



Article Influence of Nanosized CoTiO₃ Synthesized via a Solid-State Method on the Hydrogen Storage Behavior of MgH₂

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Abstract: Magnesium hydride (MgH₂) has received outstanding attention as a safe and efficient material to store hydrogen because of its 7.6 wt.% hydrogen content and excellent reversibility. Nevertheless, the application of MgH₂ is obstructed by its unfavorable thermodynamic stability and sluggish sorption kinetic. To overcome these drawbacks, ball milling MgH₂ is vital in reducing the particle size that contribute to the reduction of the decomposition temperature. However, the milling process would become inefficient in reducing particle sizes when equilibrium between cold-welding and fracturing is achieved. Therefore, to further ameliorate the performance of MgH₂, nanosized cobalt titanate (CoTiO₃) has been synthesized using a solid-state method and was introduced to the MgH₂ system. The different weight percentages of CoTiO₃ were doped to the MgH₂ system, and their catalytic function on the performance of MgH₂ was scrutinized in this study. The MgH₂ + 10 wt.% CoTiO₃ composite presents the most outstanding performance, where the initial decomposition temperature of MgH₂ can be downshifted to 275 °C. Moreover, the MgH₂ + 10 wt.% CoTiO₃ absorbed 6.4 wt.% H₂ at low temperature (200 °C) in only 10 min and rapidly releases 2.3 wt.% H₂ in the first 10 min, demonstrating a 23-times-faster desorption rate than as-milled MgH2 at 300 °C. The desorption activation energy of the 10 wt.% CoTiO₃-doped MgH₂ sample was dramatically lowered by 30.4 kJ/mol compared to undoped MgH₂. The enhanced performance of the MgH₂-CoTiO₃ system is believed to be due to the in situ formation of MgTiO₃, CoMg₂, CoTi₂, and MgO during the heating process, which offer a notable impact on the behavior of MgH₂.

Keywords: MgH₂; hydrogen storage; catalytic activity; CoTiO₃

1. Introduction

In recent decades, hydrogen has emerged as the most viable energy carrier, especially in the transportation sector [1]. As far as we are concerned, the usage of fossil fuels has led to a global energy crisis and environmental pollution [2]. Thus, energy transition from fossil fuel-based to renewable energy is required. As environmentally-friendly energy storage, the best solution is to convert energy from "green" sources into chemical storage [3]. Hydrogen has received outstanding interest as an energy carrier because it has a high energy content (142 MJ/kg) [4]. Hydrogen might supersede natural gas and solid fuels as an energy source by 2050. It is anticipated that it will be extensively used in the transportation, chemical, and long-term aviation and maritime sectors [5]. The use of hydrogen as an energy carrier will ultimately aid humankind in achieving a "low" or "zero" carbon future. Recently, various countries have started using hydrogen energy, particularly in transportation. For instance, the Hyundai Nexo hydrogen fuel cell vehicle (FCV) sold 1000 units in South Korea in 2019 [6], and the company is also setting up a number of hydrogen refueling stations [7]. Nevertheless, hydrogen-based energy requires a convenient and a reliable



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). method of storing energy. How to store hydrogen is a vital phase for delivering a stock of hydrogen fuel to consumers for energy storage, fuel cell vehicles, stationary applications, and portable devices.

Commonly, hydrogen can be stored in three different forms, namely, (i) gas, (ii) liquid, and (iii) solid-state. The current hydrogen storage method for compressing gas requires high pressure, which is in the range of 350–700 bar H₂ at room temperature, whereas liquid-form storage needs low temperature for the operation $(-253 \degree C)$ [8,9]. The solid-state form appears to be the most effective technique compared to gas and liquid hydrogen because it has several benefits, including safety, high hydrogen capacity, modest working pressures, and excellent energy efficiency [10–12]. Throughout the last several decades, various types of solid-state material have been discovered. The solid-state approach of storing hydrogen has two techniques, namely, chemisorption and physisorption [13]. As a hydrogen storage technique, chemisorption in metal hydrides has drawn considerable attention. The advantage of this approach is that it can store a large amount of hydrogen in a small volume [14].

Among the various solid-state materials explored for hydrogen storage, MgH₂ has been regarded as a viable option to store hydrogen for onboard applications on the strength of its high hydrogen capacity (7.6 wt.%), high energy density (9 MJ/kg) over all the reversible hydrides, and outstanding reversibility [15]. However, the obstacles of MgH₂ for practical application include high temperature (>400 °C) to release hydrogen, sluggish sorption kinetics, and very stable thermodynamic properties ($\Delta H = 76 \text{ kJ/mol H}_2$) [16,17]. To tackle these drawbacks, several efforts, such as nanostructuring, nanoconfinement, alloying, and the addition of catalyst [18–21] have been proposed and developed to modify the Mg-based system performances. In this study, the center of interest is to reduce the decomposition temperature and improve the kinetics performance of MgH₂ by adding catalysts. Adding metal oxide [22–24], metal [25,26], metal halides [27], carbon material [28,29], and nanosized alloys [30,31] to MgH₂ as catalysts have been highlighted as notable approaches to boost its hydrogen storage performance.

