

Supercritical N₂ Processing as a Route to the Clean Dehydrogenation of Porous Mg(BH₄)₂

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Supporting Information

ABSTRACT: Compounds of interest for chemical hydrogen storage at near ambient conditions are specifically tailored to be relatively unstable and thereby desorb H₂ upon heating. Their decomposition must be performed in the absence of impurities to achieve clean dehydrogenation products, which is particularly challenging for an emerging class of microporous complex hydride materials, such as γ -phase Mg(BH₄)₂, which exhibits high surface area and readily adsorbs (sometimes undesired) molecular species. We present a novel strategy toward the purification of γ -Mg(BH₄)₂ using supercritical nitrogen drying techniques, (1) showing that clean hydrogen can be released from Mg(BH₄)₂ under mild conditions and (2) clarifying the origin of diborane among the decomposition products of stable borohydrides, a topic of critical importance for the reversibility and practical applicability of this class of hydrogen storage compounds. This technique is also widely applicable in the pursuit of the high-purity synthesis of other porous, reactive compounds, an exciting future class of advanced functional materials.

Upon heating, light metal borohydrides (M(BH₄)_x) desorb a large amount (up to 18 mass% when M = Li) of hydrogen, which has sparked very active interest in these compounds as energy storage materials for mobility.¹ Magnesium borohydride (Mg(BH₄)₂) has been intensively investigated as a hydrogen storage material due to its high gravimetric hydrogen density (14.9 mass%) and intermediate enthalpy of decomposition (40–60 kJ mol⁻¹) which is close to the ideal value for hydrogen storage at ambient conditions.^{2,3} The products of decomposition of Mg(BH₄)₂, however, vary depending on the chosen conditions, and in many cases include compounds (e.g., MgB₁₂H₁₂) that impede the reversibility of the reaction under moderate conditions.^{2,4–7} Nonetheless, the specific reaction pathways of decomposition remain an important topic of investigation toward achieving acceptable reaction conditions where it would be possible to perform reversible (de)hydrogenation.^{6,7}

One distinct characteristic of some complex borohydrides is the presence of diborane (B₂H₆) among the gaseous products evolved during the hydrogen desorption process, e.g. as observed for MZn₂(BH₄)₅^{7,8} (M = Li, Na) and many other borohydrides that desorb hydrogen readily at room temperature.⁹ The evolution of diborane has significant implications

for the practical applicability of complex borohydride materials due to its inherent toxicity and the associated irreversible loss of boron from the system. Magnesium borohydride, due to its relative thermal stability, lies within the regime expected not to evolve diborane along with H₂ upon decomposition, which has been corroborated by experiments.¹⁰ It must be noted that measurements performed in dynamic vacuum (e.g., by mass spectrometry) may not give conclusive results as to the reaction products at equilibrium, the conditions that are thermodynamically and practically relevant.

Magnesium borohydride exists in numerous (meta-)stable phases at ambient conditions, which are experimentally identified as α -Mg(BH₄)₂ (*P6₁22*), β -Mg(BH₄)₂ (*Fddd*), and γ -Mg(BH₄)₂ (*Id $\bar{3}a$*). The discovery of γ -Mg(BH₄)₂ as an open, porous structure with a large specific surface area (1160 m² g⁻¹)¹¹ has attracted heightened interest as the first member of a unique class of porous hydride materials. It exhibits both a high hydrogen content within its chemical composition and the characteristics of a high surface area sorbent; hydrogen physisorption at low temperatures can increase the total gravimetric H capacity to 17.9 mass% at 77 K.¹¹ We undertook studies of the first cycle decomposition of γ -Mg(BH₄)₂ using a combination of gravimetry and infrared (IR) spectroscopy in an open flow system, a technique that allows precise quantification of the (IR-active) components of the gas phase evolved during heating. The details of this technique have been previously reported.¹² The materials were subjected to a constant heating ramp of 2 K min⁻¹ up to 593 K under H₂ flow at 0.1 MPa (conditions chosen to focus on the release of H₂ from Mg(BH₄)₂ instead of from MgH₂, discussed in further detail in the Supporting Information (SI)).

