Catalysis with Carbon Dioxide: Opportunities and Problems

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Catalysis
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We Need More Efficient Transformations

Masstransfer in Germany

Aachener Stiftung according to World Ressource Institute, 2000 „The Weight Of Nations".

Input of Ressources into the German Industry

5.400 Mio. t/a

waste, emissions ...

4.500 Mio. t/a

products, infrastrukture,..

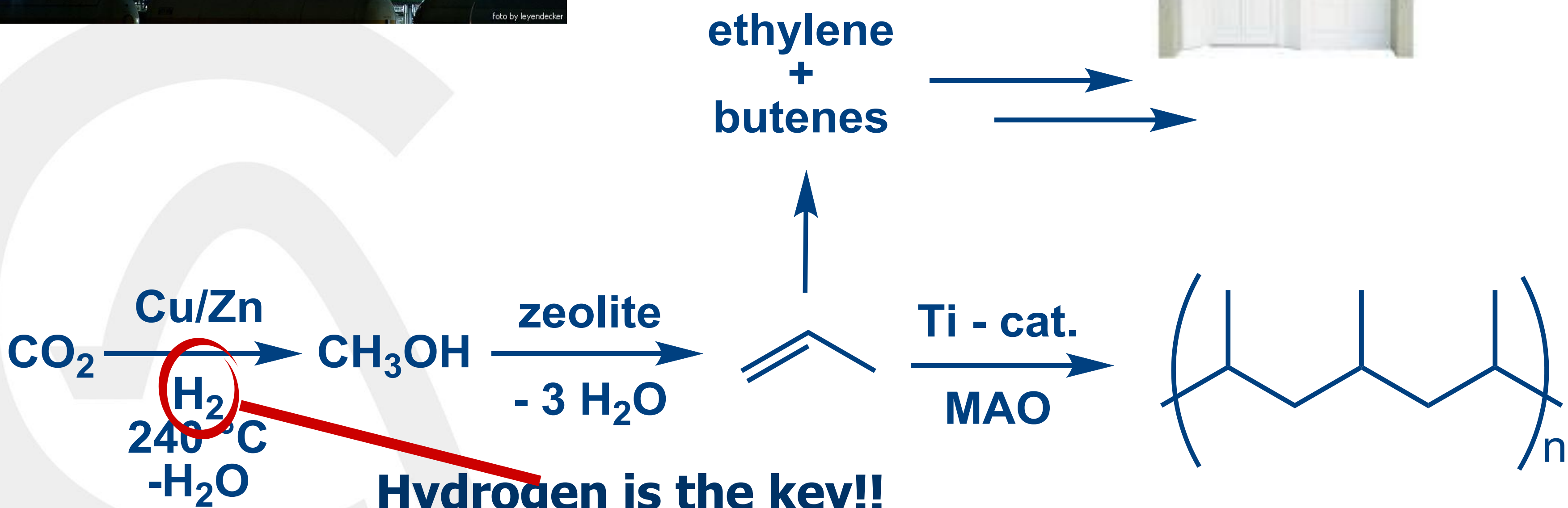
900 Mio. t/a

Carbon Dioxide: An Available Carbon Source

Nearly 44% (19%) of carbon dioxide emission came from energy (industrial) production. In 2010 around 790 Mio tons of carbon dioxide were emitted in Germany.

http://www.umweltbundesamt-daten-zur-umwelt.de

CO_2: A Carbon Feedstock for the Future ?



PP: >60 mio to/a; ca 80 billion $

Chemistry - Opportunities for the 21st Century

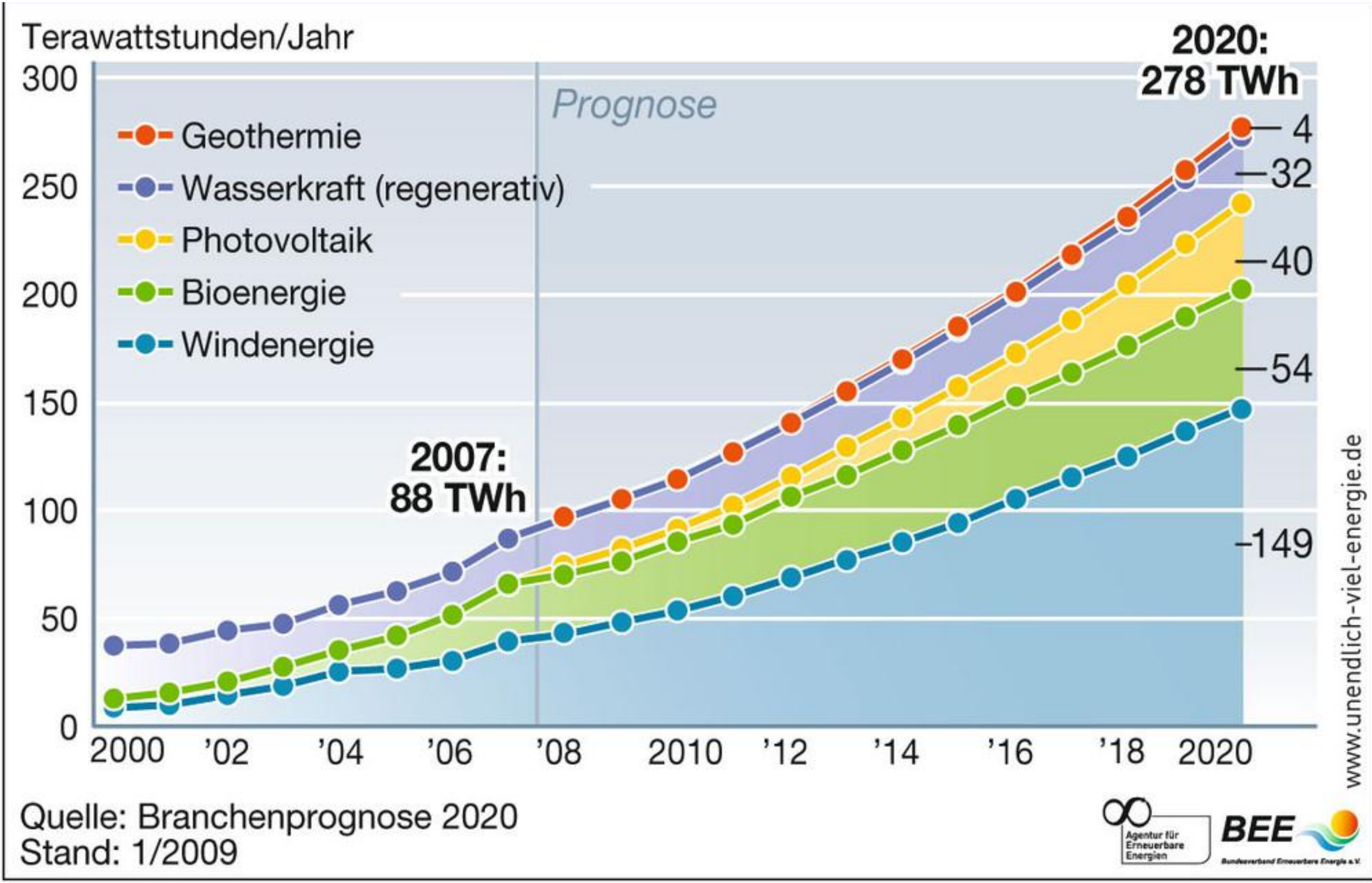
To provide and store chemical reductants in a benign and economically viable manner!

Contribute to the use of alternative energy supply
(Hydrogen-technology, fuel cells, biomass to liquid, …)

Allow for CO_2-neutral raw materials for the chemical industry (use of renewable resources, carbon dioxide, …)

