Improved H-Storage Performance of Novel Mg-Based Nanocomposites Prepared by High-Energy Ball Milling: A Review

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Abstract: Hydrogen storage in magnesium-based composites has been an outstanding research area including a remarkable improvement of the H-sorption properties of this system in the last 5 years. Numerous additives of various morphologies have been applied with great success to accelerate the absorption/desorption reactions. Different combinations of catalysts and preparation conditions have also been explored to synthesize better hydrogen storing materials. At the same time, ball milling is still commonly and effectively applied for the fabrication of Mg-based alloys and composites in order to reduce the grain size to nanometric dimensions and to disperse the catalyst particles over the surface of the host material. In this review, we present the very recent progress, from 2016 to 2021, on catalyzing the hydrogen sorption of Mg-based materials by ball milling. The various catalyzing routes enhancing the hydrogenation performance, including in situ formation of catalysts and synergistic improvement achieved by using multiple additives, will also be summarized. At the end of this work, some thoughts on the prospects for future research will be highlighted.

Keywords: hydrogen storage; ball milling; Mg-based composites; catalysts

1. Introduction

According to the Key World Energy Statistics 2020 report of the International Energy Agency, the worldwide total energy consumption has increased by 50% in the last 20 years [1]. The majority of the consumed energy is produced from non-renewable sources, mainly oil and natural gas. The associated pollution puts a significant burden on the environment as we see more and more evidence of climate change, since CO₂ emissions increased by 50% in the last 20 years. To counterbalance this issue, renewable energy sources have gained significant attention in the last few decades. For example, the energy production using renewables and biofuel has continuously increased in the EU since the early 2000s, and in 2018, these two sources accounted for 34.2% of the total energy production [2]. With the significant increment in the renewable production capacity, the inherent difficulties of these sources (location dependency, non-continuous supply) become a more pressing issue. Hence, energy storage technologies have to be developed to cope with future demands.

One of the promising prospects is the utilization of hydrogen as an energy vector [3,4]. Hydrogen has several positive features, including its outstanding energy density per mass unit (120–140 MJ/kg) and the absence of harmful byproducts when used in a fuel cell [4–7]. Although the production of hydrogen is currently largely based on techniques using fossil sources, such as hydrocarbon reforming and gasification, there are some promising methods utilizing renewable energy sources as well [5,8–10]. For example, photocatalytic water splitting and hydrogen generation from biomass are particularly attractive methods for green hydrogen generation; furthermore, there are also attempts to apply biological processes for such purpose [5,8,9]. Hydrogen can be employed in a number
of transportation and stationary applications; for example, fuel cell electric vehicles may be an alternative to internal combustion vehicles and also to electric vehicles using Li-ion batteries [6,11]. Buses, trains, trams and other similar vehicles are particularly suitable for the introduction of hydrogen fuel cells, since these applications do not need an extensive refueling infrastructure [11]. Hydrogen can also be used as a stationary energy storage medium, such as a complementary power supply for solar powered households [12] and off-grid charging stations [13], in case of the absence of sunlight. There are proposals for large scale storage of renewable energy on a daily and even seasonal basis [14,15].

One of the major problems of widespread commercialization of hydrogen-based technologies is the lack of efficient and application-friendly hydrogen storage solutions [16,17]. Depending on the use case, the hydrogen storage system should possess high storage density (either volumetrically and/or gravimetrically), fast charge/discharge rate, adequate operational cycle life and delivery temperature/pressure [4]. As an example, for light-duty vehicles, the US Department of Energy (DOE) set up technical targets for a range of system parameters [18].

There are various methods to store hydrogen, including the traditional solutions, i.e., storage of hydrogen in high-pressure vessels and storage in liquid form. Although special composite high-pressure vessels can handle pressures up to 70 MPa [19,20] and they are currently utilized in several vehicular systems [11], the size of these containers still implies a limitation for some applications. While liquid storage mitigates this issue, the considerable energy required for cooling hydrogen to 21 K and the unavoidable boil-off of H₂ make this method impractical in most cases [3,5]. Solid state hydrogen storage can be a promising alternative to the above-mentioned techniques, as they generally offer larger volumetric hydrogen densities [4,17,20,21]. Hydrogen can be adsorbed in molecular form on the surface of several carbon-based materials, such as graphite, carbon nanotubes, graphene and metal-organic frameworks (MOF) [22–24]. These systems offer good H₂ sorption rates and reversibility; however, higher capacities can usually be achieved only at lower temperatures (~77 K). Alternatively, hydrogen can be stored in the form of different metal hydrides (LaNi₅H₁₂, TiFeH₂, MgH₂, Mg₂NiH₄, etc.) [16,25–28], complex hydrides (alanates, such as LiAlH₄; borohydrides, such as LiBH₄) [4,29,30] and chemical hydrides (NH₃BH₃; amides, such as LiNH₂) [4,30,31]. The main advantage of hydrides, compared to other storage methods, is their excellent storage capacities. However, reversibility can be an issue, particularly in case of complex hydrides and chemical hydrides. Additionally, complex hydrides and some metal hydrides possess high desorption temperatures.

Among metallic hydrides, MgH₂ is considered to be one of the best candidates to be incorporated into the hydrogen-based economy due to its high storage capacity and low cost. Recent research and development targeting new approaches for improving the H₂-storage performance of Mg-based systems is comprehensively expounded [32]. It has undoubtedly been confirmed that high-energy ball milling is an ideal tool to improve the hydrogenation/dehydrogenation performance of these materials via the creation of abundant lattice defects [33].

In this review paper, first a brief summary will be given on the physics of the thermodynamics and kinetics of hydrogenation of elemental magnesium (Section 2). Since nanostructuring is an essential tool to considerably improve the kinetics of Mg-based systems, details of the most efficient top-down technique, i.e., ball milling will be highlighted in Section 3. The main body of this study (Section 4) will be dedicated to the very recent research trends (covering years from 2016 through 2021) of Mg-based hydrogen storage systems doped by conventional and innovative additives including the following:

- Transition metal-based catalysts;
- Intermetallic compound catalysts;
- Catalysts formed during in situ reactions;
- Synergistic multiple catalysts;
- Catalysts with special morphology.
At the end of the text, a brief discussion on the future prospects will be highlighted (Section 5).

2. A Short Overview of MgH$_2$ and Its Hydrogen Storage Properties

As was cited above in this review paper, solid-state hydrogen storage is still a significant technological challenge; nevertheless, numerous promising efforts have occurred thus far. Magnesium and magnesium-based alloys, compounds and composites have been extensively studied as hydrogen storage materials for several decades, including the enormous progress in the last 20 years [34]. Among metallic elements, magnesium attracts the highest interest in the field of solid-state hydrogen storage due to its very high theoretical gravimetric (7.6 wt.%) and volumetric (0.11 kg H/L) capacities. Magnesium has several other advantages, i.e., it is lightweight, non-toxic, abundant and relatively safe [26,35]. Moreover, Mg can be produced by well-established technology and the raw material cost is relatively small [27]. The reaction of Mg with H$_2$ can be inferred from the corresponding binary phase diagram (Figure 1), which has been calculated using the Thermo-Calc program PARROT [36]. At moderate pressures, the only hydride phase that co-exists with Mg in equilibrium is MgH$_2$, which has a tetragonal TiO$_2$ (rutile type) unit cell with a space group of $P4_2/mnm$. This low-pressure hydride phase is commonly designated as $\beta$-MgH$_2$ [26]. The Mg–H bonding interaction in $\beta$-MgH$_2$ is rather complex, mainly ionic, but exhibits some covalent character as well [37]. As was stated by the authors, this weak but significant covalent bonding can be a huge advantage on the hydrogenation–dehydrogenation performance of elemental magnesium. Upon increasing the pressure above 8 GPa, a polymorphic structural transformation occurs in the Mg–H system, leading to the formation of a high-pressure orthorhombic $\gamma$-MgH$_2$ phase (unit cell structure PbO$_2$) [26].

![Figure 1. Mg–H binary phase diagram [36].](image-url)
The thermodynamic aspects of metallic hydride formation can be understood from Figure 2. At the very early stages of H-absorption (when the hydrogen concentration $C_H < 0.1 \text{ H/M}$), the hydrogen atoms can occupy interstitial positions in the metallic lattice, resulting in the formation of a solid solution ($\alpha$-phase), see also the left-hand side image. By continuing the rapid pressure increase, only a limited amount of extra hydrogen atoms can be absorbed in the $\alpha$-phase; instead, the nucleation of a stoichiometric hydride phase ($\beta$-phase) commences at a critical H-concentration, which is then followed by a wide plateau. In this wide concentration range, the $\alpha$-phase and $\beta$-phase co-exist, and they are in thermodynamic equilibrium. This concentration range determines the amount of the reversible absorbed hydrogen. When the total volume of the material is transformed into the hydride phase (see the right-hand side image), a second steep pressure rise can be observed in the pressure-composition isotherms, relating to the capture of new H-atoms in interstitial sites of the $\beta$-phase. It is also envisaged from Figure 2 that the width of plateau has a strong temperature dependence, which is totally eliminated at a critical temperature, $T_C$. Above this temperature, the transition between the two phases is continuous. $p_{eq}$ at a given temperature is the pressure at which the hydride phase is in equilibrium with the gaseous H$_2$. For pressures $p < p_{eq}$, the hydride phase is thermodynamically unstable, which leads to the dehydrogenation of the $\beta$-phase. When the external pressure is larger than $p_{eq}$, hydrogen absorption becomes favorable.

