Karlsruhe Institute of Technology

Biomass to Liquid Karlsruhe

Modified MtG-processes for BtL and Power-to-Fuels

Dr. Ulrich Arnold, Dorian Oestreich, Dr. Stephan Pitter, Prof. Dr.-Ing. Jörg Sauer

Institute of Catalysis Research and Technology

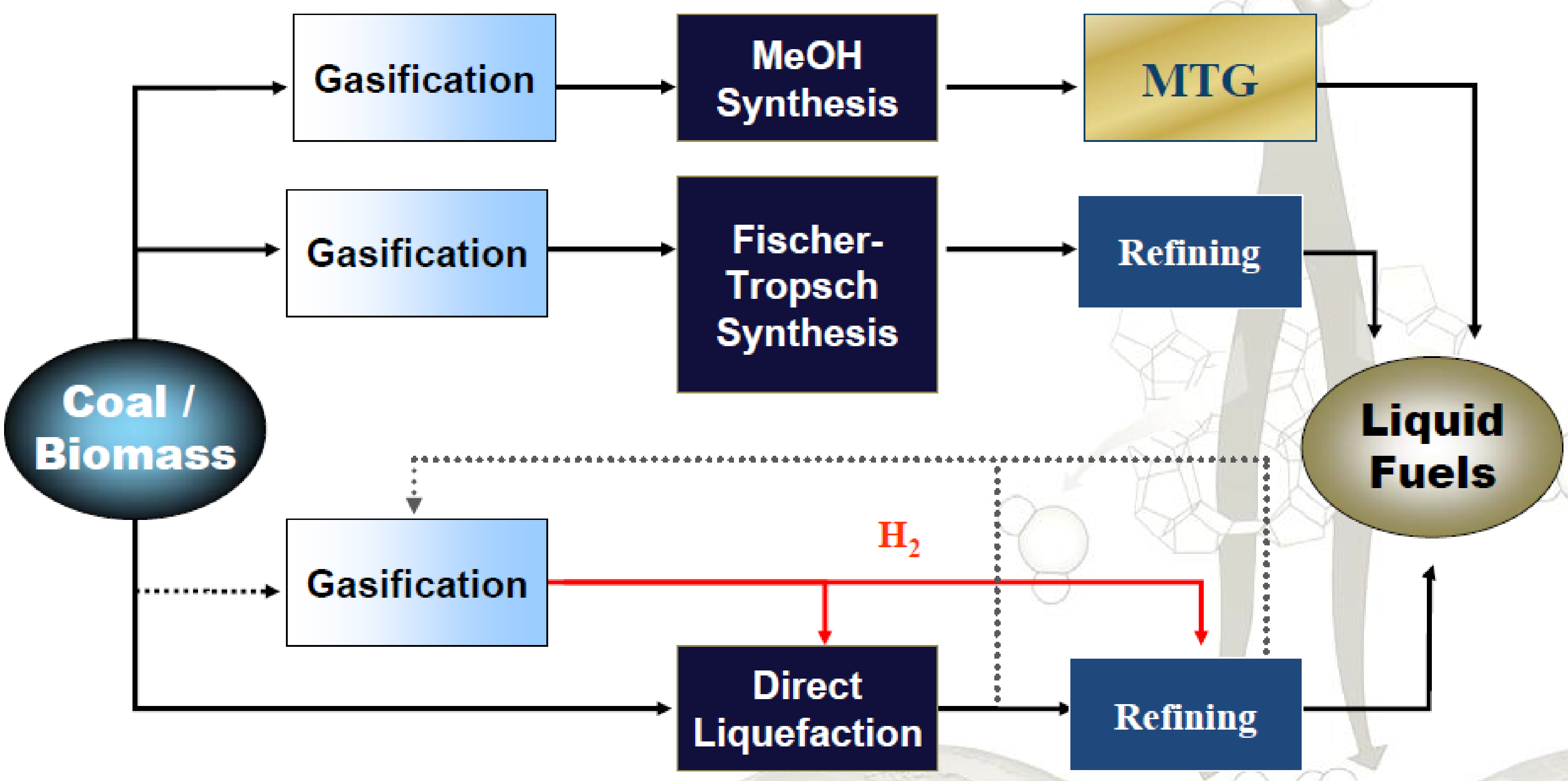
Outline

- Introduction: The Methanol-to-Gasoline Process (MtG)
- Reasons for Modifications to MtG
- Examples
- Conclusions

First Implementation of MtG in New Zealand[1]

[1] M. Hindman, Methanol-to-Gasoline-Technology, ExxonMobil Research and Engineering, World CtL-Conference, 2010, from http://www.exxonmobil.com/apps/refiningtechnologies/files/conference_2011.1204.MTG_World_CTL.pdf, retrieved on 2014-11-02

Options for CtL or BtL[1]

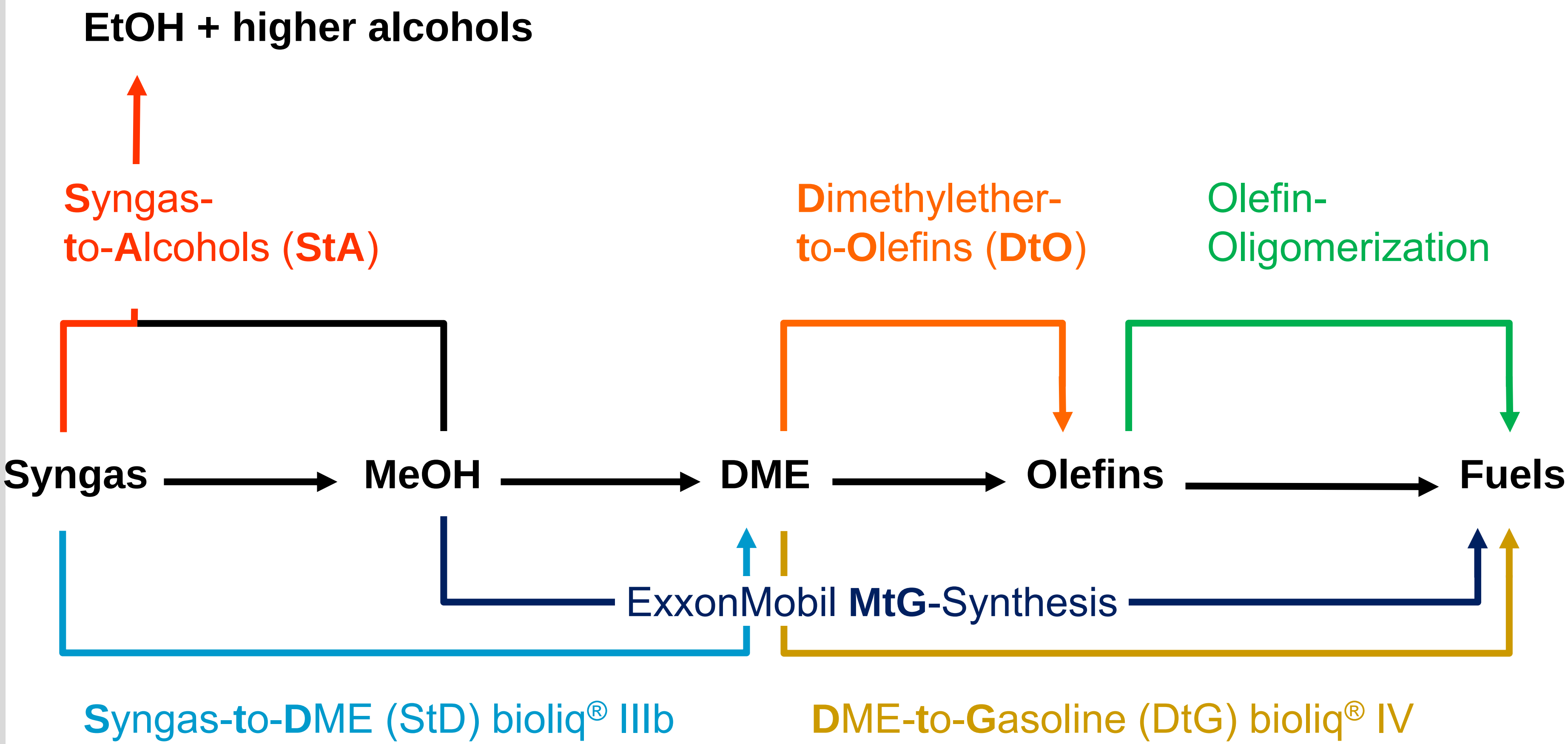


[1] M. Hindman, Methanol-to-Gasoline-Technology, ExxonMobil Research and Engineering, World CtL-Conference, 2010, from http://www.exxonmobil.com/apps/refiningtechnologies/files/conference_2011.1204.MTG_World_CTL.pdf, retrieved on 2014-11-02

