Article

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

Zhouming Hang ^{1,2,3} , Zhencan Hu ⁴, Xuezhong Xiao ^{4,*} , Ruicheng Jiang ⁴ and Meng Zhang ⁴

¹ College of Mechanical and Automotive Engineering, Zhejiang University of Water Resources and Electric Power, Hangzhou 310018, China; hangzhm@zjweu.edu.cn

² Zhejiang Engineering Research Center for Advanced Hydraulic Equipment, Zhejiang University of Water Resources and Electric Power, Hangzhou 310018, China

³ Key Laboratory for Technology in Rural Water Management of Zhejiang Province, Zhejiang University of Water Resources and Electric Power, Hangzhou 310018, China

⁴ State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China; 21726113@zju.edu.cn (Z.H.); 21726011@zju.edu.cn (R.J.); 11726062@zju.edu.cn (M.Z.)

* Correspondence: xzxiao@zju.edu.cn

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

Citation: Hang, Z.; Hu, Z.; Xiao, X.; Jiang, R.; Zhang, M. Enhancing Hydrogen Storage Kinetics and Cycling Properties of NaMgH₃ by 2D Transition Metal Carbide MXene Ti₃C₂. *Processes* **2021**, *9*, 1690. <https://doi.org/10.3390/pr9101690>

Academic Editor: Mingxia Gao

Received: 29 July 2021

Accepted: 16 September 2021

Published: 22 September 2021

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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 *P_{nma}*) 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]:

Especially, NaMgH₃ 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), NaMgH₃ 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 NaMgH₃.

Much attention has been focused on improving de/re-hydrogenation kinetics performance and cycling properties of NaMgH₃ during the last few decades [17–21]. It has been proved that adding Li or K into NaMgH₃ 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 Mg₂NiH₄ and YH₃ nanoparticles in NaMgH₃. 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 NaMgH₃ to 328 K with 153.47 kJ/mol by introduced K₂TiF₆ as a dopant. Moreover, it was confirmed that TiF₃ can significantly reduce the activation energy of NaMgH₃ 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_{n+1}X_nT_x (*n* = 1–3), where M represents a transition metal, X is carbon and/or nitrogen, and T_x stands for the surface terminations [26]. The carbide transition metal MXene, such as Ti₃C₂, 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 Ti₃C₂ on de/re-hydrogenation reactions of hydrides [29–34]. Liu et al. [29,30] observed a strong catalytic effect of Ti₃C₂ in de/re-hydrogenation kinetics properties on both MgH₂ and NaAlH₄. In particular, Ti₃C₂ tremendously improved the cycling stability of NaAlH₄, with the de/re-hydrogenation performance remaining nearly constant over 10 cycles. The superior catalytic efficiency of Ti₃C₂ has also been proven on LiNa₂AlH₆ and Li_{1.3}Na_{1.7}AlH₆ [31,32]. Therefore, the superior catalytic efficiency of the lamellar-structure Ti₃C₂ is highly anticipated to expand to the NaMgH₃.

There are indeed many other higher hydrogen storage capacity compounds, such as LiBH₄ with 18.5 wt.%, MgH₂ with 7.6 wt.% and NaAlH₄ with 5.6 wt.% [35,36]. Although the reversible hydrogen storage capacity of NaMgH₃ 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, Δ*H*(des), and entropy, Δ*S*(des), of desorption for Equation (1) were determined as 86.6 kJ·mol^{−1} H₂ and 132.2 J·mol^{−1}·H₂·K^{−1}. The enthalpy and entropy of desorption for Equation (2) correspond to those for pure NaH (Δ*H*(des) = 116 kJ·mol^{−1}·H₂ and Δ*S*(des) = 168.2 J·mol^{−1}·H₂·K^{−1}). The theoretical gravimetric heat storage capacity of Equations (1) and (2) is 2881 kJ·kg^{−1} (Equation (1) = 1721 kJ·kg^{−1}, Equation (2) = 1160 kJ·kg^{−1}). Therefore, NaMgH₃ 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 NaMgH₃ cycling properties.

