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# Simultaneous improvement of kinetics and thermodynamics based on SrF<sub>2</sub> and SrF<sub>2</sub>@Gr additives on hydrogen sorption in MgH<sub>2</sub>†

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Herein we describe and discuss the effect of significant advantages of the alkaline earth fluoride additive SrF<sub>2</sub> on the improvement of the kinetics, thermodynamics, and cyclability of the frontier hydrogen storage material MgH<sub>2</sub>. Strontium fluoride, SrF<sub>2</sub>, which has been used as an additive for the first time in the present study, has an elemental electronegativity difference of 3.04 (the highest amongst the fluorides) as compared to 2.38 for NbF<sub>5</sub>, one of the best-known catalysts so far for MgH<sub>2</sub>. Therefore, SrF<sub>2</sub> is highly ionic and will readily react with MgH<sub>2</sub>, which is not only ionic but also has a polar covalent character. SrF<sub>2</sub> reacts with MgH<sub>2</sub> to yield magnesium fluoride (MgF<sub>2</sub>) and strontium hydride (SrH<sub>2</sub>) which act as catalysts. The present investigations have revealed that both (MgF<sub>2</sub> + SrH<sub>2</sub>) and their graphene templated version, (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr, work as better catalysts for MgH<sub>2</sub> than NbF<sub>5</sub>. Thus the desorption of H<sub>2</sub> from ball-milled MgH<sub>2</sub> catalyzed by (MgF<sub>2</sub> + SrH<sub>2</sub>) corresponds to 5.30 wt% in 15 min, and for (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr the desorption is 6.01 wt% in 15 min at 290 °C. Also, the onset desorption temperatures for MgH<sub>2</sub> with (MgF<sub>2</sub> + SrH<sub>2</sub>) and (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalysts are 261 °C and 231 °C, respectively, which are 95 °C and 125 °C lower than that for ball-milled MgH<sub>2</sub>. The H<sub>2</sub> absorption for (MgF<sub>2</sub> + SrH<sub>2</sub>) catalyzed MgH<sub>2</sub> is found to be 6.00 wt% in 5 min at 290 °C. For (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalyzed MgH<sub>2</sub> the hydrogen absorption is 6.16 wt% in 2 min at 290 °C. The change in desorption enthalpy for MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr is 67.60 kJ mol<sup>-1</sup> as compared to 74.84 kJ mol<sup>-1</sup> for MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>). The storage capacity for MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr remains ~6.00 wt% even after 15 cycles, which corresponds to excellent cyclability. A feasible catalytic mechanism arising from (MgF<sub>2</sub> + SrH<sub>2</sub>) and (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalysts on hydrogen sorption in MgH<sub>2</sub> has been proposed based on X-ray diffraction, Raman spectroscopy, Fourier transmission infrared spectroscopy, and transmission/scanning electron microscopic studies. The present study is the first of its type where absorption/desorption kinetics, thermodynamics, and cyclability for MgH<sub>2</sub> have all been improved by the use of the single additive SrF<sub>2</sub> and the derived catalyst MgF<sub>2</sub> + SrH<sub>2</sub>.

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## 1 Introduction

Since the dawn of civilization, energy demands of human beings have been mostly met by fossil fuels.<sup>1,2</sup> Even if the availability of

these can be assured until the end of this century, the deleterious effect which ensues due to the emission of CO<sub>2</sub> causing climate change may prohibit their use in the coming decades.<sup>3,4</sup> At present the CO<sub>2</sub> concentration in the atmosphere is 414 ppm.<sup>5</sup>

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† Electronic supplementary information (ESI) available: Fig. S1: XRD spectra of (a) MgH<sub>2</sub>, (b) MgH<sub>2</sub>-SrF<sub>2</sub> and (c) MgH<sub>2</sub>-SrF<sub>2</sub>@Gr. Fig. S2: FTIR spectra of (a) MgH<sub>2</sub>, (b) B.M. MgH<sub>2</sub>-SrF<sub>2</sub>, (c) Gr, (d) SrF<sub>2</sub>@Gr and (e) MgH<sub>2</sub>-SrF<sub>2</sub>@Gr. Fig. S3: XRD spectra of (a) Mg-(MgF<sub>2</sub> + SrH<sub>2</sub>) (1st dehydrogenation) and (b) Mg-SrF<sub>2</sub>@Gr (1st dehydrogenation). Fig. S4: Scanning electron micrographs of (a) B.M. MgH<sub>2</sub>-SrF<sub>2</sub>, (b) 1st desorption of B.M. MgH<sub>2</sub>-SrF<sub>2</sub> (Mg-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr), (c) B.M. MgH<sub>2</sub>-SrF<sub>2</sub>@Gr, and (d) after cycling of B.M. MgH<sub>2</sub>-SrF<sub>2</sub>@Gr (MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr), (e) EDAX spectra after cycling of the MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr sample and (f) elemental mapping after cycling of MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr. Fig. S5: XRD spectra of (a) MgH<sub>2</sub>-SrF<sub>2</sub>@Gr and (b) after 15th adsorption run of Mg/MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr. Fig. S6: DSC plot of ball milled MgH<sub>2</sub> for 25 h at different heating rates: (a) 5 °C min<sup>-1</sup>, (b) 7 °C min<sup>-1</sup> and (c) 10 °C min<sup>-1</sup>. (ii) Kissinger plot for the calculation of activation energy. Fig. S7: FTIR spectra of (a) Mg-(SrH<sub>2</sub>-MgF<sub>2</sub>)@Gr (1st dehydrogenation), (b) Mg-(SrH<sub>2</sub>-MgF<sub>2</sub>)@Gr (after 14 cycles of dehydrogenation) and (c) MgH<sub>2</sub>-(SrH<sub>2</sub>-MgF<sub>2</sub>)@Gr (after 15 cycles of rehydrogenation). See DOI: 10.1039/d1ma00012h



It has to be reduced to  $\sim 200$  ppm (50% of current levels) so that by 2050 the temperature change of the environment is no more than  $2^\circ\text{C}$ .<sup>6</sup> If climate change is not checked, the earth will become uninhabitable in a few decades. Another issue is the large gap between the supply and demand of energy. This continues to increase as the human population increases. The population of the earth will be 10 billion by the year 2050.<sup>7</sup> We need clean, abundant, and renewable energy that fulfills our energy demand for the long term. Decades of research have suggested that, out of various options, the most attractive candidate is hydrogen.<sup>8</sup> Hydrogen is produced from water, and it turns back to water upon high-temperature combustion, *e.g.*, IC engines or cold combustion in fuel cells. There has been a recent upsurge in research on the production, storage, and application of hydrogen. Out of these, the storage of hydrogen is the most crucial aspect, which cuts through production/distribution, safety, and application. The storage of hydrogen in the form of metal hydrides is the most efficient and safe mode of storage.<sup>9,10</sup> However, despite the intensive search for a hydride that fulfills the essential required limits, any viable hydride has not yet emerged. The limit required by the DOE for a solid-state storage system is 4.5 wt% and  $36\text{ g H}_2\text{ L}^{-1}$ .<sup>11</sup> Such a system limit can be achieved only if the storage material shows a storage capacity higher than 4.5 wt% and  $36\text{ g L}^{-1}$  of hydrogen. Research carried out in recent years suggests that  $\text{MgH}_2$  may be such a storage material. It has a gravimetric storage capacity of 7.6 wt% and a volumetric storage capacity of  $110\text{ g H}_2\text{ L}^{-1}$  and its storage is also reversible.<sup>12</sup> Mg is abundantly available on the earth's crust and in the sea. Thus it is a viable hydrogen material, but it has two hurdles related to high sorption temperature ( $\sim 400^\circ\text{C}$ ) and sluggish kinetics ( $< 1\text{ wt\% min}^{-1}$ ).<sup>13</sup>

In the aforementioned background, many studies have been conducted to overcome the aforementioned difficulties associated with  $\text{MgH}_2$ . Partial success has been achieved in these efforts.<sup>14</sup> The most useful way in which efforts have been made to lower sorption temperature and improve kinetics is through the use of catalysts/additives. The most deployed catalysts are transition metals such as Ti, Fe, Co, Ni, Mn, Nb, V, and Zr, and their compounds.<sup>15</sup> Regarding the transition metal compounds, oxides and halides are potential candidates. Out of these,  $\text{Nb}_2\text{O}_5$  and  $\text{NbF}_5$  have received particular attention. However, it has been found that the addition of  $\text{NbF}_5$  to  $\text{MgH}_2$  leads to a better hydrogen sorption behavior than that of  $\text{Nb}_2\text{O}_5$ .<sup>16,17</sup> It has been found that, during cycling at higher temperature,  $\text{Nb}_2\text{O}_5$  starts to get dissociated, leading to the formation of an increasing amount of  $\text{MgO}$ . In yet another study by Floriano *et al.*,<sup>18</sup> the superiority of  $\text{NbF}_5$  over  $\text{Nb}_2\text{O}_5$  in regard to the hydrogen desorption characteristics of  $\text{MgH}_2$  has been elucidated.  $\text{NbF}_5$  has been generally found to be a very effective catalyst for improving the hydrogen sorption characteristics of  $\text{MgH}_2$ .<sup>17</sup> The investigation carried out by Recham *et al.*<sup>19</sup> has shown that  $\text{NbF}_5$  is a better additive than  $\text{Nb}_2\text{O}_5$  as well as  $\text{NbCl}_5$  for enhancing the hydrogen sorption kinetics. A detailed study on the effect of several transition metal halides, including  $\text{NbF}_5$ , has been conducted by Malka *et al.*<sup>20,21</sup> They have found the significant effect of  $\text{NbF}_5$  on hydrogen sorption in  $\text{MgH}_2$ .

Only  $\text{ZrF}_4$  was found to be somewhat better than  $\text{NbF}_5$ .<sup>16,17,19–23</sup> These authors have also shown that, of the two halides  $\text{NbF}_5$  and  $\text{NbCl}_5$ , the former is a better additive for  $\text{MgH}_2$ .

