

Synchrotron X-Ray Studies of Ti-Doped NaAlH₄

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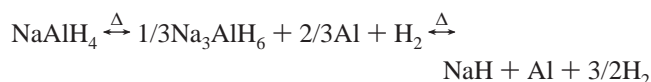
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Pure and doped NaAlH₄ with 5 mol % Ti on the basis of Ti₁₃•6THF have been investigated by means of X-ray synchrotron radiation. The Rietveld method has been used to study the possible substitution of Ti inside the NaAlH₄ structure and/or the presence of vacancies. This study indicates that there is no significant variation of the lattice parameter once the Na Alanate is doped with the Ti cluster. From the refinement of the site occupation factors, the substitution of Ti on the Na site can be excluded. A slight improvement was found when Ti was substituted on the Al site, but it is not significant enough to say that Ti definitely substitutes for Al in the Alanate phase. Additionally, there is no evidence for vacancy formation in Ti-colloid-doped sodium Alanate.

Introduction

For the use of hydrogen in mobile applications, the development of compact, light, safe, and cost-effective hydrogen storage is necessary. Different techniques for storing hydrogen on board a vehicle are being discussed and have been reviewed in several papers (e.g., Schlapbach and Züttel¹). Among the proposed methods, a principle advantage of storing hydrogen in chemical form, for example, as an atom in a metal hydride, is the high volumetric storage density which can be achieved by this method.

Some years ago, Bogdanovic and Schwickardi² found that reversible hydrogen storage is possible on transition-metal-doped NaAlH₄ under moderate conditions. Of these precursors, Ti-based materials have appeared to be the most efficient ones in terms of kinetics and hydrogen storage capacity when added to the Alanate. Since this discovery, many studies have been performed in order to understand the role of a Ti catalyst in sodium Alanate (SAH), but until now, the working mechanism is still not clear. The decomposition of Na Alanate and the reversible reaction occur through a two-steps reaction (giving 5.6 wt % of H₂)



Different scenarios have been proposed to explain the mechanism by which the doping metal might enhance the kinetics of the NaAlH₄ decomposition–recombination reaction.^{3–8} Some of the earlier studies suggested that Ti or an intermetallic Ti–Al phase would play a role as the heterogeneous catalyst. However, kinetic studies showed that noble metal catalysts, which have by orders of magnitude better hydrogen chemisorption capabilities than Ti, have almost no catalytic effect.⁹ It is therefore unlikely that the chemisorption is rate determining and splitting or recombining of the H₂ molecule cannot be the slowest step. Furthermore, SNMS and XPS measurements

showed that Ti is depleted at the outer surface by ball milling and is driven into the material. If Ti was acting as a heterogeneous catalyst at the outer surface of the Alanate particles, the Ti-doped material would be less active after extended ball milling, which is not the case.^{10,11}

Recent DFT calculations of Ti-enhanced NaAlH₄ indicated¹² that there is a certain preference for Ti to replace Al and stay at Al sites in the outer layers of an Alanate host lattice where it is able to increase the mobility of hydrogen species. Another theoretical study found that a particular local arrangement around Ti atoms may be important for the rehydrogenation reaction and that the diffusion of hydride species on the Al metallic phase and the formation of mobile alane species might play a role in the synthesis of the next products in the rehydrogenation reaction. A similar hypothesis where the hydrogen diffuses to the surface in a mobile Al–H complex where it is then dissociated by the catalyst and releases H₂ was made earlier by Gross et al.¹³ Until now, however, there is no experimental evidence for the formation of the thermodynamically unstable AlH₃ as an intermediate, and more work is needed to prove or disprove this assumption.

A third hypothesis is that the dopant enters the NaAlH₄ lattice substituting for Na¹⁴ or Al¹² with a distortion of the lattice and the formation of vacancies. Reference 12, which is a theoretical modeling of Ti-doped NaAlH₄, states that Ti substitution is predicted to be unstable in any case, but if metastable substitution did occur, then Ti substitution for Al would be more favorable than that for Na.

Following this, the aim of this work is to study if there is substitution of Ti inside the Alanate lattice and/or the formation of vacancies, by means of X-ray diffraction.

