

Chemical State and Local Structure around Titanium Atoms in NaAlH₄ Doped with TiCl₃ Using X-ray Absorption Spectroscopy

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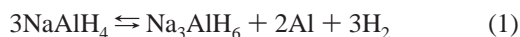
Received: March 30, 2004; In Final Form: July 30, 2004

X-ray absorption spectroscopy is applied to investigate NaAlH₄ doped with 5 mol % TiCl₃ by ball milling. XANES analysis indicates that after the ball milling Ti species are reduced from Ti (+3) to Ti (0). Release or absorption of hydrogen does not affect the chemical state obtained after ball milling. EXAFS analysis shows that the Ti atoms are associated only with Ti as next neighbors in the ball-milled state as well as during subsequent desorption and absorption of hydrogen. Furthermore, an increase of the particle size and an ordering of the local structure is seen to evolve with the desorption and the absorption of hydrogen.

Introduction

Among the hydrogen-storage technologies, low- and medium-temperature complex metal hydrides are promising because of their high storage capacity and low cost. Unfortunately, the slow kinetics and the irreversibility of the decomposition reaction at moderate conditions have limited their applications. Various attempts have been made to circumvent these disadvantages. In complex aluminum hydrides, the most successful one has been to add a transition-metal-based dopant.¹

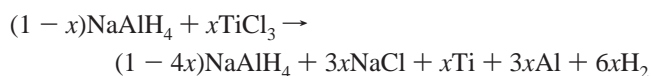
In the case of sodium alanate, Ti-based dopants are most active for improving the kinetics of the reaction. Thus, the first two hydrogen exchange reactions [(1) and (2)] can be made reversible under moderate temperatures and pressures. The third step occurring at temperatures higher than 400 °C is not considered for practical purposes.



From the first two steps a reversible hydrogen capacity of 5.6 wt % is expected. However, this amount of reversible hydrogen has never been reached experimentally and moreover decreases with increasing amount of dopants.² The values of 37 and 47 kJ/mol for the enthalpy of the decomposition reaction for the first and second step, respectively, indicate that sodium alanate is a medium-temperature hydride. The kinetics of the hydriding/dehydriding reaction depends on the nature of the precursor^{3–6} and on the doping procedure.^{3,6,7} So far, for sodium alanate the highest reaction rate for both absorption and desorption was achieved using a Ti cluster, Ti₁₃·6THF (THF = tetrahydrofuran) as a dopant.^{8,9} Indeed, around 4.5 wt % of hydrogen can be released in less than 60 min at 150 °C under

a residual hydrogen pressure of 0.5 bar and reloaded in a range of 10–15 min at 100 °C under 100 bar of hydrogen pressure.

A better understanding of the nature and the mechanism of the active catalyst will be of valuable interest in finding more effective catalysts and for modifying appropriately the properties of the material. So far, it has been suggested that a reduction of TiCl₃ occurs during the milling process² according to the following reaction:



However, X-ray diffraction (XRD),^{10,11} microscopic analysis (SEM = scanning electron microscopy),^{5,12} electron paramagnetic resonance spectroscopy (EPR),¹³ or infrared spectroscopy (IR)¹³ have not yet elucidated the chemical state and the local structure around the Ti atoms. Under these circumstances, X-ray absorption spectroscopy (XAS) appears to be well-suited to investigate the local atomic environment around Ti at different stages of the absorption/desorption reaction in sodium alanate doped with a Ti-based catalyst. Indeed, this technique is a local structural probe with elemental sensitivity. Moreover, the method allows the investigation of the chemical state and the geometric and electronic structure of small nanoparticles. Valuable information can then be gained concerning the number, the types, and the distances of neighboring atoms around the selected central site.¹⁴

In this paper, we report on the evolution of the chemical state of Ti as well as on the local structure around Ti atoms after ball milling and during two different defined stages of the absorption/desorption reaction in sodium alanate doped with 5 mol % TiCl₃.

