

REVIEW

Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH₄) solutions

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Abstract

It is clear that in order to satisfy global energy demands whilst maintaining sustainable levels of atmospheric greenhouse gases, alternative energy sources are required. Due to its high chemical energy density and the benign by-product of its combustion reactions, hydrogen is one of the most promising of these. However, methods of hydrogen storage such as gas compression or liquefaction are not suitable for portable or automotive applications due to their low hydrogen storage densities. Accordingly, much research activity has been focused on finding higher density hydrogen storage methods. One such method is to generate hydrogen via the hydrolysis of aqueous sodium borohydride (NaBH₄) solutions, and this has been heavily studied since the turn of the century due to its high theoretical hydrogen storage capacity (10.8 wt%) and relatively safe operation in comparison to other chemical hydrides. This makes it very attractive for use as a hydrogen generator, in particular for portable applications. Major factors affecting the hydrolysis reaction of aqueous NaBH₄ include the performance of the catalyst, reaction temperature, NaBH₄ concentration, stabilizer concentration, and the volume of the reaction solution. Catalysts based on noble metals, in particular ruthenium (Ru) and platinum (Pt), have been shown to be particularly efficient at rapid generation of hydrogen from aqueous NaBH₄ solutions. However, given the scarcity and expense of such metals, a transition metal-based catalyst would be a desirable alternative, and thus much work has been conducted using cobalt (Co) and nickel (Ni)-based materials to attempt to source a practical option. “Metal free” NaBH₄ hydrolysis can also be achieved by the addition of aqueous acids such as hydrochloric acid (HCl) to solid NaBH₄. This review summarizes the various catalysts which have been reported in the literature for the hydrolysis of NaBH₄.

Introduction

In recent years, global energy demand has grown at an unprecedented rate, and this trend is expected to continue long into the future [1]. At the same time, the cost of traditional energy sources such as coal, oil, and gas continues to increase. There is thus an acute need for alternative sources of energy.

One of the more widely studied alternative energy sources is hydrogen [2]. The chemical energy per unit mass of hydrogen (142 MJ kg⁻¹) is at least three times

larger than that of any other fuel (e.g., the chemical energy per unit mass of hydrocarbons is only 47 MJ kg⁻¹) [3]. The combustion of hydrogen generates only water as a by-product, and is thus environmentally benign, and its adoption as fuel in internal combustion engines, for example, would lead to a significant reduction in atmospheric pollution. However, due to its very low density, hydrogen is difficult to store in the gaseous state under standard conditions and must be heavily compressed to be stored in useful quantities on board a vehicle. Compressed gases must be stored in heavy steel

containers, partially nullifying the benefit in terms of high gravimetric energy density of using hydrogen in the first place. Alternatively, hydrogen can be stored in cryogenic containers, but these are costly and accumulate considerable “boil off” losses [4]. Both of these approaches are also hazardous and present considerable risks to the user and the public at large.

Hence alternative higher capacity methods of storing hydrogen need to be found. Materials currently under investigation for this purpose can largely be grouped into four categories, namely (a) large surface area materials onto which hydrogen molecules are absorbed, (b) intermetallic hydrides into which hydrogen molecules are absorbed by dissociation into hydrogen atoms, (c) complex metal hydrides where hydrogen atoms are chemically bonded within molecular structures and (d) chemical hydrides which react with water or alcohols to produce hydrogen [2, 5–10]. A brief description of each of these hydrogen storage methods, some example materials, and their advantages and disadvantages with respect to one another in terms of hydrogen storage is given in the following four subsections.

Hydrogen storage on large surface area materials

Carbon-based nanostructured materials such as fullerenes [11], graphene [12, 13], and nanotubes [14], mesoporous silica [15, 16], metal organic frameworks [17–19], and clathrate hydrates [20] all belong in this category. These materials can offer high gravimetric hydrogen storage densities and good reversibility cycles (of hydrogen adsorption and desorption), but typically operate at temperatures lower (below 298 K) than that is desirable for practical application.

Hydrogen storage in intermetallic hydrides

Intermetallic hydrides, also known as interstitial hydrides, absorb and liberate hydrogen under nearly ambient conditions [9, 21–23]. The hydrogen is stored in interstitial sites and thus does not affect the host lattice [5]. They are often grouped by their structure type into four categories, namely AB₅ (e.g., LaNi₅), AB (e.g., FeTi), A₂B (Mg₂Ni), and AB₂ (TiMn₂) [5]. However, the gravimetric hydrogen storage densities of such systems are too low (<5 wt%) for portable applications.