China: The application for CtL

[1] M. Hindman, Methanol-to-Gasoline-Technology, ExxonMobil Research and Engineering, World CtL-Conference, 2010, from http://www.exxonmobil.com/apps/refiningtechnologies/files/conference_2011.1204.MTG_World_CTL.pdf, retrieved on 2014-11-02

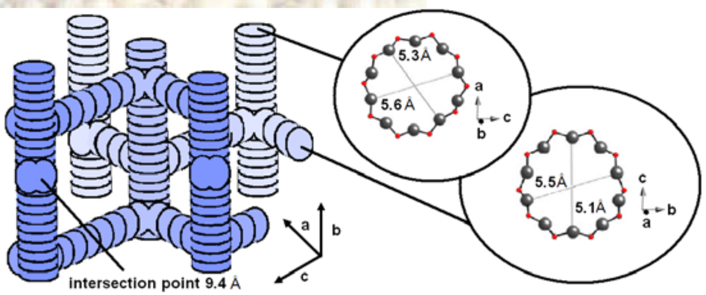
MtG-Chemistry Offers many Options[2]



[2] E. Dinjus, U. Arnold, N. Dahmen, R. Höfer, W. Wach, "Green Fuels - Sustainable Solutions for Transportation", in: *Sustainable Solutions for Modern Economies, RSC Green Chemistry Series No. 4*, (Ed.: Rainer Höfer), RSC Publishing, Cambridge, **2009**, pp. 125-163.

Catalysts

- $CO/CO_2/H_2$ to Methanol:
  - Copper-Catalysts:
    - ⇨ $Cu/ZnO/Al_2O_3$
- Methanol to DME:
  - Acidic Oxides:
    - ⇨ Al_2O_3
    - ⇨ Zeolithes
- DME to Olefins, DME to Gasoline, Olefin Oligomerization:
  - Zeolites (ZSM5)

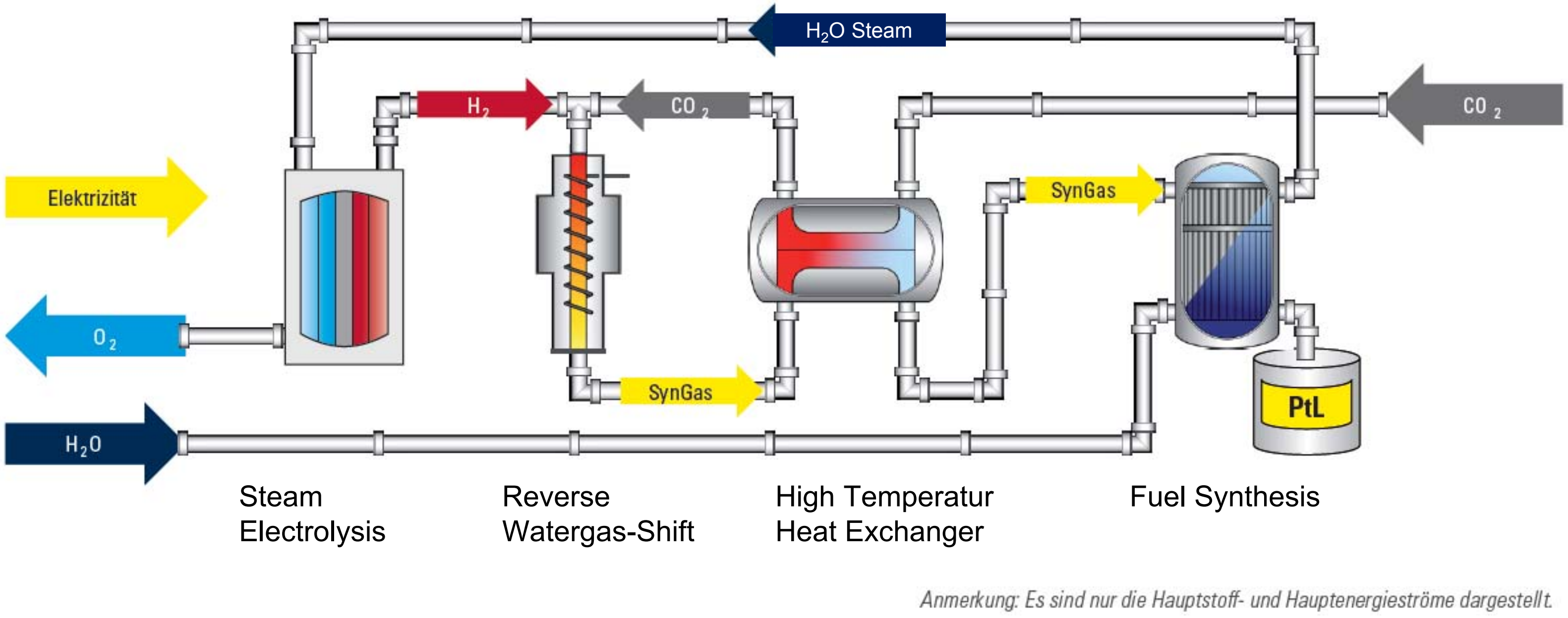


[3] http://www.catalysts.clariant.com/bu/Catalysis, retrieved 2014-11-02
[4] http://www.axens.net/our-offer/by-products/catalysts-and-adsorbents.html, retrieved 2014-11-02

Outline

- Introduction: The Methanol-to-Gasoline Process (MtG)
- Reasons for Modifications to MtG:
  - Different Feedstocks for Syngas
  - Different Syngas Qualities
  - Demands for New or Different Products
  - Scale of Implementation
- Examples
- Conclusions

Power to Liquids according to Sunfire / Bilfinger[5]



[5] http://www.sunfire.de/wp-content/uploads/BILit_FactSheet_POWER-TO-LIQUIDS_EMS_de.pdf, retrieved 2014-11-03

Existing Fuel Standards in Europe

Karlsruhe Institute of Technology

- 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

Outline

Karlsruhe Institute of Technology

- Introduction: The Methanol-to-Gasoline Process (MtG)
- Reasons for Modifications to MtG
- Examples:
  - Direct DME-Synthesis
  - Modified ZSM-5 Catalysts for Gasoline Stage
  - New Fuels from Methanol / DME
  - Homogeneous Catalysis to Methanol / DME
- Conclusions

DME direct synthesis[6]

- Favourable thermodynamics for H_2/CO ratios around 1:1
- Highly exothermal and exergonic reaction[

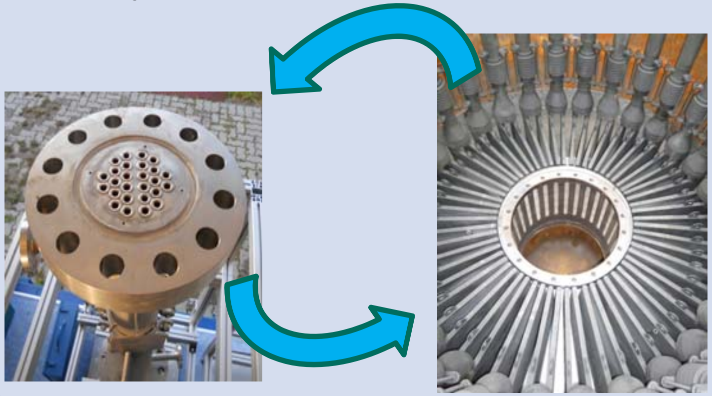
$$CO + 2\,H_2 \rightleftarrows CH_3OH \qquad \Delta_R H^0 = -95{,}0 \text{ kJ/mol}$$

$$2\,CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \Delta_R H^0 = -14{,}9 \text{ kJ/mol}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta_R H^0 = -41{,}2 \text{ kJ/mol}$$

