Hydrogen Storage

DOI: 10.1002/anie.201003074

Catalytic Solvolysis of Ammonia Borane**

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An energy source with a low environmental impact remains a crucial goal for our society. While energy consumption is a broader concern, transportation is an area of keen interest. Hydrogen is an attractive alternative to petrochemical resources because its combustion produces only water as a by-product. Unfortunately, the physical properties of hydrogen, which complicate its safe, efficient, and economical storage, remain a significant barrier toward establishing hydrogen as a viable source of energy.[1] Of the known hydrogen storage technologies (i.e. compression and liquefaction,[2] metal hydrides,[3] chemical hydrides[1b,d], and carbon nanotube adsorption[4]) chemical hydrides have the highest gravimetric storage capacity. Despite recent determinations by the Department of Energy (DOE) on the status of sodium borohydride,[5] ammonia borane remains one of the most compelling candidates for hydrogen storage because of its higher hydrogen content (19.6 wt %) and stability.[1b,d,6] Indeed, the aforementioned DOE report goes so far as to suggest that the decision to not use sodium borohydride should not impact continued research on ammonia borane (AB). Moreover, applications outside of transportation remain equally worthy of consideration, not only as a means to further the refinement of developing technologies, but also to encourage the development of critical aspects connected with the establishing of new energy sources, such as the supply and distribution channels.

Several homogeneous catalysts have been shown to catalyze the release of one equivalent of hydrogen from ammonia borane at ambient temperature. For example, a very efficient homogeneous iridium catalyst for the dehydrogenation of ammonia borane was reported by Goldberg and co-workers, who demonstrated the fast release of hydrogen within 20 minutes at room temperature.[7] Relevant pincer-type catalysts have shown similar efficacies as demonstrated by the research groups of Fagnou[8a] and Schneider.[8b] Manners and co-workers have demonstrated that pincer-based catalysts can catalyze the linear polymerization of ammonia borane to form poly(aminoborane).[9] Baker and co-workers described the acid-initiated dehydrogenation of ammonia borane[10] as well as a homogeneous nickel-containing catalyst capable of effecting the dehydrogenation of ammonia borane wherein a 94 % yield of hydrogen was observed in three hours at 60 °C.[11] Despite these advances, dehydrogenation of ammonia borane remains limited both in terms of hydrogen yield and reaction rate.

In contrast, the hydrolysis of ammonia borane in the presence of a heterogeneous catalyst can provide up to three equivalents of hydrogen per mole of ammonia borane at room temperature at satisfactory rates. Several reports have appeared (see for example Xu and Chandra,[12a,b] Manners and co-workers,[12c] Ramachandran and Gagare,[12d] and Jagirdar and co-workers[12e]), which detailed heterogeneous catalysts containing noble or basic metals and used for the hydrolysis of ammonia borane. Unfortunately, these systems require relatively high catalyst loadings and the catalysts have proven difficult to recover with no option for reuse. Recently, reusable monodisperse nickel nanoparticles have emerged as useful catalysts that display five cycles of catalytic activity.[13] Nonetheless, the most practical issue—the systemic wt % of hydrogen—is rarely addressed for hydrolysis-based systems. For example, the system wt % of hydrogen for the hydrolysis of ammonia triborane (where the system weight is defined as $NH_3B_3H_7$ + water + catalyst) is 6.1 % when a base metal heterogeneous catalyst is used. The comparison of this value with the modified DOE target of 7.5 % systemic gravimetric capacity[14] for the year 2015 shows that the systemic wt % of hydrogen is among the most significant hurdles for the development of an efficient system for the generation of hydrogen by means of hydrolytic methods. That is, the requirement for the reaction media (i.e. organic solvent or water in the case of solvolytic or hydrolytic processes), which contributes greatly to the total weight of the system, significantly diminishes the hydrogen wt % of the system.

Herein, we describe a system for the solvolysis of ammonia borane that constitutes significant progress toward addressing the issues described above. The simple and robust system displays rapid and quantitative evolution of hydrogen from ammonia borane and employs a homogeneous iridium catalyst with exceptionally low loadings and minimal use of solvent.

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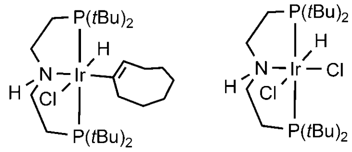
[**] Horizon Fuel Cell Technologies is acknowledged for assistance and helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003074.

