REVIEWS

Hydrogen generation from ammonia borane using nanocatalysts

Suresh Babu Kalidindi AND Balaji R. Jagirdar

Abstract | The rapidly depleting petroleum feed stocks and increasing green house gas emissions around the world has necessitated a search for alternative renewable energy sources. Hydrogen with molecular weight of 2.016 g/mol and high chemical energy per mass equal to 142 MJ/kg has clearly emerged as an alternative to hydrocarbon fuels. Means for safe and cost effective storage are needed for widespread usage of hydrogen as a fuel. Chemical storage is the one of the safer ways to store hydrogen compared to compressed and liquefied hydrogen. It involves storing hydrogen in chemical bonds in molecules and materials where an on-board reaction is used to release hydrogen. Ammonia–borane, (AB, $H_3N·BH_3$) with a potential capacity of 19.6 wt% is considered a very promising solid state hydrogen storage material. It is thermally stable at ambient temperatures. There are two major routes for the generation of H_2 from AB: catalytic hydrolysis/alcoholysis and catalytic thermal decomposition. There has been a flurry of research activity on the generation of H_2 from AB recently. The present review deals with an overview of our efforts in developing cost-effective nanocatalysts for hydrogen generation from ammonia borane in protic solvents.

1. Introduction

1.1. *Energy*

Energy is essential for human civilization and for the social progress of mankind. Man's current energy needs are by and large met by the fossil fuels such as petroleum, oil, and natural gas. These energy resources are limited and not renewable.[1] The rapidly depleting fossil fuel feed stocks and increasing green house gas levels around the world have necessitated search for alternative sources of fuel. Restructuring our energy economy towards sustainable energy sources is inevitable in the present scenario of global energy and environmental crisis.

Hydrogen is considered as one of the promising alternatives to fossil fuels because of its high energy content and environmental friendliness.[2] When hydrogen is burned with oxygen, it releases 142 MJ/kg of energy and water as a by-product. One of the major hurdles for its widespread usage for mobile applications is its storage. Physical hydrogen storage which involves storing of hydrogen as a gas or liquid is very difficult due to its low density and is unsafe for practical applications. Chemical hydrogen storage which involves storing of hydrogen in the form of chemical bonds in molecules is one of the safe alternatives to physical hydrogen storage. The requirements for an on-board hydrogen storage material for transportation include the following:

- High gravimetric and volumetric densities

- Appropriate thermodynamics

- Fast kinetics

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Scheme 1: Classification of hydrogen storage materials based on the interaction between hydrogen and the storage medium.
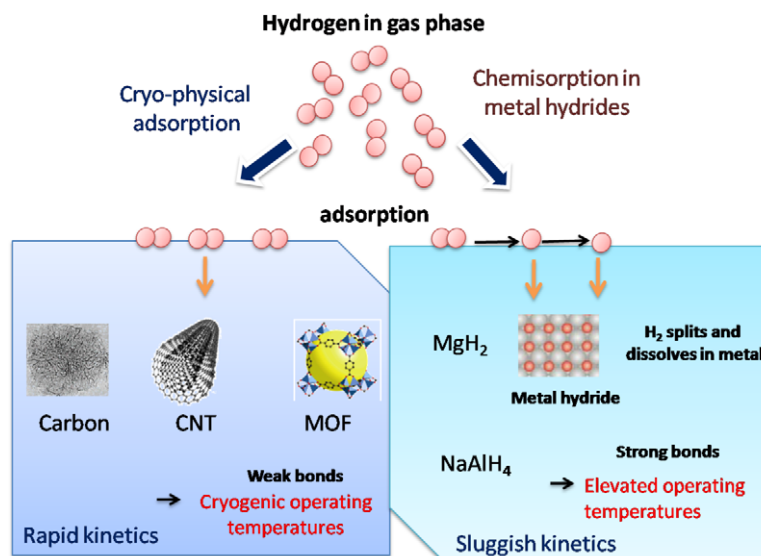
Scheme 1 shows the classification of the hydrogen storage materials based on the interaction between hydrogen and the storage material, i.e., physical adsorption and chemisorption.[3] Physisorption of hydrogen involves binding of the hydrogen molecule to adsorbent by very weak forces such as van der Waals forces. Using this approach, reasonable gravimetric hydrogen storage could be attained, but only at very low temperatures (77 K), whereas fast kinetics and reversibility are the main advantages of this approach.[4] Chemisorption of hydrogen involves dissociation of hydrogen into atoms on metal surfaces, which dissolve inside the metal lattice to form a solid solution. Atomic hydrogen stored in the interstitial sites of metal recombine at the particle surfaces during the desorption process requiring high temperatures which is the main disadvantage of this approach.[5]

