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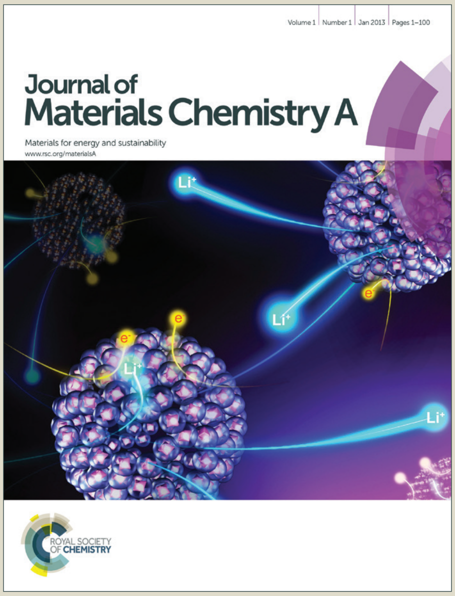

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ARTICLE TYPE

Synthesis and Hydrogen Release Properties of Alkyl-substituted Amine-boranes

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Three organic amine-boranes — diethylenetriamine-borane ($C_4H_{13}N_3{\cdot}3BH_3$, DETAB), triethylenetetramine-borane ($C_6H_{18}N_4{\cdot}4BH_3$, TETAB) and tetraethylenepentamine-borane ($C_8H_{23}N_5{\cdot}5BH_3$, TEPAB) have been synthesized via liquid-phase reaction of diethylenetriamine ($C_4H_{13}N_3$, DETA), triethylenetetramine ($C_6H_{18}N_4$, TETA), and tetraethylenepentamine ($C_8H_{23}N_5$, TEPA) with BH_3-THF solution. By using high-resolution synchrotron powder X-ray diffraction (HR-XRD), fourier transform infrared (FT-IR), elemental analysis and solid-state ^{11}B nclear magnetic resonance (NMR) measurements, the structural properties of the three compounds have been characterized. Hydrogen desorption properties of these compounds are measured by temperature programmed desorption (TPD) and thermogravimetry (TG) over the temperature range from 50 to 250 °C, in which 5.5, 6.6 and 6.9 equivalents hydrogen are released in two steps based on the combination of protic (N-H) and hydridic (B-H) hydrogens. It is confirmed by mass spectrometry (MS) results that only H_2 is liberated during the thermal decomposition of the three compounds. The dynamics are investigated by isothermal dehydrogenation at various temperatures. Compared with ammonia borane (NH_3BH_3, AB), these compounds show faster dehydrogenation rate. Regeneration study shows that DETAB can be regenerated by treating its dehydrogenated products with lithium aluminium hydride ($LiAlH_4$) and ammonium chloride (NH_4Cl) at room temperature.

Introduction

The ability, how to store hydrogen at high volumetric and gravimetric density and release it on demand,[1] is the technology vital to the widespread implementation of fuel cells as high power density portable systems.[2] Recently, extensive efforts have been focused on storing H_2 in chemical bonds in condensed phase materials.[3, 4] For instance, boron–nitrogen–hydrogen (B-N-H) compounds,[5-11] which contain both protic (N-H) and hydridic (B-H) hydrogen atoms and allow a facile H_2 elimination pathway, providing high gravimetric hydrogen capacities at relatively low temperature.[12, 13] Among these B-N-H compounds, AB[14-19] has been considered as one of the most promising hydrogen storage candidates because of its advantages,[20] such as high gravimetric density of H_2, fast kinetics at moderate temperatures, good thermal stability, facile synthesis at large scale, and safe handling under atmospheric conditions.[21, 22] Despite the fact that AB can release >12 wt.% H_2 over the temperature range from 90-150 °C with a kinetically controlled decomposition, its practical application is still frustrated by the crucial issues, such as poor reversibility,[23, 24] slow kinetics at low temperatures (below 90°C) and excessive volatile impurities (borazine, diborane and ammonia) during dehydrogenation.

