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Helmholtz-Institut Erlangen-Nürnberg

Hydrogen storage using aromatic hydrocarbons (LOHCs) – the solution for mobile applications ?

P. Wasserscheid[a,b]

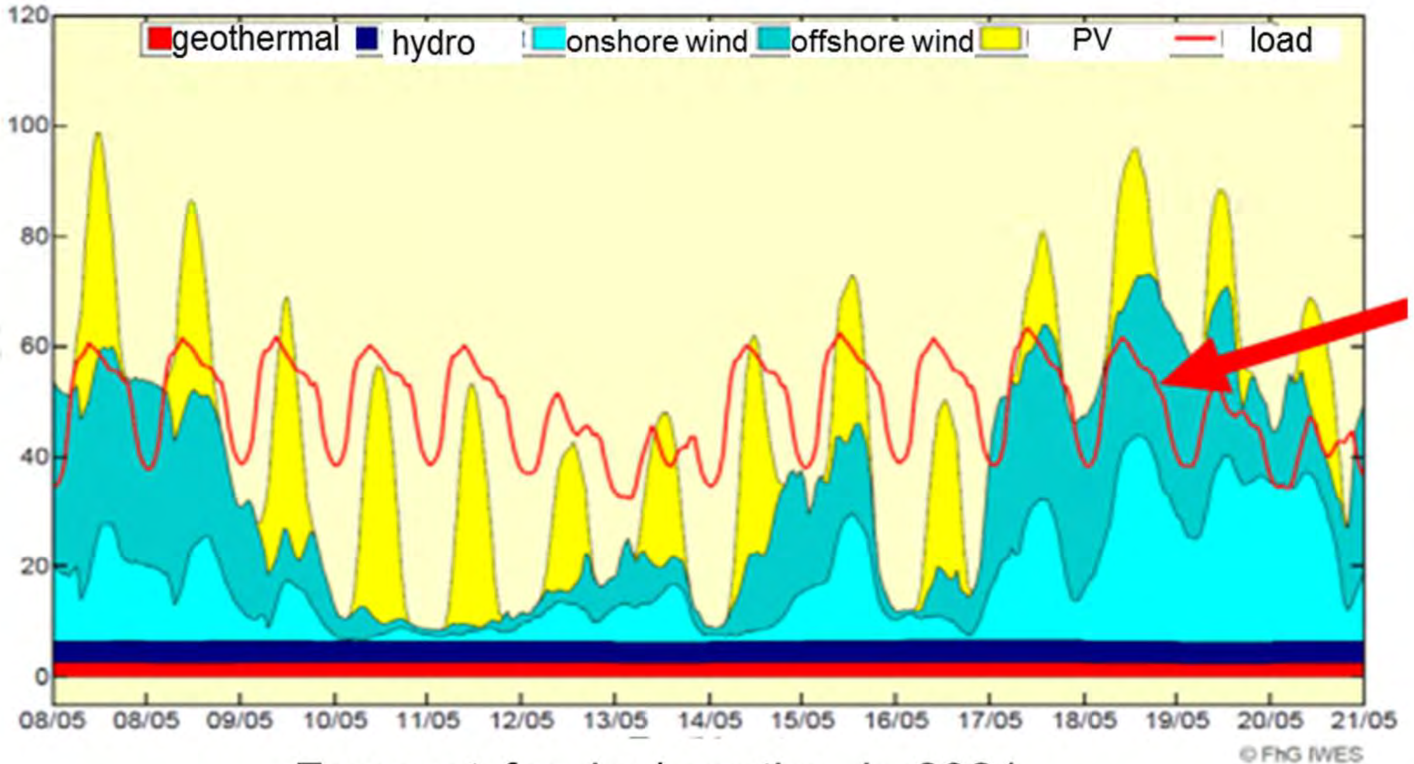
a) Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg

b) Helmholtz-Institute for Renewable Energy Production

German „Energiewende“ – energy storage is urgently needed !

Germany (2013):
regenerative capacity (peak) = 72 GW
average consumption = 71 GW

Power [GW]

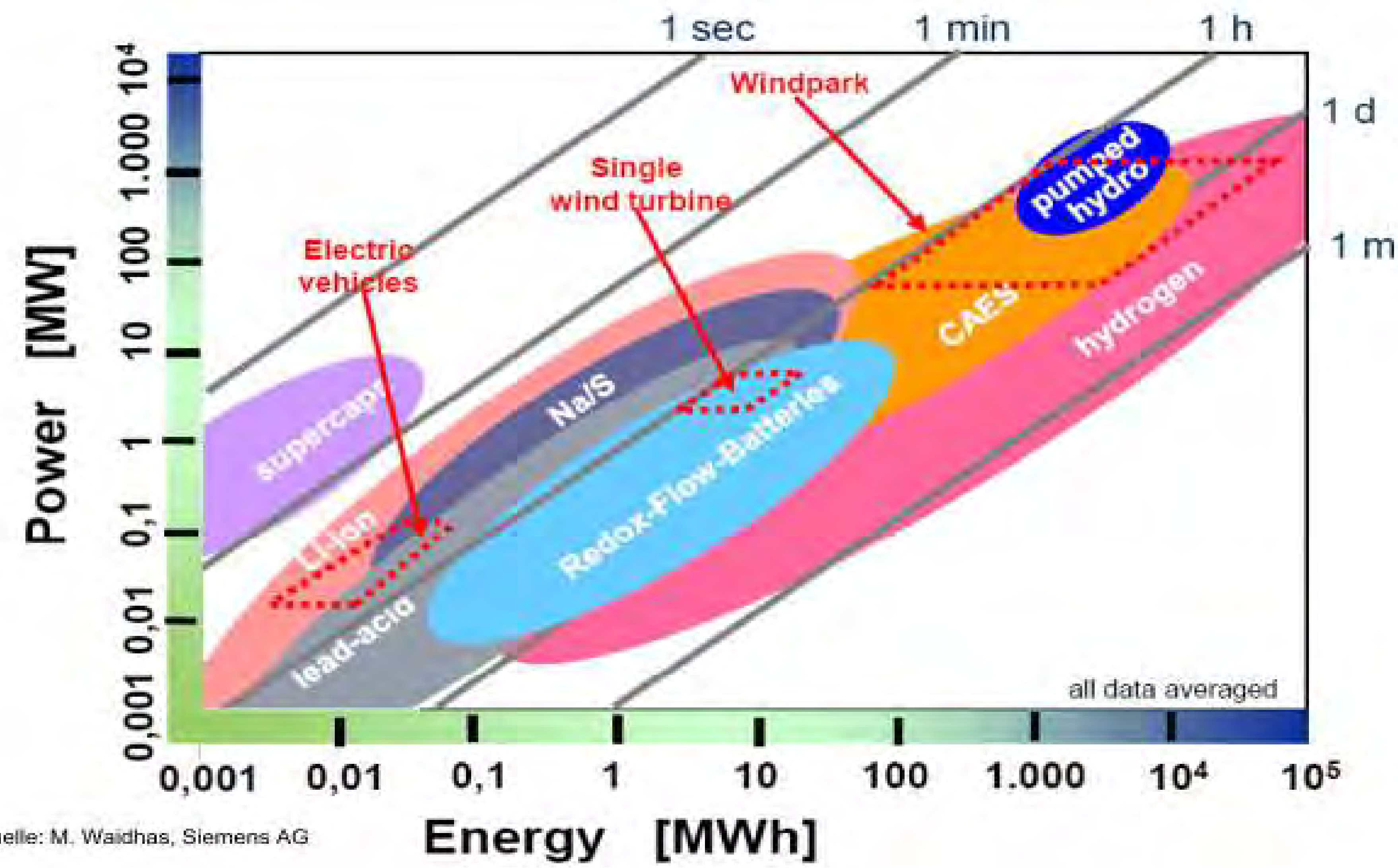


Forecast for day/months in 2021

Possible Consequences:

- Negative electricity prices at energy-rich times;
- Need for back-up capacities for energy-lean times.

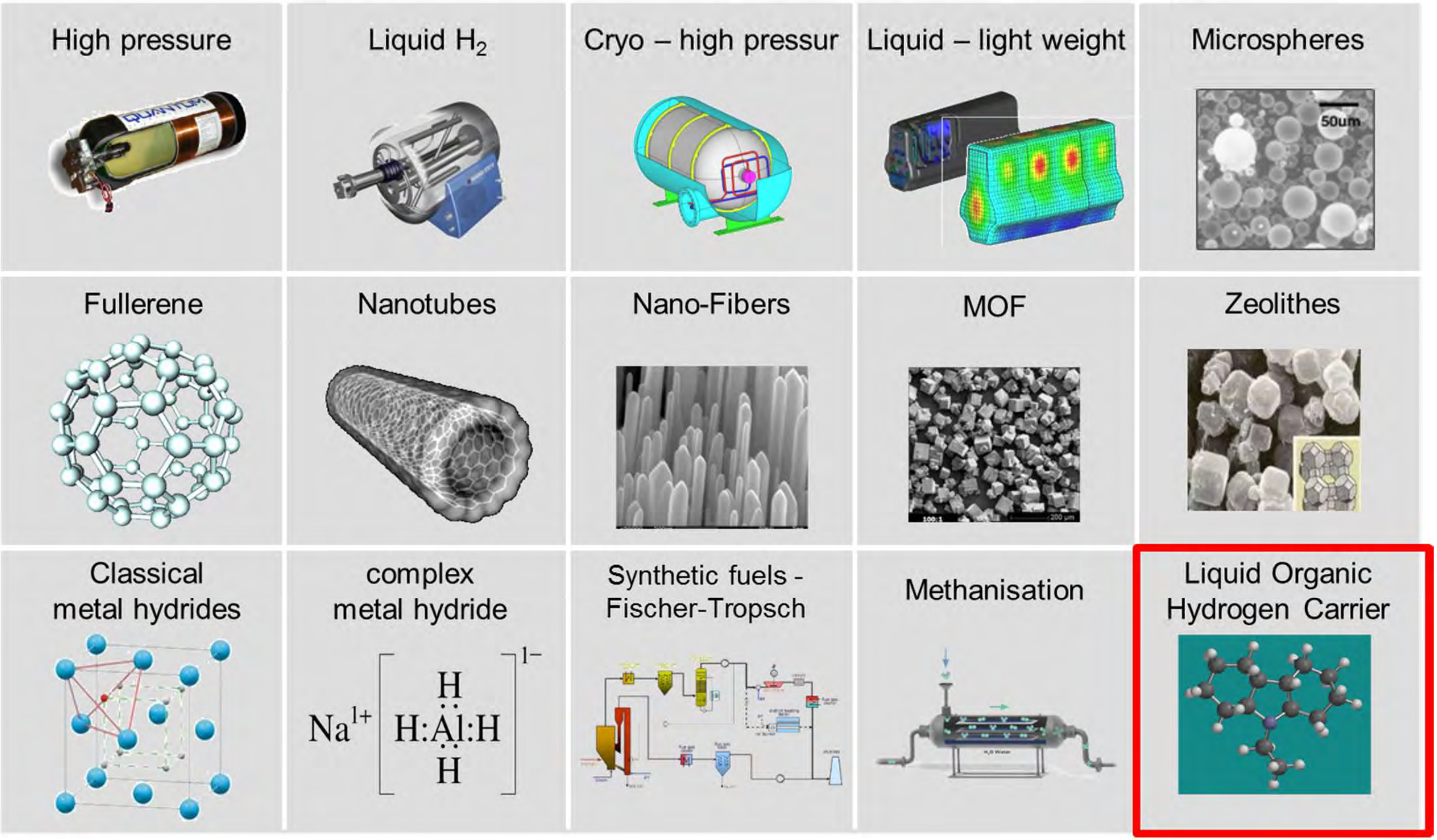
Energy storage - options



Quelle: M. Waidhas, Siemens AG

Chemical energy storage: Hydrogen as the key-compound

Problem: Volumetric storage density of hydrogen is very low



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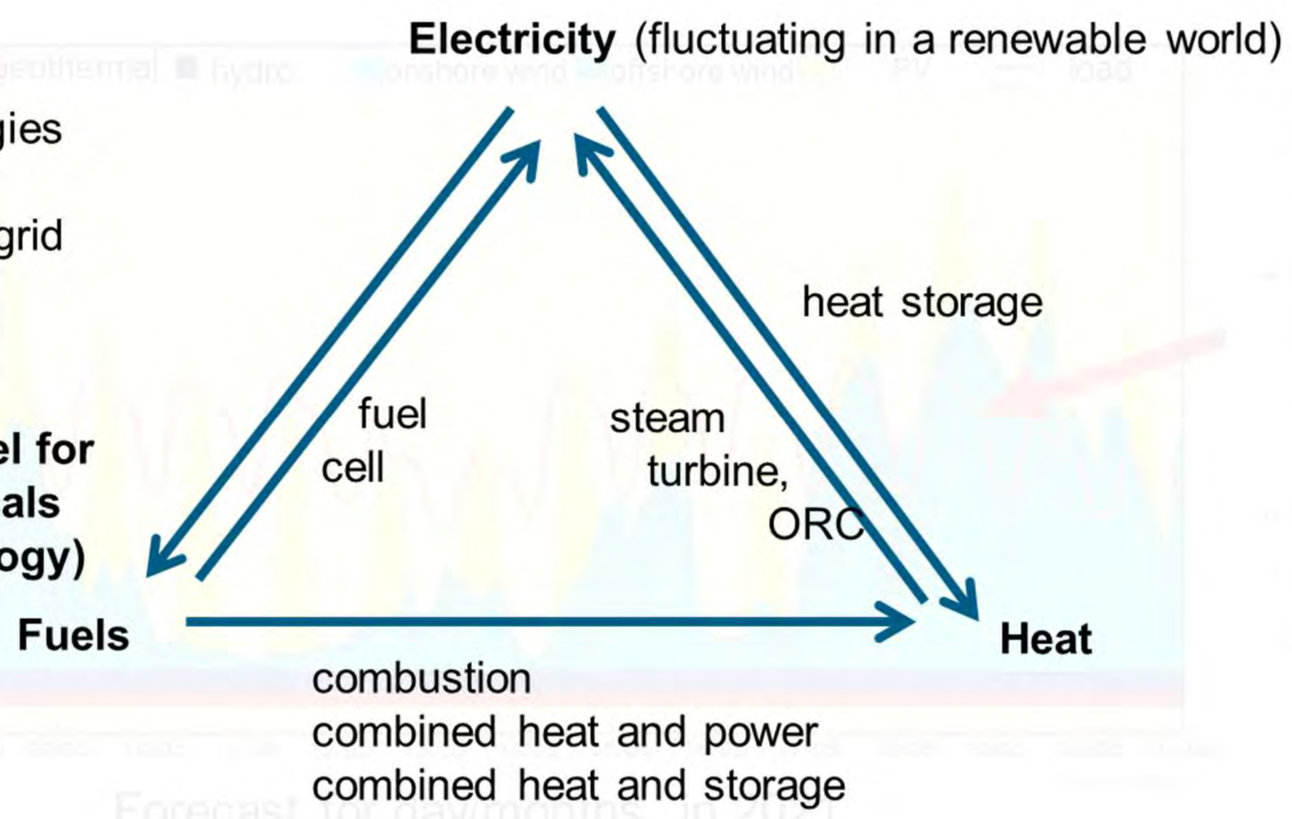
Electrolysis +
Power-to-X technologies

