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Study of the Influence of NaCl and LiCl on the Decomposition of $Sr(AlH_4)_2$

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INTRODUCTION AND MOTIVATION

Chemical storage of hydrogen in alanates is one possible solution to the problem of energy storage posed by the global energy transition. Advances in the field of mechanochemistry allowed the preparation of alanates also by ball milling. In order to characterise the alanates themselves, often simply the obtained mixtures consisting of the alanate and the by-product were investigated For that purpose, the by-product is assumed to be inert. In this study, we review the validity of this assumption for $Sr(AlH_4)_2$.

MECHANOCHEMICAL SYNTHESIS

$SrCl_2 + 2\ MAlH_4 \rightarrow Sr(AlH_4)_2 + 2\ MCl$

500 rpm, 10 h M = Li, Na

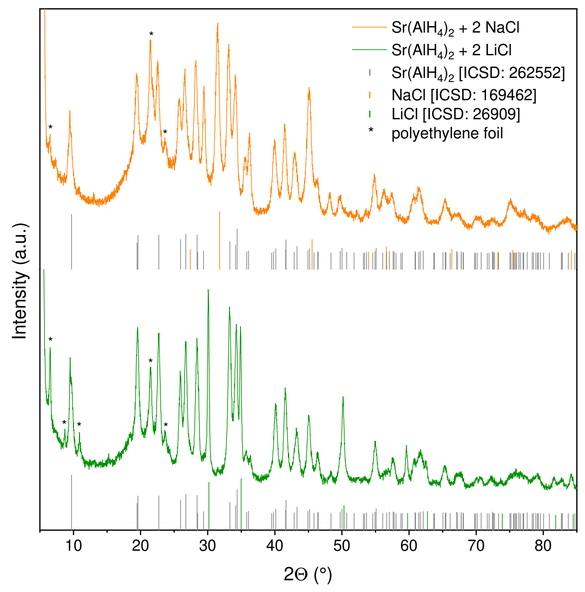
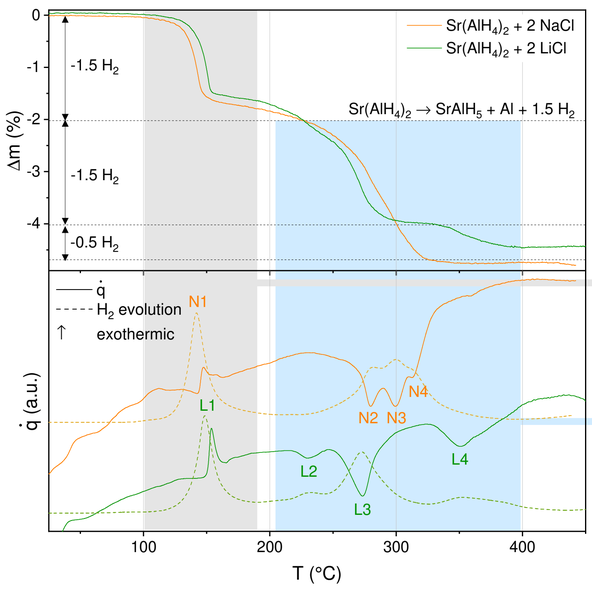


Fig. 1: XRD of $Sr(AlH_4)_2$ + 2 MCl (M = Li, Na).

THERMAL DECOMPOSITION (Setaram Sensys coupled with H_2-sensor, 5 K/min, Ar)



DEHYDROGENATION REACTIONS [1,2]

① $Sr(AlH_4)_2 \rightarrow SrAlH_5 + Al + 1.5\ H_2$
② $SrAlH_5 \rightarrow SrH_2 + Al + 1.5\ H_2$
③ $SrH_2 + 2\ Al \rightarrow 0.5\ SrH_2 + 0.5\ SrAl_4 + 0.5\ H_2$

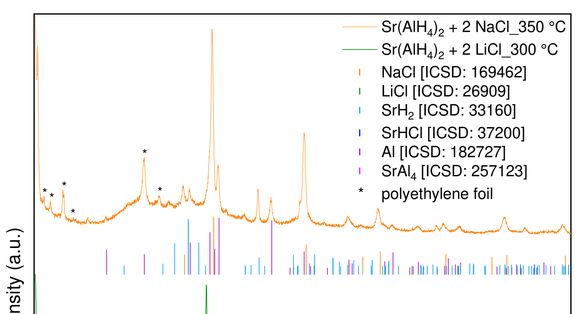
Overlap of sub-steps, possibly:
(1) $Sr(AlH_4)_2 \rightarrow SrH_2 + AlH_3$ (2) $SrH_2 + AlH_3 \rightarrow SrAlH_5$

Dehydrogenation behaviour of $SrAlH_5$ dependent on by-product:
- Steps of $SrAlH_5$ + 2 NaCl decomposition overlap
- Steps of $SrAlH_5$ + 2 LiCl decomposition can be separated

Fig. 2: TG-DSC of $Sr(AlH_4)_2$ + 2 MCl (M = Li, Na), TG normalised to $Sr(AlH_4)_2$ content.

