Catalysis – A Tool for Efficient Conversion of Renewables

Biorefinica – Platform chemicals and product lines", Deutsche Bundesstiftung Umwelt

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an der Universität Rostock

Three Major Challenges for the Future

- **Energy:**
  In short time not enough for everyone! 8 and 10% economic growth in India and China. Oil is estimated to last <100 years.

- **Health & Ageing:**
  Dramatic reduction of new drugs. Still >6 Mio people die from cancer (6.2 Mio in 2002; 10.3 Mio in 2020) and >2 Mio die from HIV/AIDS (2007; 33.2 Mio people are infected). An ageing society has additional needs (e.g. Alzheimer, Parkinson).

- **Environmental Protection:**
  More sustainable production should be realized. The increase of carbon dioxide has to be stopped, otherwise dramatic climate changes will result.

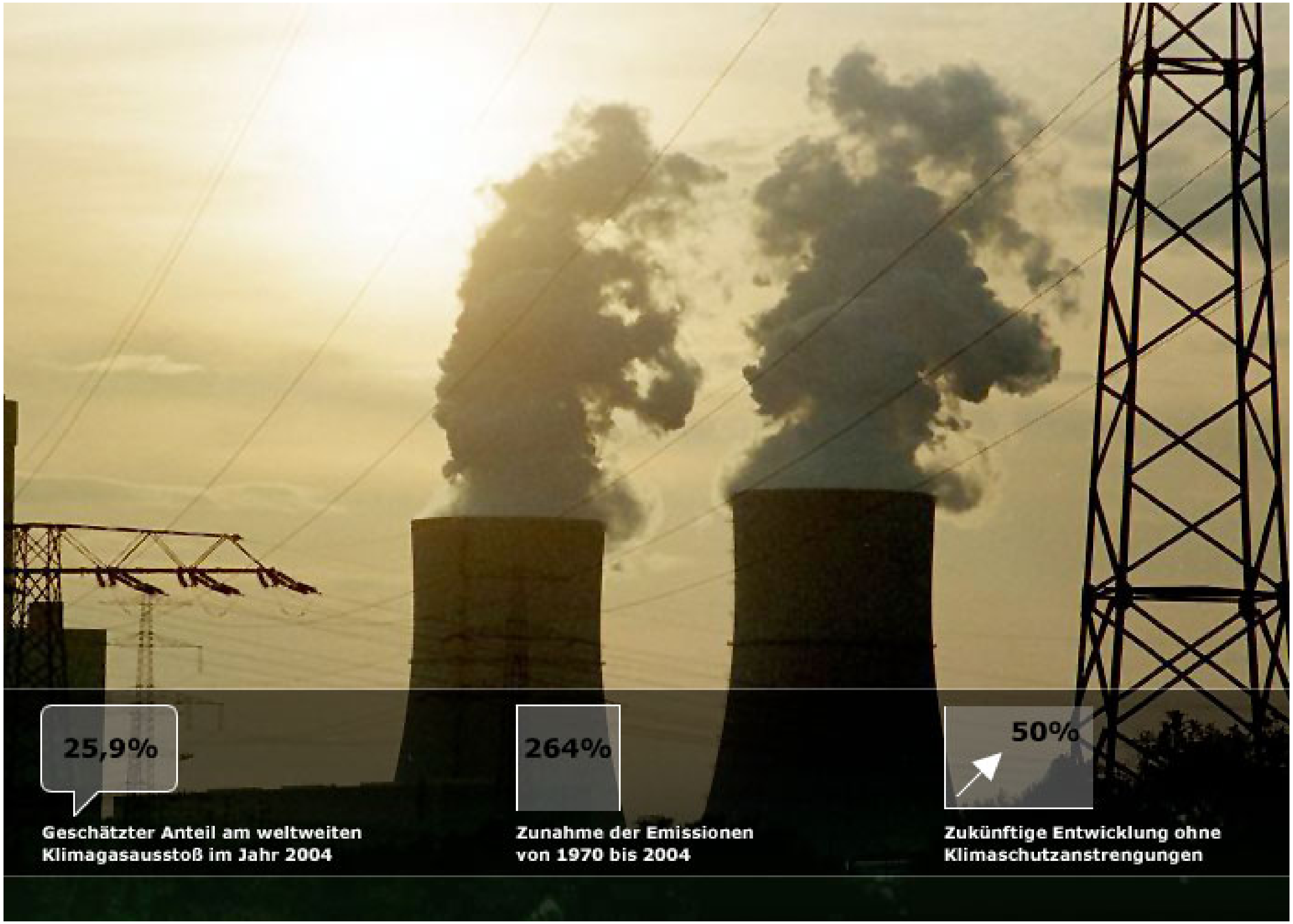
Top 10 of the Global Problems

1. Energy
2. Water
3. Food
4. Environment
4. Poverty
5. Terrorism and war
6. Health
7. Education
8. Democracy
9. Population

Problems 2-9 are direct or indirect related to energy!

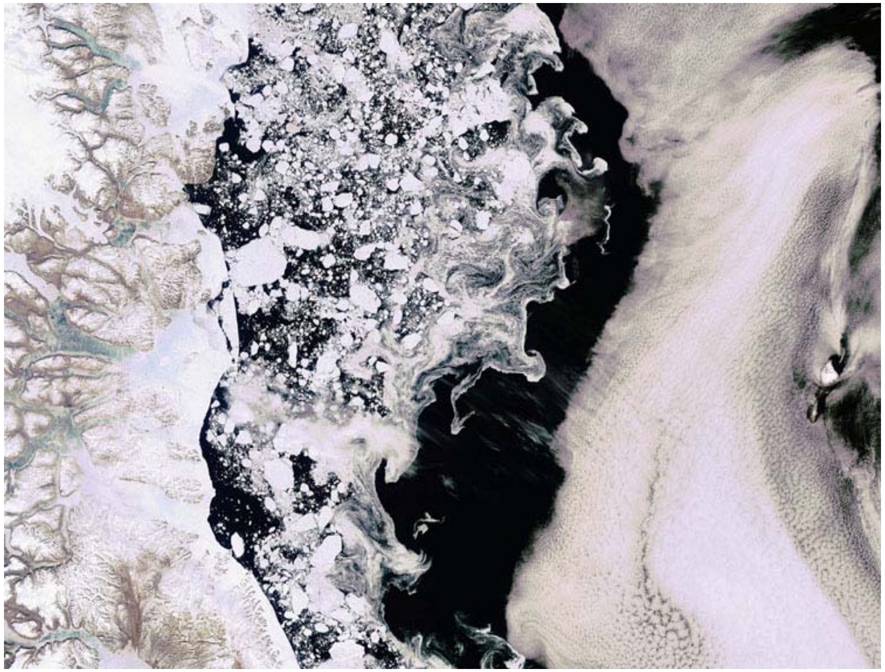
Richard. E. Smalley, MRS Bulletin **2005**, *30*, 412-417.

No Energy without Carbon Dioxide



Energy: More than 25 % of all climate relevant gases are produced for energy (2004). In the last 35 years emissions increased by a factor of 1.5. In 2030 additional 50 percent carbon dioxide and other gases will pollute our atmosphere if we do not change.

Global Problems - Local Actions



In the last ten summers the water ice area has been decreased statistically by 100.000 km² per year. In 2007 the decrease was 1 Million km².

