

An Overview of the Recent Advances of Additive-Improved $\text{Mg}(\text{BH}_4)_2$ for Solid-State Hydrogen Storage Material

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Abstract: Recently, hydrogen (H_2) has emerged as a superior energy carrier that has the potential to replace fossil fuel. However, storing H_2 under safe and operable conditions is still a challenging process due to the current commercial method, i.e., H_2 storage in a pressurised and liquified state, which requires extremely high pressure and extremely low temperature. To solve this problem, research on solid-state H_2 storage materials is being actively conducted. Among the solid-state H_2 storage materials, borohydride is a potential candidate for H_2 storage owing to its high gravimetric capacity (majority borohydride materials release >10 wt% of H_2). $\text{Mg}(\text{BH}_4)_2$, which is included in the borohydride family, shows promise as a good H_2 storage material owing to its high gravimetric capacity (14.9 wt%). However, its practical application is hindered by high thermal decomposition temperature (above 300°C), slow sorption kinetics and poor reversibility. Currently, the general research on the use of additives to enhance the H_2 storage performance of $\text{Mg}(\text{BH}_4)_2$ is still under investigation. This article reviews the latest research on additive-enhanced $\text{Mg}(\text{BH}_4)_2$ and its impact on the H_2 storage performance. The future prospect and challenges in the development of additive-enhanced $\text{Mg}(\text{BH}_4)_2$ are also discussed in this review paper. To the best of our knowledge, this is the first systematic review paper that focuses on the additive-enhanced $\text{Mg}(\text{BH}_4)_2$ for solid-state H_2 storage.

Keywords: hydrogen storage; solid-state storage; borohydrides; $\text{Mg}(\text{BH}_4)_2$; additives

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1. Introduction

1.1. Renewable and Sustainable Energy System

The rapid increase in energy consumption worldwide has already raised questions with regard to production issues, energy resource scarcity and serious environmental effects (ozone depletion, global warming, climate change, etc.) [1]. The earth's oil reserves are finite. Thus, they are not expected to last long. Moreover, it is expected that oil supply in the future will eventually peak and drop with the depletion of these reserves. On a global scale, the "greenhouse effect" is a key environmental issue due to the emission of carbon dioxide and other gases into the atmosphere. The major causes of such an impact are the burning of fossil fuels and deforestation [2].

Due to the productive relationship between clean energy and sustainable growth, renewable energy is often considered to be one of the most reliable solutions. The most urgent task is to take energy-saving measures in order to minimise energy consumption and change the demand situation that renewable energy must meet [3]. Many aspects can contribute to the realization of sustainable development. One of the most crucial aspects is the need to provide a completely sustainable energy [4–6] to reduce the world's dependence on non-renewable resources such as fossil fuel.

1.2. Hydrogen as an Ideal Energy Carrier

Like electricity, hydrogen (H_2) can be considered as a superior form of energy carrier that is extremely effective. In addition, H_2 has zero or near-zero emissions [7]. H_2 is environmentally and climatically clean when derived from green electricity or fossil fuels over the entire energy conversion chain [8]. Furthermore, it can be produced using different renewable (water and solar, wave, geothermal and biomass energies) and non-renewable (nuclear energy, natural gas and coal) resources. Its use may vary from transport and energy production systems that utilise fuel cells, turbines or internal combustion engines and water as a by-product. One of the Earth's greatest environmental challenges may be solved by H_2 's capability to replace fossil fuels in the transportation industry [9,10]. Although the importance of H_2 energy has been investigated for many years, researchers are still determining how H_2 energy can contribute to a more sustainable environment [11–15]. Some researchers have highlighted the concept of an H_2 economy as an imminent possibility [16–18]. These studies indicate that the role of H_2 energy will become increasingly significant. Numerous researchers have investigated how the world can be transformed into one where the main energy carriers in the energy system are H_2 and electricity [19].

The amount of H_2 's energy per unit mass is 143 MJ kg^{-1} , which is triple that of liquid hydrocarbons [20,21]. According to different storage capacities and application areas, three common types of H_2 storage systems can be used, namely (1) compressed H_2 gas, (2) liquified H_2 and (3) solid-state H_2 storage [22–27], each with its own benefits and drawbacks. The liquid H_2 storage method offers a high volumetric and gravimetric H_2 capacity. However, significant energy is required for the liquefying process, and an appropriate container with a sufficient insulation layer is needed to minimise the vaporisation of liquid H_2 for a long period of time [28]. Conversely, the technique using compressed H_2 gas is commonly used in our society owing to the simple storage method and low cost of the processing and transportation of H_2 gas. However, a high-pressure storage has some drawbacks, such as the inability of the required large physical volume to achieve the volumetric target, high cost and safety issues that are still under consideration [29,30].

Storing H_2 in a solid-state form is quite promising compared with liquified H_2 and compressed H_2 gas in terms of safety, energy efficiency, space and cost-effectiveness [31–33]. Solid-state H_2 storage can be divided in two particular ways: by chemical adsorption (chemisorption), which is based on the simple or complex chemical absorption of atomic H_2 in light metal hydrides, and physical adsorption (physisorption), which relies on the adsorption of molecular H_2 on high-surface-area materials [34]. Examples of chemisorption materials are metal hydrides, such as Mg_2NiH_4 , $LaNi_5$ and MgH_2 , and complex hydrides, such as $LiAlH_4$, $NaAlH_4$, $LiBH_4$, $Mg(BH_4)_2$ and $NaBH_4$. Meanwhile, carbon-based materials (e.g., carbon nanotubes (CNTs), activated carbon and graphene), zeolite and metal–organic framework (MOF) are examples of physisorption materials. Figure 1 presents the schematic of the H_2 absorption mechanism in chemisorption materials and adsorption mechanism in physisorption materials.

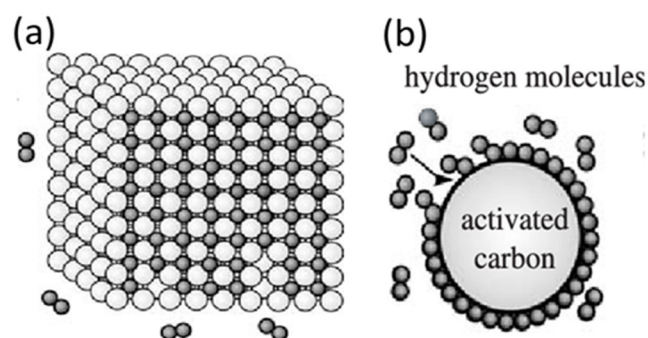


Figure 1. Schematic of hydrogen (a) absorption mechanism in chemisorption materials and (b) adsorption mechanism in physisorption materials [10].

For solid-state H₂ storage, chemisorption materials are preferable compared with physisorption materials owing to their high H₂ storage capacity and moderate temperature and pressure requirement. Chemisorption materials, especially metal hydrides and complex hydrides, have been thoroughly studied, owing to their significant H₂ density and dehydrogenation/rehydrogenation capabilities, while ignoring the requirement for high pressure or low temperature [35]. Previous studies have demonstrated that Mg-based hydrides are potential candidates for solid-state H₂ storage because of their excellent reversibility to H₂ absorption and desorption, as well as high H₂ storage capacity [36,37]. However, their high decomposition temperature and sluggish sorption kinetic properties hinder their commercial application. Meanwhile, researchers have revealed that complex hydrides have high gravimetric and volumetric capacities, enabling them to meet the capacity requirements of H₂ storage materials [38,39]. However, the disadvantage is that most complex hydride compounds do not have convenient H₂ desorption thermodynamics and/or kinetics and require high temperatures to desorb H₂. Moreover, they usually contain impurities. The reversibility of the Ti-doped NaAlH₄ catalyst system was first studied by Bogdanovic and Schwickardi [40]. Since then, researchers have exerted significant effort to investigate the properties of complex hydrides as suitable candidates for solid-state H₂ storage [41–45].

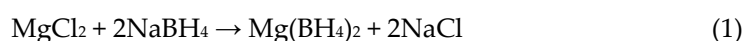
Borohydrides are an example of complex hydride materials with high H₂ storage capacity. As borohydride has high gravimetric and volumetric H₂ storage capacity, it shows promise as a good H₂ storage material [46]. Research on metal borohydride (M(BH₄)_n) (where M = Li, Na, Mg, Ca etc.) as a competitor for solid-state H₂ storage material began with lithium borohydride (LiBH₄) [47]. LiBH₄ decomposes into LiH and B, with 13.8 wt% of H₂ release along the process [41,48–52]. Mauron et al. [53] conducted a pressure–concentration–temperature (PCT) study on LiBH₄, and found that the entropy (ΔS) and enthalpy (ΔH) of dehydrogenation were 115 JK^{−1} mol^{−1} H₂ and 74 kJ mol^{−1} H₂, respectively. LiBH₄ is reversible to H₂ desorption and absorption since the dehydrogenation products, lithium hydride (LiH) and boron (B) can absorb H₂ at 600 °C under 35-MPa H₂ pressure within 12 h [50] or at 727 °C under 15-MPa H₂ pressure within 10 h [52] to form LiBH₄. The thermal and H₂ storage properties of metal borohydrides (M(BH₄)_n) (where M = Li, Na, Mg and Ca) are presented in Table 1.

Table 1. Thermal and hydrogen storage properties of metal borohydrides.