More recently, Santiago *et al.*<sup>16</sup> conducted a detailed study of the effect of  $\text{NbF}_5$ , which led to the formation of  $\text{MgF}_2$  and  $\text{NbH}_{0.9}$ , on the hydrogen sorption kinetics in  $\text{MgH}_2$ . They have used two types of  $\text{NbH}_{0.9}$  catalyst: one formed on milling  $\text{MgH}_2$  with  $\text{NbF}_5$  and the other separately synthesized. They have shown that  $\text{NbF}_5$  exhibits excellent hydrogen sorption kinetics due to the homogeneous distribution of  $\text{NbH}_{0.9}$  in the form of fine particles in  $\text{MgH}_2$ . However, they have found a significant decrease in the achievable hydrogen storage capacity. Contrary to the studies of Santiago *et al.*,<sup>17</sup> Jain *et al.*<sup>23</sup> have found that, when  $\text{MgH}_2$  and  $\text{MgF}_2$  are milled together,  $\text{MgF}_2$  remains intact, does not dissociate and persists throughout the hydrogen sorption cycling. In these studies,  $(\text{MgH}_2 + \text{MgF}_2)$  has been shown to exhibit better hydrogen sorption than  $\text{MgH}_2$  alone.

Fluorine has an electronegativity of 3.95, which is the highest out of all elements. Hence fluorides will be highly ionic and react readily with  $\text{MgH}_2$ , which is ionic but also has a polar covalent character.<sup>24</sup> As outlined above, so far,  $\text{NbF}_5$  has been found to be the most suitable additive for  $\text{MgH}_2$ .<sup>17,19</sup> Here we have used a new fluoride  $\text{SrF}_2$ . This has a larger elemental electronegativity difference of 3.05 (Sr: 0.93 and F: 3.98) as compared to  $\text{NbF}_5$ , for which it is 2.38 (Nb: 1.60, F: 3.98). In fact,  $\text{SrF}_2$  has the largest electronegativity difference out of all non-radioactive fluorides. We have shown that  $\text{SrF}_2$  works as a significantly better additive for hydrogen sorption in  $\text{MgH}_2$ . The additive  $\text{SrF}_2$  reacts with  $\text{MgH}_2$  while it is heated for dehydrogenation and produces two compounds  $\text{MgF}_2$  and  $\text{SrH}_2$ . These remain stable and are present throughout the hydrogen sorption cycling and act as catalysts. They lead to the improvement of hydrogen sorption kinetics and thermodynamics. As a further factor for the improvement of hydrogen sorption in  $\text{MgH}_2$ , we have used graphene templation of  $\text{SrF}_2$  and  $(\text{MgF}_2 + \text{SrH}_2)$ .  $(\text{MgF}_2 + \text{SrH}_2)$  and  $(\text{MgF}_2 + \text{SrH}_2)\text{@Gr}$  catalyzed  $\text{MgH}_2$  show onset desorption temperatures of  $261^\circ\text{C}$  and  $231^\circ\text{C}$ , respectively, which are  $95^\circ\text{C}$  and  $125^\circ\text{C}$  lower than that of ball-milled  $\text{MgH}_2$ , for which it is  $356^\circ\text{C}$ .  $\text{MgH}_2$  catalyzed by  $(\text{MgF}_2 + \text{SrH}_2)\text{@Gr}$  shows superior dehydrogenation kinetics. It desorbs 6.01 wt% in 15 min at  $290^\circ\text{C}$ . It also shows better rehydrogenation kinetics by absorbing 6.16 wt% in 2 min at  $290^\circ\text{C}$  and 18 atm  $\text{H}_2$  pressure. The storage capacity remains  $\sim 6\text{ wt\%}$  even up to 15 cycles. Thus  $\text{MgH}_2\text{-(MgF}_2 + \text{SrH}_2)\text{Gr}$  shows excellent cyclability. Therefore, in contrast to earlier studies with  $\text{NbF}_5$ ,<sup>16</sup> the storage capacity remains intact during cycling with the  $\text{SrF}_2\text{@Gr}$  additive. The change in desorption enthalpy for  $\text{MgH}_2\text{-7 wt\% (MgF}_2 + \text{SrH}_2)$  and  $\text{MgH}_2\text{-7 wt\% (MgF}_2 + \text{SrH}_2)\text{@Gr}$  samples was found to be  $74.84\text{ kJ mol}^{-1}$  and  $67.60\text{ kJ mol}^{-1}$ , respectively. These are significantly lower than the desorption enthalpy of  $\text{MgH}_2$ , which is  $80.66\text{ kJ mol}^{-1}$ . It may be mentioned that earlier studies<sup>16</sup> employing the  $\text{MgF}_2\text{-NbH}_{0.9}$  catalyst do not suggest any improvement in enthalpy (thermodynamics). Also, in these studies, the storage capacity significantly decreases on cycling.<sup>16</sup> The present catalysts  $(\text{MgF}_2 + \text{SrH}_2)$  and  $(\text{MgF}_2 + \text{SrH}_2)\text{@Gr}$  lead to



the improvement of both the hydrogen sorption kinetics and thermodynamics of hydrogen sorption in  $\text{MgH}_2$ . The present study forms one of the few cases and, to the best of our knowledge, the first case for a fluoride-hydride catalyst which leads to the improvement of all hydrogen sorption characteristics, namely, kinetics, thermodynamics and cyclability.

## 2 Experimental section

### 2.1. Synthesis of $\text{SrF}_2@Gr$

Strontium fluoride (Alfa Aesar) was ball-milled at 180 rpm for 24 hours with a ball-to-powder ratio of 50:1 under 5 atm hydrogen pressure before further use. High quality graphene has been routinely produced in our laboratory.<sup>25</sup>  $\text{SrF}_2$  was templated on graphene using the following steps. Firstly, sodium dodecyl sulfate (SDS) (0.004 g), Gr (0.0145 g), and dimethylformamide (DMF) ( $\sim 50$  mL) were mixed. Then the resultant solution was mixed homogeneously by using an ultrasonicator at 20 kHz for 2 hours. Finally, 0.582 g of the  $\text{SrF}_2$  base material was added to the above solution, followed by sonication at room temperature until a homogeneous dark solution was formed. The material so obtained was dried overnight in a vacuum at 60 °C, collected, and characterized. The resulting material, as confirmed by XRD and Raman spectroscopy, corresponds to  $\text{SrF}_2@Gr$ . This was further used as the additive for hydrogen sorption in  $\text{Mg}/\text{MgH}_2$ . Our previous studies have shown the synthesis protocol and detailed procedure of graphene templation.<sup>26–28</sup>

### 2.2. Synthesis of $\text{MgH}_2$ admixed with graphene templated $\text{SrF}_2$ ( $\text{SrF}_2@Gr$ )

$\text{MgH}_2$  (99.99%) was purchased from Nanoshel (UK). 7 wt% of  $\text{SrF}_2@Gr$  was added to the pure  $\text{MgH}_2$  sample.  $\text{MgH}_2\text{-SrF}_2@Gr$  was synthesized by mechanical milling of  $\text{SrF}_2@Gr$  with  $\text{MgH}_2$ . The mixture was ball-milled at 180 rpm for 25 hours with a ball-to-powder ratio of 50:1 (by weight) using a Retsch PM 400 planetary ball miller. For brevity, instead of writing 7 wt%  $\text{SrF}_2$ , we will henceforth mention it simply as  $\text{SrF}_2$ . The quantity 7 wt% will be implied. Also, all samples including Mg alone were prepared through ball milling. Hence, we will not add the suffix B.M. to the samples and it is taken to be implied. The concentration of the additive ( $\text{SrF}_2@Gr$ ) was taken to be 7 wt% of  $\text{MgH}_2$ . It was found that 7 wt% of the additive ( $\text{SrF}_2@Gr$ ) is optimum (in terms of desorption temperature and hydrogen storage capacity) for hydrogen sorption in  $\text{Mg}/\text{MgH}_2$ . To avoid contamination from air during ball milling, the vial containing materials was filled with hydrogen gas with 5 atm pressure. All samples were transferred and loaded inside a  $\text{N}_2$  filled glove box (MBRAUN MB-10 compact) with  $\text{O}_2$  and  $\text{H}_2\text{O}$  levels  $< 1$  ppm.

### 2.3. Characterization techniques

For the structural characterization of the prepared samples, XRD data were collected with a Panalytical Empyrean X-ray diffractometer equipped with an area detector ( $256 \times 256$  pixels) at 0.02 °C

step size in  $2\theta$  range from 10°–110° with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5415 \text{ \AA}$ ) operated at 40 kV, 40 mA. All the samples were wholly covered with parafilm to prevent the sample reactions from atmospheric contamination during XRD. The microstructures of the samples were studied by transmission electron microscopy (TEM), and selected area electron diffraction (SAED) patterns using TEM: TECNAI 20 G<sup>2</sup> at an accelerating voltage of 200 kV. The surface morphology and energy dispersive X-ray analysis (EDAX) with the color mapping of elements of as-prepared samples was done by using a scanning electron microscope (SEM): FEI Quanta 200 with operating voltage 25 kV in a high vacuum ( $\sim 10^{-5}$  torr). Fourier transform infrared (FTIR) spectroscopy was carried out using a PerkinElmer (Spectrum 100) spectrometer in transmission mode with wavenumbers ranging from the mid-infrared region (400–4000  $\text{cm}^{-1}$ ).

The dehydrogenation properties of the as-prepared samples were analyzed by temperature-programmed desorption (TPD) at a heating rate of 3 °C  $\text{min}^{-1}$ . TPD analysis of the catalyzed and uncatalyzed  $\text{MgH}_2$  was started under vacuum ( $10^{-3}$  torr) using dynamic heating conditions with a precision of  $\pm 0.2$  °C. Rehydrogenation kinetics was measured in the soak mode at 290 °C under 15 atm pressure. Dehydrogenation kinetics was measured using the release mode of the instrument at 290 °C under 1 atm pressure. All the de/rehydrogenation measurements were performed using an automated two-channel volumetric Sievert type apparatus supplied by Advanced Materials Corporation Pittsburgh, USA.

## 3 Results and discussion

### 3.1 (a) Synthesis of $\text{SrF}_2@Gr$

In order to verify the templation of the additive over graphene, transmission electron microscopy analysis of the  $\text{SrF}_2@Gr$  sample was performed. Fig. 1 shows a representative TEM micrograph of the templated version of nano- $\text{SrF}_2$  over graphene. Fig. 1(a) shows a representative TEM micrograph of graphene. The expected wrinkled microstructure of graphene is visible. The SAED pattern of graphene shows (002) and (110) graphitic peaks (Fig. 1(b)). Indexing of the diffraction pattern by a diffraction ring profiler can be seen in Fig. 1(c). Fig. 1(d) shows the TEM micrograph of  $\text{SrF}_2@Gr$ , which confirms the templation of  $\text{SrF}_2$  over graphene. Fig. 1(c) and (f) has been again indexed with a diffraction ring profiler. It may be noted that, during the TEM analysis, the  $\text{SrF}_2$  samples templated on graphene were taken out and then inserted again. As verified by several such runs, the  $\text{SrF}_2$  particles remained on graphene and did not fall off. This showed that the  $\text{SrF}_2$  particles are anchored on graphene (Fig. 1(d)). Fig. 1(f) has been again indexed with a diffraction ring profiler.