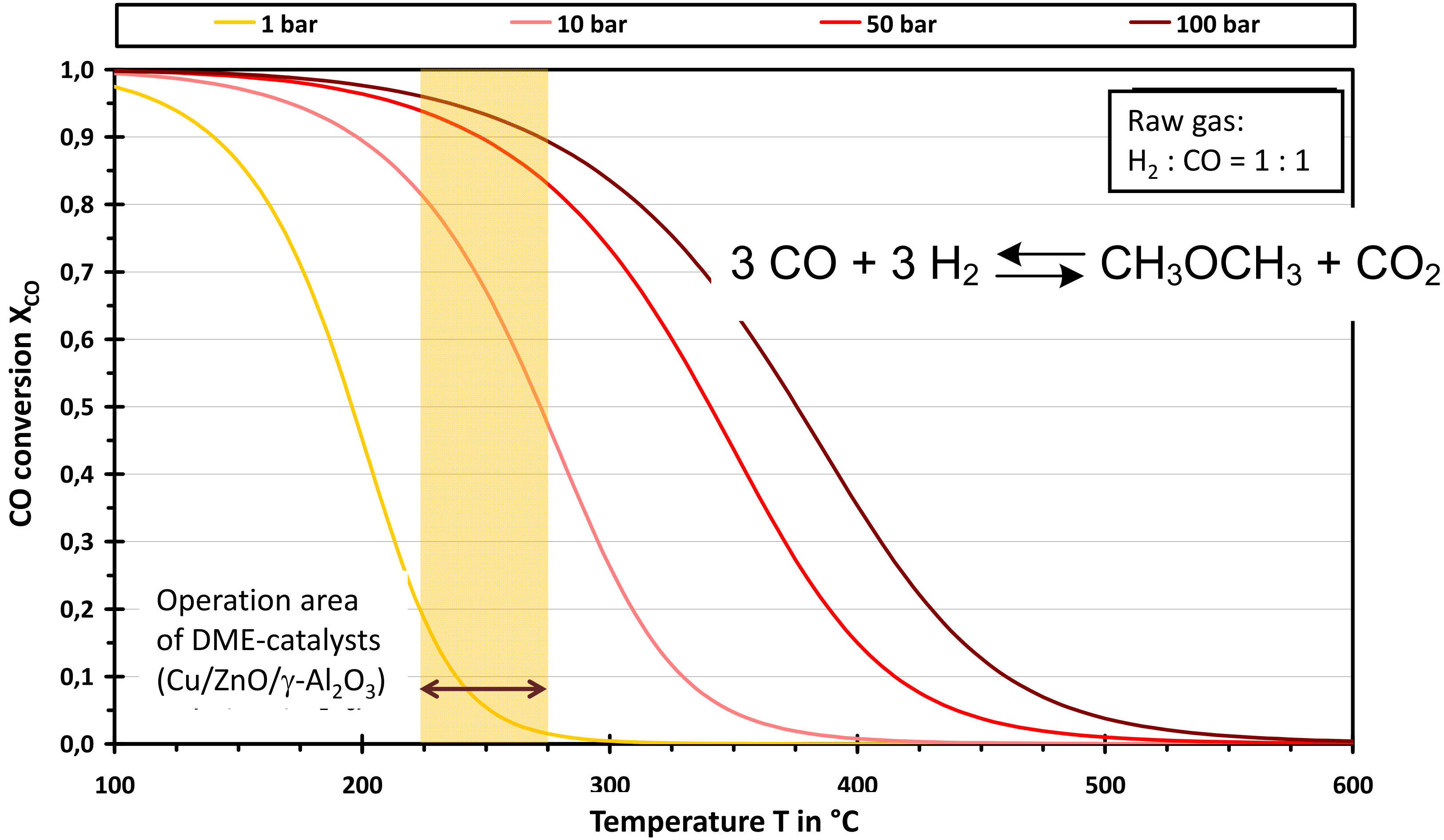
$$3\,CO + 3\,H_2 \rightleftarrows CH_3OCH_3 + CO_2 \qquad \Delta_R H^0 = -246{,}2 \text{ kJ/mol}$$

Reaction engineering and catalyst development



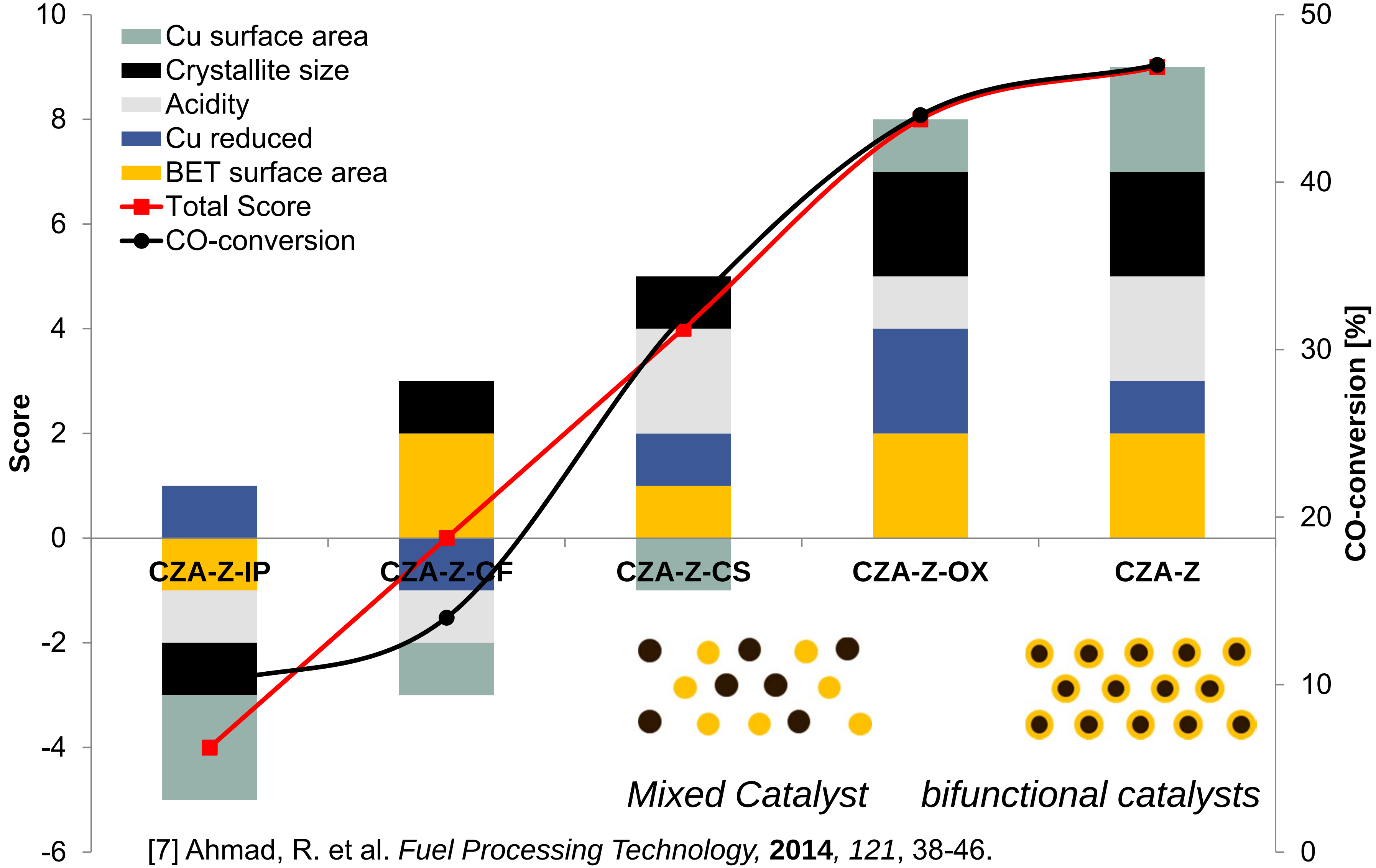
[6] Pagani, G., DE 2362944 A1, 1974, assigned to Snam Progetti S.p.A.

