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Ca(BH₄)₂–LiBH₄–MgH₂: a novel ternary hydrogen storage system with superior long-term cycling performance[†]

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A ternary hydrogen storage system, of superior cyclic stability and high capacity, was developed from a mixture of Ca(BH₄)₂, LiBH₄ and MgH₂ in molar ratios of 1:2:2. Investigation on both non-isothermal and isothermal hydrogen desorption/absorption properties shows that the hydrogen desorption starts from 320 °C and completes at 370 °C under a heating rate of 2 °C min⁻¹, releasing *ca.* 8.1 wt% H₂. The finishing temperature of desorption is much lower and the capacity much higher than any of the twohydride mixtures in the ternary system. In particular, hydrogenation of the ternary system initiates at an extremely low temperature of ca. 75 °C and the onset dehydrogenation temperature is significantly reduced by 90 °C after the initial dehydrogenation/hydrogenation cycle, which is ascribed to the formation of an active dual-cation hydride of CaMgH_{3.72} for dehydrogenation in the hydrogenation process. There is ca. 7.6 wt% H₂ absorbed at 350 °C and 90 bar H₂ for 18 h for the system postdehydrogenated at 370 °C for 30 min, demonstrating a reversibility of over 94%. The capacity seems to fade mainly in the initial few cycles and stabilizes after further cycling. The reversibility is as high as 97% and a dehydrogenation capacity of ca. 6.2 wt% H₂ at the 10th cycle. Favourable kinetics and thermodynamics of hydrogen desorption/absorption are achieved, which are responsible for the low completion temperature and the superior cycling performance. Mechanisms of the improved dehydrogenation/hydrogenation properties including the cyclic behaviour of the system are also proposed in relation to microstructural analyses.

Introduction

Ever-growing needs in energy, the cumulative depletion of fossil fuels and the rapid increase of greenhouse gases have prompted the development of clean and renewable energy sources. Hydrogen is considered one of the most promising clean energy carriers. The US Department of Energy's (DOE) targets renewed in 2009 proposed that >5.5 wt% hydrogen storage capacity with favourable cycling properties has been deemed necessary for commercial development of vehicles powered by H₂/O₂ proton exchange membrane fuel cells.1 Alkali and alkali-earth metal borohydrides, which possess high gravimetric and volumetric hydrogen densities, have attracted extensive attention as promising hydrogen storage materials.2-4 Among these, lithium borohydride, LiBH4, has been widely investigated due to its high gravimetric hydrogen density (18.5 wt%), but its dehydrogenation is hampered by unfavourable thermodynamics (74 kJ mol⁻¹ H₂), leading to a desorption temperature over 400 °C. Its absorption kinetics is also sluggish, even at 150-350 bar of hydrogen at 600-650 °C.5 The calculated dehydrogenation reaction enthalpy of calcium borohydride, Ca(BH₄)₂, is 32 kJ $mol^{-1} H_2$,⁶ which is slightly lower than the appropriate value for hydrogen desorption reaction for fuel cells (*ca.* 39 kJ mol⁻¹ H₂).⁷

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† Electronic supplementary information (ESI) available: XRD pattern of the as-synthesized Ca(BH₄)₂, XRD patterns and FTIR spectra of the selected dehydrogenation intermediates and product of the Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ ternary system at different dehydrogenation temperatures; SEM images of the as-milled Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ mixture, and its products dehydrogenated at 370 $^\circ C$ for 30 min, and re-hydrogenated at 350 $^\circ C$ for 18 h after different cycles; XRD patterns of the dehydrogenation and re-hydrogenation products of the ternary system dehydrogenated at 370 °C for 30 min, and hydrogenated at 350 °C for 18 h for different cycles, as-synthesized CaMgH_{3.72}, CaMgH_{3.72} heated to 260 $\,^\circ\text{C}$ and the 1^{st} round re-hydrogenated product of the ternary system heated to 260 °C and dwelling for 10 min; dehydrogenation curves of the individual CaMgH_{3.72} and Ca(BH₄)₂ + 2LiBH₄ + $2MgH_2$ system of the 1st and the 2nd round cycles, and the initial dehydrogenation curves of $(1 - 1.5x)Ca(BH_4)_2 + 2LiBH_4 + (2 - x)MgH_2 +$ xCaMgH_{3,72} (x = 0.1, 0.2) systems; tables of desorption rates of the main desorption stages of the different systems and the apparent activation energy (E_a) and the dehydrogenation reaction enthalpy $(\triangle H)$ of the as-milled different systems. See DOI: 10.1039/c3ta12472j

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Both the gravimetric and volumetric hydrogen densities (*ca.* 11.4 wt% and 130 kg m⁻³, respectively) of Ca(BH₄)₂ are also favourable as a hydrogen storage material.^{8,9}

Ca(BH₄)₂ decomposes into CaB₆ and CaH₂ with 9.6 wt% of hydrogen evolved upon heating to 500 °C.¹⁰ The onset decomposition temperature is theoretically <100 °C at 1 bar H₂,¹¹ which seems to satisfy the requirement for practical applications.¹ However, its sluggish kinetics, due to a high reaction barrier, leads to a high operating temperature (350 °C) and poor reversibility (*e.g.*, an initial reversibility of 60% requires hydrogenation at 400 °C for 48 h under 700 bar of H₂ with the addition of TiCl₃ and Pd as catalysts).¹²

