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Catalytic Effect of TiF_3 on Hydrogenation Properties of MgH_2

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***Abstract*- Magnesium based hydrides are attractive materials for hydrogen storage with reversible hydrogen capacity up to 7.6 wt%. However, the potential for commercial applications of MgH_2 is limited because of its high temperature of hydrogen discharge and slow desorption kinetics.**

The present work deals with investigating the catalytic effect of TiF_3 on hydrogenation properties of MgH_2. The samples are prepared by ball milling MgH_2 with varying concentration of TiF_3 at different milling time. Absorption/desorption kinetics were studied by Sievert's type apparatus under different temperatures. The subsequent changes in structural and morphological properties induced by hydrogenation / dehydrogenation are studied using XRD and SEM. Results indicate that the catalyst enhances the kinetics of pure MgH_2 with stablity in capacity. MgH_2+10wt% TiF_3 ball milled for two hour was found to absorb 3wt% hydrogen at 573K temperature.

***Keywords*- Hydrogen Storage, transition metal fluoride, Ball milling, catalyst, kinetics.**

I. INTRODUCTION

Due to high gravimetric (7.6%) and volumetric (110 kgm-^{3}) hydrogen capacity, low cost, high abundance and good reversibility MgH_2 has been considered as a one of the most promising material for hydrogen storage. However its practical onboard application for hydrogen storage is impeded by its high operating temperature and sluggish hydriding/dehydriding kinetics [1]. Various studies have been carried out to enhance the hydrogen sorption properties of nano crystalline MgH_2 by adding suitable catalysts such as transition metal, their oxides and halides. Among various additives Nb_2O_5 possesses an impressive catalytic effect on the sorption kinetics of MgH_2 [2].

Recently it has been reported that metal halide catalyst addition results in better hydrogen storage than their metal or metal oxides. Bhat *et al.* [3] compared the effect of Nb_2O_5 with its halide $NbCl_5$. They found that $NbCl_5$ shows better catalytic effect than Nb_2O_5. The influence of niobium oxide and halide on the hydrogen desorption properties of ball milled MgH_2 have been investigated by Recham *et al* [4] and found that the halides show faster kinetics and reduced hydrogen desorption temperature. It has also been found that some transition metal halides, such as $CrCl_3$, FeF_3, NiF_2, Tif_3, $NbCl_5$ and NbF_5, also show very good catalytic property [5- 12]. Jin *et al.*[13] investigated the effect of various halide additives (NiF_2, Tif_3, VF_4, NbF_5, FeF_2, ZrF_4, CrF_2, CuF_2, CeF_3, YF_3) on the decomposition temperature of MgH_2 by DSC method and found that Ni, Ti, V and Nb fluorides are more effective than Fe, Zr, and Cr, while CuF_2, YF_3 and CeF_3 do not have a significant catalytic effect.

Malka *et al.* [14] studied the influence of various halide additives (chlorides and fluorides) on the decomposition temperature of MgH_2 using the TPD method and reported that fluorides are better catalyst than chlorides. Halides having highest oxidation state reduce magnesium decomposition temperature more effectively than their counterparts with lower oxidation state. Halide from group IV and V of the periodic table are better catalysts in comparison to the other studied halide [14]. During the ball milling MgH_2 react with fluorides and formed a protective and reactive layer of MgF_2. This compound has a high affinity with hydrogen because of the F-anion, which weakens the Mg-H bonding and improves the sorption properties [15- 17].

In this paper influence of TiF_3 halide (with various concentrations) additive on the hydrogenation properties of ball milled MgH_2 at different milling time has investigated. This system possesses enhanced sorption kinetics, in particular the absorption performance at a moderate temperature range.

