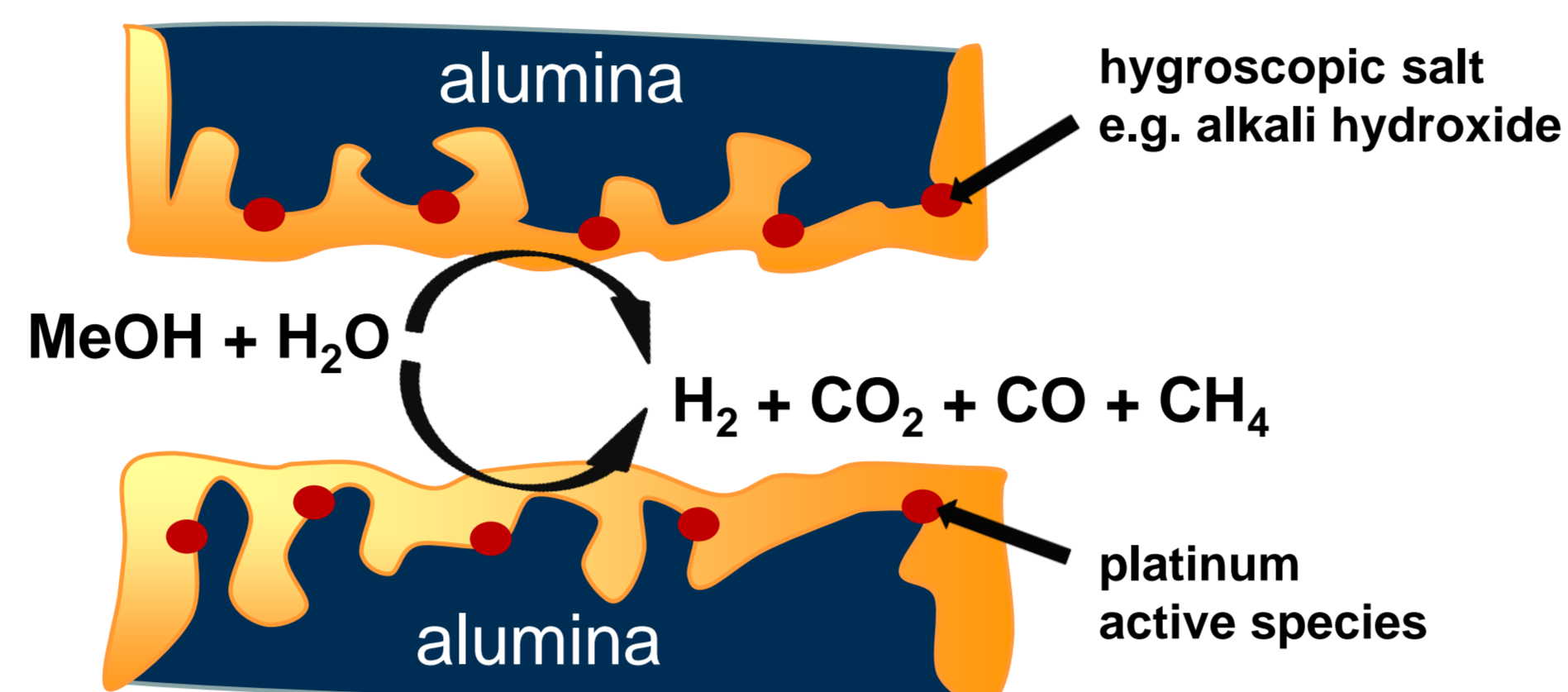


Renewable energy sources are intermittent, therefore an effective storage technology is required. One possible compound for chemical energy storage is methanol (12.5 wt% H₂-storage capacity, 6.3 kWh kg⁻¹ energy density [1]). The stored hydrogen can be released by methanol reforming, heterogeneously catalyzed.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

