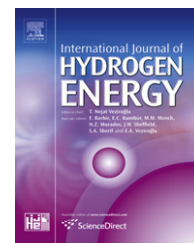


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## Dehydrogenation reactions of $2\text{NaBH}_4 + \text{MgH}_2$ system

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### ARTICLE INFO

#### Article history:

Received 20 May 2010

Received in revised form

5 November 2010

Accepted 10 January 2011

Available online 23 February 2011

#### Keywords:

Hydrogen storage

Sodium borohydride

Magnesium hydride

Thermal programmed desorption

X-ray diffraction

Infrared spectroscopy

### ABSTRACT

Reactive Hydride Composites (RHCs), ball-milled composites of two or more different hydrides, are suggested as an alternative for solid state hydrogen storage. In this work, dehydrogenation of  $2\text{NaBH}_4 + \text{MgH}_2$  system under vacuum was investigated using complementary characterization techniques. At first, thermal programmed desorption of as-milled composite and single compounds was used to identify the temperature range of hydrogen release. RHC samples annealed at various temperatures up to 500 °C were characterized by X-ray diffraction, infrared spectroscopy and scanning electron microscopy. It was found that the dehydrogenation reaction under vacuum is likely to proceed as follows:  $2\text{NaBH}_4 + \text{MgH}_2 (>250\text{ °C}) \rightarrow 2\text{NaBH}_4 + 1/2\text{MgH}_2 + 1/2\text{Mg} + 1/2\text{H}_2 (>350\text{ °C}) \leftrightarrow 3/2\text{NaBH}_4 + 1/4\text{MgB}_2 + 1/2\text{NaH} + 3/4\text{Mg} + 7/4\text{H}_2 (>450\text{ °C}) \rightarrow 2\text{Na} + \text{B} + 1/2\text{Mg} + 1/2\text{MgB}_2 + 5\text{H}_2$ . In addition, presence of  $\text{NaMgH}_3$  phase suggests the occurrence of secondary reactions.

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## 1. Introduction

A prospective of using technologies such as fuel cells for the replacement of internal combustion engines in the generation of environmentally friendly energy has highly promoted the development of novel hydrogen storage systems. Hydrogen is the ideal energy carrier due to its highest heating value ( $141.8 \cdot 10^3 \text{ kJ kg}^{-1}$ ), non-polluting combustion product ( $\text{H}_2\text{O}$ ), and its abundance [1]. However, its very low boiling point in the liquid state ( $-267\text{ °C}$ ) and its low density in the gaseous state ( $0.126 \text{ kg m}^{-3}$ ) proved to be just temporary solutions because of the low energy efficiency in case of liquid storage and safety reasons in case of gaseous storage, respectively. For commercial applications, an ideal hydrogen storage system should meet certain criteria: high storage capacity

(>5–10 wt%), good kinetics ( $<1 \text{ wt.}\% \text{ min}^{-1}$ ), reasonable thermodynamics ( $\Delta H \sim 40 \text{ kJ/mol H}_2$ ) high thermal conductivity (dissipating sorption heat), low cost ( $<2 \text{ €/kW h}$ ), reversibility (>500 cycles), and chemical stability (against oxygen, air, moisture).

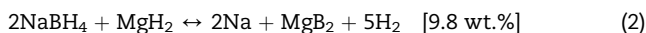
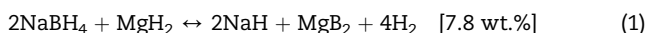
Different types of materials have been investigated, and the International Energy Agency (IEA) points a promising scenario for storage of hydrogen in solid state, even though it still needs further development [2]. Single hydrides are well known and have been already revised [3]. Complex hydrides such as alاناتes [4] and borohydrides [5] were later introduced as hydrogen storage materials. Another pioneer work in the hydrogen storage field was the use of a mixture of single and complex hydrides with amides based systems [6]. Later this approach has been extended to borohydrides systems [7],

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which were known as Reactive Hydride Composites (RHCs) [8]. Currently, one family of important materials for solid hydrogen storage being studied is Reactive Hydride Composites (AH + BXH), which are made mixing a metal AH (e.g. Mg) and a complex hydride BXH (e.g. B = Li, Na, and X = Al, N, B). The NaBH<sub>4</sub>–MgH<sub>2</sub> composite is considered a prospective material system due to its low cost, good chemical stability, high hydrogen capacity, and potential recyclability [9]. However, up to now there is limited investigation on sorption reactions [10–12] of this RHC system by experimental means.

As in the case of pure NaBH<sub>4</sub> [13], the main dehydrogenation reaction can proceed in two distinct manners:



Even though thermodynamics of this RHC for reaction (1) ( $\Delta H = -70 \text{ kJ/mol H}_2$ ) indicates an equilibrium temperature of 375 °C under 1 atm of hydrogen pressure, very recent experimental results have demonstrated distinct and controversial results [11]. The present work intends to contribute to the clarification of the sorption properties, more precisely, indicating the most probable dehydrogenation pathway for the system. Diverse experimental techniques have been used and the existence of intermediate phases will also be outlined.