Formula	Molecular Weight (g mol ^{−1})	Decomposition Temperature (°C)	Hydrogen Storage Capacity (wt%)	Ref.
LiBH ₄	21.8	320	18.5	[47]
NaBH ₄	37.8	450	10.6	[54]
Mg(BH ₄) ₂	53.9	320	14.9	[55]
Ca(BH ₄) ₂	69.8	360	11.4	[56]
KBH ₄	53.9	550	7.5	[57]

1.3. Characteristic of Mg(BH₄)₂ Hydrogen Storage System

As a member of the borohydride family, magnesium borohydride (Mg(BH₄)₂) is an extremely promising H₂ storage material owing to its high gravimetric storage density (14.9 wt%) [58–67]. Theoretically, it is predicted that H₂ can be released at rather mild conditions [68–72]. Filinchuk et al. [73] discovered a cubic phase of Mg(BH₄)₂, which is a complex hydride with a large surface area and a porous structure suitable for H₂ adsorption. Mg(BH₄)₂ can be synthesised by the metathesis of MgCl₂ and NaBH₄ in diethyl ether, as expressed in Equation (1) [74]:

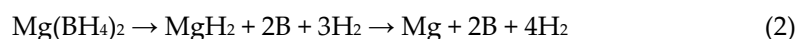


Bateni et al. [75] studied a new method for synthesis of Mg(BH₄)₂ by the milling of MgBr₂ and NaBH₄. Mg(BH₄)₂ was extracted from the reaction product (Mg(BH₄)₂ + NaBr) by Soxhlet with diethyl ether. In another report, Cerny et al. [76] synthesised the solvent-free

Mg(BH₄)₂ by the metathesis of LiBH₄ and MgCl₂ in diethyl ether, and found that their method is more efficient than the previously reported reaction from NaBH₄ and MgCl₂, which yields a solvated product that is rather amorphous.

Several theoretically predicted Mg(BH₄)₂ structures have been published, demonstrating an “outstanding divergence between experiment and theory” [60,77]. The high-pressure structures *P-4*, *I4₁/acd* [78], *I4₁/amd* [79] and *Fddd* [80] found by first-principle studies, for example, have been discovered to be more favourable than the experimentally determined *P4₂nm* phase of the ultra-dense δ-Mg(BH₄)₂ [73]. These inconsistencies can lead to an erroneous assessment of thermodynamic properties, affecting the evaluation of Mg(BH₄)₂'s hydrogen storage characteristics. It was proposed that the small size of the Mg cation, together with the close proximity of BH₄, leads to increased repulsive interactions and a condition in which the orientation of the anions plays a significant role [77,81]. Vibrational spectroscopy studies can be used to characterise the local structure of BH₄, which can be linked to the stability of the compounds.

Chłopek et al. [55] and Matsunaga et al. [63,82] reported that the H₂ desorption of Mg(BH₄)₂ occurs in a two-step pathway as expressed in Equation (2):



Several studies have shown that pure crystalline Mg(BH₄)₂ can release mostly pure H₂ at 300 °C [74,83–86]. However, the preceding and subsequent experimental research has continuously demonstrated that decomposition occurs through a two-step pathway at a temperature beyond 200 °C [87–90]. Fichtner et al. [88] reported that the two-step decomposition of Mg(BH₄)₂ yielded activation energies of 311 ± 20 and 189 ± 15 kJ mol^{−1}, whereas Ibikunle et al. [91] only obtained a value of 155.2 kJ mol^{−1} [63]. The characteristic of Mg(BH₄)₂ is that it has a wide range of crystal structures, and the number of crystals is larger than that of any other known borohydrides. The experiment and theory are presented in Table 2.

Table 2. Experimental gravimetric (q_m), specific (q) and volumetric (q_v) densities of different Mg(BH₄)₂ polymorphs.

Phase	Space Group	q _m , wt%	q, g cm ^{−3}	q _v , g L ^{−1}	Ref.
α-Mg(BH ₄) ₂	<i>P6₁22</i>	14.9	0.783	117	[92]
β-Mg(BH ₄) ₂	<i>Fddd</i>	14.9	0.761	113	[93]
γ-Mg(BH ₄) ₂	<i>Ia3a</i>	14.9	0.550	82	[73]
γ-Mg(BH ₄) ₂ -0.80 H ₂	<i>Ia3d</i>	17.4	0.565	98	[73]
δ-Mg(BH ₄) ₂	<i>P4₂nm</i>	14.9	0.987	147	[73]

1.4. Modification of the Mg(BH₄)₂ Properties

Although Mg(BH₄)₂ shows promise as a solid-state H₂ storage material, its high decomposition temperature, slow sorption kinetics and very stable thermodynamic properties hinder its commercial application. To modify the H₂ storage properties of Mg(BH₄)₂, several methods have been employed, such as particle size reduction via ball milling [74,94], the use of catalysts or additives to improve sorption kinetics [74,95–97] and alteration of the thermodynamic properties using the destabilised concept (mix of two or more complex metal hydrides) [98–108]. Among these methods, the addition of catalysts or additives to Mg(BH₄)₂ has been studied rigorously as it significantly improves the H₂ storage properties of Mg(BH₄)₂. A catalyst or additive is generally used to increase the H₂ adsorption rate by reducing the activation energy of the dehydrogenation/rehydrogenation reaction. The obvious advantage of the addition of catalysts or additives is that it helps improve the kinetic performance, while the capacity loss is negligible [109]. The authors of this article reviewed the impact of the different groups of catalysts/additives on the H₂ storage properties of Mg(BH₄)₂. In addition, the authors of this article also pointed out the role of catalysts/additives and their catalytic mechanism, and provided opinions on the

future prospect and challenges with regard to $\text{Mg}(\text{BH}_4)_2$ as a suitable material for solid-state H_2 storage.

2. Hydrogen Storage Behaviour of Additive-Enhanced $\text{Mg}(\text{BH}_4)_2$

2.1. Metals

The addition of metal as a dopant to enhance the H_2 storage properties of complex metal hydrides has been widely studied [110,111]. The role of Al was investigated by Jiang et al. [112] on the dehydrogenation and rehydrogenation of $\text{Mg}(\text{BH}_4)_2$. Table 3 presents the sorption properties of $\text{Mg}(\text{BH}_4)_2 + \text{Al}$, $\text{Mg}(\text{BH}_4)_2 + \text{LiH} + \text{Al}$, $\text{Mg}(\text{BH}_4)_2 + 1/3(\text{Li}_3\text{AlH}_6) + 2\text{Al}$, $\text{Mg}(\text{BH}_4)_2 + \text{LiAlH}_4$ and pure $\text{Mg}(\text{BH}_4)_2$. Figure 2a shows that the sample $\text{Mg}(\text{BH}_4)_2 + \text{Al}$ and $\text{Mg}(\text{BH}_4)_2 + \text{LiH} + \text{Al}$ desorption activity was comparable to $\text{Mg}(\text{BH}_4)_2$, with improved the desorption kinetic and reduced the release temperature at the second step. In comparison to $\text{Mg}(\text{BH}_4)_2$, sample $\text{Mg}(\text{BH}_4)_2 + 1/3(\text{Li}_3\text{AlH}_6) + 2\text{Al}$ had more desorption steps, which may be related to the decomposition of Li_3AlH_6 . The process started at about 150°C , which was 30°C lower than that of Li_3AlH_6 in pure LiAlH_4 . Two other desorption steps can be observed in sample $\text{Mg}(\text{BH}_4)_2 + \text{LiAlH}_4$, which may cause the decomposition of LiAlH_4 to start at approximately 140°C , which is 30°C below the decomposition temperature of pure LiAlH_4 . At 350°C , the time taken by pristine $\text{Mg}(\text{BH}_4)_2$ to release 90% of H_2 was 1911 s, whereas the other samples could complete 90% of desorption below 1700 s at the same temperature. As can be seen from Figure 2b, the rate of desorption of LiH-doped $\text{Mg}(\text{BH}_4)_2$ was significantly low compared with that of the sample containing Al and pure $\text{Mg}(\text{BH}_4)_2$ only. This indicates that Al plays a major role in the improvement of the release kinetics in the Al-doped $\text{Mg}(\text{BH}_4)_2$ samples. The Mg–B–Al–H system is considered to be somewhat reversible. Doped $\text{Mg}(\text{BH}_4)_2$ samples were able to absorb about 1.7, 5.1, 5.0 and 5.7 wt% of H_2 . The reversibility of the Mg–B–Al–H system is significantly associated with regenerated MgH_2 and LiBH_4 .

Table 3. Characteristics of hydrogen sorption from different samples [112].

Sample	Dehydrogenation		Rehydrogenation	
	Temperature Program Desorption (TPD) (wt%)	Desorption at 350°C (wt%)	Time for 90% H_2 Desorption (s)	Absorption at 350°C (wt%)
$\text{Mg}(\text{BH}_4)_2$	12.0	10.4	1911	4.1
$(\text{Mg}(\text{BH}_4)_2 + \text{Al})$	8.3	6.2	1173	1.7
$(\text{Mg}(\text{BH}_4)_2 + \text{LiH} + \text{Al})$	8.0	5.8	1699	5.1
$(\text{Mg}(\text{BH}_4)_2 + 1/3(\text{Li}_3\text{AlH}_6) + 2\text{Al})$	10.1	7.6	1277	5.0
$(\text{Mg}(\text{BH}_4)_2 + \text{LiAlH}_4)$	11.5	9.5	1316	5.7