Experimental Methods

All sample preparations were done in an argon-filled glovebox equipped with a recirculation system to keep the water and oxygen concentrations below 1 ppm. Chemical operations were performed on the bench under purified nitrogen using Schlenk tube techniques. Commercially available NaAlH₄ (Chemetall, Frankfurt, Germany) was purified by a Soxhlet extraction with

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TABLE 1: Sample Description

labels	sample description
(TiCl ₃)	TiCl ₃ as received
(Ti)	Ti metallic foil
(bm)	NaAlH ₄ + 5 mol % TiCl ₃ , ball-milled 30 min at 600 rpm
(dd)	NaAlH ₄ + 5 mol % TiCl ₃ , quenched once 2.6 wt % of hydrogen is released ($T = 150\text{ }^{\circ}\text{C}$, $p_{\text{H}_2} = 0.3\text{ bar}$)
(da)	NaAlH ₄ + 5 mol % TiCl ₃ , quenched once 2.3 wt % of hydrogen is absorbed ($T = 100\text{ }^{\circ}\text{C}$, $p_{\text{H}_2} = 100\text{ bar}$)

THF as described elsewhere.⁸ According to elemental analysis the purified NaAlH₄ contained $7.6 \pm 0.1\text{ wt \% H}$ and $0.2 \pm 0.1\text{ wt \% C}$.

The sample doped with a Ti-based catalyst was prepared using TiCl₃ (99.999%, Sigma Aldrich). In an argon glovebox, a silicon nitride vial containing balls made of the same material was filled with 2 g of purified sodium alanate and 285 mg of TiCl₃ and sealed. The ball to powder weight ratio was about 20:1. The milling was carried out in a Fritsch P6 planetary mixer/mill at 600 rpm for 30 min.

Absorption and desorption of hydrogen were carried out in a modified Sieverts apparatus. A more detailed description of the apparatus and the reactor used can be found elsewhere.^{8,15} We have investigated the evolution of the local structure around Ti on samples quenched at a defined degree of the dehydrogenation-rehydrogenation reaction (cf. Table 1).

X-ray absorption spectroscopy was performed on the samples at the Ti K-edge (4966 eV). The measurements were carried out at the ANKA-XAS beam line, Forschungszentrum Karlsruhe, Germany. The ANKA storage ring was operated with an electron beam of 2.5 GeV and a mean electron current of 100 mA. The X-ray monochromator, equipped with a pair of Si {111} crystals ($2d = 6.271\text{ \AA}$), was operated in fixed-exit mode. The Ti K-edge X-ray absorption spectrum of a Ti metal foil was measured for energy calibration in transmission mode. Ti metal was also used as a reference sample. Due to the low concentration of Ti in the doped sodium alanate samples, these spectra were taken in a fluorescence mode at room temperature, collecting Ti K α radiation ($\sim 4510\text{ eV}$) by a solid-state detector (five-element Canberra LEGe). An air-filled ionization chamber at 0.4 bar gas pressure was used to monitor the incident intensity of the beam. Spectra were recorded at 5 eV step width in the pre-edge region 1 (4816–4916 eV), 2 eV in the pre-edge region 2 (4916–4946 eV), 0.5 eV at the rising edge (4946–5006 eV), and equidistant k -steps (0.03 \AA^{-1}) in the post-edge region (5006–5941 eV). Up to nine scans were averaged to improve the signal-to-noise ratio. The sample holder was a specially designed cell, which allowed the samples to be prepared, transferred, and measured without exposing them to air. It consisted of a cavity ($15 \times 5 \times 1\text{ mm}$) carved into an Al block, which was filled with the powder. The latter was sealed with a viton O-ring and a lid consisting of an aluminum frame with a metallized polymer film window ($50\text{ }\mu\text{m}$).

