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Oxidative and catalytic effects on the thermal decomposition of metal borohydrides

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Abstract: The effects of oxidation on the hydrogen release behavior of magnesium borohydride and calcium borohydride were investigated using differential scanning calorimetry. To date, studies on the oxidation kinetics of borohydride compounds in air and the influence of oxidation on hydrogen desorption behavior have been limited. In this work, the degree of oxidation and the corresponding changes in hydrogen release temperature were analyzed based on DSC signals to evaluate the extent of oxidation and its effect on hydrogen desorption characteristics. In addition, the influence of $ScCl_3$, a commonly used metal catalyst, on the oxidation behavior of borohydrides was also examined. Both compounds were found to undergo complete oxidation within one day; however, the oxidation-induced changes in hydrogen release temperature were minimal. The addition of the $ScCl_3$ catalyst did not induce significant changes in the oxidation process, but slightly reduced the oxidation rate and led to the formation of additional intermediate phases. Further in-depth studies are required to elucidate the mechanisms underlying these phenomena.

Key words: borohydride, oxidation, hydrogen release, catalyst, DSC

1. Introduction

Metal borohydrides have attracted considerable attention as hydrogen storage materials due to their high hydrogen content. Metal borohydrides experienced many different intermediate states and the hydrogen desorption proceeded at different temperatures and energy levels.[1] For instance, magnesium borohydride releases hydrogen through several sequential decomposition steps, resulting in the formation of various intermediate products.[2] Under ambient hydrogen pressure, magnesium borohydride initially decomposes into magnesium hydride and boron at approximately 300 °C, followed by further decomposition into metallic magnesium at around 395 °C, as described below.[2]

$$Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2 \quad (1a)$$

$$MgH_2 \rightarrow Mg + H_2 \quad (1b)$$

Calcium borohydride also decomposes into calcium hydride and calcium boride in several steps between 390 and 500 °C.[3]

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$$Ca(BH_4)_2 \rightarrow 2/3\ CaH_2 + 1/3\ CaB_6 + 10/3\ H_2 \quad (2)$$

Metal borohydrides can be easily oxidized in the presence of oxygen and moisture. For example, lithium borohydride reacts with water and oxygen in air to produce products such as $LiB(OH)_4$, $H_6B_2O_6$, $LiB(OH)_2(O_2)$. These observations indicated that oxidation in air is the dominant reaction pathway, rather than gas phase hydrolysis with water.[4] Light metal hydrides and complex hydrides used for hydrogen storage are also capable of releasing hydrogen via hydrolysis.[5] For instance, $LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2$ corresponding to a hydrogen storage capacity of 8.6 wt.%. However, hydrogen loss through such reaction reduces the amount of hydrogen available for reversible hydrogen storage. Magnesium borohydride is oxidized to $Mg(OH)_2$, $Mg(BO_2)_2$, and MgO, while calcium borohydride is oxidized to $Ca(OH)_2$, $Ca(BO_2)_2$, and CaO. This oxidation not only decreases the effective hydrogen storage capacity but also adversely affects hydrogen desorption behavior. The thermal decomposition temperature of $Mg(OH)_2$ ranges from 241 to 390 °C.[6] Magnesium metaborate, $Mg(BO_2)_2$, and calcium metaborate, $Ca(BO_2)_2$, decompose into MgO and CaO at temperatures above approximately 600 °C and 1000 °C, respectively. Furthermore, MgO and CaO decompose only at extremely high temperatures, above 2852 °C and 2400 °C, respectively, which are well beyond the experimental temperature range of the present study.

The effect of catalysts on the decomposition behavior of metal borohydrides is also a critical factor in the development of hydrogen storage materials. However, the use of catalysts does not always lead to improved hydrogen storage performance. For example, the addition of $TiCl_3$ as a catalyst to $NaAlH_4$ was reported to reduce the hydrogen storage capacity due to a side reaction that releases hydrogen irreversibly.[5] It should be also noted that mechanical can reduce hydrogen storage capacity compared to unmilled MgH_2. This reduction is attributed to partial oxidation occurring during the milling process used to decrease particle size, which results in a significant loss of active hydrogen absorbing material.

