

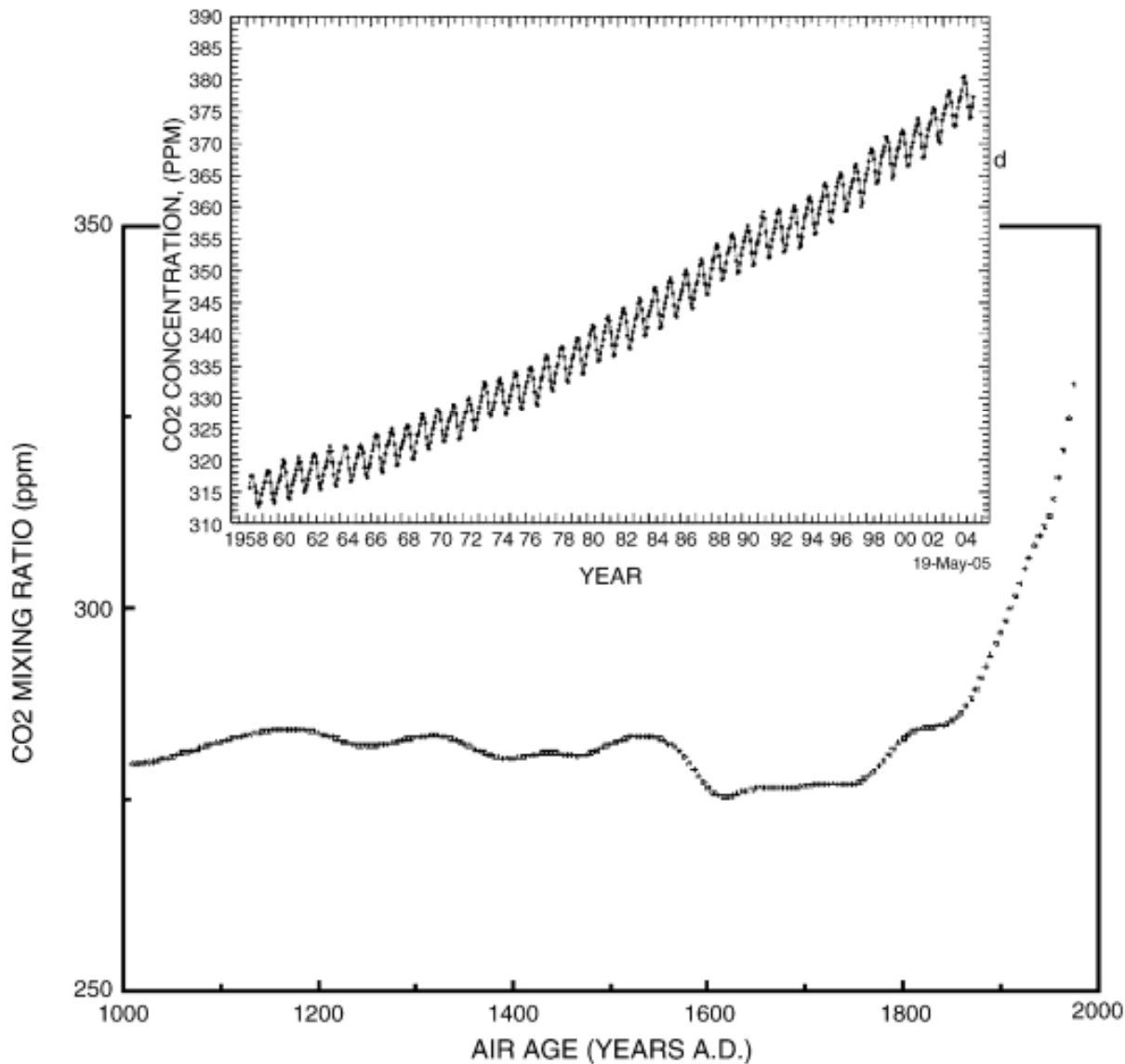


Utilization of CO₂

Lecture series: Modern Methods in
Heterogeneous Catalysis Research

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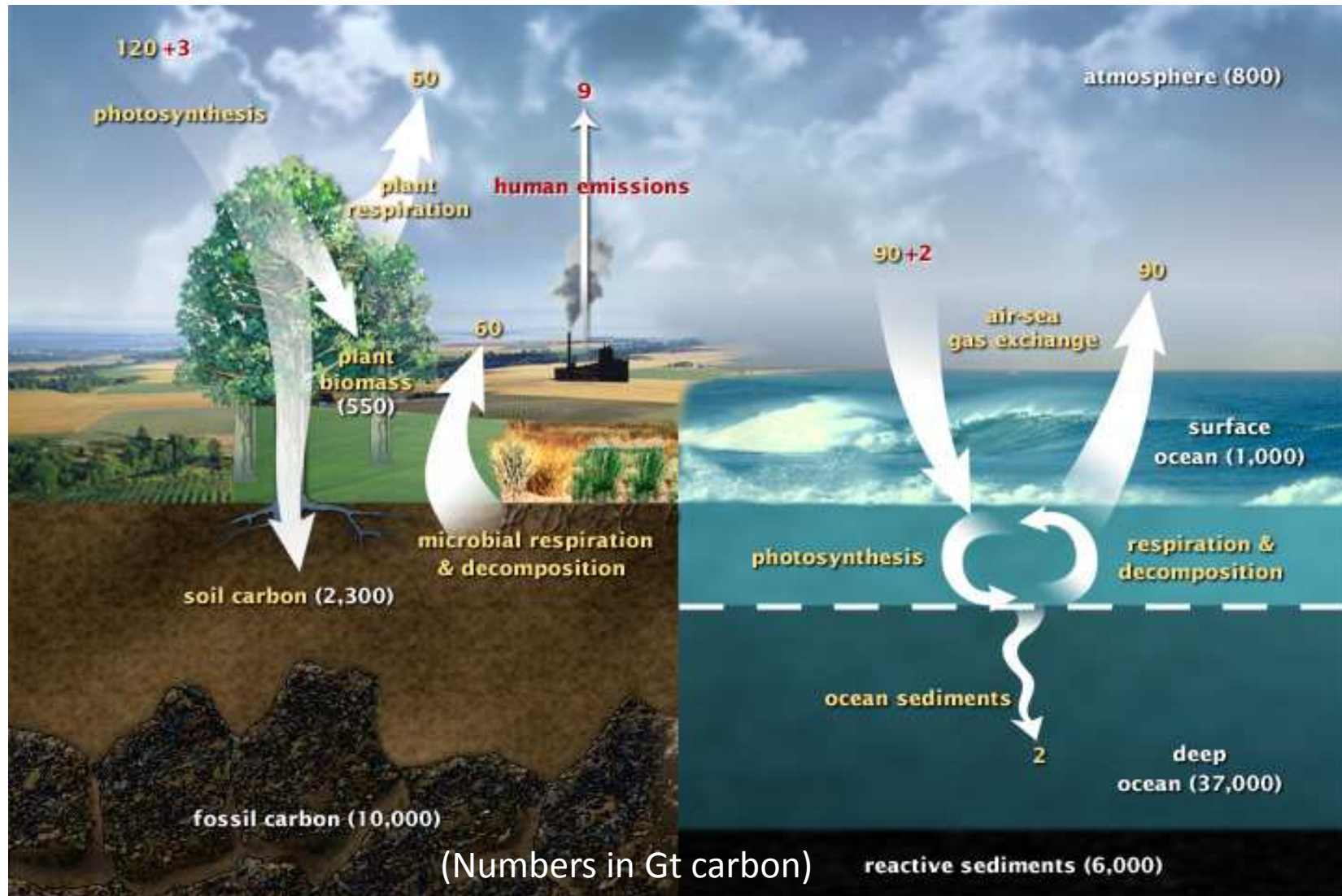
CO₂ emissions



2012:
400 ppm CO₂ in arctic
measurement

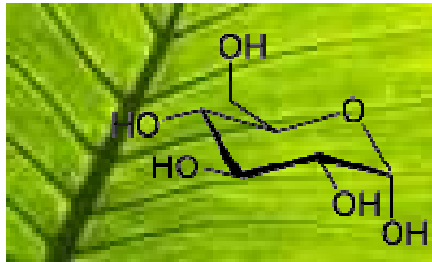
CO₂ emissions:
~ 30 Gt / year (2008)
Due to fossil fuel
combustions for
energy applications

Global carbon cycle



Wikimedia Commons, Source: <http://earthobservatory.nasa.gov/Features/CarbonCycle/>

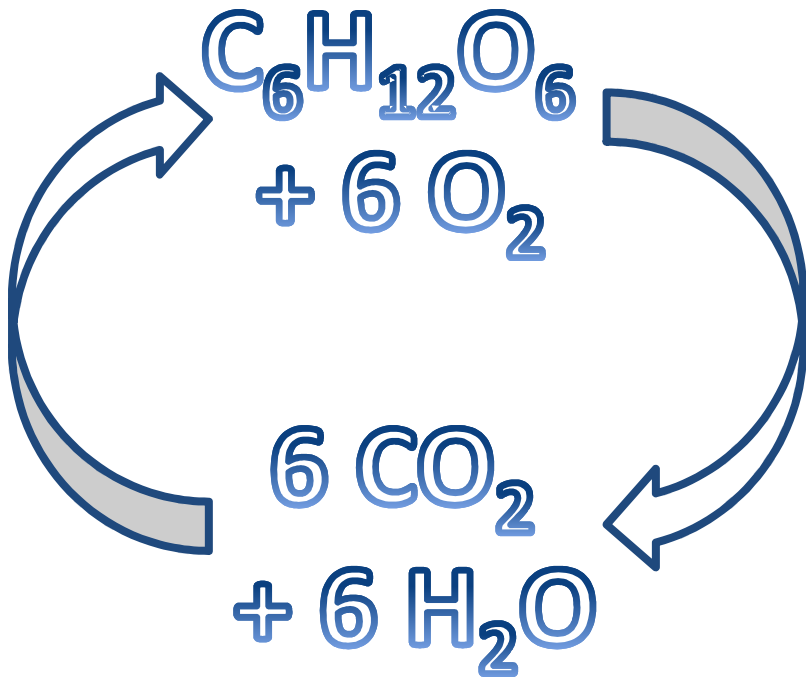
CO₂ conversion in nature: Photosynthesis



Energy

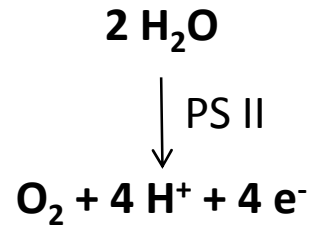


Photosynthesis

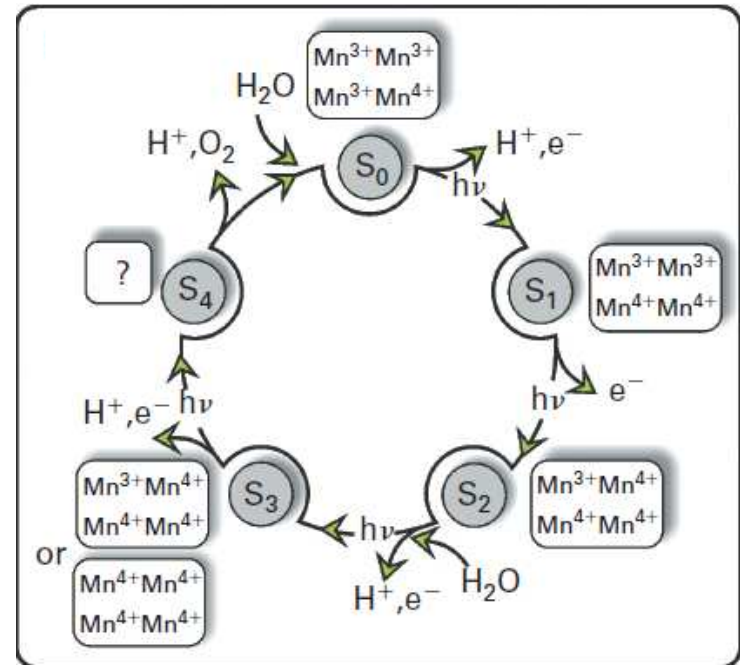


Respiration

Oxidation of water:

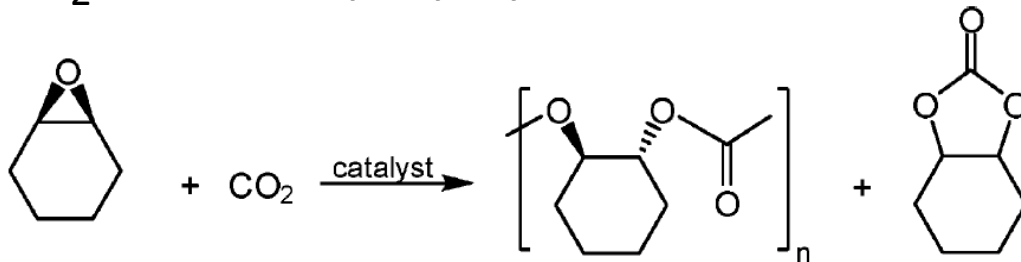


N. Cox, W. Lubitz:
„Molecular Concepts
of Water Splitting:
Nature’s Approachs“,
In: *Energy Storage
Materials*, Hrsg: R.
Schlögl, De Gruyter,
Berlin, 2012.



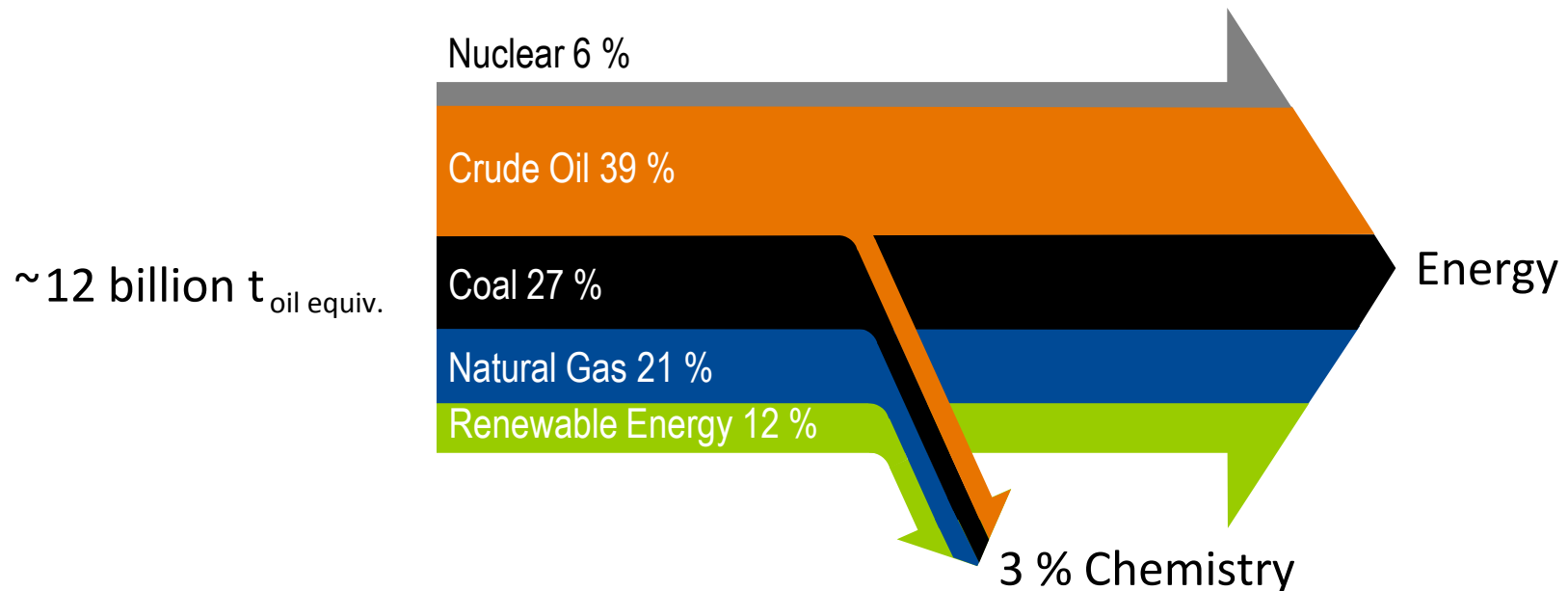
Today's industrial use of CO₂

- Synthesis of polymers (plastics)
 - For example: Copolymerization of cyclohexene oxide and CO₂ to afford poly(cyclohexene carbonate)



- Urea synthesis (70 Mt CO₂ / year)
 - $\text{CO}_2 + 2 \text{NH}_3 \rightarrow \text{H}_2\text{N-CO-NH}_2 + \text{H}_2\text{O}$
- Salicylic acid synthesis (20 kt CO₂ / year)
 - $\text{C}_6\text{H}_5\text{-OH} + \text{CO}_2 \rightarrow \text{C}_6\text{H}_4(\text{OH})\text{COOH}$
- Ca. 110 Mt / year for chemicals, inorganic pigments and methanol (**< 1% of global CO₂ emissions**)

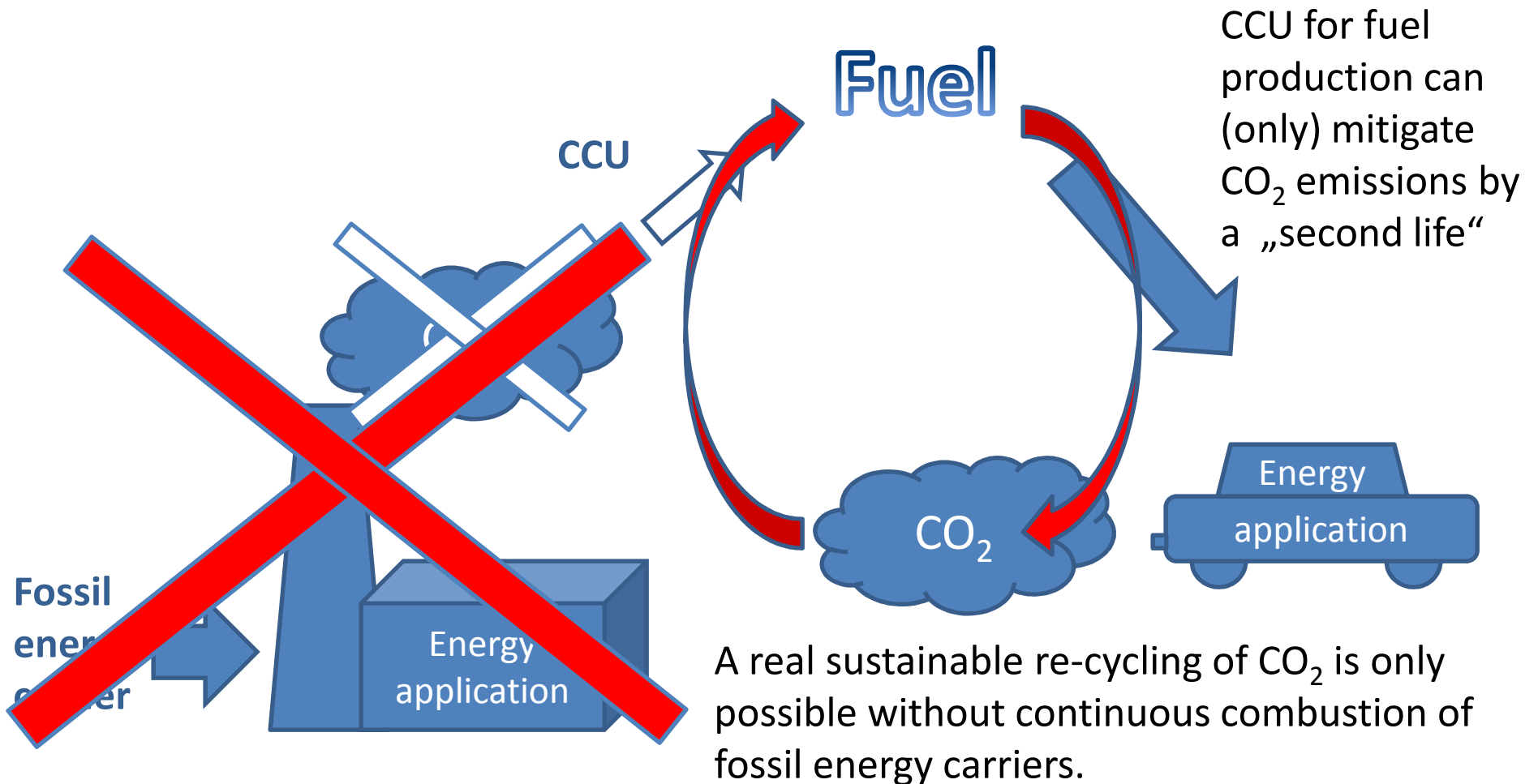
Chemicals vs. fuels



F. Seitz: „ Raw Material Change in the Chemical Industry and the Role of Biomass“, In: *Heterogeneous Catalysis for the Conversion of Biomass and Its Derivatives*, Hrsg: M. Behrens und A. Datye, Edition Open Access, Dez. 2012.

