

Graphene decorated metal nanoclusters as an effective novel catalyst for improving the hydrogen storage behaviour of MgH₂

M. Sterlin Leo Hudson*, A. Ramesh* and Keisuke Takahashi**

* Department of Physics, Central University of Tamil Nadu, Thiruvavur – 610101, India.

** Graduate School of Engineering, Hokkaido University, Sapporo 060-8278, Japan

ABSTRACT

High volumetric and gravimetric hydrogen density in MgH₂ motivates significant research attention over the recent years to make it as a viable hydrogen storage material for fuel cell applications. However, the high thermodynamic stability of MgH₂ ($\Delta H_f = 74.06 \pm 0.42$ kJmol⁻¹H₂) is a major bottleneck for its practical applications. Several metal and non-metal catalysts are being investigated for improving the hydrogen sorption kinetics and recyclability of MgH₂ for hydrogen storage applications. Here, we propose graphene decorated with Fe clusters (G-Fe) to be an effective alternative catalyst for dehydrogenation and re-hydrogenation reaction of MgH₂. Dehydrogenation kinetics of MgH₂ with 5 wt.% G-Fe is increased significantly and the formation enthalpy, ΔH_f is lowered to 50.4 ± 2.9 kJmol⁻¹H₂. Additionally, re-hydrogenation of MgH₂ with 5 wt.% G-Fe takes only 4 minutes to absorb 5 wt% of hydrogen at 300 °C and 25 atm. Hence, graphene decorated with Fe clusters is effective for both the hydrogenation and dehydrogenation processes. TEM micrograph shows that graphene decorated Fe cluster behaves like a shell while MgH₂ is its core, resulting in the reduction of crystallite growth during cycling. After six re-hydrogenation cycles, the crystallite size of MgH₂ increased only by 15 nm, showing a reduction in crystallite growth when compared to other metal and non-metal catalysts. Density functional theory shows that defects of graphene act as the active sites for dehydrogenation of MgH₂ while Fe clusters reduce the adsorption of dissociated H atoms, resulting in low temperature dehydrogenation. Thus, graphene decorated with metal clusters could open up a new way of designing a new type of catalysts which could replace transition metal catalysts.

Keywords: hydrogen storage, metal decorated graphene, catalysts, re-hydrogenation, kinetics

1 INTRODUCTION

Functionalized graphene has quickly caught much attention due to its unexpected properties in the field of catalysis [1]. Graphene oxide is a successful modification of graphene where graphene oxide shows high catalytic activity during the oxidation process [2,3]. In the same way, metal nanocluster-decorated graphene happens to have unexpected catalytic effects towards various systems [4-6]. In particular, graphene decorated with iron clusters is experimentally and theoretically found to absorb hydrogen

[7,8]. During the hydrogenation process over graphene with iron clusters, calculations revealed that H₂ dissociation occurs over iron clusters, which is considered to cause spillover towards graphene [7]. Such phenomena can be a key reaction for the hydrogenation process as the H₂ dissociation is generally a first step reaction for hydrogenation reaction. In this work, MgH₂ is chosen to evaluate the catalytic effect of graphene with Fe nano clusters. Magnesium hydride is the prototype reversible hydrogen storage material which involve MgH₂ dissociation and hydrogenation of Mg with H₂. In order to increase the kinetics of the dehydrogenation and hydrogenation reactions of MgH₂ several catalysts such as rare earth metals, rare earth metal oxides and carbon nanostructures have been extensively investigated over the recent years [9,10]. However, seeking better catalysts for accelerating kinetics, hydrogenation, and dehydrogenation of MgH₂ are still problematic issues for further practical applications. Metal nanoclusters decorated graphene catalysts could be proposed to be potential catalysts for hydrogenation reaction for such systems. The catalytic effect of graphene decorated with iron nanoclusters is experimentally investigated.

In particular, MgH₂ discharging and charging are used as proto type reactions in order to evaluate the catalytic effect towards dehydrogenation and rehydrogenation. Hydrogen absorption and desorption of MgH₂ with graphene decorated with iron clusters are experimentally tested. Temperature programmed desorption, differential scanning calorimetry and isothermal kinetic studies were carried out to study the dehydrogenation and rehydrogenation behaviour of catalyzed MgH₂. X-ray diffraction and Transmission electron microscopy was used to observe the structure and microstructure of catalyzed MgH₂ during hydrogenation cycles.

