

“Homogenous Catalysis in Energy Related Process Technology”

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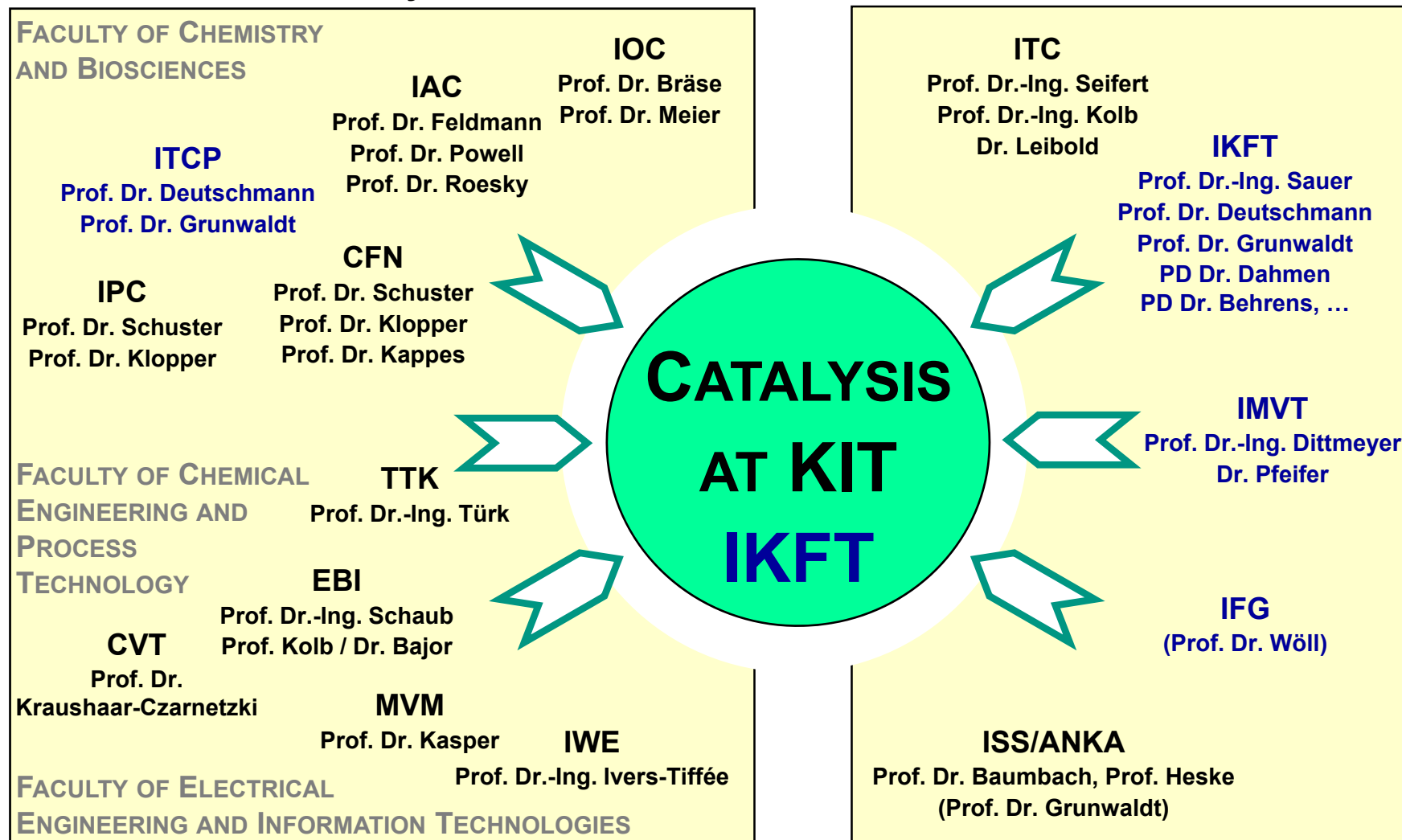
Institute of Catalysis Research and Technology



Catalysis within more than 25 Groups at KIT

University Part

Federal Labs

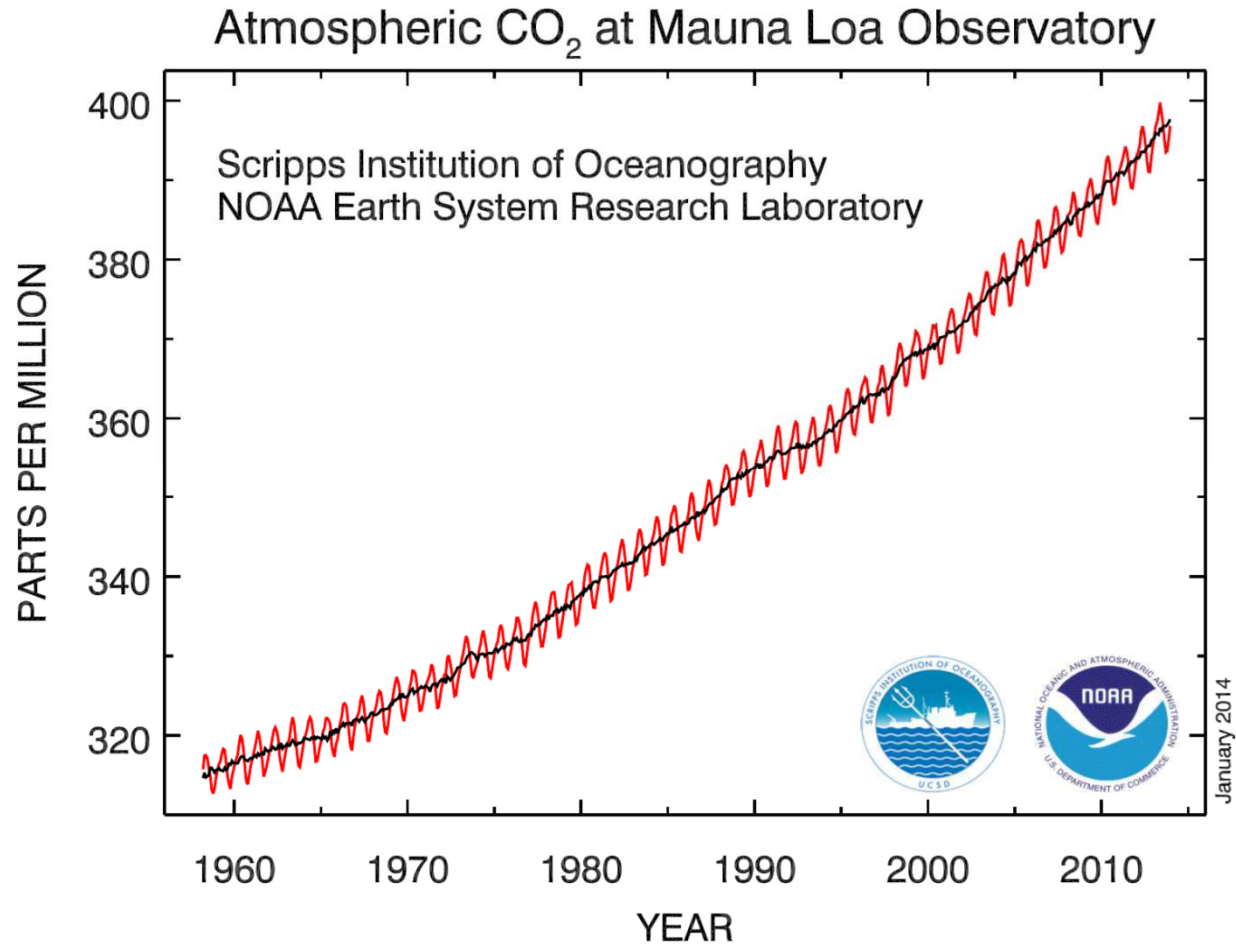


Die Mission des Instituts für Katalyseforschung und -technologie



Das Institut für Katalyseforschung und -technologie bildet am KIT die Brücke von der grundlagenorientierten und angewandten Forschung bis zur Umsetzung in neue Technologien und Produkte für die Gebiete Katalyse und Prozesstechnologie katalytischer Prozesse.

Climate Change – an Issue that is here to Stay



Political Background for Energy Research in German

- The Coalition Agreement mentions a “triangle of energy policy:
 1. Climate- and environmental protection
 2. Security of supply
 3. Affordability

- Three general technological approaches are discussed to achieve the goals of the “German Energiewende”:
 1. Renewable Energies
 2. Energy Efficiency
 3. Energy Storage, Grids, New Mechanisms for the Electricity Market