→ For a large scale reduction of CO₂ emissions, the target of CO₂ conversion must be fuels rather than chemicals

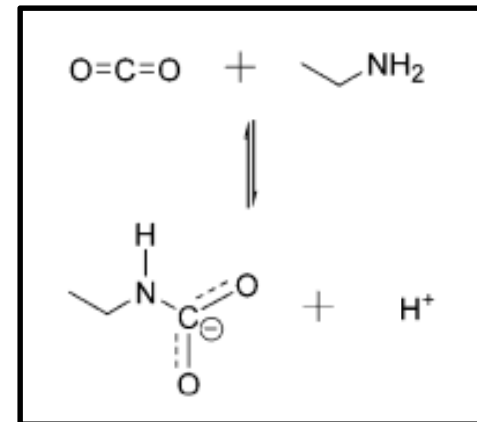
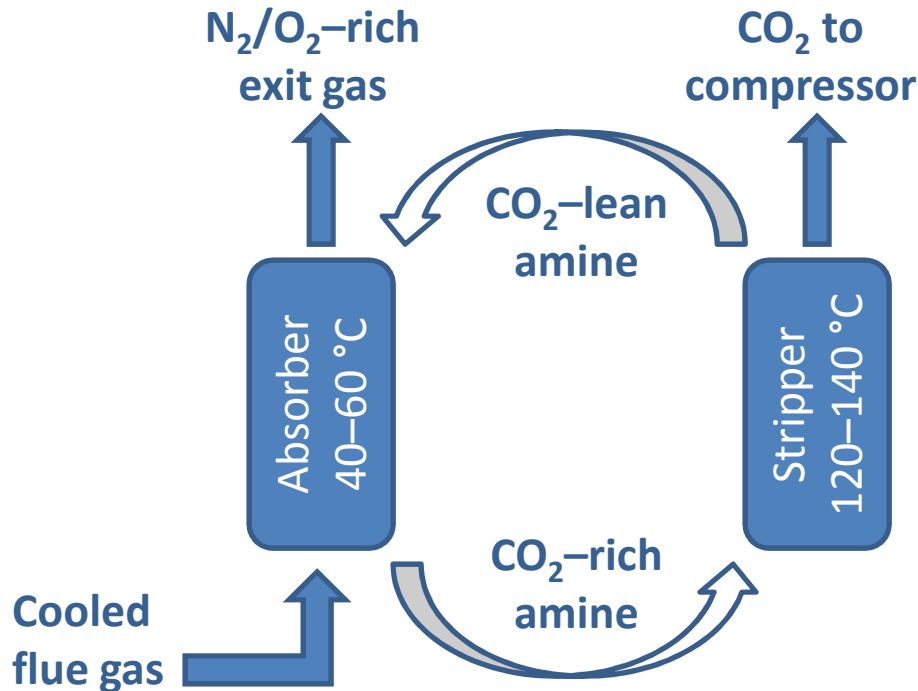
CCU = CO₂ recycling (?)



CCU is no justification to continue the use of conventional fossil power generation.

Carbon capture

- Absorption of CO_2 from flue gas in suitable adsorbent, mainly aqueous solutions of alkanolamines, e.g. 30-40% MEA (monoethanolamine) in H_2O



Drawbacks:

- Alternatively, membranes or solid adsorbents, e.g. amines grafted on porous solid supports

- low CO_2 loading capacity
- high equipment corrosion rate;
- amine degradation by SO_2 , NO_2 , and O_2 in the flue gases which induces a high absorbent makeup rate
- high energy consumption during high temperature absorbent regeneration
- large equipment size

Reactivity of CO₂

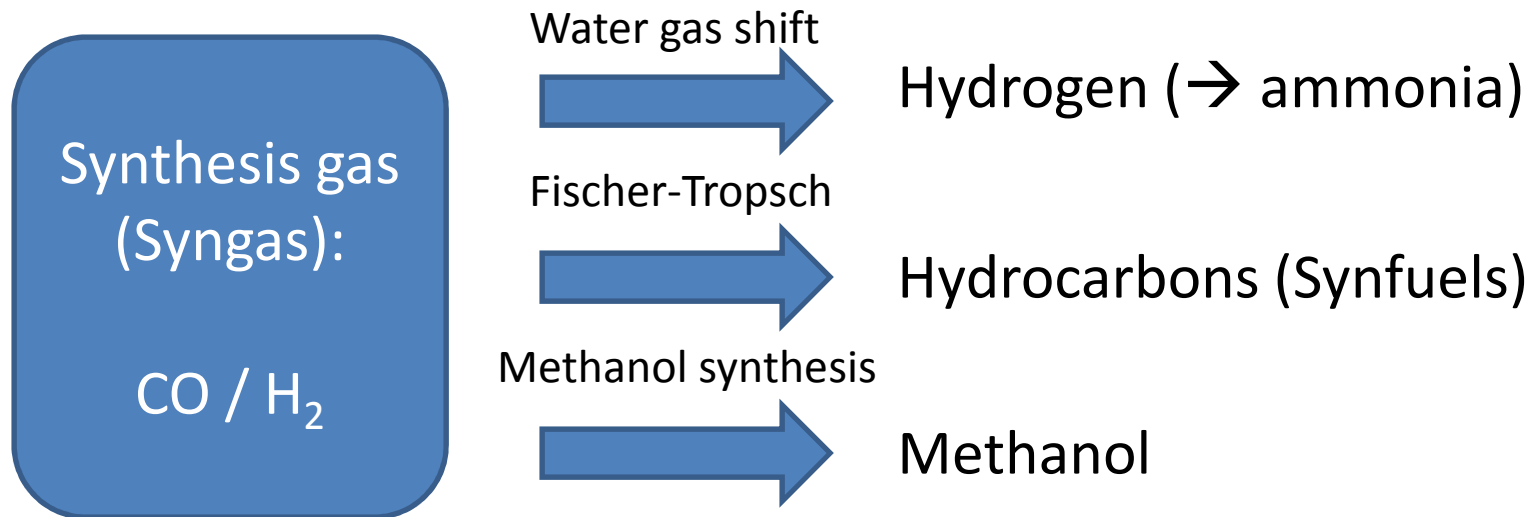
- High thermodynamic stability,
 - $\Delta H_f = -394$ kJ/mol
- Apolar, low reactivity
- But can be activated
 - Lewis basicity of the O atoms
 - C atom is electrophilic
- Reactions of CO₂ dominated by nucleophilic attack on C of electron donating reagents, surface sites or organometallic complexes
- And/or electrophilic attack on O atoms

CO₂-to-fuels: Overview

- Reduction of CO₂ to higher-energy molecules
 - Reactions with hydrogen:
 - rWGS to form CO (→ syngas chemistry → fuels)
 - Hydrogenation to form methanol, (DME)
 - Hydrogenation to form methane (Sabatier reaction)
 - Hydrogenation to form formic acid
 - Reactions with hydrocarbons:
 - CO₂-reforming of methane
- Thermochemical conversion of CO₂
- Electrochemical conversion of CO₂
- Photoelectrochemical conversion of CO₂

Syngas chemistry

- Current technology in C1 chemistry for production of fuels and chemicals



Syngas production today

- Syngas is produced from fossil sources
- Coal-derived syngas
 - $C + H_2O \rightarrow CO + H_2$
 - Gasification of coal
- Natural gas derived syngas
 - $CH_4 + H_2O \rightarrow CO + 3 H_2$
 - Steam reforming of natural gas

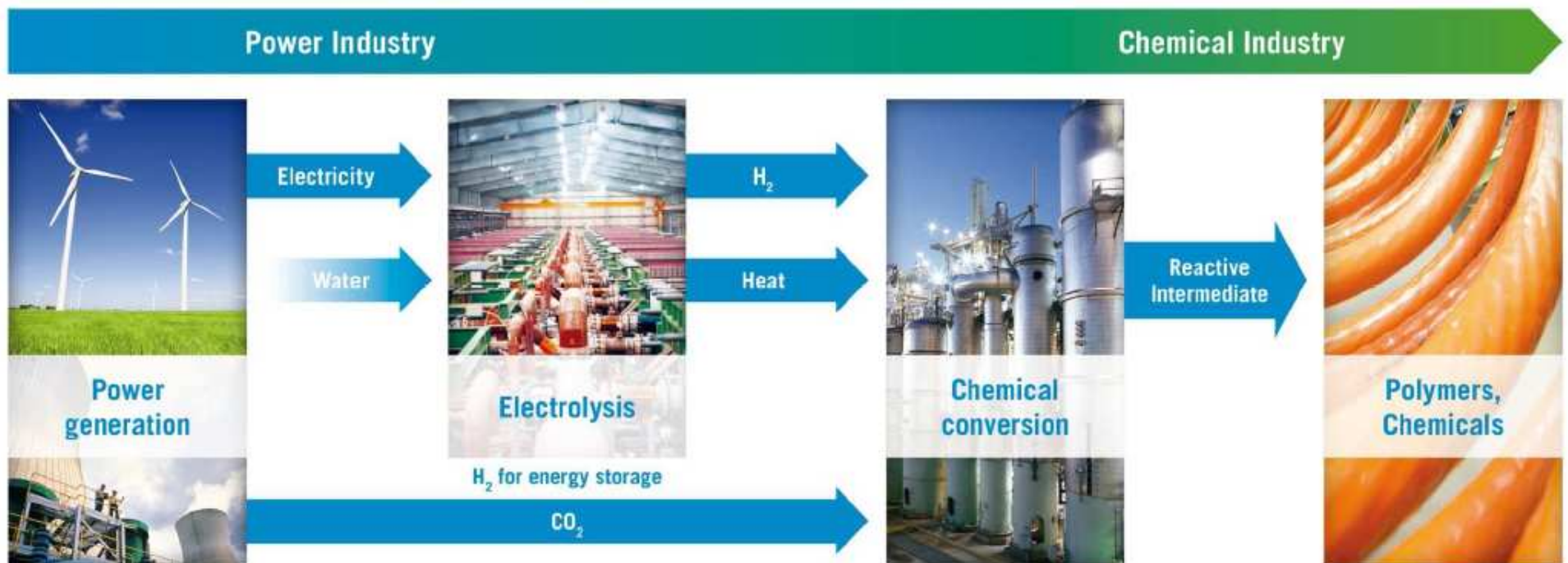


Syngas from CO₂: rWGS

- Reverse water gas shift reaction
 - $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ $\Delta H = 41.2 \text{ kJ/mol}$
- H₂/CO ratio in syngas is adjusted by the WGS equilibrium
 - Cu-Zn catalysts for low temperature shift (LTS), Fe-Cr catalysts for HTS
- Need for development of improved catalysts for rWGS (Cu/ZnO, Pt/CeO₂, ...)
- Reaction engineering approaches to improve CO yield: Removal of water

rWGS R&D activities

CO₂RRECT-Project: *CO₂-Reaction Using Regenerative Energies and Catalytic Technologies*



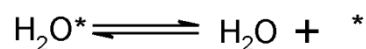
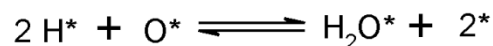
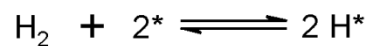
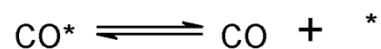
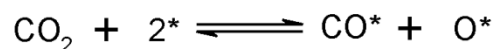
GEFÖRDERT VOM



Bundesministerium
für Bildung
und Forschung

The mechanism of rWGS

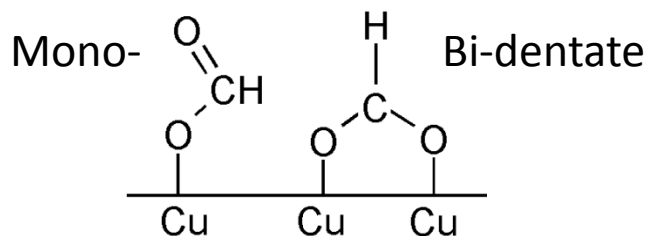
Surface redox mechanism



– subsequent CO_2/H_2 cycles

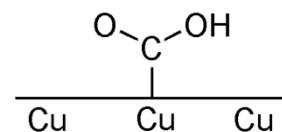
Ginés, M. et al. *Appl. Catal., A*, **1997**, 154, 155

Formate intermediates

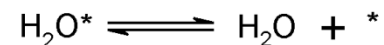
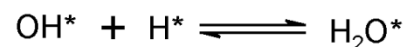
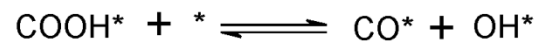
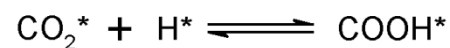
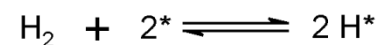
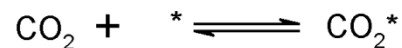