Extensive screening of a series of homogeneous catalysts indicated that the hydrogenation catalysts **1**[15] and **2** were excellent candidates for the solvolysis of ammonia borane (Scheme 1). In a typical experiment, addition of ammonia borane to a solution of a solvent/water mixture at 40 °C predosed with catalyst gave rise to immediate and vigorous evolution of hydrogen, which was measured in a water-filled graduated measuring cylinder (see the Supporting Information for the experimental setup). Within 10 minutes, 2.20 equivalents of H_2 (960 mL) was generated in THF/water (1:1; Figure 1). In EtOH/water (1:1), 2.36 equivalents of H_2 was generated, while in *i*PrOH/water(1:1), 2.93 equivalents of H_2 was generated. A reusability test showed that upon consecutive additions of ammonia borane (up to 10 additions), the same activity was maintained as both the amount of hydrogen generated and the reaction time required remained constant (Figure 2). No obvious initiation process was observed based on the apparent lack of an induction period. The remaining solution (which contained the activated catalyst, residual ammonium borate, and the solvent) was still effective in generating hydrogen from ammonia borane even after prolonged exposure to air for a few weeks.



1 **2**

Scheme 1. Catalysts for solvolysis of ammonia borane.

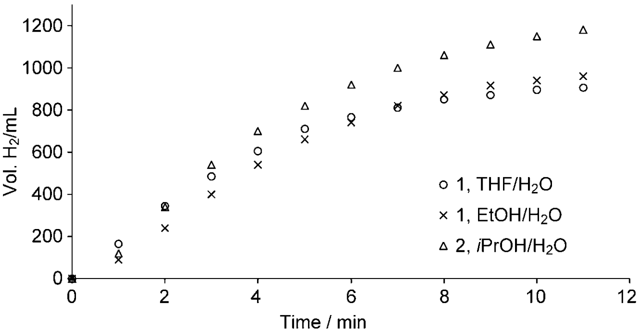


Figure 1. Solvolysis of ammonia borane catalyzed by **1** and **2** (40 °C).

Other factors such as the stability of the catalyst and the solvent system were investigated. Catalyst **1** decomposes slowly in the solid state, and relatively fast in the solution state. This observation is probably a result of the decomposition/loss of the labile cyclooctenyl ligand. Therefore, the air-stable catalyst, **2**, was investigated. Improved performance in terms of efficacy of hydrogen generation was observed with catalyst **2** along with a marked improvement in stability. The NMR sample solutions of **2** showed no observable change after heating in wet $CDCl_3$ for four days at 80 °C. Moreover, storing solid **2** at 100 °C for 30 days resulted in no observable change in both purity and activity. The solid-state structure of **2** is shown in Figure 3.[16]

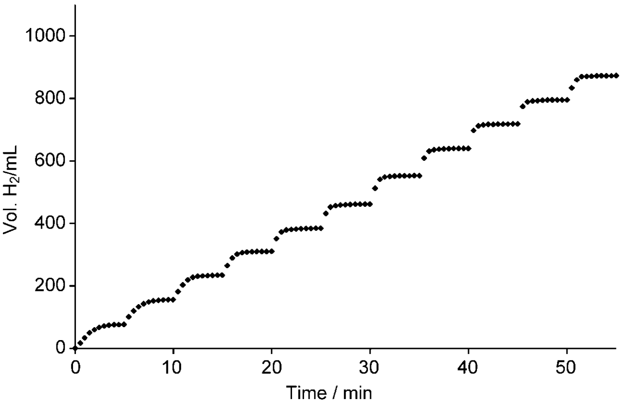


Figure 2. Consecutive solvolysis of ammonia borane catalyzed by **1** (40 °C). Ammonia borane (50 mg) was added in each time interval; [Cat] = 0.04 mol % against 500 mg total AB consumed.

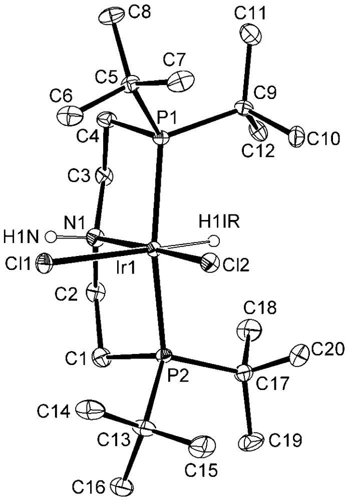


Figure 3. X-ray crystal structure of **2**. Thermal ellipsoids are set at 30 % probability. Non-nitrogen and non-iridium hydrogen atoms removed for clarity. Bond lengths are in Å: Ir1–H1Ir 1.53(7); Ir1–N1 2.094(4); Ir1–Cl1 2.5400(14); Ir1–Cl2 2.3874(13).

