Enhancing Hydrogen Storage Kinetics and Cycling Properties of NaMgH₃ by 2D Transition Metal Carbide MXene Ti₃C₂

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Abstract: Metal hydrides have recently been proposed for not only hydrogen storage materials but also high-efficiency thermal storage materials. NaMgH₃ contains a considerable theoretical thermal storage density of 2881 kJ/kg. However, its sluggish de/re-hydrogenation reaction kinetics and poor cycling stability exhibit unavailable energy efficiency. Doping with active catalyst into NaMgH₃ is deemed to be a potential strategy to mitigate these disadvantages. In this work, the enhancement of de/re-hydrogenation kinetics and cycling properties of NaMgH₃ is investigated by doping with lamellar-structure 2D carbon-based MXene, Ti₃C₂. Results shows that introducing 7 wt.% Ti₃C₂ is proved to perform excellent catalytic efficiency for NaMgH₃, dramatically reducing the two-step hydrogen desorption peak temperatures (324.8 and 345.3 °C) and enhancing the de/re-hydrogenation kinetic properties with the hydrogen desorption capacity of 4.8 wt.% H₂ within 15 min at 365 °C and absorption capacity of 3.5 wt.% H₂ within 6 s. Further microstructure analyses reveal that the unique lamellar-structure of Ti₃C₂ can separate the agglomerated NaMgH₃ particles homogeneously and decrease the energy barriers of two-step reaction of NaMgH₃ (114.08 and 139.40 kJ/mol). Especially, lamellar-structure Ti₃C₂ can improve the reversibility of hydrogen storage of NaMgH₃, rendering 4.6 wt.% H₂ capacity remained after five cycles. The thermal storage density of the composite is determined to be 2562 kJ/kg through DSC profiles, which is suitable for thermal energy storage application.

Keywords: hydrogen storage materials; NaMgH₃; MXene; lamellar-structure; cycling performances

1. Introduction

Sodium-based hydrides such as NaH, MgH₂ (simple binary hydrides), NaBH₄ (borohydride), NaAlH₄ (alanates hydride), and NaMgH₃ (perovskite hydride) have been researched as promising candidates for hydrogen storage or thermal energy storage during the past decades [1-8]. As the GdFeO₃-type perovskite (space group Pmnm) hydride, NaMgH₃ has received considerable attention for its high gravimetric and volumetric hydrogen densities (6 wt.% and 88 kg/m³) and possesses a considerable theoretical thermal storage gravimetric density (2881 kJ/kg) with reversible two-step de/re-hydrogenation process: [9-15]
\[
\text{NaMgH}_3 \rightarrow \text{NaH} + \text{Mg} + \text{H}_2 \quad (1)
\]

\[
\text{NaH} + \text{Mg} \rightarrow \text{Na} + \text{Mg} + \frac{1}{2} \text{H}_2 \quad (2)
\]

Especially, NaMgH\textsubscript{3} is considered as a potential thermal energy medium for concentration solar power (CSP) because of the high thermodynamic stability [16]. In particular, as a suitable candidate for thermal energy storage (TES), NaMgH\textsubscript{3} has several obvious advantages: high hydrogen storage capacity, low and flat hydrogen de/absorption pressure and plateau, negligible hysteresis, high thermal storage density, and low cost of raw materials [7]. In addition, de/re-hydrogenation kinetics performance and cycling properties are also important parameters to determine whether it is available to TES. However, the further applications to thermal energy storage are limited by sluggish de/re-hydrogenation kinetic performance and pronounced degradation of cycling properties of NaMgH\textsubscript{3}.

Much attention has been focused on improving de/re-hydrogenation kinetics performance and cycling properties of NaMgH\textsubscript{3} during the last few decades [17–21]. It has been proved that adding Li or K into NaMgH\textsubscript{3} would make Li or K partially take the place of the Na position and the formation of distorted perovskite structure would enhance the de-hydrogenation kinetics performance [17,18]. Li et al. [19] improved the cycling properties through in situ embedding of Mg\textsubscript{2}NiH\textsubscript{4} and YH\textsubscript{3} nanoparticles in NaMgH\textsubscript{3}. Except alkali metal and metal hydrides, the Ti-based catalysts have been found to possess remarkably high catalytic activity. Wang’s group [20] decreased the onset desorption temperature of NaMgH\textsubscript{3} to 328 K with 153.47 kJ/mol by introduced K\textsubscript{2}TiF\textsubscript{6} as a dopant. Moreover, it was confirmed that TiF\textsubscript{3} can significantly reduce the activation energy of NaMgH\textsubscript{3} to 104 kJ/mol [18].

As a new type of two-dimension materials, MXenes have been successfully synthesized through etching ternary carbides, nitrides, or carbonitrides (MAX) with HF or in situ HF [22–25]. The general formula of MXenes is M\textsubscript{n+1}X\textsubscript{n}T\textsubscript{x} (n = 1–3), where M represents a transition metal, X is carbon and/or nitrogen, and T\textsubscript{x} stands for the surface terminations [26]. The carbide transition metal MXene, such as Ti\textsubscript{3}C\textsubscript{2}, possesses a particularly lamellar structure, showing promising application as an anode material for Li-ion batteries [27,28]. Furthermore, much effort has been devoted to exploring the superior catalytic effect of Ti\textsubscript{3}C\textsubscript{2} on de/re-hydrogenation reactions of hydrides [29–34]. Liu et al. [29,30] observed a strong catalytic effect of Ti\textsubscript{3}C\textsubscript{2} in de/re-hydrogenation kinetics properties on both MgH\textsubscript{2} and NaAlH\textsubscript{4}. In particular, Ti\textsubscript{3}C\textsubscript{2} tremendously improved the cycling stability of NaAlH\textsubscript{4}, with the de/re-hydrogenation performance remaining nearly constant over 10 cycles. The superior catalytic efficiency of Ti\textsubscript{3}C\textsubscript{2} has also been proven on Li\textsubscript{2}Na\textsubscript{2}AlH\textsubscript{6} and Li\textsubscript{1.3}Na\textsubscript{1.7}AlH\textsubscript{6} [31,32]. Therefore, the superior catalytic efficiency of the lamellar-structure Ti\textsubscript{3}C\textsubscript{2} is highly anticipated to expand to the NaMgH\textsubscript{3}.