Graphite's highest sorption rate may be attributed to the formation of protective layers surrounding the particles. Graphite can encapsulate metallic particles, thereby acting as an effective barrier against oxidation. As a result, the newly generated surfaces created during the milling process may be partially protected, leading to a reduced degree of oxidation.[7] The incorporation of catalysts into metal borohydrides by ball-milling can therefore give a complicated effect on hydrogen storage capability.

In this study, the effect of oxidation on the hydrogen desorption behavior in metal borohydrides was systematically investigated using differential scanning calorimetry (DSC). In addition, the influence of a metal catalyst on both the oxidation behavior and thermal decomposition of metal borohydrides was examined.

2. Experimental

Magnesium borohydride and calcium borohydride were purchased from Sigma-Aldrich and used as received. For oxidation experiments, 50 mg of magnesium borohydride was transferred into a vial inside a glove box filled with argon. The vial was placed in a desiccator containing a saturated sodium hydrogen phosphate solution to maintain a constant relative humidity of 95 %. Oxidation was carried out at 30 °C for exposure times of 0, 1, 3, 6, 12, 18, and 24 hours. 50 mg of calcium borohydride was treated using the same procedure as used for magnesium borohydride. For catalyst-containing samples, 50 mg of calcium borohydride was mixed with scandium chloride at a molar ratio of 95:5 and ball-milled at a rotational speed of 500 rpm for 2 h. The ball-to-powder mass ratio was maintained at 40:1. Differential scanning calorimetry measurements were performed using a Scinco DSC N-650 instrument. Metal borohydride was sealed in an aluminum pan and DSC data were collected in an air atmosphere during heating from room temperature to 500 °C at a scanning rate of 10 °C/min.

3. Results and Discussion

3.1. Magnesium borohydride

Following oxidation of the metal borohydrides, DSC was performed to investigate their thermal reaction behavior. As shown in *Fig*. 1, three peaks were detected for the magnesium borohydride at approximately 100, 200, and 310 °C. In contrast, the calcium borohydride exhibited two distinct peaks at around 100 and 400 °C, as shown in *Fig*. 2. During air exposure, metal borohydride crystallites react with oxygen to form metal oxide layers on the particle surfaces. These oxides decompose at extremely high temperature, exceeding 2400 °C, which are beyond the temperature range accessible in the present experiments. In addition, compounds formed via reactions between metal borohydrides and water molecules decompose at temperatures above 600 °C. Therefore, the thermal events observed in the temperature range of 300–400 °C cannot be attributed to the decomposition of metal oxides or metal hydroxides, but are instead associated with the decomposition and hydrogen release of the metal borohydrides.

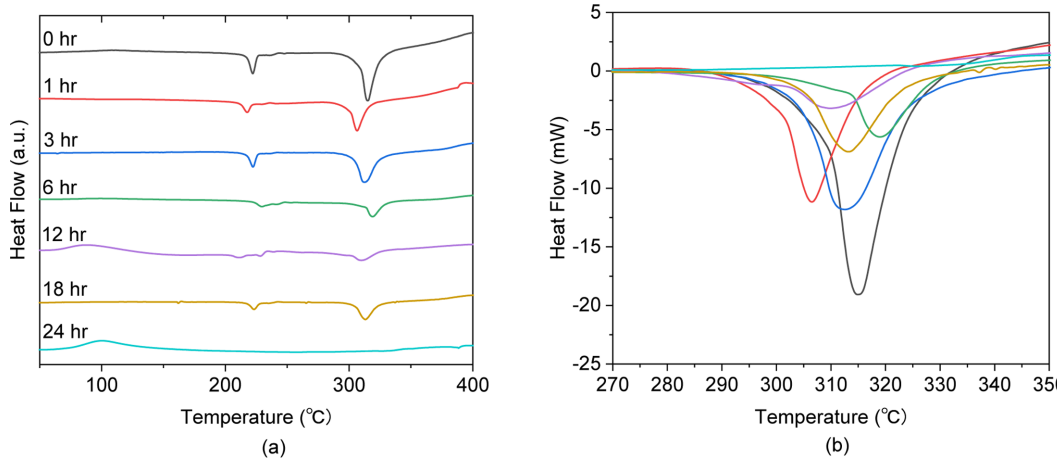

Fig. 1. DSC curves of $Mg(BH_4)_2$ at various oxidation times (a) and the curves appearing around 310 °C (b).