Hydrogen storage in complex metal hydrides

Complex metal hydrides (e.g., NaAlH₄ [24–26], LiAlH₄ [27, 28], LiBH₄ [29, 30]) generally have the formula

A_xB_yH_m, where A is an alkali metal cation and B is a metal or metalloid to which the hydrogen atoms are covalently bonded. Certain binary metal hydrides such as MgH₂ [31–33] and AlH₃ [34–36] also have covalently bonded hydrogen atoms and are thus more similar to complex metal hydrides than intermetallic hydrides in their hydrogen storage properties. Complex metal hydrides are particularly promising due to their high theoretical gravimetric and volumetric hydrogen storage densities. However, they suffer from slow uptake and release kinetics, meaning that much of the stored hydrogen is not practically accessible due to the time it would take to release it.

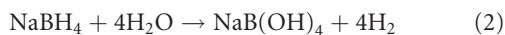
Hydrogen storage in chemical hydrides

Chemical hydrides (e.g., NaBH₄ [37], LiAlH₄ [38–40], NH₃BH₃ [41–43]) have high gravimetric hydrogen storage densities and release hydrogen by reaction with water. In effect, the hydrogen is stored both in the chemical hydride itself and the water. These reactions tend not to be easily reversible and the by-products must be extracted from the spent fuel mixture to be regenerated. However, as the reactions can be controlled by control of parameters such as rate of water addition, pH, and the use of catalysts, chemical hydrides are particularly attractive for use in portable applications, where easy “on-off” control is crucial. A particularly attractive option is hydrogen generation from the hydrolysis of aqueous sodium borohydride (NaBH₄) solutions. This brings several advantages over other potential materials such as lithium aluminum hydride, including nonflammability (of sodium borohydride solutions), stability in air, and low reactivity of reaction by-products which can (at least theoretically) be recycled.

Hydrogen Storage in Sodium Borohydride

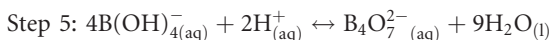
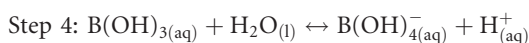
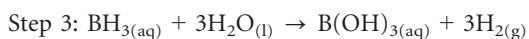
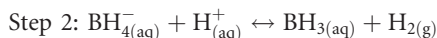
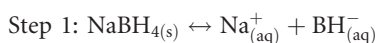
Sodium borohydride can be classified as both a complex metal hydride and a chemical hydride as it can release hydrogen by two methods: thermolysis, where the stored hydrogen is released by heating, and hydrolysis, where the stored hydrogen is released by reaction with water. The former is not attractive for portable applications since sodium borohydride is stable up to 400°C [44]. The latter is particularly attractive for three major reasons. Firstly, hydrolysis of sodium borohydride is a spontaneous, exothermic (−210 kJ mol^{−1}) [45] process that can be easily accelerated by the simple addition of a metal catalyst. Secondly, as can be seen from equation 1, half of the hydrogen comes from the water, giving sodium borohydride a relatively high theoretical hydro-

gen storage capacity of 10.8 wt%. Finally, the hydrolysis reaction can produce pure hydrogen at temperatures as low as 298 K.



However, hydrogen generation by hydrolysis of sodium borohydride is not without problems. A major issue is the volume of water required. Equation 1 shows the stoichiometric chemical reaction, but in reality at least 4 molar equivalents of water are required for each mole of sodium borohydride in the reaction. This is for two reasons. Firstly, as shown in Equation 2, sodium metaborate (NaBO_2) is rapidly hydrated. Secondly, the solubility of sodium borohydride in water is relatively low (55 g per 100 g at 25°C), requiring more water than that required by stoichiometry to ensure the sodium borohydride remains in solution (although sodium borohydride does have a considerably higher solubility than ammonia borane (33.6 g per 100 g at 25°C) [41], and other hydrolysis materials such as aluminum [46, 47] and silicon [48], which are insoluble). This is further compounded by the even lower solubility of sodium metaborate (28 g per 100 g of water at 25°C), which means that the concentration of sodium borohydride must be kept below 16 g per 100 g of water to ensure that sodium metaborate does not precipitate from the reaction mixture and foul the catalyst and reaction vessel. All of these considerations mean that in reality the gravimetric hydrogen storage capacity of sodium borohydride is far lower than the theoretical value of 10.8 wt%, and has led to a “no-go” recommendation from the United States Department of Energy for use in automotive applications [49]. Nevertheless, sodium borohydride hydrolysis remains very attractive for smaller scale portable applications such as chargers for mobile phones, tablets, and laptop computers.