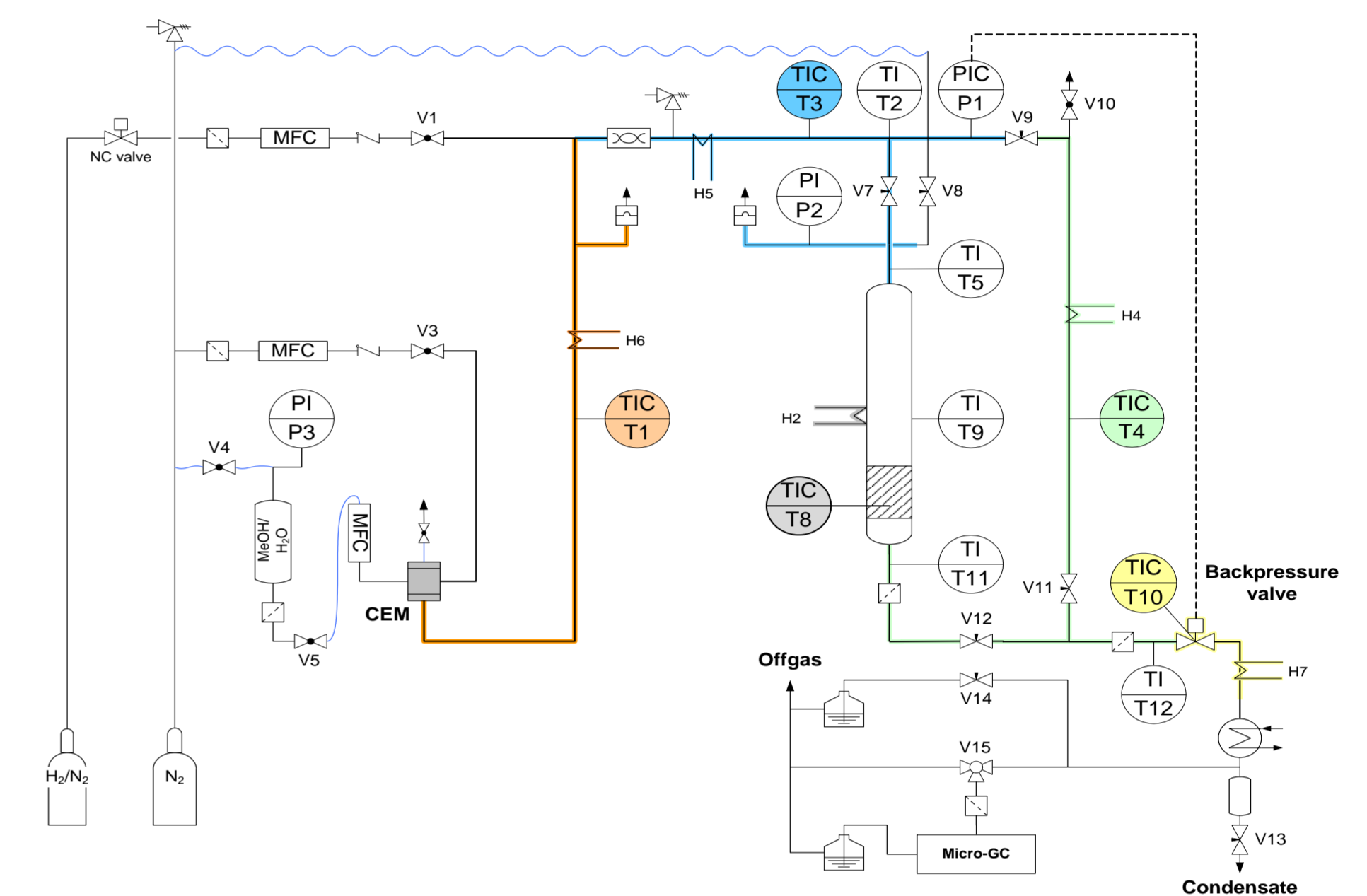
Experimental

Pt-alumina catalyst
4.86 wt% Pt on γ -alumina (Alfa Aesar)
$A_{BET} = 143 \text{ m}^2 \text{ g}^{-1}$
$V_{\text{pore,BJH}} = 0.9 \text{ cm}^3 \text{ g}^{-1}$