Even though several materials have been investigated using both approaches (physisorption and chemisorption) none of the currently-known materials seem to meet the stringent requirements of a storage material for practical applications.

1.2. Chemical hydrogen storage: hydrogen generation from ammonia borane

Generation of hydrogen from suitable carriers is a safe alternative to hazardous physical hydrogen storage. In this regard, boron hydrides with high gravimetric content of hydrogen are considered to be promising materials as carriers of hydrogen for portable applications.[6]

Ammonia borane ($H_3N \cdot BH_3$, AB) with 19.6 wt% of hydrogen has been attracting immense

interest as a hydrogen storage medium in recent years.[7] It possesses a volumetric density of 146 g H_2/lit and a gravimetric density of 196 g H_2/kg. These values are well above the US Department of Energy targets (2015) of a volumetric density greater than 82 g H_2/lit and a gravimetric density greater than 90 g H_2/kg. Ammonia borane is a stable white solid and a safe material to handle under ambient conditions, which makes it very attractive for practical applications. Ammonia borane was first synthesized by Shore and Parry in 1958 using $NaBH_4$ and NH_4Cl in ether solvent.[8] Even though Ramachandran and Gagare reported the preparation of AB using sodium borohydride and ammonium formate on a large scale (10 mol) in high purity ($>98\%$) in dioxane,[9] the cost involved is high, therefore, it is imperative to find an efficient and economical synthesis procedure for real-time applications.

Release of hydrogen from AB can be accomplished either by thermolysis (neat or metal catalyzed) in the solid state and non-aqueous medium (ethereal solvents) or metal catalyzed reactions in protic solvents (water and methanol) (Scheme 2).[7] In general, the spent products (byproducts) obtained from the thermolysis of AB are BNH_x polymers, whereas catalytic decomposition in water affords $B(OH)_3$. Calculations indicate that for AB to form $1/n [B_3N_3H_4]_n$ and release 2.3 equiv of hydrogen, the $\Delta H_{rxn} = -60.8$ kJ mol^{-1}, whereas to form $B(OH)_3$ and release 3 equiv of hydrogen, the $\Delta H_{rxn} = -227$ kJ mol^{-1}.[10] Calculations also indicate that thermolysis of AB in aprotic solvents

Scheme 2: Hydrogen generation from ammonia borane in different media.
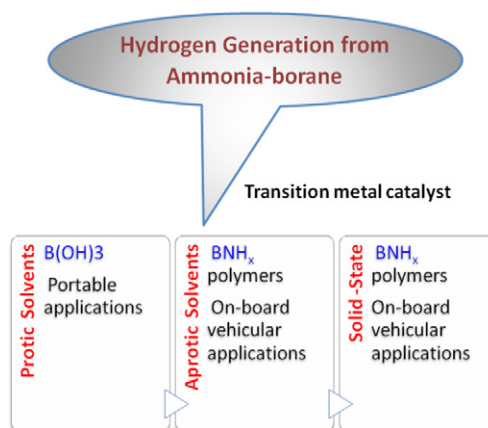
and in solid state could find applications for on-board hydrogen storage provided, energy efficient off-board regeneration routes are discovered. And with the development of a one pot regeneration process of AB from the spent material very recently demonstrated by Davis et al., AB promises to be a potential hydrogen storage material for the future generations.[11]