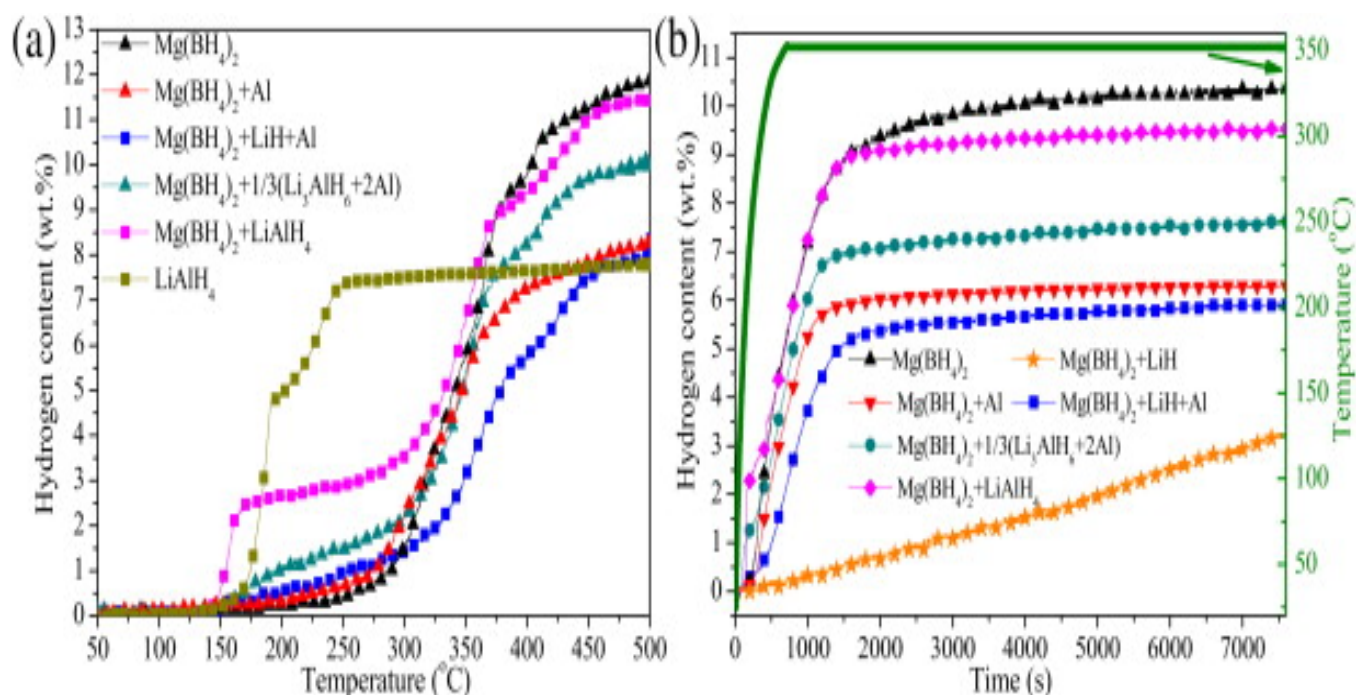


Figure 2. Dehydrogenation properties of the different samples: (a) Temperature program desorption curves and (b) isothermal desorption kinetics at 350 °C of the Mg-B-Al-H systems [112].

Ball milling is considered to be a useful technique to enhance the kinetics of H_2 reaction by altering the microstructures and surface properties [113]. Conversely, Li et al. [74] investigated the effect of ball milling and Ti-based additives on the dehydriding properties of $\text{Mg}(\text{BH}_4)_2$. Compared with the initial dehydriding temperature of the as-synthesised $\text{Mg}(\text{BH}_4)_2$, no significant difference was observed in the sample mixed with Ti, TiH_2 and TiB_2 , whereas the addition of TiO_2 reduced the initial dehydriding temperature by about 50 °C. However, the addition of TiCl_3 reduced the initial dehydriding temperature from 262 °C to 88 °C, which indicates a reduction of approximately 174 °C. The improvement may be due to the reaction between $\text{Mg}(\text{BH}_4)_2$ and TiCl_3 , forming unstable $\text{MgTi}_x(\text{BH}_4)_{(2+nx)}$, which is consistent with the study by Li et al. [114], in which $\text{ZrLi}(\text{BH}_4)_5$ was formed.

Recently, Wang et al. [115] investigated the influence of Ti nanoparticles on the dehydrogenation kinetic and reversibility of $\text{Mg}(\text{BH}_4)_2$, and found that the Ti-doped $\text{Mg}(\text{BH}_4)_2$ sample showed better desorption kinetics than the undoped $\text{Mg}(\text{BH}_4)_2$. The Ti-doped $\text{Mg}(\text{BH}_4)_2$ sample also showed a great improvement in terms of capacity released, in which at 270, 280, and 290 °C, as shown in Figure 3, the doped sample could desorb more H_2 within 35 h than $\text{Mg}(\text{BH}_4)_2$ does for each temperature. Moreover, the activation energy for hydrogen release from $\text{Mg}(\text{BH}_4)_2$ also decreased after the addition of Ti nanoparticles. Based on the Arrhenius plot, the activation for Ti-doped $\text{Mg}(\text{BH}_4)_2$ sample was 56.5 kJ/mol, which was lower than that of undoped $\text{Mg}(\text{BH}_4)_2$ (61.1 kJ/mol). From the experimental results, Wang et al. concluded that during the milling and heating process, Ti nanoparticles react with $\text{Mg}(\text{BH}_4)_2$ to generate in situ Ti-based species ($\text{TiH}_{1.924}$ and TiB_2). It is believed that TiB_2 could act as a heterogeneous nucleation agent, and $\text{TiH}_{1.924}$ could act as a hydrogen pump during the rehydrogenation process. Table 4 presents the effect of several metal catalysts on the desorption and absorption of $\text{Mg}(\text{BH}_4)_2$.

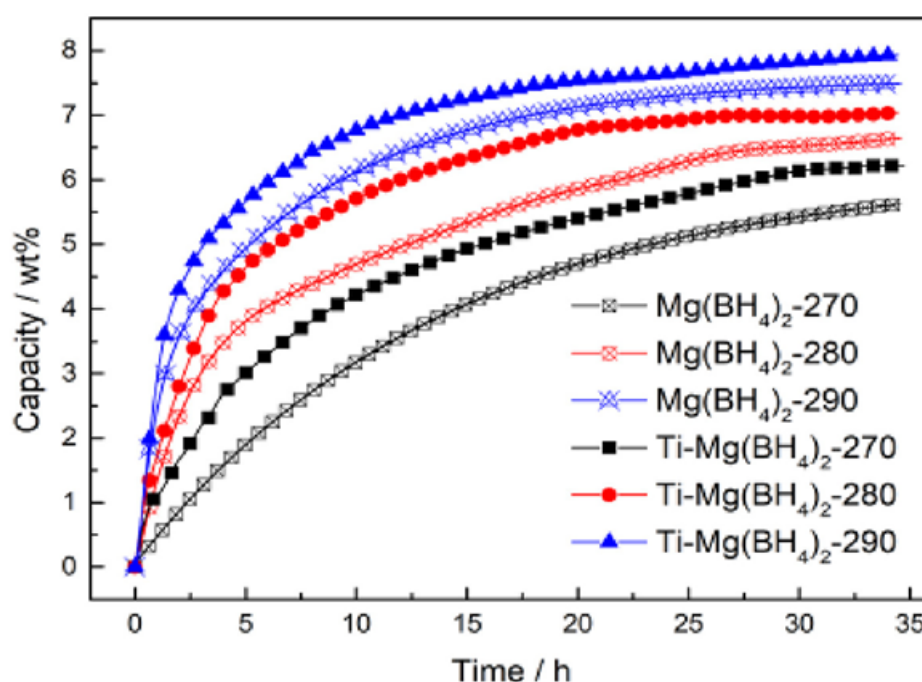


Figure 3. The dehydrogenation kinetic curves of the undoped $\text{Mg}(\text{BH}_4)_2$ and Ti-doped $\text{Mg}(\text{BH}_4)_2$ samples at 270, 280 and 290 °C, respectively [115].

Table 4. Effect of several metals on the desorption and absorption kinetic of $\text{Mg}(\text{BH}_4)_2$.

Additive		Desorption of $\text{Mg}(\text{BH}_4)_2$			Absorption of $\text{Mg}(\text{BH}_4)_2$			Ref.
Name	Mol. %	Time, min	Temperature, °C	H_2 , wt%	Time, min	Temperature, °C	H_2 , wt%	
Al	50	125	350	6.2	100	350	1.7	[112]
Ni	2	3600	256	2.7	1200	251	1.3	[116]
Ti	-	900	270	4.0	900	270	4.23	[115]

2.2. Metal Oxides

Previous studies have demonstrated that among the catalysts/additives used to improve the H_2 storage properties of metal hydrides and complex hydrides, metal oxides are rigorously applied [94,117]. Zavorotynska et al. [118,119] focused on the study of cobalt-based additives used to enhance the sorption properties of $\text{Mg}(\text{BH}_4)_2$ in three cycles, as shown in Figure 4. The first cyclic absorption isotherm (Figure 4b) demonstrates that the grinding of undoped $\text{Mg}(\text{BH}_4)_2$ can increase the rehydrogenation kinetics by two to five times, whereas all additives, except Co_3O_4 , decrease it.

