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Calcium Borohydride for Hydrogen Storage: Catalysis and Reversibility

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We demonstrate a new solid-state synthesis route to prepare calcium borohydride, $Ca(BH_4)_2$, by reacting a ball-milled mixture of CaB_6 and CaH_2 in a molar ratio of 1:2 at 700 bar of H_2 pressure and 400–440 °C. Moreover, doping with catalysts was found to be crucial to enhance reaction kinetics. Thermogravimetric analysis and differential scanning calorimetry revealed a reversible low-temperature to high-temperature endothermic phase transition at 140 °C and another endothermic phase transition at 350–390 °C associated with hydrogen release upon formation of CaB_6 and CaH_2 , as was evident from X-ray diffraction analysis. Thus, since $Ca(BH_4)_2$ here is shown to be prepared from its anticipated decomposition products, the conclusion is that it has potential to be utilized as a reversible hydrogen storage material. The theoretical reversible capacity was 9.6 wt % hydrogen.

Hydrogen storage is accepted to be a key enabling technology for the advancement of hydrogen and fuel cell power technologies in transportation, stationary, and portable applications. The U.S. Department of Energy (DOE) is focusing the efforts primarily on on-board vehicular hydrogen storage systems that will allow for a driving range of at least 300 miles. This has stimulated many research groups to attempt to find new practical metal hydrides or other hydrogen storage materials that will meet the U.S. DOE system target of 6 wt % of reversible hydrogen capacity at around 100 °C and 1-10 atm.¹ With respect to the weight percent of hydrogen, the most promising class of metal hydrides to meet this target is the complex hydrides. Recently investigated materials with high gravimetric densities include alanates,² amides,³ and metal borohydrides.⁴ We will here focus on the metal borohydrides, specifically calcium borohydride. Among the metal borohydrides, the features of the alkali borohydrides, that is, LiBH₄, NaBH₄, and KBH₄, are relatively well explored.⁵ While sodium and potassium borohydrides cannot be rehydrided, lithium borohydride has been shown by Muller et al. to be hydrogenated at 600-650 °C at 100–160 bar.⁶ By destabilizing LiBH₄ with MgH₂ upon formation of MgB₂, LiH, and hydrogen gas, Vajo et al.⁷ showed a system capable of reversibly storing 8-10 wt % of hydrogen at 350-450 °C. Also, Mg(BH₄)₂ has been investigated for its reversible properties,^{8,9} but so far, there is no evidence for reversibility in the literature. Another interesting highhydrogen-content compound is Ca(BH₄)₂, but little information is available regarding fundamental properties. Calcium borohydride can be prepared by reacting calcium hydride¹⁰ or alkoxides¹¹ with diborane, which is a poisonous gas. Another preparation method is reaction in THF,¹² forming Ca(BH₄)₂-(THF)₂, which is commercially available. Recently, calcium

borohydride was more conveniently prepared by reacting MgB₂ with CaH₂ at 350 bar of H₂ pressure and 400 °C upon obtaining MgH₂ as a byproduct;¹³ thus, the maximum hydrogen capacity would be 8.3 wt %. Nakamori et al.¹⁴ prepared calcium borohydride by ball milling LiBH₄ with CaCl₂, obtaining LiCl as a byproduct, thus preventing reversibility. We will here for the first time demonstrate how to prepare calcium borohydride from its decomposition products without forming byproducts, thus obtaining a theoretical reversible capacity of 9.6 wt % of hydrogen.

Theoretical calculations showed that calcium borohydride may form by reacting CaB₆ with CaH₂, resulting in a reaction enthalpy (at T = 0 K) of ~53 kJ (mol H₂)⁻¹ for the following reaction:¹⁵

 $CaB_6(s) + 2CaH_2(s) + 10H_2(g) \rightarrow 3Ca(BH_4)_2(s)$

This encouraged us to prepare this material by solid-state reactions. We discovered that it was possible to prepare calcium borohydride by following a specific synthesis route, previously not reported in the literature. The synthesis route involved three consecutive steps, which could not be excluded in order to prepare calcium borohydride. The starting materials were CaB₆ (99.5% Alfa Aesar) and CaH₂ (99.99%, Aldrich), mixed in a 1:2 molar ratio. All sample handlings were performed in an argon-filled glove box monitored to have oxygen and water levels below 1 ppm. First, the mixture of CaB₆ and CaH₂ was ball milled in a SPEX mill for 30 min. Second, the powder was mechanically pressed into a pellet of 10 mm in a hydraulic Carver press to form better contact between the particles. Third, the pellet was placed in a steel crucible further enclosed in a commercial AE Closure (Snap-tite, Inc.), which was attached to a high-pressure hydrogenation system and placed in a furnace. The autoclave was initially pressurized to 350 bar of H₂ pressure before being heated up to 400-440 °C, and the obtained

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Figure 1. Powder X-ray diffraction pattern of a sample made by reacting $CaB_6 + 2CaH_2 + 4$ wt % of $TiCl_3 + 4$ wt % of Pd at 70MPa and 440 °C. The sample contains $Ca(BH_4)_2$ (|) + CaB_6 (O) + CaH_2 (\bullet) + CaO (x).



