High-pressure DSC study of hydrogen sorption/desorption properties of doped sodium alanate

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The development of energy storage systems has become the subject of intensive research due to the progressing usage of regenerative energy sources with non-continuous availability. In many respects, hydrogen appears to be a promising solution. However, the lack of practical hydrogen storage systems is the main challenge to the implementation of a hydrogen based energy economy. Sodium alanate is one of the most thoroughly investigated solid hydrogen carriers due to its low cost and weight, high hydrogen content and auspicious operating conditions. However, several challenges and severe problems, associated with the properties of this material, remain unsolved, among which the slow sorption/desorption kinetics is particularly prominent. It is known from literature that dopants like titanium significantly improve the sorption/desorption kinetics, however, the mechanism of dopant action is still not fully understood. Therefore, this study was intended to contribute to a more detailed understanding of the hydrogen sorption/desorption thermochemistry in doped sodium alanate.

It has often been described in the literature that in the Ti-doped $NaAlH_4$ system, titanium reacts with aluminum forming the stable Al_3Ti phase [1], in addition, other metastable phases with higher Al content were also detected [2]. The consumption of Al for the formation of these phases lowers the hydrogen storage capacity, hence, an excess of Al can improve this situation [3]. To gain more information on the effect of Al addition in Ti-doped sodium alanate, the dehydrogenation and hydrogenation behavior of this system was studied using high-pressure differential scanning calorimetry (HP-DSC). Several thermal effects were separately identified during heating or cooling, depending on the applied hydrogen pressure. From the van't Hoff plot the enthalpy of reaction of the hydrogenation process was calculated. The analysis of PCI (pressure-composition isotherm) data clearly shows that the addition of Al increases the hydrogen storage capacity in Ti-doped samples. These results also evidenced that the Al content is the limiting factor for the second step of hydrogenation (from Na_3AlH_6 to $NaAlH_4$) since some of the Al is consumed for the formation of the Al-rich $Al_{(1-y)}Ti_y$ phase ($y<0.25$). Thus, the present study contributes to the understanding of the hydrogenation and dehydrogenation behavior of doped sodium alanate with the perspectives that the findings are also applicable to other related doped alanates.

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