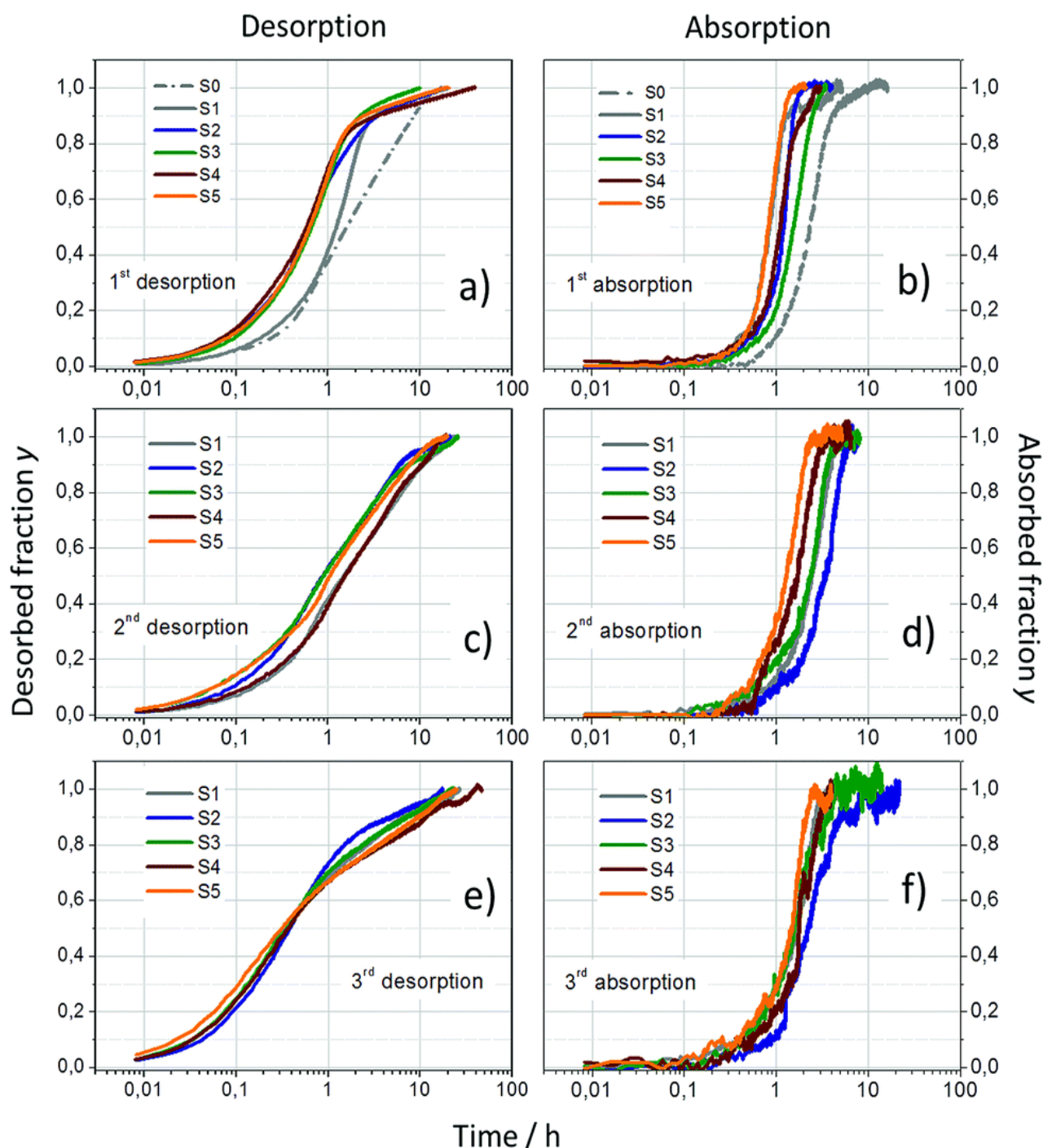


Figure 4. Isothermal desorption kinetics (a,c,e) and absorption kinetics (b,d,f) of different sample S0–S5 during 3 cycles. γ -Mg(BH₄)₂ as received (S0), γ -Mg(BH₄)₂ ball-milled (S1), and γ -Mg(BH₄)₂ + 2 mol% X (X = CoF₃ (S2), Co₂B (S3), CoCl₂ (S4), Co₃O₄ (S5)) [118].

In the second cycle, the desorption process of all samples (Figure 4c) was even slower than that in the first cycle, as 90% of the desorption process was completed within 10 h. Although Co₂B did not seem to have any major influence and CoF₃ slowed down the kinetic rate, Co₃O₄ and CoCl₂ seemed to improve the absorption kinetics. In the third cycle, the desorption kinetics were quicker than those in the second cycle, with a slightly enhancing effect on CoF₃ and Co₂B, whereas CoCl₂ and Co₃O₄ were slightly negative. Overall, in the first cycle, the desorption kinetic rates were the highest, declining in the second cycle and increasing again in the third cycle. Most additives slightly improved the kinetics in the first cycle but had little effect in the second cycle. CoF₃ and Co₂B slightly improved

the reaction rate in the last cycle, whereas other additives declined the kinetics. Likewise, in the first cycle, the absorption kinetics were the fastest, and then they decreased significantly in the second cycle, whereas in the third cycle, the kinetic rate was the same as that in the first cycle. Additives mainly slowed down the absorption kinetics, and only Co_3O_4 significantly enhanced the kinetics in all three cycles. It should be noted that the curve in Figure 4 behaved differently in all cycles, especially in desorption. This indicates that the reaction was controlled by a different mechanism, which explains the inconsistency of the reaction rate with the cycle.

Saldan et al. [120] studied the reversible H_2 desorption–adsorption of $\gamma\text{-Mg}(\text{BH}_4)_2$ ball-milled with MoO_3 and TiO_2 . As can be seen from Figure 5, $\gamma\text{-Mg}(\text{BH}_4)_2\text{-MoO}_3$ first desorbed H_2 at 267°C , which released approximately 5.1 and 5.6 wt% of H_2 after 10 and 15 h, respectively. At a slightly lower temperature, pristine $\gamma\text{-Mg}(\text{BH}_4)_2$ released about ~4.6 and about ~5.2 wt% of H_2 at the same time.

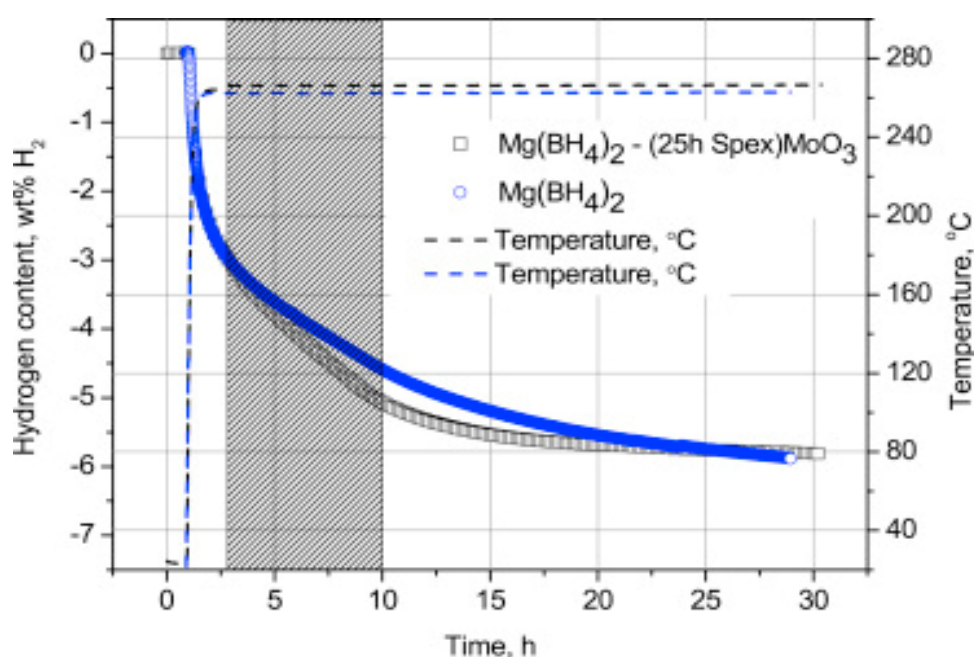


Figure 5. Hydrogen desorption curves of pristine $\gamma\text{-Mg}(\text{BH}_4)_2$ and $\gamma\text{-Mg}(\text{BH}_4)_2 + 2 \text{ mol}\% \text{MoO}_3$ [120].

The H_2 desorption–absorption properties of the mixture of pre-milled TiO_2 and $\gamma\text{-Mg}(\text{BH}_4)_2\text{-TiO}_2$ were also studied (Figure 6). Most of the H_2 release occurred at 270°C – 300°C , and the H_2 cycle occurred at 271°C . The first vacuum desorption released about 4.0 wt% of H_2 after about 40 h and then performed rehydrogenation in about 140 bar of H_2 . After dehydrogenation, about 2.4 wt% of H_2 was reversible in about 70 h. From the solid-state ^{11}B NMR data after the first H_2 desorption, there were two peaks at approximately -20 and -50 ppm. These peaks corresponded to the presence of $(\text{B}_3\text{H}_8)^-$ and higher anionic polyboranes.

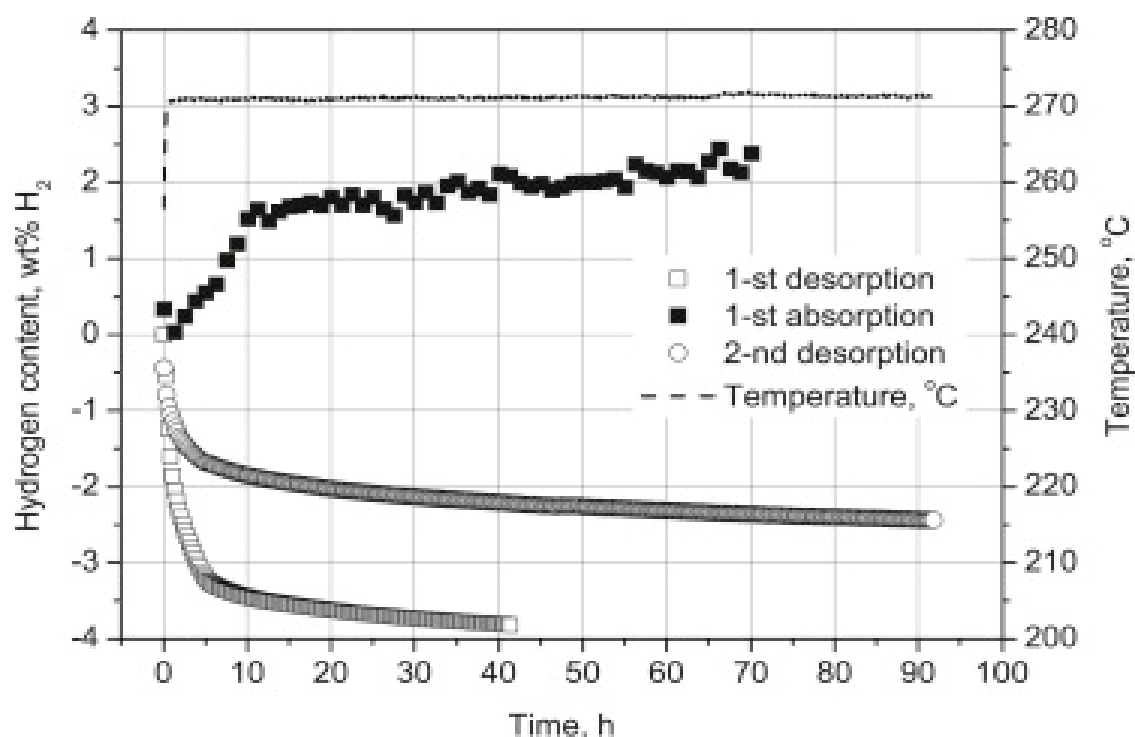


Figure 6. Cycling properties of hydrogen sorption of γ -Mg(BH₄)₂ + 2 mol % TiO₂ [120].

