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ARTICLE TYPE

The role of $MgB_{12}H_{12}$ in the hydrogen desorption process of $Mg(BH_4)_2$

Yigang Yan,*[a] Arndt Remhof,[a] Daniel Rentsch[b] and Andreas Züttel[ac]

$MgB_{12}H_{12}$ has often been considered as the major obstacle for the reversible hydrogen storage in $Mg(BH_4)_2$. This communication provides evidence that $MgB_{12}H_{12}$ phase (monomers) does not exist in the decomposition products of $Mg(BH_4)_2$ at 265 to 400°C, and thereby it will not act as a dead end.

Due to the combined high volumetric and gravimetric hydrogen densities, light-metal complex hydrides have been widely investigated for solid-state hydrogen storage.[1-3] Among them, magnesium borohydride $Mg(BH_4)_2$ with a hydrogen density of 14.9 wt% is currently one of the most discussed light metal complex hydrides.[4-11] In the overall decomposition reaction, $Mg(BH_4)_2$ exhibits an enthalpy change of −39 kJ/mol H_2 enabling hydrogen desorption to occur already at around room temperature.

In order to develop a reversible storage system toward the practical applications, the hydrogen desorption pathway and the key intermediates involved need to be known. Many efforts have been raised to identify the reaction intermediates during the decomposition process of $Mg(BH_4)_2$.[5, 6, 9, 12-19] Magnesium dodecaborate $MgB_{12}H_{12}$ has been widely considered as the main reaction intermediate in the hydrogen sorption cycle of $Mg(BH_4)_2$.[5, 6, 9, 12-14, 19] This point was supported by NMR observation of the $[B_{12}H_{12}]^{2-}$ species in the aqueous solutions of decomposition products of $Mg(BH_4)_2$.[6, 9, 12] However, phase identification by solution-state NMR is hindered by possible reaction products between the solvent and the investigated sample. It cannot be ruled out that the $[B_{12}H_{12}]^{2-}$ species observed in the aqueous solution resulted from the hydrolysis of the decomposition products, but were not present in the solid-state samples.

In a recent study, we found that $MgB_{12}H_{12}$ decomposes above 400°C. This does not match with any of the hydrogen desorption events of $Mg(BH_4)_2$ which shows three major desorption steps between 250 to 400°C.[20] For hydrogen storage application, the stable $MgB_{12}H_{12}$ would be an unwanted byproduct as it acts as boron sink in the hydrogen sorption cycle and deteriorate the reversibility. Therefore, elucidating the role of $MgB_{12}H_{12}$ is of particular importance for further development of $Mg(BH_4)_2$ as a hydrogen storage material.

In present study, dimethylsulfoxide (DMSO-d_6) was used as solvent for solution-state ^{11}B NMR measurements in order to avoid the reaction between solvent and the investigated samples. Interestingly, $MgB_{12}H_{12}$, a DMSO soluble compound, was not observed in the DMSO-d_6 solutions of all decomposition products of $Mg(BH_4)_2$ from 265 to 400°C. Traces of $[B_{12}H_{12}]$ units were found, which was attributed to be a part of a polymeric intermediate product. This study provides new insights into the hydrogen desorption mechanism of $Mg(BH_4)_2$.

The decomposition of $Mg(BH_4)_2$ was carried out under dynamic vacuum at 265 to 400°C. The samples were subsequently cooled down to room temperature for NMR measurements. The hydrogen release amounts, recorded by a flow meter, were 7.4 wt% (265ºC), 9.1 wt% (285ºC), 10.2 wt% (300ºC) and 11.9 wt% (400ºC), respectively. Fig. 1 shows $^{11}B\{^1H\}$ NMR spectra of DMSO-d_6 solutions of decomposed $Mg(BH_4)_2$ and the reference $K_2B_{12}H_{12}$. In the sample of $Mg(BH_4)_2$ heated at 265°C, $Mg(B_3H_8)_2$ was observed as the main phase, identified by its chemical shift of −29.2 ppm. Undecomposed $Mg(BH_4)_2$ was observed as additional minor phase. Only traces of $Mg(B_3H_8)_2$ observed in the sample heated at 285°C, and both $Mg(B_3H_8)_2$ and $Mg(BH_4)_2$ disappeared above 285°C. The closo-compound $MgB_{12}H_{12}$ was not detected in the DMSO-d_6 solutions of all the decomposition products. This observation agrees with the results from FT-IR measurements, where no B-H vibration modes of $[B_{12}H_{12}]^{2-}$ were found in all the decomposition products of $Mg(BH_4)_2$ (Fig. S1, †ESI).
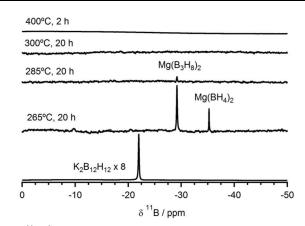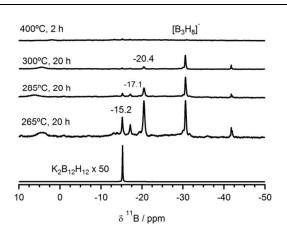

Fig. 1 $^{11}B\{^1H\}$ NMR spectra of DMSO-d_6 solutions of $Mg(BH_4)_2$ heated at 265 to 400°C, referred to $K_2B_{12}H_{12}$. Resonance assignments: −35.2 ppm $[BH_4]^-$, −29.2 ppm $[B_3H_8]^-$,[20] and −15.3 ppm $[B_{12}H_{12}]^{2-}$.