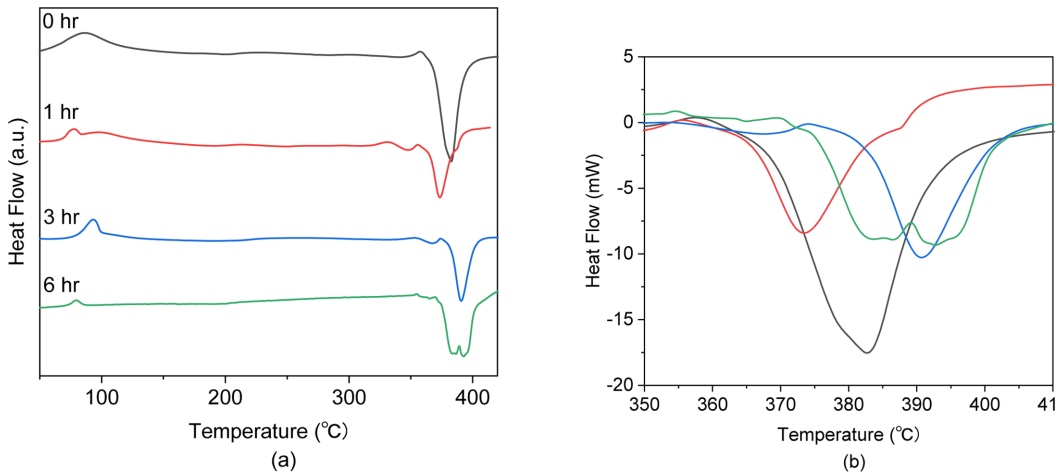

Fig. 2. DSC curves of $Ca(BH_4)_2$ at various oxidation times (a) and the curves appearing around 380 °C (b) in the absence of $ScCl_3$.

A broad exothermic peak was observed near 100 °C for magnesium borohydride. Two possible processes may account for this feature. One is the crystallization of an amorphous phase into the γ-phase.[8] The other potential exothermic process at approximately 100 °C is the reaction of magnesium borohydride with water molecules.[9] The negligible shift in this thermal feature with increasing oxidation time indicates that partial oxidation of the magnesium borohydride crystallites does not significantly affect these low-temperature reactions.

The second peak in *Fig.* 1 appears at approximately 220 °C. Magnesium borohydride is known to exhibit multiple thermally induced phase transitions. For instance, the low-temperature α-$Mg(BH_4)_2$ phase transforms into the high-temperature orthorhombic β phase (space group Fddd) upon heating to approximately 180 °C. Porous γ-$Mg(BH_4)_2$ undergoes thermally-induced phase transitions to the ε phase at 153 °C and subsequently to β' phase (allegedly a disordered form of the β phase) at around 185 °C.[8] In addition, transformation of the α phase to the ζ phase has been reported to occur near 224 °C.[10] The thermal peak observed at approximately 220 °C in *Fig.* 1 is therefore likely associated with one of these phase transitions. Notably, this peak exhibits no significant change with increasing oxidation time, indicating that partial oxidation of magnesium borohydride crystallites does not appreciably influence phase transitions within the crystal structure.

The third peak, appearing around 310 °C, corresponds to the hydrogen release process. The extent of oxidation of magnesium borohydride during air exposure was determined by integrating the hydrogen release peak at approximately 310 °C. The corresponding reaction temperatures and degrees of oxidation are summarized in *Table* 1. The degree of oxidation was quantified based on the decrease in the DSC peak area corresponding to hydrogen release. The oxidation degree at time t was defined as

$$\text{Oxidation degree (\%)} = (1 - I_t/I_0) \times 100,$$

where I_0 and I_t are the hydrogen-release peak integrals at 0 h and time t, respectively. For all DSC measurements, a nominal sample mass of 50 mg was used, and the integrals were normalized by this constant mass. Due to experimental constraints, each DSC measurement at a given oxidation time was performed once. Therefore, the oxidation degrees and peak temperatures reported here should be regarded as indicative of general trends rather than statistically averaged values. Future work will include repeated measurements and uncertainty evaluation to quantify the experimental scatter more rigorously.