One step DME synthesis with bi-functionals catalyst



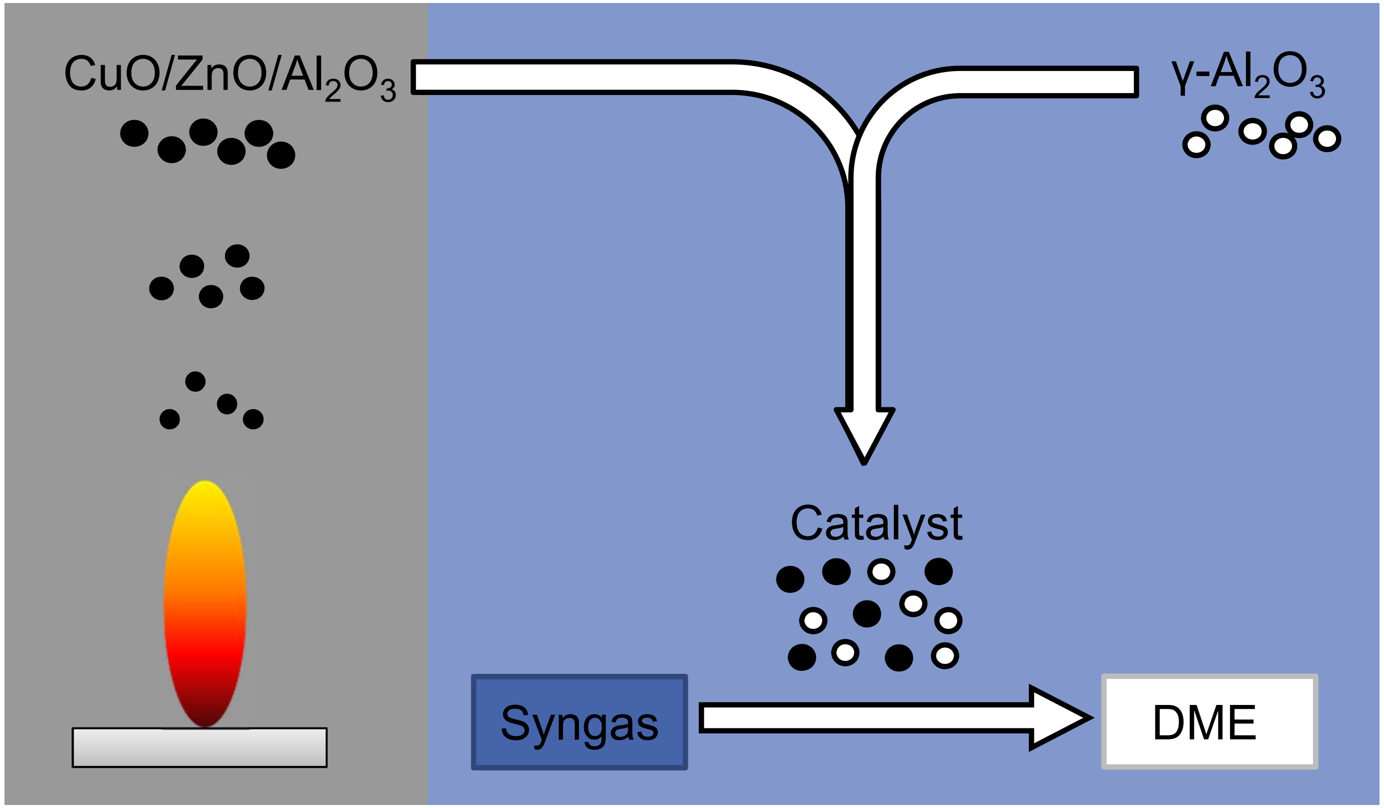
Equilibrium calculations, AspenOne, species involved: MeOH, DME, CO_2, CO, H_2, H_2O

Catalyst development with Hybrid Materials[7]



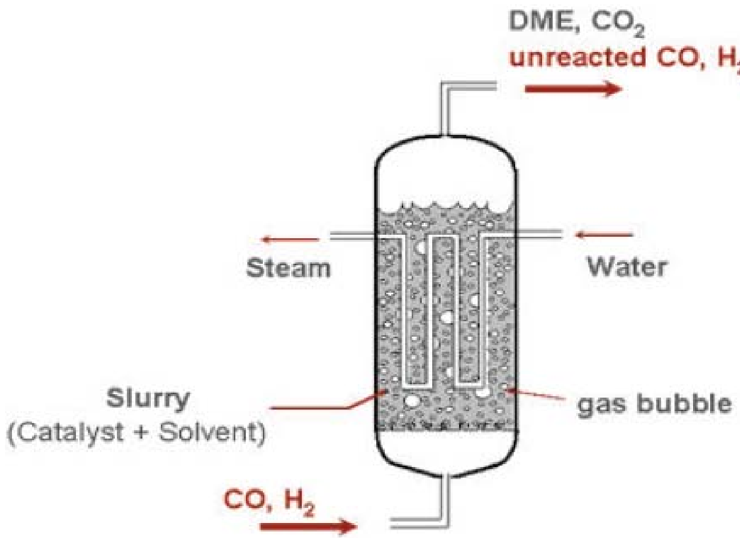
[7] Ahmad, R. et al. *Fuel Processing Technology*, **2014**, *121*, 38-46.

Innovative Routes to Multifunctional Catalysts Flame-spray-Synthesis[8]

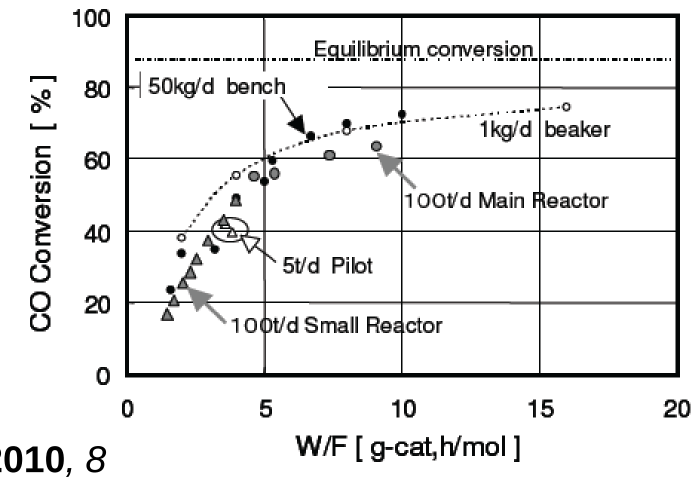


[8] R. Ahmad, R. et al., Catal. Commun. 43 (2014) 52-56.

Three Phase Slurry Reactor for DME[9]



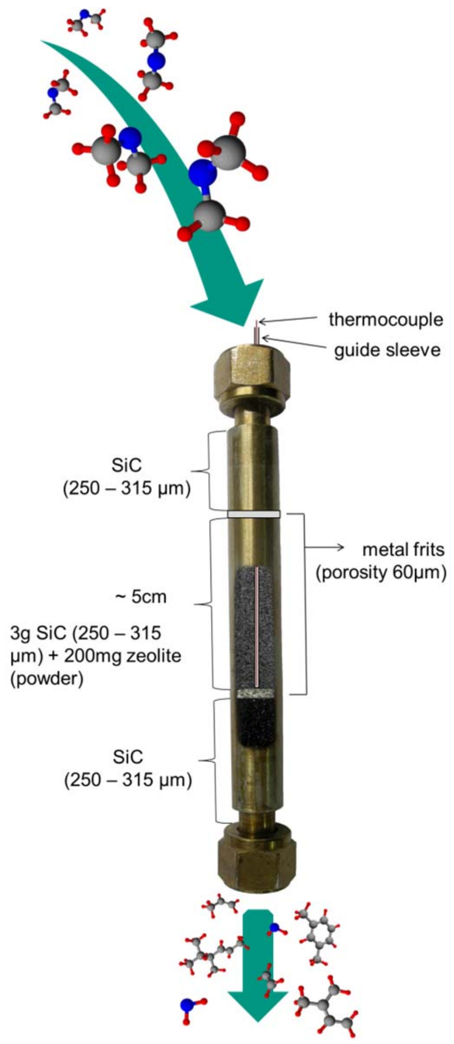
100t/d Pilotplant of JFE near Kushiro, Japan 2003-06



[9] Yagi, H.; Ohno, Y.; Inoue, N.; Okuyama, K. & Aoki, S., *International Journal of Chemical Reactor Engineering,* **2010**, *8*

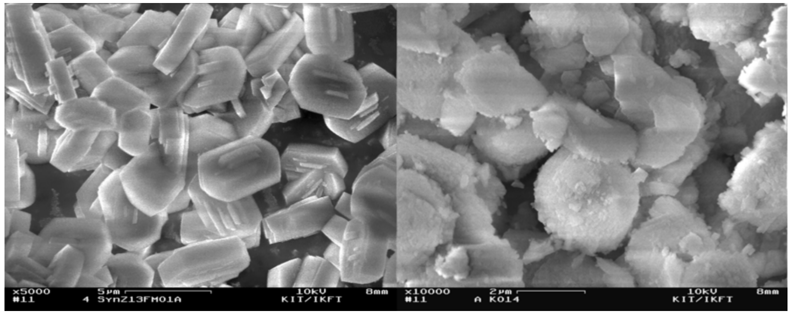
Gasoline from Dimethylether

- Compared to the MtG process, the DtG process (dimethyl ether to gasoline) offers advantages in terms of heat of reaction, reactor design and process conditions.
- The reaction typically occurs on zeolites of the H-ZSM-5 type, producing hydrocarbons up to C_{10} units.
- Hierarchic structures (micro- and meso-porores) change diffusion properties in zeolites and consequently product selectivity in catalysis



