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Thermodynamics, kinetics and modeling studies of KH- RbH- and CsH-doped $2LiNH_2/MgH_2$ hydrogen storage systems

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ABSTRACT

In this study, the effects of several alkali metal hydride dopants on the thermodynamics and kinetics of the $2LiNH_2/MgH_2$ system were determined. The results showed that the stabilities of the doped $2LiNH_2/MgH_2$ system are in the order: KH < RbH < CsH. Kinetics measurements showed that the absorption and desorption rates are in the order: RbH > KH > CsH, with absorption rates being about twice as fast as desorption from the corresponding materials. As expected, the activation energies for the reactions were in the order: RbH < KH < CsH with the activation energies for absorption being less than that for the corresponding desorption reaction. Modeling studies revealed that desorption reactions are controlled by diffusion during the entire process. However, for absorption reactions the rate-controlling process changed during the course of the reactions. The rate-controlling process in the first 70% of the absorption reactions was reaction at the phase boundary whereas diffusion controlled the rate in the latter stages.

Introduction

Lithium amide ($LiNH_2$) and its modifications are promising hydrogen storage materials for on-board vehicular applications because of their relatively high theoretical hydrogen storage capacities and low cost [1–5]. It has been found that the partial substitution of Li in $LiNH_2$ by Mg greatly improves its thermodynamic properties [6]. Equations (1) and (2) show the chemical reactions for the $2LiNH_2/MgH_2$ system that involve hydrogen absorption and desorption.

$$2LiNH_2 + MgH_2 \rightarrow Mg(NH_2)_2 + 2LiH \quad (1)$$

$$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2 \quad (2)$$

The first step in Equation (1) produces $Mg(NH_2)_2$ irreversibly. The $Mg(NH_2)_2$ is then involved in the reversible absorption and release of hydrogen in Equation (2). Scientists have found that hydrogen can be released from this system at an onset temperature of 130 °C, which is considerably lower than that for other complex hydrides such as borohydrides. However, this operating temperature and it's relatively slow kinetics are still not sufficient to meet DOE's goals for hydrogen storage. Therefore efforts have been made to develop dopants that would lower the operating temperature even further and

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improve kinetics. A number of dopants have been studied [7–10] but the most effective ones to date have been those based on alkali metal hydrides. P. Chen and colleagues [11] observed that potassium hydride had a great effect thermodynamically and kinetically when introduced into the $2LiNH_2/MgH_2$ hydrogen storage system. Scientists such as Luo et al. [12] and Durojaiye et al. [13] also studied the KH-doped lithium amide-magnesium hydride hydrogen storage system. They found that potassium hydride is a more effective dopant for the $2LiNH_2/MgH_2$ (2:1) complex than the $LiNH_2/MgH_2$ (1:1) system for desorption studies. Durojaiye et al. [14] also discovered that rubidium hydride was a very effective catalytic additive for the $2LiNH_2/MgH_2$ system. They found that the hydrogen desorption rate from the RbH-doped sample was approximately twice as fast as that from the KH-doped sample and about 60 times faster than that from the un-doped sample. They also found that the addition of 3 mol % RbH lowered the desorption temperature of the system by 94 °C. Hayes et al. [15] did kinetics and modeling studies on the RbH-doped $2LiNH_2/MgH_2$ system and found that diffusion was the rate-controlling process for absorption and release of hydrogen at 160 °C. Other researchers have studied the effects of Rb-related additives such as RbF [16] and dopants RbH–KH on the $2LiNH_2/MgH_2$ system [17]. In these studies, they also saw that RbH plays a significant role in lowering the reaction temperature and speeding up the process.

In a recent paper, Goudy and group members [18] reported that cesium hydride is an effective dopant for the lithium amide-magnesium hydride storage system. This was the first time that cesium hydride was reported to be an effective dopant for the $2LiNH_2/MgH_2$ system. It was found that CsH was very effective in lowering the desorption enthalpy and in improving the reaction rates.