Among the catalysts, metal oxide has attracted growing interest because of its profound influence on the behavior of MgH₂. Moreover, transition metals and their compounds have been proven to ease hydrogen dissociation and recombination [32]. Transition metals and their oxides are able to provide more sites for Mg and MgH₂ nucleation, which ameliorates the hydrogen sorption kinetics [33]. Moreover, these transition metal oxide are easily reduced and converted into low-valence transition metal oxide or hydride due to the high reductivity of Mg/MgH_2 , which has been identified as a promising catalyst for dehydrogenation of MgH_2 [34]. This is due to the significant interaction between the s-states of H and the d-states of low-valence transition metals, which could weaken the Mg-H bonds of MgH₂ and enhance its reversible hydrogen storage performance. As reported by the earliest study, doping Ti, Mn, V, Fe, and Ni presents a rapid desorption process of MgH₂ [35]. Thereafter, another series of transition metals, Co, Cu, and Nb, display remarkable catalytic function on the hydrogen release of MgH₂ [36,37]. It is predicted that the oxides of transition metals proffer efficient catalytic activity on the performance of MgH₂. For instance, adding TiO₂ could speed up the absorption and desorption process of MgH₂, enable the absorption of 5.3 wt.% H₂ in only 44 s, and release 6.4 wt.% H₂ in 700 s. Moreover, Yan et al. [38] demonstrated that adding NiTiO₃ could lower the temperature for the release of hydrogen as well as the activation energy of MgH_2 and result in faster hydrogen desorption and absorption. Furthermore, Shan et al. [39] reported that the presence of CoFe₂O₄ could speed up the hydrogen dehydriding of MgH₂. The composite sample of MgH₂ + 9 mol CoFe₂O₄ began to decompose at 150 $^{\circ}$ C, which was lower than undoped MgH₂ (340 °C), and it is capable of desorbing 6.11 wt.% H₂. Then, Ismail et al. [40] conducted a further study on transition metal oxide. The addition of CuFe₂O₄ could reduce the temperature for release hydrogen from 340 °C to 250 °C. They concluded that the enhancement of the MgH₂ behavior was due to the formation of MgO, Fe and Mg–Cu alloy that accelerates the hydrogen desorption of MgH₂. Therefore, transition metal oxide

catalysts are favorable in ameliorating the hydrogen storage behavior of MgH_2 by boosting the electron transfer between Mg and H [32].

In this study, it is of interest to examine the catalytic activity of another transition metal oxide, $CoTiO_3$. What is noteworthy, is that the catalytic efficiency is influenced by the dispersion of catalytic activity on the system. Nanocatalysts offer noticeably more active catalytic sites and intimate interaction because of their increased surface area. Thus, in this study, we synthesized nanosized $CoTiO_3$ via a solid-state method. The addition of $CoTiO_3$ was projected to remarkably boost the behavior of MgH_2 by lowering the initial decomposition temperature and rapid hydrogen absorption/desorption kinetics. Although there is a previous study reported on the effect of $CoTiO_3$ [41], there remains a lack of mechanism of interaction between MgH_2 and $CoTiO_3$. Furthermore, different synthesis methods present different catalytic activities. This study broadens the way to explore the effect of $CoTiO_3$ and demonstrates the different catalytic activities of $CoTiO_3$ on the hydrogen storage behavior of MgH_2 . Hence, in this paper, the influence of different weight percentages of $CoTiO_3$ was systematically explored.

2. Materials and Methods

MgH₂ (95% pure), Co₃O₄ (99.99% pure), anatase TiO₂ (99.95% pure), and citric acid monohydrate (>98% pure) provided by Sigma Aldrich, St. Louis, MO, United States were used without any pretreatment. The nanosized CoTiO₃ was synthesized using the solidstate method. The stoichiometric amount of Co₃O₄ and TiO₂ were ground together for 15 min. Thereafter, citric acid monohydrate was added and continuously ground for 15 min. The powder was then calcined at 850 °C for 5 h. Thereafter, different weight percentages of CoTiO₃ (5, 10, 15, and 20 wt.%) were added with MgH₂ to study its catalytic activity on the hydrogen storage behavior of MgH₂. The mixture was milled together in a planetary ball mill (NQM-0.4) at 400 rpm for 1 h.

Sievert-type pressure-composition-temperature apparatus from Advanced Materials Corporation, Pittsburgh, PA, United States which is also known as Gas Reaction Controller (GRC) apparatus, was used to conduct the temperature-programmed desorption (TPD) measurement and the hydrogen absorption and desorption experiment. The GRC provides a reliable and convenient way to evaluate desorption/absorption characteristics of materials. Temperature, capacity, and time data obtained through TPD measurements were used to determine the capacity, kinetics, and thermodynamic properties of material. The TPD measurement was conducted in a vacuum chamber heated to 450 °C (heating rate: $5 \,^{\circ}$ C/min). For the isothermal tests, experiments were conducted at 200 °C, 33.0 atm hydrogen pressure (absorption kinetics), and 300 °C, 1.0 atm hydrogen pressure (desorption kinetics).

