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Effect of SrFe₁₂O₁₉ nanopowder on the hydrogen sorption properties of MgH₂

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Abstract

In this study, the effects of different contents (5, 10, 15, 20 and 50 wt.%) of an $SrFe_{12}O_{19}$ nanopowder, doped into MgH₂ and prepared by the ball milling method, were investigated with the aim of improving hydrogen storage properties. The results indicated that 10 wt.% SrFe₁₂O₁₉ showed the best performance, compared with un-doped MgH₂ in terms of the onset dehydrogenation temperature. The desorption temperature of MgH₂ + 10 wt.% SrFe₁₂O₁₉ decreased to about 270 °C compared to the 350 °C and 420 °C for as-milled and as-received MgH_2 , respectively. The de/rehydrogenation kinetics of MgH_2 also improved after doping with SrFe₁₂O₁₉. Increasing the doping amount of SrFe₁₂O₁₉ to 15, 20 and 50 wt.% initiated negative effects, such as lower capacity and slower sorption rates. From the Kissinger plot differential scanning calorimetry, the apparent activation energy was 133.31 kJ/mol for as-milled MgH₂ and 114.22 kJ/mol for MgH₂ + 10 wt.% SrFe₁₂O₁₉, indicating that SrFe₁₂O₁₉ addition decreased the activation energy for hydrogen desorption of MgH₂. From the X-ray diffraction results, it is believed that the formation of a new phases of Fe, $MgFe_2O_4$ and SrO during the dehydrogenation process might be responsible for the catalytic effects which further enhanced the hydrogen storage properties of MgH₂.

1. Introduction

Being environmentally-friendly, numerous efforts have been made to realize the potential of hydrogen as a major energy carrier, in both mobile and stationary applications.¹ However, hydrogen storage is still a major problem and three main approaches currently exist, high pressure, cryogenics and chemical compounds, which reversibly release H₂ upon heating (solid-state storage). Storing hydrogen in a solid state offers several benefits over compressed and liquid forms, particularly in terms of safety, cost and high volumetric and gravimetric density.² Various types of material have been proposed and are currently under investigation. Among them MgH₂ has been a research hotspot due to its large gravimetric density (7.6 wt.%), superior reversibility and low cost.^{3,4}

Nevertheless, its high temperature of hydrogen release (> 400 °C) and slow rehydration and dehydration kinetics are two main problems that limit the use of MgH₂ as a hydrogen storage material in practical applications.⁵ In an attempt to improve the hydrogen storage properties of MgH₂, a lot of studies have been performed. One of the strategies is the addition of a catalyst. Various catalysts have been doped into MgH₂ via ball milling, such as metals,⁶⁻¹⁰ metal oxides,¹¹⁻ ¹⁵ metal halides,¹⁶⁻²³ carbon-based materials,^{24, 25} and alloys.²⁶⁻²⁸ To date, metal oxides, especially the ternary oxide known as ferrite, have attracted attention because of the role they play in enhancing the hydrogen storage properties of materials.

In a previous report by Wan et al.,²⁹ the dehydrogenation performance of MgH₂ was significantly improved after doping with NiFe₂O₄ nanoparticles. Meanwhile, Li et al.³⁰ also reported that addition of MnFe₂O₄ nanoparticles significantly enhanced the dehydrogenation properties of MgH₂. Furthermore, in a study by Zhang et al.³¹ on the dehydrogenation mechanism of ball milled MgH₂ doped with ferrite nanoparticles (CoFe₂O4, ZnFe₂O4, MnFe₂O4

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and $Mn_{0.5}Zn_{0.5}Fe_2O_4$), the result indicated that all ferrites can significantly reduce the desorption temperature of MgH₂, and that CoFe₂O₄ showed the best catalytic performance of the ferrites. Shang et al.³² also found that addition of 7 mol% CoFe₂O₄ enhanced the hydrogen storage properties of MgH₂ by reducing the onset desorption temperature to 160 °C, 200 °C lower than as-milled MgH₂.

Although some ferrites have a positive effect on the hydrogen storage properties of MgH₂, they still do not fulfil the requirements for practical application as suitable hydrogen storage materials. Therefore, it is important to find other types of catalyst that can improve the hydrogen storage properties of MgH₂. Therefore, in this study another type of ferrite, $SrFe_{12}O_{19}$, was selected as a catalyst for MgH₂. There is no existing research into the effect of $SrFe_{12}O_{19}$ nanoparticles on MgH₂ properties. A recent study suggests that improvement in the hydrogen storage properties of MgH₂ doped with 7 mol% NiFe₂O₄ is related to in situ formed intermetallic Fe₇Ni₃ and (Fe,Ni) phases from the reaction between NiFe₂O₄ and MgH₂ during the desorption process, and that these phases act as a real catalyst.²⁹ So, it can be speculated that $SrFe_{12}O_{19}$ reacts with MgH₂ during the desorption process to form a new active species.

