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Role of $Li_2B_{12}H_{12}$ for the Formation and Decomposition of $LiBH_4$

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By in situ X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy, the role of $Li_2B_{12}H_{12}$ for the sorption of $LiBH_4$ is analyzed. We demonstrate that $Li_2B_{12}H_{12}$ and an amorphous $Li_2B_{10}H_{10}$ phase are formed by the reaction of $LiBH_4$ with diborane (B_2H_6) at 200 °C. Based on our present results, we propose that the $Li_2B_{12}H_{12}$ formation in the desorption of $LiBH_4$ can be explained as a result of reaction of diborane and $LiBH_4$. This reaction of the borohydride with diborane may also be observed for other borohydrides, where $B_{12}H_{12}$ phases are found during decomposition.

Introduction

The investigations of complex hydrides as potential energy carriers[1,2] were intensified after Bogdanovic et al. discovered in 1997 the catalytic effect of Ti on the hydrogen sorption of sodium alanate.[3] More recently, borohydrides ($M(BH_4)_x$) such as $LiBH_4$ were proposed as lightweight hydrogen storage materials[4] with volumetric hydrogen densities well above the density of liquid hydrogen. The gravimetric hydrogen density of $LiBH_4$ (18.4 mass%) exceeds even the one of gasoline. However, the hydrogen absorption and desorption mechanism is not well understood.

The overall reaction for the formation and decomposition of $LiBH_4$ can be expressed by the following equation:

$$LiBH_4 \leftrightarrow LiH + B + 3/2H_2 \qquad (1)$$

Different groups showed the reversibility of this reaction[5-7] and investigated the hydrogen sorption mechanism of the compound. Based on this research $Li_2B_{12}H_{12}$ was proposed as reaction intermediate[8-12] and its formation was observed during desorption of $LiBH_4$ by Raman measurements[9] and NMR spectroscopy.[10] The reaction including the intermediate is as follows:

$$LiBH_4 \leftrightarrow 1/12Li_2B_{12}H_{12} + 5/6LiH + 13/12H_2 \leftrightarrow LiH + B + 3/2H_2 \qquad (2)$$

In recent investigations we showed that diborane plays a major role in the formation and decomposition of borohydrides.[13,14] The proposed modified reaction not including $Li_2B_{12}H_{12}$ as an intermediate is as follows:

$$LiBH_4 \leftrightarrow LiH + 1/2B_2H_6 \leftrightarrow LiH + B + 3/2H_2 \qquad (3)$$

This reaction is based on different observations and experimental results on the formation and decomposition of $LiBH_4$ and other borohydrides.

For the *decomposition* it is known that less stable borohydrides, which desorb at lower temperatures, release a considerable amount of diborane in the desorbed gas, whereas more stable borohydrides desorb at higher temperature and release mainly hydrogen.[15,16] This can be explained by the stability of diborane. Diborane is reported to decompose at approximately 250 °C by thermal decomposition[17] and is therefore not observed as a decomposition product at higher temperatures. Decreasing the desorption temperature of stable borohydrides leads to the

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emission of diborane. This is observed for LiBH4 mixed with silica-gel.[18]

For the *formation*, the synthesis of borohydrides by exposing metal hydrides to diborane in ether is known since 1953, when Schlesinger et al. published their work on the synthesis of borohydrides.[19] We demonstrated the solvent free synthesis of $LiBH_4$ at low temperature by milling[14] or heating[13] of LiH in diborane atmosphere. Milling of LiH in diborane[14] at room temperature leads to almost pure $LiBH_4$. This method can be exploited for the preparation of borohydrides in general: Milling a metal hydride in diborane atmosphere leads to the formation of the corresponding borohydride, as evidenced on the example of LiH, MgH_2 and CaH_2. Heating of LiH in diborane[13] revealed a different result. Apart from an incomplete reaction (50% yield) due to the formation of a $LiBH_4$ passivation layer on the surface of the metal hydride,[20] $Li_2B_{12}H_{12}$ could be clearly observed as a reaction product. This is exactly the phase proposed by a number of groups[8−11] to be the intermediate for the formation and decomposition of $LiBH_4$.

