Hydrogen Storage

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A Self-Contained Regeneration Scheme for Spent Ammonia Borane Based on the Catalytic Hydrodechlorination of BCl_3**

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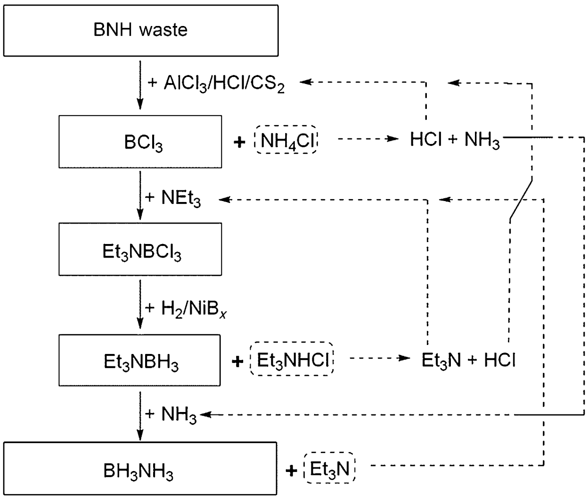
More than a decade ago, following the great interest shown by the automotive industry in hydrogen fuel-cell propelled vehicles, a quest for chemical-based hydrogen-storage and hydrogen-source systems exceeding the capacity of classical metal hydrides and complex metal hydrides began. As a compound with one of the highest hydrogen contents, ammonia borane (AB) was quickly identified as a promising candidate, especially because of its benign hydrogen-release temperatures starting at 95 °C.[1,2] The hydrogen release is exothermic, which explains why direct re-hydrogenation of spent AB is impossible. This low dehydrogenation temperature and the exothermicity both result from the simultaneous presence of hydridic and protic hydrogen in the AB molecule.

Early suggestions of recycling procedures contain three important steps that pose great challenges for their practical implementation; namely: 1) the digestion of the polymeric spent AB by the formation of oxidized, or more specifically, halogenated boron species, BX_3 (X = Cl, Br, I), 2) hydrogenation, or more precisely, the hydrodehalogenation of these compounds, and 3) replacement of the auxiliary reagents (bases) used as thermodynamic drivers in the hydrodehalogenation process by ammonia. An alternative recycling strategy was recently presented by Sutton et al., which is based on the strong reducing power of hydrazine.[3] The procedure has the advantage that the regeneration can be carried out as a one-pot synthesis. However, the use of energetically demanding, dangerously unstable, and toxic hydrazine does not make the process appear to be favorable on an industrial scale.[4] In industry, hydrazine is almost always, except for the production of rocket fuel, used as a hydrate rather than a pure compound because of safety concerns. In the hydrazine-based recycling scheme, however, it cannot be used as a hydrate because of the sensitivity to hydrolysis of the hydrazine borane adduct.[5] Consequently, a recycling scheme using inexpensive and comparably safe reagents is still highly desired.

Herein we demonstrate that the three major obstacles for the implementation of the early recycling schemes based on the break-up of spent AB by boron halogenation can be overcome leading to a self-contained recycling procedure, that is, a procedure that uses molecular hydrogen and spent AB as input materials and delivers AB utilizing only mass commodity chemicals as recyclable auxiliary reagents (Scheme 1). Because the current production of AB requires the use of expensive hydrides, the demonstrated recycling scheme also strikes a new path to potentially produce AB and other boranes more economically. Given the importance of the three major road blocks for realization of the AB regeneration scheme outlined above, discussion of the BNH-waste break-up, hydrodehalogenation of BCl_3 species, and base exchange will each start with a short overview defining the main obstacles.



Scheme 1. Regeneration of BNH waste based on the catalytic hydrodechlorinaton of BCl_3. Dashed lines indicate the recycling pathways of the by-products. Solid boxes indicate the results of the key processes, BNH break-up, addition of thermodynamic driver, hydrodechlorination, and base exchange.

