

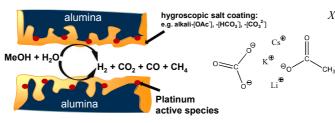
Molten salt modified catalyst systems for methanol steam reforming

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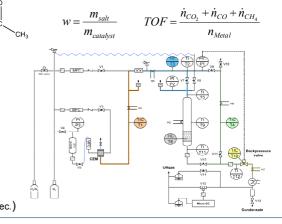
Renewable energy sources are intermittent, therefore an effective storage technology is required. One possible compound for chemical energy storage is methanol (12.5 wt% H₂-storage capacity, 6.3 kWh kg⁻¹ energy density [1]). The stored hydrogen can be released by methanol reforming, typically heterogeneously catalyzed. For this type of reaction a commercially available catalyst (5 wt% platinum on alumina) is modified by primarily alkali-acetate salts according to the SCILL-approach [2].

Experimental

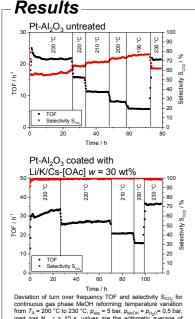
Pt-alumina catalyst 4.86 wt% Pt on y-alumina (Alfa Aesar) $A_{\rm BET}$ = 143 m² g⁻¹ $V_{\text{pore,BJH}} = 0.9 \text{ cm}^3 \text{ g}^{-1}$

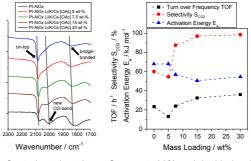


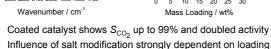
- Preparation according to the SCILL-approach [2]
- Use of Li/K/Cs-acetate (0.2/0.275/0.525) to lower the melting point ($T_{\rm m}$ = 120 °C)
- Coating of catalyst with salt layer by wet impregnation, vacuum drying
- Catalyst test experiments in continuous gas phase fixed bed reactor
- Temperature variation: T_R = 200-230 °C, p_{abs} = 5 bar, p_{MeOH} = $p_{H_{2O}}$ = 0.5 bar
- Substrate dosage via MFC with inert gas nitrogen, product analytics via GC
- Characterization of CO-adsorption with DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spec.)



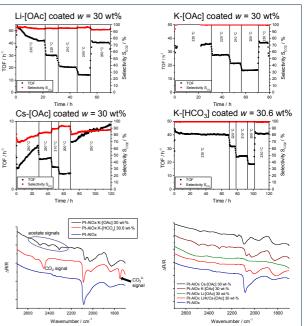
 $x_{CO_2} + x_{CO} + x_{CH_4}$







- indicated by reaction experiments and CO-DRIFTS IR-Spectra of uncoated Pt-catalyst show two CO-bands: On-top at 2080 cm⁻¹ and bridge-bonded at 1850 cm⁻¹
- Salt treated catalysts reveal a new CO-band at 2030 to 2000 cm⁻¹ shifting to lower wavenumbers for higher wt%
- At higher salt loadings (15 and 30 wt%): on-top band suppressed, bridge-bonded band enhanced
- These effects are known for alkali-doping: CO adsorption on potassium influenced platinum [3]



Conclusion / Outlook

- ▶ Low melting salt mixture Li/K/Cs-[OAc] not neccessary for an efficient reaction
- > Stable operation and pronounced enhancement of activity and selectivity for K-[OAc] (T_m = 292 °C) coated catalyst even at T_R = 200 °C in an humid atmosphere
- ▶ DRIFT spectra of K-[OAc] and Li/K/Cs-[OAc] coated catalyst nearly identical
- ▶ DRIFT spectra of K-[OAc] and K-[HCO₃] treated catalyst show similar CO-bands
- > Potassium reveals the most significant influence on the active platinum species
- Salt modified catalysts show enhanced bridge-bonded adsorption of probe molecule CO
 - → one fact that might explain the high CO₂-selectivities

- Analyse the catalysts with MeOH-DRIFTS
- ▶ Determine the influence of adsorbed H₂O
- Inspect the influence of the hygroscopic nature of the salt coating
- Extend the concept towards other salts
- Apply the approach to other reactions

[1] G.A. Olah, Beyond Oil and Gas: The Methanol Economy, Wiley-VCH, 2009. [2] U. Kernchen et al., Solid Catalyst with Ionic Liquid Layer (SCILL) — A New Concept to Improve Selectivity Illustrated by Hydrogenation of Cyclooctadiene, Chem. Eng. Technol. 30(8), 2007, 985-994 [3] H.P. Ronzel Alkali-Metal-Affected Adsorption of Molecules on Metal Surfaces. Surface Science Reports 8. 1987. 43-125