To overcome the above drawbacks, plenty of research works have been conducted on investigating the thermal decomposition of AB,[25, 26] which guide us in understanding the complex dehydrogenation mechanism[27] of AB and finding efficient ways to suppress the emission of poisonous impurities.[28-30] Recently, modifying the structure of AB to adjust the kinetics and thermodynamics of H_2 release has also been investigated. For example, replacing one H atom on the N of AB with a metal cation generates metal amidoborane, such as, $LiNH_2BH_3$,[31] $NaNH_2BH_3$,[32, 33] and $Ca(NH_2BH_3)_2$,[34] etc., which not only have fast kinetics and decreased enthalpy for H_2 release, but also suppress the emission of impurities.[35] In addition, the development of derivatives of AB with alkyl-N substitution, such as methylamine-borane ($CH_3NH_2{\cdot}BH_3$, MeAB),[36] ethane 1,2-di-amine-borane ($C_2H_8N_2{\cdot}2BH_3$, EDAB)[37] etc, have been reported. For these compounds, the introduction of alkyl-N groups is expected to disrupt the dihydrogen bonding network, which not only lowers the dehydrogenation exothermicity and activation energy, but also enhances the B-N dative bond resulting in decreasing volatile nitrogen impurities during decomposition.[38, 39]

Inspired by the works above, we design a series of alkyl-substituted amine-boranes including DETAB, TETAB and TEPAB. In this paper, we report our results on the synthesis, characterization, dehydrogenation properties and possible dehydrogenation mechanism of these compounds systematically. Our investigations on these series compounds will expand the C-B-N systems and pave way of fulfilling the goal of utilizing hydrogen as a promising environmental-friendly energy carrier.

Experimental Section

Reagents and synthesis

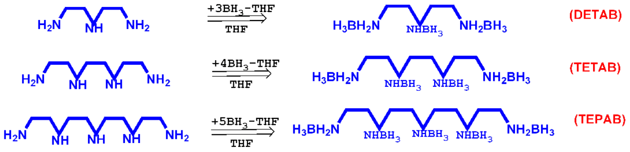
The BH_3-THF solution (1M/L), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA),

Journal of Materials Chemistry A Accepted Manuscript

CO_2H_2, $LiAlH_4$-$C_4H_{10}O$, NH_4Cl and anhydrous tetrahydrofuran (THF, ≥ 99.9%) were purchased from Sigma-Aldrich. All reactions were performed in an inert atmosphere using standard Schlenk line and glovebox techniques.

The DETAB, TETAB and TEPAB were prepared (as shown in scheme 1) according to literature procedures[37] with minor modifications. In the experiments, BH_3-THF solutions were dropped into DETA, TETA and TEPA respectively in the molar ratio 1 : 1 under stirring. Subsequently, these reaction flasks were kept at room temperature and stirred for 24 h. Then, the THF solvents were removed to yield viscous and transparent liquids. Finally, after 6 days of evaporation under vacuum at room temperature, white solids of DETAB, TETAB, and TEPAB were obtained.

Scheme 1. Procedure for the synthesis of DETAB, TETAB and TEPAB.



Regeneration of the dehydrogenation residues

A suspension of thermal decomposition products of DETAB (0.133 g, 0.001 mol) [the molar mass was calculated based on the amount of H_2 released during dehydrogenation] NH_4Cl (0.107 g, 0.002 mol) and HCOOH (0.006 mol) in THF (5ml) was stirred at 60 °C for 24 h. A solution of lithium aluminium hydride-diethyl ether (0.006 mol) was added to the solution then keeping stirring at RT for 2h. After completing the reaction, THF was removed under vacuum, and the solid residue was filtered with diethyl ether.

Instrument and analysis

The high-resolution synchrotron powder X-ray diffraction data were collected by a Mythen-II detector with a wavelength of λ = 1.0315 Å at the powder diffraction beam line, Australian Synchrotron. Fourier transform infrared (FT-IR) spectroscopy (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bonds. Samples were pressed with KBr and then loaded into a sealed chamber filled with argon to be measured. Thermal property measurements were performed by thermogravimetry (TGA, STA 409C)/mass spectroscopy (MS, QMS403) with a heating rate of 5 °C min^{-1} under 1 bar of argon. Dehydrogenation properties for the samples were evaluated using Sievert's volumetric methods with a heating rate of 5 °C min^{-1} under argon. Approximately 0.03 g of the sample was loaded and heated with a heating rate of 5 °C min^{-1} from room temperature to 250 °C. The pressure data (P) and the temperature data (T) were recorded automatically at every other 6 s. Finally, according to the equation: PV = nRT, where R is the gas constant, the mol (n) of the gas released from the sample could be calculated. Solid-state ^{11}B-NMR results were collected on a Bruker Avance 300 MHz spectrometer, using a Doty CP-MAS probe with no probe background. The powder samples collected after the decomposition reaction were spun at 5 kHz, using 4 mm ZrO_2 rotors filled up in a purified argon atmosphere glove box. A 0.55 µs single-pulse excitation was employed, with repetition time of 1.5 s.