In this work, MgH₂ was mixed with SrFe₁₂O₁₉ to improve its hydrogen storage properties. The aim was to combine the in situ active species factors and thus enhance the de/hydrogenation properties of MgH₂. The hydrogen storage properties and reaction pathways of MgH₂ were investigated using Sievert-type pressure-composition-temperature (PCT) apparatus, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The possible mechanism behind the catalytic effect of SrFe₁₂O₁₉ on MgH₂ is also discussed.

2. Experimental Details

2.1 Preparation of samples

The starting maetrials, MgH₂ (98% purity), SrFe₁₂O₁₉ were purchased from Sigma-Aldrich and were used as received. All handling of the powder, including weighing and loading, was performed in an argon atmosphere using an MBraun Unilab glovebox to prevent from humidity and oxidation. The MgH₂ powder was ball milled with different wt.% of SrFe₁₂O₁₉ (5, 10, 15, 20 and 50 wt.%) in a planetary ball mill (NQM-0.4) for 1 h, by milling for 15 min, resting for 2 min and then milling for another 15 min. This process was conducted in 3 cycles in a different direction at a rotation speed of 400 rpm using hardened stainless steel vials and stainless steel balls. The ratio of the weight of the balls to the weight of the powder was 40:1.

2.2 Characterizations of sample

desorption (TPD) rehydrogenation For the temperature-programmed and the and dehydrogenation kinetic measurements, about 100 mg of the sample was loaded into a sample vessel in the glovebox. The experiments were performed in a Sievert-type PCT apparatus (Advanced Material Corporation). For the TPD experiment, all the samples were heated in a vacuum chamber and the amount of desorbed hydrogen was measured to determine the lowest decomposition temperature. The heating rate for the TPD experiment was 5 °C/min and the samples were heated from 25 °C to 450 °C. The de/rehydrogenation kinetics measurements were conducted at the desired temperature with initial hydrogen pressures of 1.0 atm and 30 atm, respectively.

The phase structures of the samples before and after desorption as well as after rehydrogenation were performed using a Rigaku MiniFlex X-ray diffractometer with Cu K_{α} radiation. θ -2 θ scans were carried out over diffraction angles from 20° to 80° at a speed of 2.00

°/min. All the samples were prepared in the glovebox in order to minimise the oxidation of the sample. To avoid exposure to the air during the measurement, the sample was spread uniformly on the sample holder and covered with scotch tape and sealed in plastic wrap.

Differential scanning calorimetry (DSC) analysis of the dehydrogenation process was carried out on a Mettler Toledo TGA/DSC 1. About 2–6 mg of sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove box to the DSC apparatus. An empty alumina crucible was used as the reference material. The samples were heated from room temperature to desire temperature under an argon flow of 50 ml/min, and different heating rates were used. The microstructures of the samples were characterized by using a scanning electron microscope (SEM; JEOL JSM-6360LA) by setting the samples on carbon tape and then coating them with gold spray under a vacuum

3. Results and Discussion

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3.1 Dehydrogenation temperature

Fig. 1 shows the TPD patterns for the dehydrogenation of as-received MgH₂, as-milled MgH₂, MgH₂ + 5 wt.% SrFe₁₂O₁₉, MgH₂ + 10 wt.% SrFe₁₂O₁₉, MgH₂ + 15 wt.% SrFe₁₂O₁₉, MgH₂ + 20 wt.% SrFe₁₂O₁₉ and MgH₂ + 50 wt.% SrFe₁₂O₁₉. The as-received MgH₂ started to release hydrogen at about 420 °C, with a total dehydrogenation capacity of 7.42 wt.% H₂ by 450 °C. After milling, the onset desorption temperature of MgH₂ was reduced to about 350 °C with the total capacity of hydrogen desorbed about 6.68 wt.%, indicating that the milling process also influences the onset desorption temperature of MgH₂, as reported by Huot et al.³³ It is obvious that after doping with different percentages of SrFe₁₂O₁₉ the onset desorption

