Influence of the aluminum addition on the hydrogenation/dehydrogenation behavior of doped sodium alanate

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Complex aluminum hydrides have attracted significant attention as hydrogen storage materials after the discovery of Ti-catalyzed $NaAlH_4$ [1]. However, the hydrogen release and uptake pathways from doped metal alanates are complicated and thus remain not fully understood. Therefore, the present work is focused on the investigation of the dehydrogenation and hydrogenation processes in the Ti-doped $NaAlH_4$ system by means of High-Pressure-DSC and a Sieverts-type apparatus for the determination of pressure-composition-isotherms (PCI).

The doping of $NaAlH_4$ with higher amounts of a catalyst can significantly improve the hydrogenation/dehydrogenation kinetics [2,3]. However, it also significantly reduces the hydrogen storage capacity of the system, due to the additional weight of the dopant and the formation of undesirable byproducts. It has been confirmed that in a case of $TiCl_3$-doped $NaAlH_4$, $Al_{(1-y)}Ti_y$ phases with the various compositions [4] can be formed, resulting in the decrease of the hydrogen storage capacity. We therefore decided to investigate this problem in more detail and prepared samples containing relatively high amounts of the dopant (10 and 15 mol% of $TiCl_3$). PCI curves recorded for $NaAlH_4$ with different doping levels confirmed that with increasing dopant content the hydrogenation/dehydrogenation rates increase and the gravimetric storage capacity decreases. The critical amount of $TiCl_3$ for the total conversion of $NaAlH_4$ was calculated to be above 33 mol%, however, the experimental results showed that already at 15 mol% of $TiCl_3$ only one hydrogenation/dehydrogenation step is present. Therefore, it was assumed that $NaAlH_4$ was consumed for the formation of $Al_{(1-y)}Ti_y$ phases ($y<0.25$). In order to confirm this assumption, measurements with the addition of pure Al were performed. The presented results clearly indicate, that the excess of Al increases the amount of cyclable hydrogen.

The HP-DSC traces measured for Ti-doped $NaAlH_4$ samples under various hydrogen pressures until the temperature of 400 °C showed the expected effects, which can be well interpreted and quantified. The measurements with added Al to Ti-doped $NaAlH_4$ samples showed an additional heat effect, which is not yet fully understood.

In summary, the HP-DSC has proved to be a useful technique that can improve the understanding of hydrogen release and uptake properties as well as phase transitions in metal alanate systems.

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