Nanolayer-like-shaped MgFe$_2$O$_4$ synthesised via a simple hydrothermal method and its catalytic effect on the hydrogen storage properties of MgH$_2$

N. A. Ali,$^a$ Nurul Hayati Idris,$^a$ M. F. Md Din,$^b$ N. S. Mustafa,$^a$ N. A. Sazelee,$^b$ F. A. Halim Yap,$^a$ N. N. Sulaiman,$^a$ M. S. Yahya$^a$ and M. Ismail$^a$  

In this study, the effect of nanolayer-like-shaped MgFe$_2$O$_4$ that is synthesised via a simple hydrothermal method on the performance of MgH$_2$ for hydrogen storage is studied. MgH$_2$ + 10 wt% MgFe$_2$O$_4$ is prepared by using the ball milling method. The MgFe$_2$O$_4$-doped MgH$_2$ sample started to release H$_2$ at approximately 250 °C, 90 °C and 170 °C lower than the milled and pure MgH$_2$ respectively. At 320 °C, the isothermal desorption kinetic study has shown that the doped sample has desorbed approximately 4.8 wt% H$_2$ in 10 min while the milled MgH$_2$ desorbed less than 1.0 wt% H$_2$. For isothermal absorption kinetics, the doped sample can absorb approximately 5.5 wt% H$_2$ in 10 min at 200 °C. Meanwhile, the undoped sample absorbs only 4.0 wt% H$_2$ in the same condition. The activation energy of 10 wt% MgFe$_2$O$_4$-doped MgH$_2$ composite is 99.9 kJ mol$^{-1}$, which shows a reduction of 33.1 kJ mol$^{-1}$ compared to the milled MgH$_2$ (133.0 kJ mol$^{-1}$). X-ray diffraction spectra display the formation of new species which are Fe and MgO after dehydrogenation, and these new species are believed to act as the real catalyst that plays a crucial role in improving the sorption performance of the MgFe$_2$O$_4$-doped MgH$_2$ system by providing a synergetic catalytic effect.

1. Introduction

To prepare for the future and ensure global environmental viability, energy systems have to be reliable, clean, low cost, environmentally friendly and flexible. Humanity is expected to use 40 TW of power (40 billion of kW) in the future. To satisfy this demand, different sources of renewable energy, such as hydrogen, are needed. Sustainable hydrogen is an ideal clean energy carrier because there is no carbon dioxide or other greenhouse gas emission at the end-user level. Commonly, there are 3 forms of storing hydrogen which is high-pressure gas, cryogenic liquid hydrogen in tanks (stored at 21.2 K) and as solid state hydrogen storage by either reacting with chemical compounds or absorbing. Among these approaches, solid-state hydrogen storage has higher potential for higher hydrogen density and may yield greater utility towards the practical implementation of hydrogen storage. Among the various materials for solid-state hydrogen storage, MgH$_2$ considered as one of the most potential material due to its high hydrogen storage capacity (7.6 wt%), excellent reversibility and low cost. However, MgH$_2$ is restricted by the decomposition temperature, which is high with slow sorption kinetics and is excessively stable thermodynamically. Many research have been conducted to overcome these disadvantages by altering the thermodynamics and improve the kinetic properties by producing nanostructures and utilizing catalysts such as carbon-based materials, metal oxides, metal hydrides, metal oxides and nanosized alloys.

