Thermodynamic Investigation of Vanadium Hydrogenation

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Chemical hydrogen storage in complex hydrides is a widely discussed option for energy storage targeted applications to foster the transition to a renewable energy based economy. The thermodynamics of the dehydrogenation and hydrogenation reactions of the e.g. alkali and earth alkali metal alanates have already been investigated in some detail. In contrast, for the majority of transition metal alanates not even the pathway of dehydrogenation is clear yet. [1]

The most stable transition metal alanates have decomposition temperatures of 50 to 130 °C [2]. This fact combined with their tendency to form stable solvent adducts makes the synthesis of the pure alanates very challenging. Hence the direct synthesis of the alanates from aluminium and the transition metal under high hydrogen pressure is desirable. To investigate this synthesis route vanadium seems to be a promising candidate due to its promoting influence on the re-hydrogenation of sodium alanate.

Since the first step of the direct synthesis of vanadium alanate would be the hydrogenation of vanadium, the investigation of this reaction is the main subject of this study. Two samples containing different levels of oxygen were used. The characterization of the phase transition $\beta \rightleftharpoons \gamma$ ($VH_x \rightleftharpoons VH_2$) was carried out by HP-DSC measurements at hydrogen pressures from 50 to 180 bar. Additionally, PCI curves at temperatures from 30 to 100 °C were volumetrically measured by a Sieverts apparatus.

The molar enthalpies related to hydrogen for the phase transition $\beta \rightleftharpoons \gamma$ were determined by Van't Hoff plots using HP-DSC as well as the volumetric results. The experiments showed, in agreement with Asano et al. [3], that the oxygen content of the vanadium metal used, seems to strongly effect the hydrogenation behaviour. Merely the results for the sample containing only traces of oxygen are in good agreement with literature values reported by Reilly and Wiswall [4] as well as Luo et al. [5].

References

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