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1 Introduction

Complex metal borohydrides have been regarded as one of the most promising systems for hydrogen storage in the light of their high hydrogen capacities.^{1,2} During the past decades, intensive research has been performed on the synthesis and modification of these compounds so as to enhance their hydrogen storage properties.^{3–5} The dehydrogenation temperatures of these candidates are still too high for practical low-temperature applications, because of their thermodynamic stability due to the strong B–H interactions, which is the main source for hydrogen release from borohydrides.^{6–8} Recently, a credible correlation between the dehydrogenation temperature and the Pauling electronegativity, χ_p , (since the decomposition temperature of metal borohydrides decreases with increasing χ_p of the metal cations) was provided by means of

Stabilization of NaZn(BH₄)₃ via nanoconfinement in SBA-15 towards enhanced hydrogen release[†]

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In the present work, the decomposition behaviour of NaZn(BH₄)₃ nanoconfined in mesoporous SBA-15 has been investigated in detail and compared to bulk NaZn(BH₄)₃ that was ball milled with SBA-15, but not nanoconfined. The successful incorporation of nanoconfined NaZn(BH₄)₃ into mesopores of SBA-15 was confirmed by scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, ¹¹B nuclear magnetic resonance, nitrogen absorption/desorption isotherms, and Fourier transform infrared spectroscopy measurements. It is demonstrated that the dehydrogenation of the space-confined NaZn(BH₄)₃ is free of emission of boric by-products, and significantly improved hydrogen release kinetics is also achieved, with pure hydrogen release at temperatures ranging from 50 to 150 °C. By the Arrhenius method, the activation energy for the modified NaZn(BH₄)₃ was calculated to be only 38.9 kJ mol⁻¹, a reduction of 5.3 kJ mol⁻¹ compared to that of bulk NaZn(BH₄)₃. This work indicates that nanoconfinement within a mesoporous scaffold is a promising approach towards stabilizing unstable metal borohydrides to achieve hydrogen release with high purity.

> first-principles calculations and experiments on the thermodynamic stability of metal borohydrides, $M(BH_4)_n$ (M = Li, Na, K, Cu, Mg, Zn, Sc, Zr, and Hf, n = 1-4), demonstrating a viable strategy for the development of new metal borohydrides with advantageous dehydrogenation properties *via* regulating the χ_p of the relevant metal cations.⁹ It is also well known, however, that less stable metal borohydrides, due to the presence of relevant metal cations with high χ_p , release considerable amounts of diborane by-products in conjunction with the liberation of hydrogen, prohibiting their practical application as hydrogen storage materials in fuel cells.¹⁰ Thus, a feasible approach is also desirable to achieve a compromise between the favorable release of hydrogen and the thermodynamic stability of metal borohydrides.

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Recently, a series of dual-cation (M, Zn) compounds (M = Li, Na) formed by ball milling ZnCl₂ and MBH₄ (M = Li, Na), along with MCl (M = Li, Na) by-products, *i.e.*, LiZn₂(BH₄)₅, NaZn₂(BH₄)₅, and NaZn(BH₄)₃, in which Zn²⁺ has a high χ_p of 1.65, were demonstrated experimentally and theoretically to undergo thermal decomposition of hydrogen below 100 °C, which is much lower than that for other pure metal borohydrides, *e.g.*, LiBH₄, NaBH₄, Mg(BH₄)₂, and Ca(BH₄)₂, giving these dual-cation compounds remarkable potential to be practical for hydrogen storage applications.^{11–15} We have recently realized the purification of NaZn(BH₄)₃ using a wet-chemical route with separation of the NaCl formed during synthesis, which significantly increases the practical hydrogen capacity of this system.¹⁶ It has to be borne in mind, however, that as a result of the instability of Zn-based borohydrides, large

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 $[\]dagger$ Electronic supplementary information (ESI) available: XRD of sediments during preparation of NaZn(BH_4)_3–THF solution and pure NaZn(BH_4)_3 decomposed at 200 $\,^{\circ}\text{C}$, and TEM images of NaZn(BH_4)_3 loaded into SBA-15. See DOI: 10.1039/c2ta00195k

amounts of boranes are released during pyrolysis, which is substantially harmful to proton exchange membrane fuel cells (PEMFC), reduces the effective hydrogen capacity, and decreases possibilities for reversibility. Therefore, suppression of boranes released during its decomposition is of vital importance for the application of NaZn(BH₄)₃ as a hydrogen storage material.