II. EXPERIMENTAL

Pure MgH_2 (purity 98%) and TiF_3(98%)were purchased from Alfa Aesar. Ball milling was carried out, nominally at Room Temperature (RT) using planetary (Retsch PM 100 type) ball mill. The vial and ball materials were hardened chromium steel. To start with MgH2 was milled in Argon (Ar) atmosphere for 20 hours at RT. Then MgH_2+ x wt% TiF_3 (x = 5, 10 & 15) were ball milled for 2 and 5 h under Ar atmospheric condition. The powder specimen was loaded into the vial then sealed using an O-ring covered with a thin layer of sealing grease in an Ar filled homemade Glove box at our laboratory in University of Rajasthan Jaipur, India. The ball-to-powder mass-charge ratio (BPR) was approximately 40:1 and the milling speed has been maintained at 300 rpm for different milling periods.

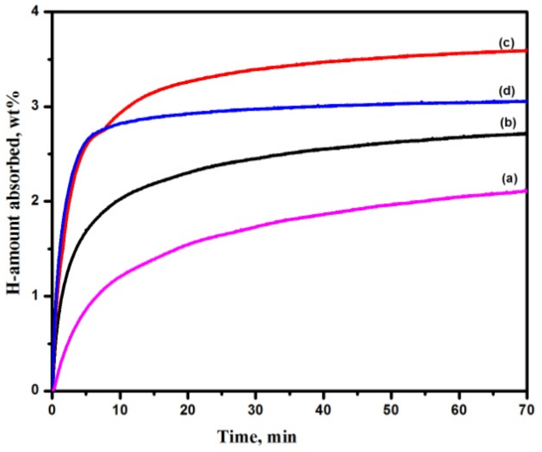

Fig.1. Hydrogen absorption curves at 573 K of (a) 20 hrs milled MgH_2, (b)-(d) 2 hrs milled MgH_2 + xwt% TiF_3 (x = 5, 10, 15).

Hydrogenation storage properties of TiF_3 doped MgH_2 were investigated at different temperatures by using a Sievert-type apparatus which was built up in our lab. Prior to study the whole system was evacuated to 10^{-6} Torr vacuum at 673 K for 2 h and the samples were introduced for hydrogenation in the chamber. To perform hydrogenation measurement one gram of the as-milled sample was kept in a stainless steel cylindrical vial (5 ml capacity) and closed with a filtered stainless steel cap and inserted in the stainless steel high pressure reactor (20 ml capacity). Before measurements sample was completely desorbed at 350 ^{0}C under vacuum of $1x10^{-6}$ Torr.

The structures of the samples were characterized by X-ray Diffraction (XRD, Panalytical Make X' Pert PRO MPD) analysis using CuKα radiation (λ= 1.54 Å). Particle size and surface topology of all the samples were investigated using Scanning Electron Microscope (SEM, ZEISS with EHT 20.00 Kv).

III. RESULTS AND DISCUSSION

A. Effect of the addition of TiF_3

The hydrogen sorption kinetics of MgH_2, by mechanical milling with additives can be markedly improved at near room temperature. The catalytically enhanced kinetic performance was found to persist in the absorption/desorption cycles. But the catalytic mechanism has not yet been well established. The absorption curves of 20 and 2 hrs milled MgH2 and MgH_2+ x wt% TiF_3 (x = 5, 10, 15) are shown in Fig. 1 respectively.

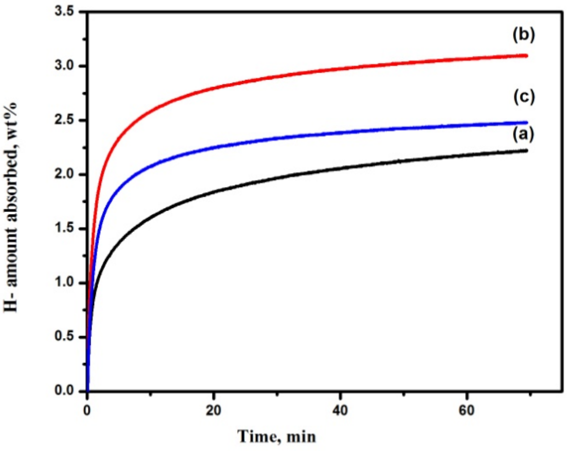

Fig.2. Hydrogen absorption curves at 523 K of 2 h milled MgH_{2+}x wt% TiF_3(a)–(c) for 5, 10 and 15wt%.

