



Kinetics and modeling studies of the $\text{CaH}_2/\text{LiBH}_4$, $\text{MgH}_2/\text{LiBH}_4$, $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ systems

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ABSTRACT

Borohydrides of alkali and alkaline-earth elements are of interest because of their high hydrogen holding capacities. However, their usefulness for hydrogen storage applications is often limited by high thermodynamic stabilities and slow kinetics. In this study comparisons have been made of the physical and chemical characteristics of $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, and mixtures of $\text{LiBH}_4/\text{MgH}_2$ and $\text{LiBH}_4/\text{CaH}_2$. Temperature programmed desorption, TPD, analyses showed that samples containing Mg generally had lower onset temperatures than the corresponding samples containing Ca. Pressure Composition Temperature, PCT, isotherms showed that these materials displayed well defined two phase plateau regions. Therefore, kinetics measurements were done to determine the hydrogen desorption rates in the two phase plateau region. All kinetics determinations were done using constant pressure thermodynamic forces in which the ratios of the plateau pressure to the applied hydrogen pressure were kept the same for all samples. In all these measurements the pressure ratio was set at 3 and the temperature was 450 °C. Under these conditions the reaction rates were in the order: $\text{Mg}(\text{BH}_4)_2 > \text{Ca}(\text{BH}_4)_2 > \text{LiBH}_4/\text{MgH}_2 > \text{LiBH}_4/\text{CaH}_2$. An attempt was also made to determine the rate-controlling process in these samples by doing kinetic modeling. The results showed that diffusion was the rate-controlling process in $\text{Mg}(\text{BH}_4)_2$ whereas reaction at the phase boundary controlled reaction rates in $\text{Ca}(\text{BH}_4)_2$. In $\text{LiBH}_4/\text{MgH}_2$ and $\text{LiBH}_4/\text{CaH}_2$, reaction at the phase boundary controlled reaction rates initially whereas diffusion controlled rates in the latter stages.

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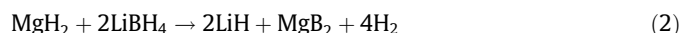
1. Introduction

Alkaline earth and alkali metal borohydrides are of interest for hydrogen storage because of their high gravimetric and volumetric hydrogen contents [1–9]. However, their potential application to solid state hydrogen storage for automobiles has been hindered by unfavorable thermodynamics and kinetics. Notable borohydrides that are being studied include LiBH_4 , $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$, which contain 18.4, 14.9 and 11.6 wt% hydrogen respectively [2,4,6]. LiBH_4 releases 13.9 wt% hydrogen according the equation:

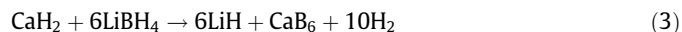


In order to improve the hydrogen storage properties of LiBH_4 , one common approach has been doping with catalysts/additives such as metal halides, amides and hydrides [8]. Reilly and Wiswall [10] first reported the destabilizing effects of additives on metal hydrides and since then this approach has become widely used in hydrogen storage. Theoretical studies using first principles have also been used to predict a number of borohydride systems that should have favorable thermodynamics [11–14]. Some of these

reactions have been experimentally studied and were found to have some interesting hydrogen storage properties. One such system is $\text{LiBH}_4/\text{MgH}_2$. This system with or without other dopant/catalyst additives has been studied extensively [15–20]. It releases hydrogen according to the equation:



Au et al. [21,22] has also investigated LiBH_4 modified with metal oxides and chlorides. LiBH_4 has also been destabilized with CaH_2 [23,24] in a reaction with theoretical hydrogen capacity of 11.7 wt% according the equation:



This system releases 9 wt% hydrogen reversibly when doped with TiCl_3 . Hydrogen gas is the only species identified by mass spectrometry. Yang et al. [25] showed that increasing the amount of TiCl_3 catalyst lowers the desorption temperature and the activation energy of the system. But this is offset by reduction in the amount of hydrogen released.

