

IV.H.15 In Situ NMR to Understand Hydrogen Storage Chemistry

Mark Conradi (Primary Contact), Eric Sorte,
Tim Ivancic, David Shane, Laura Rayhel, Bob Corey
Washington University
Department of Physics
St. Louis, MO 63130
Phone: (314) 935-6292
Email: msc@wustl.edu

DOE Program Manager: Dr. Refik Kortan
Email: refik.kortan@science.doe.gov

Objectives

- To understand the hydrogen chemistry of hydrogen storage solids.
- To develop nuclear magnetic resonance (NMR) techniques for in situ probing of these systems.

Technical Barriers

- Reaction intermediate species may have very low concentrations and/or short lifetimes.
- Intermediate may be difficult to study by an array of analytical techniques.

Abstract

We have used in situ NMR of ^{27}Al to discover a new mobile species in the hydrogen chemistry of NaAlH_4 . This species is identified by its aluminum chemical shift of 105 ppm, S105. It appears that this is a defect-ridden form of NaAlH_4 itself. This species is likely the long-sought mechanism by which metal atoms are transported in the dehydriding and rehydriding reactions of the alanate. Structure searching has identified a new structure of NaAlH_4 that has a chemical shift in good agreement with S105. It is not yet clear what makes the defect concentration unusually large in this structure. We have developed a new method of measuring the rate of exchange between metal-hydrides and the surrounding gas phase. The H nuclear spins in the hydride have two paths for relaxation: (1) intrinsic (and usually slow) relaxation in the hydride, and (2) exchange with H from the very rapidly relaxing gas phase. In this technique, the observed effective relaxation rate in the hydride is a good estimate of the rate of exchange from the hydride to the gas phase. We have applied the method to PdH_x and PdD_x and find overall exchange activation energies of 0.32 eV in both.

The gamma phase of $\text{Mg}(\text{BH}_4)_2$ has 33% open space, suggesting that BH_4 diffusion may be substantially enhanced

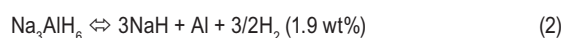
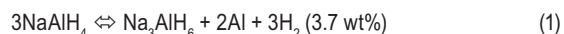
in this phase. However, our hydrogen NMR lineshapes and T_{1D} (slow-motion) measurements show no evidence of diffusion (to 100 s^{-1}) at temperatures to 150°C . The borohydride group reorientations in this phase have a large barrier energy, much like the alpha phase, as measured through the hydrogen T_1 relaxation. At and above 175°C , the gamma phase transforms to something equal or very similar to the beta phase, as demonstrated by the hydrogen T_1 and X-ray diffraction.

Sodium hydride is one of the simplest hydrides, yet little is known about its H and Na diffusion. We report H and ^{23}Na lineshapes and T_1 , as well as hydrogen $T_{1\rho}$ for commercial samples of NaH and a sample of pure and ball-milled NaH from Jensen in Hawaii. For the commercial material, there is an increasing fraction of mobile H as the temperature is increased. The remainder of the H line narrows between 250 and 300°C . By 300°C , the sodium line is only narrowed by a factor of 2, showing that Na-Na interactions are not being averaged (the Na are not yet diffusing). The UH sample of ball-milled NaH displays line narrowing of the hydrogen at a remarkably lower temperature (about 130°C).

Progress Report

NaAlH_4

NaAlH_4 is a complex hydride, having covalently bonded AlH_4^- anions ionically bonded with the Na^+ counterions. While the (complex) LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ systems have larger theoretical reversible hydrogen mass fractions (18.4 and 14.9%), NaAlH_4 (5.6 wt%) remains the archetypal complex storage system when doped with titanium or other metals. Its status reflects the early discovery of the catalysis effect, the large amount of subsequent NaAlH_4 research, and the prospect of operation near 100°C , using waste heat from a polymer electrolyte membrane hydrogen fuel cell. The decomposition of this system occurs in two generally distinct steps, each releasing H_2 gas and Al metal:



Despite years of intense study, the mechanism of the above reactions and the role of the catalyst remain uncertain. Good reviews of the current knowledge on NaAlH_4 have appeared.