INVESTIGATION OF THE DECOMPOSITION PATHWAY USING XRD AND THERMODYNAMIC COMPUTATIONS

The XRDs of the decomposition products and the thermodynamic assessment of the dehydrogenation pathway show $SrAlH_5$ + 2 NaCl to directly decompose into 0.5 SrH_2 and 0.5 $SrAl_4$ as SrH_2 is already unstable at N2 from a thermodynamic point of view.
In contrast, $SrAlH_5$ + 2 LiCl first forms SrHCl, LiH and Al. Since the decomposition of the formed SrHCl + LiH is only thermodynamically feasible at temperatures above L2, the decomposition steps are separated for $SrAlH_5$ + 2 LiCl.



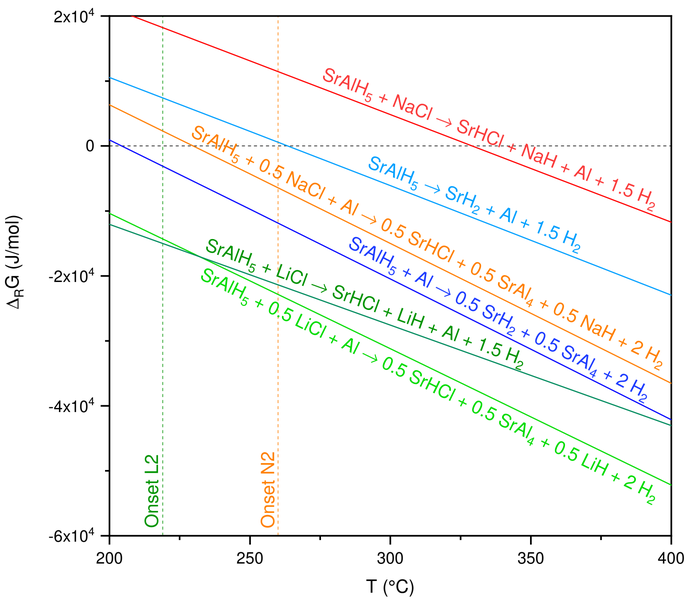
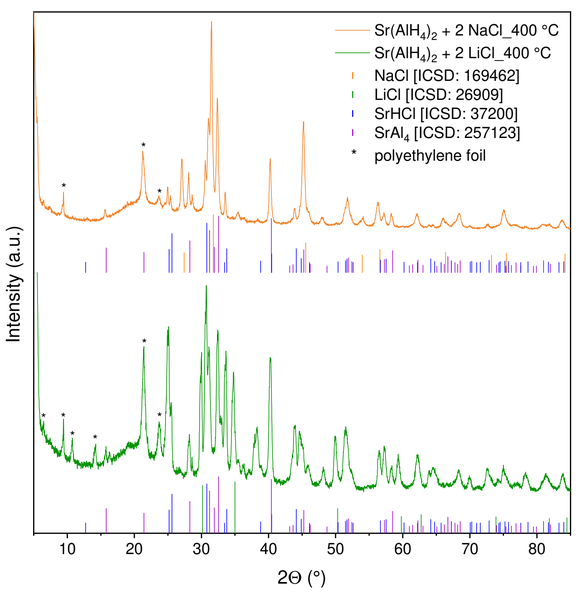


Fig. 3: left: XRD of $Sr(AlH_4)_2$ + 2 MCl (M = Li, Na) after heating to 300 °C (LiCl) and 350 °C (NaCl), right: Thermodynamic assessment of the decomposition of $SrAlH_5$ + 2 MCl.



