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Effect of Magnesium Fluoride on Hydrogenation Properties of Magnesium Hydride

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Abstract: A cost effective catalyst is of great importance for consideration of MgH_2 as potential hydrogen storage material. In this regard, we investigated the catalytic role of alkaline metal fluoride on the hydrogen storage behavior of MgH_2. Samples were synthesized by admixing 5 mol % MgF_2 into MgH_2 powder using planetary ball mill. Hydrogenation measurements made at 335 °C showed that in comparison to only 70% absorption by pure MgH_2, catalyzed material absorbed 92% of theoretical capacity in less than 20 min and desorbed completely in almost the same time. Sorption studies done at lower temperatures revealed that complete absorption at temperature as low as 145 °C is possible. This is due to uniform distribution of MgF_2 nano particles within the MgH_2 powder. X-ray diffraction patterns also showed the presence of stable MgF_2 phase that does not decompose upon hydrogen absorption-desorption. Cyclic measurements done at 310 °C showed negligible loss in the overall storage capacity with cycling. These results reveal that the presence of the chemically inert and stable MgF_2 phase is responsible for good reversible characteristic and improved kinetics.

Keywords: magnesium hydride; magnesium fluoride; hydrogen storage; metal hydrides; kinetics

1. Introduction

Magnesium hydride is a potential candidate for hydrogen storage because of its high gravimetric and volumetric capacities. Pure magnesium's low environmental impact and abundant availability makes it very attractive for hydrogen storage application. However, high working temperature and slow kinetics limit its potential as hydrogen storage material for practical applications. Therefore, research is required to circumvent these difficulties and make MgH_2 a viable hydrogen storage material. Nano-structuring of MgH_2 is one of the most adopted methods to improve the hydrogenation performance [1]. However, this method has a limitation to achieve the nanocrystalline size (<5 nm) required for destabilization of MgH_2 [2].

Further improvements in sorption behaviour have been achieved by adding a wide variety of pure transition metals [3,4], their oxides [5] and halides [6–8]. The remarkable catalytic effect of transition metal oxide, Nb_2O_5 has been well reported. However, during cycling at elevated temperatures, reduction of Nb_2O_5 occurs with augmentation of MgO content [5]. Later, it was found that some transition metal halides, such as FeF_3, $CrCl_3$, NiF_2, $NbCl_5$ and $TiCl_3$ possess better catalytic activity than pure metals or their oxides [6–8]. In the case of halides, Malka *et al.* [9] showed that fluorides are better catalysts than chlorides for MgH_2. Addition of transition metal fluorides during milling helps to lower the hydrogen release temperature and increase the rate of hydrogen uptake

by MgH_2. It has been shown by different groups [7–9] that during milling of MgH_2 with transition metal fluorides, the formed MgF_2 phase replaces the original oxide layer and provides a reactive and protective fluorinated surface for hydrogen uptake. This compound possesses high affinity with hydrogen because of the F-anion, which weakens the Mg-H bonding and improves the sorption properties [9].

However, not much work has been done on direct use of MgF_2 as an additive for MgH_2. Ivanov *et al*. [10] reported that addition of 5 wt % MgF_2 to pure Mg during milling leads to 5 wt % hydrogen absorption in over 20 h but has an insignificant effect on dehydrogenation kinetics of MgH_2. Loss in absorption capacity from the second cycle onwards was also observed. Recently, Ma *et al*. [11] investigated the catalytic effects of MgF_2 and TiH_2 to understand the kinetic improvements obtained when MgH_2 was ball milled with 4 mol % TiF_3. They reported that sole addition of 6 mol % MgF_2 has negligible catalytic effect on MgH_2 at an operating temperature of 150 °C.

The limited and inconsistent results attained on catalytic effect of MgF_2 on MgH_2 shows that more work needs to be done to understand this system both from hydrogenation and material perspective. The present work is aimed to investigate the microstructural, morphological and hydrogenation behaviour of MgH_2 when MgF_2 is used as additive.

2. Results

2.1. Comparison of Undoped and 5 mol % MgF_2 Doped MgH_2 at 335 °C

The X-ray diffraction (XRD) patterns of MgH_2 without and with 5 mol % MgF_2 prepared by 1 h ball milling are shown in Figure 1. For the undoped sample, the diffraction pattern peaks are associated with main phase of β-MgH_2 and some unreacted Mg. There is no evidence of the metastable γ-MgH_2 phase. This is due to the short milling time and low milling intensity. A broad peak centered at 43° is attributed to MgO. The crystallite size of β-MgH_2 is evaluated from Rietveld refinement to be 23.4 ± 0.3 nm. Milling with MgF_2 additive was even more effective for reduction of crystallite size of MgH_2 that was evaluated as 10.9 ± 0.3 nm. During milling there is physical interaction between the different species during the repeating collisions. Therefore, the MgF_2 has also some mechanical effect on MgH_2. Unfortunately, the alloying of brittle-brittle system is poorly understood [12]. However, from the present experiment it seems that addition of small amount of MgF_2 improves crystallite size reduction but the exact mechanism is still unclear.