There are indeed many other higher hydrogen storage capacity compounds, such as LiBH\textsubscript{4} with 18.5 wt.%, MgH\textsubscript{2} with 7.6 wt.% and NaAlH\textsubscript{4} with 5.6 wt.% [35,36]. Although the reversible hydrogen storage capacity of NaMgH\textsubscript{3} is about 6 wt.%, it exhibits other engineering feasibility in heat storage, accompanying the reversible hydrogen storage process [37]. From pressure–composition isotherm (PCI) measurements, the enthalpy, ΔH\textsubscript{des}, and entropy, ΔS\textsubscript{des}, of desorption for Equation (1) were determined as 86.6 kJ·mol\textsuperscript{-1}·H\textsubscript{2} and 132.2 J·mol\textsuperscript{-1}·H\textsubscript{2}·K\textsuperscript{-1}. The enthalpy and entropy of desorption for Equation (2) correspond to those for pure NaH (ΔH\textsubscript{des} = 116 kJ·mol\textsuperscript{-1}·H\textsubscript{2} and ΔS\textsubscript{des} = 168.2 J·mol\textsuperscript{-1}·H\textsubscript{2}·K\textsuperscript{-1}). The theoretical gravimetric heat storage capacity of Equations (1) and (2) is 2881 kJ·kg\textsuperscript{-1} (Equation (1) = 1721 kJ·kg\textsuperscript{-1}, Equation (2) = 1160 kJ·kg\textsuperscript{-1}). Therefore, NaMgH\textsubscript{3} would be an ideal thermal storage medium during the hydrogen storage process. However, further applications for thermal energy storage are limited by sluggish de/re-hydrogenation kinetic performance and pronounced degradation of NaMgH\textsubscript{3} cycling properties.
In this work, the 2D MXenes TiC$_2$ with a unique lamellar-structure was introduced into NaMgH$_3$ for enhancing its de/re-hydrogenation kinetics and cycling behaviors for the first time. Five composites including NaMgH$_3$-x wt.% TiC$_2$ (x = 0, 3, 5, 7, and 9) were synthesized via ball-milling. Among them, the 7 wt.% TiC$_2$-containing NaMgH$_3$ shows the optimal de/re-hydrogenation storage performance as it can desorb 4.8 wt.% H$_2$ in 15 min at 365 °C and then can be easily hydrogenated at 300 °C under 80 bar H$_2$. More importantly, the reversible hydrogen storage performance stays at a relatively high level after 5 cycles. It is confirmed that the 2D TiC$_2$ can disperse the agglomerated NaMgH$_3$ particles homogeneously, decrease the activation energy of NaMgH$_3$, and prevent Na from separating Mg during the cycles. Moreover, the thermal storage density for NaMgH$_3$-7 wt.% TiC$_2$ is evaluated to be 2562 kJ/kg through DSC profile.

2. Materials and Methods

The lamellar-structure TiC$_2$ was prepared via etching the Ti$_3$AlC$_2$ (98% purity, Lai-zhou Kai Xi Ceramic Materials Co., Ltd., Laizhou, China) with the HF, which was mixed by combining 15 mL HCl (12 M), 15 mL deionized water and 1.98 g LiF. Then 3 g Ti$_3$AlC$_2$ precursor was immersed into the in situ HF and transferred to a 100 mL Teflon-lined autoclave. The Ti$_3$AlC$_2$ was treated with a 48-hour heat treatment in an oil bath at 60 °C. After heat treatment, the precursor was washed with deionized water through centrifugation treatment. The final pH of this precursor should reach 6 and then further drying could be carried out. The drying process was operated at 80 °C for 24 h under vacuum.

The as-formed lamellar-structure TiC$_2$ was doped into NaMgH$_3$ as a catalyst to enhance de/re-hydrogenation kinetics and cycling properties. Five composites of NaMgH$_3$-x wt.% TiC$_2$ (x = 0, 3, 5, 7, and 9) were synthesized by milling with stainless steel balls of which the weight ratio to composites was 40:1 under 10 bar H$_2$ for 12 h at 400 rpm using a planetary ball mill (QM-3SP4, Nanjing, China).

The phase transformations, structures and morphological features of TiC$_2$ and NaMgH$_3$-x wt.% TiC$_2$ (x = 0, 3, 5, 7, and 9) composites were characterized via X-ray diffraction (XRD, PANalytical, The Netherlands, Cu Kα) and scanning electron microscopy (SEM, Hitachi FSEM, SU-70, Tokyo, Japan). During the XRD and SEM analyses, all samples were protected by a laboratory-made container filled with argon for preventing samples from reacting with oxygen and water. Additionally, the de/re-hydrogenation performance of NaMgH$_3$-x wt.% TiC$_2$ (x = 0, 3, 5, 7, and 9) composites were examined by a homemade Sieverts-type apparatus. The temperature-programmed desorption (TPD) analyses were tested with the heating rate of 5 °C/min from 25 to 450 °C under vacuum. The hydrogen desorption kinetics of all composites were examined at 365 and 350 °C with a base pressure of 3 × 10$^{-2}$ bar H$_2$. The hydrogen absorption kinetics were examined at 400, 350, and 300 °C under 80 bar H$_2$ for 1 h. The cycling property tests were determined by a repeated de/re-hydrogenation procedure at 400 °C, but changing the back pressure from 3 × 10$^{-2}$ to 60 bar H$_2$. The gravimetric heat storage capacity and heat change of composites were determined using a differential scanning calorimeter (DSC).