On the other hand, after several years of exploration, entrapping hydrogen storage materials within the nanopores of solid mesoporous templates has been found to serve as an effective tool for enhancing the hydrogen storage properties of these materials, in such aspects as improved kinetics and thermodynamics for the hydrogen release reaction, as well as effective suppression of volatile gases.¹⁷⁻³⁰ For example, by confining ammonia borane (AB) in templates such as Li-doped mesoporous carbon (Li-CMK)31 and metal organic frameworks (JUC-32-Y),³² the dehydrogenation kinetics of ammonia borane at lower temperature was substantially increased, together with the total suppression of both borazine and ammonia. Moreover, the recyclable dehydrogenation of ammonia borane was effectively achieved within graphene oxide-based hybrid nanostructures.³³ In regards to the pure borohydrides, numerous encouraging nanostructured or nanoporous materials, such as carbon nanotubes, carbon fibers, mesoporous silica, nanoporous carbon, and metal-organic frameworks (MOFs) have been adopted to modify the hydrogen storage properties of LiBH₄, demonstrating that nanoconfinement is an effective way to improve the hydrogen desorption/absorption properties of borohydrides.³⁴⁻³⁸ In particular, LiBH₄ that is nanoconfined via SBA-15 as a scaffold exhibits enhanced hydrogen desorption properties, with desorption starting at 150 °C, which is more than 200 °C reduction compared with the bulk LiBH4, confirming that SBA-15 is a suitable template for nanoconfinement of hydrogen storage materials.36 Therefore, by taking advantage of the unique properties of hydrogen storage materials as nanoparticles, specifically based on their high surface-tovolume ratios, leading to shorter diffusion paths for hydrogen liberation from substrates, SBA-15 was applied as a scaffold to investigate the size effect on the desorption properties of $NaZn(BH_4)_3$ on the nanoscale.

2 Experimental

Materials

NaBH₄ (98%) and anhydrous $ZnCl_2$ (99.99%) were purchased from Sigma-Aldrich and used in as-received form without further purification. Tetrahydrofuran (THF; 99.999%; Sigma-Aldrich) was further dried over sodium before using and stored under Ar atmosphere. SBA-15 was obtained from Nanjing XFNANO Materials Tech Co., Ltd, China, and vacuum-dried at 150 °C for 6 h in advance before using.

Preparation of NaZn(BH₄)₃-THF solution

For the preparation of $NaZn(BH_4)_3$ in THF, anhydrous THF (~16 mL) was first transferred in an argon atmosphere to a 50 mL ball-milling vessel containing 11 mm diameter stainless steel

spheres, with a ball-to-powder ratio of 30:1, followed by the addition of NaBH₄ (1.135 g) and ZnCl₂ (1.3631 g). To minimize heating in the vessel, the milling process was paused for 12 min after every 30 min milling, with 40 cycles at 300 rpm. After the ball-milling procedure, centrifugation was performed for around 30 min in a sealed tube under Ar atmosphere to separate the transparent NaZn(BH₄)₃–THF solution from the precipitated by-products (*e.g.*, NaCl), which were characterized by X-ray diffraction (XRD) as shown in Fig. S1 in the ESI.[†] Pure NaZn(BH₄)₃–THF solution (Fig. S2[†]) under vacuum at room temperature for 48 h.

