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Dehydrogenation and reaction pathway of Perovskite-Type $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ Chengguang Lang^{a,c}, Yi Jia^{b,c,*}, Jiangwen Liu^a, Hui Wang^a, Liuzhang Ouyang^{a,c,*}, Min Zhu^{a,c}, Xiangdong Yao^{b,c}^a School of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou 510641, China^b School of Natural Sciences and Queensland Micro, and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia^c China-Australia Joint Laboratory for Energy & Environmental Materials, Joint Venture of Griffith University and South China University of Technology, Nathan, QLD 4111, Australia

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ABSTRACT

Perovskite-type borohydride, $\text{NH}_4\text{Ca}(\text{BH}_4)_3$, is considered as a promising hydrogen storage material due to its high gravimetric hydrogen capacity (15.7 wt%). In this work, the dehydrogenation performance and reaction pathway of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ have been systematically investigated. It is found that the initial decomposition temperature is only 65 °C, suggesting a low thermodynamic stability of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$. The desorption kinetics conducted by differential scanning calorimetry (DSC) indicates that the activation energy of decomposition is about 226.1 kJ/mol. The dehydrogenation pathway of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ characterized by fourier-transform infrared spectroscopy (FTIR) and solid-state nuclear magnetic resonance (NMR) shows a stepwise decomposition process, in which the initial dehydrogenation is due to destabilization of H^+ in NH_4 and H^- in BH_4 followed by the subsequent dehydrogenation steps arising from the decomposition of homologous NH_3BH_3 and the final decomposition of $\text{Ca}(\text{BH}_4)_2$ at a high temperature, respectively.

1. Introduction

Metal borohydrides $\text{M}(\text{BH}_4)_n$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{Ca}, \text{etc.}$) have tremendous potential in the realm of clean fuels due to their low molecular weight and high hydrogen storage capacity. For example, LiBH_4 as a solid state hydrogen storage material can release 13.8 wt% of hydrogen according to the dehydrating reaction as below [1–4]:



However, the metal borohydrides need high temperature to release hydrogen owing to their high thermal stability and slow kinetics. The first-principles calculations reveal that the charge transfer from M^{n+} cations to $[\text{BH}_4]^-$ anions is a key feature to determine the stability of $\text{M}(\text{BH}_4)_n$. Specifically, there exists a positive linear relationship between the formation enthalpy ΔH_{boro} of $\text{M}(\text{BH}_4)_n$ and the Pauling electronegativity χ_p of the cation, $\Delta H_{\text{boro}} = 248.7\chi_p - 390.8$ [5,6]. Moreover, the thermal desorption experiments of $\text{M}(\text{BH}_4)_n$ indicate that the hydrogen desorption temperature T_d has a negative correlation with χ_p [7]. For example, LiBH_4 needs to be heated to above 673 K to release most of the hydrogen due to the high enthalpy of 75 kJ/mol, which is unsuitable for practical applications in the automotive sector.

Presently, NH_3BH_3 (AB) has been regarded as a promising hydrogen storage media for on-board applications owing to its remarkable high hydrogen content (19.6 wt%) and satisfactory air stability. Unfavorably, the thermal dehydrogenation of AB is accompanied with the emission of toxic gases (e.g. NH_3 , B_2H_6 , $\text{B}_3\text{H}_6\text{N}_3$) which is harmful to fuel cell, and the kinetics of dehydrogenation of AB is also sluggish. To address above issues, substantial efforts have been made to optimize the dehydrogenation performance of AB. The effect of metal chloride additives and metal hydride additives on dehydrogenation performance of AB was studied systematically by Yuki Nakagawa *et al.* The results indicated that the halide with higher χ_p of cation and MAlH_4 ($\text{M} = \text{Na}, \text{Li}$) could not only decrease the onset temperature of hydrogen release but also effectively suppress the emission of toxic gases [8,9]. For the halide, M^{n+} in MCl_n can work as a Lewis acid site to initiate the AB dehydrocoupling reaction by inducing changes in the electronic state of N. In addition, nanoconfinement is another effective strategy to optimize the dehydrogenation performance of AB. For instance, Gutowska *et al.* reported nanoconfinement of AB in mesoporous silica could significantly decrease the dehydrogenation temperature [10]. Our group also performed the research on nanoconfinement to modify the thermodynamics and kinetics of AB and indicated that the pore size,

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* Corresponding authors.

