Isotope Exchange Reactions in Ca(BH$_4$)$_2$

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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 Ca(BH$_4$)$_2$ and Ca(BD)$_2$ 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 (Ca(BH$_4$)$_2$ → Ca(BD)$_2$) was found to be 82.1 ± 2.7 kJ mol$^{-1}$ (P = 35 bar) and the one for the backward reaction (Ca(BD)$_2$ → Ca(BH$_4$)$_2$) was found to be 98.5 ± 8.3 kJ mol$^{-1}$ (P = 35 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: Ca(BH$_4$)$_2$ + D$_2$ ⇌ $K_f$ Ca(BD)$_2$ ⇌ $K_r$ Ca(BD$_4$)$_2$.

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, Ca(BH$_4$)$_2$ is of prime interest because of its favorable dehydrogenation enthalpy (32 kJ mol$^{-1}$).$^{5,6}$ Ca(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 ≥ 200, 350, 500, 132 °C respectively).$^{12-15}$ We have reported the isotope exchange between Mg(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 Ca(BH$_4$)$_2$ + D$_2$ → Ca(BD)$_2$ and the reverse reaction in detail. It is shown that Ca(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 Ca(BH$_4$)$_2$. Ca(BH$_4$)$_2$ was prepared by heating a commercial sample of Ca(BH$_4$)$_2$·2THF 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 Ca(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 Ca(BH$_4$)$_2$ was placed inside an autoclave. The autoclave was tightly sealed, and
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 Ca(BD₄)₂, which was formed by the complete deuteration of Ca(BH₄)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 Cu Kα₁ 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 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 Ca(BH₄)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 1750 cm⁻¹ corresponds to the B–D stretching mode. 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(D₂).

![Figure 1. Powder diffraction data shown for initial Ca(BH₄)₂ and fully deuterated Ca(BD₄)₂. Inset: the smaller lattice of Ca(BD₄)₂ is manifested in a clear shift of Bragg peaks to higher angles.](image1)

![Figure 2. IR spectra showing the B–H and B–D stretching region at different times during Ca(BH₄)₂ deuteration at 1 bar and 200 °C. The spectra were normalized at 1700 cm⁻¹ to highlight the relative intensity changes.](image2)

![Figure 3. Progress of the Ca(BH₄)₂ deuteration reactions as a function of time at 200 °C and different pressures.](image3)

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. 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.

\[
\text{Ca(BH}_4\text{)}_2 + \text{D}_2 \xrightarrow{K_i} \text{Activated Complex} \xrightarrow{K_r} \text{Ca(BD}_4\text{H}_{(4-x)}\text{)}_2
\]

The rate constant of deuteration was obtained by comparing the curves with the first-order rate equation \([H] = [H]_0 e^{-kt}\).

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\[
\frac{1}{K} = \frac{1}{K_2} + \frac{K_2 + K_{-1}}{K_2 K_r \text{P(D}_2\text{)}}
\]

(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/K₂ = 3.05 and (K₂ + K₋₁)/K₂ = 2.70. It appears that for the pressures above ca. 30–35 bar, the rate constant does not increase. In our previous study on the isotope exchange in Mg(BH₄)₂, the reaction rate did not change when increasing...
The reversible isotopic exchange reaction between Ca(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. 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 Mg(BH$_4$)$_2$ of 51 ± 15 kJ mol$^{-1}$. It appears thus that the nature of the metal ion plays an important role in this reaction.

## CONCLUSIONS

The reversible isotopic exchange reaction between Ca(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. The pressure-and temperature-dependent study shows a two-step reaction process.

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## ASSOCIATED CONTENT

### Supporting Information

X-ray powder diffraction of Ca(BH$_4$)$_2$ and Ca(BD$_4$)$_2$. FT-IR spectra of Ca(BH$_4$)$_2$-$D_2$ 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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## REFERENCES