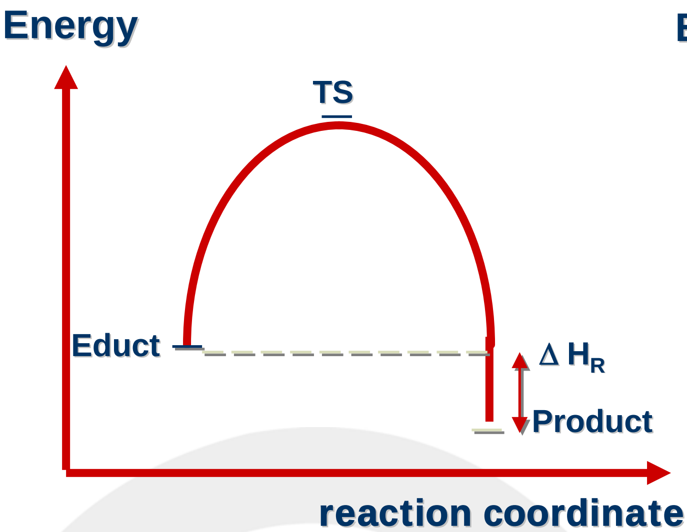
The Potential Impact of Carbon Dioxide

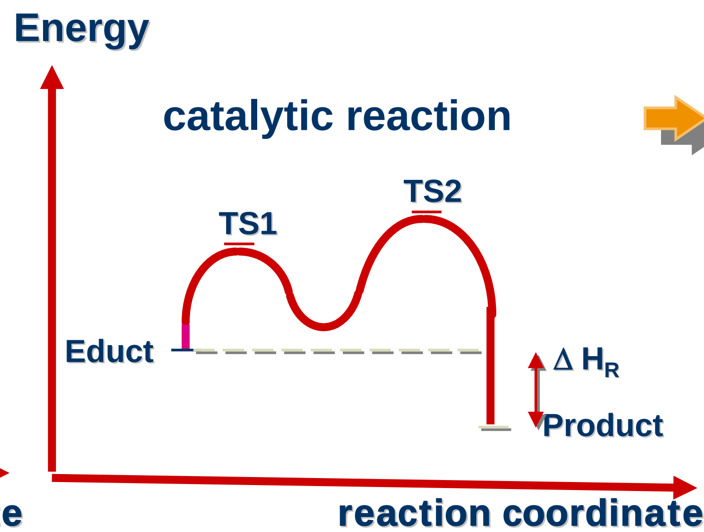
Stabilization level (ppm CO_2-eq)	Global mean temp. increase at equilibrium (°C)	Year CO_2 needs to peak	Year CO_2 emissions back at 2000 level	Reduction in 2050 CO_2 emissions compared to 2000
445 – 490	2.0 – 2.4	2000 - 2015	2000- 2030	-85 to -50
490 – 535	2.4 – 2.8	2000 - 2020	2000- 2040	-60 to -30
535 – 590	2.8 – 3.2	2010 - 2030	2020- 2060	-30 to +5
590 – 710	3.2 – 4.0	2020 - 2060	2050- 2100	+10 to +60
710 – 855	4.0 – 4.9	2050 - 2080		+25 to +85
855 – 1130	4.9 – 6.1	2060 - 2090		+90 to +140

The next 20-30 years will determine the concentration of carbon dioxide for a long time!

K. Thambimuthu, Centre for Low Emission Technology, Queensland/Australien; 17th WHEC 15.-19. Juni 2008, Brisbane

Catalysis = Saving Energy





economically and ecologically improved processes

better raw material and energy usage; minimization of waste

- The science of accelerating chemical reactions.
- More than 80% of all processes in the chemical and pharmaceutical industry make use of catalytic reactions.
- The value of products made by catalysis exceeds 2.5 x 10^6 Mio $.
- Key technology for life sciences and environmental industries.

Catalysis - Solutions for the 21st Century

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, ...)

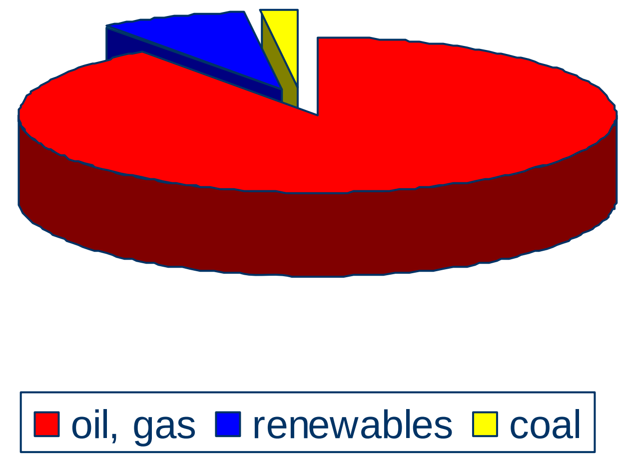
Enable new pharmaceuticals (Alzheimer, cancer, HIV, ...), **materials** (polymers), **and consumer electronics**

More sustainable processes for bulk and fine chemicals
(aniline, phenol, caprolactam, propylene oxide, polyurethane, ...)

Raw Material Basis of the Chemical Industry

Today dominant:

- Fossil Fuels
- Olefines
- Starting from small building blocks to high value products



In the future (next 20 years):

- Still fossil fuels
- Alkanes
- Renewable ressources, CO_2

Change of feedstocks needs the development of new and drastically improved catalytic transformations!

How to Use Biomass

- Biomass and CO_2 are the only carbon-containing renewable raw materials.
- If want to make an impact we have to choose the „right“ feedstock! Preferable feedstocks are: Cellulose, Hemi-Cellulose, Lignin, Chitin, agricultural and municipal solid wastes, Algae (?).
- Bulk chemicals and synthetic bio-fuels are most useful products for establishing renewables on large scale!
- Biomass will have to be accessed in a way that does not compete with land and agricultural resources for food and feed production.
- Application of known technologies and products is preferable. Integration into existing value-added chains.
- Catalysis and engeneering will be key issues.

Biomass Conversion - General

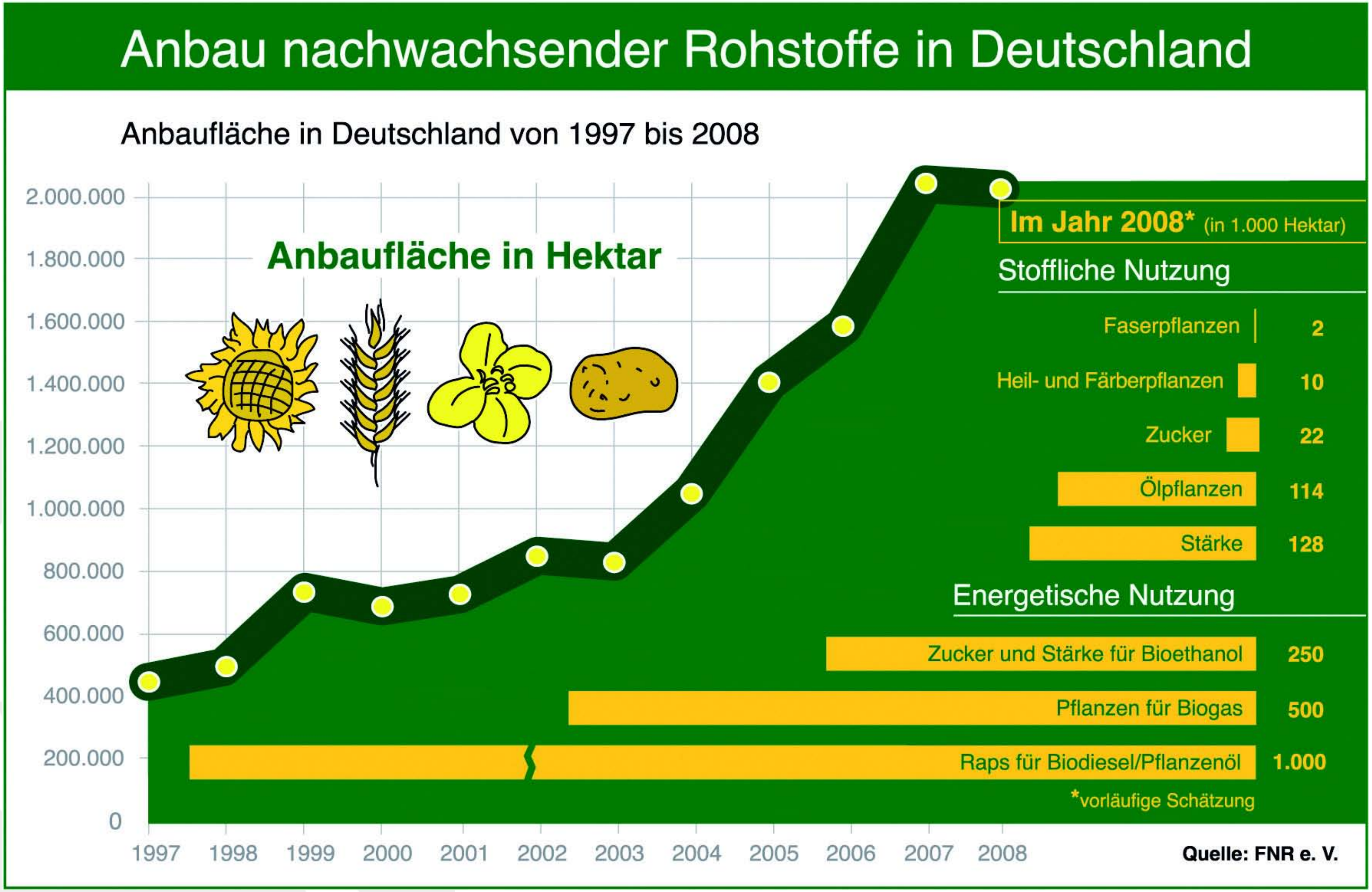
- Biomass conversion is based on molecular chemistry and catalysis!

- There are 9 fundamental elementary steps to convert biomass: hydrolysis, dehydration, hydrogenation, aldol condensation, isomerization, decarbonylation, decarboxylation, oligomerization, WGS.

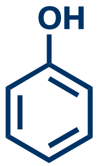
- Currently we do not use the most efficient renewable ressources; e.g. cost on energy basis: oil > starch >> cellulose. There is huge potential for improvement!

- Example biofuels: 25 MHa are used for bio-fuels (5.000 MHa for food); controversial debate on the use of crops and palm oil (World Bank states biofuels are responsible for 75% rise of food price. It is not true!)

