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Effects of milling, doping and cycling of NaAlH₄ studied by vibrational spectroscopy and X-ray diffraction

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Abstract

The effects of milling and doping NaAlH₄ with TiCl₃, TiF₃ and Ti(OBu^{*n*})₄, and of cycling doped NaAlH₄ have been investigated by infrared (IR) and Raman spectroscopy and X-ray powder diffraction. Milling and doping produce similar effects. Both decrease the crystal domain size (~900 Å for milled and ~700 Å for doped, as compared to ~1600 Å for unmilled and undoped NaAlH₄) and increase anisotropic strain (by a factor >2.5, mainly along *c*). They also influence structure parameters such as the axial ratio *c/a*, cell volume and atomic displacement amplitudes. They show IR line shifts by ~15 cm⁻¹ to higher frequencies for the Al–H asymmetric stretching mode ν_3 , and by ~20 cm⁻¹ to lower frequencies for one part of the H–Al–H asymmetric bending mode ν_4 , thus suggesting structural changes in the local environment of the [AlH₄]⁻ units. The broad ν_3 bands become sharpened which suggests a more homogeneous local environment of the [AlH₄]⁻ units, and there appears a new vibration at 710 cm⁻¹. The Raman data show no such effects. Cycling leads to an increase in domain size (1200–1600 Å), IR line shifts similar to doped samples (except for TiF₃: downward shift by ~10 cm⁻¹) and a general broadening of the ν_3 mode that depend on the nature of the dopants. These observations support the idea that some Ti diffusion and substitution into the alanate lattice does occur, in particular during cycling, and that this provides the mechanism through which Ti-doping enhances kinetics during re-crystallisation. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrogen storage materials; Infrared and Raman spectroscopy; X-ray diffraction; Alanates

1. Introduction

Doping of sodium tetrahydrido aluminate (NaAlH₄) with titanium based catalysts such as Ti(OBu^{*n*})₄, TiCl₃ and TiF₃ improves its hydrogen release properties [1–6]. The doping process usually consists of milling the alanate in the presence of few mole percent of catalysts. However, several studies indicate that milling NaAlH₄ in the absence of catalysts also improves hydrogen release [7–9]. Furthermore, there appears to exist an optimum milling time to introduce the dopant into the hydride, extended milling times leading to a spontaneous

hydrogen loss [9]. Up to now, the mechanism of action of the Ti dopants has not been established. In particular, the location of titanium dopants has been a subject of a great deal of speculation and controversy. One school of thought has held that the remarkable enhancement of the hydrogen cycling kinetics in Ti doped NaAlH₄ is due to surface-localized catalytic species consisting of elemental titanium or a Ti–Al alloy [1,4,6,10]. Alternatively, it has been hypothesized that doping involves the substitution of titanium into the bulk of the hydride [11–13]. The present work represents an attempt to measure possible structural and microstructural changes in NaAlH₄ induced by milling, doping and cycling. For this purpose various samples of untreated, doped, milled and cycled hydrides and deuterides were investigated by using

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vibration spectroscopy (IR and Raman) and X-ray powder diffraction.

2. Experimental

2.1. Preparation, milling, doping and cycling

Sodium aluminium hydride was obtained from Albemarle Corp. and recrystallized from tetrahydrofuran prior to use (samples 1-3 called "pure", see experiment Nos. 1-4 in Tables 1 and 4). The deuteride NaAlD₄ (>99% D, sample 4, see experiment No. 5 in Table 1) was synthesized by the literature method [14]. X-ray powder diffraction (XPD) analvsis (see Table 1) indicated that the hydride samples were single phase while the deuteride sample contained ~ 5 wt.% NaF and \sim 25 wt.% metallic Al. Milling was performed by grinding the pure hydride and deuteride samples 2 and 4, respectively, in a ceramic mortar during 20 and 40 min in an argon filled glove-box (called "milled" samples thereafter, see experiment Nos. 6-9 in Tables 1 and 4). XPD analysis showed that these samples contained no new phases. Doping was performed by ball-milling the pure hydride samples 1 and 3 in the presence of $Ti(OBu^n)_4$ (2 and 6 mol%, Aldrich, purity 97%), TiCl₃ (2 mol%, Aldrich, purity 99.999%) and TiF₃ (6 mol%, Aldrich, purity 99%) as described in [2,15]. XPD analysis on these samples (called "doped" samples thereafter, see experiment Nos. 11-13 in Tables 1 and 4) revealed the presence of metallic Al (up to 7 wt.%) and TiF₃ (1 wt.%) for one doped sample (experiment No. 13). Cycling was performed on the 2 mol% doped sample 3 according to a dehydrogenation by heating at 160 °C for 5 h and a rehydrogenation upon standing under 100 bar of H₂ at 100 °C for 12 h (with three successive cycles). XPD analysis on these samples (called "cycled" samples thereafter, see experiment Nos. 14-16 in Tables 1 and 4) indicated the presence of the decomposition products Na_3AlH_6 (up to 35 wt.%), metallic Al (up to 12 wt.%) and NaCl (5 wt.%). Given the scarcity of spectroscopy literature on sodium hexahydrido-aluminate (only one reported Raman spectrum [16]) the compound was synthesized by the method of Huot et al. [17] and investigated by IR and Raman spectroscopy. The sample contained about 5 wt.% of NaH impurity. All measurements were performed within less than 1 month after sample preparation. Measurements performed a few months later confirmed that the samples changed their phase compositions over time, in particular the cycled ones for which the Na₃AlH₆ phase disappeared at the expense of metallic Al.

