

Liquid-Phase Chemical Hydrogen Storage: Catalytic Hydrogen Generation under Ambient Conditions

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There is a demand for a sufficient and sustainable energy supply. Hence, the search for applicable hydrogen storage materials is extremely important owing to the diversified merits of hydrogen energy. Lithium and sodium borohydride, ammonia borane, hydrazine, and formic acid have been extensively investigated as promising hydrogen storage materials based on their relatively high hydrogen content. Significant advances,

such as hydrogen generation temperatures and reaction kinetics, have been made in the catalytic hydrolysis of aqueous lithium and sodium borohydride and ammonia borane as well as in the catalytic decomposition of hydrous hydrazine and formic acid. In this Minireview we briefly survey the research progresses in catalytic hydrogen generation from these liquid-phase chemical hydrogen storage materials.

1. Introduction

The world's energy consumption is dramatically increasing owing to the rising standards of living and the growing population. This increasing energy demand will require enormous growth in the energy generation capacity, more secure and diversified energy sources, and a successful strategy to decrease greenhouse gas emissions. Among the various alternative energy strategies, hydrogen, a globally accepted clean fuel and a primary carrier that connects plenty of energy sources to different end uses, such as hydrogen fuel cell vehicles and portable electronics, will enable a secure and clean energy future.^[1]

Vehicular applications and off-board uses enforce scientific efforts to discover hydrogen storage materials that can store and release hydrogen in a safe and efficient way. During recent decades, there have been a large number of publications on hydrogen storage materials, such as metal hydrides,^[2,3] metal organic frameworks (MOFs),^[4,5] on-board reforming of hydrocarbon into hydrogen,^[6] and organic materials.^[7] However, none of these materials have been demonstrated to meet all the necessary transportation requirements, such as volumetric and gravimetric hydrogen capacities, handling pressure and temperature, recycling of byproducts, costs, and others.

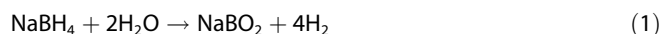
Chemical hydrogen storage materials are expected to provide a much needed breakthrough in the solid-state storage of hydrogen owing to their high hydrogen content.^[8,9] However, their performance for practical use is severely limited by the high temperatures required to desorb hydrogen and, in particular, their limited kinetics for recharging. Therefore, searching for effective liquid-phase hydrogen storage materials to conveniently release hydrogen under mild conditions is urgently desired. The hydrolysis of aqueous boron and nitrogen-based compounds, such as Li/NaBH₄ and NH₃BH₃, has received much attention.^[10–15] Recently, hydrous hydrazine (H₂NNH₂·H₂O), with a hydrogen content as high as 8.0 wt%, has been shown to be a promising hydrogen carrier for storage and transportation, and selectively decomposes to hydrogen and nitrogen at room

temperature.^[16,17] In addition, formic acid (HCOOH), containing 4.4 wt% of hydrogen, has the advantage over other substrates that it is environmentally and biologically benign and has also been shown to be a promising hydrogen storage material.^[18–21]

This Minireview discusses the research advances on hydrogen generation from these liquid-phase hydrogen storage materials. The respective advantages and drawbacks of these materials are also discussed.

2. Catalytic Hydrolysis of Sodium and Lithium Borohydrides

Borohydrides, such as NaBH₄ and LiBH₄, have received considerable research interest as potential hydrogen storage materials owing to their high hydrogen capacities. Compared to LiBH₄, NaBH₄ has been more widely studied because it provides a safe and low cost route to the production of hydrogen.^[22] NaBH₄ is a NaCl-type crystalline material with a density of 1.074 g cm⁻³.^[11] In the absence of an alkaline solution, NaBH₄ spontaneously reacts with water.^[23] The hydrolysis of NaBH₄ can effectively liberate hydrogen at room temperature in the presence of a catalyst via the following reaction [Equation (1)].^[10,12,22,24–26]



Schlesinger et al. discovered that the NaBH₄ hydrolysis reaction can be significantly accelerated by the addition of acid.^[23] Following this, only a few investigations on homogeneous catalysts have been carried out owing to the difficulty in control-