Biomass Used in Germany – Non-Food Area



Challenge: „New Catalytic Dream Reactions“

- $H_2O \longrightarrow H_2 + O_2$
- Lignin ⟶  + Arenes

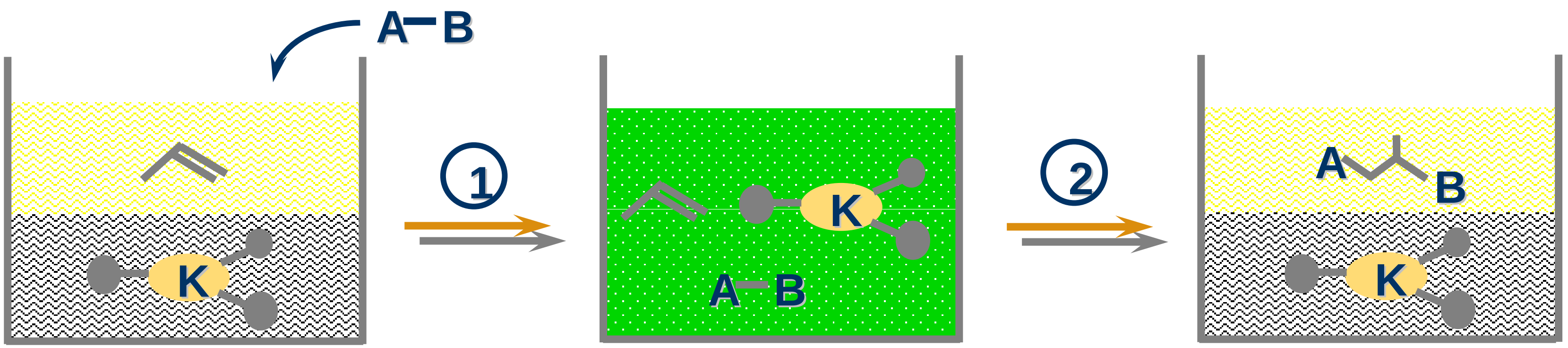
- Cellulose (Hemi-Cellulose) $\xrightarrow{H_2}$ Alkanes
- Cellulose or  ⟶ 

- CO_2 / $H_2 \longrightarrow$ LAO´s
- Selective oxidation of methane to methanol
- Selective oligomerization of ethylene to LAO´s
- $H_2 + N_2 \xrightarrow{\text{low temperature}} NH_3$
- Selective catalytic hydrogenation and deoxygenation alcoholes and carboxylic acid derivatives under mild conditions

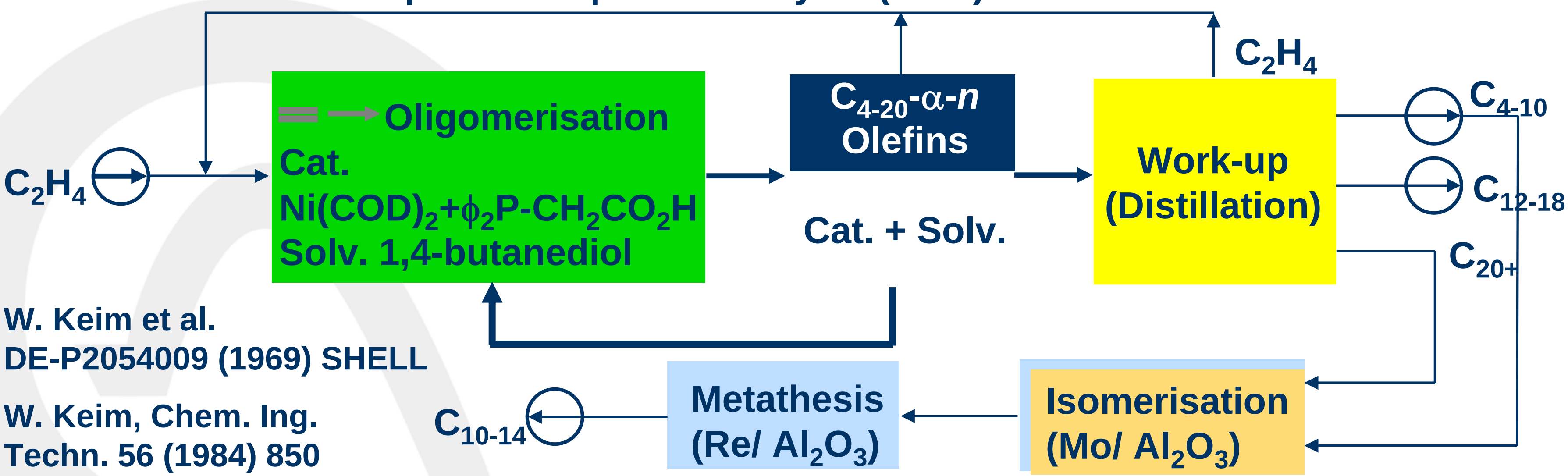
Biomass for Existing Value-added Chains: 1-Octen

- Polyolefins based on ethylene/1-hexene or ethylene/1-octene have improved properties and are produced increasingly. Production volume in 2006 >100 Mio to/a.
- The main current industrial process for these monomers is not selective and needs several steps.
- Biomass is a potential feedstock for both co-monomers.
- Route 1: Ethanol to ethylene followed by selective oligomerization.
- Route 2: Ethanol to 1,3-butadiene followed by telomerization.

Shell Higher Olefin Process (SHOP)



First industrial example of two phase catalysis (1968)

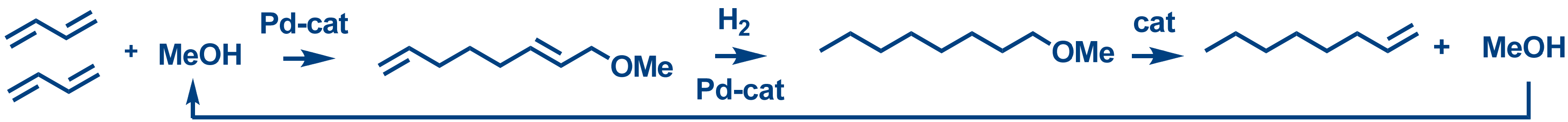


W. Keim et al.
DE-P2054009 (1969) SHELL

W. Keim, Chem. Ing. Techn. 56 (1984) 850

A Green Process for 1-Octene

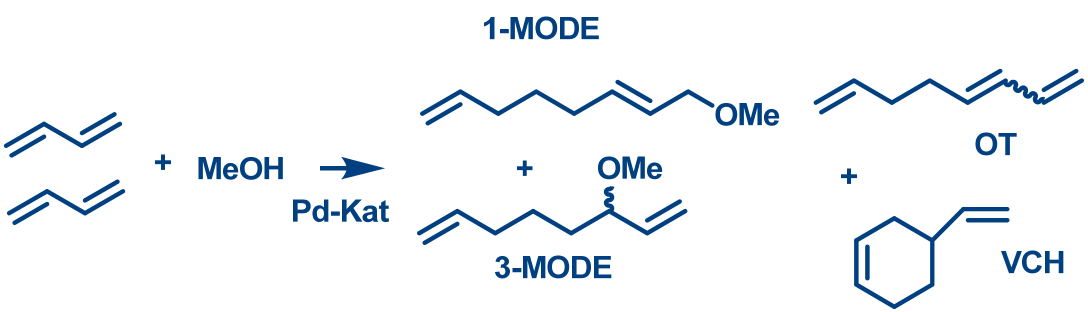
The overall process:

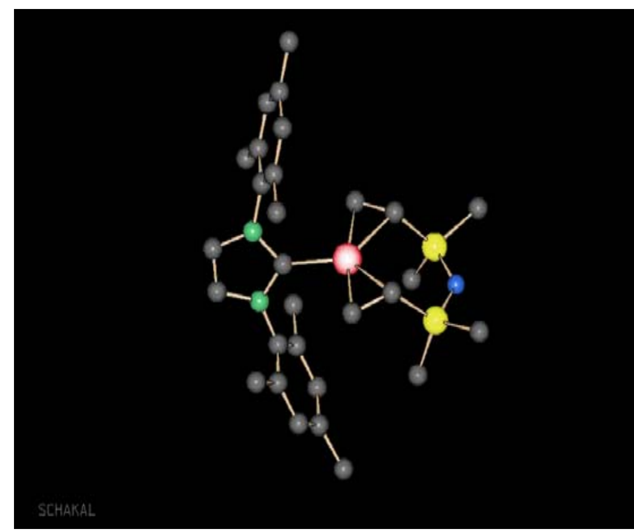


100 % atom efficient

R. Jackstell, M. Gomez Andreu, A. Frisch, H. Klein, K. Selvakumar, A. Zapf, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, *Angew. Chem. Int. Ed.* 2002, *41*, 986-989.