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temperature of MgH₂ dramatically reduced compared with that as-milled and as-received. With 5 wt.% SrFe₁₂O₁₉ the onset desorption temperature initiated at about 300 °C, but the addition of 10 wt.% caused a reduction to 270 °C. By increasing the doping amount of SrFe₁₂O₁₉ to 15 and 20 wt.%, the desorption temperature reduced to about 285 °C for both samples. Meanwhile, by increasing the additive amount to 50 wt.%, hydrogen started to desorb at about 300 °C but with a reduction in released hydrogen content. It can be speculated that when the desorption capacity of the samples with 20 and 50 wt.% SrFe₁₂O₁₉ dropped slightly to about 4.7 wt.%, this was due to the excessive catalytic effect of added amounts of SrFe₁₂O₁₉.

3.2 De/rehydrogenation kinetics

Isothermal dehydrogenation kinetic curves for the as-milled MgH₂ and MgH₂ doped with 5, 10, 15, 20 and 50 wt.% SrFe₁₂O₁₉ were studied at a constant temperature of 320 °C under 1 atm pressure, as shown in Fig. 2. The results show that the samples doped with 5 and 10 wt.% SrFe₁₂O₁₉ released 2.8 and 4.3 wt.% hydrogen, respectively, within 15 min. Meanwhile, for the samples doped with 15 and 20 wt.% SrFe₁₂O₁₉, the capacity of hydrogen released was about 2.1 wt.% for both samples over the same time period. By increasing the SrFe₁₂O₁₉ content to 50 wt.%, the amount of hydrogen released reduced to 1.9 wt.% in 15 min and about 3.1 wt.% after 60 min. In contrast, only 0.2 wt.% hydrogen was released from as-milled sample at this temperature in 15 min. It can be seen that the addition of SrFe₁₂O₁₉ improved the dehydrogenation kinetics of MgH₂ and that samples doped with 10 wt.% SrFe₁₂O₁₉ showed the fastest desorption.

In order to investigate the reversibility of the samples, isothermal rehydrogenation kinetics for as-milled MgH_2 and doped- MgH_2 were measured at a constant temperature of 320°C, under a 30 atm H₂ pressure, as shown in Fig. 3. It is obvious that the MgH_2 doped with 5

and 10 wt.% SrFe₁₂O₁₉ had better rehydrogenation kinetics than undoped MgH₂. The samples doped with 5 and 10 wt.% SrFe₁₂O₁₉ absorbed approximately 4.6 and 4.8 wt.% hydrogen, respectively, within 1 h, while the hydrogen absorbed by the as-milled MgH₂ was about 4.2 wt.% under the same conditions. However, the samples of MgH₂ doped with 15 and 20 wt.% SrFe₁₂O₁₉ showed slow rehydrogenation kinetics compared with MgH₂, with only 3.6 wt.% and 3.1 wt.% hydrogen absorbed within 1 h, respectively. When the amount of SrFe₁₂O₁₉ was increased to 50 wt.%, the sample only absorbed about 2.8 wt.% hydrogen at 1 h, i.e. a slower absorption rate than as-milled MgH₂ and MgH₂ doped with 15 and 20 wt.% SrFe₁₂O₁₉. The decreasing hydrogen capacity and slower rehydrogenation kinetics in the 15, 20 and 50 wt.% samples was due to a superfluous catalytic effect brought about by the relatively large amount of added SrFe₁₂O₁₉, blocking the diffusion path of hydrogen to some extent, and thereby reducing the reaction between Mg and hydrogen.³⁴ This same phenomenon was reported in our previous paper ³. These results indicate that the addition of a minimum amount of SrFe₁₂O₁₉ can also improve the rehydrogenation kinetics of MgH₂.

Therefore, the results of the onset decomposition temperature reduction and hydrogen sorption kinetics, show that 10 wt.% $SrFe_{12}O_{19}$ is optimum for enhancement of MgH₂ hydrogen storage properties. Thus, this sample was chosen for further analysis to determine exactly how this catalyst affects MgH₂ properties.