- to hydrogen in gas grid
- to methane
- to diesel

- **to hydrogen as fuel for mobility or chemicals (via LOHC-technology)**



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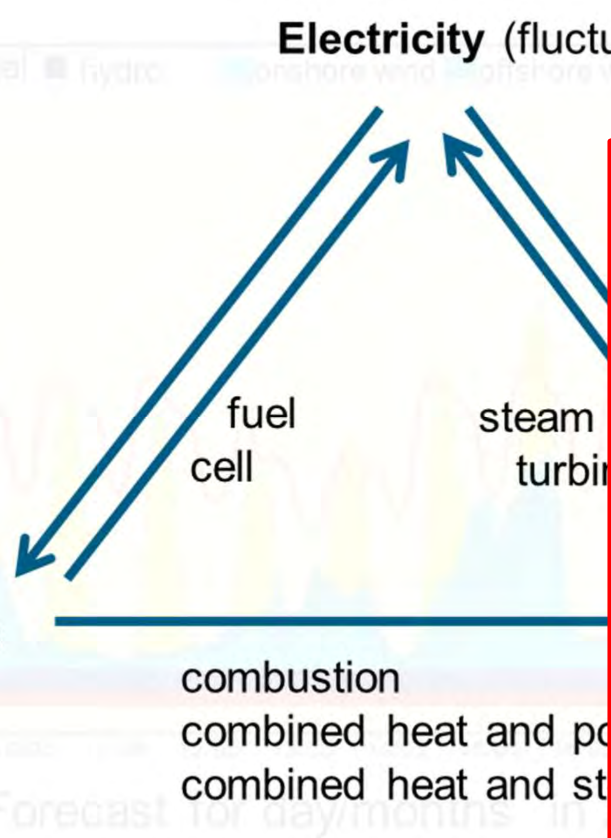


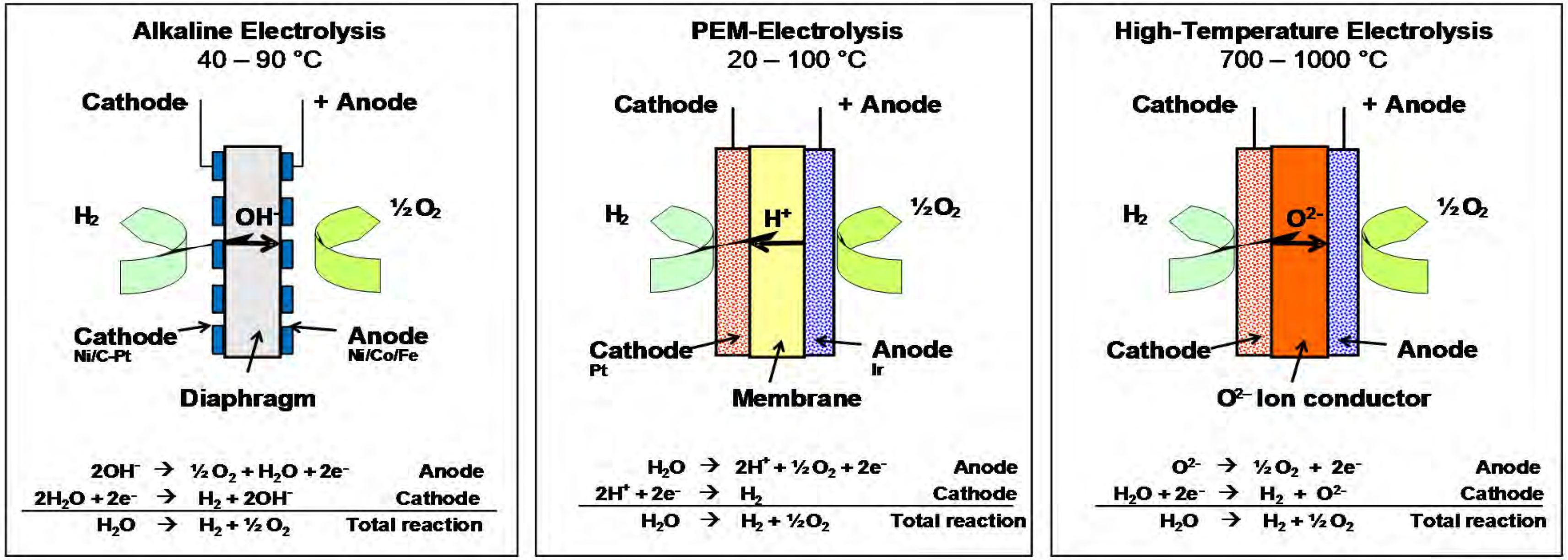
Some rough economics:

1 kg H_2 from electroysis (2015)= 3 - 5 €
1 kg H_2 is 33,3 kWh

(neglecting conversion losses):
33,3 kWh methane = ca. 1,3 €
33,3 kWh diesel= 1,5 €

If you like power to gas / power to diesel technologies you should work on cheaper/better electrolyser technologies !

Key-scientific challenges to optimize water electrolysis !



- to drastically **reduce the precious metal content** or to replace precious metals (IrO_2/PtO ⇒ e.g. Mn-, Co-oxides) while keeping energetic efficiency;
- to **realize dynamic operation** in a highly efficient manner;
- to **realize very high durability** (> 50.000 h) ⇒ avoid electrochemical corrosion processes;
- to **produce hydrogen under high pressure** (> 50 bar);
- to **reduce investment costs** by using cheap materials (membranes, electrodes etc.) and efficient manufacturing processes.

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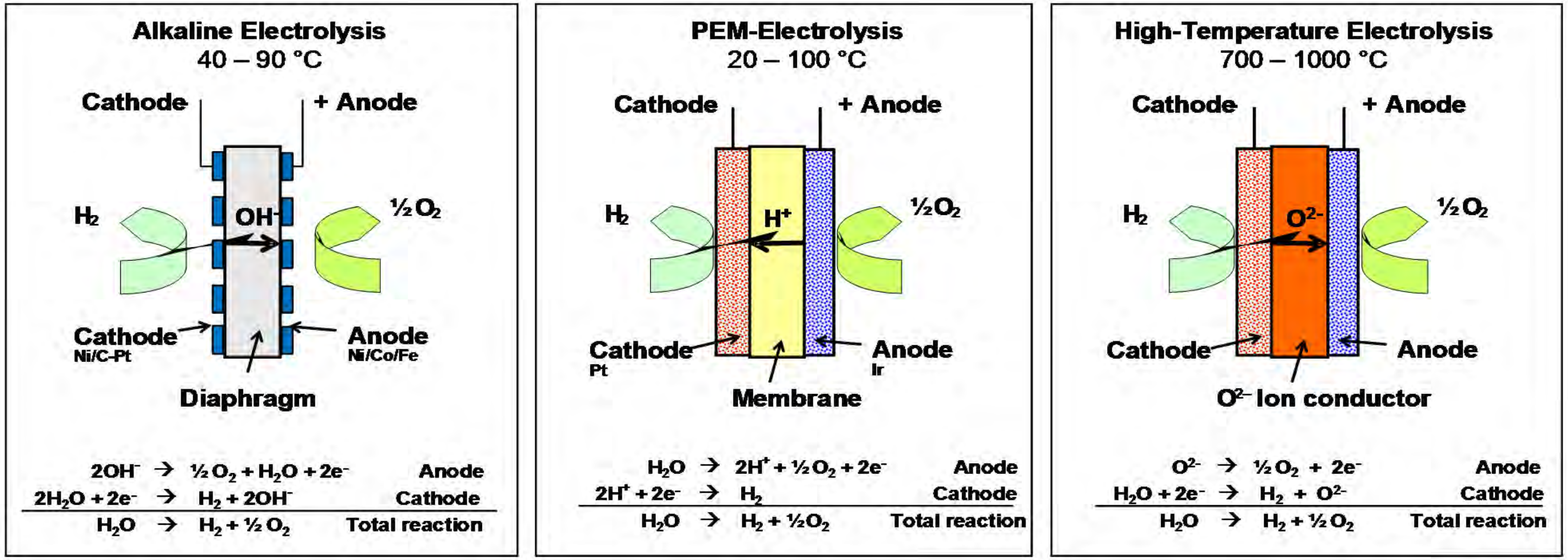
Key-scientific challenges to optimize water electrolysis !



– to drastically reduce the precious metal content or to replace precious metals

rgetic efficiency:

Meeting these challenges requires an intense interaction of materials and process sciences along the value chain

–

a deeper molecular understanding translates into new material concepts and later into new processes for manufacturing.

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als (membranes,
electrodes etc.) and efficient manufacturing processes.

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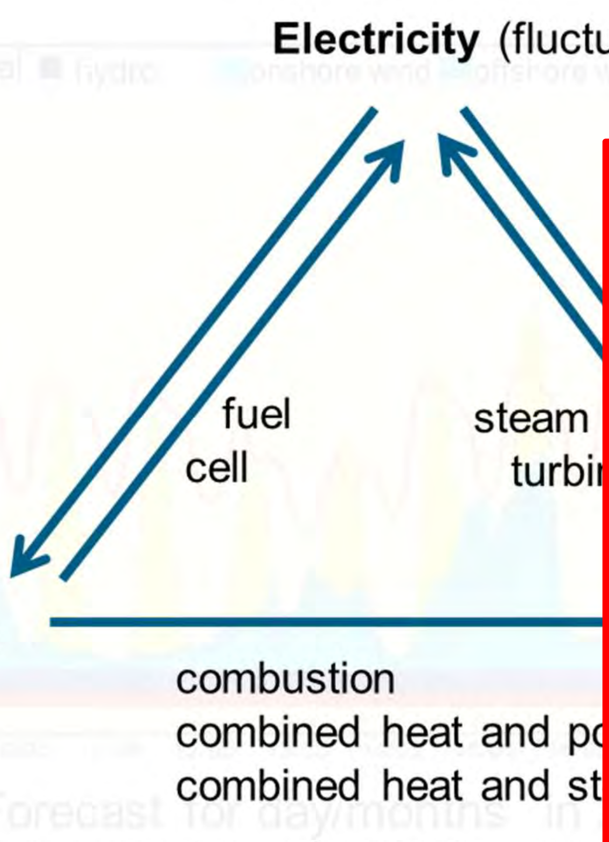

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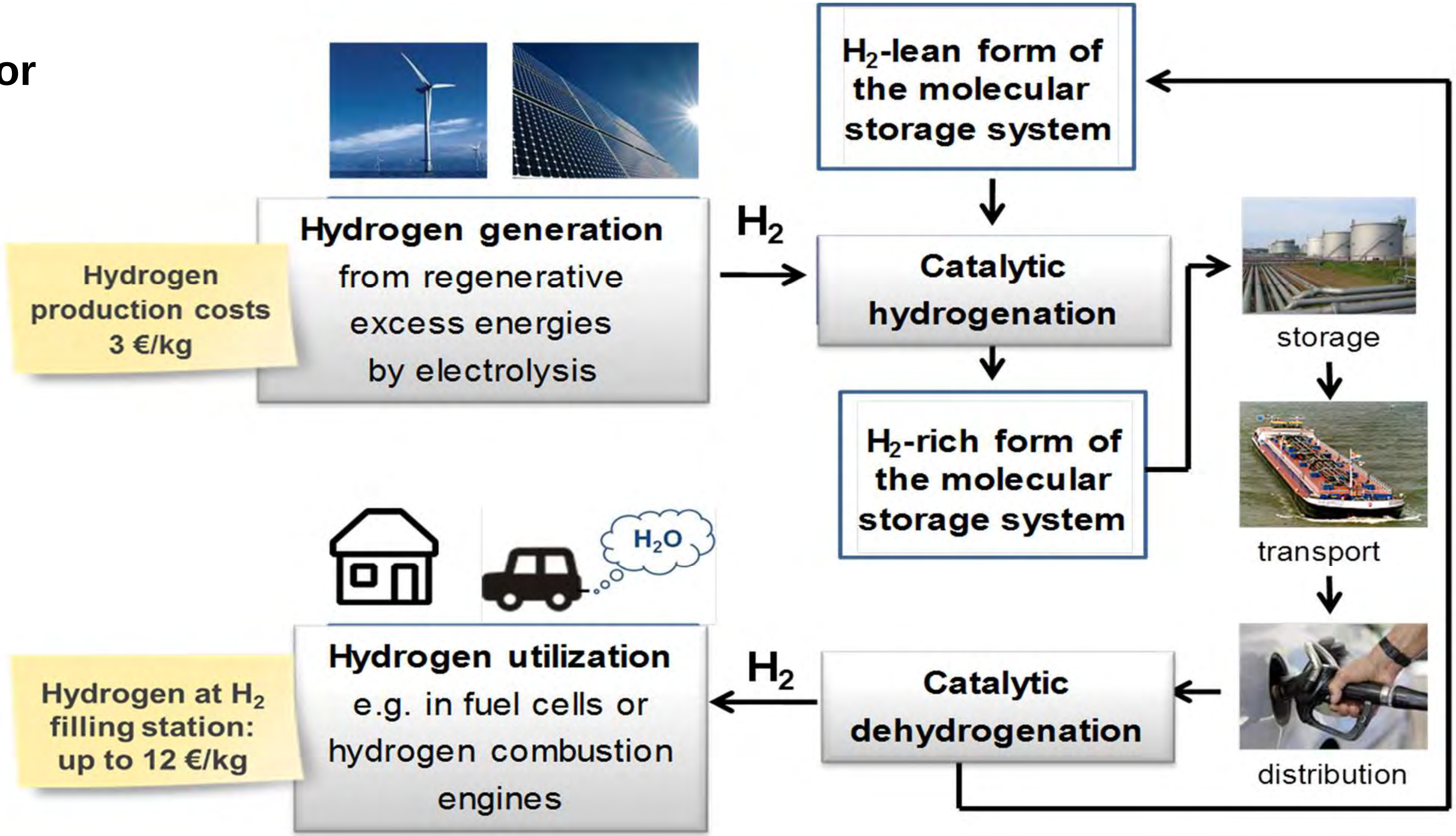
If you like power to gas / power to diesel technologies you should work on cheaper/better electrolyser technologies !