3. Results and Discussion

First, the successful synthesis of lamellar-structure MXene TiC$_2$ was confirmed through XRD and SEM analyses (Figure 1). It is obvious that the strongest and sharpest XRD diffraction peaks of Ti$_3$AlC$_2$ at $2\theta = 39^\circ$ totally disappeared after etching treatment, which were replaced by another curve, the XRD pattern of TiC$_2$. The diffraction peaks of as-formed TiC$_2$ belonging to (002) and (004) are significantly broadened and shift to lower angles. Especially, the diffraction (002) peak was much stronger than before. Furthermore, the insert SEM image obviously suggests that the as-formed TiC$_2$ exhibited a 2D lamellar-structure morphology, which was etched by in situ HF treatment and effectively separated by LiF [22].
Five composites of NaMgH$_3$-x wt.% Ti$_3$C$_2$ (x = 0, 3, 5, 7, and 9) were formed/synthesized by doping the as-prepared Ti$_3$C$_2$ into NaMgH$_3$ by ball milling, and the phase components and structures were determined by XRD, as displayed in Figure 2. As can be seen from the XRD analyses, only NaMgH$_3$ and MgO can be obviously identified in all five composites. The appearance of MgO phase is due to the impurity of Mg powders during the synthesis of pure NaMgH$_3$. It is almost impossible to find the diffraction peaks belonging to lamellar-structure Ti$_3$C$_2$ in these five patterns due to the small amounts of Ti$_3$C$_2$ additive [34]. The other possibility is that the ball milling destroyed the multilayered structure of Ti$_3$C$_2$. Therefore, the XRD results indicate the successful synthesis of the five composites without any other impurity peaks.

After assessing the phase components and morphology of NaMgH$_3$-x wt.% Ti$_3$C$_2$ (x = 0, 3, 5, 7, and 9) samples, the hydrogen desorption kinetics of all samples were evaluated
by DSC, TPD, and isothermal dehydrogenation measurements (Figure 3). As expected, doping a certain amount of TiC2 remarkably decreases the hydrogen desorption temperature in contrast to pure NaMgH3 (Figure 3a). The first- and second-step dehydrogenation temperatures of NaMgH3-3 wt.% TiC2 decreased from 372.3 and 380.3 °C to 344.5 and 358.4 °C, exhibiting 27.8 and 21.9 °C reduction, respectively. With increasing the TiC2 content to 5, 7, or 9 wt.%, the first-step dehydrogenation temperatures are further reduced to 327.5, 324.8 and 320.3 °C, respectively. Meanwhile, the second-step dehydrogenation temperatures of these samples declined to 341.3, 345.3, and 341.8 °C, respectively.

**Figure 3.** (a) DSC, (b) TPD, and isothermal dehydrogenation curves at (c) 365 °C and (d) 350 °C for NaMgH3-x wt.% Ti3C2 (x = 0, 3, 5, 7, and 9) samples.

Combined with the TPD results (Figure 3b), more hydrogen desorption kinetic properties of NaMgH3 undoped/doped with TiC2 are revealed. First, doping with 3 wt.% TiC2 reduces the onset dehydrogenation temperature of pure NaMgH3 tremendously, from 350 °C to 250 °C. In particular, further increasing the content of TiC2 to 5, 7, or 9 wt.% allows around 3.5 wt.% H2 to release (first-step decomposition reaction) below 350 °C. Importantly, the TiC2 sample containing 7 wt.% performs faster dehydrogenation kinetics than that of others below 350 °C. Nevertheless, the dehydrogenation capacity suffers a small loss, from 5.6 wt.% H2 to 5.4, 5.3, 5.2, and 5.1 wt.% H2, for the NaMgH3-x wt.% TiC2 (x = 3, 5, 7, and 9) samples, respectively, which is mainly due to the dead weight of TiC2 and existence of MgO.

More specific dehydriding kinetic characterizations were carried out through the isothermal dehydrogenation measurements at 365 and 350 °C (Figure 3c,d). Just as shown by the earlier research, the sample containing 7 wt.% TiC2 exhibits the best dehydriding kinetic properties at 365 and 350 °C, desorbing 4.8 wt.% H2 in 15 min and 3.4 wt.% H2 in 5 min, respectively. However, for the pure NaMgH3, only 0.6 wt.% H2 is released in 15 min at 365 °C. As the temperature decreases to 350 °C, the pure NaMgH3 sample only desorbs 0.2 wt.% H2 in 5 min.
As a result, it is obvious that doping of 7 wt.% Ti3C2 leads to a tremendous improvement in the dehydridding kinetic properties of NaMgH3. Furthermore, considering the observed results, including the dehydrogenation temperatures, dehydrogenation kinetic performance, and dehydrogenation capacities, the NaMgH3-7 wt.% Ti3C2 composite exhibits the best energy efficiency and represents the optimal constituent.