3.3 Differential Scanning Calorimetry

Fig. 4 presents the thermal properties of as-received MgH₂, as-milled MgH₂ and MgH₂ + 10 wt.% SrFe₁₂O₁₉, identified by DSC at heating rate of 20°C/min within a temperature range of 25–500°C and under an argon flow of 50 ml/min. The DSC curves of all samples display only a single strong endothermic peak which corresponds to the decomposition of MgH₂. The DSC

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curve of as-received MgH₂ shows the peak temperature at approximately 458.4°C. Meanwhile, the hydrogen desorption temperature of the as-milled MgH₂ and MgH₂ + 10 wt.% SrFe₁₂O₁₉ show the peak of the DSC curves shifted to the lower temperatures compared with as-received MgH₂. The DSC curves for the as-milled MgH₂ and MgH₂ + 10 wt.% SrFe₁₂O₁₉ samples had strong endothermic peaks at 426.7°C and 409.5°C, which decreased by approximately 31.7°C and 48.9°C, respectively. The reduction of the peak temperature in the DSC results indicate that the dehydrogenation properties of MgH₂ were significantly enhanced by adding SrFe₁₂O₁₉. However, the onset desorption temperature of the samples from the DSC results were slightly higher than from TPD. These phenomena may be due to the different atmospheres and heating rates used in the two types of measurements as explained in our previous paper.³⁵⁻³⁸

In order to determine the effects of $SrFe_{12}O_{19}$ addition on the activation energy of MgH₂, Kissinger analysis³⁹ was used according to the following equation:

$$\ln[\beta/T_{\rm p}^{2}] = -E_{\rm A}/RT_{\rm p} + A \tag{1}$$

where β is the heating rate, T_p is the peak temperature in the DSC curve, *R* is the gas constant, and *A* is a linear constant. Thus, the activation energy, *E*_A, could be obtained from the slope in a plot of $\ln[\beta/T_p^2]$ versus 1000/*T*_p. The DSC traces at different heating rates for as-received MgH₂, as-milled MgH₂ and MgH₂ + 10 wt. % SrFe₁₂O₁₉ used for calculation of the activation energy, *E*_A, are shown in Fig. 5.

From the Kissinger plot of the DSC data, Fig. 6, the apparent activation energy for the asreceived MgH₂ and as-milled MgH₂ was found to be 183.0 kJ/mol and 133.3 kJ/mol, respectively. Meanwhile, the apparent activation energy for MgH₂ + 10 wt. % SrFe₁₂O₁₉ was 114.2 kJ/mol, significantly lower by comparison than the other samples which were reduced by

68.8 and 19.1 kJ/mol, respectively. This result indicates that the apparent activation energy is reduced after doping with $SrFe_{12}O_{19}$ and thus the dehydrogenation behaviour of MgH₂ improves.

3.4 Scanning Electron Microscope

Fig. 7 shows the morphologies of the as-received MgH₂, as-received SrFe₁₂O₁₉, as-milled MgH₂ and as-milled MgH₂ + 10 wt.% SrFe₁₂O₁₉. The SEM images show that the as-received MgH₂ particles had an angular shape, with an average particle size larger than 100 μ m. Meanwhile, the particle size of the as-received SrFe₁₂O₁₉ was smaller than 5 μ m. In addition, the MgH₂ particle size drastically reduced after ball milling for 1 h. However, the particle size was not homogenous and some agglomeration existed. By comparison, the MgH₂ sample doped with 10 wt.% SrFe₁₂O₁₉ had a smaller particle size and appeared to have less agglomeration. It has been reported that reduction in particle agglomeration and growth results in improvement of the hydrogen storage properties of light metal hydrides ⁴⁰. Meanwhile, a smaller particle size helps to improve hydrogen absorption and desorption, as it reduces the diffusion length and offers a larger particle surface.^{34, 41} Hence, it can be speculated that the hydrogen storage properties of MgH₂ are improved after adding the SrFe₁₂O₁₉ due to a reduction in particle size and less agglomeration.

3.5 X-ray diffraction

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To investigate the catalyst effect on the improvement of MgH₂, Fig. 8 represents the XRD pattern of as-milled MgH₂ + 10 wt.% SrFe₁₂O₁₉ after 1 h ball milling, after dehydrogenation at 450 °C and after rehydrogenation at 320 °C under 30 atm. The result shows that after 1 h ball milling, Fig. 8 (a), in addition to the MgH₂ peaks, a few peaks corresponding to the SrFe₁₂O₁₉ phase exist. After dehydrogenation at 450 °C, Fig. 8 (b), there was a distinct Mg

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peak, indicating that the dehydrogenation of MgH_2 was complete. The transformation of MgH_2 to Mg is represented by the following equation:

$$MgH_2 \rightarrow Mg + H_2$$
 (2)

Meanwhile, new diffraction peaks of MgO, MgFe₂O₄ and Fe were detected after the dehydrogenation process, indicating that MgH₂ and SrFe₁₂O₁₉ may have reacted. For the rehydrogenated sample, Fig. 8 (c), it can be seen that the Mg peak was largely transformed into MgH₂. The peaks of MgFe₂O₄ and Fe, with a small amount of MgO, were still present after the rehydrogenation process.