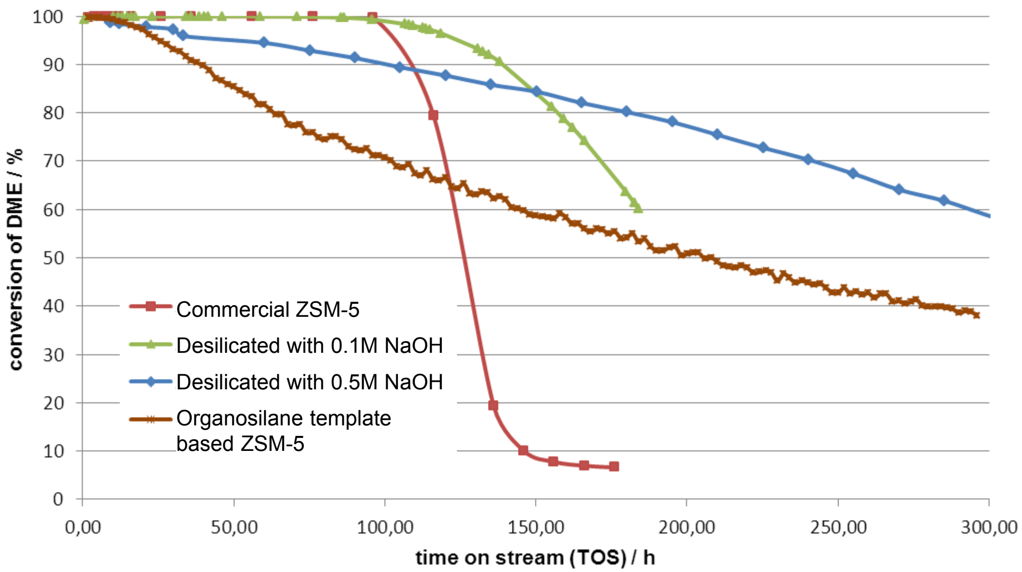
Gasoline from Dimethylether

- Systematic investigation of zeolite materials and their modification
- Different synthetic approaches with characterization



Unmodified ZSM-5 catalyst

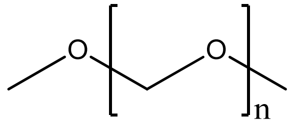
Modified ZSM-5 catalyst with enlarged mesopores



- Studies on lab-scale fuel synthesis
- Dependency of catalyst suitability by structural parameters
- Long-term experiments, coking and regeneration studies

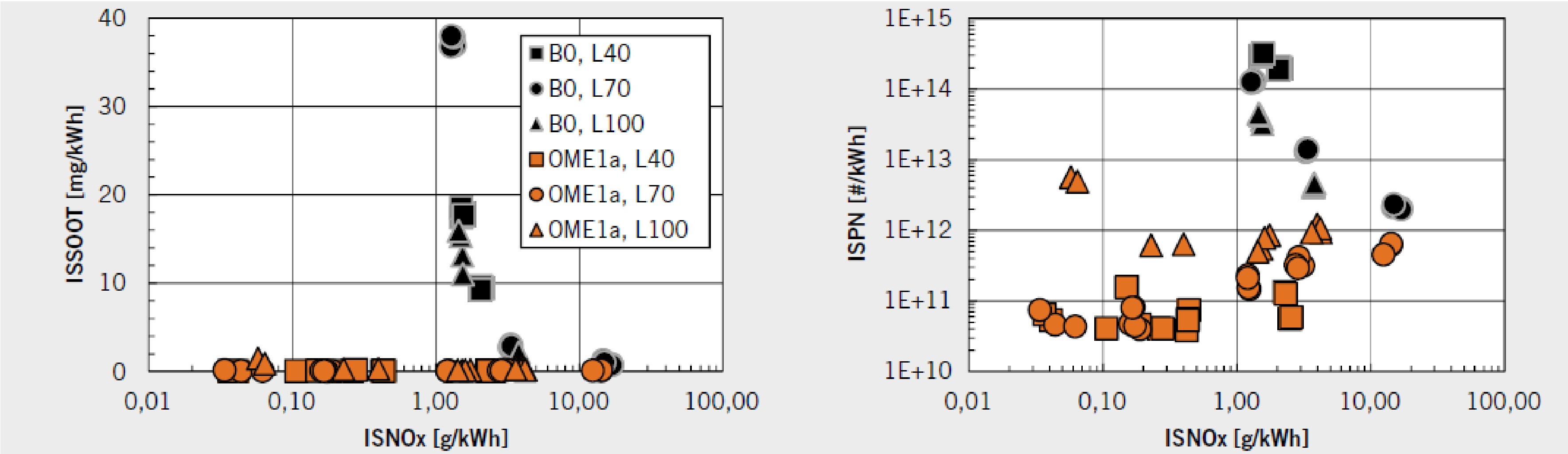
Why oxymethylene ethers?

- Because of the absence of carbon-carbon bonds,
- similar properties as conventional diesel,
- unlimited miscibility with diesel,
- non-corrosivity, non-toxicity.



Properties	MeOH	DME	OME 1	OME 3-4	Diesel [EN 590]
Molecular weight [g/mol]	32	46	76	149	~ 233
Density [kg/l, 15 °C]	0.80	0.67	0.86	1.04	0.84
O-content [%]	50	35	42.1	48	0
Calorific value [MJ/kg]	20	28	23	18	30
Calorific value [MJ/l]	16	18	20	19	36
Diesel equivalent [l]	2.3	1.9	1.8	1.9	1
Flash point [°C]	11	-41	-18	54	> 55
Boiling point [°C]	65	-25	42	155/200	170 - 390
Cetane number [CN]	5	55	50	80	51

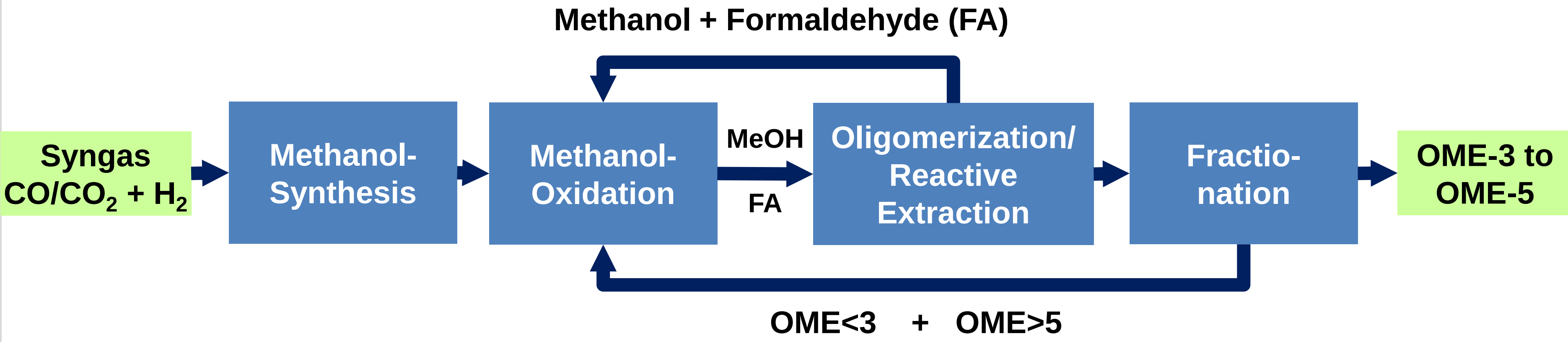
Why oxymethylene ethers[10]?



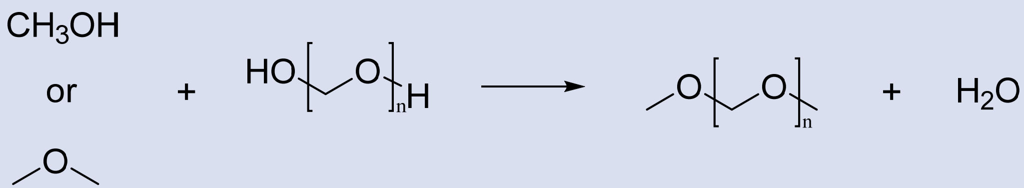
Engine tests at a research engine with variation of the exhaust-gas-recirculation, variing the air ratio between 0.9 and 1.7

[10] Härtl, M.; Seidenspinner, P.; Wachtmeister, G. & Jacob, E. *Motortechnische Zeitschrift (MTZ)*, **2014**

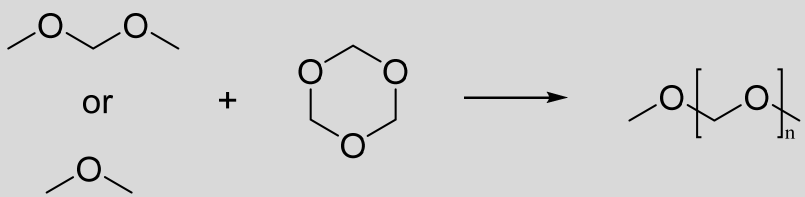
Routes to OME-3 to OME-5



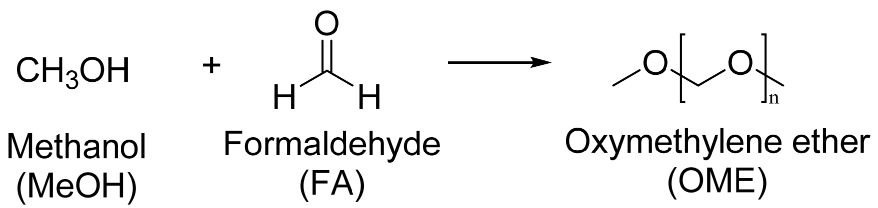
aqueous route:

