Dynamics of defects in alanates

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Abstract

Anelastic spectroscopy experiments on the dehydrogenation process of undoped and catalysed NaAlH$_4$ revealed the formation of a highly mobile species during decomposition. This species, as indicated also by isotope effect measurements, was identified as a hydrogen containing defect complex. In particular, the most likely defect complex may be of type AlH$_x$, in which fast local dynamics of H-vacancies can occur.
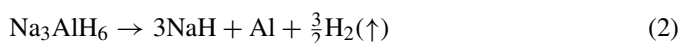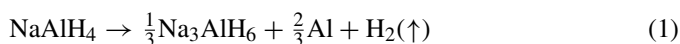
The formation of such defects begins at temperatures much lower in Ti-doped than in undoped samples. The catalyst atoms decrease the energy barrier to be overcome by H to break the bond, thus enhancing the kinetics of the chemical reactions and decreasing the temperature at which the dehydrogenation processes take place.

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1. Introduction

Sodium alanate NaAlH$_4$ is one of the promising materials for hydrogen storage [1] due to its high hydrogen weight capacity and low cost. Its dehydrogenation process is compatible with mobile hydrogen storage applications and occurs according to the following chemical reactions [2]:

$$NaAlH_4 \rightarrow \tfrac{1}{3}Na_3AlH_6 + \tfrac{2}{3}Al + H_2(\uparrow) \tag{1}$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + \tfrac{3}{2}H_2(\uparrow) \tag{2}$$

The addition of a catalyst [2] like Ti makes the dehydrogenation of NaAlH$_4$ reversible and enhances the kinetics of the solid state hydrogenation and dehydrogenation processes. In spite of the great number of theoretical and experimental studies carried out on this material, the mechanism of action and the occupancy of the catalyst in the NaAlH$_4$ system are still matter of debate. Some works suggest that Ti occupies the Na sites in the bulk lattice [3,4] or on the surface [5], whilst the formation of TiAl$_3$ [6] compound on the surface of the system is also reported. Moreover transmission electron microscope observations revealed that in NaAlH$_4$ doped with 2 mol% TiF$_3$, the Ti is initially distributed as TiF$_3$ crystallites and, only in a minor proportion, as dispersed Ti atoms incorporated into the alanate phase [7].

At the present information is still lacking on the decomposition steps, but there is general agreement that a mobile species should be operative to rapidly readjust the symmetries during the decomposition transformation. Recently we observed [8,9], by anelastic spectroscopy, the formation of a new species with a fast dynamics involving hydrogen, which appears during the thermal decomposition of NaAlH$_4$ and may help to understand the microscopic mechanism governing this reaction. This species has been identified in off-stoichiometric AlH$_x$ units, giving rise to fast H vacancy local dynamics. The formation of such stoichiometry defects starts at temperatures much lower in Ti doped than in undoped samples, and concomitantly with the decomposition reaction. The catalyst atoms decrease the energy barrier to be overcome by H to break the bond, thus enhancing the kinetics of the chemical reactions and decreasing

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the temperature at which the dehydrogenation processes take place.

The role of Ti as a trap for H has been corroborated by *ab initio* calculations in sodium alanates [10], which revealed that substitutional Ti is a powerful hydrogen attractor. Indeed, theoretical studies [4,11], Raman scattering and *ab initio* calculations [12] in undoped NaAlH$_4$ suggest that the enhanced absorption and desorption kinetics be due to the effectiveness of Ti in weakening the strength of the covalent bond between Al and H atoms thus allowing the hydrogen to desorb at a lower temperature.

2. Experimental

Sodium aluminium hydride was obtained from Albemarle Corp. The aluminium metal was removed from the raw hydride via Soxlet extraction with dry, oxygen-free tetrahydrofuran (THF) under a nitrogen atmosphere using the standard Schlenk technique. The final purification was accomplished through recrystallization from THF/pentane. NaAlD$_4$ was synthesized from LiAlD$_4$ (Aldrich, 99.8% isotopic purity) and NaF as described in the literature [13]. Sodium aluminium hexahydride Na$_3$AlH$_6$ was synthesized and purified by the method of Huot et al. [14]. Doping of all the powders was performed by the mechanical milling method [15–17] in which the hydride (deuteride) was combined with 2 mol% TiF$_3$ (Aldrich, purity 99%) and ball-milled under an argon atmosphere in a stainless steel bowl using a Fritsch 6 planetary mill at 400 rpm and a grinding ball-to-powder ratio of 35:1.