![Figure 2. Hydrogen absorption pressure-composition isotherms for a typical metal–hydrogen system, together with the Van’t Hoff plot [38].](image)

The temperature dependence of $p_{eq}$ corresponding to the $\alpha \leftrightarrow \beta$ reaction can be given using the following Van’t Hoff equation [38]:

$$\ln\left(\frac{p_{eq}}{p_{0eq}}\right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R},$$

(1)

where $\Delta H$ and $\Delta S$ are the formation enthalpy and entropy of the hydride phase and $p_{0eq}$ is a reference pressure, usually taken as the normal atmospheric pressure. From the slope and the intercept of the $\ln\left(\frac{p_{eq}}{p_{0eq}}\right)$ vs. $\frac{1}{T}$ function, $\Delta H$ and $\Delta S$ can be determined, see Figure 2. As $\Delta S$ mainly corresponds to the formation of molecular H$_2$ gas dissolved in the solid state and vice versa, it can be approximated using the standard entropy of hydrogen for all metal-hydride systems: $\Delta S = -0.135 \text{ kJ mol}^{-1}\text{K}^{-1}\text{H}_2$ [38]. On the other hand, the $\Delta H$ enthalpy term, covering a wide range for different metals, corresponds to the stability of
the metal–hydrogen bond. Based on Equation (1), to reach $p_{eq} = 1$ bar at room temperature, $\Delta H$ should be taken as $-39$ kJ mol$^{-1}$H$_2$.

Since the formation enthalpy of tetragonal MgH$_2$ phase is relatively high ($\Delta H = -74.5$ kJ mol$^{-1}$ H$_2$ [39]), one can conclude that to desorb H$_2$ under the applied pressure of $p = 1$ bar, magnesium hydride should be heated to 550 K, see the corresponding Figure 3. It is also recognized that for $p_{eq} = 10$ bar, an applied temperature of $\sim 640$ K is required. Thus, it is evident that due to the high stability of the Mg–H bonds, the hydrogenation/dehydrogenation process of elemental magnesium can only operate at elevated temperatures.

Figure 3. Temperature dependence of the equilibrium pressure for the Mg$\leftrightarrow$MgH$_2$ reaction [39].

When a hydrogen molecule approaches the magnesium surface (at a distance $\sim 0.2$ nm), a physisorbed state is formed by a weak Van der Waals force [38]. At shorter distances, the H$_2$ molecule has to overcome an energy barrier ($E_{act}$) for dissociation and the formation of a new Mg–H bond. The magnitude of $E_{act}$ strongly depends on the type of the metal involved in the hydrogenation process. In the next step, these chemisorbed hydrogen atoms penetrate into the subsurface layer and then diffuse towards the interstitial sites of metal lattice, forming the intermetallic hydride phase. Since $E_{act}$ for the hydrogenation and dehydrogenation of elemental Mg/MgH$_2$ is rather high: $E_{abs}^{act} = 90$ kJ/molH and $E_{des}^{act} = 152–180$ kJ/molH [40–47], respectively, the hydrogen absorption/desorption kinetics are poor at ambient temperatures. The above described thermodynamical limitations of hydrogenation in magnesium and the sluggish sorption kinetics are the common drawbacks of the on-board commercialization of MgH$_2$ [25]. In order to overcome these difficulties, the key issue is the simultaneous development of both the kinetic and thermodynamic performance of Mg-based systems.
One possible solution to alter the thermodynamics in the favorable direction without a significant capacity loss is reducing the crystallite size to nanometric regimes. Thus far, a huge amount of research has been targeting the nanostructuring process \[48–50\]; however, it was shown that the reduction in the \(\Delta H\) hydride formation enthalpy is significant only for clusters containing \(~10\) Mg atoms \[51\]. Anyway, nanocrystallization has a more enhanced effect on the sorption kinetics, since it increases the surface area and promotes the formation of lattice defects (dislocations, vacancies), which positively influences the diffusion of hydrogen along the grain boundaries into the bulk of the Mg particles \[52,53\]. The different coordination number of the Mg and H atoms in the grain boundary regions, coupled with a unique surface morphology, are responsible for the improved kinetic performance of Mg-nanoparticles \[54\]. In some cases, especially when the crystallite size reduction is manifested by high-energy ball milling, the formation of a metastable orthorhombic \(\gamma\)-MgH\(_2\) phase also takes place, which results in the weakening of the Mg–H bonds and a decrease in the hydrogen sorption temperature \[55\].

Alternatively, \(\Delta H\) can also be reduced if Mg is alloyed with another element. In the classical case, transition metals, such as Ni, were applied \[56–58\], leading to the formation of the intermetallic Mg\(_2\)Ni compound, where the formation enthalpy of the hydride phase is reduced to \(\Delta H = -64.5\) kJ mol\(^{-1}\)H\(_2\). Unfortunately, the maximum storage capacity is also significantly reduced (3.6 wt.\%) at the same time. The destabilization of magnesium hydride without a significant capacity loss is the most important challenge by the selection of the proper additive. High-energy ball milling of Mg or MgH\(_2\) with a small number of catalysts (up to 5–10 mol\%) such as metal oxides, metal halides and many others has been used to improve the kinetic performance. During this nanocrystallization process, a homogeneous dispersion of the catalyst particles occurs throughout the whole composite material, increasing the number of contact sites with the hydride phase. Nevertheless, ball milling still exhibits some limitations for certain Mg-based systems, i.e., hydrogenation cycling can destroy the defect structure generated during the deformation process \[32\].

3. High-Energy Ball Milling

High-energy ball milling (HEBM) or mechanical attrition produces nanostructured materials by structural decomposition of coarse-grained structures as the result of severe plastic deformation (SPD). This has become a widely used technique to synthesize nanocrystalline powders because of its simplicity, the relatively inexpensive equipment and the applicability to essentially all classes of materials \[59\]. During milling, only crystallite size reduction is required; therefore, reasonably short milling times are sufficient. Nevertheless, in some cases, the following serious problems are usually cited: contamination from milling media and/or milling atmosphere, potential fire risk and the need to consolidate the powder product with maintaining its original nanostructural feature.

3.1. Ball Milling Devices

A variety of different types of ball mills have been applied extensively in the last couple of decades for the mechanical processing of powders, including vibratory mills/shaker mills, planetary mills and attritors. The most common ball mills used for experimental studies are vibratory mills, such as the SPEX 8000 mill. In these mills, a cylindrical vial of about 0.1-liter capacity undergoes a vibratory motion in the horizontal direction (see Figure 4, left). The vial contains typically 1 g of powder and 5–20 g of grinding ball(s), resulting in a 5:1–20:1 ball to powder mass ratio and vibrates at a frequency and amplitude of approximately 20 Hz and 10–50 mm, respectively \[60\]. Vibratory mills are convenient for laboratory experiments; however, they have not been scaled up to a larger size yet. A significantly larger amount of powder material can be processed in planetary mills, which can exhibit \(~0.25–1.0\) L of vial capacity. In some cases, 2–4 such containers are rotated about two separated parallel axes, similarly to the rotation of the Earth around the Sun (see Figure 4, right). The diameter of the grinding balls is larger than in vibratory mills, and consequently, the ball to powder mass ratio can also be much higher. Attritor mills are
widely used for ultrafine grinding of ceramics and industrial minerals. Milling occurs in a stationary container filled up with a huge number of grinding balls, which are mixed by impellers attached to a vertical drive axis. A major problem experienced using vertical-axis attritor mills for dry grinding is the gravity-driven segregation of the powder to the bottom of the mill [59]. Nevertheless, these devices are especially capable of the large-scale production of up to tons of milled powders.

3.2. Formation of Nanoparticles during Ball Milling

The process of HEBM is characterized by repeated collisions between the grinding balls, the vial and the powder particles. Until now, several extensive models describing the dynamics of ball milling and its influence on microstructural changes of milled powders have been carried out [60–63]. These studies have pointed out that the products are dependent on the physical and mechanical properties of the milled powder and the type of the grinding media. Parameters associated with the milling process, such as impact velocity, impact force, collision energy, ball mass and density, ball to powder mass ratio and vial temperature were examined [64,65] and studied using computer simulations [66]. Using a free falling experiment, a close analogy to the collision events occurring in vibratory mills indicated the magnitude of the impact force increases with an increasing ball size for any impact velocities [64]. It was also concluded that the impact between the ball and the plate is significantly influenced by the thickness of the powder layer.