2 EXPERIMENTAL

2.1 Sample Preparation

MgH₂ powder of purity 98% and Fe nanopowder (APS 10-30 nm) of purity 99.9% were purchased from Alfa Aesar. Graphene decorated with Fe nanoclusters (G-Fe) were synthesized in an electric arcing chamber using graphite electrodes. To ablate the material, an electric arc was generated using a DC source of 100A and 25V between a pure graphite rod (cathode) placed opposite to a grounded anode rod made of graphite impregnated with Fe nanopowder in an arcing chamber filled with Ar (99.999% purity) partial pressure of ~300 torr. After 8-10 min of the

arcng process, the flake like carbon material was found deposited around the walls of the arcng chamber which was later confirmed as G-Fe. The MgH₂ powder was ball-milled together with 5 wt.% G-Fe under 5 atm hydrogen pressure in a custom fabricated stainless steel vial of volume 250 cm³ (capable of retaining up to 60 atm pressure) using a Retsch PM 400 planetary ball-miller at an operating speed of 150 rpm for a period of 60 minutes (6 ×10 minutes ball-milling with 15 minutes interval in-between). The ball to powder ratio was kept at 30:1, where the weight of the sample was around 2.5 grams. Ball-milling under hydrogen atmosphere prevents MgO formation. For comparative analysis, MgH₂ (without G-Fe) was ball-milled under identical experimental conditions for 5 hours (30×10 minutes ball-milling with 15 minutes interval in-between). Handling of the samples was done in mBraun MB10 compact Ar filled glove box (H₂O and O₂ levels < 1 ppm).

2.2 Dehydrogenation and Rehydrogenation Analysis

Dehydrogenation and reabsorption kinetics of the samples were analyzed through temperature programmed desorption (TPD) and isothermal absorption kinetics using an auto-mated Sieverts type apparatus supplied by Advanced Materials Corporation. TPD analysis of sample was done at the initial pressure of 10⁻³ torr under dynamic heating condition with an accuracy of ±0.2°C. Rehydrogenation kinetics were measured at different temperatures by charging the dehydrogenated MgH₂ samples with 20 atm hydrogen pressure. Thermal analyses of samples were conducted using a differential scanning calorimeter (DSC 8000, PerkinElmer). The samples were heated from room temperature to about 500°C with a set heating rate under flowing argon of 20ml/min.

2.3 Structural and Microstructural Characterization

Structural characterizations of the samples were investigated by X-ray diffraction using PANalytical X'Pert PRO diffractometer with a Cu K α beam ($\lambda = 1.5415 \text{ \AA}$) operated at 40 kV and 40 mA. The samples were loaded in airtight sample holders sealed by a fine layer of parafilm (Pechiney plastic packing) to prevent the sample from oxygen and moisture contamination. Microstructures of the samples were analyzed through bright field imaging and selected-area electron diffraction (SAED) using a FEI Tecnai 20G2 transmission electron microscope (TEM) operated at 200 keV.

3 RESULTS AND DISCUSSIONS

TPD of MgH₂ samples was performed from room temperature (25°C) to 450°C under dynamical heating condition at the heating rate 2°C/min. A comparative TPD

profiles of MgH₂ pristine, 5 hours ball-milled MgH₂ (uncatalyzed) and MgH₂+5wt.% G-Fe is shown in Fig. 1.

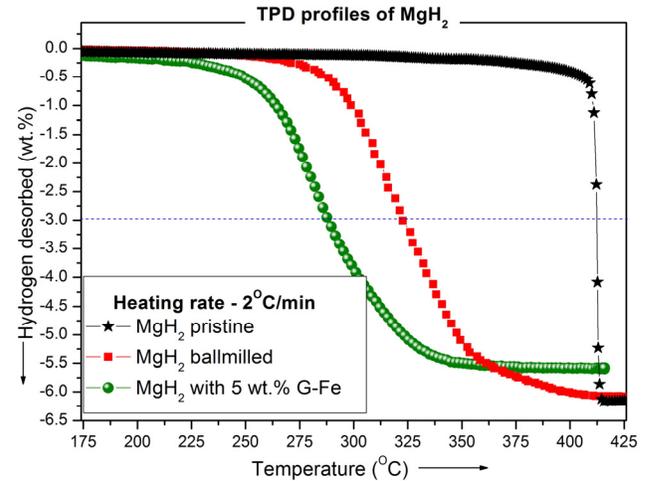


Figure. 1: Comparative temperature programmed hydrogen release profiles of MgH₂

It has been observed from Fig. 1 that the dehydrogenation temperature of MgH₂ with 5wt.% G-Fe is significantly lower than pristine and ball-milled MgH₂. The peak temperature (shown in blue dotted line) of MgH₂ catalyzed with 5wt.% G-Fe is 281.7°C, whereas that of 5 hours ball-milled MgH₂ shows peak temperature at 322.3°C. This suggest that graphene together with Fe nanoclusters exhibit superior catalytic effect in improving the dehydrogenation behaviour of MgH₂.