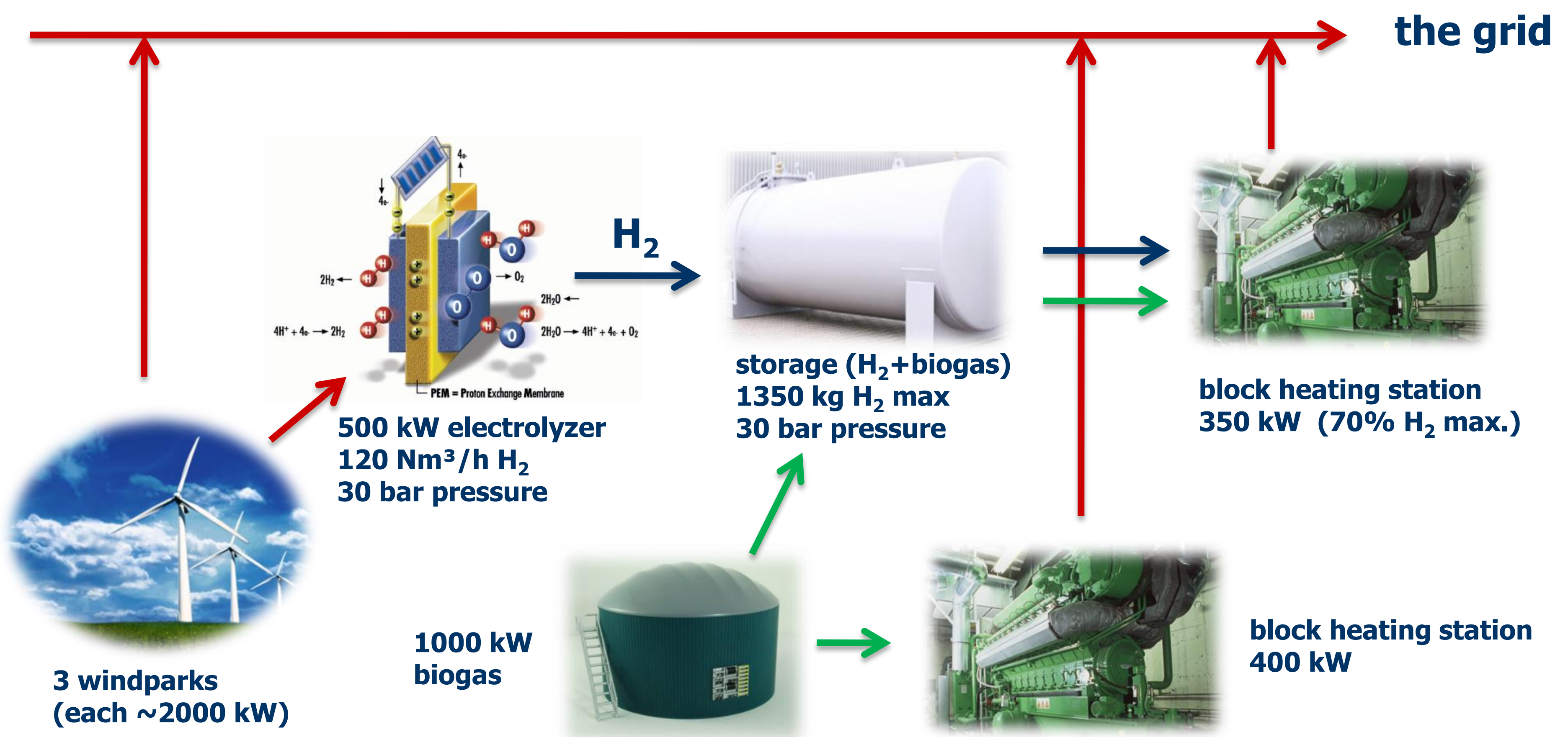
Enable new efficient materials for energy storage (batteries, bio-fuels, …), **energy saving applications** (polymers), **and energy usages** (OLEDS, PS, photovoltaics, …)

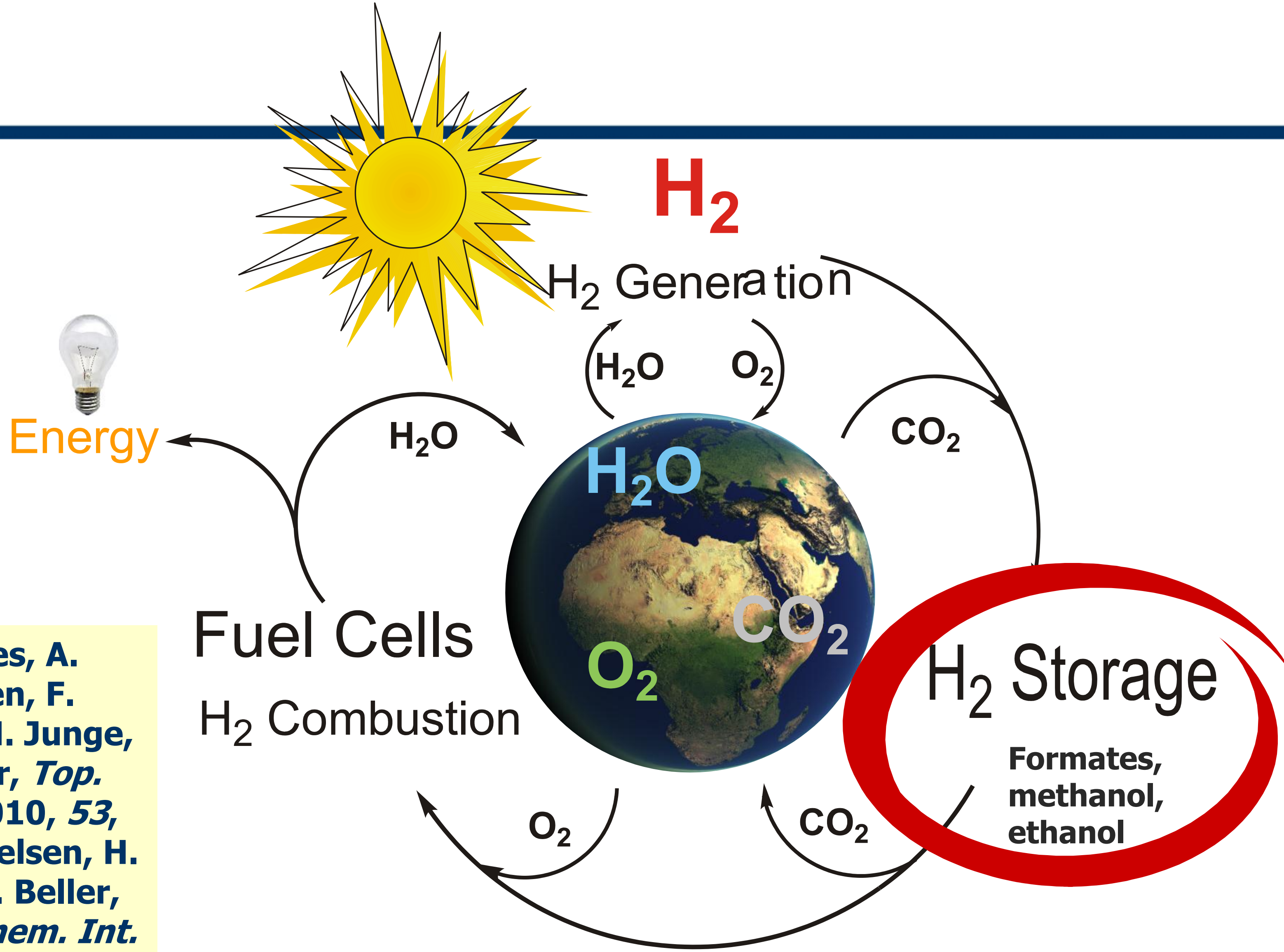
Renewable Energy in Germany 2020



Benchmark for „Green“ Hydrogen

World first hybrid power plant by ENERTRAG in Prenzlau, Brandenburg





B. Loges, A. Boddien, F. Gärtner, H. Junge, M. Beller, *Top. Catal.* 2010, *53*, 902; M. Nielsen, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* 2012, in press.

Hydrogen Storage

Physical storage

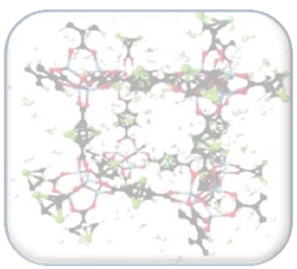
Compressed H_2

- aluminium cylinders 6.7 wt % (500 bar)
- steel cylinder 2.5 wt % (11.000 bar)
- composite materials 6.0 wt % (700 bar)

Liquid H_2

- steel cylinder
- stored at 22.4 K
- boil off 0.4 % (50 m³ tank)
- 40 % of the energy needed for cooling

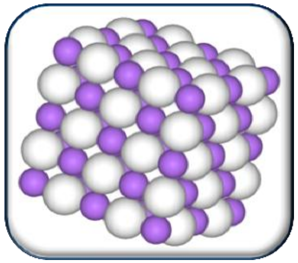
Cryo-adsorption



- Zeolithe
- MOFs
- PIMs
- SWCNTs, MWNTs, GNFs

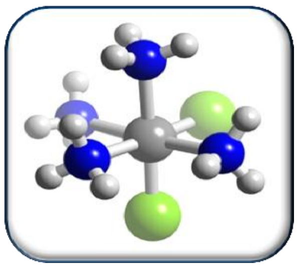
Chemical storage

Hydrides



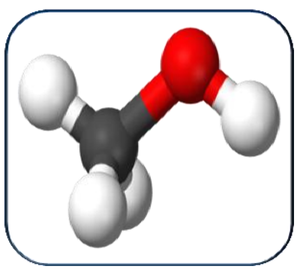
- Metal hydrides (MgH_2, …)
- Complex hydrides ($NaAlH_4$, …)