$Li_2B_{12}H_{12}$ seems to play a role in the formation and decomposition of $LiBH_4$ and also for other borohydrides, where $[B_{12}H_{12}]^{2-}$ species are predicted and observed. Latter is the case for $Mg(BH_4)_2$[10,21,22] and $Ca(BH_4)_2$[23] for instance. In this work the origin of the formation of $Li_2B_{12}H_{12}$ and its role for the decomposition and formation of $LiBH_4$ is analyzed. Therefore the reaction of $LiBH_4$ with diborane is observed during in situ X-ray diffraction (XRD) and subsequent ^{11}B magic angle spinning nuclear magnetic resonance (MAS NMR).

Experimental Section

Sample Preparation. $LiBH_4$ used in this work was prepared by milling of LiH (purchased from Sigma-Aldrich) in a diborane/hydrogen atmosphere according to our recently published work on the solvent free, room temperature synthesis of borohydrides.[14] For the XRD measurement $LiBH_4$ is exposed to a diborane/hydrogen atmosphere in a closed cell, which is heated to 200 °C in a capillary furnace (MRI Physikalische Geräte GmbH, Germany), equipped with X-ray transparent windows, to enable XRD during heating. Figure 1 shows a schematic illustration of the custom-made cell used for the diffraction experiment.

The cell consists of a capillary of 1 mm in diameter filled with $LiBH_4$, which is attached to a 6 mm stainless steel tube filled with $LiZn_2(BH_4)_5$ as a diborane source. $LiZn_2(BH_4)_5$ emits diborane and hydrogen when heated above 85 °C according to following reaction:[13,24]

$$LiZn_2(BH_4)_5 \rightarrow 2Zn + 2LiH + 5B_2H_6 + 4H_2 \qquad (4)$$

It is prepared by milling $ZnCl_2$ and $LiBH_4$ with a stoichiometric ratio of 5:2 for 90 min in a SPEX mill according to the work of Ravnsbaek et al.[24] For the experiment the cell was sealed with a high temperature glue and heated to 200 °C while monitoring the sample by XRD. Unfortunately, with this setup a monitoring of the pressure was not possible. In order to avoid mixing of $LiBH_4$ and $LiZn_2(BH_4)_5$ during the reaction, the diborane source was separated from the $LiBH_4$ by glass wool. The volume of the 6 mm tube was allowed to use a sufficient amount of $LiZn_2(BH_4)_5$ to ensure an excess of diborane during the reaction.

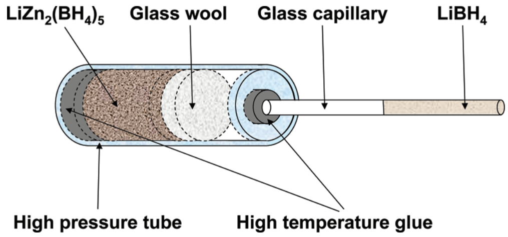

Figure 1. Schematic illustration of the setup used for the in situ high pressure and temperature X-ray diffraction measurements. The cell containing the diborane source ($LiZn_2(BH_4)_5$) attached to a capillary filled with $LiBH_4$.

The sample for the NMR measurements was prepared analogous to the XRD measurement but in a stainless steel container. A detailed description of the preparation can be found in our previously published work.[13]

Sample Characterization. The reaction of diborane with $LiBH_4$ was investigated by in situ X-ray diffraction (XRD), using a Bruker D8 diffractometer with a Goebel mirror, selecting Cu−K_α radiation with a wavelength of $\lambda Cu_{K\alpha}$ = 1.5418 Å (weighted average of Cu−$K_{\alpha 1}$ and Cu−$K_{\alpha 2}$ radiation). All samples were treated under inert Ar atmosphere. The phase fractions were extracted from the initial and the final XRD pattern by a quantitative analysis using the TOPAS software. The structural parameters for $LiBH_4$ and $Li_2B_{12}H_{12}$ were taken from Hartman et al.[25] and Her et al.,[12] respectively.

Solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance 500 MHz spectrometer with a wide bore 11.7 T magnet and employing a boron-free Bruker 4 mm CPMAS probe. The spectral frequency was 160.50 MHz for ^{11}B nucleus, and the NMR shifts are reported in parts per million (ppm) externally referenced to $BF_3 \cdot O(CH_2CH_3)_2$ at 0 ppm for ^{11}B nucleus. The powder material was packed into a 4 mm ZrO_2 rotor in an argon-filled glovebox and was sealed with a tight fitting Kel-F cap. Sample spinning was performed using dry nitrogen gas. The one-dimensional (1D) ^{11}B MAS NMR spectra were acquired after a 0.5 μs single pulse ($<\pi/12$) with application of a strong ^1H decoupling pulse of the two pulse phase modulation (TPPM) scheme.[26]

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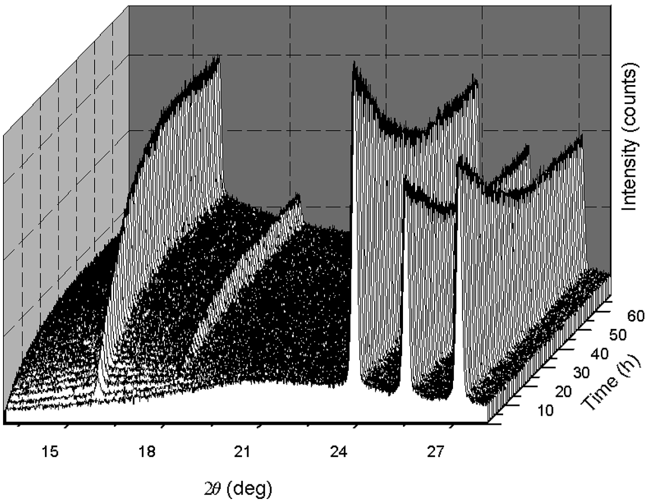

Figure 2. Crystalline phase evolution during the reaction of $LiBH_4$ with diborane at 200 °C observed by in situ X-ray diffraction.

The MAS spectrum reported in this paper was measured with the sample at room temperature.

Results and Discussion

Figure 2 shows the reaction of $LiBH_4$ with diborane at 200 °C investigated by XRD.

It can be observed that upon diborane exposure at 200 °C the $LiBH_4$ reflections decrease, while $Li_2B_{12}H_{12}$ reflections evolve as a new phase. At the same time as $Li_2B_{12}H_{12}$ is formed, the background is increasing for smaller angles indicating the progressive formation of amorphous or nanocrystalline species. After approximately 40 h the reaction stops, most probably due to the formation of a passivation layer on the surface of the remaining $LiBH_4$.

$Li_2B_{12}H_{12}$ is an example of a closoborane salt, which is usually synthesized from decaborane ($B_{10}H_{14}$), triethylamine, and toluol.[12,27] The similar sodium dodecaborate $Na_2B_{12}H_{12}$ has been prepared in wet chemical processes by the action of various boranes and fragments thereof on $NaBH_4$ in solution.[28,29] Here we demonstrate that the reaction does not require a liquid medium. Analogous to the suggestion of Miller et al. for the reaction of $NaBH_4$ with B_2H_6 we propose the formation of $Li_2B_{12}H_{12}$ to follow:

$$2LiBH_4 + 5B_2H_6 \rightarrow Li_2B_{12}H_{12} + 13H_2 \qquad (5)$$

$Li_2B_{12}H_{12}$ has been observed in the thermal decomposition of $LiBH_4$ and has been suggested as a reaction intermediate.[8-11] Based on this new result and from our understanding of diborane during the formation of $LiBH_4$,[13] we propose an alternative hypothesis: The $LiBH_4$ decomposition involves the emission of borane, similar to the decomposition of less stable borohydrides.