![Figure 4. Schematic illustration and working principle of a (left) SPEX 8000 vibratory mill and (right) Fritsch planetary mill [67].](image)

The deformation process of a powder agglomerate during an impact with the milling balls can be inferred from Figure 5. When the ball impacts the powder first, the powder behaves as a porous material, as illustrated in Figure 5 left. During the impact, powder particles slide and rotate, rearranging their positions due to particle interactions [68]. As a result, the porosity of the powder decreases, while some particles may escape from the contact area. The porous structure of the powder will be altered until it is compressed to a critical height of h’ (Figure 5, center). In this stage, the fraction of the kinetic energy of the ball is dissipated. As the impact progresses further, the elastic and plastic deformation of the individual powder particles trapped in the contact area commences (Figure 5, right).
The significantly improved absorption–desorption behavior with respect to pristine Mg is attributed to the nano-engineered surface of the magnesium particles. These homogeneously distributed nano-Fe particles on the Mg surface indicate the homogeneous activation of the material. At the same time, a negligible capacity loss is observed up to 50 full sorption cycles, while dehydrogenation can be ascribed by a three-dimensional controlled diffusion. A nanocomposite mixture of MgH2, Mg2FeH6 and Fe has been achieved by planetary milling of Mg and Fe under 30 bar H2 pressure [76]. It was demonstrated that the amount of the Mg2FeH6 complex hydride increased with the increasing milling time. In situ synchrotron XRD experiments upon heating showed that MgH2 is the first hydride to decompose. These nanocomposites present very fast sorption kinetics, i.e., desorption is
completed within 2 min at 350 °C. By analyzing the hydrogen uptake measurements of Mg catalyzed by 10 wt.% Fe$_2$O$_3$ taken at different temperatures, it was established that a rate limiting step of the initial absorption is the dissociative chemisorption of the H$_2$ molecules on the particle surfaces [77]. On the other hand, results obtained from the absorption rate function revealed that the initial hydrogenation stage is followed by the diffusion of H-atoms through the MgH$_2$ layer.

TiO$_2$ is considered as one of the best metal-oxide catalysts to enhance the hydrogenation/dehydrogenation properties of magnesium, including the reduction in the onset of the desorption temperature. Very recently, aside from the type and crystallite size of the catalyst additives, it was also confirmed that the shape and morphology of these particles may show a strong correlation with the intrinsic H-storage properties of the host material [78]. In the research of Z. Ma and coworkers, TiO$_2$ nanosheets exposed with different amounts of [001] and [101] facets have been synthesized and ball milled with MgH$_2$. The authors have found that a huge number of H-absorbing active sites and defects formed on the surface of the high surface energy [001] facets dominated TiO$_2$, which can significantly accelerate the hydrogen dissociation and recombination, see the schematic image in Figure 6 [79]. In addition, the hydrogen desorption activation energy of MgH$_2$ is also remarkably reduced to $-67.6$ kJ/mol when TiO$_2$ nanosheets exposed with [001] facets doped into MgH$_2$ [80].

When MgH$_2$ was milled together with a porous carbon-supported TiO$_2$ nanocomposite catalyst, the onset of the dehydrogenation temperature is reduced by 95 °C, while the cyclic stability has improved significantly [42]. In the corresponding density functional calculations, the main absorption structures of an MgH$_2$ molecule on low free surface energy rutile (110) TiO$_2$ and anatase (101) TiO$_2$ surfaces were constructed, and the results indicated that the Mg–H bonds are extended and weakened, in agreement with the experimental observations. These findings confirmed that TiO$_2$ acts as an important catalytic additive to lower the kinetic barrier of the dehydrogenation of MgH$_2$. When Mg is catalyzed by Ti$_3$AlC$_2$ MAX-phase, the kinetic mechanism of hydrogen desorption can be ascribed using the Johnson–Mehl–Avrami process with an exponent $n = 3.09$, corresponding to a constant nucleation rate and three-dimensional growth [81]. On the contrary, the contracting volume model describes the dehydrogenation performance of the pristine nanocrystalline MgH$_2$, indicating that the MAX-phase promotes a change in the hydrogen sorption mechanism.

A couple of years ago, titanium isopropoxide (TTIP), as an organic alkoxide, was used as an additive to MgH$_2$ and its effect was compared to the benchmark Nb$_2$O$_5$ catalyst [82]. The authors found that only a very small amount (0.5 mol%) of TTIP milled with MgH$_2$ was sufficient to enhance the kinetics, producing equally good results as Nb$_2$O$_5$ and it has a superior hydrogen capacity. Since TTIP is liquid at room temperature, it may disperse more readily among the MgH$_2$ crystalline particles than most powder additives. In addition, a simple hand mixing of TTIP with the hydride powder demonstrated excellent desorption behavior, most probably due to complete and continuous coverage of the MgH$_2$ particles by the liquid additive. A study by the same authors on the effect of the HEBM gas environment (Ar, H$_2$) was conducted on MgH$_2$ milled together with different additives, such as TTIP, Nb$_2$O$_5$ and fullerene C$_{60}$ [83]. It was found that the milling environment has very little effect on the dehydrogenation performance of the hydride phase; however, a significant difference takes place in the absorption kinetics when Nb$_2$O$_5$ is milled with MgH$_2$ under a H$_2$ or Ar atmosphere. It is interesting that an Ar milling environment has a superior effect on the hydrogenation of MgH$_2$ catalyzed by Nb$_2$O$_5$. In a parallel investigation, another alkoxide liquid, i.e., Nb(V) ethoxide [Nb(OCH$_2$–CH$_3$)$_5$], was hand mixed with pre-milled MgH$_2$ in order to combine the positive influence of Nb-based catalysts on the hydrogen storage properties with the highly dispersed state achieved by liquid additives [84]. Upon heating, Nb(OCH$_2$–CH$_3$)$_5$ reacts with MgH$_2$, releasing C$_2$H$_6$. The absorption and desorption activation energies are significantly reduced, and the dehydrogenation occurs 80 °C below the decomposition temperature of HEBM MgH$_2$. Irrespective of the amount of the Nb(V) ethoxide additive (0.1–1 mol%), the decomposition
of MgH$_2$ occurs 90 °C below the value of pure hydride [85]. An excellent reversibility is obtained (5.3 and 5.1 wt.% for absorption and desorption) at 300 °C in 3 min.

Figure 6. Schematic illustration of hydrogen dissociation and recombination on the TiO$_2$ sheet [79].

A notable improvement in the reduction in the H-desorption temperature can be achieved when MgH$_2$ is cryo-milled together with fluoride additives [86]. NbF$_5$ and FeF$_3$ have a stronger mechanical effect on the formation of a very fine microstructure than the corresponding oxides (Nb$_2$O$_5$ and Fe$_2$O$_3$), since they act as a lubricant agent during the milling process.

In a detailed study on the hydrogen storage performance of nanocrystalline MgH$_2$ catalyzed by different amounts of TiH$_2$, it was pointed out that an optimal TiH$_2$ content exists (0.025 mol%) [87]. As seen in Figure 7, increasing the TiH$_2$ content decreases the H-capacity of Mg/MgH$_2$ due to the higher atomic weight of Ti compared to Mg and the formation of irreversible TiH$_2$ takes place. On the contrary, TiH$_2$ addition enhances the sorption kinetics due to the faster hydrogen diffusion in TiH$_2$ than in MgH$_2$ and improves the reversible cycling stability, which leads to a well-determined optimum TiH$_2$ content. Using different processing devices (planetary and oscillating ball mills) for the mechanical grinding of the MgH$_2$–TiH$_2$ system, it was found that the kinetics of hydrogen absorption are more dependent on the raw starting components than the manufacturing processing parameters [88].

A different amount of TiO$_2$ addition (x = 0–10 wt.%) to a rare-earth containing a Mg$_{80}$Ni$_{10}$La$_7$Ce$_3$ alloy by mechanical milling yields the improvement on the thermodynamics and hydride stability, reaching the minimum dehydrogenation enthalpy and the minimum onset desorption temperature for x = 5 wt.% [89]. XRD and complimentary HRTEM analysis of the hydride state revealed a multi-step reaction pathway, including the formation of several hydrides, i.e., MgH$_2$, Mg$_2$NiH$_4$, LaH$_3$ and CeH$_3$. It was also established that the phase interfaces of the latter two hydrides provide low activation energy diffusion channels for the hydrogen atoms. A novel VNbO$_5$ ternary oxide was synthesized by annealing of pre-milled mixture of V$_2$O$_5$ and Nb$_2$O$_5$ in a 1:1 molar ratio and then was HEBMed to commercial MgH$_2$ [90]. The catalytic effect of VNbO$_5$ is remark-
able, since the desorption temperature of the doped MgH$_2$ decreased to 200 °C after the first hydrogenation cycle, which is in correlation with the good dispersion of the catalyst particles in the whole system.