A wide range of solvent mixtures were examined and it was found that the optimal combination is either ethanol/water or isopropanol/water in an approximately 1:1 mixture. In both cases, similar results were obtained. For example, in isopropanol/water the reaction afforded up to 2.93 equivalents (1220 mL, with catalyst **2**) of hydrogen (Figure 1). Decreasing the volume to as low as 1 mL does not significantly affect the rate, however the total volume of the hydrogen released remains the same (Figure 4). Elemental analysis of the residual ammonium borate showed little carbon content, thus suggesting that, under these conditions, the alcohol cosolvent is not significantly incorporated into the by-product through the solvolysis reaction.[17] Where purely

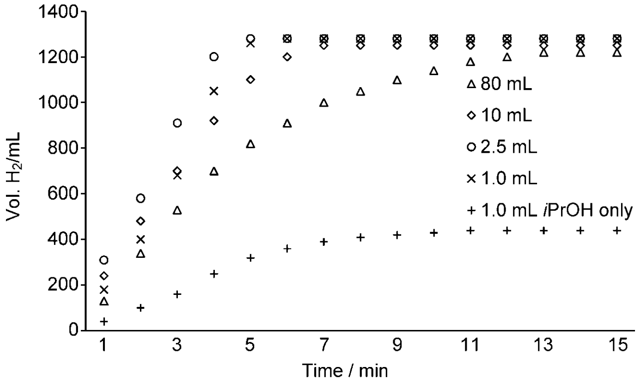


Figure 4. Effect of solvent volume on volume of H_2 produced in the solvolysis of ammonia borane with **2** in *i*PrOH/H_2O (1:1; v/v) at 40 °C.

organic solvent (*i*PrOH) is used, the activity is significantly diminished although some hydrogen is generated (Figure 4).

A key feature of any portable hydrogen generation system is the hydrogen wt % (i.e. for transportation purposes, the DOE target is 7.5 % for the year 2015).[18] In an effort to reduce the solvent requirement, we have examined the possibility of using only water vapor as the reaction medium to support the action of the catalyst on ammonia borane. The appeal of a system operating in this manner is that the water vapor could be recovered from the fuel cell (i.e. little or no water would need to be stored as part of the system), thereby further reducing the total weight of the system. To this end, ammonia borane (1 g) and catalyst **2** (1 mg) were thoroughly mixed together as solids with a mortar and pestle and were then placed in a sealed flask containing a water-soaked wick (which never made physical contact with the solid). From this freshly prepared mixture, nearly three equivalents of hydrogen was generated in four hours with stirring of the solid mixture and in seven hours without stirring (Figure 5). This corresponds to approximately 9.1 wt % of hydrogen. For comparison, sodium borohydride blended with catalyst **2** shows no evolution of hydrogen whatsoever under the same conditions, thus highlighting the selectivity of the catalyst toward ammonia borane solvolysis/hydrolysis. The derived hydrogen contained 0.2–0.5 % of NH_3, which was easily removed by passing the generated hydrogen through a filter of solid citric acid.[17]

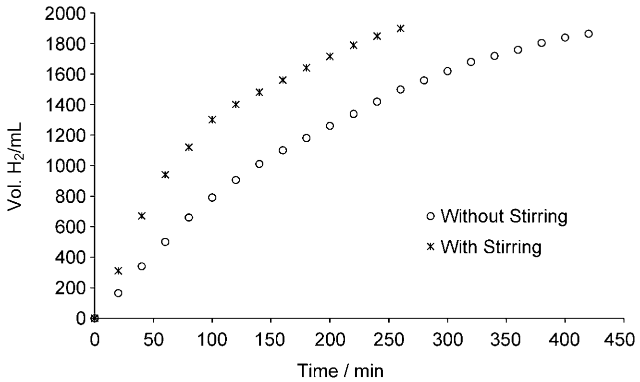


Figure 5. Solid-state solvolysis of 1 g of ammonia borane by catalyst **2** and water vapor (25 °C).

In summary, we have developed a system which, through the solvolysis of ammonia borane, results in the immediate and quantitative evolution of hydrogen. This system employs a simple and highly robust catalyst with minimal solvent requirements, an exceptional reusability profile, and high gravimetric hydrogen content. Studies on the elucidation of the mechanism and on the nature of the active catalyst are ongoing.