The apparent activation energy (*E_a*) of ball-milled MgH₂ and MgH₂ with 5 wt.% G-Fe was determined from DSC profiles using the Kissinger method [11]. Fig. 2 presents the DSC curves of MgH₂ with 5 wt.% G-Fe determined at different heating rates (2, 5, 10 and 15°C/min).

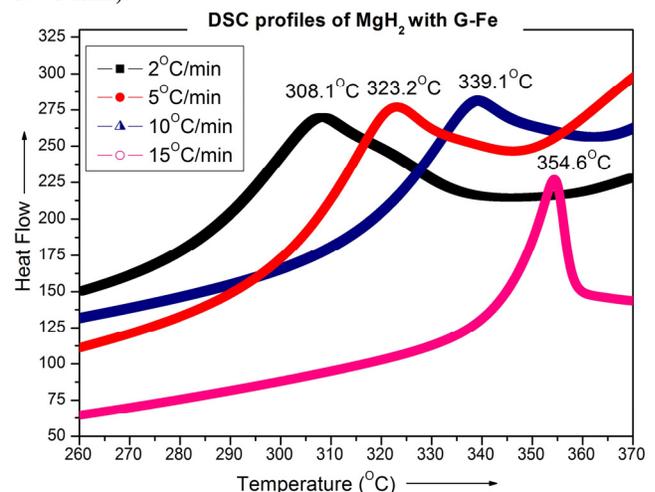


Figure. 2: DSC of MgH₂ with 5 wt.% G-Fe measured at different heating rates (2, 5, 10 and 15°C/min).

The peak desorption temperatures (*T_p*) determined from the DSC curves and the corresponding heating rates (β) are

the two parameters required for finding E_a using the Kissinger equation given below.

$$\ln(\beta/T_p^2) = (-E_a/T_p) + \ln(k_0) \quad (1)$$

Where, k_0 is a constant. A plot of $\ln(\beta/T_p^2)$ vs $1/T_p$ has a negative slope. Here, we have used 2, 5, 10 and 15°C/min DSC heating rates for calculating activation energy of the samples. Corresponding $\ln(\beta/T_p^2)$ vs $1/T_p$ plot of MgH₂ with 5wt.% G-Fe and MgH₂ without catalyst (ball-milled under identical conditions) are shown in Fig. 3.

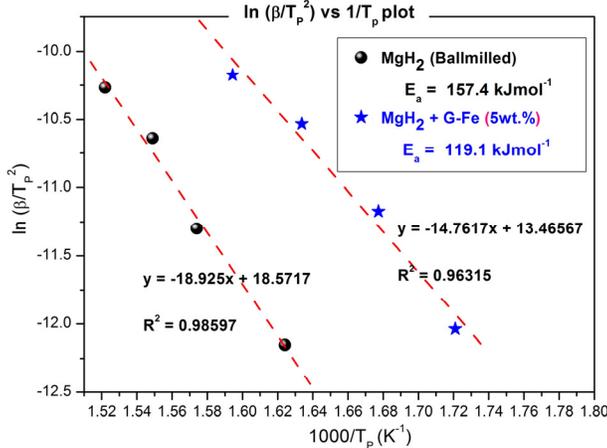


Figure. 3: $\ln(\beta/T_p^2)$ vs $1/T_p$ plot of MgH₂ with 5wt.% G-Fe and MgH₂ without catalyst (ball-milled under identical conditions).

The desorption activation energy of ball-milled MgH₂ (w/o additive) and MgH₂ catalyzed with 5 wt.% G-Fe determined from DSC profiles using Kissinger method are 157.4 and 119.1 kJmol⁻¹, respectively. Thus the addition of 5 wt.% G-Fe significantly lowers the desorption activation energy of MgH₂.

Fig. 4 presents the isothermal reabsorption kinetic curves of dehydrogenated MgH₂ with 5wt.% G-Fe determined at different temperatures with 20 atm hydrogen pressure.