Yoshihara, J. & Campbell, C.T. *J. Catal.*, **1996**, 161, 776

Carboxyl mechanism



Gokhale, A.A. et al. *J. Am. Chem. Soc.*, **2008**, 130, 1402



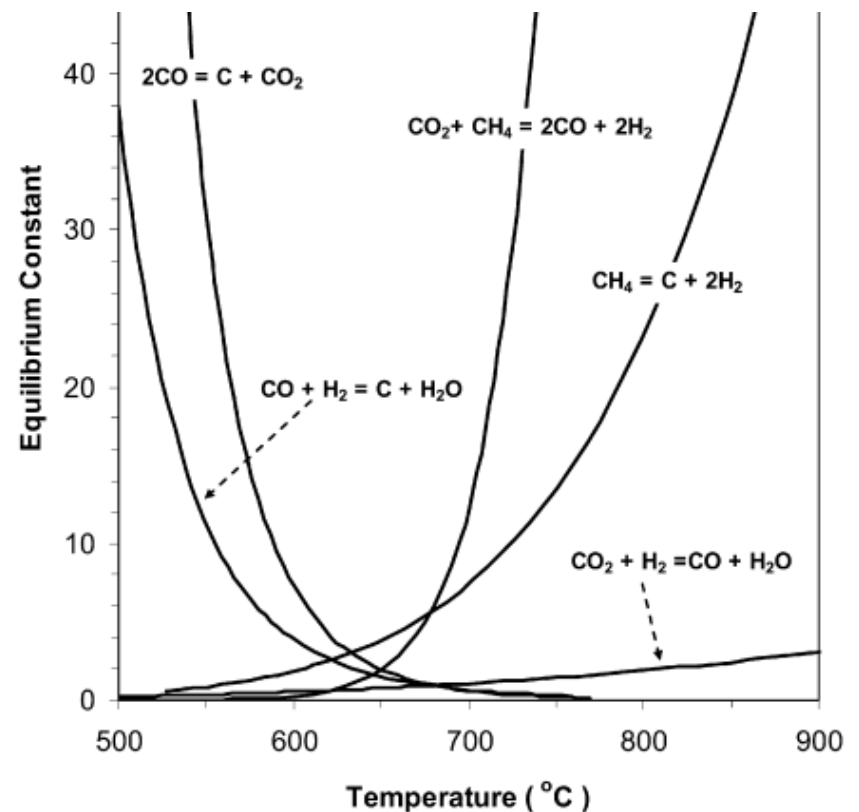
Yang, Y. et al. *Phys. Chem. Chem. Phys.*, **2010**, 12, 9909

Syngas from CO₂: Dry reforming

- Reduction of CO₂ with CH₄



- Highly endothermic
- High temperatures required (>700°C)
- Noble (Ru, Rh) and base metal (Ni) catalysts are active
- Strong influence of the support
- Challenges: Limited stability due to sintering and carbon deposits



Combined dry and steam reforming pilot plant in Japan

- Addition of steam



- Syngas is produced with lower CO₂/Carbon and H₂O/Carbon molar ratios.
低CO₂/炭素比、低スチーム/炭素比の原料から合成ガスの製造が可能
- Newly-developed catalyst has high resistance to carbon deposition under severe CO₂/Steam reforming condition.
炭素析出の起こりにくい新触媒を開発



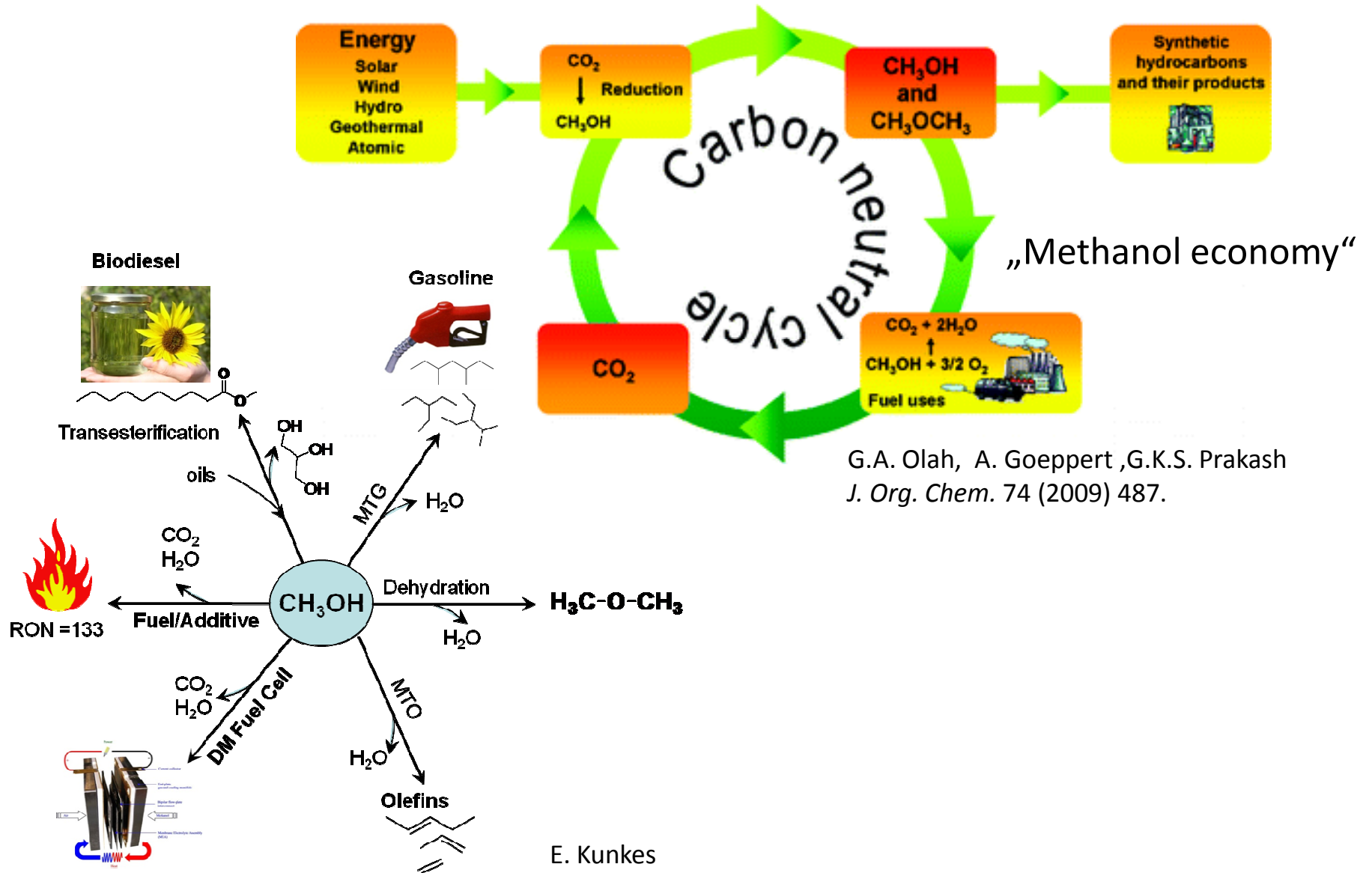
Temperature (Catalyst bed outlet) : 865~895°C, Pressure : 1.5~1.9MPaG
Feed Molar Ratio Hydrocarbon/CO₂/H₂O = 1.0/0.4~0.6/1.15~1.64

Catalyst:
Rh/Ru/MgO

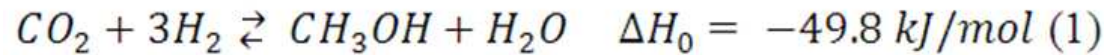
http://japan-gtl.com/pdf/Brochure_niigata_nippon_gtl.pdf

- Addition of O₂: „Tri-reforming“

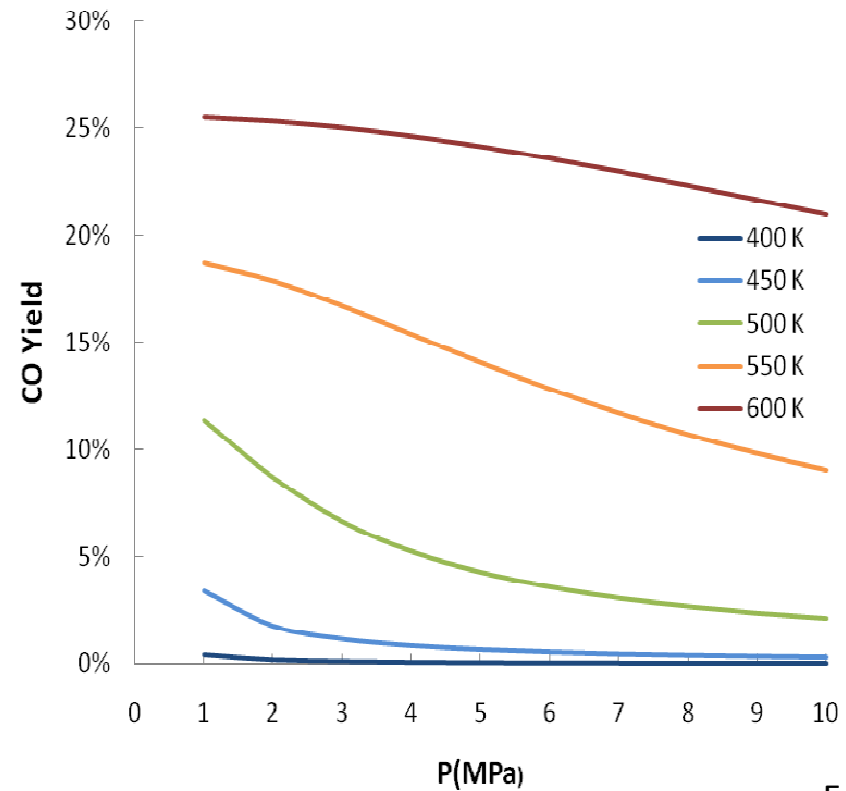
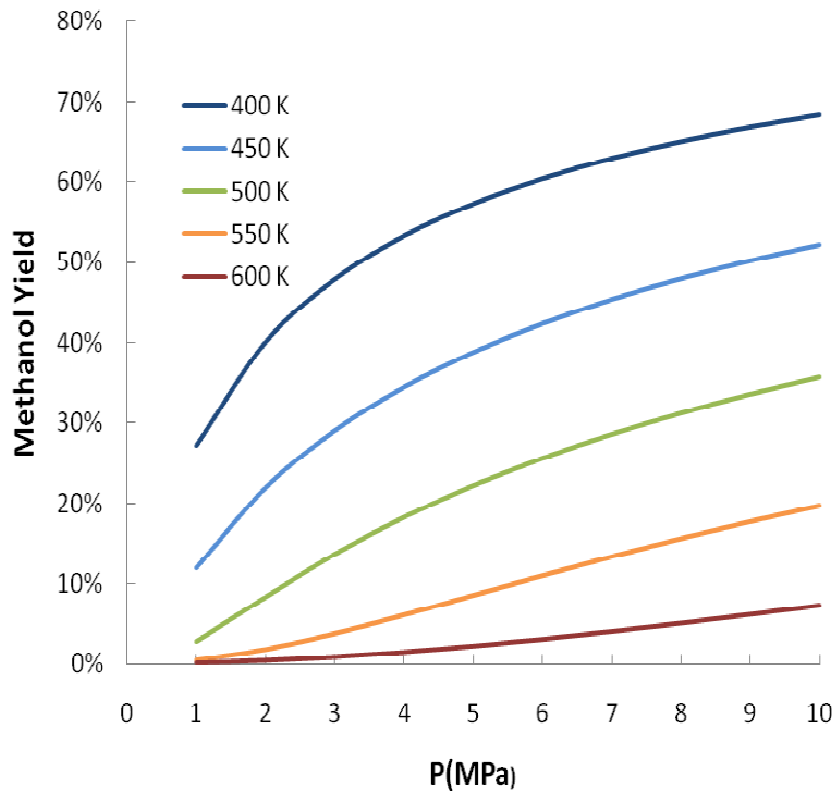
CO₂ hydrogenation to methanol