The $\text{Mg}(\text{BH}_4)_2$ system has also been extensively studied [26,27]. The complete dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ produces MgB_2 and hydrogen according to the following equation:

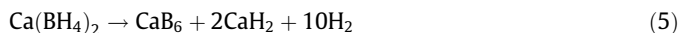


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Bardají et al. [26] studied the effect of several metal chlorides on the thermal decomposition of α - $\text{Mg}(\text{BH}_4)_2$. They showed that a mixture of titanium and niobium chloride lowered the decomposition temperature by up to 125 °C. Thermal decomposition of $\text{Mg}(\text{BH}_4)_2$ under helium and hydrogen flow was found to show the same final decomposition product of MgB_2 according to Hanada et al. [27].

The $\text{Ca}(\text{BH}_4)_2$ system has recently been studied extensively for hydrogen storage. It decomposes according to the following equation:



Ronnebro and Majzoub [6] prepared $\text{Ca}(\text{BH}_4)_2$ from ball-milled CaB_6 and CaH_2 under 700 bar hydrogen at 400–450 °C, suggesting that these species are the decomposition products. The decomposition of $\text{Ca}(\text{BH}_4)_2$ was reported to involve two steps [28,29]. Kim et al. [28] reported the formation of CaH_2 and an unknown intermediate in the first step, while CaH_2 was the only crystalline intermediate in the second step.

More recently it has been found that mixtures of borohydrides can release hydrogen at reduced temperatures [30–33]. A $\text{LiBH}_4/\text{Ca}(\text{BH}_4)_2$ composite system was found to desorb 10 wt% of hydrogen at temperature below 400 °C which is lower than decomposition temperature of either of the constituents [30]. A recent study by Ibikunle et al [31] similarly showed that a mixture of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ released hydrogen at a lower temperature than either constituent. Zhang et al. [32] used Density Functional Theory (DFT) to predict different decomposition pathways of $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$. Fang et al. [33] reported that a dual-cation borohydride is formed when a 1:1 mixture of LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ is mechanically milled and heated. The dual-cation was reported to have lower onset dehydrogenation temperature than its constituents. Much has been reported about the thermodynamics of borohydride mixtures but there have been very few studies on their kinetics.

In this study, the thermodynamics and kinetics properties of LiBH_4 destabilized with CaH_2 and MgH_2 as well as Ca and Mg based borohydride are being presented. Modeling studies to determine the processes controlling their dehydrogenation have also been attempted. The overall goal is to compare and contrast the hydrogen storage properties of these systems under the same conditions.

2. Experimental

LiBH_4 ($\geq 90\%$), MgH_2 , $\text{Ca}(\text{BH}_4)_2$ and CaH_2 (99.9% trace metal base) were obtained from Sigma–Aldrich and were used without further treatment. $\text{Mg}(\text{BH}_4)_2$ was prepared using the method described by Chłopek et al. [34]. All samples were handled in an argon-filled Vacuum Atmospheres glove box. Sample milling was done for 10 h in a SPEX 8000D mixer/mill. In order to determine the plateau pressures of the systems, PCT isotherms were determined using an Advanced Materials Corporation Gas Reaction Controller-PCI unit. Temperature programed desorption analyses (TPD) of the systems were also done on the PCI unit by heating the samples at

the rate 4 °C/min. Differential Thermal Analysis (DTA) was done using a Lab System–Diamond TG/DTA. The DTA scans were done at different heating rates and the results were used to determine the activation energies of the systems under study.