In this work, the 2D MXenes Ti₃C₂ with a unique lamellar-structure was introduced into NaMgH₃ for enhancing its de/re-hydrogenation kinetics and cycling behaviors for the first time. Five composites including NaMgH₃-*x* wt.% Ti₃C₂ (*x* = 0, 3, 5, 7, and 9) were synthesized via ball-milling. Among them, the 7 wt.% Ti₃C₂-containing NaMgH₃ shows the optimal de/re-hydrogenation storage performance as it can desorb 4.8 wt.% H₂ in 15 min at 365 °C and then can be easily hydrogenated at 300 °C under 80 bar H₂. More importantly, the reversible hydrogen storage performance stays at a relatively high level after 5 cycles. It is confirmed that the 2D Ti₃C₂ can disperse the agglomerated NaMgH₃

particles homogeneously, decrease the activation energy of NaMgH₃, and prevent Na from separating Mg during the cycles. Moreover, the thermal storage density for NaMgH₃-7 wt.% Ti₃C₂ is evaluated to be 2562 kJ/kg through DSC profile.

2. Materials and Methods

The lamellar-structure Ti₃C₂ was prepared via etching the Ti₃AlC₂ (98% purity, Laizhou 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 Ti₃AlC₂ precursor was immersed into the in situ HF and transferred to a 100 mL Teflon-lined autoclave. The Ti₃AlC₂ 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 Ti₃C₂ was doped into NaMgH₃ as a catalyst to enhance de/re-hydrogenation kinetics and cycling properties. Five composites of NaMgH₃-x wt.% Ti₃C₂ (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 H₂ for 12 h at 400 rpm using a planetary ball mill (QM-3SP4, Nanjing, China).

The phase transformations, structures and morphological features of Ti₃C₂ and NaMgH₃-x wt.% Ti₃C₂ (x = 0, 3, 5, 7, and 9) composites were characterized via X-ray diffraction (XRD, PANalytical, The Netherlands, Cu K α) 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 NaMgH₃-x wt.% Ti₃C₂ (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 H₂. The hydrogen absorption kinetics were examined at 400, 350, and 300 °C under 80 bar H₂ 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 H₂. 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 Ti₃C₂ was confirmed through XRD and SEM analyses (Figure 1). It is obvious that the strongest and sharpest XRD diffraction peaks of Ti₃AlC₂ at $2\theta = 39^\circ$ totally disappeared after etching treatment, which were replaced by another curve, the XRD pattern of Ti₃C₂. The diffraction peaks of as-formed Ti₃C₂ 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 Ti₃C₂ exhibited a 2D lamellar-structure morphology, which was etched by in situ HF treatment and effectively separated by LiF [22].

Five composites of NaMgH₃-x wt.% Ti₃C₂ (x = 0, 3, 5, 7, and 9) were formed/synthesized by doping the as-prepared Ti₃C₂ into NaMgH₃ 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 NaMgH₃ 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 NaMgH₃. It is almost impossible to find the diffraction peaks belonging to lamellar-structure Ti₃C₂ in these five patterns due to the small amounts of Ti₃C₂ additive [34]. The other possibility is that the ball milling destroyed the multilayered structure of Ti₃C₂.

Therefore, the XRD results indicate the successful synthesis of the five composites without any other impurity peaks.

Figure 1. XRD patterns of (a) Ti_3AlC_2 and (b) as-prepared Ti_3C_2 . The insert is the SEM image of Ti_3C_2 .

Figure 2. XRD patterns of (a) pure NaMgH_3 , (b) NaMgH_3 -3 wt.% Ti_3C_2 , (c) NaMgH_3 -5 wt.% Ti_3C_2 , (d) NaMgH_3 -7 wt.% Ti_3C_2 , and (e) NaMgH_3 -9 wt.% Ti_3C_2 .

After assessing the phase components and morphology of NaMgH_3 -x wt.% Ti_3C_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 Ti_3C_2 remarkably decreases the hydrogen desorption temperature in contrast to pure NaMgH_3 (Figure 3a). The first- and second-step dehydrogenation

temperatures of NaMgH_3 -3 wt.% Ti_3C_2 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 Ti_3C_2 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 NaMgH_3 -x wt.% Ti_3C_2 (x = 0, 3, 5, 7, and 9) samples.

Combined with the TPD results (Figure 3b), more hydrogen desorption kinetic properties of NaMgH_3 undoped/doped with Ti_3C_2 are revealed. First, doping with 3 wt.% Ti_3C_2 reduces the onset dehydrogenation temperature of pure NaMgH_3 tremendously, from 350 °C to 250 °C. In particular, further increasing the content of Ti_3C_2 to 5, 7, or 9 wt.% allows around 3.5 wt.% H_2 to release (first-step decomposition reaction) below 350 °C. Importantly, the Ti_3C_2 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.% H_2 to 5.4, 5.3, 5.2, and 5.1 wt.% H_2 , for the NaMgH_3 -x wt.% Ti_3C_2 (x = 3, 5, 7, and 9) samples, respectively, which is mainly due to the dead weight of Ti_3C_2 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.% Ti_3C_2 exhibits the best dehydriding kinetic properties at 365 and 350 °C, desorbing 4.8 wt.% H_2 in 15 min and 3.4 wt.% H_2 in 5 min, respectively. However, for the pure NaMgH_3 , only 0.6 wt.% H_2 is released in 15 min at 365 °C. As the temperature decreases to 350 °C, the pure NaMgH_3 sample only desorbs 0.2 wt.% H_2 in 5 min.

