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Graphene decorated with Fe nanoclusters for improving the hydrogen sorption kinetics of MgH₂ – experimental and theoretical evidence†

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Graphene decorated with Fe clusters is proposed to be a possible alternative catalyst for the hydrogenation and dehydrogenation reactions of MgH₂. In particular, graphene decorated with Fe clusters is effective for both hydrogenation and dehydrogenation processes of MgH₂. The change in enthalpy and entropy values of hydrogen absorption determined for MgH₂ with 5 wt% graphene decorated with Fe clusters is −50.4 ± 2.9 kJ per mole of H₂ and 99.8 ± 5.2 J K⁻¹ per mole of H₂, respectively. This is significantly lower than those for well-established metal catalysts and nano-interfacial confined MgH₂. Moreover, the graphene decorated with Fe clusters facilitates the fast rehydrogenation kinetics of MgH₂, which reabsorbed 90% of the total reabsorption capacity in less than 4 minutes at 300 °C and 20 atm. In addition, TEM analysis reveals that MgH₂ particles are covered by graphene with Fe clusters, resulting in the reduction of grain growth. Density functional theory shows that the defects in graphene act as the active sites for the dehydrogenation of MgH₂, while the 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 catalyst which could replace transition metal catalysts.

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 oxidation processes.² In the same fashion, metal cluster-decorated graphene happens to have unexpected catalytic effects on various systems.³–⁶ In particular, graphene decorated with iron clusters is experimentally and theoretically found to store hydrogen.⁷,⁸ During the hydrogen absorption process over graphene with iron clusters, calculations also revealed that H₂ dissociation occurs over iron clusters, which is considered to cause spillover towards graphene.⁷ Such a phenomenon can be a key reaction for the hydrogenation process as H₂ dissociation is generally the first reaction step of the hydrogenation reaction. Here, magnesium hydride (MgH₂) is chosen to evaluate the catalytic effect of graphene with Fe nanoclusters. Magnesium hydride is a potential hydrogen storage material containing 7.6 wt% H₂ (theoretical capacity). However, an effective catalyst is required to overcome the high thermodynamic stability and slow hydrogenation reaction kinetics of MgH₂. The reaction of magnesium hydride is a prototype hydrogenation reaction which requires Mg, H₂ and MgH₂ dissociation. In order to improve the kinetics of the hydrogenation and dehydrogenation of magnesium hydride, tremendous amounts of catalysts have been extensively investigated.⁹–¹⁴ However, the search for better catalysts to accelerate the kinetics, hydrogenation, and dehydrogenation of MgH₂ is still a problematic issue for further practical applications. Metal-decorated graphene catalysts could be proposed to be potential catalysts for the hydrogenation reaction of such systems. The catalytic effect of graphene decorated with iron clusters is experimentally and theoretically investigated.

In particular, MgH₂ is used as a prototype reaction in order to evaluate the catalytic effect of graphene decorated with iron towards the hydrogenation and dehydrogenation process. Hydrogen absorption and desorption of MgH₂ with graphene decorated with iron clusters are experimentally tested. Transmission electron microscope imaging is used to observe the microstructure of graphene, iron, and MgH₂. Density functional theory is implemented in order to reveal the physical and chemical origin of the reaction

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mechanism. Although the study utilizes iron-decorated graphene and MgH₂, the catalytic effect and mechanism of graphene with metal systems should be generalized to further develop metal-decorated graphene catalysts.

Experimental

MgH₂ powder of 98% purity and Fe nanopowder (APS 10–30 nm) of 99.9% purity were purchased from Alfa Aesar. Graphene decorated with Fe nanoclusters (G-Fe) was synthesized in an electric arcing chamber using graphite electrodes. To ablate the material, an electric arc was generated using a DC source of 100 A and 25 V 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) with a partial pressure of ~300 torr. After 8–10 min of the arcing process, a flake-like carbon material was found to be deposited around the walls of the arcing 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 250 cm³ volume (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 minute 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 minute interval in-between). Handling of the samples was done in an mBraun MB10 compact Ar-filled glove box (H₂O and O₂ levels <1 ppm).