Deutschlands Zukunft gestalten

Koalitionsvertrag
zwischen CDU, CSU und SPD

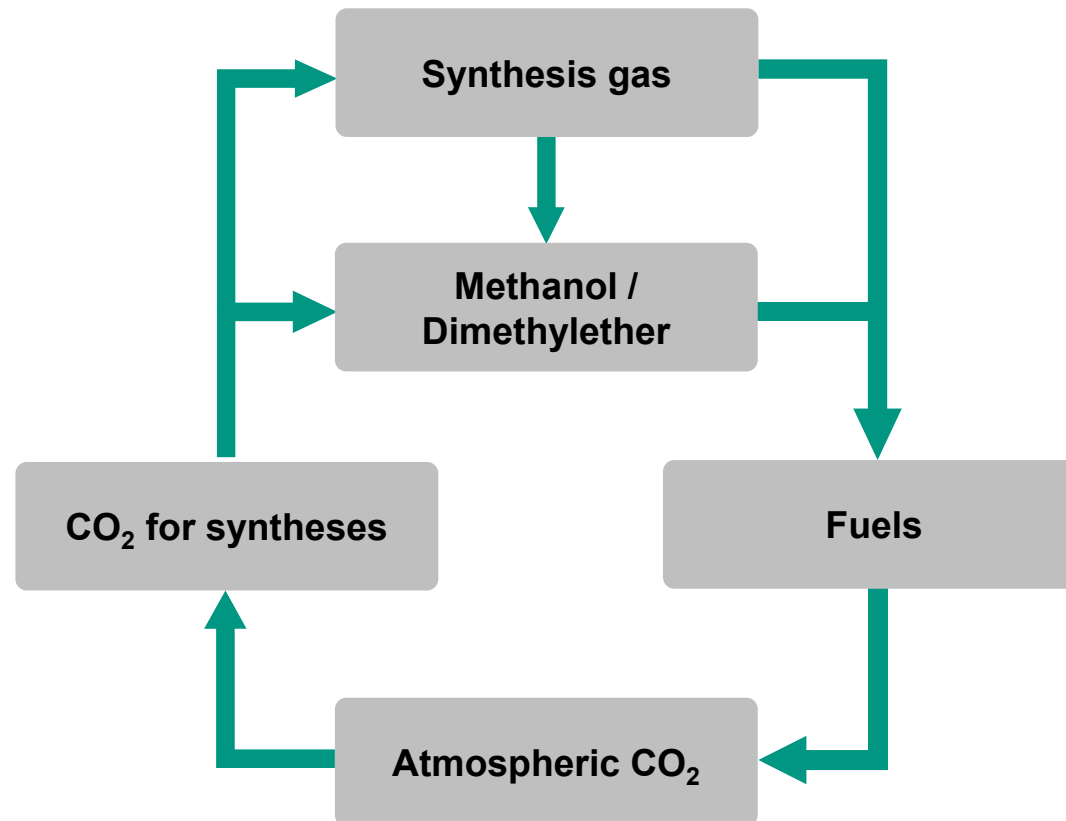
18. Legislaturperiode

Contribution of Catalysis to „Energiewende“ in Germany



- Optimized processes for existing products or intermediates
- New processes for existing products
- New processes for new intermediates

A sustainable carbon cycle



Aktuelle Änderungen in den Rahmenbedingungen

- 2015 wird in Deutschland der Systemwechsel zu einer verbindlichen **Verringerung der Treibhausgasemissionen durch Treibstoffe** vollzogen (Gesetz zur Förderung von Biokraftstoffen von 2009):
 - 2015/16: „Klimaschutzquote“ 3%
 - 2017/18/19: 4,5%
 - Ab 2020: 7,5%
- Die seit 2009 in Kraft getretene „ Biokraftstoff-Nachhaltigkeitsverordnung“ sorgt dafür, dass ab 2017 nur noch Biokraftstoffe angerechnet werden können, deren **Beitrag zur Reduzierung der Treibhausgas-Emissionen größer als 50%** ist
- Vorschlag der Europäische Kommission für die Änderung der „Directive 2009/28/EC on the promotion of the use of energy from renewable“:
 - Berücksichtigung der **“Indirekt Land-Use-Changes” ILUC**
 - **Obergrenzen für Biokraftstoffe** der ersten Generation

■ ...

Relevante Strategiepaper der Bundesregierung



The cover of the document features the logo of the Federal Ministry for Transport, Building and Urban Development on the left and the 'Energie für Deutschland' logo on the right. The title 'Die Mobilitäts- und Kraftstoffstrategie der Bundesregierung (MKS)' is prominently displayed in white text on a dark blue background. Below the title, the slogan 'Energie auf neuen Wegen' is visible. The bottom section of the cover contains a quote and the document's title and year.

Bundesministerium für Verkehr, Bau und Stadtentwicklung

Energie für Deutschland

Die Mobilitäts- und Kraftstoffstrategie der Bundesregierung (MKS)

Energie auf neuen Wegen

“Die Forschung zur marktnahen Herstellung innovativer Biokraftstoff- und Bioraffineriekonzepte mit besonderem Fokus auf Lignocellulose sowie biogene Rest- und Abfallstoffe sollen ausgeweitet werden.”

Die Mobilitäts- und Kraftstoffstrategie der Bundesregierung (MKS), 2013.



The cover features a photograph of a biomass processing facility with large metal tanks and pipes. The title 'Roadmap Bioraffinerien' is written in white on a green background at the bottom. A quote is overlaid on the image, and the document's title and year are at the bottom.

Die Bundesregierung

“Biomasse ist erneuerbar, aber [...] limitiert. Dieser Aspekt und darüber hinaus die Konkurrenz mit anderen Flächennutzungen [...] erfordern neben nachhaltigen Ertragssteigerungen eine hocheffiziente Nutzung der knappen Ressource Biomasse.”

Roadmap Bioraffinerien, 2012.

Roadmap Bioraffinerien

im Rahmen der Aktionspläne der Bundesregierung zur stofflichen und energetischen Nutzung nachwachsender Rohstoffe

But Standards are Important

■ Gasoline: DIN EN 228

- ROZ > 95
- Density >720kg/m³, <755kg/m³
- Aromatic Compounds < 35% (v/v)
- Oxygen Content <3,7% (w/w)
- Fuel Classes (summer/winter) A-F



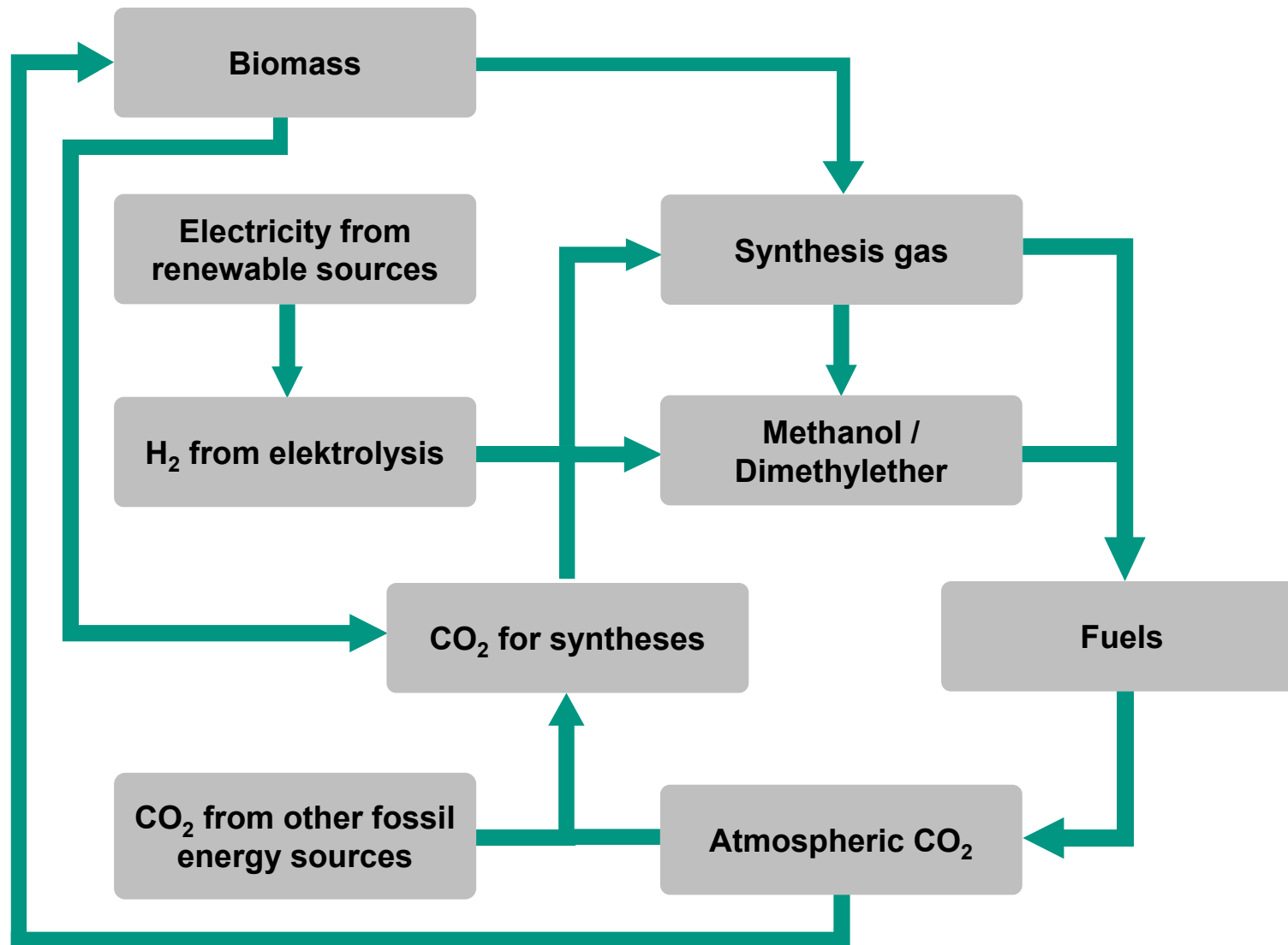
■ Diesel-Fuel: DIN EN 590

- Cetan-Number > 51
- Density >820kg/m³, <845kg/m³
- Boiling range 250°C (65%) ... 360° (95%)
- CFPP A-F