Previous research has proved that catalyst based on ternary metal oxides greatly improved the hydrogen storage performance of MgH$_2$. Zhang et al. demonstrate that ferrite nanoparticles ($\text{Fe}_3\text{O}_4$, $\text{ZnFe}_2\text{O}_4$, $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{CoFe}_2\text{O}_4$) can greatly lower the decomposition temperature of MgH$_2$. $\text{CoFe}_2\text{O}_4$ provides the best catalytic effect compared with other ferrites. New by-products are found after the dehydrogenation process, and its phase shows a great catalytic effect on the properties of hydrogen storage of MgH$_2$. Furthermore, Li et al. shows a significant improvement in the desorption performance of MgH$_2$ when catalysed with $\text{MnFe}_2\text{O}_4$. X-ray photoelectron spectroscopy and X-ray diffraction (XRD) tests show that $\text{Fe}_{0.87}\text{O}$ and $\text{Mg}_2\text{MnO}_4$ phases take part as a remarkable effect in improving the hydrogen storage performance of MgH$_2$. Interestingly, our result showed that Fe metal formed after dehydrogenation instead of $\text{Fe}_{0.87}\text{O}$ species, as claimed by Li et al. This variation paved the way for the debate.
on how ternary metal oxides, particularly ferrites, work as catalysts in improving the hydrogen sorption performance of MgH₂. Moreover, the difference in the synthesis method of the catalysts may also provide a different effect in the catalytic role.

Inspired by the role of active species that formed during the heating process in the MgH₂-ternary metal oxides catalyst system, it is quite interesting to investigate the use of other ferrites (e.g. MgFe₂O₄) as catalysts to improve the hydrogen sorption performance of MgH₂. Therefore, in this work, MgFe₂O₄ was synthesised by using a simple hydrothermal method, and its catalytic effects on the hydrogen sorption performance of MgH₂ were systematically studied. To the best of authors’ knowledge, this paper is the first to study the hydrogen sorption performance of MgH₂ catalysed with MgFe₂O₄. The possible catalysis mechanisms of MgFe₂O₄ in the sorption performances of MgH₂ are also discussed in this paper.

2. Experimental details

The nanolayer-like-shaped MgFe₂O₄ was synthesised via a hydrothermal method. In a typical synthesis, a stoichiometric amount of Mg(NO₃)₂·6H₂O (Sigma-Aldrich) and Fe(NO₃)₃·9H₂O (Sigma-Aldrich) were dissolved in 50 ml distilled water. A total of 10 ml of H₃N₂·H₂O (Sigma-Aldrich) was added dropwise to the above solution to attain the resultant pH of >9. The mixture was then transferred into a sealed Teflon lined stainless-steel autoclave (125 ml capacity) and heated for 12 h at 180 °C. The final product was washed several times with deionised water and dried overnight at 60 °C under vacuum. A total of 10 wt% of as-prepared MgFe₂O₄ was mixed with 300 mg of MgH₂ (95% pure; Sigma-Aldrich) and undergo intensive ball milling for 1 h in a planetary ball mill at the rate of 400 rpm. For comparison, pure MgH₂, and MgH₂ added with 10 wt% Fe (Alfa Aesar) and 10 wt% MgO (R&M Chemicals), respectively were also prepared under the same conditions. All preparations, including loading and weighing, were conducted in an argon atmosphere glove box (MBraun Unilab).

The onset decomposition temperature and sorption kinetic measurement for doped and undoped samples were characterised by using Sievert-type pressure–composition–temperature apparatus (Advanced Materials Corporation). For onset decomposition temperature measurement, the samples were heated from room temperature to 450 °C at a heating rate of 5 °C min⁻¹ in vacuum chamber. Meanwhile, the sorption kinetics was conducted under 1.0 atm at 320 °C for desorption kinetic measurement and under 33.0 atm at 200 °C for absorption kinetic measurement. The thermal properties of the doped and undoped samples were performed using differential scanning calorimeter (DSC)/thermogravimetric analysis from Metler Toledo. With a flow of 50 ml min⁻¹ argon, the samples

![Fig. 1](a) XRD pattern, (b) SEM image, (c) FTIR spectra and (d) Raman spectra of MgFe₂O₄.
were heated with 15, 20, 25 and 30 °C min⁻¹ heating rate from 25 °C to 500 °C.