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ling the reaction process. Ruthenium(III) acetylacetonate has been studied as a homogeneous catalyst for the NaBH₄ hydrolysis reaction.^[24] An alkaline NaBH₄ gel with a CoCl₂ catalyst precursor solution was found to show a higher generation rate and less impurities in the hydrogen compared to the alkaline NaBH₄ solution, and the NaBH₄ gel also successfully powered a NaBH₄-air battery.^[27] The homogeneous catalysis for NaBH₄ hydrolysis is good for the continuous production of hydrogen, however, it is not a suitable supply of hydrogen on demand because the NaBH₄ hydrolysis reaction usually becomes uncontrollable owing to the difficulty in suspending the reaction process.^[28] Therefore, the application of heterogeneous catalysts is regarded as a convenient method to control the hydrolysis reaction of NaBH₄ by controlling the contact between the catalyst and reaction solution. It is reported that 4 equivalents of hydrogen can be completely generated in 16 min in the presence of 1.5 wt% Pt-LiCoO₂, one of the most active catalysts for this reaction (molar ratio: Pt/NaBH₄ = 0.0002).^[26] For Pt-based catalysts, the catalytic activity was increased by decreasing the Pt particle size.^[26,29] Palladium supported on carbon powder (Pd/C) and palladium in the forms of Pd and Pd-C thin films synthesized by pulsed laser deposition (PLD) were also employed to study the hydrogen generation by the catalytic hydrolysis of an alkaline NaBH₄ solution. It was found that the cone-like structure on the surface of the Pd film, which developed through Ar⁺ ion bombardment, did not enhance the catalytic activity of the Pd, and Pd/C films showed higher catalytic activity in comparison to Pd/C powders when the same amount of catalyst was used.^[30] Besides the Pt- and Pd-based materials, some other non-noble transition metals, especially Co, also exhibit good activities.^[31–36] With a fluorinated cobalt catalyst, hydrogen can be released from an aqueous NaBH₄ solution within 2.5 min (molar ratio: Co/NaBH₄ = 0.0056).^[25] The effect of particle size on the catalytic activity of a Co-based catalyst has also been reported.^[37] A thin film of Co-B was prepared by the PLD technique and the obtained catalyst had a catalytic activity 2.5 times higher than that of the Co powder catalyst.^[37] Recently, it was found that a Cr-doped Co-B powder showed catalytic activity ca. 4 times higher than that of the pure Co-B catalyst for the production of hydrogen by the hydrolysis of NaBH₄.^[38] The increased catalytic activity is related to the formation of chromium oxide, which favors the dispersion of Co-B particles on the catalyst surface, resulting in high catalyst surface area.^[38] Besides Co-based materials, Ni, Fe, and their alloys, have also shown good catalytic activities for the hydrolysis of NaBH₄.^[39,40]

Among the borohydrides, the hydrogen content in LiBH₄ reaches a value of up to 18 wt%. LiBH₄ is a hygroscopic crystalline material with a density of 0.66 g cm⁻³ at room temperature. This chemical hydride is stable because of its bonding properties. High temperatures, up to 673 K, are required for the dehydrogenation of pure LiBH₄.^[41] An alternative way to generate hydrogen from LiBH₄ is via hydrolysis [Equation (2)]:^[42]



Considering the weight of water in the reaction, the amount of hydrogen generated in this system is 13.9 wt%. Studies found that the hydrolysis reaction of LiBH₄ with a stoichiometric amount of water had a higher yield of hydrogen than that when water exceeding the stoichiometric amount was used. The gravimetric and the volumetric hydrogen densities increased followed by a decrease when increasing water was added (H₂O/LiBH₄).^[42] It was reported that the hydrolysis reaction of LiBH₄ barely produced more than 50% of the theoretical yield because the products and the unreacted LiBH₄ formed a solid mass that clogged the reaction vessel, thus limiting the full utilization of this hydride.^[43]

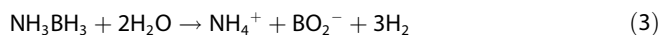
Based on investigations to date, hydrogen generation from the hydrolysis of NaBH₄ at room temperature appears an excellent candidate for portable application. The first apparatus for the supply of hydrogen by experimental bench tests on the basis of sodium borohydride has been reported.^[44] However, it needs a highly basic NaOH solution to stabilize the starting material, NaBH₄. In addition, an effective regeneration process for recycling NaBO₂ back to NaBH₄ is required for the successful implementation of this system.^[45] Therefore, large scale practical application is still a big challenge.