Preparation of control sample

A mixture of NaZn(BH₄)₃ with SBA-15 as a control sample with a weight ratio of 1 : 3 was ball milled *via* a planetary QM-1SP2 for 1 h. The ball-to-powder ratio was 30 : 1 with a milling speed of 250 rpm. Due to the relatively lower onset temperature of decomposition (approximately 100 °C),^{5,12,16} the milling procedure was carried out by alternating between 6 min of milling and 6 min of rest. In order to prevent contamination by air, all handling and manipulation of the materials were performed in an argon-filled glove box with a recirculation system to keep the H₂O and O₂ levels below 1 ppm.

Preparation of loaded NaZn(BH₄)₃/SBA-15 composite

In this case, NaZn(BH₄)₃ was loaded into SBA-15 by the typical infusion method *via* capillary action. Typically, 25 drops of NaZn(BH₄)₃–THF solution were added to SBA-15 (\sim 0.2 g) in the glove box, the mixture was then ultrasonicated for 2 h at around 25 °C, and finally, the solvent was removed at room temperature under vacuum over 48 hours to yield the target compound. Meanwhile, the weight of the sample before and after every treatment was monitored using an electronic balance.

Characterization

Simultaneous thermogravimetric analysis and mass spectrometry (TGA-MS, Netzsch STA 449C) were conducted at room temperature, using a heating rate of 2 °C min⁻¹ under dynamic argon with a purge rate of 50 mL min⁻¹. Volumetric release for quantitative measurements of hydrogen desorption from samples was carried out on a homemade Sievert's type apparatus under 1 atm Ar atmosphere. Desorption properties of the samples were also evaluated using Sievert's volumetric methods, with a heating rate of 2 $\,^\circ \mathrm{C}$ min^{-1} under argon atmosphere. Before measurement, the system was calibrated by a LiAlH₄ standard, with the experimental error less than 1%. Approximately 0.15 g of the sample was loaded, and during decomposition upon heating, the pressure data and the temperature data were recorded automatically at every 6 s. Finally, according to the equation PV = nRT, where R is the gas constant and V is the intrinsic volume of the equipment, the moles (n) of the gas released from the sample could be calculated. Nitrogen absorption/desorption isotherms (Brunauer-Emmett-Teller³⁹ (BET) technique) at the temperature of liquid nitrogen via a Quantachrome NOVA 4200e instrument were collected to characterize the pore structure of the samples. The

phase composition of the powders was analyzed by X-ray diffraction (D8 Advance, Bruker AXS) with Cu Ka radiation. Amorphous tape was used to prevent any possible reactions between the sample and air during the XRD measurement. Fourier transform infrared (FTIR, Magna-IR 550 II, Nicolet) analysis was conducted to determine the chemical bonding. During the FTIR measurements (KBr pellets), samples were loaded into a closed tube with KBr for measurement in the argon-filled glove box. Solid-state ¹¹B nuclear magnetic resonance (NMR, DSX 300) results were collected using a Doty crosspolarization magic angle spinning (CP-MAS) probe with no probe background. All those solid samples were spun at 12 kHz, using 4 mm ZrO₂ rotors filled up in a purified argon atmosphere glove box. A 0.55 µs single-pulse excitation was employed, with a repetition time of 1.5 s. The morphology of the samples was evaluated using a field emission scanning electron microscope (FE-SEM, JEOL 7500FA, Tokyo, Japan) and a transmission electron microscope (TEM, JEOL 2011 F, Tokyo, Japan). Highresolution X-ray diffraction data were collected on the powder beamline of the Australian synchrotron using a Mythen detector.