Saldan et al. [121] also conducted a further temperature-programmed desorption (TPD) analysis on Mg(BH₄)₂ doped with transition metal oxide (TMO). They found that Mg(BH₄)₂ + TMO (TMO = TiO₂ and MoO₃) had the same H₂ decomposition temperature as pristine Mg(BH₄)₂ with different intensity distributions of H₂. However, the addition of ZrO₂ to Mg(BH₄)₂ slightly reduced its decomposition temperature by about 10 °C, with the same intensity of H₂ distributed as pure Mg(BH₄)₂. Conversely, Mg(BH₄)₂ doped with Nb₂O₅ increased the thermal decomposition temperature. The result also indicated that there was no chemical reaction between the additives with Mg(BH₄)₂ during the milling process for all the TMO-doped Mg(BH₄)₂ composites. Table 5 summarises the effect of several metal oxides on the desorption and absorption of the Mg(BH₄)₂ species.

Table 5. Effect of several metal oxides on the desorption and absorption of Mg(BH₄)₂.

Additive		Desorption of Mg(BH ₄) ₂			Absorption of Mg(BH ₄) ₂			Ref.
Name	Mol. %	Time, min	Temperature, °C	H ₂ , wt%	Time, min	Temperature, °C	H ₂ , wt%	
TiO ₂	2	2400	271	3.8	4200	271	2.4	[120]
Co ₃ O ₄	2	1260	288	3.9	120	285	1.6	[118]
MoO ₃	2	1800	267	5.1	-	-	-	[120]
ZrO ₂	2	250	299	-	-	-	-	[121]
Nb ₂ O ₅	2	250	309	-	-	-	-	[121]

2.3. Metal Halides

Metal halides are a common type of catalyst/additive used to improve the H₂ storage properties of metal hydrides and complex hydrides [122,123]. Al-Kukhun et al. [124] investigated the influence of VCl₃, NbF₅ and CoCl₂ as additives on the improvement of H₂ release from Mg(BH₄)₂. The weight percentage of H₂ desorbed was observed at 300 °C after 90 min, where 7.30, 7.30, 8.00 and 10.10 wt% of H₂ was liberated from pure Mg(BH₄)₂ and Mg(BH₄)₂ doped with VCl₃, CoCl₂ and NbF₅, respectively. Although VCl₃ do not enhance the release of H₂, the kinetics and degree of H₂ release were improved by CoCl₂ and NbF₅. It should be mentioned that when NbF₅ was introduced, the H₂ release at 100 °C was 2.6 wt%, whereas the H₂ release of other samples was only 0.09 wt%. This proves that

the H₂ storage properties of Mg(BH₄)₂ can be improved with NbF₅ as a catalyst. From the NMR spectrum, the addition of NbF₅ to Mg(BH₄)₂ resulted in the formation of MgB₁₂H₁₂ intermediate phases during the heating process.

Wang et al. [125] also studied the influence of NbF₅ on amorphous Mg(BH₄)₂ that formed in situ to enhance H₂ storage performance. They found that the initial decomposition temperature of pure Mg(BH₄)₂ was 283 °C, whereas amorphous Mg(BH₄)₂ and NbF₅-doped amorphous Mg(BH₄)₂ began to release H₂ at 127 °C and 120 °C, respectively. However, as a result, the amount of H₂ released was slightly decreased to 10.04 wt% for the NbF₅-doped amorphous Mg(BH₄)₂ sample as compared with 10.28 and 10.80 wt% for pure Mg(BH₄)₂ and amorphous Mg(BH₄)₂, respectively. From the FTIR result, it was proven that the intermediate MgB₁₂H₁₂ is regenerated during the hydrogenation process. The formation of intermediate MgB₁₂H₁₂ is believed to exert negative effects on the reversibility process in the Mg(BH₄)₂. However, Yan et al. [126] proved that the intermediate MgB₁₂H₁₂ does not form as a dehydrogenation product of Mg(BH₄)₂ in their study. The results also indicated that the addition of NbF₅ changed the dehydrogenation pathway of Mg(BH₄)₂ and two new species (MgF₂ and NbB₂) that formed in situ during the dehydrogenation process. It is believed that the MgF₂ and NbB₂ species play a major catalytic role in improving the H₂ storage properties of NbF₅-doped Mg(BH₄)₂ composite.

Another study by Newhouse et al. [127] focused on the H₂ storage properties of Mg(BH₄)₂ with ScCl₃ and TiF₃ as catalysts. The addition of 5 mol% TiF₃ and ScCl₃ can significantly increase both the amount of H₂ releases and the rate of H₂ desorption of Mg(BH₄)₂. Mg(BH₄)₂ added with the catalyst released 9.7 wt% of H₂ after being placed at 300 °C for 17 h, whereas pristine Mg(BH₄)₂ desorbed 7.7 wt% of H₂. Compared with the undoped sample that required 10 h, the sample with additives had 95% of the H₂ completely desorbed in the first 2 h. The dehydrogenated species, MgB₂, fully absorbed the H₂ for the sample with and without additives. The formation of Mg(BH₄)₂ after the hydrogenation process was confirmed via NMR spectroscopy, Raman spectroscopy and power X-ray diffraction. However, the use of additives was beneficial to the formation of stable B–H₂ intermediates during the absorption process.

The effects of metal fluorides (CaF₂, ZnF₂ and TiF₃) as additives on the H₂ release process of Mg(BH₄)₂ and its corresponding microstructure evolution were explored by Zhang et al. [128]. It can be seen from Figures 7a and 8a that the first peak that appeared near 150 °C was the polymorphic transition to ε-Mg(BH₄)₂ from γ-Mg(BH₄)₂, with 0.65 wt% of H₂ released. The second transformation occurred at 200 °C, which was the polymorphic transition to β-Mg(BH₄)₂, releasing 0.35 wt% of H₂. When the sample was kept at 295 °C for 5 h, a large quantity of H₂ (8.8 wt%) was liberated, as shown in Figure 8a. In comparison with pure Mg(BH₄)₂, the addition of fluoride triggered the reduction of the decomposition temperature. The addition of CaF₂ demonstrated an identical pattern to that of pure Mg(BH₄)₂, whereas TiF₃ and ZnF₂ reduced the onset temperature to 50 °C. However, under the same conditions, 4.5 wt% of H₂ was released during the transformation from γ-Mg(BH₄)₂ to the amorphous Mg(BH₄)₂, as compared with 9.80 wt% for pristine Mg(BH₄)₂. From the TEM results, all the additives reacted with amorphous Mg(BH₄)₂ during the dehydrogenation process, confirming that CaF₂, ZnF₂ and TiF₃ acted as additives rather than as catalysts in this study.

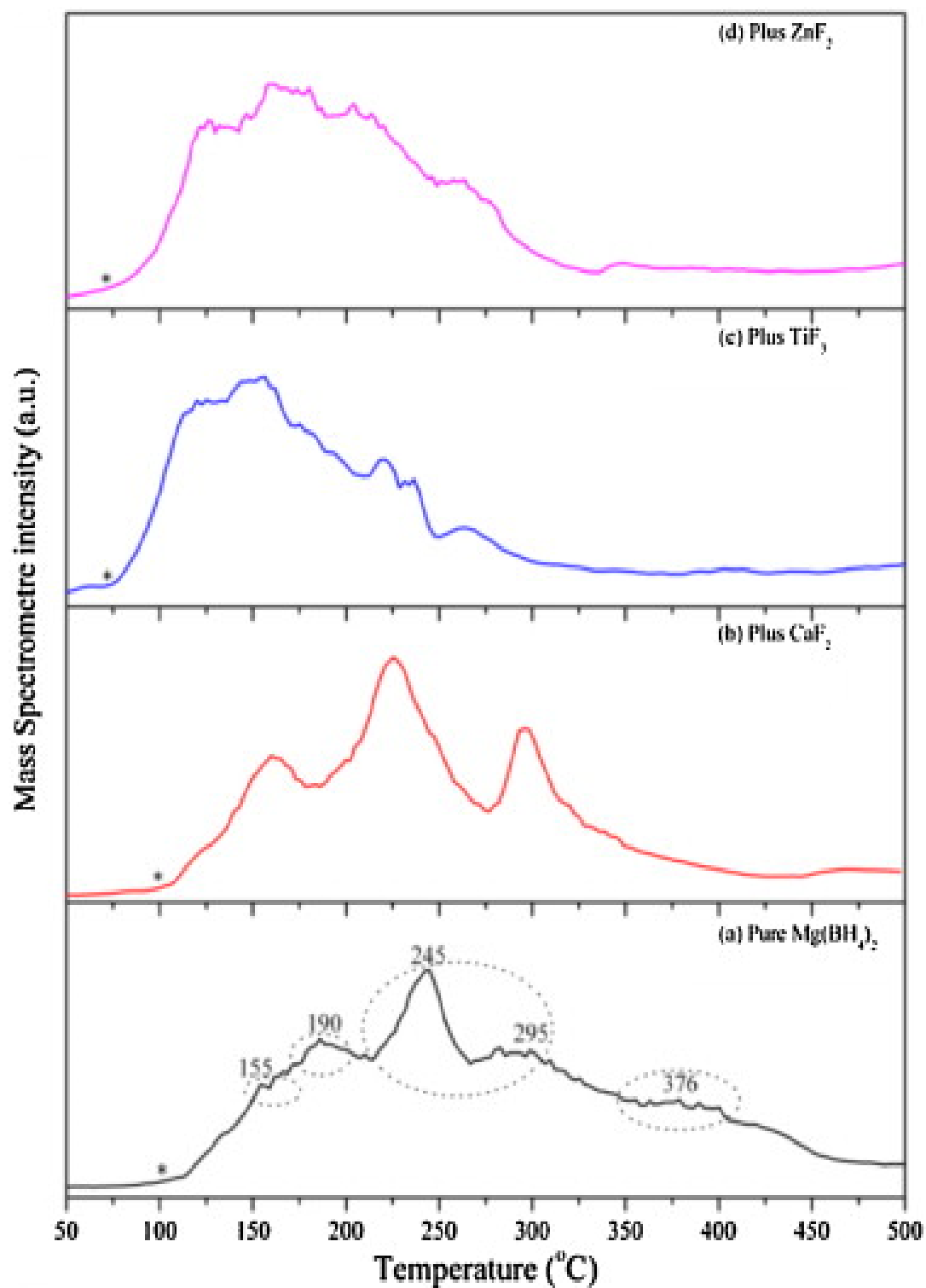


Figure 7. Temperature desorption curves for (a) pristine $\text{Mg}(\text{BH}_4)_2$ and fluoride-doped $\text{Mg}(\text{BH}_4)_2$: (b) CaF_2 ; (c) TiF_3 and (d) ZnF_2 [128].