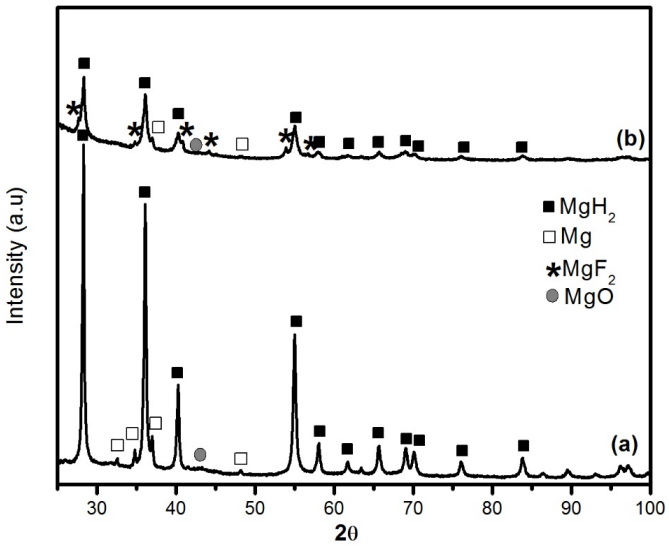

Figure 1. XRD patterns of ball milled samples milled 1 h: (**a**) pure MgH_2 and (**b**) MgH_2 + 5 mol % MgF_2.

In practical applications, desorption will be performed under a pressure of at least 100 kPa of hydrogen. However, in order to study the behaviour of MgH_2–MgF_2 system, we decided to fully dehydride the samples after ball milling. Therefore, after milling the samples were completely desorbed at 335 °C under dynamic vacuum before investigating their hydrogenation properties. Representative hydrogenation and dehydrogenation characteristics are shown in Figure 2.

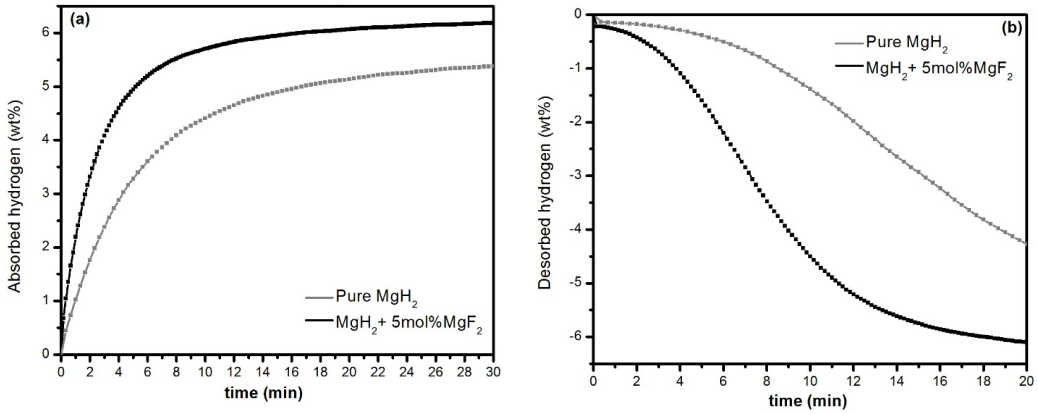

Figure 2. Hydrogen sorption kinetics at 335 °C of 1 h milled MgH_2 without and with 5 mol % MgF_2. (**a**) First absorption under 1000 kPa H_2; (**b**) desorption under 100 kPa H_2.

It is observed that at 335 °C under 1000 kPa H_2 pressure MgH_2 + 5 mol % MgF_2 system absorbs 6.2 wt % hydrogen in 30 min in comparison to only 5.3 wt % absorption by pure MgH_2. This shows a large improvement in absorption capacity is achieved, yielding 92% of the theoretical capacity in comparison to 70% for the pure MgH_2. In addition, significant improvement in desorption kinetics is achieved with complete desorption of the hydride phase in less than 20 min in presence of MgF_2. Thus, the beneficial effect of MgF_2 is clearly evident on the hydriding/dehydriding aspect of MgH_2.

Figure 3 shows the diffraction patterns of the doped sample in its desorbed and reabsorbed states. The desorbed pattern shows a small amount of un-desorbed MgH_2. The interesting fact is that MgF_2 is still present in the sample. This could be expected because it is known that for MgH_2-transition metal (TM) fluoride systems, milling or dehydrogenation induces the formation of MgF_2 and TM hydride [4,11]. Thus, MgF_2 is a stable compound and does not react to form MgH_2.

