

Isotope Exchange Reactions in $\text{Ca}(\text{BH}_4)_2$

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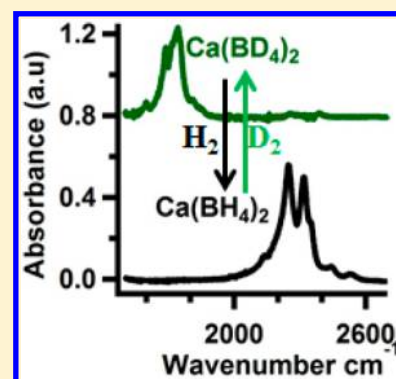
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Supporting Information

ABSTRACT: Borohydrides are actively considered as potential hydrogen storage materials. In this context, fundamental understanding of breaking and forming the B–H bond is essential. Isotope exchange reactions allow the isolation of some steps of this reaction without introducing major structural or chemical changes. Experiments were performed on $\text{Ca}(\text{BH}_4)_2$ and $\text{Ca}(\text{BD}_4)_2$ as a function of temperature and pressure. A complete exchange can be realized in about 9 h at 200 °C using a deuterium pressure of 20 bar. The activation energy, estimated using first-order kinetics, for the forward reaction ($\text{Ca}(\text{BH}_4)_2 \rightarrow \text{Ca}(\text{BD}_4)_2$) was found to be $82.1 \pm 2.7 \text{ kJ mol}^{-1}$ ($P = 35 \text{ bar}$), and the one for the backward reaction ($\text{Ca}(\text{BD}_4)_2 \rightarrow \text{Ca}(\text{BH}_4)_2$) was found to be $98.5 \pm 8.3 \text{ kJ mol}^{-1}$ ($P = 35 \text{ bar}$). A pressure-dependent study shows that the reaction rate increases with increasing pressure up to 35 bar. This behavior is consistent with a first adsorption step prior to diffusion into the solid and isotope exchange according to the

following scheme: $\text{Ca}(\text{BH}_4)_2 + \text{D}_2 \xrightleftharpoons[K_{-1}]{K_1} \text{Activated Complex} \xrightarrow{K_2} \text{Ca}(\text{BD}_x\text{H}_{4-x})_2$.



INTRODUCTION

The high gravimetric and volumetric content of hydrogen allows alkali and alkaline earth metal borohydrides to qualify as potential hydrogen storage materials.^{1–4} Among these borohydrides, $\text{Ca}(\text{BH}_4)_2$ is of prime interest because of its favorable dehydrogenation enthalpy (32 kJ mol^{-1}).^{5,6} $\text{Ca}(\text{BH}_4)_2$ has been subjected to various theoretical and experimental investigations to study its dehydrogenation pathway and the effect of catalysts on dehydrogenation and the reversibility (rehydrogenation).^{7–11}

Breaking of the B–H bond is potentially one of the first steps involved in dehydrogenation (and the last one during the reverse reaction) of borohydrides. A detailed kinetic and thermodynamic study of this process is required to improve the understanding of dehydrogenation. The deuteration of borohydrides is a process which involves breaking of B–H bonds and formation of B–D bonds without having to consider the chemical and structural changes associated with a thermal decomposition reaction. Because this process is also involved in dehydrogenation (and rehydrogenation) of borohydrides, the thermodynamic and kinetic study of this step can aid in reaching a better understanding of dehydrogenation (and rehydrogenation) process.

Isotope exchange reactions in borohydrides have been studied previously for borohydrides of Li, Na, K and Mg ($T \geq 200, 350, 500, 132 \text{ °C}$ respectively).^{12–15} We have reported the isotope exchange between $\text{Mg}(\text{BH}_4)_2$ and D_2 gas at 40 bar and found an activation energy of 50 kJ mol^{-1} .¹⁵

In this work, we study the reaction $\text{Ca}(\text{BH}_4)_2 + \text{D}_2 \rightarrow \text{Ca}(\text{BD}_4)_2$ and the reverse reaction in detail. It is shown that $\text{Ca}(\text{BH}_4)_2$ can also be deuterated at a pressure as low as 1 bar. The analysis of temperature and pressure dependence of the reaction is presented. Theoretical density functional theory (DFT) calculations on model systems in the gas phase have also been performed to explore possible transition states for the isotope exchange reaction.

