High temperature supported molten salt catalysts for hydrogen generation

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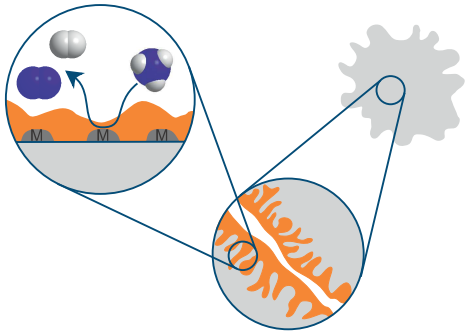
Introduction

One approach to **chemical energy storage** is binding hydrogen in organic compounds such as **methanol** or **ammonia**, to be released on demand in a **dehydrogenation** reaction such as **methanol steam reforming (MSR)**. These reactions however pose some challenges:

- Dehydrogenation reactions often require relatively **high temperatures** (500 - 600 K)
- **Limited thermal stability** of classical **homogeneous catalysts**
- **Selectivity** issues with classical heterogeneous catalysis

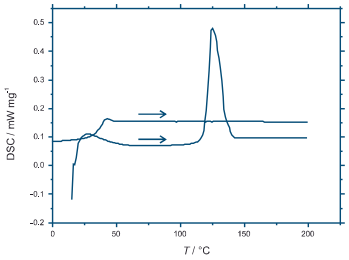
Potential solution: **SCILL** or **SILP** type catalysts in which a homogeneous or heterogeneous transition metal **catalyst is modified with a molten** salt.



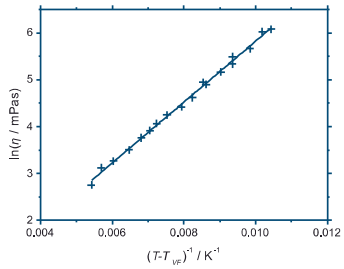
One such potential candidate: $Li_{0.2}K_{0.525}Cs_{0.575}OAc$

While the **process works** in principle (see poster M. Kusche) the **role of the salt is unclear!**

Properties of the pure salt

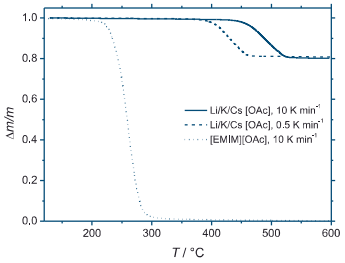


Very close to **eutectic composition.**
T_G = 33 °C, T_m = **119 °C**



Viscosity in excellent agreement with VFT equation.
η_0 = 0.510 mPas,
B = 650 K, T_0 = 323 K

$$\eta = \eta_0 \cdot e^{\frac{B}{T - T_0}}$$



Markedly **higher thermal stability** than classical ionic liquids.

Conclusion

The isolated salt mixture has a:

- **Low (eutectic) melting point**
- **Low viscosity** under reaction conditions
- **High thermal stability**

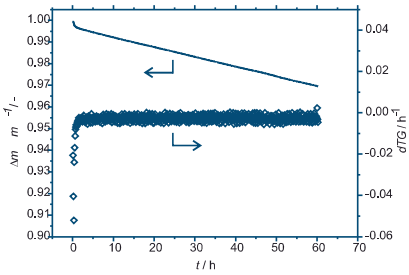
Should be **suitable for modification of catalysts.**

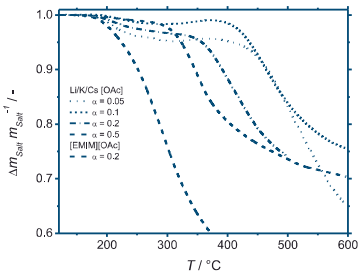
NMR, IR and IC indicate:

- **Partial decomposition of acetate** anion into carbonate and other species
- State of adsorbed **CO changes qualitatively** after heating of the catalyst
- Does a liquid salt layer remain under reaction conditions?

Exact state of salt so far unclear!

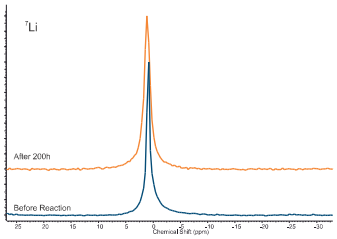
Under reaction conditions

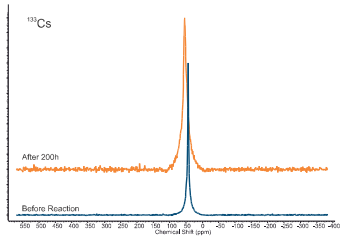


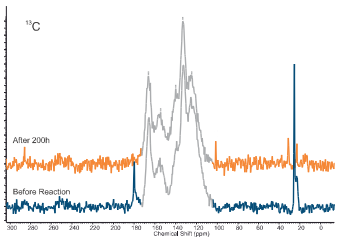


- Good **long term stability** at 300 °C
- Excellent **stability on AlOx support** at various loadings

Molten salt phase can be **expected to be stable** under reaction conditions





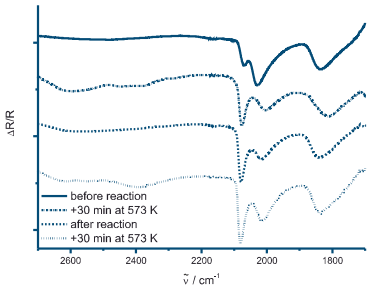


Solid state NMR spectra of Pt/AlOx MSR catalyst before and after reaction indicate

- **Change in chemical environment** of cations
- **Loss of ^{13}C acetate signals**
- Solution ^{1}H signals (not shown) show severely **reduced acetate intensity**

DRIFT IR Spectra of CO adsorbed on Pt/AlOx catalyst before and after 200 h in MSR reactor with and without surface cleansing at 573 K under Ar:

- **Significant change of spectra after treatment in reactor**
- Same effect after just 30 min at 573 K under Ar



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