To further understand the reason for such a huge dehydrogenation property gap between NaMgH3-7 wt.% Ti3C2 and pure NaMgH3, the DSC analyses were measured at different heating rates (1, 2, 5, and 8 °C/min) (Figure 4a,b). The activation energy (Ea) corresponding to the two-step dehydrogenation reactions of both two composites are quantitatively shown in Figure 4c and Table 1, determined by Kissinger fitting methods [38] (Equation (3)).

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right)$$  \hspace{1cm} (3)  

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where $\beta$ is the heating rate, $T_p$ represents peak temperature, $A$ is the pre-exponential factor, and $R$ represents the gas constant.

![Figure 4. DSC curves for (a) pure NaMgH3; (b) NaMgH3-7 wt.% Ti3C2 at different heating rates; and Kissinger plots of (c) first- and second-step dehydrogenation of both samples.](image)

**Table 1.** Activation energies ($E_a$) for the dehydrogenation of the NaMgH3 sample undoped and doped with 7 wt.% Ti3C2.

| Dopant               | Apparent Activation Energy $E_a$ (kJ/mol) |
|----------------------|------------------------------------------|
|                      | NaMgH3 (First-Step) | NaMgH3 (Second-Step) |
| Undoped              | 158.45                  | 165.16                  |
| 7 wt.% Ti3C2         | 114.08                  | 139.40                  |
Based on these data, the values of $E_a$ of the first-step hydrogen desorption reaction of NaMgH$_3$ and NaMgH$_3$-7 wt.% Ti$_3$C$_2$ are calculated to be 158.45 and 114.08 kJ/mol, respectively. For the second-step reaction, the value of $E_a$ declines from 165.16 to 139.40 kJ/mol by doping with 7 wt.% Ti$_3$C$_2$. The reduction of $E_a$ for both two reactions demonstrates that the improved dehydriding properties of NaMgH$_3$ can be ascribed to the Ti$_3$C$_2$ dopant by reducing the second-step dehydrogenation energy barrier.

The role played by unique lamellar-structure Ti$_3$C$_2$ during the dehydrogenation reactions was researched and explored. Figure 5a,b shows the SEM images of the pure NaMgH$_3$ sample, in which some small particles with average size of approximately 1 µm agglomerate together to form a larger cluster. In Figure 5c, the results of EDS analyses further confirm the results of the XRD measurements noted above, suggesting the successful synthesis of NaMgH$_3$. In contrast, the large layer-structure (about 10 µm wide) of Ti$_3$C$_2$ is completely broken into smaller lamellar-structure (about 2 µm wide) during the ball-milling procedure, with some tiny NaMgH$_3$ particles attached, as shown in Figure 5d,e. Furthermore, after 12 h ball milling, the agglomerated NaMgH$_3$ particles were separated homogeneously by the lamellar-structure Ti$_3$C$_2$. The following EDS analyses (Figure 5f) prove the existence of NaMgH$_3$ and Ti$_3$C$_2$. Based on the significant reduction of operating temperature and the superior enhancement of dehydrogenation kinetics properties in the Ti$_3$C$_2$ doped sample, it can be proposed that Ti$_3$C$_2$ plays the role of catalyst to improve the dehydrogenation kinetics properties of NaMgH$_3$ hydride, which is in agreement with our previous papers in Ti$_3$C$_2$-doped Mg(BH$_4$)$_2$ [33] and sodium alanate systems [34]. Apparently, the exploration of the SEM and EDS results described above indicate that the significant reduction of operating temperature and the superior enhancement of dehydrogenation kinetics properties of the 7 wt.% Ti$_3$C$_2$ doped sample can be mainly due to the unique lamellar-structure. The detailed microstructure information of Ti$_3$C$_2$ could not be easily revealed after the re/dehydrogenation process due to the small amounts of Ti$_3$C$_2$ additive; thus, the catalytic mechanism remains undiscovered. We hope that the catalytic mechanism of NaMgH$_3$-x wt.% Ti$_3$C$_2$ composite can be revealed in the future by a X-ray absorption near-edge structure (XANES) spectrum.

Figure 5. SEM images of (a,b) NaMgH$_3$ and (d,e) NaMgH$_3$-7 wt.% Ti$_3$C$_2$; EDS results of (c) NaMgH$_3$ and (f) NaMgH$_3$-7 wt.% Ti$_3$C$_2$.

Figure 6 shows the isothermal hydrogenation curves of pure NaMgH$_3$ and NaMgH$_3$-7 wt.% Ti$_3$C$_2$ samples at different temperatures. It is obvious that the hydrogen absorption kinetics of NaMgH$_3$ can be enhanced by doping with Ti$_3$C$_2$, resulting in the high capacity achieved at the same hydrogenation condition. Figure 6a shows the isothermal hydrogenation curves of pure NaMgH$_3$ and NaMgH$_3$-7 wt.% Ti$_3$C$_2$ samples at 300 °C. The 7 wt.% Ti$_3$C$_2$-containing composite can quickly absorb approximately 3.5 wt.% H$_2$ within 6 s.
However, the pure NaMgH$_3$ displays unacceptably slow re-hydrogenation kinetics, storing 3.0 wt.% H$_2$ in 15 min. This result suggests that only the first-step hydrogenation reaction is thermodynamically available at 300 °C. As the hydrogenation temperature increases to 350 °C, the hydrogenation kinetics of two dehydrogenated samples are improved, approximately 3.8 and 4.3 wt.% H$_2$ stored for NaMgH$_3$ and NaMgH$_3$-7 wt.% Ti$_3$C$_2$ samples, respectively. The results reveal that first- and second-step hydrogenation reactions of the samples are feasible in thermodynamics, as the temperature increases to 350 °C. However, the second-step hydrogenation kinetics of both samples are too slow to desorb more hydrogen within 30 min. When the hydrogenation temperature rises to 400 °C, the Ti$_3$C$_2$-containing sample exhibits excellent hydrogenation kinetics, absorbing 4.9 wt.% H$_2$ in 8 min, confirming that the first- and second-step hydrogen absorption kinetics have been further improved. The hydrogenation capacity of pure NaMgH$_3$ is found to be 4.2 wt.% H$_2$ in 15 min, with the second-step hydrogen absorption kinetics still being sluggish. In summary, Ti$_3$C$_2$ has obvious catalytic efficiency on the enhancement of both first- and second-step hydrogenation kinetic properties of NaMgH$_3$ under 80 bar H$_2$ at 300, 350, and 400 °C.