All the produced powders cannot be sintered at high temperature; therefore, to obtain the prismatic bars suitable for the measurement of the complex dynamic modulus, two different methods were followed. In the case of the Na$_3$AlH$_6$ sample doped with 2% TiF$_3$ (labelled Ti 2% H-1hexa) and the NaAlD$_4$ sample doped with 2% TiF$_3$ (labelled Ti 2% D-1), the alanate was mixed in a 1:1 volume ratio with pure KBr powder, which acts as a compactant, and then pressed. For the two Ti doped NaAlH$_4$ samples (labelled Ti 2% H-6 and Ti 2% H-8) and the undoped NaAlH$_4$ sample (labelled UH-2), the alanate powder was pressed alone. After pressing, all the samples were self-sustained bars 40 mm long, 5 mm wide and 0.7–1.5 mm thick. As the alanate powder reacts with oxygen and water vapor, all operations were accomplished in a glove bag in flowing nitrogen atmosphere.

Anelastic spectroscopy measurements are conducted suspending the bars on thin wires located at the nodal lines of flexural vibration modes and electrostatically exciting the corresponding mechanical resonances of the samples. The sample vibration produces an alternate stress which interacts with the local lattice distortions introduced by the mobile entities and perturbs their site energies in such a way that the sites that are energetically favoured in the first half period become unfavoured in the second half. The system then looks for the equilibrium redistribution among the perturbed levels. At the temperature at which the relaxation rate τ^{-1} of the species is equal to the angular vibration frequency ω ($\omega\tau = 1$) the stimulated atomic migration is able to follow, by thermal activation, the sample vibration, and the coefficient of elastic energy dissipation Q^{-1} reaches its maximum value. The energy dissipation (or reciprocal of the mechanical quality factor Q) is measured from the decay of the free oscillations or from the width of the resonance peak. The measurement of the dynamic Young modulus E' is simultaneously obtained from the angular vibration frequency $\omega^2 = kE'/\rho$, where ρ is the mass density, and k a numerical factor depending on the sample geometry [18]. The independent and concomitant measurements of Q^{-1} and E' allow the complex modulus $E = E' + iE''$ to be derived, being $Q^{-1} = E''/E'$. For a single relaxation time, τ, Q^{-1} is given by

$$Q^{-1} = gv_0(\lambda_1 - \lambda_2)^2 \frac{cn_1n_2}{kT} E' \frac{(\omega\tau)^\alpha}{1 + (\omega\tau)^{2\alpha}} \tag{3}$$

where c is the molar concentration of the jumping atoms and n_1 and n_2 their equilibrium fractions in sites 1 and 2; λ_1 and λ_2 are the elastic dipoles [18] of the defects in their two configurations; g is a factor of the order of 1/2 depending on the geometry of the jump and the type of sample vibration, v_0 the unit cell volume, τ a parameter equal to 1 for a single-time Debye process, and k the Boltzmann constant. For classical processes is $\tau = \tau_0 e^{W/kT}$, being W is the
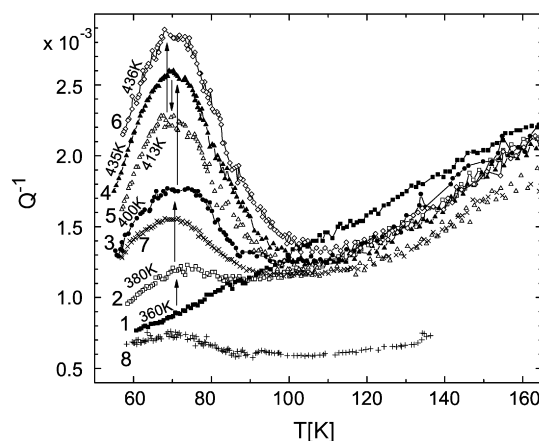