Experimental Section

Chemical operations were performed on the bench under purified N₂ using Schlenk tube techniques. Tetrahydrofuran (THF) was dried by distillation over sodium before use. NaAlH₄ was purified from a commercial product (95% purity, Albe-marle, Belgium) by Soxhlet extraction with THF. The solvent was drawn off slowly under vacuum, and large colorless crystals of NaAlH₄ were obtained from the extract. The crystals were

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dried at ambient temperature under vacuum until a residual pressure of 1×10^{-3} mbar was reached. Ti clusters were prepared by the reduction of a $\text{TiBr}_4(\text{THF})_2$ complex, following published procedures.⁴ According to chemical analysis by ICP-OES, $\text{Ti}_{13}\cdot 6\text{THF}$ used in this work contained 44 wt % Ti, 1.4 wt % B, and 7.9 wt % K.

Sample preparations were done in an argon-filled glovebox equipped with a recirculation system to keep the water and oxygen concentrations below 1 ppm during operation.⁴ The pure SAH-p and doped SAH-d samples were ball milled for 30 min at 600 rpm in a Fritsch P6 planetary mill using a silicon nitride vial with a ball to a powder weight ratio of about 20:1. The vial was filled with the powder and silicon nitride balls and sealed in the glovebox under an argon atmosphere. The doped sample was cycled eight times in a modified Sieverts apparatus and quenched in the absorbed state. Desorption measurements were performed at 150 °C under a residual hydrogen pressure of 0.4 bar and absorption measurements at 100 °C under a hydrogen pressure of 100 bar.

XRD powder diffraction measurements have been performed at room temperature at the Swiss-Norwegian beam line (BM1B) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The samples were kept in rotating 0.5 mm boron-silica glass capillaries. The capillaries were filled and sealed on the bench under a nitrogen atmosphere using the Schlenk tube technique. A wavelength of 0.49957 Å was obtained by a channel-cut Si(111) monochromator. Intensities were measured in steps of 0.008° and 0.005° in 2θ for samples SAH-p and SAH-d, respectively. In each case, up to 12 scans were averaged to improve the signal-to-noise ratio. Rietveld refinement was done using the GSAS program¹⁵ using an EXPGUI¹⁶ interface.

Results

XRD data of the SAH-p sample showed the presence of only the tetragonal NaAlH_4 phase, while for the SAH-d sample qualitative inspection of the X-ray data indicated that different phases had formed. A comparison with the JCPDS-ICDD powder diffraction data bank¹⁷ evidenced the presence of a NaAlH_4 phase, a Na_3AlH_6 monoclinic phase, and metallic Al, indicating that part of the sodium Alanate had decomposed to the hexahydride form and/or the hydrogenation reaction was not complete. Traces of NaBr were present as well.

Rietveld refinement was performed for both samples (see Figure 1 for an example of an SAH-d specimen); the starting crystallographic structures for the different phases were taken from the literature,^{18,19} NaAlH_4 has a tetragonal structure, space group $I4_1/a$, Al in the 4b position (0, 1/4, 5/8) Na in 4a (0, 1/4, 1/8), and H in 16f (x , y , z). Crystallographic details for the other structures are reported in Table 2. The quality of least-squares refinement is given by the goodness of fit defined as

$$\chi^2 = \frac{\sum w(I_o - I_c)^2}{(N_{\text{obs}} - N_{\text{var}})}$$

(where I_o and I_c are the observed and calculated intensities, w values are the weights, N_{obs} is the total number of observations, and N_{var} is the number of variables in the least-squares refinement). The quality of the refined structure is given by the R_{Bragg} factor which is calculated considering only the Bragg contribution to the diffraction pattern (I_b is the background contribution to the profile)

$$R_{\text{Bragg}} = \sqrt{\sum w(I_o - I_c)(I_o - I_b)/I_o^2 / \sum w(I_o - I_b)^2}$$