Results and Discussion

Structure Characterization

Table 1. Elemental analysis results of DETAB, TETAB and TEPAB.

Sample	Element	Measured (wt %)	Calculated (wt %)
DETAB	C:	34.19	33.21
	H:	14.98	15.33
	N:	28.43	29.05
TETAB	C:	36.45	35.75
	H:	14.90	15.00
	N:	26.65	27.79
TEPAB	C:	37.85	37.17
	H:	14.69	14.82
	N:	26.46	27.09

DETAB, TETAB and TEPAB are synthesized based on the reactions as shown in Scheme 1. To the best of our knowledge, the three compounds are synthesized and reported for the first time. The HR-XRD results of these compounds are shown in Fig. 1(a). The broad peaks between 10° and 30° in the patterns demonstrate their amorphous structures and our attempts to solve the structures of these compounds failed due to their poor crystallinity of the samples. The FT-IR spectra of DETAB, TETAB and TEPAB (Supporting Information Fig. S1) have shown that the three compounds have very similar structures and compositions. The peak intensities become weaker with the increase of carbon chains. The structure features of DETAB, TETAB and TEPAB can be revealed clearly by the N-H stretching vibration (3300-3000cm^{-1}), -CH_2- stretching vibration (3000-2800cm^{-1}) and B-H bending vibration (730 cm^{-1}). There is an obvious BH_3 stretching vibration in the region between 2600 cm^{-1} and 2250 cm^{-1} in the FT-IR spectra, which demonstrates that BH_3 groups in BH_3-THF solution have reacted with NH_2 groups in these organic amine compounds resulting in the formation of these organic alkyl-substituted amine-boranes. It is supposed that the new compounds are formed based on the N-B bond. The stretching vibration shifts of B-H and N-H are similar to that in ammonia borane reported in the literature.[39] The successful synthesis of these expected compounds have also been demonstrated by the elemental analysis (Table 1), in which the measured results of C, N, H elements in DETAB, TETAB and TEPAB agree well with their theoretical contents. Although the FT-IR and elemental analysis have initially characterized the structure feature of DETAB, TETAB and TEPAB, solid-state ^{11}B NMR test is further conducted to clarify the compositions of these compounds. The ^{11}B NMR results in Fig. 1(b) clearly show the appearance of resonances assigned to -NH_2BH_3 at -20.2, and -20.7 ppm for DETAB, while the similar resonances for TETAB and TEPAB are observed at -19.6 and -19.4 ppm. The other resonances for DETAB, TETAB and TEPAB at -17.2, -16.5 and -16.4 ppm are all ascribed to =$NHBH_3$, which are similar to previously reported data for other amino boranes, indicating the successful coordination of BH_3 groups on the NH_2 groups.

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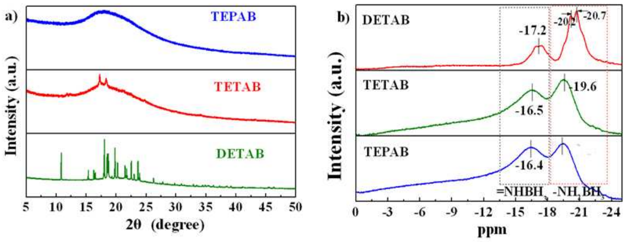

Fig. 1 HR-XRD (a), and solid state ^{11}B NMR spectra(b) of DETAB, TETAB and TEPAB.