3. Catalytic Hydrolysis of Ammonia Borane

Ammonia borane (NH₃BH₃, AB) is a stable solid at room temperature and soluble in relatively polar solvents, such as water and methanol.^[46] It has a density of 0.780 g cm⁻³ and a melting point of 110–125 °C.^[10,13] AB is nontoxic, stable, and environmentally benign, and can be safely handled at room temperature. AB has recently been considered as a promising hydrogen storage material because it possesses a low molecular weight (30.9 g mol⁻¹) and high hydrogen content (19.6 wt%), which is higher than those for LiBH₄ and NaBH₄.^[10,12,13,47] There are significant reports on the generation of hydrogen from the thermal decomposition of AB, and the thermal decomposition temperature of AB can be lowered in an organic solution or ionic liquid.^[48] Loading AB into mesoporous silica (SBA-15), mesoporous carbon (CMK-3), or Li-doped AB/CMK-3 can benefit the thermal decomposition of AB, where the temperature threshold for the generation of hydrogen and volatile byproducts are obviously lower than those for neat AB.^[49,50] Metal amidoboranes, such as LiNH₂BH₃, derived from the reaction between NH₃BH₃ and metal hydrides (such as LiH, NaH,^[51] or CaH₂^[52]) can effectively generate up to 11 wt% hydrogen with a much lower emission of borazine byproduct. In particular, LiNH₂BH₃ and NaNH₂BH₃, can generate hydrogen below 368 K without significant borazine emission.^[51] In all these reports, thermal dehydrogenation of AB usually required high temperatures and the reaction was relatively difficult to control. In contrast, there have been a lot of research activities on the generation of hydrogen from AB under milder conditions, mostly at room temperature upon hydrolysis.

The hydrolysis of AB occurs at an appreciable rate only in the presence of a suitable catalyst at an ambient temperature, thus one of the major obstacles for the practical application of this system is to develop efficient, economical, and easily recy-

clable catalysts to further improve the kinetic properties under moderate reaction conditions.^[10–14,53–68] The reaction can be briefly expressed as follows [Equation (3)]:^[53]



Compared to other noble metal catalysts (such as Rh, Pd, and Au),^[46,64] Pt-based materials, such as Pt/C, PtO₂, Pt black, and K₂PtCl₄, are reported to exhibit the highest activities for the hydrolysis of AB with the completion time ranging from 2 to 15 min (molar ratio: catalyst/AB = 0.018).^[46] The catalytic activities are in the order of 20 wt% Pt/C > 40 wt% Pt/C > PtO₂ > Pt black > K₂PtCl₄. It is considered that the precatalysts, PtO₂ and K₂PtCl₄, are reduced by AB during the reaction to produce Pt clusters and/or colloids, similar to the case of [Rh(1,5-COD)(μ-Cl)]₂.^[46] Recently, the small size and narrow size distribution of half-naked rhodium nanoclusters within zeolite were found to have good catalytic activity for this reaction.^[67]

To lower the cost of the catalysts, first row transition metals have been extensively investigated in the last 3–4 years. First row metals, such as Fe, Co, Ni, and Cu, are found to have good catalytic activities for the hydrolysis of AB, and the catalytic activities are highly dependent on their particle sizes and compositions. Cobalt powder does not show catalytic activity in the hydrolysis of AB,^[46] whereas Co nanoparticles (NPs) on supports such as γ-Al₂O₃, SiO₂, and C, result in active catalysts,^[53] with which hydrogen is released with an almost stoichiometric amount from aqueous AB and the reaction is complete in 55–70 min (molar ratio: metal/AB = 0.018). Among the supports of γ-Al₂O₃, SiO₂, and C, the C support gives the most active Co catalyst.^[53] Supported Ni NPs are almost equally active but supported Cu NPs show lower activity. In contrast with the supported Co, Ni, and Cu catalysts, Fe/γ-Al₂O₃ NPs are catalytically inactive for this reaction.^[53] Recently, we found that amorphous Fe NPs, synthesized in situ using a mixture of NaBH₄ and NH₃BH₃ as the reducing agents without any supports, have Pt-like catalytic activity, with which the hydrolysis reaction can be completed within 8 min (molar ratio: metal/AB = 0.12, Figure 1a).^[58] The amorphous Fe catalyst can be readily recycled without any obvious loss of catalytic activity after being recycled 20 times in air.^[58] This could be because the amorphous catalyst has a much greater structural distortion and therefore a much higher concentration of active sites for the catalytic reaction than its crystalline counterpart, pre-synthesized using NaBH₄ as the reducing agent (Figure 1b).^[58] In addition, the amorphous Co, Ni, and Fe–Ni alloy NPs also exhibit much better