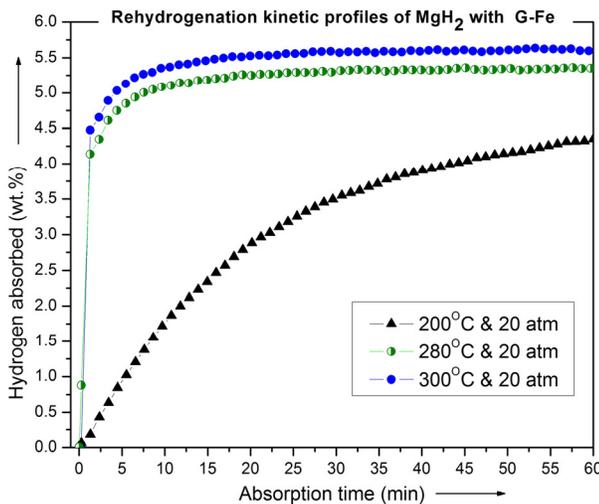


Figure. 4: Reabsorption kinetic curves of dehydrogenated MgH₂ catalyzed with 5 wt.% G-Fe

It has been observed that the dehydrogenated MgH₂ with G-Fe sample shows fast absorption kinetics. The sample absorbed more than 5 wt.% hydrogen in less than 4 minutes at 300°C and 20 atm. Whereas, that of un-catalyzed (ballmilled without additive) dehydrogenated MgH₂ sample took nearly 20 min to absorb 5 wt.% hydrogen at 300°C and 20 atm (not shown here). This reveals that the G-Fe exhibit superior catalytic effect on MgH₂ both for hydrogen release and uptake.

The change in formation enthalpy and entropy values for the formation of MgH₂ derived from Vant Hoff plot (not given here) are -50.4 ± 2.9 kJmol⁻¹ H₂ and 99.8 ± 5.2 JK⁻¹mol⁻¹ H₂, respectively. It should be mentioned that the change in formation enthalpy and entropy value for as-received bulk MgH₂ is -74.06 ± 0.42 kJmol⁻¹ H₂ and 133.4 ± 0.7 JK⁻¹mol⁻¹ H₂, respectively [12]. However, change in formation enthalpy and entropy of MgH₂ was reported for element coated Mg. For Fe coated Mg, the formation enthalpy and entropy of MgH₂ was -59.9 ± 1.9 kJmol⁻¹ H₂ and 112.3 ± 3.1 JK⁻¹mol⁻¹ H₂, respectively [13]. Recent publication shows that reduced enthalpy and entropy values of -45 ± 3 kJmol⁻¹ H₂ and 84 ± 5 JK⁻¹mol⁻¹ H₂, respectively were observed for MgH₂-Ti nanocomposites produced by spark discharge [10].

It is known that the thermodynamic properties of the Mg-to-MgH₂ hydrogenation reaction may change dramatically at the nanoscale due to its modified structure at the nano dimension and the dominant contribution of the surface (or interface) structure and local bond lengths at the smallest sizes [10]. In the present investigation, the observation of low reaction enthalpy and entropy values for the hydrogenation reaction of Mg is due to the nanosize and intermixed character of the disordered graphene and Fe nanoparticles. The presence of Fe nanoparticles and graphene is expected to have a synergetic effect in improving the dehydrogenation behavior and in enhancing the hydrogenation of Mg to MgH₂ through spillover effect [14,15].

Fig. 5 shows the X-ray diffractogram of MgH₂ with 5wt.% G-Fe during different stages of hydrogenation cycles. It was noticed that after sixth dehydrogenation and rehydrogenation cycles, the diffraction peak intensity increases, suggesting the grain growth of MgH₂. The crystallite size of MgH₂ was calculated from XRD peaks using the Scherrer equation [16]. The average grain size of as-prepared MgH₂ with G-Fe (Fig. 5(a)) is 19 nm and after sixth cycles (Fig. 5(c)), the crystallite size of MgH₂ increases to 34.8 nm. Liu et al. [17] observed that after six hydrogenation cycles, the grain size of pure-MgH₂ (w/o additives) was increased three times (from 10.8 nm to 32 nm after six cycles). Thus in the present work, the presence of graphene decreases the grain growth when compared to

pure-MgH₂ during hydrogenation cycles, improving the fast the hydrogenation kinetics of Mg.

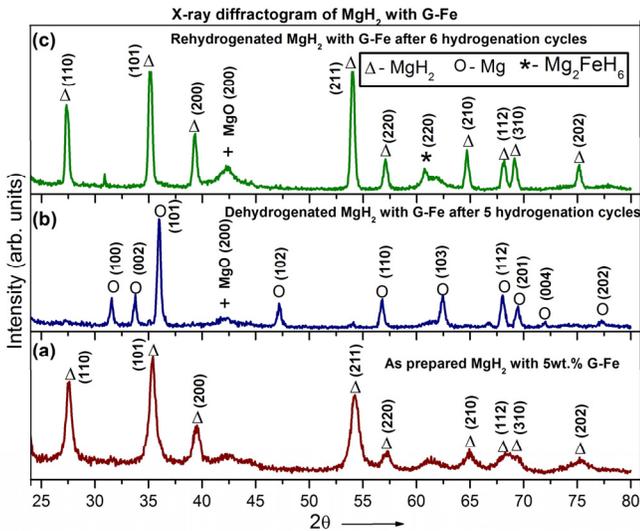


Figure. 5: Powder X-ray diffraction pattern of MgH₂ with 5 wt.% G-Fe (a) as-prepared (b) Dehydrogenated after five hydrogenation cycles and (c) Rehydrogenated after 6 hydrogenation cycles.

