

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 catalyst system functionalized by a molten salt (lithium/potassium/cesium-acetate) is presented.

Experimental

Simple preparation process

Impregnation
Incipient wetness

Vacuum drying
p = 250-80 mbar, T = 45-60 °C

Transfer to test rig

In-situ reduction
T = 230 °C, 5% H₂ in N₂

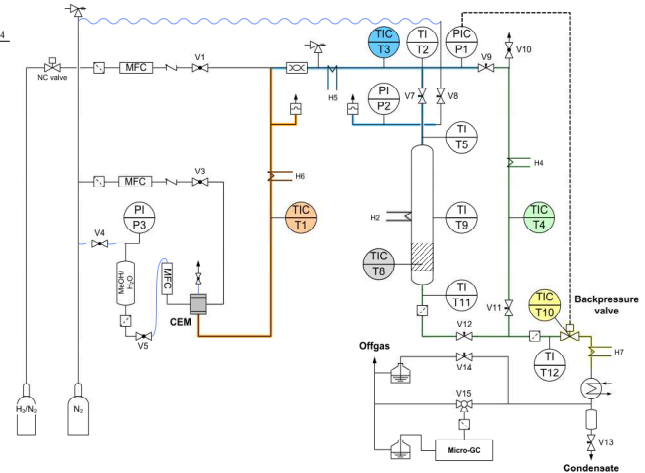
| support | modifying salt |
|--|---|
| γ-alumina | Li/K/Cs-acetate |
| A _{BET} = 100 m ² g ⁻¹ | 0.2/0.275/0.525 mol% |
| V _{pore,BJH} = 0.75 cm ³ g ⁻¹ | T _{melt} = 120 °C [2] |
| Point of zero charge ≈ 9 | ρ _{200 °C} = 2.06 g cm ⁻³ [2] |

$$X_{MeOH} = \frac{\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4}}{\dot{n}_{MeOH,in}}$$

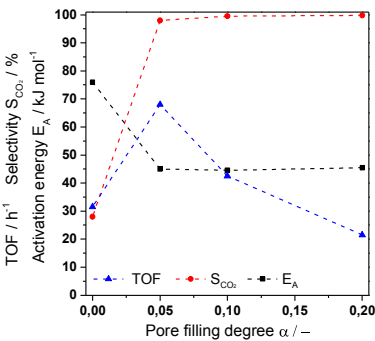
$$TOF = \frac{\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4}}{n_{Metal}}$$

$$S_{CO_2} = \frac{x_{CO_2}}{x_{CO_2} + x_{CO} + x_{CH_4}}$$

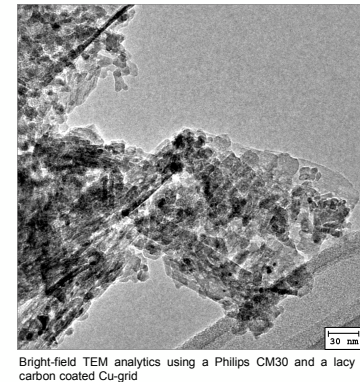
- ▶ Preparation similar to SILP-approach [3] - pore filling degree: $\alpha = \frac{V_{salt}}{V_{pore}}$
- ▶ Dissolving of salt mixture in water, addition of precursor PtCl₄
- ▶ Coating of γ-alumina with salt layer and Pt as active species
- ▶ Catalyst testing in continuous gas phase fixed bed reactor
- ▶ Temperature variation: 200-250 °C, p_{abs} = 10 bar, p_{MeOH} = p_{H₂O} = 1 bar
- ▶ Substrate dosage via MFC with inert gas N₂, product analytics via GC



