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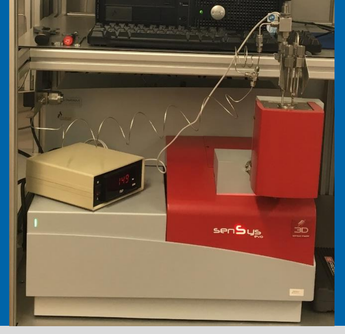

Influence of the aluminum addition on the hydrogenation/dehydrogenation behavior of doped sodium alanate

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1. Introduction and motivation

The development of energy storage systems as enablers for various energy technologies has become the subject of intensive research to overcome negative consequences of the consumption of fossil fuels. In many respects, hydrogen technologies appear to be a promising solution. The main challenge for the implementation of a hydrogen based energy economy is the lack of practical hydrogen storage systems. 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, the hydrogen release and uptake pathways are complicated and remain not fully understood. The presented study was intended to address the question to which degree the common titanium additives do have catalytic or thermodynamic impact on the (de)hydrogenation of sodium alanate.

2. Preparation and characterization

Sample preparation:

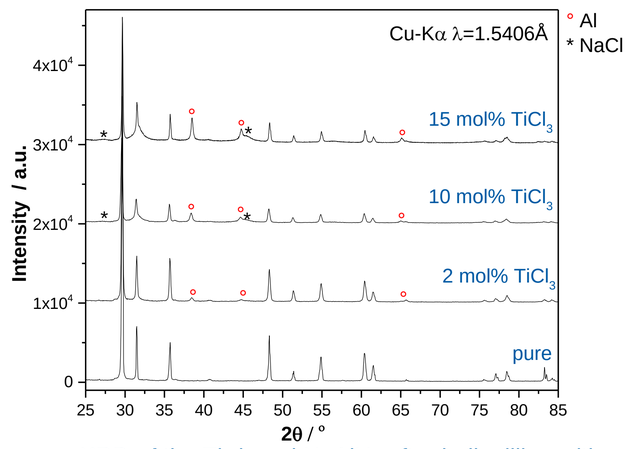
- Purified $NaAlH_4$ was mixed with x mol% $TiCl_3$ (x =2, 10, 15) in 1 g quantities
- Ball milling in a Fritsch P6 planetary mill at 650 rpm for a period of 3 h
- XRD characterization with Bruker D2 Phaser X-ray diffractometer
- Possible settings for protecting the samples from oxidation

HP-DSC measurements:

- DSC (Setaram Sensys Evo) with the samples of 30–40 mg
- High Pressure Gas Panel up to 1000 bar (Setaram PVHP-50-100-V2)
- Isobaric measurement (± 0.1bar) with a heating/cooling rate 2 $^oC\ min^{-1}$

Hydrogenation experiments:

- PCI curves were recorded using a homemade Sievert's type apparatus
- Samples mass 150–200 mg
- Isothermal measurement at 160^{o}C (± 0.1^{o}C)



XRD of the Ti-doped $NaAlH_4$ after ball milling with the different $TiCl_3$ content

3. HP-DSC measurements

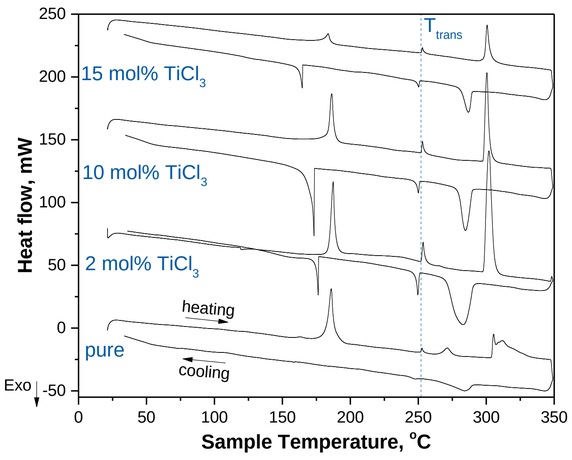
4. Hydrogen sorption behavior

Influence of the dopant content

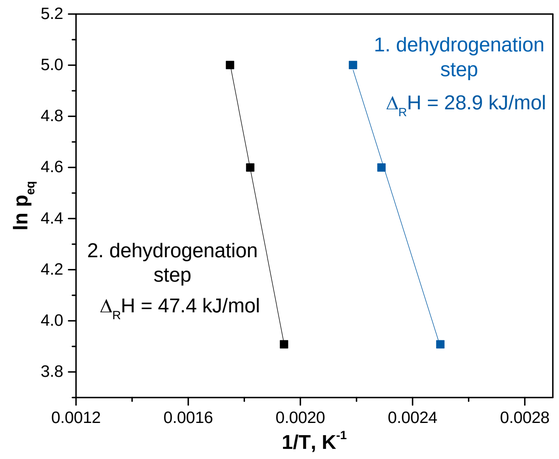
Owing to the reversibility of the doped sodium alanate, the peaks observed during heating/cooling are related to the decomposition/formation of $NaAlH_4$:

$$\underset{\text{2. hydrogenation step}}{NaAlH_4} \rightleftharpoons \underset{\text{2. dehydrogenation step}}{1/3\ Na_3AlH_6 + 2/3\ Al + H_2} \rightleftharpoons \underset{\text{1. hydrogenation step}}{NaH + Al + 3/2\ H_2}$$

Structural transformation of Na_3AlH_6 - the phase transition from the monoclinic α-Na_3AlH_6 to the orthorhombic β-Na_3AlH_6 appears in between desorption/absorption steps.



High-pressure DSC plots (150 bar) of Ti-doped $NaAlH_4$



Van´t Hoff plots of 10 mol% doped $NaAlH_4$

The enthalpies for the first and second dehydrogenation steps of 10%-doped $NaAlH_4$ are estimated to be 28.9 ± 1.3 and 47.4 ± 0.4 kJ/mol H_2, respectively. These values are in a good agreement with the ones experimentally obtained by Rongeat et al. 28.4 ± 1.5 and 51.9 ± 1.2 kJ/mol H_2 [1].

The PCI curves exhibit two distinctive plateaus in accordance with the two-step decomposition/hydrogenation of the system (first hydrogenation step - lower plateau, second hydrogenation step - higher plateau). The doping of $NaAlH_4$ with higher amounts of $TiCl_3$ 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:

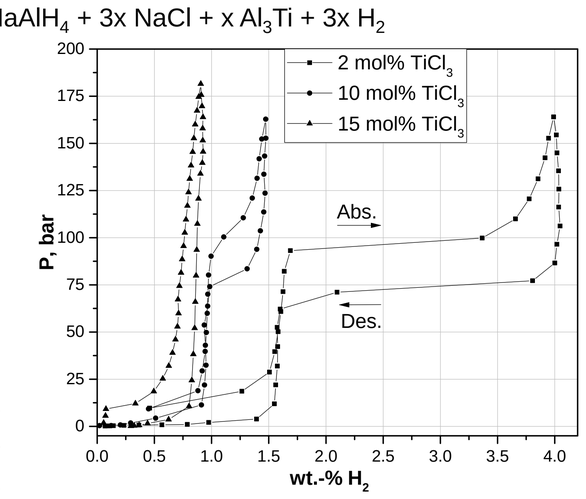
$$NaAlH_4 + x\ TiCl_3 \rightarrow (1\text{-}3x)\ NaAlH_4 + 3x\ NaCl + x\ Al_3Ti + 3x\ H_2$$

Theoretical hydrogen storage capacity

$TiCl_3$ content, mol%	wt.-%, H_2 theor.
0	5.60
2	4.98
10	3.05
15	2.16
33.3	0

The lower hydrogen storage capacity is assumed to be caused by the formation of a Al-rich $Al_{(1-y)}Ti_y$ phase (y<0.25) [4]. If this phase is stable, there will be an insufficient amount of Al for the reverse reaction with Na_3AlH_6:

$$NaAlH_4 + x\ TiCl_3 \rightarrow (1\text{-}kx)\ NaAlH_4 + 3x\ NaCl + x/y\ Al_{1-y}Ti_y + lx\ Na_3AlH_6 + (2k\text{-}3l)x\ H_2$$



PCI curves of Ti-doped $NaAlH_4$ with the different $TiCl_3$ content recorded at 160^{o}C

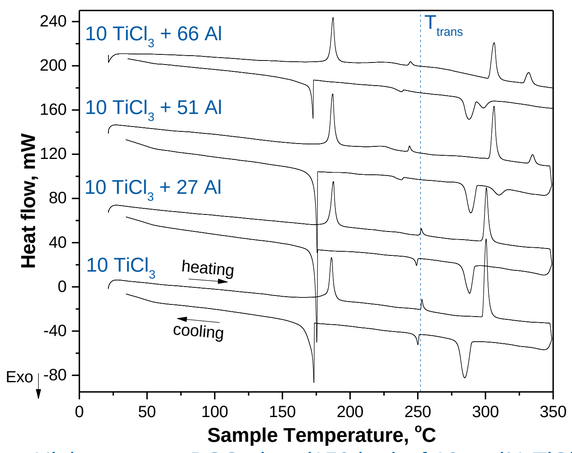
Influence of the aluminum addition

The addition of the higher amounts of Al leads to an additional signal in the DSC measurement which takes place at around 330 ^{o}C (at 150 bar). The fourth event is reversible and pressure dependent, thus must probably appear due to the decomposition of NaH or an unknown Na-Al-H phase.