3 Results and discussion

Sample determination

In order to confirm the successful infiltration of NaZn(BH₄)₃ into mesoporous SBA-15, XRD, FTIR, NMR, BET, SEM, and TEM measurements on pure SBA-15, and the loaded and ball-milled NaZn(BH₄)₃/SBA-15 composites were conducted. From the increased weight of SBA-15 after NaZn(BH₄)₃ incorporation, a weight loading rate of 24 wt% is deduced for the loaded composite. In the XRD results, as shown in Fig. 1, a broad peak was present in the range of 20 from 20° to 40° for all samples involving SBA-15, as a consequence of the components for amorphous silica that are present in SBA-15. With respect to the control sample of the ball-milled NaZn(BH₄)₃/SBA-15



composite, peaks belonging to NaZn(BH₄)₃ are present, indicating that only a physical mixture was produced during the ball-milling process. In contrast to the ball-milled composite, peaks indexed to NaZn(BH₄)₃ are absent from the loaded NaZn(BH₄)₃/SBA-15 sample, which can be attributed to the nanoconfinement of $NaZn(BH_4)_3$ inside the pores of SBA-15, indicating the superior dispersion of NaZn(BH₄)₃ in the mesopores in comparison to the control sample. In the search for further evidence for the effective infiltration of NaZn(BH₄)₃ into the pores of SBA-15, N2 adsorption/desorption analysis was employed to verify the specific surface area together with the cumulative pore volume of the mesoporous SBA-15. As we can see from Fig. 2 and Table 1, both the BET surface area and the cumulative pore volume of SBA-15 after encapsulation of $NaZn(BH_4)_3$, 13.6 m² g⁻¹ and 0.03 cm³ g⁻¹, respectively, are substantially reduced, concurrent with a significant reduction of the intensity of the BJH pore size distribution, in comparison to SBA-15 without loading, providing further confirmation of successful encapsulation of NaZn(BH₄)₃ in the mesopores of SBA-15.

Owing to the amorphous state of nanoconfinement of $NaZn(BH_4)_3$ into SBA-15 on the basis of the XRD results, both FTIR and NMR spectra were collected to further characterize the $NaZn(BH_4)_3$ inside the pores of SBA-15. In addition to the peak at $\sim 1100 \text{ cm}^{-1}$ assigned to the vibration of the Si–O–Si moiety as shown in the FTIR spectrum (Fig. 3), peaks of B-H bonds at 1120 cm^{-1} , attributed to bending modes, and in the region of 2200-2400 cm⁻¹, also attributed to bending modes, which were quite analogous to those of the as-prepared NaZn(BH₄)₃, were observed after the infiltration of NaZn(BH₄)₃ into SBA-15, suggesting that NaZn(BH₄)₃ exists inside the pores of SBA-15 as fine crystallites. Moreover, for the as-prepared and nanoconfined $NaZn(BH_4)_3$, the absence of characteristic peaks of C-H bonds (Fig. S3⁺) in the range of 2800–3000 cm⁻¹ indicates the complete removal of THF. It is interesting to see, however, that the intensity of B-H vibrations of nanoconfined NaZn(BH₄)₃ was significantly decreased compared with pure $NaZn(BH_4)_3$,



Fig. 2 Pore size distributions for (a) the mesoporous SBA-15 and (b) the loaded NaZn(BH₄)₃/SBA-15 composite from the BET results. The inset shows the corresponding nitrogen adsorption and desorption isotherms.

Table 1 BET and Langmuir surface areas, and total pore volume of the meso-porous SBA-15 with and without NaZn(BH_4)_3 loading

Samples	Surface area $(m^2 g^{-1})$		Tatal name
	BET	Langmuir	volume (cm ³ g ⁻¹)
Mesoporous SBA-15 Loaded NaZn(BH ₄) ₃ /SBA-15	274.6 13.6	442.1 22.1	0.4596 0.0293



Fig. 3 FTIR (left) and ¹¹B MAS solid-state NMR (right) spectra of SBA-15, ballmilled NaZn(BH₄)₃/SBA-15 composite, and loaded NaZn(BH₄)₃/SBA-15.

