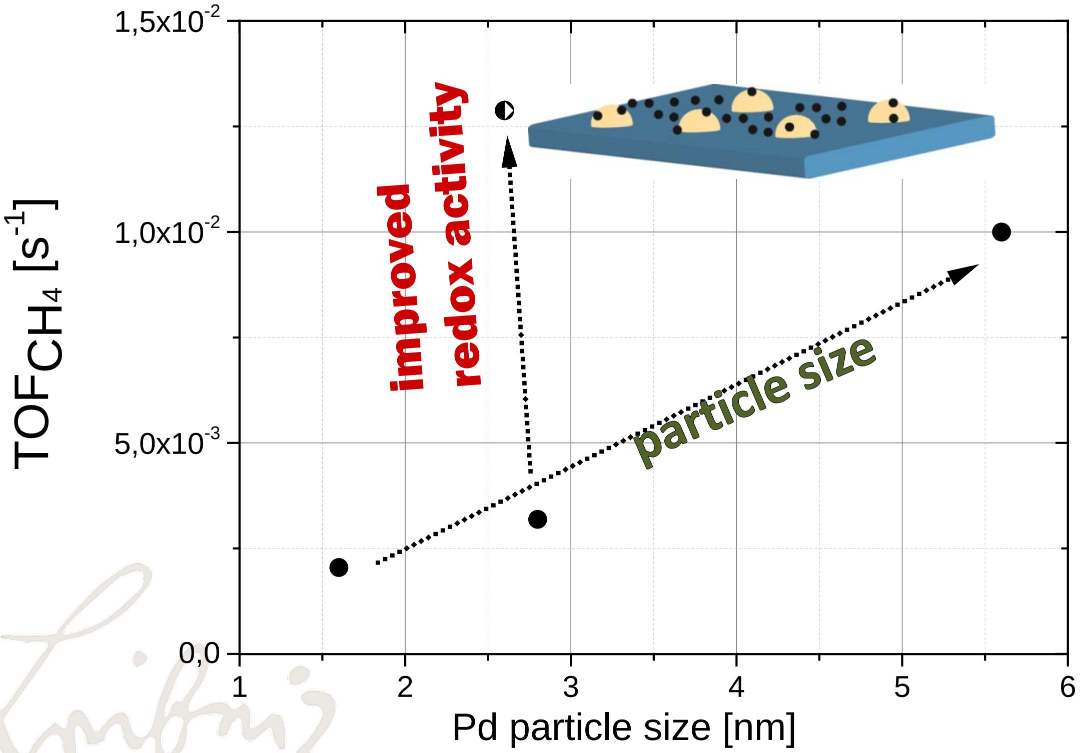
Light-off curves of CH_4 conversion

Heating and cooling ($10°C\ min^{-1}$)

GENERALLY VALID?

M. Cargnello, J.J.D. Jaén, J.C.H. Garrido, K. Bakhmutsky, T. Montini, J.J.C. Gámez, R.J. Gorte, P. Fornasiero, *Science* **2012**, 337,713.

Improving the catalyst activity

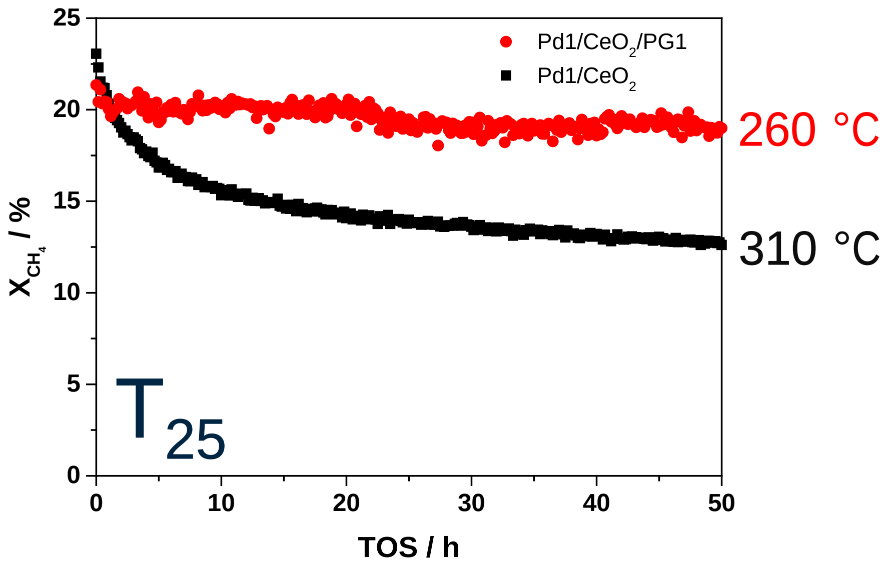


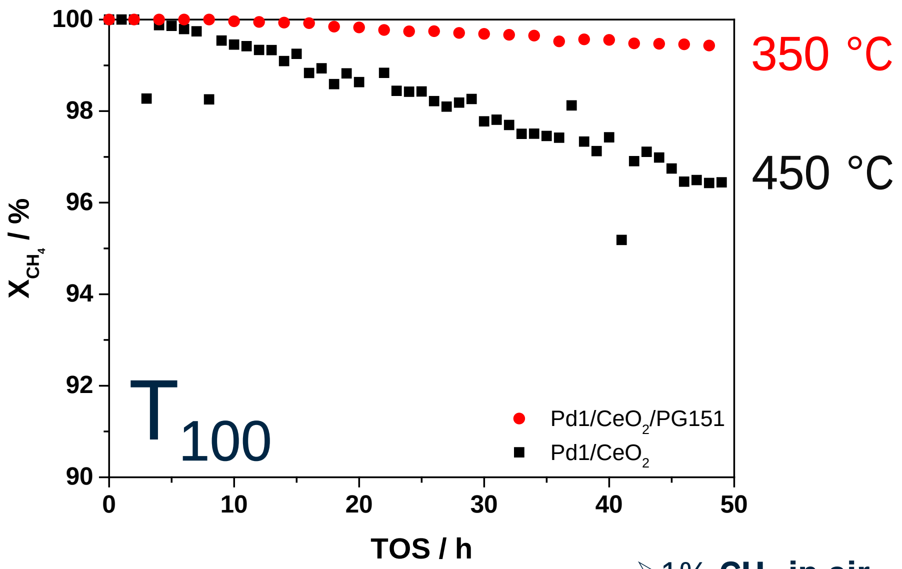
- 1% CH_4 **in air**
- $Pd/CeO_2/PG1$
- 250 °C
- GHSV = 33.000 h^{-1}

M. Hoffmann, S. Kreft, G. Georgi, G. Fulda, M.-M. Pohl, D. Seeburg, C. Berger-Karin, E. V. Kondratenko, S. Wohlrab, *Applied Catalysis B, Environmental*; **2015**, 179, 313-320.

Improving the long term stability

CH_4
in exhaust gas





- 1% CH_4 in air
- 75 ml/min
- GHSV = 33.000 h^{-1}

- conventional Pd/CeO_2 shows deactivation after a few hours on stream
- Pd and CeO_2 in glass shows improved performance over 50 h on stream

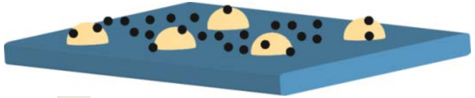
Generation 2: long term stability under wet conditions