To study the thermal properties and to calculate the activation energy, differential scanning calorimetry (DSC, Mettler Toledo, Columbus, OH, United States)(DSC/TGA 1) was used. Six to eight milligrams of the sample were placed in a crucible and heated to 500 °C under an argon flow of 50 mL/min at four different heating rates (15 °C/min, 20 °C/min, 25 °C/min, and 30 °C/min). Rigaku MiniFlex, Tokyo, Japan, X-ray diffraction (XRD) with Cu K α radiation was used to examine the phase structure. The patterns were scanned over diffraction angles from 20° to 80° at 2.00°/min. The sample microstructure and morphology were examined using a scanning electron microscope (SEM; JEOL, Akishima, Tokyo, Japan) (JSM-6350LA). The particle size distributions of the samples were calculated using Image J software. The SEM images was used to calculate the distributions size of the sample, where a number of measurements were collected for the diameter of the particle. Fourier transform infrared (FTIR) spectrometry was conducted in the range of 400–2000 cm⁻¹ using IR Tracer-100, Shimadzu, Kyoto, Japan and Raman spectra were conducted at room temperature (0.1% power laser) using Renishaw Raman spectroscopy (532 nm radiation).

3. Results and Discussion

3.1. Synthesis of CoTiO₃

The phase composition of the as-synthesized CoTiO₃ was investigated using XRD, as presented in Figure 1a. The diffraction peaks at 20 of 23.9° , 32.7° , 35.3° , 40.5° , 48.9° , 53.4° , 56.8° , 61.8° , 63.5° , 68.7° , 70.9° , and 74.8° correspond to the crystallographic plane of (012), (104), (110), (113), (024), (116), (018), (214), (300), (208), (1010), and (220). Evidently, all the peaks matched well with the spinel structure of CoTiO₃ (JCPDS 15-866). No other peak was detected, confirming the formation of pure CoTiO₃. The average crystallite size of the CoTiO₃ was approximately 28.7 nm, calculated using the Scherrer formula (Equation (1)), as follows [42]:

L

$$= K\lambda/\beta\cos\theta \tag{1}$$

where L, K, λ , β , and θ are referring to the average crystallite size, Scherer constant (0.94), X-ray wavelength, full width at half maximum, and diffraction angle, respectively. The FTIR spectrum of the as-synthesized $CoTiO_3$ is presented in Figure 1b. The bands between 400 and 800 cm⁻¹ are the typical peaks of CoTiO₃ that correspond to the stretching vibrations of the metal ions [43]. The FTIR spectrum exhibited bands between 640 and 450 cm^{-1} , which is due to Ti–O–Ti and Co–Ti–O band formation [44]. The strong band at around 431 cm^{-1} corresponds to the bond of Co–O [45]. Maensiri et al. [46] and Rashad et al. [47] stated that the peaks in the range of 450–600 cm⁻¹ were ascribed to the Ti–O–Ti bond. Thus, the peaks at 473 cm^{-1} are assigned to the Ti–O–Ti bond [48] and the peaks at 626 cm⁻¹ correspond to the Ti–O–O bond [46]. Moreover, the Raman spectra in Figure 1c confirm the formation of CoTiO₃ [44]. The strongest Raman modes observed around 692 cm⁻¹ were attributed to the high frequency of the vibrational mode of the CoO₆ octahedra, known as the symmetry stretching mode, while other remaining Raman modes correspond to the lattice vibrations of the phonon modes [43]. The SEM image (Figure 1d) of the as-synthesized CoTiO₃ revealed that the as-synthesized nanosized CoTiO₃ comprises a good dispersion of eclipse-like grain shape. The particle size of the as-synthesized $CoTiO_3$ is measured using Image J software, with an average particle size of 0.16 µm. The distributions of the particle sizes are depicted in a histogram in Figure 1e. The results show that it is relevant to conclude that pure nanosized CoTiO₃ was successfully synthesized using the solid-state method.



Figure 1. (a) XRD profile, (b) FTIR spectra, (c) Raman spectra, (d) SEM image, and (e) particle size distribution of as-synthesized CoTiO₃.

