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# Improved hydrogen release from magnesium borohydride by ZrCl<sub>4</sub> additive



HYDROGEN



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#### ABSTRACT

Thermal dehydrogenation of  $Mg(BH_4)_2$  was investigated with  $ZrCl_4$  as a catalyst in vacuum and argon gas flow conditions. The results have been compared with the thermal dehydrogenation of pure- $Mg(BH_4)_2$  under similar experimental conditions. Two endothermic peaks were observed for pure  $Mg(BH_4)_2$  before the actual dehydrogenation reaction whereas; in the case of catalyzed  $Mg(BH_4)_2$ , an exothermic followed by endothermic peaks appeared. Marginal hydrogen was evolved during these low-temperature events. The actual dehydrogenations of pure- $Mg(BH_4)_2$  were started at 235 °C and ended at 450 °C with three clear dehydrogenation steps. However; in the case of catalyzed  $Mg(BH_4)_2$  dehydrogenation started very early (onset 197 °C) and completed before 400 °C with merely two visible dehydrogenation steps. The lower dehydrogenation temperature of catalyzed  $Mg(BH_4)_2$  was attributed to the reduced apparent activation energy as compared to the pure  $Mg(BH_4)_2$ .

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#### Introduction

Hydrogen storage and delivery technology based on the solid material has been considered as one of the best options to realize the hydrogen-based energy system [1-3]. In this regards, bcc alloys were sufficiently explored, however, failed to reach the desired sets goal of DOE as per the hydrogen storage capacity is a concern [4-7]. The complex hydrides

such as alanates, borohydrides, and amides have attracted the attention of scientists and engineers all over the world as per the hydrogen storage capacity are concern [8,9]. However; the thermodynamics and hydrogenation-dehydrogenation kinetics need to be fine-tuned to lower the working temperature for onboard applications [10]. Among others; magnesium borohydride (Mg(BH<sub>4</sub>)<sub>2</sub>), has a great potential to be developed for solid hydrogen storage application [11–15]. The reason

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being: low materials cost, high hydrogen gravimetric (14.8) & volumetric (112 g/L) density, and favorable enthalpy of dehydrogenation which is estimated empirically as 40 kJ/mol of hydrogen. The thermal decomposition of pure Mg(BH<sub>4</sub>)<sub>2</sub> was studied earlier by many researchers by simultaneous TGA–DTA and TGA–DSC in combination with in situ XRD [12,16–24]. The Mg(BH<sub>4</sub>)<sub>2</sub> desorbs hydrogen via multiple steps intermediated with complex magnesium borohydride formation as per the reaction (1) given below:

$$\begin{array}{l} Mg(BH_{4})_{2} \leftrightarrow 1/6MgB_{12}H_{12} + 5/6MgH_{2} + 13/6H_{2} \leftrightarrow \\ MgH_{2} + 2B + 3H_{2} \leftrightarrow Mg + 2B + 4H_{2} \end{array}$$

Although; the reports on thermal dehydrogenation of  $Mg(BH_4)_2$  are a bit contradictory, all the researchers had agreed on the formation of  $MgH_2$  as one of the intermediate. Depending upon the dehydrogenation condition, the *in situ* formed  $MgH_2$  further dehydrogenated into Mg, or  $MgB_2$  [22–24]. The dehydrogenation of *in situ* formed  $MgH_2$  is an essential step affecting the overall hydrogen storage capacity of  $Mg(BH_4)_2$  [25–27].

Recently, it has been demonstrated that ZrCl<sub>4</sub> is one of the best catalysts for the thermal dehydrogenation of MgH<sub>2</sub> [28,29]. Among other catalytic properties of ZrCl<sub>4</sub>, it has proven as an excellent grain refiner which is attributed to its sublimation characteristics at relatively low temperature. The present investigation deals with the catalytic effect of ZrCl<sub>4</sub> on thermal dehydrogenation of Mg(BH<sub>4</sub>)<sub>2</sub>. It was found that merely two hours ball milling of Mg(BH<sub>4</sub>)<sub>2</sub> with one mole % ZrCl<sub>4</sub> substantially decreases the dehydrogenation temperature as compared to pure Mg(BH<sub>4</sub>)<sub>2</sub> under similar experimental conditions. The improved kinetics of thermal dehydrogenation of catalyzed Mg(BH<sub>4</sub>)<sub>2</sub> has been explained on the basis of a surface modification of Mg(BH<sub>4</sub>)<sub>2</sub> and grain refinement during ball milling. In the whole manuscript, p-Mg(BH<sub>4</sub>)<sub>2</sub> and c-Mg(BH<sub>4</sub>)<sub>2</sub> are used for 2 h ball milled pristine Mg(BH<sub>4</sub>)<sub>2</sub> and 2 h ball milled Mg(BH<sub>4</sub>)<sub>2</sub> with mole % ZrCl<sub>4</sub> catalyst respectively.