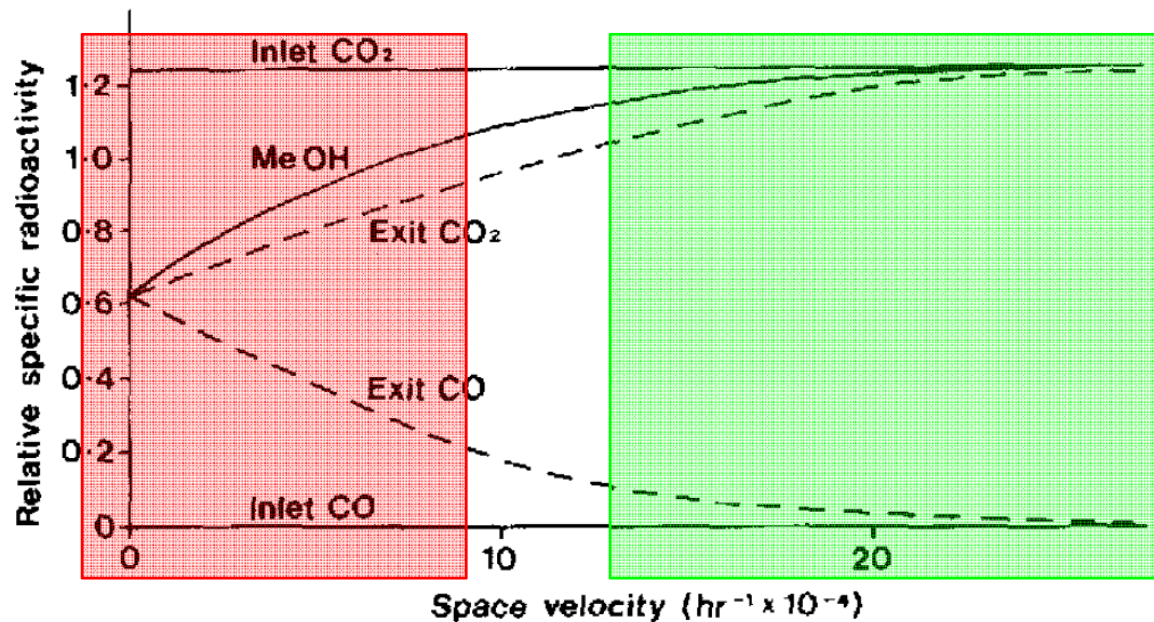
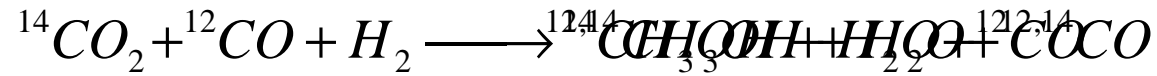
Thermodynamics of CO₂ hydrogenation



Equilibrium yields
from 1:3 CO₂/H₂



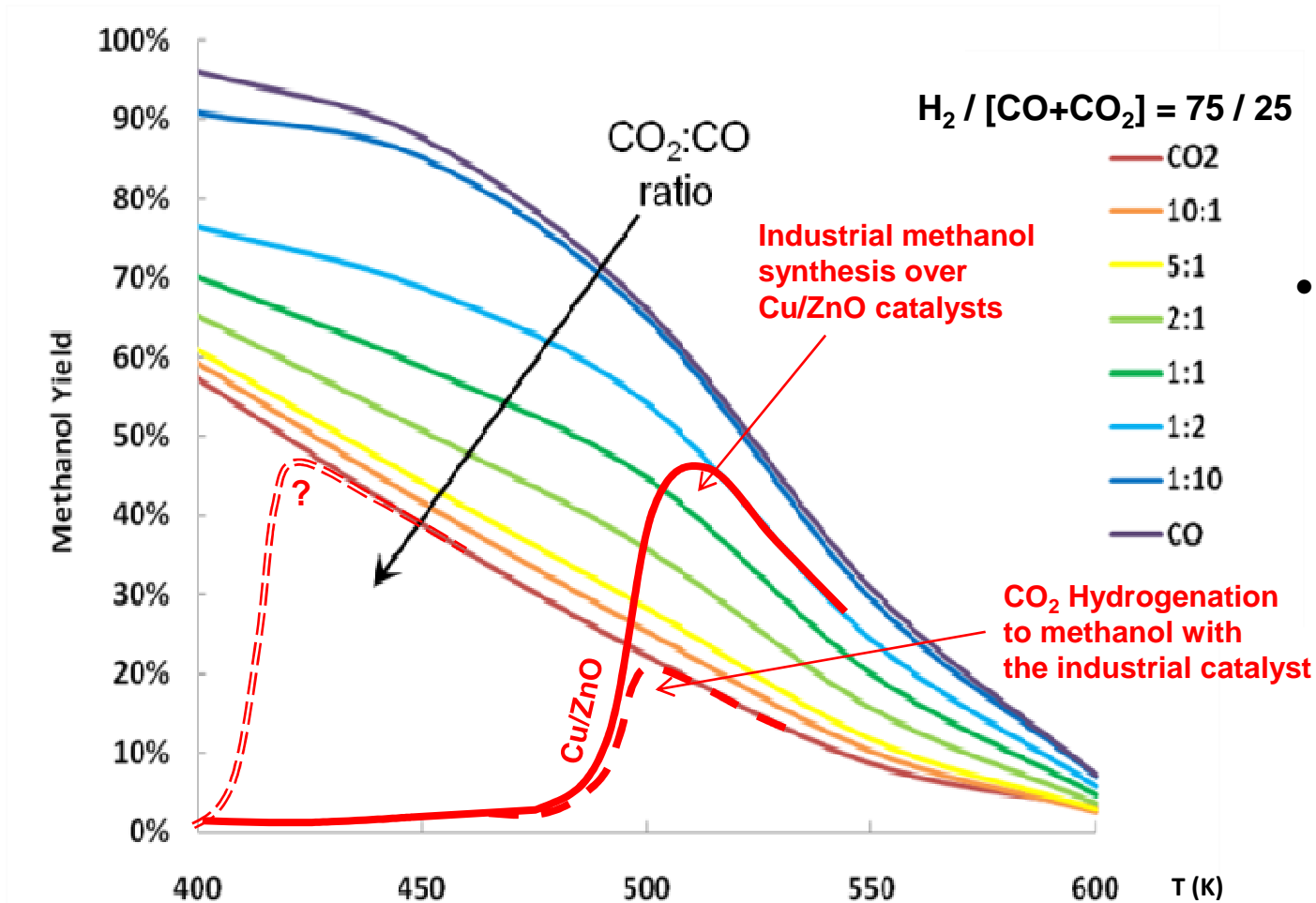
The carbon source for methanol



- On Cu Catalysts, CO₂ is observed to react much faster than CO to form methanol

G. C. Chichen, et. al. *Applied Catalysis* 30 (1987) 333-338

Methanol: Challenges

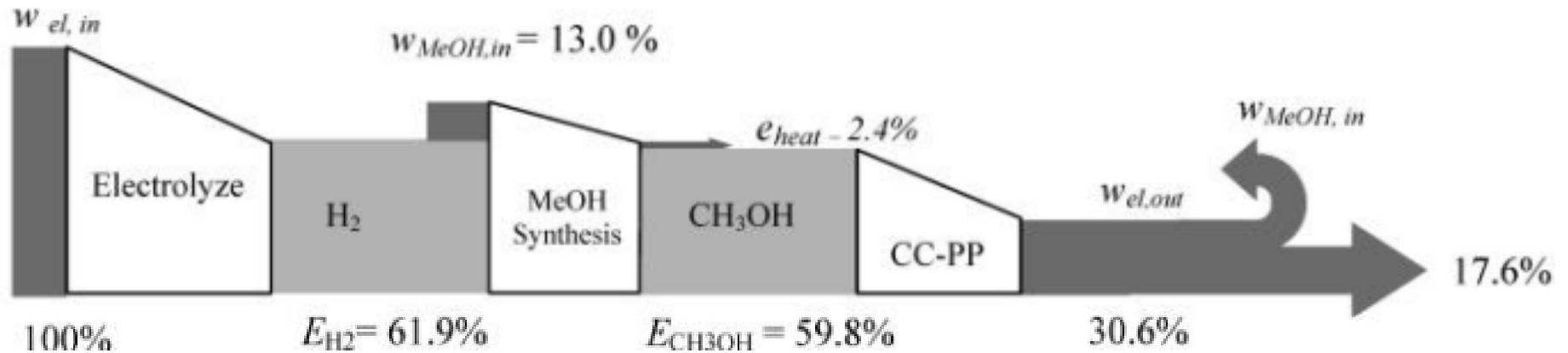


• Challenges

- low temperature activity
- product inhibition by water
- selectivity to methanol vs. CO

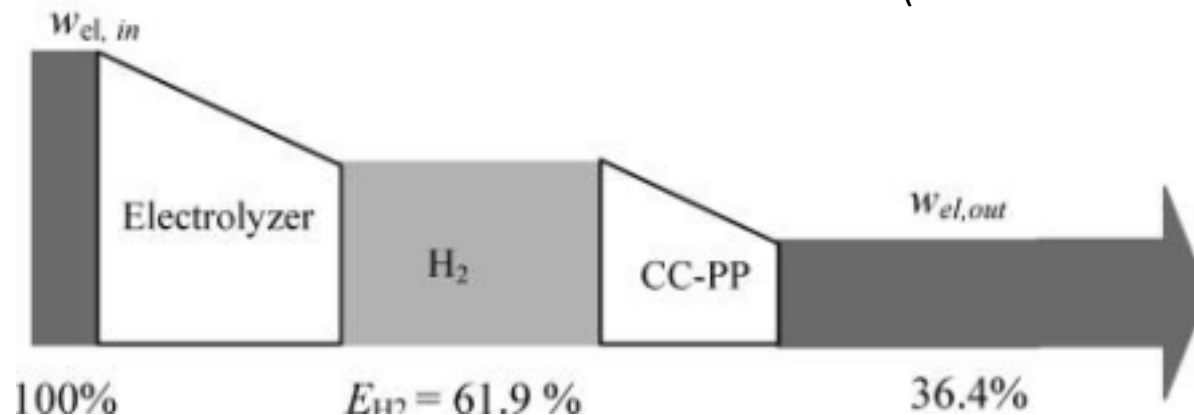
Renewable energy storage in MeOH

Methanol



Hydrogen

(CC-PP: Combined Cycle Power Plant)