Figure 6. Isothermal hydrogenation curves of pure NaMgH$_3$ and NaMgH$_3$-7 wt.% Ti$_3$C$_2$ at different temperatures. (a) 300 °C (b) 350 °C (c) 400 °C.

The reversible dehydrogenation properties of NaMgH$_3$ are remarkably enhanced because of the superior catalytic activity of Ti$_3$C$_2$ with lamellar-structure. To obtain the cycling properties of NaMgH$_3$ with or without dopant, the cycling isothermal dehydrogenation curves and hydrogen capacities of two samples are displayed in Figure 7. In the first cycle, pure NaMgH$_3$ desorbs 5.5 wt.% H$_2$ in 15 min at 400 °C. After hydrogenation at 400 °C under 60 bar H$_2$, it releases only 2.6 wt.% H$_2$ in 60 min, losing approximately half of its initial capacity. The dehydrogenation kinetic property of pure NaMgH$_3$ also suffers tremendous degradation in the second cycle, especially in the latter 3rd, 4th and 5th cycles, 3.8, 4.0, and 3.75 wt.% H$_2$ were desorbed in 20 min, respectively. The dehydrogenation kinetics and capacity of pure NaMgH$_3$ in the latter three cycles are recovered from the poor second cycle. For the Ti$_3$C$_2$ doped NaMgH$_3$, in the first cycle, about 5.1 wt.% H$_2$ is released in 5 min. The difference is that the Ti$_3$C$_2$ doped sample does not suffer tremendous capacity loss in the second cycle. In the latter four cycles, the Ti$_3$C$_2$ doped sample desorbs 4.3, 4.4, 4.4, and 4.6 wt.% H$_2$ in 20 min, respectively. In five cycles, pure NaMgH$_3$ suffers a huge capacity loss from 5.5 to 4.1 wt.% H$_2$ losing a quarter of its initial capacity. It is well known that a material with faster kinetics will release more hydrogen within a fixed time. Hence, Ti$_3$C$_2$ can relieve the degradation of dehydrogenation capacity to some extent due to its improved dehydrogenation kinetics. However, it is clear that the lamellar-structure Ti$_3$C$_2$ can effectively enhance the cycling stability of NaMgH$_3$ in five cycles. The expectation of the dehydrogenation kinetics and cycling stability of NaMgH$_3$ remaining unchanged is not achieved. Therefore, further investigation of enhancing the cycle stability of NaMgH$_3$ should be explored.
The pronounced degradation of dehydrogenation performance and hydrogen capacity in the second cycle for the pure NaMgH$_3$ is abnormal. There should be some phase separations during hydrogenation after the first cycle dehydrogenation. Furthermore, it was found that pure NaMgH$_3$ would segregate into separate NaH and Mg during the high-temperature cycling tests [39]. In order to confirm the phase transformation of Ti$_3$C$_2$ doped/undoped NaMgH$_3$ samples during hydrogen storage process, XRD characterization was carried out for the re-hydrogenated sample. In Figure 8a,b, the NaMgH$_3$, NaH, Mg, and MgO phases can be seen in the XRD patterns of the pure NaMgH$_3$ sample after the second and third hydrogenations. The separation of NaH and Mg phases after hydrogenation can explain the reason why abnormal degradation occurs. Therefore, the detailed reaction process can be proposed as follows. When pure NaMgH$_3$ dehydrogenates at 400 °C, both of the two step decomposition reactions occur quickly, forming molten Na and solid Mg. The drastic molten Na covers the outside surface of solid Mg particles to form the compact Na layer so that most Na and Mg are separated; the residual Na would be hydrogenated to form the solid NaH during the subsequent hydrogenation process, which hinders the further absorption of H$_2$, making the formation of MgH$_2$ and NaMgH$_3$ much more difficult, thereby decreasing the hydrogen capacity of NaMgH$_3$ [37]. Therefore, the formation of the NaH layer must be responsible for the pronounced degradation of dehydrogenation performance in the second cycle for the pure NaMgH$_3$. This hypothesis can be proved by the strong diffraction peaks of NaH in the second hydrogenation sample (Figure 8). Moreover, the enhanced dehydrogenation performance of the pure NaMgH$_3$ sample in the latter three cycles would be due to the distillation of molten Na making the NaH layer thinner [37]. In contrast, the XRD patterns of the hydrogenated NaMgH$_3$-7 wt.% Ti$_3$C$_2$ sample displays the diffraction peaks of NaMgH$_3$, MgH$_2$, and MgO, without any diffraction peaks belonging to NaH (Figure 8c,d). The weak diffraction peaks of MgH$_2$ are caused by the distillation of molten Na during the cycles. Meanwhile, to confirm the separation phenomenon of Na and Mg, the dehydrogenation processes at 400 °C can be observed through a homemade quartz tube. It can be observed that after hydrogenation the pure NaMgH$_3$ appears as a light-yellow metal layer ingoting with metallic luster, corresponding to the existence of NaH (Figure S1a,b). However, the deposition of NaH disappears in the Ti$_3$C$_2$-doped NaMgH$_3$ sample (Figure S1c,d). Herein, the XRD results and dehydrogenation observation indicate that the existence of lamellar-structure Ti$_3$C$_2$ can effectively prevent Na from separating Mg to form the insular NaH layer, largely preserving the cycling dehydrogenation properties of NaMgH$_3$.  

