Catalytic Effect of TiF₃ on Hydrogenation Properties of MgH₂

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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 MgH₂ is limited because of its high temperature of hydrogen discharge and slow desorption kinetics. The present work deals with investigating the catalytic effect of TiF₃ on hydrogenation properties of MgH₂. The samples are prepared by ball milling MgH₂ with varying concentration of TiF₃ 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 MgH₂ with stability in capacity. MgH₂+10wt% TiF₃ 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 MgH₂ 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 MgH₂ by adding suitable catalysts such as transition metal, their oxides and halides. Among various additives Nb₂O₅ possesses an impressive catalytic effect on the sorption kinetics of MgH₂ [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 Nb₂O₅ with its halide NbCl₅. They found that NbCl₅ shows better catalytic effect than Nb₂O₅. The influence of niobium oxide and halide on the hydrogen desorption properties of ball milled MgH₂ 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 CrCl₃, FeF₃, NiF₂, TiF₃, NbCl₅ and NbF₅, also show very good catalytic property [5-12]. Jin et al.[13] investigated the effect of various halide additives (NiF₂, TiF₃, VF₄, NbF₅, FeF₂, ZrF₄, CrF₂, CuF₂, CeF₃, YF₃) on the decomposition temperature of MgH₂ by DSC method and found that Ni, Ti, V and Nb fluorides are more effective than Fe, Zr, and Cr, while CuF₂, YF₃ and CeF₃ 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 MgH₂ 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 MgH₂ react with fluorides and formed a protective and reactive layer of MgF₂. 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 TiF₃ halide (with various concentrations) additive on the hydrogenation
properties of ball milled MgH\textsubscript{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\textsubscript{2} (purity 98\%) and TiF\textsubscript{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\textsubscript{2}+ x wt\% TiF\textsubscript{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.

III. RESULTS AND DISCUSSION

A. Effect of the addition of TiF\textsubscript{3}

The hydrogen sorption kinetics of MgH\textsubscript{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 MgH\textsubscript{2} and MgH\textsubscript{2}+ x wt\% TiF\textsubscript{3} (x = 5, 10, 15) are shown in Fig. 1 respectively.

![Fig.1. Hydrogen absorption curves at 573 K of (a) 20 hrs milled MgH\textsubscript{2}, (b)-(d) 2 hrs milled MgH\textsubscript{2} + xwt\% TiF\textsubscript{3} (x = 5, 10, 15).](image)

Hydrogenation storage properties of TiF\textsubscript{3} doped MgH\textsubscript{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\textsuperscript{-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 0C under vacuum of 1x10\textsuperscript{-5} Torr.

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

![Fig.2. Hydrogen absorption curves at 523 K of 2 h milled MgH\textsubscript{2}+x wt\% TiF\textsubscript{3}(a)–(c) for 5, 10 and 15wt\%.](image)

It is observed that the addition of different amount of Catalyst improved the absorption kinetics of MgH\textsubscript{2}. From 5- 10 wt\% of TiF\textsubscript{3} hydrogen absorption capacity increased as well as absorption kinetics but further with increasing concentration of catalyst hydrogen capacity
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. 2. Hydrogen desorption curves at 573 K of MgH$_2$+x wt% TiF$_3$ for x = 5, 10, 15 in (a), (b) and (c).](image1)

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 °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. 3. Hydrogen desorption curves at 573 K of MgH$_2$+x wt% TiF$_3$ for x = 5, 10, 15 in (a), (b) and (c).](image2)

![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.](image3)

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](image4)
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.](image)

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.

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\text{MgH}_2 + \frac{2}{3} \text{TiF}_3 \rightarrow \text{MgF}_2 + \frac{2}{3} \text{TiH}_2 + \frac{1}{3} \text{H}_2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots ..
particle size can enhance the rates of hydrogenation-dehydrogenation.

The microstructure and XRD analysis show that MgF₂ and TiH₂ phases form in the dehydrogenation process for the 2 h milled MgH₂-10 wt% TiF₃ sample.

IV. CONCLUSIONS

Titanium fluorides that readily react with MgH₂ to form hydrides or metal–hydrogen solid solutions tend to exert a significant catalytic effect on the hydrogenation kinetics of MgH₂.

It is concluded that the various concentration of catalyst (TiF₃) improved the absorption/desorption kinetics of MgH₂. The 2 h milled MgH₂+10 wt% TiF₃ 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 MgH₂+10 wt% TiF₃ at operating temperature 573 K is decreased with increasing milling time and decreased by ~1.7 wt% in 10 minutes.

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VI. REFERENCES