Surprisingly, a significant, specific release of diborane was observed upon heating between 350 and 500 K for all of the γ -Mg(BH₄)₂ materials studied, while not at any temperatures below 600 K in identical measurements for α -Mg(BH₄)₂ and β -Mg(BH₄)₂. The quantifiable components of the gaseous products of decomposition at an illustrative temperature of 400 K are shown in Figure 1a. The release of diborane is observed to occur before both solid phase transitions of γ -Mg(BH₄)₂ to ϵ -Mg(BH₄)₂ (423 K) and β -Mg(BH₄)₂ (533 K),¹³ making it a unique feature of the γ -phase.

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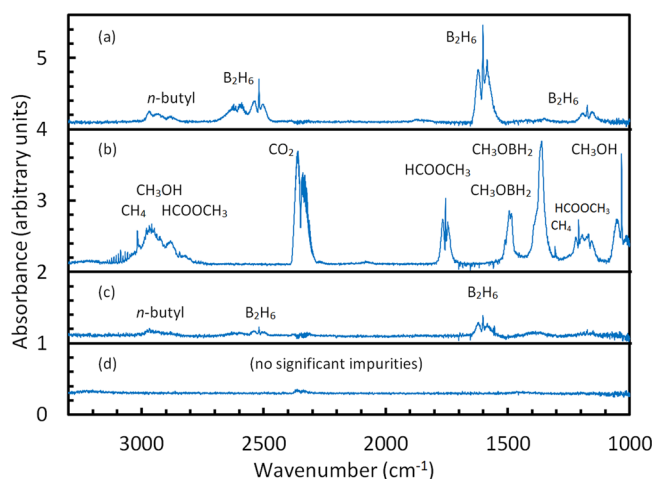


Figure 1. Infrared spectra of the gas mixture evolved during heating of untreated γ -Mg(BH₄)₂ (a), CScD-treated γ -Mg(BH₄)₂ (b), and 1x (c) and 3x (d) NScD-treated γ -Mg(BH₄)₂ at 400 K, with the components of the mixture identified (see Supporting Information for detailed analysis). The bulk of the mixture is H₂.

The observation of diborane among the decomposition reaction products of Mg(BH₄)₂ in the γ -phase is of critical importance in understanding the reaction pathways of decomposition of borohydrides. Under the chosen thermodynamic conditions, Mg(BH₄)₂ is not expected to emit diborane⁹ but the highly nontrivial reaction pathways^{3,6} of this system, complex phase diagram, and sensitivity to conditions arouse many uncertainties. To determine the origin of the presence of diborane in the decomposition of γ -Mg(BH₄)₂, we employed a strategy based on the hypothesis that B_xH_y-containing impurities (e.g., DMS-BH₃) remain trapped in its porous structure after synthesis, and which are not removed by standard purification methods: heating to 353 K in vacuo.¹¹ The identification of “*n*-butyl” impurities (see SI) in the gas stream upon decomposition was a strong indication that new techniques to purify the materials before decomposition were in any case necessary to separate decomposition reaction products from leftover impurities related to synthesis.

Supercritical drying (ScD) or extraction methods¹⁴ have long been established as effective in numerous applications for the, among others, synthesis,^{15,16} activation,¹⁷ and catalytic activity enhancement¹⁸ of porous materials. Typically, a drying agent is chosen based on the close proximity of its supercritical point to ambient temperature and pressure, such as CO₂. Carbon dioxide is also nontoxic, nonflammable, low in cost, and known as an effective solvent of many organic molecules typical of ScD purification applications. The general ScD method¹⁴ comprises exposing the porous (impurity-containing) material to the drying agent in liquid (or near-liquid supercritical) phase, where its high density is correlated with the high solubility of the target solute (or solutes). The liquid solution containing the impurities is then heated (and in turn compressed) above the critical point in a closed container. From the supercritical state, the pressure is slowly reduced to vacuum, and the fluid solution (then containing a certain concentration of impurities) escapes the porous structure without encountering a phase boundary or surface tension effects along the way. With success in dissolving the impurity molecules in the pores, the remaining material is left impurity-free, activated, or otherwise dried of its past guests.