The dehydrogenation and reabsorption kinetics of the samples were analyzed through temperature-programmed desorption (TPD) and pressure–composition isotherm (PCI) measurement using an automated four channel volumetric Sievert-type apparatus supplied by Advanced Materials Corporation. TPD analysis of the sample was done at an initial pressure of 10⁻³ torr under dynamic heating conditions with an accuracy of ±0.2 °C. The rehydrogenation kinetics was measured at different temperatures by charging the dehydrogenated MgH₂ samples with 20 atm hydrogen pressure. Thermal analyses of the 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 20 ml min⁻¹.

Structural characterization of the samples was performed by X-ray diffraction using a PANalytical X’Pert PRO diffractometer with a Cu Kα beam (λ = 1.5415 Å) operated at 40 kV and 40 mA. The samples were loaded in air-tight sample holders sealed by a fine layer of paraffilm (Pechiney plastic packing) to prevent the sample from being contaminated by oxygen and moisture. The 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.

Results and discussion

TPD of MgH₂ samples was performed from room temperature (25 °C) to 450 °C under dynamic heating conditions at a heating rate of 2 °C min⁻¹. A comparison of the TPD profiles of pristine MgH₂, 5 hour ball-milled MgH₂ (un-catalyzed) and MgH₂ + 5 wt% G-Fe is shown in Fig. 1(a) & (b).

It has been observed from the TPD profiles that the dehydrogenation temperature of MgH₂ + 5 wt% G-Fe is significantly lower than those of pristine and ball-milled MgH₂. The peak temperature of MgH₂ + 5 wt% G-Fe is 281.7 °C, whereas that of 5 hour ball-milled MgH₂ is 322.3 °C. This suggests that graphene together with Fe nanoclusters exhibits superior catalytic effect in improving the dehydrogenation behaviour of MgH₂.

Fig. 2(a) & (b) present the DSC curves of 5 hour ball-milled (un-catalyzed) MgH₂ and MgH₂ + 5 wt% G-Fe, respectively, determined at different heating rates (2, 5, 10 and 15 °C min⁻¹). The apparent desorption activation energy (Ea) of ball-

![Fig. 1](image-url) Comparative TPD profiles of MgH₂ (a) hydrogen release capacity and (b) peak temperature.
milled MgH$_2$ and MgH$_2$ + 5 wt% G-Fe was determined using the Kissinger method.\textsuperscript{15}

The peak desorption temperature (TPD) determined from the DSC curves and the corresponding heating rates ($\beta$) are the two parameters required for determining $E_a$ using the Kissinger equation given below.

$$\ln(\beta/T_P^2) = (-E_a/RT_P) + \ln(k_0)$$

where $k_0$ is a constant. The 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$^{-1}$ DSC heating rates for calculating the desorption activation energy of the samples. The corresponding $\ln(\beta/T_P^2)$ vs. $1/T_P$ plot of ball-milled MgH$_2$ and MgH$_2$ + 5 wt% G-Fe is shown in Fig. 2(c).

The desorption activation energy of ball-milled MgH$_2$ (w/o additive) and 5 wt% G-Fe admixed MgH$_2$ determined from the DSC curves using the Kissinger method is 157.4 and 119.1 kJ mol$^{-1}$. For pristine MgH$_2$, it is ~187 kJ mol$^{-1}$.\textsuperscript{16,17} Table 1 gives the summary of the calculated apparent desorption activation energy of MgH$_2$ determined from DSC curves using the Kissinger equation.

It should be noted that 1 hour ball-milled MgH$_2$ + 5 wt% graphene nanosheets (without metal decoration) shows the peak desorption temperature at 358 °C for the DSC heating rate of 5 °C min$^{-1}$.\textsuperscript{18} Meanwhile, in the present case, 1 hour ball-milled MgH$_2$ + 5 wt% G-Fe shows the peak desorption temperature at 323 °C for the DSC heating rate of 5 °C min$^{-1}$ (refer to Fig. 2(b)). Thus the presence of Fe nanoclusters on graphene greatly lowers the dissociation temperature of MgH$_2$.