It is observed that the addition of different amount of Catalyst improved the absorption kinetics of MgH_2. From 5- 10 wt% of TiF_3 hydrogen absorption capacity increased as well as absorption kinetics but further with increasing concentration of catalyst hydrogen capacity decreased .The absorbed amount of hydrogen are 2, 3 and 2.8 wt% for MgH_{2+}x wt% TiF_3 (x = 5, 10, and 15) in first 10 minutes. Here we report additional results at lower operating temperature (523 K) and found that the absorbed amount of hydrogen is decreased to about 1.5, 2.5 and 2.0 wt% for the additives concentration (x = 5 – 15) of TiF_3 as shown in Fig.2. It is concluded that the highest storage capacity is 3 wt% for the MgH_2-10 wt% TiF_3. The results also show that the high concentration of TiF_3 catalyst will degrade the hydrogen storage capacity of the material, as seen from the profile of the sample containing 15 wt% TiF_3.

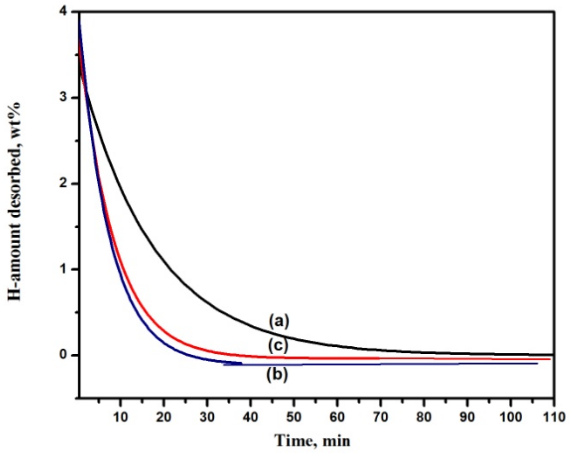

Fig. 3. Hydrogen desorption curves at 573 K of MgH_2+x wt% TiF_3 for x = 5, 10, 15 in (a), (b) and (c).

Therefore, 2 h milled MgH_2+10 wt% TiF_3 is selected for further investigation of structural properties of as-milled and hydrogenated/ de-hydrogenated samples and hydrogen storage capacity at different operating temperatures (below 300 ^{0}C).

The pronounced catalytic enhancement arising upon adding of TiF_3 was also observed on the hydrogen desorption properties. Fig. 3 shows the desorption curves at 573 K of 2 h milled MgH_2+ x wt% TiF_3 (x = 5, 10, 15). It is clear from the desorption results, that more hydrogen is released in the same time limit from the 10 wt% TiF_3 than the other ones. Addition of TiF_3 improved the desorption kinetics of MgH_2 by accelerated desorption rate and reduced operating temperature.

B. *Effect of milling time*

The effect of milling time on MgH_2+10 wt% TiF_3 for 2 and 5 hrs are shown in Fig. 4. Apparently, a longer milling time leads to a more pronounced kinetic enhancement in particular during the initial periods.

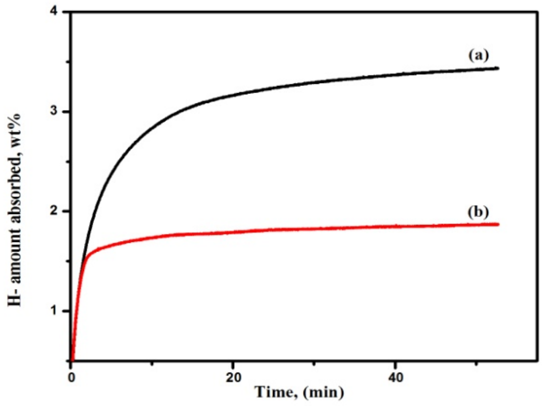

Fig.4. Comparision of hydrogen absorption of ball milled MgH_2+10 wt% TiF_3 at 573 K for (a) 2 h (b) 5 h.

