

Effects of catalysts on the dehydriding of alanates monitored by proton NMR

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Abstract

In situ studies of the transition from NaAlH₄ to Na₃AlH₆ are performed by proton NMR for samples doped with TiCl₃ and with Ti₁₃-nanoclusters. The local hydrogen dynamics in the different compounds is studied by the nuclear spin-lattice relaxation. For the Ti-doped NaAlH₄ samples a double-exponential recovery of the nuclear magnetization is observed, indicating two fractions of hydrogen with different mobilities. In Na₃AlH₆ a transition from hindered rotation of the AlH₆ groups to full isotropic reorientation of these groups is observed in the temperature range 200–260 K.

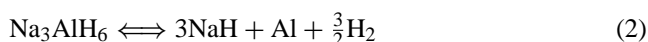
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1. Introduction

Sodium alanate NaAlH₄ is a promising candidate for the development of a reversible hydrogen storage system for mobile applications. It decomposes in two steps, first into the hexahydride Na₃AlH₆, which further decomposes into NaH as follows:



The interest in NaAlH₄ for hydrogen storage increased drastically in 1997, when it was discovered that the inverse of reactions (1) and (2) can be catalysed by the addition of a small amount of Ti-based complexes [1]. Until quite recently, the addition of Ti³⁺ cations in the form of chlorides was considered to hold the highest potential for rapid release and absorption of hydrogen gas [2–4]. Very recently,

however, it has been demonstrated that the hydrogen storage properties of Ti-doped NaAlH₄ could be considerably improved by using Ti₁₃-nanoclusters as doping agents [5,6].

Nuclear magnetic resonance (NMR) has seen wide application to study the structural and dynamical properties in classical interstitial hydrides (see e.g. [7]). However, only very few studies have been performed on complex chemical hydrides. The structure and hydrogen dynamics in Na₃AlH₆ has been studied by ¹H NMR [8]. First solid-state magic angle spinning (MAS) NMR spectra of ²⁷Al have been measured on LiAlH₄ by Balema et al. [9]. Recently, ²³Na and ²⁷Al MAS-NMR has been used by Bogdanović et al. [10] to study the effect of discharging and recharging of NaAlH₄. The present paper reports on first ¹H NMR studies of the starting material NaAlH₄, the intermediate product Na₃AlH₆ and the final product NaH. The effect of different catalysts on the proton NMR spectra and their temperature dependent time evolution is investigated. Furthermore, the influence of the catalysts on the hydrogen dynamics is studied by measuring the spin-lattice relaxation rate Γ_1 .

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2. Experimental details

NaAlH_4 material was purchased as powder (Chemetall, Frankfurt) and purified by a Soxhlet extraction with THF [6]. The Na_3AlH_6 sample was prepared by mechanical alloying (ball milling) of appropriate amounts of NaAlH_4 and NaH [11]. The NaH sample was obtained by ball milling of purified NaAlH_4 followed by thermal desorption under vacuum at 443 K.

Two types of Ti-doped samples were prepared by ball milling of NaAlH_4 with small amounts of TiCl_3 and Ti_{13} -nanoclusters, respectively. Details about the preparation of the small Ti_{13} -clusters are given in [6]. The titanium concentration was 2.0 mol% for the TiCl_3 -doped sample and 1.8 mol% for the Ti-cluster-doped sample.

The proton NMR measurements were performed at 67.7 MHz and the spectra were obtained by Fourier transformation of the free-induction decay (FID) following a single 90° r.f.-pulse after a dead time of typically $10 \mu\text{s}$. The spin-lattice relaxation was measured by using an inversion-recovery pulse sequence. In case of a single-exponential recovery the relaxation rate Γ_1 was obtained by fitting

$$M(\tau) = M_0[1 - 2 \exp(-\tau \cdot \Gamma_1)] \quad (3)$$

to the magnetization values measured as a function of the recovery time τ .