In the rehydriding direction, spent NaH + Al metal under excess H_2 gas pressure combine to form NaAlH_4 . Therefore, spatially separated Na and Al atoms are somehow brought into intimate (stoichiometric) contact. This transport of metal atoms has been identified as the likely reaction

bottleneck, according to H-D isotopic scrambling and other measurements. Therefore, we and others have hypothesized the existence of a mobile, Al- or Na-bearing species that is a key intermediate in the reaction(s).

We report here the discovery by in situ ^{27}Al NMR spectroscopy of just such a mobile, Al-bearing species. Crucially, the new species (i.e. not one of the well-known species of reactions 1 and 2), formed at elevated temperature and pressure, can be retained for further study at ambient pressure and temperature.

Taken together, the results suggest that S105 is a highly mobile, Al- and H-bearing entity with an ^{27}Al chemical shift very near that of NaAlH_4 itself. S105 accounts for $\sim 10\%$ of the aluminum spins for undoped NaAlH_4 melted under excess H_2 pressure. We propose that S105 is a highly defective form of NaAlH_4 . In particular, following the calculations of Guyadin et al, the defects are AlH_3 vacancies. Such vacancies were calculated to diffuse on the several picosecond time scale; this would lead to rapid motion of a much larger number of Al and H atoms. This proposal provides natural explanations for the ^{27}Al shift of S105 being close to that of NaAlH_4 , motionally narrowed resonances of S105 in ^{27}Al and hydrogen (but not ^{23}Na) NMR, the large number of Al spins in the S105 line, and the disorder apparent in X-ray diffraction. Crucially, such AlH_3 vacancies would promote the aluminum atom transport needed for rehydriding in reaction 1.

The NMR of S105 shows, for the first time, direct spectroscopic evidence of a mobile chemical intermediate in the hydrogen reactions of NaAlH_4 . Importantly, the new species can be harvested under ambient conditions for further study.

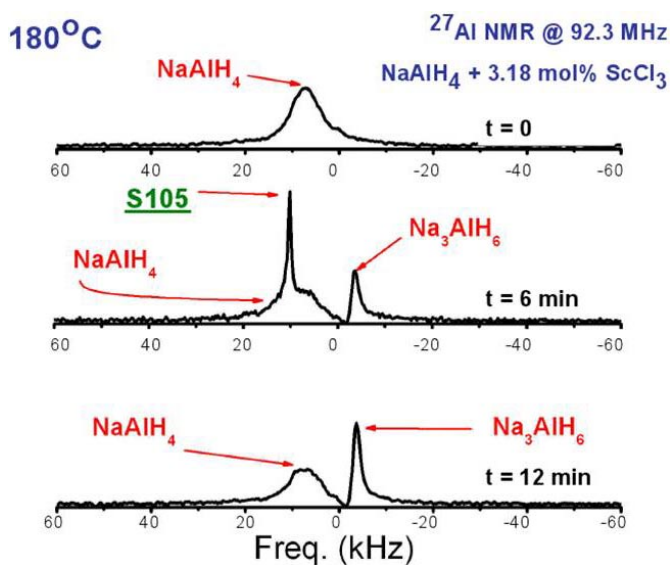


FIGURE 1.

Hydride to Gas Exchange

At thermal equilibrium, many metal-hydrides and deuterides are surrounded by H_2 or D_2 gas at a considerable pressure. Exchange of H or D between the solid and gas phases provides a new pathway for nuclear spin relaxation, beyond the processes that are intrinsic to the solid phase, because of the extremely rapid spin relaxation of the gas at typical conditions. A crucial requirement is that the number of spins in the gas phase must be of the same order as the number of spins in the solid. Thus, the solid powder particles (where H or D is at high density compared to the gas) should be spread out in space, supported on a substrate in dilute fashion.

This effect, an increase in the apparent relaxation rate by exchange with the surrounding gas, has been observed. More recently, it was used to determine the exchange rate K_{pg} (from palladium to gas) of H in PdH_x in equilibrium with H_2 gas. The probability of successful crossing of the surface barrier (from palladium to gas) was estimated as 2.8×10^{-7} at 20°C , in agreement with earlier work based on H,D exchange.