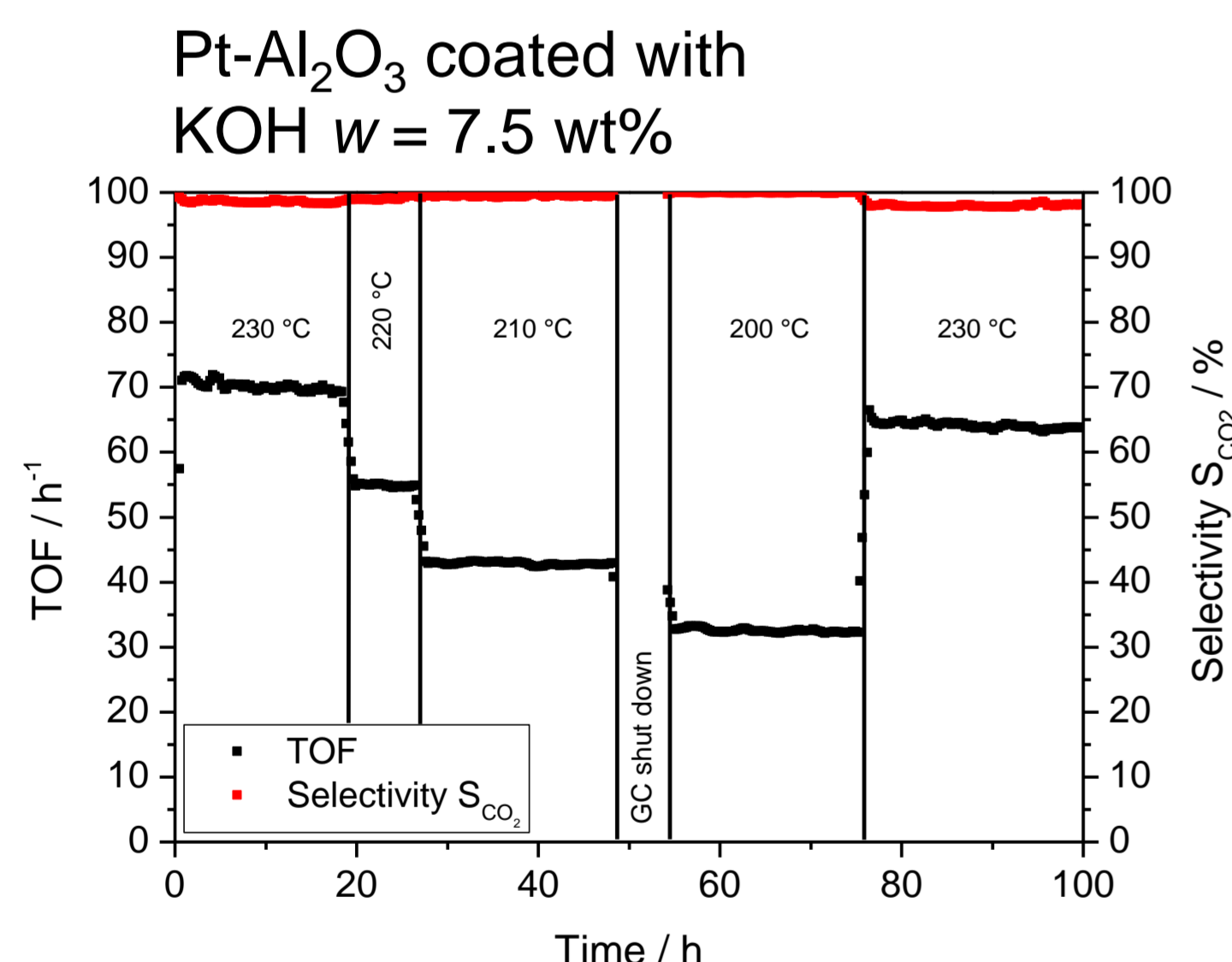
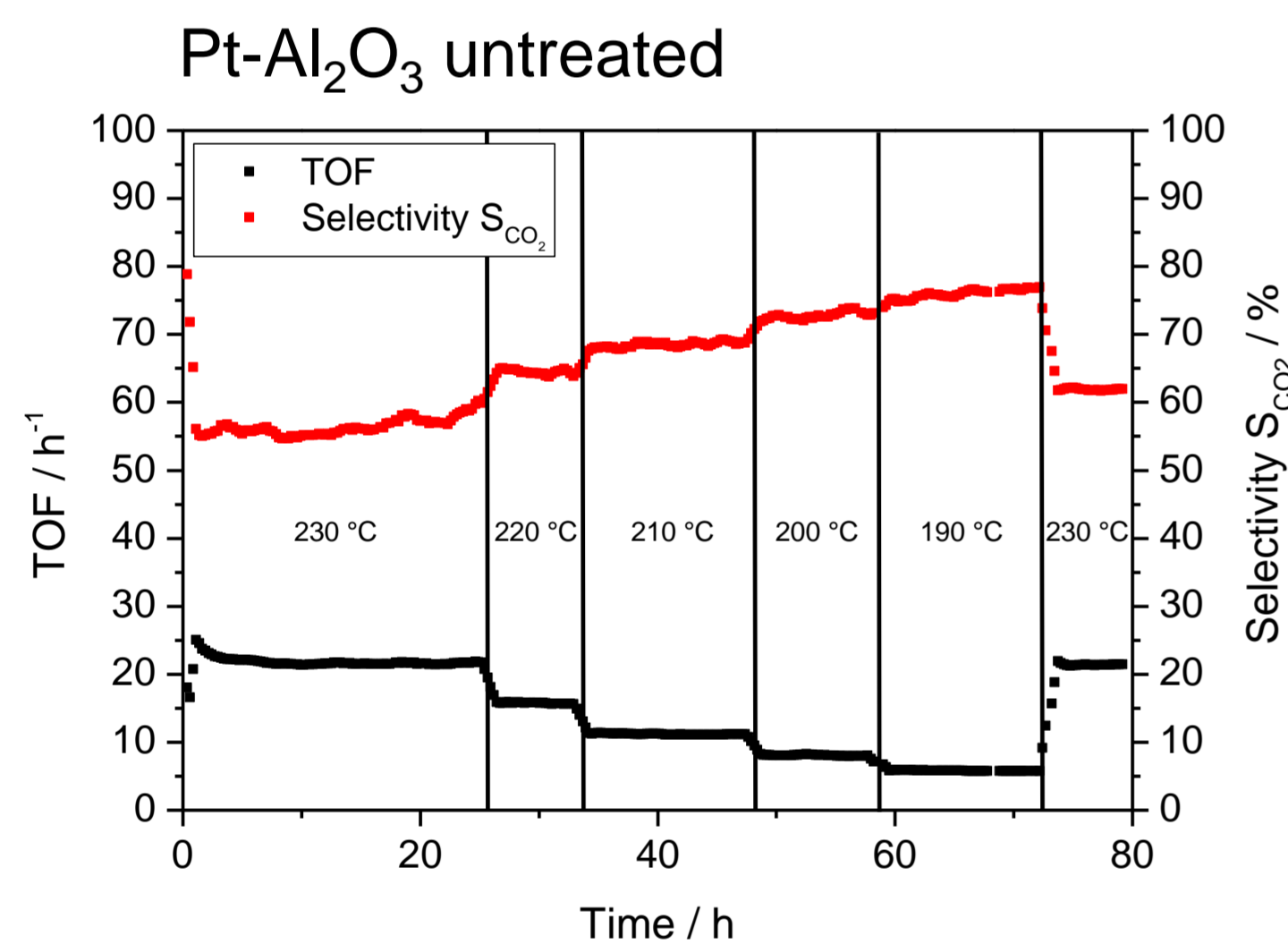
$$X_{\text{MeOH}} = \frac{\dot{n}_{\text{CO}_2} + \dot{n}_{\text{CO}} + \dot{n}_{\text{CH}_4}}{\dot{n}_{\text{MeOH,in}}} \quad S_{\text{CO}_2} = \frac{x_{\text{CO}_2}}{x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{CH}_4}}$$