Hydrazine, Aminoborane, Ammonia



- NH_3, N_2H_4
- NH_4BH_4
- $[Mg(NH_3)_6]Cl_2$, $NaBH_4$

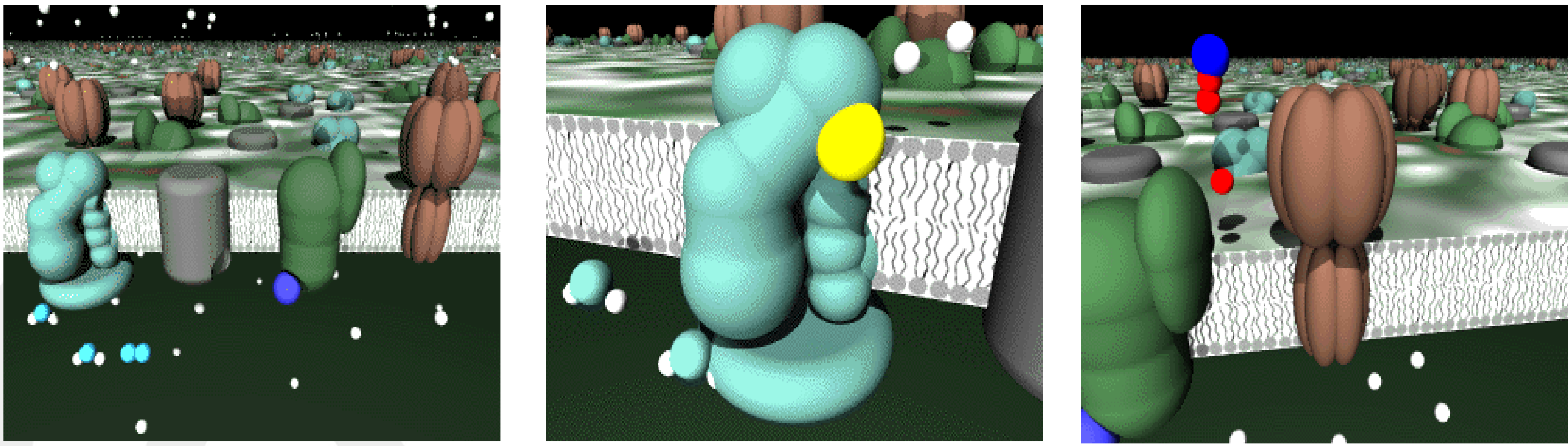
„Organic Hydrides“



- MeOH, EtOH
- Decaline, Methylcyclohexane
- Formic Acid

Energy Storage in Nature

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

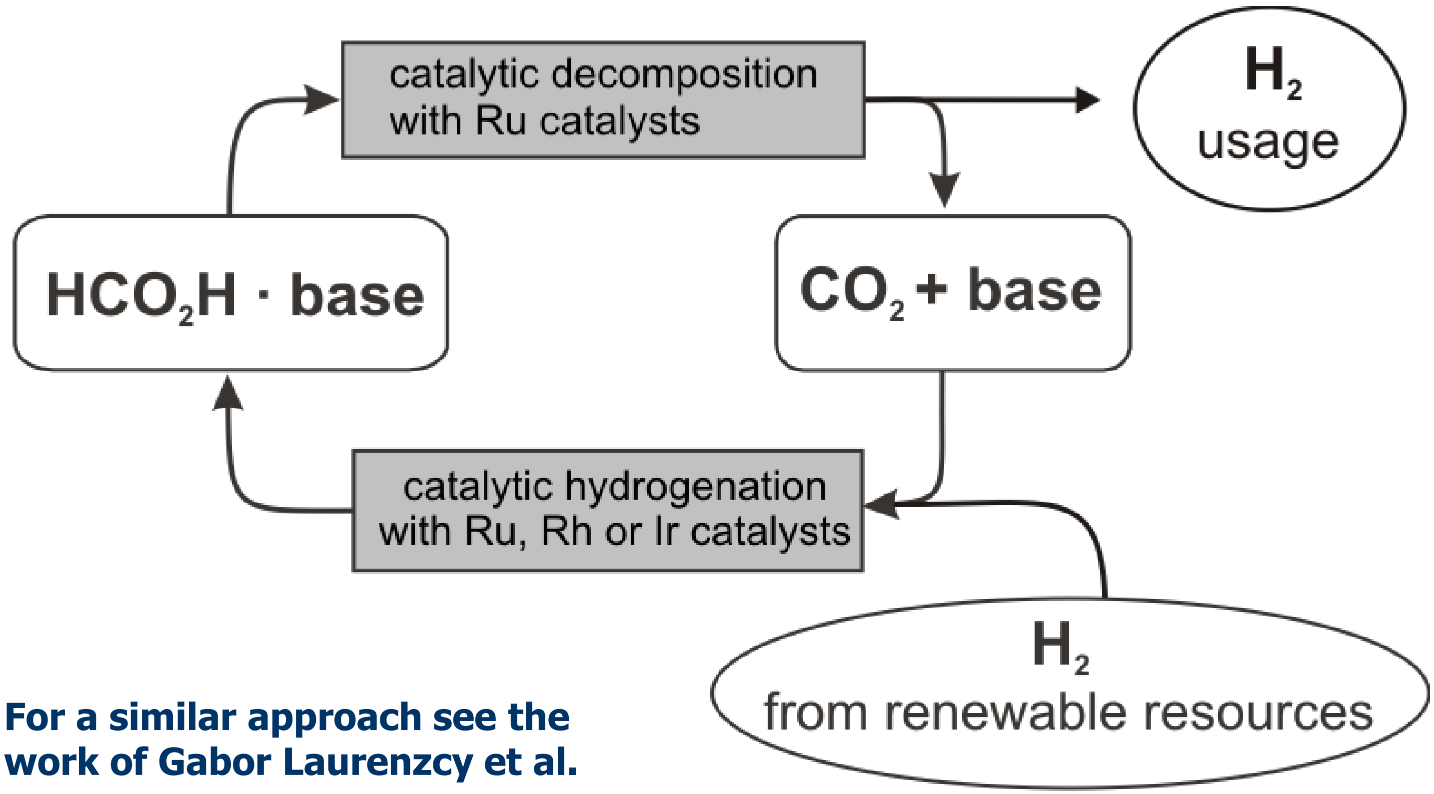


- Only visible light is used (400 – 700nm): 50% loss
- Reflection, absorption and transmission by leaves: 20% loss
- Limited light reaction efficiency (8-10 photos per CO_2): 72-77% loss
- Respiration required for translocation and biosynthesis: 40% loss

Total theoretical efficiency is not more than 5.5-6.6% (reality: 0.6%)

A Concept for Hydrogen Storage

B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* 2008, *120*, 4026-4029; *Angew. Chem. Int. Ed.* 2008, *47*, 3962; A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* 2008, *1*, 751; B. Loges, A. Boddien, H. Junge, J. R. Noyes, W. Baumann, M. Beller, *Chem. Commun*. 2009, 4185.



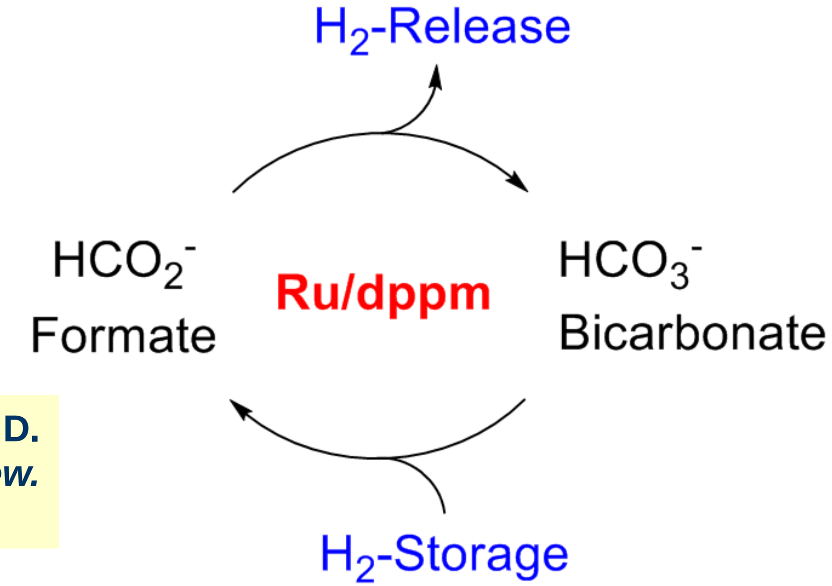
Dr. Henrik Junge

For a similar approach see the work of Gabor Laurenzcy et al.