Ammonia borane is highly soluble and quite stable in protic solvents such as water and methanol. The ^{11}B NMR spectrum remains unchanged in water for more than 80 days under an argon atmosphere, indicating the high stability of AB in water.[12] In the presence of transition metal catalysts, AB undergoes dissociation in protic solvents (R–OH) to liberate three equivalents of hydrogen and $B(OR)_3$ as the byproduct.[13] Since regeneration of AB from $B(OR)_3$ type of products is a highly energy intensive process, this route can be used only for mobile applications to meet short term energy needs, rather than for vehicular on-board applications. The hydrogen generated using this route can be used in polymer electrolyte membrane fuel cell (PEMFC) as a fuel. The advantages associated with this system are: (i) it does not need an external base (NaOH) to stabilize the starting material and the pH of the solution is close to neutral; (ii) rapid hydrogen generation could be achieved even at room temperature in the presence of suitable catalysts; (iii) this system has a high hydrogen capacity, which releases hydrogen with an $H_2/AB = 3.0$.

1.3. *Nanocatalysis*

Heterogeneous catalytic reactions play pivotal roles in many industrial processes like energy production, pharmaceutical drug synthesis, environmental remediation, etc.[14] Although heterogeneous catalysis is understood to a lesser extent compared to homogeneous catalysis, the interaction of molecules with single crystalline surfaces of metal is well established, thanks to advanced characterization techniques such as atomic force microscopy. In these processes, the interaction of molecules with the surface of a solid (catalyst) is decisive. The fields of catalysis and nanoscience are inextricably linked to each other. Nanocatalysts with large surface area and a variety of defect sites are expected to show improved catalytic properties compared to conventional catalysts comprising of micron sized particles.[15] The major breakthrough in this field was reported in the late 1980s by Haruta et al.: Au nanoparticles (<5 nm) supported on Fe_2O_3 were found to be very active for CO oxidation below room temperature.[16] Since then, many reactions were studied using transition metal nanocatalysts. Most catalysts are based on precious metals (Pt, Rh, Ru, Pd and Ag);[17] their use is limited from the standpoint of both cost and material availability on a global scale. Thus, more work needs to be done towards developing first row transition metal based catalysts which are less expensive and more abundant. The present review deals with an overview of our efforts in developing cost-effective nanocatalysts for hydrogen generation from ammonia borane in protic solvents.

2. Catalytic hydrogen generation from ammonia borane in protic solvents

2.1. *Precious metal catalysts*

The addition of catalytic amount of suitable precious metal catalysts such as Pt, Rh, and Ru to aqueous AB solution leads to vigorous release of about 3 equivalents of hydrogen gas (eq. (1))[18]

$$H_3N \cdot BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2. \quad (1)$$
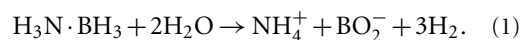
The course of AB hydrolysis reaction can be easily monitored by ^{11}B NMR spectroscopy. After

the completion of reaction, the 1:1:1:1 quartet signal at $\delta - 23.9$ ppm corresponding to AB disappears and a singlet resonance appears between 8 and 18 ppm due to products such as H_2BO_3, BO_2^- and other borate species in equilibrium in the solution. Xu and co-workers studied the hydrolysis of AB using various supported precious metal nanoparticles.[18] Among those nanocatalysts, γ-Al_2O_3 supported Ru, Rh, and Pt nanoparticles (2 wt%) were found to be highly active towards AB hydrolysis, effecting hydrogen release of $H_2/AB = 3.0$ in 3.0, 1.3 and 0.75 min, respectively (metal/AB = 0.018). The Pd/Al_2O_3 and Au/Al_2O_3 nanocatalysts showed lower catalytic activities, releasing hydrogen of $H_2/AB = 2.9$ in 120 min and $H_2/AB = 1.9$ in 610 min, respectively (metal/AB = 0.018). The order of activity towards hydrogen release was found to be $Pt/Al_2O_3 > Rh/Al_2O_3 > Ru/Al_2O_3 > Pd/Al_2O_3 > Au/Al_2O_3$. No significant deactivation was observed for the recycled noble metal catalysts, making them attractive for long term use. Various Pt based catalysts were also found to be highly active towards AB hydrolysis reaction and the order of activity was found to be $Pt/C > PtO_2 > Pt$ black > K_2PtCl_4.[19]