EXPERIMENTAL SECTION

Synthesis of $\text{Ca}(\text{BH}_4)_2$. $\text{Ca}(\text{BH}_4)_2$ was prepared by heating a commercial sample of $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ progressively up to 130 °C under vacuum. X-ray diffraction of the desolvated material (Supporting Information) shows that the phase composition of the resulting powder is a mixture of α , β , and γ phase of $\text{Ca}(\text{BH}_4)_2$ with 47.7(8), 45.6(7), and 6.7(5) mole %, respectively. All experiments were performed with samples of this batch. After full deuteration, this composition changed to 30.03(5), 58(8), and 11.7(4) mole % respectively. This change is likely due to the temperature applied and the stabilization of the high-temperature β -phase.

Deuterium Exchange Reactions. These reactions were performed in a manner similar to that used in our previous study.¹⁵ A vial containing 150 mg of $\text{Ca}(\text{BH}_4)_2$ was placed inside an autoclave. The autoclave was tightly sealed, and

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deuterium gas was introduced into the autoclave after evacuating it once. The deuterium pressure was monitored with a pressure gauge attached to the autoclave. The autoclave was introduced into the preheated furnace. It was removed from the furnace after a regular time interval (3 h). A small sample was removed (under an inert atmosphere of argon) for X-ray diffraction and infrared (IR) characterization.

In one set of experiments (first set), the furnace temperature was kept constant at 200 °C and pressure was varied (1, 5, 10, and 20 bar). In another set of experiments (second set), the pressure was kept constant at 30 bar and the temperature was varied (140, 170, and 200 °C). Both sets of experiments were repeated for $\text{Ca}(\text{BD}_4)_2$, which was formed by the complete deuteration of $\text{Ca}(\text{BH}_4)_2$.

IR spectra were obtained with a Biorad Excalibur Fourier transform infrared (FT-IR) instrument equipped with a Specac Golden Gate ATR setup. The spectral resolution was set to 1 cm^{-1} . Samples were loaded under an inert atmosphere of nitrogen. Powder X-ray diffraction patterns were obtained on a STOE STADI P diffractometer in Debye–Scherrer geometry with monochromated $\text{Cu K}\alpha_1$ radiation. The phase composition was determined with the Rietveld method using the software FullProf.¹⁶

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns of both hydride and deuteride phases are shown in Figure 1. The slight shift of

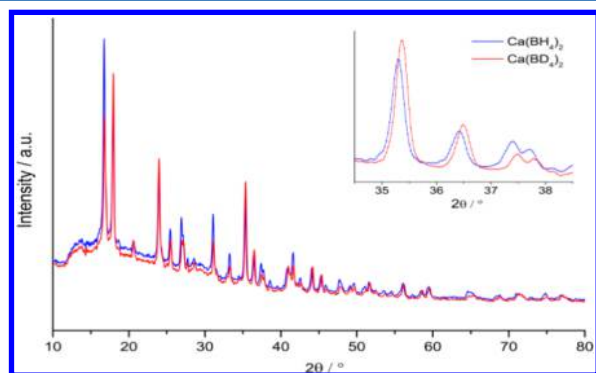


Figure 1. Powder diffraction data shown for initial $\text{Ca}(\text{BH}_4)_2$ and fully deuterated $\text{Ca}(\text{BD}_4)_2$. Inset: the smaller lattice of $\text{Ca}(\text{BD}_4)_2$ is manifested in a clear shift of Bragg peaks to higher angles.

lattice parameters to higher angle is due to the relatively heavier deuterium nucleus.¹⁷ Importantly, powder diffraction demonstrates that the crystallinity is not affected by the isotope exchange; hence, the kinetics of the reaction are expected to be comparable in both phases.

Figure 2 compares the IR spectra of $\text{Ca}(\text{BH}_4)_2$ during deuteration at 1 bar pressure and 200 °C at different times. The spectra were normalized at 1700 cm^{-1} to highlight the relative intensity changes. The band around 2330 cm^{-1} corresponds to the B–H stretching modes, while the band around 1750 cm^{-1} corresponds to the B–D stretching mode.^{18,19} Figure S3 of the Supporting Information compares the IR spectra¹⁸ of selectively labeled $\text{Ca}(\text{BH}_3\text{D})_2$ and $\text{Ca}(\text{BD}_3\text{H})_2$ to highlight the spectral differences for different isotopomers. The wide separation of stretching frequency in these two cases helps in easy identification of each species. The relative intensities of these peaks can be related to the mole fraction of hydrogen and deuterium present in the sample.¹⁵

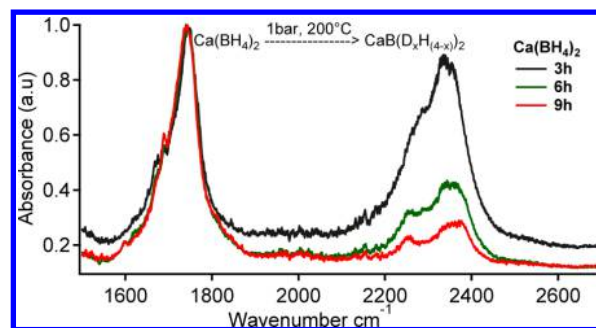


Figure 2. IR spectra showing the B–H and B–D stretching region at different times during $\text{Ca}(\text{BH}_4)_2$ deuteration at 1 bar and 200 °C. The spectra were normalized at 1700 cm^{-1} to highlight the relative intensity changes.