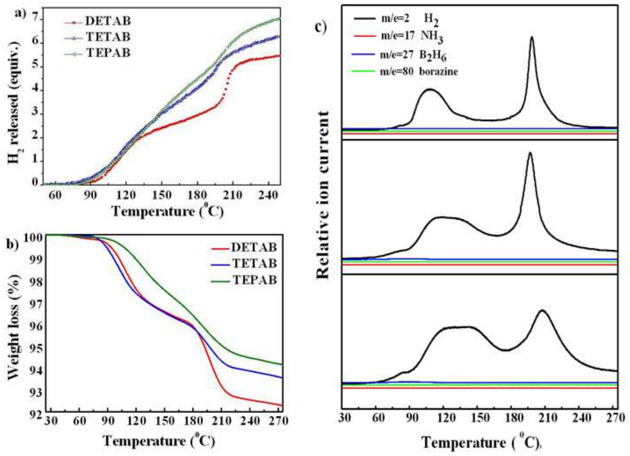

Fig. 2. TPD (a), TG (b) and MS (c) results for DETAB, TETAB and TEPAB with a heating rate of 5 °C/min in nitrogen.

Hydrogen Release Properties

The dehydrogenation properties of DETAB, TETAB and TEPAB are investigated using TPD, TG and MS measurements at temperature range from 50 to 250 °C with a heating rate of 5 °C/min. As shown in Fig. 2(a), the TPD curves present that there are 5.5, 6.6 and 6.9 equivalents hydrogen (corresponds to 7.6, 6.8 and 5.9 wt %) in two-step processes released from DETAB, TETAB and TEPAB, respectively. These results are agree well with the TG results as shown in Fig. 2(b), in which the total weight loss for DETAB, TETAB and TEPAB are 7.6, 6.4 and 5.8 wt %, respectively. The MS spectra in Fig. 2(c) show similar two-step decomposition processes for the three compounds, in which the first step occurs between 90 to 150 °C and the second step is from 170 to 230 °C. This two-step decomposition is similar to the dehydrogenation reaction of EDTA.[19] As shown in the MS curves, during the decomposition, no impurities such as NH_3, B_2H_6 and $B_3N_3H_6$ are detected under our experimental conditions, showing great advantages compared with the decomposition of AB, in which hydrogen gas is contaminated by NH_3, B_2H_6 and $B_3N_3H_6$ and so forth.[14] Furthermore, unlike AB, the decomposed residue of DETAB after TPD test shows no foaming, which is beneficial to the practical application for this compound as hydrogen storage material.

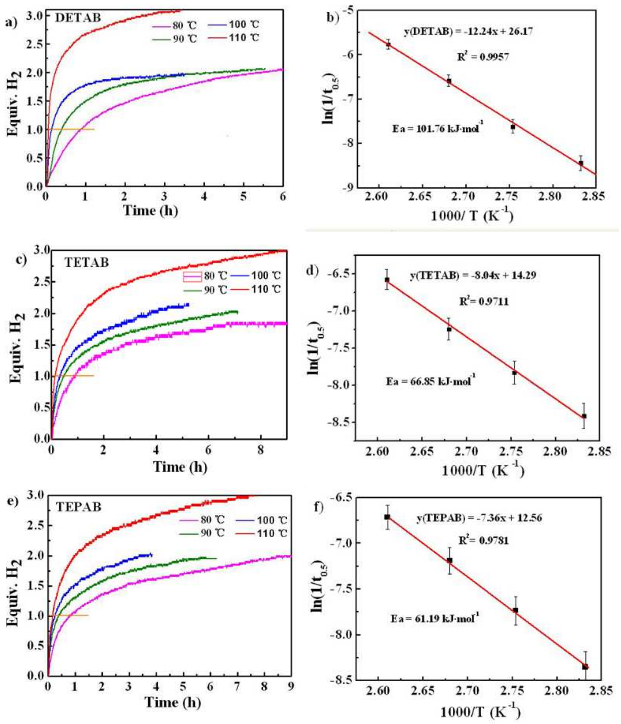

Fig. 3. Isothermal dehydrogenation results for DETAB (a), TETAB (b) and TEPAB (c) at 80, 90, 100 and 110 °C.