### 3.1 (b) Characterization of $\text{MgH}_2$ admixed with $\text{SrF}_2$ templated on graphene ( $\text{MgH}_2\text{-SrF}_2@Gr$ )

A quantity of 7 wt% of  $\text{SrF}_2$  was added to  $\text{MgH}_2$ . The concentrations of the additives  $\text{SrF}_2$  and  $\text{SrF}_2@Gr$  were found to be





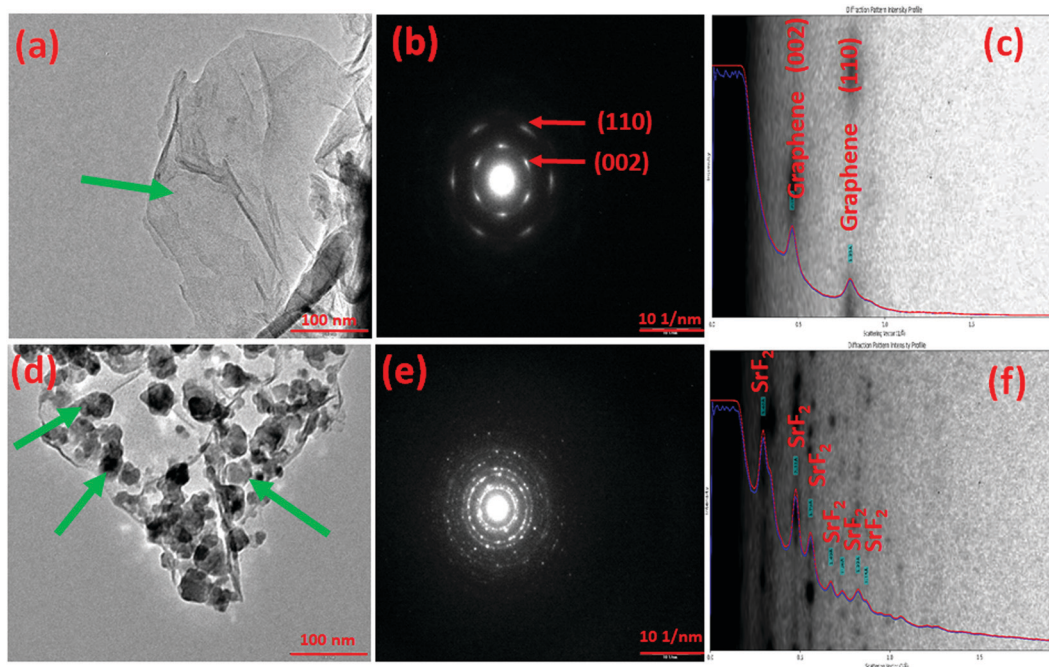


Fig. 1 TEM micrographs of (a) graphene, (b) SAED pattern of graphene, (c) diffraction ring profiler indexing of graphene, (d) SrF<sub>2</sub>@Gr, (e) SAED pattern of SrF<sub>2</sub>@Gr, and (f) diffraction ring profiler indexing of SrF<sub>2</sub>@Gr.

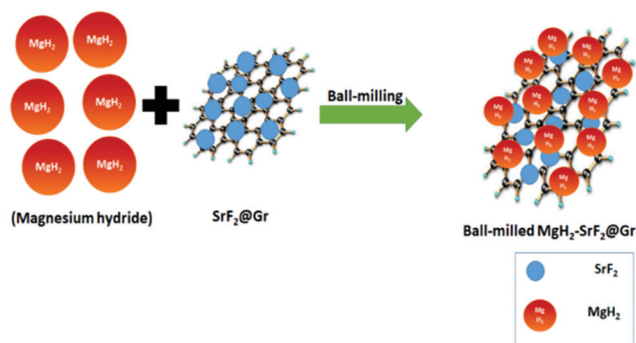


Fig. 2 Schematic diagram for MgH<sub>2</sub> admixed with SrF<sub>2</sub> templated on graphene (MgH<sub>2</sub>-SrF<sub>2</sub>@Gr).

optimum for catalyzing MgH<sub>2</sub>. A schematic diagram of the templation of SrF<sub>2</sub> on Gr is shown in Fig. 2.

To check the obtained XRD data with the standard crystallographic data and phases present in the sample, we performed multiphase Le Bail fitting of the XRD patterns using JANA software.<sup>26</sup> The XRD data ( $2\theta = 20\text{--}80^\circ$ ) for MgH<sub>2</sub> and the admixed version of MgH<sub>2</sub> samples are also shown in Fig. S1(i) (ESI<sup>†</sup>). Fig. 3(a)–(c) show the XRD fitting (difference plot with model and experimental data) of MgH<sub>2</sub> and the admixed version of the MgH<sub>2</sub> sample. The peak from  $20^\circ$  to  $25^\circ$  has been left intentionally as  $2\theta = 21.16^\circ$  and  $23.50^\circ$ , which corresponds to the peak of the parafilm, which is used as a cover on the XRD holder to avoid contamination of the sample from air and moisture. Fig. 3(a)–(c) and Fig. S1(a)–(c) (ESI<sup>†</sup>) show the XRD patterns of the ball-milled MgH<sub>2</sub> additive with SrF<sub>2</sub> and SrF<sub>2</sub>@Gr. Fig. 3(a) shows the XRD pattern of the ball-milled MgH<sub>2</sub>, where all the XRD peaks tally with the known XRD peaks

of  $\beta$ -MgH<sub>2</sub>. No evidence of high-pressure  $\gamma$ -MgH<sub>2</sub> has been found. Fig. 3(b) shows the XRD pattern of SrF<sub>2</sub> admixed with MgH<sub>2</sub>, where the phases of SrF<sub>2</sub> and MgH<sub>2</sub> have been indexed in XRD. Fig. 3(c) shows the XRD pattern of MgH<sub>2</sub> admixed with SrF<sub>2</sub> templated on graphene (SrF<sub>2</sub>@Gr). The phases of MgH<sub>2</sub> and SrF<sub>2</sub> can be clearly seen in the XRD pattern. The analysis of the XRD pattern of SrF<sub>2</sub>@Gr added MgH<sub>2</sub> indicates that all the peaks are of MgH<sub>2</sub> and SrF<sub>2</sub> NPs. The Gr peaks are very weak and broad (Fig. 1). They get obliterated in the background and with peaks of MgH<sub>2</sub> and SrF<sub>2</sub>.

Fig. 4 shows the Raman spectra of graphene (Gr) and the SrF<sub>2</sub>@Gr added MgH<sub>2</sub> sample. Fig. 4(a) shows the Raman spectrum of graphene. As is known, the G band corresponds to the in-plane vibration of sp<sup>2</sup> hybridized carbon. The D band represents the vibrations of carbon atoms at defect sites, including the carbon at the edge atoms forming dangling bonds.<sup>28,29</sup> The D and G bands together with the 2D band can be seen in Fig. 4(a). Fig. 4(b) shows the Raman spectrum of the ball-milled SrF<sub>2</sub>@Gr with added MgH<sub>2</sub> sample. The D and G bands are present together as a 2D band. It can be said that the Raman spectra helps to identify the nanostructured carbon catalyst, which has not been clearly revealed from the XRD results. If we compare Fig. 4(a) and (b), the  $I_D/I_G$  ratio is less than one ( $I_D/I_G < 1$ ) for graphene and greater than one ( $I_D/I_G > 1$ ) for SrF<sub>2</sub>@Gr with added MgH<sub>2</sub>. This may be due to the creation of defects during ball milling due to which the intensity of the D band is enhanced. This reveals the fact that there is an interaction between Gr and SrF<sub>2</sub>, which may lead to the displacement of carbon atoms in graphene. The TEM micrographs shown in Fig. 1(a)–(f) show SrF<sub>2</sub> nanoparticles located on graphene (Gr). Even when the sample (SrF<sub>2</sub>@Gr) was taken out from the TEM and inserted again, there was no



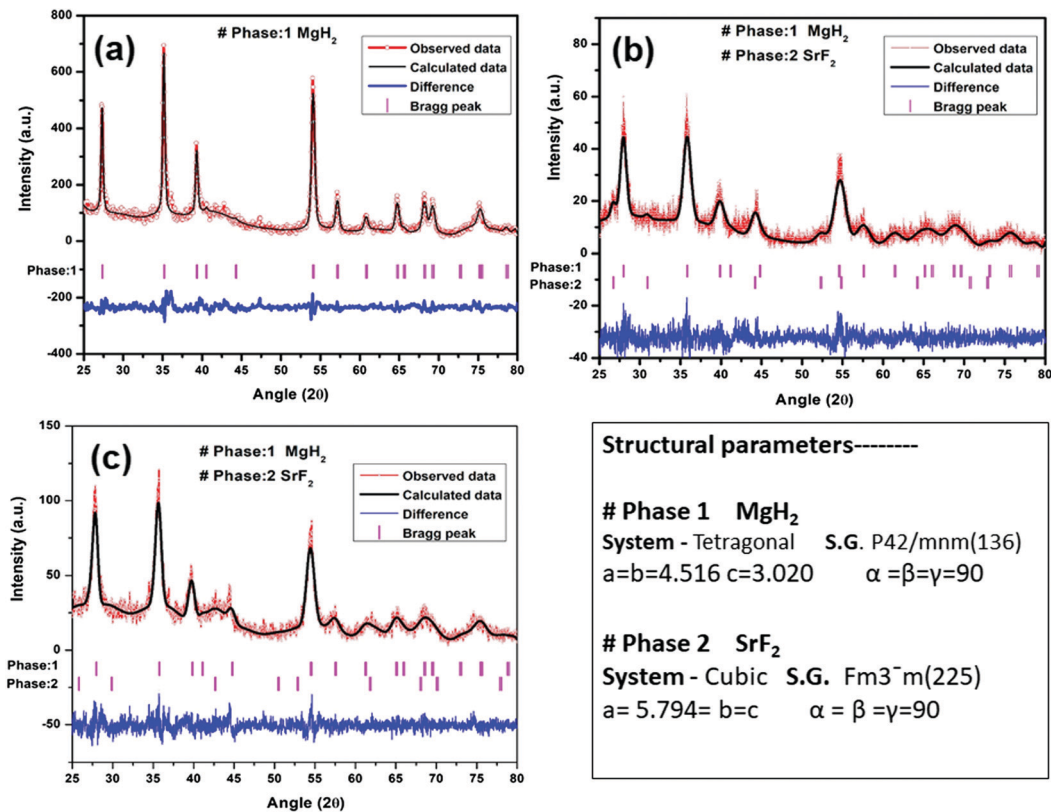


Fig. 3 XRD patterns of  $\text{MgH}_2$  admixed with  $\text{SrF}_2$  and  $\text{SrF}_2$  templated on graphene ( $\text{SrF}_2$ @Gr) with Le Bail fitting using Jana software: (a)  $\text{MgH}_2$ , (b)  $\text{MgH}_2$ - $\text{SrF}_2$ , and (c)  $\text{MgH}_2$ - $\text{SrF}_2$ @Gr.