The „CAMERE“ Process (Korea)

Ind. Eng. Chem. Res. **1999**, *38*, 1808–1812

- Carbon dioxide hydrogenation to form **methanol** via a **reverse-water-gas-shift** reaction

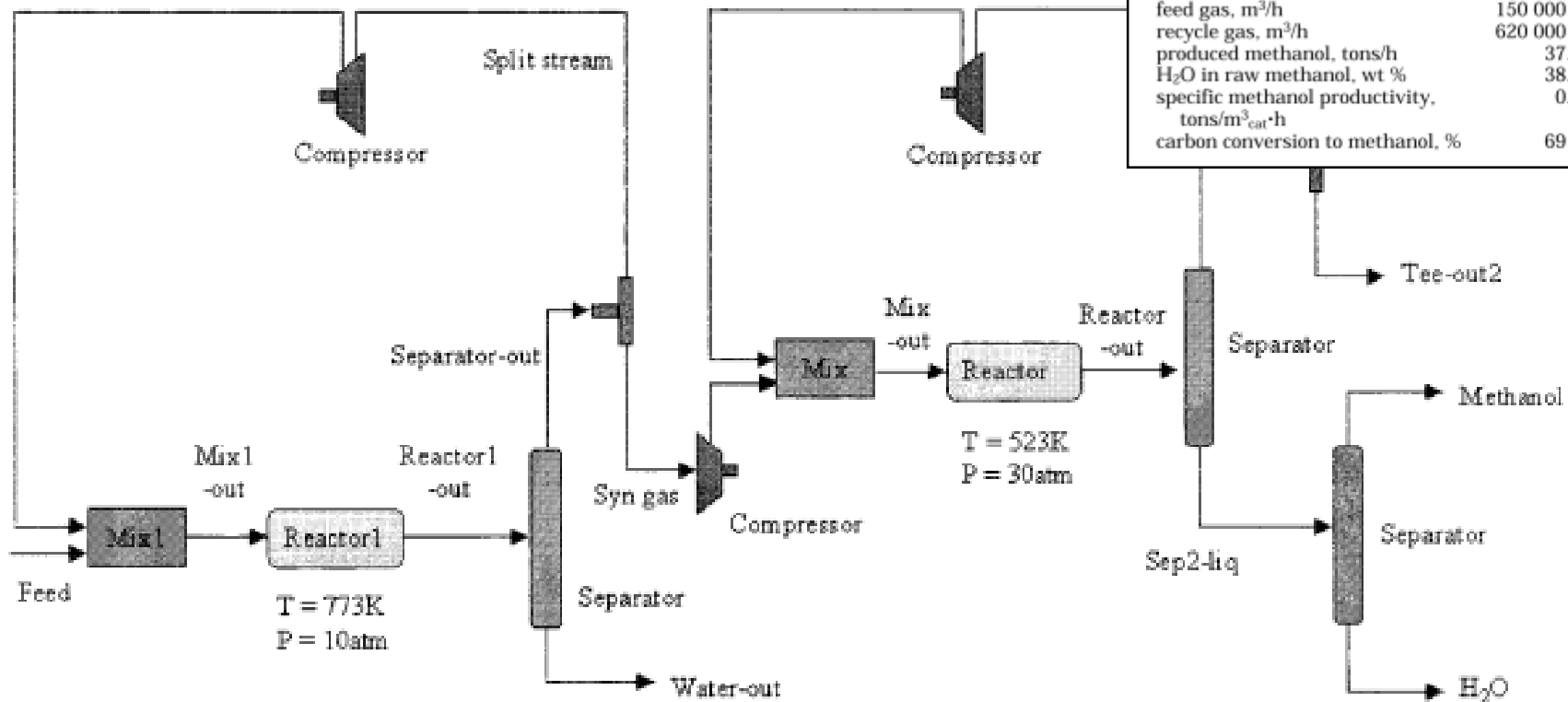


Table 1. Comparison of the CAMERE Process with the Direct CO₂ Hydrogenation

	direct	CAMERE process
1. Reverse-Water-Gas-Shift Reaction		
catalyst, m ³		30
pressure, atm		20
feed gas, m ³ /h	150 000	
space velocity, h ⁻¹		5000
condensed water, tons/h		18.5
conversion of CO ₂ to CO, %		61
2. Methanol Synthesis with Recycle		
catalyst, m ³	80	80
feed gas, m ³ /h	150 000	127 000
recycle gas, m ³ /h	620 000	506 000
produced methanol, tons/h	37.01	47.87
H ₂ O in raw methanol, wt %	38.2	15.3
specific methanol productivity, tons/m ³ _{cat} ·h	0.46	0.6
carbon conversion to methanol, %	69	89

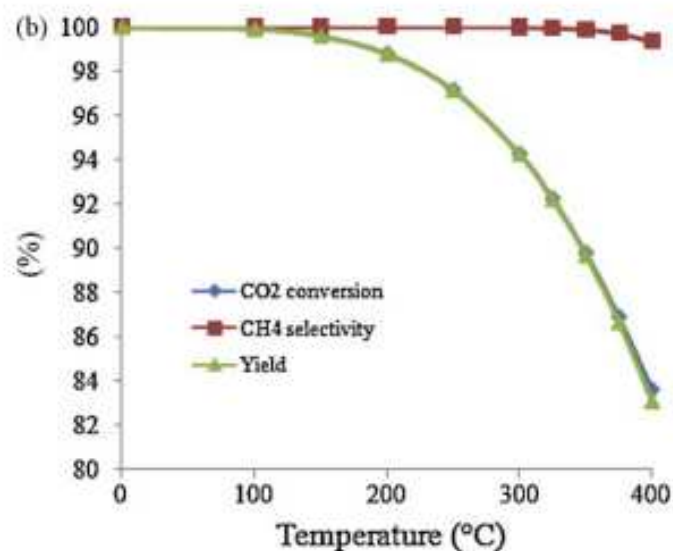
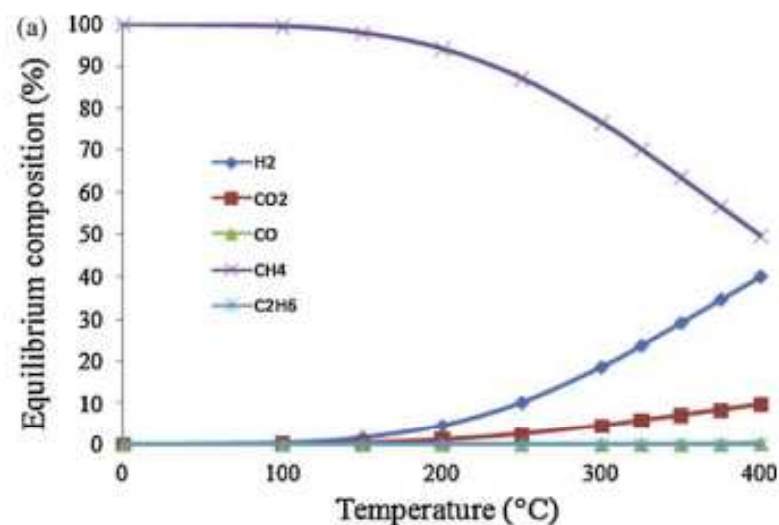
CO₂-to-methane (Sabatier reaction)



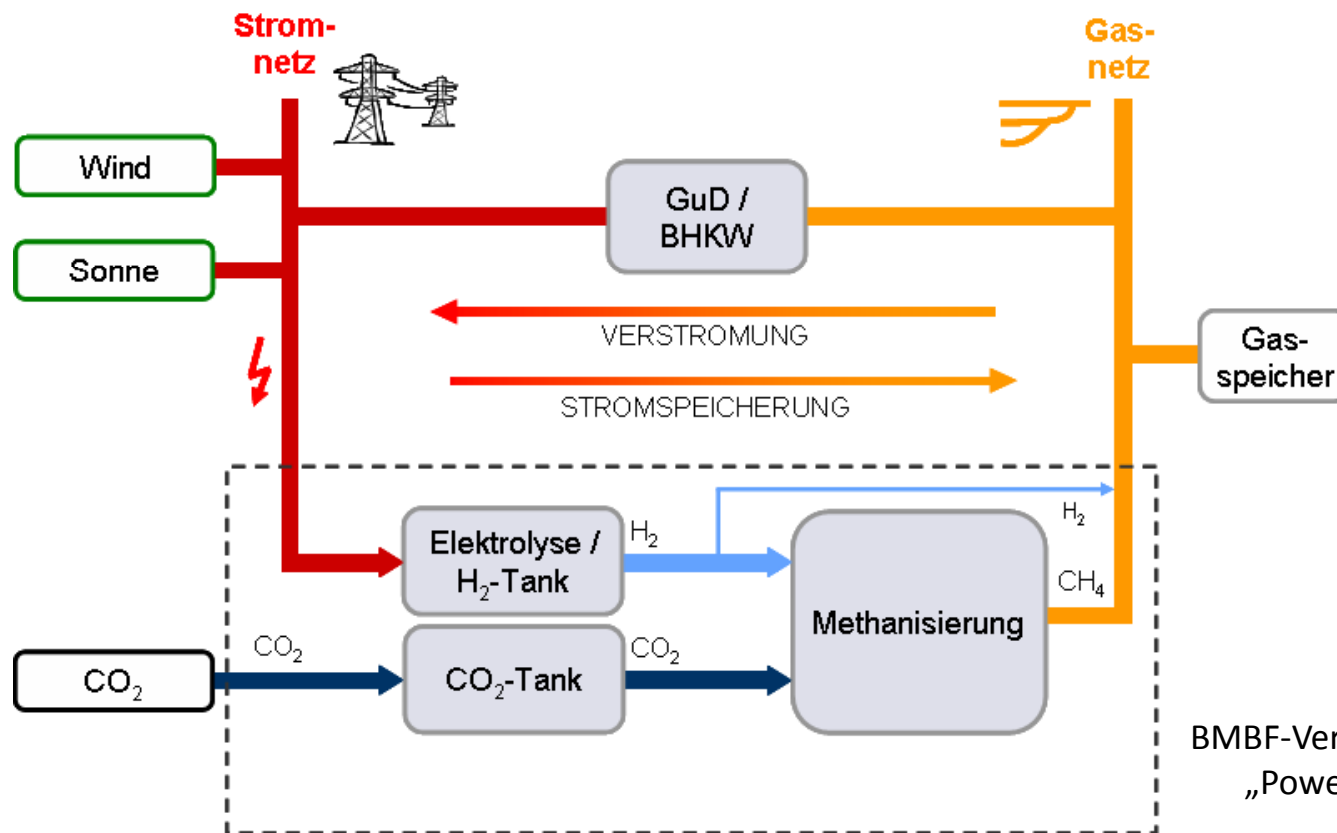
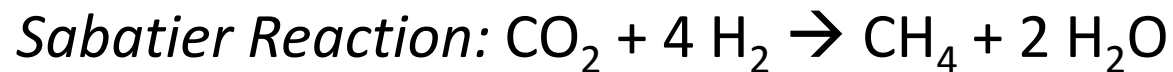
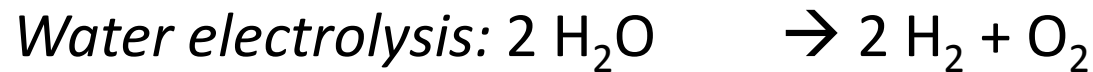
$$\Delta H_{298\text{ K}} = -252.9 \text{ kJ/mol}$$