For the first set of experiments, IR spectra were measured at different reaction times (3, 6, 9 h) for different pressures (1, 5, 10, 20 bar). The mole fraction of hydrogen in the sample was calculated by taking the ratio of relative intensity of B–H and B–D stretching bands. This mole fraction was used to plot the curves showing the progress of the reaction with time (Figure 3). The rate constant of deuteration was obtained by comparing

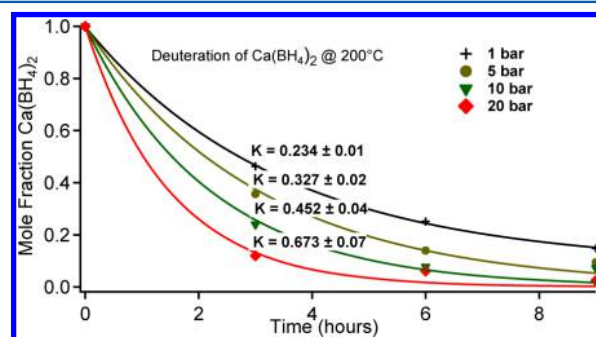


Figure 3. Progress of the $\text{Ca}(\text{BH}_4)_2$ deuteration reactions as a function of time at 200 °C and different pressures.

the curves with the first-order rate equation $[\text{H}] = [\text{H}]_0 e^{-kt}$. Figure 3 reveals that as pressure was decreased, the rate constant of the reaction also decreased. This behavior is consistent with the reaction scheme in which an intermediate is in equilibrium with the reactants.



The pressure above which increase in pressure would not affect the reaction rate significantly can be estimated by analyzing the variation of the initial reaction speed estimated from the exchanged amount after 3 h. Variation of effective rate constant, k , was plotted (Figure 4) against deuterium pressure $P(\text{D}_2)$.

$$\frac{1}{K} = \frac{1}{K_2} + \frac{K_2 + K_{-1}}{K_1 K_2 P(\text{D}_2)} \quad (1)$$

Figure 4 shows the variation of the initial rate constant (measured after 3 h) with deuterium pressure. The solid red line corresponds to a fit of these data sets using eq 1 with $1/K_2 = 3.05$ and $(K_2 + K_{-1})/K_1 = 2.70$. It appears that for the pressures above ca. 30–35 bar, the rate constant does not increase. In our previous study¹⁵ on the isotope exchange in $\text{Mg}(\text{BH}_4)_2$, the reaction rate did not change when increasing

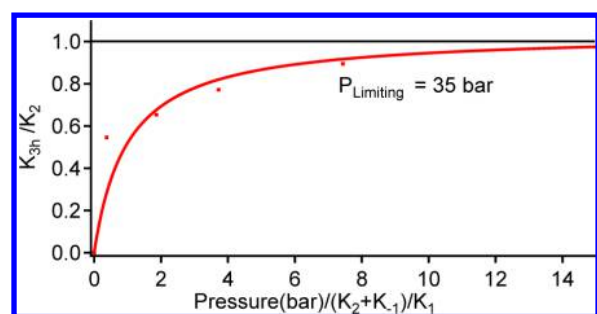


Figure 4. Variation of effective rate constant with pressure.

the pressure from 40 to 80 bar, which is then consistent with the present observations.

Equation 1 implies a reversible first reaction step. In a typical gas–solid reaction, the initial step is the adsorption followed by further reactions (such as the dissociation of the hydrogen molecule before the diffusion into the solid). Assuming that the slow step is the dissociation reaction, the amount of hydrogen available for diffusion is dictated by the pressure-dependent adsorption equilibrium until the entire surface is covered with hydrogen at pressures of about 30 bar. Alternate models could be proposed, such as adsorption followed by the diffusion of hydrogen molecules.