Table 1. Reaction temperature, normalized integral, and oxidation degree of $Mg(BH_4)_2$ at various oxidation times

Oxidation (hr)	Reaction temperature	Normalized integral	Oxidation degree (%)
0	315	100	0
1	307	60	40
3	313	18	82
6	319	14	86
12	310	7	93
18	313	18	82
24	-	0	100

Approximately 50 % of the magnesium borohydride was rapidly oxidized within the first hour of air oxidation, after which the remaining fraction underwent oxidation at a slower rate, reaching near-complete oxidation after one day. Despite of the progressive oxidation, the hydrogen release temperature (*Table* 1) exhibited only minor variations. These results indicate that oxidation occurs not only at the particle surface and but also within the interior of the crystallites. The minimal change in hydrogen release temperature suggests that partially oxidized structures within the crystallites do not significantly influence hydrogen generation from the local $Mg(BH_4)_2$ framework, the migration process of hydrogen gas from the crystallite interior to the surface, or the subsequent release of hydrogen gas from the particle surface. Overall, these findings demonstrate that partial structural and chemical modifications of the crystallites have a negligible impact on the macroscopic hydrogen release behavior.

3.2. Calcium borohydride

Similar to magnesium borohydride, an exothermic

signal appeared near 100 °C for calcium borohydride may be attributed to reactions with water molecules leading to hydrogen release or to other structural changes.[9] Calcium borohydride is known to undergo several polymorphic phase transitions, including transformation from the α to the α′ phase at approximately 222 °C, from α′ to β between 278 and 300 °C, and from γ to δ between 290 and 330 °C.[11] However, such phase transitions were not detected under the present experiment conditions. The β phase of calcium borohydride decomposes at 380 °C, while δ phase decomposes in the range of 400–480 °C.[12] Kim et al. reported that this decomposition process results in the formation of hydrogen gas, CaH_2, and intermediate compounds.[3] Accordingly, the peak observed near 390 °C is attributed to the hydrogen release reaction of β phase calcium borohydride. The extent of oxidation of calcium borohydride was quantified by integrating the hydrogen release peak near 390 °C, using the same analytical approach applied to magnesium borohydride. The corresponding reaction temperatures and degrees of oxidation are summarized in *Table* 2. Approximately 50 % of calcium borohydride was oxidized within the first hour of air exposure, similar to the behavior observed for magnesium borohydride, although the oxidation rate was slightly higher. As oxidation progressed, the decomposition temperature near 380 °C remained essentially unchanged, indicating that partial oxidation did not significantly affect the hydrogen release temperature.

Table 2. Reaction temperature, normalized integral, and oxidation degree of $Ca(BH_4)_2$ at various oxidation times.

Oxidation (hr)	Reaction temperature	Normalized integral	Oxidation degree (%)
0	383	100	0
1	373	51	49
3	391	19	81
6	389	10	90

3.3. Catalytic effect

As shown in *Fig.* 3, the thermal signal near 100 °C transitioned from exothermic to endothermic after one day oxidation. This behavior suggests that, during the early stages of oxidation (less than one day), calcium borohydride reacts with a limited amount of adsorbed water to form $Ca(BO_2)$, resulting in an exothermic signal. In contrast, at more advanced stages of oxidation (greater than one day), the presence of a large amount of water within the oxidized calcium borohydride leads to surface water evaporation near 100 °C, producing an endothermic signal.

The hydrogen release temperature and degree of oxidation of calcium borohydride ball-milled with scandium chloride are summarized in *Table* 3. The

