A Single-Component Liquid-Phase Hydrogen Storage Material

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Ⓢ Supporting Information

ABSTRACT: The current state-of-the-art for hydrogen storage is compressed H_2 at 700 bar. The development of a liquid-phase hydrogen storage material has the potential to take advantage of the existing liquid-based distribution infrastructure. We describe a liquid-phase hydrogen storage material that is a liquid under ambient conditions (i.e., at 20 °C and 1 atm pressure), air- and moisture-stable, and recyclable; releases H_2 controllably and cleanly at temperatures below or at the proton exchange membrane fuel cell waste-heat temperature of 80 °C; utilizes catalysts that are cheap and abundant for H_2 desorption; features reasonable gravimetric and volumetric storage capacity; and does not undergo a phase change upon H_2 desorption.

Scheme 1. A Single-Component Liquid-Phase Hydrogen Storage Material

Safe, efficient storage and delivery of hydrogen is essential for the development of a hydrogen-based energy infrastructure. Storage of hydrogen as a compressed gas (up to 10 000 psi/700 bar) is the current state-of-the-art,[1,2] but to increase the storage density and mitigate the risks associated with storage and transport of high-pressure gas, numerous condensed-phase hydrogen storage approaches are currently under investigation. These include metal hydrides,[3] sorbent materials,[4] and chemical hydride[5] systems.[6] Boron- and nitrogen-containing chemical hydrides have attracted much attention because of their high gravimetric hydrogen densities and favorable kinetics of hydrogen release.[7,8] Ammonia borane (H_3N-BH_3, AB), with a gravimetric density of 19.6 wt % H_2, is one of the most promising candidates among the chemical hydride materials. AB has both hydridic and protic hydrogens, facilitating H_2 release under mild conditions. However, while the release of H_2 from AB and its derivatives has been extensively investigated,[9,10] AB is a solid material that releases H_2 at its melting point and cannot serve as liquid fuel without dilution (e.g., with a solvent), which necessarily reduces its hydrogen storage capacity.[11]

The appeal of a safe, liquid-phase hydrogen storage material is clear.[12] The U.S. has a network of over 150 000 miles (244 000 km) of pipeline dedicated to delivering liquid petroleum products, and many nations worldwide have similar networks in place.[13] The transition to a hydrogen-based energy economy will be greatly facilitated if it can take advantage of the existing liquid-based distribution channels such as pipelines, tankers, and retail outlets. Two potential liquid-phase hydrogen storage materials that have received recent attention in the literature are formic acid, HCO_2H,[14] and hydrous hydrazine, $N_2H_4 \cdot H_2O$.[15] One disadvantage of these compounds is that they have decomposition pathways that potentially generate side products that are toxic to fuel cell catalysts (e.g., CO and NH_3) in addition to safety
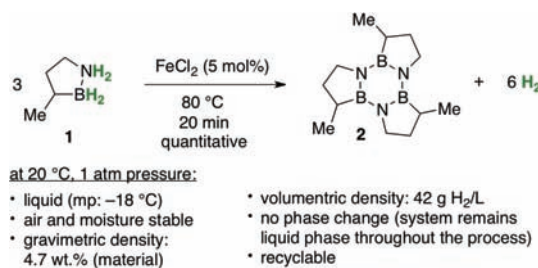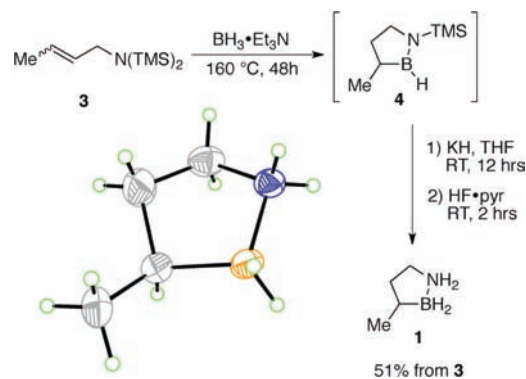
concerns (e.g., for hydrazine[16]). Liquid organic hydrides (i.e., hydrocarbons) are another class of potential hydrogen carriers, but for carbon-rich systems, the hydrogen liberation step is strongly endothermic, typically requiring reaction temperatures of 350−500 °C,[17] well above the "waste heat" temperature of 80−90 °C provided by a standard proton exchange membrane (PEM) fuel cell. This limitation can be overcome somewhat by the incorporation of heteroatoms into the carbon scaffold. Pez, Scott, and Chang of Air Products Corporation have studied the use of 9-ethylcarbazole as a hydrogen storage material and demonstrated the dehydrogenation of 9-perhydroethylcarbazole at 150−200 °C in a series of patents.[18,19] In 2010, Tsang et al. published a method to regenerate spent 9-ethylcarbazole fuel using molecular H_2 and an alumina-supported ruthenium catalyst.[20] One drawback to 9-ethylcarbazole hydrogen storage is that the spent fuel material is a solid at temperatures up to 60 °C.

