In Situ NMR Study on the Interaction between LiBH_4 – $\text{Ca}(\text{BH}_4)_2$ and Mesoporous Scaffolds

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S Supporting Information

ABSTRACT: We discuss the use of nuclear magnetic resonance (NMR) spectroscopy to investigate the physical state of the eutectic composition of LiBH_4 – $\text{Ca}(\text{BH}_4)_2$ (LC) infiltrated into mesoporous scaffolds and the interface effect of various scaffolds. Eutectic melting and the melt infiltration of mixed borohydrides were observed through in situ NMR. In situ and ex situ NMR results for LC mixed with mesoporous scaffolds indicate that LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ exist as an amorphous mixture inside of the pores after infiltration. Surprisingly, the confinement of the eutectic LC mixture within the mesopores is initiated below the melting temperature, which indicates a certain interaction between the borohydrides and the mesoporous scaffolds. The confined borohydrides remain inside of the pores after cooling. These phenomena were not observed in microporous or nonporous materials, and this observation highlights the importance of the pore structure of the scaffolds. Such surface interactions may be associated with a faster dehydrogenation of the nanoconfined borohydrides.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

Complex hydrides have received attention as promising hydrogen storage materials because of their high gravimetric/volumetric hydrogen densities. In a recent effort to improve their hydrogen storage properties, nanoconfinement effects have been extensively explored using various meso-/nanoscaffolds.^{1–12} A reduced particle size decreases the diffusion lengths required for an interphase reaction and thus boosts the reaction kinetics.¹³ The nanoconfinement of hydrides into nanopores has been often shown by the disappearance of X-ray diffraction (XRD) peaks^{4,7,9,10,12} and by the loss of the bulk properties such as phase-transition or melting signals in differential scanning calorimetry (DSC) data.^{2,7,9,10} The origin of those phenomena and the physical states of the hydrides after incorporation or infiltration into the nanopores are not yet fully understood. Although the interface between the nanoconfined hydrides and scaffolds and the reduction in particle size are both recognized as important factors for altering the hydrogen storage properties of these materials, spectroscopic characterization of this observation has rarely been reported.¹¹ Therefore, the physical state of the hydrides upon infiltration into the nanopores must be further investigated to understand the interface/surface effect of various scaffolds.

Recently, we observed enhanced hydrogen desorption and absorption properties for a eutectic $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ composite (LC) co-infiltrated into CMK-3, an ordered mesoporous carbon.⁹ The dehydrogenation process was

accelerated, and the desorption temperature was significantly reduced to $\sim 300^\circ\text{C}$, compared with $\sim 400^\circ\text{C}$ for pure LC. In addition, the XRD peak intensity of the borohydrides weakened, and the eutectic melting was hardly seen in the DSC data even after the composite was ball-milled with CMK-3. The peaks were completely lost after melt infiltration. Nuclear magnetic resonance (NMR) spectroscopy is indispensable in understanding these phenomena and in probing the local environment of the $[\text{BH}_4]^-$ anions. The system was found to be suitable for the application of in situ variable temperature (VT) NMR because of the lowered melting temperatures of the two borohydrides ($\sim 200^\circ\text{C}$) and because of the wide separation of the ^{11}B NMR shifts for the $[\text{BH}_4]^-$ anions (~ 10 ppm) in LiBH_4 and $\text{Ca}(\text{BH}_4)_2$. Because nanoconfinement is often achieved through the introduction of hydride particles into host scaffold pores using a melt infiltration method, such in situ spectroscopic observation is believed to be highly valuable. In this work, we used solid-state magic angle spinning (MAS) NMR to elucidate the local environment of the ionic species in the LC composite and the way in which they interact with the support materials. The composite borohydrides, combined with the scaffold materials exhibiting a wide range of porosities, were carefully examined at different stages by in situ and ex situ

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NMR. We also demonstrate the nanoconfinement effect on the hydrogen storage ability of the investigated composite material.

Figure 1 presents the ex situ ^{11}B MAS NMR spectra for ball-milled LC and LC/CMK-3. The ^{11}B NMR spectra of LC/

Figure 1. Ex situ ^{11}B MAS NMR spectra of the ball-milled $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ without CMK-3 (black) and with CMK-3 (red). The reference spectra of $\alpha\text{-Ca}(\text{BH}_4)_2$, $\beta\text{-Ca}(\text{BH}_4)_2$, and $o\text{-LiBH}_4$ are shown in pink, brown, and blue, respectively. Spinning sidebands are marked by the *.