![Figure 7](image_url)

**Figure 7.** Reversible and irreversible contributions to the hydrogen storage of the (1–y) MgH$_2$ + y TiH$_2$ nanocomposite [87].

### 4.2. Intermetallic Compounds as Catalysts for the H-Sorption of MgH$_2$

Very recently, various intermetallic compounds were also added to MgH$_2$ by ball milling to improve its H-sorption properties. Mg–40 wt.% TiFe nanocomposites with different milling parameters have been synthesized by adding TiFe intermetallic compound to Mg by HEBM. As a first step, the TiFe intermetallic compound was produced by pre-milling of TiH$_2$ and Fe powders [91]. When the TiFe catalyst is synthesized under ethanol to improve its refinement level, no traces of untransformed Mg were detected after hydrogenation at room temperature. This can be explained by the thermal activation of the Mg/TiFe interface that enhances the initial diffusion of decomposed hydrogen during the absorption process. The best initial hydrogenation kinetics can be attained when the Mg–TiFe nanocomposite was prepared in a planetary mill (3 wt.% after 60 min of absorption); nevertheless, the maximum overall capacity (4.0 wt.%) can be reached after HEBM in a shaker mill [92].

Very recently, El-Eskandarany et al. successfully synthesized a new synthetic binary Mg–5 wt.% TiMn$_2$ nanocomposite system with an advanced hydrogenation/dehydrogenation performance [93]. The beneficial effect of TiMn$_2$ addition on the cyclability is outstanding, with respect to pure milled nanocrystalline Mg, the nanocomposite powder shows almost zero degradation of the achieved H-storage capacity after 1000 sorption cycles. Even at this stage, the TiMn$_2$ nanoparticles are homogeneously adhered onto the surface of the MgH$_2$ powders. Based on additional microstructural experiments, the authors concluded that this system neglects any undesired grain-coarsening, which is crucial from the point of view of industrial applications. To attain this purpose, the as-synthesized nanocomposite powder was employed as a source in a complete hydrogen storage system for fuel-cell applications. A mixture of $\gamma$-MgH$_2$ and $\beta$-MgH$_2$ with a nanosized crystallite structure
was stabilized by the addition of 10 wt.% ZrNi$_5$ powders by reactive milling under a hydrogen gas atmosphere [94]. The corresponding HRTEM study presented in Figure 8 confirms the formation of intimate fine crystals (5–15 nm). The as-milled MgH$_2$–10 ZrNi$_5$ nanocomposite exhibits an outstanding H-absorption performance, i.e., full absorption can be reached within 1 min at 275 °C. As a continuation of this research, Ti$_2$Ni metallic glassy nanopowders were added to MgH$_2$ via cryo-milling [95]. Structural investigations revealed that the short-range order atomic structure was preserved after the severe plastic deformation during the HEBM procedure. In addition, this disordered structure is stable up to 400 °C. Similar to the prior results, the Mg–10 wt.% Ti$_2$Ni system also possesses excellent life-time cyclic stability, achieving more than 80 full hydrogenation/dehydrogenation cycles without any degradation, which can directly be associated with the stable nanomorphology of the MgH$_2$ nanoparticles. Similar results have been obtained when 7 wt.% amorphous LaNi$_3$ was milled to MgH$_2$, i.e., increased milling time promotes the uniform distribution of the amorphous nanoparticles in the hydride matrix [96]. In addition, these hard LaNi$_3$ nanoparticles are capable of penetrating through the MgO layer, which facilitates excellent H-absorption (6 wt.% at 200 °C) and extraordinary long cyclic lifetime.

Large scale applications of Mg-based nanocomposites have been targeted by the HEBM synthesis of Mg$_x$(Fe$_{20}$V$_{80}$) material [97]. The increased addition of FeV to Mg facilitates the hydrogenation performance of MgH$_2$, including faster kinetics and lower activation energy of hydride decomposition, while the H-absorption mechanism changes from random nucleation and 3D growth (undoped MgH$_2$, Avrami exponent $n = 4$) to diffusion controlled (Mg–10 wt.% (Fe$_{20}$V$_{80}$), Avrami exponent $n = 2.5$). HEBM of 5 at.% VTiCr with MgH$_2$ was carried out under high pressure (100 bar) hydrogen gas. The excellent hydrogenation kinetics and cyclic stability of MgH$_2$ doped by a bcc VTiCr alloy is attributed to the perfectly distributed nano-sized catalyst particles [98]. In this research, it was demonstrated that this VTiCr–MgH$_2$ alloy can absorb hydrogen at pressures as low as 0.04 bar, due to the thermodynamically feasible reactions. Pre-milled Zr$_{0.67}$Ni$_{0.33}$ amorphous powder was added as a precursor to nanocrystalline MgH$_2$ via shaker mill [99]. Structural and morphological experiments showed that the addition of 10 wt.% amorphous powder led to the formation of very fine MgH$_2$ nanoparticles and resulted in enhanced sorption kinetics. This composite can absorb 4 wt.% H$_2$ within a minute at 250 °C. The nucleation of a small amount of ZrO$_2$ can further catalyze the hydrogenation process by reducing the activation energy of hydrogen dissociation. Furthermore, a synergistic effect between the amorphous Zr-Ni particles and the possible dissolution of Ni can destabilize the MgH$_2$ phase. Combined ball milling and hydride combustion was successfully applied to synthesize a novel MgH$_2$–MgC$_{0.5}$C$_{0.5}$ composite in order to ameliorate the hydrogenation performance of MgH$_2$ [100]. Compared to the nanocrystalline MgH$_2$, the onset temperature of dehydrogenation of the composite material is as low as 237 °C. At the same time, the MgC$_{0.5}$C$_{0.5}$ additive was stable; no phase transformation occurred during several sorption cycles.

4.3. Formation of Catalysts during In Situ Reactions

In certain cases, an in situ reaction can take place between several additives during the HEBM process, resulting in a compositional change. In other cases, a reduction of the catalyst by MgH$_2$ can also occur either during the ball milling procedure or during the dehydrogenation/hydrogenation cycling.

It was demonstrated in a systematic study that, under special circumstances, the high-energy ball milling can induce a reaction between MgH$_2$ and a stable metal oxide additive Nb$_2$O$_5$ [101]. Reduction of the metal oxide by MgH$_2$ occurs over a wide composition range, and as a result Mg$_x$Nb$_y$O$_{x+y}$ rock salt phase forms. However, 10 h of milling was necessary for this transformation to occur, and by further extending the milling time (30 h), an increased yield of the rock salt phase could be achieved. The newly formed Mg$_x$Nb$_y$O$_{x+y}$ promotes the dehydrogenation of MgH$_2$, as was indicated by the decreased desorption peak temperature (~35 °C reduction). Changing the material of the grinding medium
and the vial (from steel to zirconia) enables the modification of the in situ reaction, as it results in a blend of several rock salt products with different stoichiometries [102]. A similar observation was made in case of TiO\textsubscript{2} additive mixed to MgH\textsubscript{2} via a planetary mill using a relatively high ball to powder weight ratio (70:1), i.e., reduction of TiO\textsubscript{2} and in situ formation of Ti dissolved MgO (Mg\textsubscript{3}Ti\textsubscript{y}O\textsubscript{x+y} phase) occurred during prolonged (30 h) milling [103]. Such a product was shown to enhance the desorption kinetics of MgH\textsubscript{2} and to lower the desorption temperature [104]. In case of both Nb\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2}, it was suggested that the metal dissolved MgO is a catalytically active phase [102,104]; additionally, the dissolution of Nb leads to the expansion of the MgO lattice, which can cause cracks in the MgO layer, enhancing the diffusion of hydrogen [102].

Another study investigated the catalytic effect of TiVO\textsubscript{3.5} oxide on the hydrogen sorption of MgH\textsubscript{2} [41]. It was found that during ball milling, TiVO\textsubscript{3.5} is reduced by MgH\textsubscript{2}, and very fine metallic Ti and V nanoparticles are created. These nanoparticles can improve the dissociation and recombination of H\textsubscript{2} molecules and act as a hydrogen pump for the magnesium hydride. It was also pointed out that the catalytic activity of the in situ formed Ti and V nanoparticles are superior to those added directly to MgH\textsubscript{2}, as it is difficult to reduce the particle size down to several nanometers and disperse them homogeneously by ball milling only. In some cases, the reduction of the additive and the formation of in situ species do not take place during the HEBM treatment, but rather during the following desorption–absorption cycling, as was demonstrated in ref. [105]. To be specific, after 20 cycles, the 5 wt.% of Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} catalysts are completely reduced to metallic Fe.