Research in our lab focuses on the fundamental chemistry and applications of boron−nitrogen heterocycles (i.e., cyclic molecules containing carbon, boron, and nitrogen).[21−27] We recently reported the synthesis of 1,2-BN-cyclohexane,[28] a cyclic amine borane. Cyclic amine boranes have not been as extensively explored as AB and its acyclic derivatives in H_2 storage applications, arguably because of the lack of synthetic access. We noted that 1,2-BN-cyclohexane (mp: 63 °C) cleanly releases hydrogen to form a trimer when thermally activated. As part of an ongoing program directed toward hydrogen storage by BN heterocycles,[29,30] we disclose herein the development of BN-methylcyclopentane (**1**) (Scheme 1), which is an air- and moisture-stable liquid at room temperature. We report that **1** is capable of releasing 2 equiv of H_2 per molecule of **1** (4.7 wt %) both thermally, at temperatures above 150 °C, and catalytically using a variety of cheap and abundant metal halides, at temperatures

Scheme 2. Synthesis of Charged Liquid Fuel 1

Figure 1. Automated volumetric buret measurements of H_2 release catalyzed by metal chloride complexes.

below 80 °C. The exclusive product of dehydrogenation is the trimer **2**, which is also a liquid at room temperature. We also demonstrate that the conversion of the spent fuel **2** back to the charged fuel **1** can be accomplished in high yield under relatively mild conditions, making this system a viable candidate for liquid-phase hydrogen storage in mobile and carrier applications.

The synthesis of **1** is illustrated in Scheme 2. Treatment of the bis-N-protected amine **3** with neat $BH_3 \cdot Et_3N$ at 160 °C for 48 h generated heterocycle **4**, which was not isolated. The crude mixture was diluted with THF, and then KH and HF·pyridine were added to generate the charged fuel **1**. The product was purified by column chromatography under ambient conditions (i.e., in the presence of oxygen and moisture), and **1** was isolated in 51% overall yield from **3**. Compound **1** is a liquid at room temperature with a melting point of −18 °C. At lower temperatures, we were able to grow crystals of **1** that were suitable for single-crystal X-ray diffraction (XRD) analysis, thus unambiguously confirming our structural assignment (see the ORTEP in Scheme 2).

We determined that heterocycle **1** is thermally stable at 35 °C as a neat liquid [see the Supporting Information (SI) for details]. However, upon heating at 150 °C for 1 h in the absence of solvent, each of three molecules of **1** releases 2 equiv of H_2 in forming the trimer **2** (eq 1), which is also a liquid at room temperature (mp: 9 °C). Thus, the hydrogen desorption from charged fuel **1** to form the spent fuel **2** does not involve a phase change, a critical property for a liquid-phase H_2 carrier in terms of actual application in fuel cells.[11,31] Additionally, **1** and **2** display low volatility, with boiling points of approximately 335 and 378 °C, respectively (determined at reduced pressure and extrapolated to 1 atm), reducing the risk of introducing potential fuel cell poisons into the H_2 stream.