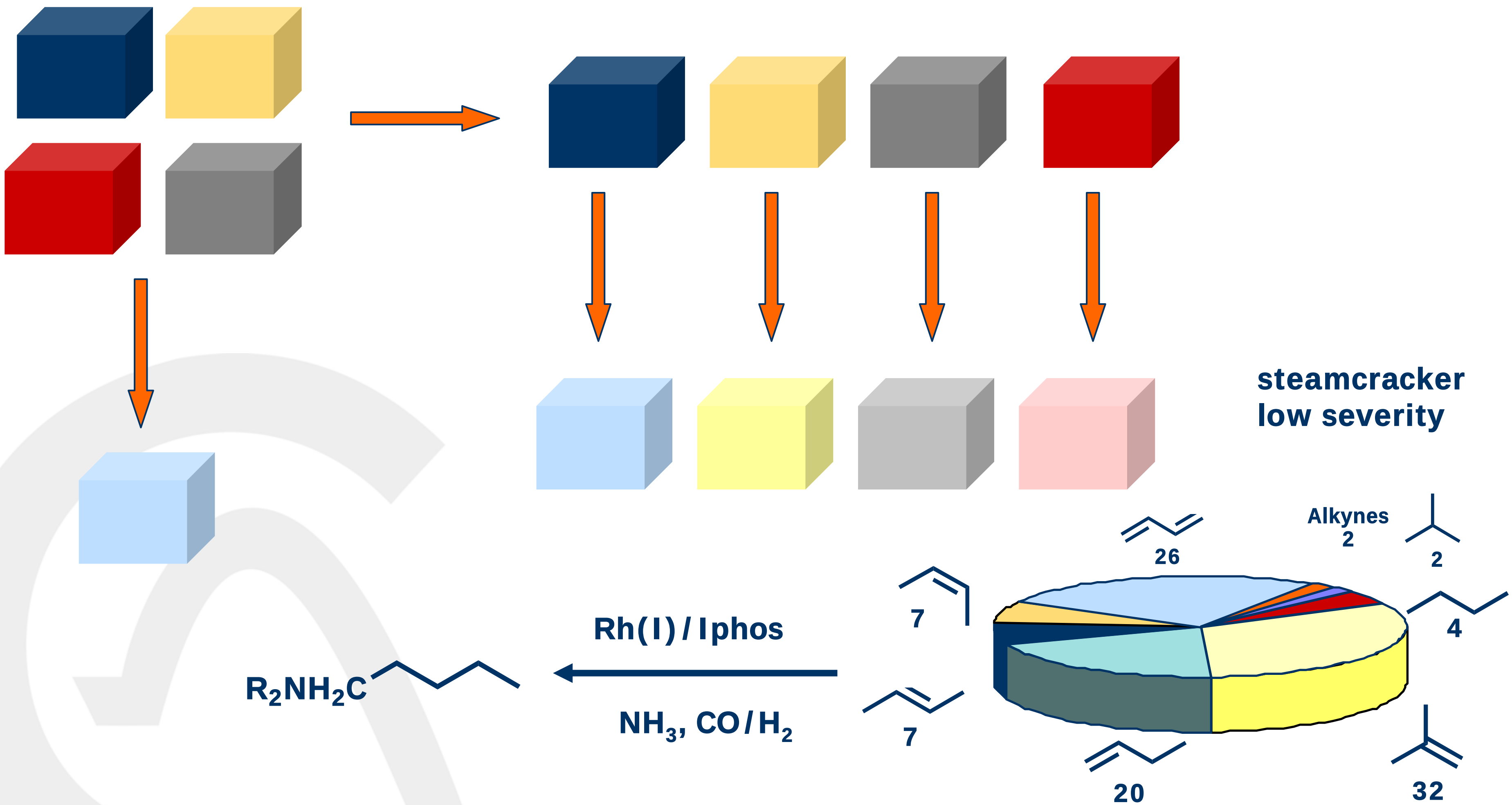
MeOH Telomerisation:





>25.000 kg of telomerization products have been so far produced.

Use Mixtures Instead of Pure Feedstocks



A. Seayad, M. Ahmed, H. Klein, R. Jackstell, T. Gross, M. Beller, Science, 2002, 297, 1676-1678.

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Renewable Hydrogen is Available

Island Utsira, Norway

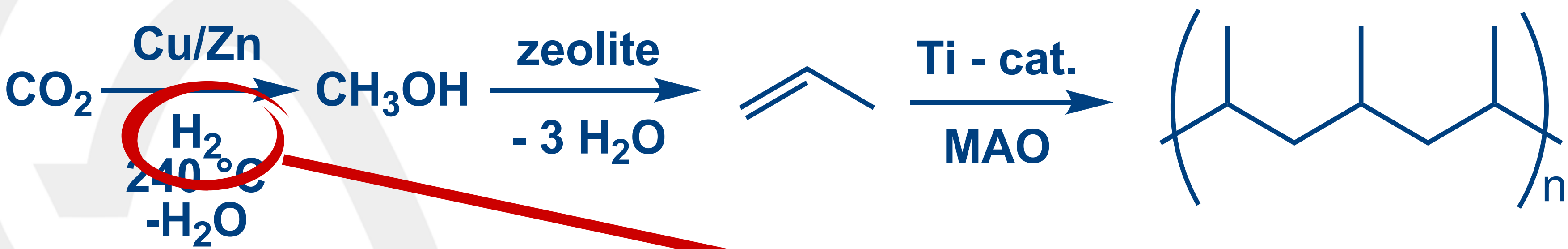
Energy efficiency:
- **Electrolysis: 60-70%**
- **Si-Photovoltaik: <20%**
- **Organic-Photovoltaik: <10%**

Hydrogen-Infrastructure / Safety Issue

Carbon Dioxide: Available from Industry

Industry: Nearly 20% of carbon dioxide emission came from industry (2004). It increased from 1970 bis 2004 by 164% (9 billion tons of CO_2 in 2004). If we do not change we will increase emissions up to 14 billion tons in 2030.

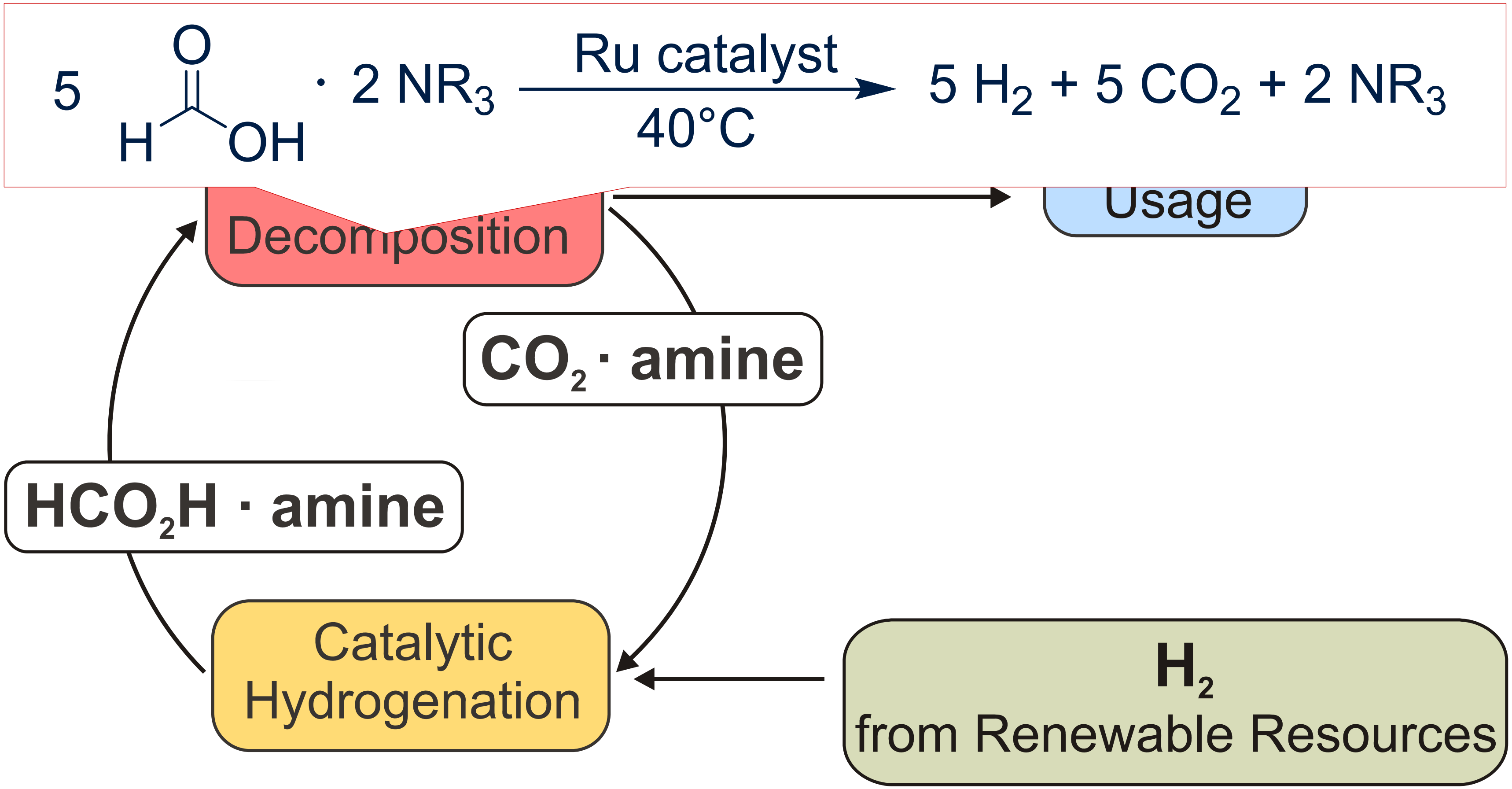
CO_2: Feedstock for the Future ?