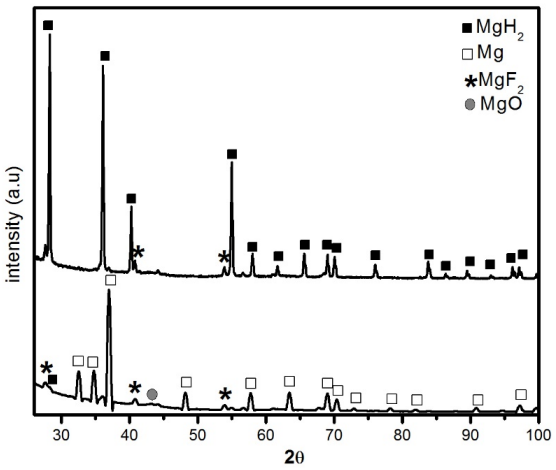

Figure 3. XRD patterns of MgH_2 + 5 mol % MgF_2 (**a**) after desorption at 335 °C under 100 kPa H_2 and (**b**) after re-hydrogenation at 335 °C under 1000 kPa H_2.

This is confirmed by the diffraction pattern of fully hydrided sample. The phases present are MgH_2 and MgF_2 along with small amount of unreacted Mg. Compared to the patterns of Figure 1 we see that the peaks of patterns of Figure 3 are not as broad, implying that the crystallite size increased. From Rietveld analysis we found that the crystallite size of Mg in the dehydrided pattern is 49.1 $\pm$ 0.8 nm while the crystallite size of MgH_2 in the reabsorbed pattern is 64 $\pm$ 2 nm. This shows that there is grain growth compared to the as-milled sample. This may be due to the high temperature of hydrogenation and also because of desorption/absorption itself.

Figure 4 shows the SEM images of MgH_2 + 5 mol % MgF_2 composite in (Figure 4a) desorbed state and (Figure 4b) after re-hydrogenation at 335 °C in comparison with pure MgH_2 (Figure 4c). The images show that ball milling with additive leads to effective decrease in particle size. In addition, energy dispersive X-ray (EDX) mapping done at higher magnification (Figure 5) shows that agglomerates consist of smaller MgH_2 particles and additive.

Elemental mapping made on MgH_2 + 5 mol % MgF_2 in both the desorbed state (Figure 5a) and re-hydrogenated state (Figure 5b) confirms homogenous distribution of MgF_2.

High energy milling leads to uniform dispersion of MgF_2 phase in MgH_2 matrix which may act as a catalytic layer and contributes in improving sorption properties. Chemical analysis performed by EDX spectroscopy during transmission electron microscopy (TEM) investigation of the desorbed sample gave the average atomic composition of different elements as 9.8% O, 14.7% F and 75.7% Mg which is very close to the nominal composition (86% Mg and 14% F). The presence of oxygen in EDX pattern in comparison to its small trace in XRD pattern could be due to small crystallite size of MgO making it peak difficult to distinguish from the background. A similar EDX investigation was performed on a sample that has been submitted to five dehydrogenation/hydrogenation cycles. Because abundances vary from point to point, we average over four different localisations. We found that, after cycling, the atomic composition of different elements was 15% $\pm$ 4% O, 11% $\pm$ 4% F and 74% $\pm$ 6% Mg. Within experimental error, these values are similar to the ones before cycling. However, this may be an indication that cycling induces a loss of MgF_2 and increase of MgO. Typical TEM micrographs presented in Figure 6 shows the morphology of the desorbed sample.

The image shows presence of large number of particles agglomerated together with no visibility clear particle boundaries. These observations are quite similar to those reported recently by Grzech *et al*. [13]. High resolution pictures taken over region-1 in Figure 6 and its corresponding selected area electron diffraction (SAED) patterns shows reflections at *d*-spacing 2.45, 1.90, 1.60, 1.36 and 1.22 Å which are characteristic of Mg (101), (102), (110), (112) and (202) planes respectively along with reflections at d values 2.10 and 1.48 Å, corresponding to MgO (200) and (220) planes. Thus, the surface consists of small crystallites of MgO (forming well defined ring and represented by red rings) surrounding the large crystallites of Mg (seen as discontinuous spots and represented by white rings). While the multiple SAED patterns acquired from the region-2 were well indexed as a mixture of large crystallite Mg and small crystallite of MgF_2 (seen as well-defined rings and colored yellow). The absence of oxide in region-2 is evidence that presence of fluoride limits MgO only to the surface. Both structural and morphological studies support the presence of MgF_2 phase even after complete hydrogen absorption/desorption cycle at 335 °C.