As a result, it is obvious that doping of 7 wt.% Ti_3C_2 leads to a tremendous improvement in the dehydriding kinetic properties of NaMgH_3 . 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 (E_a) 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)).

$$\ln(\beta/T_p^2) = -E_a/RT_p + \ln(AR/E_a) \quad (3)$$

where β 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.

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)	
	NaMgH ₃ (First-Step)	NaMgH ₃ (Second-Step)
Undoped	158.45	165.16
7 wt.% Ti ₃ C ₂	114.08	139.40

Based on these data, the values of E_a of the first-step hydrogen desorption reaction of NaMgH₃ and NaMgH₃-7 wt.% Ti₃C₂ are calculated to be 158.45 and 114.08 kJ/mol, respec-

tively. 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_3C_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_3C_2 dopant by reducing the second-step dehydrogenation energy barrier.

The role played by unique lamellar-structure Ti_3C_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_3C_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_3C_2 . The following EDS analyses (Figure 5f) prove the existence of NaMgH_3 and Ti_3C_2 . Based on the significant reduction of operating temperature and the superior enhancement of dehydrogenation kinetics properties in the Ti_3C_2 doped sample, it can be proposed that Ti_3C_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_3C_2 -doped $\text{Mg}(\text{BH}_4)_2$ [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 kinetic properties of the 7 wt.% Ti_3C_2 doped sample can be mainly due to the unique lamellar-structure. The detailed microstructure information of Ti_3C_2 could not be easily revealed after the re/dehydrogenation process due to the small amounts of Ti_3C_2 additive; thus, the catalytic mechanism remains undiscovered. We hope that the catalytic mechanism of NaMgH_3 -x wt.% Ti_3C_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_3C_2 ; EDS results of (c) NaMgH_3 and (f) NaMgH_3 -7 wt.% Ti_3C_2 .

Figure 6 shows the isothermal hydrogenation curves of pure NaMgH_3 and NaMgH_3 -7 wt.% Ti_3C_2 samples at different temperatures. It is obvious that the hydrogen absorption kinetics of NaMgH_3 can be enhanced by doping with Ti_3C_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_3C_2 samples at 300 $^{\circ}\text{C}$. The 7 wt.% Ti_3C_2 -containing composite can quickly absorb approximately 3.5 wt.% H_2 within

6 s. However, the pure NaMgH₃ displays unacceptably slow re-hydrogenation kinetics, storing 3.0 wt.% H₂ 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.% H₂ stored for NaMgH₃ and NaMgH₃-7 wt.% Ti₃C₂ 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 Ti₃C₂-containing sample exhibits excellent hydrogenation kinetics, absorbing 4.9 wt.% H₂ in 8 min, confirming that the first- and second-step hydrogen absorption kinetics have been further improved. The hydrogenation capacity of pure NaMgH₃ is found to be 4.2 wt.% H₂ in 15 min, with the second-step hydrogen absorption kinetics still being sluggish. In summary, Ti₃C₂ has obvious catalytic efficiency on the enhancement of both first- and second-step hydrogenation kinetic properties of NaMgH₃ under 80 bar H₂ at 300, 350, and 400 °C.

Figure 6. Isothermal hydrogenation curves of pure NaMgH₃ and NaMgH₃-7 wt.% Ti₃C₂ at different temperatures. (a) 300 °C (b) 350 °C (c) 400 °C.