To lower the operating temperature and improve the reversibility of Ca(BH₄)₂, various methods have been adopted, such as the addition of catalysts,¹³⁻¹⁵ combination with metal amide hydrides^{16,17} and other borohydrides.¹⁸⁻²⁰ Our recent work reveals that the main desorption temperature of Ca(BH₄)₂ is reduced by more than 50 °C via an in situ formed super-fine TiO₂ and a porous structure by the introduction of Ti(OEt)₄.¹⁴ However, the reversibility and reversible capacity still need to be further improved. The combination of Ca(BH₄)₂ with LiBH₄ was found to possess a decreased dehydrogenation temperature and an increased reversible hydrogen storage capacity, controversially due to the existence of eutectic melting18 or the formation of a dual-cation borohydride LiCa(BH₄)₃.¹⁹ Enhanced kinetics is also obtained from a mixture of $Ca(BH_4)_2$ and $Mg(BH_4)_2$, which is superior to either of the individual constituents.²⁰ However, the previous reported improvements in hydrogen desorption/ absorption properties of binary Ca(BH₄)₂ systems with other hydrides usually require catalysts,16,18 which reduces the overall capacity to some extent. Even for some high capacity systems, the reversibility is still very limited. For example, only 3.2 wt% H_2 was absorbed for a 0.02NbF₅-doped 0.4LiBH₄ + 0.6Ca(BH₄)₂ composite under 400 $^{\circ}C$ and 90 bar of H₂ in the first cycle,18 though its theoretical hydrogen content is as high as ca. 8.0 wt%.

The hydrogen storage capacity of MgH₂ is 7.6 wt%, lower than those of either $LiBH_4$ or $Ca(BH_4)_2$. The onset and completion dehydrogenation temperatures of pristine MgH₂ are high, and its kinetics is relatively low.²¹ However, MgH₂ plays effective roles in improving the hydrogen sorption properties of LiBH₄ and Ca(BH₄)₂. Vajo et al.²² proposed firstly a concept of destabilizing the $2LiBH_4 + MgH_2$ system so that $LiBH_4$ can be reversibly dehydrogenated and re-hydrogenated with a reduced reaction enthalpy by the addition of MgH₂. It is suggested that the formation of MgB₂ in the system due to the introduction of MgH₂ stabilizes the dehydrogenated state and destabilizes effectively the LiBH₄. This approach is also helpful in identifying ways of improving the sorption properties of $Ca(BH_4)_2$. For the Ca $(BH_4)_2$ + MgH₂ system, studies from different groups^{23,24} show that the dehydrogenation pathway, in other words, the dehydrogenation product, depends on the dehydrogenation parameters, such as the presence of hydrogen in the reaction atmosphere, or the addition of additives/catalysts. The onset dehydrogenation temperature of the Ca(BH₄)₂ + MgH₂ system is not visibly different from that of $Ca(BH_4)_2$ alone. However, the initial reversibility of the dehydrogenation/hydrogenation of the

Ca(BH₄)₂ + MgH₂ system was significantly improved compared with that of Ca(BH₄)₂, despite the different synthesis methods and dehydrogenation processes of the systems tested.^{23,24} An initial reversibility of 60% was obtained at 350 °C and 90 bar of H₂ for 24 h without association of catalysts for the Ca(BH₄)₂ + MgH₂ system post-dehydrogenated at 400 °C, whereas Ca(BH₄)₂ was not reversible under the same conditions.²⁴ However, the reversibility of the Ca(BH₄)₂ + MgH₂ system is still too harsh, even without considering the long-term cyclic properties.

So far, progress has been made in improving hydrogen sorption capacity, reversibility and reducing the operating temperature of LiBH₄ and Ca(BH₄)₂ systems, via catalysis, hydride mixing, and reactive hydride composites, etc. However, previous investigations of the reversibility focus mostly on the initial cycle. In the present study, we develop a ternary system of $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ (in molar ratios). By simply mixing these three hydrides, the obtained system possesses favourable overall hydrogen storage performance, including a relatively narrow temperature range and a low completion temperature of dehydrogenation, a significantly low hydrogenation temperature, especially a remarkably reduced dehydrogenation temperature after the initial cycle with superior long-term cyclic stability. A systematic study was performed on the nonisothermal and isothermal hydrogen desorption/absorption properties of the ternary system, along with microstructural characterization during desorption/absorption. A mechanism for the sorption process is proposed for further improvement of the system.

Experimental section

LiBH₄ (95%) and MgH₂ (98%) were commercially purchased from Sigma-Aldrich and Alfa-Aesar, respectively. Ca(BH₄)₂ (96%) was synthesized by the metathesis reaction of CaCl₂ and NaBH₄ in tetrahydrofuran according to our previous work.¹⁴ A mixture of Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ in molar ratios was ballmilled for 24 h on a planetary ball mill (QM-3SP4, Nanjing) rotating at 500 rpm. The ball-to-powder weight ratio was 120 : 1.

X-ray diffraction (XRD, Phillips X' pert Pro) using Cu K α radiation at 40 kV/40 mA with a step width of 0.05° was carried out to determine the phase structure of the as-milled Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ and its products at different desorption/ absorption stages and cycling conditions. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Tensor 27 unit. A scanning electron microscope (SEM, Hitachi-4800, Japan) equipped with an energy-dispersive spectrometer (EDS) was applied for morphology and composition characterization of the as-milled Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ and its desorption/ absorption products at different cycles.