Use of green hydrogen in mobility is a potential economic scenario !

Competing technologies: **Compressed H_2** 300-500 bar **Cryogenic H_2** - 253 °C **Pipeline transport**

LOHC technology for hydrogen logistics:



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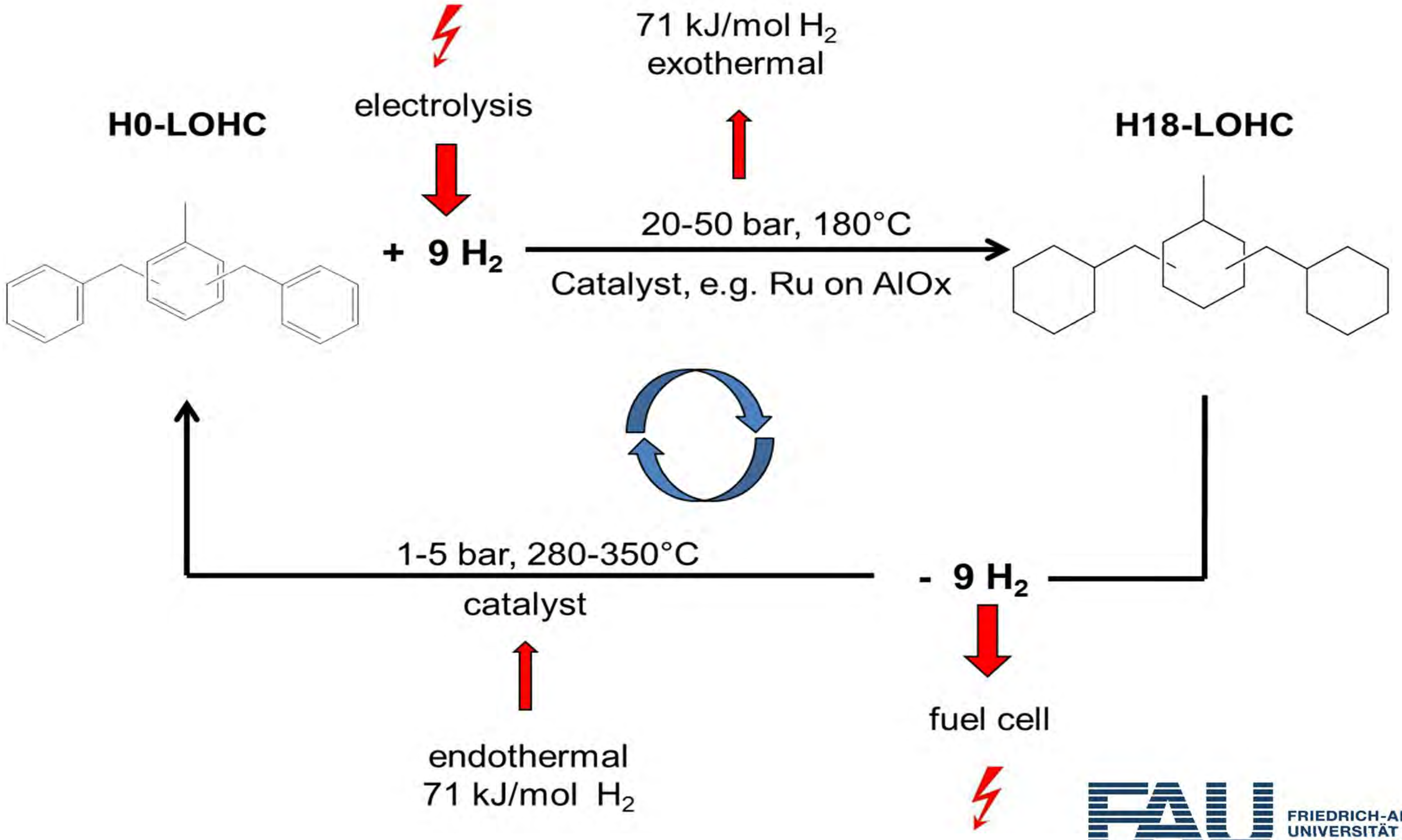
Dibenzyltoluene(H0-LOHC) – Perhydro-Dibenzyltoluene(H18-LOHC)

H0-LOHC is a commercial heat transfer oil e.g. Marlotherm © by SASOL



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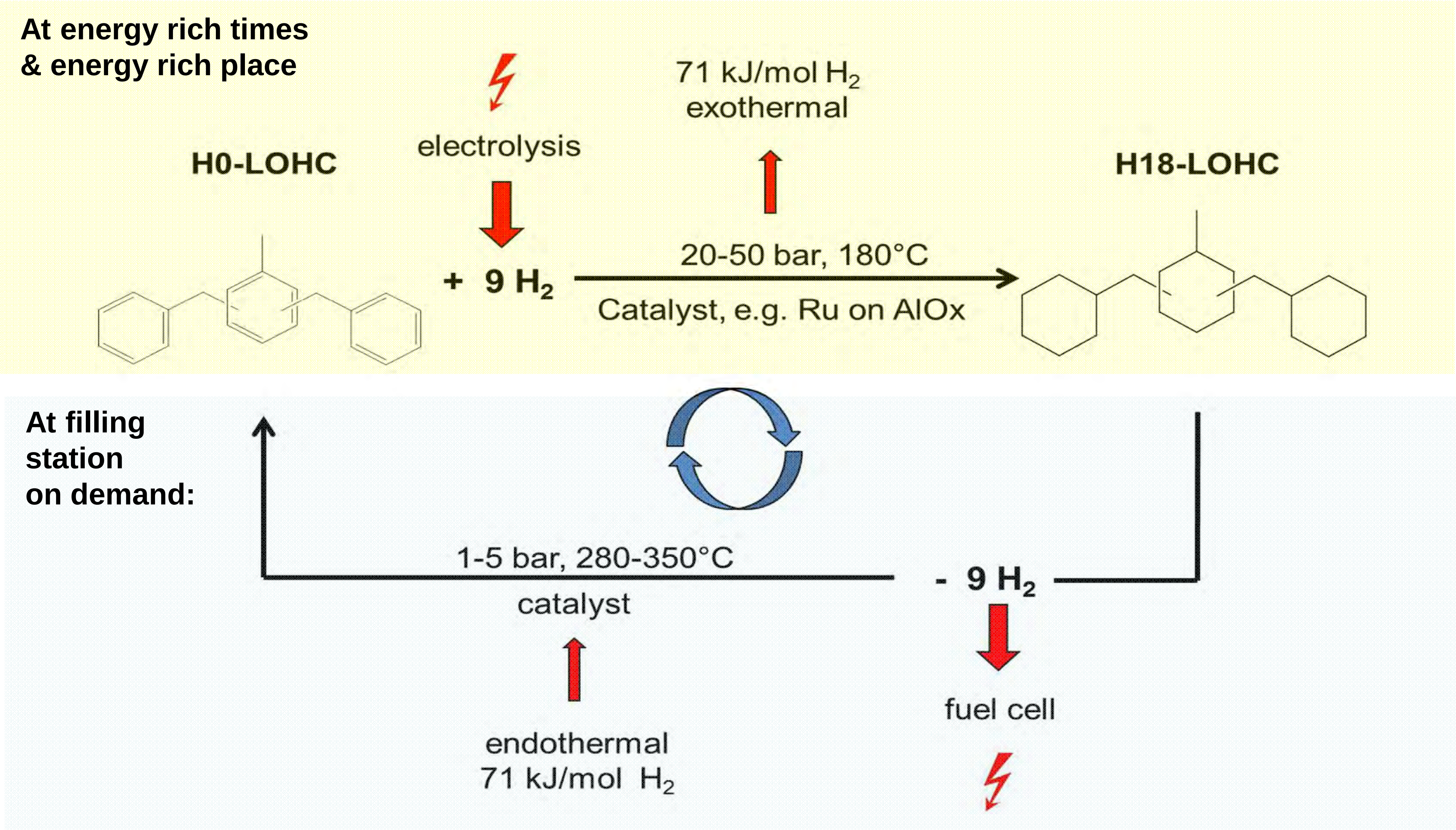

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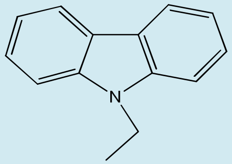
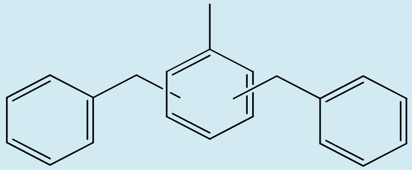
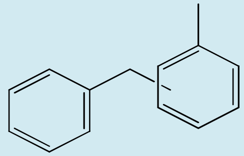
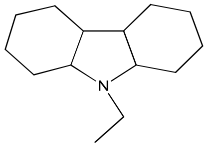
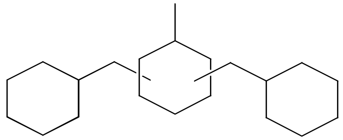
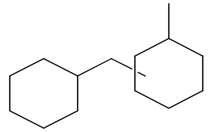
LOHC systems under detailed investigation

LOHC system	NEC/H12-NEC	MSH/H18-MSH	MLH/H12-MLH
H_2-lean form			
H_2-rich form			
mp (H_2-lean form)	68 °C	-34 °C	-30 °C
bp (H_2-lean form)	270 °C	390 °C (diesel: 170 – 390 °C)	280 °C
H_2-capacity / wt%	5.8	6.2	6.2
Energy content / kWh kg^{-1}	1.91	2.05 (comm. Li ion battery= 0.15)	2.05
heat of hydro-genation / kJ mol^{-1} H_2	55	71	71
Cost €/ kg (1 ton scale)	ca. 40	ca. 4	ca. 4
hazard symbols H_2-lean form	Xn	- (diesel: Xn, Otto-fuel: toxic)	Xn

Brückner, Obesser, Bösmann, Teichmann, Arlt, Dungs, PW, ChemSusChem, **2014** , 7(1), 229-235..

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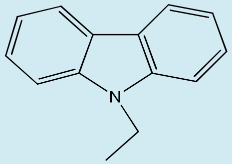
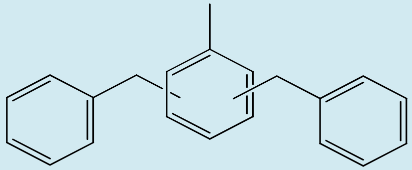
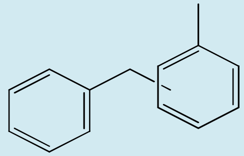
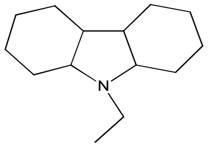
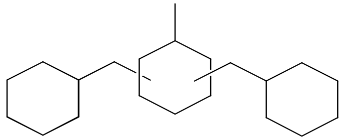
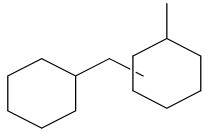
H_2-lean form			
H_2-rich form			
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Truck load of 30.000 kg equals 1,860 kg of H_2

(compared to 300-600 kg in truck with H_2 high pressure containers)

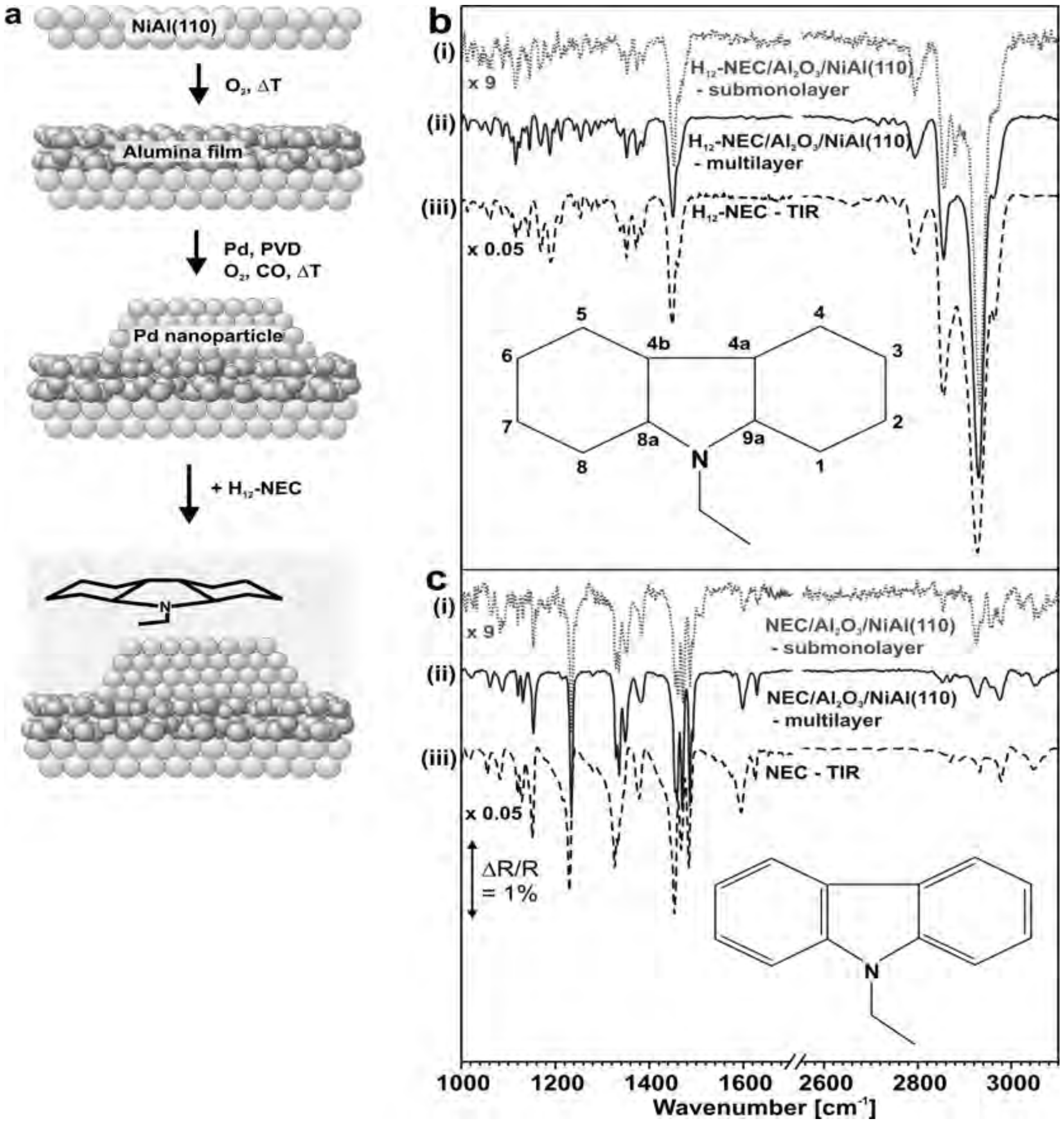
Brückner, Obesser, Bösmann, Teichmann, Arlt, Dungs, PW, ChemSusChem, **2014** , 7(1), 229-235..

