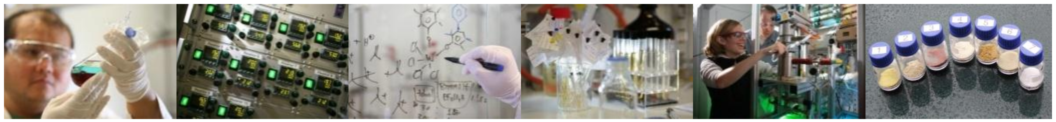

Low-Temperature Methanol Reforming using Molten Salt modified Catalysts

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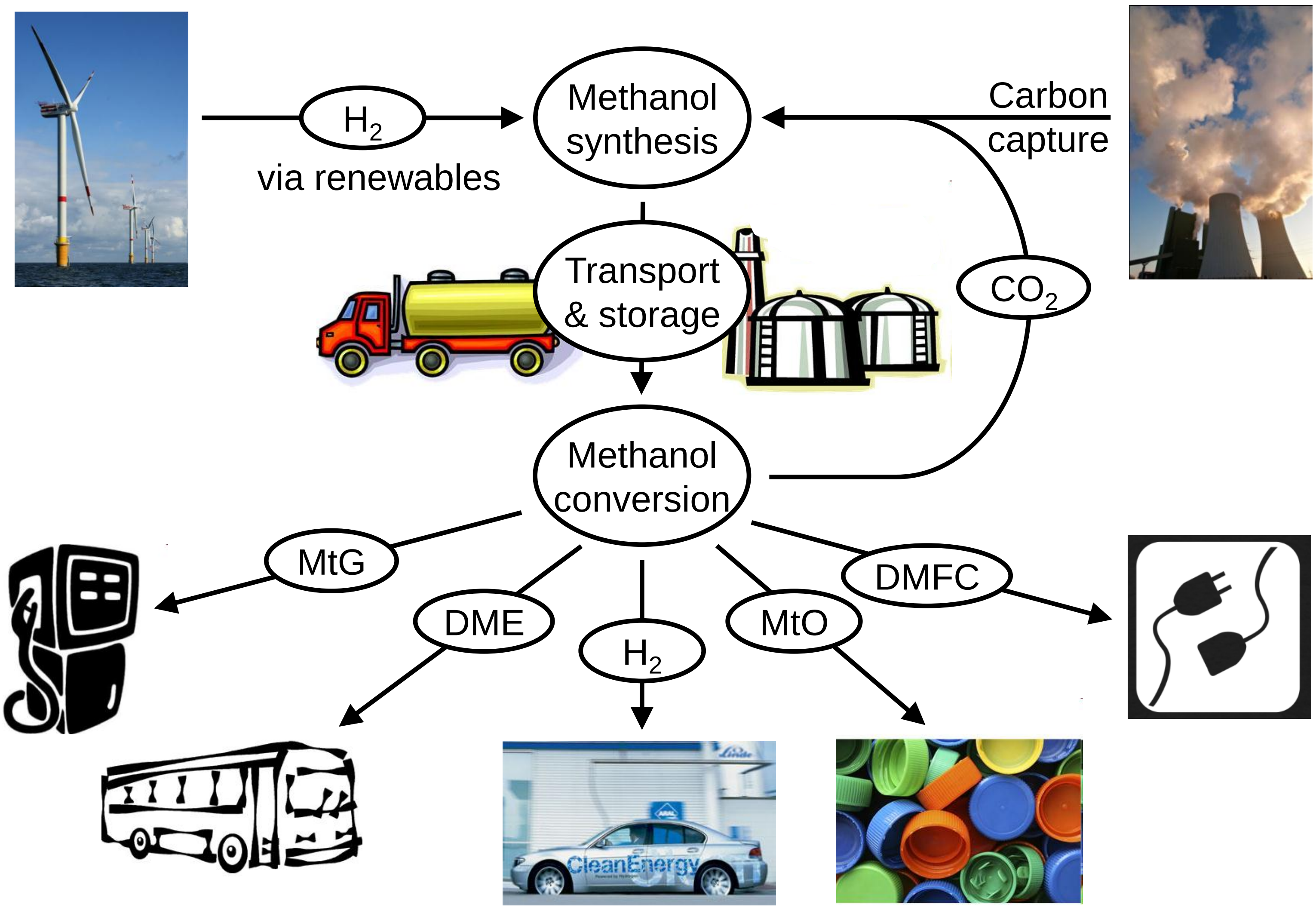
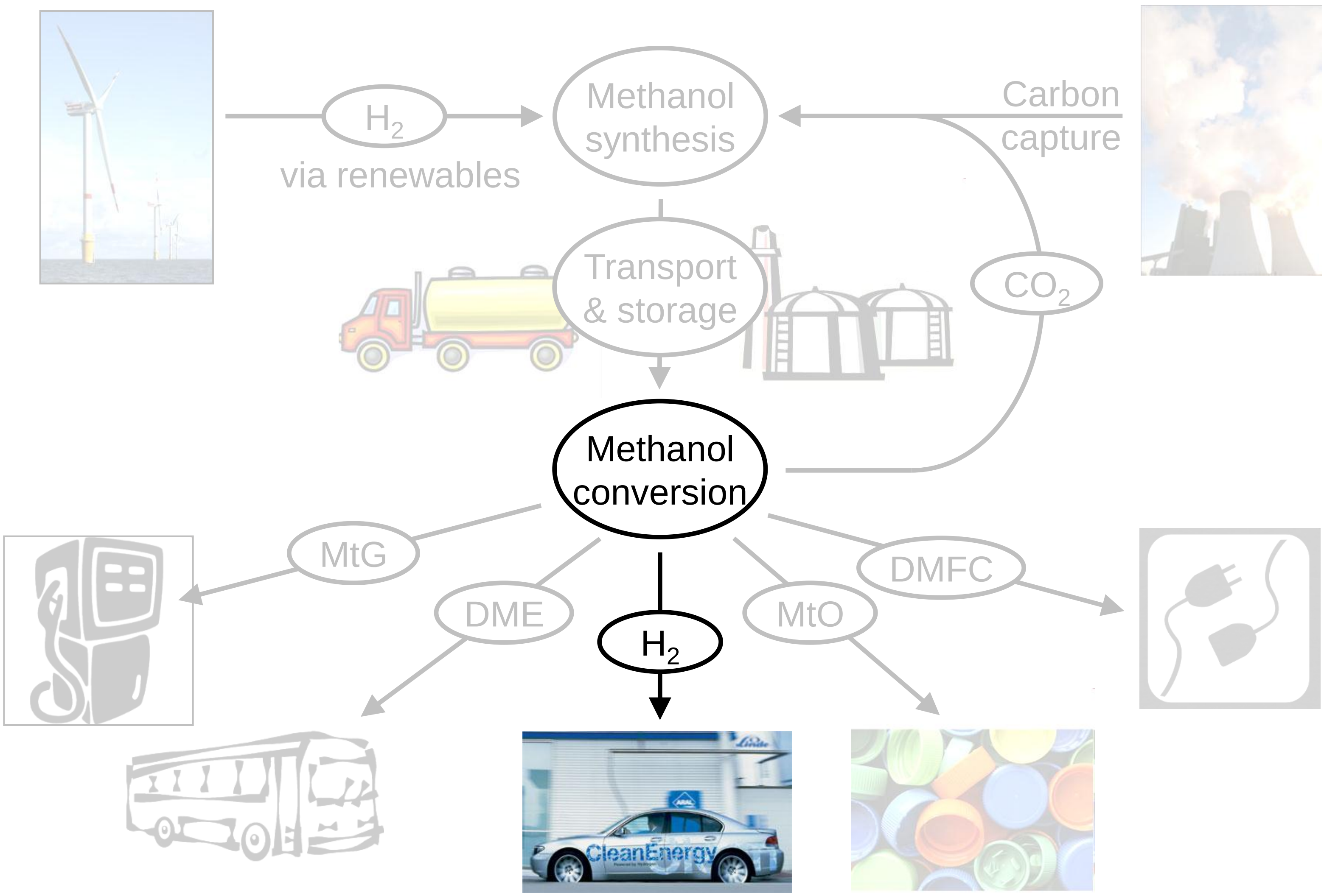
Motivation: The Methanol Economy[1]