Fig. 1. Low-temperature dependence of the elastic energy loss. Sample Ti 2% H-6 after a thermal treatment (TT) up to 360 K (($\blacksquare$) 1). Sample Ti 2% H-8 after the following subsequent TT's up to: 380 K (($\square$) 2); 400 K (($\bullet$) 3); 435 K (($\blacktriangle$) 4); 413 K (($\triangle$) 5); 436 K (($\diamond$) 6). Sample Ti 2% H-5 (mixed with KBr) after TT up to 436 K (($\times$) 7). Sample UH-2 after TT at 447 K of 480 min as described in Ref. [9] (($+$) 8).

activation energy. As τ is temperature dependent for thermally activated processes, the relaxation condition ($\omega\tau = 1$) is satisfied at low temperatures for fast processes and at high temperatures for slow processes.

3. Results

The elastic energy loss of the as received NaAlH$_4$ doped with 2% mol of TiF$_3$ measured below room temperature shows a smooth background which rises with increasing temperature. The sample was then progressively heated to temperatures between 360 and 436 K, to follow the evolution of the anelastic spectrum with progression of the chemical reactions. After each thermal treatment, Q^{-1} was measured in the temperature range between 300 and 60 K. After a thermal treatment (TT) at 380 K a broad peak centered around 70 K for a vibration frequency of 1 kHz was observed. After increasing the TT to 435 K, the peak height increase proceeds. Instead, a subsequent heating to a temperature lower than that of the previous TT (413 K), in which decomposition did not proceed as indicated by the modulus [8,9] visibly reduces the peak height. This result indicates regression of the concentration of the mobile species produced by decomposition. After a further increase of the ageing temperature, the peak height keeps increasing again.

The 70 K peak could be stimulated also in the undoped NaAlH$_4$, even though thermal treatments to higher temperatures for long times (447 K for 4 h) were required (Fig. 1) to make it detectable over the background dissipation. The maximum height obtained (after TT at 447 K for 8 h) for the peak in the undoped sample is however much lower than those obtained for the Ti-doped sample (for a comparison see Fig. 1). This fact implies that the concentration of the relaxing species is much lower in undoped samples than in catalyzed specimen.

The peak is caused by a thermally activated process [8], as it shifts towards higher temperature at for a vibration mode with a higher frequency (Fig. 2). It is very broad with respect to a single Debye process, indicating strong elastic interactions
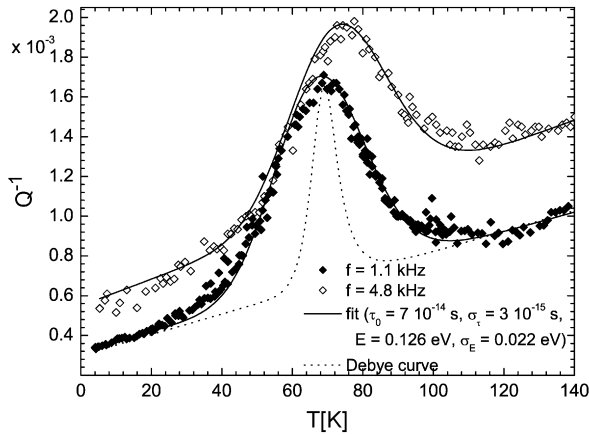
Fig. 2. The elastic energy loss of the thermally treated Ti-doped alanate (symbols) and best fits (solid lines) obtained by means of the model with Gaussian distribution functions of the activation energy and relaxation time. For comparison the corresponding Debye curve is reported (dotted line).

or/and multiple jumping type of the mobile entity. Indeed the peak can be fitted [8] considering a Gaussian distribution for both the activation energy and the relaxation time. The best fit values of the mean activation energy and the pre-exponential factor are $E_a = 0.126$ eV and $\tau_0 = 7 \times 10^{-14}$ s [8], while the standard deviation of the distribution are $\sigma(E) = 0.022$ eV and $\sigma(\tau_0) = 3 \times 10^{-15}$ s. The order of magnitude of τ_0 is typical of point defect relaxation.