BNH-waste break-up: Several groups suggested procedures consisting of a digestion step preceding the separate hydrogenation of the boron- and nitrogen-carrying moieties.[6–8] One fundamental problem for breaking up spent AB lies in the very different waste products that result from the various dehydrogenation processes. For example, if AB is decomposed by thermal treatment at 95 °C, the main component of the residue was identified as polyaminoborane $(BH_2NH_2)_x$.[9] Thermal treatment at 150 °C of AB or $(BH_2NH_2)_x$ leads to the formation of cross-linked polyborazylene (PB).[10–12] Another product obtained from the dehydrogenation processes is borazine, which is equally difficult to break-up into smaller borane- and nitrogen-

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containing units because of its tendency to dehydropolymerize. If the dehydrocoupling is performed in solution using certain solvents and catalysts, the main product is also PB.[13–15] A possible means to break the stable B–N bonds in these compounds is the hydrolysis of the spent fuel leading to the formation of even more stable B–O bonds.[6,8] Although the conversion of B–O bonds into B–H bonds is in principle possible using strong reducing agents, that is, metal hydrides such as $LiAlH_4$, the problem is then only shifted to the recycling of other high energy materials. We therefore focused on break-up procedures aiming at the formation of B–X bonds (X = Cl, Br, I), which are weaker than B–O bonds, assuming that these systems would be more easily accessible for the catalytic generation of B–H bonds. In contrast to the hydrazine-based recycling procedure, the successful recycling scheme should also be capable of digesting strongly dehydrogenated AB, that is, heavily cross-linked polyborazylene which is insoluble in common solvents. To achieve this goal the Sneddon group suggested the use of Brønsted acid (HBr and HCl) based superacids.[6] To date, the systems $AlBr_3/HBr/CS_2$ and $AlCl_3/HCl$/toluene were investigated, but no significant break-up of strongly dehydrogenated AB materials, such as borazine or PB was achieved by the superacid treatment.[6,16]

Since the difference in the break-up between less-dehydrogenated material, such as $(BH_2NH_2)_x$, and a more strongly dehydrogenated one has proven to be of importance, we took great care to obtain the more strongly dehydrogenated type of material in a well-defined and reproducible way. We therefore first dehydrogenated AB at 95 °C for 24 h to obtain predominantly $(BH_2NH_2)_x$ (checked by NMR and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, see Figure S2 and S4 in the Supporting Information) and then continued the dehydrogenation at 150 °C for 20 h under vacuum (10^{-3} mbar) to obtained strongly cross-linked PB that is not soluble in THF (checked by DRIFT; Figure S4, S1).

Herein, we report an improved procedure for the regeneration of strongly dehydrogenated species, such as borazine, PB, and cross-linked PB by using the $AlCl_3/HCl/CS_2$ superacid/solvent system running at 40 bar HCl pressure and 80 °C. The superacid protonates the nitrogen atoms in the material and the excess of HCl ensures chlorination of all boron atoms leading to the formation of NH_4Cl and BCl_3 with a yield of 90 % BCl_3 (for details concerning the quantification procedures please see Section S 6.2 of the Supporting Information). The formation of NH_4Cl was confirmed by powder X-ray diffraction (PXRD; Figure S6) and that of BCl_3 was quantitatively determined from the integration of the ^{11}B NMR signals. The monitoring of the process by ^{11}B NMR spectroscopy is displayed in Figure 1. During the first 3 h of the reaction almost no soluble components were detected in the reaction solution. After another hour, signals at $\delta = 32$ ppm, $\delta = 29.8$ ppm, and $\delta = 25.4$ ppm appeared from which the formation of B-chlorinated borazanaphthalene ($B_5N_5H_4Cl_4$; see Figure S5) and of smaller soluble chlorinated PB fragments can be concluded.[17,18] The chlorination of borazine to 2,4,6-trichloroborazine $(BCl_3NH)_3$ was conducted as a control experiment, which, beside the possibility to break-up this compound also showed that the only effect of the chlorination is the conversion of the borazine doublet $^{11}B\{^1H\}$ NMR at $\delta = 32$ ppm (see Figure S3) into a singlet essentially with no effect on the signal position. This fact allows us to conclude that a significant amount of chlorinated BN ring species has formed after 4 h.