The PdD_x/D_2 system has a larger ratio of the intrinsic relaxation rate of the gas to the intrinsic relaxation rate of the solid, compared to the PdH_x/H_2 system. Thus, the exchange rate of D atoms from the solid metallic phase to the gas phase, K_{pg} , can be followed over a wider range of temperatures and rates. This allows a more accurate determination of the activation energy for the exchange

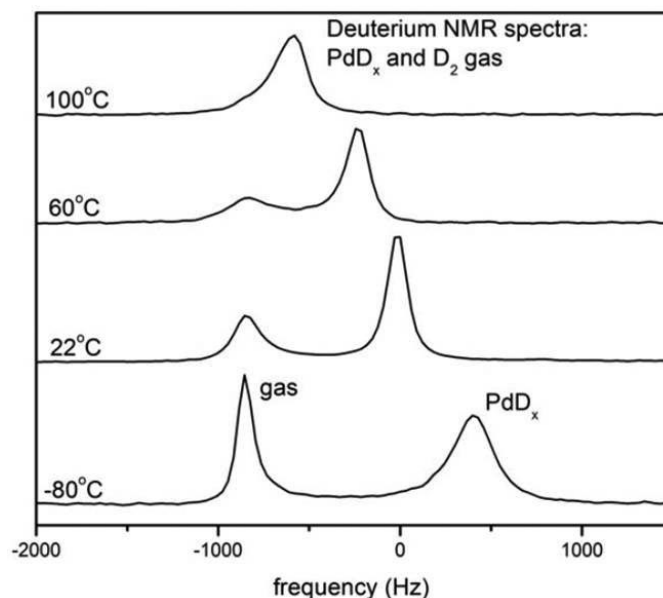


FIGURE 2. Deuterium NMR spectra of PdD_x and the surrounding D_2 gas at several temperatures. The 22°C spectrum shows that there are about half as many D nuclear spins in the gas as in the deuteride. At -80°C , PdD_x broadens due to the slowing of the internal motions. At 60°C , the gas resonance is broadened by gas-deuteride exchange; by 100°C , the resonances are partially merged.

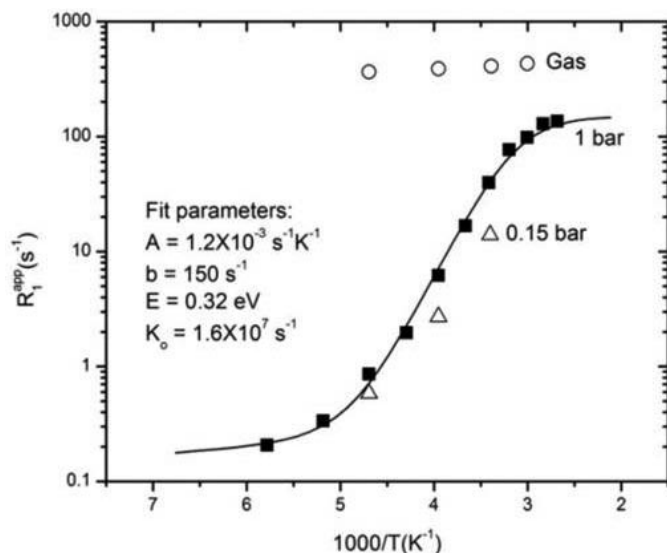


FIGURE 3.

process. Here in PdD_x/D_2 , we follow K_{pg} over about three decades and find (Figure 3) K_{pg} to have $E = 0.32 \text{ eV} \pm 10\%$. A re-analysis of the relaxation data from the PdH_x/H_2 system (Figure 4) shows very similar exchange rates and activation energy, compared to the deuterium system.

$\gamma\text{-Mg}(\text{BH}_4)_2$

Metal borohydrides are attractive candidates for hydrogen storage for transportation and other applications, due to their typically large mass fractions of hydrogen. The utilization of metal borohydrides is often hampered by slow hydrogen release and uptake kinetics, which call for fundamental studies of mobility and dynamics of hydrogen and the complex tetrahydridoborate anions, BH_4^- , in this class of materials.

Magnesium borohydride has an extreme structural flexibility (several polymorphs have been observed) and high gravimetric hydrogen storage density of $\rho_{\text{m}} = 14.9 \text{ wt}\% \text{ H}_2$, and it stores hydrogen reversibly. It is therefore considered one of the most interesting hydrogen storage materials. However, hydrogen uptake (from the dehydrided state) has up to now only been realized at relatively harsh conditions (400°C and 950 bar).