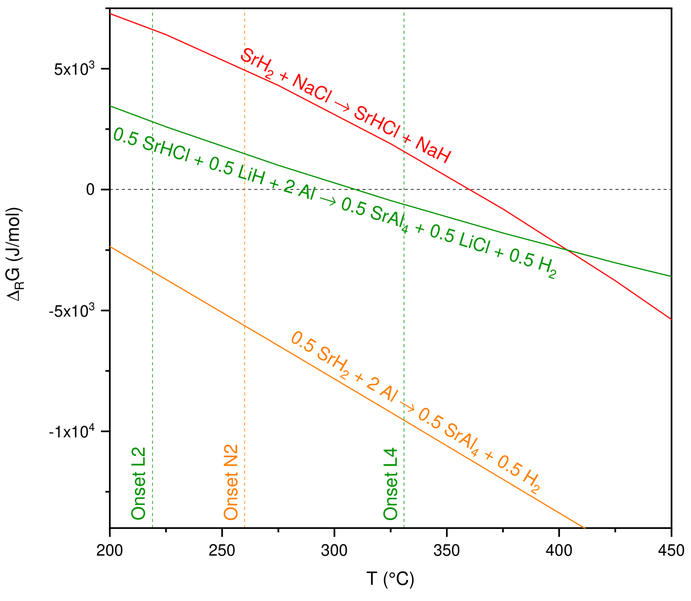
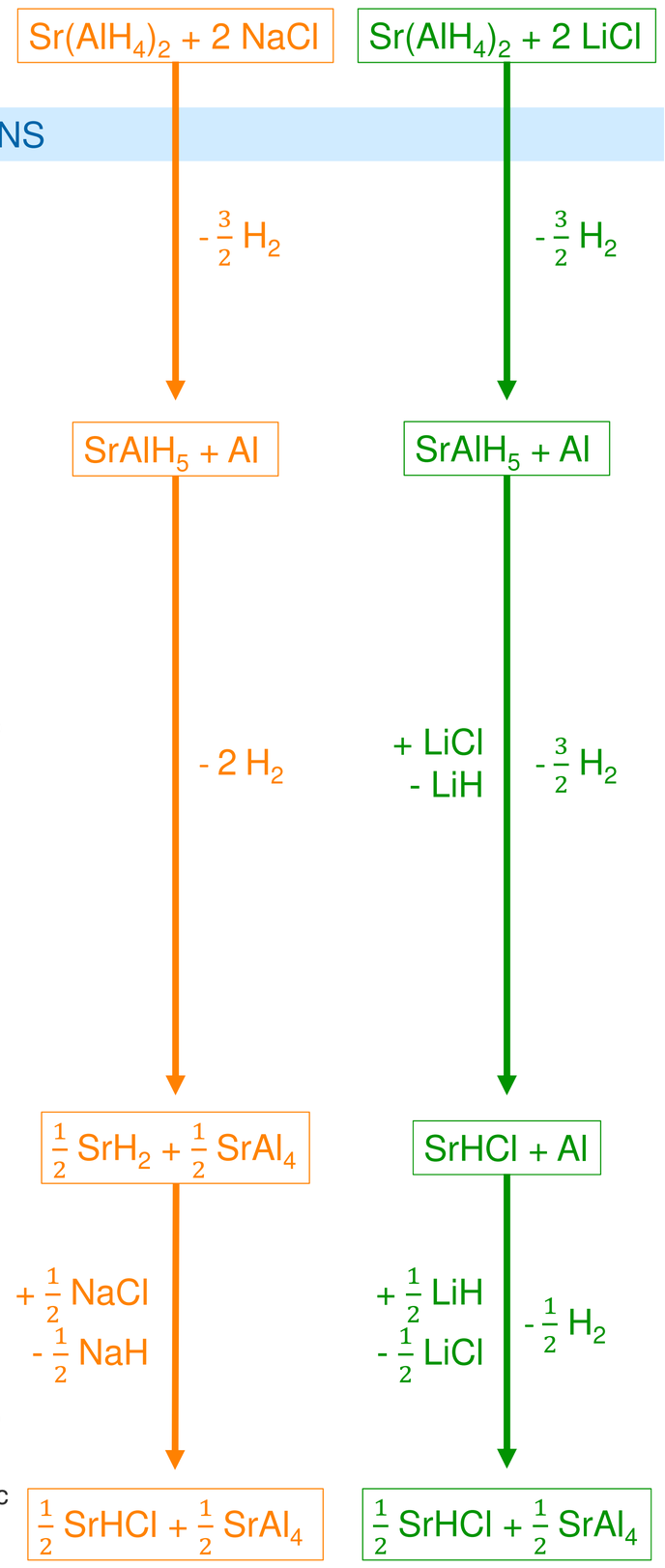


Fig. 4: left**:** XRD of $Sr(AlH_4)_2$ + 2 MCl (M = Li, Na) after heating to 400 °C, right: Thermodynamic assessment of the decomposition of SrHX (X = H, Cl) considering MCl.



CONCLUSION

In contradiction to the common assumption of inert by-products, we found LiCl to affect the decomposition pathway of $Sr(AlH_4)_2$. The different effects of LiCl and NaCl correspond to the differing stability of LiH ($\Delta_f H°(298)$ = -90.5 kJ/mol [3]) and NaH ($\Delta_f H°(298)$ = -56.4 kJ/mol [3]). Due to the high stability of LiH its formation is thermodynamically favoured and thus the addition of LiCl changes the decomposition reactions of $Sr(AlH_4)_2$.

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