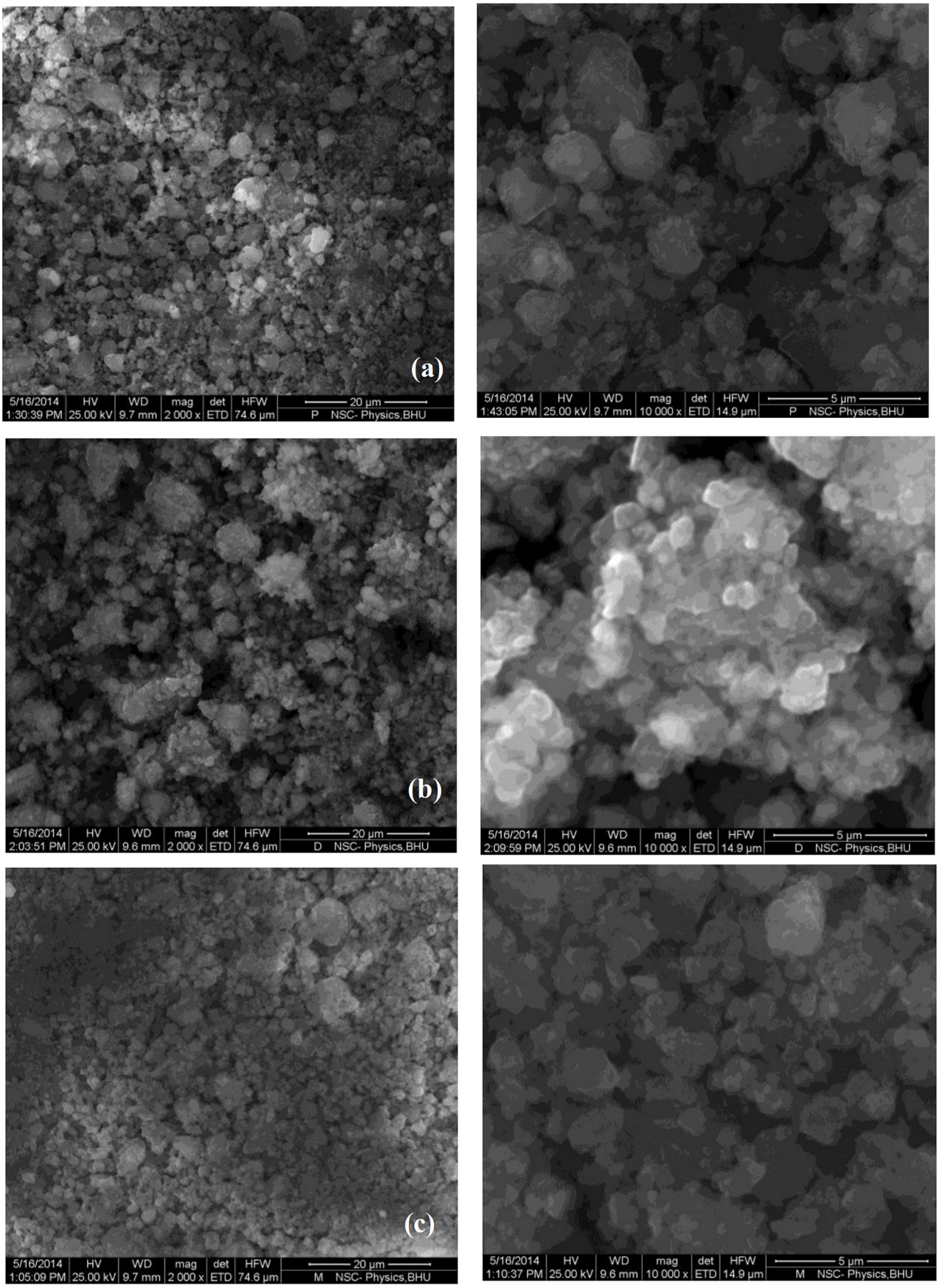

Figure 4. SEM images for MgH_2 + 5 mol % MgF_2 in (**a**) desorbed state and (**b**) re-hydrogenated state in comparison to (**c**) pure MgH_2.

