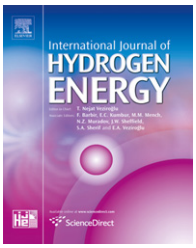
Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Thermochemical transformations in $2MNH_2$–$3MgH_2$ systems (M = Li or Na)

Oleksandr Dolotko [a], *Neil Paulson* [b], *Vitalij K. Pecharsky* [a,c,*]

[a] *The Ames Laboratory, U.S. Department of Energy Iowa State University, Ames, IA 50011-3020, USA*
[b] *Olin College, Needham, MA 02492, USA*
[c] *Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011-2300, USA*

ARTICLE INFO

Article history:
Received 7 December 2009
Received in revised form
18 February 2010
Accepted 20 February 2010
Available online 1 April 2010

Keywords:
Hydrides
Hydrogen release
Amides
X-ray diffraction
Temperature programmed dehydrogenation

ABSTRACT

Thermochemical reactions between alkali metal amides and magnesium hydride taken in 2:3 molar ratios have been investigated using pressure-composition-temperature, X-ray powder diffraction and residual gas analysis measurements. The thermally induced reactions in both title systems are stoichiometric and proceed as a following solid state transformation: $2MNH_2 + 3MgH_2 \rightarrow Mg_3N_2 + 2MH + 4H_2\uparrow$. A total of 6.45 wt.% of hydrogen is released by the $2LiNH_2$–$3MgH_2$ system beginning at 186 °C, and a total of 5.1 wt.% H_2 is released by the $2NaNH_2$–$3MgH_2$ system starting at 130 °C. Combined structure/property investigations revealed that the transformation in the lithium containing system proceeds in two steps. In the first step, lithium amide reacts with MgH_2 to form $Li_2Mg(NH)_2$ and hydrogen. In the second step, reaction between $Li_2Mg(NH)$ and MgH_2 leads to the formation of the Mg_3N_2 nitride, lithium hydride and additional gaseous hydrogen. The transformation in the sodium containing system appears to proceed through a series of competing solid state processes with formation of $Mg(NH_2)_2$ and $NaMgH_3$ intermediates. Partial rehydrogenation in 190 bar hydrogen pressure leading to formation of the MgNH imide was observed in the dehydrogenated $2NaNH_2$–$3MgH_2$ system at 395 °C.

1. Introduction

Hydrogen-storage materials hold a promise to support many new technologies, including clean and efficient hydrogen fuel cells for automobiles. Global research toward this goal includes understanding the basic mechanisms that underlie reversible hydrogen storage in several families of complex hydrides [1,2].

Currently, a main factor limiting the development of hydrogen-based energy technologies, such as fuel cells, is the absence of a material suitable to store a sufficient amount of hydrogen in a way that allows for easy and safe refueling. Among the most promising classes of materials are complex metal hydrides. These are light-weight complex hydrides, such as alanates $[AlH_4]^-$, amides $[NH_2]^-$, imides $[NH]^{2-}$, and borohydrides $[BH_4]^-$, all of which are quite attractive for hydrogen storage due to their ability to store and release large amounts of hydrogen. The total hydrogen contents are 10.5, 8.7 and 18.1 wt.% for $LiAlH_4$, $LiNH_2$ and $LiBH_4$, respectively.

Recently, metal–N–H systems have been under considerable attention as new families of hydrogen-storage materials since the Chen's report in 2002 that lithium nitride absorbed and desorbed a large amount of hydrogen [3]. This is a two-step reaction, which can be expressed as follows:

* *Corresponding author*. The Ames Laboratory, U.S. Department of Energy Iowa State University, Ames, IA 50011-3020, USA. Tel.: +1 515 294 8220; fax: +1 515 294 9579.
E-mail address: vitkp@ameslab.gov (V.K. Pecharsky).
0360-3199/$ – see front matter © 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2010.02.104

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \quad (R1)$$

However, the kinetic and thermodynamic properties of the Li–N–H system require further improvement for practical applications. The strongly endothermic nature of the reactions mentioned above requires high operation temperatures. To lower the temperature, the thermodynamic properties of the reaction must be altered. Nakamori et al. [4,5] noted that the dehydrogenation reaction of $LiNH_2$ can be promoted by substituting Li with Mg, which is the element with larger electronegativity. This proved to be the case, and the $2LiNH_2$–MgH_2 system was found to be reversible over nine cycles at 200 °C and 32 bar H_2 with gravimetric capacity of 4.5 wt.%. The proposed reaction R2, where $Li_2Mg(NH)_2$ and hydrogen form, has a reduced reaction enthalpy compared with the equivalent $LiNH_2$/LiH reaction.

$$2LiNH_2 + MgH_2 \leftrightarrow Li_2Mg(NH)_2 + 2H_2\uparrow \quad (R2)$$

The existence of the ternary lithium magnesium imide as the dehydrogenation product was corroborated in other experiments without further characterization [6,7]. Ensuing studies of the Li–Mg–N–H system [8–10] showed that initial dehydrogenation reaction between $LiNH_2$ and MgH_2 taken in a 2:1 molar ratio leads to the formation of the same $Li_2Mg(NH)_2$ ternary imide, which can be further rehydrogenated to $Mg(NH_2)_2$/LiH mixture. Therefore, the reversible process is actually between $[Li_2Mg(NH)_2 + 2H_2]$ and $[Mg(NH_2)_2 + 2LiH]$, as described in equation R3:

$$2LiNH_2 + MgH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2\uparrow \leftrightarrow Mg(NH_2)_2 + 2LiH \quad (R3)$$

As reported later by Xiong et al. [11], the $2LiNH_2$–MgH_2 system does not release much hydrogen during ball milling, but 5.3 wt.% of hydrogen may be desorbed during heating of the sample from 100 to 170 °C.