Fig. 3 presents the isothermal reabsorption kinetic curves of dehydrogenated MgH$_2$ + 5 wt% G-Fe determined at different temperatures (200, 280 and 300 °C) and 20 atm hydrogen pressure. It has been observed that the dehydrogenated

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
& Pristine MgH$_2$ & MgH$_2$ + G-Fe (5 wt\%) \\
\hline
Activation energy (kJ mol$^{-1}$) & ~187 (ref. 16 and 17) & 157.4 & 119.1 \\
\hline
\end{tabular}
\caption{Summary of desorption activation energy determined for MgH$_2$ using the Kissinger method.}
\end{table}
MgH$_2$ + 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. Meanwhile, the ball-milled (un-catalyzed) dehydrogenated MgH$_2$ sample took nearly 20 min to absorb 5 wt% hydrogen at 300 °C and 20 atm. This reveals that G-Fe exhibits superior catalytic effect on MgH$_2$ for both hydrogen release and uptake.

Fig. 4(a) & (b) represent the PCI isotherms and Van’t Hoff plot of MgH$_2$ + G-Fe, respectively. From the Van’t Hoff plot (Fig. 4(b)), the formation enthalpy and entropy values of MgH$_2$ with 5 wt% G-Fe were derived. The change in enthalpy and entropy values is $-50.4 \pm 2.9$ kJ per mole of H$_2$ and $99.8 \pm 5.2$ J K$^{-1}$ per mole of H$_2$, respectively, for the formation of MgH$_2$. It should be mentioned that the change in formation enthalpy and entropy values for as-received bulk MgH$_2$ is $-74.06 \pm 0.42$ kJ per mole of H$_2$ and $133.4 \pm 0.7$ J K$^{-1}$ per mole of H$_2$, respectively. However, the change in formation enthalpy and entropy of MgH$_2$ was reported for element-coated Mg. For Fe-coated Mg, the formation enthalpy and entropy of MgH$_2$ were $-59.9 \pm 1.9$ kJ per mole of H$_2$ and $112.3 \pm 3.1$ J K$^{-1}$ per mole of H$_2$, respectively.

Zhao-Karger et al. reported that MgH$_2$ nanoparticles (<3 nm) confined in an activated carbon fiber scaffold system exhibited reduced enthalpy and entropy values of $-63.8$ kJ per mole of H$_2$ and 117.2 J K$^{-1}$ per mole of H$_2$, respectively. Jia et al. observed that MgH$_2$ nanoparticles with ordered mesoporous carbon, CMK-3, exhibit a reduced enthalpy and entropy of $-55.4$ kJ per mole of H$_2$ and 105.7 J K$^{-1}$ per mole of H$_2$, respectively. Recently, reduced enthalpy and entropy values of $-45 \pm 3$ kJ per mole of H$_2$ and 84 $\pm 5$ J K$^{-1}$ per mole of H$_2$, respectively, were observed for MgH$_2$-Ti nanocomposites produced by spark discharge.

It has been pointed out that the thermodynamic properties of the Mg-to-MgH$_2$ hydrogenation reaction can be dramatically improved at the nanoscale due to the dominant contribution of the high surface to volume ratio. In accordance with previous reports, it is known that Fe nanoparticles and graphene are very good catalysts for the MgH$_2$ system. Therefore, 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 synergistic effect in improving the dehydrogenation behavior and in enhancing the hydrogenation of Mg to MgH$_2$ through the spillover effect.

Fig. 5(a) shows the XRD patterns of as-prepared MgH$_2$ + 5 wt% G-Fe, Fig. 5(b) presents the XRD pattern of dehydrogenated MgH$_2$ + G-Fe (5 wt%) after five rehydrogenation cycles and Fig. 5(c) shows its XRD pattern after six rehydrogenation cycles.