EXAFS (extended X-ray absorption fine structure) data analysis was based on standard least-squares fit techniques¹⁶

using the UWXAFS¹⁷ program package. To extract the EXAFS signal $\chi(k)$, the atomic background function $\mu_0(E)$ was optimized with respect to spurious contributions below $\sim 1\text{ \AA}$ in the k -weighted Fourier transform (FT) of the data using *autobk* utility (Automated Background Removal for XAFS data). The ionization energy E_0 , the origin for calculation of the $\chi(k)$ function, was fixed at the first maximum in the derivatives of spectra of the Ti metal foil and the doped alanates. In the case of TiCl₃ it was settled to the maximum of the white line. The region investigated was up to about 800 eV above the Ti K-edge ($k \sim 13.5\text{ \AA}^{-1}$). Metric parameters (neighboring atomic distances R_i , mean square radial displacements or EXAFS Debye–Waller factors σ_i^2 , and coordination numbers N_i for the coordination shell i) were determined using the *feffit* code. Backscattering amplitude and phase shift functions for single scattering paths in a three-shell *hcp*-Ti metal cluster and a three-shell TiCl₃ cluster were obtained from FEFF8.2^{18,19} calculations (the phase of the TiCl₃ sample was determined from the diffraction pattern to be the β one with the following parameters: *hcp* cell with $a = 6.27\text{ \AA}$, $c = 5.82\text{ \AA}$, space group $P6_3/mcm$, $d(\text{Ti–Cl}) = 2.45\text{ \AA}$, $d(\text{Ti–Ti}) = 2.91\text{ \AA}$).²⁰ Prior to analysis, the k^2 -weighted EXAFS functions were Fourier-transformed over a k -space range of $\sim 2.5\text{--}13.5\text{ \AA}^{-1}$, using symmetric square windows with $\Delta k = 0.2\text{ \AA}^{-1}$ “Hanning sills”. All EXAFS refinements were performed in R -space over the individual radial distance ranges given in Table 2. The quality of the fit, “ R -factor” (last column of Table 2), which is χ^2 scaled by the magnitude of data, was evaluated with *feffit*.²¹ Typical values are a few percent, and a value of $R = 0.02$ signifies that the experimental and the theoretical value agree within 2%.

XANES spectra (X-ray absorption near-edge structure, i.e., the region which ends roughly 50 eV above the edge) for all samples were isolated from XAFS scans by subtraction of the pre-edge background absorption (approximated by a polynomial function) and normalization of the edge jump to unity to allow quantitative comparison.

Results and Discussion

Figure 1 represents the normalized Ti K-edge XANES of doped sodium alanate after ball milling (bm) and at different stages of the dehydrogenation (dd) and hydrogenation (da) reactions. The spectra are compared with the spectrum of TiCl₃ and the spectrum of metallic titanium (Ti), which is taken as reference. From the first derivatives of the spectra (not shown), it can be clearly seen that the first inflection point in the spectrum (bm) is lowered from 4972 eV for TiCl₃ to 4966 eV, coinciding with the position of Ti metal (Ti). This confirms earlier assumptions, that during ball milling the TiCl₃ is decomposed and the valence state of Ti is changed from (+3) to (0). Moreover, the analysis of the first inflection point in spectra (dd) and (da) shows that this valence state does not change neither during desorption nor absorption of hydrogen. Additionally, we can see that in the range from 4967 to 4973 eV (inset of Figure 1) the absorption curves of (bm), (dd), and

TABLE 2: Data Range and Metric Parameters Obtained by EXAFS Least-Squares Fit (S_0^2 Fixed at 0.6)

sample labels	fit range $R - \Delta$ (\AA)	shell	R ($\pm 0.02\text{ \AA}$) (\AA)	N (± 0.2)	σ^2 (\AA^2)	ΔE (eV)	R -factor
(TiCl ₃)	1.25–2.62	Cl	2.42	5.9	0.0028	5.3	0.02
(Ti)	1.4–3.2	Ti	2.91	12.0	0.0078	6.5	0.01
(dd)	1.65–2.91	Ti1	2.84	2.9 ^a	0.0056	−6.7 ^a	0.03
		Ti2	3.0	2.9 ^a	0.0049	−6.7 ^a	
(da)	1.36–2.91	Ti1	2.84	5.3 ^a	0.0050	−9.2 ^a	0.008
		Ti2	2.99	5.3 ^a	0.0042	−9.2 ^a	

^a Denotes that fit parameter are forced to be equal for both shells.