[1] G.A. Olah, Beyond Oil and Gas: The Methanol Economy, Wiley-VCH, 2009.

Motivation: The Methanol Economy[1]



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[1] G.A. Olah, Beyond Oil and Gas: The Methanol Economy, Wiley-VCH, 2009.

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Methanol Steam Reforming

- Production of hydrogen in high yields
- Reactions involved

Methanol steam reforming	$CH_3OH + H_2O \rightleftharpoons 3\,H_2 + CO_2$
Methanol decomposition	$CH_3OH \rightleftharpoons 2\,H_2 + CO$
Water gas shift reaction	$CO + H_2O \rightleftharpoons H_2 + CO_2$

- Typical reaction conditions
  - Temperature: 200 to 300 °C
  - Catalyst: Cu/ZnO or transition metals on support

Challenges for methanol steam reforming in decentralized applications

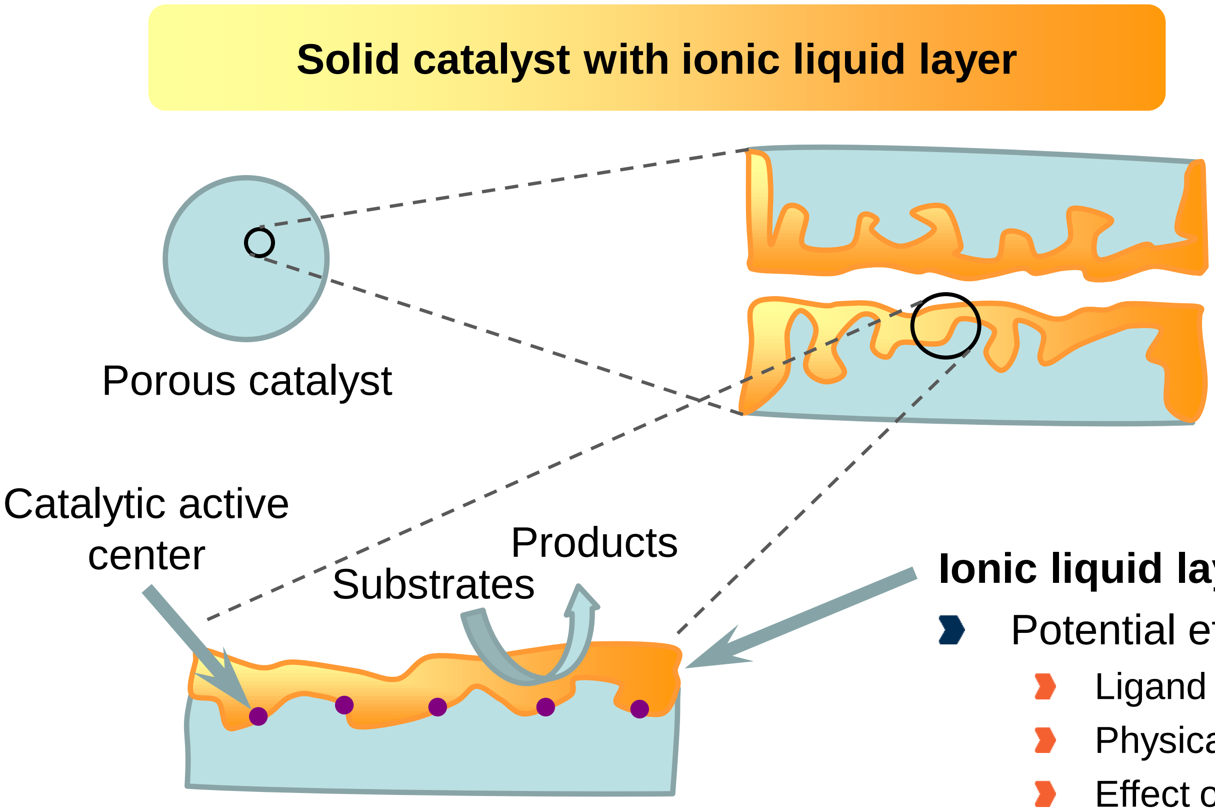
Activity
- High activity at low temperatures < 200 °C
- Enabling heat integration with high temperature PEM fuel cells (~ 180 °C)