CMK-3 differ significantly from those of pure LC with respect to peak broadness and peak shift, and the appearance of a new peak is observed (marked by an arrow). A similar feature also appears in the ^1H and ^7Li NMR spectra (see Figure S1, Supporting Information). Notably, the new peak in the ^{11}B NMR spectrum was not detected when the individual borohydride was milled separately with CMK-3, such as $\text{LiBH}_4/\text{CMK-3}$ or $\text{Ca}(\text{BH}_4)_2/\text{CMK-3}$ (see Figure S2, Supporting Information). This result indicates that the ball milling process may induce local melting, such that part of the borohydrides can come into close contact with the carbon surface, similar to what occurs during melt infiltration. In fact, after milling with CMK-3, most of the LC becomes amorphous, as observed from the drastically reduced XRD peak intensities (see Figure S3, Supporting Information). Such changes in the characteristic NMR signatures and amorphization observed through XRD raise the question of whether the appearance of the new peak is a consequence of the nanoconfined eutectic mixture. To answer this question, we applied an in situ VT NMR method to obtain direct and valuable insights into the borohydride particles that infiltrate into the pores and become confined.

The in situ ^{11}B VT MAS NMR spectra of hand-mixed LC (without CMK-3) are presented in Figure 2. The mixture could be readily assessed based on the ^{11}B spectra of the pure borohydrides shown in Figure 1. For the anion $[\text{BH}_4]^-$, we use a notation such as $[\text{BH}_4]_{\alpha\text{-Ca}}^-$ to denote the $[\text{BH}_4]^-$ in the $\alpha\text{-Ca}(\text{BH}_4)_2$ crystalline phase. The room-temperature spectrum indicates that $[\text{BH}_4]_{\alpha\text{-Ca}}^-$, $[\text{BH}_4]_{\beta\text{-Ca}}^-$, and $[\text{BH}_4]_{\text{Li}}^-$ (in this case, $o\text{-LiBH}_4$) all remain intact, as indicated by peaks at -30 , -33 , and -42 ppm, respectively. When the temperature is increased to 100°C , the $o\text{-LiBH}_4$ peak suddenly becomes sharp, which indicates an approximately 10-fold reduction (330 to 35 Hz) in its full width at half-maximum (fwhm). This change may be related to the increased mobility of $[\text{BH}_4]_{\text{Li}}^-$ that could result in

Figure 2. In situ ^{11}B VT MAS NMR spectra of the hand-mixed $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ without CMK-3. The peak positions of $\alpha\text{-Ca}(\text{BH}_4)_2$, $\beta\text{-Ca}(\text{BH}_4)_2$, and $o\text{-LiBH}_4$ are marked by “ α ”, “ β ”, and “ o ”, respectively. The measurements were taken from room temperature to 170°C and again at room temperature after the sample was cooled. The illustration in the inset schematically describes the mechanism for the appearance of a new peak at -36.4 ppm.

the efficient averaging of line-broadening sources,¹⁴ such as B–H, B–B, and B–Li dipole couplings and a ^{11}B quadrupole interaction ($I = 3/2$). However, this observation is unexpected because no sudden increase in boron mobility at such a low temperature has been previously reported in the literature.^{14,15} The line width broadens slightly (to 62 Hz fwhm) at temperatures higher than 140°C . B–H J -coupling was not observed upon the removal of ^1H decoupling; thus, as expected, the LiBH_4 is not in the liquid or liquid-like phase at 100°C . Similar line narrowing was observed in a ^7Li MAS NMR spectrum at the same temperature of 100°C (data not shown), whereas noticeable line narrowing in the ^1H MAS NMR spectrum occurred only after the temperature was increased to higher than 170°C (see Figure S4, Supporting Information). Therefore, rapid diffusion of the entire $[\text{BH}_4]_{\text{Li}}^-$ unit can be excluded as the mechanism for the line narrowing in the ^{11}B NMR spectrum. Because a rapid Li^+ diffusion is known to occur at approximately 120°C for LiBH_4 due to a polymorphic phase transition,¹⁶ the change in the ^7Li line width can be understood, although the temperature in this case is slightly lower. Rapid Li^+ diffusion appears to be coinciding with such efficient averaging of the anisotropic spin–spin interaction for boron in $[\text{BH}_4]_{\text{Li}}^-$ of the LC eutectic mixture. However, the exact mechanism requires further exploration.