Figure 7. Isothermal dehydrogenation cycle curves of (a) NaMgH$_3$ and (c) NaMgH$_3$-7 wt.% Ti$_3$C$_2$ at 400 °C; cycle capacity curves of (b) NaMgH$_3$ and (d) NaMgH$_3$-7 wt.% Ti$_3$C$_2$. 

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In addition to its use as a hydrogen storage application, NaMgH₃ can also be a potential candidate for thermal energy storage (TES) owing to the theoretical thermal storage density as high as 2881 kJ/kg [37]. In Figure S2a,b, the thermal storage densities of as-formed pure NaMgH₃ and NaMgH₃-7 wt.% Ti₃C₂ samples are calculated to be 2727 and 2562 kJ/kg through DSC profiles, respectively. The reduction of ~6.0% thermal storage density for the NaMgH₃-7 wt.% Ti₃C₂ sample is mainly due to the dead weight of Ti₃C₂ and existence of MgO. Even with this reduction, as-formed NaMgH₃-7 wt.% Ti₃C₂ sample exceeds the thermal storage properties of most other candidates (Table 2). Meanwhile, Ti₃C₂ dramatically enhances the de/re-hydrogenation kinetics and cycling performance of NaMgH₃, making it more suitable for TES application [40].

Table 2. Thermal energy storage densities of different thermochemical energy storage materials [41–44].

| Type of Thermal Energy Storage (TES) | Example of TES Materials | Total Thermal Storage Capacity (kJ/kg) |
|------------------------------------|--------------------------|--------------------------------------|
| Sensible heat                      | Molten salt mixtures     | 153 *                                 |
| Latent heat/phase change materials | NaNO₃                    | 282 *                                 |
| Thermochemical                     | Oxidation of Co₃O₄       | 1055 *                                |
|                                   | NaMgH₃-7 wt.% Ti₃C₂      | 2562 *                                |
| Metal hydrides                     | NaAlH₄                   | 711 *                                 |
|                                   | Mg₂NiH₄                  | 1157 *                                |
|                                   | Mg₂FeH₆                  | 2090 *                                |

* Theoretical thermal storage capacity.

4. Conclusions

NaMgH₃ is considered a potential candidate for hydrogen storage and thermal storage, but further practical applications are limited by its poor de/re-hydrogenation kinetics...
and cycling performance. An investigation of enhancing the re/dehydrogenation kinetics and cycling performance of NaMgH3 through doping with Ti3C2 was carried out by using XRD, SEM, TPD, DSC, isothermal de/re-hydrogenation measurements and cycling tests. The NaMgH3-7 wt.% Ti3C2 sample exhibits the optimal dehydrogenation performance, reducing the two-step desorption peak temperatures from 372.3 and 380.3 °C to 324.8 and 345.3 °C, respectively. The NaMgH3-7 wt.% Ti3C2 can release 4.8 wt.% H2 in 15 min and 3.4 wt.% H2 in 5 min at 365 °C and 350 °C, respectively. The unique lamellar-structure of Ti3C2 can separate the agglomerated NaMgH3 particles homogeneously and decrease the activation energy of NaMgH3 to 114.08 and 139.4 kJ/mol for the first- and second-step dehydrogenation reactions, respectively. The addition of Ti3C2 also dramatically enhances the hydrogen storage kinetics of NaMgH3 at 300, 350, and 400 °C. Approximately 3.5 wt.% H2 is absorbed in 6 s for the NaMgH3-7 wt.% Ti3C2 sample at 300 °C. The poor cycling properties of NaMgH3 are improved by Ti3C2, with 4.6 wt.% H2 capacity remaining after five cycles. Lamellar-structure Ti3C2 can homogeneously separate aggregated NaMgH3 particles and prevent Na from separating Mg after dehydrogenation. Furthermore, NaMgH3-7 wt.% Ti3C2 with its high thermal storage density of 2562 kJ/kg and fast kinetics can be a potential candidate for TES.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/pr9101690/s1, Figure S1: Photographs of pure NaMgH3 and NaMgH3-7 wt.% Ti3C2 (a and c) before and (b and d) after dehydrogenation at 400 °C. Figure S2: DSC profiles of (a) pure NaMgH3 (b) NaMgH3-7 wt.% Ti3C2 at a heating rate of 5 °C/min.