(1)

charged fuel ⟶ spent fuel

−6 H_2
150 °C, 1 hr
98% yield

no phase change

liquid at 20 °C | liquid at 20 °C

bp: 70 °C at 0.18 torr
extrapolated: 335 °C at 1 atm

bp: 93 °C at 0.16 torr
extrapolated: 378 °C at 1 atm
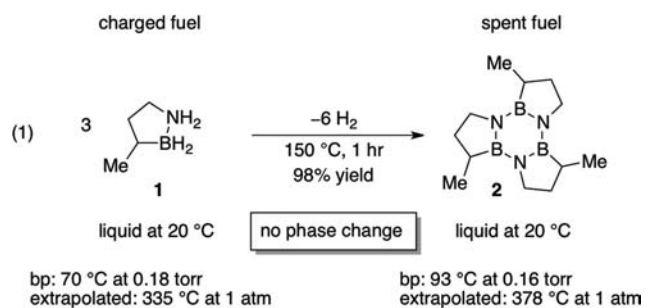
Metal-catalyzed dehydrogenation of AB has attracted growing attention from the perspective of hydrogen storage. Although many important advances have been made with Pd, Ru, Ir, and
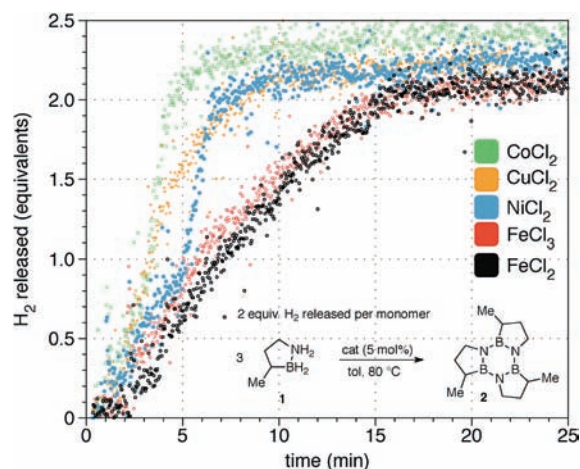
other noble-metal catalysts,[9] the development of convenient-to-handle, cheap, abundant, and efficient catalysts with low toxicity is of considerable interest. Our research has focused on first-row transition-metal halide catalysts.[32] To our knowledge, there have been only a limited number of publications discussing the dehydrogenation AB with these metal salts. Ramachandran and co-workers reported the use of $NiCl_2$ and $CoCl_2$ as catalysts for methanolysis of AB,[33] and Jagirdar et al. used $CoCl_2$, $NiCl_2$, and $CuCl_2$ as reactants to assist in the hydrolysis of AB.[34] The use of iron halide salts for AB dehydrogenation in the solid state has recently been reported by Chen et al.[35]

To find the most effective metal halide catalyst for the dehydrogenation of **1**, we screened anhydrous F, Cl, Br, and I complexes of Fe, Co, Ni, and Cu at 5 mol % catalyst loading in toluene.[36] We monitored the reaction progress by ^{11}B NMR spectroscopy. The postulated dimer intermediate **5** (Table S1 in the SI) was visible in the ^{11}B NMR spectrum (96 MHz, toluene; 3.0 ppm, doublet, $^{1}J_{BH} = 117$ Hz) but could not be isolated.[37−41] The conversions after 5 min at 80 °C are listed in Table S1. We found that in general, bromide complexes are the most reactive toward formation of **2**, followed by chloride and then iodide complexes, and that fluoride complexes are almost completely inactive. Copper, nickel, and cobalt halides are more reactive than iron halides. The two most active catalysts in this study were $NiBr_2$ and $CuBr$, both of which achieved 76% conversion to **2** in 5 min. All of the selected chloride, bromide, and iodide complexes can completely dehydrogenate **1** to release 2 equiv of H_2 per molecule of **1** in less than 30 min. The presence of a catalyst was essential for H_2 desorption at 80 °C. No H_2 release was observed after 1 h at 80 °C without a catalyst.