E-mail addresses: y.jia@griffith.edu.au (Y. Jia), meouyang@scut.edu.cn (L. Ouyang).<https://doi.org/10.1016/j.pnsc.2018.02.002>

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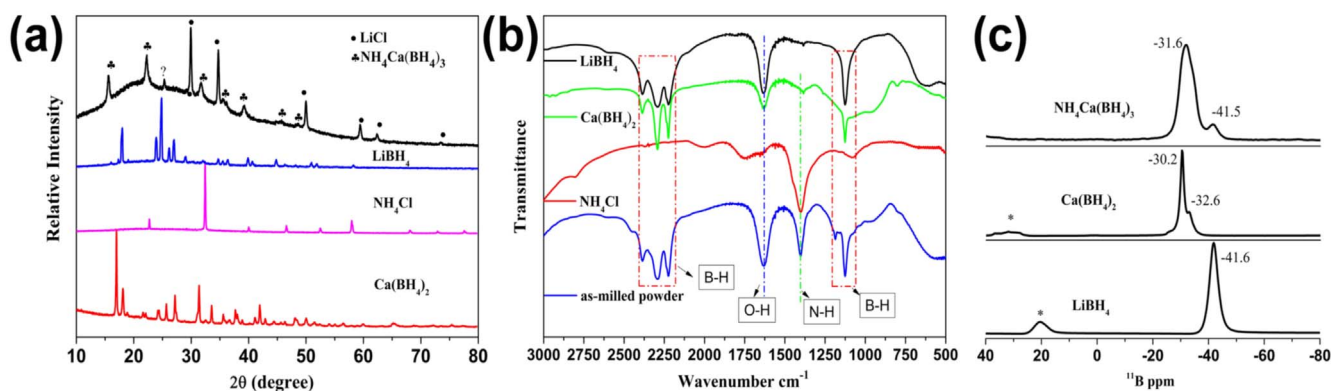


Fig. 1. (a) XRD patterns of starting materials and as-milled sample; (b) FTIR spectra of starting materials and as-milled sample; (c) ^{11}B NMR spectra of LiBH_4 , $\text{Ca}(\text{BH}_4)_2$, and $\text{NH}_4\text{Ca}(\text{BH}_4)_3$. Side bands are indicated by *.

unsaturated bonds and metal ions are key to achieve this modification [11–13]. It is reported that the improved dehydrogenation performance of AB confined by a metal organic framework (MOF: JUC-32-Y), which lowers the onset temperature of nanoconfined system to only $\sim 50^\circ\text{C}$ while the dehydrogenation of neat AB is at $\sim 100^\circ\text{C}$ [11]. Furthermore, loading AB into low-density porous aromatic framework (PAF-1) can significantly improve the overall hydrogen gravimetric capacity due to the light C and H elements in PAF-1 host as compared to heavy MOF based scaffolds [9]. Lithium-catalyzed dehydrogenation of AB within mesoporous carbon framework (Li-CMK-3) is also a good tactics, and the dehydrogenation capacity of Li-CMK-3 nanoconfined AB system can reach to $\sim 7\text{ wt\%}$ at around 60°C . Simultaneously, the undesirable volatile byproducts can be entirely suppressed due to the synergistic effects of nanoconfinement and Li catalysis [13].

Ammonium borohydride (NH_4BH_4), possessing the highest gravimetric hydrogen content (24.5%), is another promising candidate for hydrogen storage. NH_4BH_4 was firstly reported to be synthesized by a metathesis reaction between NH_4F and NaBH_4 in 1958 [14]. However, NH_4BH_4 is unstable above -40°C and will decompose at room temperature. Therefore, stabilization of NH_4BH_4 is an important prerequisite to realize its practical application. Recently, it is reported that solid NH_4BH_4 is stable for weeks at room temperature under a pressure of 0.5 GPa [15,16], whereas it is not a practical approach via such an extreme condition. Nielsen *et al.* tried to stabilize NH_4BH_4 by nanoconfinement in mesoporous silica but it was not achievable [15]. However, dual-cation borohydrides seem to be a feasible method to stabilize the borohydrides. Knight *et al.* successfully synthesized $\text{KAl}(\text{BH}_4)_4$ hypersalt, which could stabilize the volatile liquid aluminum borohydride into a manageable solid by combination with KBH_4 , enhancing remarkably the thermal stability [17]. Using the same method, Schouwink *et al.* synthesized complex borohydride $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ which is stable at room temperature [18,19], but the hydrogen release from this compound has not been systematically investigated.