The phase composition of the samples was analysed by XRD via a Rigaku MiniFlex X-ray diffraction apparatus equipped with Cu Kα radiation. Data were collected in the 2θ range 20° to 80° at 2° min⁻¹. The morphologies of the samples were observed by scanning electron microscopy (SEM) (JEOL JSM-6350LA). Fourier transform infrared (FTIR) spectrometry was recorded on an IR Shimadzu Tracer-100 between 400 and 2000 cm⁻¹. Raman spectra were recorded on Renishaw Raman spectroscopy (532 nm radiation) extended with 0.1% power laser measurement at room temperature.

3. Results and discussion

Before milling with MgH₂, the phase structure of MgFe₂O₄ was confirmed by XRD, as shown in Fig. 1(a). The crystallographic planes of (220), (311), (400), (422), (511), (440) and (533) correspond to the diffraction peaks at 2θ of 30.1°, 35.4°, 43.1°, 53.5°, 57.0°, 62.6° and 74.1°, respectively. This result is in good agreement with the standard cubic spinel structure (JCPDS 71-1232). No other peaks were detected in the sample. The average crystallite size of MgFe₂O₄ was approximately 19 nm, as determined by using Scherrer’s formula:

\[ L = \frac{k\lambda}{B \cos \theta}, \]

where \( L \) is the average crystallite size (nm), \( \theta \) is the angle of diffraction, \( k \) is Scherrer’s constant (\( k = 0.94 \)), \( \lambda \) is the X-ray wavelength (0.15405 nm) and \( B \) is the full width at half maximum of the diffraction peak in radian (FWHM). The SEM image (Fig. 1(b)) reveals that the MgFe₂O₄ forms a large layer with a nanosized thickness. From the FTIR spectrum (Fig. 1(c)), two typical peaks of MgFe₂O₄ were observed at the low wave-number, thus indicating the formation of spinel ferrite structure. The peak at 417 cm⁻¹ can be ascribed to the Fe–O vibration in the octahedral site, and the peak at 538 cm⁻¹ can be assigned to the Fe–O vibration in the tetrahedral and octahedral sites. Furthermore, the Raman peaks (Fig. 1(d)) at 475 and 694 cm⁻¹ can be assigned to the characteristic peaks of MgFe₂O₄ whereas the peak at 283 cm⁻¹ corresponding to the stretching vibration of the Mg–O chemical bond.

The XRD, FTIR and Raman spectroscopy results confirm that pure MgFe₂O₄ was successfully synthesised by the hydrothermal method.

Fig. 2(a) shows the onset decomposition temperature results for the pure MgH₂, milled MgH₂ and MgH₂ with 10 wt% MgFe₂O₄. Before milling, pure MgH₂ started to desorb hydrogen at approximately 420 °C. The total amount of hydrogen desorbed is approximately 7.0 wt%. After milling for 1 h, the onset decomposition temperature of MgH₂ was decreased to approximately 340 °C. This phenomenon demonstrate that the sorption performance of MgH₂ also influenced by the milling.
From the curve, it can be seen that after milling, the amount of hydrogen desorb of MgH₂ slightly decreases. This might be ascribed to the hydrogen released from MgH₂ during the milling process. After doping with 10 wt% of MgFe₂O₄, it is clear that the onset decomposition temperature of the MgH₂ was dramatically reduced to 250 °C, 90 °C and 170 °C lower than that for the milled and pure MgH₂, respectively. However, the hydrogen desorption capacity decrease slightly to approximately 6.5 wt% because the dopant used in this study, namely, MgFe₂O₄, does not contain hydrogen.

From Fig. 2(a), it can be concluded that MgFe₂O₄ additive plays a positive role in decreasing the decomposition temperature of MgH₂.