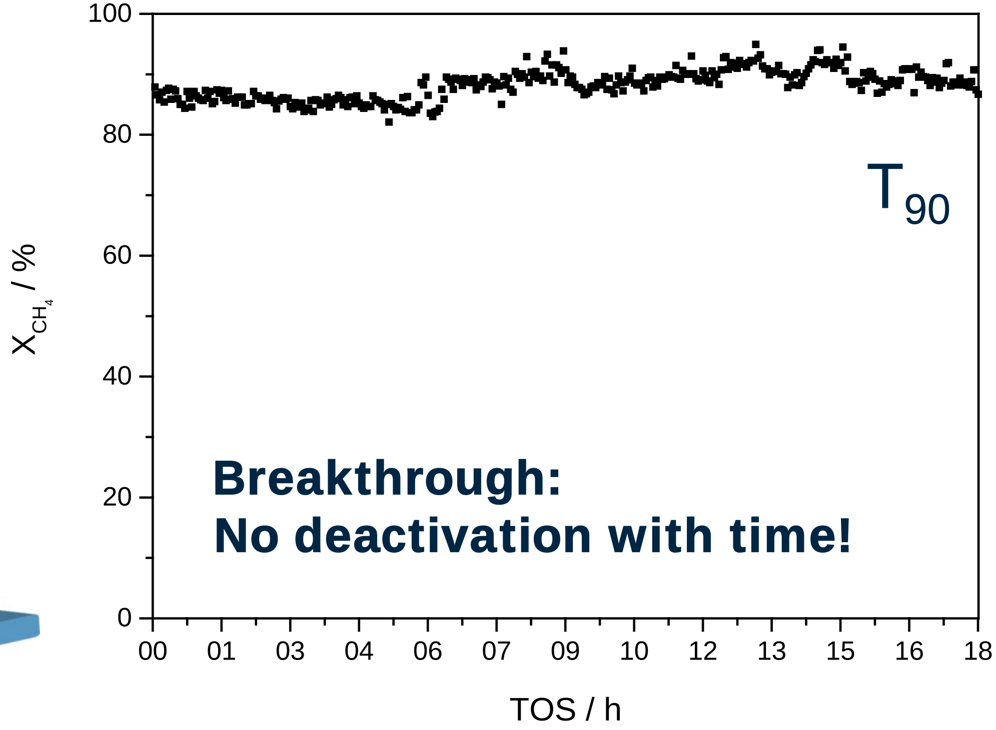
CH_4
in exhaust gas

$N_2:O_2:CO_2:$**$CH_4:H_2O$**

74,9: 9,0: 5,5: **0,1: 10,5 vol%**

m_{Cat} = 200 mg
F_{total} = 300 ml/min
GHSV ~ 81000 h^{-1}



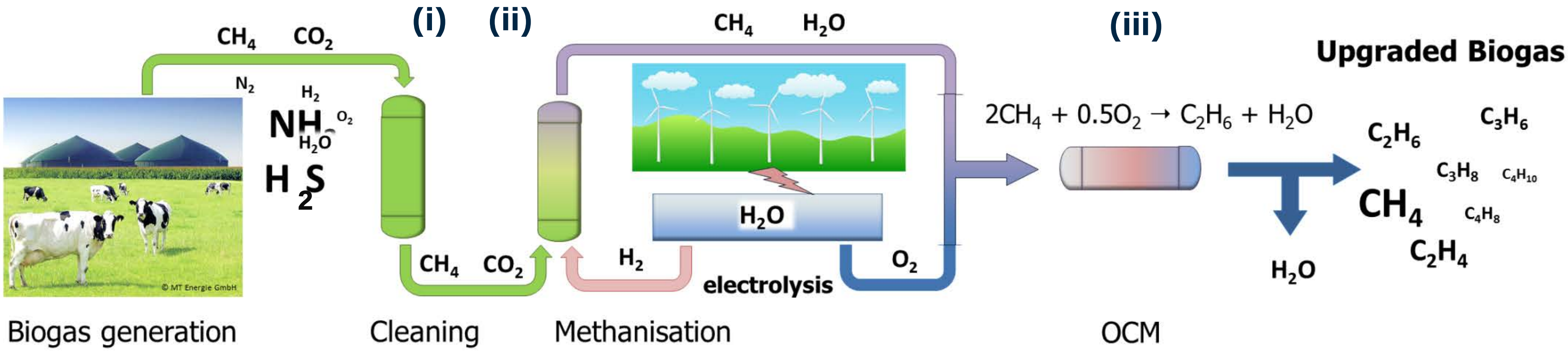


Biogas conditioning

Gas grid
Injection of CH_4

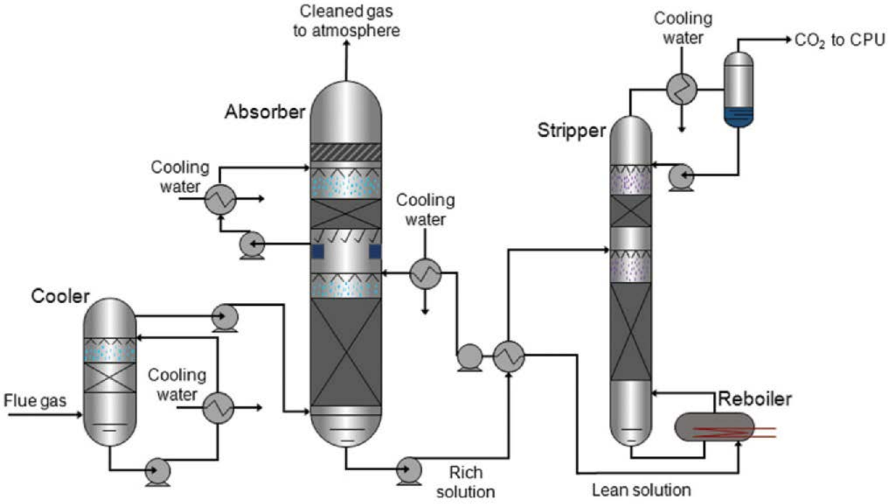
biogas generation

(i) Cleaning – O_2 removal
(ii) CO_2-methanation
(iii) Oxidative coupling of methane (OCM) to C_{2+} hydrocarbons



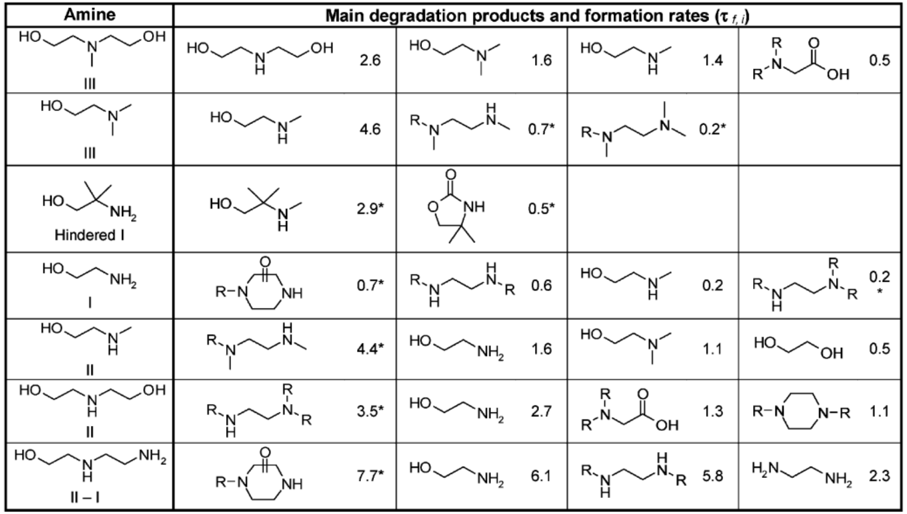
i) Oxygen removal

Amine scrubbing



Kohl A and Nielsen R , Gas Purification , 5th Edn , Gulf Publishing Company , Houston , pp. 41 – 48 (1997).

Problem: Oxidation of amines in presence of oxygen



Main Degradation Products of Ethanolamine-H_2O-Air Systems

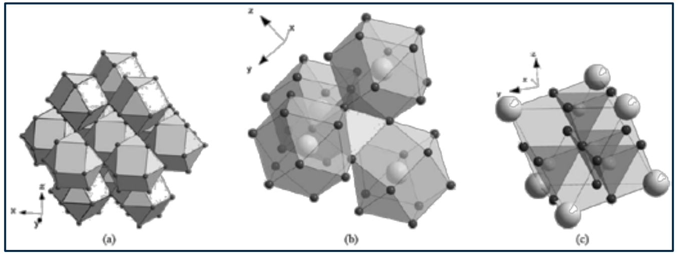
Lepaumier et al. *Ind. Eng. Chem. Res.* **2009,** *48,* 9068–9075

Catalysis Leibniz-Institut für Katalyse e.V. LIKAT

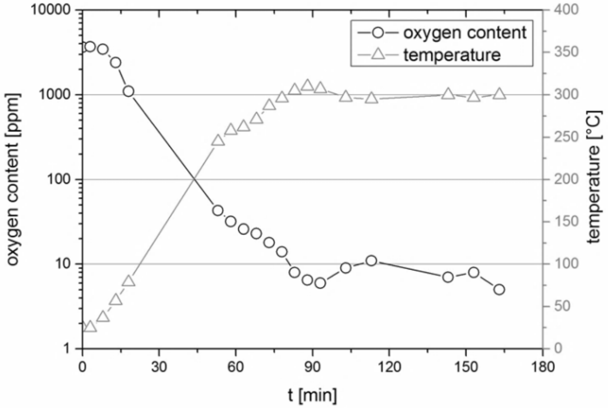
i) Oxygen removal

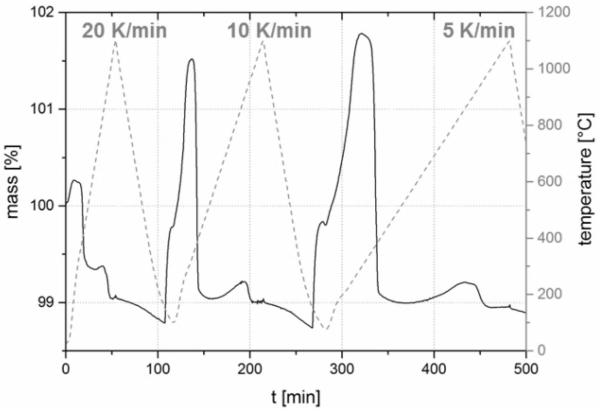
Gas grid
Injection of CH_4

$YBaCo_4O_{7+\delta}$ as substance for absorptive oxygen removal



- Oxygen removal from $CH_4/CO_2/O_2$ mixtures
- constant O_2 flux of 0.4 vol.%
- GHSV of 6000 L kg^{-1} h^{-1}
- CH_4:CO_2 = 70:30.