It was found that along with the main MgH$_2$ phase, the MgO phase is detected. It was noticed that after six...
dehydrogenation and rehydrogenation cycles, the diffraction peak intensity increases, suggesting the grain growth of MgH₂. Assuming that the MgH₂ particles were spherical, the size of the grains were calculated from the XRD peaks using Scherrer’s equation.²⁷ This suggests that the average grain size of as-prepared MgH₂ + G-Fe (Fig. 5(a)) is 19 nm and after six cycles (Fig. 5(c)), the grain size of MgH₂ increases to 34.8 nm. Liu et al.²⁸ observed that after six hydrogenation cycles, the grain size of pure-MgH₂ (w/o additives) increased three times (from 10.8 nm before cycling to 32 nm after cycles).

The nucleation and growth of the Mg₂FeH₆ phase was observed in the cycled MgH₂ + G-Fe sample, due to the reaction between elemental Mg and Fe during the hydrogenation process, suggesting that the Fe particles were not free during hydrogenation. However, during dehydrogenation, Mg₂FeH₆ completely transformed into elemental Mg and Fe, benefiting the initial stage of the rehydrogenation process.²⁸

Microstructural analysis of the sample was carried out using TEM. Fig. 6 presents the TEM microstructures of the as-synthesized graphene sheets decorated with Fe nanoparticles (Fig. 6(a)), MgH₂ ball-milled for 5 hours (Fig. 6(b)), MgH₂ + 5 wt% G-Fe (Fig. 6(c)) and MgH₂ + 5 wt% G-Fe after five dehydrogenation/rehydrogenation cycles (Fig. 6(d)).

It was found from the TEM micrograph (Fig. 6(a)) that the Fe nanoparticles (indicated by blue arrows) in G-Fe were distributed throughout the graphene surface. The size of Fe nanoparticles ranges from 5 to 15 nm. The hexagonal pattern observed in the SAED pattern (inset of Fig. 6(a)) confirms that the synthesized sample is graphene. EDAX spectral analysis confirms that the composition of Fe nanoparticles in graphene is 2 wt%. The grid spacing is set to 0.20 Å with 0.00 eV of smearing. The Γ point is implemented for the sampling of the Brillouin zone. Exchange-correlation of Perdew–Burke–Ernzerhof (PBE) with spin polarization calculations is applied for all calculations.¹⁰ Charge transfer analysis is performed using Bader charge analysis.³¹,³²

The adsorption energies of the MgH₂ cluster and one H atom are calculated using eqn (2)

\[
E_{\text{ad}} = E_{\text{Surface+adsorbate}} - E_{\text{Surface}} - E_{\text{Adsorbate}}
\]

The reaction between Fe-decorated graphene and MgH₂ takes place by using the mechanical ball milling process in the experiment. In general, the ball milling process destroys the structure of the material. Hence, atomic clusters are implemented in order to consider the complicated unusual structures. The MgH₂ cluster is used in order to understand the fundamental dehydrogenation properties over the Fe-decorated catalysts as MgH₂ clusters have been shown to be an effective model to understand the hydrogenation and dehydrogenation properties of MgH₂ systems.¹⁰ In addition, graphene within non-periodic boundary conditions is considered. In particular, asymmetric graphene consisting of 32 carbon atoms, shown in Fig. 7(a), is constructed within non-periodic boundary conditions.

### Computational results

The MgH₂ cluster is adsorbed on non-defected graphene with/without an Fe atom, single defected graphene, Fe-doped graphene and large graphene with/without an Fe atom. The adsorption energies of the MgH₂ cluster and H atom over each graphene model are collected in Table 2. The structural models are shown in Fig. 7(a–f). The different sizes of defects and the adsorption of Fe monomers are considered based on the graphene in Fig. 7(a).
The MgH$_2$ cluster is adsorbed on the edge of non-defected graphene where one of the H atoms is dissociated and adsorbed on the C atom. The adsorption energy of the MgH$_2$ cluster and the H atom on non-defected graphene is calculated to be $-4.21$ eV and $-0.55$ eV, respectively. Upon the introduction of Fe atom onto non-defected graphene, both H atoms are fully dissociated from MgH$_2$ clusters, as shown in Fig. 7(c). In particular, it is interesting that the adsorption energy of the MgH$_2$ cluster and H atom dramatically decreased and was $-1.36$ eV and $0.06$ eV compared to the one without Fe. Thus, a dramatic decrease of H adsorption energy is predicted to allow low temperature dehydrogenation. Single C defect is created at the edge of graphene shown in Fig. 7(d). Both H atoms are dissociated over the single C defect graphene. It is interesting that the adsorption energy of the MgH$_2$ cluster on single defect graphene is calculated to be $-5.38$ eV as single defect enhances the MgH$_2$ cluster adsorption energy by $-1.17$ eV as compared to the MgH$_2$ cluster on non-defected graphene. Furthermore, H adsorption energy is calculated to be $-0.83$ eV where H atoms are adsorbed at the edge of graphene shown in Fig. 7(d). However, a decrease of H adsorption energy is not observed in the single defect case compared to the case of Fe-decorated graphene.