while there was also increased intensity of the O-H vibrations compared with pure SBA-15, which presents only a slight peak due to O-H vibrations. This is indicative of weakened B-H bonds and a possible attractive interaction between O of SBA-15 and H of the BH4 group after incorporation of nanoscale NaZn(BH₄)₃ into SBA-15. Furthermore, ¹¹B NMR spectra revealed that typical resonances of BH_4^{-1} groups centered at -42 ppm and -45.2 ppm for the synthesized NaZn(BH₄)₃ could be assigned to BH₄ groups related to Na⁺ and Zn²⁺, respectively, in agreement with the literature,16 while the resonances of BH₄⁻¹ groups of NaZn(BH₄)₃ after infiltration into SBA-15 have a roughly 1.6 ppm shift to the downfield region, which was also observed for a LiBH₄-MgBH₄ mixture after infiltration into carbon pores.40 This result indicates the increased electron density of boron in NaZn(BH₄)₃ due to the different chemical environment induced upon nanoconfinement compared to pure NaZn(BH₄)₃. The downfield shift of BH₄ groups in the NMR spectra can be mainly attributed to (1) the attractive interaction between O of SBA-15 and H of the BH4 moiety, as indicated by the FTIR spectra, which will weaken the electron withdrawal by H from B in the BH₄ group and, vice versa, result in increased electron density of atomic B; and (2) the possible shielding effect of lone-pair electrons of O atoms from SBA-15 on the resonances of boron in the NaZn(BH₄)₃ inside the pores of SBA-15, at least to a certain degree, indirectly demonstrating the successful infiltration of NaZn(BH₄)₃ into SBA-15. In addition, a low peak with a broad shoulder pertaining to amorphous

boron in the region of 16 to -20 ppm appears in the NMR spectra of nanoconfined NaZn(BH₄)₃ in SBA-15, originating from possible decomposition during solid state NMR measurements, owing to its relatively much lower dehydrogenation temperature in contrast to pure NaZn(BH₄)₃ (as discussed below).

The surface morphology changes for the nanoconfined $NaZn(BH_4)_3$ before and after dehydrogenation were obtained through SEM and high resolution TEM (HRTEM) images. As shown in Fig. 4b, after vacuum drying, agglomeration due to the thus-crystallized NaZn(BH₄)₃ is obviously absent on the surfaces of SBA-15, while the Si map agrees well with the structure of the SBA-15 and the Zn map corresponds well with the Si map from the energy dispersive spectroscopy (EDS) elemental maps for the loaded compound (Fig. 4d-f), suggesting good dispersion of NaZn(BH₄) inside the pores of SBA-15. The TEM images in Fig. 5 show the distribution of NaZn(BH₄)₃ in the channel pores of the samples before and after dehydrogenation. The characteristic hexagonal arrays of uniform channels with the typical honeycomb appearance of SBA-15 material (Fig. S4⁺), presenting a channel diameter of around 6.5 nm, were definitely observed, in accordance with the average pore diameter of approximately



Fig. 4 SEM images of (a) pure SBA-15 for comparison, (b) loaded NaZn(BH₄)₃/ SBA-15 after vacuum drying, (c) the products after dehydrogenation to 200 °C, and the corresponding EDS maps of Si (e) and Zn (f), corresponding to image (d), collected before dehydrogenation.



Fig. 5 HRTEM images at different magnifications of the loaded NaZn(BH₄)₃/ SBA-15 before (a and b) and after (c and d) dehydrogenation; TEM image before dehydrogenation (e) and the corresponding EDS maps of Si (f), Zn (g), and Na (h).

6 nm derived from the BET results. Additionally, dark domains and spots inside the mesopores of SBA-15, resulting from the nanoconfined NaZn(BH₄)₃ and/or its decomposed products, denoted by arrows, are apparent, with EDS elemental maps of Si coinciding with those of Zn and Na, providing strong confirmation for the incorporation of NaZn(BH₄)₃ into SBA-15. Moreover, it should be pointed out that the pore structure of the loaded samples, after heat treatment to 200 °C (Fig. 5c and d), remains intact, which agrees well with the SEM images of the loaded samples (Fig. 4b and c) regardless of whether or not they had experienced heat treatment, demonstrating that SBA-15 can effectively maintain its nanoconfinement effects on the NaZn(BH₄)₃ inside its pores throughout the process of hydrogen desorption.