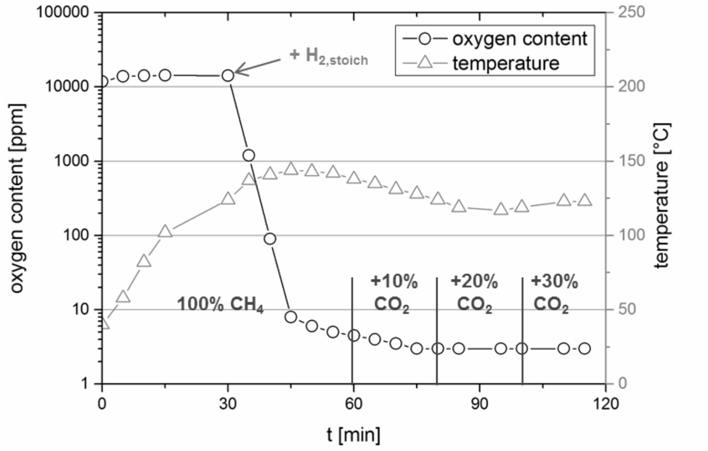
- Thermo-gravimetric experiments clearly showed the ability of $YBaCo_4O_{7+\delta}$ to absorb oxygen from air
- $YBaCo_4O_7 + 0.5O_2 \rightarrow YBaCo_4O_8$ (theoretical Δm = 2.8 wt.%)
- oxygen absorption between 270 and 350 °C
- oxygen release above 400 °C

Peppel, T.; Seeburg, D.; Fulda, G.; Kraus, M.; Trommler, U.; Roland, U.; Wohlrab, S. Chemical Engineering & Technology 2017, 40, 153-161.

i) Oxygen removal

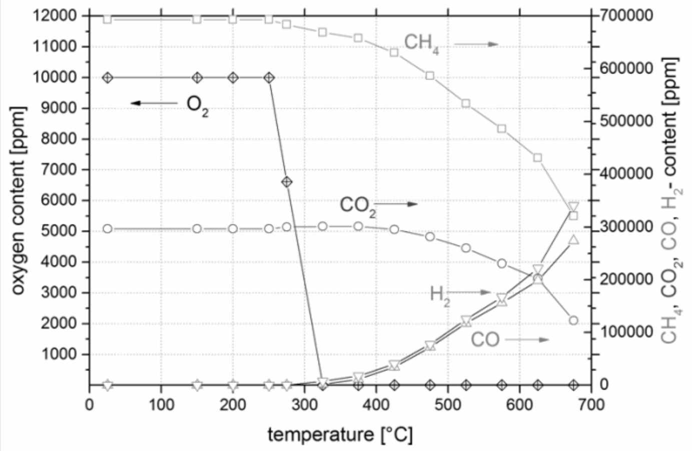
Catalytic approaches (catalyst: Pt/γ-Al_2O_3)

$O_2 + 2H_2 \rightarrow 2H_2O$



-From CH_4/CO_2/O_2/H_2 mixtures
-constant O_2 flux of 1 vol.%
-GHSV of 6000 L kg^{-1} h^{-1}

$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$

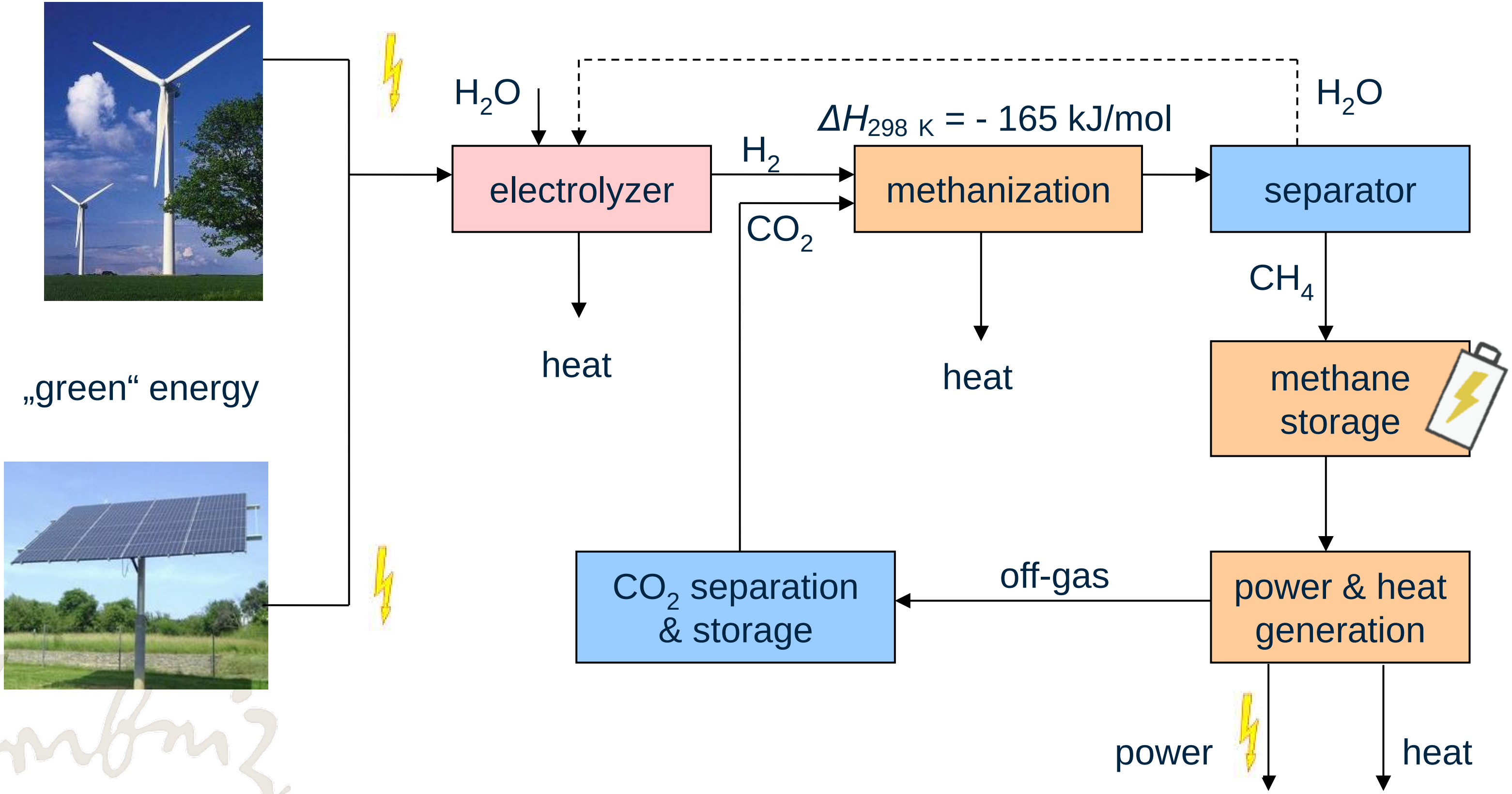


-From CH_4/CO_2/O_2 mixtures
-constant O_2 flux of 1 vol.%
-GHSV of 22.500 L kg^{-1} h^{-1}

Peppel, T.; Seeburg, D.; Fulda, G.; Kraus, M.; Trommler, U.; Roland, U.; Wohlrab, S. Chemical Engineering & Technology 2017, 40, 153-161.

