Supplemental information

Towards a structure-performance relationship for hydrogen storage in Ti-doped $NaAlH_4$ nanoparticles

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Sample preparation

For the “Ti first” sample, the pore volume of the CNF (fishbone structure, pore volume 0.6 ml/g, prepared from syngas over Ni/SiO_2) was impregnated with $Ti(OBu)_4$ (≥97%, Sigma-Aldrich) in diethylether (0.15 mM. 10 mol % $Ti(OBu)_4$ compared to $NaAlH_4$) until the pore volume was completely filled. The diethylether was removed by drying the impregnated sample at room temperature. Subsequently, 8 wt% $NaAlH_4$ was impregnated using THF (1 ml solution per gram CNF) as a solvent. Next the sample was dried by cooling to -40 °C in an acetone-dry-ice bath followed by slow heating form -40 to 15 °C over a period of 3 h under reduced pressure (6 mbar). The sample will be referred to as “$NaAlH_4$-Ti/CNF”. All sample handling was performed in an inert atmosphere either using Schlenk techniques or using a glove box.

The “alanate first” sample of identical composition was prepared by reversing the impregnation order of $NaAlH_4$ and $Ti(OBu)_4$. CNF were first impregnated with $NaAlH_4$ in THF and dried at low temperature (-40 to 15 °C, see above) . Next, the material was allowed to heat up in an Ar atmosphere to room temperature and the $Ti(OBu)_4$ dissolved in diethylether was impregnated on the $NaAlH_4$/CNF. The sample was immediately cooled to -40 ^{o}C and dried as described above. This sample will be referred to as “Ti-$NaAlH_4$/CNF”. An undoped nano-$NaAlH_4$ with a similar $NaAlH_4$ loading of 8 wt% was prepared using the same procedure. This sample will be referred to as “$NaAlH_4$/CNF” and had alanate particle sizes from 20 - 30 nm.[3] For comparison, a bulk sample was prepared by ball milling $TiCl_3$ with purified $NaAlH_4$ (Ti:Al= 4.5 mol%) using a SPECS ball milling apparatus as described by Haiduc *et al.*[26] This sample will be referred to as “ball milled $TiCl_3$-$NaAlH_4$”.

Reloading of samples

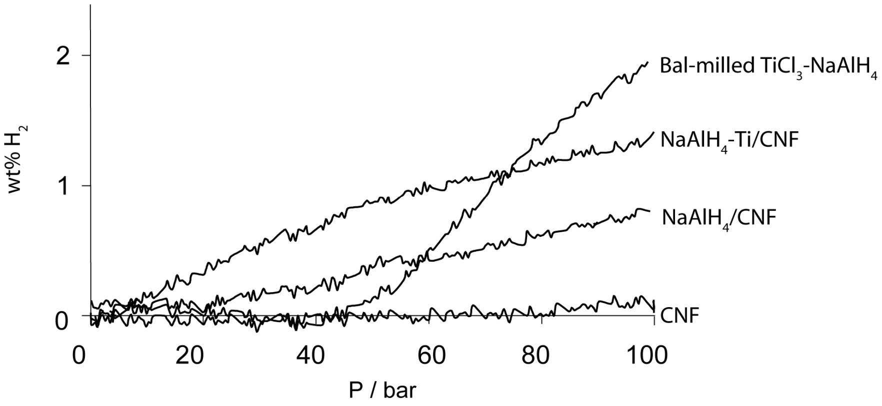

Figure S1: H_2 absorption for 1st absorption step at 115 °C. $\Delta P/\Delta t$ = 1.38 bar·min^{-1}; the uptake has been normalized to the mass of $NaAlH_4$

Figure S1 shows H_2 uptake profiles at 115 °C, after the first desorption at 250 °C, as function of pressure for $NaAlH_4$/CNF, $NaAlH_4$-Ti/CNF, ball-milled $TiCl_3$-$NaAlH_4$, and CNF. CNF (without $NaAlH_4$ or $Ti(OBu)_4$ deposition) did not shown any appreciable uptake from 0.1 to 100 bar H_2. Ball-milled $TiCl_3$-$NaAlH_4$ started to absorb H_2 from 45 bar H_2 pressure and absorbed 1.90 wt% H_2 at 100 bar.

$NaAlH_4$/CNF absorbed H_2 from a pressure of 20 bar and absorbed 0.85 wt% H_2 (normalized to the mass of $NaAlH_4$) at 100 bar. Table S1 shows that the absorption capacities in the second and third cycles were respectively 0.18 and 0.26 wt% H_2.

NaAlH4-Ti/CNF could be reloaded at an unprecedented low pressure of 10 bar; 1.38 wt% H2 could be reabsorbed after the first desorption. This number decreased to 0.76 and 0.53 wt % after the 2nd and 3rd cycle (Table S1). XPS studies (not shown here) indicated that after desorption NaH was highly dispersed over the support. This might make the recombination of NaH and Al with H_2 to $NaAlH_4$ difficult thus decreasing the hydrogen storage capacity in the next cycle.