$$W = \frac{m_{\text{salt}}}{m_{\text{catalyst}}} \quad \text{TOF} = \frac{\dot{n}_{\text{CO}_2} + \dot{n}_{\text{CO}} + \dot{n}_{\text{CH}_4}}{n_{\text{Metal}}}$$



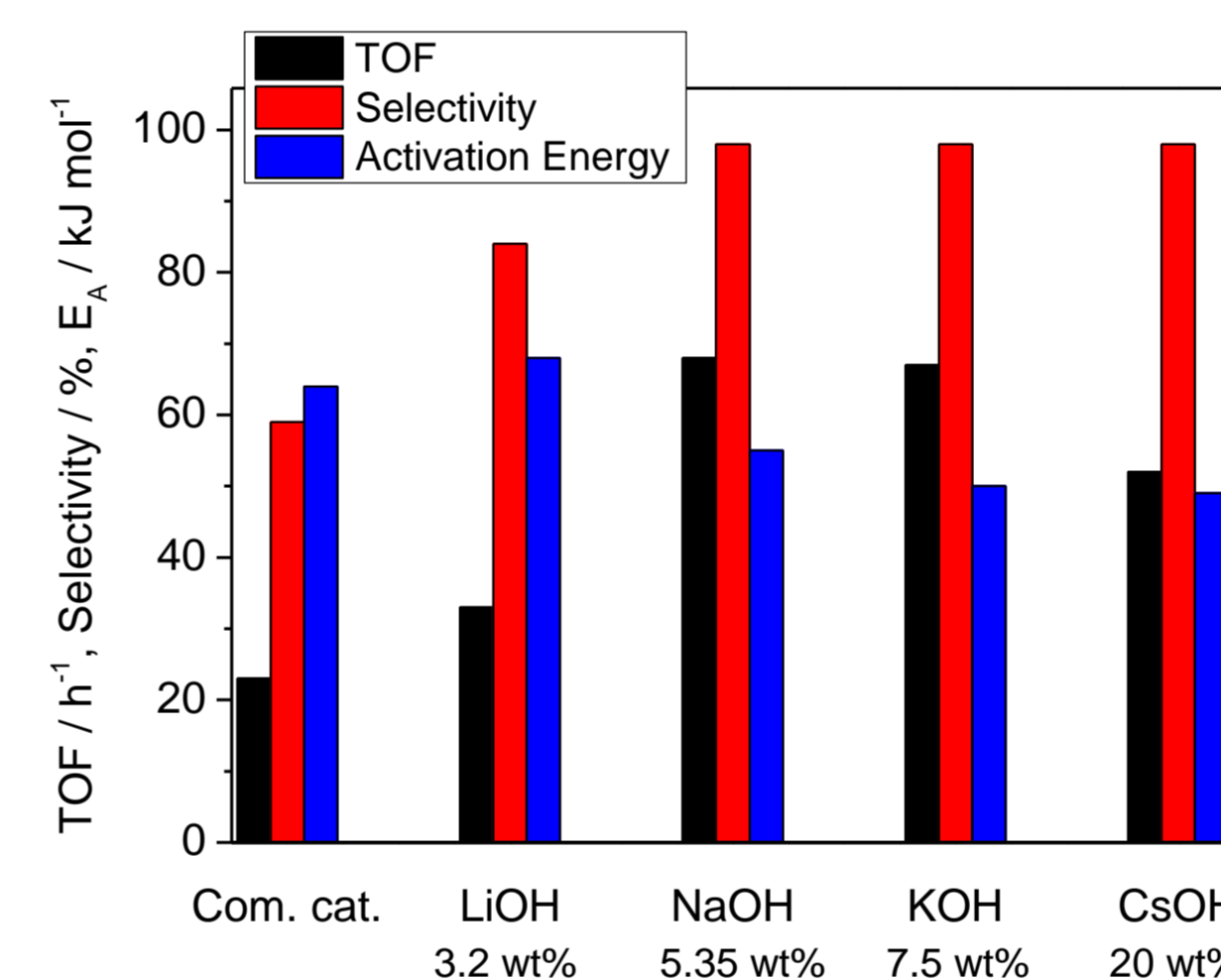
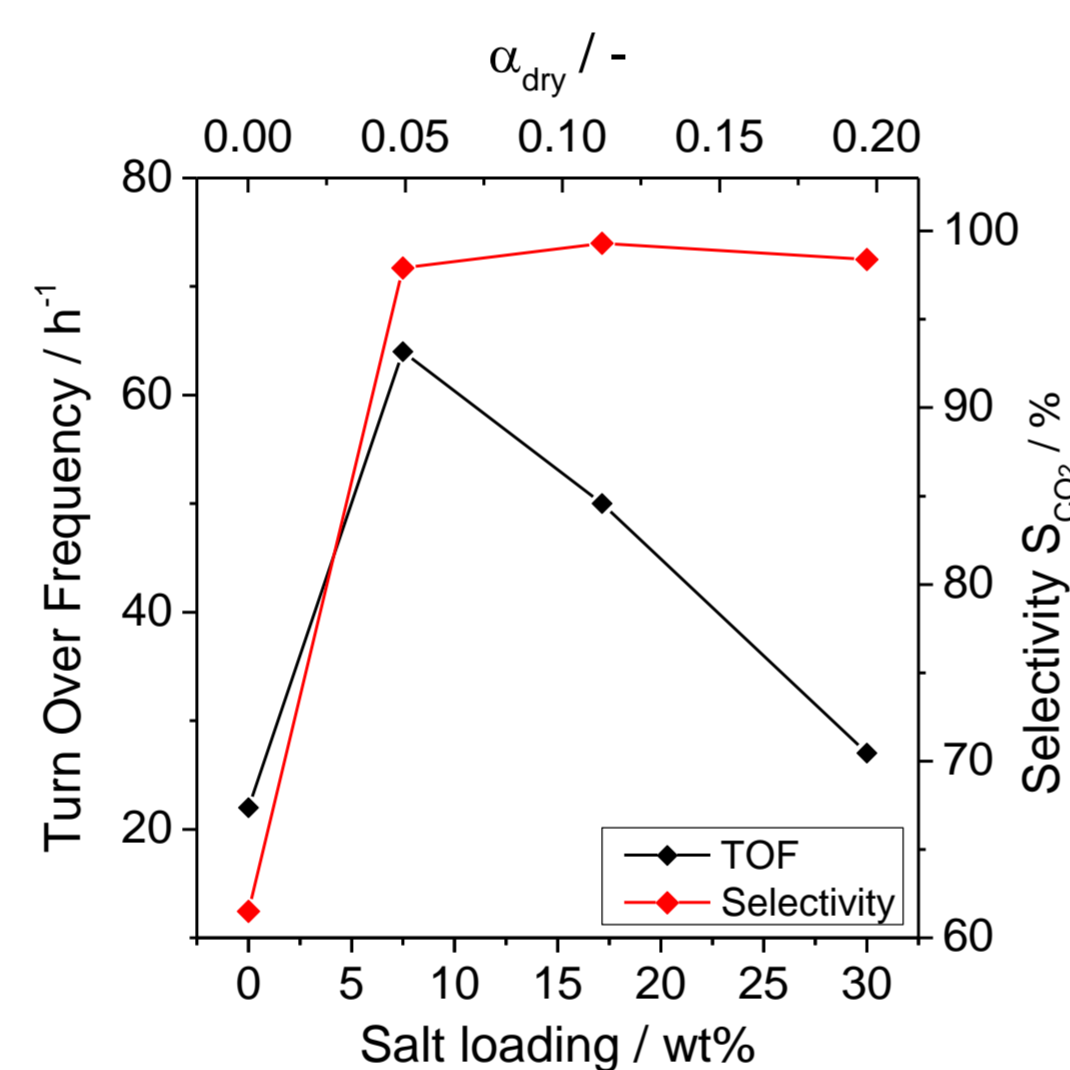
- Coating of catalyst with alkali hydroxides by wet impregnation
- Catalyst test experiments in continuous gas phase fixed bed reactor
- Temperature variation: $T_R = 200\text{-}230 \text{ }^\circ\text{C}$, $p_{\text{abs}} = 5 \text{ bar}$, $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5 \text{ bar}$
- Substrate dosage via MFC with inert gas nitrogen, product analytics via GC
- Investigation of CO-adsorption with DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy)