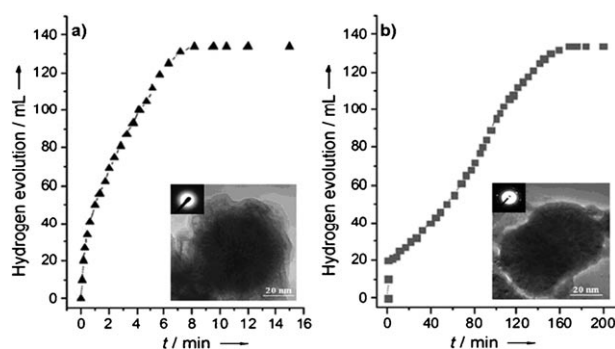


Figure 1. Generation of hydrogen via the hydrolysis of aqueous AB (0.16 M, 10 mL) in the presence of a) in situ synthesized Fe catalysts; and b) the pre-synthesized (Fe/AB = 0.12) at room temperature under Ar. Inset: TEM images and the corresponding selected area electron diffraction (SAED) patterns of the Fe NPs.^[58]

catalytic activity than their crystalline counterparts.^[61–63] The generation of hydrogen from aqueous AB catalyzed by non-noble metals is summarized in Table 1.

Besides metal catalysts, solid acids such as cation exchange resins and zeolites, and carbon dioxide are reported to have activities for the generation of hydrogen from an aqueous AB solution.^[68]

Recently, methanolysis of AB, a reaction similar to its hydrolysis, has been reported to generate pure hydrogen at room temperature according to Equation (4).^[69,70]

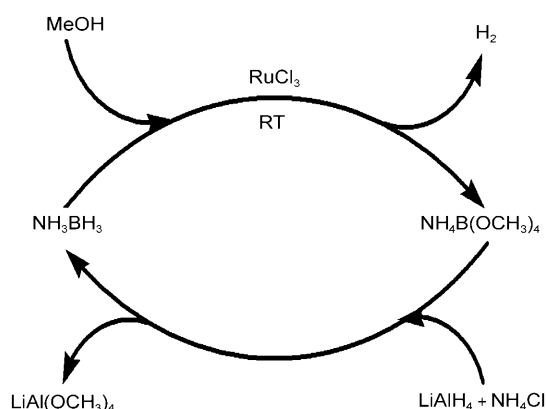


The hydrogen capacity of the above system was calculated to be approximately 3.9 wt%, which is lower than that from the hydrolytic system (8.9 wt%). It is reported that RuCl₃, RhCl₃, CoCl₂, NiCl₂, Pd/C, and Raney Ni act as catalysts for the methanolysis of AB; RuCl₃ shows the best activity.^[70] The authors also

Table 1. Catalytic activities of non-noble metal catalysts for the generation of hydrogen from aqueous AB.