In the second set of experiments, the pressure was kept constant at 35 bar and the temperature was varied. The rate constants at different temperatures were calculated as mentioned above. The activation energy for this reaction was calculated (using the Arrhenius equation $k = Ae^{-E/RT}$) and found to be $82.1 \pm 2.7 \text{ kJ mol}^{-1}$. It should be noted here that our sample is in fact a mixture of several polymorphs; thus, our value corresponds to an average value, as different polymorphs may show different kinetics. This value is, as expected, significantly lower than the activation energy for the first dehydrogenation step for $\text{Ca}(\text{BH}_4)_2$ at ca. $370 \text{ }^\circ\text{C}$ which was reported to be 225 kJ mol^{-1} .²⁰ Llamas-Jansa et al.²¹ calculated activation energy to be 184(14), 192(3), and 230(1) kJ mol^{-1} for the γ , α , and β polymorphs of $\text{Ca}(\text{BH}_4)_2$, respectively.

The same procedure was repeated for the reverse reaction, and the corresponding activation energy is observed to be $98 \pm 8.4 \text{ kJ mol}^{-1}$. Figure 5 illustrates the IR spectra before and after the deuteration reaction, as well as after the rehydrogenation reactions, showing that this exchange reaction is fully reversible.

With the aim of obtaining an estimate of the order of magnitude expected for the activation energy of an isotope

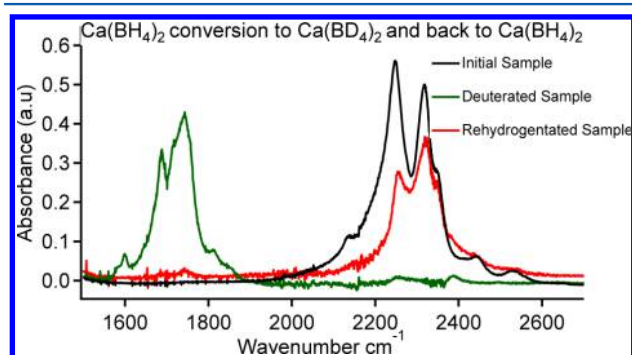


Figure 5. IR spectra showing complete conversion of $\text{Ca}(\text{BH}_4)_2$ to $\text{Ca}(\text{BD}_4)_2$ and complete rehydrogenation leading back to $\text{Ca}(\text{BH}_4)_2$ formation ($200 \text{ }^\circ\text{C}$, 20 bar).

exchange reaction for the BH_4^- ion, we have performed a DFT calculation for the reaction of a deuterium atom with the BH_4^- , yielding a transition state similar to the one of a SN_2 reaction. The value obtained (97 kJ mol^{-1}) is in the range of our observed values for $\text{Mg}(\text{BH}_4)_2$ ¹⁵ (50 kJ mol^{-1}) and $\text{Ca}(\text{BH}_4)_2$ (82 and 97 kJ mol^{-1}).

The difference of the values of the activation energy obtained for $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ is quite important. It is important to note in this context the difference of crystal structures, in the sense that the structure of $\text{Mg}(\text{BH}_4)_2$ ²² is relatively open (volume per formula unit, ca. 115 \AA^3) and potentially offers easier diffusion paths for hydrogen (and deuterium) compared to that of $\text{Ca}(\text{BH}_4)_2$ ^{23,24}, which has a rather compact crystal structure (volume per formula unit, less than 113 \AA^3). It must also be noted that the Ca^{2+} ions are much larger than the Mg^{2+} ions. Hydrogen adsorption at low temperatures has been observed in the γ phase of $\text{Mg}(\text{BH}_4)_2$.²⁵ It appears thus that the higher activation energy observed for $\text{Ca}(\text{BH}_4)_2$ may be related to a higher barrier for the diffusion of hydrogen in the crystal, as compared to that of $\text{Mg}(\text{BH}_4)_2$.

CONCLUSIONS

The reversible isotopic exchange reaction between $\text{Ca}(\text{BH}_4)_2$ and D_2 has been studied. Complete deuteration can be easily achieved. It is important to note that deuterated borohydrides can be interesting deuterium storage materials.²⁶ The pressure- and temperature-dependent study shows a two-step reaction process.

The first step depends on the deuterium pressure, but at pressures above 35 bar, the rate constant does not change. The activation energy estimated for the deuteration reaction is found to be around 82 kJ mol^{-1} , which is larger than the previously found value for $\text{Mg}(\text{BH}_4)_2$ of $51 \pm 15 \text{ kJ mol}^{-1}$. It appears thus that the nature of the metal ion plays an important role in this reaction.

ASSOCIATED CONTENT

Supporting Information

X-ray powder diffraction of $\text{Ca}(\text{BH}_4)_2$ and $\text{Ca}(\text{BD}_4)_2$, FT-IR spectra of $\text{Ca}(\text{BH}_{4-x}\text{D}_x)_2$ samples, and details of the DFT calculations. 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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