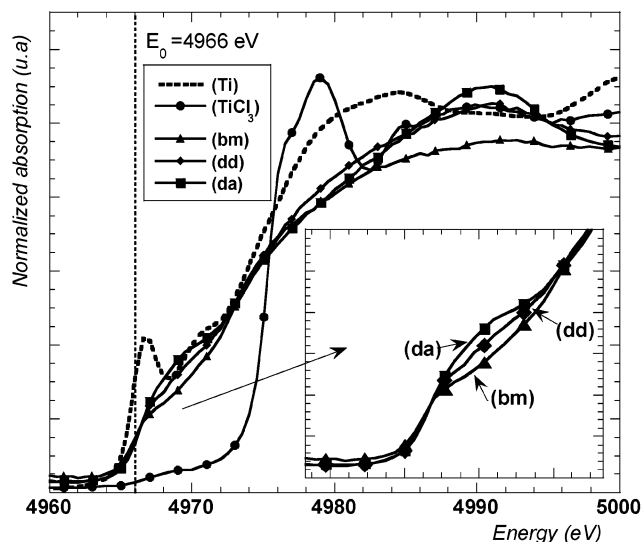


Figure 1. Normalized Ti K-edge XANES spectra of NaAlH₄ doped with 5 mol % of TiCl₃ at different stages. Samples are ball-milled (bm), after 2.6 wt % of hydrogen was released at 150 °C under a residual hydrogen pressure of 0.3 bar (dd) and after 2.3 wt % of hydrogen was reabsorbed at 100 °C under 100 bar of hydrogen (da). For comparison the spectra of TiCl₃ as received (TiCl₃) and pure Ti metal are presented (Ti). The vertical dashed line at 4966 eV corresponds to the first inflection point in the Ti K-edge XANES spectrum of the pure metal.

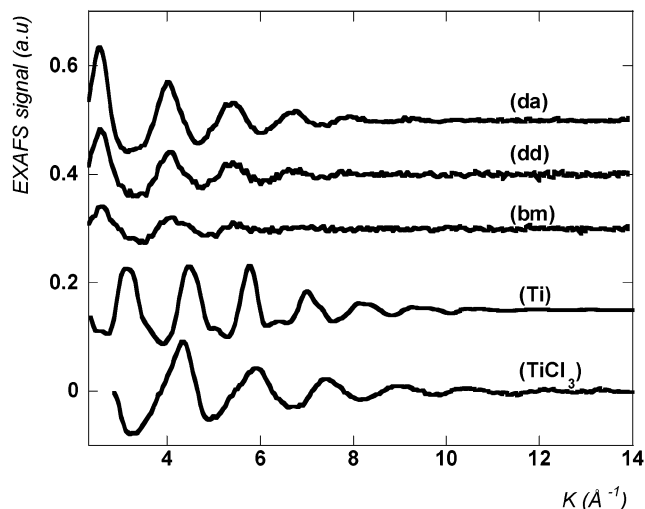


Figure 2. EXAFS spectra $\chi(k)$ of NaAlH₄ doped with 5 mol % of TiCl₃ at different stages corresponding to those of Figure 1.

(da) samples show differences in the shoulder at the rising edge. These low-energy features of 3d transition metals are due to changes in the electronic band structure (4p/3d hybridization) which depend on the particle size.²² Hence, the observed evolution may indicate that a growth or ordering of the Ti particles occurs going from sample (bm) over (dd) to (da). As shown in the following section, this is in agreement with the observation of the EXAFS amplitude increasing from (bm) via (dd) to (da).

Figure 2 displays the EXAFS functions $\chi(k)$ of the samples corresponding to those of Figure 1. Comparison of (TiCl₃) and (bm) spectra shows that the environment around Ti atoms changes significantly during the milling process. The strong reduction of the EXAFS amplitude indicates the strong distortion of the local order in that state. Furthermore, as the decomposition occurs in (dd), one can see that the oscillations reflecting the different structure in sample (bm) are intensified, becoming even more pronounced for the sample quenched during the rehydro-