Catalyst	Crystallinity	Average metal particle size [nm]	Maximum H ₂ /AB molar ratio	Time to completion [min]	Catalyst/AB molar ratio
10 wt% Co/γ-Al ₂ O ₃ ^[53]	crystalline	13	2.9	70	0.018
10 wt% Co/SiO ₂ ^[53]	crystalline	12	2.9	70	0.018
10 wt% Co/C ^[53]	crystalline	2.5	2.9	55	0.018
10 wt% Ni/γ-Al ₂ O ₃ ^[53]	crystalline	3.8	2.9	65	0.018
10 wt% Cu/γ-Al ₂ O ₃ ^[53]	crystalline	17	2.9	590	0.018
10 wt% Fe/γ-Al ₂ O ₃ ^[53]	crystalline	16	0		0.018
Fe ^[58]	amorphous	60	3	8	0.12
Fe ^[58]	crystalline	< 100	ca. 3	160	0.12
Ni in starch ^[61]	amorphous	< 10	3	6	0.1
Co ^[63]	amorphous	< 10	3	1.7	0.04
Fe _{0.5} Ni _{0.5} ^[63]	amorphous	3	3	2.2	0.12
hollow Ni/SiO ₂ nanospheres ^[59]	amorphous	< ca. 3	ca. 3	22	0.05
Ni/SiO ₂ nanospheres ^[59]	amorphous	no data	2.0	76	0.05
Ni/SiO ₂ ^[59]	amorphous	no data	1.9	120	0.05
Ni@SiO ₂ nanospheres ^[66]	no data	very small	2.7	23	0.065
MOF-based Ni NPs ^[64]	amorphous	ca. 100	3	5	0.10
Ni hollow sphere ^[65]	crystalline	no data	0.6	120	ca. 0.025

report an efficient one-pot regeneration of AB from the methanolysis intermediate, ammonium tetramethoxyborate (Scheme 1). Addition of NH_4Cl as an ammonia source is necessary to improve the yield.^[70]



Scheme 1. Ammonia borane hydrogen cycle.^[70]

Surfactant-free Co–Co₂B, Ni–Ni₃B, and Co–Ni–B show good catalytic activities for the methanolysis of AB.^[69] When the molar ratio of catalyst/AB is 0.2, three moles of hydrogen were liberated in 2.5, 4.2, and 1.5 min for Co–Co₂B, Ni–Ni₃B, and Co–Ni–B, respectively. The catalysts are recyclable and their activities remain almost unchanged, even after 20 cycles.^[69] Other catalysts, such as Cu, Cu/Cu₂O, and PVP-stabilized Pd, have also been reported for the methanolysis of AB.^[71,72]

In conclusion, the hydrolysis of AB presents a high hydrogen capacity up to 8.9 wt% of the starting materials, AB and H₂O, which is higher than that from its methanolysis. Moreover, hydrolysis of AB does not require a highly basic solution to stabilize the starting material AB, which is an advantage to the hydrolysis of NaBH₄. Further experimental and theoretical research towards its practical application, the mechanism of the reaction, and the development of a high performance system consisting of a reactor, solution supplier, and reaction controller, as well as the regeneration of AB are desired.

4. Catalytic Decomposition of Hydrous Hydrazine

Anhydrous hydrazine, H₂NNH₂, a liquid at room temperature, has a hydrogen content as high as 12.5 wt%. Hydrazine was investigated as a monopropellant for use in satellite propulsion using an Ir-based catalyst.^[73] Various research groups have explored the catalytic decomposition of anhydrous hydrazine, for which Shell405 (30 wt% Ir/Al₂O₃)^[74] was a milestone during the catalyst development. It has been shown that hydrazine can be decomposed in two ways: the complete decomposition [Equation (5)]:



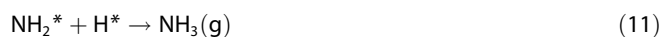
and the incomplete decomposition [Equation (6)]:



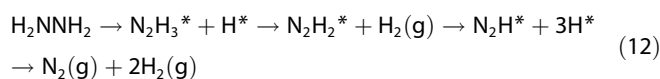
It has been reported that the two decomposition reactions [Equations (5) and (6)] may proceed through various pathways depending upon the catalysts used and the reaction conditions.^[74–81] In one pathway, firstly the N–N bond breaks to form the NH₂ species on the surface [Equation (7)], which further decomposes to nitrogen and hydrogen [Equation (8)]. Upon thermal activation, the surface adsorbed nitrogen and hydrogen species recombine to desorb N₂ and H₂ [Equations (9) and (10)].



In the second pathway, the surface adsorbed NH₂ species react with hydrogen species to desorb NH₃ [Equations (7), (9), and (11)].



In the third pathway, N₂ is formed intra-molecularly and not by the recombination of nitrogen species. The N–H bonds break first, forming species such as N₂H₃^{*}, N₂H₂^{*}, N₂H^{*}, and N₂ [Equation (12)].