Hydrogen is the key!!

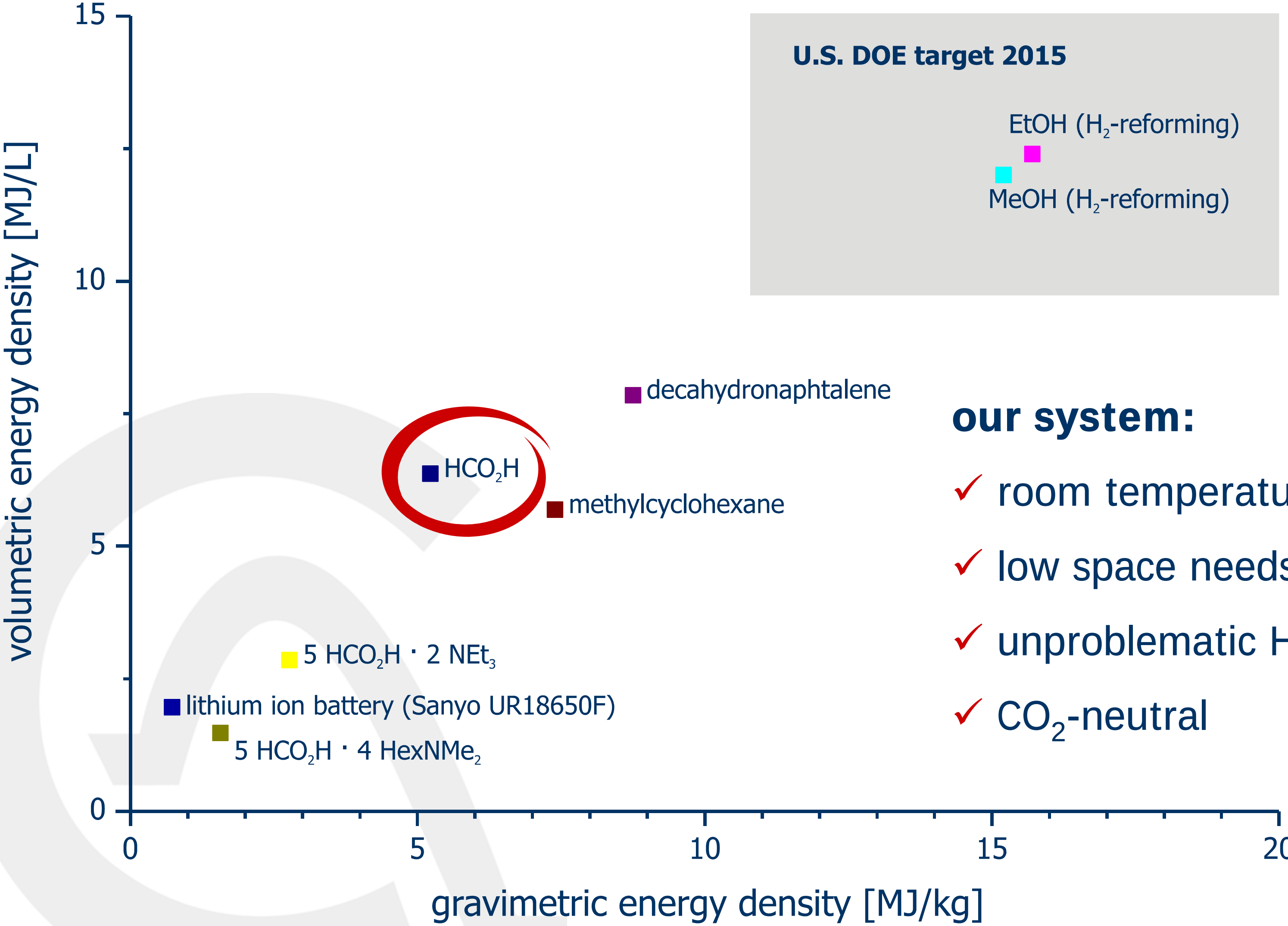
PP: >30 Million to / Jahr

A CO_2-Neutral Cycle for H_2-Storage



B. Loges, A. Boddien, H. Junge, M. Beller, Angew. Chem. Int. Ed. 2008, 47, 3962-3965 („Hot paper“). See also for a parallel development: C. Fellay, P. J. Dyson, G. Laurency Angew. Chem. Int. Ed. 2008, 47, 3965-3967.

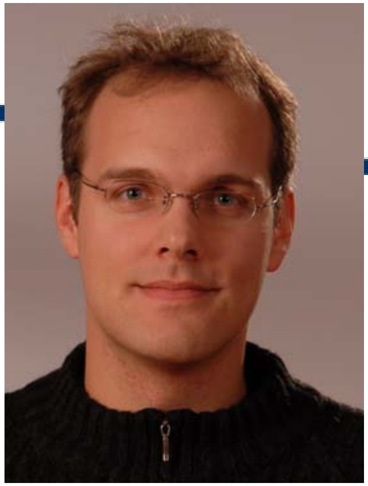
Theoretical Energy Content of Different Substrates



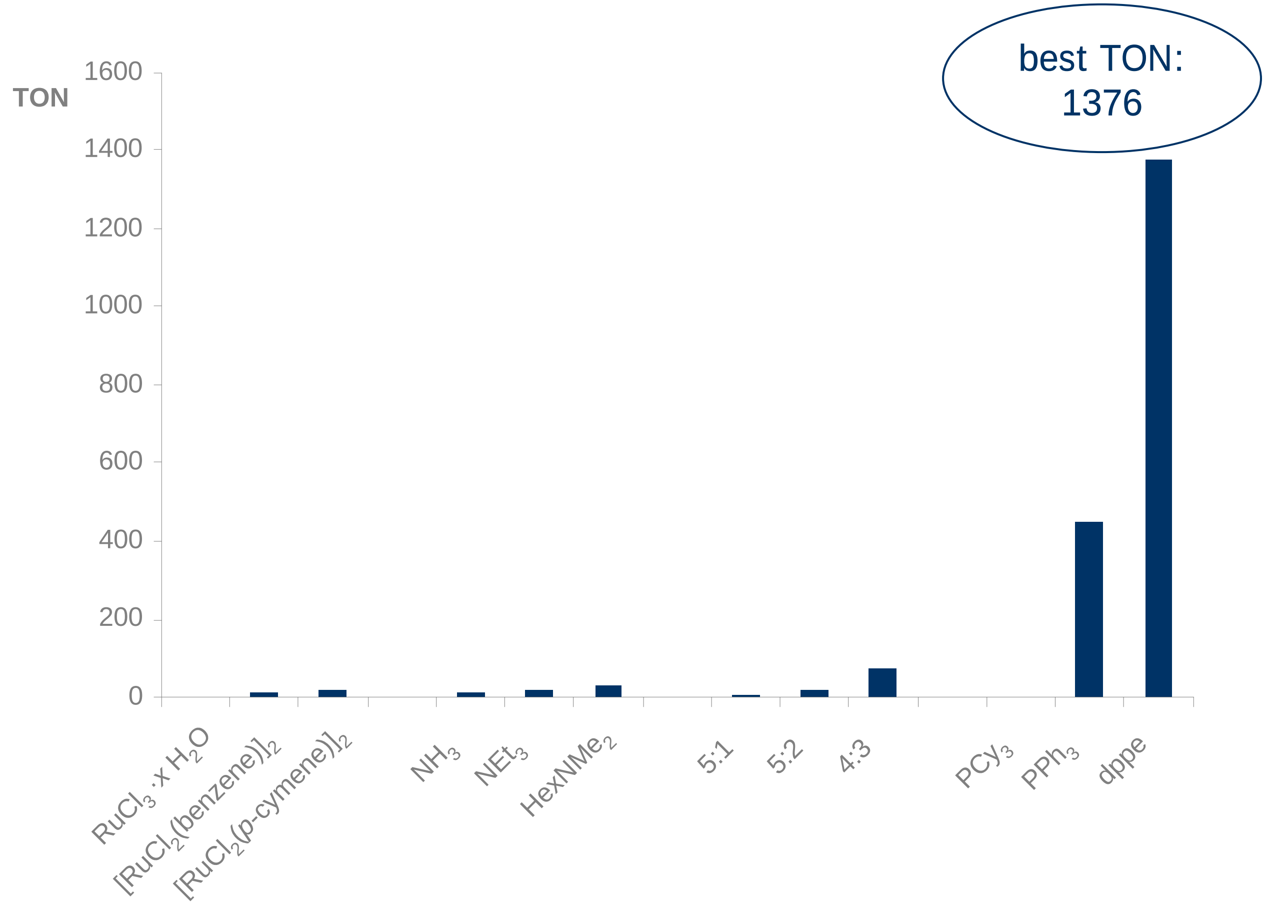
our system:

- ✓ room temperature
- ✓ low space needs
- ✓ unproblematic H_2-cleaning
- ✓ CO_2-neutral

Towards an Optimized Catalyst



- Metal source
- Amine
- Ratio HCO_2H:Amine
- Ligand



Reaction conditions: 5 mL substrate, 19 – 59.5 µmol metal, 0-6 eq. phosphine, 40 °C, 3 h

B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026-4029; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962-3965.
A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* **2008**, *1*, 751-758.