In this work, a dual-cation perovskite-type borohydride, $\text{NH}_4\text{Ca}(\text{BH}_4)_3$, was fabricated via ball milling of $\text{Ca}(\text{BH}_4)_2$, LiBH_4 and NH_4Cl according to the literatures [18,19]. Due to the high theoretical hydrogen content of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$, it is demanded to study its dehydrogenation property and dehydrating pathway. The initial dehydrogenation temperature of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ is relatively low (at about 65°C), whereas the overall activation energy of decomposition is still about 226.1 kJ/mol, suggesting a stepwise dehydrating pathway of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$. The further FTIR and NMR results reveal that the initial dehydrogenation is due to the destabilization of H^+ in NH_4 and H^- in BH_4 followed by the subsequent dehydrogenation steps arising from the decomposition of homologous NH_3BH_3 (the rest NH_3 from NH_4 and BH_3 from one BH_4) and $\text{Ca}(\text{BH}_4)_2$ at a high temperature, respectively.

2. Experimental section

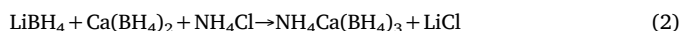
$\text{Ca}(\text{BH}_4)_2$ (product NO. 695254) and LiBH_4 (95%) were used as purchased from Sigma-Aldrich. NH_4Cl was purchased from Tianjin Damao Chemical Reagent Factory. The starting materials were used as received without further purification. $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ was synthesized in according with the reference [18]. $\text{Ca}(\text{BH}_4)_2$, LiBH_4 and NH_4Cl (1 g in total) were mixed and put into a stainless ball milling jar. The ball-to-powder mass ratio was set to 50:1 at the start. The mechanochemical reaction was then undertaken at 500 rpm for 2 h using a type of planetary ball mill (QM-3SP4, Nanjing, China) at room temperature. To prevent overheating, the milling process was performed every 2 min milling by breaking 5 min for 60 cycles. All sample handling was performed in an Ar-filled glovebox.

The ball milled product was analyzed by powder diffractometer (XRD, PANalytical X'PERT) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The qualitative analysis of FTIR using an iS50 Fourier transform infrared spectrometer was applied to the samples in our experiments. Differential scanning calorimetry (DSC) analysis was performed using a high-pressure differential scanning calorimetry (SETARAM, France). Temperature programmed desorption (TPD) measurement was conducted on an automatic Sieverts-type apparatus (AMC, HP2000). The isothermal dehydrogenation kinetic test was conducted initially under vacuum at differently specific temperature. About 230 mg sample was put into sample holder. ^{11}B solid-state NMR experiments were carried out at room temperature on a Bruker Advance 400 NMR spectrometer operating at 9.7 T. Scanning electron microscopy (SEM) was carried out on a Philips XL-30 FEG

3. Results and discussion

3.1. Synthesis of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$

Synthesis of $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ from LiBH_4 , $\text{Ca}(\text{BH}_4)_2$ and NH_4Cl is based on a metathesis reaction as following Eq. (2):



The X-ray diffraction (XRD) characterization was applied to the starting materials and the as-milled sample. As shown in Fig. 1a, the peaks of NH_4Cl , LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ have completely disappeared and new peaks appeared after ball-milling the starting materials for 2 h. The new XRD peaks shown in Fig. 1b are assigned to $\text{NH}_4\text{Ca}(\text{BH}_4)_3$ and by-product LiCl respectively, which is in agreement with the reported data [19]. In addition, a broad peak centered at approximately 20 degree is attributed to the tape used to protect the sample from being exposed to air.

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