In order to ascertain whether the mobile species giving rise to the anelastic peak involves hydrogen, we performed measurements on deuterated samples. The NaAlD$_4$ sample doped with Ti was thermally treated from the as-prepared state with subsequent cycles up to 323, 345, 368 and 441 K. Only after the last treatment (441 K for 100 min) the deuterated sample exhibited the peak. A comparison with the peak in the Ti-doped NaAlH$_4$ (Fig. 3) displays an isotope shift of 7 K (at practically the same
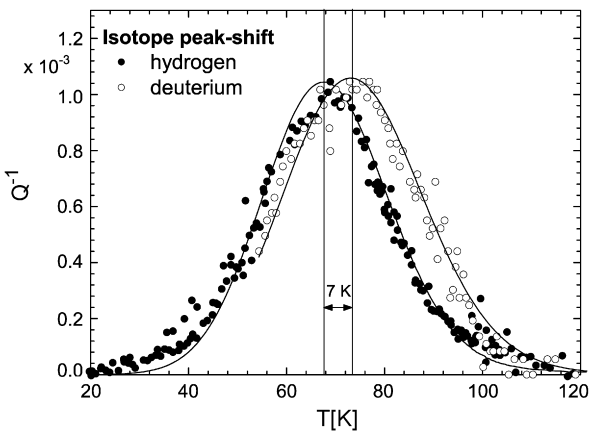
frequency), which is well above the experimental uncertainty of the temperature measurement (0.1 K). This result shows that the relaxation at low temperature is caused by the dynamics of a complex containing hydrogen.

In the deuterium containing sample we fitted the experimental data (Fig. 3), after subtraction of a linear background, considering a Gaussian distribution for both the activation energy and the relaxation time, similarly to the case of NaAlH$_4$. The best fit values of the mean and of the standard deviation of the energy distribution are $\bar{E}_D = 0.136$ eV and $\sigma(E_D) = 0.025$ eV [9], to be compared with $\bar{E}_H = 0.126$ eV and $\sigma(E_H) = 0.022$ eV, obtained for hydrogen. For the mean and the standard deviation of the relaxation time distribution we fixed the values obtained from the hydrogenated sample.

4. Discussion

The peak at 70 K cannot be ascribed to a stoichiometric phase produced by the chemical reactions; in fact, the Q^{-1} spectra of NaAlH$_4$, Na$_3$AlH$_6$, Al and NaH show only a smooth increase of the dissipation with increasing T (Fig. 4). Moreover, the peak cannot be due to reorientation of H in Ti complexes as it is present also in the Ti-free samples. The possibility of a H relaxation in Al should be ruled out, as the solubility of H in bulk Al is extremely low (H/Al = 10^{-6} to 10^{-8} at 660 °C) and the intense peak observed cannot be thought to be produced by defects present at ppm levels. Finally the relaxation cannot be due to the compression of the powder to obtain the consolidated samples, because the compressed NaAlH$_4$ powders do not show the peak.

For all the above reasons the peak should be caused by a defect present in one of the crystal structures involved in the chemical reactions. One can exclude a defect of NaH as XRD measurements [19] do not reveal a significant amount of sodium hydride after ageing at 380 K for a short time, while the peak is already present in the anelastic spectra. Therefore the most likely defect complex involving hydrogen may be of type AlH$_x$, which forms during the tetra- to hexa-hydride transformation. Precisely, the relaxation peak may be due to the H vacancy dynamics within
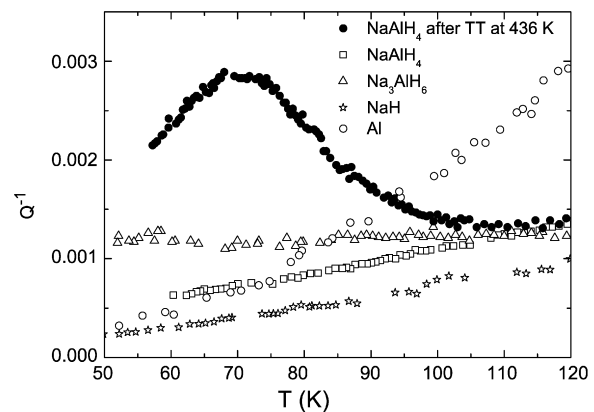

Fig. 3. Elastic energy loss of Ti doped NaAlH$_4$ after a thermal treatment at 436 K (●) and of Ti doped NaAlD$_4$ after a thermal treatment at 441 K ((○) 1.1 kHz). A linear background has been subtracted. The heights of the two peaks measured at 1.1 kHz have been normalized. Lines are the best fit considering a Gaussian distribution for both the activation energy and the relaxation time. The vertical lines mark the position of the maxima of the peaks in the hydrogenated and deuterated samples.