Another significant problem is the rate of reaction. Sodium borohydride undergoes self-hydrolysis upon the addition of water, and is thus typically stabilized by the addition of sodium hydroxide (the self-hydrolysis reaction rate drops to negligible above pH 13) [50]. The mechanism of self-hydrolysis has been described as follows [51]:



The decrease in the amount of protons in basic media results in Step 2 of the self-hydrolysis being disfavored

and the hydrogen generation process thus slowed. By increasing the amount of protons and thus accelerating Step 2, the addition of homogenous acid catalysts to aqueous sodium borohydride solutions results in an increase in the rate of hydrolysis.

Heterogeneous catalysts can be added to reduce the activation energy and accelerate the generation of hydrogen. Removal of the catalyst leads to an increase in the activation energy and a stabilization of the reaction. Various kinetic models have been used to describe the process of metal catalyzed hydrolysis and these have been well summarized by Rangel *et al.* [51]. The “on-off” control obtained by adjusting the pH or the contact with a heterogeneous catalyst makes sodium borohydride a very attractive hydrogen storage material for portable applications. In the past 15 years a host of different heterogeneous catalyst systems have been reported for sodium borohydride hydrolysis, the majority of them based on ruthenium and cobalt. The mechanism of many of these reactions is still poorly understood, and thus this remains a rich field of research. Acids can be used as homogenous catalysts for the hydrolysis reaction as they lower the pH and destabilize the sodium borohydride solution.

The physical form of heterogeneous catalysts also plays a large role in controlling the sodium borohydride hydrolysis process. In particular, the “on-off” functionality required for portable applications is far more difficult to achieve with loose powder catalysts than with supported catalysts as it is easier to remove the latter from solution (though powders can be pelletized to overcome this). However, supported catalysts are generally more susceptible to being blocked by a layer of sodium metaborate by-product, and can have lower accessible catalyst surface than powders.

Reactions of sodium borohydride with water vapor have been reported [52–54]. This hydrolysis method is promising as it increases the gravimetric hydrogen storage capacity by decreasing the amount of water required, and also do not require catalytic activation. However, the hydrogen yields are much poorer than those of liquid phase hydrolysis and the reactions must be carried out with water temperatures of above 110°C, and thus vapor phase hydrolysis of sodium borohydride has not been heavily investigated.

Noble Metal Catalysts: Ruthenium (Ru) and Platinum (Pt)

Several ruthenium-based catalysts giving high initial rates of hydrogen generation have been reported. The most active catalyst in terms of initial hydrogen generation rate was reported by Ozkar *et al.* [55], who achieved maximum hydrogen generation rates of 96,800 mL min⁻¹ (g cata-

lyst)⁻¹ using water dispersible ruthenium(0) nanoclusters at ambient temperatures. The next highest performing ruthenium-based catalyst in terms of hydrogen generation rate is a ruthenium catalyst generated from a ruthenium salt by reduction with sodium borohydride, followed by an annealing step. In powder form this gave a maximum hydrogen generation rate of 18,600 mL min⁻¹ (g catalyst)⁻¹ [56].

A number of immobilized ruthenium-based catalysts have also been reported, though none can match the activity of Ozkar's nanoclusters. Liang et al. [57] attached ruthenium(0) to graphite powder via an aminosilane chain. Though in this case a powder was used, if the same methodology could be employed to functionalize graphite rods then a viable "on/off" mechanism could easily be envisaged. This system achieved hydrogen generation rates of 969 mL min⁻¹ (g catalyst)⁻¹. Supported catalyst systems have also been very popular due to their practicality. A higher performing system (in terms of hydrogen generation rate) using carbon as the support was reported by

Li et al. [58], who converted Ni/C to Ru-RuO₂/C by galvanic replacement, generating hydrogen at a rate of 2800 mL min⁻¹ (g catalyst)⁻¹. Park et al. [59] used sodium borohydride to reduce various metal salts to form catalytic alloys on activated carbon fiber (ACF) in situ. A tertiary alloy of composition Ru₆₀Co₂₀Fe₂₀ showed the highest hydrogen release of 5030 mL min⁻¹ (g catalyst)⁻¹.

Several catalysts formed of ruthenium on support materials such as carbon papers and polymer beads have been reported [60–67], but most of these suffer from poor catalytic performance in terms of hydrogen generation rate (see Table 1). Amendola et al. [61] dispersed a ruthenium boride catalyst onto various anionic and cationic resin beads, which they then dispersed in solutions of sodium borohydride stabilized with sodium hydroxide. IRA 400 resin beads were found to be the highest performing, giving hydrogen generation rate of 189 mL H₂ min⁻¹ (g catalyst)⁻¹. Chen et al. [63] obtained a higher hydrogen generation rate of

Table 1. Noble metal catalysts for sodium borohydride hydrolysis.