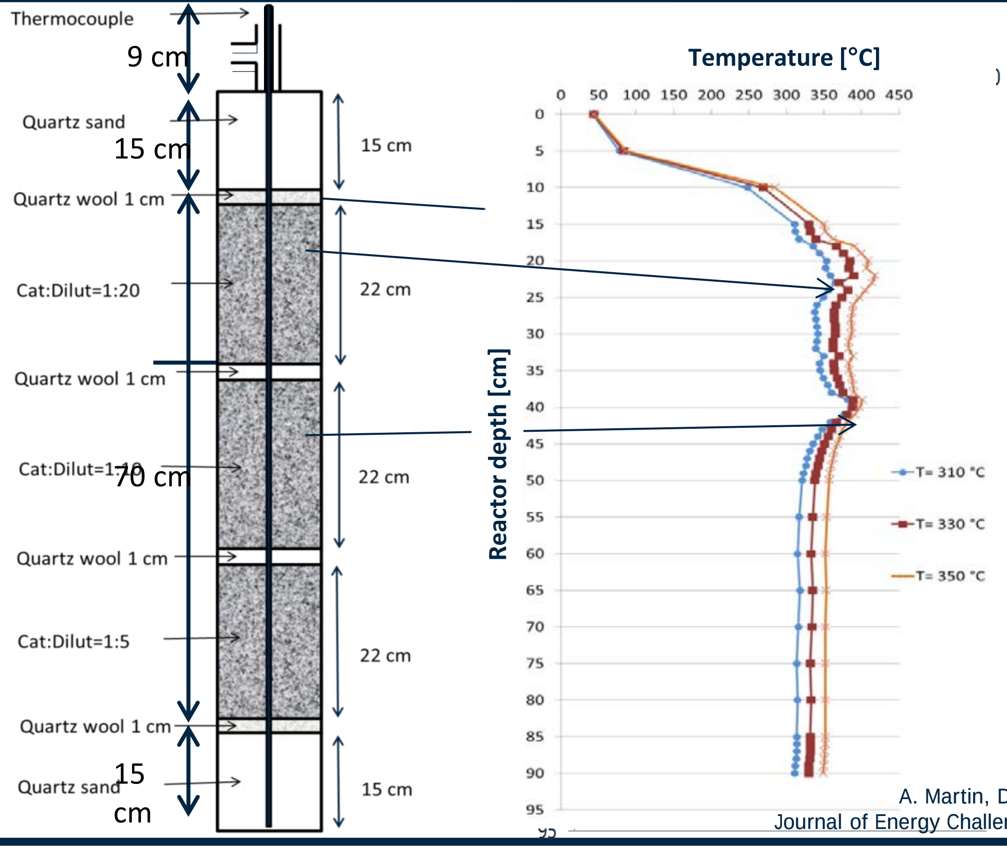
ii) CO_2 Methanation

Gas grid
Injection of CH_4



ii) CO_2 Methanation

8000 h^{-1}
46,32 Nl/h CO_2
188,4 Nl/h H_2
25,36 Nl/h N_2



@ 310-350 °C
50-51 l/h Methan

Hot spot: 50 K

A. Martin, D. Türks, H. Mena, U. Armbruster
Journal of Energy Challenges and Mechanics 3 (2016) 29

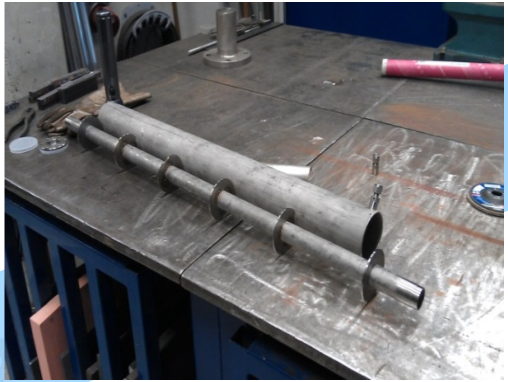
ii) CO_2 Methanation

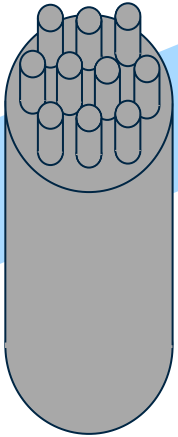
Gas grid
Injection of CH_4

EUROPÄISCHE UNION
Europäischer Fonds für
Regionale Entwicklung

Lab-Reactor
(1-4 ml Catalyst)
1-5 Nl_{SNG}/h

Lab-Reactor
(>100 ml Catalyst) 50 Nl_{SNG}/h





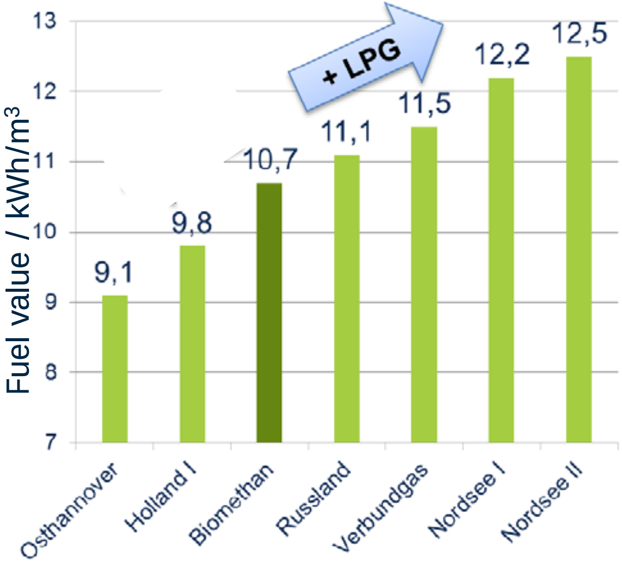
Aiml:
Scale-up of bundle of pipes (10x)
500 Nl_{SNG}/h (= $5kW_{el}$)

iii) Oxidative coupling of methane (OCM) to C_{2+} hydrocarbons

Gas grid
Injection of CH_4

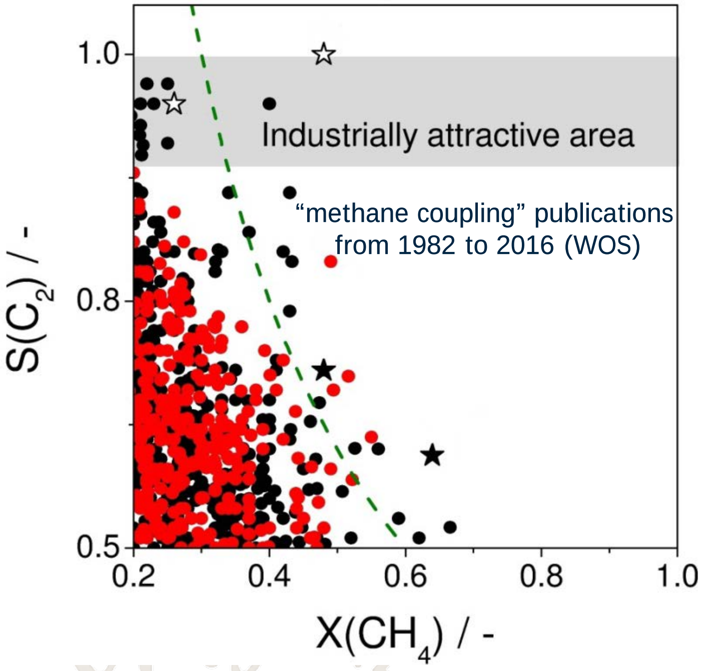
Add-mixing of bio-methane to the federal gas distribution net is less economical because the fuel value (HS) of so obtained methane is 10.7 kWh/m³, which is lower than 11.20 kWh/m³ delivered by Russian natural gas.

Biogas generation



DVGW Arbeitsblatt G 260; Ursprung des Biomethans: 3 % Restkohlendioxid z.B. Druckwechseladsorption, Druckwasserwäsche

Coupling of methane – close to industrialization?



Possible ways towards applications

1) Working at low conversion (X) and high selectivity (S)

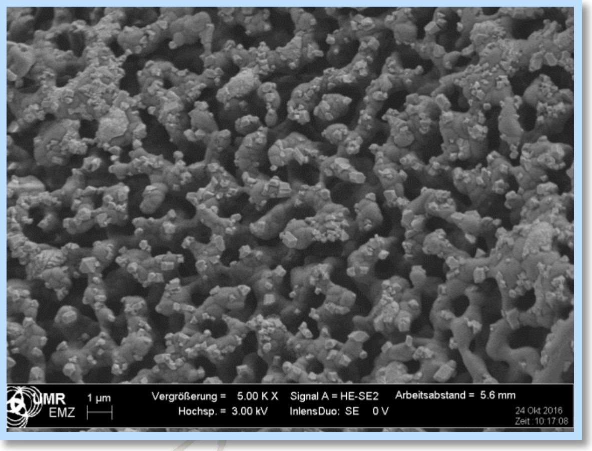
2) Oxygen free conversion

• data obtained after 2010
☆ absence of oxidants or
★ subsequent CO_x hydrogenation

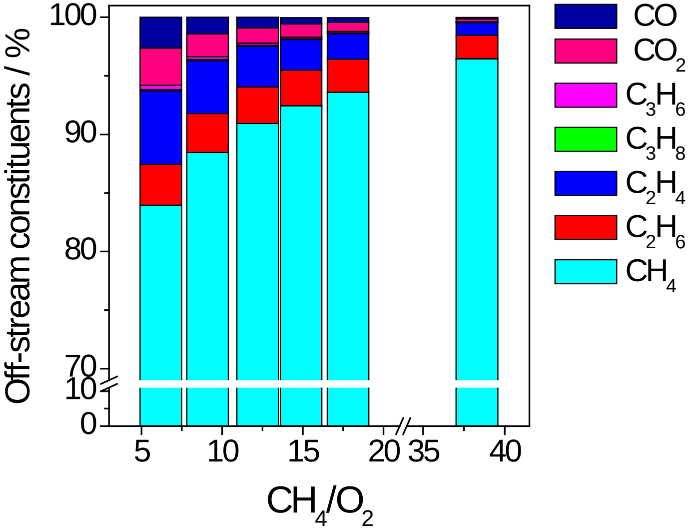
E.V. Kondratenko, T. Peppel, D. Seeburg, V.A. Kondratenko, N. Kalevaru, A. Martin, S. Wohlrab, *Catal. Sci. Technol.* **2017**, 7, 366-381.