Following the phase transition of LiBH_4 , the α -to- β phase transition of $\text{Ca}(\text{BH}_4)_2$ occurs at $\sim 140^\circ\text{C}$, approximately the same temperature as measured using DSC.⁹ At this point, a new peak begins to appear at -35 ppm and shifts gradually upfield with increasing temperature. At 170°C , only a single sharp peak exists at -36.4 ppm, located between the peaks of LiBH_4 and $\text{Ca}(\text{BH}_4)_2$. The B–H J -coupling (82 Hz)^{14,17} was also observed, which indicates that the eutectic melting has taken place. Thus, both borohydrides are expected to be well mixed in the liquid state. The origin of the new peak in the in situ ^{11}B NMR of LC can be explained using the schematic illustration in the inset of Figure 2. At room temperature, Li^+ and Ca^{2+}

cations form stable and strong ionic bonds with $[\text{BH}_4]_{\text{Li}}^-$ and $[\text{BH}_4]_{\text{Ca}}^-$, respectively. However, as the temperature is increased, the cation exchange slowly progresses up to the melting point, where a uniformly mixed state is reached. The cation exchange is apparently initiated at temperatures lower than the melting temperature possibly due to the accelerated diffusion of the Li^+ ions. The appearance of a small peak at -35.5 ppm at 140°C hints at the formation of a solid solution that contains LiBH_4 and $\text{Ca}(\text{BH}_4)_2$, which may act as a seed for large-scale ion exchange. Finally, near the eutectic melting temperature, a random mixture of cations renders $[\text{BH}_4]^-$ anions completely indistinguishable in the liquid. After the mixture was cooled, the ^{11}B spectrum indicated the separate recrystallization of the two borohydrides. The thermodynamically stable $\alpha\text{-Ca}(\text{BH}_4)_2$ phase was favorably formed over the starting material of $\beta\text{-Ca}(\text{BH}_4)_2$ because the presence of LiBH_4 facilitates the polymorphic phase transition.^{18,19}

Figure 3 shows that mixing with the CMK-3 (LC/CMK-3) results in a notable change in the in situ VT ^{11}B NMR spectra.

Figure 3. In situ ^{11}B VT MAS NMR spectra of the hand-mixed $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ with CMK-3. The peak positions of $\alpha\text{-Ca}(\text{BH}_4)_2$, $\beta\text{-Ca}(\text{BH}_4)_2$, and $o\text{-LiBH}_4$ are marked by “ α ”, “ β ”, and “ o ”, respectively. The illustration in the inset schematically describes the mechanism for the appearance of a new peak at -38.5 ppm at a relatively low temperature.

A new peak (-38.5 ppm) emerges at temperatures as low as 80°C , compared with 140°C for LC in the absence of a carbon support, as shown in Figure 2. This result indicates that contact with the carbon surface may promote the formation of a solid solution before any significant increase in the ionic mobility, for example, that of Li^+ in LiBH_4 , occurs. As the temperature reaches 170°C , the new peak grows rapidly, while the peaks for $\text{Ca}(\text{BH}_4)_2$ and LiBH_4 diminish and leave small traces. Notably, the peak position shifts upfield from -36.4 ppm for LC alone due to the influence of the CMK-3 surface. Surprisingly, the new peak at -38.5 ppm in the hand-mixed LC/CMK-3 persists after the mixture is cooled, which is in contrast to the LC, in which a clear phase separation is observed. The position of the new peak is close to the -38 ppm peak for the ball-milled LC/CMK-3 shown in Figure 1. As previously mentioned, we can infer that cation mixing that is similar to eutectic melting may

occur during ball milling and that the presence of CMK-3 can stabilize the mixed state, possibly via nanoconfinement.