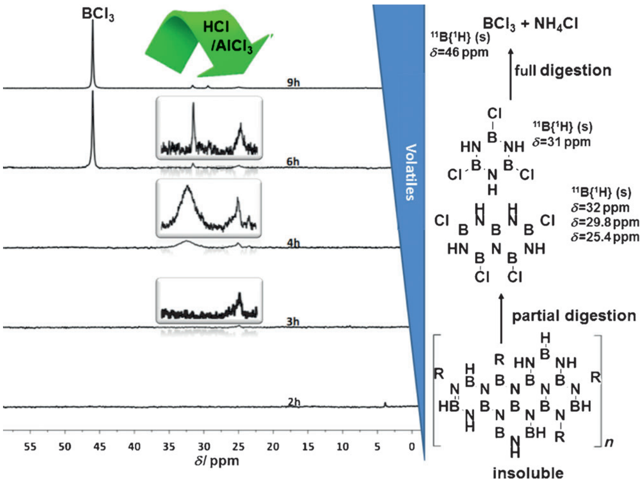

Figure 1. Temporal development of the digestion of cross-linked polyborazylene by the superacid system $HCl/AlCl_3/CS_2$, recorded by ^{11}B NMR (C_6D_6) spectroscopy.

The reaction proceeds by the formation of BCl_3, detected by the development of the intense signal at $\delta = 46$ ppm and the fading out of the original resonance signals. The overall yield of the reaction is greater than 90 % BCl_3. The solid residue was determined by PXRD (Figure S6) to be $AlCl_3$ and ammonium chloride. Its inductively coupled plasma–optical emission spectroscopy (ICP-OES) analysis gave a boron content of 0.03 wt %.

All volatile components were collected by a cryo trap allowing the determination of the overall yield to be more than 90 % (by ^{11}B NMR spectroscopy and ICP-OES). We also tested if a break-up of less-dehydrogenated material, in this case $(BH_2NH_2)_x$, is achievable at milder conditions. For this material, a yield of BCl_3 of at least 80 % was accomplished at ambient temperature and 30 bar HCl pressure within 4 h. For borazine, a yield of 90 % BCl_3 at $p_{HCl} = 30$ bar and 80 °C was obtained in 4 h. Thus, the applicability of the superacid digestion is demonstrated for essentially all types of relevant spent AB material.

Hydrodehalogenation of BCl_3: The second major obstacle to an efficient recycling route for spent AB based on the superacid concept is the successful hydrodehalogenation of the halogenated boron species, in this case BCl_3, formed during the spent-fuel break-up. Since the direct hydrogenation of BCl_3 to (di)borane is thermodynamically unfavorable ($BCl_3 + 3H_2 \rightarrow {}^1/_2 B_2H_6 + 3HCl \quad \Delta_R G°(298\,K) = +148.0\ kJ\,mol^{-1}$),[19] the reaction will need an auxiliary reactant as a thermodynamic driver. It is clear that for a self-contained regeneration scheme, this auxiliary reactant needs to be easily recoverable.[20] For the proof of concept, we chose the relatively strong Lewis base triethylamine that forms a B–N adduct with BCl_3. The regeneration scheme was intended to avoid expensive or difficult to handle (solid, toxic etc.) hydrogenation compounds, such as metal hydrides or hydrazine, and to conduct the hydrogenation preferably with molecular hydrogen. As a comparably inexpensive hydrogenation catalyst, finely dispersed nickel appeared to be a possible choice, but elemental nickel forms nickel borides in the presence of Et_3NBH_3. Since nickel boride itself was shown to be a catalyst for the hydrogenation of alkenes,[21] with the boron serving as a structural promoter to prevent the coarsening of the finely dispersed material, a phenomenon observed, for example, in the case of Raney nickel,[22] we decided to try Ni_3B as the catalyst for the hydrodechlorination step. From the presence of chloride, a certain risk of poisoning the nickel boride catalyst by the irreversible formation of nickel chloride surface species must be assumed. The comparably fast kinetics (Figure 2) over the course of the reaction and the fact that X-ray photoelectron spectroscopy (XPS) investigations of the catalyst after the completion of the reaction did not show any signs of chloride formation, illustrate that this type of catalyst poisoning is not relevant for this system. It is safe to assume that the presence of the large amounts of triethylamine protects the catalyst. Some information on the cycle life and catalyst leaching can be found in the Supporting Information.