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References
1. Santos, D.M.F.; Sequeira, C.A.C. Sodium borohydride as a fuel for the future. Renew. Sust. Energ. Rev. 2011, 15, 3980–4001.
2. Ahluwalia, R.K. Sodium alanate hydrogen storage system for automotive fuel cells. Int. J. Hydrogen Energy 2007, 32, 1251–1261.
3. Liu, Y.; Wang, S.; Li, Z.; Gao, M.; Liu, Y.; Sun, W.; Pan, H. Enhanced hydrogen storage performance of MgH2 by the catalysis of a novel Intersected Y2O3/NiO hybrid. Processes 2021, 9, 892.
4. Hu, Z.C.; Qin, H.Y.; Xiao, X.Z.; Chen, M.; Liu, M.J.; Jiang, R.C.; Chen, L.X. Excellent catalysis of various TiO2 dopants with Na0.46TiO2 in situ formed on the enhanced dehydrogenation properties of NaMgH3. J. Phys. Chem. C 2019, 123, 22832–22841.
5. Zhang, X.; Liu, Y.; Ren, Z.; Zhang, X.; Hu, J.; Huang, Z.; Lu, Y.; Gao, M.; Pan, H. Realizing 6.7 wt% reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides. Energy Environ. Sci. 2021, 14, 2302–2313.
6. Huang, X.; Xiao, X.; He, Y.; Yao, Z.; Ye, X.; Kou, H.; Chen, C.; Huang, T.; Fan, X.; Chen, L. Probing an intermediate state by X-ray absorption near-edge structure in nickel-doped 2LiBH4–MgH2 reactive hydride composite at moderate temperature. Mater. Today Nano 2020, 12, 100090.
7. Poupin, L.; Humphries, T.D.; Paskevicius, M.; Buckley, C.E. A thermal energy storage prototype using sodium magnesium hydride. Sustain. Energy Fuels 2019, 3, 985–995.
8. Chen, W.; Xiao, X.; He, J.; Dong, Z.; Wang, X.; Chen, M.; Chen, L. A dandelion-like amorphous composite catalyst with outstanding performance for sodium borohydride hydrogen generation. Int. J. Hydrogen Energy 2021, 46, 10809–10818.
9. Reshak, A.H. NaMgH3 a perovskite-type hydride as advanced hydrogen storage systems: Electronic structure features. Int. J. Hydrogen Energy 2015, 40, 16383–16390.
10. Ikeda, K.; Kogure, Y.; Nakamori, Y.; Orimo, S. Reversible hydriding and dehydriding reactions of perovskite-type hydride NaMgH3. Scr. Mater. 2005, 53, 319–322.
11. Bouamrane, A.; Laval, J.P.; Soulje, J.P.; Bastide, J.P. Structural characterization of NaMgH2F and NaMgH3. Mater. Res. Bull. 2000, 35, 545–549.
12. Wu, H.; Zhou, W.; Udoovic, T.J.; Rush, J.J.; Yildirim, T. Crystal chemistry of perovskite-type hydride NaMgH5: Implications for hydrogen storage. *Chem. Mater.* 2008, 20, 2335–2342.

13. Pottmaier, D.; Pinatel, E.R.; Vitillo, J.G.; Garroni, S.; Orlova, M.; Baró, M.D.; Vaughan, G.B.M.; Fichtner, M.; Lohstroh, W.; Baricco, M. Structure and Thermodynamic Properties of the NaMgH4 Perovskite: A Comprehensive Study. *Chem. Mater.* 2011, 23, 2317–2326.

14. Bouhadda, Y.; Fenineche, N.; Boudouma, Y. Hydrogen storage: Lattice dynamics of orthorhombic NaMgH5. *Phys. B Condens. Matter* 2011, 406, 1000–1003.

15. Wang, Z.; Tao, S.; Li, J.J.; Deng, J.Q.; Zhou, H.; Yao, Q. The Improvement of Dehydriding the Kinetics of NaMgH5 Hydride via Doping with Carbon Nanomaterials. *Metals* 2017, 7, 9.

16. Sheppard, D.; Paskevicius, M.; Buckley, C.E. Thermodynamics of hydrogen desorption from NaMgH5 and its application as a solar heat storage medium. *Chem. Mater.* 2011, 23, 4298–4300.

17. Wang, Z.; Li, J.J.; Tao, S.; Deng, J.Q.; Zhou, H.; Yao, Q. Structure, thermal analysis and dehydriding kinetic properties of Na-\textit{Li}MgH\textit{X} hydrides. *J. Alloys Compd.* 2015, 660, 402–406.

18. Tao, S.; Wang, Z.M.; Wan, Z.Z.; Deng, J.Q.; Zhou, H.; Yao, Q. Enhancing the dehydriding properties of perovskite-type NaMgH5 by introducing potassium as dopant. *Int. J. Hydrogen Energy* 2017, 42, 3716–3722.

19. Li, Y.; Zhang, L.; Zhang, Q.; Fang, F.; Sun, D.; Li, K.; Wang, H.; Ouyang, L.; Zhu, M. In situ embedding of Mg\textit{Ni}H\textit{X} and YH\textit{X} nanoparticles into bimetallic hydride NaMgH5 to inhibit phase segregation for enhanced hydrogen storage. *J. Phys. Chem. C* 2014, 118, 22635–23644.

20. Wang, Z.; Tao, S.; Deng, J.; Zhou, H.; Yao, Q. Significant improvement in the dehydriding properties of perovskite hydrides, NaMgH5, by doping with K/TiF\textit{X}. *Int. J. Hydrogen Energy* 2017, 42, 8554–8559.

21. Ismail, M.; Zhao, Y.; Yu, X.B.; Dou, S.X. Improved hydrogen storage performance of Mg\textit{Li}–NaAlH\textit{X} composite by addition of TiF\textit{X}. *Int. J. Hydrogen Energy* 2012, 37, 8395–8401.

22. Allabeb, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y. Guidelines for synthesis and processing of 2D titanium carbide (TiS\textit{X}N\textit{X}MXene). *Chem. Mater.* 2017, 29, 7633–7644.