The ^7Li NMR spectra shown in Figure 4 can aid in understanding the status of cations in the borohydrides

Figure 4. ^7Li MAS NMR spectra of $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ mixed with CMK-3 (a) ex situ results of the infiltrated (upper, in orange) and ball-milled (lower, in olive) samples and (b) in situ results of the hand-mixed samples at 20°C (black) and 170°C (red) and after cooling (blue). The peak positions marked by the dotted line correspond to Li^+ in the bulk LiBH_4 crystalline phase.

incorporated into the CMK-3. The spectrum of the infiltrated LC/CMK-3 indicates a new peak at -4 ppm and is clearly distinguished from the spectrum of the hand-mixed LC/CMK-3. The ^7Li spectrum of the ball-milled LC/CMK-3 resembles the ^{11}B spectrum of the same sample in Figure 1 in that the newly formed peak after ball milling coexists with the bulk LiBH_4 peak at -1.2 ppm. In the in situ results in Figure 4b, the spectrum of the hand-mixed LC/CMK-3 at 170°C shows a new peak, similar to the spectrum of the infiltrated sample. The spectrum of the cooled LC/CMK-3 retains this new peak, which demonstrates the nanoconfinement of the LC in the CMK-3. This result is consistent with that found in the ^{11}B NMR spectra, and we confirm that the new peaks in the ^{11}B NMR (Figure 3) and ^7Li NMR (Figure 4) spectra for LC/CMK-3 originate from the nanoconfined eutectic mixture in which $[\text{BH}_4]^-$ forms random ionic bonds with both Li^+ and Ca^{2+} cations.

Thus, we can understand the unusual DSC profiles of LC/CMK-3 reported in Figure 7 of the work by Lee et al.⁹ The previously described NMR results indicate that when the LC composite is infiltrated inside of the pores, $[\text{BH}_4]^-$ becomes indistinguishable; LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ do not exist as separate crystalline phases but instead form an amorphous mixture. Therefore, we cannot expect any phase transition or melting in the DSC measurement.^{9,20} The gradual growth of a new peak with increasing temperature and without any clear indication of melting in the in situ ^{11}B NMR spectra shown in Figure 3 appears to explain the broad exothermic peak^{2,9,10} found via DSC; even the exothermic infiltration process could have

Figure 5. (a) In situ and (b) ex situ ^{11}B VT MAS NMR spectra of the hand-mixed $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ composite with mesoporous MCM-41 (see the Supporting Information for experimental details for the ex situ ^{11}B VT MAS NMR). In situ ^{11}B MAS NMR spectra of the hand-mixed $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ with (c) microporous pure silica zeolite and (d) nonporous graphite.

occurred over a wide temperature range because no well-defined melting temperature exists for an amorphous phase. Though it is not yet conclusive, we believe that this amorphous state inside of the pores is thermodynamically stable rather than kinetically frozen by restricted mobility; the applied cooling rate is slow enough for phase separation to occur in the case of LC, and the in situ NMR results in Figure 3 show that the contact with carbon pore walls could make ion diffusion even faster.¹¹ The results thus far clearly support a significant surface interaction between the LC and the carbon pores.

In order to investigate whether such a strong interaction is due to the surface chemistry or the pore structure, various scaffolds, such as mesoporous MCM-41,²¹ microporous zeolite, nonporous quartz glass powder, and nonporous graphite, were employed, and similar NMR experiments were conducted. The experimental details are described in the Supporting Information. Among the materials tested, only the LC/MCM-41 produced ^{11}B NMR results (Figure 5a,b) similar to those for LC/CMK-3 shown in Figure 3. The signature peak at -36.5 ppm for the solid solution appeared at ~ 80 °C and grew continuously. When the melt phase was cooled after the sample was heated to only 120 °C for the ex situ NMR (Figure 5b), peaks remained at approximately -37 ppm. The NMR spectra of zeolite (Figure 5c), crushed quartz glass powder (data not shown), and graphite (Figure 5d) are similar to those of pure LC; a new peak from the eutectic melt of LC appears near the melting temperature and disappears after the samples are cooled. This result demonstrates that the high mobility of the borohydrides at such low temperature is catalyzed by contact with the porous scaffold surface irrespective of the chemical composition, at least within our study, and that after the solid solution forms, it maintains the eutectic composition rather than recrystallizing back to the separate LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ phases.

Having determined the enhanced interface interaction accompanied by the nanoconfinement, we examined its effect on hydrogen desorption using thermogravimetry (TG)

combined with mass spectrometry (MS). The TG-MS data for pure LC and LC ball-milled with CMK-3 or graphite are presented in Figure 6. The temperature of the main

Figure 6. TG-MS data for the ball-milled pure $0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$ (black), with CMK-3 (red), and with graphite (blue). Release of H_2 is indicated by the normalized ion current.

dehydrogenation is lower for LC/graphite than that for pure LC, and the LC/CMK-3 outperforms the LC/graphite. We note that the hydrogen release at 255 °C in LC/graphite results from partial oxidation of borohydrides by oxygen impurities;^{22,23} similar mass drop in TG data is seen for pure LC and also for LC/CMK-3, though it appears more broadly.