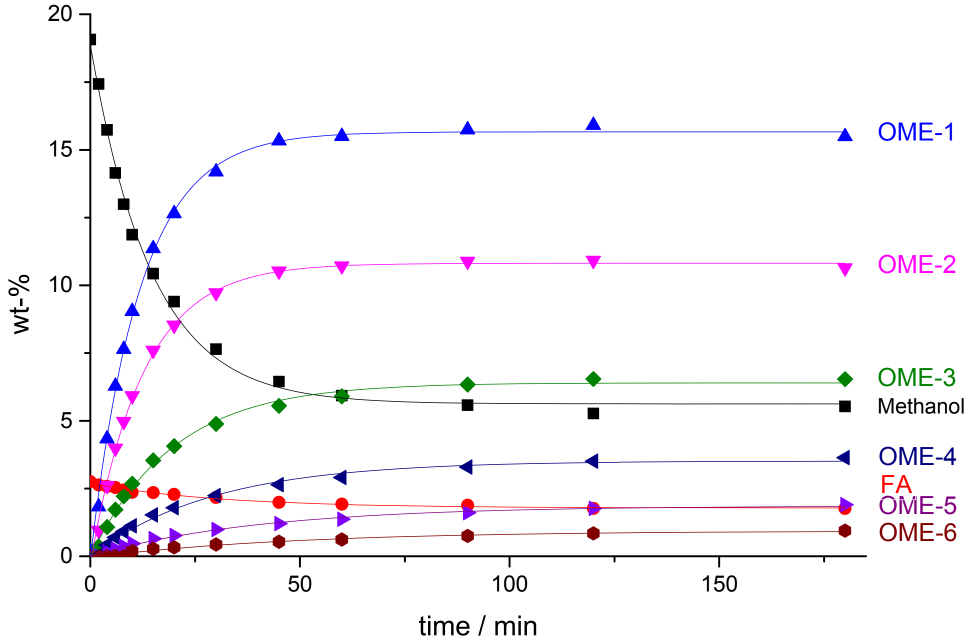


aqueous-free route:



Results

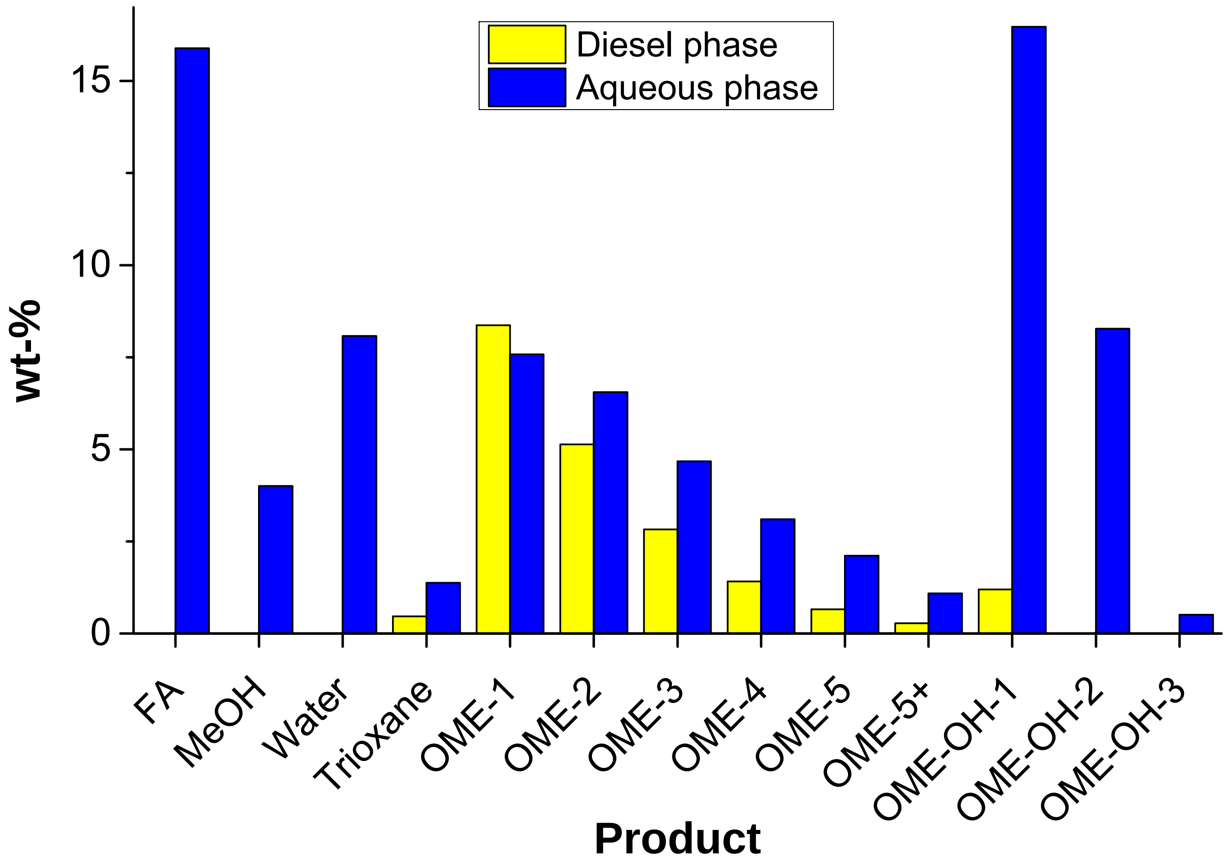


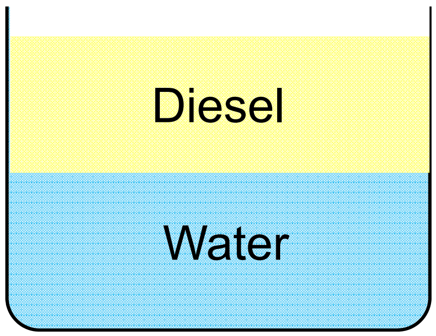


T = 80 °C
p = 0 … 0.2 MPa
Cat.: Amberlyst

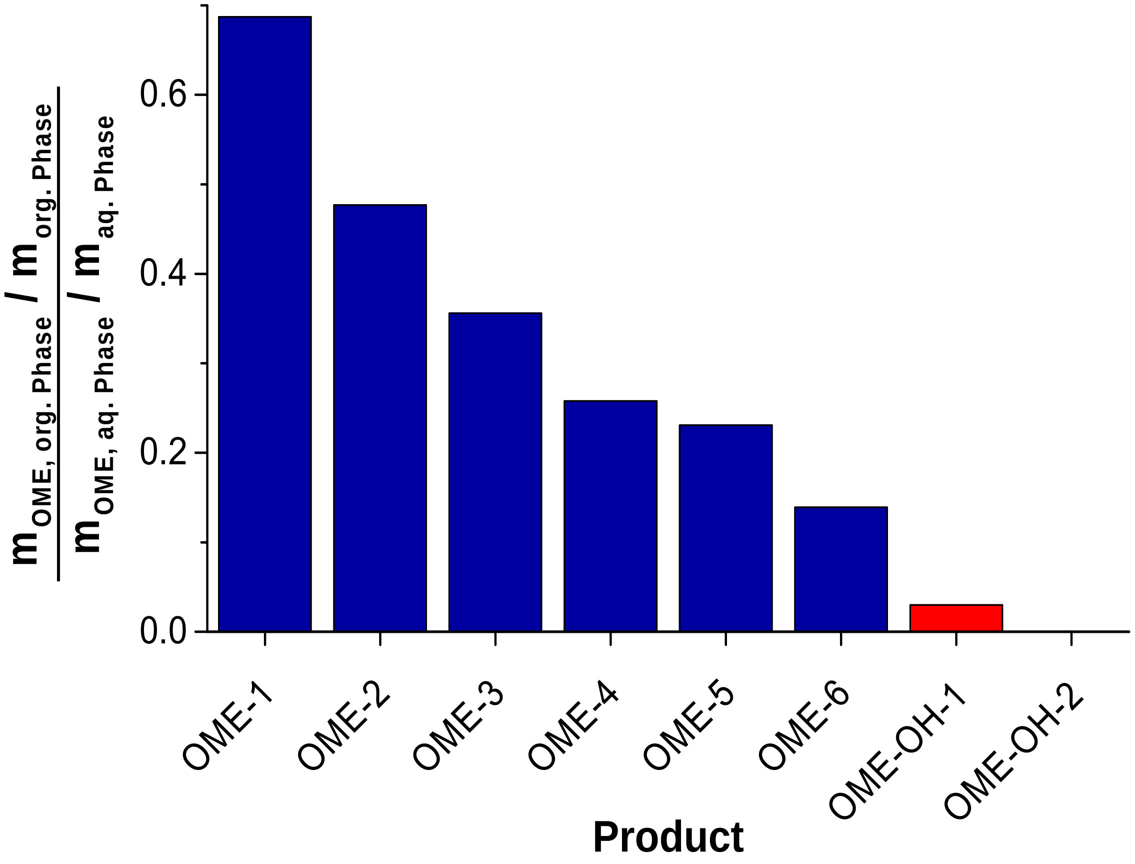
Edukts:
Cat. = 0.5 g
MeOH = 40 g
p-Formaldehyde = 60 g