In the fourth pathway, hydrazine is directly hydrogenated in a concerted reaction to form ammonia. It has been reported that different catalyst surfaces promote different reaction pathways.^[78–80]

Most of the reports on the decomposition of hydrazine show the presence of ammonia as a product, whereas the selective decomposition of hydrazine to exclusive hydrogen is scarce.^[77] Zhang and co-workers have explored in detail the gas phase catalytic decomposition of hydrazine diluted in argon (3% v/v) over a range of SiO₂- and Al₂O₃-supported catalysts of ferrous and platinum group metals.^[77] They found that the supported Fe, Ru, Co, and Rh metal catalysts exhibited 100% selectivity for hydrogen only at high temperatures (> 300 °C). In contrast, the SiO₂-supported Ni, Pd, and Pt catalysts were active at around room temperature and the Ni/SiO₂ catalyst showed 90% selectivity for hydrogen at 50 °C. Interestingly, the selectivity for hydrogen sharply declined at temperatures above 50 °C, where the incomplete hydrazine decomposition [Equation (6)] was proposed. It was found that the catalytic activity or hydrogen selectivity did not significantly depend on the support (SiO₂, Al₂O₃, and carbon), metal loading, and reduction temperature of the catalysts.^[77] The same group has

reported supported iron-nitride catalysts for hydrazine decomposition, but a 100% selectivity for hydrogen could only be achieved above 400 °C, presumably through the decomposition of ammonia produced via the incomplete decomposition of hydrazine.^[81]

However, anhydrous hydrazine (>98%) is explosive when exposed to a metal catalyst, making it difficult to safely apply. Hydrous hydrazine, such as hydrazine monohydrate, $\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}$, still containing a large amount of hydrogen, 8.0 wt%, is much safer^[73] and might be a promising hydrogen carrier for storage and transportation. The easy recharging and the availability of the current infrastructure of liquid fuels for recharging as well as the only production of nitrogen that does not require recycling, besides hydrogen, are distinguished advantages of hydrous hydrazine. As water molecules may lower the activity of catalysts and the reactivity of hydrazine, the development of efficient and selective catalysts for hydrogen generation from hydrous hydrazine, is of critical importance. Despite having encouraging properties as a hydrogen storage material, hydrous hydrazine has received very little attention, especially for its selective decomposition to hydrogen.^[16,17,82] It has been reported that an $\text{Ir}/\text{Al}_2\text{O}_3$ catalyst is active for hydrazine monohydrate decomposition.^[82] We have recently explored the catalytic decomposition of hydrous hydrazine over various metal (Fe, Co, Ni, Cu, Ru, Rh, Ir, Pt, and Pd) NPs at room temperature.^[16] As shown in Figure 2, among the

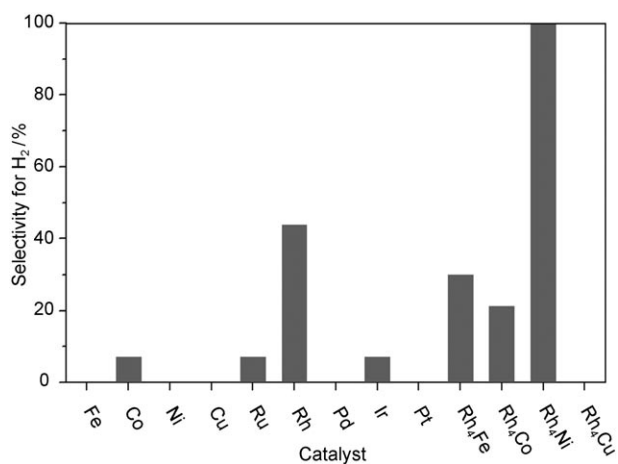


Figure 2. Comparative selectivity of different metal NP-based catalysts for hydrogen generation from hydrous hydrazine at room temperature.

various NPs examined, the Rh NPs (diameter ca. 16 nm) were found to be the most selective (44%) for hydrogen release from hydrous hydrazine decomposition. Reducing the particle size to 5 nm by employing a surfactant in the preparation of the Rh catalyst, enhances the activity of the Rh NPs catalyst and the reaction completion time is reduced by three fold.^[16] Other metal NPs, such as Co, Ru, and Ir, exhibited only 7% selectivity for hydrogen, and Fe, Cu, Ni, Pt, and Pd were totally inactive under the described reaction condition.^[16]