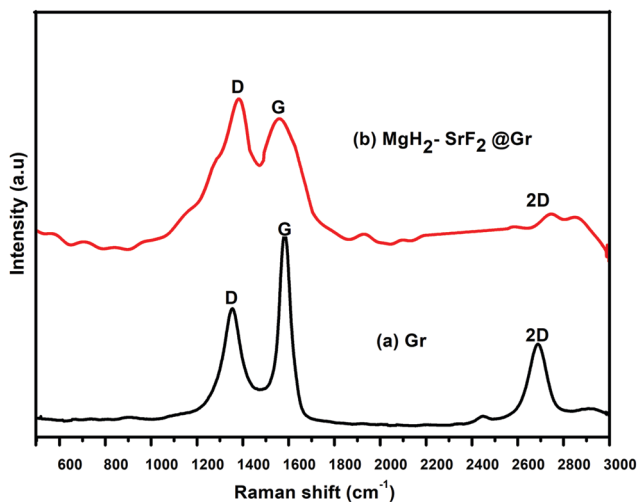


Fig. 4 Raman spectra of (a) graphene (Gr) and (b)  $\text{MgH}_2$ - $\text{SrF}_2$ @Gr.

displacement of  $\text{SrF}_2$  nanoparticles. This shows that  $\text{SrF}_2$  (NPs) are anchored on graphene. Experiments covering several de/rehydrogenation samples have shown that  $\text{SrF}_2$  (NPs) remain anchored on graphene.

### 3.2 Hydrogen sorption studies

**3.2 (a) Formation of  $\text{MgF}_2$  and  $\text{SrH}_2$ .** It may be mentioned that, in previous studies on fluoride as an additive for  $\text{MgH}_2$ ,

it has been found that on heating for dehydrogenation of  $\text{MgH}_2$  the fluoride generally dissociates yielding new compounds.<sup>16,17,19</sup> On the other hand, there have been some studies where the fluoride additive/catalyst remains intact.<sup>23</sup> In order to check the status of  $\text{SrF}_2$  on heating with  $\text{MgH}_2$ , for dehydrogenation, the XRD patterns of the dehydrogenated samples were taken. The dehydrogenation was done at  $290^\circ\text{C}$  at which complete dehydrogenation was found to take place. Fig. 5(a) and (b) or Fig. S3(a) and (b) (ESI<sup>†</sup>) show the representative XRD patterns of dehydrogenated  $\text{MgH}_2$ - $\text{SrF}_2$  and  $\text{MgH}_2$ - $\text{SrF}_2$ @Gr, respectively. Indexing the XRD peaks revealed that, on dehydrogenation where heating at high temperature ( $\sim 300^\circ\text{C}$ ) is involved,  $\text{SrF}_2$  was no longer present. Instead two products  $\text{MgF}_2$  and  $\text{SrH}_2$  were formed. Studies involving several dehydrogenation runs showed that, after dehydrogenation of  $\text{MgH}_2$ - $\text{SrF}_2$  and  $\text{MgH}_2$ - $\text{SrF}_2$ @Gr,  $\text{MgF}_2$  and  $\text{SrH}_2$  together with Mg are invariably present. For the graphene templated version the formed products will be located on Gr. It may be pointed out that the reaction of  $\text{MgH}_2$  and  $\text{SrF}_2$  is not expected to be instantaneous. There is every possibility of formation of the metastable phase  $\text{Sr}(\text{F}_x\text{H}_{2-x})$  as reported by Santiago *et al.*<sup>16</sup> This metastable phase  $\text{Sr}(\text{F}_x\text{H}_{2-x})$  then dissociates so as to form  $\text{SrH}_2$  (and the other associated compound  $\text{MgF}_2$ ). However, due to the low concentration of  $\text{SrH}_2$  the trace of  $\text{Sr}(\text{F}_x\text{H}_{2-x})$  could not be found in the present study.

The reaction of  $\text{MgH}_2$  and  $\text{SrF}_2$  can be described as follows.

(1) When  $\text{MgH}_2$  reacts with  $\text{SrF}_2$  (molar ratio 1 : 1) it forms



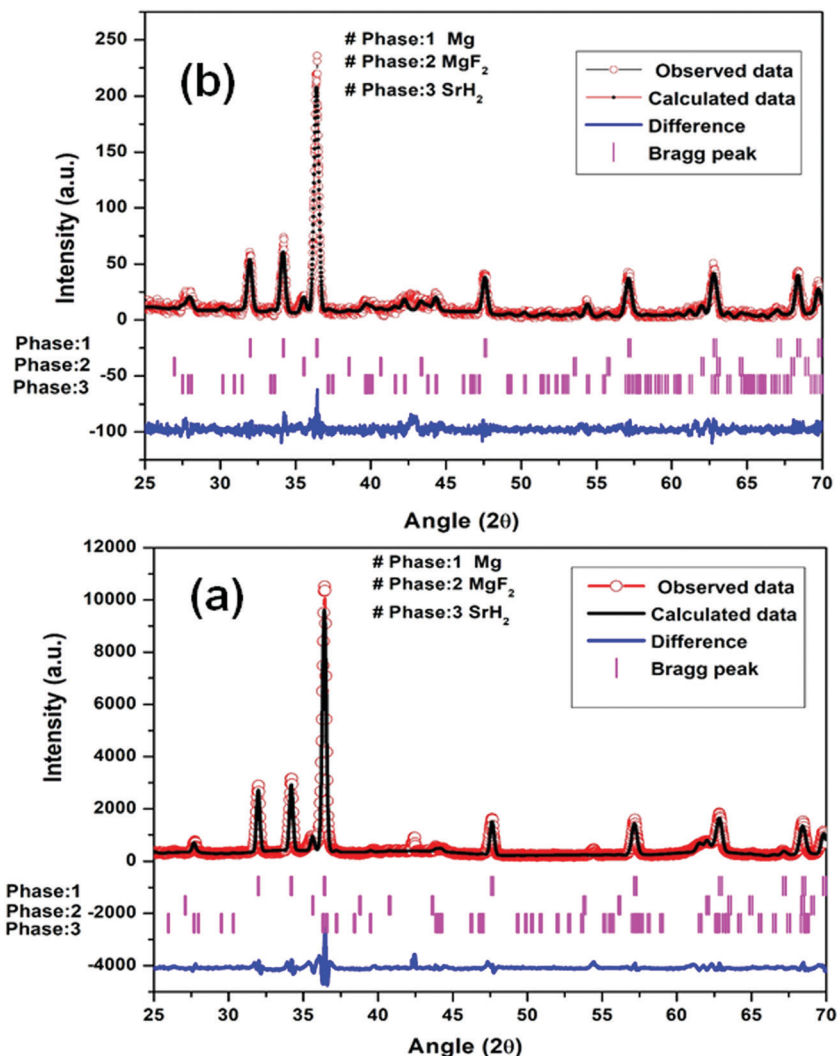
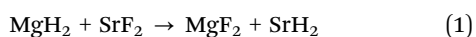
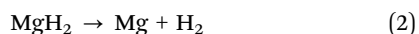


Fig. 5 Le Bail fitting of XRD patterns using JANA software at different steps: (a) Mg-(MgF<sub>2</sub> + SrH<sub>2</sub>) (1st dehydrogenation) and (b) Mg-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr (1st dehydrogenation).



(2) When MgH<sub>2</sub> desorbs to Mg, it forms



Attempts were made to determine the stage of dehydrogenation at which the products MgF<sub>2</sub> and SrH<sub>2</sub> were formed. It was found that, when the peak desorption temperature (Fig. 6(ii)) was reached, the conversion of (MgH<sub>2</sub> + SrF<sub>2</sub>) to (MgF<sub>2</sub> + SrH<sub>2</sub>) invariably takes place. It may be pointed out that, as is known, the fluoride additive lowers the desorption temperature for all Mg based storage materials.<sup>21</sup> Thus it may be considered that initially SrF<sub>2</sub> may decrease the desorption temperature of MgH<sub>2</sub>. However, once the reaction starts MgH<sub>2</sub> + SrF<sub>2</sub> is converted into MgF<sub>2</sub> + SrH<sub>2</sub> corresponding to the quantity of the additive taken. This conversion is completed when the peak desorption temperature is reached. Similar is the case for ball-milled MgH<sub>2</sub>-SrF<sub>2</sub>@Gr.

It may be pointed out that, after the first dehydrogenation reaction, besides Mg, the products which result, namely, MgF<sub>2</sub>

and SrH<sub>2</sub>, are present in all absorption/desorption runs. Further hydrogen (absorption/desorption) runs showed a significant improvement in kinetics, thermodynamics, activation energy and cyclability. Apparently the improvements in hydrogen sorption in MgH<sub>2</sub> are due to (MgF<sub>2</sub> + SrH<sub>2</sub>) and (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr which act as catalysts.

We now proceed to describe and discuss hydrogen sorption studies in (MgF<sub>2</sub> + SrH<sub>2</sub>) and (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalyzed MgH<sub>2</sub>.

### 3.2 (b) Temperature programmed desorption (TPD).

In order to estimate the onset of desorption for (MgF<sub>2</sub> + SrH<sub>2</sub>) catalyzed MgH<sub>2</sub>, the hydrogenation of the product, namely, Mg (MgF<sub>2</sub> and SrH<sub>2</sub>), was conducted at 300 °C and 20 atm hydrogen pressure for 4 hours. The samples were brought to room temperature. After this temperature programmed desorption was carried out as follows.