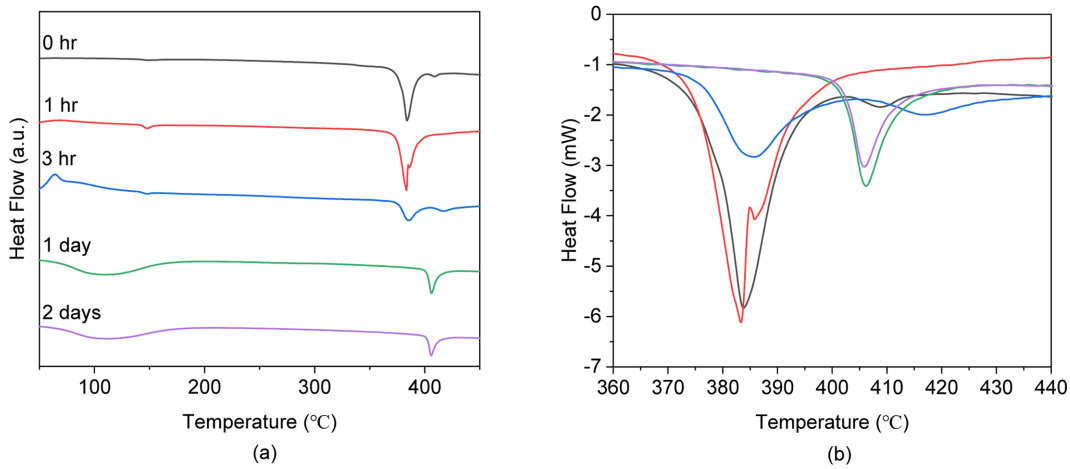

Fig. 3. DSC curves of $Ca(BH_4)_2$ at various oxidation times (a) and the curves appearing around 400 °C (b) in the presence of $ScCl_3$.

Table 3. Reaction temperature, normalized integral, and oxidation degree of $Ca(BH_4)_2$ in the presence of $ScCl_3$ at various oxidation times

Oxidation (hr)	Reaction temperature	Normalized integral	Oxidation degree (%)
0	384	100	0
1	383	104*	-
3	386	40	60
24	406	36	64
48	406	28	72

*For the $ScCl_3$-containing sample at 1 h, the normalized integral slightly exceeded 100 %, which is attributed to overlapping exothermic processes and baseline uncertainty. This anomalous point was therefore excluded from quantitative evaluation of oxidation degree.

presence of scandium chloride slightly reduced the oxidation rate of calcium borohydride compared to samples without catalyst, with a final oxidation degree of 72 %, lower than the approximately 90 % observed in the absence of scandium chloride. After one day of oxidation, an additional thermal peak emerged at 406 °C, compared to 384 °C for the uncatalyzed sample. Although the exact origin of this peak remains unclear, it likely associated with the decomposition of intermediate compounds into crystalline CaH_2 and amorphous boron and/or amorphous calcium boride,[3] reflecting a combined effect of catalysis and oxidation. The hydrogen release temperature remained largely unchanged until a substantial fraction of calcium borohydride had been oxidized. Overall, scandium chloride did not exert a significant influence on the intrinsic hydrogen release behavior of calcium borohydride when compared to the hydrogen release temperature and oxidation rate of the uncatalyzed material.

In this work, we focus primarily on reporting the observed effects of $ScCl_3$ on the oxidation behavior and hydrogen release of $Ca(BH_4)_2$. A detailed mechanistic analysis of how $ScCl_3$ modifies surface oxidation, diffusion processes, or reaction pathways is beyond the scope of the present study and will be addressed in future investigations.

It should be noted that the chemical identities of the intermediate phases proposed in this study were not directly confirmed by independent characterization techniques such as XRD or FTIR. The assignments are based on previously reported decomposition and oxidation pathways of metal borohydrides in the literature. Therefore, the discussion of intermediates in Sections 3.2 and 3.3 should be regarded as tentative and qualitative. A more rigorous identification of the oxidation products and intermediate phases will be the subject of future work.

4. Conclusions

More than 50 % of both magnesium and calcium borohydrides was oxidized after several hours of exposure to air. However, this partial oxidation did not lead to a measurable change in the hydrogen release temperature. This observation suggests that magnesium and calcium oxide phases, partially formed at or beneath the particle surface, do not significantly influence hydrogen generation within the crystallites or the subsequent migration of hydrogen through the internal crystal matrix. The catalytic effect of scandium chloride introduced by ball milling was manifested as a delay in the oxidation process, resulting in a higher hydrogen release amount compared to uncatalyzed borohydrides. Nevertheless, scandium chloride did not exert a significant influence on the intrinsic hydrogen release reaction.

Acknowledgements

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