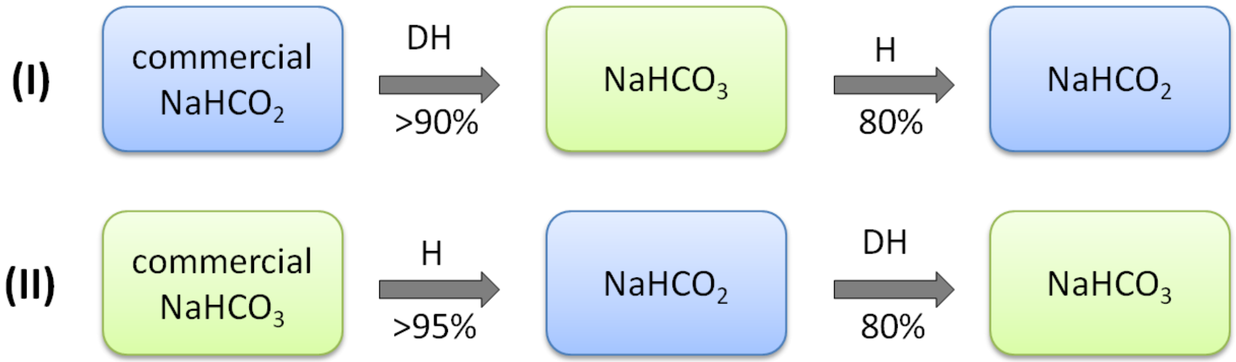
D. Preti, S. Squarcialupi, G. Fachinetti, *Angew. Chem. Int. Ed.* 2010, *14*, 2581; C. Federsel, R. Jackstell, A. Boddien, G. Laurenczy, M. Beller, *ChemSusChem* 2010, 3, 1048-1050.

A CO_2-Neutral Cycle for H_2-Storage

A single ruthenium-based catalyst is capable catalyzing both reactions at room temperature!



A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem. Int. Ed*. 2011, 50, 6411-6415.



Hydrogenation

Full conversion; TON: 1108

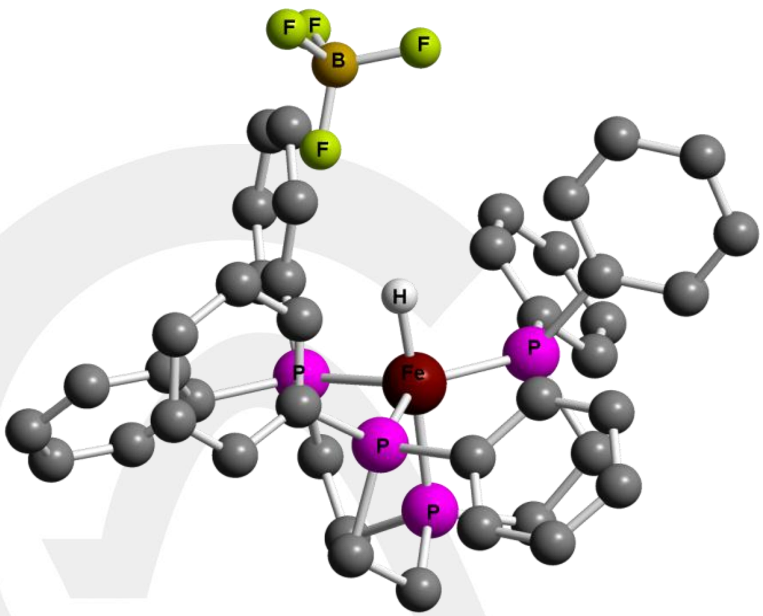
Dehydrogenation

Full conversion; TOF: 2592 h^{-1}

Fe-Catalyzed Hydrogenation of CO_2 and HCO_3^-

$CO_2 + H_2 \xrightarrow[\text{MeOH, Base}]{\text{Fe cat.}} HCO_2H\text{-Base} \xrightarrow{\text{ROH / NHR}'_2} HCO_2R \text{ / } HCONR'_2$

80°C, 60 bar H_2; yield 88%; 610 TON



product	yield	TON
HCO_2Me	56	585
HCO_2Et	16	167
HCO_2Na	88	610
DMF	75	727

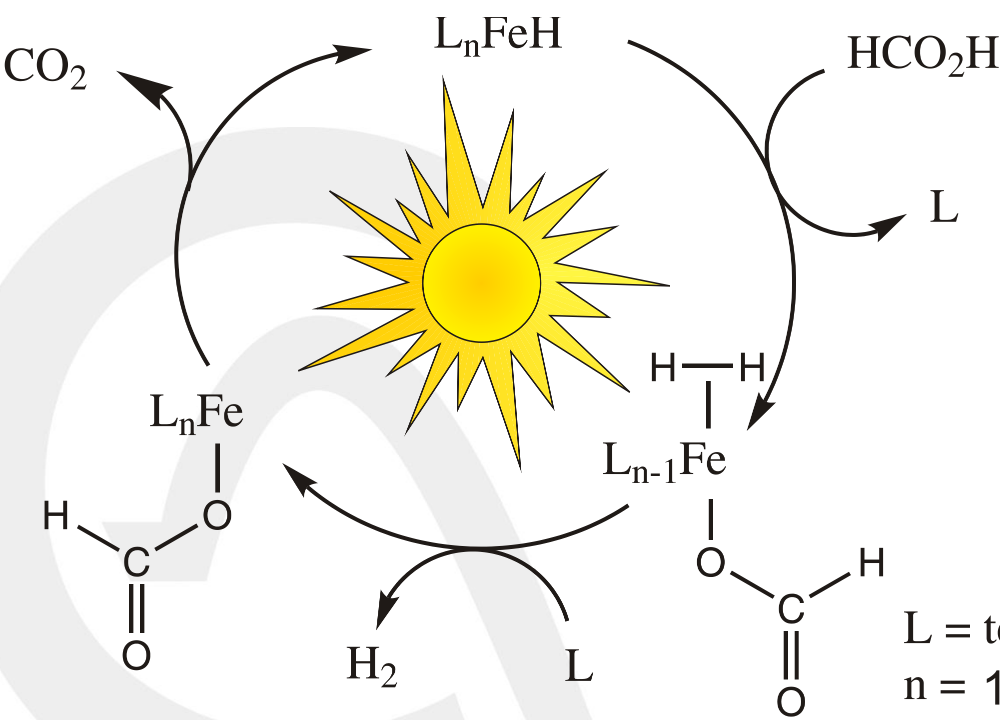
Best previous result: 6 TON.*

* G. O. Evans, C. J. Newell, *Inorg. Chim. Acta* 1978, *31*, L387.

C. Ferdersel, A. Boddien, R. Jackstell, R. Scopelliti, P. J. Dyson, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.* 2010, *49*, 9777-9780. see also C. Bianchini, M. Peruzzini for alkyne hydrogenation

Hydrogen from Formic Acid: Fe Catalysts

$$Fe_3(CO)_{12} \xrightarrow[\text{- 3 eq.CO; - }CO_2]{h{\bullet}\nu \atop \text{terpy, }PPh_3\text{, }HCO_2H\text{, }NEt_3} [FeH(terpy)(PPh_3)(CO)] + \ldots$$



