IV.I.13 NMR of Hydrogen Storage Systems: Ionic Hydrides and Mobile Species

Major Accomplishments for Period 01 September 2008 – 15 April 2009

In the past, hydrogen storage solids were almost exclusively *interstitial metallic hydrides*. These are noted for their generally good hydrogen diffusion kinetics; here we report $\omega_H$, the rate of atomic-level hydrogen hopping events. This is nicely demonstrated in Figure 1, where $\omega_H$ appears on a logarithmic scale for the prototypical ionic system MgH$_2$ and in the metallic systems ScH$_2$, Mg-ScH$_x$, and LaNi$_5$H$_6$. Clearly, MgH$_2$ has much slower dynamics than the metals, and a much higher activation energy. Remarkably, MgH$_2$ can be converted from the rutile (ionic) structure to the fluorite (metallic) structure with as little as 20% Sc, though Figure 1 is for 35% Sc; the H hopping in the metallic phase is much faster than in MgH$_2$ and is even a bit faster than in ScH$_2$.

While the metallic hydrides show good H kinetics, an essential feature of any hydrogen storage system, the mass-fraction of H, is too small. Thus, interest has turned to the lightweight hydrides, such as LiH, MgH$_2$ (7.6 w/w%), NaMgH$_3$, and LiBH$_4$ (18 w/w%). These are all *ionic or complex* hydrides. We examined coarse-grained MgH$_2$ as the prototypical ionic hydride. The rate $\omega_H$ of H hopping remains too slow to narrow the hydrogen NMR line up to 400°C, so $\omega_H < 10^5 \text{s}^{-1}$. This confirms the reputation of MgH$_2$ for slow kinetics – rehydridding Mg metal often is halted once a thin skin of MgH$_2$ forms and blocks further reaction progress.

To detect and measure such slow motions, we turned to the ultraslow motion experiment of Ailion and Slichter. Standard spin Zeeman-order is converted to spin dipolar-order at the start of the experiment. This order is found to decay with time constant $T_{1D}$. Because dipolar order is a correlation between a spin’s orientation and the local dipolar field from its neighbors, and because the local field varies from site-to-site with little correlation, a single atomic jump destroys a given spin’s contribution to the dipolar order. Thus, the measured relaxation rate $1/T_{1D}$ is essentially equal to the rate of atomic jumps for a typical H atom.

Results are presented in Figure 2 for coarse-grain MgH$_2$. The straight-line region represents thermally activated H motion, from $0.1 \text{s}^{-1}$ at 250°C to $400 \text{s}^{-1}$ at 400°C; these are indeed slow motions. The activation energy is $1.72 \text{ eV} (\pm 7\%)$, a high value that explains the slow kinetics of MgH$_2$. At lower temperatures, the data curve and are no longer controlled by H kinetics; the
dipolar order decays through coupling to the $^{25}\text{Mg}$ spins and the quadrupolar $T_1$ process. The overall fit to the data incorporates both mechanisms and is excellent.

We investigated a number of ball-milled MgH$_2$ materials supplied by collaborators at Savannah River, Université de Québec Trois Rivieres, and GKSS (Germany). Lineshape data are presented in Figure 3a for the most “accelerated” system – MgH$_2$ with 0.5 mol% Nb$_2$O$_5$ from GKSS. Already at 100°C, a line-narrowed component appears, indicating a small fraction of mobile H atoms (here “mobile” means $\omega_H > 10^5$ s$^{-1}$). With increasing temperatures, the fraction of intensity in the narrowed line (see graph in Figure 3b) increases up to ~31% at 400°C. Two aspects are worthy of note: mobile H atoms appear already at low temperature (100°C) and the sample is inhomogeneous, with some slow-moving H and some fast moving. Presumably, the sample inhomogeneity reflects a very broad distribution of local environments, due to the aggressive mechanical activation process.

In addition, the relaxation time $T_1$ decreases from 3,000 s to 0.1 s in the ball-milled GKSS material. This rapid relaxation, only weakly temperature dependent, demonstrates a large concentration of unpaired electron spins from mechanical rupture of the bonds.

The behavior of ball-milled MgH$_2$ is similar to NaMgH$_3$, ball-milled from 1:1 NaH and MgH$_2$. The hydrogen NMR line narrows starting below 100°C. The narrowing is inhomogeneous up to 275°C, beyond which the rest of the line narrows rapidly. The $T_1$ of NaMgH$_3$ is a few seconds, remarkably short for such a ‘rigid’ spin system; presumably, a large concentration of unpaired electrons are present here as well.

LiBH$_4$ has much faster atomic motions. At all temperatures above -100°C, the tetrahedral BH$_4$ units reorient rapidly, as shown in earlier work. At a solid-solid transition at 109°C, the Li$^+$ motion increases dramatically. As in Figure 4, the $^7\text{Li}$ resonance narrows so that quadrupolar satellites at ±10 kHz are clearly resolved. Thus, the high-temperature (HT) phase may be superionic, though the Li$^+$ motion is $\approx 10^9$ s$^{-1}$, far below the liquid-like rates of some superionics.

The H and $^{11}\text{B}$ resonances also narrow from 170-240°C, well into the HT phase (see Figures 5, 6, and 7). The activation energy extracted from H linewidth and $T_1D$ data is 0.72 eV, ±5%. The narrowing of the $^{11}\text{B}$ resonance is crucial: if the BH$_4$ units were not diffusing and the H were moving by exchanging between neighboring BH$_4$ units, the $^{11}\text{B}$ linewidth could not decrease below that predicted from B-B dipolar interactions. This limiting width is calculated to be 1,600 Hz, while the narrowest line in Figure 7 is 300 Hz (all values FWHM). So, the BH$_4$ are diffusing as intact units.
Measurements in molten LiBH₄ at 285°C rule out rapid H-exchange between BH₄ units. As displayed in Figure 8, the ¹¹B spectrum has 5 lines of intensity ratio 1:4:6:4:1. This is unambiguous evidence that each BH₄ has long-lived spin states of the 4 H atoms (i.e., 4 up, 3 up + 1 down, 2 up + 2 down, etc.). Rapid exchange would lead to collapse (averaging, narrowing) of the 5-line pattern. From the linewidth in Figure 8, the BH₄ lifetime against H-exchange is at least 16 ms. From spin-echo experiments, the lifetime is at least several seconds. Thus, exchange in the melt is slow; in the solid the exchange will be even slower. Thus the previously observed isotopic scrambling of BH₄, BH₃D, BH₂D₂, etc does not occur through rapid H-exchange.

Separate NMR isotope scrambling experiments starting with mixed LiBH₄ and LiBD₄ powders find nearly complete isotopic mixing in 30 minutes or less. Thus, in the melt, H-exchange falls in between the several second and 30 minute time scales.

Publications


People Working on DOE Project

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