Example:
N-Ethylcarbazol (NEC) – Perhydro-N-Ethylcarbazol (H12-NEC)

LOHC-systems are **Diesel-like liquids** (high boiling point, low flammability, viscosity, density, materials compatibility), that can store significant amounts of hydrogen by reversible, catalytic hydrogenation/dehydrogenation reactions.

What happens at the catalytic site in H_2 –release from LOHCs ?

Fundamental aspects of catalytic H12-NEC dehydrogenation



Sobota, Nikiforidis, Amende, Zanon, Staudt, Höfert, Lykhach, Papp, Hieringer, Laurin, Assenbaum, PW, Steinrück, Görling, Libuda, Chemistry— A European Journal **2011**, 17(41), 11542-11552.

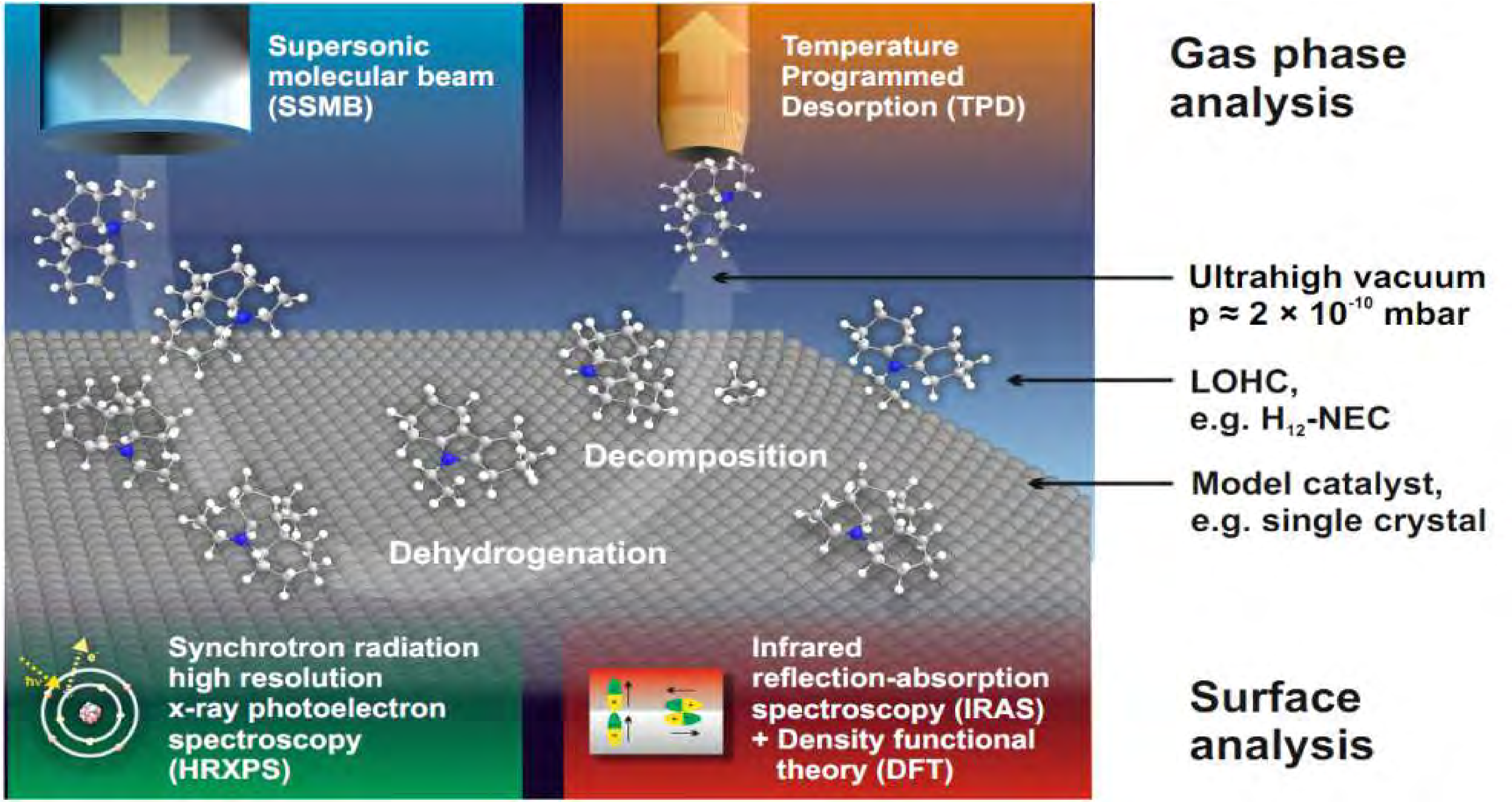
Gleichweit, Amende, Schernich, Zhao, Lorent, Höfert, Brückner, PW, Libuda, Steinrück, ChemSusChem **2013**, 6(6), 974-977.

Gleichweit, Amende, Bauer, Schernich, Höfert, Lorenz, Zhao, Müller, Koch, Bachmann, PW, Libuda, Steinrück, Papp, Journal of Chemical Physics **2014**, 140(20), 204711/1-204711/9.

Amende, Gleichweit, Schernich, Höfert, Lorenz, Zhao, Koch, Obesser, Papp, PW, Steinrück, J. Libuda, Journal of Physical Chemistry Letters **2014**, 5(8), 1498-1504.

Fundamental aspects of catalytic H12-NEC dehydrogenation

- overview of applied surface science approaches -



C. Papp, PW, J. Libuda, H.-P. Steinrück, Chemical Record **2014**, 14(5), 879-896.

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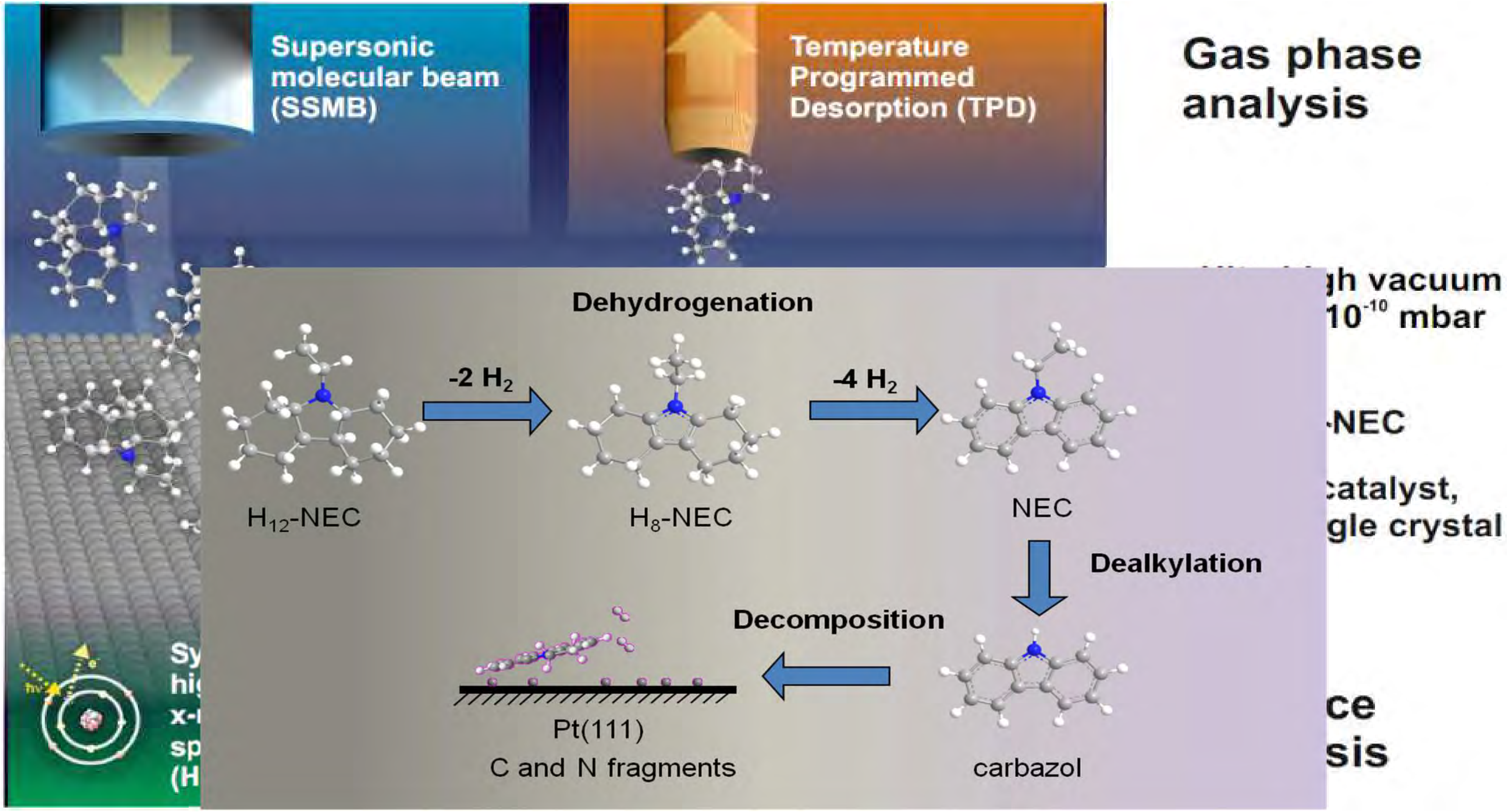

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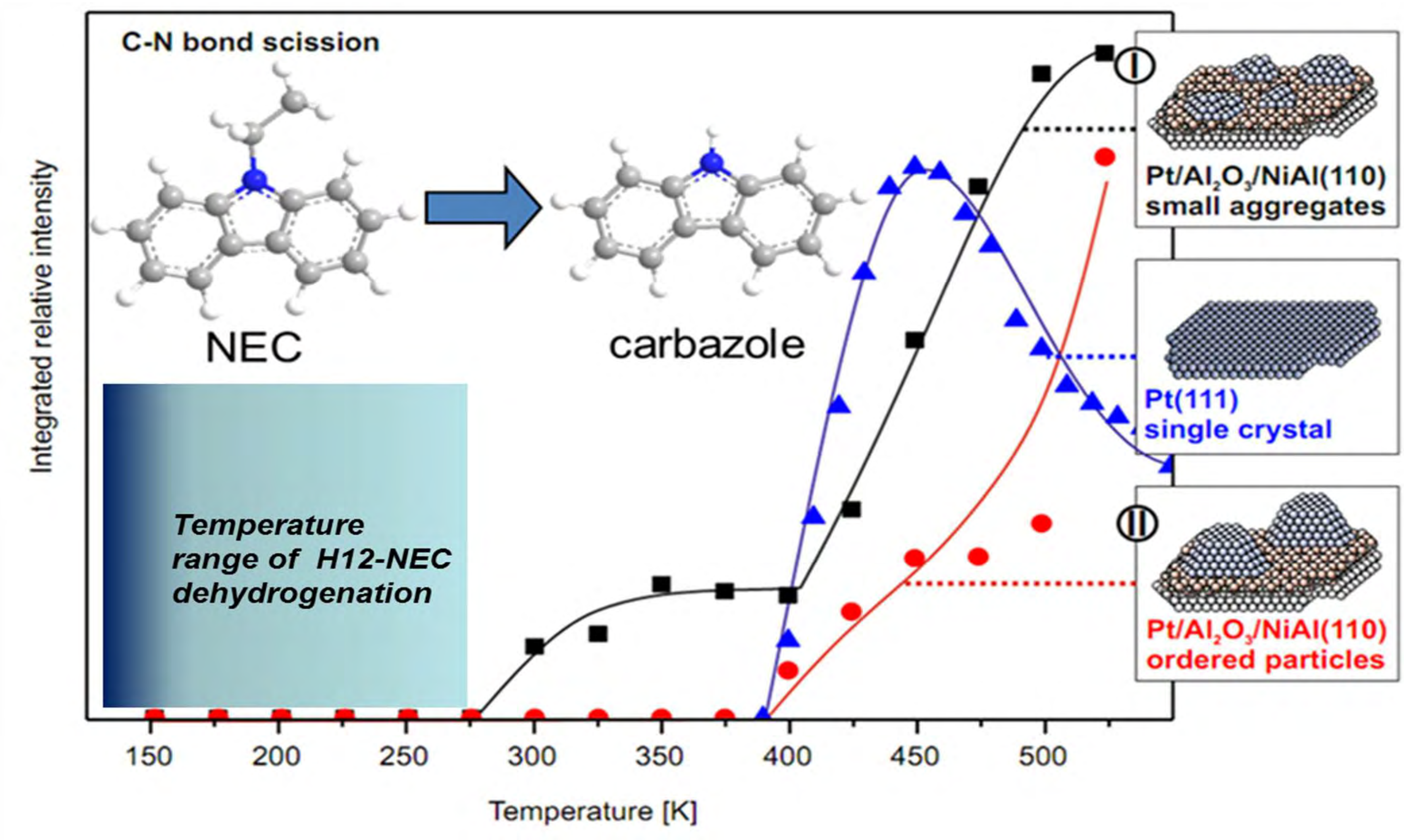
Fundamental aspects of catalytic H12-NEC dehydrogenation