To further examine the sorption properties of the MgFe₂O₄-doped MgH₂ sample, the isothermal absorption kinetic was studied. The amount of hydrogen absorbed from the milled MgH₂ and the MgFe₂O₄-doped MgH₂ sample was measured under 33.0 atm H₂ and at constant temperature of 200 °C, as shown in Fig. 2(b). The MgFe₂O₄-doped MgH₂ sample shows better absorption kinetics than undoped MgH₂. For the MgFe₂O₄-doped MgH₂ sample, the amount of 5.5 wt% H₂ was absorbed in 10 min, whereas the milled MgH₂ only absorbed approximately 4.0 wt% H₂ within the same time. From the result, it clearly shows that the addition of MgFe₂O₄ enhanced the rehydrogenation kinetics of MgH₂.

For further studies on the catalytic effect of MgFe₂O₄ on the sorption kinetic of MgH₂, isothermal desorption kinetic was performed under 1.0 atm at 320 °C. As shown in Fig. 2(c), the MgFe₂O₄-doped MgH₂ sample shows significant enhancement compared with the milled MgH₂. The results shows that the undoped MgH₂ released less than 1.0 wt% H₂ after 10 min, whereas the doped sample can released approximately 4.8 wt% H₂ under the same condition. In contrast, it can be seen that MgFe₂O₄ also plays a significant role in enhancing the dehydrogenation kinetic of MgH₂.

The catalytic effect of MgFe₂O₄ was further studied with the cycling performances of MgFe₂O₄-doped MgH₂ system. Fig. 3(a) presents the isothermal absorption kinetics of the 10 wt% MgFe₂O₄ doped with MgH₂ at 320 °C under a hydrogen pressure of 33.0 atm over 10 cycles. From the result, it can be seen that after the ten cycles, the absorption kinetics show a small reduction in the hydrogen capacity. After completing the 10th cycle, the system is able to absorb 5.6 wt% of hydrogen in 60 minutes. The result shows that the doped system displays good absorption properties even after 10 cycles. As for the desorption kinetics, Fig. 3(b) shows the isothermal desorption kinetics for 10 cycles that was carried out at 320 °C and under 1.0 atm of pressure. Like the absorption kinetics, a small hydrogen capacity degradation is shown after completing the 10th cycle. The doped system possesses a good performance after completing the 10th cycle as it is able to desorb about 5.5 wt% of hydrogen within 60 minutes. These results demonstrated that MgFe₂O₄ plays a vital catalytic role for the cycle life of MgH₂.

The thermal properties of the 10 wt% MgFe₂O₄-doped MgH₂ and undoped MgH₂ sample were further studied by DSC at heating rate of 30 °C min⁻¹ and under a flow of 50 ml min⁻¹ argon (Fig. 4). Obviously, the DSC trace for the pure MgH₂ showed one endothermic peak at approximately 482.9 °C. This strong endothermic peak related to the released of hydrogen
from the MgH$_2$. Similar to the pure MgH$_2$, DSC traces of the milled MgH$_2$ and MgFe$_2$O$_4$-doped MgH$_2$ showed only one strong endothermic peak at 438.8°C and 393.3°C respectively. The peaks correlated to the decomposition of MgH$_2$ but at lower temperatures.

The improvement in desorption behaviour is correlated with the kinetic barrier of the hydrogen desorbed from the MgH$_2$. By doping MgH$_2$ with MgFe$_2$O$_4$, low value of activation energy for released hydrogen is obtained. Kissinger analysis (eqn (2)) was conducted to determine the activation energy of doped and undoped MgH$_2$ samples.

\[
\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_A}{R} + A,
\]

where $\beta$ is the heating rate, $E_A$ is the activation energy, $R$ is the gas constant, $T_p$ is the peak temperature of DSC curves and $A$ is the linear constant. Fig. 5 illustrates the curves of DSC for the milled MgH$_2$ and MgH$_2$ doping with 10 wt% MgFe$_2$O$_4$ samples at heating rates of 15, 20, 25, and 30 °C min$^{-1}$. From the Kissinger plot of the DSC data (Fig. 5(c)), it can be perceived that the activation energy, $E_A$, for the MgFe$_2$O$_4$-doped MgH$_2$ composite is 99.9 kJ mol$^{-1}$, which is decrease 33.1 kJ mol$^{-1}$ compared with the milled MgH$_2$ (133.0 kJ mol$^{-1}$). The result indicates that addition of MgFe$_2$O$_4$ reduces the decomposition activation energy and boost the desorption performances of MgH$_2$.