A large defect is created in graphene in order to completely break the structure of graphene where six carbon atoms are taken from graphene consisting of 32 C atoms. The structure of graphene is greatly deformed. The adsorption of MgH$_2$ cluster on the large defected graphene particularly shows a high adsorption energy of $-7.89$ eV where both H atoms are dissociated from the MgH$_2$ cluster, as shown in Fig. 7(e). H adsorption energy is calculated to be $-2.08$ eV. This also confirms that the edge of the defected graphene is reactive against the MgH$_2$ cluster. However, high H adsorption energy could require higher temperatures for further dehydrogenation processes. An Fe atom is then adsorbed on the large defected graphene shown in Fig. 7(f). The adsorption energy of the MgH$_2$ cluster and H atom over the large defected graphene with Fe is dramatically decreased to $-2.84$ eV and $-0.53$ eV, respectively, where full dehydrogenation of the MgH$_2$ cluster is also observed. Thus, one can suggest that the introduction of Fe atom decreases the dehydrogenation temperature of the MgH$_2$ cluster over defected graphene.

Bader charge analysis is performed for the large defected graphene with/without Fe in order to reveal the physical origin of the effect of Fe. Bader analysis indicates that the Fe atom is positively charged by 0.8 electrons. This indicates that electrons from Fe atoms are transferred to C atoms near Fe atoms. One could suggest that Fe atoms fill and stabilize the defects of graphene. As a result, graphene is less active. On the other hand, electrons in the d-orbital of Fe atoms could enhance the dehydrogenation of the MgH$_2$ cluster. Thus, the catalytic activities of defected graphene could be controlled by Fe.

**Conclusions**

Graphene decorated with Fe clusters is experimentally and theoretically proven to be a possible low cost and alternative catalyst towards the hydrogenation reaction compared to transition metal catalysts. Experiments show that graphene decorated with Fe clusters decreases the dehydrogenation temperature of MgH$_2$ from 322.3 °C to 281.7 °C where the activation energies are experimentally measured to be 119.1 kJ mol$^{-1}$. Furthermore, the rehydrogenation of MgH$_2$ with graphene decorated with Fe clusters is dramatically improved where it takes only 4 minutes to absorb 5 wt% hydrogen at 300 °C and 20 atm. After six rehydrogenation cycles, the grain size of MgH$_2$ increased only 15 nm, showing low order grain growth during cycling. This is advantageous for MgH$_2$ in maintaining cycling stability, making it suitable for hydrogen storage applications. TEM analysis confirms the low order grain growth of MgH$_2$ and shows that the graphene decorated with Fe clusters behaves like a shell while MgH$_2$ is its core. Density functional theory calculations reveal that the location of the active site – the defect in graphene – and the presence of iron clusters at the defect site of graphene are the key factors for the dehydrogenation of MgH$_2$, as the Fe clusters reduce the adsorption of dissociated H atoms, thus resulting in low-temperature hydrogen release. This suggests that other transition metals could also be effective if charge transfers from the transition metal to graphene are involved. Thus, graphene decorated with Fe clusters could be a
potentially alternative for transition metal catalysts for hydrogenation reactions and the possibility of utilizing graphene decorated with other metal clusters could further be explored.

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Notes and references

23. M. Ismail, N. Juahir and N. S. Mustafa, Improved Hydrogen Storage Properties of MgH2 Co-Doped with FeCl3 and...