Selectivity
- High selectivity to CO_2
- Mitigation of CO (catalyst poison for PEM fuel cells)

Flexibility
- No pre-reforming should be required
- Good start-stop behavior under dynamic operation conditions

Aim of the present Study

- Apply SCILL[1] concept (**s**olid **c**atalyst with **i**onic **l**iquid **l**ayer) to methanol steam reforming
- Extending the SCILL concept towards higher reaction temperatures > 200 °C



Ionic liquid layer on the pore surface

- Potential effects
  - Ligand effect on active centers
  - Physical solvent effect for reactants
  - Effect on activity and selectivity

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[1] U. Kernchen et al., Chem. Eng. Technol. 30 (2007), 985-994.

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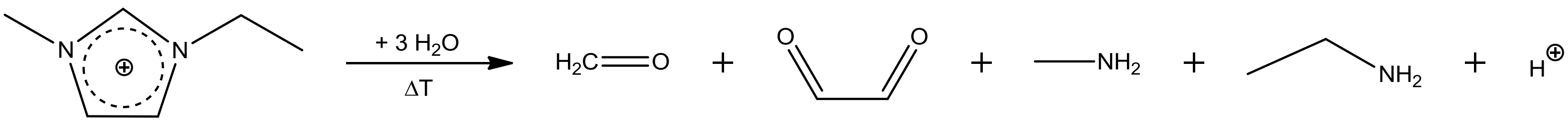
Why using Low-Temperature Molten Salts?

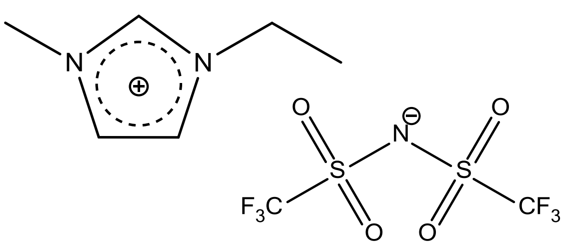
- Organic ionic liquids are not stable at typical reaction conditions of steam reforming
  - Temperatures > 200°C and hydrolytic environment due to the presence of steam
  - Hydrolysis of imidazolium leads to the formation of amines (“Retro-Radziszewski” reaction)

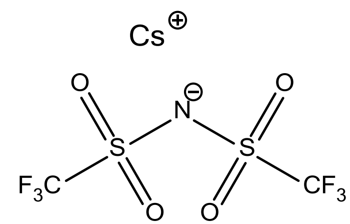


- Way out of the stability problem: use of inorganic cations

Ionic liquids
- Organic cation + anion
- T_{melt} < 100 °C
- T_{stable} < 250 °C

Low-temperature molten salts
- Inorganic cation + organic anion
- 100 °C < T_{melt} < 250 °C
- T_{stable} > 250 °C





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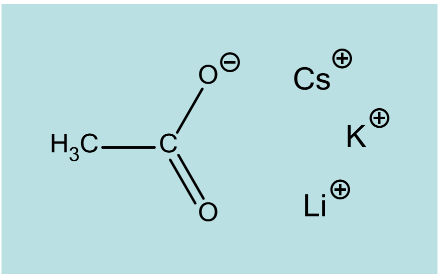
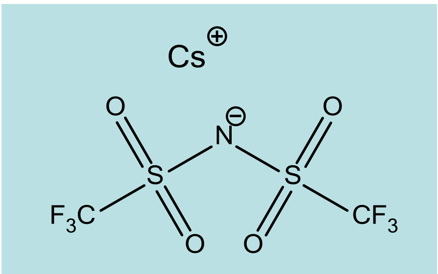
Molten Salt physical Properties

- Molten salts used in this study
  - Cesium/potassium/lithium acetate (lower melting point by eutectic mixture)



  - Cesium bis(trifluoromethylsulfonyl)imid ($Cs-NTf_2$)



- Characterization of molten salts
  - Differential scanning calorimetry
  - Density measurement (Archimedes principle)
  - High-temperature viscosimetry
  - Thermal gravimetric analysis