Fig. 6 presents the microstructures of the pure and milled MgH$_2$, and MgFe$_2$O$_4$-doped MgH$_2$. From the images, it can be seen clearly that the particle size of the pure MgH$_2$ is around 50-100 μm (Fig. 6(a)). Fig. 6(b) shows the image of the MgH$_2$ after 1 h ball milling. The size of the milled MgH$_2$ was decreased dramatically compared to the pure MgH$_2$. However, the image shows agglomeration and inconsistent particle sizes. Fig. 6(c) shows that the particle size of 10 wt% MgFe$_2$O$_4$-doped MgH$_2$ was the smallest and had less agglomeration than the pure and milled MgH$_2$. Smallest particle size gives a larger region of contact to the MgH$_2$, thus resulting in the higher rate of reaction of MgH$_2$.

To investigate the phase structure, XRD measurement was performed on the 10 wt% MgFe$_2$O$_4$-doped MgH$_2$ sample, as shown in Fig. 7. From Fig. 7(a), it can be observed that the MgH$_2$ and MgFe$_2$O$_4$ phases are present in the as-milled MgFe$_2$O$_4$-doped MgH$_2$ sample. No additional peaks were found from the spectra. After dehydrogenation at 450 °C (Fig. 7(b)), the XRD pattern showed that the MgH$_2$ was completely dehydrogenated to Mg. This result demonstrates that the decomposition of MgH$_2$ was completed after heating for up to 450 °C. Furthermore, a small peak of MgO and Fe formed after the desorption process, thus demonstrate that the partial reaction of MgH$_2$ with MgFe$_2$O$_4$ may occur during the heating process as follows:

\[
4\text{MgH}_2 + \text{MgFe}_2\text{O}_4 \rightarrow \text{Mg} + 4\text{MgO} + 2\text{Fe} + 4\text{H}_2 \quad (3)
\]

The standard Gibbs Free energy, $\Delta G^f$, of MgH$_2$, MgFe$_2$O$_4$ and MgO are -35.9824, -1317.1232 and -569.024 kJ mol$^{-1}$,
respective.43 The total change $\Delta G$ correlated with the reaction in eqn (3) is $-815.0168$ kJ mol$^{-1}$. These values can confirm the possibility of the reaction in eqn (3) from thermodynamic potentials. Fig. 7(c) shows the XRD patterns for the rehydrogenated sample under 33.0 atm $\text{H}_2$ at 320 °C. The result illustrates that the phase of Mg was fully converted into MgH$_2$. Furthermore, the peak of Fe and MgO still remained after undergoing rehydrogenation.

From the above analyses, the improvements in the sorption properties of MgH$_2$ doped with 10 wt% MgFe$_2$O$_4$ may be resulted from the formations of Fe and MgO. Fe and MgO may act as the real catalysts that play a vital role in the improvements of MgH$_2$ sorptions. Therefore, to verify the effect of Fe and MgO on MgH$_2$, samples of 10 wt% MgO-doped MgH$_2$ and 10 wt% Fe-doped MgH$_2$ were prepared and the TPD profiles for the dehydrogenations were shown as in Fig. 8. It is clearly seen that the decomposition temperature of MgH$_2$ are reduced with the addition of MgO or Fe as compared to the pure and milled MgH$_2$. However, the performance of these MgO and Fe are not significant as the sample of 10 wt% of MgFe$_2$O$_4$ doped with MgH$_2$. This demonstrated that the \textit{in situ} generated MgO and Fe from the reaction of MgH$_2 + 10$ wt% of MgFe$_2$O$_4$ may play a significant role that introduce a synergetic catalytic effect that cause a significant improvement on the dehydrogenation performances of MgH$_2$ doped with 10 wt% of MgFe$_2$O$_4$. In addition, the \textit{in situ} formed Fe and MgO in the MgH$_2 + 10$ wt% of MgFe$_2$O$_4$ sample are speculated to have a higher degree of dispersion and more compact phase segregation as compared to the milled MgH$_2 + 10$ wt% Fe and milled MgH$_2 + 10$ wt% MgO. This would be likely to lead the improvement of the sorption kinetics.