The reversible dehydrogenation properties of NaMgH₃ are remarkably enhanced because of the superior catalytic activity of Ti₃C₂ with lamellar-structure. To obtain the cycling properties of NaMgH₃ 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 NaMgH₃ desorbs 5.5 wt.% H₂ in 15 min at 400 °C. After hydrogenation at 400 °C under 60 bar H₂, it releases only 2.6 wt.% H₂ in 60 min, losing approximately half of its initial capacity. The dehydrogenation kinetic property of pure NaMgH₃ 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.% H₂ were desorbed in 20 min, respectively. The dehydrogenation kinetics and capacity of pure NaMgH₃ in the latter three cycles are recovered from the poor second cycle. For the Ti₃C₂ doped NaMgH₃, in the first cycle, about 5.1 wt.% H₂ is released in 5 min. The difference is that the Ti₃C₂ doped sample does not suffer tremendous capacity loss in the second cycle. In the latter four cycles, the Ti₃C₂ doped sample desorbs 4.3, 4.4, 4.4, and 4.6 wt.% H₂ in 20 min, respectively. In five cycles, pure NaMgH₃ suffers a huge capacity loss from 5.5 to 4.1 wt.% H₂, 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, Ti₃C₂ can relieve the degradation of dehydrogenation capacity to some extent due to its improved dehydrogenation kinetics. However, it is clear that the lamellar-structure Ti₃C₂ can effectively enhance the cycling stability of NaMgH₃ in five cycles. The expectation of the dehydrogenation kinetics and cycling stability of NaMgH₃ remaining unchanged is not achieved. Therefore, further investigation of enhancing the cycle stability of NaMgH₃ should be explored.

Figure 7. Isothermal dehydrogenation cycle curves of (a) NaMgH₃ and (c) NaMgH₃-7 wt.% Ti₃C₂ at 400 °C; cycle capacity curves of (b) NaMgH₃ and (d) NaMgH₃-7 wt.% Ti₃C₂.

The pronounced degradation of dehydrogenation performance and hydrogen capacity in the second cycle for the pure NaMgH₃ is abnormal. There should be some phase separations during hydrogenation after the first cycle dehydrogenation. Furthermore, it was found that pure NaMgH₃ would segregate into separate NaH and Mg during the high-temperature cycling tests [39]. In order to confirm the phase transformation of Ti₃C₂ doped/undoped NaMgH₃ samples during hydrogen storage process, XRD characterization was carried out for the re-hydrogenated sample. In Figure 8a,b, the NaMgH₃, NaH, Mg, and MgO phases can be seen in the XRD patterns of the pure NaMgH₃ 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 NaMgH₃ 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 H₂, making the formation of MgH₂ and NaMgH₃ much more difficult, thereby decreasing the hydrogen capacity of NaMgH₃ [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 NaMgH₃. 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 NaMgH₃ 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 NaMgH₃-7 wt.% Ti₃C₂ sample displays the diffraction peaks of NaMgH₃, MgH₂, and MgO, without any diffraction peaks belonging to NaH (Figure 8c,d). The weak diffraction peaks of MgH₂ 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 NaMgH₃ 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 Ti₃C₂-doped NaMgH₃ sample (Figure S1c,d). Herein, the XRD results and dehydrogenation observation indicate that the existence of lamellar-structure Ti₃C₂ can effectively prevent Na from separating Mg to form the insular NaH layer, largely preserving the cycling dehydrogenation properties of NaMgH₃.

Figure 8. XRD patterns of pure NaMgH₃ before the (a) second and (b) third dehydrogenations at 400 °C. XRD patterns of NaMgH₃-7 wt.% Ti₃C₂ before the (c) second and (d) third dehydrogenations at 400 °C.

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	NaNO ₃	282 *
Thermochemical	Oxidation of Co ₃ O ₄	1055 *
	NaMgH ₃ -7 wt.% Ti ₃ C ₂	2562
Metal hydrides	NaAlH ₄	711 *
	Mg ₂ NiH ₄	1157 *
	Mg ₂ FeH ₆	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 <https://www.mdpi.com/article/10.3390/pr9101690/s1>, Figure S1: Photographs of pure NaMgH₃ and NaMgH₃-7 wt.% Ti₃C₂ (a,c) before and (b,d) after dehydrogenation at 400 °C. Figure S2: DSC profiles of (a) pure NaMgH₃ and (b) NaMgH₃-7 wt.% Ti₃C₂ at a heating rate of 5 °C/min.

Author Contributions: The experimental work, original draft preparation, and modification, Z.H. (Zhouming Hang) and Z.H. (Zhencan Hu); methodology for experiments, manuscript review, and editing, X.X. and R.J.; conceptualization and data analysis, resources, project administration, and funding acquisition, X.X.; data analysis, M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: This work is supported by the National Key Research and Development Program (2018YFB1502100), the National Natural Science Foundation of China (52171223), and the Zhejiang Provincial Natural Science Foundation of China (LZ21E010002).

Conflicts of Interest: The authors declare no conflict of interest.

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