Another major study focused on an entirely different starting ratio of $Mg(NH_2)_2$ to LiH, i.e. 3:8 molar and in so doing mapped out a new reaction pathway that significantly increases the limit of stored hydrogen in the Li–Mg–N–H system [12,13]. The reaction R4 yields a reversible capacity of 7 wt.% hydrogen, where H_2 begins to desorb at 140 °C, and the desorption peaks at 190 °C. The reverse hydrogenation can be achieved at 200 °C under 30 bar hydrogen pressure.

$$8LiH + 3Mg(NH_2)_2 \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2 \quad (R4)$$

Continuing studies in the Li–Mg–N–H system followed two main pathways. One is investigating the effect of the ratio between the amide and the hydride, the other focusing on developing an understanding of the kinetics and mechanisms of these reactions. Following their earlier Mg doping studies [5,14,15], Orimo and co-workers considered higher ratios of Li_3N:Mg_3N_2 as a binary system for hydrogenation [16,17]. After extensive X-ray investigations of different nitride mixture ratios prepared under different temperature regimes, the reversible reaction R5 was found to yield both a maximum gravimetric capacity (9.1 wt.%) and a minimum dehydrogenation temperature.

$$4Li_3N + Mg_3N_2 + 12H_2 \leftrightarrow 12LiH + 3Mg(NH_2)_2 \quad (R5)$$

The dehydrogenation temperature could be lowered by ball milling with 1 mol% Ti, although the maximum in the evolved hydrogen occurs at 270 °C and gas continues to be desorbed above 430 °C. Hydrogenation of the mixture of Li_3N and Mg_3N_2 after heat treatment at 560 °C can be carried out at 250 °C in 350 bar H_2 pressure.

Here we focus on hydrogen desorption properties of $2MNH_2$–$3MgH_2$ systems (where M = Li and Na). Our previous report [18] showed that destabilization of alkali metal aluminohydrides by amides leads to the formation of aluminum nitride, alkali metal hydrides and gaseous hydrogen (R6):

$$MNH_2 + MAlH_4 \rightarrow AlN + 2MH + 2H_2\uparrow \quad (R6)$$

Based on these studies, we have successfully designed and developed MNH_2–MgH_2 systems (where M = Li or Na) in a previously unexplored 2:3 molar ratio of components. Existence of the magnesium nitride Mg_3N_2 prompted us to investigate mixtures of alkali metal amides and magnesium hydride in molar ratios from which the corresponding compound may be produced. Thermochemical solid state transformations in these systems were studied by using the pressure-composition-temperature (PCT), X-ray powder diffraction (XRD), and residual gas analysis (RGA) measurements.

2. Materials and methods

The starting materials $LiNH_2$ (95 wt.% purity) and $NaNH_2$ (>90 wt.% purity) were purchased from Sigma–Aldrich; MgH_2 powder with 98 wt.% purity was purchased from Alfa-Aesar. Due to air sensitivity of the starting materials and the products, all manipulations have been carried out under a continuously purified and monitored argon atmosphere in a glove box.

The alkali metal amide was mixed with magnesium hydride in a 2:3 molar ratio (~1 g of mixture total) using ball milling in a 50 ml hardened-steel vial for 15 min in an 8000 M SPEX mill. The 20 g of steel balls (2 large balls weighing 8 g each and 4 small balls weighing 1 g each) were used for ball milling. To check whether the components react during the mechanochemical treatment, X-ray powder diffraction analysis was used. No reaction between starting materials during the ball milling for 15 min was observed. Powdered and well mixed samples were pressed into 6 mm diameter pellets weighing approximately 0.2 g.

For the preparation of the $NaMgH_3$ compound the mixture of the NaH and MgH_2 (~1 g) taken in a 1:1 molar ratio was ball milled for 3 h.

The kinetics of hydrogen desorption was measured using the PCTPro-2000 system – a fully automated Sieverts instrument, which enables experiments in the temperature region from 25 to 400 °C and up to 200 bar of hydrogen pressure. While still in the glove box, a pellet of starting mixture was placed in a PCTPro-2000 autoclave. Closed autoclave was then connected to the PCT instrument and evacuated. Volume calibration using high purity helium gas was performed at room temperature before every kinetic measurements.

Quantitative analysis of the released gas was carried out using the RGAPro-2500 residual gas analyzer, connected to the