Catalyst	Form	Activity (mL H ₂ min ⁻¹ (g catalyst) ⁻¹)	NaBH ₄ conc./wt%	NaOH conc./wt%	Temperature/°C	Year	Reference
Ru	Supported on IRA 400 resin	189	20	10	25	2000	[61]
Pt-LiCoO ₂	Powder	3100	20	10	22	2002	[70]
Pt/C	Powder	23,090	10	5	Not stated	2004	[69]
Ru NPs	Powder	96,800	0.75	0	25	2005	[55]
Pt/Ru-LiCoO ₂	Catalyst dispersed on a nickel mesh	2400	5	5	25	2005	[72]
Pt/C	Powder	23,000	10	5	25	2006	[68]
Ru(0) nanoclusters	Powder	4	0.57	10	25	2006	[75]
Pt/C	Powder	6000	9	Not stated	25	2007	[76]
Pt/Pd-CNT	Supported on CNT paper	126	0.1	0.4	29	2007	[73]
Pt/C	Powder	170	5	5	30	2007	[77]
Ru/C	Powder	770	1	3.75	25	2007	[65]
Ru ₆₀ Co ₂₀ Fe ₂₀ alloy	Supported on activated carbon fibers	5030	10	4	25	2008	[59]
Ru	Powder	18,600	5	5	60	2008	[56]
Pt-Ru	Powder	150	2	4	20	2008	[64]
Pt/Ru-LiCoO ₂	Catalyst bed	3000	10	5	25	2008	[78]
Ru	Supported on ion exchange resin beads	132	5	1	25	2008	[67]
Ru	Supported on polymer beads	216	1	1	Not stated	2009	[63]
Ru(0) nanoclusters confined in zeolites	Powder	130	1.1	5	25	2009	[79]
Ru on graphite	Supported on graphite	969	10	5	30	2010	[57]
Rh/TiO ₂	Immobilized onto titanium dioxide support to form a catalyst bed	210	15	5	23	2010	[80]
Alumina carrier Ru composite	Supported on alumina	68.2	12.5	1	25	2012	[81]
Ru/C	Powder	570	10	4	25	2012	[66]
Ru-RuO ₂ /C	Powder	2800	5	1	30	2013	[58]

Table 2. Nonnoble metal catalysts for sodium borohydride hydrolysis.

Catalyst	Form	Activity (mL H ₂ min ⁻¹ (g catalyst ⁻¹))	NaBH ₄ conc. (wt%)	NaOH conc. (wt%)	T/°C	Year	Reference
Ni-B	Powder	330	1.5	20	25	2003	[119]
Co-B	Powder	2970	2	5	15	2005	[120]
Co-B	Powder	875	20	5	20	2005	[121]
Raney Ni	Powder	228.5	1	10	20	2006	[122]
Raney Co	Powder	267.5	1	10	20	2006	[122]
Co-B/Ni foam	Dip coated	7200	25	3	20	2007	[123]
Co-B	Thin film prepared by pulsed laser deposition	3300	0.1	Not stated	25	2007	[124]
Ni-Co-B	Powder	2608	2.7	15	28	2007	[125]
Co-B	Powder	2400	20	5	20	2007	[126]
Co-B	Supported on carbon black	2073	0.75	8	25	2007	[114]
Co-P	Electroplated on copper	954	10	1	30	2007	[127]
Co-B	Powder	26,000	15	5	30	2008	[86]
Ni-B	Powder	1300	10	5	60	2008	[56]
Co-B	Powder	6000	5	5	60	2008	[56]
Co-W-B/Ni foam	Electrolessly plated	15,000	20	5	30	2008	[91]
Co-B/Ni foam	Electrolessly plated	11,000	20	10	30	2008	[128]
Co-B/MWCNTs	Powder	5100	20	3	30	2008	[113]
Co-B	Thin film prepared by pulsed laser deposition	5016	0.1	4	25	2008	[129]
Co/PPX-Cl	Metallized films	4250	2.5	10	25	2008	[130]
Ni(0) nanoclusters	Stabilized on PVP	4250	0.57	0	25	2008	[131]
Co-B/Pd	Dry dip coated	2875	20	4	30	2008	[132]
Co on activated C	Powder	3600	5	1	30	2008	[133]
Co-B	Carbon supported	166	1	5	25	2008	[134]
Co-B	Powder	39,000	5	0	40	2009	[85]
Co-P-B	Powder	2120	0.95	1	25	2009	[135]
Co-Cr-B	Powder	3400	0.95	1	25	2009	[136]
Co-Ni-P	Electrodeposited	2479	10	10	30	2009	[104]
Co-Ni-P-B	Powder	2400	0.95	1	25	2009	[105]
Co-B	Electrolessly plated	1640	10	5	25	2009	[137]
Co-Ni-B	Powder	1175	0.95	1	25	2009	[138]
Ni-Ru	Electrolessly plated	400	10	5	35	2009	[62]
Co-Fe-B	Powder	1300	0.95	1	25	2010	[139]
Fe-Co-B/Ni foam	Electrolessly plated	22,000	15	5	30	2010	[90]
Co-P-B	Thin film prepared by pulsed laser deposition	4320	0.95	1	25	2010	[140]
Co-P/Ni foam	Electrolessly plated	3584	10	1	30	2010	[141]
Co-W-B	Powder	2570	0.95	1	25	2010	[139]
Co-Mo-B	Powder	2875	0.95	1	25	2010	[139]
Co-Cu-B	Powder	2210	0.95	1	25	2010	[139]
Co-P on Cu sheet	Electrolessly plated	1846	5	1	25	2010	[142]
Co-B	Supported on attapulgate clay	3350	5	10	25	2010	[143]
Co-alumina on Cu plates	Electrodeposited	383	3	1	80	2010	[144]
Co-B	CoCl ₂ solution added to a solid powder mixture of NaOH and NaBH ₄	23,333	50	5	Unregulated	2011	[87]
Co NPs embedded on a B thin film	Pulsed laser deposition	3375	0.095	0	25	2011	[106]
Co-B	Powder	9000	10	5	Unregulated	2011	[145]
Co-B NPs	Powder	4928	3	5	25	2011	[146]
Co-B NPS	Supported on hydrogels	120	0.19	5	30	2011	[147]