Molten salt	Molar composition[1]	Density @ 200 °C	Viscosity @ 200 °C	Melting point
Cs/K/Li-OAc	52.5/27.5/20.0 %	2.21 g cm^{-3}	42 mPa s	119 °C
$Cs-NTf_2$		2.06 g cm^{-3}	15 mPa s	120 °C

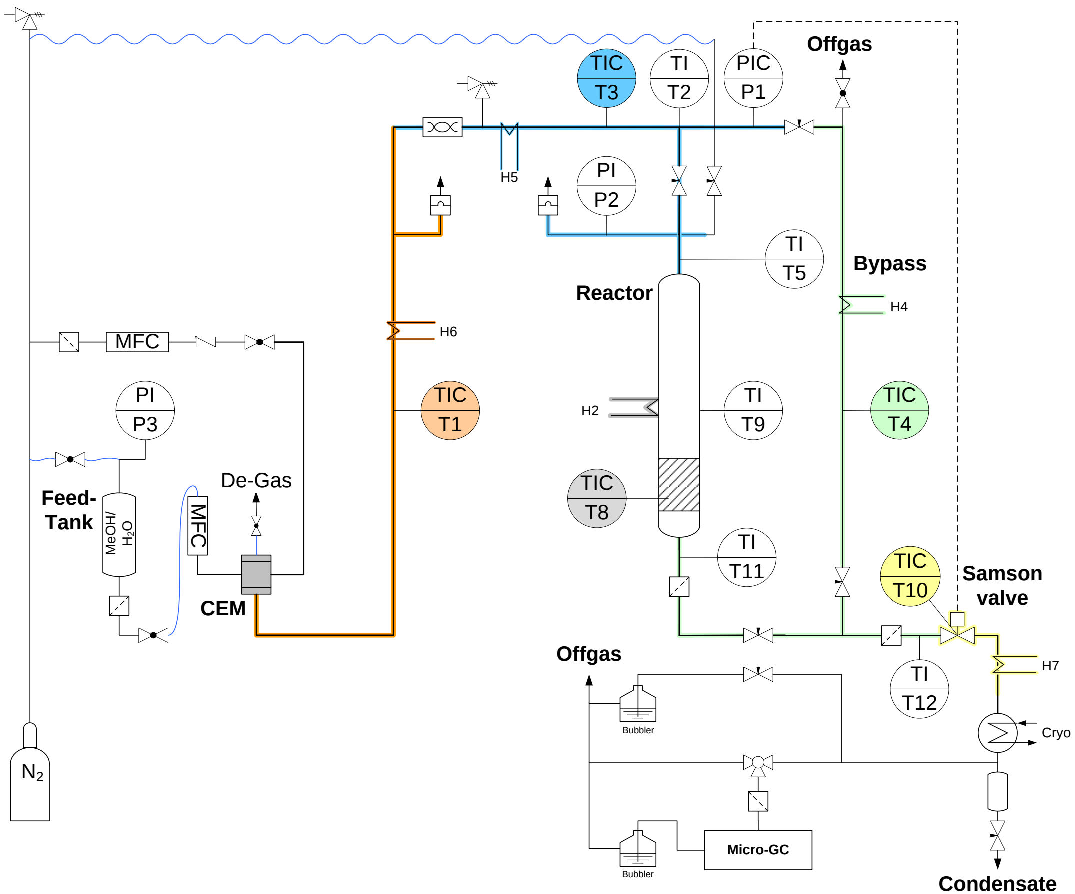
[1] J.G. Janz et al., Nat. Stand. Ref. Data Ser. 61 (1978), Part I.

Preparation of the Molten Salt coated Catalyst

- Heterogeneous catalyst: Pt/Pd (30 wt.-%) on carbon black
  - Used as received

- Coating procedure
  - Careful mixing of heterogeneous catalyst and salt in methanol solution
  - Removal of methanol by rotary evaporator
  - Subsequent drying in vacuo
  - Result: free flowing catalyst particles
  - Salt content on catalyst 10 wt.-%

Continuously operated Fixed-Bed Reactor for Methanol Steam Reforming



Typical reaction conditions
Catalyst loading: 100 mg
diluted with 2 g Al_2O_3 as inert material
Steam to methanol ratio 1:1
p_{tot} = 10 bar, $p_{MeOH} = p_{H2O}$ = 2.7 bar
balance nitrogen
WHSV = 22.2 $g_{Feed}\ g_{Cat}^{-1}\ h^{-1}$

Methanol conversion: $X_{MeOH} = \frac{\dot{n}_{CO_2} + \dot{n}_{CO}}{\dot{n}_{MeOH,Feed}}$

