

Structure of Ti in TiCl₃ Doped NaAlH₄

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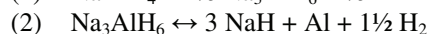
Abstract. To elucidate the structure of Ti in Ti-doped sodium alanate used for hydrogen storage, XAFS studies were performed. In freshly prepared samples the majority of the Ti is present in interstitial positions in the NaAlH₄. By increasing the desorption temperature, thus increasing the extent of hydrogen desorption, Ti migrates into the Al, finally forming a less active TiAl₃ alloy.

Keywords: Enter Keywords here. Titanium, XAFS, EXAFS, hydrogen storage, sodium alanate

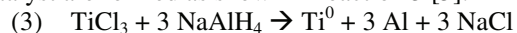
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INTRODUCTION

Hydrogen is regarded as a promising energy carrier for future society. The challenge to overcome is the safe storage of hydrogen with limiting energy losses during the storage and release process for transportation purposes. Sodium alanate (NaAlH₄) is a potential candidate for storage, since it has suitable thermodynamics and a satisfactory storage capacity [1,2]. However, the main difficulty with sodium alanate is the slow kinetics for hydrogen release and absorption. The steps in which hydrogen is desorbed are shown in equations 1 and 2.



The unfavorable hydrogen desorption and absorption rates can be improved by decreasing the NaAlH₄ particle size [3] or by adding a Ti-catalyst to the alanate, for example TiCl₃ [1,4]. The most active catalyst is prepared via ball-milling. When NaAlH₄ is ball milled with TiCl₃, NaCl, Al-metal and the Ti-catalyst are formed as shown in reaction 3 [5].



The exact role and composition of the catalytic Ti species have been heavily researched in the past years but has not been elucidated so far. In literature, the characteristics of Ti in sodium alanate have resulted in contradictory results. In some experiments Ti has been found to remain on the surface of the alanate crystallites [6] whereas in others Ti has been found to exchange with the Na sites [7]. Other experimental studies indicate that Ti alloys with Al upon doping [4,8]. Although the characteristics of the various Ti species have been investigated separately, the

distribution of the Ti over the various locations has not been addressed and is described here.

This study deals with the investigation of the local structure of Ti in TiCl₃ ball milled NaAlH₄ as a function of desorption temperature. The latter is of crucial importance since the desorption temperature has a significant effect on the rate of the subsequent absorption step [4]. Fast desorption is favored by high temperatures (>225°C), however, the rates for the subsequent hydrogen absorption step of the material are then significantly lowered and might be related to the state of the Ti catalyst. The local environment of Ti after desorbing samples at different temperatures has been studied with XAFS at the Ti K-edge.

EXPERIMENTAL

Sample Preparations

All sample preparations were performed under a nitrogen or argon atmosphere in a glovebox. Chemical operations were conducted using Schlenk techniques. The samples were obtained from the authors of ref. 4 to ensure a fair comparison of results. The freshly doped sample is referred to as 'SAH-start'. After desorbing this sample at either 125 °C, 225 °C or 475 °C with a ramp of 5°C/min. the samples are respectively called 'SAH-125', 'SAH-225' and 'SAH-475'. The XRD diffraction patterns, desorption curves of the first desorption step and hydrogen storage capacities were identical to those in [4] (not shown here).

EXAFS

X-ray absorption spectroscopy was performed on the Ti-K-edge at station E4 of the DESY synchrotron (Hamburg, Germany). The storage ring was operated at 4.4 GeV with a mean current of 120 mA. The measurements were performed at 77 K in flowing He using a Si (111) double crystal monochromator, which was detuned to 80% to suppress higher harmonics. The samples (11 mg of Ti-doped NaAlH₄ or 6 mg TiAl₃) were diluted with BN and had a total absorption of 2.55. All sample preparations were done in a glovebox, and transferred to the beam-line in a closed cell.

Extraction of the EXAFS data (average of three scans) from the measured absorption data was performed with the XDAP program [9]. The Ti-Al backscattering amplitude and phase shift were calculated using the FEFF 8.2 code [10] and calibrated using an experimental measured spectrum of TiAl₃ at 77 K, i.e. the input parameters v_r , S_0^2 and the Debye Waller factor were adjusted in such a way that the structural parameters for the reference compound match the crystallographic data, $\Delta\sigma^2=0$ and $E_0=0$ eV. An experimentally recorded Ti foil at room temperature was used to calibrate the Ti-Ti calculated reference. The used FEFF input parameters were similar to those in [8] and [11].

Experimental data was fitted in k^2 using the difference file technique in R-space [12] from $3 < k < 10$ or $3 < k < 12$ ($\text{\AA}^{-1}$) depending on the quality of the data. The quality of the fit was checked by applying k^1 , k^2 and k^3 weightings.

RESULTS AND DISCUSSION

An XRD study (data not shown) confirmed that our samples show identical behavior to those reported by

Geerlings and coworkers [4]. However, using XRD to characterize the amorphous Ti phase is cumbersome. This challenge can be addressed using XAFS spectroscopy since it does not need long range ordering of the atoms in the samples.

Figure 1 shows the k^1 weighted Fourier transform data of SAH-start, SAH-125, SAH-225 and SAH-475 (top panel magnitude; lower panel the imaginary part). From the changes in the magnitude, and position of the nodes in the imaginary part it can be concluded that the local environment around Ti changed significantly as function of desorption temperature.