iii) Oxidative coupling of methane (OCM) to C_{2+} hydrocarbons

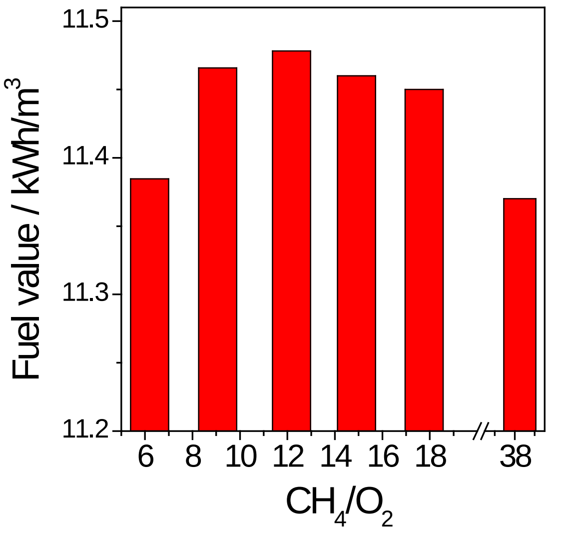
Increasing biogas heating value through conversion of methane into higher hydrocarbons



Porous silica as support for OCM-catalyst particles



Maximum H_S of 11.49 at CH_4/O_2 of 12. However, CH_4/O_2 = 38 yields H_S = 11.37, which is well above 11.2

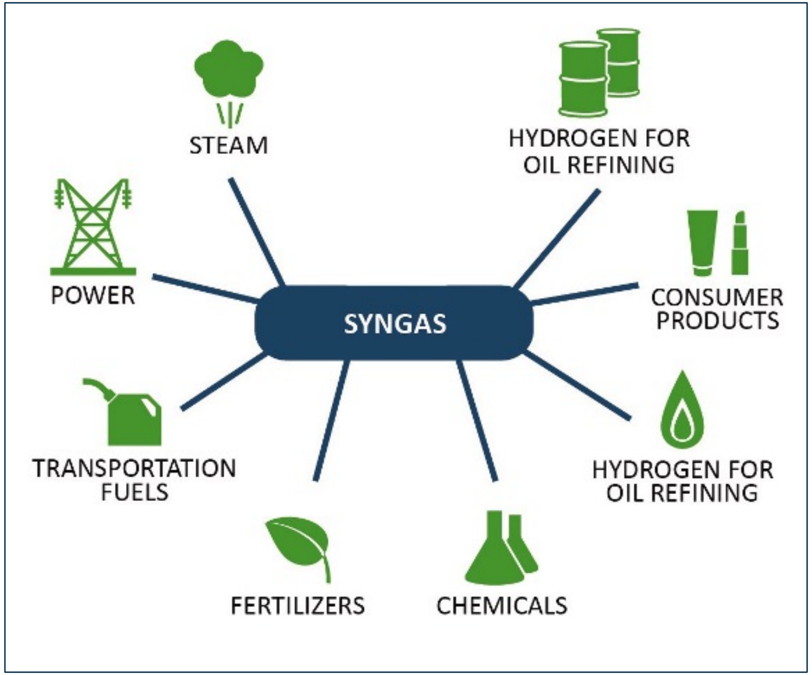


CO_x drops with increasing CH_4/O_2 to 0.24% CO_2 and 0.13% CO at CH_4/O_2 = 38

Syngas production

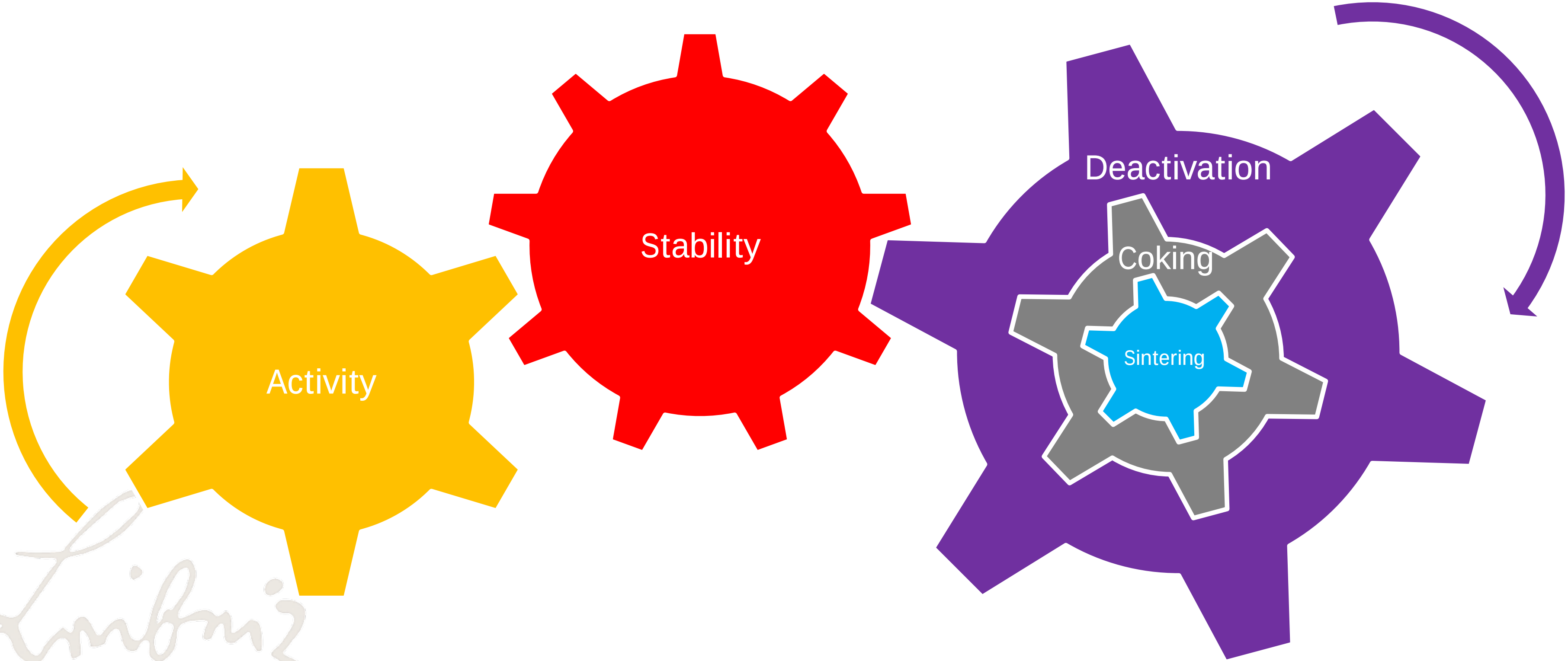
- Increasing demand of syngas, the main intermediate for chemicals, fuels and H_2.
- ➢ Dry reforming of methane (**DRM**) with CO_2 is promising.

- Application of Ni-based catalysts due to low cost and availability.
- Fast deactivation of Ni-based catalysts.
- ➢ Development of highly stable catalysts that can prevent coke deposition.



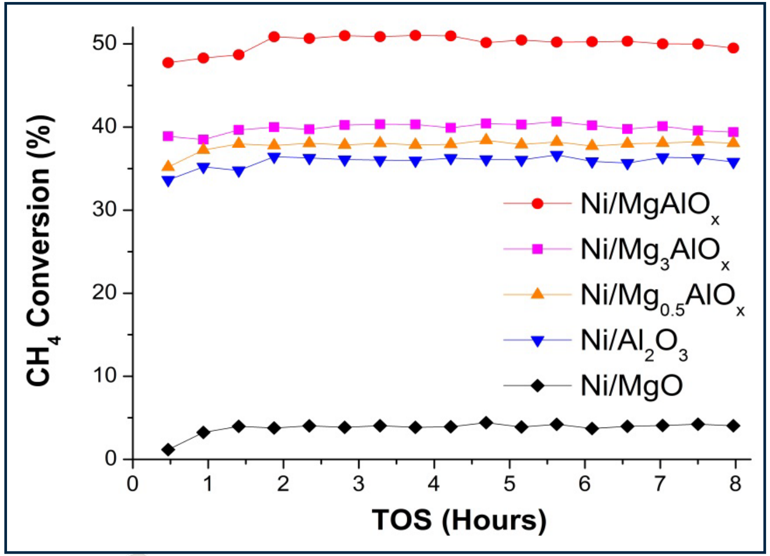
What determines a good catalyst?

Syngas ($CO + H_2$) production

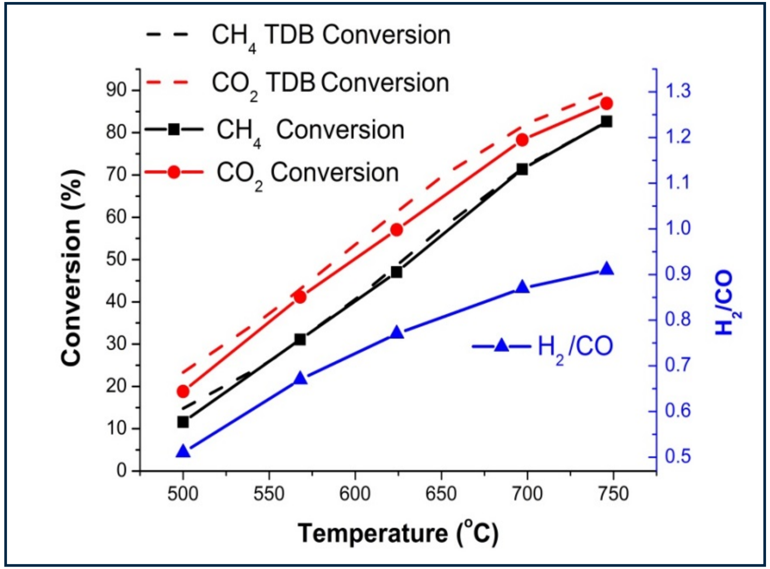


Catalysis LIKAT Leibniz-Institut für Katalyse e.V.