2.2. First-row transition metal catalysts

Although several efficient precious metal catalysts are known, a catalyst with greater stability comprising cheaper and more abundant first-row transition metals is highly desirable. Recent focus on the catalyst design has been on the use of non-precious metals. In many cases, it was found that the surface morphology and composition have tremendous effects on the activities. It is quite challenging to realize the activities of precious metals using first row transition metals.

The copper nanoparticles synthesized using the Solvated Metal Atom Dispersion (SMAD) method have been employed for the hydrolysis of ammonia borane.[20] Controlled oxidation of the as-prepared nanoparticles resulted in the formation of $Cu@Cu_2O$ core-shell nanoparticles. Whereas bubbling air through the Cu-butanone colloid for about 30 min resulted in the formation of Cu_2O nanoparticles. All these three catalysts were characterized using transmission electron microscopy (TEM) and powder XRD techniques. Figure 1 shows the characterization data of these catalysts.[21]

The specific areas of the catalysts obtained using the BET method[22] are 91.1 m^2/g, 79.0 m^2/g, and 60.5 m^2/g respectively for Cu, $Cu@Cu_2O$ core shell, and Cu_2O nanoparticles. Figure 2 shows a comparison of the activities of these three catalysts towards AB hydrolysis reaction.

During hydrolysis of AB, the surface of the catalyst $Cu@Cu_2O$ nanoparticles gets reduced to Cu(0) as evidenced by the XRD pattern. A plausible mechanism of H_2 release in this case is shown in Scheme 3. As shown in the scheme, the reduction of Cu_2O to Cu(0) is due to the transient Cu–H intermediate. The catalysts were highly recyclable and the activity remained nearly the same even after 8 cycles.