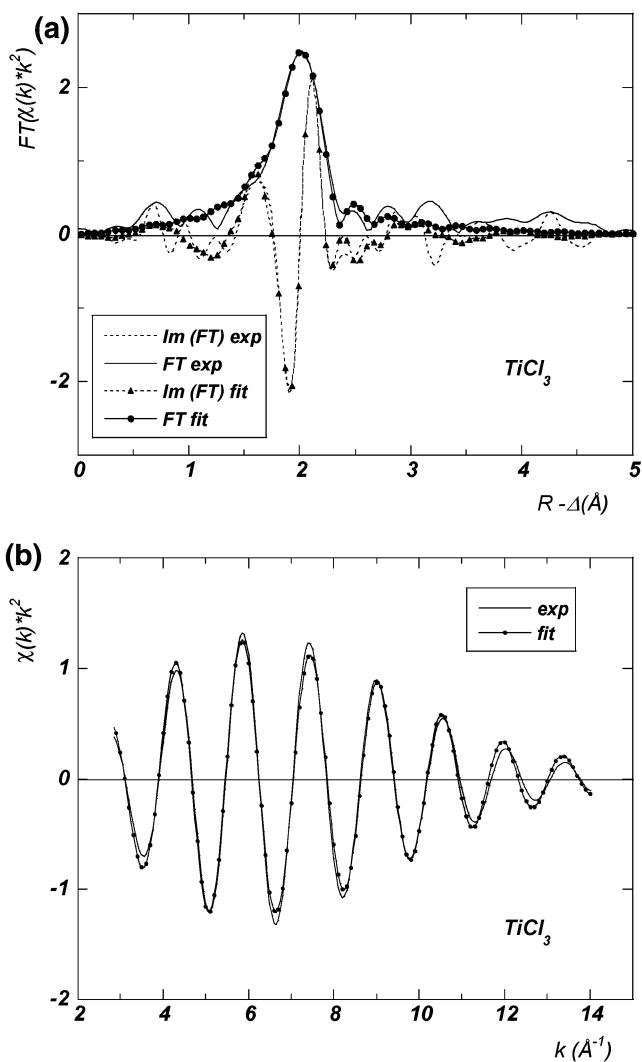


Figure 3. (a) FT magnitude and imaginary part, R -space fit magnitude and imaginary part of the TiCl₃; (b) Fourier filtered data and fit in k -space.

genation step (da). We conclude that the local order around Ti in TiCl₃ is destroyed after ball milling and another one is formed. This new local structure is even more pronounced during subsequent desorption and absorption of hydrogen.

EXAFS data fit analysis was carried out on samples (TiCl₃), (Ti), (dd), and (da). Analysis of sample (bm) was not attempted. The amplitude reduction factor²³ S_0^2 was determined to be about 0.6 in order to reproduce the theoretical coordination number of 12 for the first Ti neighbor shell in the metal and 6 for the first Cl neighbor shell in the TiCl₃. Such a low value for S_0^2 has also been reported by Carlson et al. for neighboring element of Sc ($S_0^2 = 0.62$).²⁴

The metric parameters obtained from the least-squares fitting are presented in Table 2. Figures 3a, 4a, and 5a represent the magnitude and imaginary part of the Fourier transform as well as the fit in R space of samples (TiCl₃), (Ti), and (da), respectively. Figures 3b, 4b, and 5b display the corresponding Fourier filtered data and the fit in k -space.

Figure 3 represents the result for the TiCl₃. The coordination number and the Ti–Cl interatomic distance were found to be 5.9 and 2.42 Å, respectively (cf. Table 2). These extracted structural parameters obtained by fitting the EXAFS signal from TiCl₃ powder are in agreement with the published crystallographic data (six Cl with $d(\text{Ti}–\text{Cl}) = 2.45$ Å).²⁰