The TPD of MgH<sub>2</sub> catalyzed by (MgF<sub>2</sub> + SrH<sub>2</sub>) and also (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr was conducted at a heating rate of 3 °C min<sup>-1</sup>. Fig. 6(i, a-c) show the TPD of ball-milled MgH<sub>2</sub> and the catalyzed versions of MgH<sub>2</sub>. Fig. 6(i-a) showing the TPD of the ball-milled MgH<sub>2</sub> sample exhibits the onset of desorption at





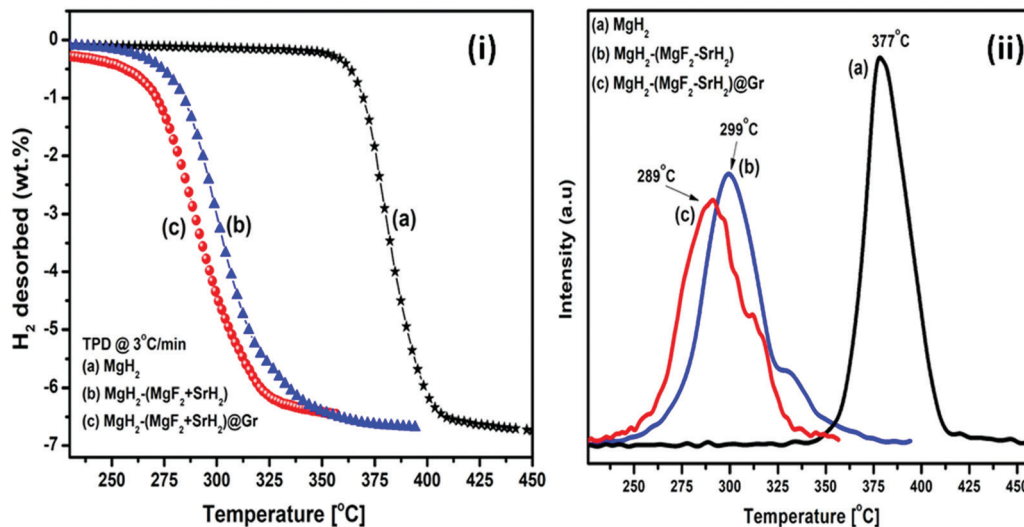


Fig. 6 (i) TPD of  $\text{MgH}_2$  catalyzed by (a)  $\text{MgH}_2$ , (b)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ , (c)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  and (ii) TPD (peak intensity vs. temperature) of (a)  $\text{MgH}_2$ , (b)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ , and (c)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ .

356 °C. The complete dehydrogenation of  $\text{MgH}_2$  has been found at 418 °C with a desorption capacity of 6.60 wt%. The onset desorption temperature for  $\text{MgH}_2$  catalyzed by  $(\text{MgF}_2 + \text{SrH}_2)$  has been found at 261 °C. The complete dehydrogenation takes place at 351 °C showing a storage capacity of 6.41 wt%. The onset desorption temperature for  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  catalyzed  $\text{MgH}_2$  has been found to be 231 °C. Nearly 3.41 wt% of hydrogen is desorbed at the temperature of 292 °C, showing a complete dehydrogenation capacity of 6.32 wt% is obtained at 320 °C. The onset desorption temperature for  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  catalyzed  $\text{MgH}_2$  has been found to be lower by 125 °C and 30 °C than those for  $\text{MgH}_2$  and  $(\text{MgF}_2 + \text{SrH}_2)$  catalyzed  $\text{MgH}_2$ , respectively. Thus it can be said that the hydrogen sorption characteristics of  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$

catalyzed  $\text{MgH}_2$  are superior to those of  $(\text{MgF}_2 + \text{SrH}_2)$  alone. It may be pointed out that the present onset desorption temperature of 231 °C is one of the lowest onset temperatures observed for  $\text{MgH}_2$  catalyzed by various catalysts.<sup>23,26–28,30–35</sup>

**3.2 (c) De/rehydrogenation kinetics.** The rehydrogenation/dehydrogenation kinetics profiles are shown in Fig. 7(i) and (ii), respectively. Fig. 7(i, a–c) show the rehydrogenation kinetics of  $\text{MgH}_2$ ,  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ , and  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  samples, respectively. The rehydrogenation kinetics was measured at 290 °C and 1.8 MPa  $\text{H}_2$  pressure. In the present investigation, invariably ball-milled samples of  $\text{MgH}_2$ ,  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$  were used, we will henceforth, for brevity, write  $\text{MgH}_2$ ,  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$  instead of B.M.  $\text{MgH}_2$ , B.M.  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ . Also for all samples the catalyst quantity

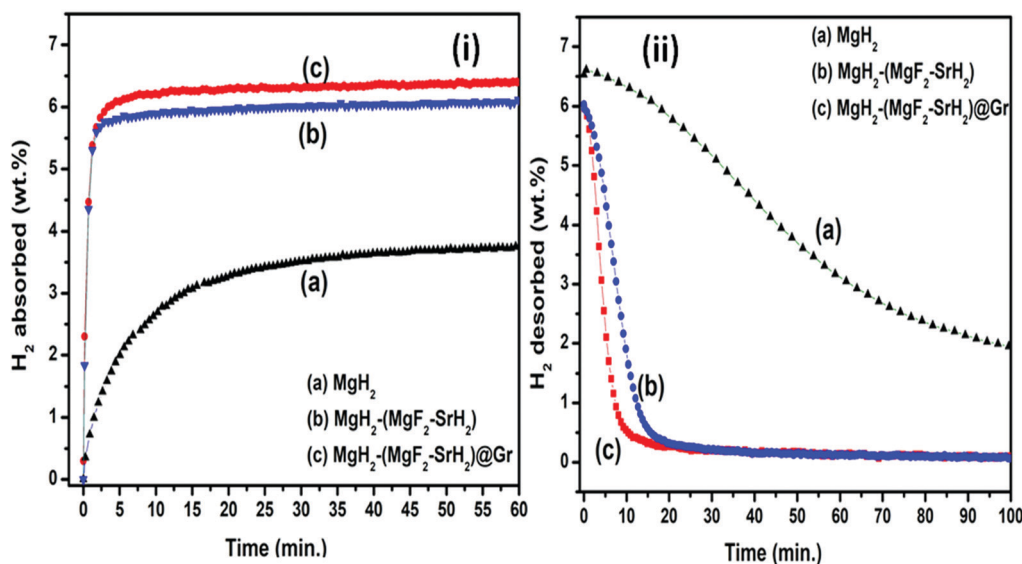


Fig. 7 De/rehydrogenation kinetics profile. (i) Rehydrogenation kinetics curve at 290 °C and 1.8 MPa  $\text{H}_2$  pressure: (a)  $\text{MgH}_2$ , (b)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ , and (c)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ . (ii) Dehydrogenation kinetics curve at 290 °C and 0.1 MPa  $\text{H}_2$  pressure: (a)  $\text{MgH}_2$ , (b)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ , and (c)  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ .



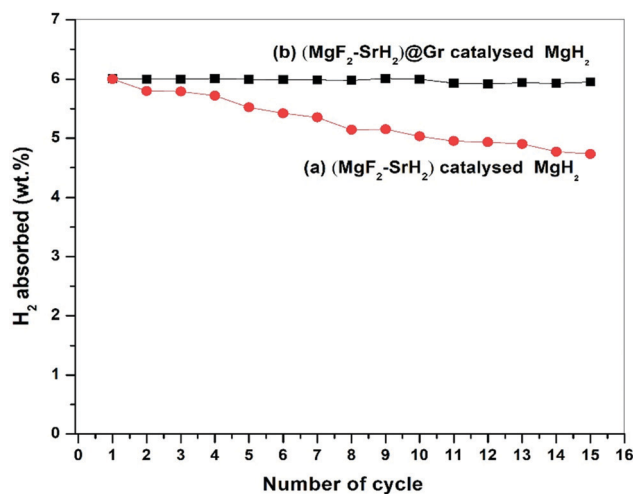
**Table 1** Comparison of rehydrogenation kinetics at  $\sim 300$  °C in 2 min with different metal fluorides

S. no.	Catalyst/additive used	Rehydrogenation kinetics in 2 min (wt%)	Ref.
1.	TiF <sub>3</sub>	4.5	32
2.	VF <sub>4</sub>	3.5	32
3.	NbF <sub>5</sub>	4.5	17 and 32
4.	NiF <sub>2</sub>	3.2	32
5.	ZrF <sub>4</sub>	3.6	32
6.	CrF <sub>2</sub>	3.1	32
7.	FeF <sub>2</sub>	3.2	32
8.	CeF <sub>3</sub>	4.6	33
9.	LaF <sub>3</sub>	4.5	33
10.	MgF <sub>2</sub>	3.0	23
11.	MgF <sub>2</sub> + SrH <sub>2</sub>	5.9 ( $T_{\text{abs}} -290$ °C)	Present study
12.	MgF <sub>2</sub> + SrH <sub>2</sub> @Gr	6.2 ( $T_{\text{abs}} -290$ °C)	Present study

of 7 wt.% has been used. In view of this the prefix: corresponding to 7 wt.% for the catalysts will be taken as implied. The rehydrogenation kinetics of the MgH<sub>2</sub> sample is slow (Fig. 7(i-a)), *i.e.*, it only absorbs 2.02 wt% in 5 min and 3.05 wt% in 15 min. Nearly 3.76 wt% of H<sub>2</sub> is absorbed in 20 min. Fig. 7(i-b) show the rehydrogenation kinetics of the MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>) sample, the rehydrogenation kinetics of the catalyst system (MgF<sub>2</sub> + SrH<sub>2</sub>) is improved, and it can absorb 5.90 wt% in 2 min and 6.00 wt% in 5 min. Fig. 7(i-c) show the rehydrogenation kinetics of (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalyzed MgH<sub>2</sub> where very fast kinetics takes place. The MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr adsorbs 6.16 wt% in 2 min. The rehydrogenation kinetics of the MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr sample shows better rehydrogenation compared to our recent and other studies.<sup>23,26–28,30–35</sup> Rehydrogenation of 5.90 wt% and 6.20 wt% for MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>) and MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr, respectively, in 2 min represents one of the fastest H<sub>2</sub> absorption processes for Mg. A comparison of the absorption kinetics for MgH<sub>2</sub> with different catalysts/additive is shown in Table 1.