With this strategy in mind, we first subjected γ -Mg(BH₄)₂ to a typical CO₂ ScD (CScD) routine, the details of which can be found in the SI. However, the subsequent decomposition of CScD- γ -Mg(BH₄)₂ under flowing H₂ resulted in the evolution of a series of carbon- and oxygen-containing gases (e.g., see Figure 1b) which is clear evidence of a reaction having occurred between Mg(BH₄)₂ and the supercritical CO₂. The role of borohydrides (and likewise alanes¹⁹) as strong hydride transfer agents for the reduction of CO₂ at mild temperatures (<330 K) is interesting in itself, but nonetheless, the standard ScD methodology with CO₂ is clearly not suitable for use on Mg(BH₄)₂ due to its inherent reactivity.

We therefore sought a different ScD fluid which is not reactive with γ -Mg(BH₄)₂. Nitrogen has only occasionally been alluded to as an alternative drying agent to CO₂,^{20–22} predominantly in the context of above ambient temperatures where it exhibits a much lower solvent power toward commonly extracted organic compounds. However, the solvent power of N₂ or any solvent increases with density, which implies that near cryogenic temperatures are necessary to realize the full potential of N₂ as an ScD fluid. Nitrogen has a similar molecular size, liquid density, and critical pressure to CO₂, and its critical temperature (126 K) is easily accessible with the use of a liquid nitrogen cooled cryostatic bath; thus, N₂ is indeed a promising candidate for inert supercritical fluid extraction.

The as-synthesized γ -Mg(BH₄)₂ was subjected to a N₂ ScD (NScD) routine as follows (further details found in the SI). A 200 mg sample was degassed at room temperature and then exposed to liquid N₂ at 2 MPa and 110 K in a closed vessel for 4 h. After heating to 150 K (and with the pressure held to <8 MPa), the sample was immersed in supercritical N₂ for 1 h and then slowly degassed at 150 K to 0.1 Pa over 12 h. This process was iterated in certain instances to determine the effects of multiple treatments (1x, 3x, etc.).

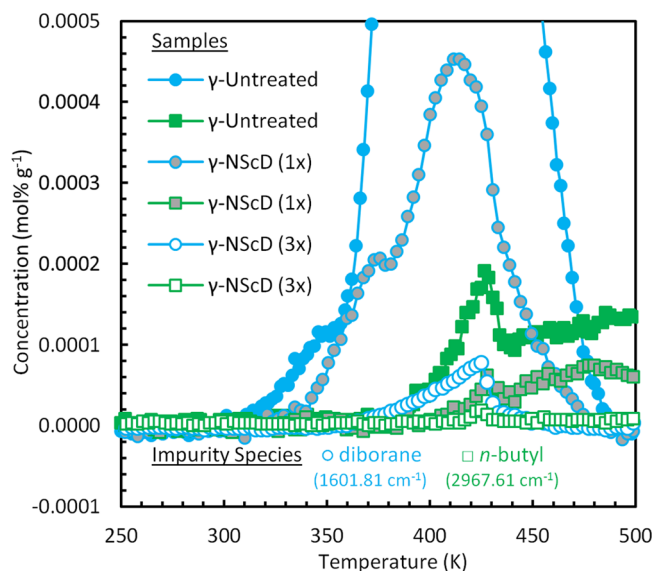


Figure 2. Temperature-dependent concentration of diborane (blue) and *n*-butyl (green) gases measured by IR absorbance in the downstream flow of H₂ under heating of γ -Mg(BH₄)₂ at 2 K min⁻¹: untreated (filled symbols), 1x NScD-treated (gray filled symbols), and 3x NScD-treated (unfilled symbols).