Development of a highly active Ni/MgAlO$_x$ catalyst



CH_4 conversion of the catalysts with different Mg/Al ratio.



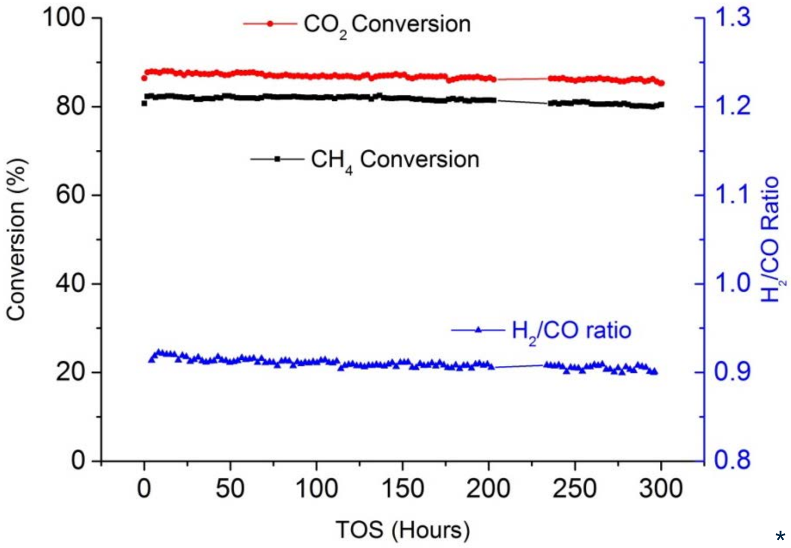
Ni/MgAlO$_x$ catalytic activity performance in comparison with thermodynamic balance (TBD) **
1 bar, CH_4/CO_2 = 1, WHSV = 100 L/(g_{cat}×h).

* Q. L. M, Ha et al., *Catalysts* **2017**, *7* (5), 157-173

Long term stability of a tailor made Ni/MgAlO$_x$ catalyst

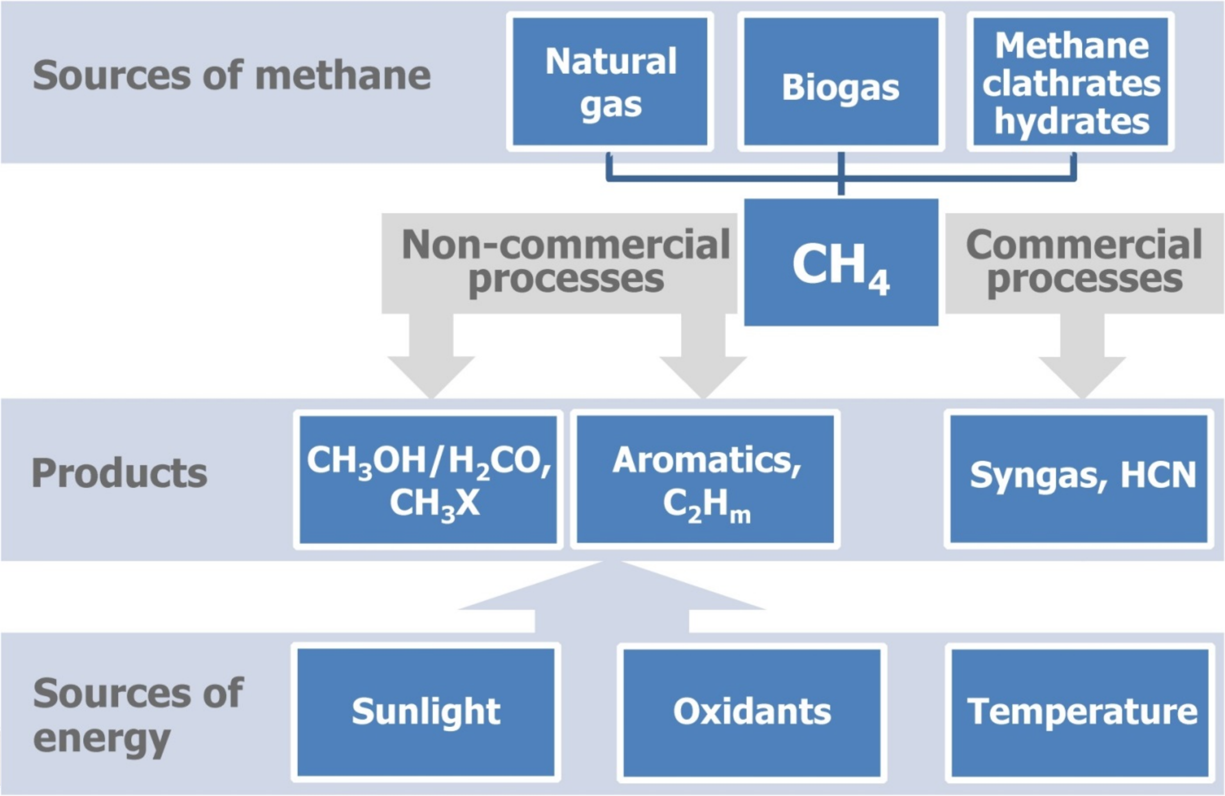
- **Ni/MgAlO$_x$.CA** (LIKAT type) shows high and stable DRM activity over 300 hours at high WHSV.
- Negligible carbon deposition (< 1%) after 300 h on stream, reflecting the high coking resistance, probably due to contribution of CO_2 gasification and stable dispersion of Ni species.

DRM conditions:
700 °C, 1 bar,
CH_4/CO_2 = 1,
WHSV = 170 L/(g_{cat}×h).



* Q. L. M, Ha et al., *Catalysts* **2017**, *7* (5), 157-173

Methane processing



X stands for $OOCCF_3$ or OSO_3H

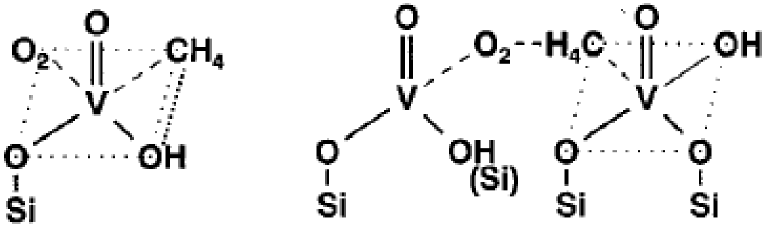
m = 2,4,6

Dream reactions: The formaldehyde issue

- Industrial production of CH_2O (ca. 25 Mio t/a)

$$CH_4 \xrightarrow[\text{Kat., T}]{+H_2O} CO + 3H_2 \xrightarrow[\text{Kat., T}]{-H_2} CH_3OH \xrightarrow[\text{Kat., T}]{+0{,}5O_2,\ -H_2O} CH_2O$$

- Direct oxidation of methane to formaldehyde using silica supported VO_X*

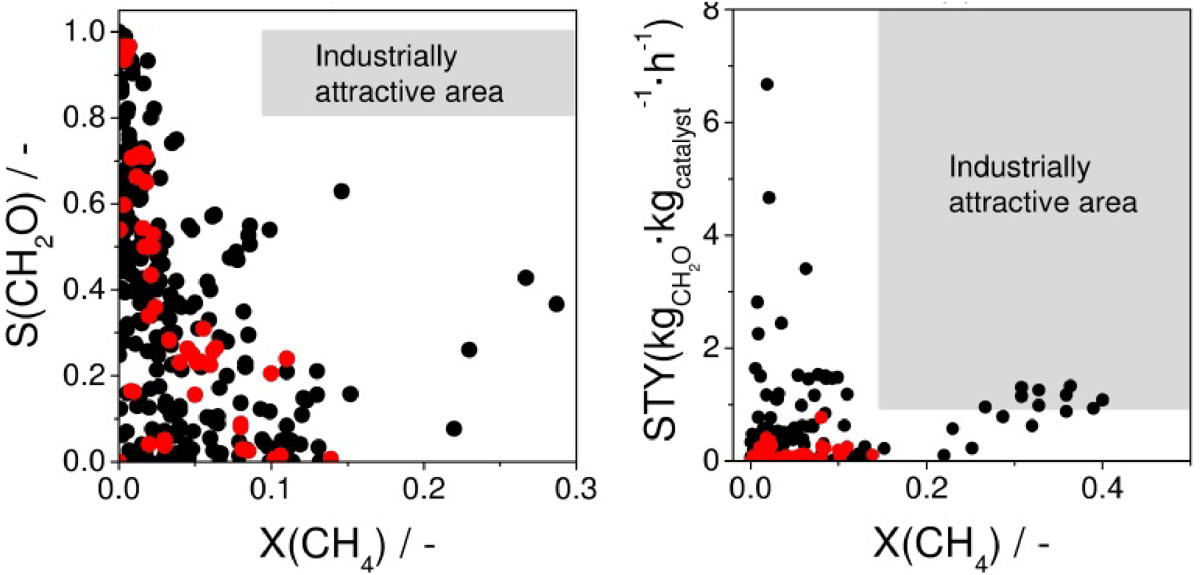


C. Pirovano, E. Schönborn et al. *Catalysis Today* **2012,** *192*, 20-27. P. Wallis, E. Schoenborn et al. *RSC Adv.* **, 2015**, 5, 69509-69513.
P. Wallis, S. Wohlrab et al. *Catalysis Today* **2016,** *278*, 120-126.
E.V. Kondratenko, T. Peppel et al. *Catal. Sci. Technol.* **2017**, 7, 366-381.