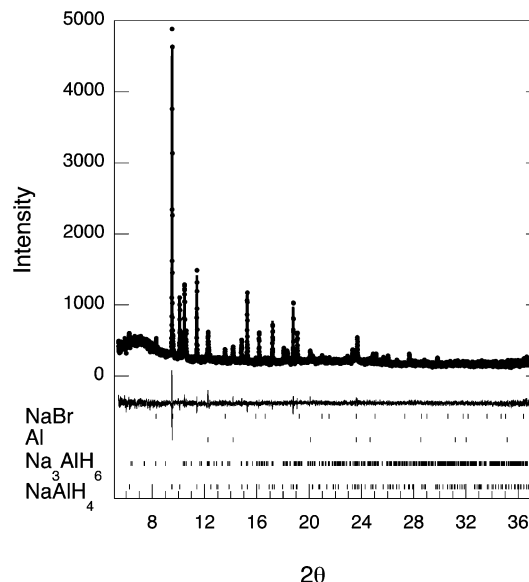


Figure 1. Rietveld refinement of an SAH-d sample. Dots represent the experimental data, and the thick line represents the calculated pattern. Residuals and phase tick marks are also shown.

TABLE 1: Results Obtained by Rietveld Refinement for an SAH-p Sample

site	x	y	z	B_{iso}
NaAlH_4 , $I4_1/a$, $a = 5.02507(6)$, $c = 11.3539(2)$				
Al (4b)	0	1/4	5/8	1.78(7)
Na (4a)	0	1/4	1/8	3.2(1)
H (16f)	0.2372	0.3836	0.5469	2.45

For both samples, the background was described employing a Chebyshev polynomial, while the profile shape was described using the Thomson-Cox-Hastings function. The general refinement procedure adopted here was first to minimize global parameters (like background parameters and the general scale factor common for all the phases) and then scale factors for each of the phases, lattice parameters, and profile functions (no refinement was necessary for strain and anisotropy) to obtain a fairly good description of the data. Then the thermal parameters, B_{iso} , for the various atoms present (not for hydrogen) in the main phases (NaAlH_4 , Na_3AlH_6 , and Al) were refined checking for the presence of possible high correlations (no correlations greater than 57% were found). The results, together with quantitative phase analysis in the case of the SAH-d sample, are reported in Tables 1 and 2.

When the fit converged, the thermal parameters were kept fixed together with the scale factors and the refinement of site occupation factors of Na or Al for the NaAlH_4 phase was performed; no attempts were made to refine the H atomic positions and/or site occupation factor. The presence of vacancies without any Ti inside the structure was also tested, both for the Na site and for the Al site and for both SAH-d and SAH-p; results for the site occupation factors and the corresponding R_{Bragg} factors are reported in Table 3.

In the case of SAH-d, different possibilities were explored to check for the Ti substitution inside the sodium Alanate lattice and Ti was substituted for Na atoms and for Al atoms. Some authors¹⁴ suggested the substitution of Na by Ti atoms; others²⁰ claim that in terms of crystal chemistry this substitution is quite improbable, while the replacement of Al atoms by Ti seems to be more plausible. In the refinement, Ti was substituted in one case on the Al crystallographic site 4b and in the other trial on the Na 4a site. Since a fully occupied crystallographic site is calculated by GSAS using a site occupation factor equal to 1,

TABLE 2: Results Obtained by Rietveld Refinement for an SAH-d Sample^a

site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}	phase amount wt %
NaAlH ₄ , <i>I</i> ₄ / <i>a</i> , <i>a</i> = 5.02508(6) <i>c</i> = 11.3571(2)					
Al (4b)	0	1/4	5/8	1.2(4)	59.7(2)
Na (4a)	0	1/4	1/8	2.6(4)	
H (16f)	0.2372	0.3836	0.5469	2.45	
Na ₃ AlH ₆ , <i>P</i> ₂ ₁ / <i>n</i> , <i>a</i> = 5.4145(3), <i>b</i> = 5.5402(3), <i>c</i> = 7.7620(4), <i>β</i> = 89.871(4)					
Al (2a)	0	0	0	1.2(5)	25.1(2)
Na (2b)	0	0	1/2	1.9(6)	
Na (4e)	−0.00129(5)	0.46129(4)	0.25008(4)	2.1(4)	
H (4e)	0.0918	0.0352	0.2207	3.099	13.7(2)
H (4e)	0.2220	0.3283	0.5454	3.099	
H (4e)	0.1649	0.2689	0.9500	3.099	
Al Fm $\bar{3}$ m <i>a</i> = 4.0499(2)					13.7(2)
NaBr Fm $\bar{3}$ m <i>a</i> = 5.9863(4)					1.6(1)