3.2. Hydrogen Storage Properties

The catalytic activity of the as-prepared CoTiO₃ on MgH₂ was studied by TPD experiments, as depicted in Figure 2a. The performance of the modified MgH₂ with CoTiO₃ was significantly enhanced compared to undoped MgH₂. In terms of decomposition temperature, commercial MgH₂ started decomposing at 420 °C, whereas as-milled MgH₂ started at approximately 340 °C. This outcome implies that the process of ball milling for 1 h is beneficial in lowering the decomposition temperature of MgH₂ as it decreased by 80 °C when compared with commercial MgH₂. This result is consistent with a prior study that found that enhanced performance of metal/complex hydride is due to the milling process, which is effective in refining the particle size [49]. The milling process in essential in reducing the particle size, which contributes to the decrease of the decomposition temperature. However, the milling process would become inefficient in reducing particle sizes when the equilibrium between cold-welding and fracturing is achieved [50]. A previous study also reported that increasing the milling time causes the decomposition temperature to shift to higher temperatures due to the agglomeration of particles and reduction of their free surface area [51]. After augmenting MgH₂ with 5 wt.% of CoTiO₃, the onset decomposition temperature downshifted to 298 °C. The reduction in the decomposition temperature was more significant when the amount of $CoTiO_3$ was increased to 10 wt.%. The MgH₂ + 10 wt.% CoTiO₃ sample began to decompose at 275 °C. For the 15 wt.% CoTiO₃-doped MgH₂, the decomposition temperature was almost similar to the MgH₂ + 10 wt.% CoTiO₃. The influence of different wt.% on the performance of MgH₂ was further explored with 20 wt.% of CoTiO₃. The composite sample of $MgH_2 + 20$ wt.% CoTiO₃ also began to release hydrogen lower than undoped MgH₂, which started to release at 295 °C. However, the onset decomposition for the MgH₂ + 20 wt.% CoTiO₃ was slightly higher than MgH₂ + 10 wt.% CoTiO₃. This outcome was comparable with a previous study that found that the decomposition temperature for the 15 wt.% and 20 wt.% SrFe₁₂O₁₉-doped MgH₂ was slightly higher than $MgH_2 + 10$ wt.% SrFe₁₂O₁₉ [52]. Sulaiman et al. [53] also claimed the same condition, where the decomposition temperature for the MgH₂ + 50 wt.% Na₃FeF₆ was slightly higher than for MgH₂ + 10 wt.% Na₃FeF₆ and MgH₂ + 20 wt.% Na₃FeF₆. This condition may be due to the excessive catalyst that may block the diffusion path of hydrogen, which limits the hydrogen diffusion [54]. Even the temperature for the hydrogen release for the 20 wt.% of catalyst was higher than that for the 10 wt.%; the temperature for the MgH₂ to release hydrogen doped with a different weight percentage of CoTiO₃ was significantly reduced when compared with undoped MgH₂. Of note is the fact that the presence of $CoTiO_3$ could modify the performance of MgH₂ and be beneficial in lowering the decomposition temperature of MgH₂.



Figure 2. (a) TPD, (b) hydrogen absorption at 200 °C under 33.0 atm H₂ pressure, and (c) hydrogen desorption curve at 300 °C under 1.0 atm H₂ pressure of the MgH₂–CoTiO₃ system.

The reversibility of the MgH₂-CoTiO₃ system was further studied via an absorption kinetic experiment conducted at a low temperature (200 °C). The doped sample was studied with a different weight percentage of CoTiO₃, as demonstrated in Figure 2b. Among the four different wt.%, $MgH_2 + 10$ wt.% CoTiO₃ produces the fastest absorption rate and represents improved absorption kinetics performance than does undoped MgH₂. As shown in Figure 2b, in the first 10 min, the as-milled MgH₂ absorbed 4.3 wt.% H₂, whereas the $MgH_2 + 10$ wt.% CoTiO₃ sample absorbed 6.4 wt.% H₂. Even after completing the 60 min duration, the as-milled MgH₂ could not attain as high capacity as that of the MgH₂-doped 10 wt.% CoTiO₃. In the meantime, the hydrogen absorbed for the 5, 15, and 20 wt.% of catalyst were 2.5, 4.1, and 6.0 wt.% H₂, respectively, in the first 10 min. For the 5 wt.% of CoTiO₃, the MgH₂ + 5 wt.% CoTiO₃ shows faster kinetics than milled MgH₂ in the first 11s and intercept with the MgH₂ at 12s and become slower than undoped MgH₂. It can be concluded that the hydrogen absorption behavior was affected by the amount of catalyst. In the context of desorption kinetics, as depicted in Figure 2c, the MgH₂-doped CoTiO₃ composite displays a rapid desorption rate compared to undoped MgH₂. Similar to the performance of the absorption kinetics, the $MgH_2 + 10$ wt.% CoTiO₃ presents a faster desorption kinetics rate compared to the 5, 15, and 20 wt.% CoTiO₃-doped MgH₂ samples. In the first 10 min, the undoped MgH₂ roughly desorb hydrogen (<0.1 wt.%). Meanwhile, the MgH₂ + 10 wt.% CoTiO₃ sample desorbed at approximately 2.3 wt.% H₂, which represents a 23-times-faster desorption rate when compared with undoped MgH₂. In the same period, the 5, 15, and 20 wt.%-doped MgH₂ desorbed 0.8, 1.8, and 1.2 wt.% H₂, respectively, which is also faster than undoped MgH₂. Table 1 summarizes