However, it is also observed that increasing milling time causes a substantial decrease in the hydrogen capacity. Hydrogen storage of MgH_2 +10 wt% TiF_3 at 573 K is observed to be 3.0 wt% in 10 minutes for 2 hrs milled while for 5 hrs milled it's decreased to ~1.7 wt%.

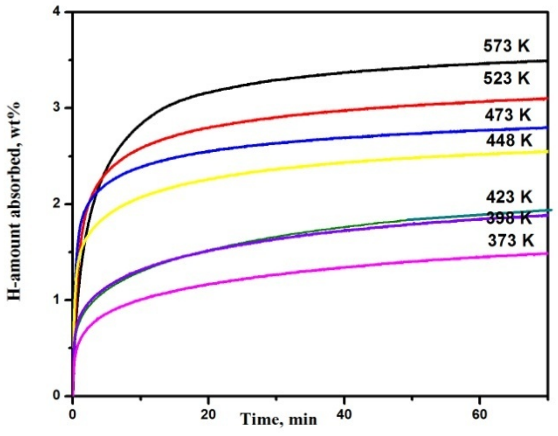

Fig. 5. Hydrogen absorption curves of MgH_2+10 wt% TiF_3 at temperature range from 573 K to 373 K in the curves of (a) – (g) respectively

C. Hydrogen storage performance

Hydrogen storage performance of 2 hour milled MgH_2+ xwt% TiF_3 was further investigated for the temperature range from 573 K to 373 K which are shown in fig. 5 from (a)-(g). Generally pre-activation is required for the pure MgH_2 however, in case of MgH_2 catalyzed with TiF_3 or any other transition metal halides pre-activation is not required and sample is directly used for the measurements after complete desorption at 573 K for 2 h. In case of 2 h milled MgH_2+10 wt% TiF_3 the absorbed hydrogen amount was found 3 wt% within 10 minutes and was about to saturate in one hr for the temperature range 523–448 K. The hydrogen capacity of this material is decreased by half of the above capacity in the temperature range from 423 – 373 K. It is concluded from the results that the increment in hydrogen storage capacity is due to the catalytic effect of TiF_3 on MgH_2 in the starting time periods (~10 minutes).

D. Structural characterization

The catalytic effect of 10 wt% TiF_3 on structural properties of MgH_2 have been investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Fig.6 shows the diffraction patterns of 2 h milled MgH_2-+10wt% TiF_3 for as-prepared, hydrogenated and dehydrogenated samples. It is clear from the results that diffraction pattern of as-milled sample is quite similar to MgH_2. The qualitative result obtained from weak and broad peaks shows that the grain size decreases and lattice strain increases [18].

In the case of the as-milled sample, the most intense Bragg peaks are identified as tetragonal β-MgH_2 and a metastable orthorhombic phase γ-MgH_2 which has been previously reported to form upon milling MgH_2 [19]. It is observed from the diffraction patterns that the intensity of β-MgH_2 peak increased after hydrogenation and disappeared after dehydrogenation. Besides, the formation of a γ- MgH_2 induced by high energy milling is also observed and disappears in the dehydrogenation process as in case of β-MgH_2 peak.

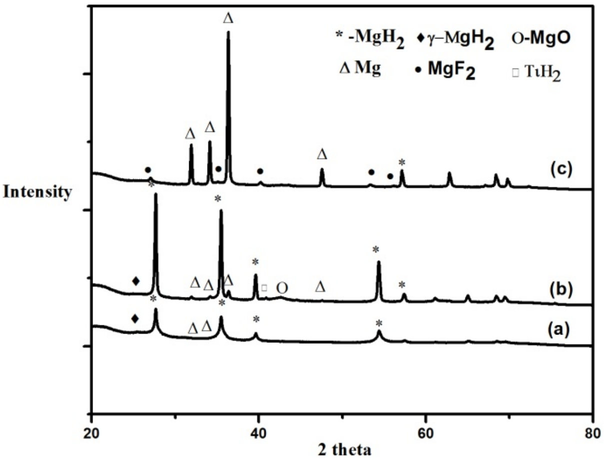

Fig.6. XRD patterns of the MgH_2+10wt% TiF_3 (a) as prepared, (b) hydrogenated and (c) after desorption.