Based on the above-mentioned characterization, we can therefore conclude that $NaZn(BH_4)_3$ was indeed incorporated into SBA-15 in the nanoscale form and/or blocked the pores of SBA-15 by dint of infusion through the capillary effect.

Hydrogen desorption properties

To explore the effects of SBA-15 as a scaffold on the hydrogen storage properties of nanoconfined NaZn(BH₄)₃, a comparison of the thermal decomposition performance of the as-prepared

 $NaZn(BH_4)_3$, the $NaZn(BH_4)_3$ loaded into SBA-15, and the ballmilled NaZn(BH₄)₃/SBA-15 composite as a control sample was conducted by employing TGA and MS in tandem with volumetric measurements, as shown in Fig. 6 and 7a. The decomposition of the as-prepared $NaZn(BH_4)_3$ in the temperature range of 80-200 °C is similar to what was previously reported,16 with a weight loss of \sim 29 wt%, accompanied by the release of a multitude of borane families, e.g., BH_3 and B_2H_6 , which is further verified by the much lower amount of hydrogen release in comparison with its theoretical content, with only 1.35 mol of gas liberated during the thermolysis procedure, according to the volumetric results expressed with respect to the content of $NaZn(BH_4)_3$ in the sample under the same conditions, indicating a significantly reduced amount of effective hydrogen. In the case of the ball-milled mixture of NaZn(BH₄)₃ with SBA-15, as most NaZn(BH₄)₃ is present outside of the SBA-15, instead of being incorporated into the nanopores of SBA-15, it undergoes a decomposition process that is comparable with that of pure $NaZn(BH_4)_3$, exhibiting a 24.1 wt% weight loss, which is much more than its theoretical hydrogen storage capacity (9.1 wt%), but with only 1.4 mol of released gas from volumetric results. In contrast, from the MS spectra of NaZn(BH₄)₃ nanoconfined in SBA-15, only hydrogen was detected over the whole thermolysis process, coupled with a total suppression of BH₃ and/or B₂H₆. In addition, the onset decomposition temperature of NaZn(BH₄)₃ infiltrated into SBA-15 decreased to around 50 °C, along with one peak at 112 °C, which is slightly lower than those of pure NaZn(BH₄)₃ and the control sample (\sim 120 °C). Furthermore, the weight loss (6 wt%) is in good agreement with the volumetric results, with around 3.98 mol of gas released upon heating, accounting for 99% of theoretical hydrogen capacity, which further confirms the complete repression of release of boric by-products. The weight loss process for dehydrogenation ends before 150 °C, in concurrence with the MS spectra, which is much lower than that of pure $NaZn(BH_4)_3$,



Fig. 6 TGA (left) and MS (right) results for pure NaZn(BH₄)₃ (black line), ballmilled NaZn(BH₄)₃/SBA-15 (red line), and loaded NaZn(BH₄)₃/SBA-15 (blue line), with a heating rate of 2 °C min⁻¹ under dynamic argon atmosphere. The right axis of the TGA chart gives the amount of weight loss relative to the mass of NaZn(BH₄)₃ only.

Fig. 7 (a) Volumetric gas release measurements for pure NaZn(BH₄)₃(black line), ball milled NaZn(BH₄)₃/SBA-15 (red line) and loaded NaZn(BH₄)₃/SBA-15 (blue line), with a heating rate of $2 \,^{\circ}$ C min⁻¹ under 1 atm argon, expressed with respect to the content of NaZn(BH₄)₃ only, and (b) isothermal volumetric results for gas release from the loaded NaZn(BH₄)₃/SBA-15 composite at 80 °C, 90 °C, 100 °C, and 110 °C, and for pure NaZn(BH₄)₃ at 110 °C. The inset shows a comparison of the Arrhenius plots of the temperature-dependent rate data of the loaded NaZn(BH₄)₃/SBA-15 composite (\bullet) and the pure NaZn(BH₄)₃ (O).

clearly demonstrating that the nanoconfinement of $NaZn(BH_4)_3$ facilitates the kinetics of hydrogen release.