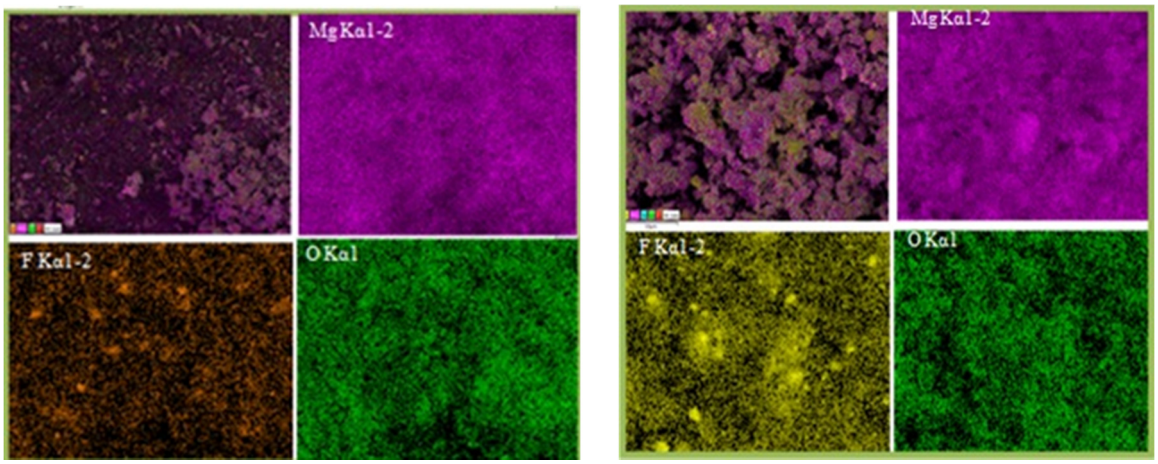

Figure 5. Elemental mapping showing particle morphology and distribution of 1 h milled MgH_2 + 5 mol % MgF_2: (**a**) after desorption and (**b**) after re-hydrogenation at 335 °C.

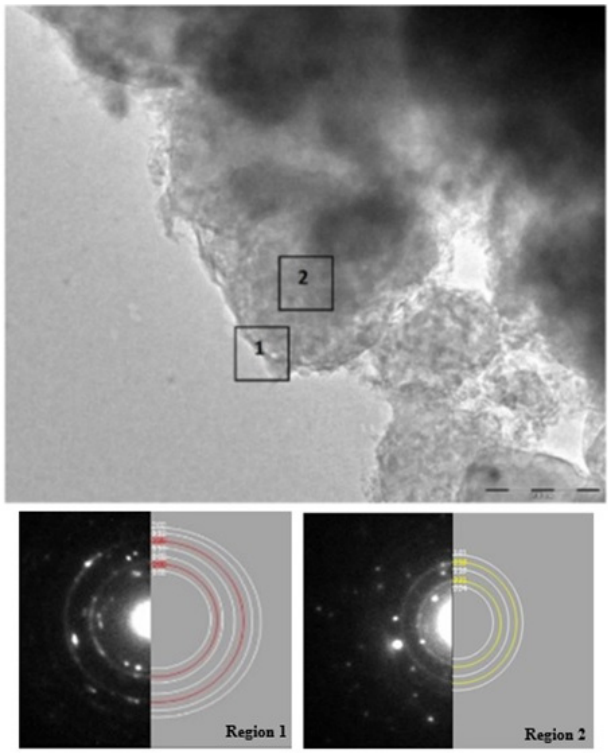

Figure 6. Transmission electron microscopy (TEM) micrograph of MgH_2 + 5 mol % MgF_2 sample after desorption at 335 °C with selected area electron diffraction (SAED) patterns and simulations. Region 1 is composed of Mg (**white rings**) covered with MgO layer (**red rings**) in simulated data while Region 2 shows diffraction rings corresponding to Mg (**white rings**) and MgF_2 (**yellow rings**).

2.2. Hydrogenation Characteristics of MgH_2 + 5 mol % MgF_2 at Lower Temperatures

The catalytic effect of 5 mol % MgF_2 on hydrogen sorption properties of MgH_2 was further investigated at lower temperatures. Figure 7 shows the absorption kinetics at 335, 310, 285 and 145 °C under 1000 kPa of hydrogen.

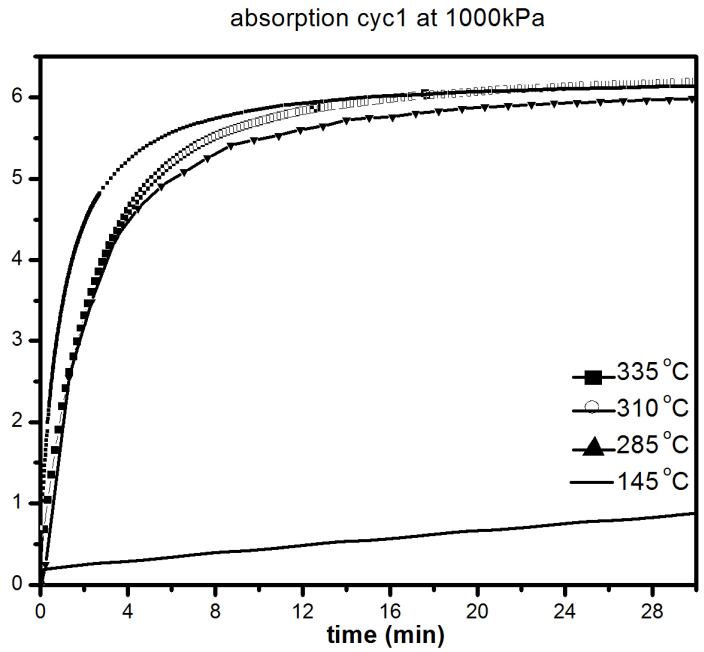

Figure 7. First absorption under 1000 kPa H_2 at different temperatures of 1 h milled MgH_2 + 5 mol % MgF_2. The insert is a compete absorption curve at 145 °C.

