Molten salt modified catalysts for hydrogen generation from ammonia and methanol

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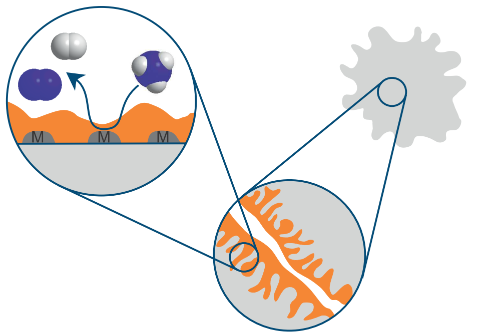
Introduction

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)** or **decomposition of ammonia**. 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

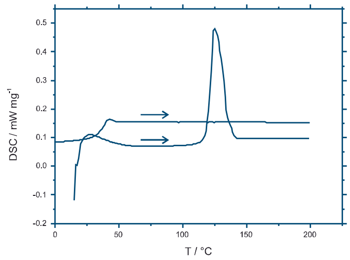
Potential solution: **SCILL** or **SILP** type catalysts in which a homogeneous or heterogeneous transition metal **catalyst is modified with a molten** salt.



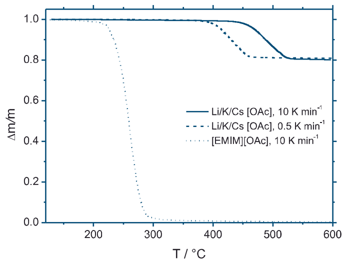
One such potential candidate: **$Li_{0,2}K_{0,275}Cs_{0,525}OAc$**

While the **process works** in principle the **role of the salt is unclear!**

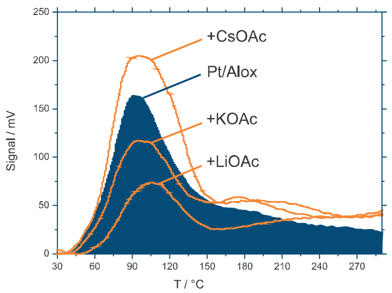
Properties of the salt



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

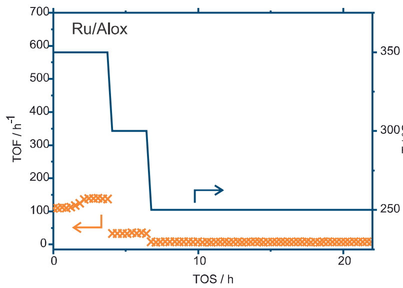


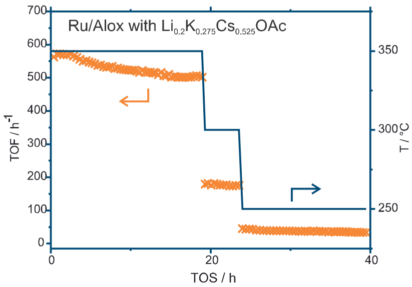
Markedly **higher thermal stability** than classical ionic liquids.

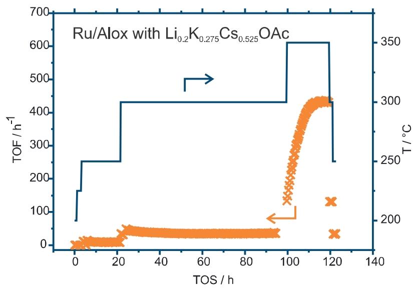


Marked influence of the different salt species on the CO TPD measurements.

Application

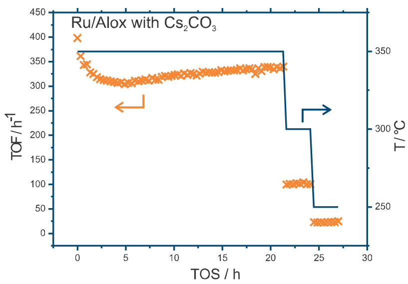


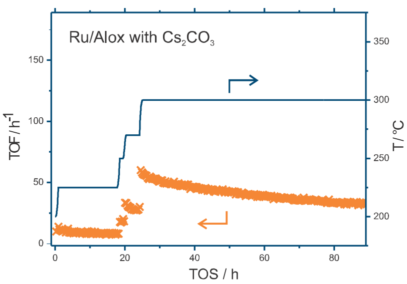




Improved catalytic performance on addition of the acetate melt!

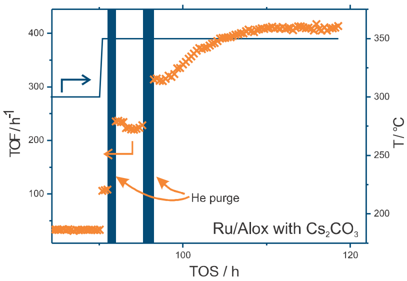
Significant **influence of thermal history**. When run from low temperatures the salt decreases the performance. **Drastic permanent activation after heating to 350°C.**





Systems loaded with Cs_2CO_3 equally show a **dependence on thermal history**. At elevated temperatures **both systems converge to the same performance**.

Potential **thermal decomposition or chemical reaction**.



All experiments run on a continuous gas-phase fixed bed reactor, p = 1 bar, gas flow = 60 ml/min, He:NH3 = 1:2, α = 0,2 for the acetate mix, equal molar amount of Cs_2CO_3

Conclusion

The isolated salt mixture has a:

- **Low (eutectic) melting point**
- **Low viscosity** under reaction conditions (not shown)
- **High thermal stability**
- Salt modification **changes the coordinating properties** of the metal

Suitable for modification of catalysts.

The thermal history of the catalyst strongly influence the catalytic performance.

Thermal decomposition and chemical modification have a strong influence on the process.

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