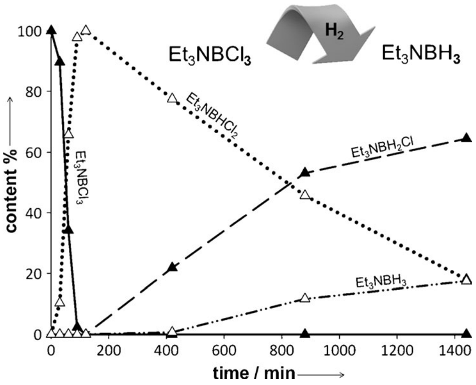

Figure 2. Temporal development of the stepwise hydrodechlorination of Et_3NBCl_3 using molecular hydrogen and Ni_3B as a catalyst. $T = 130\,°C$, $p(H_2) = 60$ bar. [1]

Hydrodechlorination experiments with triethylamine in various solvents showed that an excess of this base also helped to prevent the formation of Et_3NHBCl_4 as an ionic by-product. Consequently, we conducted subsequent experiments solvent free, that is, with triethylamine also assuming the role of the solvent as well as its role as a thermodynamic driver.

Figure 2 illustrates that the reaction proceeds stepwise from Et_3NBCl_3 via the intermediates Et_3NBHCl_2 and Et_3NBH_2Cl to the product Et_3NBH_3. Some optimization with respect to the reaction rate and the formation of by-products was carried out by investigating the reaction at 60 bar hydrogen pressure and $T = 60$, 100, 139, 160 °C. The corresponding maxima of the first intermediate, the Et_3NBHCl_2 adduct, were reached at 600, 270, 90, 30 min, respectively. At 180 °C the reaction already proceeded too fast for well-resolved curves to be obtained by extracting and characterizing individual samples from the reaction solution in the autoclave. Also, at 180 °C, the established decomposition of all triethylamine adducts, that is, $BCl_xH_{3-x}NEt_3$ ($x = 1,2,3$), under the formation of molecular HCl, ethene, and cyclic N-alkyl-B-chloroborazines sets in.[23,24]

In Figure 3 the hydrodechlorination of BCl_3 at 130 °C and 60 bar hydrogen pressure is shown (for a corresponding experiment at 160 °C see Figure S15 in the Supporting Information). In experiments leaving out only the catalyst or the hydrogen gas, no hydrodechlorination was detected, which demonstrates the decisive role of these two components. Long-term experiments show that the equilibrium even in the case of the 130 °C experiment is practically reached within 48 h. (Equilibrium composition Et_3NBHCl_2/Et_3NBH_2Cl/Et_3NBH_3: (at 130 °C) 12 %/70 %/18 %, (at 160 °C) 0 %/70 %/30 %). A single subsequent removal of the produced Et_3NHCl and continued reaction, shifts the equilibrium composition to 15 %/40 %/45 % at 130 °C and 0 %/52 %/48 % at 160 °C.

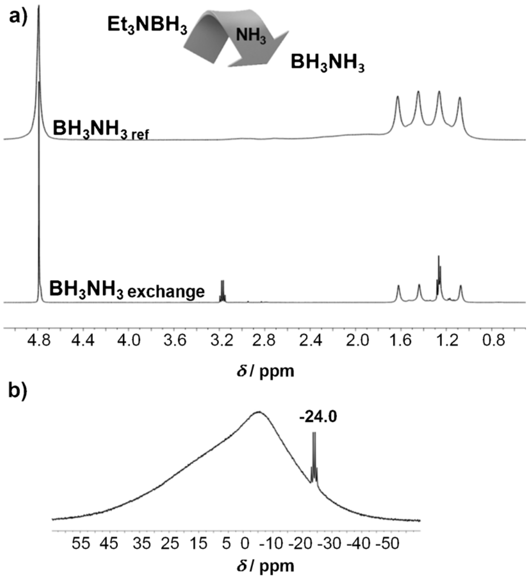

Figure 3. a) Comparison of the ^1H NMR (D_2O) coupled spectra of BH_3NH_3 obtained from the recycling process and produced by the standard salt metathesis.[25] b) The $^{11}B\{^1H\}$ NMR (D_2O) spectrum of the product of the NEt_3–NH_3 exchange reaction.