A new nanoporous polymorph of magnesium borohydride denoted $\gamma\text{-Mg}(\text{BH}_4)_2$ was recently discovered. This polymorph crystallizes with space group symmetry $I\bar{d}\text{-}3a$ and has a remarkably low material density of $\rho = 0.55 \text{ g/cm}^3$ due to a three-dimensional net of interpenetrating channels of $\sim 8 \text{ \AA}$ diameter giving $\sim 33\%$ empty void space.

The large void space in the γ -phase crystal structure suggests that rapid diffusion of BH_4 units, as observed in LiBH_4 but not in α or $\beta\text{-Mg}(\text{BH}_4)_2$, may occur at an enhanced

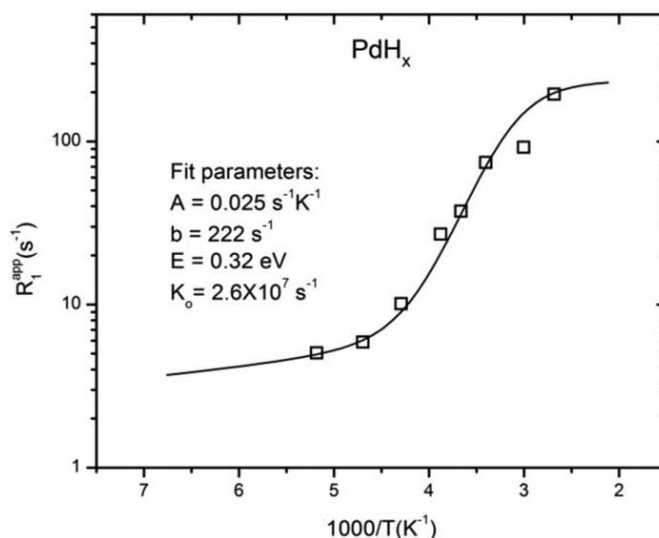


FIGURE 4. Nuclear spin-lattice relaxation data for PdH_x surrounded by 0.9 bar H_2 (at 20°C). The points are data from reference 3; the solid curve is a fit using equations (5) and (6) with the listed parameters.

rate in the γ -phase. Rapid diffusion of BH_4 could have a positive effect on the kinetics of dehydriding and rehydriding of this material. This has prompted our present investigation of hydrogen NMR lineshape and T_{1D} (T_{1D} is sensitive to motions which are too slow to narrow the line). Hydrogen T_1 is also reported, because it is determined by and can report upon reorientations of the BH_4 units.

Hydrogen NMR lineshapes reveal no motional narrowing due to translational self-diffusion in the main part of the resonance, up to 175°C. “Slow” motion measurements by means of the hydrogen T_{1D} indicate the absence of translational motions faster than 10^2 s^{-1} up to this temperature. Thus, despite the large amount (33%) of open volume in $\gamma\text{-Mg}(\text{BH}_4)_2$, we find no evidence for rapid diffusion.

The hydrogen T_1 is controlled by the rate of BH_4 reorientation. Observation of a deep minimum in T_1 at 50°C demonstrates that the mean rate of reorientation is about 10^9 s^{-1} at 50°C. The T_1 behavior of γ -phase is similar to that reported in α -phase, where activation energies for BH_4 reorientation were found to be 0.12, 0.20, and 0.36 eV. By comparison, in β -phase $\text{Mg}(\text{BH}_4)_2$, a T_1 minimum occurs at -135°C and is described by an 0.12 eV activation energy. Thus, the mean activation energy for BH_4 reorientation in γ -phase is high, as in α -phase. The ^{11}B T_1 shows a minimum at 50°C, as well. This is as expected, because the intramolecular B-H dipole interaction, modulated by BH_4 reorientations, drives (in part) both the hydrogen and ^{11}B spin-lattice relaxations.