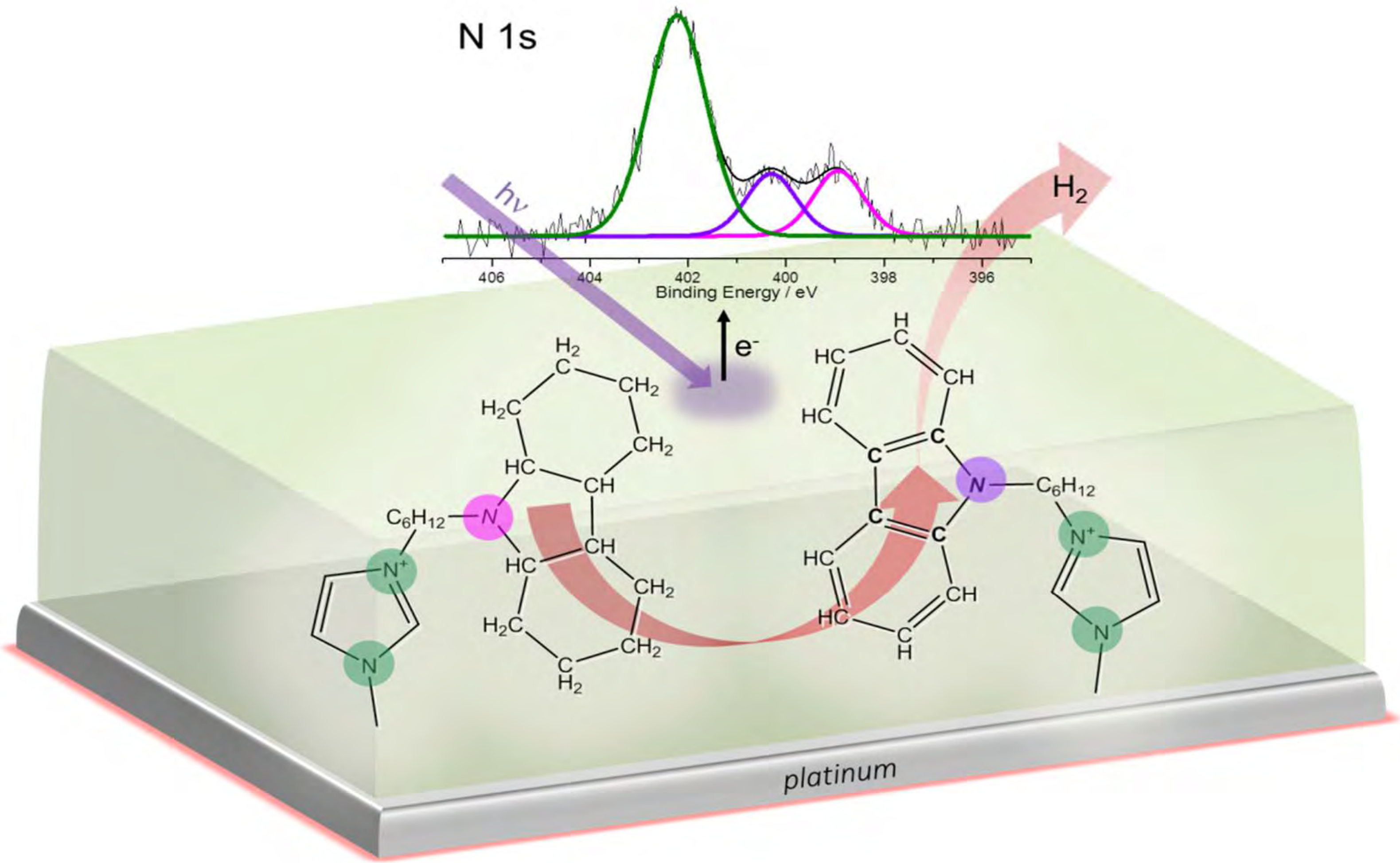
- effect of Pt particle size under surface science conditions -



Under surface science conditions, the catalytic dehydrogenation occurs at much lower temperatures compared to the real dehydrogenation experiments

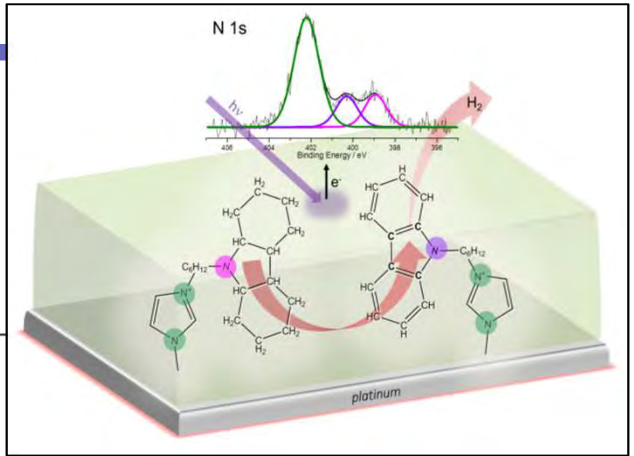
XPS studies of catalytic H12-NEC dehydrogenation -

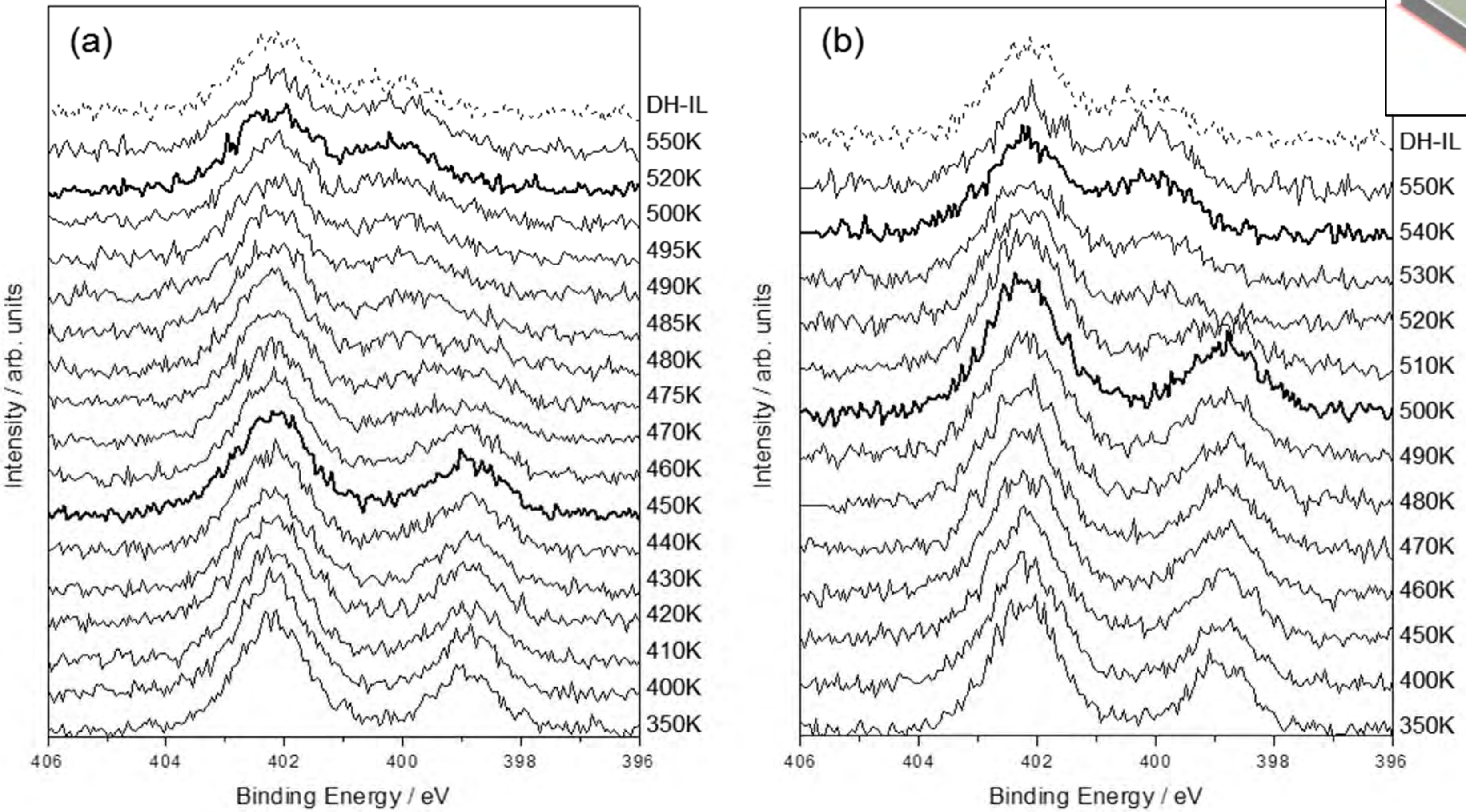
Perhydrocarbazol N-linked to an ionic liquids cation to mimic a condensate phase in the UHV experiment



Matsuda, Schwegler, Taccardi, PW, Steinrück, Maier, ChemPhysChem, **2015**, in press. (10.1002/cphc.201500236)

XPS study of perhydro-carbazole bound to an IL-linker to mimic a condensate phase





Dehydrogenation temperature on Pt-foil is close to real catalysis conditions !

Dehydrogenation on Pt starts 50 K lower than on Au !

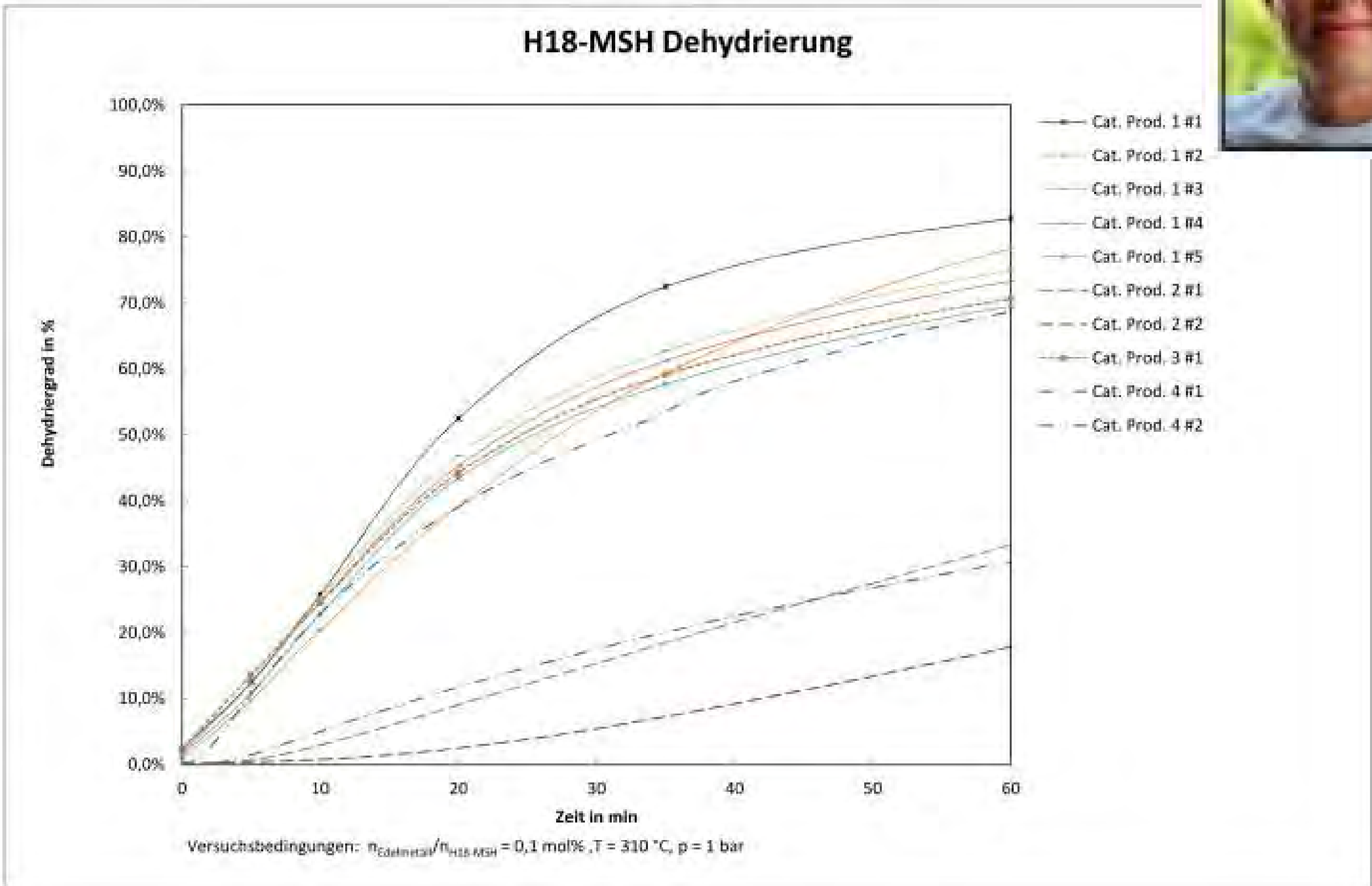
N 1s spectra of H12-NEC on (a) Pt foil and (b) Au foil.
Dehydrogenation start and end spectra are marked by bold lines; Dashed spectra are N 1s spectra of H0-NEC on Au foil at 500 K (mean heating rates are 0.002 K/sec)

What happens in the catalyst pellet ?

Screening of commercial
Pt on AlOx
catalyst samples

Perhydro-dibenzyltoluol dehydrogenation

@ same conditions:
310 °C, 1 bar
@ same total Pt content

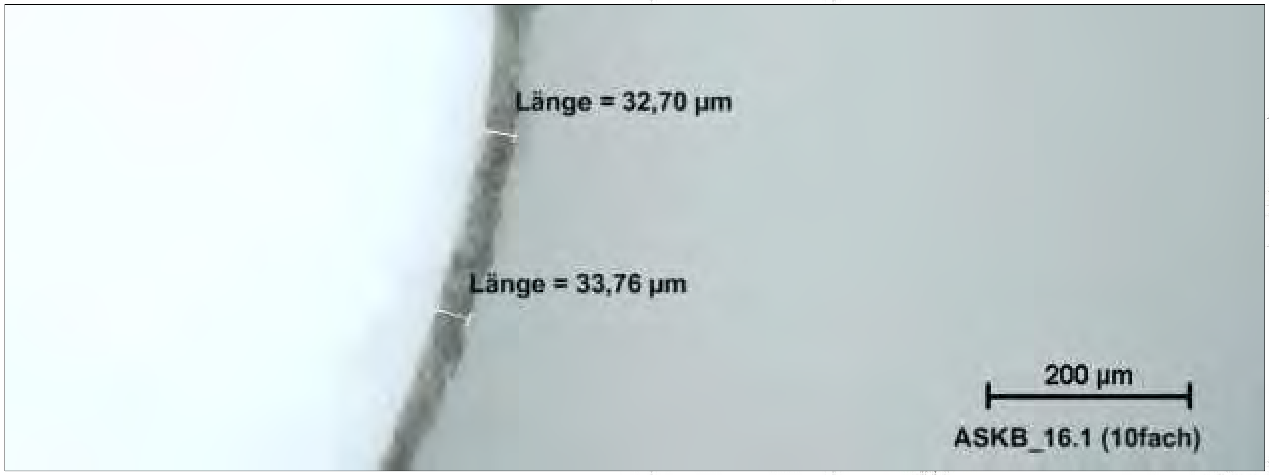


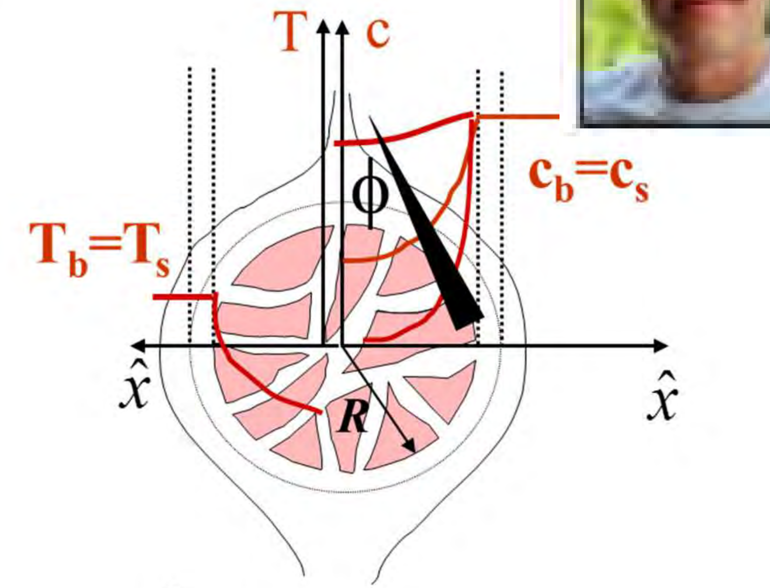
All „good“ catalysts are egg-shell systems

The thinner the shell, the better the catalyst performance.