CO_2 selectivity: $S_{CO_2} = \frac{x_{CO_2}}{x_{CO_2} + x_{CO}}$

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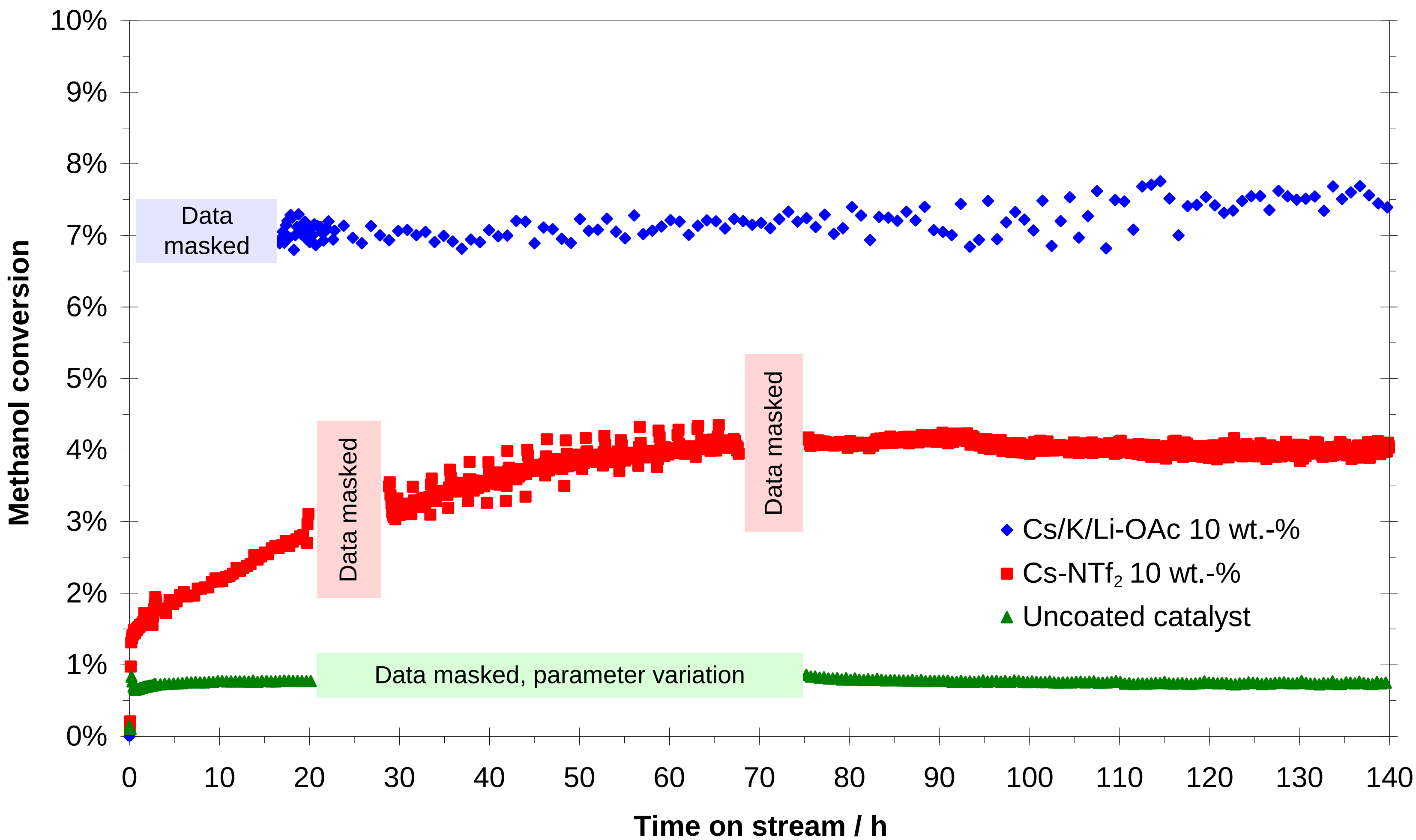
Methanol Conversion using different Catalyst Systems



Reaction conditions: T = 230 °C, p_{tot} = 10 bar, p_{MeOH} = p_{H2O} = 2.7 bar, balance nitrogen, m_{Cat} = 100 mg, WHSV = 22.2 g_{Feed} g_{Cat}^{-1} h^{-1}

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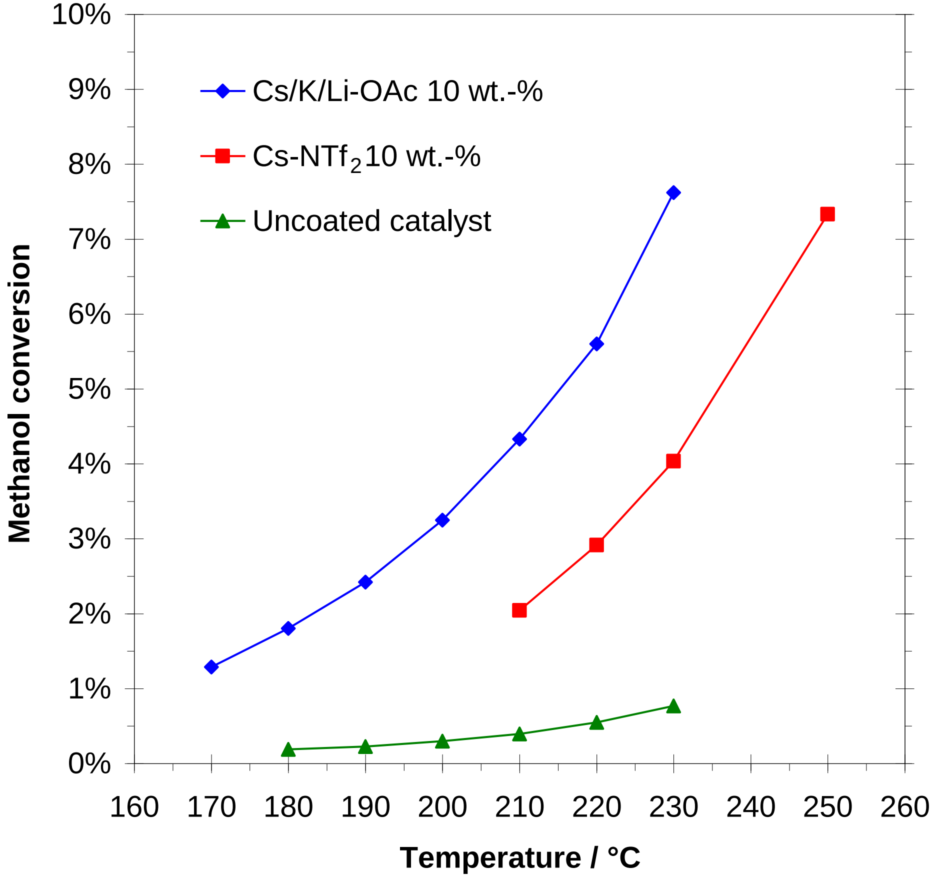
Temperature Dependency of Conversion