the hydrogen storage behavior of undoped and doped MgH₂ with a difference percentage of CoTiO₃. Notably, low catalyst content is also beneficial in ameliorating the kinetics performances of MgH₂. Similar to the TPD result, the MgH₂ + 10 wt.% CoTiO₃ performs the fastest absorption and desorption rate. These findings are in line with a previous study that demonstrated $MgH_2 + 0.5$ mol Nb_2O_5 performs superior desorption kinetics than MgH_2 doped with 0.05, 0.1, 0.2, and 1.0 mol Nb_2O_5 [55]. Similar to a study conducted by Ranjbar et al. [54], the desorption behavior of the MgH₂ with 10 wt.% of SiC presents a faster desorption rate, which becomes slower when doping with 20 wt.% of SiC. They indicated that excessive catalysts in the composite may restrict the hydrogen diffusion to some extent, limiting the Mg–H reaction. From the findings, noticeably, the performance of MgH_2 can be affected by the amount of the catalyst. By comprehensively considering the absorption/desorption hydrogen performance, the MgH₂ with 10 wt.% of the CoTiO₃ sample demonstrates the ultimate absorption/desorption performance. Thus, in this study, the MgH₂ + 10 wt.% CoTiO₃ sample is applied to examine the catalytic activity of CoTiO₃ on the hydrogen storage behavior of MgH₂. These results are similar to previous studies, in which 10 wt.% was an optimum amount of additive to provide a synergetic catalytic effect on the hydrogen storage performance of a metal hydride and a complex hydride [56,57]. Moreover, an excessive amount of additive may limit the diffusion of hydrogen to some extent, thereby reducing the reaction between the Mg and the hydrogen [54].

Table 1. The hydrogen storage behavior of undoped and doped MgH₂ with different weight percentage of CoTiO₃.

Sample	Decomposition Temperature (°C)	Absorption Capacity (wt.%) in 10 min	Desorption Capacity (wt.%) in 10 min
Commercial MgH ₂	420	-	-
As-milled MgH ₂	340	4.3	< 0.1
MgH ₂ + 5 wt.% CoTiO ₃	298	2.5	0.8
MgH ₂ + 10 wt.% CoTiO ₃	275	6.4	2.3
MgH ₂ + 15 wt.% CoTiO3	276	4.1	1.8
MgH ₂ + 20 wt.% CoTiO ₃	295	6.0	1.2

The effect of CoTiO₃ was further explored with the cycling performance of MgH₂ + 10 wt.% CoTiO₃, as shown in Figure 3. As reported previously, the cyclability of the undoped MgH₂ is poor, where the performance would erode drastically after undergoing the first cycle [58]. Therefore, the cyclability of the undoped MgH₂ is not included in this study because it desorbs only a small amount of hydrogen for the first cycle. Figure 3a shows the absorption kinetics curve of MgH₂ + 10 wt.% CoTiO₃ over the ten cycles. Surprisingly, after completing the 10th cycle, there is only a small amount of degradation in the hydrogen capacity for the absorption kinetics performance. The MgH₂ + 10 wt.% CoTiO₃ was able to absorb 7.1 wt.% H₂ after the 10th cycle. Figure 3b shows the desorption kinetics curve of the MgH₂ + 10 wt.% CoTiO₃ for the ten cycles. The MgH₂ + 10 wt.% CoTiO₃ composite maintain good cyclability, with the ability to desorb 5.7 wt.% H₂, even after completing the 10th cycle. It is evident that the addition of CoTiO₃ is beneficial in maintaining a superior cyclability of MgH₂.

To explore the kinetics mechanism of the $MgH_2 + 10$ wt.% CoTiO₃ composite further, the sorption kinetics performance was analyzed using the kinetics model. For instance, a previous study has demonstrated the kinetic model characterization for the absorption/desorption time for the alloys materials [59,60]. A series of kinetics models have been widely explored and reviewed by Pang and Li [61] in their study. In this study, the kinetics mechanism was studied using Johnson–Mehl–Avrami (JMA) and contracting volume (CV) models, as indicated in Table 2. The JMA and CV models were considered because they are suitable for the experimental data and are precise without requiring further assumptions

or approximations [61]. Moreover, other researchers have utilized this method extensively in prior studies to understand the rate-limiting step of the researched materials [62]. With kinetic equations such as CV and JMA, the rate-limiting step of the kinetics can be derived from the experimental data. In this study, the rate-limiting step is determined using the best linear plot of the experimental data with the kinetics equations.



Figure 3. Cycling performance of MgH₂ + 10 wt.% CoTiO₃ for (**a**) absorption kinetics curve at 320 °C under 33.0 atm H₂ pressure and (**b**) desorption kinetics curve at 320 °C under 1.0 atm H₂ pressure.

Table 2. Kinetic model used for sorption kinetics of current study, where α , t, and k refer to reacted fraction, time, and reaction rate constant, respectively. Based on [62].

