

Thermodynamic Study of the Dehydrogenation Reactions of the Complex Hydrides Mg(AlH₄)₂ and Ca(AlH₄)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(AlH₄)₂ and Ca(AlH₄)₂ are already investigated to some extent, several details concerning their dehydrogenation behaviour still remain unclear.

In the case of Mg(AlH₄)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(AlH₄)₂ however has not yet been investigated as a pure compound.

Since neither Mg(AlH₄)₂ nor Ca(AlH₄)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(AlH₄)₂ was successful via both routes although only the synthesis in solution yielded pure Ca(AlH₄)₂. In contrast, the complete conversion of the starting materials to Mg(AlH₄)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(AlH₄)₂ is due to the overlapping of endothermic and exothermic partial reactions. We propose the steps to be Mg(AlH₄)₂ → Mg + 2 Al + 4 H₂ (endothermic) and Mg + H₂ → MgH₂ (exothermic), respectively.

The investigation of the dehydrogenation of different Ca(AlH₄)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

- [1] Y. Kim, E.-K. Lee, J.-H. Shim, Y. W. Cho, K. B. Yoon, *J. Alloys Compd.* **2006**, *422*, 283.
- [2] M. Mamatha, B. Bogdanovic, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schuth, C. Weidenthaler, *J. Alloys Compd.* **2006**, *407*, 78.
- [3] M. Fichtner, O. Fuhr, *J. Alloys Compd.* **2002**, *345*, 286.
- [4] Y. Liu, Y. Pang, X. Zhang, Y. Zhou, M. Gao, H. Pan, *Int. J. Hydrogen Energy* **2012**, *37*, 18148.
- [5] K. Komiya, N. Morisaku, Y. Shinzato, K. Ikeda, S. Orimo, Y. Ohki, K. Tatsumi, H. Yukawa, M. Morinaga, *J. Alloys Compd.* **2007**, *446-447*, 237.
- [6] N. Morisaku, K. Komiya, Y. Z. Li, H. Yukawa, M. Morinaga, K. Ikeda, S. Orimo, *Adv. Mater. Res.* **2007**, *26-28*, 869.