Fig. 7(ii, a–c) show the dehydrogenation kinetics of MgH<sub>2</sub>, MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>), and MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr samples, respectively. The dehydrogenation kinetics was performed at 290 °C and 0.1 MPa H<sub>2</sub> pressure. Fig. 7(ii-a) shows the dehydrogenation kinetics profile of the MgH<sub>2</sub> sample. As shown in Fig. 7(ii-a), the MgH<sub>2</sub> sample desorbs 0.19 wt% in 5 min and 0.56 wt% in 15 min. The desorption of 4.69 wt% of H<sub>2</sub> has been observed in 100 min. Fig. 7(ii-b) shows the dehydrogenation kinetics of the MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>) sample, the dehydrogenation kinetics for this sample is improved, and it desorbs 1.68 wt% in 5 min and 5.59 wt% in 15 min. Fig. 7(ii-c) shows the dehydrogenation kinetics of (MgH<sub>2</sub>)-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr. The MgH<sub>2</sub> sample with the graphene templated catalyst (MgF<sub>2</sub> + SrH<sub>2</sub>) desorbs 4.08 wt% in 5 min and 6.01 wt% in 15 min. MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr desorbs 6.11 wt% in 25 min. Thus the dehydrogenation kinetics of MgH<sub>2</sub> catalyzed by the (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr sample shows better dehydrogenation compared to our recent and other studies.<sup>23,26–28,30–35</sup>

**3.2 (d) Cycling stability.** To check the cycling stability of (MgF<sub>2</sub> + SrH<sub>2</sub>) and (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalyzed MgH<sub>2</sub> samples, we performed continuous de/rehydrogenation experiments at 290 °C as shown in Fig. 8. The dehydrogenation of the optimum



**Fig. 8** Cycling stability up to 15 cycles of (a) (MgF<sub>2</sub> + SrH<sub>2</sub>) catalysed MgH<sub>2</sub> and (b) (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr catalysed MgH<sub>2</sub>.

material MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr was performed at 290 °C and 0.1 MPa H<sub>2</sub> pressure. The rehydrogenation was carried out at 290 °C and 1.8 MPa H<sub>2</sub> pressure. In order to compare the cycling stability of MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>) and MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr, repeated de/rehydrogenation experiments were performed up to 15 cycles. The MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>) sample in the first cycle absorbs 6.01 wt% and 5.72 wt% in the 10th cycle. In the 15th cycle, the absorption capacity of the MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>) sample is lowered, reaching 4.73 wt%. However, with the graphene templated version, the cycling stability of the sample is improved. The MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr sample absorbs 6.12 wt% in the first cycle and about the same quantity after the 15th cycle (even after 15 cycles it remains  $\sim 6.10$  wt%). Thus there is almost no decrement of the storage capacity on cycling. The remarkable cycling stability is due to graphene on which the catalyzed particles are anchored. Similar to the case of SrF<sub>2</sub> templated on graphene (Section 3.1(a)), TEM studies show that MgF<sub>2</sub> and SrH<sub>2</sub> remain templated and hence anchored on graphene. Thus there is no agglomeration of MgF<sub>2</sub> and SrH<sub>2</sub>.

**3.2 (e) Differential scanning calorimetry for the calculation of activation energy.** To understand the improvement in dehydrogenation kinetics, the lowering of the activation energy barrier in the presence of the catalyst (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr in MgH<sub>2</sub> was determined by differential scanning calorimetry. The DSC was performed under nitrogen flow (20 mL min<sup>-1</sup>) at heating rates of 5 °C min<sup>-1</sup>, 7 °C min<sup>-1</sup>, and 10 °C min<sup>-1</sup>.

To find the activation energy using the Kissinger equation<sup>36,37</sup> the peak desorption temperature at different heating rates was used.

$$\ln(\beta/T_p^2) = (-E_a/RT_p) + \ln(k_0) \quad (3)$$

where  $T_p$  is the corresponding peak desorption temperature and  $\beta$  is the heating rate. The slope obtained from the plot between  $\ln(\beta/T_p^2)$  and  $1000/T_p$  is used for calculating the desorption activation energy and is shown in Fig. 10(ii). The activation energy for (MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr is 79.92 kJ mol<sup>-1</sup>. This signifies the better





catalytic activity of  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  over  $\text{MgH}_2$  nanoparticles. The activation energy of  $79.92 \text{ kJ mol}^{-1}$  implies that we have to apply  $79.92 \text{ kJ mol}^{-1}$  energy to overcome the energy barrier for the conversion of  $\text{MgH}_2$  into  $\text{Mg}$  in the case of  $\text{MgH}_2$  catalyzed by  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ . However, the activation energy of the ball-milled  $\text{MgH}_2$  (25 hours) is  $160.06 \text{ kJ mol}^{-1}$  as shown in Fig. S6 (ESI†). This activation energy ( $79.92 \text{ kJ mol}^{-1}$ ) is significantly lower as compared to other catalysts, e.g.  $130 \text{ kJ mol}^{-1}$ ,<sup>38</sup>  $131 \text{ kJ mol}^{-1}$ ,<sup>39</sup> and  $111 \text{ kJ mol}^{-1}$ .<sup>40</sup>

**3.2 (f) Thermodynamic stability.** To understand the thermodynamic stability of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$  and  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ , enthalpy changes were evaluated and compared. The change in enthalpy for the de/rehydrogenation was calculated by pressure composition isotherm (PCI). Representative PCI curves for different samples are shown in Fig. 11(i) and (ii).

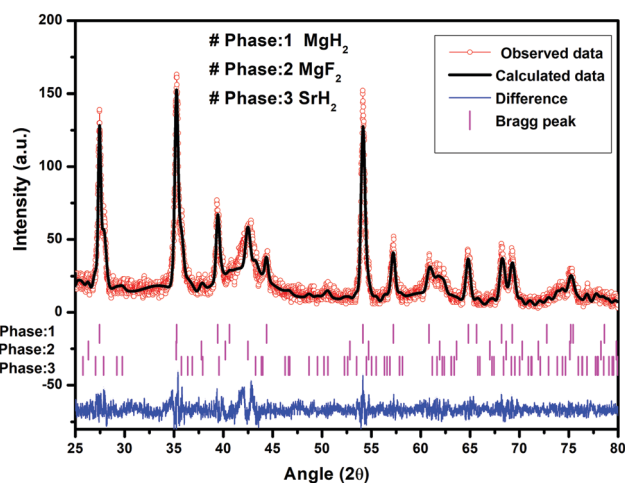


Fig. 9 Le Bail fitting of the XRD pattern using JANA software after 15 cycles of  $\text{H}_2$  de/rehydrogenation of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ .

The PCI was carried out at  $282 \text{ }^\circ\text{C}$ ,  $302 \text{ }^\circ\text{C}$ , and  $320 \text{ }^\circ\text{C}$  for the  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$  sample to calculate the change in the enthalpy of the sample. The enthalpy change in the process of de/re-rehydrogenation has been evaluated using the van't Hoff plot. The enthalpy change for the dehydrogenation of  $\text{MgH}_2/\text{Mg}$  with  $(\text{MgF}_2 + \text{SrH}_2)$  has been found to be  $74.84 \text{ kJ mol}^{-1}$  (Fig. 11(i, a and b)). However, the enthalpy change for rehydrogenation ( $\text{Mg}$  to  $\text{MgH}_2$ ) with  $(\text{MgF}_2 + \text{SrH}_2)$  is  $67.99 \text{ kJ mol}^{-1}$  (Fig. 11(i, c and d)). In order to calculate the enthalpy change of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$ , PCI was performed at  $288 \text{ }^\circ\text{C}$ ,  $311 \text{ }^\circ\text{C}$ , and  $321 \text{ }^\circ\text{C}$ . The enthalpy change for the dehydrogenation of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  has been found to be  $67.60 \text{ kJ mol}^{-1}$  (Fig. 11(ii, a and b)). However, the enthalpy change for the rehydrogenation of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  is  $61.54 \text{ kJ mol}^{-1}$  (Fig. 11(ii, c and d)). Thus the desorption enthalpy change for  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  has been found to be lower by  $7.42 \text{ kJ mol}^{-1}$  as compared to  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ . The change in the enthalpy of  $\text{MgH}_2/\text{Mg}$  has been found to be superior to those reported in several other studies.<sup>26,27,31–35</sup> Thus it can be said that the graphene templation of  $(\text{MgF}_2 + \text{SrH}_2)$  plays a vital role in promoting the whole reaction.

## 4 Proposed mechanism for the hydrogen sorption of $\text{MgH}_2$ with the additive $\text{SrF}_2@\text{Gr}$ derived catalyst $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$

The de/rehydrogenation of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  can be understood based on the results obtained from XRD, TEM, SEM, FTIR and Raman spectroscopic studies conducted in the present investigation.

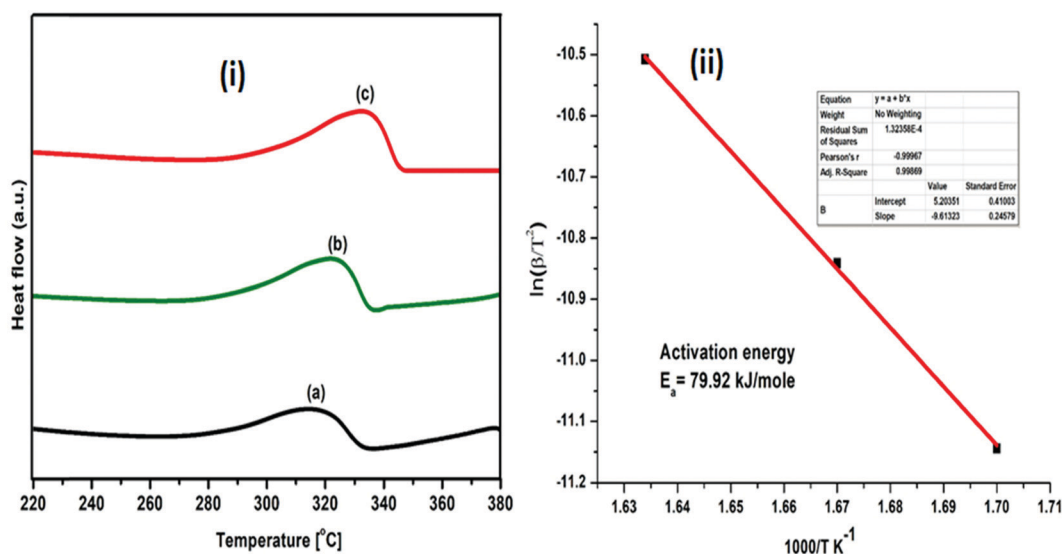


Fig. 10 (i) DSC profiles of  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  catalyzed  $\text{MgH}_2$  under heating at (a)  $5 \text{ }^\circ\text{C min}^{-1}$ , (b)  $7 \text{ }^\circ\text{C min}^{-1}$  and (c)  $10 \text{ }^\circ\text{C min}^{-1}$ ; (ii) Kissinger plot for evaluating activation energy.