EXAFS analysis

Table S1. Cycle tests of hydrogen absorption of $NaAlH_4$/CNF and $NaAlH_4$-Ti/CNF after desorption at 250 °C.

	1st Abs[+]	2nd Abs[+]	3rd Abs[+]
	wt% H_2	wt% H_2	wt% H_2
$NaAlH_4$-Ti/CNF [*]	1.38	0.76	0.53
$NaAlH_4$/CNF [#]	0.85	0.18	0.26

[*] The maximum H_2 absorption capacity is 2.50 wt% H_2.

[#] Maximum capacity is 5.6 wt% H_2 normalized to $NaAlH_4$ (assuming $NaAlH_4$ decomposes to NaH).

[+] In each desorption step > 90% of amount of hydrogen was released.

Table S2. Ti K-edge EXAFS fit of as prepared $NaAlH_4$-Ti/CNF and Ti-$NaAlH_4$/CNF. Δk= 3.3-11 $Å^{-1}$.

	Fitrange / Å	Atom	N	$\Delta\sigma^2$ / 10^3 $Å^{-2}$	R / Å	E_o / eV	k^2 variance Im.	k^2 variance Abs.
$NaAlH_4$-Ti/CNF	1.5-3.8	Ti-C	2.3	4.48	2.39	8.75	0.40	0.17
		Ti-Al	2.9	3.36	2.69	3.42		
		Ti-Al	1.6	9.08	3.09	1.81		
		Ti-Ti	0.7	-0.90	3.63	-3.10		
Ti-$NaAlH_4$-/CNF	1.3-2.9	Ti-O	3.9	7.03	2.02	2.18	0.09	0.07
		Ti-C	6.2	0.30	2.49	-12.20		

Ti-Ti	3.0	6.01		2.85	-0.13

Maximum free parameters is 18 or 19.

The EXAFS (data collected at station E4 at hasylab, Hamburg) fit of $NaAlH_4$-Ti/CNF revealed that Ti is on average surrounded with 2.3 C/O atoms at 2.39 Å in its first shell (Table S2). In the next two shells, 2.9 Al atoms at 2.69 Å and 1.6 Al atoms at 3.09 Å were fitted. The first Ti atom was found at 3.63 Å with a coordination number of 0.7. The fit parameters of Ti-$NaAlH_4$/CNF reveal that Ti is surrounded with 3.9 O/C atoms at 2.02 Å and 6.2 C/O atoms at 2.49 Å. In the next shell, 3 Ti atoms are present at 2.85 Å.

The absence of Na or Al atoms in the local structure of Ti-$NaAlH_4$-/CNF indicates that Ti did not interact with the $NaAlH_4$ to a level detectable by EXAFS (10%). Since the local structure comprised the same atoms as the original Ti-precursor ($Ti(OBu)_4$), it is concluded that the majority of “Ti” was present as nanoparticles of $Ti(OBu)_4$, or a decomposition product thereof, in the as-prepared Ti-$NaAlH_4$/CNF. The large value of E_0 for the Ti-C absorber-scatter pair indicates that the nature of the Ti-C bond is different from that in the used reference compound (TiC).

Fitting of the EXAFS of $NaAlH_4$-Ti/CNF revealed that 2.3 C atoms at 2.39 Å surround the Ti atom in its first coordination shell. Please note that C and O are indistinguishable but chemical knowledge is used to discriminate between C and O. The Ti-C shortest bond distance in TiC is 2.16 Å.[S1] The strong deviation to the Ti-C distance of 2.39 Å in $NaAlH_4$-Ti/CNF indicates that TiC did not form. Most logically, the carbon atom originated from the CNF support, implying that the Ti species was highly dispersed on the surface of the CNF. This might also explain the large E_0 value i.e. the Ti-C bond in the sample is dissimilar to that in the Ti-C reference. In addition the carbon scatterer in this sample is also different from that in Ti-$NaAlH_4$/CNF as seen from the Ti-C bond length and different E_0 values. Part of the difference in E_0 values can beexplained by a difference in oxidation state of the Ti, which is higher in butoxide-doped samples, as observed before for bulk samples.[S2] In the next shells 2.9 Al atoms were fitted at 2.69 Å and 1.6 Al atoms at 3.09 Å. The presence of Al atoms in the local structure indicates that the $Ti(OBu)_4$ reacts with $NaAlH_4$ during the synthesis.

Ti-Al distances in ball milled $TiCl_3$-$NaAlH_4$ range from 2.71 to 2.92 Å.[S2-5] The shortest distance is comparable to that found for the first Ti-Al shell present in our samples. However the longer Ti-Al distance in our samples (3.09 Å; Table 4) is significantly longer than reported before. It has been calculated however, that Ti-Al distances differ for Ti in $NaAlH_4$ nanoparticles in comparison to bulk Ti-doped $NaAlH_4$.[S6] The total coordination number of all the closest shells around Ti is 7.5, which is considerably smaller than the coordination number of 12 in bulk materials. Thus suggesting that our particles deviate significantly from bulk material. Therefore the long Ti-Al distance observed in this study might be the result of the changed properties of nano-sized alanate.[S7]

Since our samples have a total Ti-Al coordination number of 4.5 and a Ti-Ti coordination number of 0.7 the total Ti:Al ratio in our particles is ~1:6.4. Thus the TiAlx species have an average stoichiometry of $TiAl_{6.4}$.