Coordination and activation of CH_4 and O_2 at VO_X species

State of the art

CH$_4$ conversion

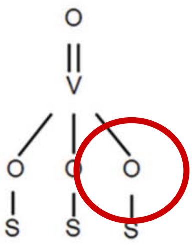


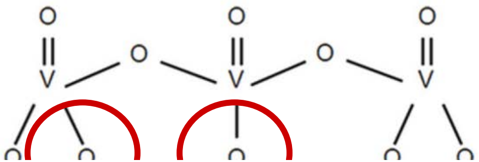
(a) Selectivity (S) to formaldehyde and (b) space-time-yield (STY) of formaldehyde obtained over various materials at different degrees of CH$_4$ conversion (X). The black and red datapoints are used to distinguish between studies before and after 2010, respectively.

Methane oxidation over V/Ti-SBA-15

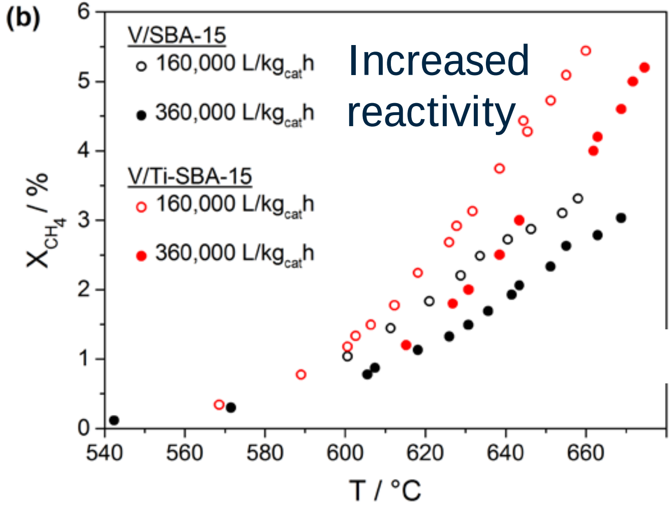
CH_4 conversion

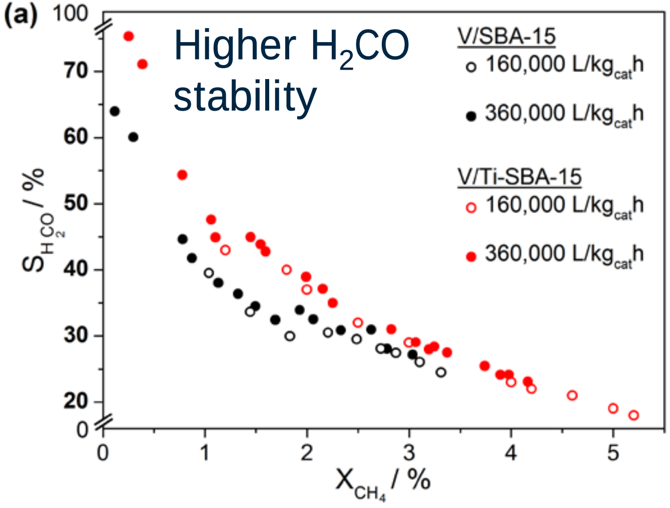
Better activation of **V-O-S**upport bonds
by lower electronegativities of the support





CH_4: O_2 = 9: 1
~ 2.8 wt% V

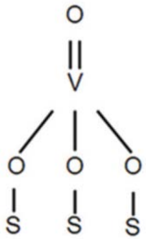




Hetero-Atom doping

Dopants of mesoporous silica (SBA-15)

Ti	783 m²/g	2,9 Gew%
V	844 m²/g	0,84 Gew%
Cr	861 m²/g	1,6 Gew%
Mn	458 m²/g	2,5 Gew%
Fe	649 m²/g	1,6 Gew%
Co	641 m²/g	2,8 Gew%
Ni	748 m²/g	2,7 Gew%
Cu	430 m²/g	2,9 Gew%
Zn	748 m²/g	3,1 Gew%
Zr	961 m²/g	3,4 Gew%
Nb	733 m²/g	3,6 Gew%
Mo	714 m²/g	Spuren
W	692 m²/g	6,2 Gew%