Microstructural analysis of the sample was carried out using TEM. Fig. 6 presents the TEM microstructures of as-synthesized graphene sheets decorated with Fe nanoclusters (Fig. 6(a)), MgH₂ with 5wt.% G-Fe (Fig. 6(b)) and MgH₂ with 5 wt.% G-Fe after six dehydrogenation and rehydrogenation cycles (Fig. 6(c))

It has been observed from the TEM micrograph (Fig. 6(a)) that the Fe nanoparticles (indicated by blue arrow) in G-Fe were found to get decorated throughout the graphene surface. The size of Fe nanoparticles are in the range of 5 to 15 nm. The distribution of graphene sheets (shown by white arrow) can be readily distinguished in the as-prepared and cycled MgH₂ with G-Fe samples (Fig. 6(b) & 6(c)). The corresponding SAED patterns (insets in Fig. 6(b) & 6(c)) shows the fine grain distribution of the samples. The ring patterns arise in the SAED patterns due to the presence of Fe nanoparticles and the bright patterns are from MgH₂ particles. It has been observed from the TEM micrograph of cycled sample that the graphene is intercalated between MgH₂ particles, possibly reducing the agglomeration of MgH₂ particles during cycling.

In accordance with the earlier study by other researchers, it has been observed that the presence of graphene reduces the grain growth of MgH₂, suggesting graphene is a very good crystal growth inhibitor during dehydrogenation/ rehydrogenation cycles of MgH₂ [14,15].

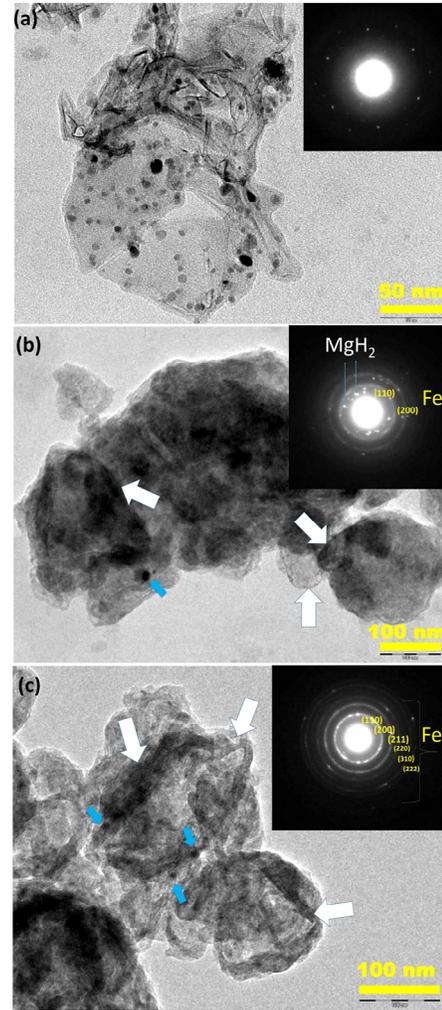


Figure. 6: TEM microstructure of (a) as-synthesized G-Fe, (b) as-prepared MgH₂ with 5 wt.% G-Fe and (c) MgH₂ with 5 wt.% G-Fe after six rehydrogenation cycles.

4 CONCLUSIONS

Graphene decorated with Fe clusters is experimentally proven to be a possible low cost and alternative catalyst towards the hydrogenation reaction compared to transition metal catalysts. Experiment shows that graphene decorated Fe clusters decrease the dehydrogenation temperature of MgH₂ from 322.3°C to 281.7°C where activation energies are experimentally measured to be 119.1 kJmol⁻¹. Furthermore, the rehydrogenation of MgH₂ with 5 wt.% graphene decorated Fe clusters is dramatically improved where it takes only 4 minutes to absorb 5 wt% of hydrogen at 300°C and 20 atm. After the six rehydrogenation cycles, the grain size of MgH₂ increased only 15 nm, showing a low order crystalite growth during cycling. This is advantageous for MgH₂ in withstanding cycling stability, suitable for hydrogen storage applications. The TEM analysis confirms the low order grain growth of MgH₂ due to the presence of graphene which behaves like a shell while MgH₂ is its core.

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