Product separation by extraction





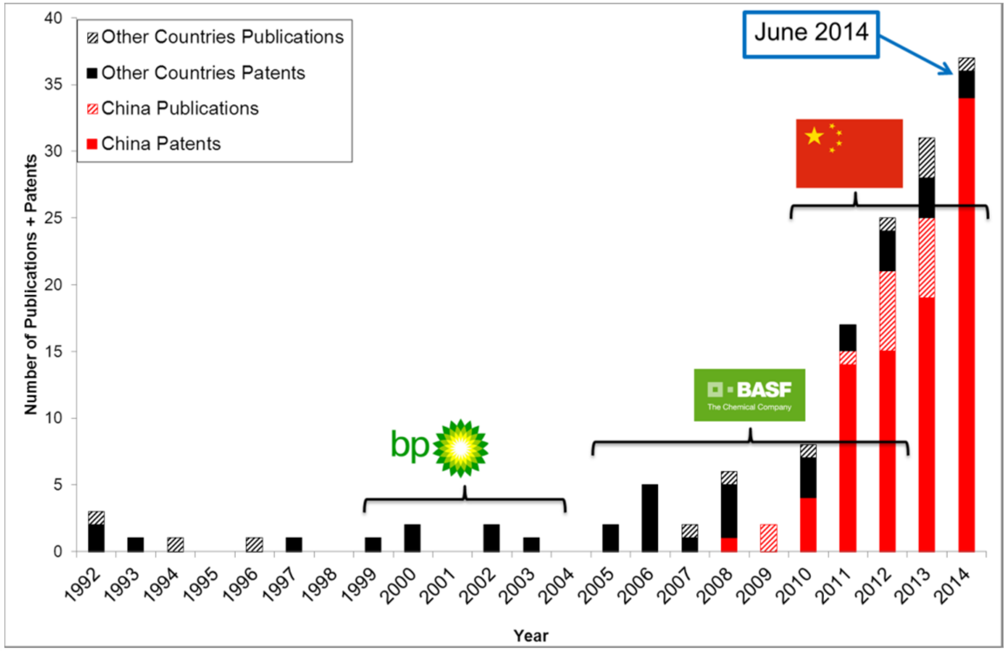
Extraction with diesel

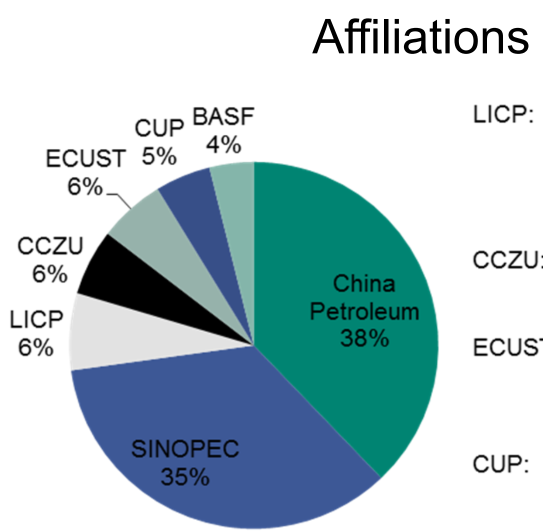


Overview of literature

Karlsruhe Institute of Technology

Publications : Patents = 1 : 3





LICP: Lanzhou Institute of Chemical Physics Chinese Academy of Sciences, China

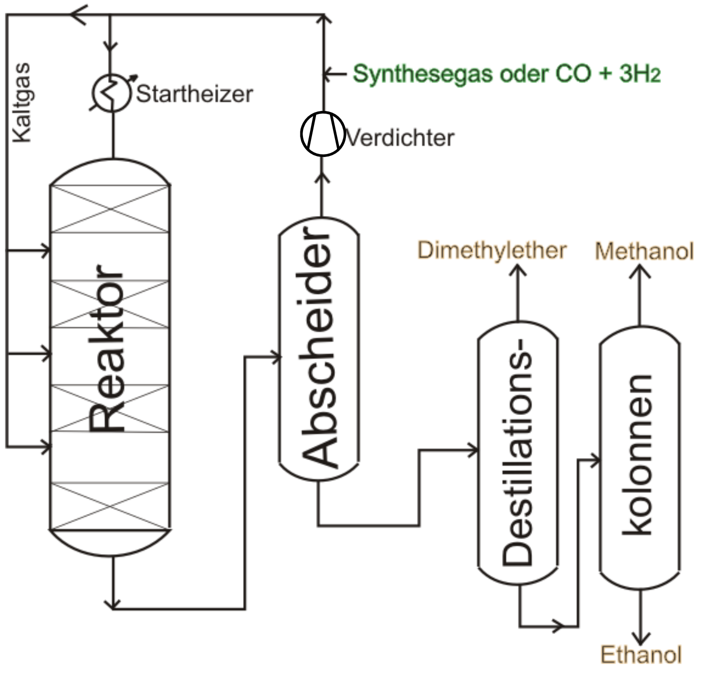
CCZU: Changzhou University, China

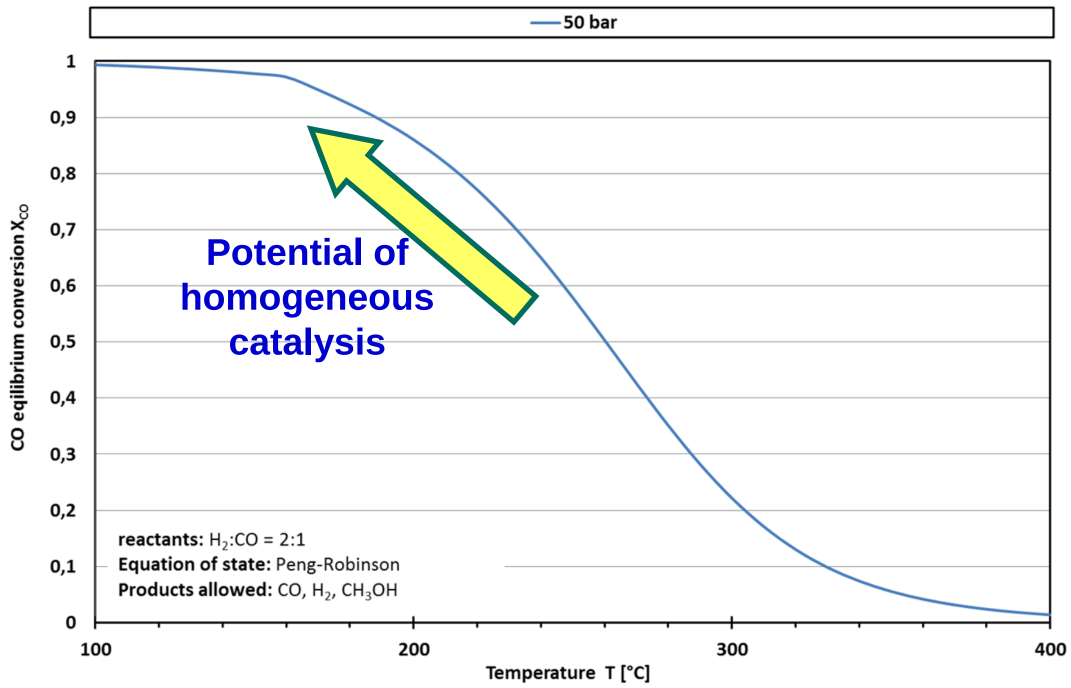
ECUST: East China University of Science and Technology, China

CUP: China University of Petroleum (Huadong)

Conventional MeOH process

- Today, the most widely used heterogeneous catalyst are based on Cu, ZnO, and Al_2O_3 (introduced by ICI in 1966).