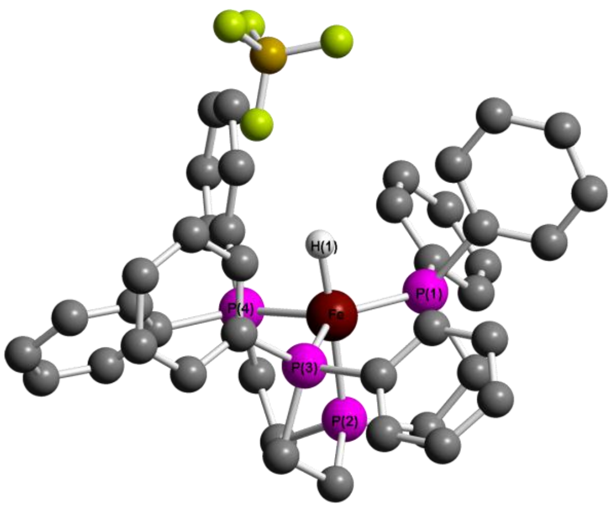
L = terpy, PPh_3, CO
n = 1-3

TON 150
TOF ca. 10h^{-1}

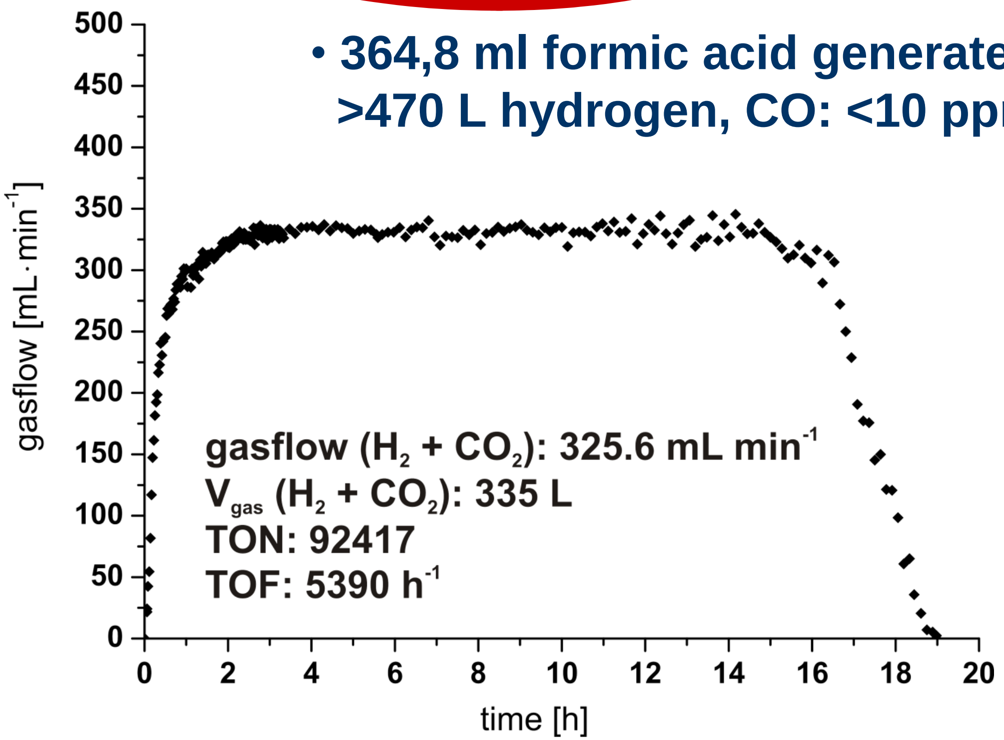
B. Loges, A. Boddien, B. Loeges, F. Gärtner, A.-E. Surkus, H. Junge, M. Beller, *J. Am. Chem. Soc.* 2010, *132*, 8924-8934. Editors choice in Science August 2010.

State-of-the-Art-Fe-Catalysts

$$HCO_2H \underset{\text{Fe cat. / base}}{\overset{\text{Fe cat.}}{\rightleftarrows}} CO_2 + H_2$$



- TON: >90.000
- TOF: >10.000 h^{-1}
- 364,8 ml formic acid generate >470 L hydrogen, CO: <10 ppm

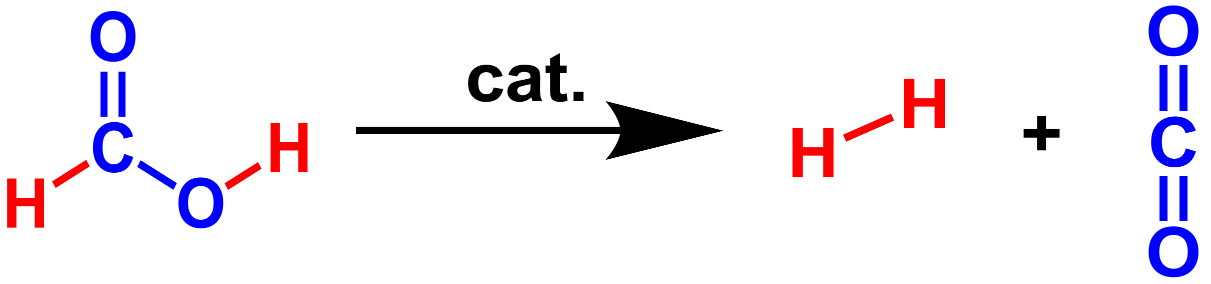


A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science* 2011, 1733-1736; C. Federsel, A. Boddien, R. Jackstell, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.* 2010, *49*, 9777-9780.

Chemistry is Fun, too …

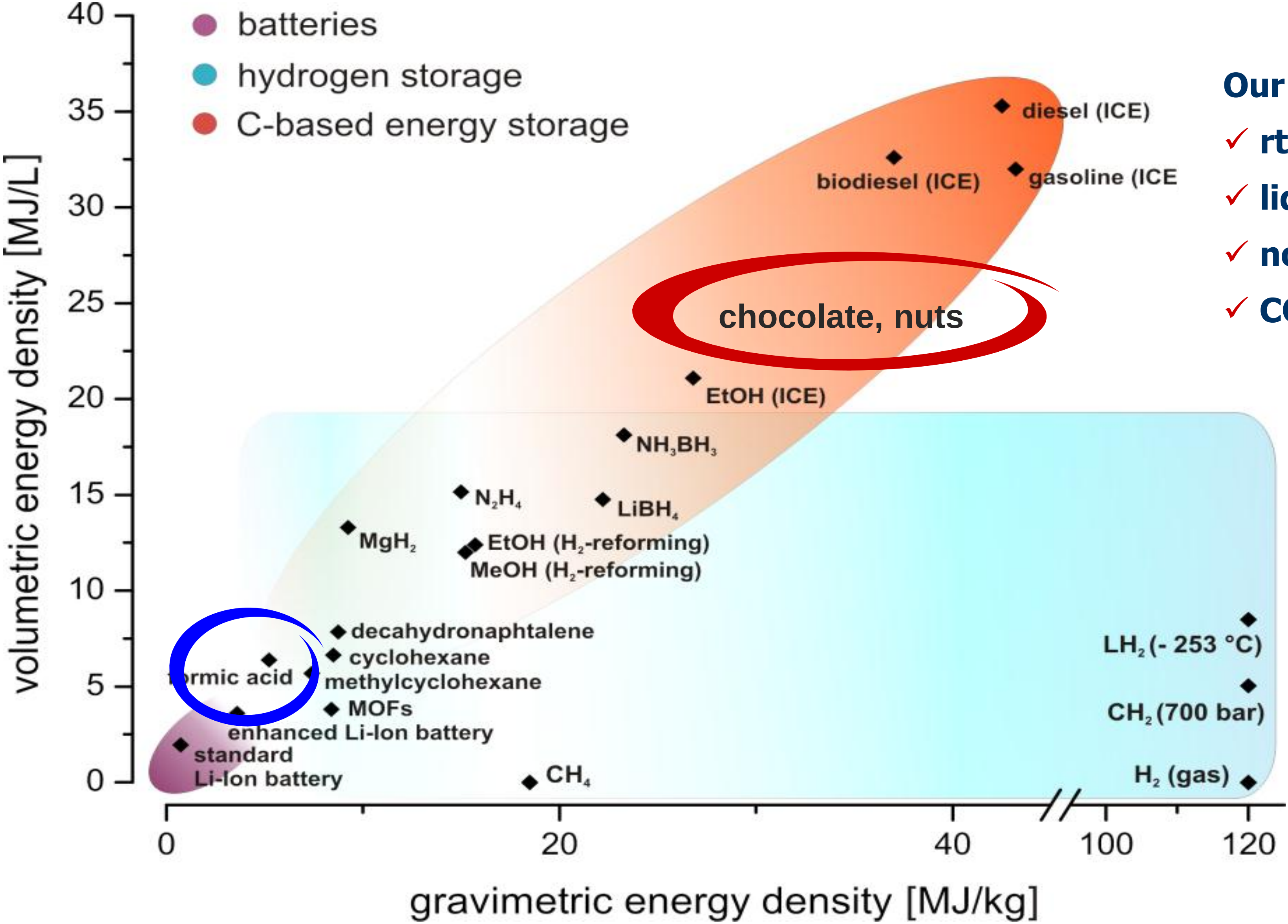
Formic Acid as Energy Carrier

- liquid
- non-toxic
- 1.77 kWh/l
- 4.4 wt H_2
- no H_2 to water



What is your favorite Food?