In order to investigate the phase structure in more detail, a sample of MgH₂ doped with 50 wt.% SrFe₁₂O₁₉ was prepared, as only slight MgFe₂O₄ and Fe peaks were detected and no Srcontaining phase appeared in the XRD phase composition of the 10 wt.% SrFe₁₂O₁₉. Fig. 9 shows the XRD patterns of MgH₂ doped with 50 wt.% SrFe₁₂O₁₉ after 1 h ball milling, after dehydrogenation at 450 °C, and after rehydrogenation at 320 °C. The results indicate that after 1 h ball milling, the peak intensity of MgH₂ and SrFe₁₂O₁₉ gradually enhanced after increasing the amount of SrFe₁₂O₁₉ to 50 wt.%, Fig. 9 (a), compared to the MgH₂ + 10 wt.% SrFe₁₂O₁₉ sample. After dehydrogenated at 450 °C, the diffraction peaks of Mg slightly decline and those of the Fe, MgFe₂O₄ and MgO phases are more discernible, while a new phase of SrO appears due to the higher SrFe₁₂O₁₉ concentration. The MgH₂ + 10 wt.% SrFe₁₂O₁₉ sample shows no Sr-containing species. Meanwhile, after rehydrogenated at 320 °C, the Fe, MgFe₂O₄ and SrO diffraction peaks remain unchanged and the Mg peak is largely transformed to MgH₂. MgO is still observed, probably due to oxygen contamination during sample preparation. From this result, it can be assumed that MgH₂ reacts with SrFe₁₂O₁₉ during the heating process forming Fe, MgFe₂O₄ and

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$$9MgH_2 + 2SrFe_{12}O_{19} \rightarrow 9MgFe_2O_4 + 2SrO + 6Fe + 9H_2$$
(3)

The standard state free energy of reaction, ΔG° , can be calculated from the standard state free energies using the equation below:

$$\Delta G^{\circ} = \sum \Delta G^{\circ}{}_{\text{fproducts}} - \sum \Delta G^{\circ}{}_{\text{freactants}}$$
(4)

The values of standard Gibbs free energy, ΔG°_{f} , of MgH₂, SrFe₁₂O₁₉, MgFe₂O₄ and SrO are -35.98, -5015.88, -1317.12 and -562.41 kJ/mol, respectively, have been obtained from the literature.⁴² Thus, by using eqn (4), the total change, ΔG , associated with the reaction in equation (3) will be -2623.34 kJ/mol of MgH₂. The possibility of the reaction stated in eqn (3) is proven by the results obtained from the thermodynamic potentials.

Based on the above analyses, the improvement in hydrogen storage properties acquired in this study may be attributed to a few factors. First, the reduction in particle size after ball milling and addition of a catalyst may contribute to a high density of surface defects and more grain boundaries. It is believed that a large number of defects introduces a large number of nucleation sites at the surface of MgH₂ and provides hydrogen diffusion channels for dehydrogenation.³⁰

Second, the new active species of Fe, MgFe₂O₄, and SrO, formed after de/rehydrogenation, might act as real catalysts for improving the hydrogen sorption properties of MgH₂ as they can create surface activation and form a large number of nucleation sites at the surface of the MgH₂ matrix.⁴¹ The in situ Fe particles, with a higher peak intensity than the MgFe₂O₄ and SrO species as shown in the XRD pattern, may play an important role as it has been reported that Fe is one of

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the good catalysts for improvement in MgH₂ hydrogen storage properties.^{43, 44} Bassetti et al.⁴⁵ reported that proper combination of Fe and MgH₂ leads to a significant increase in the desorption kinetics of MgH₂ where almost the whole H content is released in less than 1000 seconds at 300 °C. Meanwhile, previous studies also discuss transition metal catalysts such as Fe, Ni, Co and Pd that play an important role in enhancing MgH₂ hydrogen storage properties.⁴⁶⁻⁴⁸ In addition, MgFe₂O₄ and SrO may also have an extra catalytic effect on MgH₂. Previous studies have shown that MgH₂ with metal oxide addition gives as good or even faster hydrogenation kinetics than their metallic counterpart.^{12, 49, 50} So, the catalytic effect of Fe may further combine with the catalytic functions of MgFe₂O₄ and SrO to generate a synergetic catalytic effect. Thus, it is reasonable to conclude that these newly developed products act as real catalysts and doping with SrFe₁₂O₁₉ can result in significant improvement in MgH₂ desorption properties.