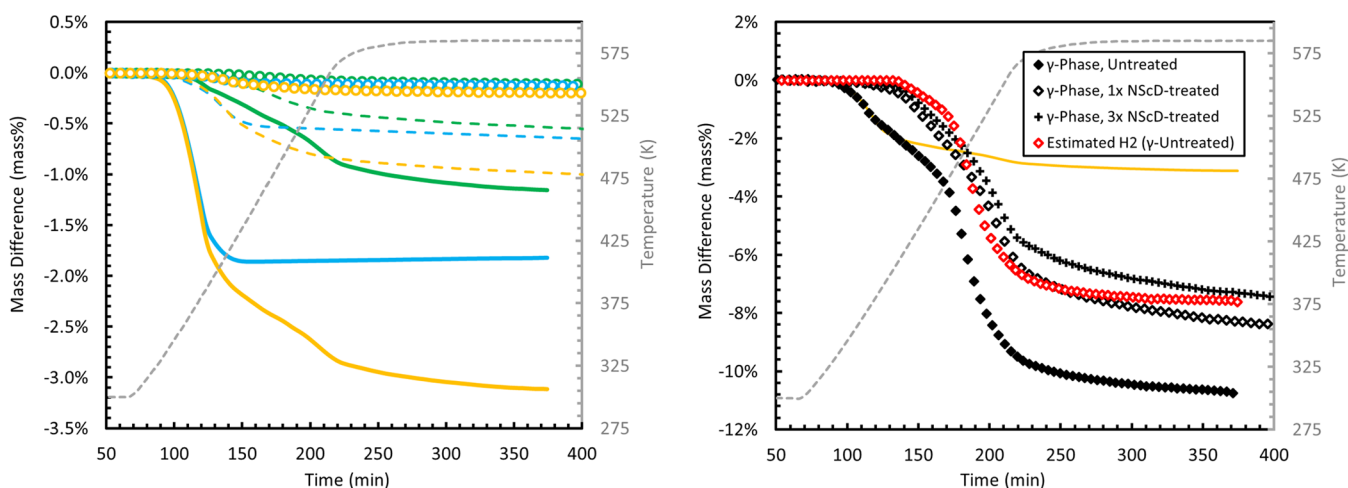
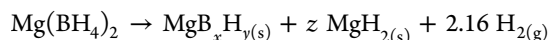


Figure 3. (Left) Time-dependent mass loss during heating of untreated γ -Mg(BH₄)₂ (solid lines), 1x NScD-treated γ -Mg(BH₄)₂ (dashed lines), and 3x NScD-treated γ -Mg(BH₄)₂ (unfilled circles) corresponding to diborane (blue), *n*-butyl impurities (green), and total IR-detectable impurities (yellow). The temperature profile is shown in gray. (Right) Total mass loss during heating of untreated γ -Mg(BH₄)₂ and 1x and 3x NScD-treated γ -Mg(BH₄)₂, measured by gravimetry. The temperature ramp is shown in gray. The mass loss of the untreated γ -Mg(BH₄)₂ due to total IR-detectable impurities (as shown in Figure 3) and the remainder (\sim H₂) is also shown.

The results of the subsequent decomposition of NScD- γ -Mg(BH₄)₂ in flowing H₂ are shown in Figures 1–3. In contrast to the results after CScD treatment, the concentrations of all IR active species in the gaseous decomposition products after only a single NScD treatment are significantly reduced, including that of diborane. As anticipated, no reaction products between N₂ and Mg(BH₄)₂ were observed (see Figure 1c and 1d). The temperatures associated with the mass loss from both diborane and *n*-butyl impurities in the NScD sample are identical to those of the untreated sample, indicating that the sample was not crucially altered except in reducing the concentration of impurities. This was further confirmed with powder X-ray diffraction (XRD) studies (see SI), which show that γ -Mg(BH₄)₂ is highly crystalline before and after NScD treatments, and with N₂ adsorption measurements, which show an increase in BET surface area due to NScD treatments. Iterated NScD treatments were found by ATR-IR spectroscopy to show a cumulative reduction of impurity species (see SI), where after three iterations the diborane release was reduced to near the detection limit of the methods used (\sim 2.5% of the original amount): see Figure 2.

The total mass loss during decomposition as measured by gravimetry is compared to the calculated mass loss from IR quantification analyses for the untreated γ -Mg(BH₄)₂ and the NScD-treated γ -Mg(BH₄)₂ in Figure 3. The lack of IR active gas species during the decomposition of NScD-treated γ -Mg(BH₄)₂ between 298 and 593 K is strong evidence that this phase decomposes to form only solid products (except H₂), without emitting diborane. The dehydrogenation reaction is centered at 500 K and proceeds to a final mass loss of 8 mass% following:



where MgB_xH_y contains a variety of [B_xH_y] units.⁶

The release of diborane (1.9 mass%), an *n*-butyl containing impurity (1.2 mass%), and a trace amount of methane (<0.1 mass%) during the heating of untreated γ -Mg(BH₄)₂ is ultimately reduced after three NScD treatments to 0.1, <0.1, and 0.0 mass%, respectively. The estimated mass loss corresponding to the dehydrogenation reaction in untreated

γ -Mg(BH₄)₂ is also centered at \sim 500 K (see Figure 2), indicating that impurity species do not significantly change the reaction mechanism of decomposition. The lower temperature release of hydrogen in the γ -phase material compared to the β -phase (\sim 600 K)¹³ can be attributed to an advantage of higher surface area or a well activated surface for hydrogen release.