Table 2. Continued.

Catalyst	Form	Activity (mL H ₂ min ⁻¹ (g catalyst ⁻¹))	NaBH ₄ conc. (wt%)	NaOH conc. (wt%)	T/°C	Year	Reference
Co-Ni-P/Pd-TiO ₂	Electrolessly plated	460	1.13	10	25	2011	[102]
Co-B NPs	Supported on TiO ₂	12,500	1	3.75	30	2012	[99]
Co-B NPs	Supported on Al ₂ O ₃	11,650	1	3.75	30	2012	[99]
Co-B NPs	Supported on CeO ₂	10,390	1	3.75	30	2012	[99]
Co	Supported on colloidal carbon spheres	1911	1	10	20	2012	[112]
Co-B	Impregnation onto carbon supports	1358	1	8	27	2012	[111]
CoO nanocrystals	Powder	8333	10	10	30	2012	[116]
Co-Pd-B	Powder	2920	0.57	5	25	2012	[89]
Co-Mo-Pd-B	Powder	6023	0.57	5	25	2012	[89]
Co-W-P on Cu substrates	Electrolessly plated	5000	10	10	30	2012	[103]
Co-B	Solution plasma process	4380	2	7	25	2012	[148]
Co-B	Powder	4300	0.76	0.1	30	2012	[149]
Ni-B	Powder	3400	0.76	0.1	30	2012	[149]
Co-ZIF-9	Solvothermal	182	0.5	5	30	2012	[150]
Ni-Fe-B	Powder	2910	5	4	25	2012	[151]
Co-Mn-B	Powder	35,000	7	7	70	2012	[97]
Co(II)-Cu(II)-based complex catalyst	Powder	188	2.5	5	30	2012	[152]
Fe-Co NPs	Powder	1433	5	0	30	2012	[153]
Co-Mo-B	Powder	19,000	5	5	30	2013	[92]
Co NPS on aerogels	Powder	2010	1	10	25	2013	[107]
Co-P	Electrodeposition	5965	10	10	30	2013	[154]
Co-Ni-P	Electrolessly plated	3636	10	10	30	2013	[155]
Zr/Co	Impregnation onto carbon supports	1708	5	2	Not stated	2013	[156]
Co-La-Zr-B	Powder	1500	10	2	40	2013	[94]
Co-La-Zr-B	Powder	133	5	0	20	2013	[93]
Co-B	Supported on carbon black	8034	10	5	25	2014	[115]
Co-B-TiO ₂ framework	Powder	1980	5	1.5	30	2014	[157]
Ni-Co-P	Supported on alumina	6600	2	4	55	2014	[158]
PAN/CoCl ₂ -CNT nanofibers	Electrospun	1255	1	0	25	2014	[159]
Oleic acid stabilized Co-La-Zr-B nanoparticle	Powders	102	5	2	20	2014	[160]
Co-B/Ni foam	Electrolessly plated	24,400	15	5	30	2014	[98]
Co/Ni foam	Magnetron sputtered	2650	3.8	4.5	23	2014	[161]
Co ₃ O ₄	Solution combustion synthesized powder	1240	0.6	0	20	2014	[162]
Co NPs	Supported on a polyacrylamide hydrogel network	537	3.8	5	30	2014	[163]
Co-Ru-B	Powder	8075	0.57	0.4	25	2014	[95]
Au/Ni NPs	Powder	2597	0.11	Not stated	30	2014	[164]