A homemade temperature-programmed desorption (TPD) instrument was employed to measure the temperature-dependent hydrogen desorption of the as-milled product. The sample was loaded into a tube reactor housed in a tube furnace, and heated from RT (room temperature) to 550 °C. To evaluate the apparent activation energy (E_a), various heating rates (1, 2, 3, 5, 7.5 °C min⁻¹) were used. DSC (differential scanning calorimetry) measurement was performed on a Netzsch STA 200 F3

instrument to obtain the thermal properties and enthalpy change during the hydrogen desorption from RT to 500 °C. A constant flow of pure argon was supplied as protective gas for TPD and DSC tests during heating. Both non-isothermal and isothermal sorption properties were evaluated by volumetric method on a homemade Sieverts-type apparatus at a temperature range of RT to 320-550 °C. In the non-isothermal testing, the temperature was elevated at a rate of 2 °C min⁻¹ for dehydrogenation and a rate of 1 °C min⁻¹ for hydrogenation. Static vacuum and a hydrogen pressure of 90 bar were used for dehydrogenation and hydrogenation, respectively. For isothermal testing, samples for dehydrogenation and hydrogenation were all heated at a rate of 10 $^\circ C\ min^{-1}$ to the given temperature and dwelt during the measurement. For hydrogenation testing, samples were post-dehydrogenated at a heating rate of 2 °C min⁻¹ to 370 °C and dwelling for 30 min, and then hydrogenated at 350 °C for 18 h.

For comparison, selected parallel experiments were also performed on the individual $Ca(BH_4)_2$, $2LiBH_4 + MgH_2$, $Ca(BH_4)_2 + MgH_2$ and $Ca(BH_4)_2 + 2LiBH_4$ mixtures, which were ball-milled under identical conditions to the ternary $Ca(BH_4)_2 +$ $2LiBH_4 + 2MgH_2$ system. To avoid air and moisture contamination, all of the samples were manipulated in a glovebox (MBRAUN). The concentration of O₂ and H₂O in the glovebox was below 1 ppm.

Results and discussion

Phase transformation during ball milling

Fig. 1 shows the XRD pattern of the ball-milled ternary Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ system. For comparison, those of the ballmilled Ca(BH₄)₂, Ca(BH₄)₂ + MgH₂ and 2LiBH₄ + MgH₂ systems are also shown. The as-synthesized Ca(BH₄)₂ is composed of α , β and γ polymorphic hybrid with β -Ca(BH₄)₂ as the main phase,¹⁴ as shown in Fig. S1.† However, the pattern of the ball-milled Ca(BH₄)₂ (Fig. 1) is identical to single β -Ca(BH₄)₂,²⁵ indicating a phase transformation from α/γ - to β -Ca(BH₄)₂ during the ball-



Fig. 1 XRD patterns of the ball-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$, $Ca(BH_4)_2$, $Ca(BH_4)_2 + MgH_2$ and $2LiBH_4 + MgH_2$ systems.

milling process, which is in agreement with the results reported by other researchers.^{9,13} Different from the individual $Ca(BH_4)_2$, the polymorphic $Ca(BH_4)_2$ in the ternary $Ca(BH_4)_2 + 2LiBH_4 +$ MgH₂ system is transformed to single γ -Ca(BH₄)₂ after ball milling. Whereas, for the ball-milled $Ca(BH_4)_2 + MgH_2$ system, besides the dominant phase of γ -Ca(BH₄)₂, a small amount of β -Ca(BH₄)₂ remains, and the peaks of γ -Ca(BH₄)₂ are broader than those in the ternary system, indicating improved crystallinity of γ -Ca(BH₄)₂ in the ternary system. Therefore, it is inferred that the introduction of either single MgH₂ or the LiBH₄ + MgH₂ mixture renders a crystal transformation from α / β -Ca(BH₄)₂ to γ -Ca(BH₄)₂ during the present ball milling. Conversion from α/β - to γ -Ca(BH₄)₂ by ball milling was also mentioned in the VF₄-doped Ca(BH₄)₂¹⁵ and Ca(BH₄)₂ + *x*LiBH₄¹⁸ systems. However, differently, major β -Ca(BH₄)₂ with minor γ -Ca(BH₄)₂ were obtained in a ball-milled Ca(BH₄)₂ + MgH₂ system reported by Minella et al.,²⁶ which is probably due to its shorter ball-milling time (3 h) than the present (24 h). Moreover, the diffraction peaks in Fig. 1 and S1[†] show that except for the polymorphic transformation of $Ca(BH_4)_2$, diffraction peaks of LiBH₄ and MgH₂ are visible in either the ternary system or the binary systems after ball milling, indicating that there is almost no chemical reaction taking place between the different hydrides during ball milling.