Fig. 2 $^{11}B\{^1H\}$ NMR spectra of D_2O solutions of $Mg(BH_4)_2$ heated at 265 to 400°C, referred to $K_2B_{12}H_{12}$. Resonance assignments: –41.7 ppm $[BH_4]^-$, –15.2 ppm $[B_{12}H_{12}]^{2-}$, –17.1

5 ppm $[B_{11}H_{11}]^{2-}$,[21] and –30.6 ppm $[B_3H_8]^-$.

The solubility of $MgB_{12}H_{12}$ and other dodecaborates (e.g. $Y_2(B_{12}H_{12})_3$) in DMSO-d_6 has been shown by solution-state ^{11}B NMR.[20, 22] Moreover, DMSO-d_6 was effectively used to extract

10 $MgB_{12}H_{12}$ from a heterogeneous mixture of magnesium hydrides and polyboranes.[20] Since $MgB_{12}H_{12}$ was reported in the aqueous solutions by ^{11}B NMR, additional ^{11}B NMR measurements were carried out after dissolution of samples in D_2O (Fig. 2). Again, $[B_3H_8]^-$ was observed as the main phase for the samples

15 decomposed at 265 to 300°C. Additionally, more species were observed in these samples, i.e., $[B_{12}H_{12}]^{2-}$ (–15.2 ppm) and $[B_{11}H_{11}]^{2-}$ (–17.1 ppm). The resonance at –20.4 ppm also showed a J_{B-H} of 125 Hz (not shown), indicating a phase with a B : H ratio of 1 to 1 and closo structure same to $[B_{12}H_{12}]^{2-}$; it may be

20 assigned to $[B_9H_9]^{2-}$.[21] Furthermore, when temperature for the decomposition was increased, less soluble species were observed in the decomposition products, as shown in Table 1. In the sample decomposed at 400°C, no water soluble species were detected.

25 The difference between ^{11}B spectra of DMSO-d_6 and D_2O solutions may be closely related to the difference between DMSO and water concerning the reactivity. Water is a polar protic solvent, which easily offers H^+ (D^+ for D_2O) making it more reactive than the aprotic DMSO-d_6. DMSO-d_6 can only extract

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Table 1. Contents (mol%) of boron atoms belonging to different species, detected by solution-state ^{11}B NMR. A DMSO (12 mM) and an aqueous solution (46 mM) of $K_2B_{12}H_{12}$ were used as external references. The phases including $[B_{11}H_{11}]^{2-}$ and the

35 species at –20.4 ppm were classified into others.

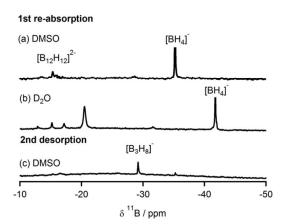| $Mg(BH_4)_2$ samples	boron contents from different species / mol%			
	$[BH_4]^-$	$[B_3H_8]^-$	$[B_{12}H_{12}]^{2-}$	Others
(DMSO)				
265°C, 20h	0.5	5.3	-	-
300°C, 20h	-	-	-	-
(D2O)				
265°C, 20h	1.3	10.9	2.7	18.2
300°C, 20h	0.4	5.2	0.6	8.1

Fig. 3 $^{11}B\{^1H\}$ NMR spectra of sample ($Mg(BH_4)_2$ decomposed at 265°C for 20 h) after 1st re-absorption and 2nd desorption. The measurements were carried out after dissolution of samples in

40 DMSO and D_2O, respectively.

monomers, e.g., $[BH_4]^-$ and $[B_3H_8]^-$ phases (Fig. 1). When using water as solvent, the hydrolysis of the measured samples cannot be ruled out. The dissolution of pure $Mg(BH_4)_2$ in water was

45 investigated, which only resulted in formation of $[B(OH)_4]^-$ (Fig. S2, †ESI). Additionally, we investigated a sample at early-stage decomposition, where $Mg(BH_4)_2$ was heated at 265°C for 2h. In the DMSO-d_6 solution of this sample (Fig. S3, †ESI), $[BH_4]^-$ and $[B_3H_8]^-$ were detected, which did not convert to the closo-species

50 in the aqueous solution. These observations agree with the report in the literature that the hydrolysis of aracho or nido-boranes leads to the formation of boric acid but not $[B_{12}H_{12}]^{2-}$.[23]