Figure 1: TEM bright field image of (a) Cu nanoparticles; (b) $Cu@Cu_2O$ nanoparticles; (c) Cu_2O nanoparticles; (d) Stack plot of XRD patterns of Cu, $Cu@Cu_2O$, and Cu_2O nanocatalysts.
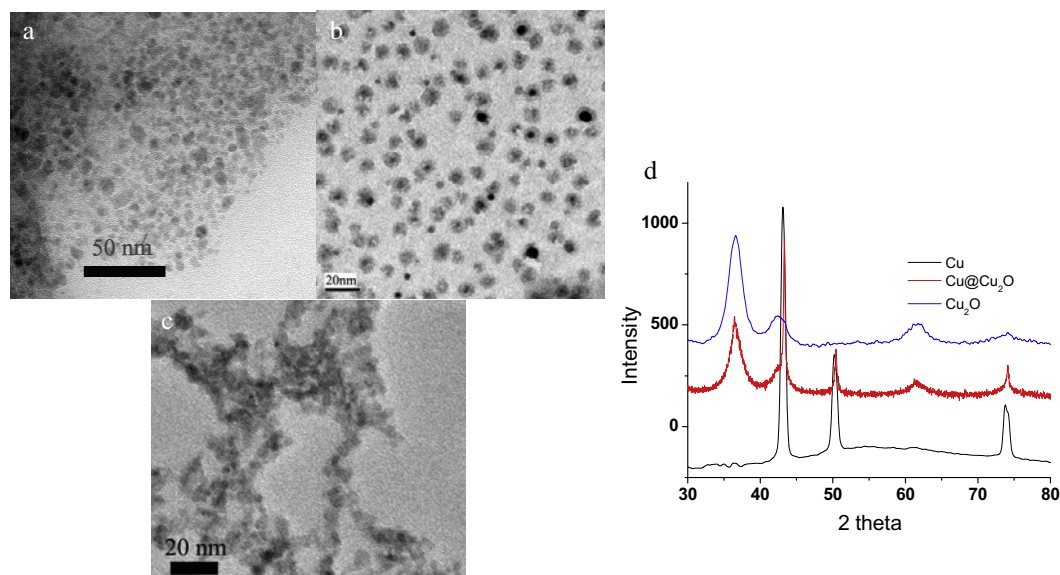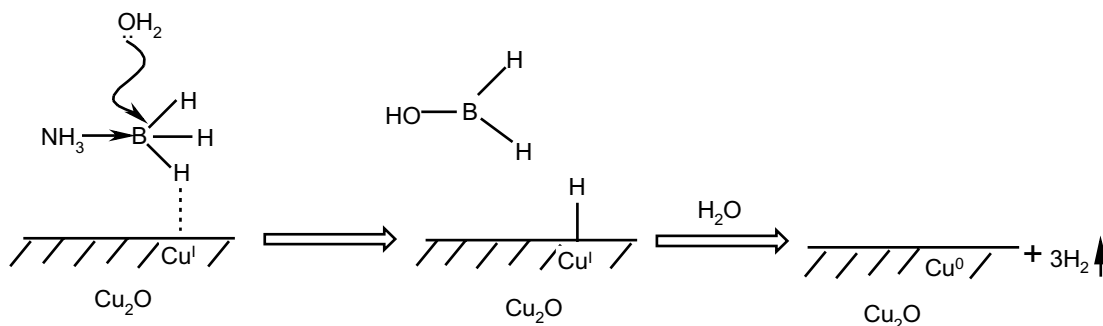
Scheme 3: Plausible mechanism for the release of H$_2$ from Cu$_2$O catalyzed hydrolysis of AB.

Figure 2: Comparison of the catalytic activities of Cu, Cu@Cu$_2$O and Cu$_2$O from hydrolysis of AB (1.0 mmol in 30 mL water; 15 mol% catalyst).
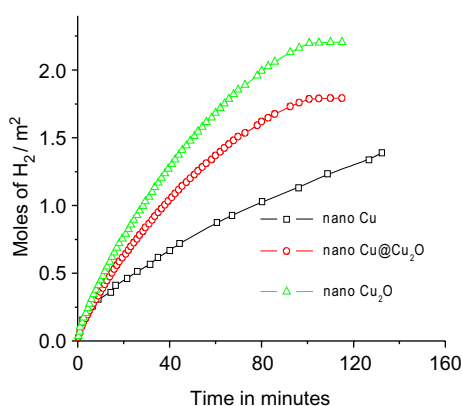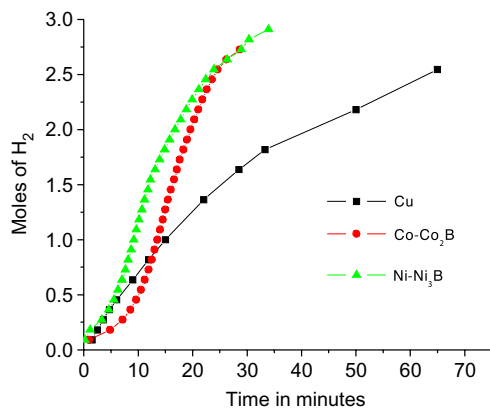