Hydrogen desorption/absorption properties

Fig. 2 shows the TPD (a) and volumetric desorption (b) results of the ball-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system, along with the corresponding performances of the ball-milled $Ca(BH_4)_2$, $Ca(BH_4)_2 + MgH_2$ and $2LiBH_4 + MgH_2$ systems. As seen from Fig. 2a, all systems exhibit a distinguishable multi-step dehydrogenation process. The ternary system starts to dehydrogenate at *ca.* 320 °C and completes at *ca.* 370 °C in a narrow temperature range of *ca.* 50 °C. Three peaks, centered at 339,



Fig. 2 TPD (a) and volumetric dehydrogenation (b) curves of the ball-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$, $Ca(BH_4)_2$, $Ca(BH_4)_2 + MgH_2$ and $2LiBH_4 + MgH_2$ systems.

349 and 358 °C, which are partially overlapped, are observed for the ternary system. The onset dehydrogenation temperature of the ternary system is almost the same as those of the individual $Ca(BH_4)_2$ and $Ca(BH_4)_2 + MgH_2$ systems, and is slightly higher than that of the 2LiBH₄ + MgH₂ system as seen from Fig. 2, and is comparable to pristine MgH₂,²¹ but is certainly lower than LiBH₄.⁵ Though the first step of the individual Ca(BH₄)₂ and $Ca(BH_4)_2 + MgH_2$ systems, which is also the main dehydrogenation step, is also located in the same temperature range of 320-370 °C as that of the ternary system, broad humps are vaguely seen in their TPD curves at temperatures higher than 370 °C in a large temperature range up to at least 450 °C. The second-step dehydrogenation of the two systems completes at a much higher temperature than the completion dehydrogenation temperature of the ternary system (370 °C). For the 2LiBH₄ + MgH₂ system, there are two distinguishable peaks visibly observed. The relatively sharp peak at 310-340 °C is proposed from the decomposition of MgH₂ and the broad peak ranging from 350-420 °C is from the dehydrogenation of LiBH₄ by reference to a previous result obtained from a catalyzed LiBH₄-MgH₂ system,²⁷ in which LiBH₄ and MgH₂ interacted with each other and lowered the main dehydrogenation temperature of both of them. It is further seen in Fig. 2a that the decomposition peak of MgH₂ occurring in the 2LiBH₄ + MgH₂ system is not observed in the same temperature range in both the $Ca(BH_4)_2$ + $2LiBH_4 + 2MgH_2$ and $Ca(BH_4)_2 + MgH_2$ systems. This indicates that the existence of either the Ca(BH₄)₂ + LiBH₄ mixture or the individual $Ca(BH_4)_2$ does not facilitate the decomposition of MgH₂ toward a low temperature as LiBH₄ does in the 2LiBH₄ + MgH₂ system. But anyway, it is clear that the Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ ternary system possesses a considerably lower completion dehydrogenation temperature than the other systems. The dehydrogenation of the ternary system is not a simple accumulation of the desorption of its composed individual hydrides. The composed hydrides interacted with each other in the dehydrogenation process and played a synergetic role in lowering the dehydrogenation temperature range.

The volumetric dehydrogenation curves shown in Fig. 2b confirms that the main dehydrogenation of the ternary system almost completes at 370 °C with *ca.* 8.1 wt% H₂ released, which is 83% of the theoretical capacity of the system. Further increasing the temperature to 550 °C only results in an additional desorption of 1.6 wt% H₂. However, for the individual Ca(BH₄)₂ and Ca(BH₄)₂ + MgH₂ systems, there is only 5.7 and 6.2 wt% H₂, respectively, upon heating to 370 °C. For the 2LiBH₄ + MgH₂ system, dehydrogenation liberates only 2.7 wt% H₂ in the 1st step at 300–330 °C, originated from the decomposition of MgH₂ according to a previous study,²⁷ only *ca.* 4.0 wt% H₂ in total up to 370 °C, and 8.1 wt% H₂ till *ca.* 420 °C. Therefore, the ternary system not only shows lower completion temperature of dehydrogenation, but also much higher dehydrogenation capacity at a given temperature than the others.

DSC curves of the as-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$, $Ca(BH_4)_2$, $Ca(BH_4)_2 + MgH_2$ and $2LiBH_4 + MgH_2$ systems are presented in Fig. 3. It is seen that all reactions involved in the as-milled ternary system are endothermic, indicating that the system may be mostly reversible. The peak centered at 120 °C is



Fig. 3 DSC curves of the as-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$, $Ca(BH_4)_2$, $Ca(BH_4)_2 + MgH_2$, $2LiBH_4 + MgH_2$ systems and the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system after 1st round hydrogenation (a); the Gaussian–Lorentzian fitting line of the DSC curve for the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system (b). Regions of A–D are the domains of integration in calculating the reaction enthalpy.