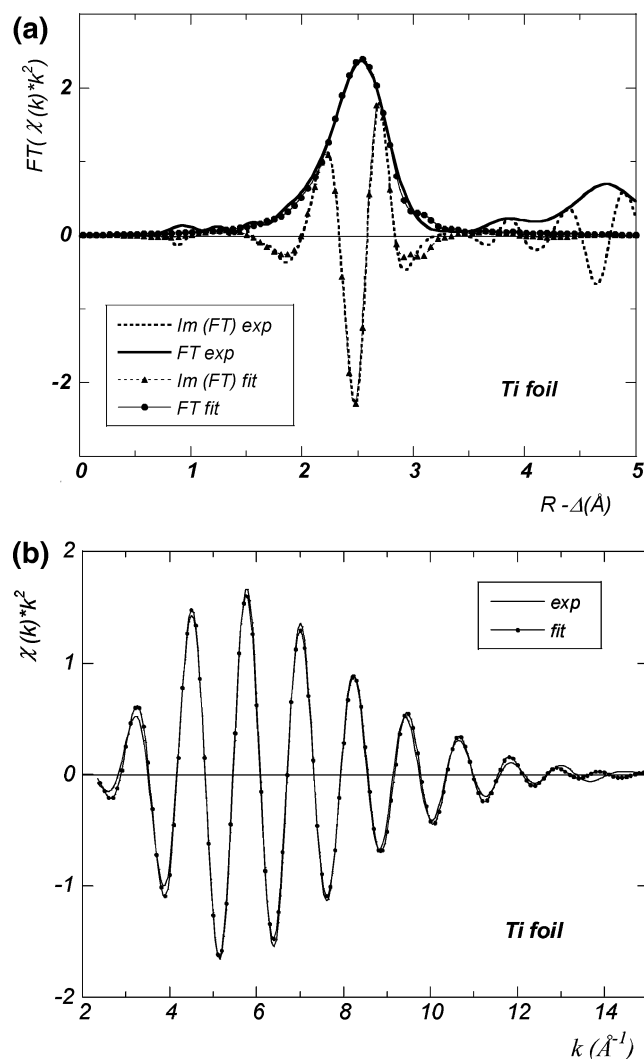


Figure 4. (a) FT magnitude and imaginary part, R -space fit magnitude and imaginary part of the Ti foil; (b) Fourier filtered data and fit in k -space.

Figure 4 refers to the metallic Ti. The coordination environment in that case is characterized by the slight distance splitting of the *hcp* structure (12 atoms) between the six first neighbors at 2.896 Å, which are in a plane and the six second next neighbors at 2.95 Å, which are above (three of the six atoms) and below (three others) the previous plane. This slight distance deviation within the first coordination sphere can be seen from the beat node²⁵ in the Fourier-filtered data visible above 14 Å⁻¹ (Figure 4b). However, the bond length resolution in EXAFS defined by $\Delta R \approx \pi/2k_{\text{max}}$ is limited to 0.11 Å in this study. That is why the fitting of the Ti metal first shell was carried out with a single distance (2.91 Å) of Ti neighbors. The latter explains the relatively high Debye–Waller factor of 0.0078 Å², Table 2, for the 12 Ti atoms at a mean distance of 2.91 Å.

Comparison of both the FT magnitude peak, $FT(\chi(k)k^2)$, and the corresponding filtered data, $\chi(k)k^2$, of samples (dd) (not shown) and (da) shown in Figure 5 a,b with the metal (Figure 4a,b) and TiCl₃ (Figure 3a,b) reveal the much higher asymmetry in the Ti first coordination sphere of these samples quenched during the decomposition and the absorption of hydrogen. From the beat node around 11 Å⁻¹, the presence of two closely spaced backscatterers with the same atomic number must be assumed. The distance separation between the two atoms can be derived from $\delta R \approx \pi/2k_{\text{bn}}$, where k_{bn} denotes the beat-node position in k -space. For sample (dd) we found a distance separation of 0.154