Figure 3: Comparison of activities of amorphous Co–Co$_2$B, Ni–Ni$_3$B and Cu nanoparticles, generated in-situ during the hydrolysis of AB (metal/AB = 0.3).
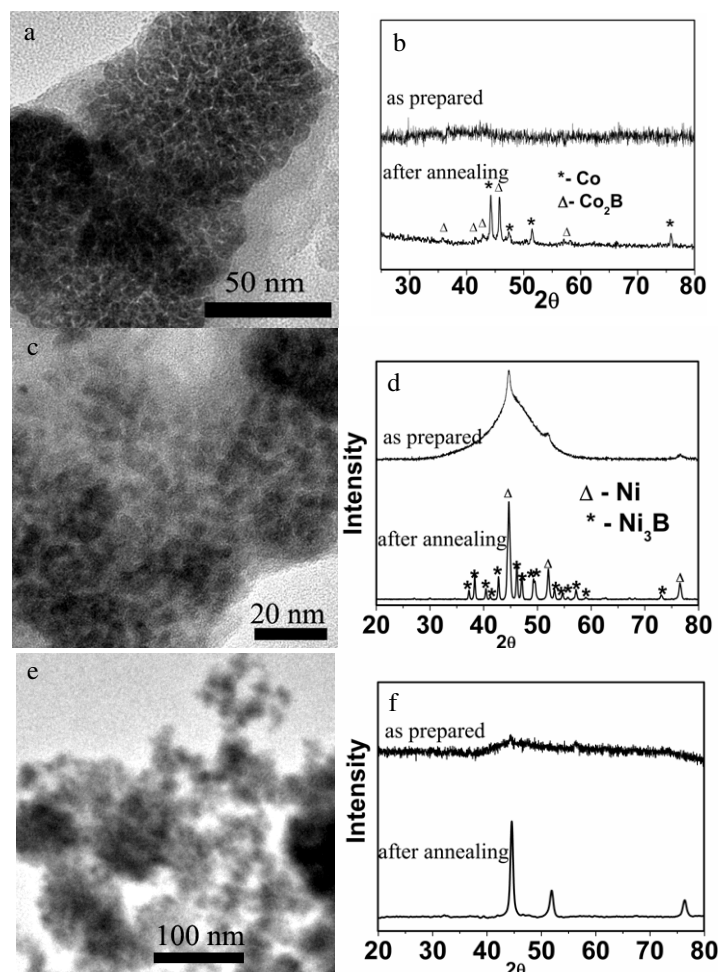

Co^{2+}, Ni^{2+} and Cu^{2+} ions were found to be highly active towards AB hydrolysis.[23] These ions were transformed into metal atoms/clusters upon hydrolysis and the in-situ produced nanoparticles were found to catalyze the AB hydrolysis. Cu^{2+} ions react almost instantaneously, whereas Co^{2+} ($\sim$1 h) and Ni^{2+} ($\sim$2–3 h) ions showed induction periods. Without taking into account the induction period, Co^{2+} is more active than Ni^{2+} and Cu^{2+} in the case of reactions using 7, 15, and 30 mol% of the respective salt. However, at higher mol% of the ions, Cu^{2+} is more active than Co^{2+} and Ni^{2+}. In case of Cu^{2+}, AB hydrolysis was found to be fast initially, slowing down after ca. 5 min. Changes in pH take place during the hydrolysis reactions. While the pH remains within the 8.5–9.0 range in the case of Co^{2+} and Ni^{2+} systems, large variations (8–2.5) in pH take place in the case of Cu^{2+} system. Addition of Cu^{2+} to AB solution results in the generation of H$^+$ which was evident from a drop in the pH during the initial 2–3 min that is responsible for the initial rapid H$_2$ evolution.[24] After about 5 min of reaction time, hydrogen evolution slowed down and the reaction was catalyzed by in-situ generated Cu nanoparticles. In the cases of Co^{2+} and Ni^{2+} assisted AB hydrolysis, amorphous powders are formed that are highly catalytically active for hydrogen generation. Figure 3 shows a comparison of the activities of Cu, Co and Ni nano powders.