ascribed to the phase conversion of LiBH₄ from orthorhombic (o) to hexagonal (h) according to a previous report.²⁷ Similar peaks also exist in the 2LiBH₄ + MgH₂ system. The peak centered at 200 °C is assigned to the eutectic melting of Ca(BH₄)₂ and LiBH₄.¹⁸ The formation of the eutectic melt may be the reason why the LiBH₄ in the ternary system is not effective in lowering the dehydrogenation temperature of MgH₂ as it does in the $2LiBH_4 + MgH_2$ system. The sharp peak centered at 340 °C and the broad peak around 360 °C correspond to different dehydrogenation stages. Moreover, careful observation shows that the broad peak is composed of two partially overlapping peaks. The appearance of three endothermic reactions for dehydrogenation of the ternary system is also consistent with the appearance of three peaks in its TPD curve where the two in the high temperature range are mostly overlapped. The sharp peak occurring at ca. 290 °C in the 2LiBH₄ + MgH₂ system, which is ascribed to the melting of h-LiBH₄ according to the previous report,²⁷ does not occur in the ternary system, due probably to its eutectic melting with $Ca(BH_4)_2$ at a low temperature of 200 °C as mentioned before. In addition, the sharp peak centered at 340 °C in the ternary system is located at a slightly higher temperature than a similar one in the 2LiBH₄ + MgH₂ system, which is also consistent with the TPD result that the 1st-step dehydrogenation of the ternary system is at a slightly higher temperature than that of the 2LiBH₄ + MgH₂ system. In addition, the first endothermic peak of either the $Ca(BH_4)_2 + MgH_2$ system or the individual $Ca(BH_4)_2$ is located at higher temperature than the one of the ternary system. The existence of the downward humps at ca. 400 and 430 °C in the Ca $(BH_4)_2$ + MgH₂ system and individual Ca $(BH_4)_2$, respectively, and the broad peak in the 2LiBH₄ + MgH₂ system are also in good agreement with the features of the 2nd-step dehydrogenation obtained from their TPD results.

The isothermal desorption curves of the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ and the reference systems performed at 320 °C are shown in Fig. 4. It is seen that the hydrogen desorption kinetics of the ternary system is much superior to the others. There is *ca*.



Fig. 4 Isothermal desorption curves of the ball-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$, $Ca(BH_4)_2$, $Ca(BH_4)$

6.9 wt% H₂ evolved within 110 min for the ternary system, whereas there are only 5.4, 5.6, 3.6 and 3.4 wt% H₂ evolved for the Ca(BH₄)₂, Ca(BH₄)₂ + MgH₂, Ca(BH₄)₂ + 2LiBH₄ and 2LiBH₄ + MgH₂ systems, respectively, under the same conditions. The desorption rates of the main desorption stages of the different systems obtained from the tangent slopes of the main desorption parts of the curves are summarized in Table S1 in ESI.† The much higher dehydrogenation rate of the ternary system also indicates that mutual interaction exists among the Ca(BH₄)₂, LiBH₄ and MgH₂ phases during the isothermal process which leads to the evident improvement of dehydrogenation kinetics.

Fig. 5 represents the absorption curves upon heating to $350 \,^{\circ}\text{C}$ at a heating rate of $1 \,^{\circ}\text{C} \min^{-1}$ and dwelling for 18 h at 90 bar of H₂ of the Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ system as well as the individual Ca(BH₄)₂ which are all post-dehydrogenated at 370 $\,^{\circ}\text{C}$ for 30 min (a), and their isothermal hydrogenation curves heating to 350 $\,^{\circ}\text{C}$ at a rate of 10 $\,^{\circ}\text{C} \min^{-1}$ and dwelling for 18 h at 90 bar of H₂ (b). As shown in Fig. 5a, hydrogenation



Fig. 5 Hydrogenation curves of the Ca(BH₄)₂ + 2LiBH₄ + 2MgH₂ system as well as individual Ca(BH₄)₂ upon heating to 350 °C at a heating rate of 1 °C min⁻¹ and dwelling for 18 h (a) and isothermal dwelling at 350 °C for 18 h with a heating rate of 10 °C min⁻¹ to 350 °C (b).

initiates at *ca*. 75 °C for the ternary system, and there is already 3.8 wt% H₂ absorbed into the post-dehydrogenated product upon heating to 350 °C. There is almost no hydrogen absorbed for the individual $Ca(BH_4)_2$ under the same heating conditions. Fig. 5b further shows that the post-dehydrogenated $Ca(BH_4)_2$ + 2LiBH₄ + 2MgH₂ system absorbs 3.3 wt% H₂ within 60 min at 350 °C (including the *ca.* half an hour of heating process), meanwhile, the absorbed H₂ is only 0.8 wt% for the individual $Ca(BH_4)_2$. When the absorption time is prolonged to 1080 min, there is ca. 7.6 wt% H₂ absorbed for the ternary system, which is equivalent to 94% of the hydrogen evolved during the initial dehydrogenation (8.1 wt% as seen from Fig. 2b), whereas there is only 3.4 wt% H₂ absorbed for the individual $Ca(BH_4)_2$ under the same conditions (Fig. 5b). In addition, the contents of hydrogen absorbed after 18 h of dwelling at 350 °C with different heating rates are almost the same for both the two systems, as seen from Fig. 5a and b. The present result shows that both the initial reversibility and hydrogenation capacity of the ternary system are evidently higher than those of the reported catalyzed-Ca(BH₄)₂ and Ca(BH₄)₂ combination systems to date, such as the $0.02NbF_5 + Ca(BH_4)_2$ (a hydrogenation capacity of 3.0 wt% H2 at 400 °C and 90 bar for 24 h with a reversibility around 40%),¹³ 0.02NbF₅ + 0.6Ca(BH₄)₂ + 0.4LiBH₄ (a hydrogenation capacity of 3.2 wt% H₂ at 400 °C and 90 bar for 20 h with a reversibility around 40%)¹⁸ and Ca(BH₄)₂ + MgH₂ (a hydrogenation capacity of 4.9 wt% H₂ at 350 °C and 90 bar H₂ for 24 h with a reversibility around 60%)²⁴ systems, despite the facts that longer hydrogenation time with higher or at least the same hydrogenation temperature were used in the reported systems.