Kinetics measurements were done with an in-house designed stainless steel Sieverts apparatus. The apparatus used to perform the kinetics measurements is described in Fig. 1. It consists of a stainless steel manifold with ports for adding hydrogen, venting and evacuating. High and low pressure transducers are used to monitor the pressure in various parts of the apparatus. In desorption kinetics, the pressure in the sample reactor is initially adjusted to a value just slightly above the dissociation pressure (often called the plateau pressure) of the hydride, in order to assure that we are starting with the fully hydrided material. Then the reactor is sealed. A regulator is used to adjust the applied pressure to a fraction of the dissociation pressure. When the sample reactor valve is re-opened, hydrogen flows through the regulator and into an evacuated reservoir. The regulator serves to keep the applied pressure constant during the measurement. The ratio of the dissociation pressure, P_m , to the applied pressure, P_{appl} , is defined as the *N*-Value in these experiments. Further details about the procedures used for the kinetics measurements can be found elsewhere [35–38].

3. Results and discussion

TPD curves were constructed for all the samples in order to determine the temperatures at which hydrogen is released. Fig. 2 shows the TPD curves for the systems under study. The results show that $\text{Mg}(\text{BH}_4)_2$ has a lower onset temperature than $\text{Ca}(\text{BH}_4)_2$. $\text{MgH}_2/\text{LiBH}_4$ has a lower onset temperature than $\text{CaH}_2/\text{LiBH}_4$. The onset temperature is the temperature at which hydrogen begins to desorb. Onset temperatures for all the samples are listed in Table 1 along with other experimental data.

Kinetics and modeling studies were also done. Prior to these measurements PCT isotherms were constructed to determine if a plateau region existed. The plateau region would correspond to the dissociation pressure of the hydride. Using these isotherms, it was possible to measure the kinetics of hydrogen desorption in the two-phase region at constant pressure thermodynamic driving force. The PCT isotherm for the $\text{Mg}(\text{BH}_4)_2$ sample at 450 °C is shown in Fig. 3 and the isotherm for $\text{Ca}(\text{BH}_4)_2$ is shown in Fig. 4. The isotherms for the $\text{LiBH}_4/\text{CaH}_2$ and $\text{LiBH}_4/\text{MgH}_2$ mixtures are reported elsewhere and are not reported here [23,40].

Using the PCT isotherm in Fig. 3 for the $\text{Mg}(\text{BH}_4)_2$ sample at 450 °C, it is possible to illustrate how the kinetics measurements were done. Kinetics measurements were done in the two-phase plateau region of the isotherm between points “a” and “b”. A hydrogen pressure was applied (shown as point “c” on the isotherm) that was a fraction of the plateau pressure. When moving along the isotherm between points “a” and “b”, the pressure remained constant. As was stated earlier, the ratio of the plateau pressure, P_m , to the applied pressure, P_{appl} , has been defined as the *N*-Value. In these experiments, all kinetics measurements were done at 450 °C and at an *N*-Value of three. Since ΔG is a measure of the thermodynamic driving force and since it is proportional to

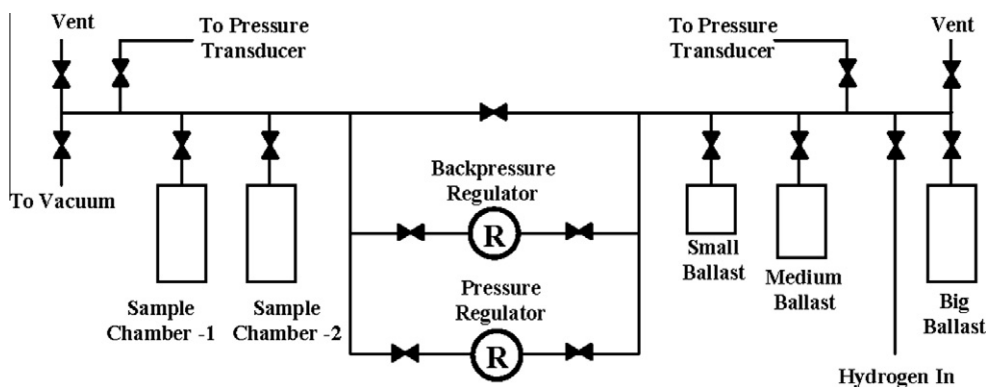


Fig. 1. Schematic diagram of the apparatus used to perform kinetics experiments.

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