Complex metal oxides were recently investigated as additives for MgH\textsubscript{2} due to their ability to react with the hydride during the desorption process and produce in situ formed phases. A partial reduction of MnFe\textsubscript{2}O\textsubscript{4} occurred during the dehydrogenation (T = 450 °C) of 10 wt.% MnFe\textsubscript{2}O\textsubscript{4} catalyzed MgH\textsubscript{2} [106]. According to the authors, the produced Fe particles and Mg\textsubscript{0.8}Mn\textsubscript{0.2}O\textsubscript{3} oxide phase may be the real active species, enhancing the sorption properties of the hydride. A similar study was conducted on CuFe\textsubscript{2}O\textsubscript{4} doped MgH\textsubscript{2}, in which case, CuFe\textsubscript{2}O\textsubscript{4} is partially reduced to Mg\textsubscript{2}Cu, Fe and MgO during the desorption process (see the XRD patterns in Figure 9) [107]. It was suggested that the formation of these catalytically active phases may be reason of the decreased desorption temperature and improved kinetics. N.A. Ali and co-workers synthesized MgNiO\textsubscript{2} nanoflakes using hydrothermal method and doped to MgH\textsubscript{2} [108]. The MgNiO\textsubscript{2} reacts with MgH\textsubscript{2} during the H-sorption and as a result MgO and NiO form. It was demonstrated that the absorption/desorption rate increased, and the desorption activation energy decreased significantly, compared to the as-milled MgH\textsubscript{2}. It is interesting to note that samples catalyzed with only MgO or NiO do not show significant improvement in the desorption performance over the as-milled MgH\textsubscript{2}, which indicates that these in situ created phases have a remarkable synergistic catalytic effect as well.

Several works have demonstrated that a reaction can take place between Ni additive and MgH\textsubscript{2} during the dehydrogenation process, namely the additive is reduced and an Mg\textsubscript{2}Ni intermetallic phase forms [109–115]. In general, this transformation occurs in the course of the first desorption, while in case of the subsequent cycles, a reversible conversion of Mg\textsubscript{2}Ni ↔ Mg\textsubscript{2}NiH\textsubscript{4} takes place alongside the Mg ↔ MgH\textsubscript{2} reaction. The kinetic measurements of such composites show excellent absorption/desorption behavior; for example, MgH\textsubscript{2} doped by NiMoO\textsubscript{4} nanorods is able to absorb 5.5 wt.% hydrogen in 10 min at 150 °C and 3.2 MPa [114]. Similarly, MgH\textsubscript{2} catalyzed by carbon encapsulated iron-nickel nanoparticles (Fe\textsubscript{0.6}Ni\textsubscript{0.36}@C) has reached an absorption capacity of 5.18 wt.% hydrogen in 20 min at 150°C and 3 MPa [44]. P. Yao et al. investigated the catalytic effect of Ni@rGO (Ni nanoparticles anchored on reduced graphene oxide) on the H-storage properties of MgH\textsubscript{2}, they measured a good absorption rate (3.7 wt.% in 10 min) even at a temperature as low as 100 °C (p = 3 MPa) [112]. The desorption kinetics was also fast, i.e., 6.1 wt.% hydrogen could be desorbed in 15 min (T = 300 °C, p = 0.0004 MPa). It was indicated that the in situ formed Mg\textsubscript{2}Ni/Mg\textsubscript{2}NiH\textsubscript{4} can improve the catalytic activity over unreacted Ni [112]. Even better dehydrogenation properties were attained for Ni/TiO\textsubscript{2}...
nanocomposite-doped MgH$_2$, namely, the amount of desorbed hydrogen can reach 6.5 wt.% in 7 min at 265 °C and 0.002 MPa [109]. In such composites, the remarkable H-storage performance is generally attributed to the in situ formed phase (i.e., Mg$_2$Ni/Mg$_2$NiH$_4$). The catalytic mechanism was well explained in ref [116]; accordingly, the Mg$_2$NiH$_4$ phase decomposes earlier than MgH$_2$ during the desorption process; the newly created Mg$_2$Ni can assist the dehydrogenation of MgH$_2$ in a way that H atoms first diffuse to the Mg$_2$Ni and then to the solid–gas interface. This mechanism is often referred to as a “hydrogen pump” [44,117,118], since the intermetallic phase acts as a diffusion channel for hydrogen and also serves as a heterogeneous nucleation site. It was also pointed out that the micro-strain associated with the volume change occurring during the Mg$_2$Ni→Mg$_2$NiH$_4$ transformation is beneficial for the diffusion of H and, thus, the kinetic performance of the composite [110,119]. When using Ni-containing additives, besides the formation of Mg$_2$Ni, other in situ formed phases can also appear, such as MgS in MgH$_2$ catalyzed by carbon supported Ni$_3$S$_2$ [120] and α-Fe in MgH$_2$ doped by a transition metal-based MOF (metal-organic framework) [121]. These catalytic species play an important role in the hydrogenation/dehydrogenation process and usually provide active sites for the nucleation reaction. Doping nanocrystalline Mg$_2$FeH$_6$ by Ni promotes the reaction of Ni with MgH$_2$ and Fe, resulting in the formation of Mg$_2$NiH$_4$ and FeNi$_3$ phases, respectively [122]. The Mg$_2$FeH$_6$–20Ni alloy possesses a two-step dehydrogenation sequence, in contrast to the single-step reaction of the as-prepared material. The reaction between Mg$_2$Ni (from the decomposition of Mg$_2$NiH$_4$) and Mg$_2$FeH$_6$ forms a new Mg-Fe-Ni-H quaternary hydride with a significantly lower onset dehydrogenation temperature.

Other material classes have also shown the ability to form in situ phases in combination with MgH$_2$; for example, a recent paper studied different transition metal sulfides (such as TiS$_2$, NbS$_2$, MoS$_2$, MnS, CoS$_2$ and CuS) as additives [123]. In situ formed phases such as MgS, TiH$_2$, NbH, Mo, Mn, Mg$_2$CoH$_5$ and MgCu$_2$ can be viewed as an effective catalyst of the (de)hydrogenation reaction, as the sorption kinetics significantly improved, mainly at lower temperatures. MgS and TiH$_2$ are suggested to serve as nucleation sites for Mg/MgH$_2$ and diffusion channels for hydrogen, Nb/NbH and Mg$_2$CoH$_5$/Mg$_2$Co mainly act as hydrogen pump, while Mo, Mn and MgCu$_2$ can facilitate the decomposition of MgH$_2$ by weakening the Mg-H bond. There are also examples of desorption-induced phases in cases of fluoride (K$_2$SiF$_6$ [124], K$_2$NbF$_7$ [125]), and chloride (HfCl$_4$) [126] materials, where KH, MgF$_2$, Mg$_2$Si, Nb and MgCl$_2$ phases appear, respectively. Investigations on MgH$_2$ catalyzed by FeB [127], CoFeB [128] and Co/CNT [129] indicated that in situ generated phases also appear in case of transition metal borides. The formed Fe [127,128], B [127,128], CoFe [128] and Co$_3$MgC [128,129] phases are considered to provide additional nucleation sites for the Mg$\leftrightarrow$MgH$_2$ phase transformation, while Fe can also enhance the dissociation of H$_2$ molecules.

Based on the above presented reports, it is clear that in situ formed (either during ball milling or H-sorption) catalysts have a remarkable ability to improve the hydrogen sorption performance of Mg-based materials. In terms of catalytic activity, they often surpass those additives that are not formed in situ, but only mixed with MgH$_2$ through ball milling. The reason behind this observation can have multiple origins: (i) the in situ formed phases have altered the electronic structure compared to the original additive [41,102,109,128], which could be beneficial to the interaction with hydrogen atoms/molecules; (ii) the small size and uniform distribution (which were observed in multiple cases [41,109,110,117,128]) are also an important feature for in situ generated catalysts, since more interphase regions and a larger surface area covered by these products lead to an enhanced overall catalytic activity.
Figure 8. (a) HRTEM image of MgH$_2$/10 wt.% ZrNi$_5$ nanocomposite powders obtained after 50 h of ball milling time. The FFT lattice images for zones I, II, III, IV, V and VI shown in (a) are displayed in (b–g), respectively [94].
Figure 9. XRD profiles of 10 wt.% CuFe$_2$O$_4$-doped MgH$_2$ sample (a) after ball milling, (b) after desorption at 450 °C and (c) after re-absorption at 250 °C [107].

4.4. Utilization of Synergy between Multiple Catalysts

As was also presented in Section 4.1, additives such as transition metals, transition metal oxides and carbon-based materials are effective catalysts for the dehydrogenation of MgH$_2$. However, an increasing number of publications demonstrated that greater improvements can be achieved in the sorption properties by combining different additives than using a single catalyst. These observations were attributed to a synergistic catalytic mechanism occurring during the (de)hydrogenation process.