The cyclic properties of the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system are shown in Fig. 6a. It is found that the reversible hydrogen capacity decreases from 8.1 to 6.6 wt% in the first 5 cycles, a capacity fading of less than 0.4 wt% H₂ per cycle, and then tends to be stable in the following cycles (from 6.6 to 6.2 wt% in the further 5 cycles), a capacity fading of less than 0.1 wt% H₂ per cycle. Retention of 77% is attained after 10 cycles. The retention after 10 cycles of the present system is much higher than the initial reversibility of the 0.02NbF₅ + Ca(BH₄)₂, 0.02NbF₅



Fig. 6 Cycling properties of the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system: (a) the dehydrogenation capacity at different dehydrogenation/hydrogenation cycles; (b) dehydrogenation curves at the 1st, 2nd and 10th cycles upon heating to 370 °C and dwelling for 30 min; (c) hydrogenation curves of the 1st and 9th cycles upon heating to 350 °C and dwelling for 18 h at 90 bar H₂.

+ 0.6Ca(BH₄)₂ + 0.4LiBH₄ and Ca(BH₄)₂ + MgH₂ systems as mentioned previously.

An interesting finding worthy of note is that, after the first desorption/absorption cycle, the starting dehydrogenation temperature of the ternary system in the following cycles up to the 10 cycles is remarkably lowered to 230 °C, reduced by ca. 90 °C compared with the initial one, as shown in Fig. 6b, the dehydrogenation curves of the 1st, 2nd and 10th cycles upon heating to 370 °C and then dwelling for 30 min. Moreover, Fig. 6b further shows that the dehydrogenation features of the 2nd and 10th cycles are almost identical in the initial dehydrogenation process at temperature lower than ca. 300 °C. Slightly decreased capacity and kinetics occur only at temperature over ca. 300 °C. This phenomenon indicates that there should be some highly reversible hydrides with comparatively low dehydrogenation temperature after the first round hydrogenation. The 1st and 9th hydrogenation curves in the heating and dwelling process are shown in Fig. 6c. It is seen that the hydrogen absorbed at the 1st and 9th cycles are 3.8 wt% and 2.7 wt%, respectively, during the heating to 350 °C. The difference in the amount of hydrogen absorbed between the 1st and 9th cycles is slightly increased with the temperature, indicating that the content of hardly hydrogenated phase increases with cycling. With a further isothermal hydrogenation at 350 °C for 18 h, the total amounts of hydrogen absorbed are 7.6 and 6.2 wt% for the 1st and 9th cycles, respectively, which are also almost the equilibrium values. Combining the dehydrogenation capacity of the 9th cycle shown in Fig. 6a, it is found that the reversibility of the 9th cycles is 97%, which is slightly higher than that of the initial one. It reveals that the reversibility of the ternary system is significantly high, especially after the initial several cycles. Such superior long-term cycle performance and high capacity are rarely found in the previous literature related to the light metal boron hydride systems based on the best of our knowledge.

Chemical reactions in the dehydrogenation/hydrogenation process and mechanism of the improved hydrogen storage properties

XRD analysis of the selected dehydrogenation intermediates of the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ ternary system are shown in Fig. S2a.[†] The intermediates at 250 °C are still composed of γ -Ca(BH₄)₂, LiBH₄ and MgH₂. There is no newly formed crystal phase detected in the intermediates at 250-320 °C, though ca. 0.67 wt% H₂ is released (Fig. 2b). A small amount of H₂ releasing from Ca(BH₄)₂ might not change the main crystal structure of $Ca(BH_4)_2$,¹⁴ or it is probable that an amorphous phase is formed. However, when the temperature is increased by only 10 °C to 330 °C, new diffraction peaks originating from CaH₂ and Mg appear, along with those of the remaining Ca(BH₄)₂, LiBH₄ and MgH₂. The relative peak intensity of Ca(BH₄)₂ is rapidly weakened, whereas that of the LiBH₄ phase remains the same. The phenomenon implies that $Ca(BH_4)_2$ reacts firstly with partial MgH₂, generating CaH₂, Mg and H₂. Further elevating the temperature by only another 10 °C to 340 °C, the diffraction peaks of Ca(BH₄)₂, LiBH₄ and MgH₂ all disappear in the intermediates, leaving only those of the CaH₂ and Mg phases.

However, FTIR test (Fig. S3[†]) shows that B-H bonds exist in the intermediates, indicating the formation of amorphous B-H containing intermediates accompanying the evident liberation of H₂ (Fig. 2b). For the intermediates at 350–370 °C, CaH₂ and Mg are still the only crystal phases detected, and a B-H containing phase is also detected by FTIR test (Fig. S3[†]) in the intermediates at 350 °C, whereas there is almost no B-H containing phase detected in intermediates at 370 °C. Combining its dehydrogenation curve (Fig. 2b), this is reasonable, as dehydrogenation has almost completed at 370 °C. The B-H containing phase decomposed and no boron-containing phase is detected by XRD in the intermediates of Ca(BH₄)₂ at 400 °C due to its amorphous feature.²⁸ For the dehydrogenation product at 550 °C, besides the remaining CaH₂ and Mg phases, CaB₆ and LiH are also detected. Fig. S2b[†] shows its amplified pattern, in which diffractions of CaB₆ and LiH are clearly seen. Due to the poor crystallinity of CaB₆, their diffraction peaks are broad. Certainly, there is no B-H containing phase detected by FTIR (Fig. S3[†]) due to the full decomposition of the B-H containing phase. Formation of nanocrystalline CaB₆ was also reported by Kim et al.²⁴ in the dehydrogenation product of $Ca(BH_4)_2$ at 480 °C.