3. Results and discussion

A comparison of the room-temperature proton NMR spectra of the starting material NaAlH_4 , the intermediate product Na_3AlH_6 and the final product NaH is given in Fig. 1. A common feature of these spectra is the existence of the narrow central line superimposed on the much broader component. In each case, the central line accounts only for a few percent of the total spectrum area and may be attributed to impurities or remaining solvent from the purification process. The intensity of this central line is different for NaAlH_4 samples purified in different batches.

The main components of the room-temperature NMR spectra of all three compounds are quite different with respect to their widths and shapes. The spectrum of NaAlH_4 represents a Pake-like doublet with a splitting of approximately 50 kHz. A similar splitting has been seen previously in the NMR spectrum of AlH_3 [12], which is also a non-metallic hydride. The intermediate compound, Na_3AlH_6 , produces a broad unresolved line with a halfwidth of approximately 17 kHz. The spectrum of the final product, NaH , is again unresolved, with the halfwidth of about 35 kHz.

Although the spectra shown in Fig. 1 were measured at a rather low resolution, the observed differences are clear enough to distinguish between the compounds. This property is a crucial prerequisite for an efficient in situ study of the decomposition processes. At room temperature

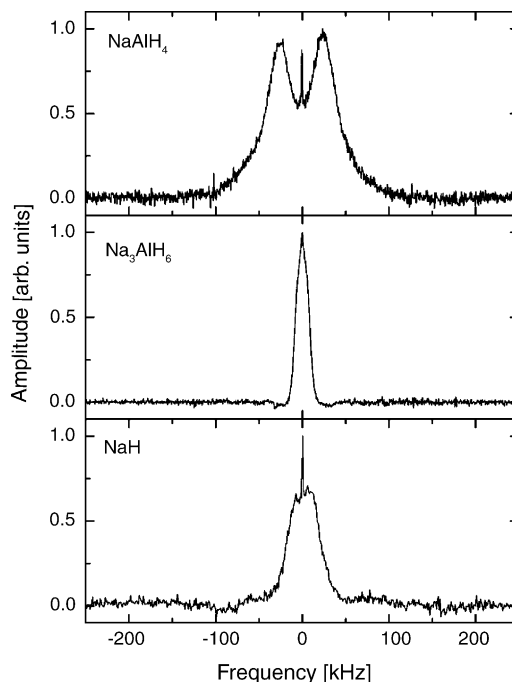


Fig. 1. Proton NMR spectra of NaAlH_4 , Na_3AlH_6 and NaH .

the decomposition reaction of NaAlH_4 occurs very slowly. This is evident from Fig. 2, which shows the proton NMR spectrum of Na_3AlH_6 together with the spectra of the TiCl_3 -doped NaAlH_4 measured directly after ball-milling and after having stored the sample in the glove box for 5 months. Even after 5 months at room temperature the transformation from NaAlH_4 to Na_3AlH_6 is not yet completed. While the central line characteristic of Na_3AlH_6 has already been formed, the doublet structure of NaAlH_4 is still visible as shoulders. A faster decomposition of NaAlH_4 to Na_3AlH_6 occurs at higher temperatures and by using Ti-clusters as doping

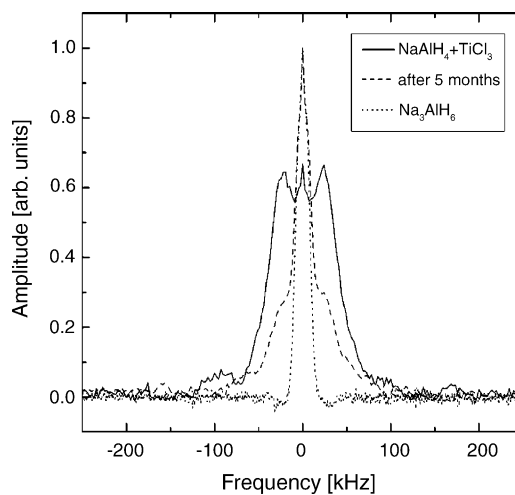


Fig. 2. Proton NMR spectra of Na_3AlH_6 and NaAlH_4 with 2.0 mol% TiCl_3 . The TiCl_3 -catalysed NaAlH_4 was measured right after the preparation as well as after 5 months.