- Increase in activity by the factor of 10 using Cs/K/Li-OAc coated catalyst
- Conversion at temperatures as low as 170 °C even higher compared to uncoated system at 230°C
- Measured activation energy lies in the range of 50 to 70 kJ mol^{-1} for all systems

Reaction conditions: p_{tot} = 10 bar, p_{MeOH} = p_{H2O} = 2.7 bar, balance nitrogen, m_{Cat} = 100 mg, WHSV = 22.2 g_{Feed} g_{Cat}^{-1} h^{-1}

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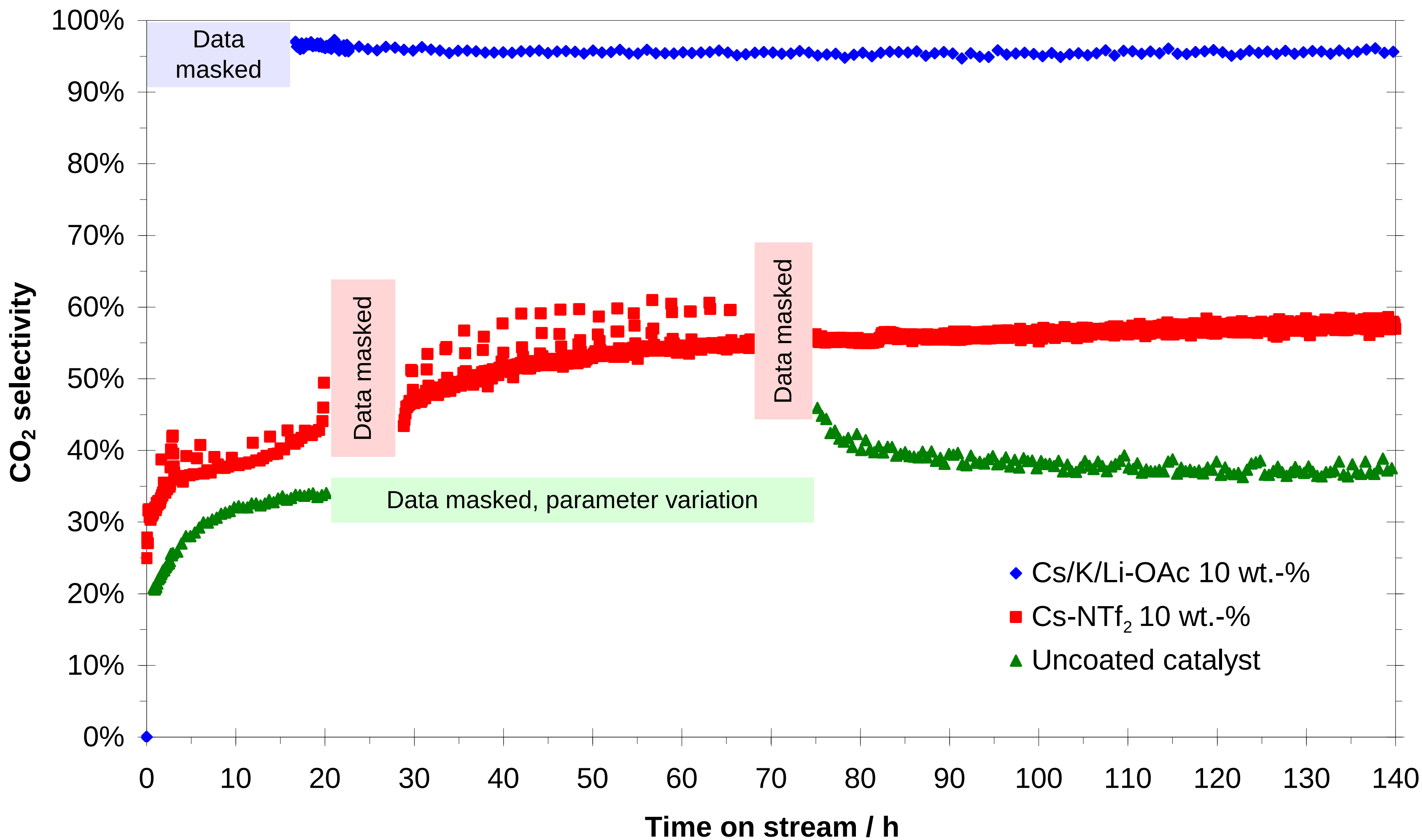
CO_2 Selectivity using different Catalyst Systems