The outer surface of the CMK-3 is known to have a graphite-like, polyaromatic character similar to that of carbon black or carbon fibers.²⁴ The graphitic nature of the CMK-3 surface has been confirmed via Raman spectroscopy and is primarily composed of carbon atoms in an sp^2 hybrid state with a

reduced quantity of disordered bonding.^{24,25} Therefore, we assume that the surface interactions between the LC and the CMK-3 and between the LC and graphite could be similar. However, the stronger ring current of the aromatic carbons²⁶ in graphite, which are much less disordered than those of CMK-3, results in a highly dispersed ¹¹B NMR spectra (Figure Sd). As has been suggested, the catalytic effect^{27,28} of carbon can improve the dehydrogenation characteristics. One explanation suggests that cations partially transfer their charges to the carbon surface instead of to the anions, which results in weaker ionic and covalent bonding (e.g., Al–H or B–H) in the complex anions and ultimately lowers the hydrogen desorption energy. The reduced dehydrogenation temperature of the LC/graphite compared with that of pure LC demonstrates the catalytic effect of nonporous graphite. However, the TG-MS results suggest that a nanoconfinement effect must be considered as the primary effect for any further decrease in the dehydrogenation temperature of the LC/CMK-3. Comparison between LC/CMK-3 and LC/MCM-41 is also of interest. After melting, partial dehydrogenation due to reactive surface groups can occur, and different surface groups in CMK-3 and MCM-41 can lead to different behavior. However, this reaction appeared very minor, and we did not see any noticeable NMR signal (¹¹B, ¹H, ⁷Li, and ¹³C) changes for both cases up to 190 °C. At higher temperatures, irreversible reactions between borohydrides and SiO₂ render such comparison impossible.²⁹

Besides the shifts observed for ¹¹B nuclei, the interaction between [BH₄][−] and the carbon surface could be further probed by correlation NMR between ¹³C nuclei of the carbon and either ¹H or ¹¹B nuclei of the anions. Our preliminary probe of ¹³C MAS and ¹H–¹³C cross-polarization (CP) MAS spectra of CMK-3 before and after infiltration (see Figure S5, Supporting Information) reveals the changes of the carbon surface after infiltration. ¹H–¹³C CPMAS signal, which was not seen for the carbon-only case, was detectable by the [BH₄][−] units that are in close contact with the carbon surface, while the improved ¹³C MAS NMR signal detectability indicates the delocalization of electron density of the carbon surface over the anions. With ¹³C labeling on the carbon material to some extent, we believe that further exploration using ¹³C–¹H or ¹³C–¹¹B distance measurements is possible and provides quantitative access to the local geometry and the interaction. Finally, we note that our carbon scaffold material (CMK-3) did not show any chemical modification upon confining of borohydrides and after dehydrogenation reactions as ¹³C MAS and CPMAS NMR spectra showed (see Figure S5, Supporting Information). The result confirms the inertness of the carbon surface, which is distinguished from the cases of the C=C reduction reaction observed for fullerenes.³⁰

In summary, we investigated the eutectic 0.68LiBH₄ + 0.32Ca(BH₄)₂ composite with and without various scaffolds using ¹¹B, ⁷Li, and ¹H NMR spectroscopy. Eutectic melting and nanoconfinement of the borohydrides were clearly captured in situ NMR spectroscopy. The NMR results for LC mixed with CMK-3 confirm the formation of a LC solid solution at temperatures lower than the eutectic melting point and the subsequent confinement of the solid solution. From these results, we conclude that such confinement can occur even during a ball milling treatment of borohydrides with scaffold materials and that the solid solution remains confined after cooling. This behavior differs from that of pure LC, which recrystallizes back into two separate borohydrides phases. The results imply that the surface interaction of LC with CMK-3 is

significant. The confinement of the solid solution occurs only in mesoporous scaffolds (not in microporous and nonporous materials), irrespective of the chemical composition of the supports, which further emphasizes the importance of the pore structure of the scaffolds. With respect to the hydrogen storage properties of the composites, thermogravimetric analyses of the LC/CMK-3 and LC/graphite indicate that the interaction between the borohydrides and the mesoporous scaffolds, as revealed by NMR, may partly account for the rapid dehydrogenation of the nanoconfined borohydrides.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details and Figures S1–S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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