From the result obtained, we postulate that formation of fresh and fine MgO and Fe species which resulted from the reaction between MgH$_2$ and MgFe$_2$O$_4$ during the dehydrogenation process may play significant role in improving the sorption performances of MgH$_2$. Numerous studies have claimed that the newly active species formed during the deabsorption process may play as a real catalyst in the enhancement of MgH$_2$ sorption.$^{44}$ Many works have proven that Fe is...
an excellent catalyst for sorption performance in MgH2.7–9 It is believed that the presence of fresh and fine Fe could interact with H2 molecules, thus possibly leading to the dissociation of H2 molecules and the improvement of the de/rehydrogenation kinetic. Furthermore, previous studies have shown that the sorption performance in MgH2 can be enhanced with the addition of MgO. Ares-Fernández and Aguey-Zinsou10 claimed that the addition of MgO to MgH2 during the milling process led to an enhancement of sorption kinetics because of the high electronegativity MgO. In another study, the same group also claimed that during the milling process, MgO may act as a process control agent that can lead to the reduction of the particle agglomeration of MgH2 by an optimal breakage rate, thus aiding the high stability of these particles and evading the use of cold welding.11 Shan et al.12 also revealed that MgO has a great catalytic effect on the MgH2 sorption performance. Their study showed that during the heating process in CoFe2O4-doped MgH2 composite system, MgO is formed. The catalytic effect of MgO could work together with the catalytic role of the Fe metal to create a synergistic effect. Therefore, the in situ active species of Fe and MgO may actually act as real catalysts and further enhance the hydrogen sorption performance of MgH2. However, further studies are needed to elucidate more details on the exact role of MgFe2O4 addition in MgH2.

4. Conclusion

In this study, nanolayer-like-shaped MgFe2O4 was successfully synthesised through a rapid, simple hydrothermal method. The addition of 10 wt% as-synthesised MgFe2O4 to MgH2 reduces the onset decomposition temperature and enhances sorption kinetics. The MgFe2O4-doped MgH2 sample has started to release H2 at approximately 250 °C, 90 °C and 170 °C lower than milled and pure MgH2 respectively. In a duration of 10 min, the isothermal desorption kinetic study showed that the doped sample can release approximately 4.8 wt% H2 at 320 °C while the milled MgH2 only desorbed less than 1.0 wt% H2 under the same condition. For isothermal absorption kinetics, the doped sample can absorb approximately 5.5 wt% H2 in 10 min at 200 °C. By contrast, the milled MgH2 sample absorbed only 4.0 wt% H2 in the same condition. From the Kissinger analysis, the apparent activation energies, EA, for the MgFe2O4-doped MgH2 sample were calculated to be 99.9 kJ mol−1 compared with the milled MgH2 (133.0 kJ mol−1). The XRD exploration displays the formation of new species of Fe and MgO after the dehydrogenation process, and these species remained unchanged after rehydrogenation. It is believed that the new species of Fe and MgO play a synergistic role in enhancing the hydrogen storage performances of MgH2.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Ministry of Higher Education of Malaysia for financial support through the Fundamental Research Grant Scheme (FRGS 59362). The authors also would like to give appreciation to Universiti Malaysia Terengganu for the good facilities to accomplish this project.

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