In this study, the alkali metal dopants KH, RbH, and CsH were added to the $2LiNH_2/MgH_2$ system in order to compare their effectiveness in improving the thermodynamics and kinetics of hydriding and dehydriding from the $2LiNH_2/MgH_2$ system. Each doped system was studied at several temperatures in order to determine activation energies. Modeling studies were used to determine the rate-controlling process for hydrogen absorption and desorption.

Materials and methods

The materials used in this research were obtained from the Sigma Aldrich Corporation. The $LiNH_2$ was 95% pure whereas the MgH_2 powder was hydrogen storage grade containing less than 0.1% trace metal contaminants. The KH dopant was obtained commercially whereas the RbH and CsH dopants were prepared in the laboratory using a procedure that was described in a previous publication [18]. The concentration of dopants used in all the reactions was 3.3 mol%. Sample handling was performed in a Vacuum Atmospheres argon-filled glove box that was capable of achieving less than 1 ppm oxygen and moisture. The $LiNH_2/MgH_2$ doped mixtures were prepared by milling each sample mixture for up to 10 h in a SPEX 8000M Mixer/Mill. This mill had an argon-filled stainless steel pot containing four small stainless steel balls. A Perkin Elmer Diamond TG/DTA was used to determine the thermal stability of the mixtures. Pressure Composition Isotherm (PCI) and Temperature Programmed Desorption (TPD) analyses were done in a gas reaction controller unit to determine the hydrogen desorption properties of the mixtures. This fully automated apparatus was manufactured by the Advanced Materials Corporation in Pittsburgh, PA. The TPD analyses were done in the 30–450 °C range at a temperature ramp of 4 °C/min. Kinetics experiments were performed in an all stainless steel Sievert's apparatus. It contained ports for adding hydrogen, venting and evacuating and it also contained pressure regulators for controlling the hydrogen pressure applied to the sample. The kinetics was monitored by measuring the rate of pressure change in remote reservoirs as gas was absorbed or released from the sample. High purity hydrogen gas of 99.999% purity was used throughout the analyses. Further details about the procedures described here can be found elsewhere [18–20].

Results

Pressure-composition isotherms (PCIs) and van't Hoff plots

Figs 1 and 2 contain pressure-composition absorption and desorption isotherms for the KH-, RbH-, and CsH-doped systems at 180 °C. Isotherms were also determined in the 160–180 °C range for each system. Desorption isotherms have been reported for these systems [18] but this is the first time that absorption isotherms have been reported for the CsH-doped system. The plots in Figs. 1 and 2 show that the plateau pressures at 180 °C for the doped materials are in the order: KH > RbH > CsH. According to Equation (3), a plot of Ln P vs 1/T should be linear.

$$\ln P = -\Delta H/RT + C \quad (3)$$

P represents the mid-plateau pressure, ΔH is the enthalpy, R is the gas constant and T is the absolute temperature. The

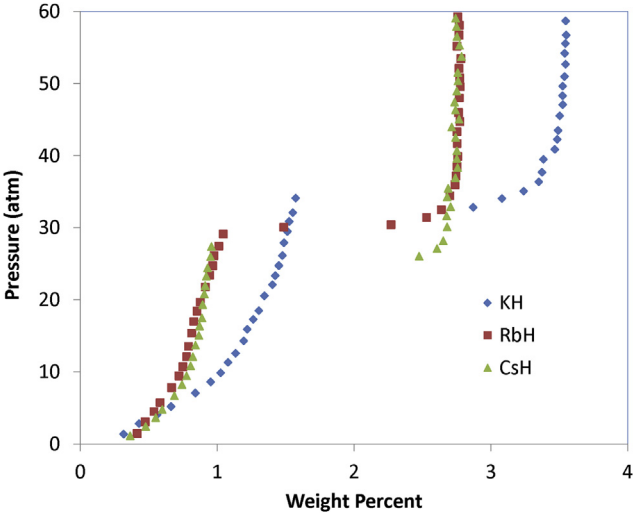

Fig. 1 – PCI absorption curves for $2LiNH_2/MgH_2$ mixtures at 180 °C.