## 2. Experimental

### 2.1. Materials

RHC samples were prepared by ball milling using a planetary ball mill P5, inside an argon glovebox, with a sample-per-ball ratio of 1:10, rotation speed of 300 rpm, for 20 h. Starting materials NaBH<sub>4</sub> (98 wt.%) from Alfa-Aesar and MgH<sub>2</sub> (95 wt.%) from Goldschmidt were utilized without any additional purification.

### 2.2. Heat treatment

Thermal Programmed Desorption (TPD) was acquired using a Quadropole Mass Spectroscopy coupled to a furnace (Catlab Hiden Analysis). In order to run the TPD analysis, each sample was prepared by making a pellet of the powder and then crushing it. TPD runs were performed in a continuous mode up to 600 °C at a heating rate of 5 °C/min, with a helium flow of 50 mL/min. Hydrogen release was quantified using MgH<sub>2</sub> as calibration standard, assuming a single decomposition reaction  $\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$  (7.6 wt.%). The RHC samples were heat treated at different temperatures, in the range of temperature identified by TPD, in a laboratory glass vacuum line. Small quantities of the RHC were placed inside several quartz tubes and fitted with a Young's tap. This system was used to avoid air exposition of the samples during transport to the vacuum line, as all sample preparation was protectively conducted inside an argon glovebox. Each RHC sample was evacuated to 10<sup>-4</sup> mbar and heat treated up to a maximum temperature

of 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C at a heating rate of about 10 °C/min and kept for 1 h for temperature homogenization.

### 2.3. Characterization techniques

Ex-situ characterization of heat treated RHC samples was performed with different techniques. Powder X-Ray Diffraction (XRD) measurements were performed using a Cu radiation X'Pert (Panalytical Instruments) with a capillary spin stage. XRD patterns were taken at 0.017° step size and 60 s step time. Samples were individually placed inside 0.5 mm glass capillaries, and spin mode was used during measurements to avoid preferential orientation of the crystallites. Infrared (IR) measurements were performed using an Attenuated Total Reflection (ATR) cell instrument (Nicolet 6700) with a ZnSe crystal. IR spectra were obtained in 4 cm<sup>-1</sup> resolution and 252 scans. Samples were prepared inside an argon glovebox and a protective system (PE bag) was used to prevent exposition of the samples to air during measurements. Micrographs were taken by Scanning Electron Microscopy (SEM) using a Stereo Scan (LEICA 410) in Secondary Electrons (SE) mode, with a mean working distance of 10 mm and EHT of 15 kV. Mapping of the heavier elements (Na, Mg) was obtained with a coupled Electron Dispersion X-ray (EDX) detector.

## 3. Results and discussion

### 3.1. Thermal programmed desorption

A first TPD in continuous mode was used as guideline, in order to identify the main temperature region for hydrogen release from the 2NaBH<sub>4</sub> + MgH<sub>2</sub> system. In addition, TPD of the single compounds (NaBH<sub>4</sub>, MgH<sub>2</sub>) was also performed and used for comparison. Respective TPD curves are shown in Fig. 1. Pure MgH<sub>2</sub> releases hydrogen at about 370 °C, whereas pure NaBH<sub>4</sub> shows a main dehydrogenation reaction at about 500 °C. The TPD profile of RHC sample presents a broad peak, starting at

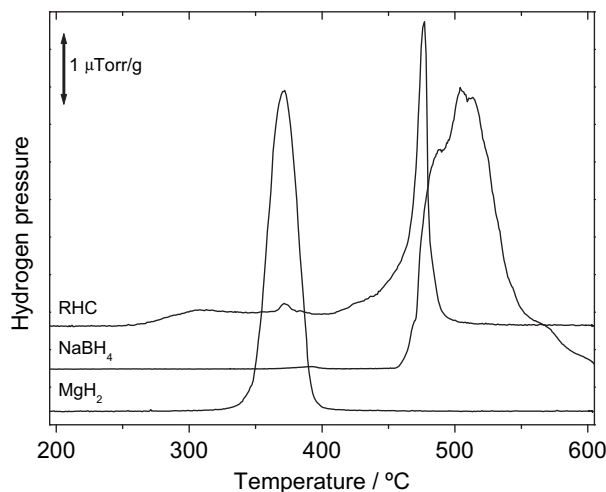


Fig. 1 – TPD of RHC sample (2NaBH<sub>4</sub> + MgH<sub>2</sub>) and single compounds (NaBH<sub>4</sub>, MgH<sub>2</sub>).

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