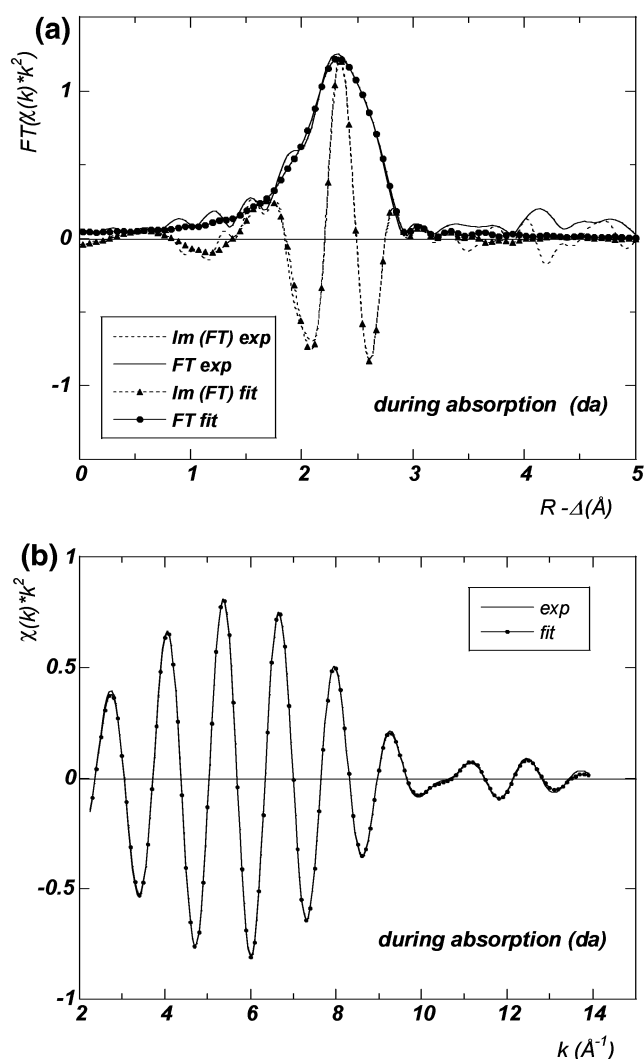


Figure 5. (a) FT magnitude and imaginary part, R -space fit magnitude and imaginary part of sample da; (b) Fourier filtered data and fit in k -space.

Å and for sample (da) a distance separation of 0.14 Å. Hence, inclusion of two scattering paths is mandatory to model the EXAFS data. The fit results, Table 2, with two Ti backscatterers are in agreement with the estimated distance separation from the beat-node position. It should be noted that the fit fails upon inclusion of Cl backscatterers as well as for an Al shell. These results indicate that neither significant amounts of TiCl₃ are present in samples (bm), (dd), and (da) nor formation of a Ti/Al alloy takes place. As already concluded from XANES, EXAFS confirms the significantly higher local order around Ti in sample (da) as compared to sample (dd) (see apparent coordination numbers and Debye–Waller factors in Table 2), indicating that a partial annealing takes place upon the hydrogen exchange. The local order in the ball-milled samples is somehow compatible with a strongly distorted *hcp* structure, reflecting the strain as a consequence of the mechanical stress exerted by the milling procedure.

In the literature, two hypotheses have been suggested concerning the chemical state of the titanium species when used as catalyst in alanates. The first speculates that during the doping procedure Ti(0) species are formed and that the active catalyst is a Ti/Al alloy.^{1,11} The second one claims that the dopants are substituted into the lattice of the bulk hydride.^{26,27} From the XAS measurements, it is shown that Ti(0) species are effectively formed during the doping procedure, and it remains zerovalent

during desorption and absorption of hydrogen. The formation of an alloy with Al or the formation of TiH_2 is not supported from the present EXAFS data.

Conclusions

In the present study, the chemical state of Ti in NaAlH_4 doped with TiCl_3 has been identified using XANES spectroscopy. It has been shown that a reduction of the initial TiCl_3 occurs during the ball-milling process. This result has been confirmed, meanwhile, by XPS measurements. After ball milling the Ti is in the zero-valence state and remains so during the desorption and absorption of hydrogen. Moreover, the local order around Ti is more pronounced in the absorbed state as compared to the decomposed or the ball-milled one. This may be due to the formation of larger particles upon hydrogen uptake. EXAFS analysis indicates that the local structure around the Ti atoms consists only of Ti neighbors after ball milling and during subsequent release and uptake of hydrogen. The structure formed after ball milling is close to that of metallic titanium but in a more distorted state. However, the local order evolves and tends to a higher order from the ball-milled state to the absorbed one. There are no hints indicating the formation of an alloy with Al or the formation of TiH_2 .

Acknowledgment. Financial support by the “Forschungsallianz Brennstoffzelle Baden-Württemberg” is gratefully acknowledged. We appreciate beam-time allotment by ANKA and experimental assistance by Stefan Mangold and the ANKA-ISS staff.

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