Kinetic Equation	Rate Limiting Step	
$\alpha = kt$	Surface controlled.	
$1 - (1 - \alpha)1/3 = kt$	CV three-dimensional (3D): contracting volume, 3D growth with constant interface velocity.	
$1 - (1 - \alpha)1/2 = kt$	CV two-dimensional (2D): contracting volume, 2D growth with constant interface velocity.	
$1-(2\alpha/3)-(1-\alpha)2/3 = kt$	CV 3D (variable velocity): contracting volume, 3D growth diffusion controlled with decreasing interface velocity.	
$[-\ln(1-\alpha)]1/3 = kt$	JMA 3D: 3D growth of existing nuclei with constant interface velocity.	
$[-\ln(1-\alpha)]1/2 = kt$	JMA 2D: 2D growth of existing nuclei with constant interface velocity.	

Figure 4 present the kinetics curve that was calculated on the basis of the equation in Table 2. The absorption and desorption kinetics curves of the MgH₂ + 10 wt.% CoTiO₃ were calculated for reacted fractions ranging from 0% to 80% [63]. From the figure, for the absorption kinetics at 200 °C, the rate-limiting step is best represented using the 3D growth diffusion controlled with decreasing interface velocity, whereas the desorption kinetics of the MgH₂ + 10 wt.% CoTiO₃ at 300 °C was best described using the 2D growth of existing nuclei with constant interface velocity. These results suggest that hydrogen diffusion through the MgH₂ + 10 wt.% CoTiO₃ was fast. The nanosized CoTiO₃ may be beneficial in allowing a faster dissociation rate of hydrogen and hence fasten the diffusion of hydrogen, which results in faster kinetic performance.

The thermal characteristics of MgH₂ + 10 wt.% CoTiO₃, performed using DSC (heating rate: 30 °C/min), are presented in Figure 5. The DSC trace demonstrates one endothermic peak correlated to the hydrogen release of MgH₂. The peak of hydrogen release of MgH₂ + 10 wt.% CoTiO₃ happens at a lower temperature (382 °C) compared with as-milled



MgH₂ (445 $^{\circ}$ C), indicating that the dehydrogenation kinetics of MgH₂ was enhanced by milling with CoTiO₃.

Figure 4. Plot of the resulting curves of different kinetics equations applied to experimental (**a**) absorption kinetics at 200 °C and (**b**) desorption kinetics at 300 °C of MgH₂ + 10 wt.% CoTiO₃.



Figure 5. Thermal event of as-milled MgH₂ and MgH₂ + 10 wt.% CoTiO₃ (Heating rate: $30 \degree C/min$) under 50 mL/min of Argon flow.

The enhancement in the dehydrogenation kinetic is associated with the energy barrier for hydrogen released from MgH₂. In this study, the activation energy for hydrogen release from the doped and undoped MgH₂ was evaluated using the DSC results. Figure 6a,b display the DSC curve of as-milled MgH₂ and MgH₂ + 10 wt.% CoTiO₃ at four different heating rates. The Kissinger equation (Equation (2)) is used to evaluate the activation energy during decomposition.

$$\ln \left[\beta/T_{\rm p}^{2}\right] = -E_{\rm A}/RT_{\rm p} + A \tag{2}$$

where E_A is the activation energy, R is the gas constant, T_p is the endothermic peak corresponding to the decomposition temperature, β is the heating rate, and A is a linear constant. Thereafter, the activation energy is determined on the basis of the Kissinger plot of ln $[\beta/T_p^2]$ versus $1000/T_p$, as in Figure 6c. The activation energy of the MgH₂ + 10 wt.% CoTiO₃ and as-milled MgH₂ were calculated to be 104.6 and 135.0 kJ/mol, respectively. The activation energy of MgH₂ was decreased by 23% with the presence of CoTiO₃ compared with undoped MgH₂. Adding CoTiO₃ into MgH₂ remarkably reduces the energy barrier, which led to reduced activation energy and enhanced kinetic performance.



Figure 6. DSC curve of (**a**) as-milled MgH₂, (**b**) MgH₂ + 10 wt.% CoTiO₃ (Heating rate: 15, 20, 25, and 30 $^{\circ}$ C/min) and (**c**) Kissinger plot of undoped MgH₂ and MgH₂ + 10 wt.% CoTiO₃.

Lower activation energy provided the reduction in the desorption barrier, which results in a dramatic decrease in the decomposition temperature. Low decomposition temperature indicates the weakening of the hydride stability [64]. As the bond energy of the Mg–H is the decisive factor in hydride stability, the reduction in hydride stability is attributed to the bond weakening between Mg and H. Typically, the addition of transition metal elements or their oxides helps in decreasing the binding energy between the Mg and H due to the electron exchange process between the MgH₂ and additives in oxidation or reduction reactions [65]. As reported by a previous study, adding a catalyst is the most favorable approach for promoting the dissociation of the MgH₂ stability and decomposition temperature [66]. Thus, it is reasonable to conclude that the addition of CoTiO₃ is beneficial in promoting the superior performance of MgH₂ by lowering the energy barrier.