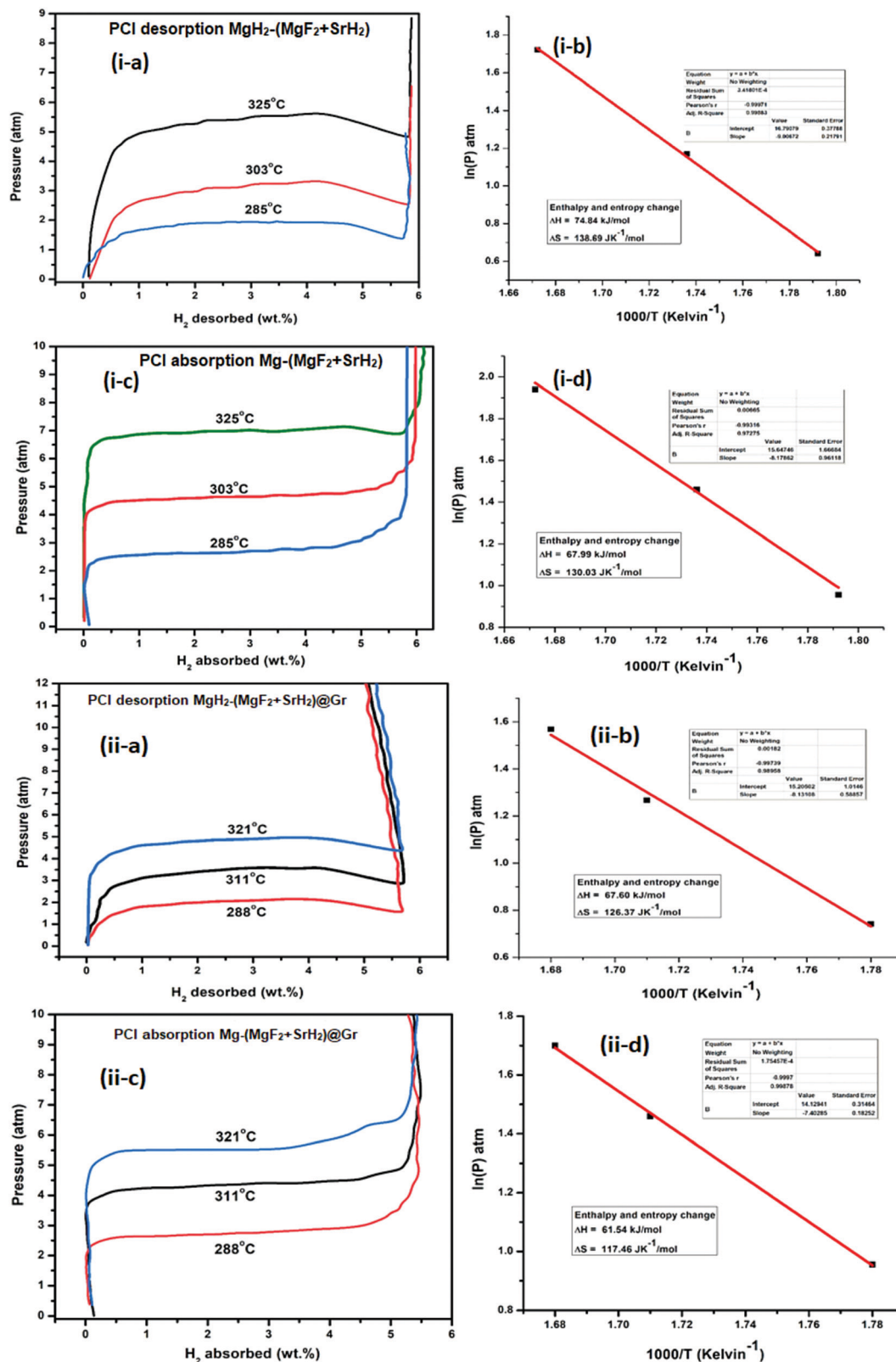


Fig. 11 PCI isotherm of  $\text{MgH}_2$  catalysed with: (i-a) PCI desorption at three different temperatures for the  $\text{MgH}_2\text{-(MgF}_2\text{+SrH}_2\text{)}$  sample; (i-b) van't Hoff plot for the calculation of change in enthalpy; (i-c) PCI absorption at three different temperatures for the  $\text{MgH}_2\text{-(MgF}_2\text{+SrH}_2\text{)}$  sample; (i-d) van't Hoff plot for the calculation of change in enthalpy; (ii-a) PCI desorption at three different temperatures for the  $\text{MgH}_2\text{-(MgF}_2\text{+SrH}_2\text{)@Gr}$  sample; (ii-b) van't Hoff plot for the calculation of change in enthalpy; (ii-c) PCI absorption at three different temperatures for the  $\text{MgH}_2\text{-(MgF}_2\text{+SrH}_2\text{)@Gr}$  sample; and (ii-d) van't Hoff plot for the calculation of change in enthalpy.



The microstructure of  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  catalyzed  $\text{MgH}_2$  before and after cycling was analyzed by employing TEM. Fig. 12(a)–(i) show the typical TEM micrographs and the related selected area electron diffraction (SAED) patterns after ball milling and cycling. Also the EDAX analysis of  $(\text{MgF}_2 + \text{SrH}_2)@\text{Gr}$  catalyzed  $\text{MgH}_2$  was

conducted (Fig. 12(j)). The EDAX analysis is in keeping with the XRD studies (Fig. 3(c) and Fig. S1(c), ESI†) wherein the presence of  $\text{MgH}_2$  and  $\text{SrF}_2$  has been found through SAED patterns.

The presence of  $\text{MgF}_2$  and  $\text{SrH}_2$  even after cycling as evidenced by (Fig. 12(g)–(i))  $\text{MgH}_2$  and  $\text{SrF}_2$  shows that these

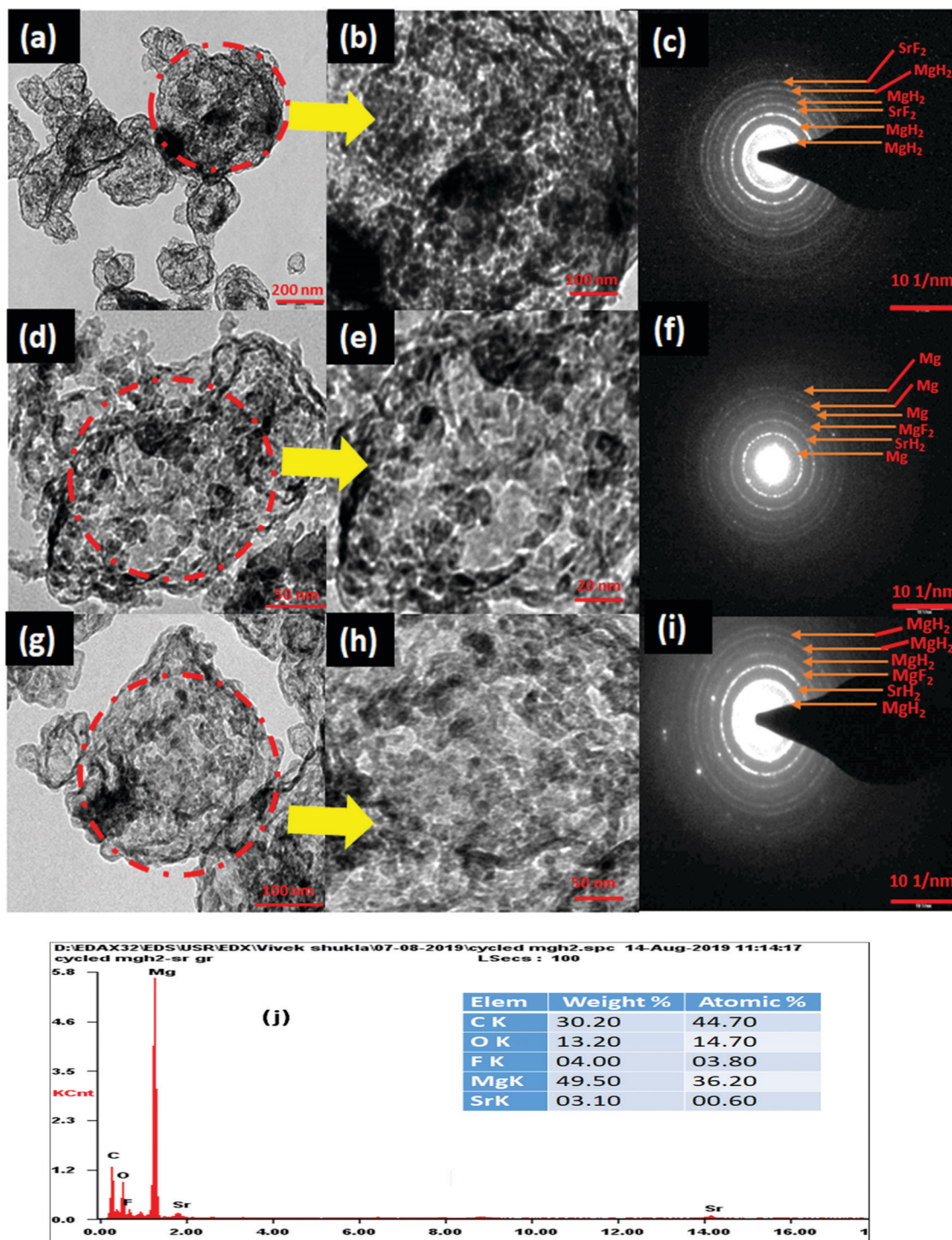


Fig. 12 TEM micrographs of (a and b)  $\text{MgH}_2\text{-SrF}_2$ , (c) SAED pattern of  $\text{MgH}_2\text{-SrF}_2$ , (d and e)  $\text{Mg-(MgF}_2 + \text{SrH}_2)\text{Gr}$  (1st dehydrogenation), (f) SAED pattern of  $\text{Mg-(MgF}_2 + \text{SrH}_2)\text{Gr}$  (1st dehydrogenation), (g and h)  $\text{MgH}_2\text{-(MgF}_2 + \text{SrH}_2)@\text{Gr}$  (15 cycles of rehydrogenation), (i) SAED pattern of  $\text{MgH}_2\text{-(MgF}_2 + \text{SrH}_2)@\text{Gr}$  (15 cycles of rehydrogenation), and (j) EDAX spectrum after 15th cycle of rehydrogenation of  $(\text{MgF}_2 + \text{SrH}_2)\text{Gr}$  catalyzed  $\text{MgH}_2$ .





catalysts leads to improvements in hydrogen sorption all through. This confirms that they are indeed the catalysts. Also as shown in Fig. 12(g) and Fig. S4(c) (ESI<sup>†</sup>), there is no agglomeration of MgF<sub>2</sub> and SrH<sub>2</sub>. This implies that MgF<sub>2</sub> and SrH<sub>2</sub> are anchored on graphene. Fig. 12(g) and Fig. S4(c) (ESI<sup>†</sup>) show that MgF<sub>2</sub> and SrH<sub>2</sub> after 15 cycles (Fig. 12(g) or Fig. S4(c), ESI<sup>†</sup>) are nearly homogeneously dispersed. From the SAED patterns and EDAX analysis of SEM (Fig. 12(j) and Fig. S4(c), ESI<sup>†</sup>), one can also identify the presence of Mg, Sr, C, and F (some oxygen is also present, which may be due to some oxidation during the transfer of the specimen in the TEM and SEM chambers), showing that the catalysts remain stable even after 15 cycles of de/rehydrogenation. Because of the aforementioned feature, the catalytic activity will not degrade and the storage capacities will not vary with cycling as observed in our investigation (Fig. 8).