It should be pointed out that the samples were initially desorbed at 335 °C in order to ensure that full desorption was achieved before all absorption measurements. We notice only a slight loss in absorption capacity with reduction of temperature from 335 °C (6.2 wt % H_2) to 285 °C (5.8 wt % H_2). As seen in Figure 7, there was slight loss in kinetics and capacity in the temperature range 335–285 °C with the material reaching its complete capacity in less than 30 min. However, at 145 °C, the kinetics are much slower, but after 20 h, a capacity of 5.5 wt % is reached, as shown in Figure 7b. Desorption kinetic under 100 kPa H_2 at 285, 310 and 335 °C are shown in Figure 8.

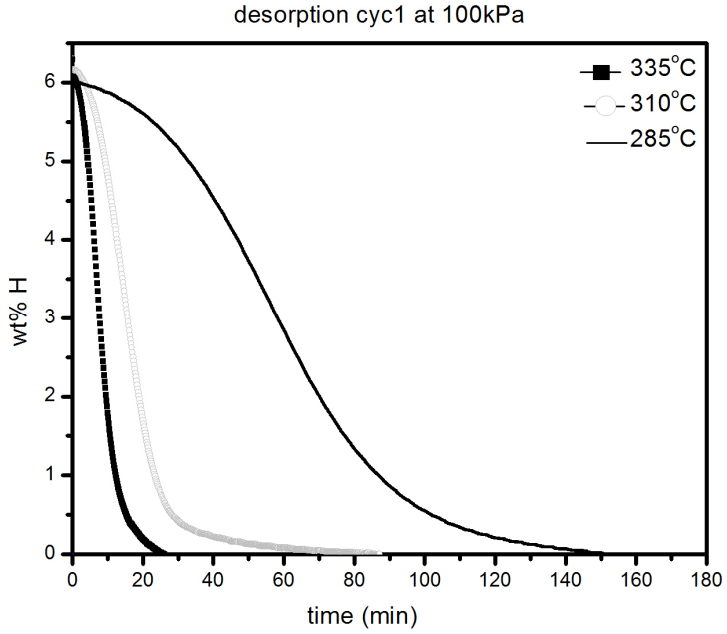

Figure 8. Desorption under 100 kPa H_2 at different temperatures of 1 h milled MgH_2 + 5 mol % MgF_2.

As expected, the kinetics are getting slower as temperature decreases but is still relatively fast even at 285 °C were complete desorption takes place in less than 3 h. These results reveal that even by sole addition of alkaline metal fluorides, improvements in hydrogenation characteristics of magnesium hydride can be achieved.

2.3. Cyclic Stability of MgH_2 + 5 mol % MgF_2 at T = 310 °C

Micro structural results have confirmed that MgF_2 phase does not decompose and no new phase formation occurs during hydrogen absorption/desorption measurements for MgH_2 + 5 mol % MgF_2 system. Therefore, cyclic performance of catalyzed magnesium hydride was examined at moderate operating temperature of 310 °C at pressure of 1000 kPa (for absorption) and 10 kPa (for desorption) to evaluate performance stability. Prior to the measurements the sample was completely desorbed at 335 °C. Figure 9 shows that the absorption capacity goes down from 5.9 wt % in first cycle to 5.6 wt % in the 10th cycle.