The dehydrogenations of DETAB, TETAB and TEPAB are further investigated using isothermal volumetric hydrogen release measurements at various temperatures (80, 90, 100 and 110 °C) as presented in Fig. 3(a, c and e). In the case of DETAB, about 2.0 equivalent hydrogen gas is released within 240 min at 80 °C. At elevated temperatures (from 90 to 110 °C), the hydrogen release time can be reduced from 90 to 15 min, accompanied by an increase in the volume of hydrogen released. About 3.0 equivalent hydrogen can be released within 150 min at 110 °C for DETAB. In contrast to DETAB, the dehydrogenation of TETAB and TEPAB show sluggish kinetics. About 3.0 equivalent of H_2 from TETAB and TEPAB can be liberated within 8h at the temperature of 110 °C. However, as shown in Fig. 3(b, d and f), the apparent activation energy (Ea) for the hydrogen release with Kissinger's method is determined to be 101.76, 66.85 and 61.19 kJ/mol, indicating that TEPAB and TETAB are more reactive than DETAB. One possible explanation is that the carbon backbone destabilizes the polyamine borane (PAB)-like products by decreasing the ability to form di-hydrogen bonds. A decrease in the di-hydrogen bonding contributions in PAB has also been suggested to be responsible for the observed decrease in reaction enthalpy for solid AB in nano-confined silica scaffolds.[40] By comparison of the decomposition dynamics of DETAB, TETAB and TEPAB, we can see that about total 2 equivalent of H_2 is liberated from DETAB, TETAB and TEPAB at temperatures of 80, 90 and 100 °C, and about 3 equivalent of H_2 is liberated at temperature of 110 °C for the three compounds. In addition, no induction period is observed for the isothermal

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dehydrogenation profile at the experimental temperature, showing certain advantages over AB, which exhibits an induction period of about 15 min during the isothermal dehydrogenation at 100 °C.

Decomposition Mechanism and Thermodynamics

To understand the decomposition process and the final products of DETAB, TETAB and TEPAB, FT-IR and solid-state ^{11}B NMR measurements are conducted after heating the samples to various temperatures. Fig. 4(a) shows the FT-IR spectra of the samples acquired at room temperature (RT), 80 °C and 250 °C, respectively. Upon heating the samples to 80 °C, the vibrations assigned to B-H, N-H and C-H almost keep unchanged, while after heating to 250 °C, N-H vibrations nearly disappeared, suggesting excessive supplement of B-H in each sample. The FT-IR results are consistent with the step-wise dehydrogenation indicated by the TPD and MS results (Fig. 2(a) and (b)).

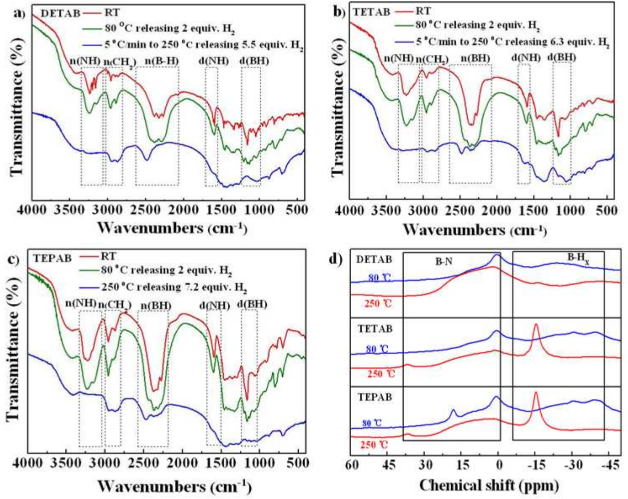
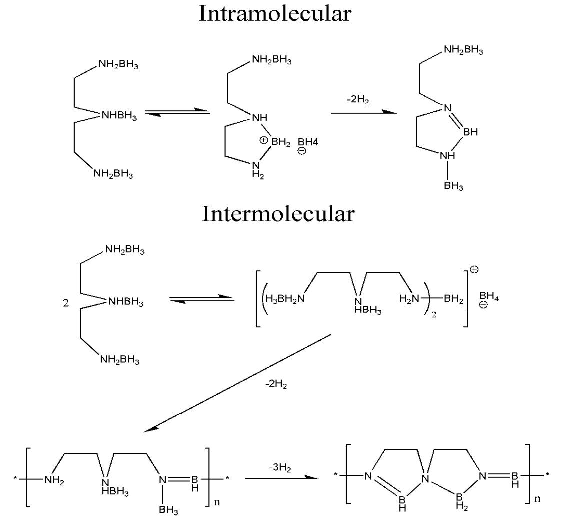


Fig. 4. FT-IR spectra for DETAB (a), TETAB (b) and TEPAB (c) at different states with a heating rate of 5 °C min^{-1}. (d) is the ^{11}B NMR spectra for DETAB, TETAB and TEPAB acquired at 80 °C and 250 °C, respectively.