4. Conclusion

The effects of different contents (5, 10, 15, 20 and 50 wt.%) of an $SrFe_{12}O_{19}$ additive on the hydrogen storage properties of MgH₂, prepared by the ball milling method, were investigated for the first time. It was found that the hydrogen sorption properties of MgH₂ improved significantly after $SrFe_{12}O_{19}$ addition, and that compared with un-doped MgH₂, 10 wt.% $SrFe_{12}O_{19}$ resulted in optimum performance in terms of onset dehydrogenation temperature and de/rehydrogenation kinetics. The onset desorption temperature of MgH₂ + 10 wt.% $SrFe_{12}O_{19}$ was reduced to 270 °C, decreasing by about 80 °C and 150 °C for as-milled and as-received MgH₂, respectively. The isothermal dehydrogenation kinetics show that a 10 wt.% $SrFe_{12}O_{19}$ doped sample can release 4.3 wt.% H₂ in 15 min, whereas as-milled MgH₂ can only release 0.2 wt.% within the same time. Regarding rehydrogenation kinetics, the sample doped with 10 wt.% $SrFe_{12}O_{19}$ absorbed

approximately 4.8 wt.% hydrogen within 1 h at 320 °C, while the hydrogen absorbed by the asmilled MgH₂ was about 4.3 wt.% under the same conditions. From the Kissinger plot of DSC, the apparent activation energies for as-received MgH₂ and as-milled MgH₂ were 183 kJ/mol and 133.31 kJ/mol, respectively. This reduced to 114.22 kJ/ mol for MgH₂ + 10 wt.% SrFe₁₂O₁₉, indicating that SrFe₁₂O₁₉ addition decreased the activation energy for hydrogen desorption of MgH₂. In addition, particle size reduction and less agglomeration may help improve the hydrogen sorption properties of MgH₂. From the XRD results, it is believed that the formation of a new species of Fe, MgFe₂O₄ and SrO during ball milling or the de/rehydrogenation process might actually be responsible for the catalytic effects and thus, further enhanced the hydrogen storage properties of the MgH₂. It can be concluded that SrFe₁₂O₁₉ is one of the promising additives for MgH₂ as it tends to reduce the onset desorption temperature and significantly improves the kinetic performance.

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References

- 1. L. Mai, X. Tian, X. Xu, L. Chang and L. Xu, *Chem. Rev.*, 2014, **114**, 11828-11862.
- 2. L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353-358.
- 3. M. Ismail, Int. J. Hydrogen Energy, 2014, 39, 2567-2574.
- 4. B. Sakintuna, F. Lamari-Darkrim and M. Hirscher, *Int. J. Hydrogen Energy*, 2007, **32**, 1121-1140.
- 5. G. Principi, F. Agresti, A. Maddalena and S. Lo Russo, *Energy*, 2009, **34**, 2087-2091.
- H. Gasan, O. N. Celik, N. Aydinbeyli and Y. M. Yaman, *Int. J. Hydrogen Energy*, 2012, 37, 1912-1918.
- 7. A. Ranjbar, Z. P. Guo, X. B. Yu, D. Attard, A. Calka and H. K. Liu, *Int. J. Hydrogen Energy*, 2009, **34**, 7263-7268.
- 8. L. E. A. Berlouis, P. Honnor, P. J. Hall, S. Morris and S. B. Dodd, *J. Mater. Science*, 2006, **41**, 6403-6408.
- 9. L. Z. Ouyang, X. S. Yang, M. Zhu, J. W. Liu, H. W. Dong, D. L. Sun, J. Zou and X. D. Yao, *J. Phys. Chem. C*, 2014, **118**, 7808-7820.
- 10. V. Koteski, J. Belosevic-Cavor, K. Batalovic, J. Radakovic and A. Umicevic, *RSC Adv.*, 2015, **5**, 34894-34899.
- 11. N. Juahir, N. S. Mustafa, A. Sinin and M. Ismail, *RSC Adv.*, 2015, 5, 60983-60989.
- 12. K. S. Jung, E. Y. Lee and K. S. Lee, J. Alloys Compd., 2006, 421, 179-184.
- 13. V. V. Bhat, A. Rougier, L. Aymard, G. A. Nazri and J. M. Tarascon, *J. Alloys Compd.*, 2008, **460**, 507-512.
- 14. A. Patah, A. Takasaki and J. S. Szmyd, Int. J. Hydrogen Energy, 2009, 34, 3032-3037.
- 15. B.-H. Chen, Y.-S. Chuang and C. o.-K. Chen, J. Alloys Compd., 2016, 655, 21-27.
- 16. M. Ismail, *Energy*, 2015, **79**, 177-182.
- 17. M. Ismail, N. S. Mustafa, N. Juahir and F. A. H. Yap, *Mater. Chem. Phys.*, 2016, **170**, 77-82.