In the present case MgO was detected in both samples except dehydrogenated sample, which is likely due to the slight oxygen contamination. No peak related to TiF_3 is identified in as-milled sample. After dehydrogenation process MgF_2 and TiH_2 peak were observed, suggesting that MgH_2 reacts with TiF_3 to produce MgF_2. When MgH_2 reacts with fluorides, MgF_2 is usually formed as a protective and reactive layer during the reaction between MgH_2 and titanium or metal fluoride [3, 4, 6, 20]. This compound possesses a high affinity with hydrogen because of the F- anion, which weakens the Mg-H bonding and improves the sorption properties [4]. The formation of these two phases should follow reaction (1). It is highly expected that this reaction can occur during milling process due to collision between vial, balls and among the balls produced high energy environment.

$$MgH_2 + 2/3\ TiF_3 \rightarrow MgF_2 + 2/3\ TiH_2 + 1/3\ H_2 \ldots\ldots (1)$$

Fig.7 shows the SEM micrographs of 2 h milled MgH_2+10%wt TiF_3 and subsequently hydrogenated-dehydrogenate at 573 K. The results indicate that the particle size of MgH_2 is effectively decreased after ball milling and found many particles distribution at the surface of the composite matrix. The decrease of particle size can enhance the rates of hydrogenation-dehydrogenation.

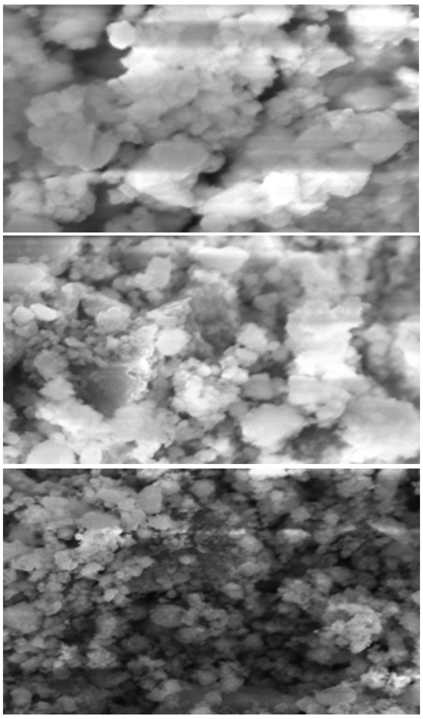

Fig.7. SEM images of 2h milled MgH_2+10 wt% TiF_3 (a) as milled (b) hydrogenated and (c) dehydrogenation.

IV. CONCLUSIONS

Titanium fluorides that readily react with MgH_2 to form hydrides or metal–hydrogen solid solutions tend to exert a significant catalytic effect on the hydrogenation kinetics of MgH_2.

It is concluded that the various concentration of catalyst (TiF_3) improved the absorption/ desorption kinetics of MgH_2. The 2 h milled MgH_2+10 wt% TiF_3 absorbed hydrogen 3 wt% within 10 minutes and about to saturate in one hr at below operating temperature while the hydrogen desorption was the same wt% in time limit. The storage capacity of MgH_2 +10 wt% TiF_3 at operating temperature 573 K is decreased with increasing milling time and decreased by ~1.7 wt% in 10 minutes.

The microstructure and XRD analysis show that MgF_2 and TiH_2 phases form in the dehydrogenation process for the 2 h milled MgH_2-10 wt% TiF_3 sample.

V. ACKNOWLEDGEMENT

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