Selected Energy Storage Materials

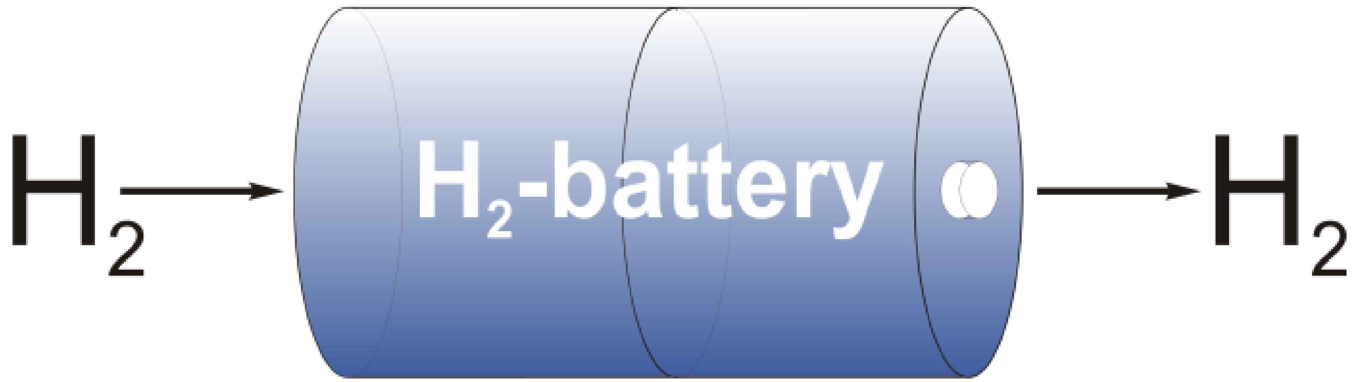


Our system:

- ✓ rt
- ✓ liquid
- ✓ non toxic
- ✓ CO_2 neutral

Towards the Development of a Hydrogen Battery

$$H_2 + CO_2 \rightleftharpoons HCO_2H \cdot amine \rightleftharpoons H_2 + CO_2$$

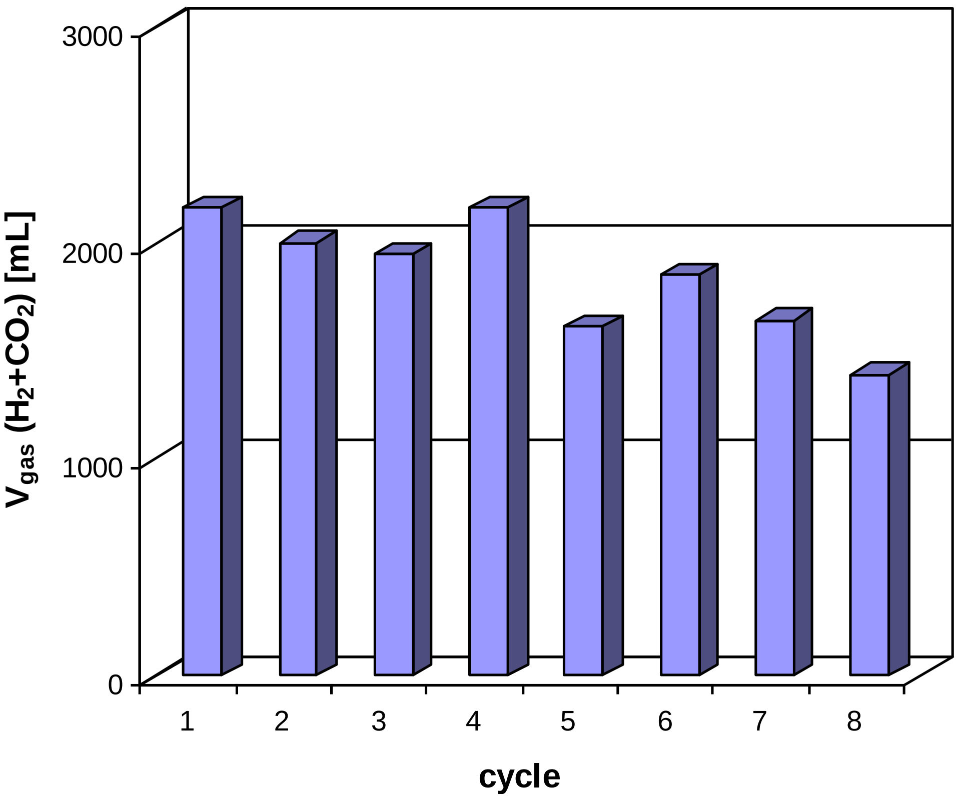


	energy content [MJ/kg]	storage efficiency [%]
$H_2 + CO_2 \rightleftharpoons HCO_2H$	5.22	100
$3H_2 + CO_2 \rightleftharpoons CH_3OH + H_2O$	15.2	66.6
$4H_2 + CO_2 \rightleftharpoons CH_4 + 2H_2O$	30.15	50

Carrier/energy content based on maximum evolved H_2 and lhv (33.33 kWh/kg).

State-of-the-Art Ru-catalyzed CO_2 Hydrogenation

No	Cat	Cond.	mmol FA	AAR
1	5.2	2h 100 °C, 0.4h RT	2	0.07
2	5.2	20h RT	7	0.20
3	5.2	2h 100 °C, 20h RT	20	0.56
4	5.2	20h 100 °C, 20h RT	19	0.54
5	10.4	2h 100 °C, 2h RT	67	1.86
6[b]	10.4	2h 100 °C, 2h RT	39	2.69



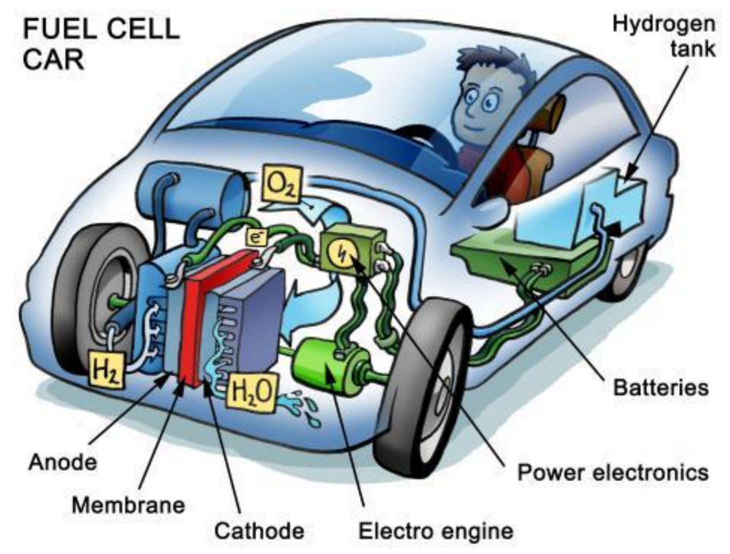
10.4 µmol [RuC_{l2}(benzene)]$_2$ / 4 equiv. dppm in 36 mmol NEt_3 and 20 mL DMF, stirring speed: 400 rpm, 30 bar H_2 pressure and 30 bar CO_2 pressure at RT (total of 60 bar pressure). [b] 14.4 mmol NEt_3 used.

A. Boddien, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, G. Laurenczy, M. Beller, manuscript submitted; see also work of W. Leiter.

Fuel Cells: Opportunities for Catalysis

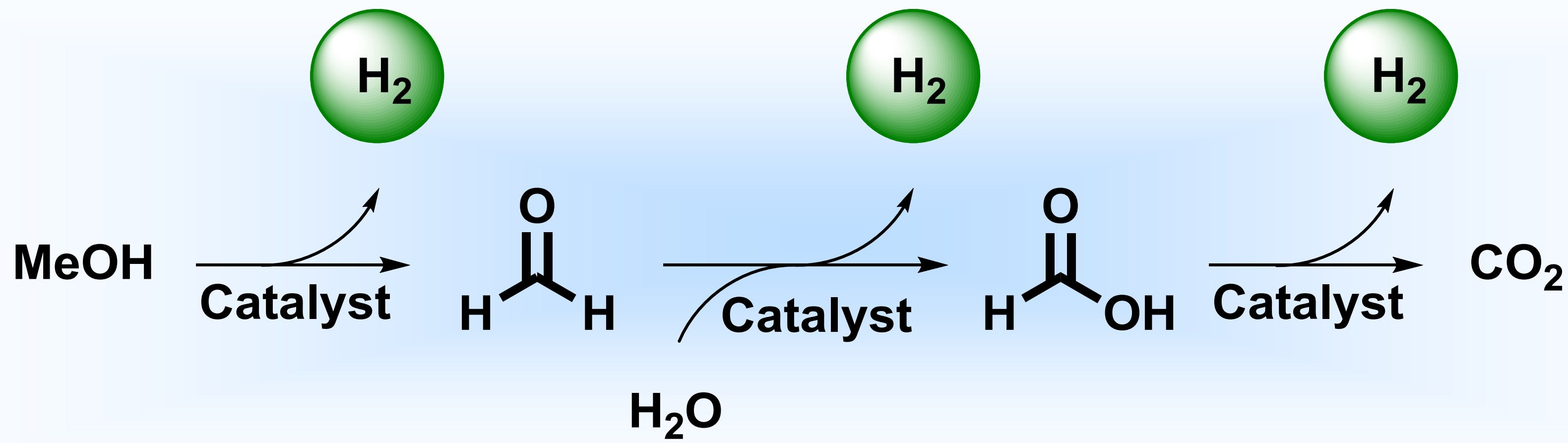
- **Convert chemical energy into electricity**
  - » **Hydrogen: PEMFC (Proton Exchange Membrane Fuel Cell)**
  - » **Methanol: DMFC (Direct Methanol Fuel Cell)**
  - » **Hydrogen from methanol: RMFC (Reformed Methanol Fuel Cell)**

- **2010: $750 million market worldwide**



- **Current state-of-the-art efficiency:**
  - » **PEMFC: 70%**
  - » **DMFC: 10-30%; too low efficiency**
  - » **RMFC: 25-40%; low efficiency; reforming requires >200 °C**

MeOH-Reforming by Homogeneous Catalysts



State-of-the-art: Dumesic and co-workers, Nature, 2003.