216 mL H₂ min⁻¹ (g catalyst⁻¹) by depositing ruthenium (0) nanoparticles onto monodisperse polystyrene microspheres, though it was only tested in a 1 wt% solution of sodium borohydride (rather than the 20 wt% solution of Amendola et al.) and could thus perhaps be capable of producing hydrogen at a faster rate if placed in a more

concentrated solution. Higher rates of hydrogen generation have been obtained using ruthenium catalysts supported on carbon. For example, Fisher et al. [65] obtained commercially available Ru/C catalyst powder and found that grinding it to a particle size of 35 μm minimized internal diffusion effects to give a maximum

hydrogen generation rate of $770 \text{ mL H}_2 \text{ min}^{-1} (\text{g catalyst}^{-1})$.

Several platinum-based catalysts with high hydrogen generation rates have also been reported. Wu *et al.* [68, 69] utilized Pt/C powders to obtain hydrogen generation rates of $\sim 23,000 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$. Kojima *et al.* coated Pt(0) onto LiCoO_2 and used the resultant powder to generate hydrogen at a maximum rate of $3100 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$ [70]. This system was subsequently coated onto a honeycomb monolith and incorporated into a 10 kW scale hydrogen generator [71]. Another promising adaptation of this catalytic system was reported by Krishnan *et al.* [72]. They dispersed the catalyst onto a nickel mesh which could then be dipped in and out of solution in response to the demand for hydrogen generation. Pena-Alonso *et al.* [73] have also reported a promising system in which they deposited platinum and palladium atoms onto carbon nanotubes and achieved hydrogen generation rates of $126 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$. Saha *et al.* [74] have recently reported a highly stable graphene-Pt-Co nanohybrid catalyst which shows exceptional stability and a very high catalytic activity ($\text{TOF} = 107 \text{ min}^{-1}$). These catalysts are synthesized in a fairly simple manner and show great promise.

Nonnoble Metal Catalysts: Cobalt (Co) and Nickel (Ni)

Noble metals are scarce and expensive. Hence the use of catalyst systems based on the cheaper transition metals is highly desirable. Specifically, cobalt and nickel have been the most commonly employed transition metals to date due to their low cost and abundance compared to noble metals, whilst an increasing amount of research is being carried out on iron-based systems.

Cobalt borides (Co-B) have been heavily studied as catalysts for sodium borohydride hydrolysis reactions. The exact structure of these compounds and the mechanism of hydrogen generation remains a subject of debate. The current state of the art in terms of our understanding of the catalyst structure and mechanism has been well summarized by Demirci and Miele [37, 82, 83]. Cobalt boride-based catalysts are generally formed by reduction in cobalt(II) salts in aqueous solution with sodium borohydride, and it has been reported that the critical factor contributing to their catalytic activity is that the cobalt ought to be fully reduced [84]. The highest performing Co-B catalyst reported to date had a hydrogen generation rate of $39,000 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$, though given that this value was obtained in the absence of stabilizing sodium hydroxide and at an elevated temperature of 40°C , it is difficult to make a direct comparison with other systems [85]. Liu *et al.* [86] obtained a maximum

HGR of $26,000 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$ in a sodium hydroxide stabilized solution of sodium borohydride with a super fine Co-B catalyst obtained via the formation of a colloidal Co(OH)_2 intermediate.

An adaptation of these systems used cobalt chloride (CoCl_2) in aqueous solution as catalyst, but with aluminum powder as well as sodium borohydride to accelerate the rate of generation of hydrogen [87]. However, after only three cycles the hydrogen generation rate had dropped to 20% of the maximum rate. The authors attributed this loss to the buildup of reaction by-products on the surface of the powder mixture. Bic have patented a fuel cartridge design which overcomes this problem, and allows the on-demand generation of hydrogen from an aqueous sodium hydroxide stabilized solution of sodium borohydride using CoCl_2 as catalyst without excessive surface by-product build up [88].