"CO_2-neutral Cycle" for Storage of Hydrogen

membrane processes

H_2

$H_2 + CO_2$

H_2 from renewable resources

for example: H. Lin, E. Van Wagner, B. D. Freeman, L. G. Toy, R. P. Gupta, *Science* 2006, 311, 639.

homogeneous hydrogenation of CO_2

Our task: controlled decomposition of formic acid into hydrogen and carbon dioxide at low temperatures

HCOOH

P. G. Jessop in *Handbook of Homogeneous Hydrogenation*, Vol. 1, (Eds. J. G. de Vries, C. Elsevier), Wiley-VCH, Weinheim 2007, pp. 489-511; see also: Leitner et al.; Noyori et al.

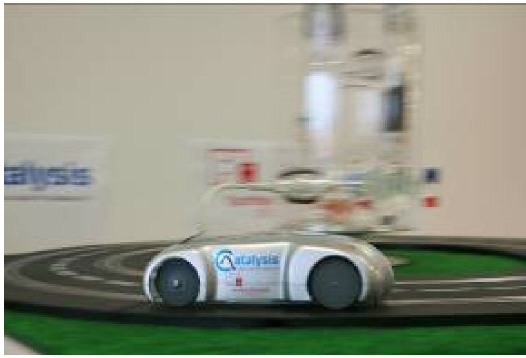
Applications?

Combination of hydrogen generation and fuel cell technology:

Mid term:
mobile and portable applications
e.g. laptop, cell phones

Long term?
A car needs ca. 1 kg H_2 / 100 km
– ca. 120 kg formic acid per 500 km
or 20 L per 100 km

Demonstration: Toy car

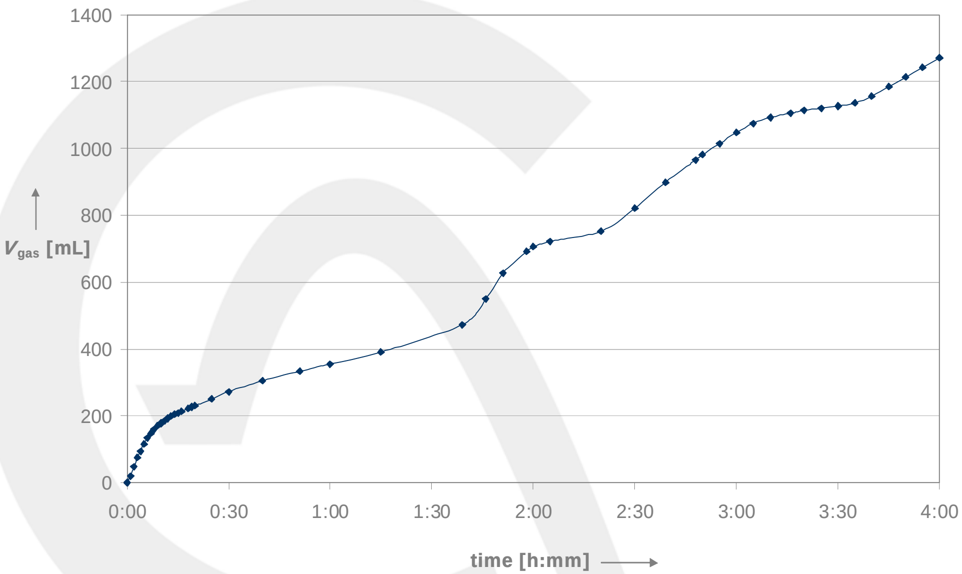


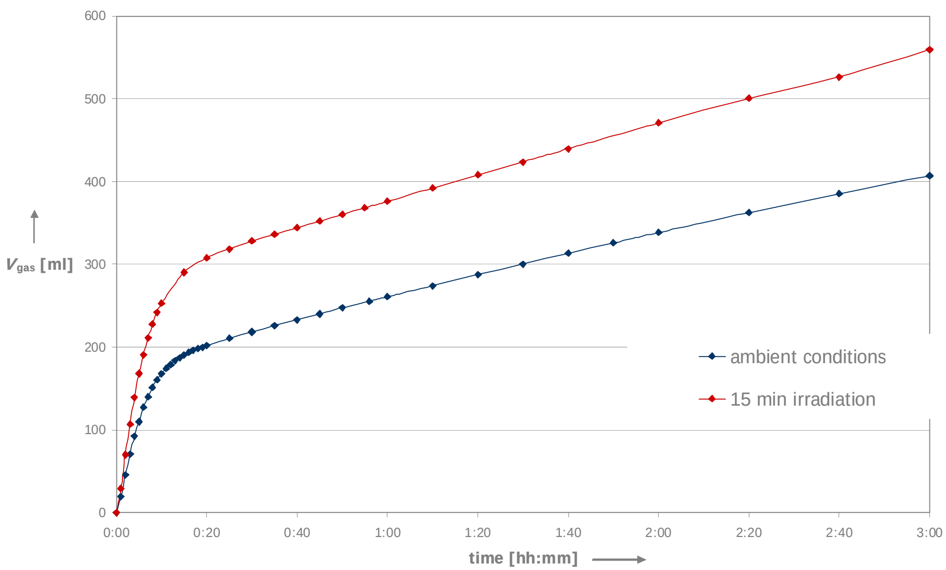
Visit of the German President at LIKAT on 26.10.2008

New Results

One day, Albert Boddien obtained a result that did not fit into our previous investigations.

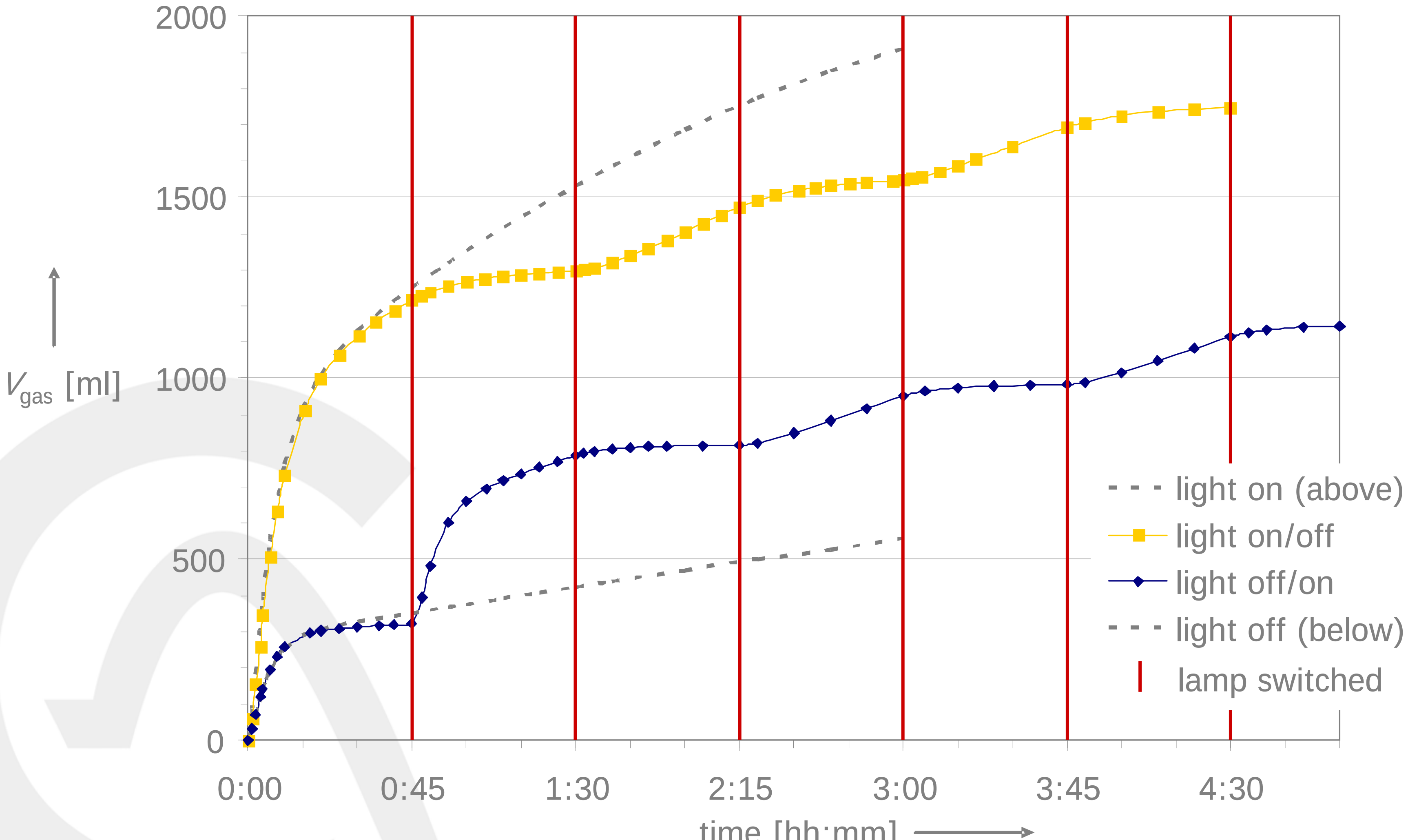
A few days later, this result could be reproduced while we took photos (with flash) of our apparatus.