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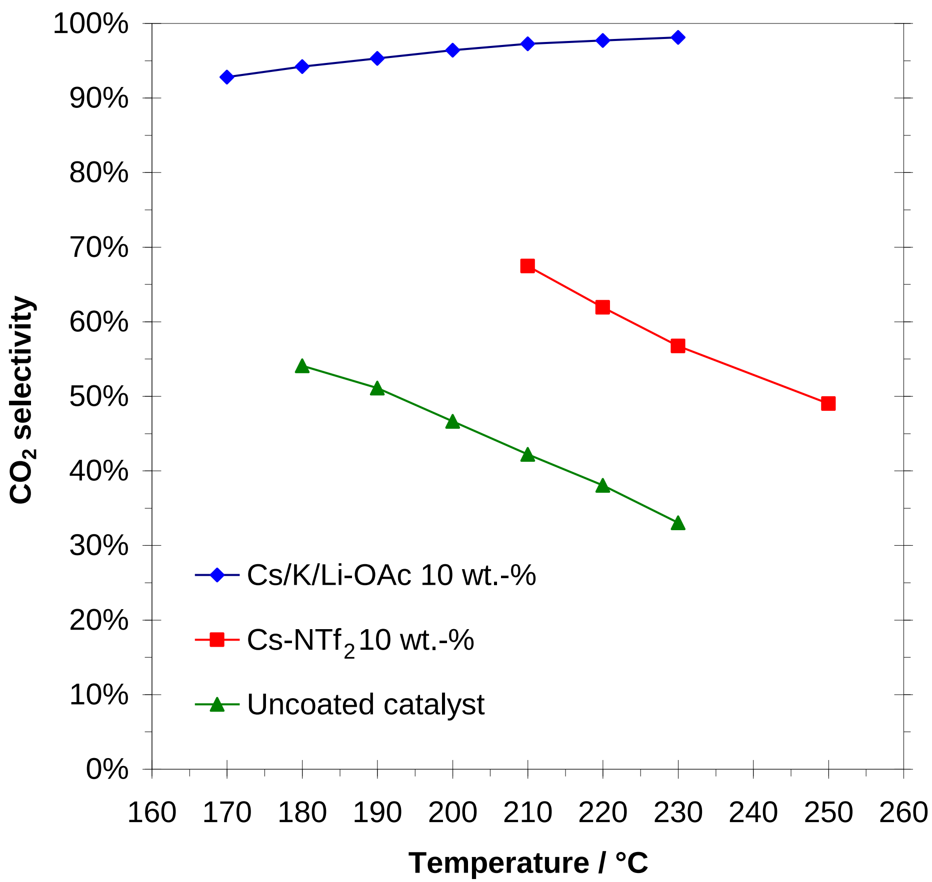
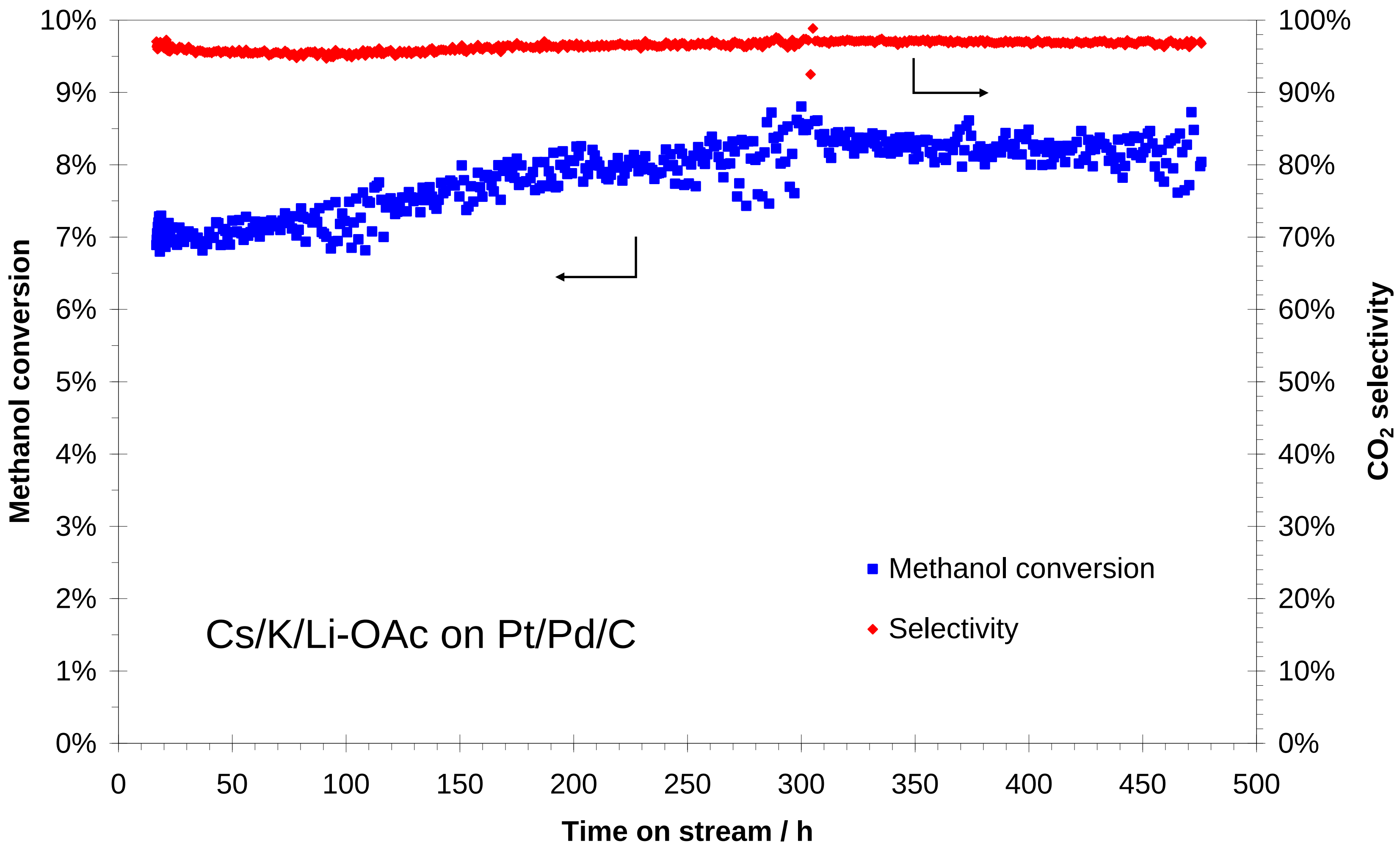
Temperature Dependency of Selectivity