Various alloy systems based on Co-B have been reported, such as Co-Mo-Pd-B [89], Co-Pd-B [53], Co-Fe-B [90], Co-W-B [91], Co-Mo-B [92], Co-La-Zr-B [93, 94], Co-Ru-B [95], Co-Cr-B [96], and Co-Cu-B [89]. The best performance of this type of catalyst reported to date is a Co-Mn-B powder, giving an HGR of $35,000 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$ [97]. There have been several reports of highly performing Co-B-based catalysts being deposited on Ni foam by electroless plating. This highly porous structure is ideal for conferring on/off functionality to the hydrogen generation reaction by simply dipping and removing the catalyst into and out from the aqueous borohydride solution. Co-B/Ni foam gave a maximum hydrogen generation rate of $24,400 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$ [98], whilst Co-Fe-B/Ni foam was used to obtain a maximum hydrogen generation rate of $22,000 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$ [90]. Other substrates have also shown promising hydrogen generation rates, and could be deployed in a similar way for "on/off" hydrogen generation. Nanosized Co-B catalyst has also been prepared on TiO_2 , giving an HGR of $12,500 \text{ mL min}^{-1} (\text{g catalyst}^{-1})$. The authors [99] noted that supported Co-B catalysts perform better in the sodium borohydride hydrolysis reaction than unsupported catalysts. Chen *et al.* have investigated the effects of varying different synthesis conditions on the effect of catalyst activity of Co-B deposited on ion exchange resins [100]. They found that a slower reduction time gives a higher surface area, more active catalytic Co-B species.

A series of Co-P systems have also been reported, such as Co-P [101], Co-Ni-P [102], and Co-W-P [103], and also some mixed Co-P-B systems such as Co-P-B [104] and Co-Ni-P-B [105], but in general these systems have been poorer performing than the boron alloys in terms of hydrogen generation rates.

Cobalt nanoparticles have also been reported to be effective at catalyzing hydrogen generation. These are typically deposited initially as Co(II) ions on a support material and then reduced chemically to Co(0). Patel *et al.* [106] used pulsed layer deposition to coat a boron sheet with cobalt nanoparticles, obtaining an HGR of $3375 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$. Zhu *et al.* [107] deposited cobalt nanoparticles onto carbon-based aerogels using an impregnation-reduction method, obtaining an HGR of $2010 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$. Jaworski *et al.* [108] impregnated a hydroxyapatite support with cobalt nanoparticles which showed reasonably good durability, attaining 75% of their maximum performance after 3 weeks of use. This system was improved further by Rakap *et al.* [109], who synthesized a hydroxyapatite-supported cobalt nanoparticle catalyst providing 25,600 turnovers in the hydrolysis of basic sodium borohydride. Bennici *et al.* [110] have reported a better performing polyanion complex (in terms of hydrogen generation rate) as a support for cobalt nanoparticles, but the large weight of the support per g of cobalt metal would probably render such systems unsuitable for portable applications which are becoming increasingly popular at present.

Several carbon-supported cobalt nanoparticle catalysts have been reported, which have the advantage of being relatively low in cost. Niu *et al.* [111] observed a HGR of $1358 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$ with such a system, whereas Zhu *et al.* [112] impregnated colloidal carbon spheres obtained from glucose with cobalt with a greater HGR of $1911 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$. Cobalt boride has also been synthesized on carbon supports [113, 114], and these were found to be more highly performing than the carbon-supported Co NP systems; for example, Baydaroglu *et al.* attained a HGR of $8034 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$ at room temperature [115]. Cobalt oxide (CoO) nanocrystals have also been found to be an effective catalyst [116], with an HGR of $8333 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$.

Cobalt, nickel, and iron are all ferromagnetic materials, and it has been suggested that this property could be used as a catalytic “on/off” switch by using a magnet to remove the catalyst from the solution when hydrogen generation is no longer required. In a recent study [117], cobalt, nickel, and iron were deposited onto SiO_2 by an impregnation/chemical reduction process. These catalysts gave HGR values of 8700, 300, and $130 \text{ mL min}^{-1} (\text{g metal})^{-1}$, respectively. Silicon dioxide is a very attractive catalyst support material due to its low molecular mass, low cost and chemical stability.

Various other nickel-based catalysts have been reported [118], but cobalt-based catalysts have generally been found to be superior in terms of maximum hydrogen

generation rate, rendering cobalt the catalyst of choice for sodium borohydride hydrolysis.