To understand further the differences between various iron, cobalt, nickel, and copper chloride complexes, we performed several dehydrogenation experiments using an automated gas buret apparatus.[42] Chloride complexes were chosen for this study because they are significantly cheaper than bromide complexes. In a general procedure, we dissolved 75 mg of **1** in toluene with 5 mol % catalyst and submerged the reaction flask in an 80 °C oil bath. Varying the metal resulted in markedly different hydrogen release profiles (Figure 1). $CoCl_2$ promoted the release of 2 equiv of H_2 from **1** in ca. 7 min, and the $CuCl_2$- and $NiCl_2$-catalyzed reactions were complete in under 10 min. The reactions with iron complexes were slower; both $FeCl_3$ and $FeCl_2$ promoted the
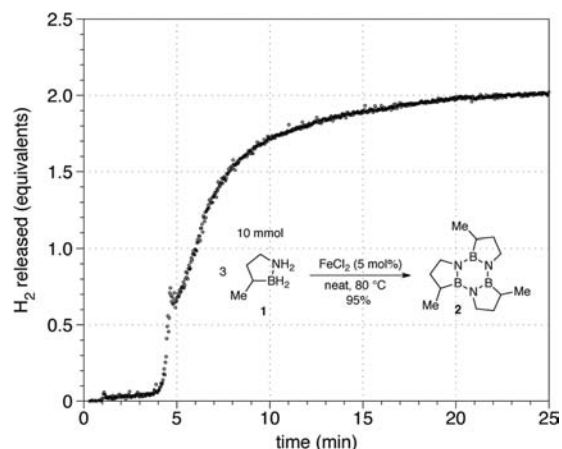
Figure 2. Large-scale dehydrogenation of **1** using 5 mol % FeCl$_2$ without solvent.
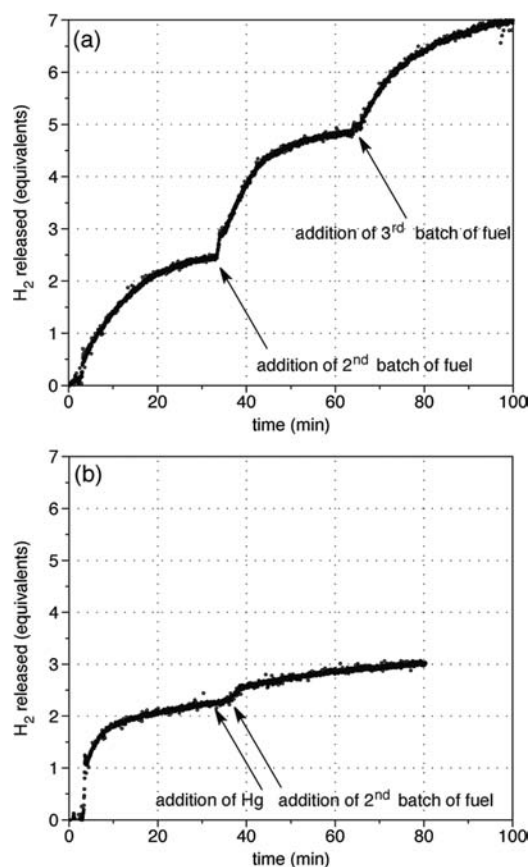

Figure 3. (a) H$_2$ evolution trace for sequential addition of charged fuel **1**. (b) H$_2$ evolution trace with Hg poisoning of the catalyst.

desorption of 2 equiv of H$_2$ in ca. 15 min. Interestingly, for the cobalt- and nickel-catalyzed reactions, the initial rate of H$_2$ desorption (i.e., from $t = 0$ to t for 1.0 equiv of H$_2$) is apparently lower than the rate over the time period from 1.0 to 2.0 equiv. We repeated the automated buret measurement experiments illustrated in Figure 1 at 50 °C and noted that the time required for complete H$_2$ desorption exceeded 4 h for all catalysts (see the SI for details). This suggests that the reaction temperature has a significant effect on the rate of dehydrogenation.