The temperatures during decomposition of 10 mol% $TiCl_3$+ 66 mol% Al doped $NaAlH_4$

Pressure, bar	Onset temperature, ^{o}C			
	$T_{1\ des}$	T_{trans}	$T_{2\ des}$	$T_{3\ des}$
100	179.8	242.8	280.8	307.7
120	182.1	242.2	290.4	318.6
150	184.5	242.9	302.8	328.2
200	186.4	-	339.5	351.8

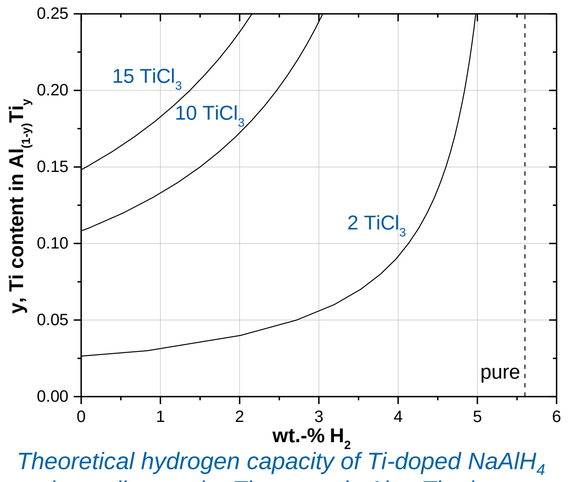
It is important to note that with 27 mol% of Al excess in 10 mol% doped $NaAlH_4$ the additional event is not present. It appears when 51 mol% of Al was added and becomes more pronounced with 66 mol%.



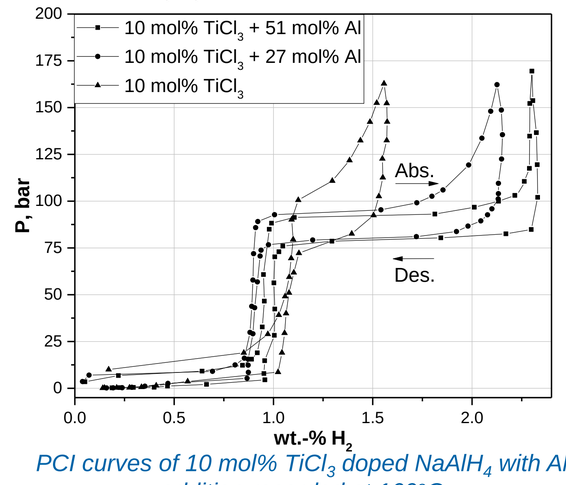
High-pressure DSC plots (150 bar) of 10 mol% $TiCl_3$ doped $NaAlH_4$ with Al addition

Based on the cyclable hydrogen content it can be estimated which phase was formed. From this assumption the lacking amount of Al can be calculated and the necessary Al excess can be added:

$$NaAlH_4 + x\ TiCl_3 + 2lx\ Al \rightarrow (1\text{-}3x)\ NaAlH_4 + 3x\ NaCl + x/y\ Al_{1-y}Ti_y + 2kx\ H_2,\ k=(3\text{-}6y)/2y,\ l=(1\text{-}4y)/2y$$



Theoretical hydrogen capacity of Ti-doped $NaAlH_4$ depending on the Ti content in $Al_{(1-y)}Ti_y$ phase



PCI curves of 10 mol% $TiCl_3$ doped $NaAlH_4$ with Al addition recorded at 160^{o}C

5. Conclusion

In this study the hydrogen storage capacity of doped $NaAlH_4$ was improved noticeably by adding excess of Al, this impact is related to the possible Al-rich $Al_{(1-y)}Ti_y$ phase (y<0.25) formation. With the help of HP-DSC an additional reversible process was detected when a higher amount of Al was added to the system. The present study shows that the previously observed increase of the equilibrium pressure is not due to a destabilization of sodium alanate but results from a lack of aluminum. The observed phenomenon in the sodium alanate system will presumable be also applicable to related doped alanates.

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