Results

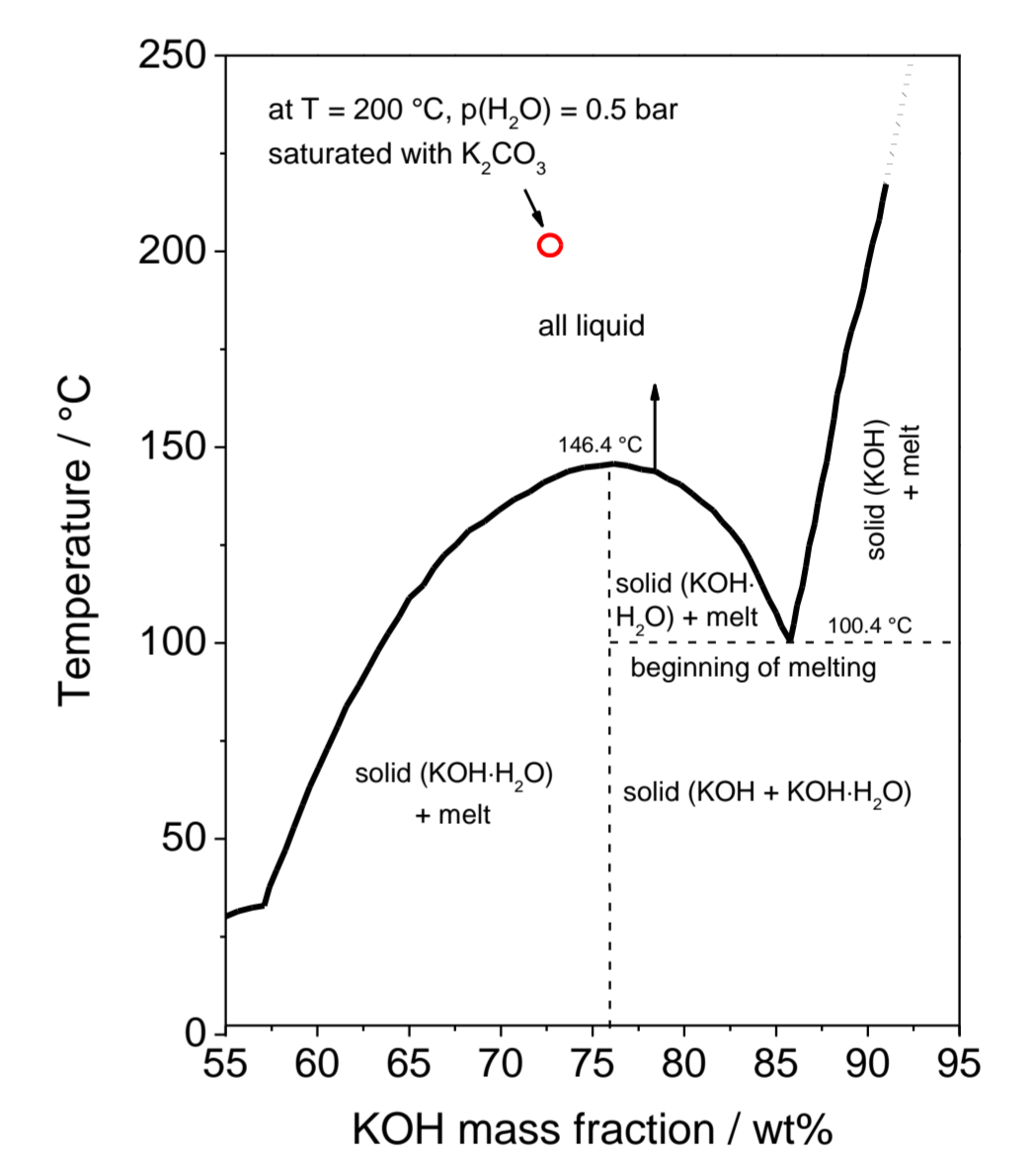


Deviation of turn over frequency TOF and selectivity S_{CO_2} for continuous gas phase MeOH reforming; temperature variation from $T_R = 200 \text{ }^\circ\text{C}$ to $230 \text{ }^\circ\text{C}$, $p_{\text{abs}} = 5 \text{ bar}$, $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5 \text{ bar}$, inert gas N_2 , $\tau = 10 \text{ s}$, values are the arithmetic average of 5 data points; same conditions for experiments on the right

Results under comparable conditions: $T = 230 \text{ }^\circ\text{C}$, same molar amount of MOH $n_M/n_{\text{Pt}} = 5.4$