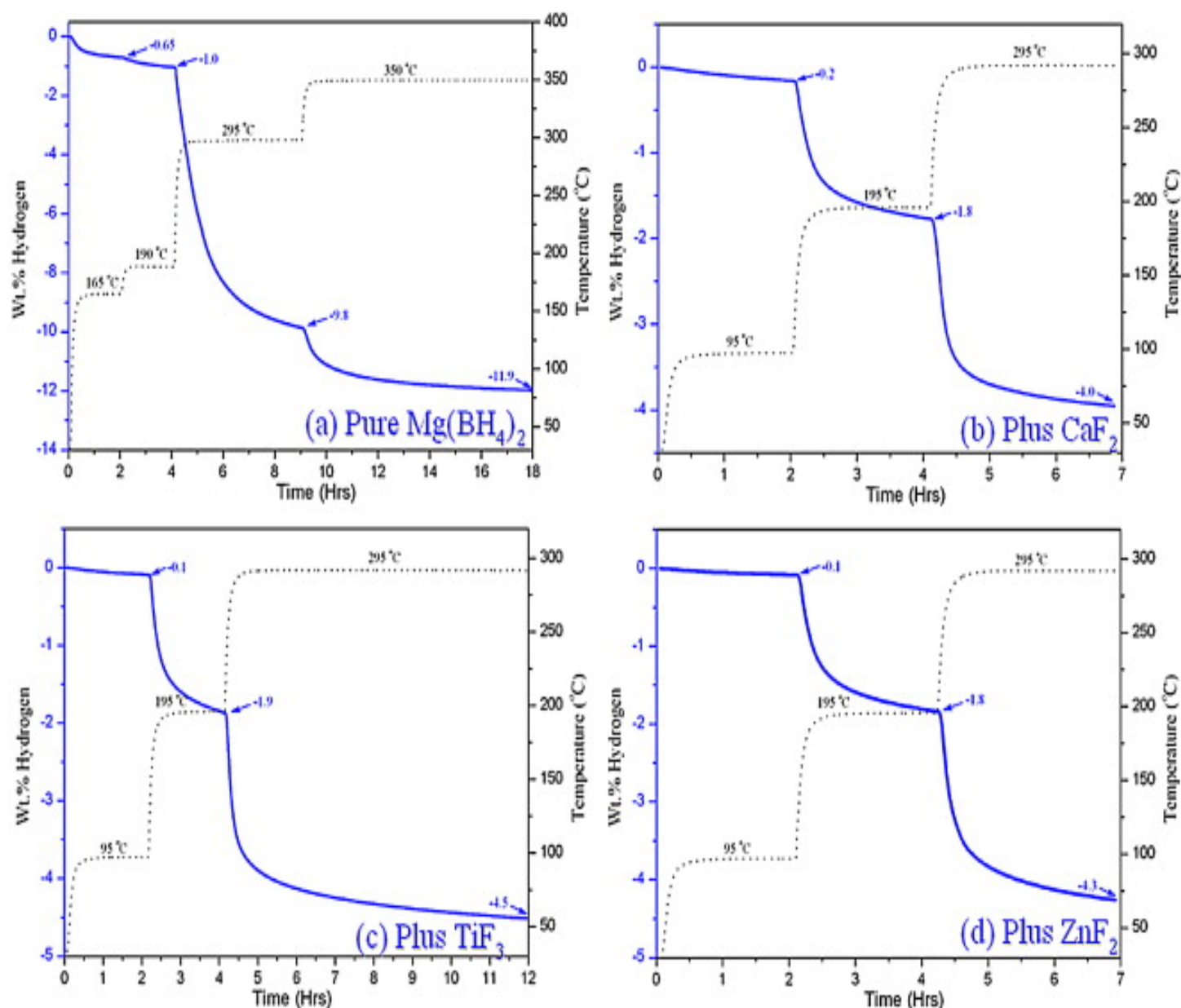


Figure 8. Hydrogen desorption profiles for (a) pristine $\text{Mg}(\text{BH}_4)_2$ and fluoride-doped $\text{Mg}(\text{BH}_4)_2$: (b) CaF_2 ; (c) TiF_3 and (d) ZnF_2 [128].

Another study by Kumar et al. [129] focused on ZrCl_4 -catalysed $\text{Mg}(\text{BH}_4)_2$ and its thermal dehydrogenation properties. As can be seen from Figure 9, the dehydrogenation process of pure $\text{Mg}(\text{BH}_4)_2$ was performed in three steps between 230 °C and 450 °C, releasing approximately 11.0 wt% of H_2 . The first dehydrogenation reaction started at 230 °C and peaked at 302 °C, releasing 4.90 wt% of H_2 . Mass spectroscopy (MS) analysis revealed that the second dehydrogenation process occurred at 330 °C, releasing 3.4 wt% of H_2 . The third endothermic events were associated with the dehydrogenation of MgH_2 generated in situ, which occurred between 365 °C and 450 °C, with 2.6 wt% of H_2 released. Compared with pure $\text{Mg}(\text{BH}_4)_2$, the onset temperature of catalysed $\text{Mg}(\text{BH}_4)_2$ was lower. The dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ with a catalyst began at 197 °C and peaked at 289 °C, releasing 5.6 wt% of H_2 . Whereas ZrCl_4 exerted mild catalytic effects at 289 °C and 337 °C in the first and second dehydrogenation phases, a solder peak observed at 360 °C indicated an impressive outcome of catalyst in the dehydrogenation of MgH_2 formed in situ. According to the Kissinger analysis, the addition of ZrCl_4 reduced the activation energy of H_2 released from $\text{Mg}(\text{BH}_4)_2$ for the first and second steps. The XPS result indicated that

ZrCl₄ reduced to ZrCl₃ and metallic Zr during the milling process. It is believed that ZrCl₃ and metallic Zr formed in situ act as real catalysts in enhancing the dehydrogenation properties of the ZrCl₄-doped Mg(BH₄)₂ composite system.

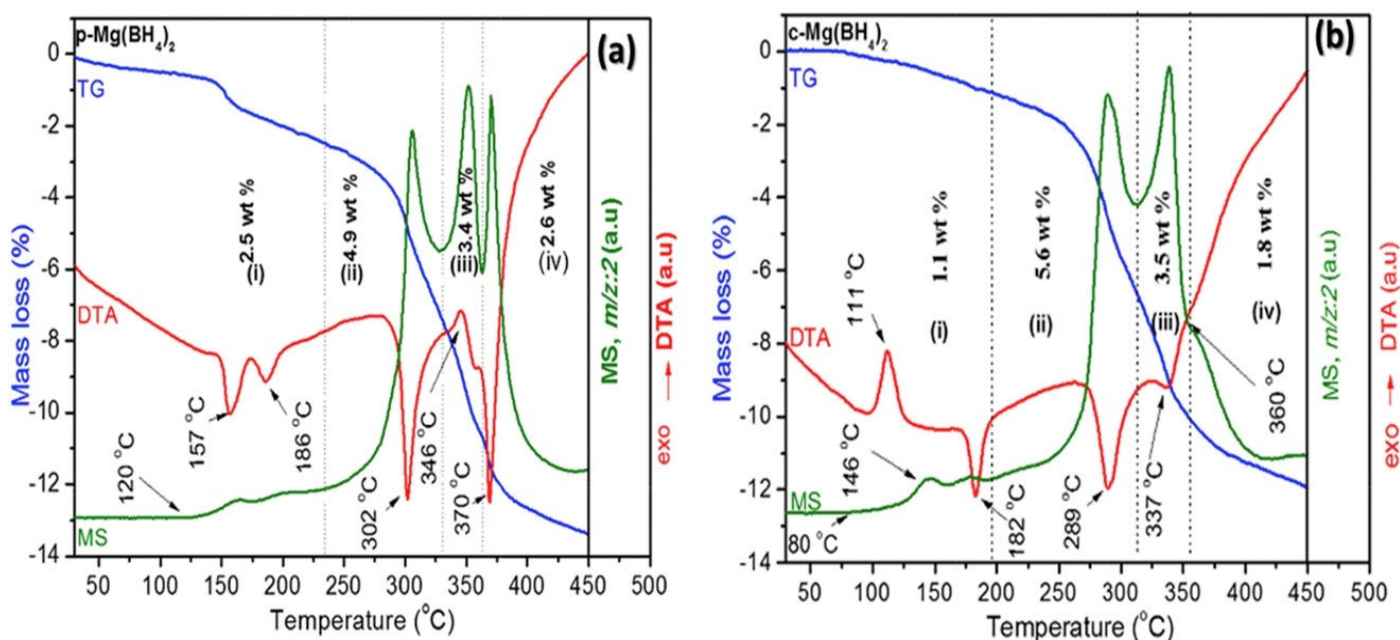


Figure 9. TG-DTA-MS measurements of (a) as-milled pure Mg(BH₄)₂, and (b) as-milled ZrCl₄-catalyzed Mg(BH₄)₂ [129].