Fig. 4. The elastic energy loss of pure NaAlH$_4$, Na$_3$AlH$_6$, NaH and Al, compared with the Q^{-1} of thermally treated alanate, showing the relaxation peak at 70 K. The dissipation of aluminum has been divided by a factor of 3.

the AlH_x groups, which would allow the remaining H atoms to reorient around Al.

The peak height increases with increase of the ageing temperature, as more off-stoichiometry AlH_x units are formed with progression of decomposition. When an annealing of the sample is made at a temperature lower than that of the previous TT, the peak height decreases (Fig. 1); this indicates that the interstitial hydrogen population previously injected in the lattice under non-equilibrium conditions, looking for equilibrium, partially migrates back to the bond sites thus reducing the concentration of the AlH_x defects. This result also shows that: (i) the bond is the deepest trap for H; (ii) hydrogen becomes mobile on a long-range scale at about 410 K or less. We propose, therefore, that the structural transformation is driven by hydrogen more than by the heavier Na or Al atoms. Obviously, for the transformation to proceed we expect also small displacements of Na and Al, even though some excess Al atoms remain dispersed and slowly cluster in form of crystals in the lattice [6,7].

The negligible height of the 70 K peak in the Ti-free sample is readily explained by the fact that the decomposition temperatures are shifted to higher values in the undoped powders. Consequently, the energy barrier that hydrogen must overcome to break the Al–H bond is expected to be lower in the catalyzed sample. It means that the strength of the chemical bonds is decreased by the Ti atoms, resulting in a decrease of the temperature at which the decomposition takes place.

The formation of hydrogen vacancies, and hence the presence of AlH_x complexes, during the dehydrogenation and rehydrogenation reactions was first proposed by anelastic spectroscopy experiments [8,9] and subsequently suggested by a recent density functional theory study [11]. The formation of AlH_3 was also hypothesized to explain decomposition and reformation of sodium alanate [20,21]. DFT calculations [22] identified hydrogen vacancies and interstistials as the predominant defect species with low formation energies and high mobility, as indicated by the calculated low energies for propagation. Furthermore, energy barriers obtained from neutron scattering in Na_3AlH_6 were found [23] in good agreement with the calculated values for local H-vacancy diffusion within the AlH_5 units.

The presently proposed model of the formation of AlH_x off-stoichiometry defects to explain the low temperature relaxation peak, seems the most likely, also in view of the subsequent theoretical and experimental studies mentioned above. However, the possibility that the peak might be due to the relaxation of hydrogen around another type of defect, for instance an impurity acting as trapping centre for hydrogen, cannot be ruled out. In this case, a thermal treatment under "quasi equilibrium" conditions would decrease the peak height (Fig. 1), as hydrogen would migrate back to fill the hypothesized AlH_x defects formed during decomposition. In the framework of this picture, the presence of the relaxation process itself would imply AlH_x formation, and the bond would result to be, again, the deepest trap.

5. Conclusions

The formation of a new species and its evolution during the decomposition reactions in Ti-doped and undoped sodium alanates was reported. This species, which gives rise to a thermally activated relaxation peak around 70 K at 1 kHz, is a point-defect complex with fast local dynamics, which according to the observed deuterium isotope shift involves hydrogen. This defect was identified as a AlH_x unit, which forms during the tetra- to hexa-hydride transformation. A comparison of the results obtained in undoped and Ti doped $NaAlH_4$ indicates that the strength of the chemical Al–H bonds is decreased by the Ti atoms, resulting in a decrease of the temperature at which the decomposition takes place.

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