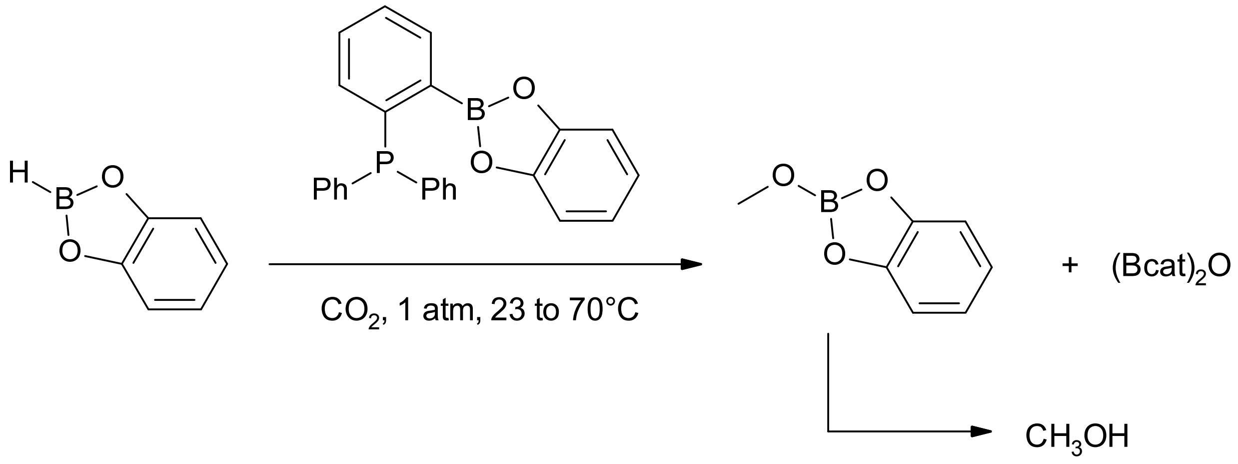




- Typical conditions: 5–10 Mpa, 250°C.
- Selectivity > 99.8 %.

Recent trends in homogeneously catalyzed CO_2 reduction (A)

- Organoborane reduction to MeOH[11]

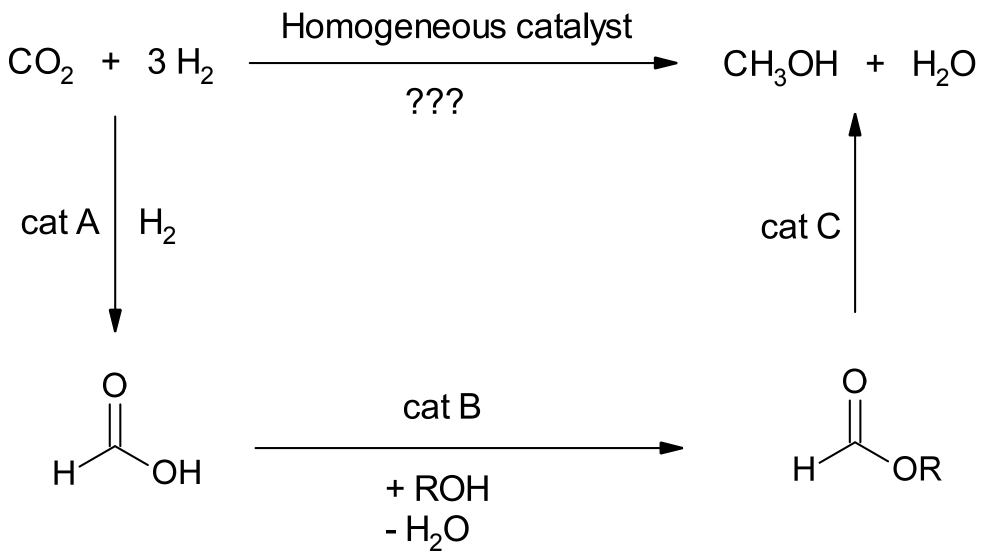


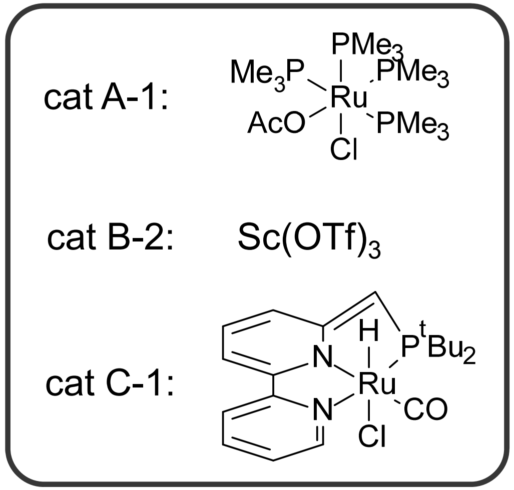
- Yield up to 99%.
- TON (turnover numbers) and TOF (turnover frequencies) reaching >2950 and 853 h^{-1}.
- Compared to the other metal-free systems, here the weak interaction between the catalyst and CO_2 is of particular importance.

[11] L. Maron, F.-G. Fontaine et al., J. Am. Chem. Soc. 2013, 135, 9326−9329.

Recent trends in homogeneously catalyzed CO_2 reduction (B)

- Homogeneous cascade catalysis to MeOH[12]



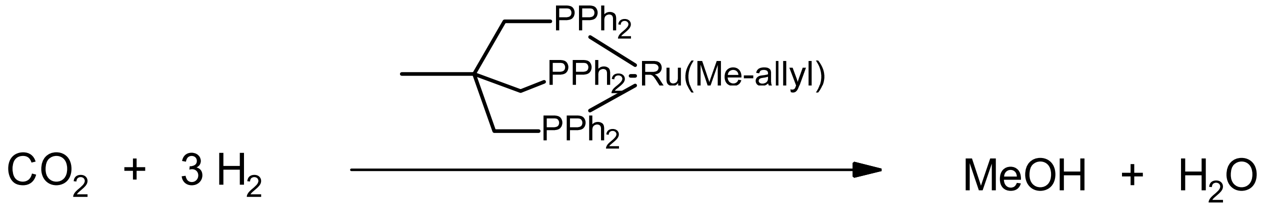


- For steps (1) and (2) a physical separation is suggested, due to the low stability of cat B-2.
- Reactions take place at 75°C for steps (1) and (2), and at 135°C for step (3).
- TON (turnover number) of the complete cascade on lab-scale amounts to 21.

[12] S. Sanford et al., J. Am. Chem. Soc. 2011, 133, 18122–18125.

Recent trends in homogeneously catalyzed CO_2 reduction (C)

- Ruthenium catalyzed hydrogenation of CO_2 to MeOH[13]



- Highest TON (turnover number) of 221 reached at 60 bar H_2, 20 bar CO_2, in a mixture of EtOH / THF, at 140°C, $HNTf_2$ added.
- In situ catalysts with triphos also active.

[13] J. Klankermayer, W. Leitner et al., Angew. Chem. Int. Ed. 2012, 51, 7499–7502

Overview

- Introduction: The Methanol-to-Gasoline Process (MtG)
- Reasons for Modifications to MtG
- Examples:
  - Direct DME-Synthesis
  - Modified ZSM-5 Catalysts for Gasoline Stage
  - New Fuels from Methanol / DME
  - Homogeneous Catalysis to Methanol / DME
- Conclusions

Conclusion: Take-home Messages

- The availability of **cheap natural gas** and an overcapacity for methanol in China drives **investments** and **R&D for new MtG-technologies**

- **The German "Energiewende"** may pave the way for **DME, Gasoline or other liquids from "synthetic syngas" (H_2+CO_2)**

- New catalysts for the "gasoline stage" give the opportunity to **increased selectivity** and **increased time-on-stream** and subsequently increased availability

- Homogeneous Catalysis **offers a potential for to overcome the present limitation by the thermodynamic equilibrium**

- **OMEs** may be a new option for **clean and efficient diesel fuels from methanol**

Acknowledgements

Karlsruhe Institute of Technology

- Funding agencies and sponsors
- Partners
- The various KIT-teams
- The audience for your kind attention!

HELMHOLTZ GEMEINSCHAFT

GEFÖRDERT VOM

Bundesministerium für Bildung und Forschung

Gefördert durch:

Bundesministerium für Ernährung und Landwirtschaft

aufgrund eines Beschlusses des Deutschen Bundestages

FNR
Fachagentur Nachwachsende Rohstoffe e.V.

Karlsruhe Institute of Technology

Karlsruher Institut für Technologie