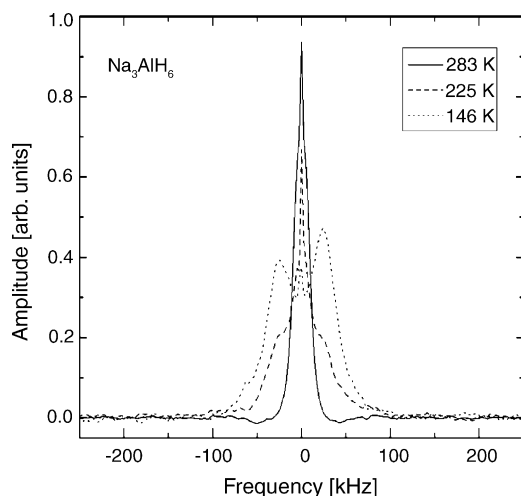


Fig. 3. Temperature dependence of the proton NMR spectrum of Na_3AlH_6 .

agents. The proton NMR spectrum of NaAlH_4 with 1.8 mol% Ti-clusters measured after having heated the sample for 1 h to 360 K already closely resembles that of Na_3AlH_6 . This allows us to conclude that the first decomposition stage of the Ti-cluster-doped NaAlH_4 is completed after 1 h at 360 K.

The proton NMR spectrum of NaAlH_4 suggests that even at room temperature the so-called rigid lattice condition is fulfilled, i.e. the characteristic rate of hydrogen motion ν_{H} is much lower than the width of the NMR spectrum $\Delta\nu \approx 50$ kHz. For Na_3AlH_6 , the proton NMR spectrum is more narrow at room temperature, but it changes substantially at lower temperatures. Fig. 3 shows a comparison of the spectra measured on Na_3AlH_6 at three different temperatures between 146 and 283 K. The 146 K spectrum of Na_3AlH_6 consists of a small central line superimposed on a doublet structure with a splitting of about 50 kHz, quite similar to the room-temperature spectrum of NaAlH_4 . The intensity of the central line grows with increasing temperature at cost of the doublet structure. Already at 225 K the doublet structure has essentially disappeared with only two shoulders left. The structure of Na_3AlH_6 suggests that this phenomenon is related to hindered rotation of the AlH_6 groups, which form nearly regular octahedra with a four-fold symmetry [13]. The phenomena of the thermally activated rotation of the AlH_6 octahedra in Na_3AlH_6 have been studied previously by proton NMR [8]. The rotation of the AlH_6 octahedra allows a given proton spin to sample different local fields, resulting in a partial averaging of the resonance frequencies. In NaAlH_4 the (local) mobility of hydrogen seems to be much lower than in Na_3AlH_6 , since the proton NMR spectra of NaAlH_4 indicate no effect of motional averaging. This result is in good agreement with the relaxation data discussed below.

In order to gain further insight into the hydrogen dynamics in the different compounds the proton spin-lattice relaxation has been measured on the same samples. In these systems the

total relaxation rate Γ_1 consists in general of the sum of two contributions

$$\Gamma_1 = \Gamma_{1,\text{para}} + \Gamma_{1,\text{dip}} \quad (4)$$

where $\Gamma_{1,\text{para}}$ results from the dynamic interaction of the proton spins with fluctuating magnetic fields arising from paramagnetic impurities. The dipolar relaxation $\Gamma_{1,\text{dip}}$ is due to the motion-induced fluctuations of the magnetic dipole–dipole interaction of a given proton with neighboring protons and with the sodium and aluminum nuclei.