What happens in the catalyst pellet ?

Screening of commercial *Pt on AlOx* catalyst samples





$$r_{obs} = \frac{1}{V_p} \int_{V_p} k(T) \cdot c(\hat{x})^n \, 4\pi\hat{x}^2 \, d\hat{x}$$

All „good" catalysts are egg-shell systems

The thinner the shell,

→ **Large influence of pore diffusion on LOHC dehydrogenation kinetics**

→ **In-house catalyst materials with very thin shell led to productivities of up to 12 g H_2/g Pt min^{-1} → 24 kW(therm) / g Pt**

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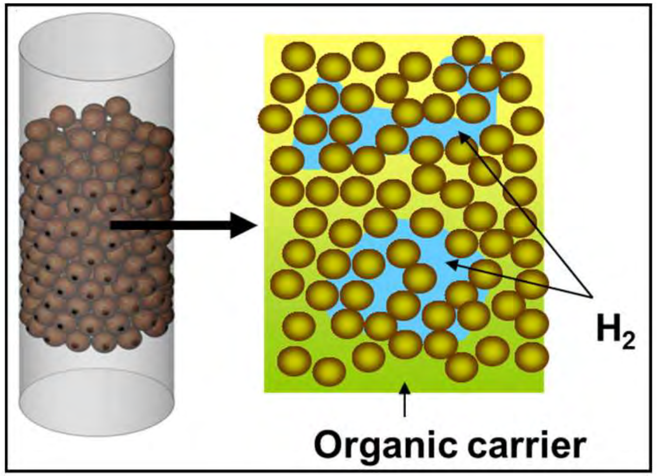
How to optimize the LOHC dehydrogenation reactor ?

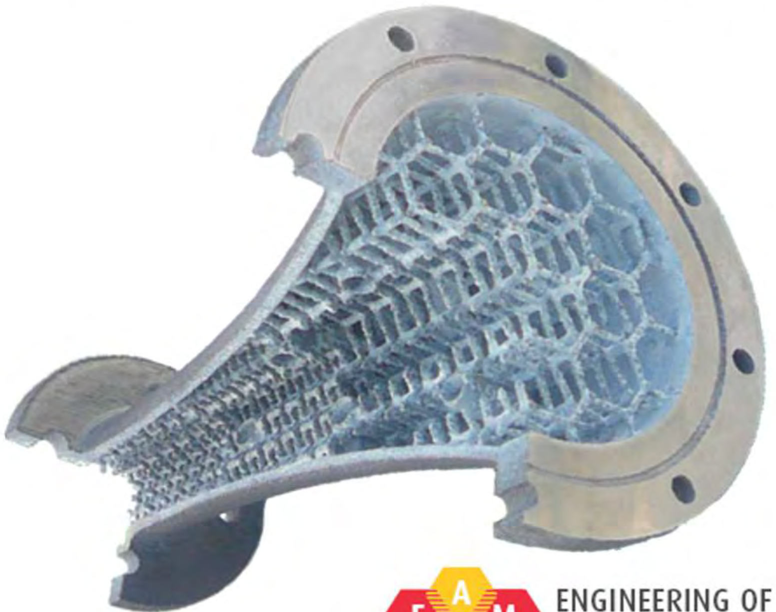
1 ml H_x-LOHC liberates > 650 ml H_2 → the reactor is a gas generation device

Negative effects in classical fixed-bed reactor !



- Loss of liquid-catalyst contact
- Residence time influence by gas formation
- Difficulties to introduce heat into a reactor that is essentially full of gas.

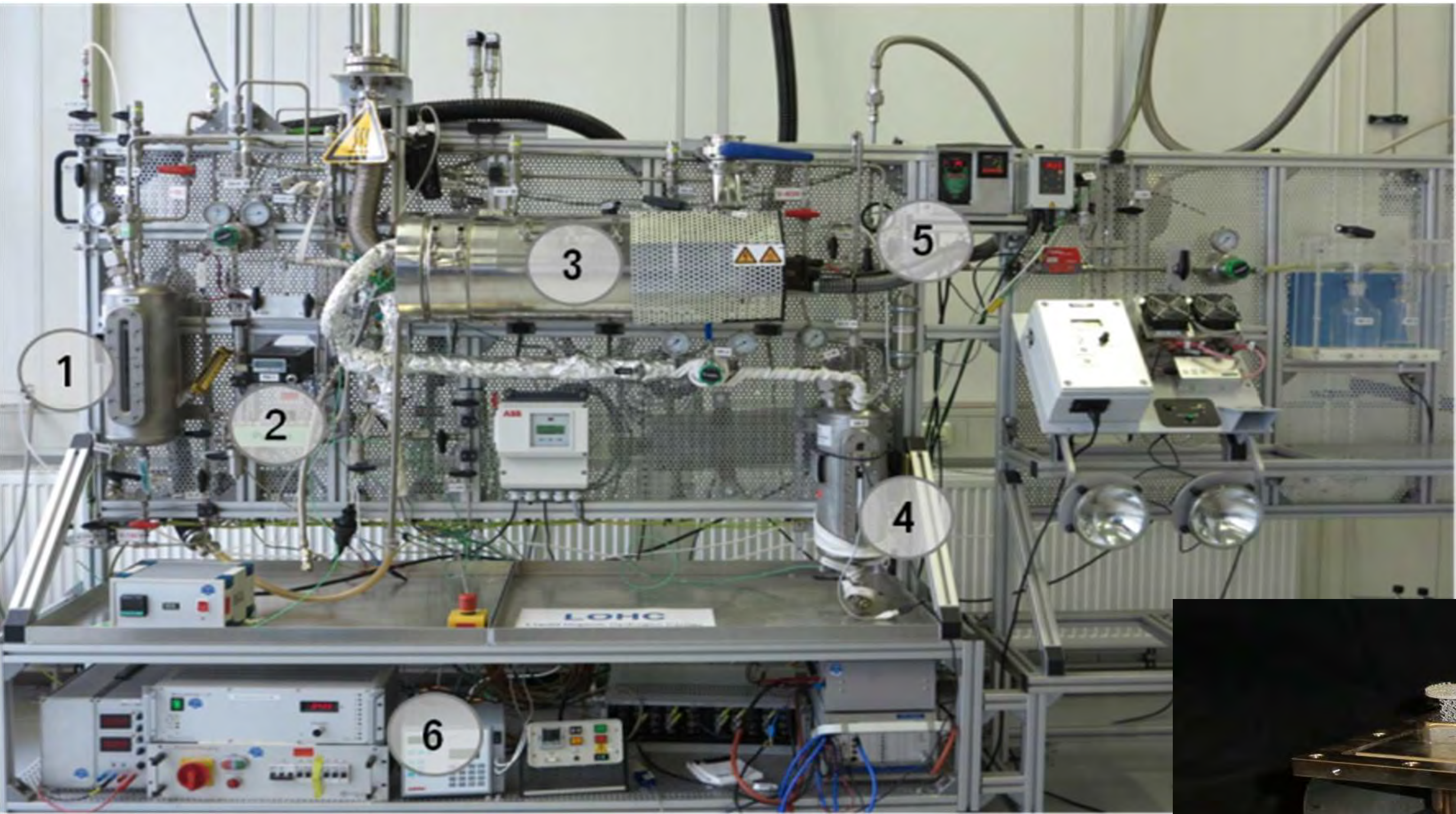
One possible solution:



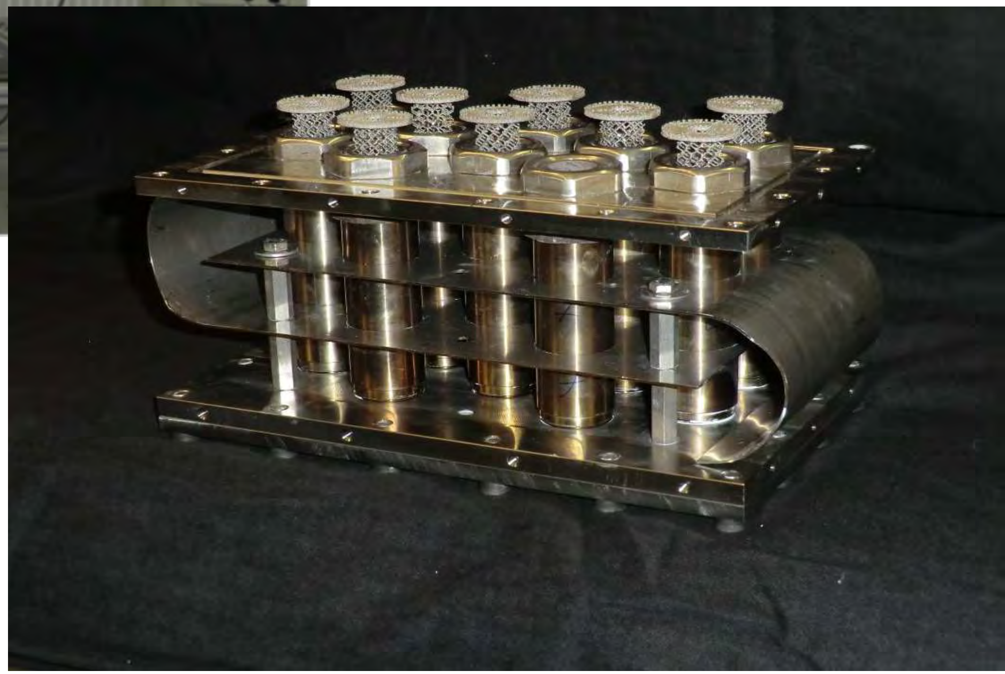
- Use open-cellular metal structure as catalyst substrate e.g. tailor-made by additive manufacturing
- Coat metal struts with porous alumina
- Deposit Pt nanoparticles on the alumina support

ENGINEERING OF ADVANCED MATERIALS

LOHC dehydrogenation test rig with connected fuel cell



Peters, Eypasch, Frank, Schwerdtfeger, Körner, Bösmann, PW, Energy & Environmental Science, **2015**, 8, 641–649.



ENGINEERING OF ADVANCED MATERIALS

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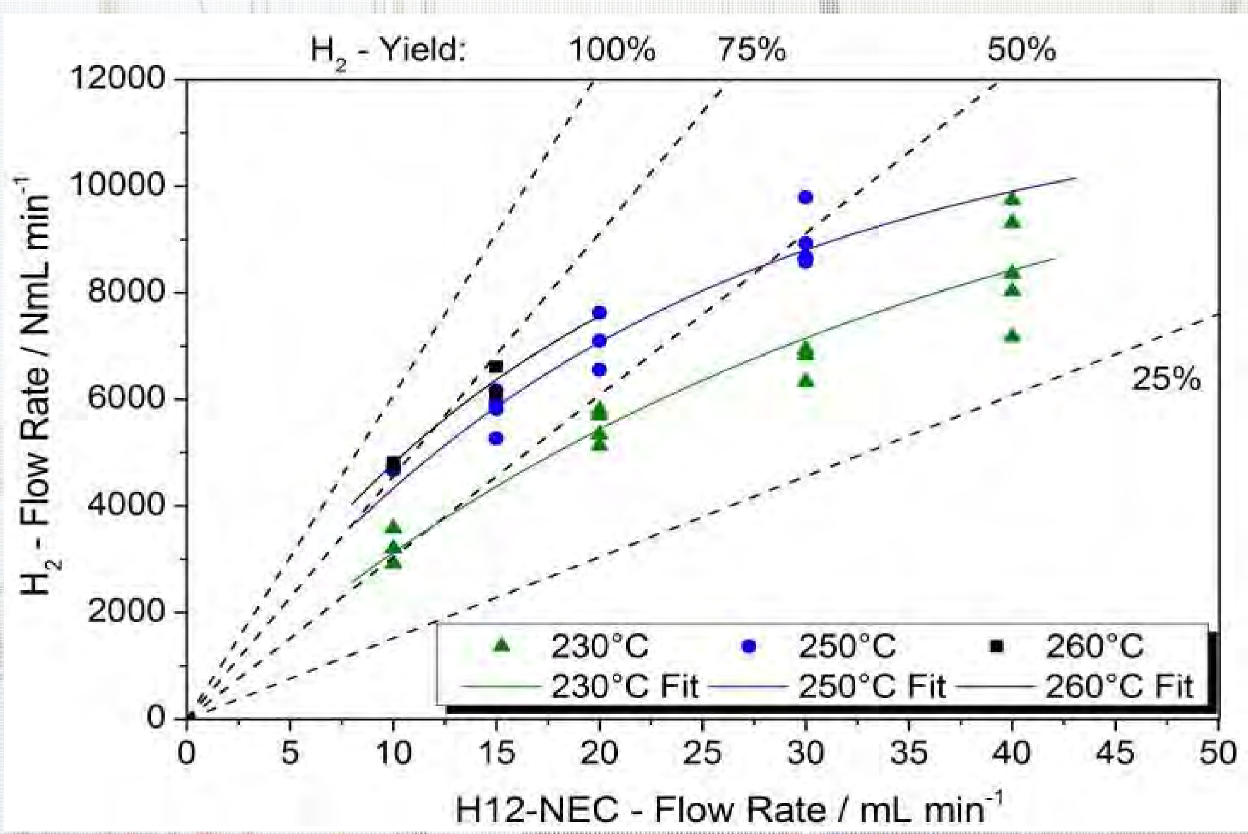
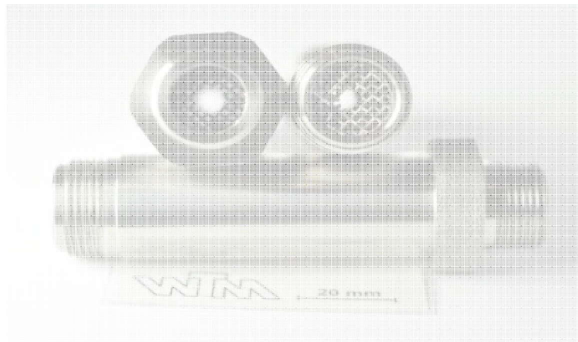




1 KW$_{ele}$ HRU (total 250 ml reactor)
→ 4 kW$_{ele}$ / liter reactor volume

Peters, Eypasch, Frank, Schwerdtfeger, Körner, Bösmann, PW, Energy & Environmental Science, **2015**, 8, 641–649.