Base exchange: The last key step to arrive at the final product AB is the exchange of the auxiliary base in the borane adduct for ammonia. Although this step is just a simple exchange reaction, reports in the literature demonstrate that it is also a major problem for the proposed recycling procedures in organic solvents. For example, it was reported the AB cannot be precipitated from a Me_2EtNBH_3/toluene solution by bubbling ammonia through it at ambient conditions.[6] Although hydrazine borane should be strongly favored in respect to the base exchange with ammonia because of its comparably weak base strength ($pK_a = 7.94$) compared to that of ammonia ($pK_a = 9.26$), no exchange was observed on exposure to liquid ammonia (at −78 °C) whereas a complete exchange was achieved at 60 °C within 24 h.[3]

From these results it is clear that for using NEt_3 ($pK_a = 10.6$) as auxiliary base, a large excess of ammonia, best put into practice by working solvent free with pure ammonia, and elevated temperatures are required. Since the product AB starts to dehydrogenate at 95 °C, a temperature of 80 °C was chosen as the upper limit. The result of such a base-exchange experiment conducted by exposing the Et_3NBH_3 adduct to liquid ammonia at 80 °C for 12 h is displayed in Figure 3. At room temperature, however, the exchange rate is very low and both types of adducts (Et_3NBH_3, H_3NBH_3) are stable even when exposed to pure liquid base of the other type. Consequently, after thermal quenching by ammonia release, the adduct obtained from the base-exchange step can be separated. The comparison of the ^{1}H NMR (D_2O) spectrum: $\delta = 1.37$ ppm (q, $^1J_{BH} = 92$ Hz) of the compound obtained with that of pure AB substantiates its formation. Weak signals of the reactant NEt_3, the triplet at $\delta = 1.27$ ppm, and a quartet at $\delta = 3.17$ ppm, are still present in the spectrum. Evidence for the synthesis of the desired product AB is given by the occurrence of the quartet at $\delta = -24$ ppm in the $^{11}B\{^1H\}$ NMR spectrum with a coupling constant of $^1J_{B,H} = 92$ Hz, a value in the typical range for BH_3 moieties. The absence of the BH_3 quartet in the $^{11}B\{^1H\}$ NMR spectrum at $\delta = -12.1$ ppm for Et_3NBH_3 gives evidence that the exchange of NEt_3 for ammonia was complete.

As a test of the overall procedure, including all separation steps, we subjected a 40 mg sample of spent AB (PB) to the full recycling sequence, that is, BNH break-up and formation of BCl_3, hydrodechlorination (without removal of Et_3NHCl), BH_2Cl disproportionation (conversion according to $2\,BH_2Cl \rightarrow BHCl_2 + 0.5\,B_2H_6$), and base exchange, and obtained 25.7 mg AB (total yield 60 %, details and thermodynamic considerations see the Supporting Information).

In summary, it was demonstrated that the superacid/solvent system $HCl/AlCl_3/CS_2$ is capable of completely digesting borazine, polyaminoborane, and even cross-linked PB, the cross-linked PB being the form of the most strongly dehydrogenated AB material. The digestion is accompanied by the simultaneous conversion of the boron content of these compounds into volatile BCl_3 with high yields. The catalytic hydrodehalogenation was achieved with the Lewis base NEt_3 as a thermodynamic driver. In contrast to expectations from the respective pK_a values, the exchange of the auxiliary base NEt_3 in its BH_3 adduct for ammonia can be conducted in a way that is fast and goes to completion. Taking these points together allows a closed regeneration scheme to be set-up that combines the advantages of using inexpensive standard chemicals (HCl, $AlCl_3$, CS_2, NEt_3, Ni_3B) and the generation of B−H bonds by direct hydrogenation, that is, by using molecular hydrogen. For the recycling scheme to be self-contained all the by-products need to be easily convertible into the main reactants without generating new undesired products. For example, the auxiliary base, in the presented case NEt_3, can be regained by the reaction of its hydrochloride with NaOH. The sodium hydroxide used in this process is obtained during the chlorine production by chloralkali electrolysis necessary for the generation of HCl used in the break-up procedure. A comparably simple technical implementation for each step in the recycling scheme can always be found.