Based on the above analyses, the overall reaction process of the ternary system is proposed to be:

$$\begin{split} Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2 \xrightarrow[\text{RT-550 °C}]{} \\ & 1/3CaH_2 + 2/3CaB_6 + 2LiH + 2Mg + 26/3H_2 \end{split}$$

The theoretical dehydrogenation capacity based on the equation is calculated to be 10.1 wt%, which is well in line with the experimental result (9.8 wt%, Fig. 2b).

Values of the apparent activation energy (E_a) of the ternary system determined by the Kissinger method,²⁹ with those of the other systems for comparison, are listed in Table S2.[†] The E_a value of *ca.* 162 kJ mol⁻¹ of the 1st-step dehydrogenation of the ternary system is close to those of the others, being in good agreement with their almost identical onset temperatures. However, the E_a value of the 2nd-step dehydrogenation of the ternary system, ca. 147 kJ mol⁻¹, is 20–60 kJ mol⁻¹ lower than those of the other systems. That of the 3rd step of the ternary system is *ca.* 143 kJ mol⁻¹. The close and low E_a values of the three reaction stages of the ternary system also explain well the narrow dehydrogenation temperature region, which also provides extra evidence that Ca(BH₄)₂, LiBH₄ and MgH₂ interact, forming intermediates which have a synergetic effect on the improvement of its kinetics and high available dehydrogenation capacity at relatively low temperature. Moreover, the $E_{\rm a}$ value of the 2nd cycle dehydrogenation of the ternary system is calculated to be *ca.* 121 kJ mol⁻¹, which is lowered by 40 kJ mol⁻¹ compared with that of the 1st cycle. The result gives the reason for the significantly lowered onset dehydrogenation temperature of *ca.* 230 °C of the 2nd cycle compared with that of 320 °C for the 1st cycle (Fig. 6b).

The overall reaction enthalpies of the different systems determined by integrating the endothermic peaks in their DSC curves marked as A–D in Fig. 3a are also listed in Table S2.† The dehydrogenation reaction enthalpy for the ternary system is 40.3 kJ mol⁻¹ H₂, which is 5–12 kJ mol⁻¹ H₂ lower than those of the others. However, it is noteworthy that desorption of the ternary system is a multi-step process. If separating its overlapped DSC curve with a peak fitting program based on the Gaussian–Lorentzian function and figuring out the hydrogen released in each step based on the desorption curve (Fig. 2b), the separated reaction enthalpy changes of the 1st, 2nd and 3rd-steps of the ternary system were calculated to be 50.1, 38.3 and 39.6 kJ mol⁻¹ H₂, respectively. The separated 1st-step reaction enthalpy of the ternary system is almost identical to the overall value of the individual Ca(BH₄)₂ (52.2 kJ mol⁻¹ H₂), related to their similar starting dehydrogenation temperatures. However, the much lower values of the 2nd/3rd stages contribute to the decrease in the completion temperature of the ternary system.

SEM images of the as-milled $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system and its products after different cycles of dehydrogenation/hydrogenation are shown in Fig. S4a-f.† The as-milled mixture is composed of particles with somewhat smooth surface and size in the range of $1-4 \mu m$ (Fig. S4a[†]). However, after 1st dehydrogenation, the particles show smaller size and irregular shape (Fig. S4b[†]). After 1st round hydrogenation, the particles tend to grow and agglomerate (Fig. S4c[†]), being larger than the starting mixture. The 2nd cycle dehydrogenated product (Fig. S4d[†]) also shows smaller size than that before dehydrogenation, but almost in the same order as that of the 1st dehydrogenation product. The reduced particle size of the dehydrogenated product should favour the hydrogenation of the system, as small particle sizes commonly favour the hydrogen storage properties due to easier diffusion.^{30,31} Though the particle size increases after the initial hydrogenation, the product still possesses lower onset dehydrogenation temperature (Fig. 6b). There must be other factors that compete in the behavior. In addition, there is a belt-like phase found (marked by arrow 1 in Fig. S4d[†] and amplified in its inset) in the 2nd dehydrogenation product. In the following cycles, the morphology of the dehydrogenation/hydrogenation products is not visibly changed, as typically shown in Fig. S4e and f⁺ for the 9th hydrogenation and 10th dehydrogenation, respectively, except that there are slightly larger amounts of belt-like phase formed in the dehydrogenated product with cycling, from an overview of the SEM observation. EDS analysis of the belt-like phase showed that it is both Mg- and O-rich.