The coexistence of several species including $[B_3H_8]^-$ and closo-species in the aqueous solutions (Fig. 2) implies the

55 presence of a polymeric Mg-B-H compound (labelled MgB_xH_y) which was splitted in water. Polymeric or clustered hydroborates composed of different B-H units have been reported. For instance, AlB_4H_{11} shows a polymeric chain of $–[B_3H_7]–Al(BH_4)–$, which gains H^+ from NH_3 and produces $[B_3H_8]^-$ and $[BH_4]^-$ in

60 liquid ammonia.[24] The occurrence of dimers, trimmers or larger clusters during the decomposition of $LiBH_4$ has also been discussed.[25] To further confirm the polymerization occurring during the hydrogen desorption process, the evolution of B-H species in a hydrogen sorption cycle was investigated. Thereby

65 the sample ($Mg(BH_4)_2$ decomposed at 265°C for 20 h) was exposed to 160 bar H_2 at 265°C (1st re-absorption) and thereafter decomposed at 265°C (2nd desorption). As shown in Fig. 3, after 1st re-absorption, the smaller aracho-borane $[B_3H_8]^-$ disappeared in both DMSO and aqueous solutions, which converted back to

70 $[BH_4]^-$. $MgB_{12}H_{12}$ phase (or $[B_{12}H_{12}]^{2-}$ monomers) did form by exposing the MgB_xH_y polymer to high pressure hydrogen. However, $MgB_{12}H_{12}$ disappeared again after 2nd desorption at 265°C (Fig. 3c), indicating the occurrence of polymerization involving $[B_{12}H_{12}]^{2-}$ during the desorption process.
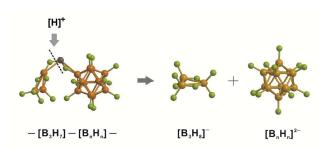
75 The polymer MgB_xH_y may be composed of aracho and closo-boranes forming a structure such as $Mg_2[B_3H_7–B_nH_n]$. It can be splitted by H^+ in water, as illustrated in Schematic 1.

80

Schematic 1. The splitting in water of MgB_xH_y polymer into $[B_3H_8]^-$ and closo-boranes $[B_nH_n]^{2-}$, where $6 \leq n \leq 12$.

Probably due to the formation of the polymeric product, the ^{11}B MAS NMR spectra of the decomposition products (Fig. S4, †ESI) at 265 to 300°C only showed broad resonances and thereby did not allow the precise phase identification. The observed two major resonances, between –30 to –60 ppm and 0 to –30 ppm, respectively, did not match with any of the reference samples.

When the decomposition temperature was increased 400°C, a broad resonance centered at around 0 ppm together with the resonance at 96.3 ppm assigned to MgB_2 (Fig. S5, †ESI) were observed. The ^{11}B CP-MAS NMR spectrum showed a resonance at –8.2 ppm, assigned to the residual of B-H species. Thereby the ^{11}B MAS NMR spectrum was de-convoluted into three individual phases, i.e., MgB_2 at 96.3 ppm, B at 1.2 ppm and the B-H species at –8.2 ppm. Approximately 63 % of the boron atoms are found as amorphous B and 30% as MgB_2. Only 7 % of the boron atoms are bound to the B-H species. This observation indicated that the MgB_xH_y polymer acts as a precursor to form amorphous B which finally converts to MgB_2. MgB_2 was identified as the only solid product at 500°C (Fig. S6, †ESI), in accordance with the results reported in literature.[6, 26]

In summary, throughout the solid-state decomposition process of $Mg(BH_4)_2$, $MgB_{12}H_{12}$ phase (or monomers) does not exist in the solid residues after decomposition. The decomposition of $Mg(BH_4)_2$ may proceed *via* a polymerization process. A small amount of $[B_{12}H_{12}]$ units were found to be present as a part of the polymeric product MgB_xH_y which decomposes into amorphous B (and MgH_2 or Mg). All B atoms finally convert into MgB_2 and therefore, no B-H species will act as dead ends for reversible hydrogen sorption of $Mg(BH_4)_2$. To accelerate the reaction kinetics toward the potential application for hydrogen storage, designing effective catalysts based on the polymerization feature during the hydrogen desorption process is of great importance.

Notes and references

[a]EMPA, Swiss Federal Laboratories for Materials Science and Technology, Hydrogen & Energy, 8600 Dübendorf, Switzerland. Fax: +41 58 765 40 22; Tel: +41 58 765 40 82; yigang.yan@empa.ch.
[b]EMPA, Swiss Federal Laboratories for Materials Science and Technology, Functional Polymers, 8600 Dübendorf, Switzerland.
[c]École Polytechnique Fédérale de Lausanne (EPFL), Institut des Sciences et Ingénierie Chimique, Lausanne, Switzerland.

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