- 18. V. V. Bhat, A. Rougier, L. Aymard, X. Darok, G. Nazri and J. M. Tarascon, J. Power Sources, 2006, **159**, 107-110.
- 19. I. E. Malka, T. Czujko and J. Bystrzycki, Int. J. Hydrogen Energy, 2010, 35, 1706-1712.
- 20. I. E. Malka, M. Pisarek, T. Czujko and J. Bystrzycki, *Int. J. Hydrogen Energy*, 2011, **36**, 12909-12917.
- 21. L. Z. Ouyang, Z. J. Cao, H. Wang, J. W. Liu, D. L. Sun, Q. A. Zhang and M. Zhu, J. Alloys Compd., 2014, 586, 113-117.
- 22. N. S. Mustafa and M. Ismail, Int. J. Hydrogen Energy, 2014, **39**, 15563-15569.
- 23. F. A. Halim Yap, N. S. Mustafa and M. Ismail, *RSC Adv.*, 2015, **5**, 9255-9260.

- 24. A. Ranjbar, M. Ismail, Z. P. Guo, X. B. Yu and H. K. Liu, *Int. J. Hydrogen Energy*, 2010, **35**, 7821-7826.
- 25. M. Lototskyy, J. M. Sibanyoni, R. V. Denys, M. Williams, B. G. Pollet and V. A. Yartys, *Carbon*, 2013, **57**, 146-160.
- 26. X. B. Yu, Y. H. Guo, H. Yang, Z. Wu, D. M. Grant and G. S. Walker, *J. Phys. Chem. C*, 2009, **113**, 5324-5328.
- 27. X. B. Yu, Y. H. Guo, Z. X. Yang, Z. P. Guo, H. K. Liu and S. X. Dou, *Scripta Mater.*, 2009, **61**, 469-472.
- 28. X. B. Yu, Z. X. Yang, H. K. Liu, D. M. Grant and G. S. Walker, *Int. J. Hydrogen Energy*, 2010, **35**, 6338-6344.
- 29. Q. Wan, P. Li, J. Shan, F. Zhai, Z. Li and X. Qu, J. Phys. Chem. C, 2015, 119, 2925-2934.
- 30. P. Li, Q. Wan, Z. Li, F. Zhai, Y. Li, L. Cui, X. Qu and A. A. Volinsky, *J. Power Sources*, 2013, **239**, 201-206.
- 31. J. Zhang, J. Shan, P. Li, F. Zhai, Q. Wan, Z. Liu and X. Qu, J. Alloys Compd., 2015, 643, 174-180.
- 32. J. Shan, P. Li, Q. Wan, F. Zhai, J. Zhang, Z. Li, Z. Liu, A. A. Volinsky and X. Qu, *J. Power Sources*, 2014, **268**, 778-786.
- 33. J. Huot, G. Liang, S. Boily, A. Van Neste and R. Schulz, *J. Alloys Compd.*, 1999, **293-295**, 495-500.