In a recent paper, Ni/TiO$_2$ core-shell particles were introduced to MgH$_2$ by ball milling and the kinetics of the composite were analyzed [130]. In the presence of the Ni/TiO$_2$ co-catalyst, a significantly faster hydrogen desorption could be observed than for single Ni or TiO$_2$ additives and the difference is more striking at lower temperatures (T = 250 °C). It was suggested that the Ni/TiO$_2$ core-shell structure can assist electron transport and, thus, enhance the recombination of hydrogen; additionally, the TiO$_2$ coating prevents grain growth and stabilizes the morphology. Another example of a synergistic catalysis is given by Chen et al., who dispersed Co nanoparticles on TiO$_2$ and this nanocomposite (Co/TiO$_2$) was added to MgH$_2$ through ball milling [131]. It was possible to achieve a lower desorption peak temperature (T$_{\text{des}}$ = 235.2 °C compared to 329.4 and 288.4 °C for Co and TiO$_2$, respectively) and faster isothermal desorption kinetics with Co/TiO$_2$ than either with Co or TiO$_2$. These improvements can be attributed to the synergistic effect of Co and TiO$_2$, i.e., Co can destabilize the MgH$_2$ owing to the higher strength of the Co–H bonds than that of Mg–H; meanwhile, the electrons from the conduction band of TiO$_2$ migrate to the Co, and as a result of the interaction of H$^-$ with the resulting holes, facilitate the recombination reaction. Another investigation was conducted on the catalytic performance of sandwich-like Ni/Ti$_3$C$_2$ in MgH$_2$, where an electron transfer was observed between Ni and Ti$_3$C$_2$ [132]. The numerous interfaces presented by the catalyst and its altered electronic state can effectively facilitate the hydrogen absorption/desorption processes.
It was also suggested that Ni has a positive effect on the dissociation of hydrogen and on the weakening of the Mg–H bond, while Ti$_3$C$_2$ can prevent the agglomeration of Ni or MgH$_2$ particles. The multiple valence states of Ti (Ti$^{0}$, Ti$^{3+}$), appearing during ball milling, can assist the conversion between Mg$^{2+}$ and Mg. The simultaneous addition of TiF$_3$ and Nb$_2$O$_5$ to MgH$_2$ via a vibratory type high-energy ball mill was studied in a recent piece of research [46]. A lower desorption temperature and dehydrogenation activation energy were found than when using only one type of catalyst. The additives are suggested to enhance the diffusion and recombination processes of hydrogen and also serve as nucleation sites for the Mg phase.

In some cases, in situ formed phases (in detail: Section 4.3) can also have a synergistic catalytic effect on the hydrogen sorption of magnesium hydride. In NiTiO$_3$-doped MgH$_2$, Mg$_2$Ni/Mg$_2$NiH$_4$ forms during the desorption/absorption process and these phases can enhance the H-sorption reactions in combination with multiple valence titanium compounds (Ti$^{4+}$, Ti$^{3+}$ and Ti$^{2+}$), which are generated during the ball milling and also during dehydrogenation [116]. Similar findings were obtained for MgH$_2$ catalyzed by Ni/TiO$_2$ [109], for which the synergistic effect was demonstrated through DSC and TPD measurements (see Figure 10), i.e., lower desorption temperatures can be found for the composite additive than for single catalysts. In both of the above cases, the underlying mechanism was proposed to be a multi-step process; firstly, the multivalent titanium facilitates the electron transfer associated with the decomposition of MgH$_2$ (H$^-$ transfers an electron to Ti$^{4+}$, while Mg$^{2+}$ obtains an electron from Ti$^{2+}$). The formed H atom can now diffuse to Mg$_2$Ni, which serves as a fast diffusion channel, also called as a “hydrogen pump” [116]. In case of transition metal-based MOF (metal-organic framework)-doped MgH$_2$, a synergistic improvement of the desorption was demonstrated for the in situ formed Mg$_2$Ni/Mg$_2$NiH$_4$ and α-Fe phases [121]. Iron primarily enhances the nucleation and growth of Mg on the interface of α-Fe and MgH$_2$, while Mg$_2$Ni, working as a “hydrogen pump”, provides channels for the migration of H atoms (see Figure 11).

Figure 10. (a) DSC and (b) TPD curves of MgH$_2$ doped by different catalysts. Note the MgH$_2$–Ni–TiO$_2$ is a simple co-milling of the additives, while Ni/TiO$_2$ was prepared using the solvothermal method [109].
A synergistic mechanism was also observed when transition metal carbides (TiC, ZrC, WC) were milled to a Mg–Ni alloy [133]. Accordingly, the desorption starts with the decomposition of Mg$_2$NiH$_4$, the stress accompanied by this phase transformation assists the dehydrogenation of MgH$_2$ together with the carbide phase, as the latter can facilitate the charge transfer between Mg$^{2+}$ and H$^–$. The carbide and Mg$_2$Ni can also act as nucleation sites for Mg/MgH$_2$.

A combination of carbon-based additives with other types of catalysts is also proven to be an effective way to achieve improved hydrogen storage properties for Mg-based materials. For example, a simultaneous application of graphene oxide-based porous carbon and TiCl$_3$ yields better desorption kinetics for MgH$_2$ than the individual use of these catalysts [134]. According to the authors, the carbon additive mainly serves as a scaffold material, thus it prevents the agglomeration of MgH$_2$ and ensures the homogeneous distribution of TiCl$_3$ particles. Similar findings were concluded when various materials supported on graphene were added to MgH$_2$ or an Mg-based alloy through ball milling. In case of TiH$_2$ templated over graphene, the graphene support effectively inhibited the agglomeration of TiH$_2$; additionally, the milling procedure introduced defects to the graphene, which is suggested to play a co-catalytic role with the TiH$_2$ [135]. Another study demonstrated that an electronic interaction exists between FeCoNi nanoparticles and their graphene support, which leads to an enhanced catalytic effect [136]. In addition to the important role of preventing agglomeration and improving the dispersion of additives, graphene can also provide numerous phase boundaries owing to its high surface area, which serves as diffusion channels for hydrogen. This feature also enables a synergistic catalytic effect with different materials that mainly improve the dissociation reaction, such as Ni [137] or TiF$_3$ [138], to improve the sorption properties of a Mg–Al alloy. Graphene can also assist the dissociation of hydrogen in combination with NbN$_{0.9}$O$_{0.1}$ when ball milled to MgH$_2$, as was reported in ref. [139]. The NbN$_{0.9}$O$_{0.1}$ phase, which was formed in situ from N-doped Nb$_2$O$_5$ nanorods, was shown to weaken the Mg–H and H–H bonds considerably, and the degree of this effect is ameliorated if graphene was also present. Synergistic improvement of the hydrogen storage properties was also reported for composites of carbon and Ni [118] or Co [118,140] nanoparticles, for which carbon layers form around the metallic catalyst. In this arrangement, the carbon can effectively prevent aggregation of the nanoparticles while maintaining their catalytic activity.
Reduced graphene oxide (rGO) was applied in several cases to support different transition metal-based catalysts, such as Ni [112], Ni$_3$Fe (see Figure 12) [119], NiS [110] and V$_2$O$_5$ [141] in Mg-based hydrogen storage materials. A decrease in the hydrogen desorption temperature and acceleration of kinetics were observed upon introduction of the co-catalysts, owing to the synergistic effect between rGO and transition metal compounds (either directly added or in situ formed). The reduced graphene oxide mainly improves the dispersion of catalyst particles and stabilizes their morphology, thus ensuring better overall catalytic activity and cyclic stability. It can also provide a diffusion channel for hydrogen; hence, H atoms dissociated on the surface of transition metal-based additives can spill over to the Mg [110].

Besides graphene, carbon nanotubes (CNT) were also combined with other additives to improve the hydrogen sorption properties of MgH$_2$. Gao et al. reported a lower dehydrogenation temperature for MgH$_2$ doped with FeB [127] or CoFeB [128] and decorated with CNTs, compared to the case where only FeB or CoFeB was used, respectively. Another paper has shown an increased absorption rate upon simultaneous application of TiF$_3$ and multiwalled carbon nanotubes in a Mg-Ni alloy [142]. For Mg–Nb$_2$O$_5$–CNT composites prepared by high-energy milling, improved kinetics was observed [143] and the use of multiple catalysts enabled a desorption capacity close to the theoretical value to be achieved (6.43 wt.%) [144]. In most of these systems, the different catalysts are believed to play different roles in the hydrogen absorption/desorption process, namely the transition metal-based compounds provide nucleation sites for MgH$_2$/Mg and can also accelerate dissociation/recombination of H$_2$ molecules at the surface. At the same time, nanotubes, owing to their morphology, are suggested to promote the diffusion of hydrogen through the interior of the particles. It was indicated that CNT may also have a positive effect on the dissociation of hydrogen [142], and can suppress extensive grain growth during cycling [144,145].

The above cited examples demonstrate the significant advantages of applying multiple catalysts to improve the hydrogen storage performance of Mg-based materials. The common key feature of these systems is the combination of different catalytic mechanisms through introducing different types of additives. It is also worth mentioning that the extent of the synergistic effect depends on the preparation conditions of the catalysts and the composite, as was shown in refs [109,112,132,134].
4.5. Catalysts with Special Morphology

Apart from the chemical composition, morphological features of the applied additives can also be an important factor to consider when one designs a novel hydrogen storage material. In the last few years, numerous works have been dedicated to catalysts with unique morphology to enhance the hydrogen ab-/desorption performance of Mg-based materials.