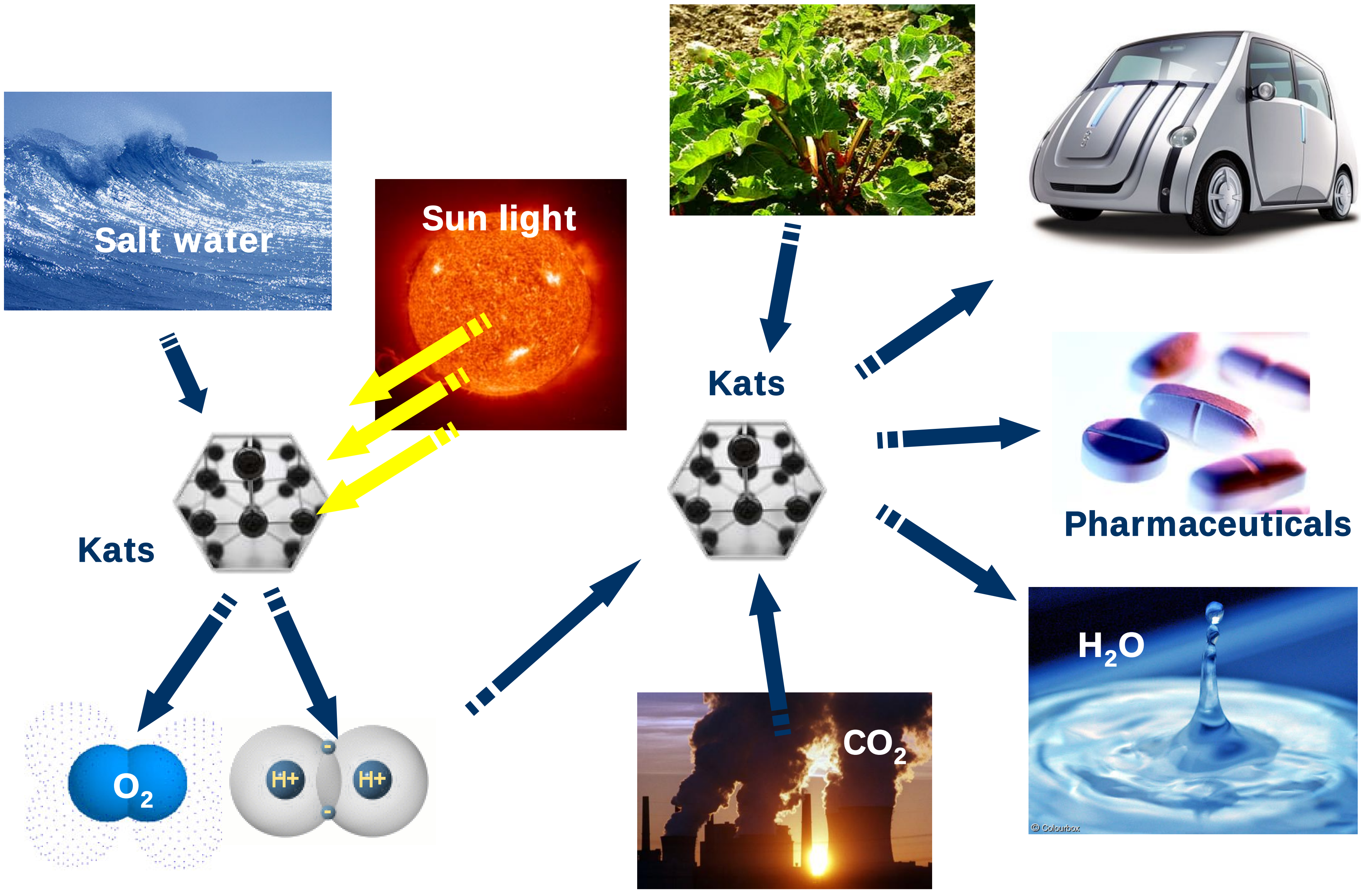
conditions: 5 mL 5 $HCO_2H \cdot 2\ NEt_3$, 19 µmol $[RuCl_2(benzene)]_2$, 6 eq. PPh_3, 40 °C - catalyst pretreated in 1 mL DMF at 80 °C, 2h

Controlling H_2 Generation with Light



conditions: 5 mL 5 $HCO_2H \cdot 2 NEt_3$, 19 µmol $[RuCl_2(benzene)]_2$, 6 eq. PPh_3, 40 °C - catalyst pretreated in 1 mL DMF at 80 °C, 2h

A Vision for Sustainability



Acknowledgements

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Industrial partners:

Drs. T. Riermeier, R. Kadyrov, W. Mägerlein, A. Cotte,

Previous funding: Mecklenburg-Vorpommern, **BMBF**, **DFG**, AIF, EU, **Degussa**, **Lanxess**, Esteve, BASF, Merck, Grünenthal, Solvias, Altana, Bayer, DSM, ...


Ostseebad
WARNEMÜNDE

An Early Vision ....

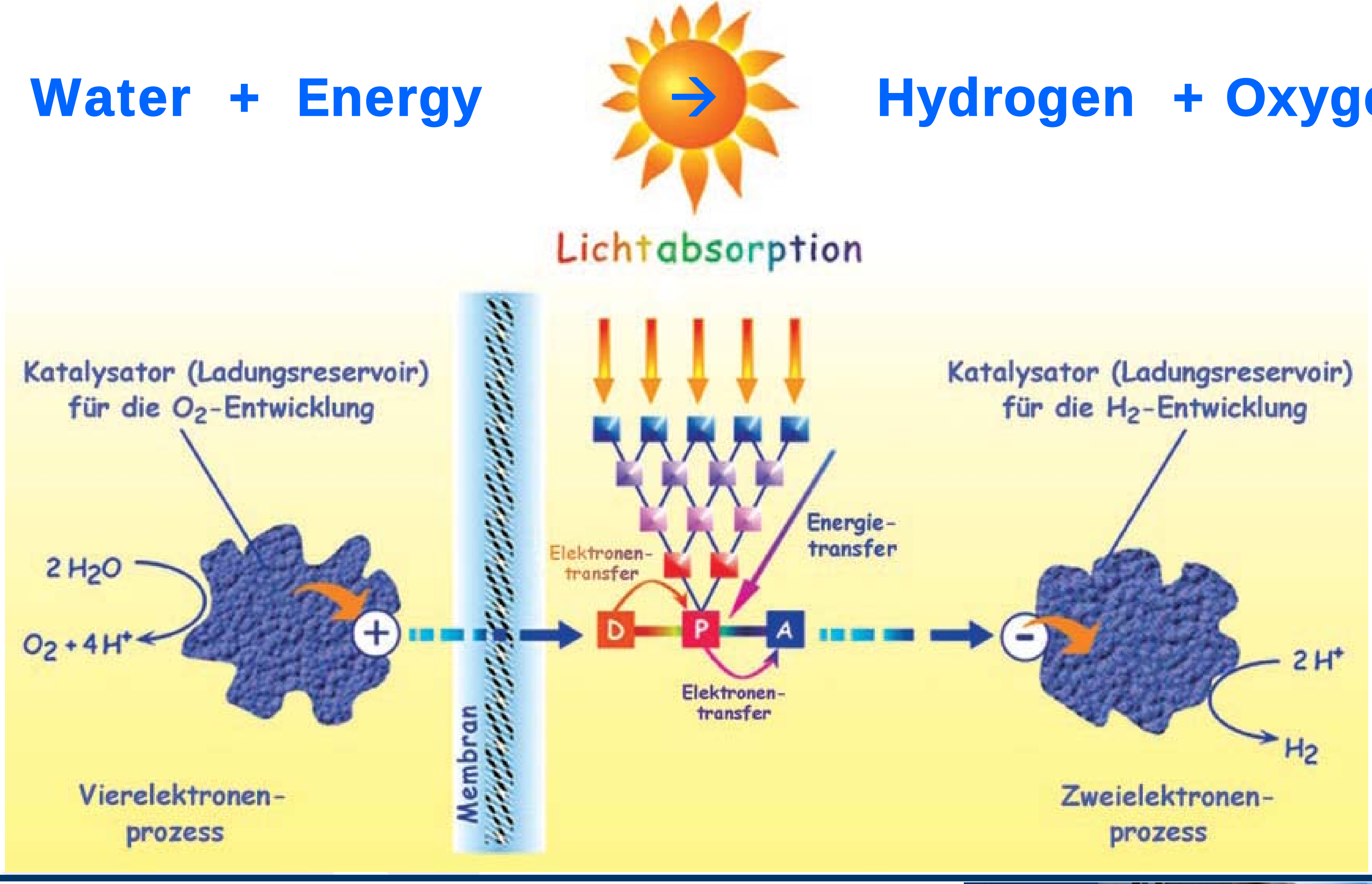
„I believe that one day hydrogen and oxygen, which are the components of water, can be used as a never ending source of heat and light; much better than coal. ...