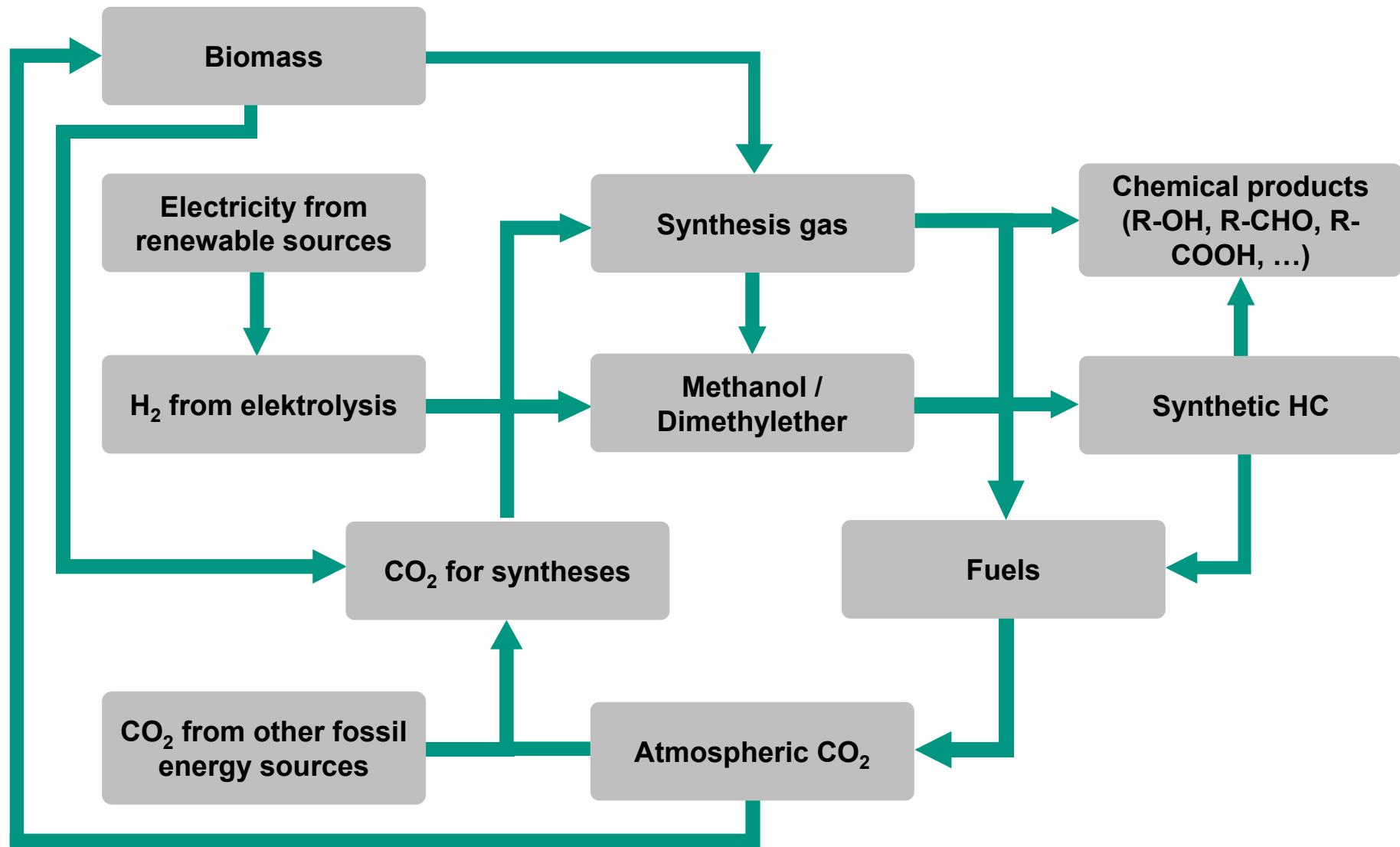
■ Jetfuel, JET-A1, ASTM D1655-13a



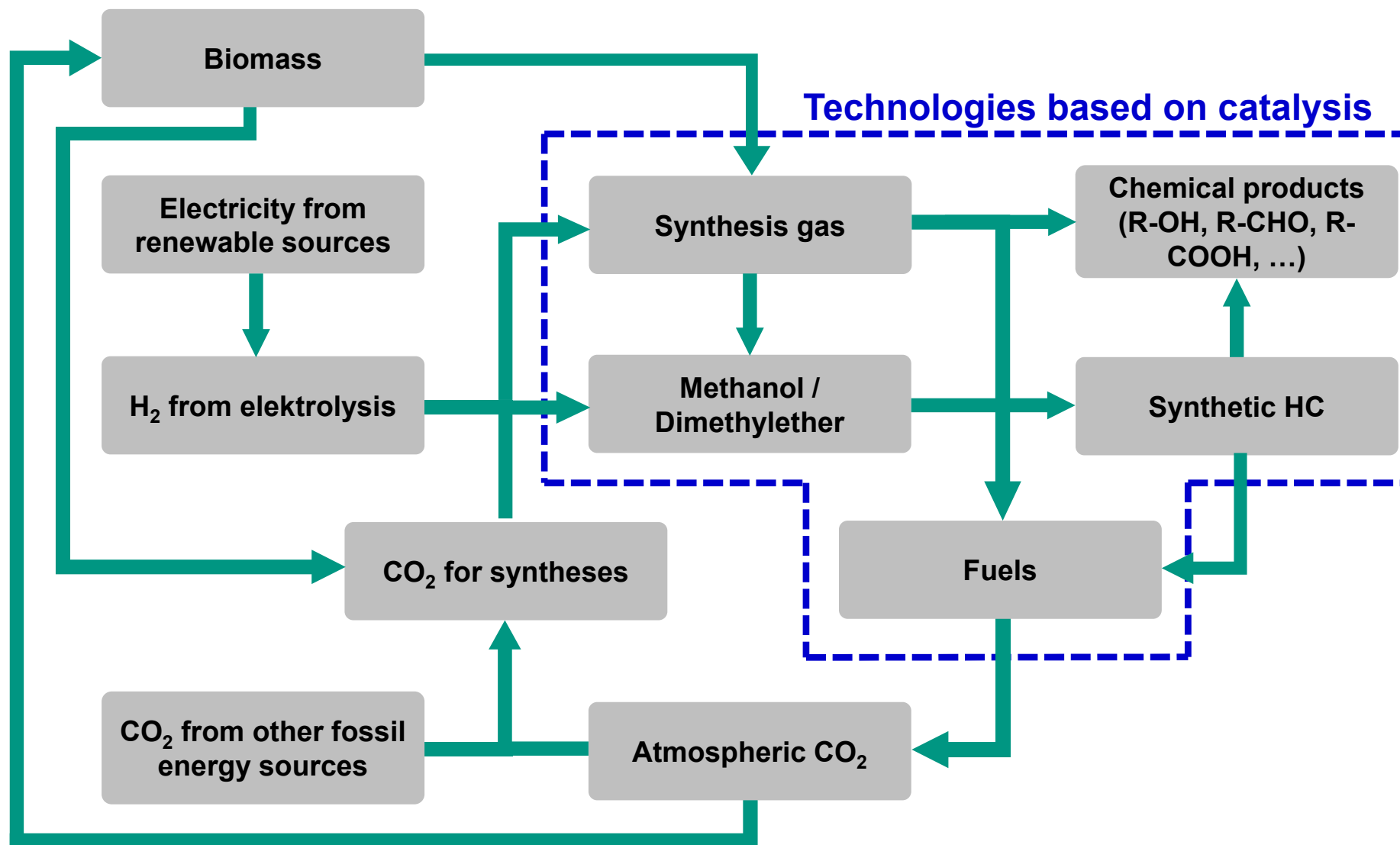
How CO₂ may be activated:



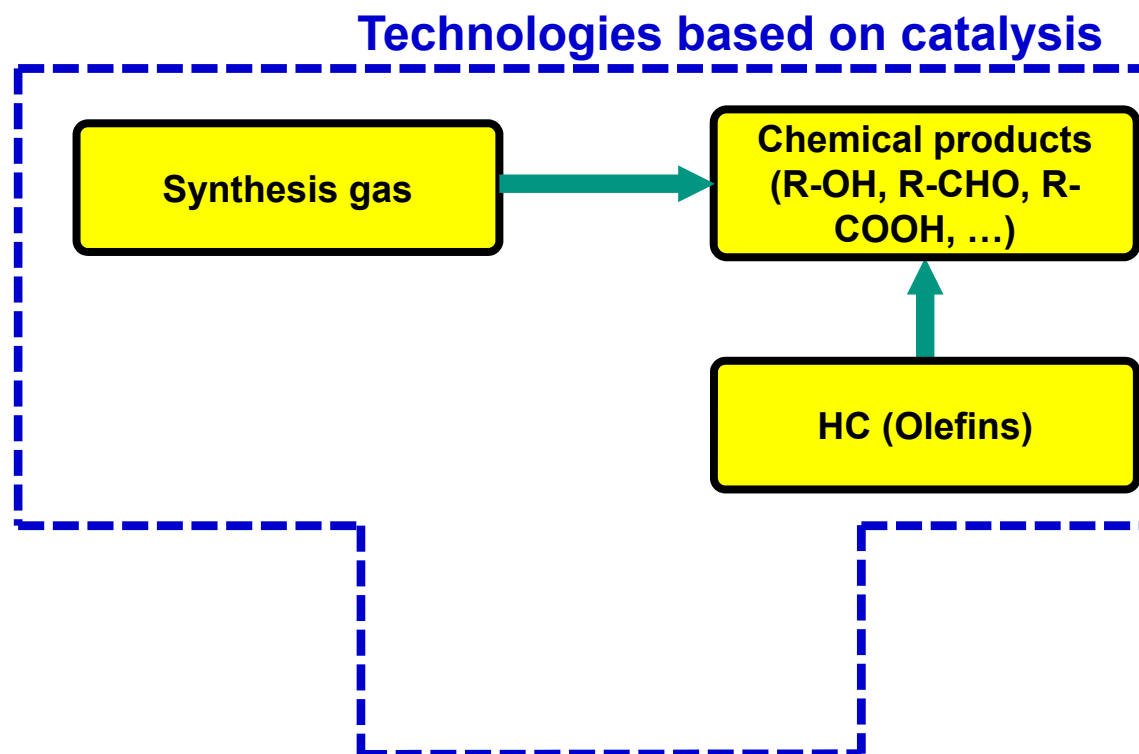
An Integrated System with Chemicals would Follow:



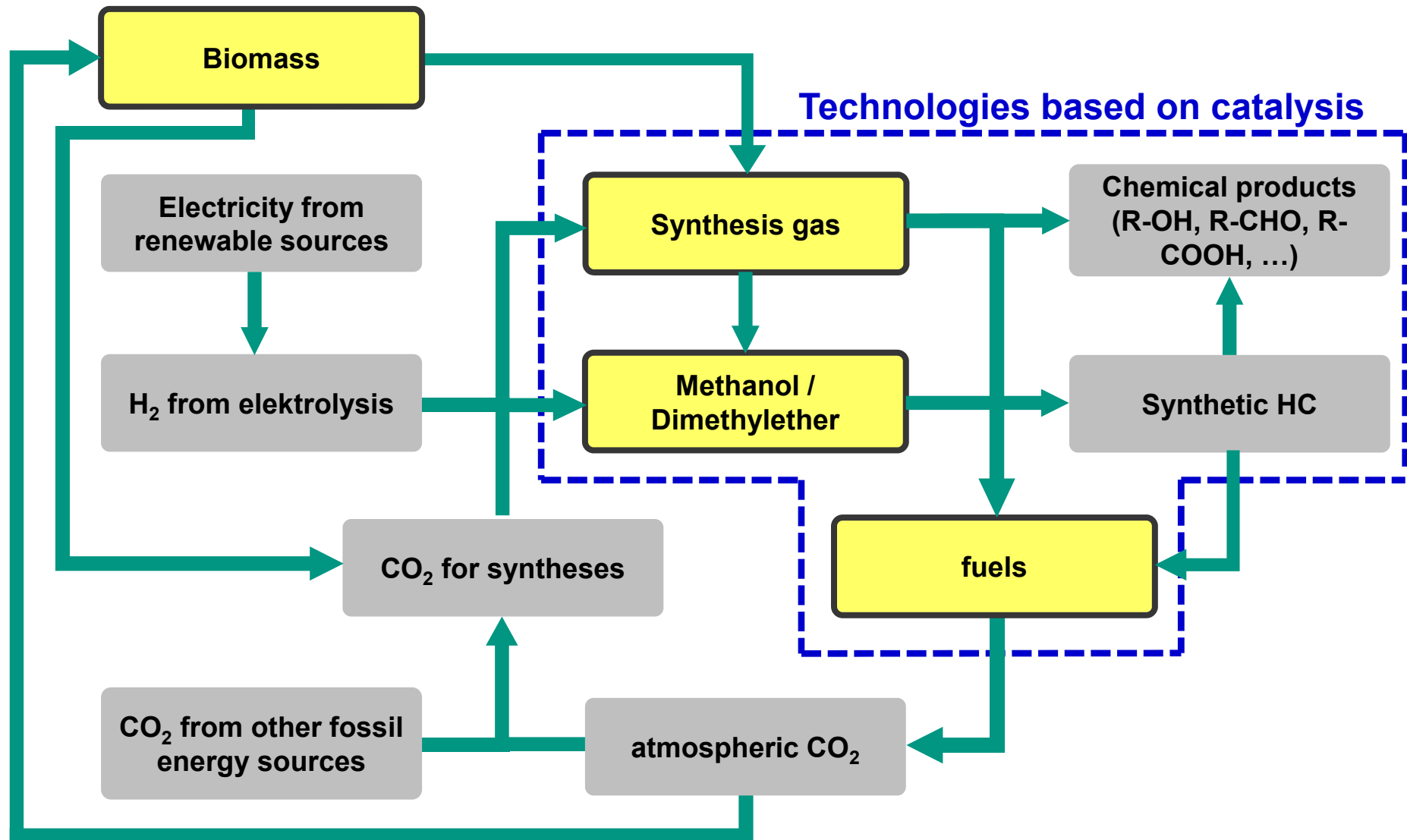
Catalysis will Play its Role



My Experience with Prozess-Technology for Homogeneous Catalysis



The Karlsruhe bioliq® Process



bioliq®-Pilot-Plant

Gefördert durch:



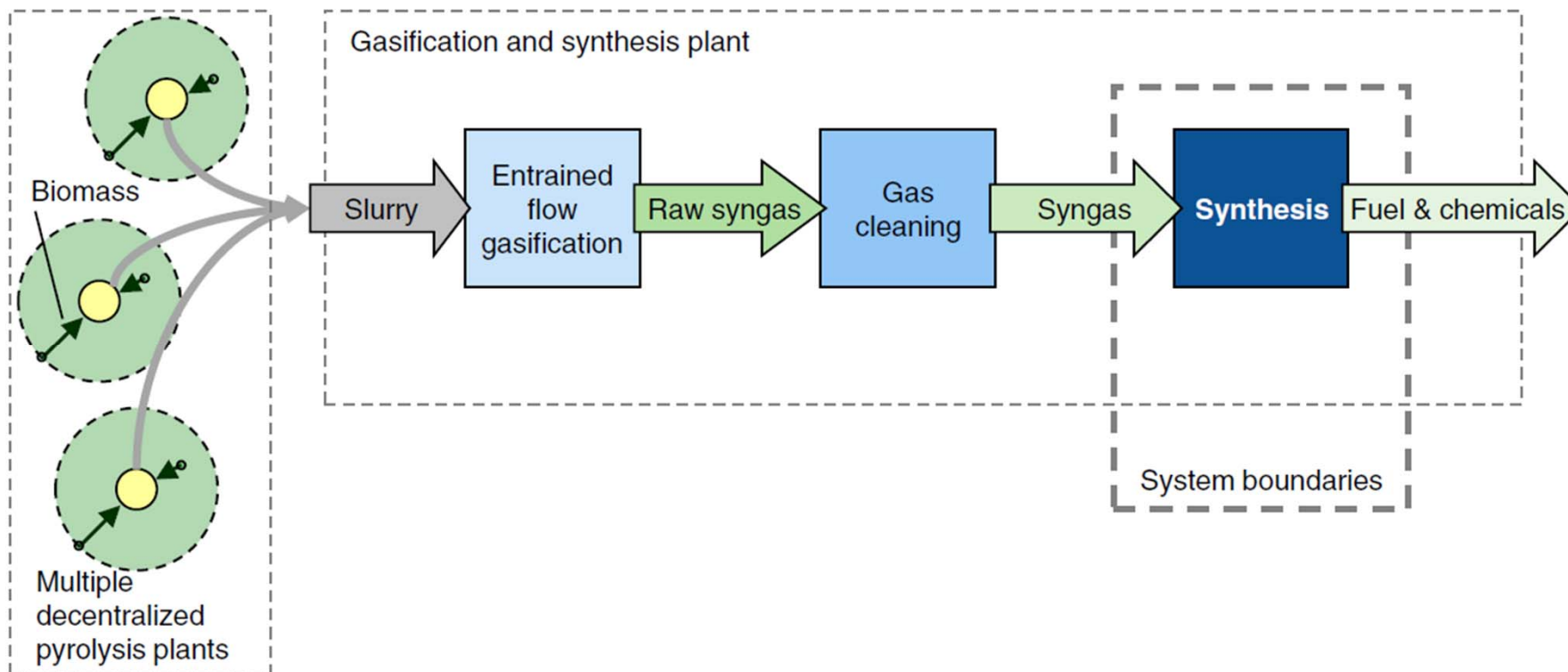
Bundesministerium für
Ernährung, Landwirtschaft
und Verbraucherschutz