2.2. Raman and infrared spectroscopy

The Raman set-up used was the same as that described previously [18,19]. It consisted of an Argon ion laser (488 nm excitation wavelength) and a Kaiser Optical Holospec monochromator equipped with a liquid nitrogen cooled CCD camera. The spectral resolution was \sim 3–4 cm⁻¹.

Additional measurements were performed by using a Labram Raman microscope using 532 nm excitation. The samples were enclosed in sealed glass capillaries with a diameter Ø1.0 mm by using a purified Ar filled glove-box. The Fourier transformation infrared (FT-IR) spectrometer used was a Paragon 1000 (Perkin-Elmer) equipped in attenuated total reflection (ATR) mode with the Golden Gate Single Reflection Diamond (P/N 10500 Graseby-Specac Series). The diamond crystal had a refractive index of 2.4 at $1000 \,\mathrm{cm}^{-1}$. The spectral resolution was 4 cm^{-1} and the spectral range $500-4400 \,\mathrm{cm}^{-1}$. The powder samples were pressed against the crystal with a calibrated strength in a purified Ar filled glove-box and protected by an airtight polyethylene film during measurement. Additional measurements in nujol suspension (prepared in a purified Ar filled glove-box and placed between two airtight NaCl plates) were done using a Bio-Rad Excalibur instrument, and KBr pellets (hand pressed in an inert atmosphere) using a Nicolet Nexus 470 FT-IR instrument. All spectra were recorded at room temperature. Both the Raman and infrared spectra were analysed by using the line fitting procedure with Lorentzian profile of the program SPECTRAW [20]. It should be noted that the Raman intensities observed for Na₃AlH₆ were much weaker than those for NaAlH₄.

2.3. X-ray powder diffraction (equipment and analysis)

The samples were analysed on a Huber Guinier Diffractometer 600 by using monochromatic Ge(111) Cu K α_1 radiation. The system was equipped with a closed-cycle helium Helix Model 22 Refrigerator. The powders were mixed with an internal silicon standard and placed between two polyethylene terephtalate foils (Goodfellow) of 0.013 mm thickness. All manipulations were performed in a purified Ar filled glove-box. In view of the instability of the samples (especially the doped and cycled ones) and the long data acquisition times (>12 h) all measurements except one (experiment No. 4) were performed at 10 K (diffraction interval $10^{\circ} < 2\theta$ $< 100^{\circ}$, step size $\Delta 2\theta = 0.02^{\circ}$, counting time per step 10 s). Samples 1-3 were studied in order to check the reproducibility of the microstructural analysis, and one of these (sample 3) was investigated at room temperature in order to check if microstructural properties such as strain were intrinsic to the NaAlH₄ phase and not induced during cooling (experiment Nos. 3–4). The following microstructure parameters were extracted from the data by conventional Rietveld analyses (program Fullprof.2k [21]): average crystallite size and anisotropic strain from diffraction line broadening, and peak shift parameter Sh (related to stacking faults [21-23]) from the displacements of certain groups of reflections (see below). The diffraction profiles (both instrumental and sample intrinsic) were modelled by using a Thomson-Cox-Hastings pseudo-Voigt function [21] (convolutions between Gaussian and Lorentzian components having different full widths at half maximum, FWHM) to simulate the peak shapes of both NaAlH₄, Si and impurities phases when present. Structural Download English Version:

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