The catalytic activity of CoTiO₃ on the microstructure of MgH₂ was further explored by SEM characterization. Figure 7 displays the micrograph of commercial MgH₂, MgH₂ after milling for 1 h, and MgH₂ + 10 wt.% CoTiO₃. Referring to Figure 7a, commercial MgH_2 are irregular in shape, with solid flake-like shaped particles. After being milled for 1 h (Figure 7c), the solid flake-like shaped particles were broken into smaller particles with some agglomerations. Before the milling process, the comparatively smooth surface of the particle is substituted by the asperities and surface defects. Because of these transformed surface structures, as-milled MgH₂ decomposes at a lower temperature than commercial MgH₂. Meanwhile, upon the addition of $CoTiO_3$ (Figure 7e), the agglomeration was reduced, and the particle size was transformed to a finer shape and size. The size of the $MgH_2 + 10$ wt.% CoTiO₃ was much smaller than ball milled MgH_2 due to the hardness of CoTiO₃, which is higher than MgH₂. The hardness of the MgH₂ was 0.58 GPa [67], while the hardness of $CoTiO_3$ was 3.4–7.5 GPa [68]. Therefore, it is speculated that the CoTiO₃ introduced the pulverization effect and helped to reduce the particle size of MgH₂. The particle size of $MgH_2 + 10$ wt.% CoTiO₃ is smaller, and they are finer in shape, even after undergoing the absorption (Figure 7g) and desorption (Figure 7i) process. No big changes occur on the particle after undergoing the absorption and desorption process. From the morphological properties, the $CoTiO_3$ is able to reduce the particle size of MgH₂ and enhances the absorption/desorption performance of MgH₂. The differences of the microstructure and morphologies of the undoped and doped MgH₂ may correspond to the presence of a catalyst that is finely dispersed on the surface of the MgH_2 particle, thus reducing the H diffusion distance and offering more reaction site and hence stimulating the faster absorption and desorption performance of MgH_2 [69]. This catalyst is embedded on the surface of MgH_2 and prevent the sample from agglomerating, indicating that $CoTiO_3$ is beneficial in distributing particles and constraining agglomeration and particle growth in the MgH_2 system [22].

The particle size of the commercial MgH₂, as-milled MgH₂, MgH₂ + 10 wt.% CoTiO₃ after milling as well as after absorption and desorption were further evaluated by Image J software. Figure 7b,d,f,h,j shows the distributions of the particle size, which are depicted in a histogram. Based on the histogram, the average particle size of commercial MgH₂, as-milled MgH₂, MgH₂ + 10 wt.% CoTiO₃ after milling, after absorption, and after desorption was calculated to be ~60, 0.47, 0.22, 0.29, and 0.28 μ m, respectively. The morphological change and drastic size reduction contribute to the high surface defects and more grain boundaries around the surface of the composite [70]. Consequently, a higher amount of reaction for the nucleation sites and better diffusion channels for the hydrogen can be achieved with amplified grain boundaries that enhance the hydrogen sorption performances of the MgH₂–CoTiO₃ composite. Similarly, a recent study found that reducing particle size improves absorption–desorption kinetics performance substantially [71,72].



Figure 7. SEM images and particle size distribution histogram of commercial MgH₂ (**a**,**b**), as-milled MgH₂ (**c**,**d**), MgH₂ + 10 wt.% CoTiO₃ after milling (**e**,**f**), MgH₂ + 10 wt.% CoTiO₃ after absorption at 200 °C (**g**,**h**), and MgH₂ + 10 wt.% CoTiO₃ after desorption at 450 °C (**i**,**j**).

To reveal the catalytic mechanism of $CoTiO_3$ for MgH₂, XRD analysis for MgH₂ + 10 wt.% CoTiO₃ was performed, as in Figure 8. The main peaks that existed after 1 h of milling (Figure 8a) were only MgH₂ and CoTiO₃. No new phase was detected, indicating that no chemical reaction occurs during the milling process. Figure 8b presents the sample of the MgH₂ + CoTiO₃ after desorption at 450 °C. Peaks of Mg were dominant, indicating that MgH₂ has been totally transformed to Mg, corresponding to the complete decomposition of MgH₂, as in (Equation (3)). Additionally, the peaks of MgO and MgTiO₃ could be detected after dehydrogenation.

$$MgH_2 \leftrightarrow Mg + H_2$$
 (3)



Figure 8. XRD patterns of (a) as-milled and (b) after desorption at 450 °C of MgH₂ + 10 wt.% CoTiO₃.

To further explore the catalytic mechanism of $CoTiO_3$ during desorption, a sample of MgH₂ + 50 wt.% CoTiO₃ was prepared. As displayed in Figure 9a, after 1 h of milling, only the parent materials, MgH₂ and CoTiO₃, were detected. No new compound was formed at this stage. After the desorption process at 450 °C (Figure 9b), the peaks of MgH₂ and CoTiO₃ disappeared and new peaks of MgO, MgTiO₃, CoMg₂, and CoTi₂ appeared.