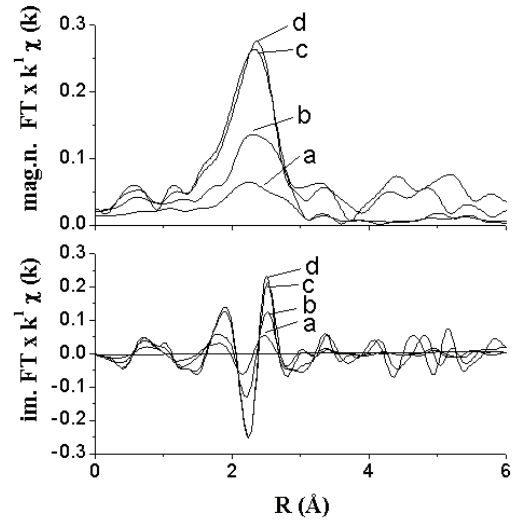


Figure 1. FT (k^1 , $k=3-12 \text{ \AA}^{-1}$) of EXAFS of SAH-start (a); SAH-125 (b); SAH-225 (c) and SAH-475 (d). Top panel: magnitude; lower panel: imaginary part.

The fit parameter for these samples are shown in Table 1. In addition the structural parameters for TiAl₃ are included in that table as well. Ti was in the first coordination shell always surrounded by Al

TABLE 1. EXAFS fits of SAH-start, SAH-125, SAH-225, SAH-475 and TiAl₃

Name	Shell	Scatterer	N	$\Delta\sigma^2$ ($10^3 \text{ \AA}^{-2}$)	R (Å)	E_0 (eV)
SAH-start	1	Al	2.3	0.04	2.71	-0.96
	2	Al	2.5	0.18	2.89	0.96
	3	Ti	1.9	0.81	3.52	1.93
SAH-125	1	Al	3.9	0.20	2.76	-1.19
	2	Al	4.6	0.20	2.92	0.23
	3	Ti	1.3	2.7	3.49	4.3
SAH-225	1	Al	4.6	0.10	2.73	1.53
	2	Al	7.8	0.82	2.84	4.97
	3	Ti	3.8	6.36	3.90	4.31
SAH-475	1	Al	4.2	0.36	2.75	3.11
	2	Al	8.3	1.95	2.89	3.70
	3	Ti	3.8	3.25	3.84	5.44
TiAl ₃	1	Al	4.0	0.00	2.73	-0.47
	2	Al	8.0	1.53	2.88	4.12
	3	Ti	4.0	4.83	3.89	1.85

Estimated errors: N:10%; $\Delta\sigma^2$: 5%; R:1%; E_0 :10%

located in two subshells at a distance of 2.7 and 2.9 Å. In the third shell, Ti was found at a longer distance. The fit for TiAl_3 exactly matches the known crystallographic data [15] of this sample (please note that the first Ti-Al shell was used to calibrate the Ti-Al reference (see experimental). The structural parameters of SAH-475 and SAH-225 are close to those of the TiAl_3 reference.

Here we will focus on the location of Ti in SAH-start. When Ti interacts with NaAlH_4 , it has been reported that Ti can substitute Na [7,13,14], or occupies an interstitial position in between three AlH_4^- units [16]. In the case that Ti substitutes Na, the resulting Al-Ti distance would be approximately 3.5 Å, which is a distance that was not observed for Ti-Al scattering in our EXAFS analysis. Therefore we conclude that the Ti did not substitute Na to a measurable extent. When Ti resides in an interstitial of the NaAlH_4 lattice, the DFT calculated Ti-Al distance is approximately 2.6 Å [16]. This distance is, within the error limits of the calculation, similar to that found in the EXAFS analysis. Three aluminum atoms surrounded the Ti in this specie. If every Ti atom would be in these interstitials, the coordination number of Ti-Al in EXAFS analysis would be 3. In our analysis, the Ti-Al coordination number is 4.8, thus the Ti must be present in another phase as well. We believe that Ti is incorporated in the surface of Al metal since then the Ti-Al distance is expected to be in the range of 2.7-2.9 Å [6], which is in agreement with our EXAFS analysis (Table 1). In this case 9 aluminum atoms surround the Ti, and the Al sphere would have a total coordination number of 9. Based on the use of fractional coordination numbers, it can be calculated that 30% of the Ti resided on the Al surface.

As can be seen in Table 1, after heat treatments the Ti-Al coordination increases with increasing desorption temperature. At the higher temperatures (225 and 475°C) the structural parameter of the samples are almost identical to that of TiAl_3 indicating the formation of an alloy at higher temperature. At the intermediate temperature the situation is more complex and will be discussed in a full paper. But it is clear that a transition occurs from Ti located in the interstitial spaces to a bulk alloy. Since the rates of hydrogen are enhanced when Ti catalyst is added, we believe that the presence of Ti in the interstitial spaces is essential for fast desorption of hydrogen. The full paper will contain additional information regarding the structure active for hydrogen absorption in sodium alanate.

CONCLUSIONS

XAFS spectroscopy is very suitable to study the evolution of the amorphous Ti-species in Ti-doped sodium alanates. Ti located in the interstitial spaces of the alanate is most likely facilitating hydrogen desorption in these samples.

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