In pure NaAlH_4 the nuclear magnetization was found to recover single exponentially according to Eq. (3) with a rather long relaxation time of $T_1 = (\Gamma_1)^{-1} \approx 3200$ s at room temperature. Shorter relaxation times and deviations from a single-exponential recovery of the nuclear magnetization were observed in less pure samples, purified in a different batch. We assume that Γ_1 in undoped NaAlH_4 is mainly due to the impurity-related paramagnetic relaxation $\Gamma_{1,\text{para}}$ with negligible contributions from the motion-induced dipolar relaxation $\Gamma_{1,\text{dip}}$.

The overall relaxation in the Ti-catalysed samples is much faster than in the untreated samples. Furthermore, rather pronounced deviations from single-exponential recovery of the nuclear magnetization are observed in the doped samples. The data can be reasonably well described by a double-exponential magnetization recovery, as shown in Fig. 4 for NaAlH_4 with 1.8 mol% Ti-clusters. The time constants obtained directly after activating the samples are about 4 and 45 s for doping with TiCl_3 and about 0.7 and 15 s for doping with Ti-clusters. The fast relaxation in the Ti-doped samples may in principle be attributed to an increase of both $\Gamma_{1,\text{dip}}$ and $\Gamma_{1,\text{para}}$. It is reasonable to assume that the hydrogen dynamics is enhanced due to the presence of catalysts, resulting in an increase in $\Gamma_{1,\text{dip}}$. Besides this effect the catalysts may act as paramagnetic centers of relaxation and thus contribute to $\Gamma_{1,\text{para}}$. However, preliminar NMR experiments show that ball milling of pure NaAlH_4 reduces T_1 even without catalysts. Moreover, the recovery of the nuclear magnetization of hydrogen in Ti-doped samples is not exceeding that measured on Na_3AlH_6 (cf. Fig. 4). The Na_3AlH_6 sample was prepared by ball milling of NaAlH_4 and NaH without catalysts, and the proton relaxation of Na_3AlH_6 can be consistently described in terms of hydrogen dynamics (see below). Finally, we found that adding the same amount of catalyst to a paraffin sample is not affecting the proton Γ_1 . Therefore, we assume that the strong increase in the relaxation rate in the case of NaAlH_4 is mainly due to an enhanced hydrogen dynamics caused by the catalysts. The processes of hydrogen dynamics in NaAlH_4 are most likely related to the rotation of the AlH_4 tetrahedra. The different time constants observed in the samples with Ti-based catalysts may be ascribed to AlH_4 tetrahedra at different positions, e.g. in the bulk and at the surface of the crystalline grains.

It is evident from Fig. 4 that after 6 weeks the recovery of the nuclear magnetization in Ti-cluster-doped NaAlH_4

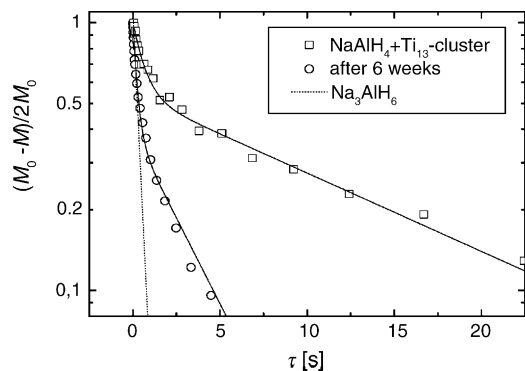


Fig. 4. Recovery of the nuclear magnetization of protons in Ti-cluster-catalysed NaAlH_4 . The measurements were performed at room temperature right after activating the sample and after storing it for 6 weeks in an argon-filled glove box. The dotted line represents the room-temperature recovery of the nuclear magnetization of protons in Na_3AlH_6 .

occurs distinctly faster than right after activating the sample. The corresponding time constants are about 0.3 and 3 s. This result may be ascribed to the more advanced decomposition of NaAlH_4 into Na_3AlH_6 , in which a fast rotational motion of the AlH_6 groups occurs. If the decomposition into Na_3AlH_6 is completed, the relaxation at room temperature is single exponential with a rather short relaxation time of $T_1 = 0.3$ s (cf. Fig. 4).