Figure 9. XRD patterns of (a) as-milled and (b) after desorption at $450 \degree C$ of MgH₂ + 50 wt.% CoTiO₃.

Figure 10 presents the MgH₂ + 10 wt.% CoTiO₃ and MgH₂ + 50 wt.% CoTiO₃ sample after absorption at 200 °C. For the MgH₂ + 10 wt.% CoTiO₃ sample (Figure 10a), the main peaks of MgH₂ were discovered, demonstrating that the Mg was fully converted to MgH₂, as per Equation (3). The peaks of MgO and MgTiO₃ were still detected. The appearance of the MgO and MgTiO₃ species occurred, indicating that MgH₂ reacts with CoTiO₃ throughout the heating process. For the MgH₂ + 50 wt.% CoTiO₃ sample, similar peaks are presented in the absorption sample (Figure 10b), which are the Mg peaks superseded by the MgH₂. New peaks of MgO, MgTiO₃, CoMg₂, and CoTi₂ were also detected, suggesting that interaction between MgH₂ and CoTiO₃ may occur during the heating process, as indicated in (Equation (4)). The mechanism of the absorption/desorption process of the MgH₂–CoTiO₃ system is shown in Figure 11.

$$11MgH_2 + 3CoTiO_3 \rightarrow 6MgO + MgTiO_3 + 2CoMg_2 + CoTi_2 + 11H_2$$
(4)



Figure 10. XRD patterns of (a) MgH₂ + 10 wt.% CoTiO₃ and (b) MgH₂ + 50 wt.% CoTiO₃ after the absorption process at 200 °C.



Figure 11. Schematic diagram of the catalytic mechanism of $CoTiO_3$ during the absorption/desorption process of the MgH₂–CoTiO₃ system. During the milling process, the MgH₂ matrix reacts with CoTiO₃. After undergoing the absorption and desorption process, MgTiO₃, MgO and CoTi₂, and CoMg₂ are formed in situ. These in situ active species may serve as an intermediate transfer getaway that accelerates the hydrogen absorption and desorption of MgH₂. With the assistance of in situ formed MgTiO₃, MgO and CoTi₂, and CoMg₂, the hydrogen storage behavior of MgH₂ is significantly improved.

On the basis of the above result, we postulate that the MgH_2 –CoTiO₃ system presents a superior hydrogen storage performance of MgH₂ due to the synergetic effect of the in situ formation of MgTiO₃, CoMg₂, CoTi₂, and MgO. These active species act like active sites at the surface of the MgH₂ matrix and provide a fast channel for the diffusion of H atoms in the absorption and desorption process [73,74]. For instance, a previous study stated that adding MgTiO₃ ameliorates the sorption kinetics performance of MgH₂ [75]. The MgH₂ + MgTiO₃ absorbed 5 wt.% of H₂ in 500 s at 307 °C. Gao et al. [69] also presented the notable performance of MgH₂ with the formation of Co-containing material after the desorption and absorption processes. It is believed that 3D electron orbitals in the transition metal stimulate the dissociation of H_2 molecules by serving as the antibonding of H₂ molecules. Thereafter, Ares-Fernandez and Aguey-Zinsou [50] presented faster absorption/desorption rates of MgH_2 when it was doped with MgO. In another work, they stated that MgO may take part as a process control agent that can reduce and prevent MgH_2 from agglomerating by achieving an optimal breakage rate [76]. The catalytic effect of MgTiO₃, CoMg₂, CoTi₂, and MgO could work together to provide a synergetic effect and further boost the performance of MgH₂. Nevertheless, more research is needed, such as applying X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy, to elucidate the catalytic function of $CoTiO_3$ on the hydrogen storage properties of MgH₂.

4. Conclusions

The hydrogen storage performance of MgH₂ was enhanced with the addition of nanosized CoTiO₃, which was synthesized via the solid-state method. The different weight percentage of CoTiO₃ was added into MgH₂, and the 10 wt.% of the CoTiO₃doped MgH₂ sample present a superior performance of hydrogen storage properties. The MgH₂ + 10 wt.% CoTiO₃ started releasing hydrogen at a temperature of 275 °C, 65 °C lower than as-milled MgH₂ (340 $^{\circ}$ C). The MgH₂ + 10 wt.% CoTiO₃ composite also presents a faster absorption and desorption rate when it can absorb 6.4 wt.% H₂ in the first 10 min and performs a 23-times-faster desorption rate when compared with as-milled MgH₂. Moreover, the activation energy of the MgH₂ decreased from 135 kJ/mol to 104.6 kJ/mol after the addition of 10 wt.% of CoTiO₃. Adding nanosized CoTiO₃ also results in a smaller and fine particle that promotes the favorable improvement of MgH₂ performance. The superior performance of MgH₂ with the addition of CoTiO₃ was also attributed to the in situ formation of MgTiO₃, CoMg₂, CoTi₂, and MgO during the heating process, which offers a synergetic catalytic role in improving the performance of MgH₂. These findings may be beneficial for the modification of the MgH₂ system for solid-state hydrogen storage in the future.

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