- CO_2 selectivity is drastically increased using molten salt coated catalysts
- Selectivity decreases with rising temperature in the cases of uncoated catalyst and $Cs\text{-}NTf_2$ coated catalyst
- **BUT:** Selectivity increases with temperature in the case of Cs/K/Li-OAc coated catalyst
- Exact reasons yet unknown, spectroscopic studies are in preparation

Reaction conditions: p_{tot} = 10 bar, $p_{MeOH} = p_{H2O}$ = 2.7 bar, balance nitrogen, m_{Cat} = 100 mg, WHSV = 22.2 $g_{Feed}\ g_{Cat}^{-1}\ h^{-1}$

Long-Term Stability proven for 20 Days on Stream



Reaction conditions: T = 230 °C, p_{tot} = 10 bar, p_{MeOH} = p_{H2O} = 2.7 bar, balance nitrogen, m_{Cat} = 100 mg, WHSV = 22.2 g_{Feed} g_{Cat}^{-1} h^{-1}

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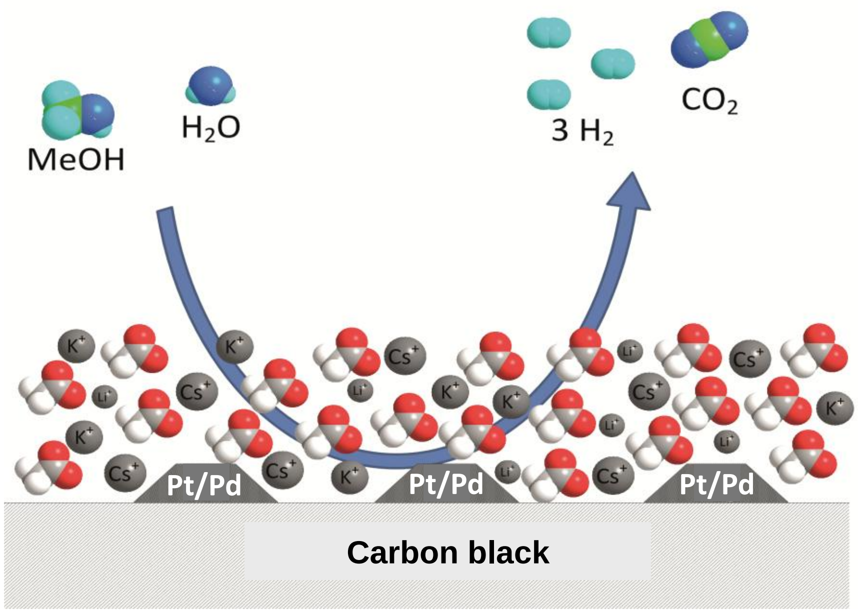
First Attempts to explain the Effect of Molten Salt Coating

- Good solubility for water (and probably methanol), enhances substrate concentration at the active center
  - Acetate salt is more hygroscopic than NTf_2 salt
- Poor hydrogen solubility might shift chemical equilibrium towards product side
  - Poor hydrogen solubility is known for many ionic liquids
- Basicity promotes WGS reaction leading to low CO content
  - Basic nature of acetate anion



Conclusion and Outlook

- SCILL concept has been extended to temperatures > 200 °C by the use of low-temperature molten salts for the first time

- Molten salt modified catalysts have been proven to be successful in methanol steam reforming
  - Increase in activity by the factor of 10
  - Increase in CO_2 selectivity to the range of 93 to 98 %
  - CO_2 selectivity for Cs/K/Li-OAc increases with rising temperature
  - Cs/K/Li-OAc coated system proven to be active and selective for 20 days on stream

- Detailed studies to reveal mechanistic effects of molten salt coating are going on
  - CO-TPD and NH_3-TPD
  - XPS analysis
  - Solubility measurements

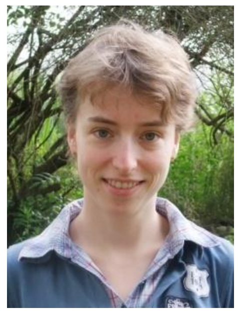
Acknowledgements

- The European Research Council is gratefully acknowledged for financial support within the ERC Advanced Grant "H_2-SMS-CAT"

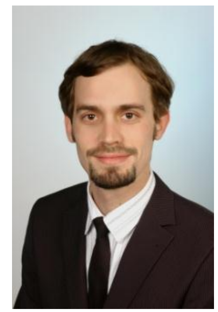
European Research Council erc

- Co-workers within the Erlangen ERC-Team

Supervisor
P. Wasserscheid



Stephanie Bajus



Matthias Kusche

Andreas Bösmann

- Please visit our poster P 05.22

- The Cluster of Excellence is acknowledged for fruitful discussions
  Visit EAM at: Central Lobby - Stand C8

EAM ENGINEERING OF ADVANCED MATERIALS

- Thank you for your kind attention!

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