Biomass to Liquid Karlsruhe

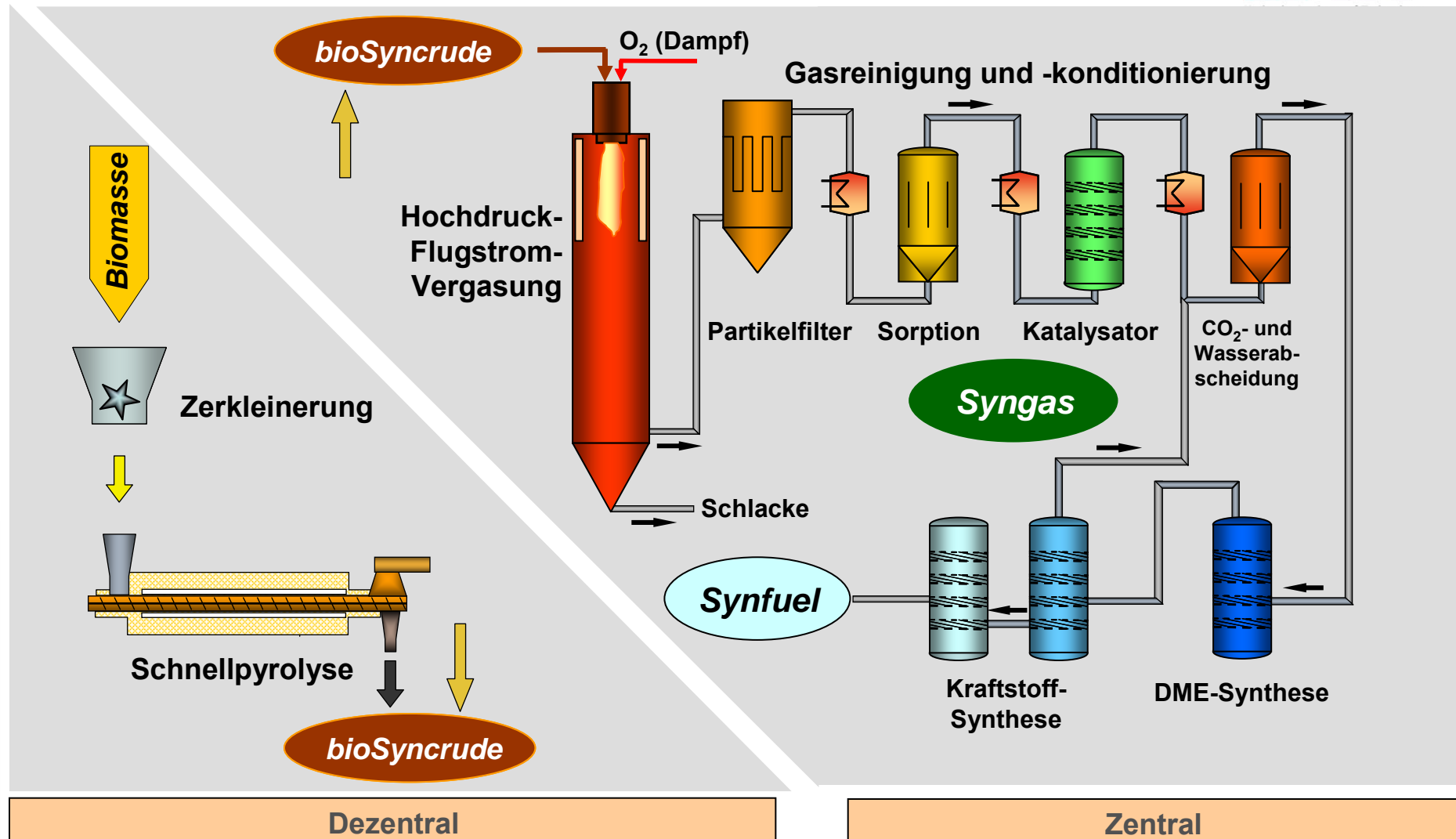


The Basic Idea behind bioliq®



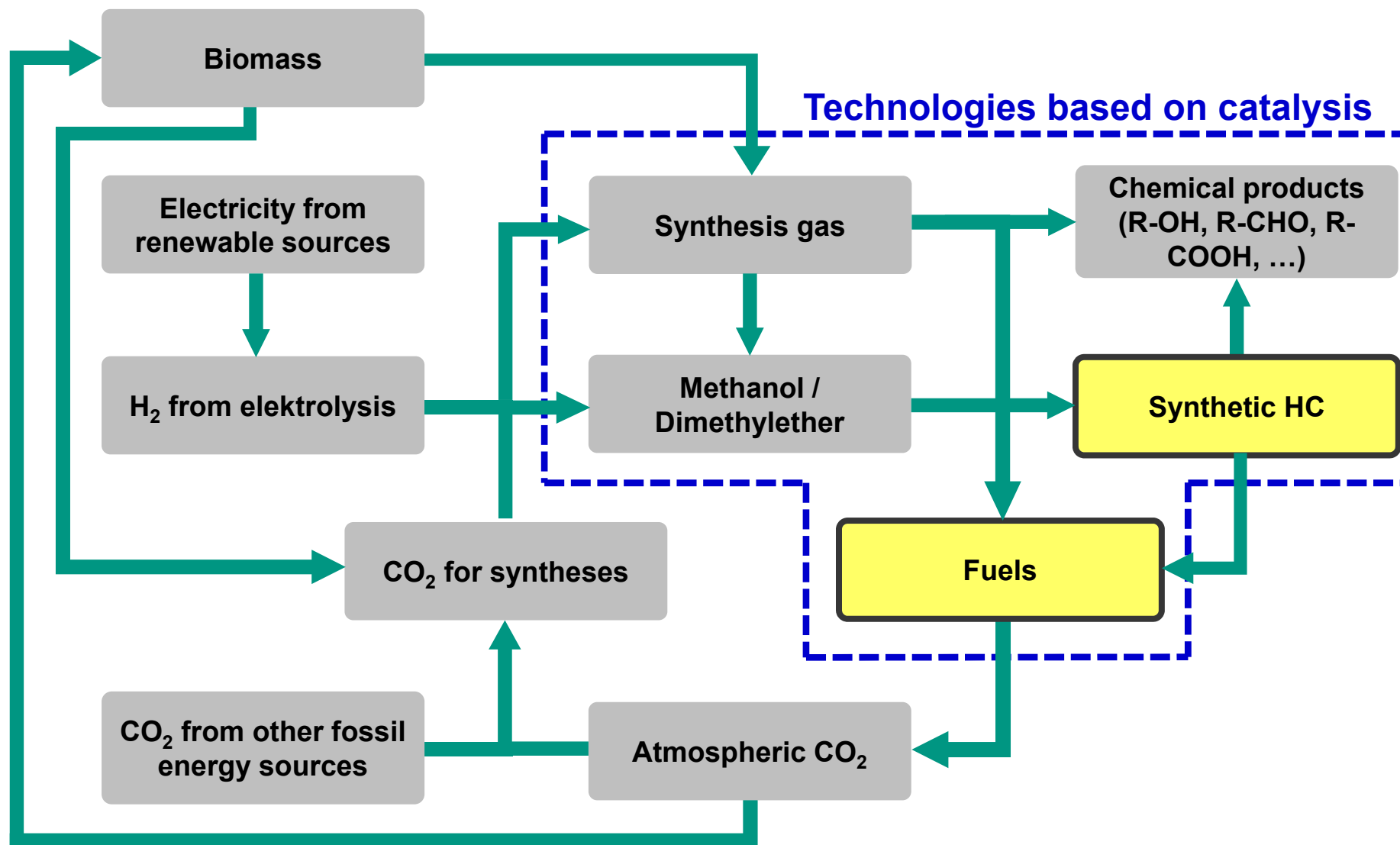
Quelle: Trippe, F.; Fruehling, M.; Schultmann, F.; Stahl, R.; Henrich, E. & Dalai, A.
„Comprehensive techno-economic assessment of dimethyl ether (DME) synthesis and Fischer-Tropsch synthesis as alternative process steps within biomass-to-liquid production“
Fuel Processing Technology, **2013**, 106, 577 - 586

bioliq-Process



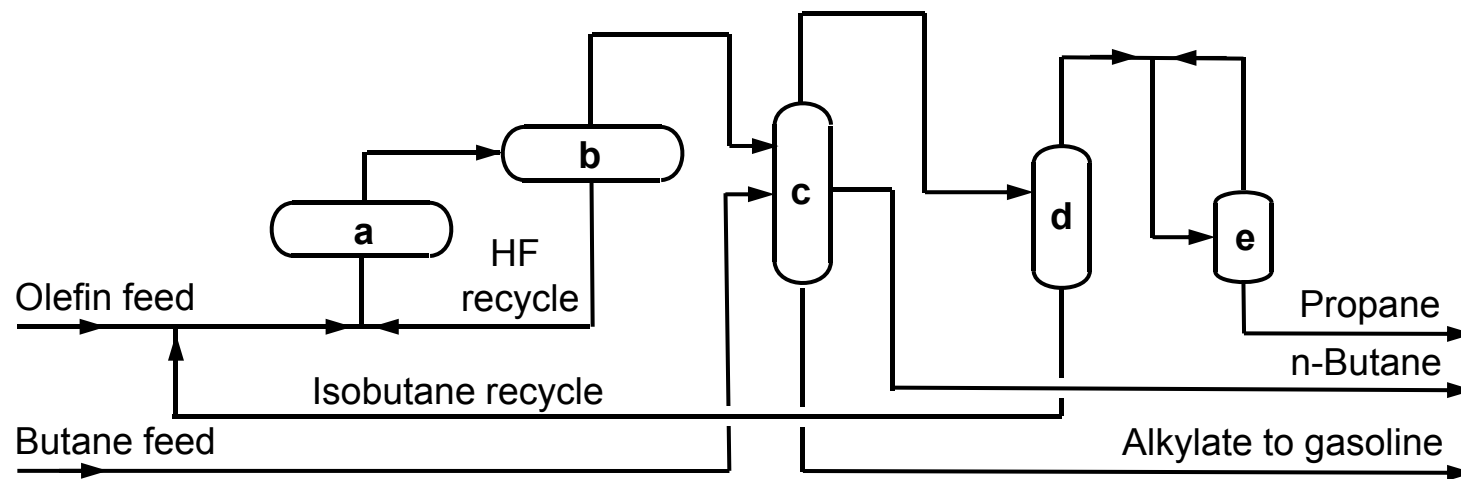
Quelle: Dahmen, N.; Dinjus, E.; Kolb, T.; Arnold, U.; Leibold, H. & Stahl, R., *Environmental Progress & Sustainable Energy*, John Wiley & Sons, Inc., **2012**, 31, 176-181

Homogeneous Catalysis in Fuel Synthesis



Homogeneous Catalysis in Fuel Synthesis

- HF catalyzed alkylation combines low-molecular-weight olefins to produce Alkylate as premium blending stock (industrially applied since late 40's).