Fig. 5 shows the Γ_1 values determined for hydrogen in Na_3AlH_6 between 130 and 380 K. Above about 260 K the nuclear relaxation is single exponential according to Eq. (3). The temperature dependence of the corresponding Γ_1 data yields an activation enthalpy of $H_a \approx 0.23$ eV. At intermediate temperatures, between about 200 and 260 K, strong deviations from a single exponential relaxation occur. The Γ_1 data included in Fig. 5 in this temperature range are

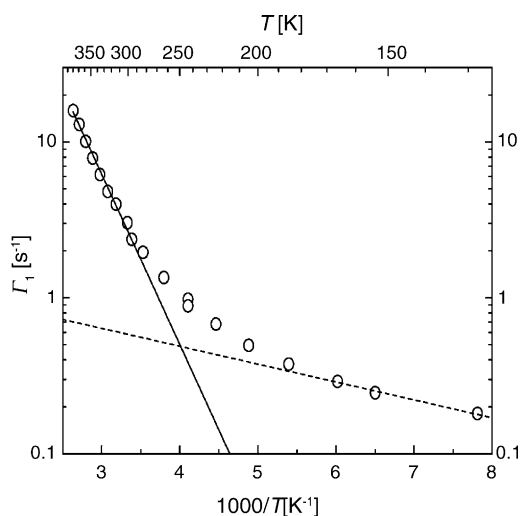


Fig. 5. Temperature dependence of the spin-lattice relaxation of hydrogen in Na_3AlH_6 . The solid and dashed lines correspond to activation enthalpies of 0.23 and 0.02 eV, respectively.

average values obtained by fitting Eq. (3) to the experimental data. Below 200 K the recovery of the nuclear magnetization shows, however, again a single-exponential behavior. These low-temperature Γ_1 data indicate a much lower activation enthalpy, of the order of $H_a \approx 0.02$ eV. The overall temperature dependence of the spin-lattice relaxation can be explained consistently within the framework of the rotation of AlH_6 octahedra in Na_3AlH_6 . Starting below 200 K, hindered rotation of the AlH_6 groups occurs, most likely around an axis with a four-fold symmetry [8]. At higher temperatures a phase change from hindered rotation to full isotropic tumbling of the AlH_6 groups appears. The temperature dependence of Γ_1 leads to activation enthalpies of about 0.02 eV for the hindered rotation and 0.23 eV for the full isotropic exchange.

Previous proton NMR studies on polycrystalline Na_3AlH_6 indicated also a transition between these two types of rotational motion of the AlH_6 octahedra [8]. However, the activation enthalpies reported in [8] for polycrystalline samples are substantially greater than the values of the present work. This result is consistent with the picture that in nanocrystalline samples, obtained by mechanical milling of the material, the local hydrogen mobility is enhanced, resulting in a reduction of the hydrogen desorption temperature.

4. Summary

NaAlH_4 , Na_3AlH_6 and NaH are well characterized by their proton NMR spectra. Thus, the NMR permits an in situ monitoring of the decomposition reactions in these complex metal-hydrides. The hydrogen dynamics in the different compounds is investigated by means of the proton spin-lattice relaxation. In Ti-doped NaAlH_4 deviations from a single-exponential recovery of the nuclear magnetization are observed, indicating at least two fractions of hydrogen with different mobilities. A rather fast local mobility is found for the AlH_6 groups in Na_3AlH_6 . Below about 200 K, the AlH_6 groups rotate around an axis with four-fold symmetry, while above about 260 K, a full isotropic reorientation of the AlH_6 groups occurs.

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