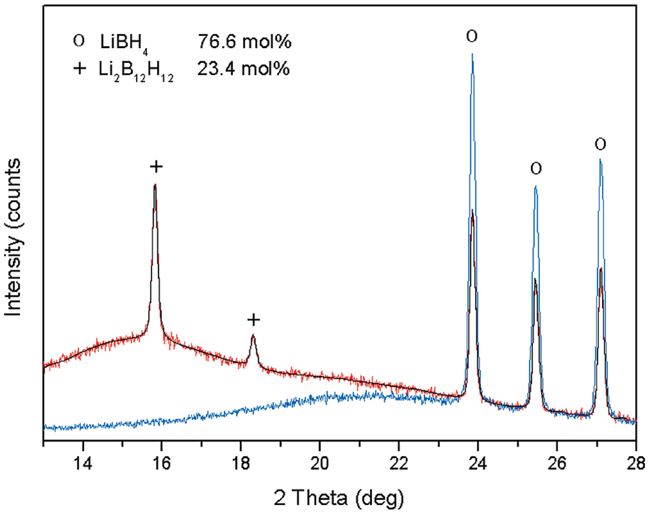

Figure 3. X-ray diffraction before and after reaction of $LiBH_4$ with diborane at 200 °C (see Figure 2).

Due to the high temperature necessary for decomposition on the one hand and the low thermal stability of borane on the other, most of the borane decomposes into the elements. Only some of it reacts with the not yet decomposed $LiBH_4$ to $Li_2B_{12}H_{12}$. As result $Li_2B_{12}H_{12}$ can be observed by Raman[9] or NMR[10] measurements in the solid residue, while in the present experiment, carried out at lower temperatures, the yield is about 50%.

In the overall reaction scheme proposed in eq 5, higher boranes are not taken into account which might participate in the reaction.[28,29]

Together with former results on the formation of $LiBH_4$ from LiH and diborane[13,14] the following reaction equation is proposed:

$$LiH \xrightarrow[RT]{1/2B_2H_6} LiBH_4 \xrightarrow[150°C]{5/2B_2H_6} \frac{1}{2} Li_2B_{12}H_{12} + 13/2H_2 \qquad (6)$$

In this reaction $LiBH_4$ is rather an intermediate in the formation of $Li_2B_{12}H_{12}$ than vice versa. From diborane desorption of $LiBH_4$ at low temperatures we know that the first part of the reaction can be reversed. Further investigations will show, if the entire reaction is reversible, that is, $Li_2B_{12}H_{12}$ decomposes finally to LiH and B, or if it is stable under normal desorption conditions. First principle studies applying density functional theory[30] (DFT) show a high stability of $Li_2B_{12}H_{12}$ and indicate that this compound remains stable even at higher temperatures.

Apart from the formation of $Li_2B_{12}H_{12}$ an amorphous or nanocrystalline material is formed, which can be seen in the significant increase of the background during the reaction. This effect can be clearly seen in Figure 3 presenting the first and the last diffraction pattern of the reaction.

The comparison of the sample before and after the reaction shows that $LiBH_4$ is significantly consumed during the formation of $Li_2B_{12}H_{12}$. The $LiBH_4$ intensity

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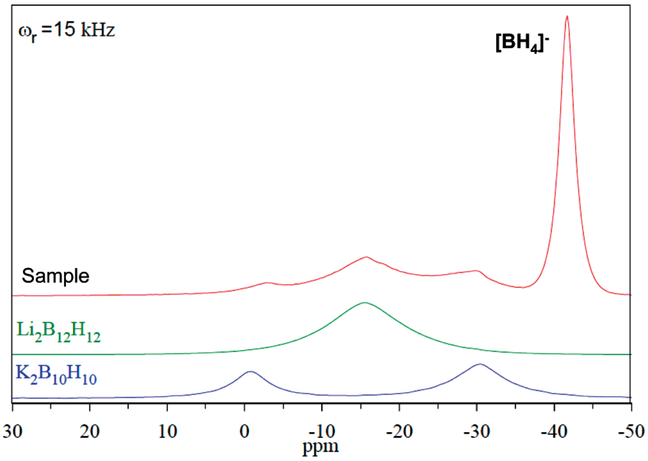


Figure 4. Solid state ^{11}B MAS NMR of LiBH$_4$ after reaction with diborane at 200 °C. Since $Li_2B_{10}B_{10}$ was not available for NMR referencing, the K analogue of $[B_{10}H_{10}]^{2-}$ compound was used for comparison.