Bimetallic catalysts might show enhanced catalytic performance in comparison to their monometallic counterparts. Since the properties of the catalyst surfaces are closely related with their catalytic activities, the precise modification of the catalyst surface by introducing a second component or by changing the morphology, could facilitate the controlled tuning of the catalytic properties. Despite Ni NPs being inactive and the low hydrogen selectivity of Rh NPs in this reaction, the alloying of Ni and Rh drastically enhances the hydrogen selectivity. The hydrogen selectivity was found to be strongly dependent on the Rh/Ni ratio, and a maximum of 100% was reached at Rh/Ni = 4:1 (Figure 3).^[17] Moreover, alloys

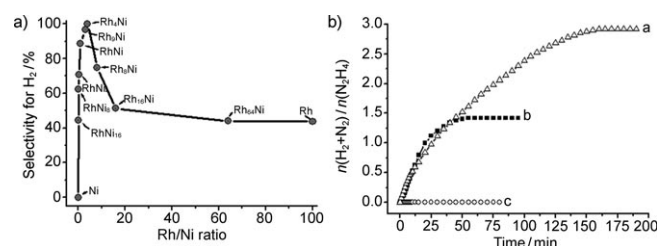


Figure 3. a) Selectivity for hydrogen generation from hydrous hydrazine (0.5 M) catalyzed by Rh_xNi_y ($x=0-64$; $y=0-16$) with $\text{Rh}/\text{N}_2\text{H}_4 = 1:10$ at room temperature. b) Time course plots for decomposition of hydrous hydrazine (0.5 M) catalyzed by a) Rh_4Ni , b) Rh ($\text{Rh}/\text{N}_2\text{H}_4 = 1:10$), and c) Ni ($\text{Ni}/\text{N}_2\text{H}_4 = 1:10$) nanocatalysts at room temperature.^[17]

of Rh with other first row transition metals, such as Fe, Co, and Cu, exhibited a loss in hydrogen selectivity, under analogous synthetic and reaction conditions.^[17] Generally speaking, alloy materials have distinct binding properties with reactants in contrast to those for monometallic metal catalysts. The strong metal–metal interactions tune the bonding between the catalyst surfaces and the reactants, where the extra stabilization of the transition state on the alloy catalysts in comparison to the corresponding interaction on the monometallic catalyst surface is an additional benefit. Therefore, it is reasonable to understand that the alloy of Rh and Ni leads to a modification of the catalyst surface and tunes the interactions of Rh with the N–N and N–H bonds as well as the stability of reaction intermediates on the catalyst surface.^[75,80] Consequently, the reaction prefers pathway (5) [Equation (5)] to pathway (6) [Equation (6)], resulting in the complete conversion of hydrazine to hydrogen and nitrogen.

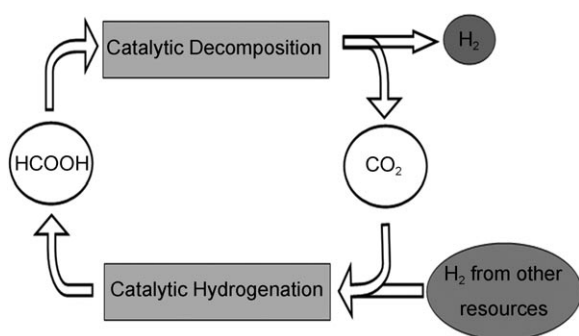
Although the current best catalyst for the complete conversion of hydrous hydrazine to hydrogen at room temperature requires the noble metal Rh, further investigations for low cost, high performance catalysts are definitely needed for the practical use of hydrous hydrazine as a safe and effective hydrogen storage material.