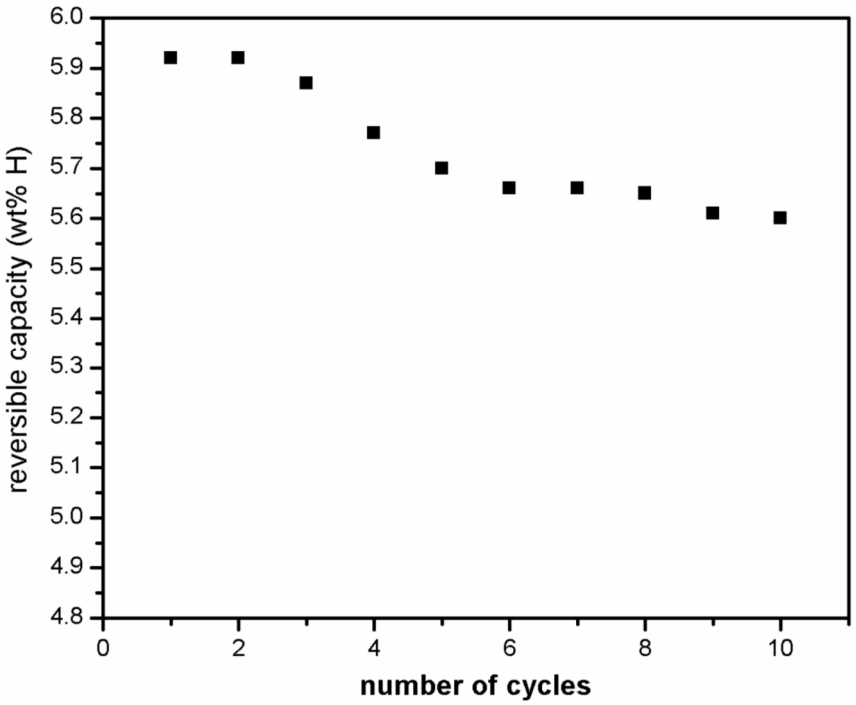

Figure 9. Hydrogen absorption kinetics at 310 °C under 1000 kPa of hydrogen of ball milled MgH_2 + 5 mol % MgF_2 for 10 cycles.

The observed loss of 0.3 wt % in capacity was reached within the first five cycles and thereafter the maximum capacity achieved by the system is more or less stabilized. These results show that magnesium hydride exhibits good hydrogen storage capacity and cyclic stability when magnesium fluoride is used as catalyst in comparison to the use of transition metal fluoride like NbF_5 or ZrF_4 where sharp decline in storage capacity was observed by Malka *et al*. [14] in the first 10 hydrogenation cycles recorded at 325 °C. X-ray diffraction patterns of the sample taken after 1st and 10th desorption cycle are presented in Figure 10. It shows that the β-MgH_2 phase and the catalytic material remain intact while small increase in content of MgO occurs. Thus, the growth of the MgO layer is mostly responsible for an observed loss in capacity.

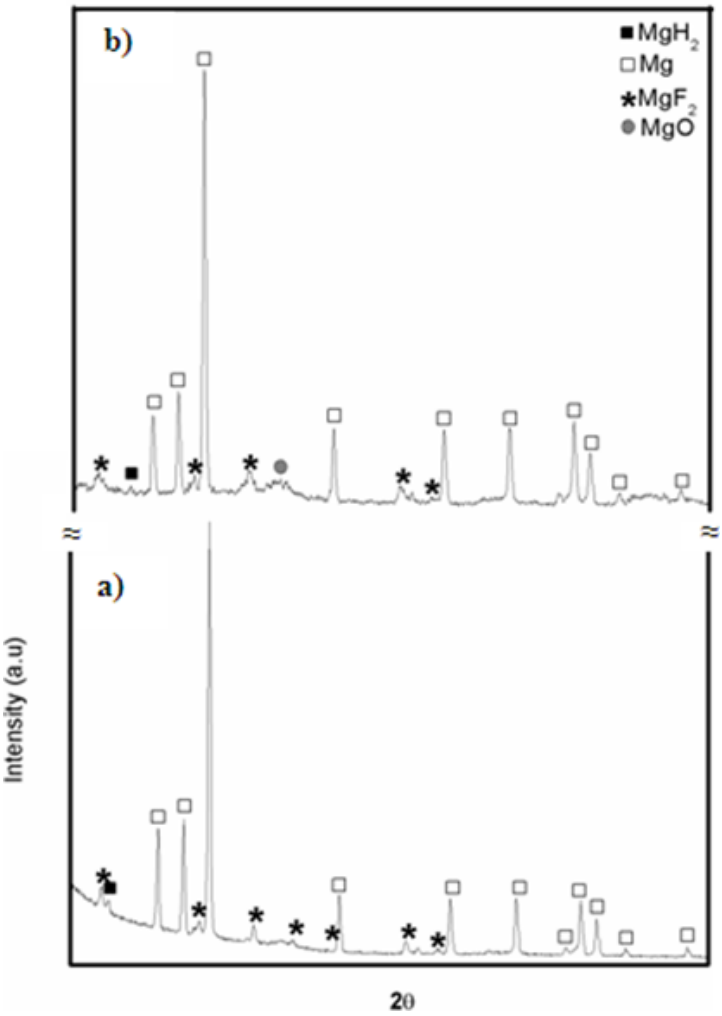

Figure 10. X-ray diffraction patterns of ball milled MgH_2 + 5 mol % MgF_2 after (**a**) one desorption and (**b**) 10 desorption cycles at 310 °C.