XRD analysis of the dehydrogenation and hydrogenation products at different cycles shows that CaH_2 and Mg are the major phases in the dehydrogenation products, and they are the only detected crystal phase in the 1st dehydrogenation product. The patterns of the 1st, 4th and 10th dehydrogenation products are representatively shown in Fig. S5a.[†] In addition, MgO is detected in the dehydrogenation product of several cycles, as shown in the 4th cycle. The peaks assigned to MgO are very evident in the dehydrogenated product of 10th cycle. Considering the Mg/O-rich belt-like phase in the SEM images of the dehydrogenated products mentioned above, it is concluded that the belt-like phase in the dehydrogenation product is MgO. The content of MgO increases with cycling as known from XRD and SEM/EDS analysis. The formation of MgO is considered to be due to the inevitable contact with air and moisture during the experimental testing process, which was also reported by Minella *et al.*²⁶ in the $Ca(BH_4)_2 + MgH_2$ system, as magnesium metal forms oxide exothermally (-601 kJ mol⁻¹).³²

It is worth noting that a newly formed dual-cation hydride of MgCaH_{3.72} is found to be always the predominant crystal phase in the hydrogenated products of the ternary system after different cycles by XRD analysis (Fig. S5b[†]), demonstrating that CaMgH_{3.72} is a highly reversible phase. γ -Ca(BH₄)₂, LiBH₄ and MgH₂ are evidently detected with relatively high intensity in the hydrogenated product of the 1st cycle. However, the relative intensities of the diffraction peaks of these three phases are gradually weakened with cycling as seen from the representative patterns of the 3^{rd} and 9^{th} hydrogenated products (Fig. S5b†). CaMgH_{3.72} formed as the main phase in the hydrogenated product rather than the full conversion of only $Ca(BH_4)_2$, LiBH₄ and MgH₂ after the first hydrogenation. To ascertain the action of CaMgH_{3.72} in the redehydrogenation process, CaMgH3.72 was synthesized according to our previous work.33 The synthesized CaMgH_{3.72} is stable in the heating process up to 260 °C as known from its XRD pattern (Fig. S6[†]) and its dehydrogenation curve (Fig. S7[†]). Dehydrogenation of CaMgH_{3.72} only occurs at ca. 320 °C (Fig. S7[†]), being much higher than 260 °C for the ternary system after the initial cycle (Fig. 6b). However, if a small amount of CaMgH_{3.72} is introduced into the ternary system to form $(1 - 1.5x)Ca(BH_4)_2 +$ $2\text{LiBH}_4 + (2 - x)\text{MgH}_2 + x\text{CaMgH}_{3.72}$ mixture (x = 0.1, 0.2) by ballmilling, it is found that the onset dehydrogenation temperature of the system is lowered by more than 30 °C, as shown in Fig. S8.† Particularly, the dehydrogenation curve of the system with x = 0.2is almost identical to the 2nd cycle dehydrogenation curve of the $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$ system. Moreover, XRD analysis of the product of the 1st round hydrogenated product of the ternary system, which is composed of CaMgH_{3.72}-Ca(BH₄)₂-LiBH₄-MgH₂, heated to 260 °C and dwelling for 10 min shows that the relative peak intensities of both Ca(BH₄)₂ and MgH₂ are weakened and that of CaMgH_{3.72} is strengthened, compared with those of the starting material (Fig. S9[†]). This result indicates that the CaMgH_{3.72} favours the decomposition of re-generated $Ca(BH_4)_2$ and MgH₂, playing an important role in lowering the onset dehydrogenation temperature of the present ternary system after the 1st cycle, which is also the reason that though the particles grow after the 1st re-hydrogenation, the onset dehydrogenation temperature of the re-hydrogenated product is still significantly lowered.

Conclusions

A ternary hydrogen storage system, $Ca(BH_4)_2 + 2LiBH_4 + 2MgH_2$, was synthesized *via* simply ball milling the three hydrides. The ternary system dehydrogenates from 320 to 370 °C, releasing *ca*. 8.1 wt% H₂, 83% of the theoretical capacity of the system. The completion temperature is much lower and the capacity considerably higher than any of the single or binary systems of the three hydrides studied so far. Enhanced desorption/ absorption kinetics and lowered reaction enthalpy are also obtained for the ternary system. Particularly, the reversibility and the cyclic stability of the ternary system are superior to the single and binary counterparts. There is about 7.6 wt% H₂ absorbed at 350 °C and 90 bar H₂ for 18 h for the ternary system initially post-dehydrogenated at 370 °C for 30 min, which is equivalent to a reversibility of 94%. The capacity fading for each cycle decreases with cycling. A reversibility of 97% and a dehydrogenation capacity of 6.2 wt% are attained for the 10th cycle. To the best of our knowledge, this is the best cycle stability for light metal boron hydride systems reported to date. $Ca(BH_4)_2$, LiBH₄ and MgH₂ in the ternary system are all reversible during cycling. Moreover, hydrogenation of the ternary system postdehydrogenation at 370 °C for 30 min initiates at an extremely low temperature of *ca.* 75 °C, and the onset dehydrogenation temperature of the re-hydrogenated product is as low as 230 °C after the 2nd cycle, with a significant reduction of 90 °C compared with the initial one, which is ascribed to the formation of an active dual-cation hydride of CaMgH_{3.72} in the hydrogenation process. The CaMgH_{3.72} is highly reversible during cycling, and favours the decomposition of $Ca(BH_4)_2$ and MgH₂. This work reveals that developing multicomponent hydrogen storage systems can be an effective approach to obtain favourable overall hydrogen storage performance.

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