Pt, 200-225 °C, 25-50 bars of pressure, <300 ppm of CO contamination

Our recent system: Full MeOH reforming to $3H_2 + CO_2$ achieved, performs <80 ºC, TOF(max) ~5000 h^{-1} (per H_2 molecule evolved), TON >500.000, catalytic system active for weeks, <1 ppm levels of CO.

M. Nielsen, E. Alberico, H. Junge, S. Gladiali, M. Beller, Science under review.

Topics of My Research Group

Catalysis for Fine Chemicals (Pd, Cu, Ru, Zn)

Catalysis for Bulk Processes (Rh, Ir, Pd)

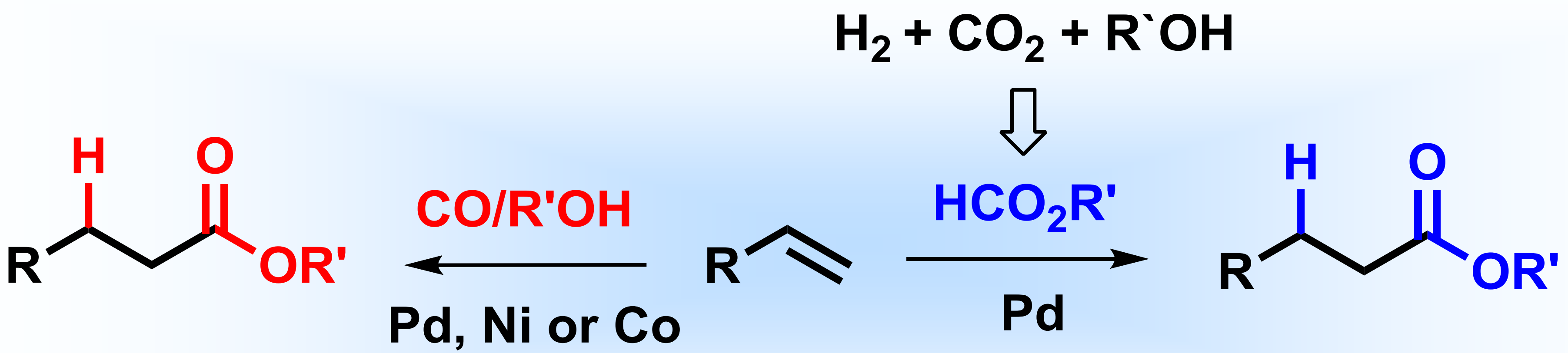
Catalysis for Energy Technologies (Ru, Fe)

Sustainable Red/Ox Catalysis (Fe, Zn, Ir, Ru)

Our goal: To provide industrially applicable methods and catalysts.

Since 2000 we have contributed to 4 „real-world“ application of catalysts on >100 kg–60.000 ton-scale and published ca 450 papers.

Carbonylations based on CO_2

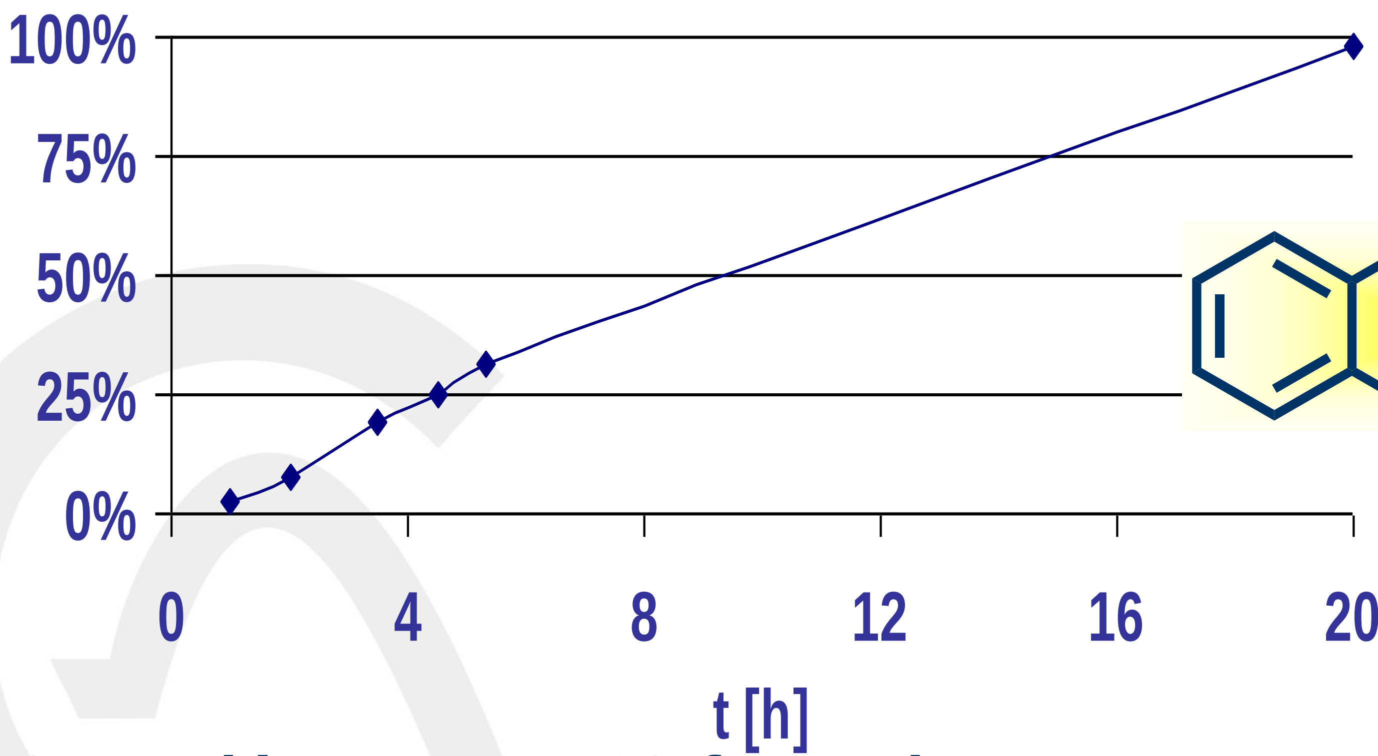


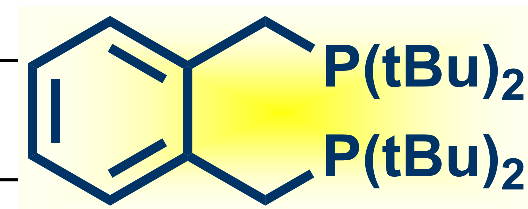
- **First report: 1983; known Pd systems need additional CO**
- **1994 one CO-free Pd-system (TON=90; ethylene)**
- **Ru-system: CO-free with TON = 1500 for ethylene**