Figure 2. Raman spectra collected from (a) high-pressure synthesis of solid-state $Ca(BH_4)_2$ and (b) a CaB_6 reference sample. Raman spectroscopy of a synthesized sample of $Ca(BH_4)_2$ showing the shifts from the $[BH_4^-]$ anion at 2280 cm⁻¹.

pressure was adjusted to 700 bar and kept for 48 h. Importantly, a chemical reaction will not occur unless a dopant of 4-8 wt % is added to the initial mixture of CaB₆ and CaH₂. As evident from powder XRD analysis, the appearance of new X-ray peaks indicated a chemical reaction. X-ray data were collected of powders contained in 0.7 mm capillaries on a rotating anode Rigaku diffractometer (RU-300) with a Cu target at 40 kV and 40 mA at 295 K. The new peaks were indexed by utilizing the trial-and-error program TREOR¹⁶ to find the unit cell parameters. Thereafter, by refining the unit cell in Pirum,¹⁷ the crystal structure was determined to be face-centered orthorhombic, with unit cell parameters a = 13.07(2), b = 8.700(2), and c = 7.52(2)Å (V = 854.4 Å³), likely of the Ba(MnO₄)₂-type, space group Fddd (No. 70), in accordance with the theoretical predictions by Vajeeston et al.¹⁸ and the Rietveld analysis by Miwa et al.¹⁹ of an adduct-free sample of calcium borohydride. The XRDpattern is shown in Figure 1. The samples were here also analyzed by Raman spectroscopy, TGA, and DSC. Raman data of a reference sample of CaB₆ and a sample of synthesized calcium borohydride were collected on a Spex model 1877 0.6 m triple spectrometer, using the 514 nm line of a Coherent Innova Ar ion laser at a power of about 10 mW at the sample. Raman spectroscopy showed the presence of the [BH₄⁻] anion in the spectra, in accordance with the literature.²⁰ The Raman peaks in Figure 2 at 785, 1150, and 1285 cm⁻¹ belong to CaB₆. The peak at 2280 cm⁻¹ belongs to the strongest BH₄ vibration in Ca(BH₄)₂.

Bogdanovic et al.² showed that by adding TiCl₃, sodium alanate, NaAlH₄, can be made reversible, obtaining 4.5 wt % at 100-200 °C. Among tried dopants to facilitate the reaction above were TiCl₃, Pd, TiCl₃ + Pd, and RuCl₃. With only TiCl₃ added, a small amount of Ca(BH₄)₂ formed, as was evident from estimating the amount of the phases by comparing relative intensities in the XRD pattern. With a mixture of $TiCl_3 + Pd$, we obtained a much higher yield of $\sim 60\%$ Ca(BH₄)₂ in relation to CaB₆ and CaH₂, and the pellet changed color from brown to gray. The XRD pattern is shown in Figure 1. By adding RuCl₃, a slightly better yield as compared to that of the $TiCl_3 + Pd$ mixture was obtained. Interesting to note is that, depending on the added catalyst/dopant, other new phases form in addition or instead of $Ca(BH_4)_2$. Only the catalyst mixture of $TiCl_3$ + Pd resulted in Ca(BH₄)₂ of the Ba(MnO₄)₂ structure type, with no other new XRD peaks present (except for unreacted CaB₆ and CaH₂). We anticipate that these other phases are polymorphs of Ca(BH₄)₂. An extensive investigation has been initiated to determine the reaction mechanism. All of the samples contained a significant amount of CaO (10-20 wt %), concluded to originate from impurities in the lines between the hydrogen bottle and the autoclave.

In order to investigate the desorption behavior, a sample of synthesized calcium borohydride was analyzed by thermal gravimetry analysis (TGA) and differential scanning calorimetry (DSC) using Mettler Toledo instruments TGA/SDTA851 and DSC822. The heating rate was 5 K/min⁻¹ in a 20 mL/hour slow stream of argon at ambient pressures. Figure 3 shows the experimental curves from analysis of a sample (<5 mg) with a composition similar to the XRD pattern in Figure 1. The DSC curve shows two phase transitions at onset temperatures of 140 and 350 °C. The TGA curve shows a weight loss at 350-390 °C, which is most likely related to hydrogen release from calcium borohydride. The increase in the TGA curve has been confirmed to be due to background effects. The decomposition products were predicted to be CaB₆ and CaH₂ by Konoplev et al.²¹ and Miwa et al.¹⁹ In order to verify this assumption, we collected XRD data at two points on the curve; samples were heated up to 150 and 400 °C, respectively, and XRD data were collected for cooled down samples. At 150 °C, the XRD pattern



Figure 3. DSC curve (- -) and TGA curve (-) showing two endothermic phase transformations at onset temperatures of 140 and at 350 °C and release of hydrogen at 350 °C.

is similar to the starting sample; thus, there is a reversible phase transition from a low-temperature form to a high-temperature form, similar to that for LiBH₄. However, at 400 °C, the XRD pattern corresponds to CaB_6 and CaH_2 without $Ca(BH_4)_2$ present. Thus, upon release of 9.6 wt % of hydrogen, we presume that calcium borohydride has completely decomposed to form CaB_6 and CaH_2 , which we now know is the starting mixture to synthesize calcium borohydride at 700 bar (70MPa) and 440 °C. The above reaction formula is thus partially reversible at the present described reaction conditions. In conclusion, this material has potential to be used as a reversible hydrogen storage material for on-board storage. High-pressure tanks up to 800 bar have been shown to be feasible for utilizing high-capacity materials, as presented by Hardy et al.²² during the 2007 DOE annual review meeting.

In summary, we have demonstrated a unique solid-state synthesis route to prepare calcium borohydride, $Ca(BH_4)_2$, for the first time without forming byproducts. The yield relative to the starting materials is estimated to 60%. We have also demonstrated that this chemical reaction can be reversed with a theoretical capacity of 9.6 wt %; the anticipated decomposition products, that is, CaB_6 and CaH_2 , can be rehydrided under high-hydrogen pressures and moderate temperatures when a catalyst is added, thus forming calcium borohydride. Next, we will explore structural changes upon decomposition in detail. Moreover, we will optimize the reaction conditions at lower pressures and temperatures and continue exploring the effect of catalysts on kinetics.

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