State of LOHC system development in 2015 – stationary applications

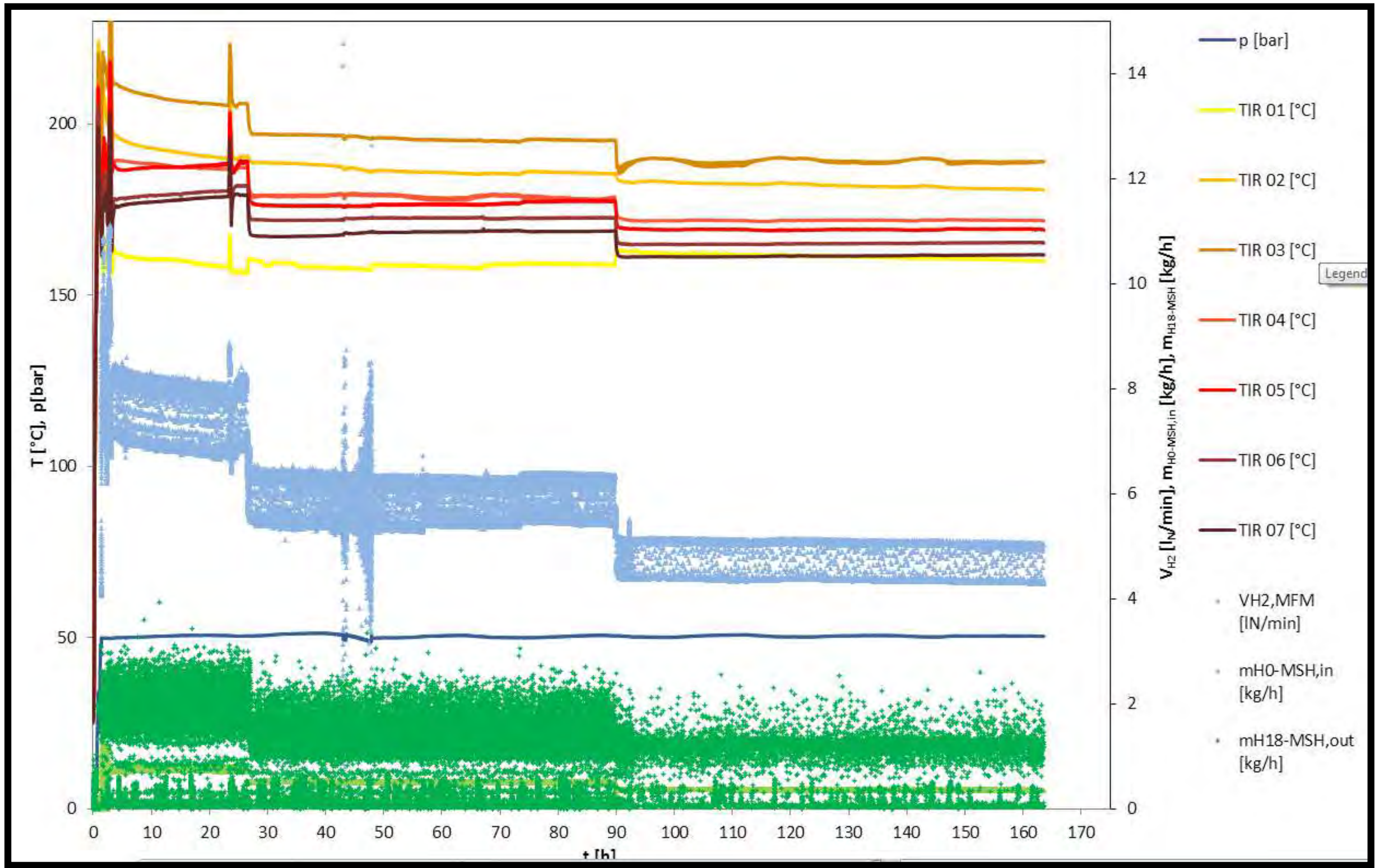
Left:
Trickle bed hydrogenation reactor to store up to 3 kW LHV H_2 in LOHC (PV of ca. 4.3 kW)

- 70 litre tank system → 144 kWh_{therm} storage
- In 2014: > 600 h dynamic operation without drop in performance, total production: ca. 700 kg H18-LOHC

Right:
Demonstrator Hydrogen Release Unit (HRU)

- Four hot oil heated tube reactors with gas/liquid separator
- Capacity: ca. 10 kW_{therm} = ca. 5.5 $kW_{electr.}$ @ connected fuel cell

State of catalyst system development in 2015



Right:
Demonstrator Hydrogen Release Unit (HRU)

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State of LOHC system development in 2015 – commercial applications

hydrogenious TECHNOLOGIES

Hydrogenious Technologies GmbH –

a FAU – spin-off and pioneer in chemical hydrogen storage

www.hydrogenious.net

- Founded in 2013; today: 15 full time employees
- Shareholders (next to founders):
  - FAU Erlangen
  - Anglo American Platinum
- Winner of several start-up competitions
  - Bavarian Founders Price
  - Science4Life Venture-Cup
  - Hochschulgründerpreis Nordbayern

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ANGLO PLATINUM

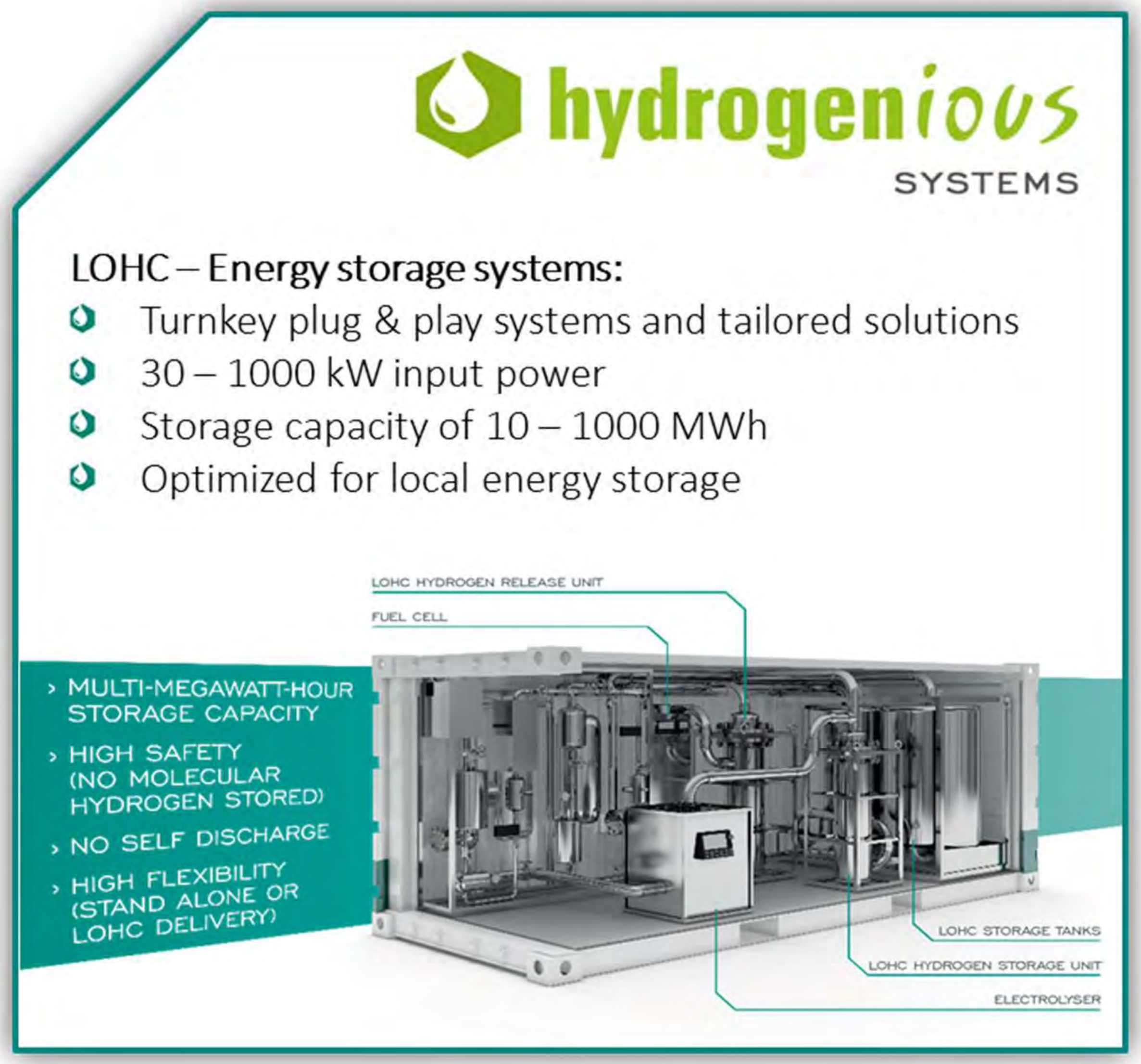
TOP START-UP DEUTSCHLAND 2014

BAYERISCHER GRÜNDER PREIS 2014 Kategorie Konzept

Science 4 Life Platz 1 Businessplanphase Hydrogenious Technologies GmbH Venture Cup 2014

Sieger Businessplan Wettbewerb netzwerknordbayern

Hydrogenious Technologies offers innovative LOHC systems for energy storage and hydrogen distribution



Main markets:

- energy self supply
- off-grid applications

e.g. power supply for mobile phone stations

Hydrogenious Technologies offers innovative LOHC systems for energy storage and hydrogen distribution

hydrogenious DISTRIBUTION

Innovative hydrogen logistics with:

- Industrial hydrogenation units up to 1.500 Nm^3/h H_2
- Easy transport by truck, train or ship – up to 1.800 kg H_2/ 40t-truck
- Safe supply of hydrogen filling stations
- Utilization of existing infrastructure

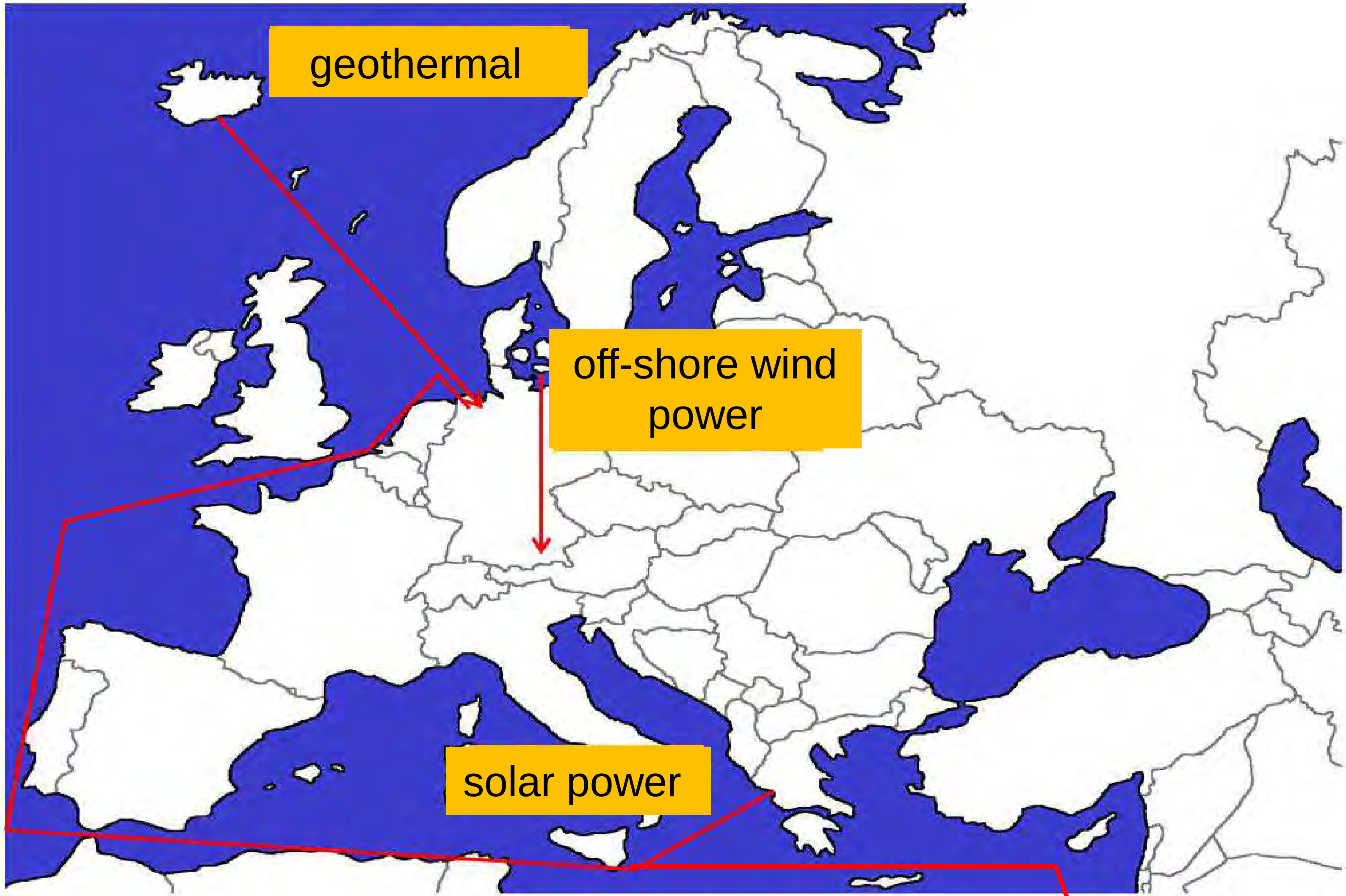
Main markets:

- Medium-sized industrial hydrogen consumer

  → **Use of charged LOHC in catalytic transfer hydrogenations is possible**

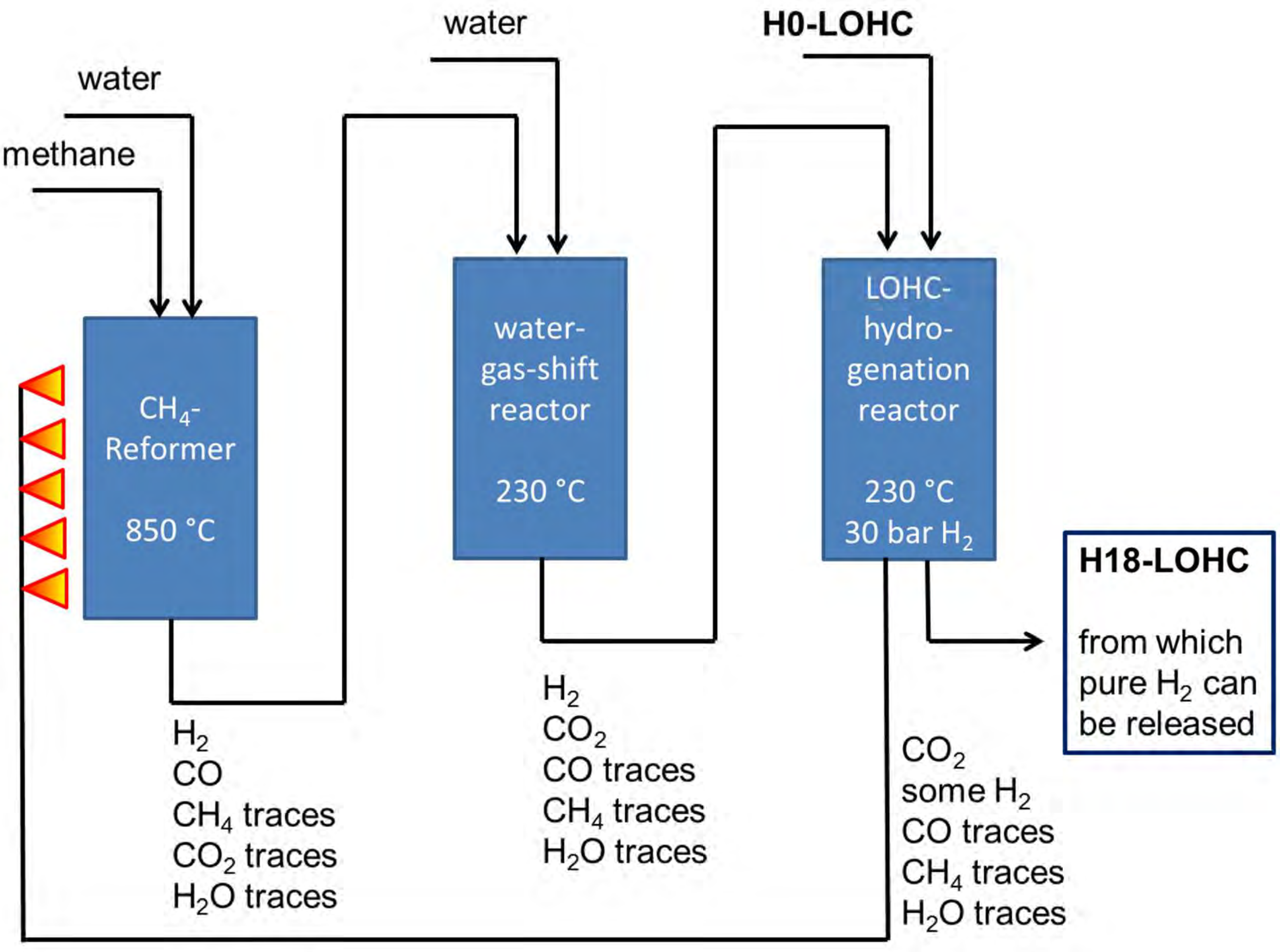
- Hydrogen filling stations
- Global hydrogen logistics

Hydrogen logistics from areas with cheap and efficient production of renewable energy



Teichmann, Arlt, PW, Int. J. of Hydrogen Energy **2012**, 37(23), 18118.

Hydrogen logistics from areas with excess energy (e.g. stranded gas)



Challenge for research:

Develop efficient hydrogenation catalyst that works in presence of CO.

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The LOHC-technology for hydrogen mobility

Two scenarios: **a) Hydrogen logistics to the H_2- filling station for on-board 700 bar technology (short to mid-term)**

Conventional technology: Compressed hydrogen

- 300-1100 bar H_2-pressure
- 300 – 1000 kg hydrogen per truck
- large high pressure storage infrastructure at filling station (inkl. compressor)

LOHC technology using perhydro-dibenzyltoluene / dibenzyltoluene

- 1 bar; safe handling in cheap, existing tanks
- 1800 kg H_2 per truck
- total infrastructure comprises:
  a) an (existing) LOHC tank;
  b) a gas, biofuel or electrical- heated dehydrogenation unit
  c) a compressor (as needed in conventional technology)
  d) a small buffer tank for compressed H_2 for the filling process

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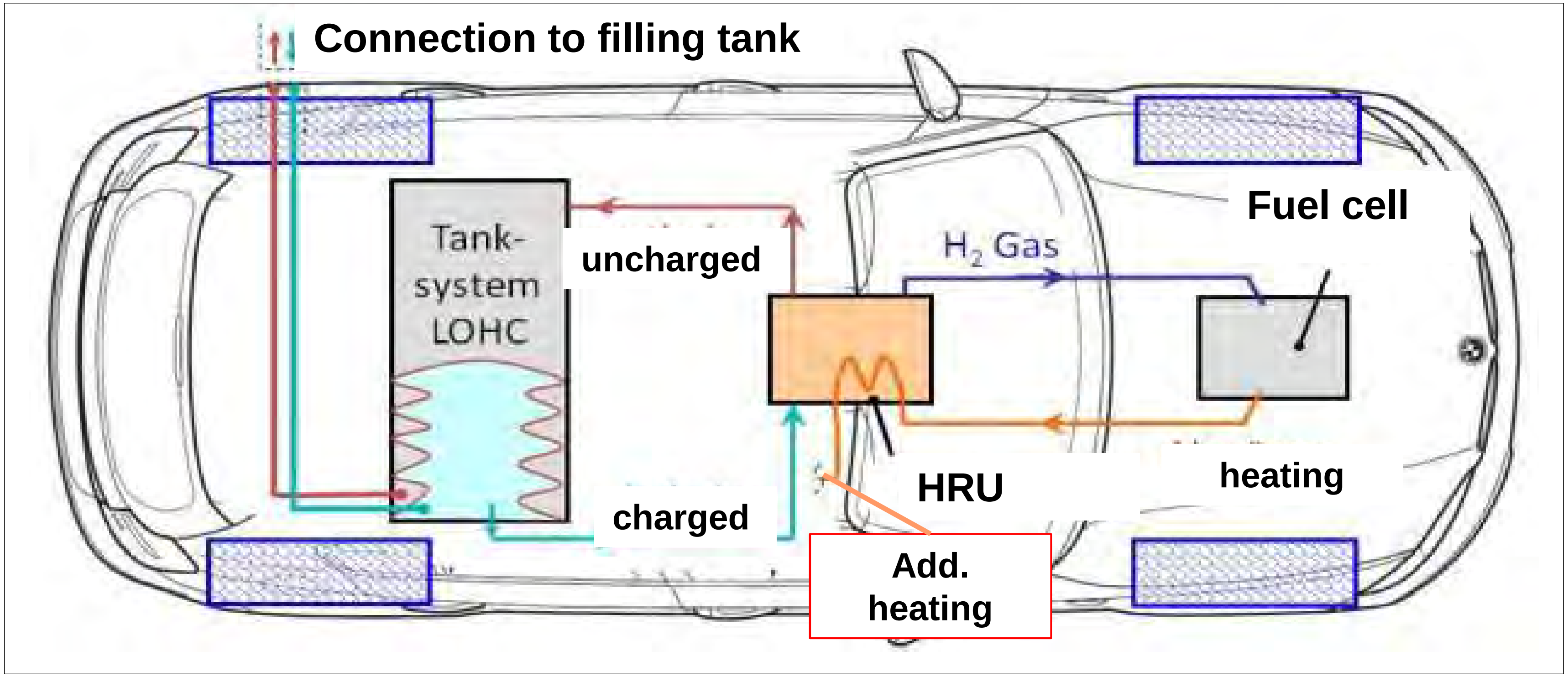
b) On board hydrogen generation (2020 +)
"Long-range, zero emission mobility"



Range Extender for electric cars: 90 liter LOHC = 600 km range

Concept for cars: zero emission range extender
Concept for trucks: LOHC + 7% biofuel

Most attractive technology option for the future:
Direct LOHC Fuel Cell technology

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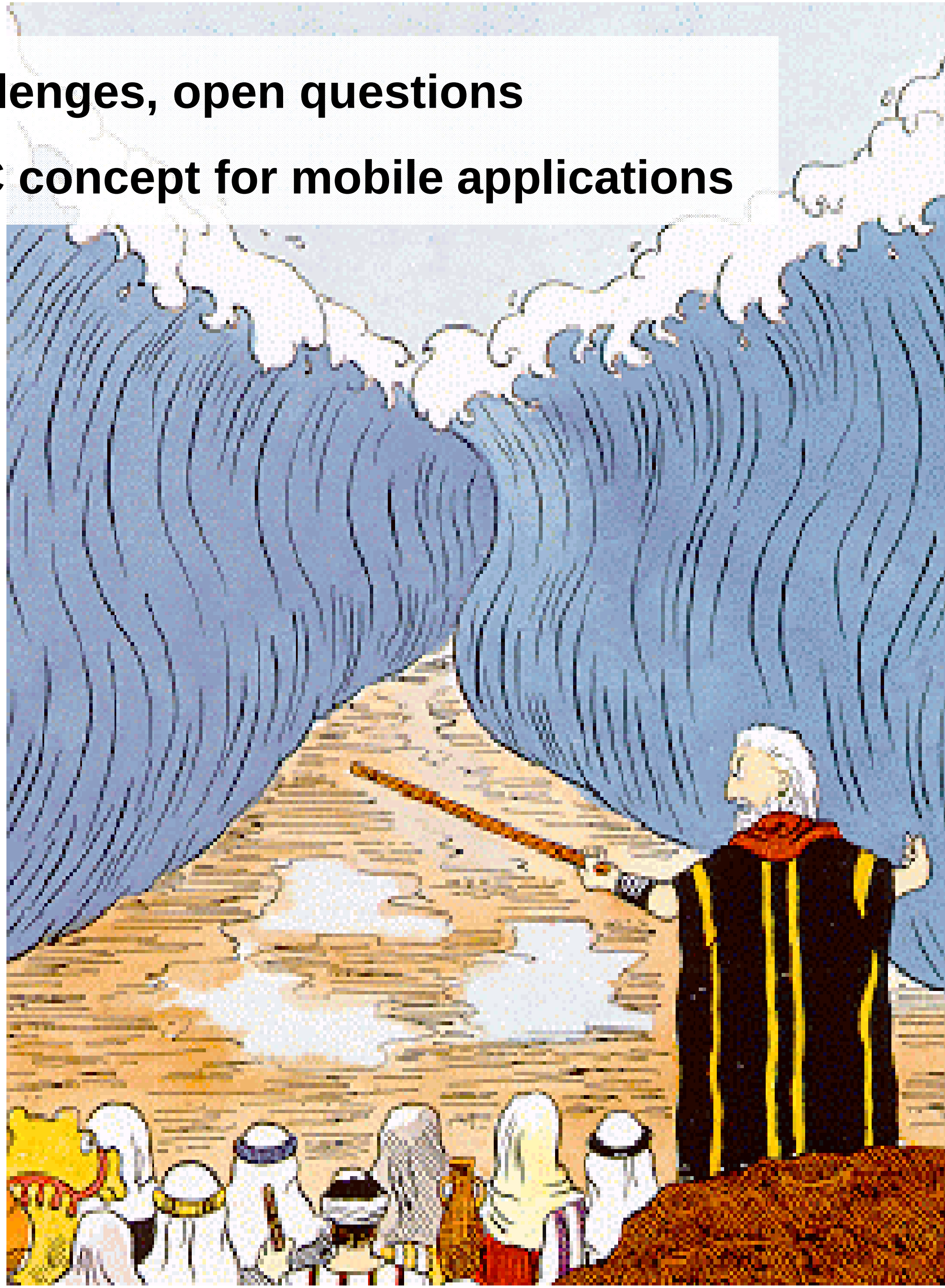
FAQs, challenges, open questions

regarding the LOHC concept for mobile applications



What do you mean
“It’s a bit muddy” ?

© Prof. Ken Seddon, Belfast

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FAQs, challenges, open questions

regarding the LOHC concept for mobile applications

- **Is the purity of the generated H_2 sufficient ?**
- **Is the overall efficiency of the energy storage system high enough ?:**

  - main losses are in electrolysis and fuel cell;
  - efficiency is probably not worse compared to a diesel car

- **Are the LOHC systems robust enough in extended hydrogenation/dehydrogenation cycles?**

  - traces of dealkylation observed for H12-NEC/NEC
  - H18 MSH/MSH is extremely robust (no sign of decomposition @ 310°C / 120 h with cat.)

- **Are there even better LOHCs systems ?**

  - 7.2 mass% H_2 is limit of aromatic/alicyclic systems
  - vapour pressure, eco-tox aspects, price, stability and hydrogenation/dehydrogenation kinetics are key factors.

Thanks to…

- **Colleagues from Chemical Engineering**
  - Prof. Dr. Eberhard Schlücker
  - Prof. Dr. Wolfgang Arlt
- **Colleagues from BMW**
  - Torsten Frank
  - Martin Eypasch
- **Colleagues from Hydrogenious**
  - Dr. Daniel Teichmann +
    all the Hydrogenious team

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Thank you for your attention !