Carbonylation of Olefins without Carbon Monoxide

Methoxycarbonylation of 1-Octene

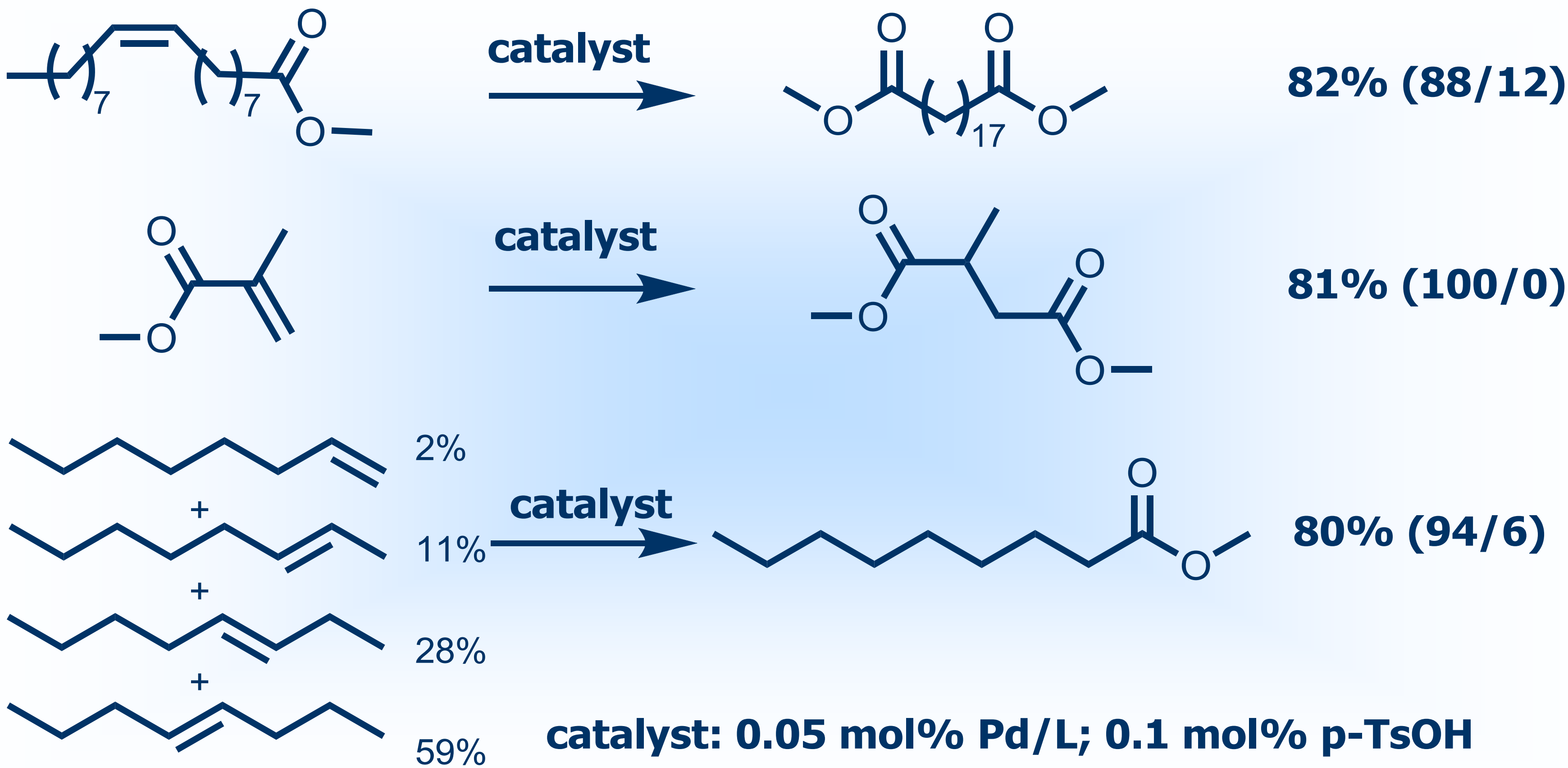
TON = 3400;
TOF = 209 h^{-1}





- **Our achievements: CO-free Pd-system; scope: 15 examples (different olefins, 3 different formates), only 1 active catalyst**

Alkoxycarbonylations with Formates

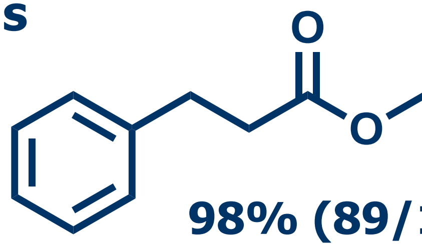


catalyst: 0.05 mol% Pd/L; 0.1 mol% p-TsOH

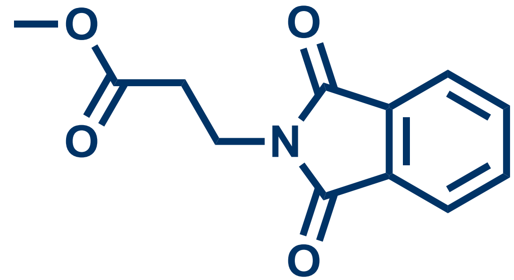
Technology has been patented together with Evonik 12/2011 cooperation R. Franke; See also D. Cole-Hamilton et al. for similar reactions with CO.

Pd-catalyzed Alkoxycarbonylation of Olefins

Selected olefins



98% (89/11)



86% (95/5)

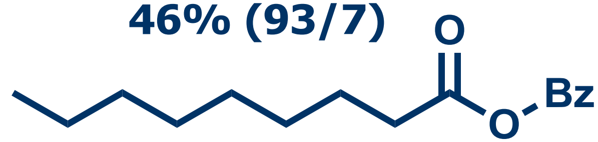
56% (100/0)

Various formates

98% (94/6)

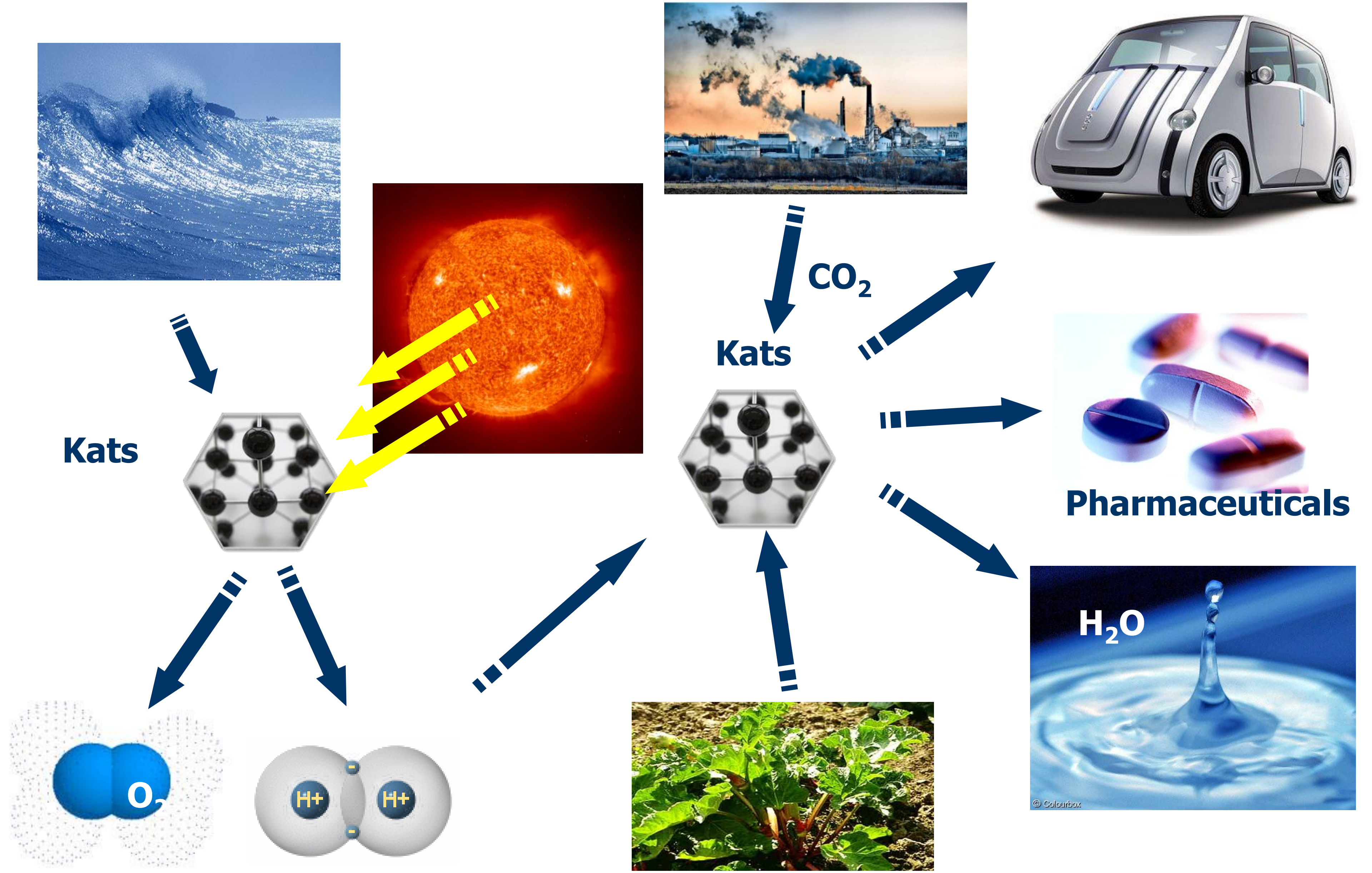
46% (93/7)

99% (95/5)



86% (92/8)

A Vision for Sustainability



Academic cooperations: S. Gladiali, G. Laurenczy, M. Costas, P. H. Dixneuf, A. Brückner, R. Ludwig, M. Bauer, H. Jiao, …
Funding: Mecklenburg-Vorpommern, BMBF, DFG, Evonik.

Thank you for the invitation and your kind attention!

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My Catalytic „Dream Reactions“

- $H_2O \longrightarrow H_2 + O_2$
- $CO_2 \longrightarrow CO$
- C (coal) $\xrightarrow{H_2}$ LAO´s at mild conditions
- Cellulose or 

- CO_2 / H_2 $\longrightarrow$ olefins, alcohols, energy-efficient FT
- Selective „oxidations“ of methane2methanol, methane2ethylene, methane2benzene, alkanes, ...
- Selective domino ismerization/functionalization reactions
- $H_2 + N_2 \xrightarrow{\text{low temperature}} NH_3$
- Selective hydrogenation and deoxygenation of alcoholes and carboxylic acid derivatives under mild conditions, low temperature methanol reforming