Thermodynamic Study of the Dehydrogenation Reactions of the Complex Hydrides $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$

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Chemical hydrogen storage in alanates is a widely discussed option for energy storage in targeted applications to foster the transition to a renewable energy based economy. Although $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ are already investigated to some extent, several details concerning their dehydrogenation behaviour still remain unclear.

In the case of $Mg(AlH_4)_2$ the thermodynamics of the first dehydrogenation step is unclear. While Kim et al. observed it as exothermic [1], Mamatha et al. reported endothermic values [2]. $Ca(AlH_4)_2$ however has not yet been investigated as a pure compound.

Since neither $Mg(AlH_4)_2$ nor $Ca(AlH_4)_2$ are commercially available they had to be synthesized first. For both alanates the synthesis was performed via the metathesis reaction in solution as well as by ball milling [3][4][5][6]. The synthesis of $Ca(AlH_4)_2$ was successful via both routes although only the synthesis in solution yielded pure $Ca(AlH_4)_2$. In contrast, the complete conversion of the starting materials to $Mg(AlH_4)_2$ only succeeded by ball milling.

The dehydrogenation reactions were investigated by TG-DSC measurements. The results show, that the contradictory literature data regarding the first step of the dehydrogenation of $Mg(AlH_4)_2$ is due to the overlapping of endothermic and exothermic partial reactions. We propose the steps to be $Mg(AlH_4)_2 \rightarrow Mg + 2\,Al + 4\,H_2$ (endothermic) and $Mg + H_2 \rightarrow MgH_2$ (exothermic), respectively.
The investigation of the dehydrogenation of different $Ca(AlH_4)_2$ samples resulted in strongly varying enthalpies for the first dehydrogenation event in the DSC measurement. It seems, that the sign of the dehydrogenation enthalpy is dependent on the synthesis route.

References

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