Ex-situ XRD

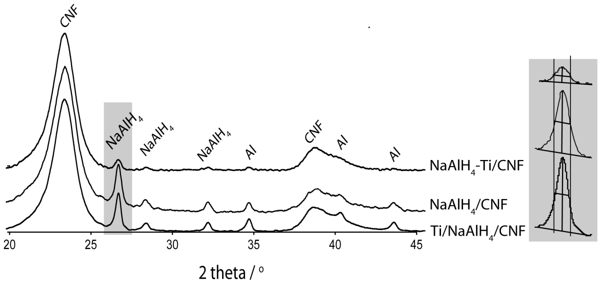

Figure S2 XRD from $NaAlH_4$/CNF, Ti-$NaAlH_4$/CNF and $NaAlH_4$-Ti/CNF at 25 °C ($\lambda = 1.4$ Å).

Figure S2 shows the X-ray diffraction patterns of as-prepared $NaAlH_4$/CNF, Ti-$NaAlH_4$/CNF and $NaAlH_4$-Ti/CNF at room temperature. Two broadened CNF diffractions were present at $2\theta = 23.55°$ and $38.86°$. $NaAlH_4$ was detected at 2θ values of 26.85°, 28.56° and 32.33°. The inset in Figure 2 shows the full width at half maximum (FWHM) of the $NaAlH_4$ diffraction and indicates that they were comparable for all measured samples. Using the Debye-Scherrer equation, a crystallite size of ~20 nm was calculated for the crystalline part of the samples. Ti containing species were never observed in the XRD studies indicating that those were XRD amorphous. Diffraction lines at $2\theta = 34.79°$, 40.34° and 43.70° were ascribed to Al and indicate that the samples lost H_2 during sample handling i.e., $NaAlH_4 \leftrightarrow NaH + Al + 1\frac{1}{2} H_2$ (eq 1).

Potential pathways for hydrogen desorption

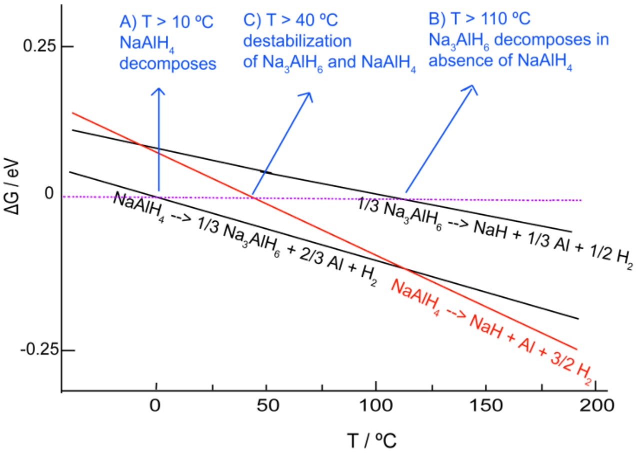

Figure S3. Temperature dependent differences for free energy change for the decompositions of $NaAlH_4$ and Na_3AlH_6 (black lines), data derived from Ke and Tanaka.[S8] Red line is the free energy change for the one-step decomposition of $NaAlH_4$ to NaH and Al.

Figure S3 shows that between (40 °C < T < 110 °C) $NaAlH_4$ can react with Na_3AlH_6 to form NaH, Al and H_2. In other words the change in Gibbs free energy of the combined reaction i.e. decomposition of $NaAlH_4$ plus decomposition of Na_3AlH_6 is more favourable. In contrast, the decomposition of Na_3AlH_6 as such has a positive ΔG in that temperature range thus does not occur spontaneously. This implies that more hydrogen can be liberated from $NaAlH_4$ by combining the two reactions at a temperature range where Na_3AlH_6 is still thermodynamically stable. A speculative explanation is that the $NaAlH_4$ reacts to Na_3AlH_6 (reaction 1) as an intermediate step followed by a very fast reaction between Na_3AlH_6 and remaining $NaAlH_4$, reaction (2). When reactions 1 and 2 are added together, it leads to the proposed direct decomposition of $NaAlH_4$ to H_2, NaH and Al (reaction 3). Apparently this combination of reactions (1) and (2) only occurs with nano-sized sodium alanate as indicated by the XRD study reported in Figure 2; bulk materials decompose via a two step mechanism with the formation of the Na_3AlH_6 intermediate.

(1) $3\ NaAlH_4 \leftrightarrow Na_3AlH_6 + 2\ Al + 3\ H_2$

(2) $[\ Na_3AlH_6 + NaAlH_4 \rightarrow 2\ NaH + 2\ NaAlH_4\ ]$

-- +

(3) $2\ NaAlH_4 \leftrightarrow 2\ NaH + 2\ Al + 3\ H_2$

The formation of NaH was not observed throughout the experiment which indicates that NaH was either amorphous, or in the form of nanoparticles smaller than 10 nm.

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