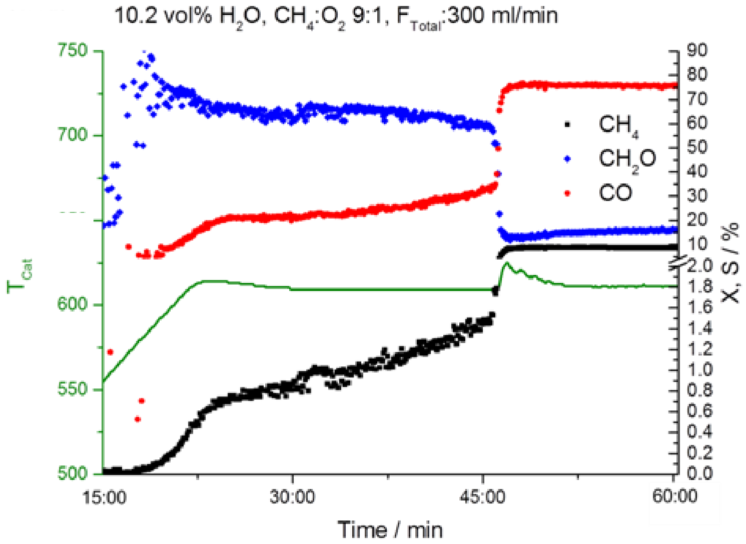


Increase in STY

blue: without H_2O

green: with H_2O

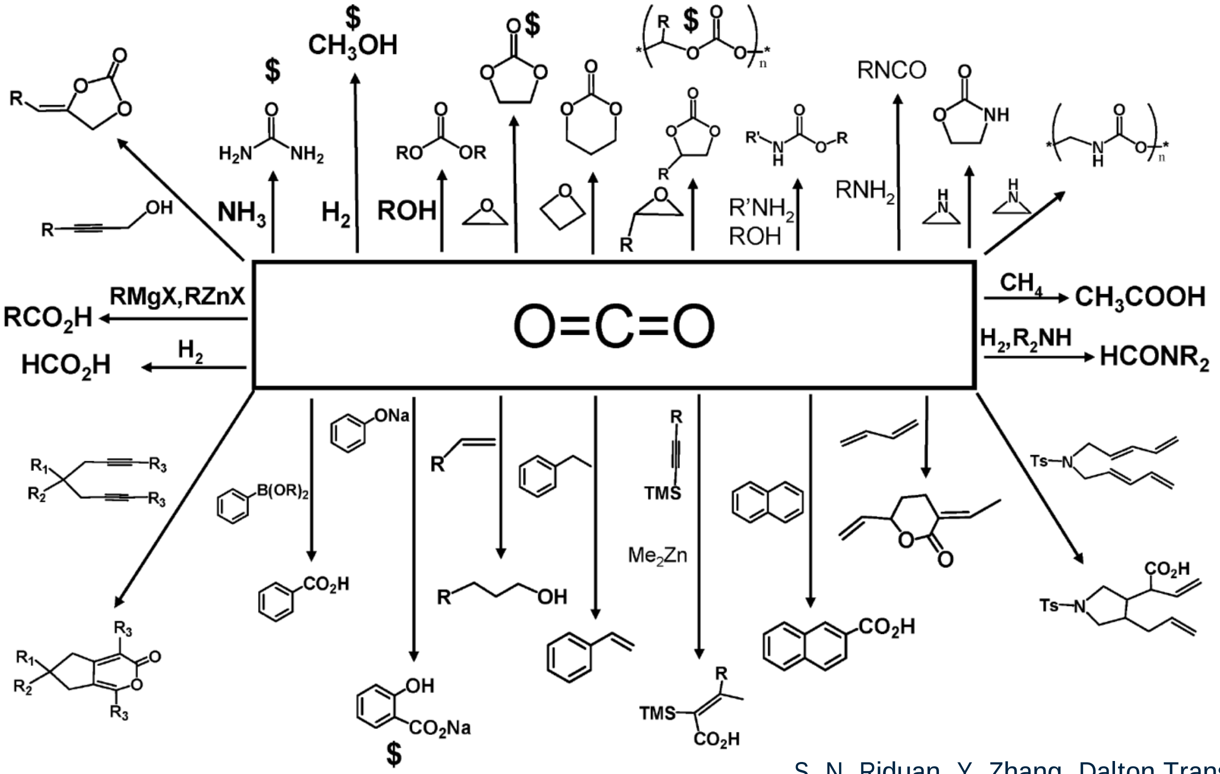
Dynamic systems



Utilization of CO_2

CO_2 conversion

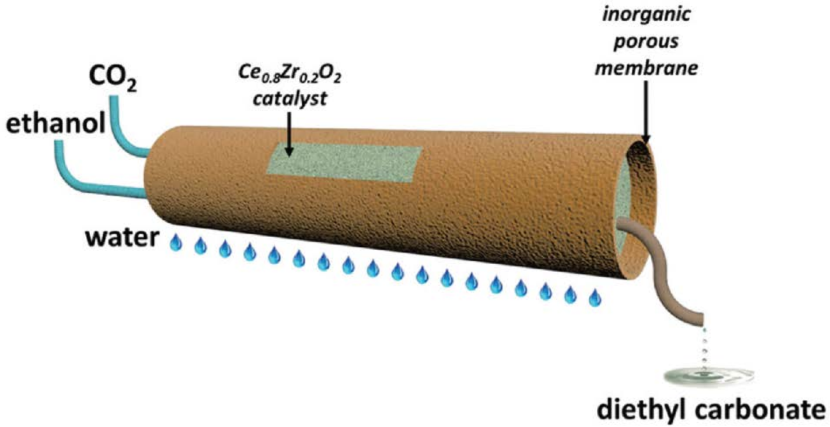
State of the art

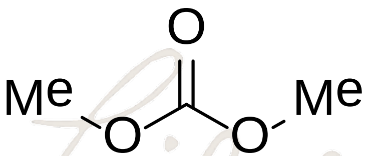


S. N. Riduan, Y. Zhang, Dalton Trans., 2010, 39, 3347-2257

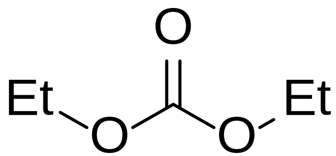
carbonic acid esters

- annual production of carbonic acid esters ca. 18 Mt
- applications:
  - » Solvents
  - » alkylation-/acylation agent
  - » fuel additive/antiknock agent
  - » Phosgene-substitute
  - » electrolyte in lithium-ion-batteries
  - » monomer for polymers (polycarbonates)





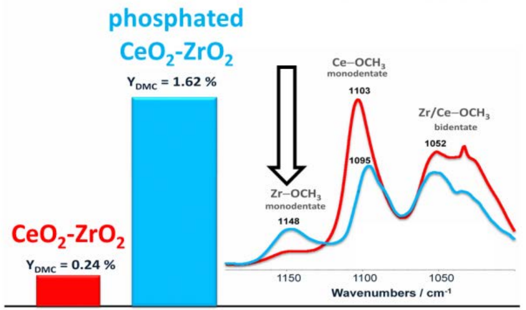
DMC



DEC

Synthesis of dialkyl carbonates from CO_2

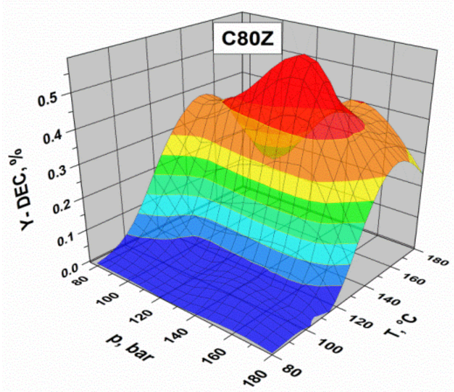
BATCH



$$2CH_3OH + CO_2 \rightleftarrows (CH_3O)_2CO + H_2O$$

I. Prymak, ..., S. Wohlrab*, *CemCatCHem, accepted*

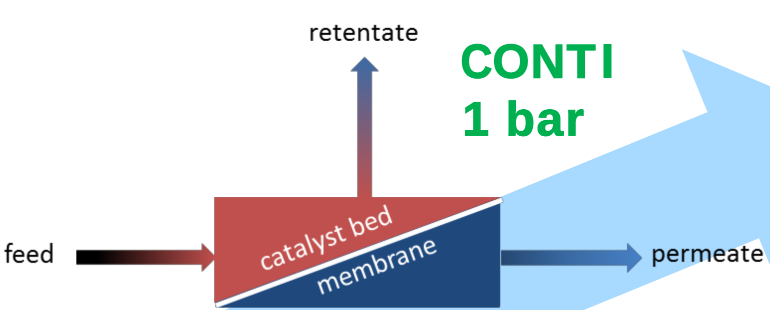
CONTI



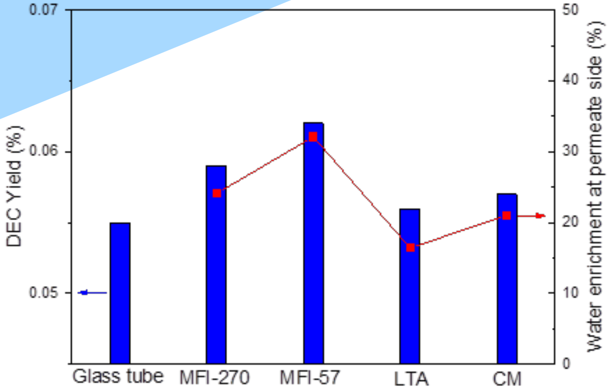
Best performance under supercritical conditions

I. Prymak, ..., S. Wohlrab*, *Catal. Sci. Technol.* **2015**, 5, 2322–2331

CONTI 1 bar



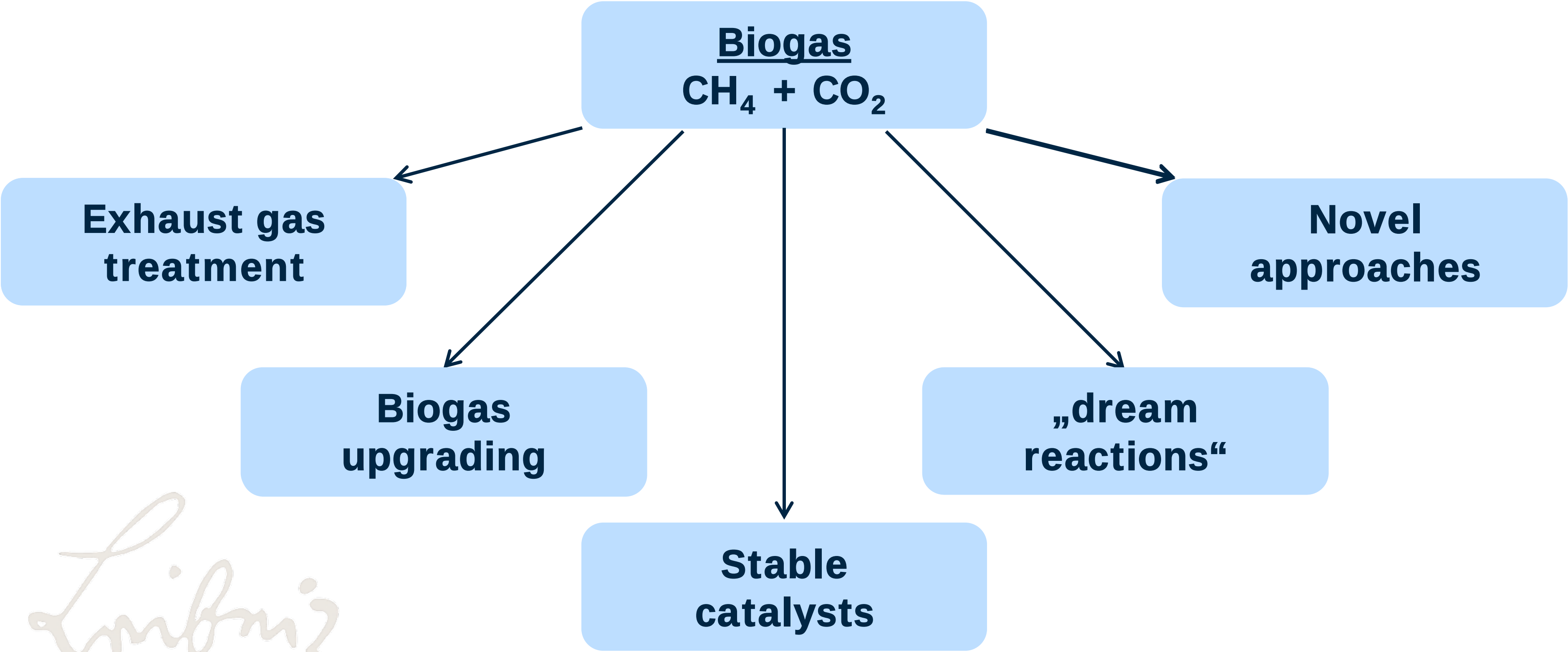
R. Dragomirova, S. Wohlrab, *Catalysts* **2015**, 5, 2161-2222



- **Increase in yield with water removal**
- **higher productivity compared to batch**

J. Wang, Z. Hao, S. Wohlrab, Green Chemistry, **2017**, 19, 3595-3600

Ways of biogas utilization



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