3. Discussion

The structural and hydrogenation results suggest that hydrogen absorption/desorption kinetics of MgF_2 doped MgH_2 is relatively slower than that attained with transition metal fluorides (TmF = TiF_3, ZrF_4, NbF_5, TaF_5). This could be explained by the presence of only one catalytically active phase in the present case (MgF_2) while two active phases are present when transition metal fluorides are used as additives. More explicitly, upon dehydrogenation the following reaction takes place in the present case.

$$MgH_2 + MgF_2 \rightarrow Mg + MgF_2 + H_2 \quad (1)$$

While, as reported by Ma *et al*. [11], when transition metal fluoride is added the reaction taking place is:

$$3MgH_2 + 2TiF_3 \rightarrow 3\,MgF_2 + 2TiH_2 + H_2 \quad (2)$$

As TiH_2 possess more negative enthalpy formation (−136 kJ/mol) than MgH_2 (−75 kJ/mol) it will remain as a stable phase during desorption of MgH_2 in later cycles [13]. Furthermore, presence and concentration of TiH_2 phase would increase on multiple absorption/desorption cycling, which results in reduction of overall storage capacity. In addition, the transition metal fluoride is very sensitive to atmospheric conditions. Ball milled MgH_2 + TM-fluoride samples require oxygen and moisture level to be less than 0.1 ppm for obtaining good hydrogenation results [7,9,11,15].

Additionally, even in the desorbed state the material is pyrophoric, which makes it difficult to handle. Moreover, transition metals are much heavier than magnesium thereby increasing the mass of entire system. It thus seems more practical to use MgF_2 as a doping agent to increase the hydrogenation/dehydrogenation kinetics than transition metal fluorides.

4. Experimental Section

The starting materials MgH_2 (99.8% purity) and MgF_2 (99.9% purity) purchased from Alfa Aesar (Ward Hill, MA, USA) were vacuum annealed for few hours at 80 °C before using them for experiments. Afterwards, MgH_2 powder with 2, 5, and 10 mol % MgF_2, was milled under Ar atmosphere using Fritsch P4 planetary mill (Idar-Oberstein, Germany) with ball to powder ratio of 50:1 at a crucible rotation speed of 220 rpm. Milling was done for 60 min with 15 min rest after every 15 min of milling. The final milled products were handled in a glove box with oxygen and moisture level below 0.1 ppm. Initial hydrogen desorption curves taken at 335 °C under 100 kPa H_2 pressure showed that with 2 mol % catalytic material the kinetics was too slow which could be improved by increasing the additive content to 5 mol %. Further increase in concentration of catalytic material to 10 mol % didn't cause any significant change in kinetics. Therefore, MgF_2 concentration was restricted to 5 mol % for further investigation.

The hydrogenation characteristics were measured on homemade Sievert-type apparatus and the cyclic studies were made on an automated-four channel apparatus called Multi Channel Hydride Evaluation System from Advanced Materials Corporation, Petersburg, VA, USA. Approximately 400 mg of powder was placed in a sample cell and completely desorbed under dynamic vacuum at 335 °C prior to any measurement. Thereafter all measurements were made under 1000 kPa H_2 pressure for absorption and 100 kPa H_2 pressure for desorption at temperatures ranging from 335 °C to 145 °C. X-ray diffraction was performed using Bruker D8 Focus X-Ray apparatus (Bruker, Madison, WI, USA) with CuKα radiation. Phase abundances were evaluated from Rietveld method using Topas software [16]. Small quantity of milled MgH_2 + 5 mol % MgF_2 (a) after desorption at 325 °C and (b) after rehydrogenation under 1000 kPa H_2 was characterized for morphological studies with chemical analysis using JEOL JSM-5500 scanning electron microscope (JEOL, Tokyo, Japan). The sample was filled in air tight bottles and taken to SEM-EDX lab were they were slightly exposed to air for loading in SEM chamber. TEM analysis was performed on FEI: Technai $20G^2$ electron microscope (FEI, Hillsboro, OR, USA), operating at 200 kV accelerating voltage. TEM samples were prepared by dry dispersion of the powder onto a carbon substrate supported by copper TEM grid. This was done in an argon glove box before the TEM session, and the prepared sample was sealed by covering with parafilm tape to be carried to TEM lab. The sample was exposed to air for short duration during loading onto the TEM holder. Thus, partially transformed samples were characterised using scanning and transmission electron microscopy.

5. Conclusions

This investigation showed that magnesium fluoride could significantly influence the hydrogen sorption properties of magnesium hydride. It has been shown that MgF_2 additive acts as a catalyst for MgH_2, thereby improving its hydrogenation/dehydrogenation kinetics. These kinetic improvements are due to the presence of chemically stable MgF_2 powder well mixed in MgH_2 matrix and MgO layer being limited only to the surface. Cyclic stability reveals that 5 mol % MgF_2 helps to accelerate the reversible kinetics of MgH_2 with higher capacity in comparison to other transition metal fluoride catalysts. This is probably due to the persistence of MgF_2 phase during hydrogen cycling. These results suggest that owing to its fast sorption properties, low sensitivity to atmospheric conditions and easy handling ability, this material can be used in applications where operation at relatively high temperature is not considered a significant issue.

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Conflicts of Interest: The authors declare no conflict of interest.

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