Our γ -phase material transformed to another phase upon standing at 175°C for 2 h in one case. Subsequent heating to 225°C completed the transformation. A second sample

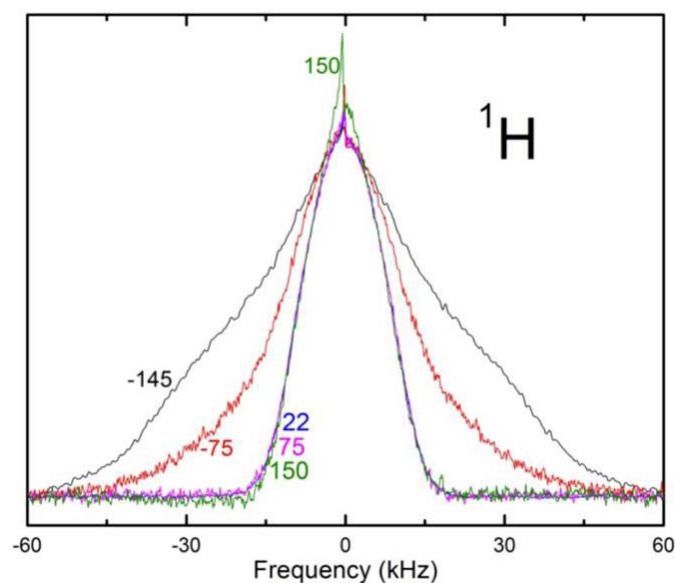


FIGURE 5. Hydrogen NMR spectra of γ -Mg(BH₄)₂ at several temperatures. At -75 and -145°C, pronounced broadening is due to slowing of the BH₄ reorientations. At and above 22°C, no further narrowing of the main resonance occurs, ruling out rapid BH₄ translational diffusion. At the highest temperature, a narrow component appears, reflecting a small fraction of mobile spins, probably from residual solvent.

of γ -phase Mg(BH₄)₂ transformed during 1 h at 250 °C. T₁ of the transformation products down to -125°C were found to be similar but not equal to T₁ of β -Mg(BH₄)₂. The data suggest that the transformation products are largely β -phase. Boron-11 magic-angle spinning NMR of the recovered transformation product demonstrates the transformed material is not significantly dehydrided; essentially all the boron atoms remain as BH₄. Powder X-ray diffraction shows that material TP2 has a crystallographic structure equal to that of the β -polymorph; an amorphous component can not be ruled out.

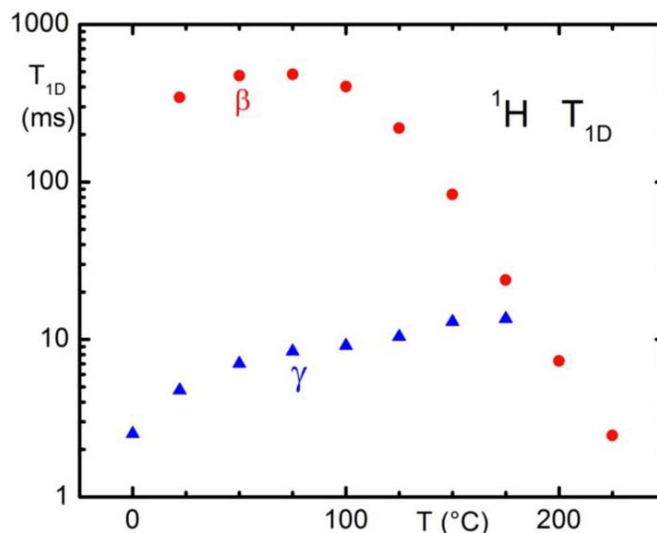


FIGURE 6. Hydrogen NMR measurements of T_{1D} in γ -Mg(BH₄)₂, together with β -polymorph data from reference 14 for comparison. In γ -phase, there is no sharp decrease in T_{1D} at elevated temperatures that would signal thermally activated diffusive hopping with rates 10² s⁻¹ or faster.

Future Directions

Our program is focusing on the complex hydrides. We will look first for systematics in the formation of S105 in NaAlH₄. We will make measurements on pure Na₃AlH₆, with the aim of excluding the hexahydride as the source of S105. Potassium alanate will be examined next, as it is the alanate most similar to sodium alanate. We will extend this work to include Li and Mg borohydrides, because of the large interest generated by those high capacity materials. In each case, the program is aimed at finding mobile intermediate species that are keys to understanding the hydrogen reactions of these storage solids.