Meanwhile, the CH$_2$ vibrations remain nearly the same during the decomposition, suggesting that the C-H did not contribute to the H$_2$ release. The mechanism of hydrogen release from solid-state AB has been described by an induction, nucleation and growth mechanistic pathway.^{27} Given that the DETAB, TETAB and TEPAB are alkyl-substituted derivatives of AB, we suppose that the three compounds show similar dehydrogenation mechanism with AB. The ^{11}B NMR spectra of TETAB and TEPAB after heating to 80 °C (Fig. 4(b)) show the resonances of BH$_4^-$ (–40 ppm), BH$_3$ (–25 ppm) and a B–N bonded (+20 ppm), which suggest that the structures of TETAB and TEPAB change firstly before decomposition. The initial stage is isomerisation to a borohydride analogous to the formation of [BH$_2$(NH$_3$)$_2$]$^+$[BH$_4$]$^-$ (DADB) from AB. This suggests that the dehydrogenation pathway of the three compounds may follow the DADB pathway similar to that of EDAB.^{37} As the mechanism proposed for EDAB, in the first dehydrogenation step, BH$_4^-$ is a reactant which releases hydrogen through reactions with NH$_2$. This mechanism may help to explain the absence of an induction period during the decomposition of DETAB, TETAB and TEPAB, since BH$_4^-$ can process dehydrogenation immediately as it is formed without the involvement of a third molecule or a mobile phase. Furthermore, the ^{11}B NMR spectrum obtained after heating to 250 °C shows that an amount of B–N bonded oligomers appear, and a new boron specie with broad resonance center at -15 ppm, ascribed to BH$_2^+$ resonance, is predominant. The ^{11}B NMR data led us to propose a reaction mechanism outlined in Scheme 2, which combines features previously observed for EDAB^{37} and AB.^{27} It has been reported previously that the BH$_4^-$ resonance of EDAB decreased upon heating and was replaced by two new resonances corresponding to the -BH$_2$ and =BH. During the whole dehydrogenation process, =BH vibrations remained nearly the same because of excessive supplement of B-H in each compound.

Scheme 2. The possible dehydrogenation pathway of DETAB, TETAB and TEPAB.



According to ^{11}B NMR analysis, although the intermediate phases are not clearly demonstrated presently, it can be concluded that the hydrogen release from DETAB, TETAB and TEPAB also occurs through the combination of B-H and N-H as other B-N-H of hydrogen storage materials. Considering the structural complexity of these new compounds, the dehydrogenation reactions may occur not only between molecules, but also involve to molecular internal self loop. During the growth period, 5.5, 6.6 and 6.9 equivalents pure hydrogen are released from DETAB, TETAB and TEPAB over the temperature range from 70 to 250 °C. It is interesting that the TPD results show a higher yield of hydrogen than 5, 6 and 7 equivalents H$_2$, based on equal reactivity of the protonic and hydridic hydrogen. The slight excess of hydrogen may result from cross-linking reactions between B-H and B-H groups in adjacent chains of the dehydrogenated structures as shown in Scheme 2.

In order to understand the thermal behaviour of the sample during decomposition, DSC test is conducted (Supporting Information Fig. S2). Thermal decomposition process of DETAB is divided into two steps, which is consistent with the

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TPD result. First of all, a clear sharp melting endothermic peak appears at 94 C, followed by a broad exothermic decomposition peak at 100-190 °C with an exothermic enthalpy, -13.4 kJ mol^{-1} H_2, corresponding to the first decomposition step based on the combination of B-H and N-H with three equivalents hydrogen release. However, at the second decomposition step at the temperature 190–220 °C, there is an endothermic peak with an enthalpy of 0.39 kJ·mol^{-1} H_2, which is in contrast with hydrogen release process based on the combination of B-H and N-H. According to the dehydrogenation mechanism analysis, the second decomposition step contains the combination of B-H and B-H groups, which may be an endothermic process. It is surprising that the enthalpies for hydrogen release in the first and second step are less than the enthalpies for hydrogen release from solid AB, about -21 kJ mol^{-1} and -11 kJ mol^{-1}, respectively.