The successful strategy to achieve the clean dehydrogenation of porous, impurity containing hydride materials upon heating is summarized in Figure 4. Impurities such as solvent molecules

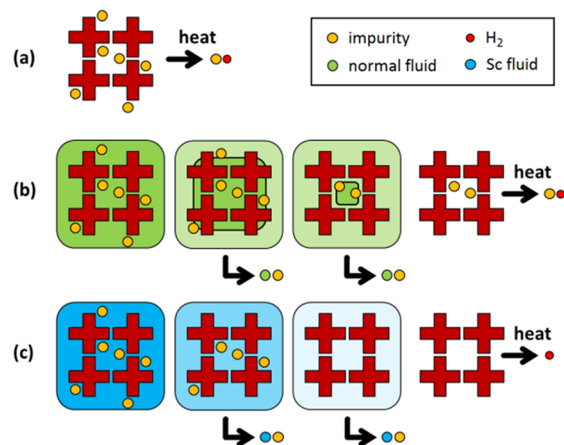


Figure 4. A schematic depicting three methods to rid a porous hydride material (shown in dark red) of its impurities: (a) heat treatment, (b) typical liquid or gas solvent treatment, and (c) NScD treatment. The gaseous products on heating (leading to decomposition) are shown at right. Gas species are shown as filled circles: impurities (e.g., B₂H₆) (yellow), H₂ (red), normal solvent fluid (green), and an inert supercritical solvent fluid (in this case N₂) (blue).

(e.g., *n*-butyl, THF, etc.), and specifically boranes (B₂H₆, etc.) in the case of complex borohydrides, are released along with hydrogen if appropriate pretreatment methods are not first performed. After liquid solvent exchange or subcritical gas/liquid exchange treatments, it is probable that impurities remain trapped in the pores due to surface tension effects and/or poor penetration of the solvent. With an appropriate supercritical

fluid exchange, however, where a fluid is chosen that will not react with the material to be purified, the impurities can be successfully removed. The products of decomposition under heating in the latter case would consist only of those expected thermodynamically under the conditions chosen (case (c) in Figure 4).

The unstable nature of boranes, including diborane which is the most stable B_xH_y species in the gas phase at ambient conditions, has caused significant difficulty in the identification and verification of the specific decomposition pathways of borohydride complex materials under heating; hence, there remains ongoing debate as to the precise role of diborane in the decomposition routes of nearly all B–H containing materials. The results presented herein shed crucial light on the matter via the investigation of $Mg(BH_4)_2$, which stands at the boundary between the borohydrides for which diborane unambiguously plays a significant role ($M = Zn, Zr$, etc.) and those for which diborane is not observed, difficult to detect, or conditions dependent. In this study we have ascertained that diborane, in a practical sense, is not a relevant decomposition product of $Mg(BH_4)_2$, except to the extent that it (or a precursor of it) exists as a removable impurity or as a fleeting intermediate undetectable at a distance from the reaction centers.

In summary, the purification of high surface area, reactive porous materials such as γ - $Mg(BH_4)_2$ is possible using supercritical N_2 as a drying fluid. The emission of diborane and other impurities in γ -phase $Mg(BH_4)_2$ during hydrogen desorption was avoided to within detection limits of the experimental methods via NScD processing methods. A clean decomposition (<0.2 mass% of impurities) yielding 8 mass% H_2 during the first cycle up to 593 K and 0.1 MPa was observed, a comparable figure to that measured for pure β - $Mg(BH_4)_2$, indicating that the reaction proceeds similarly in both cases.

The importance of ScD treatments to the clean decomposition of porous reactive materials (in this case, γ -phase $Mg(BH_4)_2$) is the key result of this study, but we also suggest the potential importance of NScD treatments for the purification of other (perhaps even nonporous) complex hydride materials or other reactive compounds where impurities are hard to remove by usual methods. We suspect that the emerging class of nanostructured, unstable materials for advanced applications such as hydrogen storage will continue to demand close attention to purification before analysis, where NScD treatments may be essential.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis methods, experimental techniques, materials characterization, IR spectra and analysis. 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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