- 34. A. Ranjbar, Z. P. Guo, X. B. Yu, D. Wexler, A. Calka, C. J. Kim and H. K. Liu, *Mater. Chem. Phys.*, 2009, **114**, 168-172.
- 35. M. Ismail, Y. Zhao, X. B. Yu and S. X. Dou, *Int. J. Hydrogen Energy*, 2010, **35**, 2361-2367.
- M. Ismail, Y. Zhao, X. B. Yu, A. Ranjbar and S. X. Dou, *Int. J. Hydrogen Energy*, 2011, 36, 3593-3599.
- 37. M. Ismail, Y. Zhao, X. B. Yu, I. P. Nevirkovets and S. X. Dou, *Int. J. Hydrogen Energy*, 2011, **36**, 8327-8334.
- 38. M. Ismail, Y. Zhao, X. B. Yu and S. X. Dou, Int. J. Electroactive Mater., 2013, 1, 13-22.
- 39. H. E. Kissinger, Anal. Chem., 1957, 29, 1702-1706.
- 40. M. Ismail, N. Juahir and N. S. Mustafa, J. Phys. Chem. C, 2014, 118, 18878-18883.
- 41. F. Zhai, P. Li, A. Sun, S. Wu, Q. Wan, W. Zhang, Y. Li, L. Cui and X. Qu, J. Phys. Chem. C, 2012, **116**, 11939-11945.
- 42. http://www.drjez.com/uco/.../StandardThermodynamicValues.
- 43. S. Deledda, A. Borissova, C. Poinsignon, W. J. Botta, M. Dornheim and T. Klassen, *Phys. Chem. Chem. Phys.*, 2005, **404-406**, 409-412.
- 44. A. Montone, A. Aurora, D. M. Gattia and M. V. Antisari, *Catalysts*, 2012, 2, 400-411.
- 45. A. Bassetti, E. Bonetti, L. Pasquini, A. Montone, J. Grbovic and M. Vittori Antisari, *Eur. Phys. J. B*, 2005, **43**, 19-27.
- 46. J.-l. Bobet, E. Akiba, Y. Nakamura and B. Darriet, *Int. J. Hydrogen Energy*, 2000, 25, 987-996.
- 47. N. Hanada, T. Ichikawa and H. Fujii, J. Phys. Chem. B, 2005, 109, 7188-7194.
- 48. N. N. Sulaiman, N. S. Mustafa and M. Ismail, *Dalton Trans.*, 2016, **45**, 7085-7093.
- 49. G. Barkhordarian, T. Klassen and R. Bormann, Scripta Mater., 2003, 49, 213-217.
- 50. Gupta R, Agresti F, Russo SL, Maddalena A, Palade P and P. G, *J. Alloys Compd.*, 2008, **450**, 310-313.

Figure captions

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Fig. 1 TPD patterns for the dehydrogenation of the as-received MgH₂, as-milled MgH₂ and MgH₂ doped with 5 wt. %, 10 wt. %, 15 wt. %, 20 wt. % and 50 wt. % SrFe₁₂O₁₉.

Fig. 2 Isothermal dehydrogenation kinetic of the as-milled MgH₂ and MgH₂ doped with 5 wt.%,

10 wt.%, 15 wt.%, 20 wt. % and 50 wt. % SrFe₁₂O₁₉ at 320 °C.

Fig. 3 Isothermal rehydrogenation kinetic of the as-milled MgH₂ and MgH₂ doped with 5 wt.%, 10 wt.%, 15 wt.%, 20 wt. % and 50 wt. % SrFe₁₂O₁₉ at 320 °C under 30 atm.

Fig. 4 DSC traces of as-received MgH₂, as-milled MgH₂ and MgH₂ + 10 wt. % SrFe₁₂O₁₉ (heating rate: 20 °C/min; argon flow: 50 mL/min).

Fig. 5 DSC traces at different heating rates for as-received MgH₂, as-milled MgH₂, and MgH₂ + 10 wt. % SrFe₁₂O₁₉.

Fig. 6 Kissinger plot of dehydrogenation for as-received MgH₂, as-milled MgH₂, and MgH₂ + 10 wt. % SrFe₁₂O_{19.}

Fig. 7 SEM images of as-received MgH₂, as-received SrFe₁₂O₁₉, as-milled MgH₂ and MgH₂+ 10 wt.% SrFe₁₂O₁₉.

Fig. 8 X-ray diffraction patterns of MgH₂+ 10 wt.% SrFe₁₂O₁₉ (a) after 1 h ball milling, (b) after dehydrogenation at 450 °C , and (c) after rehydrogenation at 320 °C.

Fig. 9 X-ray diffraction patterns of MgH₂+ 50 wt.% SrFe₁₂O₁₉ (a) after 1 h ball milling, (b) after dehydrogenation at 450 °C , and (c) after rehydrogenation at 320 °C.









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Figure 7



Figure 8



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Graphical Table of Contents (GTOC)

The desorption temperature of $MgH_2 + 10$ wt.% $SrFe_{12}O_{19}$ decreased to about 270°C compared to the 350°C and 420°C for as-milled and as-received MgH₂, respectively. The activation energy calculated by Kissinger analysis for hydrogen desorption decreased to 114.2 kJ/mol after Fe₂O₃ was added compared with the un-doped 4MgH₂-Li₃AlH₆ composite, which was 133.3 kJ/mol.