Bardaji et al. [130] studied the effect of different metal chlorides (PdCl₂, TiCl₃, VCl₃, MoCl₃, RuCl₃, CeCl₃ and NbCl₅) on the dehydrogenation properties of Mg(BH₄)₂. They found that the H₂ desorption of Mg(BH₄)₂ was slightly improved by the addition of PdCl₂, CeCl₃, VCl₃, MoCl₃ and RuCl₃. The initial decomposition temperature was reduced even further by adding NbCl₅ and TiCl₃. TiCl₃- and NbCl₅-doped samples were able to desorb 6.3 and 5.5 wt% of H₂ at 300 °C, respectively, which indicates more than 50% of Mg(BH₄)₂ H₂ storage capacity. The co-catalyst Ti–Nb nanocomposite (mix of TiCl₃ and NbCl₅) had a positive influence on the dehydrogenation properties of Mg(BH₄)₂ (decreased up to 125 °C). However, no improvement was observed on the reversibility of Mg(BH₄)₂ after the addition of catalysts.

Recently, Zheng et al. [131] investigated the effect of dual-cation transition metal fluorides K₂NbF₇ and K₂TiF₆ on the reversible hydrogen absorption/desorption properties of Mg(BH₄)₂. They discovered that 3% K₂TiF₆ and 3% K₂NbF₇-doped Mg(BH₄)₂ had an initial desorption temperature of 105 °C and 118 °C, respectively, which is approximately 200 °C lower than undoped Mg(BH₄)₂. Meanwhile, the partial reversibility of 3% K₂TiF₆-doped Mg(BH₄)₂ was enhanced to 2.7 wt% at 280 °C in 250 min, which is higher comparing to that of undoped Mg(BH₄)₂. From the XRD, FTIR and ¹¹B nuclear magnetic resonance results, Zheng et al. concluded that the improvement of reversibility performance of Mg(BH₄)₂ with the presence of K₂TiF₆ is due to the active hydrides species, KBH₄ and TiH₂. These active hydride species are formed during the dehydrogenation process by the reaction of Mg(BH₄)₂ and K₂TiF₆ and furthermore act as a real catalysing agents to accelerate the re-generation of Mg(BH₄)₂. Table 6 presents the influence of several metal halide additives on the H₂ storage properties of Mg(BH₄)₂.

Table 6. Influence of several metal halides additives on the hydrogen storage properties of $\text{Mg}(\text{BH}_4)_2$.

Additive		Desorption of $\text{Mg}(\text{BH}_4)_2$			Absorption of $\text{Mg}(\text{BH}_4)_2$			Ref.
Name	Mol. %	Time, min	Temperature, °C	H_2 , wt%	Time, min	Temperature, °C	H_2 , wt%	
TiCl_3	5	120	300	6.1	-	-	-	[130]
CoCl_3	2	2340	288	4.4	180	284	1.9	[118]
NiCl_2	2	600	258	2.7	900	253	1.2	[116]
PdCl_2	5	120	300	5.3	-	-	-	[130]
MoCl_3	5	120	300	4.2	-	-	-	[130]
NbCl_5	5	120	300	5.5	-	-	-	[130]
CeCl_3	5	120	300	3.6	-	-	-	[130]
RuCl_3	5	120	300	5.0	-	-	-	[130]
VCl_3	5	90	300	7.3	-	-	-	[124]
CoCl_2	5	90	300	8.0	-	-	-	[124]
CaF_2	3	420	295	4.0	-	-	-	[128]
TiF_3	3	420	295	4.5	-	-	-	[128]
CoF_3	2	1080	284	3.2	240	281	1.9	[118]
NiF_2	2	1800	264	6.5	600	262	2.0	[116]
ZnF_2	3	420	295	4.3	-	-	-	[128]
NbF_5	5	90	300	10.1	-	-	-	[124]
ZrCl_4	1	60	290	5.6	-	-	-	[129]
K_2TiF_6	3	200	280	6.4	250	280	2.7	[131]
K_2NbF_7	3	200	280	6.6	-	-	-	[131]

2.4. Carbon-Based Materials

There are several carbon-based materials that have been used as catalysts/additives for the $\text{Mg}(\text{BH}_4)_2$, such as CNTs [132–134], carbon nanocomposites [135], two-dimensional MXene [136,137] and graphene [97,138]. The effects of CNTs on the microstructure development and H_2 storage performance of $\text{Mg}(\text{BH}_4)_2$ were investigated by Jiang et al. [133]. The addition of CNTs reduced the decomposition temperature but suffered a decrease in H_2 desorption capacity from 9.82 to 5.98 wt%. The quickest and most effective H_2 desorption process was shown by $\text{Mg}(\text{BH}_4)_2$ doped with 5 wt% CNTs, where the initial temperature decreased to a lower temperature of about 120 °C compared with 155 °C for pristine $\text{Mg}(\text{BH}_4)_2$. The dehydriding kinetics for the sample were recorded at varying temperatures ranging from 200 °C to 300 °C. As the temperature increased, the H_2 storage capability increased, whereas the dehydrogenation kinetics accelerated. $\text{Mg}(\text{BH}_4)_2$ doped with 5 wt% CNTs released 1.32 wt% of H_2 in 30 min at a temperature of 200 °C and increased to as high as 6.04 wt% of H_2 at 300 °C for the same period. After the addition of CNTs, the activation energy, E_a , for H_2 desorption was found to be only 130.2 kJmol⁻¹, which was significantly smaller than that of H_2 desorption for pristine $\text{Mg}(\text{BH}_4)_2$, which was 451.6 kJmol⁻¹. From the results obtained, Jiang et al. [133] concluded that the improvement of the kinetic properties of CNT-doped $\text{Mg}(\text{BH}_4)_2$ was due to the change in the reaction pathway.

Yan et al. [135] studied the effect of carbon nanocomposites on the reversibility of $\text{Mg}(\text{BH}_4)_2$. The $\text{Mg}(\text{BH}_4)_2$ -carbon nanocomposites were synthesised by the milling of MgH_2 nanoparticles supported on carbon aerogel under a B_2H_6 - H_2 atmosphere. The result indicated that the decomposition temperature of as-synthesised $\text{Mg}(\text{BH}_4)_2$ -carbon nanocomposites decreased to 160 °C compared with the undoped sample. For the rehydrogenation process, the formation of $\text{Mg}(\text{BH}_4)_2$ occurred under moderate pressure and temperature (80 to 150 bar H_2 and 200 °C). From the Kissinger analysis, the apparent activation energy for the dehydrogenation process in the $\text{Mg}(\text{BH}_4)_2$ -carbon aerogel sample was reduced by 238 kJ mol⁻¹ compared with undoped $\text{Mg}(\text{BH}_4)_2$, as presented in Figure 10. According to Yan et al., the significantly improved H_2 storage properties of $\text{Mg}(\text{BH}_4)_2$ catalysed with carbon nanocomposites may be due to the effect of nanoengineering modification. It is believed that the smaller the particle size, the more the H_2 storage properties of

complex metal hydrides are improved, as proven in the previous studies on LiBH_4 and MgH_2 nanocomposite systems [139–141].

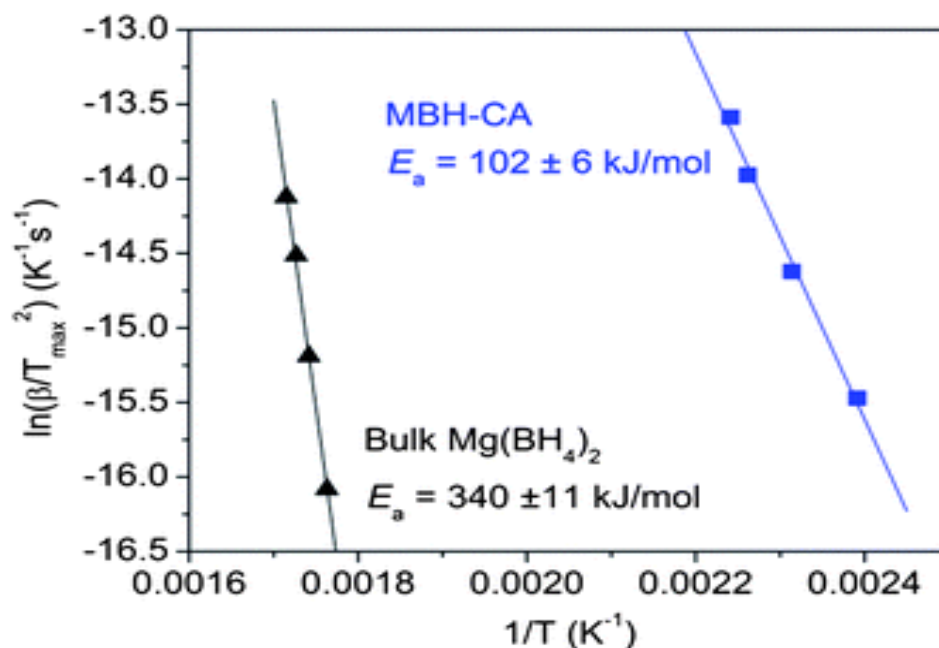


Figure 10. Kissinger analysis graph of the $\text{Mg(BH}_4\text{)}_2$ /carbon aerogel (MBH-CA) and bulk $\text{Mg(BH}_4\text{)}_2$ [135].