Acid catalysis

Acid homogenous catalysis of sodium borohydride to generate hydrogen was first reported as long ago as 1953 [165]. Unlike metal catalyzed hydrolysis of sodium borohydride, which is typically carried out in an aqueous alkaline solution, acid hydrolysis of sodium borohydride is usually conducted by adding aqueous acid solution drop wise onto solid sodium borohydride powder. The major advantages of these methods include the generation of very dry hydrogen gas, the easy control of hydrogen production and the pH neutral, environmentally benign nature of the waste products formed during the reaction. This is counterbalanced by the significant disadvantages of having to carry a reservoir of reasonably strong acid, and adding complications to the reactor design.

For example, Javed *et al.* [166] reported a system which used 6 mol/L hydrochloric acid (HCl) solution delivered at a flow rate of $1 \mu\text{L min}^{-1}$. A similar system was reported by Prosini *et al.* [167]. Such corrosive solutions are far from ideal for portable applications. Murugesan *et al.* [168] tested sulfuric, nitric, phosphoric, formic and acetic acids as catalysts for sodium borohydride. Even at high concentrations, nitric and phosphoric acid were incapable of yielding more than half of the theoretical hydrogen yield. Hydrochloric and sulfuric acid gave in excess of 95% of the theoretical hydrogen yield, but at concentrations of 3 N, which is still higher than desirable for portable applications. Even at concentrations as high as 12 N, formic and acetic acid gave only around three quarters of the theoretical hydrogen yield.

However, Akdim *et al.* [169] conducted further studies of acetic acid as an alternative to HCl and found that under the right conditions (specifically a temperature of 60°C and an acid/borohydride ratio of 2), acetic acid was found to catalyze the release of hydrogen as rapidly and to the same extent as HCl (60°C and an acid/borohydride ratio of 1). Tellingly, however, a like for like comparison of HCl and acetic acid at 60°C with an acid/borohydride ratio of 2, acetic acid yields only two-thirds of the amount of hydrogen that HCl does. More interestingly, Akdim *et al.* claim that hydrochloric and formic acid catalyzed hydrolysis produces more milliliters of hydrogen per minute than catalysis by the highest performing (in terms of hydrogen generation rate) cobalt catalysts, though direct comparisons are difficult given the nature of the two systems. If this be the case, acid hydrolysis becomes far more attractive.

Kim et al. [170] observed that when operating a PEM fuel cell using hydrogen generated by metal catalysis from an alkaline sodium borohydride solution, there is a rapid degradation in performance. They ascribe this at least in part to the presence of sodium ions in the water vapor in the hydrogen stream. They found that there were no detectable water vapor or sodium ions after condensation of the hydrogen feed generated from various organic acids, and that the cell performance degradation observed when using hydrogen generated by metal catalyzed hydrolysis was no longer observed. It is perhaps surprising that the promise of these studies has not resulted in further investigations in this area.

Summary

The highest performing heterogeneous catalyst for sodium borohydride hydrolysis was reported by Ozkar et al. [55], who achieved a maximum hydrogen generation rate of $96,800 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$ using water dispersible ruthenium(0) nanoclusters at ambient temperatures. However, due to the scarcity and expense of noble metal catalysts such as ruthenium, recent research efforts in this field have been focused on developing catalyst systems based on transition metals. Of these, cobalt boride catalysts have proved the most popular, due to their high activity (a hydrogen generation rate of $39,000 \text{ mL min}^{-1} (\text{g catalyst})^{-1}$ is the highest yet reported [84]), low cost and ease of synthesis. Immobilized cobalt boride-based catalysts are particularly promising as they offer simple reaction control, giving the “on/off” functionality required for portable applications. At present there are comparatively fewer studies of the use of homogenous catalysts such as HCl on the hydrolysis of aqueous sodium borohydride solutions. However, due to the ease of reaction control and the formation of environmentally benign reaction by-products, both of which are very attractive properties for portable applications, it seems likely that this is an area which will attract more attention in the future.

Concluding Remarks

Over the last 15 years, a great deal of effort has been directed at the synthesis and characterization of catalyst systems for sodium borohydride hydrolysis. Cobalt-based systems, in particular cobalt borides, have emerged as the catalyst of choice due to their low cost, ease of synthesis and high activity leading to high maximum hydrogen generation rates. However, several significant issues must be addressed before the widespread deployment of hydrogen generators using sodium borohydride is feasible, such as the requirement for a large stoichiometric

excess of water to ensure the sodium metaborate by-product does not foul the reactor or cover the surface of the heterogeneous catalyst and reduce the rate of reaction.

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Conflict of Interest

None declared.

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