It is to be noted that, in the reactivity series,<sup>41</sup> Sr is placed above MgH<sub>2</sub> and hence is highly reactive as compared to Mg. Therefore, there is every possibility of displacement of Mg by Sr. Therefore, the formation of MgF<sub>2</sub> and the associated compound SrH<sub>2</sub> will take place. MgH<sub>2</sub> exhibits an ionic-covalent bond<sup>42</sup> with charge densities as Mg<sup>1.509+</sup> and H<sup>-0.754</sup>. Khatabi *et al.*<sup>42</sup> have shown that the bonding between Mg and H can be weakened by using a suitable catalyst having active d orbitals. MgF<sub>2</sub> type compounds have active d orbitals in their orbital geometry.<sup>43</sup> MgF<sub>2</sub> is highly ionic owing to the elemental electronegativity difference of 2.67 (Mg: 1.31, F: 3.98), which is higher as compared to the electronegativity difference for MgH<sub>2</sub> which is 0.79 (Mg: 1.31, H: 2.10) being a polar molecule with a high electronegative character and the dominant contribution of the d orbital will readily interact with polar covalent MgH<sub>2</sub>, destabilize the Mg–H bond and improve the kinetics.

Because of the above reason, MgF<sub>2</sub> will play a dominant role in improving the kinetics. This is in keeping with the known catalytic activity of MgF<sub>2</sub> for hydrogen sorption in MgH<sub>2</sub>.<sup>23</sup> In regards to SrH<sub>2</sub> which has a lower elemental electro-negativity difference of 0.15 (Sr: 0.95, H: 2.10), it may play a minor role in destabilizing the Mg–H bond. It is known that, if MgH<sub>2</sub> assumes a smaller size in the nanoparticle range, the thermodynamics is improved.<sup>44–46</sup> Fine particles of MgH<sub>2</sub> <5 nm in size were observed in the present studies on mechanical milling. It may thus be considered that SrH<sub>2</sub> plays a major role in improving thermodynamics. This is in conformity with the results obtained in the present investigations. The formation enthalpy of the catalyzed MgH<sub>2</sub> has been found to change from 76 kJ mol<sup>-1</sup> to 61.54 kJ mol<sup>-1</sup> (an improvement of 14.46 kJ mol<sup>-1</sup>). The above discussion suggests that, whereas MgF<sub>2</sub> plays a role in improving the kinetics, SrH<sub>2</sub> helps in the positive tuning of thermodynamics. The two catalysts taken together improve the kinetics and thermodynamics. In regards to the presence of MgF<sub>2</sub> and SrH<sub>2</sub> throughout hydrogen sorption, we have already shown through XRD that these are present even after 15 sorption cycles (Fig. 9). In order to further verify this, we have performed FTIR analyses of the samples at the beginning when MgF<sub>2</sub> and SrH<sub>2</sub> were formed and then after 15 cycles of hydrogen sorption. Fig. S7 (ESI<sup>†</sup>) presents the representative FTIR spectra. The spectra were analyzed based on the known IR absorption characteristics of the various molecules embodied in the materials. The Mg–H vibration is known to give its signature from 400 to 900 cm<sup>-1</sup> and 900 to 1300 cm<sup>-1</sup>, MgF<sub>2</sub> around 1492–1500 cm<sup>-1</sup> and SrH<sub>2</sub> around 1140 cm<sup>-1</sup>.<sup>47–49</sup> The typical graphene C–H stretching vibration at 2850 and 2930 cm<sup>-1</sup> can also be noted.<sup>50</sup> The presence of all these can be clearly seen in the FTIR spectra shown in Fig. S6, ESI<sup>†</sup>.

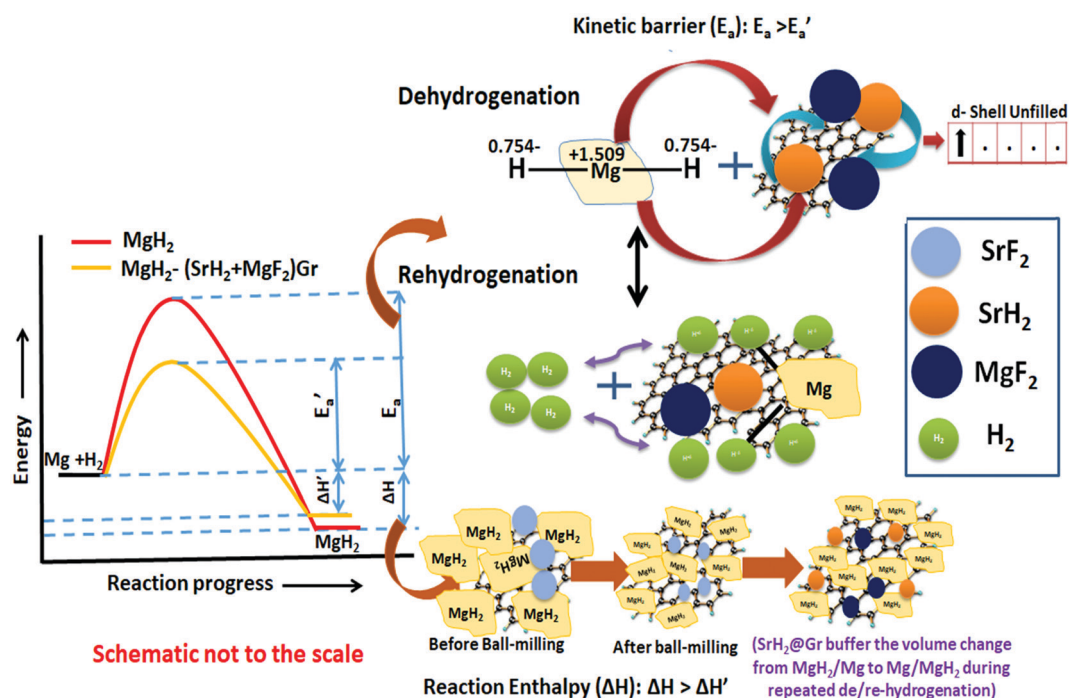


Fig. 13 Schematic diagram of the de/rehydrogenation of MgH<sub>2</sub>-(MgF<sub>2</sub> + SrH<sub>2</sub>)@Gr.



Recent studies have shown that the hydride catalyst moves from within  $\text{MgH}_2$  to the surface during dehydrogenation and *vice versa* during hydrogenation.<sup>44,45</sup> Such movement will buffer the variation of the volume of  $\text{MgH}_2$  due to repeated expansion and contraction during de/rehydrogenation. The volume change during repeated de/rehydrogenation is one of the causes for degradation in the cyclic performance of  $\text{MgH}_2$ . As discussed earlier (Sections 3.1(a) and 3.2(d)), TEM studies reveal that  $\text{MgF}_2$  and  $\text{SrH}_2$  are anchored on graphene. They do not agglomerate and as outlined earlier this improves the cyclability. The role of graphene in promoting the possible conversion of  $\text{MgF}_2$  to  $\text{MgF}_{2-x}$  and  $\text{SrH}_2$  to  $\text{SrH}_{2-x}$  cannot be ruled out. Thus the enhancement in kinetics, positive tuning of thermodynamics and very good cyclability can be attributed to the synergistic effect between  $\text{MgF}_2$ ,  $\text{SrH}_2$  and Gr. This is outlined in the schematic diagram shown in Fig. 13. The simultaneous improvement of all three crucial characteristics, namely, the kinetics, thermodynamics and cyclability, of hydrogen sorption in  $\text{MgH}_2$  makes the present investigation different than other studies on fluoride catalyzed  $\text{MgH}_2$ .

## 5 Conclusion

The present study deals with the role of one of the most ionic additives  $\text{SrF}_2$  in the formation of the catalysts  $\text{MgF}_2$  and  $\text{SrH}_2$  and their role in the improvement of hydrogen sorption in  $\text{MgH}_2$ . Besides the additive  $\text{SrF}_2$  alone and the resulting catalyst ( $\text{MgF}_2 + \text{SrH}_2$ ), their graphene templated versions were synthesized and deployed for hydrogen sorption in  $\text{MgH}_2$ . It is shown that the catalysts ( $\text{MgF}_2 + \text{SrH}_2$ ) and ( $\text{MgF}_2 + \text{SrH}_2$ )@Gr both show better hydrogen sorption characteristics than the presently known best fluoride additive/catalyst  $\text{NbF}_5/(\text{MgF}_2 + \text{NbH}_{0.9})$ . The catalyst ( $\text{MgF}_2 + \text{SrH}_2$ )@Gr shows very fast hydrogen absorption kinetics of 6.16 wt% in 2 min and desorption kinetics of 6.01 wt% in 15 min in  $\text{Mg}/\text{MgH}_2$  at 290 °C. The change in desorption enthalpy for ( $\text{MgF}_2 + \text{SrH}_2$ )@Gr catalyzed  $\text{MgH}_2$  was found to be 67.60  $\text{kJ mol}^{-1}$  (7.42  $\text{kJ mol}^{-1}$  lower than the desorption enthalpy of  $\text{MgH}_2-(\text{MgF}_2 + \text{SrH}_2)$ ). Also the storage capacity of  $\text{MgH}_2$  employing the aforementioned catalyst remains 6.10 wt% up to 15 cycles exhibiting excellent cyclability. It has been shown that, whereas  $\text{MgF}_2$  plays a major role in improving the kinetics,  $\text{SrH}_2$  allows positive tuning of the thermodynamics. All in all, the improvement of the important hydrogen sorption characteristics (kinetics, thermodynamics and cyclability) arises due to the synergistic effect of  $\text{MgF}_2$ ,  $\text{SrH}_2$  and Gr.

## Conflicts of interest

There are no conflicts to declare.

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