Regeneration of the Dehydrogenation Residues

The chemical regeneration of dehydrogenated products is then undertaken to achieve an efficient recyclable hydrogen generation system (EDTAB was chosen as an example). In general, the regeneration processes for AB take three steps of digestion, reduction and ammoniation.[41] As alkyl-N substitution derivatives of AB, EDTAB was conducted similar regenerative steps. First, we digested the dehydrogenated products by formic acid, and then reduced the products by $LiAlH_4$ in the presence of NH_4Cl. The dehydrogenation property of regeneration sample by comparison with the original sample is shown in Fig. 5(a), which shows that 76.5% of the EDTAB is converted back after the regeneration process. The dehydrogenation behaviour shows a similar appearance to the pristine one, releasing hydrogen in two steps over the temperature range from 50 to 250 °C. The successful regeneration has also been demonstrated by the FT-IR analysis as shown in Fig. 5(b), in which the typical features of N-H and B-H vibrations can be identified. Although there are lots of advances for these compounds as hydrogen storage materials, the regeneration from the dehydrogenated products is a multistep and high-energy process. Therefore, further development on seeking a simple and low-energy route to regenerate the materials is still required.

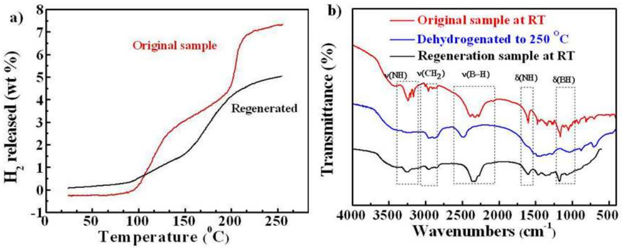

Fig. 5. (a) Comparison of TPD results for the original and regenerated sample of DETAB with a heating rate of 5 °C/min in argon; (b) FTIR spectra of EDTAB original sample, dehydrogenated (heated to 250 °C) , and regenerated sample.

Conclusions

Three new compounds, DETAB, TETAB and TEPAB were successfully synthesized via liquid-phase reactions of DETA, TETA and TEPA with BH_3-THF solution. It was found that these compounds showed pure hydrogen liberation and favourable dehydrogenation rate, suggesting that the alkyl-N modified AB derivatives have potential as chemical hydrogen storage materials. Furthermore, the dehydrogenated products can be direct regenerated by treatment with HCOOH and $LiAlH_4$ in the presence of NH_4Cl. Our investigations on DETAB, TETAB and TEPAB will expand the C-B-N systems, and pave way of fulfilling the goal to utilize hydrogen as a promising environmental-friendly energy carrier.

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Notes and references

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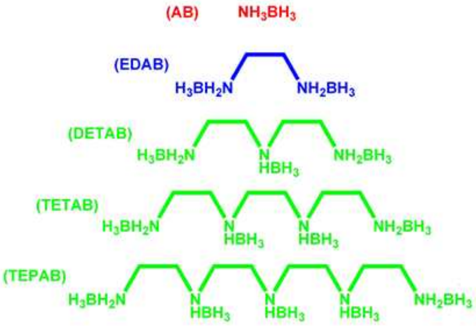

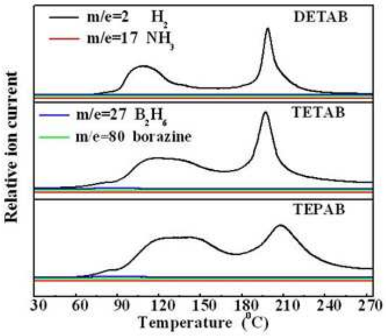

Three newly synthesized alkyl-substituted amine-boranes show favorable dehydrogenation rate with pure hydrogen release.

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