To our knowledge, the process developed demonstrates the first hydrodehalogenation of a BX_3 species based on the catalytic activation of molecular hydrogen. It will allow applications other than the one presented, such as the generation of valuable B−H containing species applicable as hydrogenation agents in organic synthesis, without the use of consumable metal hydrides.

Experimental Section

All reactants were handled under argon. The digestion processes were conducted in 15 mL stainless steel pressure vessel (alloy 59) using magnetic stirring. For the hydrodechlorination experiments the same autoclave was used with a PTFE insert. Solvents were purchased from ABCR and distilled from CaH_2 and stored under Argon. Aluminum chloride (ABCR) was sublimed prior to use. Gases: HCl 5.0 (Linde), Hydrogen 5.0 (Praxair), NH_3 3.8 (Linde), and BCl_3 5.0 (Linde) were used without further purification.

NMR spectroscopy: All NMR investigations were carried out at room temperature. ^{11}B and ^{1}H NMR spectra were recorded with a Bruker Avance III 500 MHz spectrometer. The ^{11}B shifts were referenced to BF_3OEt_2 ($\delta = 0$ ppm). For all samples spectra were measured with and without decoupling. NMR solvents were used without further purification.

Digestion of polyborazylenes (PB): PB (33 mg) was suspended in CS_2 (5 mL) and mixed with $AlCl_3$ (350 mg). The mixture was then kept at 80 °C and under 40 bar of HCl for 12 h.

The gas phase was then expanded into a cooling trap (−78 °C) which contained $CDCl_3$ (5 mL). Afterwards, the residue was identified to consist of $AlCl_3$, NH_4Cl. In the cooling trap BCl_3 ($^{11}B\{^1H\}$ NMR (C_6D_6): $\delta = 46$ ppm (s)) and small amounts of 2,4,6-trichloroborazine ($^{11}B\{^1H\}$ NMR (C_6D_6): $\delta = 32$ ppm (s)) and B-chlorinated borazanaphthalene ($^{11}B\{^1H\}$ NMR (C_6D_6): $\delta = 32$ ppm (s), $\delta = 29.4$ ppm (s), $\delta = 25.4$ ppm (s) were identified as the only compounds present. The quantification by ICP-OES showed that about 90 % of PB boron content was converted into BCl_3. The digestion of $(BH_2NH_2)_x$ and borazine was conducted analogously.

Hydrodechlorination of Et_3NBCl_3: Et_3NBCl_3 (300 mg; 1.3 mmol) of and Ni_3B (18 mg; 0.1 mmol) were added to triethylamine (7 mL) and loaded into a sealed pressure vessel with inner PTFE coating. Samples for ^{11}B NMR analysis were extracted under inert gas atmosphere every 30 min. The last sample was taken after 24 h.

Exchange of the base triethylamine for ammonia in the adduct Et_3NBH_3: Et_3NBH_3 (0.5 mL; 3.3 mmol) were dissolved in liquid ammonia (10 mL) and heated in a sealed pressure vessel using a temperature program for 12 h. Afterwards, the solution was thermally quenched by quickly releasing the NH_3 atmosphere from the pressurized vessel. Finally, BH_3NH_3, $^{11}B\{^1H\}$ NMR (D_2O): $\delta = -24$ ppm $^1J_{B,H} = 92$ Hz (q), was isolated by removing NEt_3 by vacuum distillation.

See the Supporting Information for further details.

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