#### Experimental

The Mg(BH<sub>4</sub>)<sub>2</sub> powder of purity 99.00 mass % and zirconium tetrachloride (ZrCl<sub>4</sub>) of purity 99.99 mass % obtained from Sigma–Aldrich, were used to prepare the samples. One gram of as received Mg(BH<sub>4</sub>)<sub>2</sub> was ball milled without, and with 1 mol% ZrCl<sub>4</sub> to prepare p-Mg(BH<sub>4</sub>)<sub>2</sub>, and c-Mg(BH<sub>4</sub>)<sub>2</sub> respectively. The samples were ball milled in a hardened stainless steel pot containing 20 pieces of hardened stainless steel balls of diameter 7 mm. The ball milling was carried out under an argon atmosphere at the milling frequency of 400 revolutions per minute for two hours. All the experiments and sample handling were conducted under inert atmosphere (argon gas filled glove box).

The dehydrogenation experiments were carried out in a thermoanalyser (TG-DTA; TG-8120, Rigaku) unit attached with a mass spectrometer (MS; M-QA200TS, Anelva). The system was kept inside the inert atmosphere (argon gas) glove box. The argon gas flow rate during TG analysis of all the dehydrogenation process was kept at the rate of 18 L/h to maintain the zero hydrogens back pressure. The phase analysis was carried out by powder-X-Ray diffractometer (p-XRD; RINT-2100, Rigaku, CuK<sub> $\alpha$ </sub> radiation). The powder morphology and the elemental mapping were done using scanning electron microscope (SEM; JSM-6380A, JEOL) coupled with energy dispersive spectroscopy (EDS). It has been ensured that the sample should not be exposed to an open atmosphere before and during the operations.

The apparent activation energy of dehydrogenation was evaluated by a non-isothermal process using  $H_2 - MS$  (*m/z: 2*) peak temperatures of thermal desorption mass spectroscopy conducted in the TG-DTA-MS unit. In some cases, the apparent activation energy was evaluated by the peak temperatures of differential calorimetric analysis measured in a high pressure differential calorimetric unit (HP-DSC; Q10PDSC, TA Instruments) placed inside the argon gas filled glove box. The Kissinger method was employed to calculate the kinetic parameters in the form of Equation (1) as given below:

$$\ln\frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + \ln\frac{RK_o}{E_a}$$
(1)

Where,  $T_p$  is the inset peak temperature of the events,  $\beta$  is the heating rate,  $E_a$  is the apparent activation energy,  $K_o$  is the collision frequency, and R is the universal gas constant. The chemical states of the catalyst (ZrCl<sub>4</sub>) in the ball milled c-Mg(BH<sub>4</sub>)<sub>2</sub> was determined by X-ray photoemission spectroscopy (XPS; ESCALAB 250Xi, Thermo-Fisher Scientific, Al-K<sub> $\alpha$ </sub> = 1486.6 eV) by measuring the peak positions of binding energy corresponded to Zr3d electrons.

#### **Results and discussion**

#### Sample characterization

The as received Magnesium Borohydride (Mg(BH<sub>4</sub>)<sub>2</sub>) was semicrystalline powder as analyzed by XRD and the result is presented in Fig. 1. The Mg(BH<sub>4</sub>)<sub>2</sub> powder was annealed at 100 °C up to 12 h under a dynamic vacuum condition to remove the surface adsorbed volatile solvent. The annealed sample have shown improved crystallinity as analyzed by the XRD and presented in Fig. 1. The annealed Mg(BH<sub>4</sub>)<sub>2</sub> was used for the preparation of p-Mg(BH<sub>4</sub>)<sub>2</sub> and c-Mg(BH<sub>4</sub>)<sub>2</sub>. The ball milled samples were found to be converted into amorphous powder, and it could not be analyzed by XRD. The ball milled samples were analyzed by FTIR, and the results are presented in Fig. 2. In both the samples, the stretching mode peaks were at  $2284 \text{ cm}^{-1}$ . The peaks at 1265 cm<sup>-1</sup>, 1129 cm<sup>-1</sup> would be corresponding bending mode. The FTIR peaks were identical for both the samples, except a minor peak at 2665 cm<sup>-1</sup> for p- $Mg(BH_4)_2$ . This peaks could be due to the presence of an impurity which became inactive in the case of  $c-Mg(BH_4)_2$ .

#### Thermal analysis

The TG-DTA-MS analysis of the sample  $p-Mg(BH_4)_2$  in an argon flow (flow rate: 18 liters/hours) at a heating rate of 5 °C/ min shown in Fig. 3a. The sample starts dehydrogenation

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