- Group VIII metals Ru, Rh, Pd and Ni are active
- Applied to clean hydrogen streams from CO_x
- CH₄ is a proven transportation fuel (LPG)

F. Ocampo et al./Applied Catalysis A: General 369 (2009) 90–96



CO₂-Methanation for „Power-to-gas“



Advantages:

- Developed technology for storage and grid distribution
- Easy power generation from CH₄
- Scalable to contribute to storage of fluctuating energy sources

BMBF-Verbundprojekt
„Power-to-Gas“ Gefördert durch:

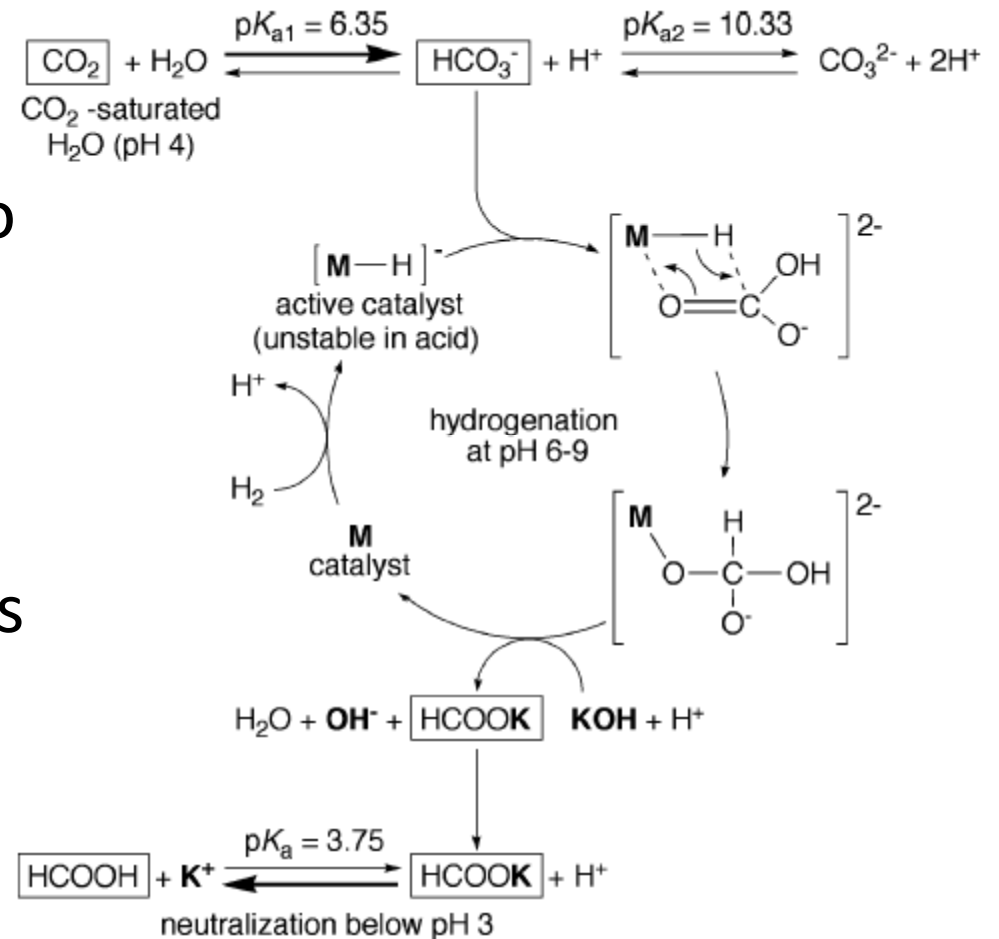


Ethanol

- Safe and proven transportation fuel or fuel additive
- Can be produced indirectly by methanol homologation (catalyzed by Co)
 - $\text{CH}_3\text{OH} + \text{CO} + 2 \text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$
- ... or directly from CO_2
 - $2 \text{CO}_2 + 6 \text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O}$
- E.g. K-promoted Cu/Fe/ZnO catalysts or Rh-based catalysts
- Catalytic synthesis competes with bio-approaches

Formic acid

- $\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$
- Low H_2 consumption, no water formation
- Potential fuel for fuel cell applications
- Promising homogeneous approaches



Thermochemical conversion

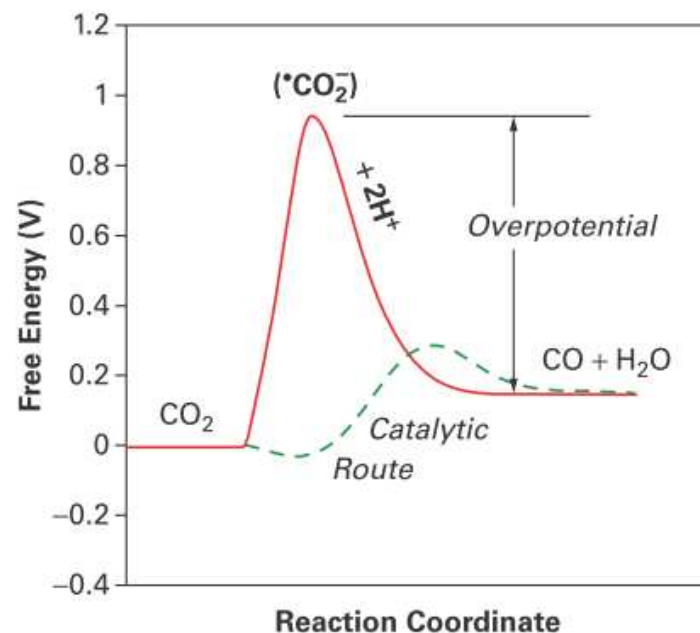
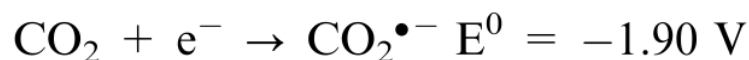
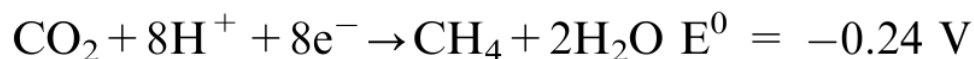
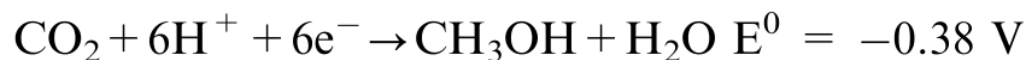
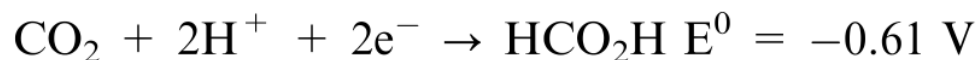
- Use of high temperature of concentrated solar power (CSP)
 - $\text{MO}_x \rightarrow \text{MO}_{x-y} + y/2 \text{O}_2$
 - $\text{MO}_{x-y} + y \text{CO}_2 \rightarrow \text{MO}_x + y \text{CO}$

 - $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$
- Cyclic operation to split CO_2
 - Thermal reduction of a transition metal oxide at high temperature with the release of O_2
 - Re-oxidation of the reduced oxide by CO_2 with the release of CO
- Feasibility proven for ZnO/Zn , $\text{Fe}_3\text{O}_4/\text{FeO}$, $\text{CeO}_2/\text{Ce}_2\text{O}_3$
- Challenge: Long-term stability at harsh conditions



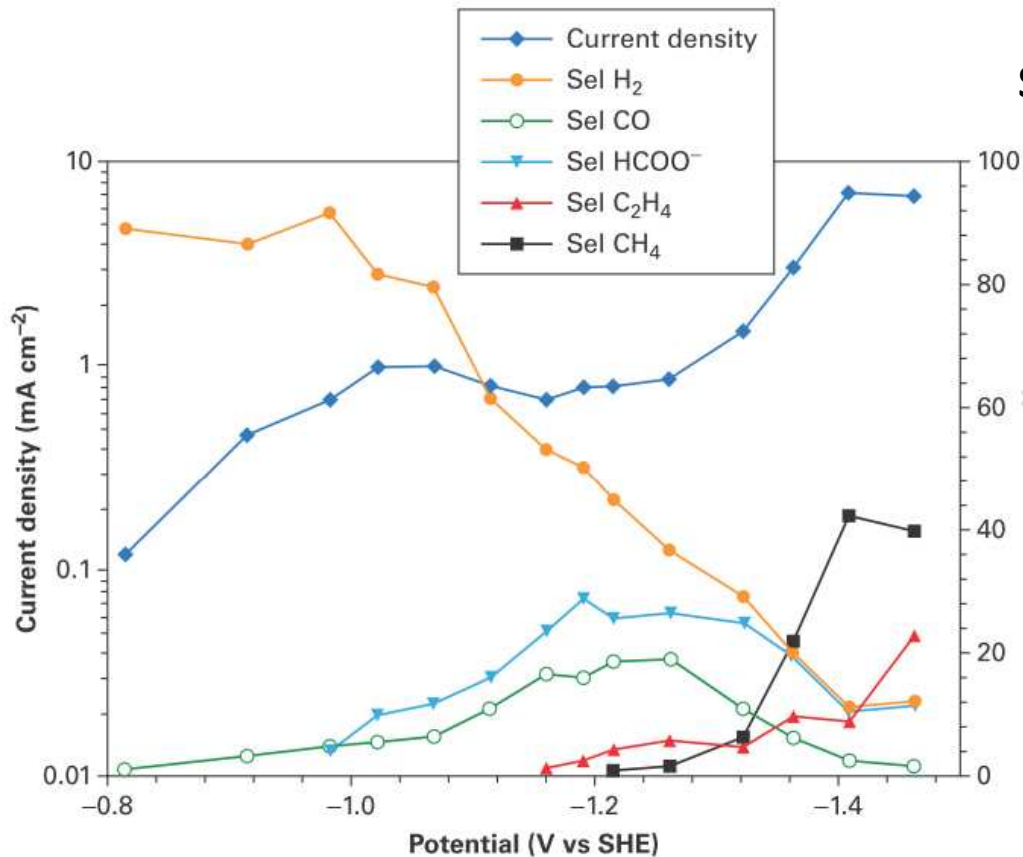
Sandia National Lab, USA

Electrochemical Approaches



- Difficult multi-electron processes
- Suitable electrocatalysts need to be developed
- Homogeneous as well as heterogeneous approaches
 - for instance heterogeneous: Cu foil