In the previous section we already mentioned some systems in which the morphology of the additives plays an important role; these are mainly catalysts with carbon support, which prevents the excessive agglomeration of particles. Core-shell structures are particularly interesting, as they can effectively separate particles that would otherwise be prone to aggregation. For example, an amorphous carbon layer is formed around transition metal nanoparticle cores such as Ni [118] and Co [118,140], which resulted in remarkable catalytic activity, as indicated by fast absorption/desorption reactions (see Section 4.4). In ref. [44], carbon was coated on an iron-nickel alloy (Fe_{0.64}Ni_{0.36}@C) and this was added to Mg by ball milling. While the milling process did not destroy the core-shell structure, it ensured the distribution of the catalyst in the Mg-based composite. A slightly different approach was presented by S. Wang and coworkers, i.e., Ni nanoparticles were dispersed on porous hollow carbon nanospheres, which were synthesized separately [115]. In this case, the Ni particles (with an average size of ~10 nm) could be found on the surface as well as in the inner cavities of the hollow carbon nanospheres; this enabled the high loading (90 wt.% of Ni with no agglomeration. Adding this catalyst to MgH₂ in a planetary ball mill yielded notable hydrogen sorption rates (6.3 wt.% hydrogen absorbed in 100 s at T = 200 °C and p = 5 MPa). In spite of the carbon shell covering the metallic particles, an in situ reaction between Mg and the transition metal could occur for all the above examples. This means that the carbon either does not form a continuous layer or can be broken, so that the core can interact with the Mg matrix as well as with hydrogen; at the same time, agglomeration of the particles is still suppressed. This is an important attribute to note for future research in this field.

M. Zhang et al. synthesized flower-like carbon wrapped TiO₂ (TiO₂@C) using a combination of the solvothermal process and low temperature pyrolysis and subsequently added this to MgH₂ thorough ball milling [146]. The flower-like structure of the catalyst is composed of numerous short rods (see Figure 13, left); however, the ball milling process destroys this morphology, and many small pieces of the catalyst are created instead, which, in turn, cover the surface of MgH₂ particles (Figure 13, right). In this way, the initial loose structure of the additive promotes the uniform distribution of the catalyst and enables the observed fast absorption rates.

![Figure 13. (left) SEM image of flower-like TiO₂@C, and (right) schematic diagram of the morphological changes during the milling process [146].](image-url)
Catalysts with layered structures were also applied to improve the sorption properties of MgH₂, for example, TiVO₃₅, with a multilayered structure, was shown to considerably decrease the adsorption/desorption temperature (e.g., the dehydrogenation temperature reduced by 75 °C) and the activation energy (59% reduction compared to pristine MgH₂) [41]. Another investigation presented a Ni/Ti₃C₂ additive with a sandwich-like structure fabricated by modified wet chemical synthesis [132]. Fast hydrogen sorption and good cyclic stability were observed for MgH₂ catalyzed by the sandwich-like Ni/Ti₃C₂. According to the authors, the layered structure of the catalyst presents plenty of interfaces that play a substantial role in the hydrogenation reaction, as these offer hydrogen diffusion paths and assist the electron transfer process (see also Section 4.4).

Catalysts with a reduced dimension have caught some attention recently, as the interaction with hydrogen can be different in these materials than in their bulk counterparts. ZrCo nanosheets prepared via a wet chemical method were ball milled to MgH₂, and as a result the hydrogen sorption properties of MgH₂ were improved, as indicated by the considerable reduction in the dehydrogenation temperature [147]. The ZrCo nanosheets covering the surface of MgH₂ were assumed to work as a hydrogen pump. Nanosheets can be also interesting, because it is possible to expose a specific high-surface-energy crystallographic plane in large quantity, as was shown in case of TiO₂ nanosheets (see also Section 4.1) [80]. Additionally, the nanosheets are also able to restrain the excessive grain growth of MgH₂ during the absorption/desorption cycling.

Carbon nanotubes are often applied as an additive to Mg-based hydrogen storage materials owing to their special tubular morphology. In many cases, they are used in combination with other, mainly transition metal-based catalysts, in order to achieve a synergistic catalytic effect (see Section 4.4) [128,142,144]. In general, it is assumed that the nanotubes can enhance the diffusion of hydrogen by serving as diffusion channels. However, a satisfactory catalytic effect can only be achieved by the breakdown of the large agglomerations of CNTs, as insufficient dispersion can lead to slow absorption/desorption kinetics [148]. On the other hand, as the dispersion process is usually ball milling, it is important to limit the milling time and intensity, because the nanotube structure can be damaged by the high-energy impacts, and amorphous carbon can form [144]. Hence, in case of such catalysts with special morphology, optimal milling parameters should be applied; the use of lower energy ball milling may be advantageous.

Not only carbon can form a nanotube structure, other materials, such as Ti-based oxides, can also have such morphology. Recently, titanate nanotubes prepared using the hydrothermal method from anatase TiO₂ was applied to improve the sorption properties of magnesium using high-energy ball milling and high-pressure torsion. The morphological differences due to the variation of the milling time were found to have a significant impact on the absorption kinetics of Mg [149]. Another group synthesized Na₂Ti₃O₇ nanotubes and nanorods using the hydrothermal and solid-state method, respectively (see Figure 14), and mixed them to MgH₂ in a planetary ball mill. It was shown that the nanotubes have a superior catalytic effect over the nanorods, as indicated by the 52.6 °C difference in the dehydrogenation peak temperature and also by the higher desorption rate [43]. The Na₂Ti₃O₇ nanotubes were more effective in catalyzing the desorption of MgH₂ than bulk Na₂Ti₃O₇, which demonstrates the advantages of the nanotube morphology. According to the authors, the Na₂Ti₃O₇ nanotubes serve as diffusion channels along Mg/MgH₂ interfaces.

Several transition metal-based nanorods were prepared and tested to improve the storage properties of MgH₂. Porous rod-like NiTiO₃ and CoTiO₃ can decrease the dehydrogenation temperature, although NiTiO₃ provides better catalytic effect (Tₐₚ = 261.5 °C and 298 °C, respectively, compared to the Tₐₚ = 322 °C of ball milled MgH₂) [116]. NiMoO₄ and CoMoO₄ nanorods similarly enhance the non-isothermal and also the isothermal desorption performance of magnesium hydride [114]. The catalytic effect in both of the above papers was mainly attributed to the in situ formed intermetallic phase; it can be assumed that the nanorod morphology, owing to its high active surface area, can promote this transformation. N-doped Nb₂O₅ nanorods were synthesized on graphene support and
were milled to MgH$_2$ [139]. A significant decrease was obtained for the dehydrogenation barrier, i.e., the apparent activation energy was changed from 139 kJ/mol (as-milled MgH$_2$) to 81 kJ/mol after the addition of the nanorod catalyst.

**Figure 14.** (a) Transmission electron micrographs of Na$_2$Ti$_3$O$_7$ nanorods and (b) nanotubes with the corresponding selected area electron diffraction patterns [43].

Carbon nanofibers, which supported Ni nanoparticles, were produced using the electrospinning method and then ball milled to MgH$_2$ [150]. The nanofibers ensured the homogeneous distribution of Ni particles around the hydride phase and also played the important role of preventing the aggregation of Ni. This effect led to fast absorption/desorption reactions and excellent cyclic stability (capacity retention of 99.8% in the first 20 cycles).

S. Hu et al. investigated the catalytic effect of ultrathin K$_2$Ti$_8$O$_{17}$ nanobelts on the H-sorption kinetics of MgH$_2$ [47]. Excellent absorption/desorption rates were observed even at lower temperatures and a marked decrease was found in the dehydrogenation activation energy, compared to the pristine MgH$_2$ (from 175.3 kJ/mol to 116.3 kJ/mol). The catalytic effect was attributed to the oxygen vacancies in the nanobelts formed during the ball milling preparation process. It was also proposed that the special morphology of the nanobelts is beneficial to expose these oxygen vacancies.

Based on the cited investigations, there is a certain potential in the catalysts with unique morphology to improve the H-storage properties of Mg-based materials. The high surface area, which is a common feature of these additives, can not only enhance the interaction with hydrogen (such as dissociation), but the increased number of interfaces can also improve the diffusion properties of the material. Hence, proper dispersion of the catalyst over the Mg matrix is of great importance; on the other hand, keeping the original morphology during the dispersion process (which is usually ball milling) is equally essential in most cases.