Water will be the coal of the future.“

Jules Verne, The Secret Island (1875)

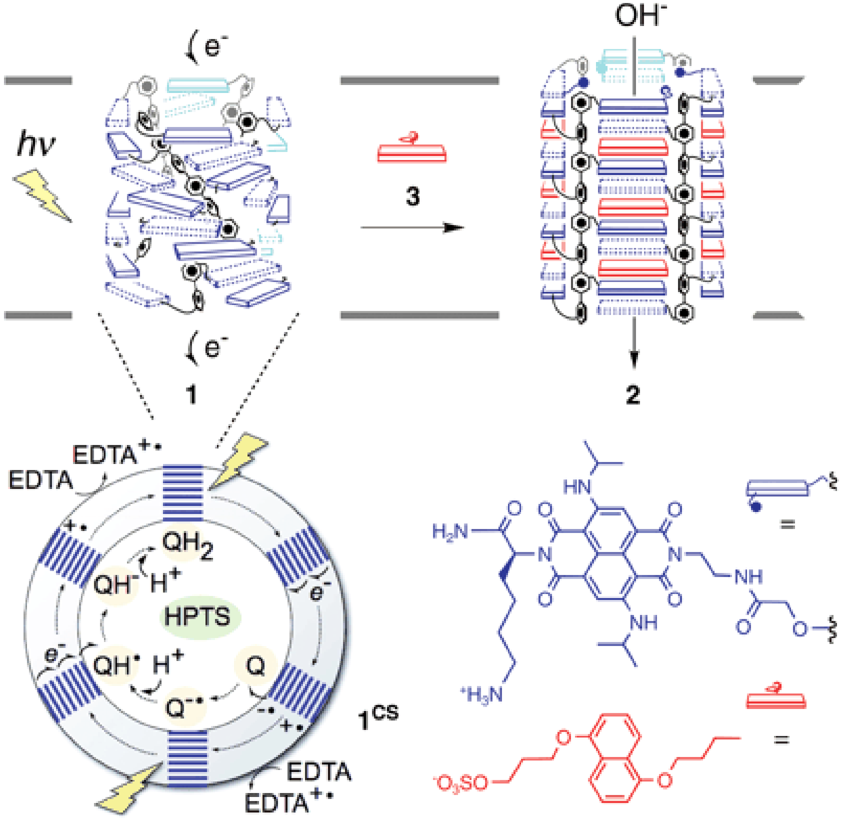
Artificial Photosynthesis

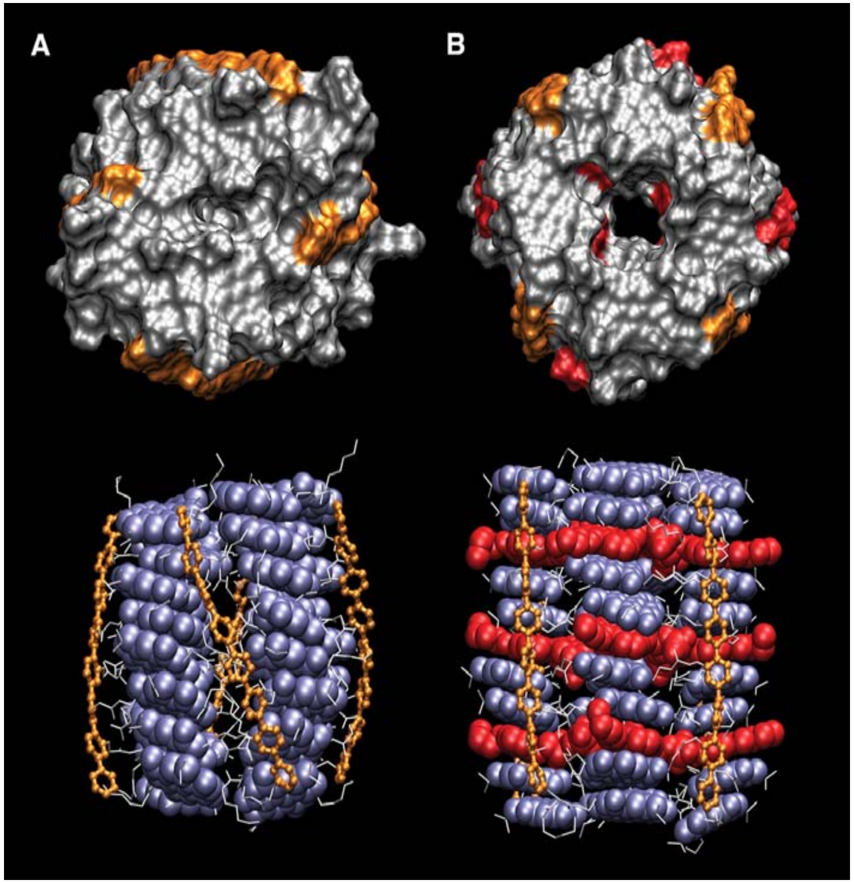
Water + Energy → Hydrogen + Oxygen



Artificial Photosynthesis: A Light-driven Electron Pump

Smart photosystem 1 with ligand-gated opening into ion channel 2 and detection of photosynthetic activity.





Molecular dynamics simulations of photosystem 1 (A) and ion channel 2 (B) with 12 ligands (red).

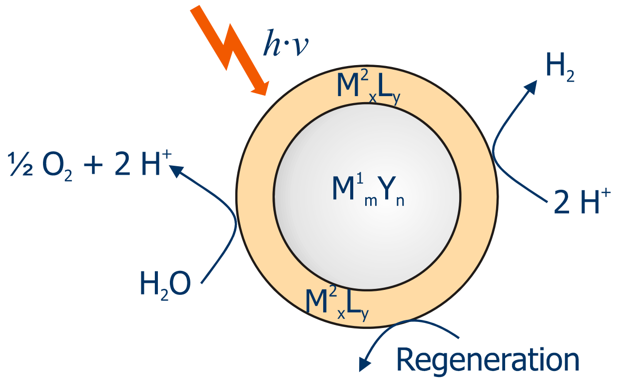
S. Bhosale, A. L. Sisson, P. Talukdar, A. Fürstenberg, N. Banerji, E. Vauthey, G. Bollot, J. Mareda, C. Röger, F. Würthner, N. Sakai, S. Matile, *Science* 2006, *313*, 84-86.

Water Cleavage: Status Today

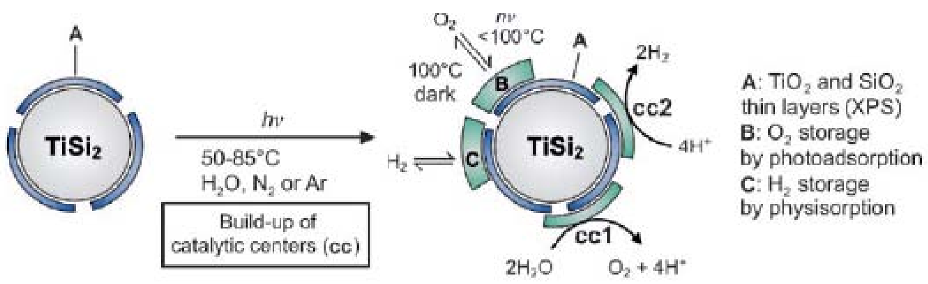
Honda-Fujishima-Effekt (UV-Light; Quantum yields up to 56 %)

$TiO_2 + 2\,h\nu \longrightarrow 2\,e^- + 2\,p^+$	(Activation)
$2\,p^+ + 2\,H_2O \longrightarrow 0{,}5\,O_2 + 2\,H^+$	(TiO_2-Electrode)
$2\,e^- + 2\,H^+ \longrightarrow H_2$	(Pt-Electrode)
$H_2O + 2\,h\nu \longrightarrow 0{,}5\,O_2 + H_2$	(overall reaction)

K. Honda, A. Fujishima, *Nature*, 1972, *238*, 37-38.



$$2\,H_2O \rightarrow H_2 + O_2$$



Visible Light (Efficiency up to 10%)

P. Ritterskamp, A. Kuklya, M.-A. Wüstkamp, K. Kerpen, C. Weidenthaler, M. Demuth, *Angew. Chem*. 2007, *119*, 7863.

Own Experiments: Plasma-treated $TiSi_2$

$$H_2O \xrightarrow{TiSi_2\ (cat.),\ h\nu} 1/2\ O_2 + H_2$$