Results

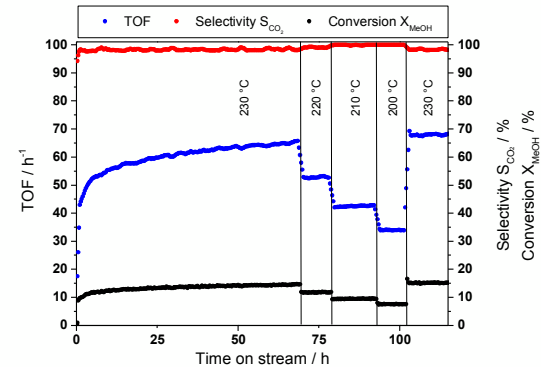


Comparison of turn over frequency TOF and selectivity S_{CO₂} for steady state gas phase MeOH reforming at T = 230 °C, activation energy E_A in the range of T = 200 °C to 250 °C, p_{abs} = 10 bar, p_{MeOH} = p_{H₂O} = 1 bar, inert gas N₂, WHSV = 31-115 h⁻¹, variation in pore filling degree α, w_{salt} respectively with constant ratio of n_{Pt}/n_{salt}:
 α = 0: w_{salt} = 0 % w_{Pt} = 0.21 %, α = 0.05: w_{salt} = 7.15 % w_{Pt} = 0.2 %
 α = 0.1: w_{salt} = 13.3 % w_{Pt} = 0.37 %, α = 0.2: w_{salt} = 23.3 % w_{Pt} = 0.64 %



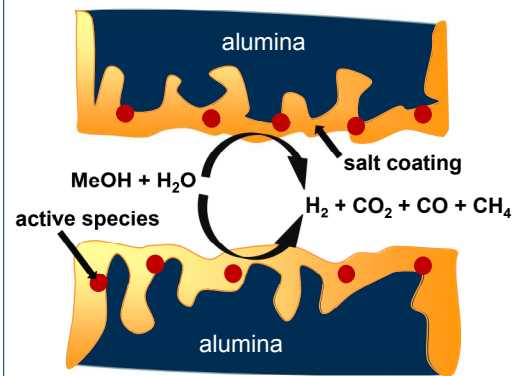
Bright-field TEM analytics using a Philips CM30 and a lacy carbon coated Cu-grid

- ▶ Impregnation as precipitation at point of zero charge of support material
- ▶ Active species is embedded in salt layer
- ▶ Distribution in pore structure is not yet clear
- ▶ Preformation yields Pt nanoparticles
- ▶ Particle size is in the range of 7 to 15 nm
- ▶ Catalysts coated with salt show high selectivity towards CO₂
- ▶ Activation energy is relatively low
- ▶ Salt modification reveals influence on reaction network
- ▶ Alkali doping effects are possible



Deviation of turn over frequency TOF, selectivity S_{CO₂} and conversion X_{MeOH} for continuous gas phase MeOH reforming, temperature variation from T = 200 °C to 230 °C, p_{abs} = 10 bar, p_{MeOH} = p_{H₂O} = 1 bar, inert gas N₂, WHSV = 115 h⁻¹, pore filling degree α = 0.05, w_{salt} = 7.15 % w_{Pt} = 0.2 %, values are the arithmetic average of 5 data points

Outlook



- ▶ Elucidate the effect of the salt coating on the active center and the reaction
- ▶ TPD experiments: CO, H₂O, MeOH
- ▶ DRIFT experiments
- ▶ EDX-TEM to show the distribution of the alkali species
- ▶ SCILL-approach [4] to eliminate the particle formation process
- ▶ Screening of various molten salts
- ▶ Extend the concept towards different reactions

[1] G.A. Olah, Beyond Oil and Gas: The Methanol Economy, Wiley-VCH, 2009. [2] S. Bajus, Doctoral Thesis, unpublished, Institute for Chemical Reaction Engineering, Erlangen, 2011. [3] M. Haumann et al., Continuous Gas-Phase Hydroformylation of 1-Butene using Supported Ionic Liquid Phase (SILP) Catalysts, Adv. Synth. & Catalysis 349(3), 2007, 425-431. [4] 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.