Hydrolysis of AB at high concentrations can lead to the liberation of small quantities of ammonia along with hydrogen. This can pose problems in fuel cell applications. Usage of methanol instead of water can circumvent this problem.[25] Co–Co$_2$B and Ni–Ni$_3$B nanocomposites were synthesized by the reaction of Co^{2+} and Ni^{2+} ions with AB in methanol. The Co–Ni–B nanocomposite was synthesized by the co-reduction of Co^{2+} and Ni^{2+} ions. The nanocomposites obtained were characterized using TEM, selective area electron diffraction (SAED), X-ray diffraction technique, and energy dispersive X-ray (EDX) analysis. All the three
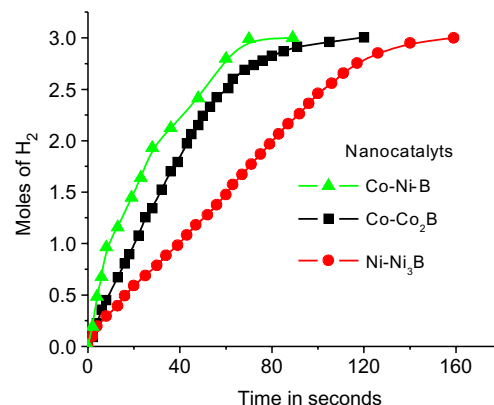
Figure 4: TEM bright field (BF) images of nanocomposites: (a) Co–Co$_2$B; (c) Ni–Ni$_3$B; (e) Co–Ni–B; XRD pattern of nanocomposites before (top) and after (bottom) annealing at 350 °C for 12 h: (b) Co–Co$_2$B; (d) Ni–Ni$_3$B; (f) Co–Ni–B.

Figure 5: H$_2$ generation from methanolysis of AB (1 mL of 1 M solution) in the presence of the nanocomposites Co–Co$_2$B, Ni–Ni$_3$B, and Co–Ni–B (catalyst/AB = 0.2).

nanocomposites were found to be amorphous in nature and the typical particle size range is 4–8 nm. The TEM bright field image and XRD patterns of Co–Co$_2$B, Ni–Ni$_3$B, and Co–Ni–B nanocomposites are shown in Figure 4.

The as-prepared nanocomposites were found to be catalytically active for the generation of H$_2$ from AB in methanol. The comparison of activities is shown in Figure 5. For catalyst/AB = 0.2, three equiv of hydrogen were liberated in 2.5, 4.2, and 1.5 min when Co–Co$_2$B, Ni–Ni$_3$B, and Co–Ni–B, respectively, were used as catalysts. The Co–Ni–B nanocomposite showed greater activity compared to the Co–Co$_2$B and Ni–Ni$_3$B systems. The Co–Ni–B system is an example of a first-row transition metal catalyst that shows the fastest kinetics for the release of H$_2$ from AB. Higher activities attained in this case could be attributed to the amorphous nature of

the catalysts, with various defect sites (active sites) on the surface of the catalysts. Corroborating this, Xu and co-workers recently found that amorphous Fe nanoparticles are more active towards hydrolysis of AB compared to their crystalline counterparts.[26] The three catalysts (Co$_2$B, Ni–Ni$_3$B, and Co–Ni–B) were also found to be highly recyclable and the activities remained almost unchanged even after 20 cycles. These are yet another set of cost-effective and stable first-row transition metal based catalysts for the generation of hydrogen from ammonia–borane in methanol.

3. Summary and future prospects

Ammonia borane with 19.6 wt% of hydrogen content is a potential hydrogen storage material for the future generations provided efficient regeneration pathways are developed. Portable PEM fuel cells based on transition metal catalyzed ammonia borane hydrolysis are expected to find applications in the near future. The major advantage with this system is that rapid reaction kinetics can be attained at ambient conditions in the presence of suitable noble metal and also non-noble metal catalysts. The development of highly active and stable first-row transition metal nanocatalysts is a major step forward in making these processes economically viable.

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