Experimental Section

[Ir(H)Cl((*t*$Bu_2PCH_2CH_2)_2$NH)(C_8H_{13})][15] (**1**): A mixture of [Ir(coe)$_2$Cl]$_2$ (0.675 g, 0.75 mmol) and HN(*t*$Bu_2PCH_2CH_2)_2$ (0.540 g, 1.49 mmol) was dissolved in toluene (5 mL) and stirred for 20 min. Hexanes (10 mL) was added and the precipitated solid was collected by filtration and dried in vacuo. Yield: 0.77 g, 74 %; ^{1}H NMR (C_6D_6): $\delta = 6.03$ (br, 1 H, N*H*), 5.51 (br, 1 H, C*H*), 3.29 (m, 2 H, CH_2), 2.34 (m, 2 H, CH_2), 2.58 (m, 2 H, CH_2), 2.12 (br, 2 H, CH_2), 1.68–1.92 (m, br, 12 H, CH_2), 1.52 (vt, $J = 6.0$ Hz, 18 H, CH_3), 1.21 (vt, $J = 6.0$ Hz, 18 H, CH_3), −25.46 ppm (t, br, 1 H, Ir*H*); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 31.6$ ppm. coe = cyclooctene.

[Ir(H)Cl_2((*t*$Bu_2PCH_2CH_2)_2$NH)] (**2**): A solution of [$H_2N(CH_2CH_2P$*t*$Bu_2)_2$]Cl (2.0 g, 5.02 mmol) in THF (5 mL) was added to a solution of [Ir(coe)$_2$Cl]$_2$ (2.25 g, 2.51 mmol) in THF (5 mL) and the mixture was stirred for 30 min. Diethyl ether (30 mL) was then added to precipitate the product. The product was further purified by recrystallization from CH_2Cl_2/diethyl ether (1:4) to obtain an off-white solid. Yield: 2.39 g, 76 %; ^{1}H NMR (CD_2Cl_2): $\delta = 6.97$ (br, 1 H, N*H*), 2.74 (m, 4 H, CH_2), 1.74 (m, 4 H, CH_2), 1.09 (vt, $J = 6.6$ Hz, 18 H, CH_3), 0.99 (vt, $J = 6.6$ Hz, 18 H, CH_3), −34.1 ppm (t, br, 1 H, Ir*H*); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 59.0$ ppm; elemental analysis calcd for $C_{20}H_{46}Cl_2IrNP_2$: C, 38.39; H, 7.41; N, 2.24; found: C, 37.81; H, 7.16; N, 2.21.

Catalytic solvolysis of ammonia borane (Figure 1 and 4): 1.0 mL (1.0 mg, 1.43×10^{-3} mmol) of a 1.0 mg mL^{-1} tetrahydrofuran solution of the desired catalyst was added in air to 80 mL of a 1:1 (v/v) mixture of organic solvent/water that had been immersed for 5 min in a water bath held at 40.0 °C. Ammonia borane (0.500 g, 16.2×10^{-3} mol) was added and the hydrogen formation was measured.

Solid-state hydrolysis of ammonia borane: A mixture of **2** (1.0 mg, 1.60×10^{-6} mol) and ammonia borane (1.034 g, 33.5×10^{-3} mol) were ground into a fine powder and placed in a conical flask equipped with a water-soaked wick (ca. 3 g). The amount of hydrogen liberated was measured in intervals of 20 min.

Quantification of liberated NH_3: The gas generated from the catalytic reaction was passed through a standardized solution of H_2SO_4 (0.0112 M) at RT. After gas generation ceased, the resulting solution was titrated with a standard solution of 0.010 M NaOH using phenolphthalein indicator. The quantity of the liberated NH_3 gas was calculated from the difference between two H_2SO_4 solutions before and after the reaction. 0.2–0.5 % of NH_3 was detected when using *i*PrOH/H_2O (1:1) and 1.5 % of NH_3 when using *i*PrOH/H_2O (3:1) as the reaction media. All the NH_3 gas was successfully trapped by passing through a filter packed with citric acid.

Received: May 21, 2010
Revised: August 30, 2010
Published online: October 4, 2010

Keywords: ammonia borane · catalytic hydrolysis · homogeneous catalysis · hydrogen storage

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[16] CCDC 776797 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Tables of bond lengths and angles can be found in the supporting information for this article.

[17] See the Supporting Information.

[18] For the sake of perspective, the U. S. DOE targets are set such that a vehicle can travel > 300 miles (480 km) without refueling, which would require 4 kg (≈45000 L) of hydrogen. If a system can evolve three equivalents of H_2 from one equivalent of AB, 18 kg of AB will be required. It should be noted however that demands for portable H_2 storage devices go beyond transportation. Powering and/or recharging hand-held or small electronic devices is an area of significant interest and such applications represent more immediate applications for ammonia-borane-based hydrogen storage technologies such as that presented here. Further, these small-quantity applications place less of an emphasis on regeneration of spent ammonia borane.