Zheng et al. [136] introduced two-dimensional MXene Ti_3C_2 to $\text{Mg(BH}_4\text{)}_2$ using a simple ball-milling technique to enhance $\text{Mg(BH}_4\text{)}_2$ dehydrogenation performance. The TPD test revealed that the initial H_2 desorption temperature of undoped $\text{Mg(BH}_4\text{)}_2$ was 286.7 °C. A significant decrease in the desorption temperature can be observed in $\text{Mg(BH}_4\text{)}_2$ - $x\text{Ti}_3\text{C}_2$ hybrids ($x = 30, 40$ and $50 \text{ wt\%}$), where H_2 starts to release at much lower temperatures of 133 °C, 125 °C and 116 °C, respectively. Isothermal dehydrogenation tests were conducted, in which, within 10 min after the temperature reached 330 °C, $\text{Mg(BH}_4\text{)}_2$ -40 Ti_3C_2 released 10.71 wt% of H_2 . In the same process, only 5.28 wt% of H_2 was detected in the pristine $\text{Mg(BH}_4\text{)}_2$. The entire dehydrogenation process of $\text{Mg(BH}_4\text{)}_2$ -40 Ti_3C_2 can be completed within 1 h, releasing 11 wt% of H_2 . Contrarily, the pristine $\text{Mg(BH}_4\text{)}_2$ released only 9.10 wt% of H_2 in 2 h, as presented in Figure 11. The improvement of the dehydrogenation properties of 40 Ti_3C_2 -doped $\text{Mg(BH}_4\text{)}_2$ composite may be due to the synergetic catalytic effect of Ti_3C_2 . According to recent reports [142,143], the metal titanium formed in situ can serve as a catalytic site, lowering the energy barrier for H-atom diffusion and weakening the stable ionic bond between Mg^{2+} and $[\text{BH}_4]^-$. Table 7 presents the effect of carbon-based metal additives on the desorption and absorption kinetic of the $\text{Mg(BH}_4\text{)}_2$.

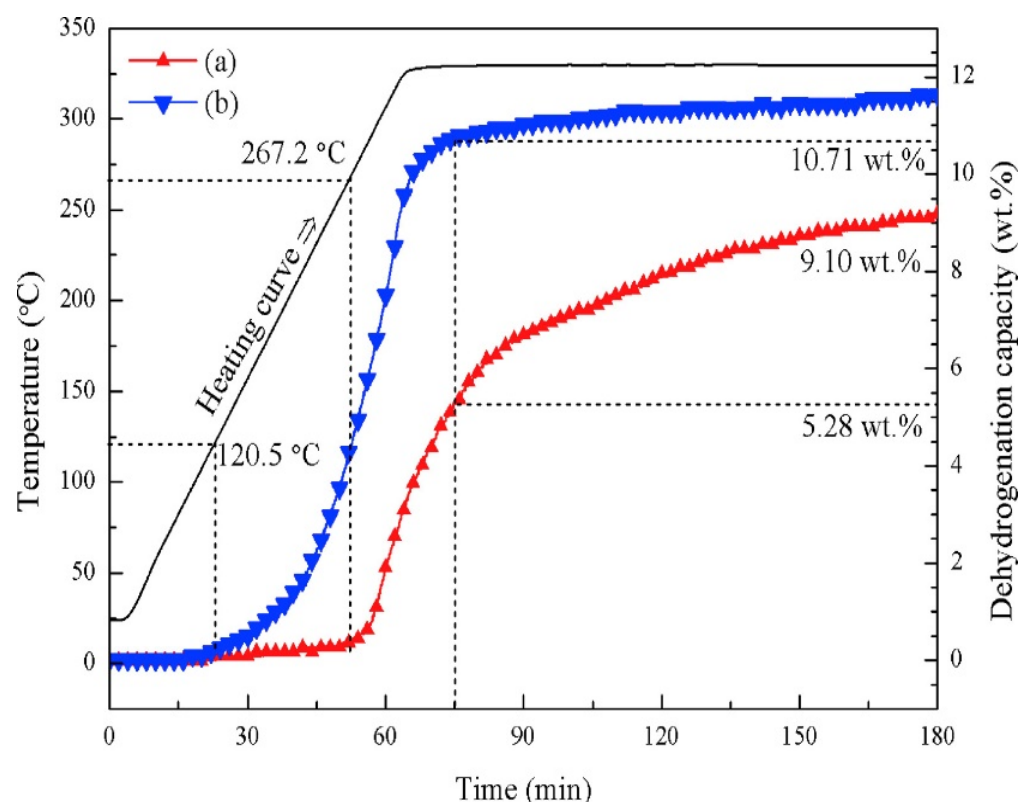


Figure 11. Isothermal dehydrogenation results for (a) pristine $\text{Mg}(\text{BH}_4)_2$ and (b) $40\text{Ti}_3\text{C}_2$ -doped $\text{Mg}(\text{BH}_4)_2$ composite at 330°C [136].

Table 7. Effect of carbon-based additives on the desorption and absorption kinetic of $\text{Mg}(\text{BH}_4)_2$.

Additive		Desorption of $\text{Mg}(\text{BH}_4)_2$			Absorption of $\text{Mg}(\text{BH}_4)_2$			Ref.
Name	Mol. %	Time, min	Temperature, $^\circ\text{C}$	H_2 , wt%	Time, min	Temperature, $^\circ\text{C}$	H_2 , wt%	
CNTs	2	50	120	5.98	120	300	2.46	[133]
Ti_3C_2	40	180	125	7.7	-	-	-	[136]

3. Future Prospects and Challenges

$\text{Mg}(\text{BH}_4)_2$ is a promising material for H_2 storage in a solid-state form owing to its high gravimetric capacity (14.9 wt%). However, its drawbacks, such as high decomposition temperature, sluggish sorption kinetics and stable thermodynamic properties, need to be solved prior to its commercial application as a medium for solid-state H_2 storage materials. Moreover, the release of other gases, such as diborane, during the dehydrogenation process is also unpleasant. Previous studies indicate that the H_2 storage properties of $\text{Mg}(\text{BH}_4)_2$ improves when doped with catalysts/additives. Different types of materials have been utilised as catalysts/additives to reduce the decomposition temperature, improve the sorption kinetics and alter the thermodynamic properties of $\text{Mg}(\text{BH}_4)_2$. The critical aspect is to adjust the thermodynamic stability to ensure the reversibility of $\text{Mg}(\text{BH}_4)_2$ and improve the kinetics at temperatures close to the acceptable and operable range. These problems need to be resolved in future research so that a favourable and convenient H_2 storage system can be realised. Some standards that should be focused on are as follows:

- Reduce the size of the particle of $\text{Mg}(\text{BH}_4)_2$. Nanostructured materials contain a large surface area, which is conducive to the uniform distribution of the catalyst, inducing more defects on the surface of the particles, uniformly mixing different composite hydrides, making the product heterogeneous nucleation and perhaps reducing the enthalpy of the reaction.

- (b) Lower the activation barrier, E_a , for the H_2 released from $Mg(BH_4)_2$, to understand the role of catalyst/additive and the mechanism of destabilization reactions in changing the properties of H_2 bonds to achieve a low temperature. The doping of the catalyst/additive changes the reaction route of the mesophase and alternate reactions. By combining with other hydride materials to form new reactions or new compounds, the thermodynamics of the reaction can be adjusted, and a H_2 reaction pathway with lower E_a can be generated.
- (c) Alter the thermodynamic properties of $Mg(BH_4)_2$. Once the kinetic barrier of H_2 desorption is overcome, the H_2 flux of desorption is proportional to the thermodynamic capability. In principle, the method to reduce the enthalpy of the H_2 reaction should also improve the kinetics for H_2 desorption under the relevant condition.
- (d) The main problem associated with borohydride as an ideal material for solid-state H_2 storage is reversible to H_2 absorption and desorption under moderate conditions. For the $Mg(BH_4)_2$, it was proven that only the second-stage reaction ($MgH_2 \leftrightarrow Mg + H_2$) is reversible to H_2 absorption and desorption under moderate conditions. Thus, a significant breakthrough is needed to ensure the whole system (first and second stages) can absorb and desorb H_2 . The use of proper catalysts/additives or engineering modification, such as nanoconfinement, might be the solution for the reversibility problem in $Mg(BH_4)_2$.
- (e) The degradation of H_2 storage capacity during the cycling process (rehydrogenation/dehydrogenation process) for the second stage of $Mg(BH_4)_2$ is also a crucial problem. It is important to find a suitable catalyst/additive that can prevent the decline in the H_2 storage capacity during the cycling process.
- (f) The release of diborane gas, which is toxic, might also have a negative effect. To prevent the release of diborane gas, the reactive hydride composite approach (mix of two or three hydride materials) might offer a good solution through the reaction between hydrides during the milling process or dehydrogenation process.

4. Conclusions

This review provides the latest developments in additive-enhanced $Mg(BH_4)_2$ for solid-state H_2 storage material. $Mg(BH_4)_2$ has shown to be promising as a potential candidate for H_2 storage owing to its high gravimetric capacity, which is 14.9 wt%. However, the application of $Mg(BH_4)_2$ is hindered by its high decomposition temperature, sluggish sorption kinetic and reversibility at a moderate temperature. To overcome these drawbacks, numerous studies have been conducted, proposing few alternatives. Whether using the ball-milling technique to reduce the particle size or by doping with catalyst/additive to reduce the activation energy of H_2 release from $Mg(BH_4)_2$, both approaches have been proven to enhance the H_2 storage capacity of $Mg(BH_4)_2$. Many studies on the ball-milling technique have demonstrated that a smaller particle size can provide a wider surface area for H_2 desorption. Other research has focused on the catalyst's/additive's efficiency in improving the H_2 storage performance of $Mg(BH_4)_2$. This article has discussed the advantages of various types of additives and their effects on the storage performance of $Mg(BH_4)_2$. The addition of the additive to $Mg(BH_4)_2$ provides a lower activation energy for H_2 release, therefore decreasing the decomposition temperature and improving the desorption properties of $Mg(BH_4)_2$. To enhance the potential of $Mg(BH_4)_2$ in advanced H_2 storage systems, further research and exploration are needed, especially in the use of proper catalysts/additives or engineering modification to ensure the whole $Mg(BH_4)_2$ (first and second stages) is reversible to H_2 absorption and desorption under moderate conditions. It is also suggested to explore a new catalyst/additive for $Mg(BH_4)_2$ to prevent the decline in H_2 storage capacity during the cycling process and to employ a reactive hydride composite approach to prevent the release of diborane gas during the dehydrogenation process of $Mg(BH_4)_2$.

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