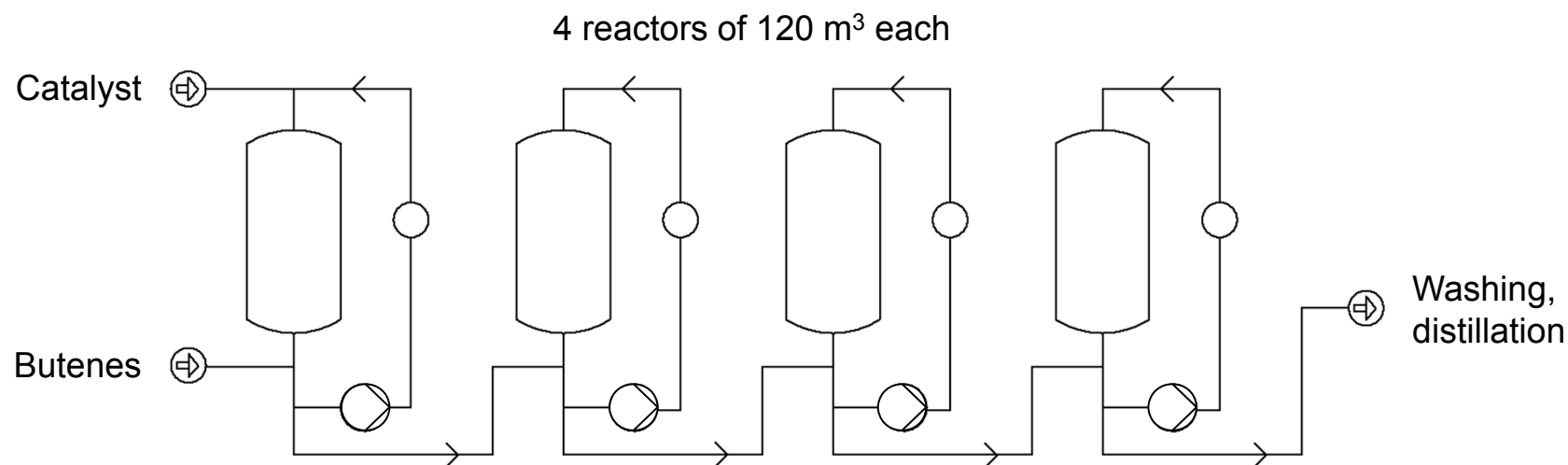


UOP Process: a) Reactor; b) Settler; c) Iso stripper; d) Depropanizer; e) HF stripper

- Reaction (liquid phase, 16°C to 40°C).
- Olefin space velocity 0.1 to 0.6 $\text{kg}_{\text{olefin}}/\text{kg}_{\text{acid}}\cdot\text{h}$.
- Catalyst productivity 1000 to 2500 $\text{kg}_{\text{alkylate}}/\text{kg}_{\text{acid}}$.
- Safety & corrosion considerations required.

Homogeneous Catalysis in Fuel Synthesis

- Dimersol olefin oligomerization (industrially applied since 1977)

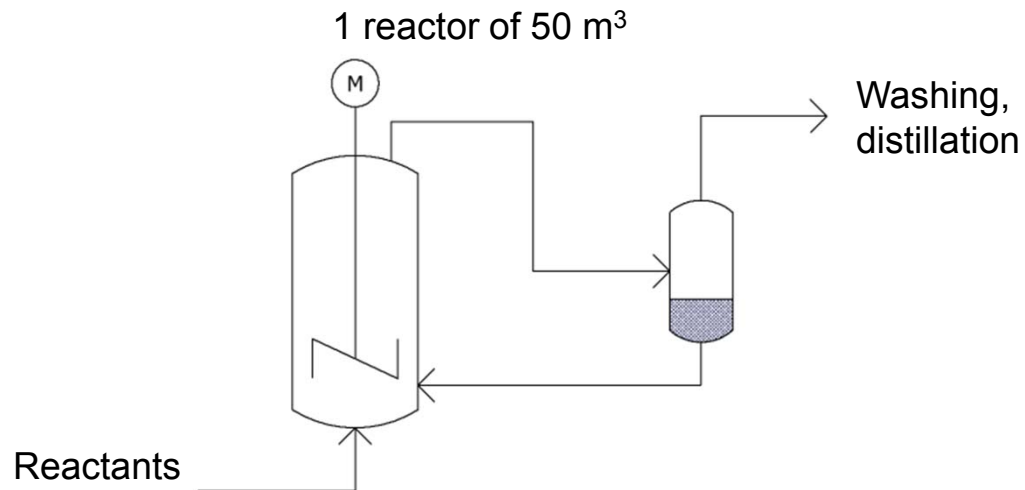


- Dimerisation reaction is catalyzed by a Ziegler-type cationic nickel complex of the general form $[\text{LNiCH}_2\text{R}_9][\text{AlCl}_4]$ ($\text{L} = \text{PR}_3$).
- Commonly operated without solvent at 50 – 70°C.
- Sensitive to any impurities.

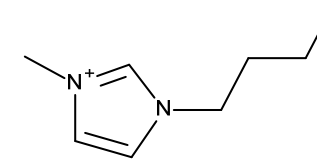
Homogeneous Catalysis in Fuel Synthesis

■ Difasol olefin oligomerization

(Chauvin Y., Einloft S., Olivier H. (1995) *Ind. Eng. Chem. Res.* **34**, 4, 1149-1155)



Catalyst:
[Ni-R][EtAlCl₃] + [C4-mim][AlCl₄]

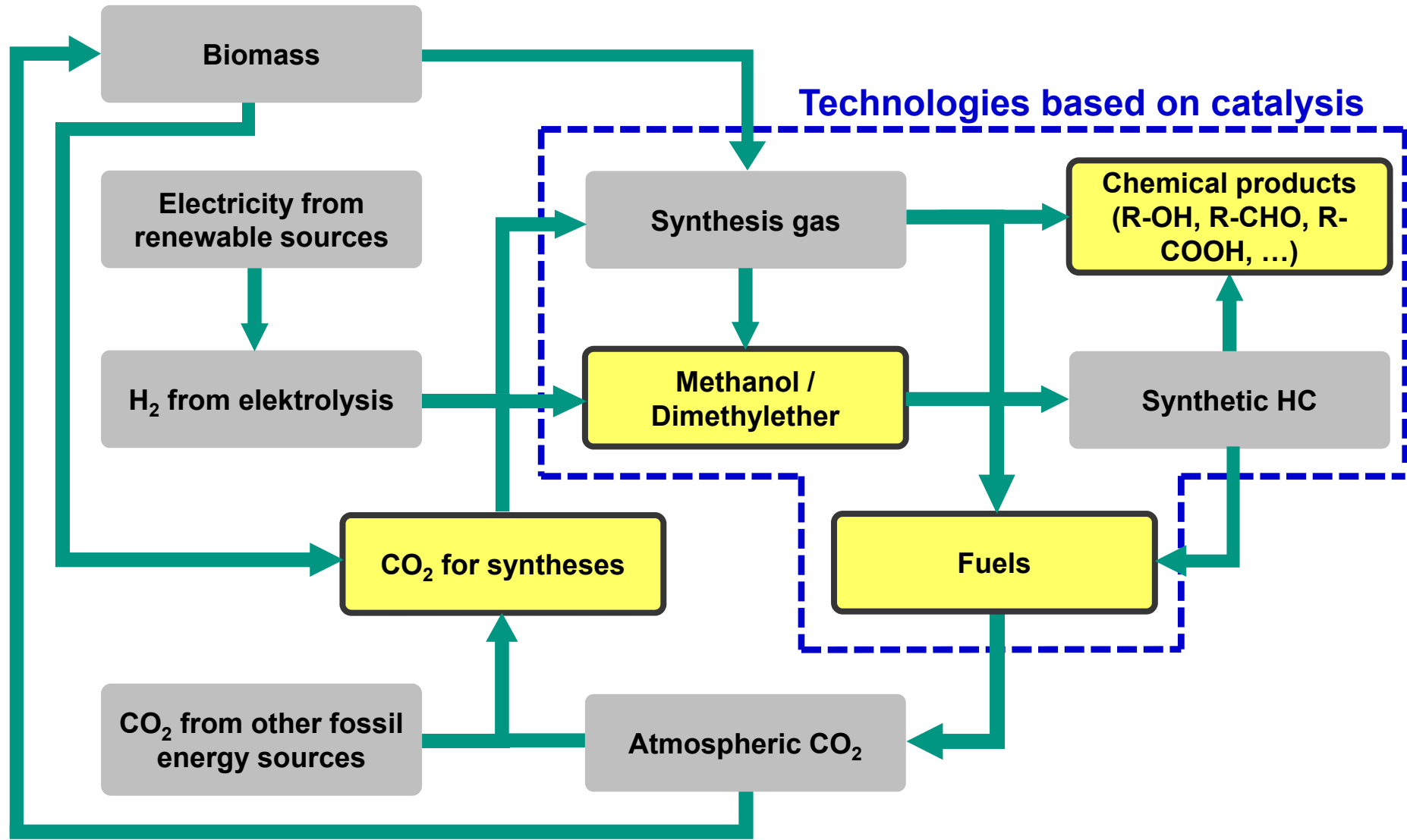


C4-mim

In comparison with the Dimersol process:

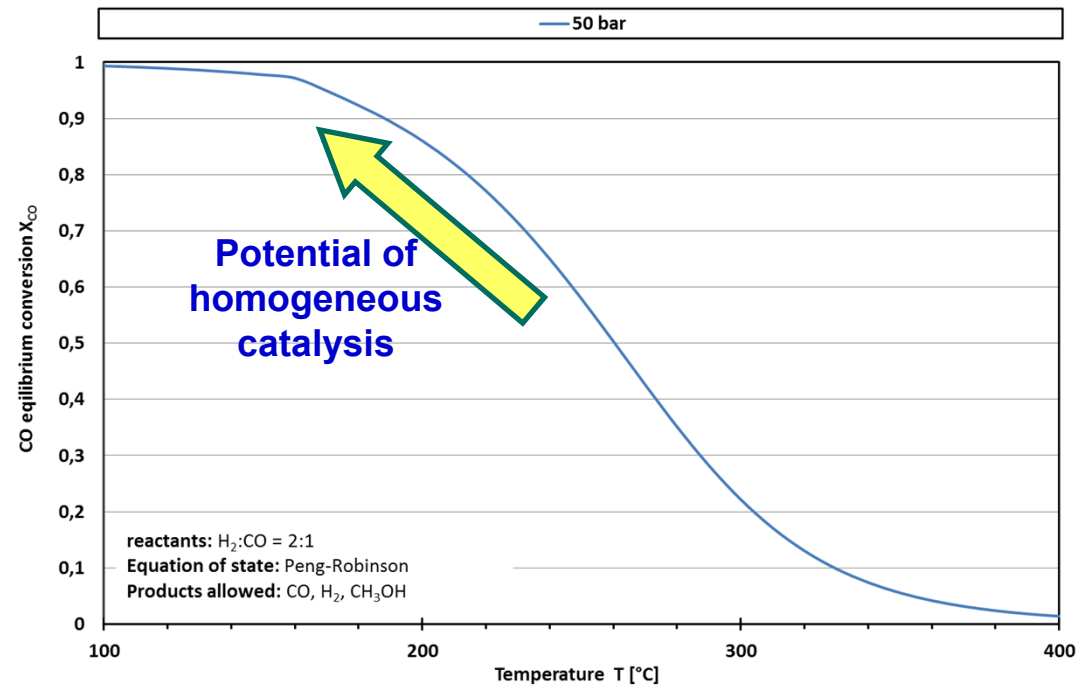
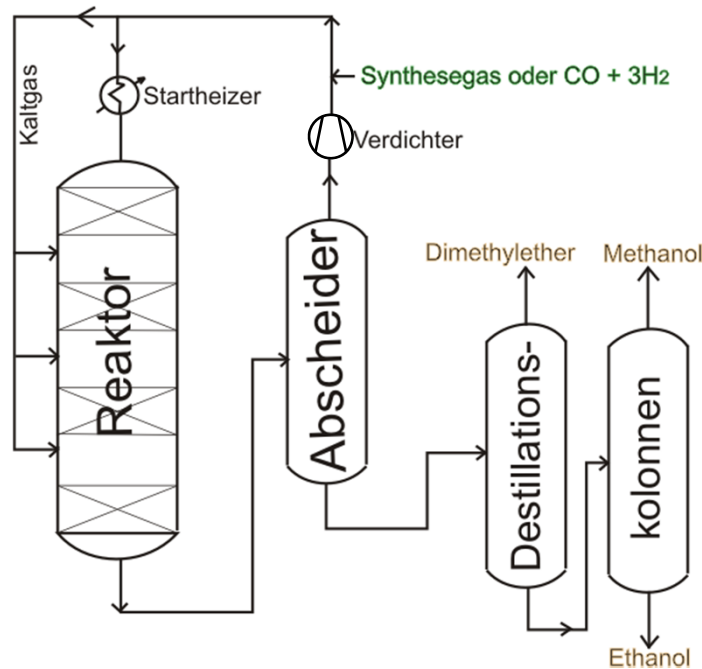
- Reduced octene solubility in ionic liquid provides increased selectivity (68 % => 75 %).
- 10-fold reduced catalyst consumption.
- Operation at low temperature and low pressure.
- Compact process design.

CO₂ as C₁ building block



Conventional MeOH process

- Today, the most widely used heterogeneous catalyst are based on Cu, ZnO, and Al₂O₃ (introduced by ICI in 1966).



- Typical conditions: 5–10 Mpa, 250°C.
- Selectivity > 99.8 %.

CO₂ reduction by (renewable) H₂

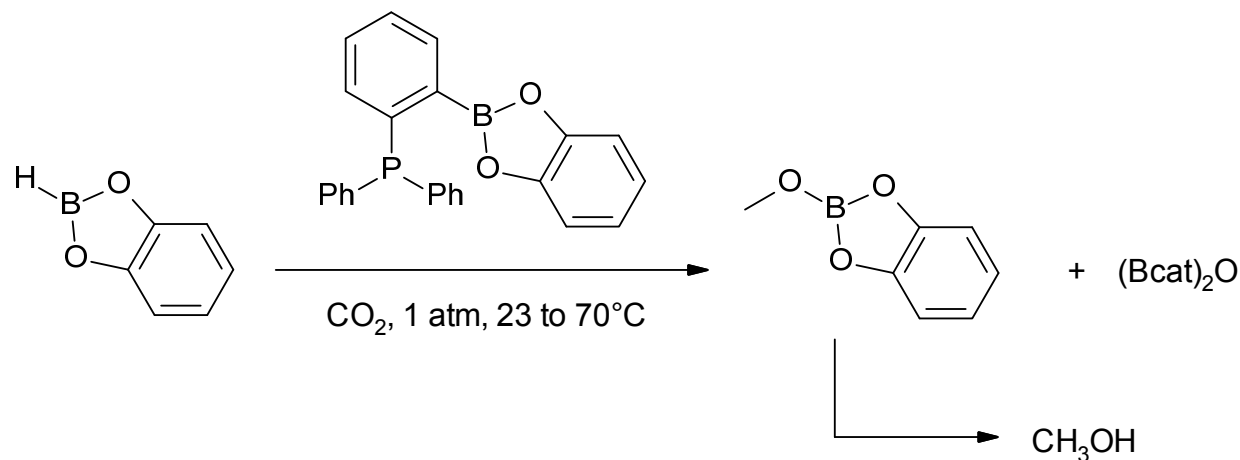
Reaction		ΔH° (kJ/mol)	ΔG° (kJ/mol)	
CO ₂ (g) + H ₂ (g)	→	HCOOH (l)	-31.0	+34.3
CO ₂ (g) + 2 H ₂ (g)	→	HCHO (g) + H ₂ O (l)	-11.7	+46.6
CO ₂ (g) + 3 H ₂ (g)	→	CH ₃ OH (l) + H ₂ O (l)	-137.8	-10.7
CO ₂ (g) + 4 H ₂ (g)	→	CH ₄ (g) + 2 H ₂ O (l)	-259.9	-132.4
CO(g) + 2 H ₂ (g)	→	CH ₃ OH (l)	-131.6	-29.9

- MeOH is typically produced by heterogeneous catalysis. Although CO is the main reactant for industrial processes, CO₂ is probably the main source for MeOH.
- Homogeneous catalysts have been mainly investigated for the production of HCOOH and derivatives.

Recent trends in homogeneously catalyzed CO₂ reduction (A)

■ Organoborane reduction to MeOH

(L. Maron, F.-G. Fontaine et al., J. Am. Chem. Soc. 2013, 135, 9326–9329)

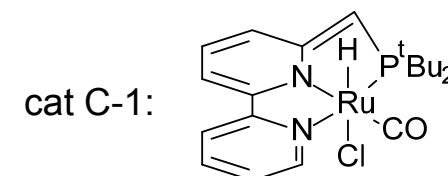
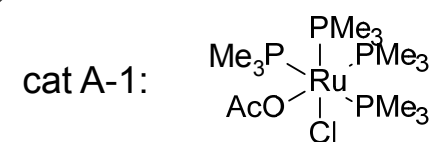
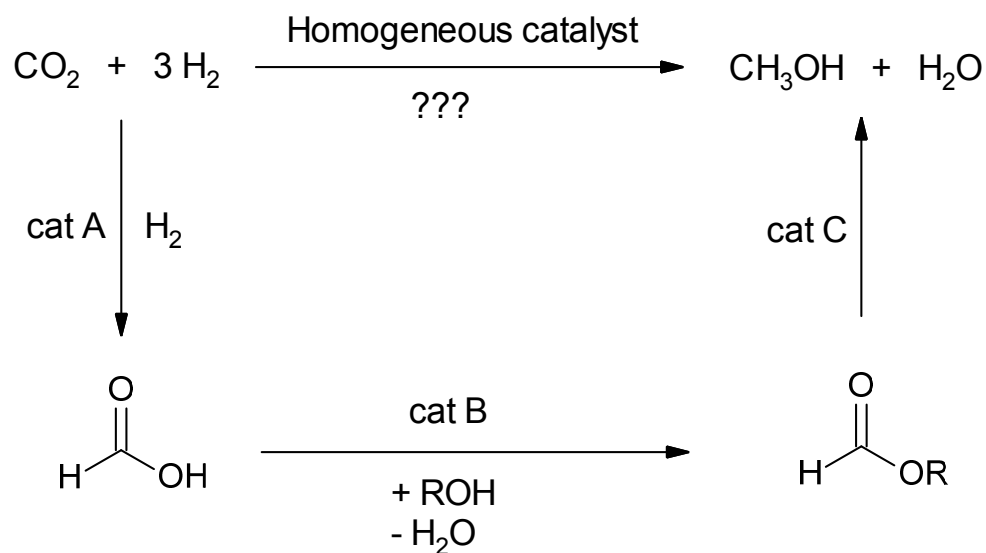


- Yield up to 99%.
- TON (turnover numbers) and TOF (turnover frequencies) reaching >2950 and 853 h⁻¹.
- Compared to the other metal-free systems, here the weak interaction between the catalyst and CO₂ is of particular importance.

Recent trends in homogeneously catalyzed CO₂ reduction (B)

■ Homogeneous cascade catalysis to MeOH

(S. Sanford et al., J. Am. Chem. Soc. 2011, 133, 18122–18125)

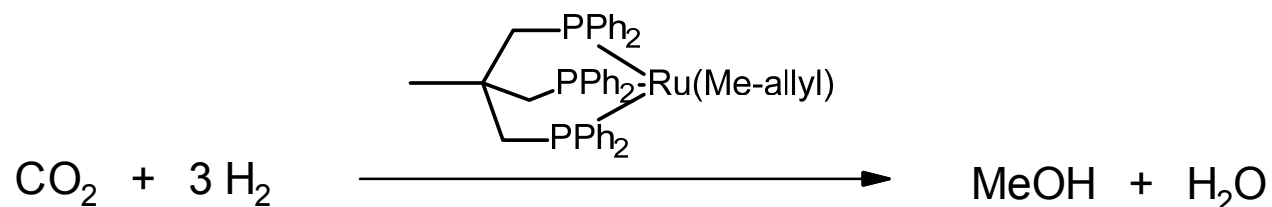


- For steps (1) and (2) a physical separation is suggested, due to the low stability of cat B-2.
- Reactions take place at 75°C for steps (1) and (2), and at 135°C for step (3).
- TON (turnover number) of the complete cascade on lab-scale amounts to 21.