(calculated by the integrated intensity) drops to approximately 50%. Assuming that the consumed $LiBH_4$ forms exclusively $Li_2B_{12}H_{12}$ about $^1/_3$ mol % of $Li_2B_{12}H_{12}$ would be expected in the final product consisting of $LiBH_4$ and $Li_2B_{12}H_{12}$. However, Rietveld analysis shows only approximately 77 mol % $LiBH_4$ and 23 mol % of $Li_2B_{12}H_{12}$. This mismatch can be explained by the amorphous or nanocrystalline phases observed as background by XRD but not taken into account in the quantification. Since these contributions are not accessible by XRD, solid state ^{11}B MAS NMR measurements were performed on the final products.

Figure 4 shows the solid state ^{11}B MAS NMR, which provides new information on the state of boron after the reaction of diborane with $LiBH_4$. The final products are compared to references of $Li_2B_{12}H_{12}$ and $K_2B_{10}H_{10}$. Latter is representative for $Li_2B_{10}H_{10}$, which was not available for this analysis as reference.

Apart from the $(BH_4)^-$ and the $(B_{12}H_{12})^{2-}$ contributions, $(B_{10}H_{10})^{2-}$ species are clearly observed in the spectrum. Quantifications of these phases result in approximately 68 mol % $LiBH_4$, 26 mol % $Li_2B_{12}H_{12}$ and 6 mol % $Li_2B_{10}H_{10}$. This result is in good agreement with the quantitative XRD results and show that the background observed by XRD (see Figure 2 and Figure 3) on the final product is mainly due to $Li_2B_{10}H_{10}$, though an amorphous contribution of $Li_2B_{12}H_{12}$ cannot be excluded. The formation of $Li_2B_{10}H_{10}$ may be described by the following reaction:

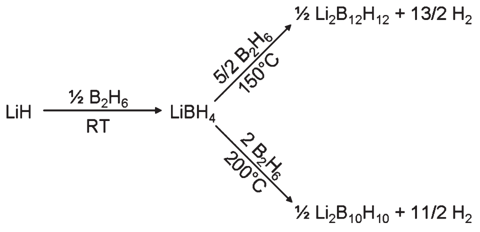
$$LiBH_4 + 2B_2H_6 \rightarrow 1/2Li_2B_{10}H_{10} + 11/2H_2 \qquad (7)$$

In this reaction, as in the formation of $Li_2B_{12}H_{12}$, it is likely that higher borane species are involved. The results agree well with thermodynamic calculations by Ohba et al.,[8] who calculated $LiBH_4$, $Li_2B_{12}H_{12}$ and $Li_2B_{10}H_{10}$ to be the most stable phases among the different existing LiB_xH_y. However, the occurrence of other unknown phases cannot be excluded.

From the work by Miller et al. on the reaction of $NaBH_4$ with B_2H_6[28,29] the formation of different polyhedral boranes is expected during a reaction of a borohydride with diborane, which we could demonstrate for the case of $LiBH_4$. In future we will investigate, if this behavior and the deduced conclusions will hold for other borohydrides as well.

Conclusions

We demonstrated that $LiBH_4$ reacts with diborane to form $Li_2B_{12}H_{12}$ and $Li_2B_{10}H_{10}$ at temperature of 150−200 °C range. Thereby $Li_2B_{10}H_{10}$ is identified as amorphous phase. Together with the synthesis of $LiBH_4$ from reaction of diborane with LiH, reported in our former work, the following reaction equation is suggested:



Based on this reaction we explain the appearance of $Li_2B_{12}H_{12}$ in the desorption of $LiBH_4$ as follows:

The decomposition of $LiBH_4$ leads to a release of diborane. Due to the high temperature ($T >$ 400 °C) desorption of $LiBH_4$, which has been known necessary for decomposition of the compound, and the low thermal stability of diborane, most of the diborane decomposes to B and H_2. However, some of the diborane or higher borane species react with the remaining $LiBH_4$ to form $Li_2B_{12}H_{12}$ and possibly $Li_2B_{10}H_{10}$, which is not detected due to the low content. If the new compound desorbs finally to LiH and B, or is a dead end of the reaction has to be analyzed in future studies. In these studies it has also to be investigated, whether the mechanism can be transferred to other borohydrides, where $B_{12}H_{12}$ phases are observed. It is reasonable to assume that diborane reacts also with other borohydrides forming the $B_{12}H_{12}$ phases during decomposition.

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