23. Yang, J.; Chen, B.; Song, H.; Tang, H.; Li, C. Synthesis, characterization, and tribological properties of two-dimensional TiS\textit{X}. *Cryst. Res. Technol.* 2014, 49, 926–932.

24. Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. Two-Dimensional Nanocrystals: Two-dimensional nanocrystals produced by exfoliation of TiS\textit{X}C\textit{X}. *Adv. Mater.* 2011, 23, 4248–4253.

25. Lin, H.; Wang, Y.; Gao, S.; Chen, Y.; Shi, J. Theranostic 2D tantalum carbide (MXene). *Adv. Mater.* 2017, 30, 1703284.

26. Anasori, B.; Lukatskaya, M.; Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* 2017, 2, 1–17.

27. Naguib, M.; Mashtalir, O.; Lukatskaya, M.; Dyatkin, B.; Zhang, C.; Presser, V.; Gogotsi, Y.; Barsoum, M. One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of MXenes. *Chem. Commun.* 2014, 50, 7420–7423.

28. Naguib, M.; Halim, J.; Lu, J.; Cook, K.M.; Hultman, L.; Gogotsi, Y.; Barsoum, M.W. New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries. *J. Am. Chem. Soc.* 2013, 135, 15966–15969.

29. Wu, R.; Du, H.; Wang, Z.; Gao, M.; Pan, H.; Liu, Y. Remarkably improved hydrogen storage properties of NaAlH\textit{X} doped with 2D titanium carbide. *J. Power Sources* 2016, 327, 519–525.

30. Liu, Y.; Du, H.; Zhang, X.; Yang, Y.; Gao, M.; Pan, H. Superior catalytic activity derived from two-dimensional TiS\textit{X}C\textit{X} precursor towards the hydrogen storage reaction of magnesium hydride. *Chem. Commun.* 2015, 52, 705–708.

31. Fan, X.; Zhang, Y.; Zhu, Y.; Guo, X.; Chen, J.; Li, L. Hydrogen storage performances and reaction mechanism of non-stoichiometric compound Li\textit{N}a\textit{N}a\textit{H}: doped with TiC\textit{X}. *Chem. Phys.* 2018, 513, 135–140.

32. Cheng, H.; Li, K.; Fan, X.; Lou, H.; Liu, Y.; Qi, Q.; Zhang, J.; Liu, J.; Yan, K.; Zhang, Y. The enhanced de/re-hydrogenation performances of LiNa\textit{N}a\textit{H} combined with two-dimension lamellar TiC\textit{X}. *Int. J. Hydrogen Energy* 2017, 42, 25285–25293.

33. Zheng, J.G.; Cheng, H.; Xiao, X.Z.; Chen, M.; Chen, L.X. Enhanced low temperature hydrogen desorption properties and mechanism of Mg(BH\textit{X})\textit{X} composed with 2D MXene. *Int. J. Hydrogen Energy* 2019, 44, 24292–24300.

34. Jiang, R.; Xiao, Z.; Zheng, J.; Chen, M.; Chen, L. Remarkable hydrogen absorption/desorption behaviors and mechanism of sodium alanates in-situ doped with Ti-based 2D MXene. *Mater. Chem. Phys.* 2020, 242, 122529.

35. Yartys, V.A.; Lotoskyy, M.V.; Akiba, E.; Albert, R.; Antonov, V.E.; Ares, J.R.; Baricco, M.; Bourgeois, N.; Buckley, C.E.; Bellosta von Colbe, J.M.; et al. Magnesium based materials for hydrogen based energy storage: Past, present and future. *Int. J. Hydrogen Energy* 2019, 44, 7809–7859.

36. He, T.; Pachuffle, P.; Wu, H.; Xu, Q.; Chen, P. Hydrogen carriers. *Nat. Rev. Mater.* 2016, 1, 1–17.

37. Sheppard, D.A.; Humphries, T.D.; Buckley, C.E. Sodium-based hydrides for thermal energy applications. *Appl. Phys. A* 2016, 122, 406.

38. Kissinger, H.E. Reaction kinetics in differential thermal analysis. *Anal. Chem.* 1957, 29, 1702–1706.

39. Ward, P.A.; Corgnale, C.; Teprovich, J.A.; Motyka, T.; Hardy, B.; Peters, B.; Zidan, R. High performance metal hydride based thermal energy storage systems for concentrating solar power applications. *J. Alloys Compd.* 2015, 645, S374–S378.

40. Aydin, D.; Casey, S.P.; Riffat, S. The latest advancements on thermochemical heat storage systems. *Renew. Sust. Energ. Rev.* 2015, 41, 356–367.
41. Harries, D.; Paskevicius, M.; Sheppard, D.; Edward Cameron Price, T.; Buckley, C.E. Concentrating solar thermal heat storage using metal hydrides. Proc. IEEE 2012, 100, 539–549.

42. Fellet, M.; Buckley, C.E.; Paskevicius, M.; Sheppard, D.A.; Research on metal hydrides revived for next-generation solutions to renewable energy storage. MRS Bull. 2013, 38, 1012-1013.

43. Sheppard, D.A.; Corgnale, C.; Hardy, B.; Motyka, T.; Zidan, R.; Paskevicius, M.; Buckley, C.E. Hydriding characteristics of NaMgH₂F with preliminary technical and cost evaluation of magnesium-based metal hydride materials for concentrating solar power thermal storage. RSC Adv. 2014, 4, 26552-26562.

44. Paskevicius, M.; Sheppard, D.A.; Williamson, K.; Buckley, C.E. Metal hydride thermal heat storage prototype for concentrating solar thermal power. Energy 2015, 88, 469–477.