Electrocatalytic reduction of CO₂

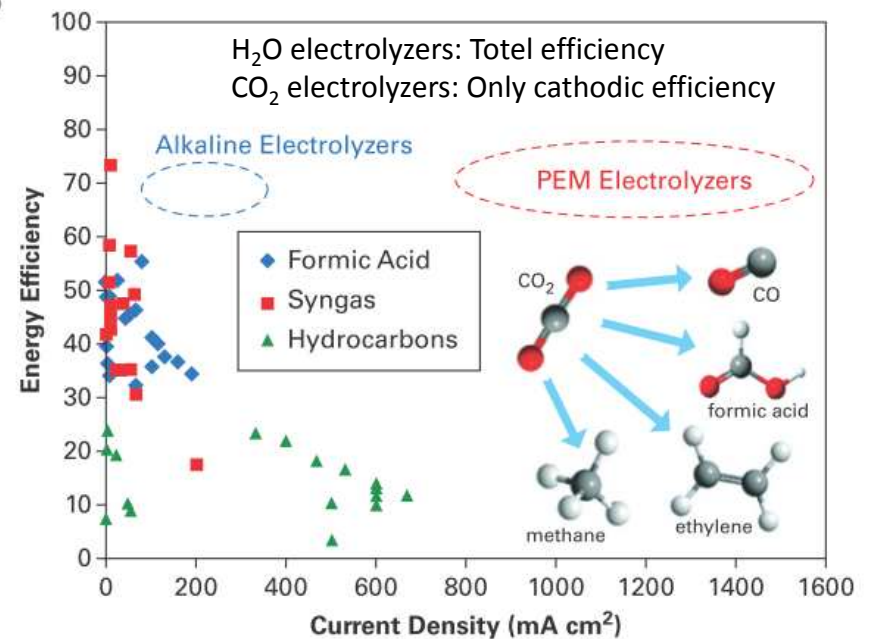


Challenges

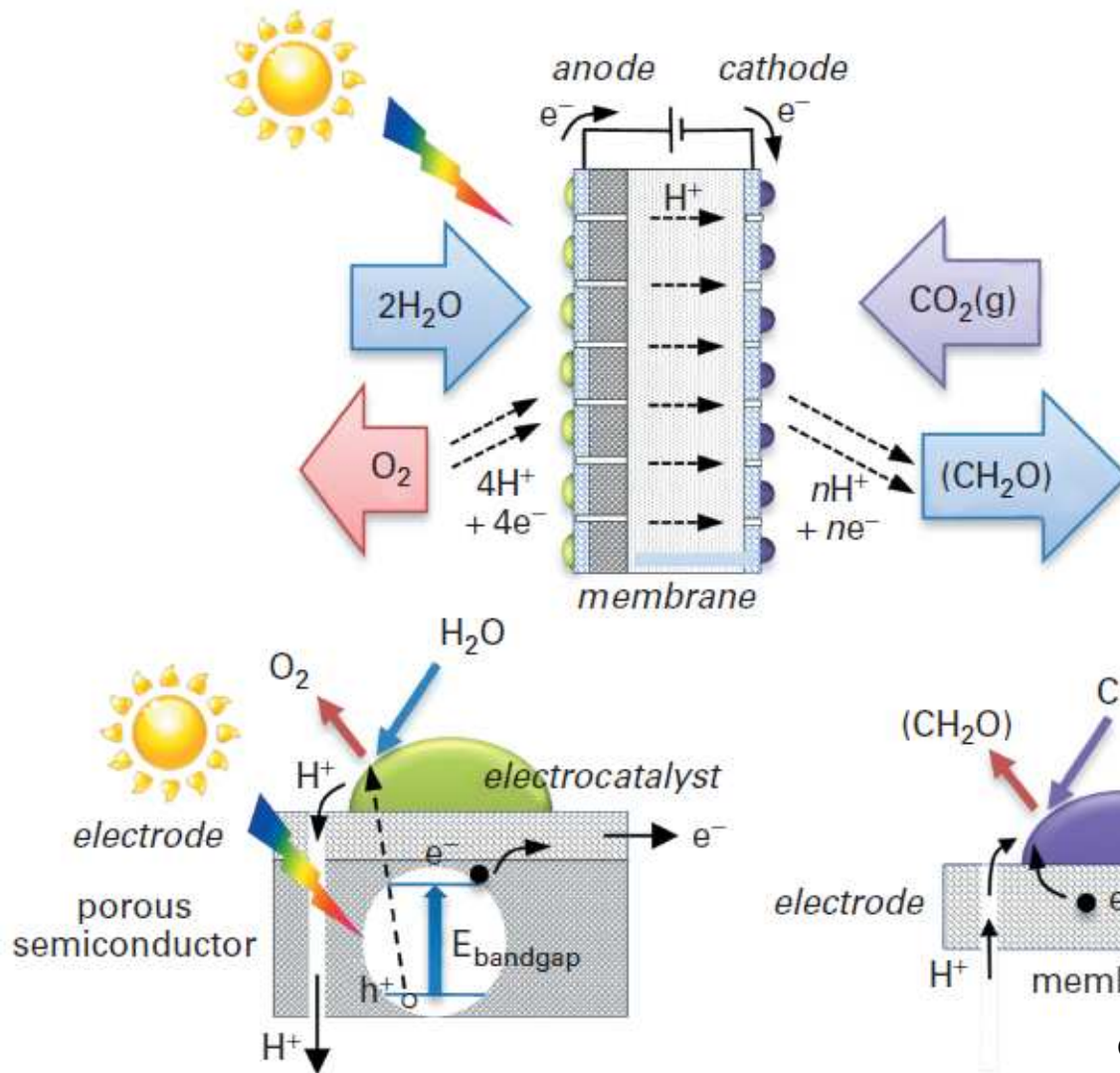
- Low CO₂ solubility in H₂O
- Low conductivity of organic solvents
- Low stability of performance

Selectivity of Cu cathode

- Reduced C1 species form at higher potential than H₂
- Selectivity depends on overpotential and the nature of the catalyst (as well as on electrolyte, p, T, ...)
- e.g., low overpotentials on Ag in inoic liquids (Science 2011, 334, 643)



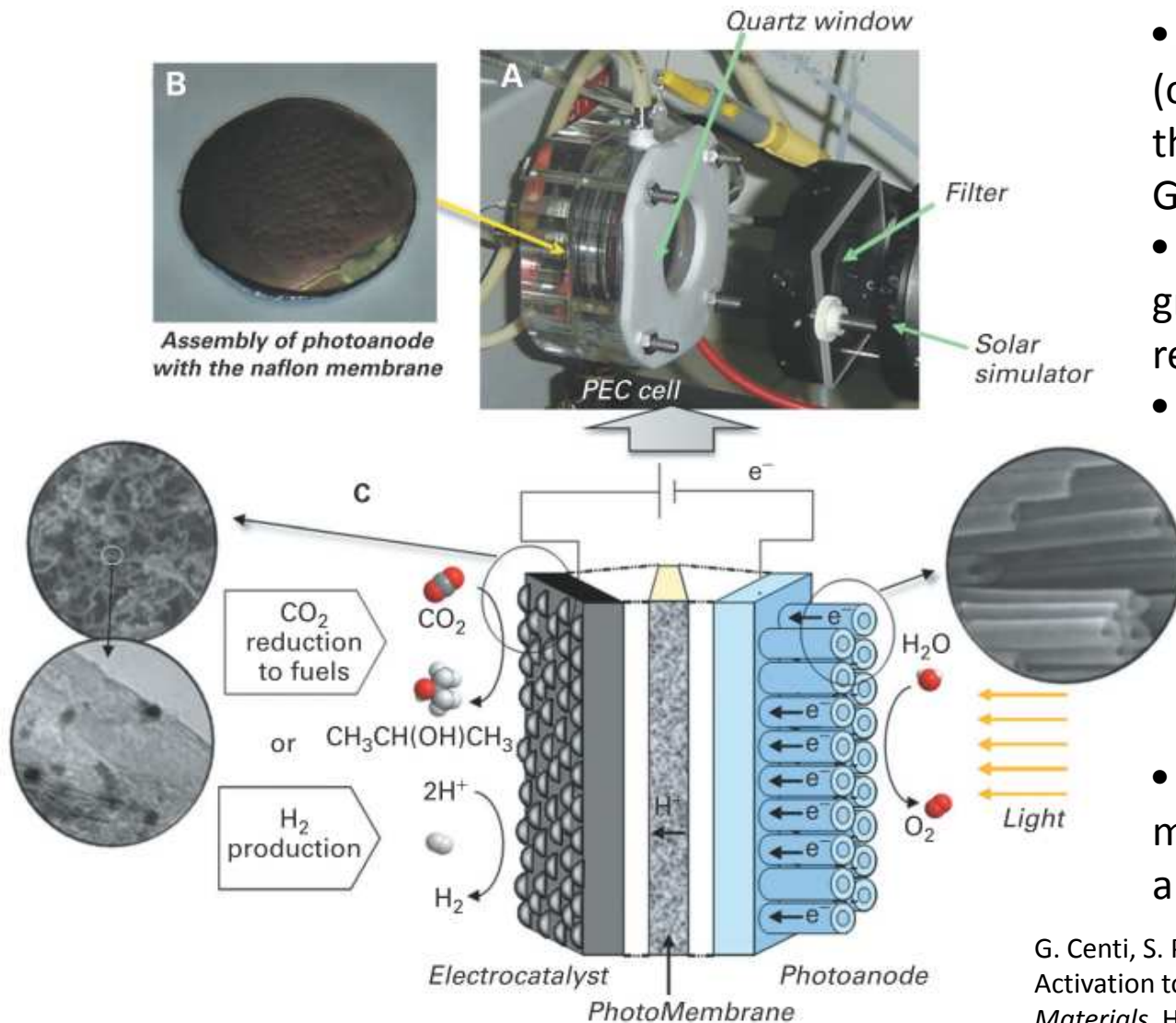
Photoelectrocatalytic (PEC) conversion



- Components of a PEC cell
 - Anode exposed to sunlight with a photocatalyst able to oxidize water and supported on a conductive support
 - Membrane to transport protons to the cathode
 - Cathode with active centres to convert CO₂
- Charge separation in semiconductor layer

G. Centi, S. Perathoner: „Photoelectro-chemical CO₂ Activation toward Artificial Leaves“, In: *Energy Storage Materials*, Hrsg: R. Schlögl, De Gruyter, Berlin, Dez. 2012.

Concept for a PEC cell for solar fuel production from CO₂



- Many cell designs proposed (often for H₂ generation rather than CO₂ conversion), see Grätzel, Nocera, Domen, ...
- The design of the Messina group (IT) involves gas phase reaction at the cathode (Fig.)
- Problems / Challenges:
 - light harvesting
 - avoid recombination
 - robust operation
 - cheap materials
 - design of electrocatalysts
 - transport
- Technique promising, but still more R&D is needed for real application

G. Centi, S. Perathoner: „Photoelectro-chemical CO₂ Activation toward Artificial Leaves“, In: *Energy Storage Materials*, Hrsg: R. Schlögl, De Gruyter, Berlin, Dez. 2012.

Summary

- Large impact of CCU technologies on global CO₂ emissions only if fuels are the target of conversion
- Several routes are possible, it is currently not clear yet, which will be the best option
- Catalytic CO₂ hydrogenation is feasible, but further R&D needed (H₂ must be “green”)
- Electrochemical or photoelectrochemical CO₂ conversion is promising, but technology still in its infancy

References

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- G. Centi, S. Perathoner, *Catal. Today* 148 (2009) 191.
- M. Aresta, A. Dibenedetto, *Dalton Trans.* (2007) 2975.
- E.E. Benson, C.P. Kubiak, A.J. Sathrum, J.M. Smieja, *Chem. Soc. Rev.* 38 (2009) 89.
- H. Arakawa et al., *Chem. Rev.* 101 (2001) 953.
- D.J. Darensbourg, *Chem. Rev.* 107 (2007) 2388.
- S. Ogo et al., *Dalton Trans.* (2006) 4657.
- R. Schlögl (Ed.): *Chemical Energy Storage*, de Gruyter, Berlin 2012.