Recent trends in homogeneously catalyzed CO₂ reduction (C)

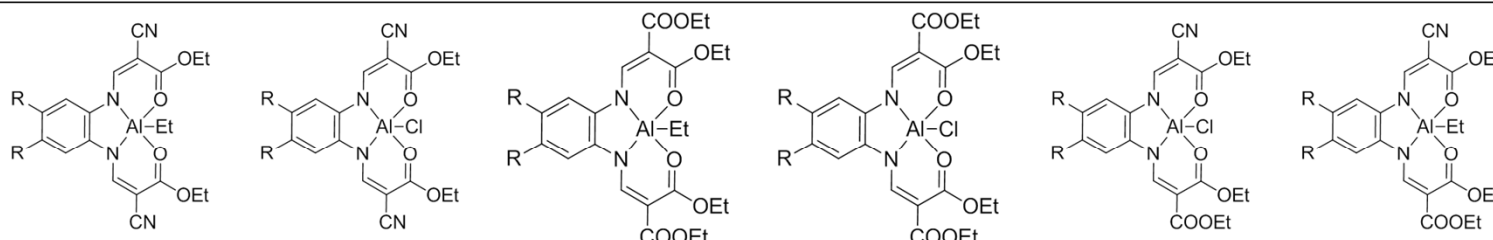
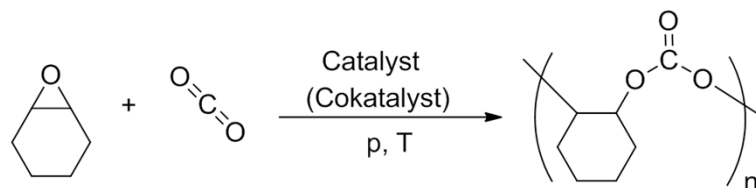
■ Ruthenium catalyzed hydrogenation of CO₂ to MeOH

(J. Klankermayer, W. Leitner et al., Angew. Chem. Int. Ed. 2012, 51, 7499–7502)



- Highest TON (turnover number) of 221 reached at 60 bar H₂, 20 bar CO₂, in a mixture of EtOH / THF, at 140°C, HNTf₂ added.
- In situ catalysts with triphos also active.

- New catalysts for the synthesis of organic Carbonates from Epoxides and CO₂ (T. A. Zevaco, E. Dinjus et al. Dalton Trans., 2014, 43, 2344-2347)



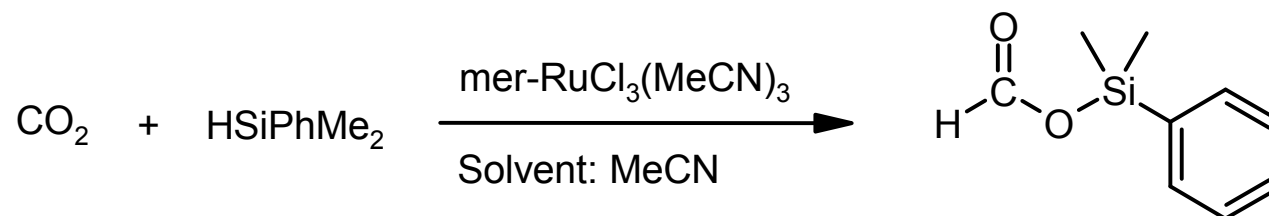
R=H	65%	63%	98%	83%	78%	88%
R=Cl	29%	73%	84%	71%	41%	50%
R=Me	46%	60%	96%	85%	79%	88%

50 bar CO₂, 80°C, 20 h, 0.2 mol% cat., Cocat.:PPNCl

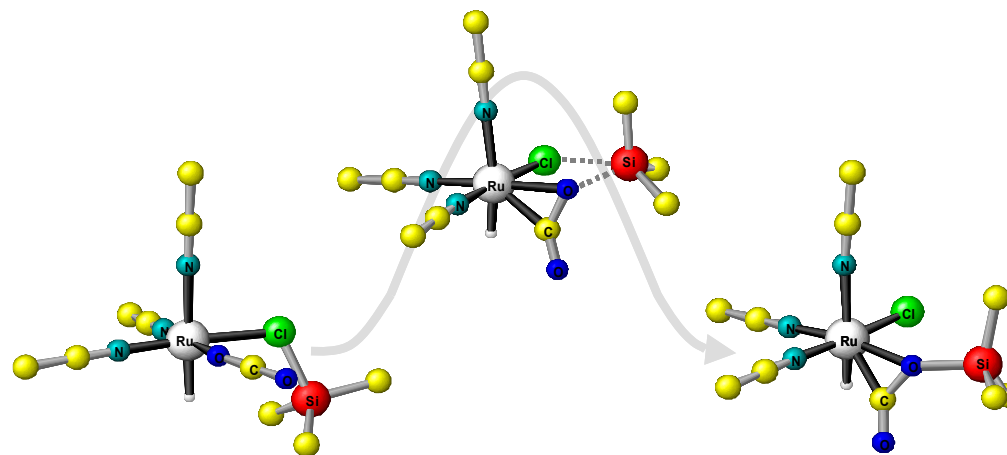
- Product: Pure polycarbonate (no ether-linkages).
- Up to almost quantitative conversion.
- Analogous Fe and Zn catalyst are suitable for transformation to cyclic carbonate.

IKFT-Research on CO₂ chemistry

- Highly active catalysts for the hydrosilylation of CO₂
(S. Pitter, P. Hofmann et al., Chem. Eu. J., 2007, 13, 2864-79)



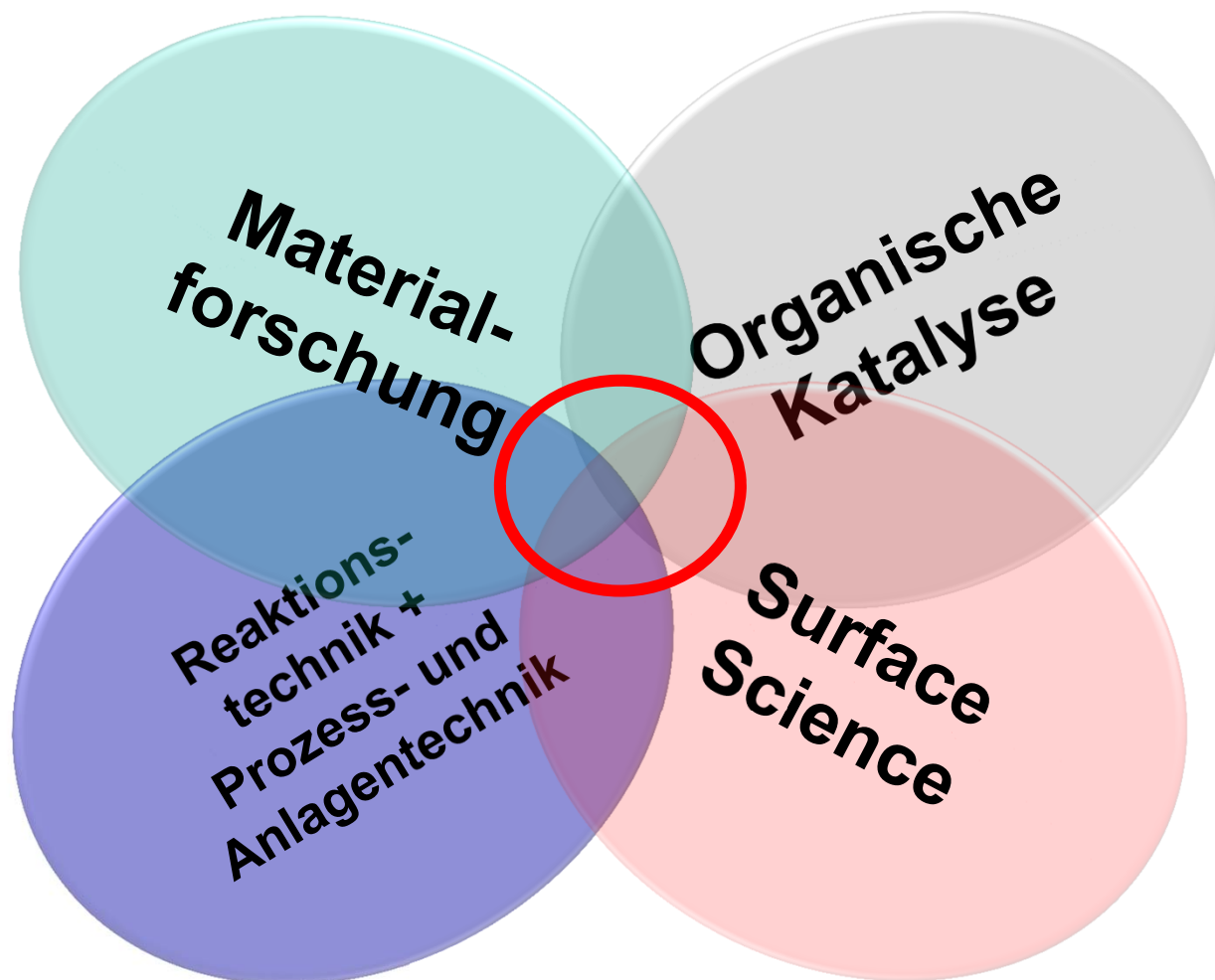
- TOF (turnover frequency) up to 3500 h⁻¹.
- Applicable as well for other H-silanes.
- Activation of silane is probably the initiating step supported by in-situ investigations
- Unusual CO₂ transfer to intermediary formed ClSiR₃ ligand is rate limiting (figure from DFT calculation below).



Conclusion

- Process technology for homogenous catalyzed processes is highly relevant for the transition of the energy system
- Homogenous catalysis may open up new process windows for more efficient, intensified processes, but the bottleneck are new catalyst systems
- bioliq is a research platform for processes from renewables to fuels and chemicals
- Partnerships with academia and industry are necessary to leverage the potential of bioliq for catalysis and process development

Unsere Mission des IKFT



Vielen Dank!

Nico Dahmen, Stephan Pitter, Tom Zevaco und...





Karlsruher Institut für Technologie

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