At the end of this review paper, we summarize the hydrogen sorption properties of some selected ball-milled Mg-based systems in Table 1. As one can recognize, reasonable hydrogenation capacities (5–6.2 wt.%) can be measured for most of the materials at absorption temperatures as low as $T_{abs} = 100–200$ °C. The lowest $T_{abs}$ values correspond to nanocrystalline Mg doped by very different types of additives, including K$_2$Ti$_8$O$_{17}$ nanobelts, CoFeB plus CNT catalysts and in situ formed N-Nb$_2$O$_5$ with graphene. On the contrary, similar capacity values (5–6.8 wt.%) for dehydrogenation can only be achieved at elevated temperatures, typically at $T_{des} = 250–300$ °C. The best performance includes catalysts, such as TiVO$_{3.5}$, sandwich-like Ni/Ti$_3$C$_2$ and K$_2$Ti$_8$O$_{17}$ nanobelts. It is also realized from Table 1 that all of the cited catalysts promote a significant reduction in the $E_{act}$ value when it is compared to pure Mg. The best performance is realized when magnesium is milled together with TiVO$_{3.5}$, NiS with reduced graphene oxide or flower-like TiO$_2$/C.
Table 1. Absorption/desorption properties and desorption activation energy of a few Mg-based hydrogen storage systems.

| Material                                           | Absorption Performance | Desorption Performance | Desorption Activation Energy (kJ/mol) | Ref. |
|----------------------------------------------------|------------------------|------------------------|--------------------------------------|------|
| MgH₂ + 10 wt.% TiVO₃,5                            | 6.3 wt.%/200 s 200 ℃/1 MPa | 6.8 wt.%/30 min 300 ℃  | 62.4                                 | [41] |
| MgH₂ + 5 wt.% Na₂Ti₃O₇ nanotube                     | 6 wt.%/60 s 275 ℃/3.2 MPa | 6.5 wt.%/6 min 300 ℃/3 kPa | 70.4                                 | [43] |
| MgH₂ + 5 wt.% K₂Ti₆O₁₇ nanobelts                    | 6.2 wt.%/12.6 min 100 ℃/2.24 MPa | 6.6 wt.%/2.4 min 280 ℃ | 116.3                                | [47] |
| MgH₂ + 5 wt.% TiO₂                                  | 6.4 wt.%/250 s 200 ℃/3 MPa | 6.5 wt.%/1000 s 300 ℃/0.005 MPa | 76.1                                 | [79] |
| MgH₂ + 1 mol.% Nb(V) ethoxide                      | 5.5 wt.%/20 min 300 ℃/1 MPa | 5.2 wt.%/10 min 300 ℃/20 kPa | 75                                    | [84] |
| La₇Ce₉Mg₈₀Ni₁₀ + 5 wt.% TiO₂                        | 4 wt.%/45 s 200 ℃/3 MPa | 3 wt.%/172 s 300 ℃/0.0001 MPa | 57.4                                 | [89] |
| MgH₂ + 10 wt.% ZrNi₅                                | 5.3 wt.%/30 min 250 ℃/0.8 MPa | 5.3 wt.%/15 min 275 ℃/0.01 MPa | 110                                  | [94] |
| MgH₂ + 10 wt.% TiNi                                | 5.1 wt.%/100 s 225 ℃/1 MPa | 5.7 wt.%/333 s 225 ℃/0.02 MPa | 87.3                                 | [95] |
| MgH₂ + 10 wt.% MnFe₂O₄                              | 5.6 wt.%/10 min 200 ℃/3 MPa | 4.6 wt.%/10 min 320 ℃/0.1 MPa | 108.4                                | [106]|
| Mg + 5 wt.% NiS/rGO                                | 5 wt.%/10 min 300 ℃/4 MPa | 4.5 wt.%/60 min 300 ℃/100 Pa | 63                                   | [110]|
| MgH₂ + 10 wt.% NiMoO₄ nanorod                      | 5.5 wt.%/10 min 150 ℃/3.2 MPa | 6 wt.%/10 min 300 ℃  | 85.9                                 | [114]|
| MgH₂ + 8 wt.% CoNi@C                               | 6 wt.%/200 s 150 ℃/3 MPa | 6.17 wt.%/1800 s 300 ℃/0.005 MPa | 78.5                                 | [117]|
| MgH₂ + 5 wt.% K₂Si₆                                 | 4.5 wt.%/2 min 250 ℃/3 MPa | 5.1 wt.%/30 min 320 ℃/0.1 MPa | 114                                  | [124]|
| Material                  | Absorption Performance | Desorption Performance | Desorption Activation Energy (kJ/mol) | Ref. |
|--------------------------|------------------------|------------------------|---------------------------------------|------|
| MgH₂ + 10 wt.% CoFeB/CNT | 6.2 wt.%/10 min 150 °C/5 MPa | 6.5 wt.%/30 min 300 °C | 83.2                                  | [128]|
| MgH₂ + 5 wt.% Ni/Ti₃C₂   | 5.6 wt.%/50 s 200 °C/3 MPa | 6.73 wt.%/2400 s 300 °C/0.005 MPa | 91.6                                  | [132]|
| Mg₉₀Ni₅ + 5 wt.% TiC     | 4.44 wt.%/1800 s 150 °C/3 MPa | 4.73 wt.%/1800 s 250 °C/0.005 MPa | 74.1                                  | [133]|
| MgH₂ + 5 wt.% FeCoNi@GS  | 6.01 wt.%/1.65 min 290 °C/1.5 MPa | 6.14 wt.%/8.5 min 290 °C/0.1 MPa | 85.4                                  | [136]|
| MgH₂ + 10 wt.% N-Nb₂O₅@C | 6.2 wt.%/60 min 100 °C/5 MPa | 6.2 wt.%/60 min 225 °C | 81                                    | [139]|
| Mg₉₀Ce₅Y₅ + 10 wt.% C@Co | 4.5 wt.%/100 min 200 °C/3 MPa | 4.5 wt.%/11 min 300 °C/0.005 MPa | 81.9                                  | [140]|
| MgH₂ + 5 wt.% flower-like TiO₂/C | 6 wt.%/40 min 150 °C/5 MPa | 6 wt.%/7 min 250 °C/1 kPa | 67.1                                  | [146]|
| MgH₂ + 10 wt.% ZrCo nanosheet | 4.4 wt.%/10 min 120 °C/3 MPa | 5.3 wt.%/5 min 300 °C | 90.4                                  | [147]|
| MgH₂ + 10 wt.% Ni@C     | 6 wt.%/800 s 300 °C/3 MPa | 6 wt.%/3500 s 300 °C | 93.1                                  | [150]|

Table 1. Cont.
5. Future Perspectives

Magnesium-based composites hold a significant potential for future applications in the field of hydrogen storage. However, substantial improvements still have to be accomplished before they can be readily utilized in practice, in spite of the remarkable research activity and progress carried out, especially in the last 5 years. Notably, the vast majority of the investigations reported here have focused on the enhancement of the kinetic properties of absorption/desorption reactions. Nevertheless, due to the low equilibrium pressure of the Mg-MgH$_2$ system, the reduction in the dehydrogenation temperature is strongly limited. Hence, changing the thermodynamic properties of this system and increasing the equilibrium pressure are highly desirable to improve the hydrogen release process.

Based on the reports discussed in this review, some important aspects can be highlighted that could support future works. Taking the advantage of the reducing ability of MgH$_2$ and the formation of in situ phases holds a significant potential for fabricating Mg-based hydrogen storage materials with improved properties. Hence, it is recommended to explore such phenomenon for other material combinations as well. A combination of multiple catalysts is also proved to be a promising way to enhance to hydrogen sorption properties of MgH$_2$. In order to find the best combinations, the effect of additives on the different rate limiting steps of the sorption reactions and the mechanism of the synergistic effect should be taken into account, thus it would be worthwhile to explore these aspects in greater detail. Additionally, the sample preparation process may also affect the synergy of the catalysts; a systematic study is needed to clarify the underlying mechanism.

6. Summary

In this paper, we have reviewed the most promising investigations, carried out in the last 5 years, on Mg-based hydrogen storage materials prepared by high-energy ball milling. There were a large number of works focusing on nanocomposites containing Mg or MgH$_2$ and a small amount (typically 5–10 wt.%) of additives. The effect of these additives has been discussed, focusing on their catalytic mechanisms. A wide range of materials has been covered, including different transition metals and transition metal-based compounds. Although these material-classes are used for a long time in this field, some novel interesting advances were attained, such as experiments on liquid additives and investigations on catalysts with specific crystallographic orientations. Additionally, various intermetallic compounds have been shown to accelerate the absorption/desorption rate. Numerous recent reports presented evidence of reactions between the host magnesium-based material and the additive, either during the milling procedure or during hydrogen cycling. It was demonstrated that various catalytically active species can be formed through these in situ reactions, which resulted in a superior hydrogen sorption performance. The utilization of multiple catalysts is another increasingly popular strategy in Mg-based systems. By carefully choosing the combination of additives and the preparation conditions, remarkable improvements can be achieved in the hydrogenation/dehydrogenation kinetics and cycling stability through the synergistic effect of catalysts. Apart from the chemical composition, morphology can also be a relevant aspect of an additive, as was demonstrated through various examples. Different types of nanorods, nanotubes, nanosheets and core-shell structures have shown the ability to enhance the H-sorption properties of MgH$_2$ and increase the cycling stability.

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