^a Goodness of fit: 1.24.**TABLE 3: *R* Factors Obtained for Ti Substitution and/or Vacancies Inside the NaAlH₄ Lattice for Pure and Doped Samples**

occupation number	<i>R</i> _{Bragg}
sample SAH-p	
fully occupied site	0.1841
Al = 1.009(3)	0.1814
Na = 0.993(5)	0.1906
sample SAH-d	
no Ti; fully occupied sites	0.276
no Ti; Al = 1.003(5)	0.275
no Ti; Na = 0.996(6)	0.277
Ti = 0.042(7) Al = 0.958(7)	0.274
Ti = 0.026(7) Na = 0.974(7) but negative values when the convergence was achieved	0.278
vacancies allowed: Ti = 0.1756(8) Al = 0.6405(8)	0.2854

the substitution of Ti for Al or Na was accomplished by placing a Ti atom in the crystallographic site 4b when we wanted to check for Al substitution and in the 4a site for the Na substitution. To have a fully occupied site, the total site occupation factor is constrained to a value of 1. To check if any vacancies are present inside the structure, this constrain is removed. The refinement procedure was done starting with the Al or Na site occupation factor equal to 0.99 and Ti equal to 0.01.

In the case of Ti substituted in the Na position after one refinement cycle, a negative value for Ti occupancy was obtained and then higher quantities as starting values for the Ti site occupation factor were tried; the best result obtained is reported in Table 3, but in any case, after a few cycles, the Ti occupation ended with a negative value. The behavior was the same also if vacancies were allowed.

The substitution of Ti in the crystallographic Al site ended with a positive site occupation factor for Ti. For this reason, we did more analysis on this crystallographic site. In a first trial, the total atomic fraction was constrained to have a fully occupied site (*Ti*_{occ} + *Al*_{occ} = 1), and in a second trial, the site was allowed to be partially occupied so as to check for the presence of vacancies (see Table 3). Even if the data showed no indication²¹ for the presence of any of the Ti–Al alloys, the refinement with the alloys phases was tried nevertheless; all the trials ended with negative scale factors.

Discussion

A previous paper¹⁴ suggesting the substitution of Ti at the Na site reported a variation in the lattice parameters in the doped NaAlH₄ with respect to the pure one. In our case, there was almost no variation of the *a* lattice parameter and only a slight change for the *c* axis (see Tables 1 and 2).

The data also indicates that the decomposition of the NaAlH₄ phase had already started or a small part of the sample was not fully rehydrogenated although SAH-d was measured in the absorbed state. The hexahydride and Al phases were formed in a molar ratio of about 1_{Na₃AlH₆}/2_{Al} (see Table 2) which corresponds to the molar ratio given by the decomposition reaction.

The values obtained for the thermal parameters were quite reasonable indicating that nonsubstantial disorder is present in the structure. From the X-ray results, there is no evidence of vacancy formation both in the pure sample and in the doped one. In the case of the SAH-p specimen, site occupation factors did not change when allowed to move and there is a little improvement, though not significant, in the *R*_{Bragg} when the Al site was refined. In the case of Na, there is a clear indication that the site is fully occupied by Na.

For the Ti-doped sample, the behavior was similar since there was no improvement in the agreement indexes when the occupancies were refined. A slight improvement was found when Ti was substituted on the Al site, but it is not significant enough (Hamilton test²²) to say that Ti definitely substitutes for Al in the Alanate phase. Our results also showed that no Ti–Al structure with long-range order was present, confirming the EXAFS analysis that only a small entity is formed between Ti and Al.¹¹

From the results so far obtained, Ti could not substitute at all or the quantity going to randomly replace Al is so low that it is not detectable by X-rays in an unequivocal way. A clear indication, instead, comes from the substitution of Ti in the Na site since the refinement always ends with negative site occupation factors for Ti and this allows us to say that, at least in our case, Ti did not substitute for Na.

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