Better information on the decomposition properties of nanoconfined and bulk NaZn(BH₄)₃ was gained via isothermal dehydrogenation at different temperatures through the method of volumetric gas release measurements, as shown in Fig. 7b and S5,[†] to investigate the dehydrogenation kinetics. As expected, the hydrogen desorption kinetics increases as the relative operating temperature increases. The results reveal that hydrogen release from the nanoconfined $NaZn(BH_4)_3$ proceeds slowly at the temperature of 80 °C, evolving about 2 wt% hydrogen within 250 min. Upon heating, nanoconfined NaZn(BH₄)₃ could release around 3 wt% hydrogen in 200 min at 90 °C and slightly more than 4 wt% within 150 min at 100 °C. Specifically, 5.7 wt% hydrogen, accounting for 95% of its theoretical hydrogen capacity, was released from NaZn(BH₄)₃ after encapsulation in SBA-15 in only 90 min, while merely 0.5 mol gas was released from pure NaZn(BH₄)₃ at the same temperature, even with time extension to 300 min, which is much less than the hydrogen release capacity of the nanoconfined NaZn(BH₄)₃ even at 80 °C. Clearly, a significant enhancement of the hydrogen release kinetics of NaZn(BH₄)₃ after encapsulation into SBA-15 is achieved due to the formation of nanocrystals, resulting in shorter diffusion paths for hydrogen spillover from the substrate, which lowers the kinetic dehydrogenation barrier. In order to quantitatively characterize the kinetic properties, Arrhenius plots of ln k were collected (where k is the reaction rate constant (s^{-1})) versus 1/T (where T is the absolute temperature for relative hydrogen release), as shown in the inset of Fig. 7b. The plots exhibit good linearity for the nanoconfined $NaZn(BH_4)_3$. By conducting a linear fit of the data points, the apparent activation energy $E_{\rm a}$ for hydrogen release from nanoconfined and bulk $NaZn(BH_4)_3$, by virtue of Arrhenius equation $(k = Aexp(-E_a/(RT)))$, can be calculated to be only 38.9 kJ mol $^{-1}$ and 44.2 kJ mol $^{-1}$, respectively. This directly confirms the enhancement of kinetics for NaZn(BH₄)₃ confined in mesopores of SBA-15. To the best of our knowledge, this is the first example of successful stabilization of a Zn-based metal borohydride via the nanoconfinement technique so as to

achieve a pure hydrogen release, in tandem with enhanced hydrogen release kinetics, making $NaZn(BH_4)_3$ a promising hydrogen storage material for practical application.