Scheme 3. Conversion of Spent Fuel 2 Back to Charged Fuel 1
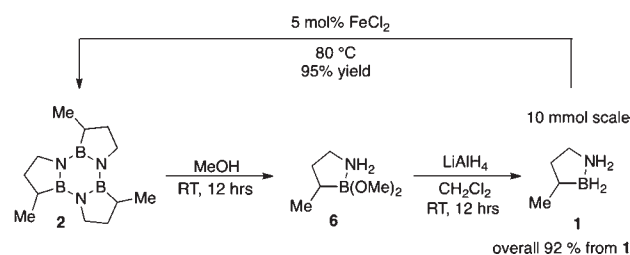
To demonstrate the potential utility of our material as a simple-to-operate, single-component liquid system, we performed a large-scale dehydrogenation of **1** (10 mmol, the maximum capacity of our buret apparatus) without additional solvent using 5 mol % FeCl$_2$ as a catalyst.[43] Figure 2 shows that 2 equiv of H$_2$ were released from the neat material in ca. 20 min at 80 °C. At the conclusion of the reaction, the spent fuel **2** was isolated in 95% yield. Noteworthy is the induction period of ca. 4 min before significant H$_2$ release was observed.[44]

The FeCl$_2$ catalyst changed form during the course of the reaction, becoming an amorphous black powder. At 5 mol % loading, the catalyst could be reused without loss of activity (Figure 3a). Adding fresh fuel **1** to the reaction flask after dehydrogenation of the old batch had completed resulted in immediate H$_2$ desorption from the new batch of fuel (tested up to three times, the capacity of our buret apparatus; see the SI for details). We also performed dehydrogenation experiments with reduced catalyst loading. With 3 mol % FeCl$_2$, the rate of dehydrogenation decreased significantly; 2 equiv of H$_2$ were released in 40 min. With 1 mol % FeCl$_2$, only 0.4 equiv of H$_2$ were released after 70 min. To probe the nature of the active catalyst species, Hg was added to the reaction mixture, and a reduced rate of hydrogen release was observed, consistent with heterogeneous catalysis (Figure 3a vs 3b).[45]

Recyclability is crucial to the success of any hydrogen storage system. For H$_2$ desorption of AB, a variety of monomeric (e.g., cyclotriborazane, cyclopentaborazane, and borazine) and polymeric (e.g., polyamino- and -iminoboranes and polyborazylene) spent fuel products can be produced depending on the dehydrogenation conditions, thus making this system less well-defined and arguably potentially more challenging to regenerate.[46] Recently, Sutton and Gordon demonstrated that one spent fuel product of AB dehydrogenation, polyborazylene, can be regenerated with hydrazine in liquid ammonia.[47−49] The hydrogen desorption of storage material **1** to form **2** is a clean process. We believe that the well-defined molecular nature of the spent fuel **2** should facilitate the development of a regeneration process. We determined that treatment of **2** with methanol for 12 h at room temperature produces the bismethoxy species **6** (Scheme 3), as confirmed by single-crystal XRD analysis.[50] Subsequent treatment of **6** with LiAlH$_4$ afforded the charged fuel **1** in 92% overall yield. This "regeneration" sequence was performed using the product of our 10 mmol-scale dehydrogenation experiment (Figure 2) to demonstrate the recyclability of our hydrogen storage system on a larger scale. We acknowledge that the described regeneration scheme is not yet optimal from an energetic point of view (i.e., the use of highly energetic LiAlH$_4$ ultimately needs to be avoided).

In summary, we have developed an air- and moisture-stable liquid-phase hydrogen storage material, **1**, that does not undergo a phase

change upon H_2 desorption. We have discovered a series of first-row transition-metal halide catalysts that are capable of releasing 2 equiv of H_2 from **1** in less than 30 min in toluene at 80 °C at modest catalyst loadings. We have demonstrated that neat liquid **1** can quantitatively release H_2 in the presence of $FeCl_2$ catalyst. Furthermore, we have shown that the spent fuel **2** can be converted back to the charged fuel **1** in good yield. The disclosed hydrogen storage material could represent a viable H_2 storage option for mobile, portable, and carrier applications. Current efforts are being directed toward developing a more cost- and energy-efficient regeneration procedure.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures, spectroscopic data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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