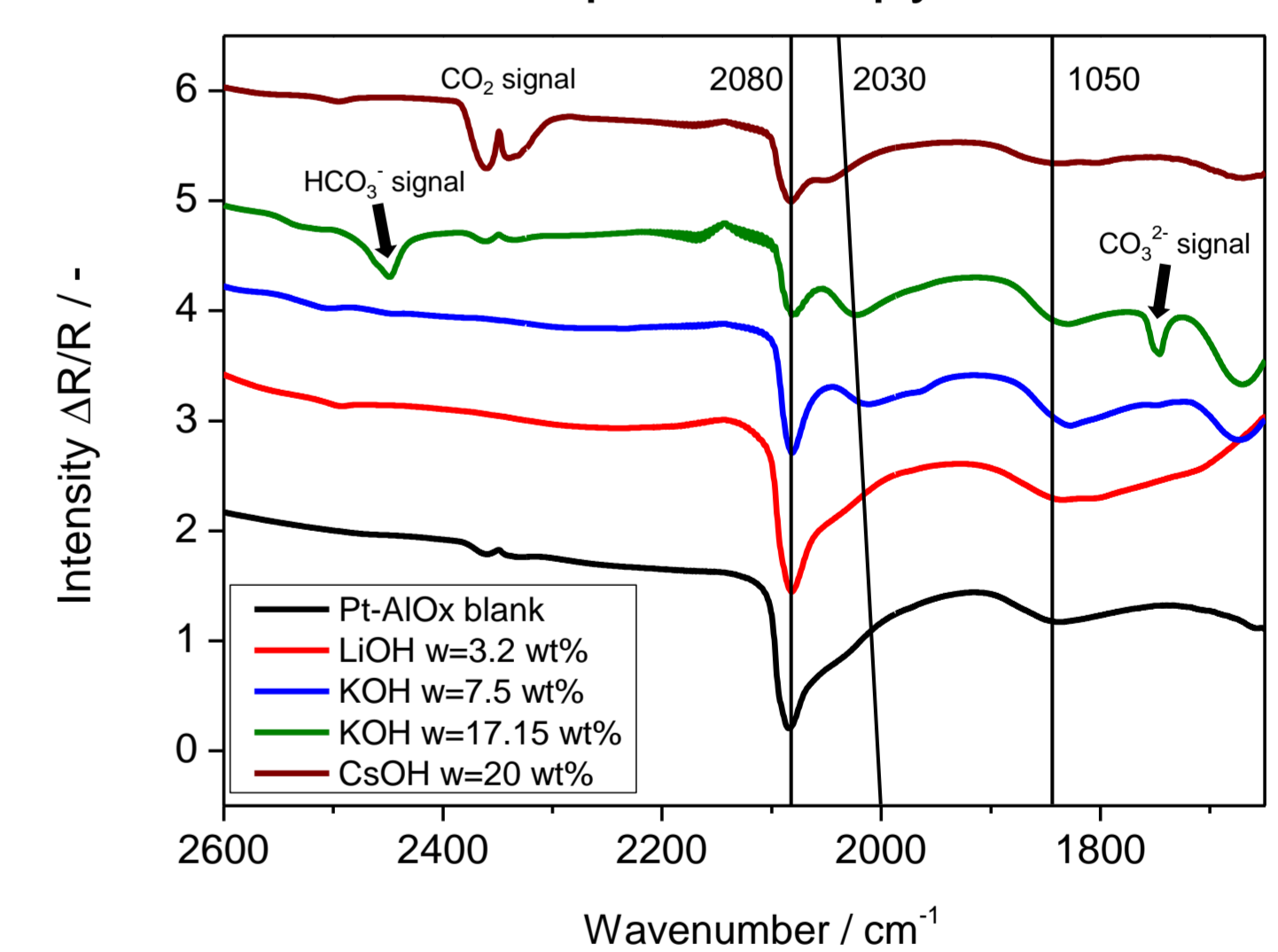


Phase diagramm KOH-H₂O [4]



- Hydroxide coated catalysts: CO₂-selectivity up to 99% and tripled activity
- KOH layer remains liquid under reaction conditions
- 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 → indication of an enhanced bonding of CO
- Effects known as alkali-doping: CO adsorption on potassium influenced platinum [3] → one explanation for higher CO₂-selectivities

CO-DRIFT spectroscopy



Conclusion

- Stable operation and pronounced enhancement of activity and selectivity for KOH coated catalyst even at $T_R = 200 \text{ }^\circ\text{C}$ in an humid atmosphere
- IR spectra of KOH reveals carbonate and bicarbonate bands
- Salt modified catalysts show enhanced bridge-bonded adsorption of probe molecule CO
- Traces of K₂CO₃ formed under reaction conditions
- So far potassium reveals the most significant influence on the active platinum species [5]
- Additionally, basic and hygroscopic nature of salt layer enhances activity / selectivity

Outlook

- Analyse the catalysts with MeOH-DRIFTS
- Determine the influence of adsorbed H₂O
- Extend the concept towards other salts
- Apply the approach to other reactions
- Investigate the effects of salt modification in the water gas shift reaction

[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. Bonzel, Alkali-Metal-Affected Adsorption of Molecules on Metal Surfaces, Surface Science Reports 8, 1987, 43-125. [4] W. M. Vogel, Some Physicochemical Properties of the KOH-H₂O System, Journal of Chemical and Engineering Data 12(4), 1967, 465-472. [5] M. Kusche, Enhanced Activity and Selectivity in Catalytic Methanol Steam Reforming by Basic Alkali Metal Salt Coatings, Angew. Chem. 2013, accepted.