Decomposition mechanism

In the light of the above discussion, the confinement of $NaZn(BH_4)_3$ in SBA-15 on the nanoscale, giving rise to shorter diffusion paths for hydrogen evolution, is the main factor responsible for enhancing the hydrogen desorption properties, similar to what has been observed in other nanoconfined hydrogen storage materials.¹⁷⁻³⁵ Further investigation of the effects of SBA-15 as a scaffold on the decomposition mechanism was conducted, in order to unravel the mechanism for improvement of the thermodynamics of hydrogen release. The XRD pattern (Fig. S6[†]) of NaZn(BH₄)₃ after decomposition to 200 °C demonstrates the formation of Zn and NaBH₄, without the appearance of any boron peaks due to its amorphous structure, which corresponds well with the results of a previous report.¹⁶ Only peaks indexed to Zn are observed, however, for the dehydrogenated product of $NaZn(BH_4)_3$ loaded into SBA-15, with no presence of NaBH₄ (Fig. 1). As apparent BH_4^{-1} groups corresponding to NaBH₄ centered at -44.2 ppm were detected in the NMR spectra, in addition to the B-H bonds in both bending and stretching modes, as witnessed by the FTIR spectra (Fig. 8), the disappearance of $NaBH_4$ from the XRD spectra may have resulted from its uniform dispersion in the mesoporous SBA-15 due to its amorphous and/or nanophase structure. This is directly confirmed by the TEM results (Fig. 5c and d), which exhibit nanocrystals of products inside the mesopores of SBA-15 after hydrogen desorption. Simultaneously, the intensity of O-H interaction vibrations was decreased with the decreasing intensity of B-H bond vibrations, suggesting that the presence of O-H interactions may promote hydrogen release from $NaZn(BH_4)_3$. With regard to the NMR spectra of the dehydrogenated products, the disappearance of peaks assigned to the BH₄ group linked to Zn^{2+} in NaZn(BH₄)₃ with and without



Fig. 8 ¹¹B MAS solid-state NMR (left) and FTIR (right) spectra of (a) pure NaZn(BH₄)₃ and (b) loaded NaZn(BH₄)₃/SBA-15 composite after decomposition to 200 °C under 1 atm argon.

infiltration into SBA-15 confirms the complete decomposition of the BH₄ group linked to Zn²⁺, demonstrating the relatively unstable character of metal borohydrides with metal cations of high Pauling electronegativity, χ_p . Compared with the products of decomposition of pure NaZn(BH₄)₃, similar phenomena were observed in the NMR spectra of the raw materials, with 0.6 ppm of downfield shift for the BH₄ group in the dehydrogenated $NaZn(BH_4)_3$ after infiltration into SBA-15. In addition, the ratio of the intensity of amorphous elemental B to that of the BH4 group increased for dehydrogenated NaZn(BH₄)₃ infiltrated into SBA-15 towards that of pure $NaZn(BH_4)_3$, illustrating that NaZn(BH₄)₃ infiltrated into SBA-15, under the attractive interaction of O in SBA-15, finds it preferable to form boron by releasing hydrogen instead of BH3 or B2H6, resulting in both suppression of gases that are detrimental to fuel cells and relatively higher hydrogen capacity. Based on the above facts, *i.e.*, the formation of NaBH₄, amorphous B, and Zn along with the release of pure hydrogen upon decomposition, the decomposition process of the nanoconfined NaZn(BH₄)₃ can be expressed as follows:

 $NaZn(BH_4)_3$ (on the nanoscale) $\rightarrow NaBH_4 + Zn + B + 2H_2$

The above decomposition reaction delivers a theoretical hydrogen capacity of 6 wt%, *i.e.*, 4 equiv. H_2 per NaZn(BH₄)₃ formula unit, agreeing well with the observed experimental results (Fig. 6 and 7a). The hydrogenation of the decomposition products, however, was unsuccessful *via* solid-state reaction at 400 °C under 10 MPa H₂.

4 Conclusion

Nanoconfinement of NaZn(BH₄)₃ in mesoporous SBA-15 was successfully realized by typical infusion *via* capillary action. Compared with pure NaZn(BH₄)₃, NaZn(BH₄)₃ infiltrated into SBA-15 displays significantly enhanced hydrogen release properties, including complete suppression of boranes and improved hydrogen release kinetics, offering pure hydrogen release in the temperature range of 50 to 150 °C. Our results indicate that nanoscale NaZn(BH₄)₃ obeys a completely different decomposition mechanism from its bulk counterpart, which enables unstable borohydrides to release pure hydrogen rather than undesirable boranes, providing a viable strategy for improving the hydrogen desorption properties of relatively unstable metal borohydrides with high Pauling electronegativity for superior hydrogen release kinetics under lower temperature by designed nanostructures.

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