5. Catalytic Decomposition of Formic Acid

Formic acid, HCOOH , a well-known chemical with numerous uses, is a liquid at room temperature and has a density of 1.22 g cm^{-3} . It is usually produced through the hydrolysis of

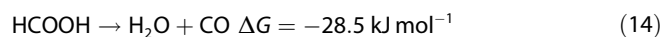
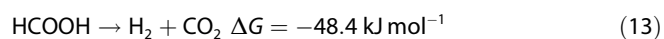
methyl formate and can also be obtained by the reduction of CO₂ with H₂ in the presence of an appropriate catalyst. Formic acid is a strong and corrosive acid. However, it is non toxic and suitable for easy transportation, handling, and safe storage. Moreover, formic acid, having 4.4 wt% of hydrogen, produces only gaseous products (H₂/CO₂) by decomposition. The H₂/CO₂ mixture can be directly applicable to fuel cells and easily separated under certain conditions.^[18]

A power supply system could be feasibly based on the catalytic processes of formation and decomposition of formic acid. Simple catalytic decomposition of formic acid produces H₂ and the byproduct CO₂, which can be recycled by repeating the reduction to formic acid. Meanwhile, CO₂ is abundant on the earth; it is cheap, and readily available. In this case, the reduction of CO₂ emissions is the use of CO₂ itself as a hydrogen carrier. Scheme 2 depicts a CO₂-neutral hydrogen storage cycle.^[19]



Scheme 2. A CO₂-neutral cycle for the storage of H₂ in formic acid system.

Nowadays, the homogeneous hydrogenation of CO₂ to formic acid with base is well established to give high catalytic activities and selectivities. The reaction was firstly studied by Inoue et al.^[83] and subsequently developed by Noyori, Jessop, Leitner, J o, and co-workers.^[84–87] However, in contrast to Li/NaBH₄, NH₃BH₃, and other H₂ storage materials, HCOOH decomposition to H₂ has received less attention. In general, the decomposition of HCOOH follows two pathways: one involves the formation of H₂ and CO₂ [Equation (13)] and the other involves the formation of CO and H₂O [Equation (14)].



To use CO₂ as a hydrogen carrier, an efficient and selective catalyst is required for the decomposition of HCOOH to selectively produce H₂ and CO₂ [Equation (13)]. There are reports on the formation of hydrogen via the homogeneous catalytic decomposition of HCOOH and, recently, the catalytic efficiency has been significantly improved.^[18–21,88–100] However, the generation of hydrogen from formic acid with heterogeneous catalysts in aqueous media remains less developed.^[101–105]

5.1 Homogeneous catalytic decomposition

Studies on the decomposition of formic acid started with the pioneering works by Coffey, Otsuka, Strauss, Trogler, and co-workers, who used Pt, Rh, Ir, and Rh-based catalysts.^[90–93] In all these early reports, the catalytic activity was generally low, except for the following two cases: with an iridium phosphine complex as a catalyst, a turnover frequency (TOF) of 1187 h^{−1} at 100–117 °C was obtained,^[90] and by using a platinum phosphine catalyst, a TOF of 100 h^{−1} after 15 min at room temperature was obtained.^[91] Over 10 years later, TOFs of around 30 h^{−1} were reported based on rhodium phosphine catalysts at room temperature and 70 °C.^[86,87] With the dinuclear complex [Ru₂(m-CO)(CO)₄(m-dppm)₂] as a catalyst for the decomposition of formic acid without a base, a TOF up to 500 h^{−1} after 20 min was observed.^[94] With a rhodium bipyridine catalyst, a TOF of 238 h^{−1} was achieved at 40 °C.^[95] In addition, it has also been found that nitrite-promoted rhodium and molybdenum phosphine catalysts can improve the reaction.^[99,100] Fukuzumi et al. reported that HCOOH selectively decomposed to afford H₂ and CO₂ in aqueous solution at room temperature in the presence of a catalytic amount of a water-soluble Rh catalyst, [Rh^{III}(Cp*)(bpy)(H₂O)]²⁺ (Cp* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine). No deterioration of the catalyst was observed during the catalytic decomposition of HCOOH in continuous runs of reaction.^[88]

Recently, noteworthy advances were made by two different groups, Beller and Laurenczy.^[19–21,89,96–98] Beller et al. investigated the decomposition of formic acid with different homogeneous catalysts at 40 °C, including RhCl₃·xH₂O, RuBr₃·xH₂O, [{RuCl₂(p-cymene)}₂], [RuCl₂(PPh₃)₃], and [{RuCl₂(benzene)}₂], in the presence of amine adducts.^[19,21,89] Variations in the ratios of amine/HCOOH, PPh₃/Ru, and different phosphine ligands, significantly changed the amount of hydrogen generated and the turnover number (TON) of the reaction. Generally, for the reaction catalyzed by [{RuCl₂(p-cymene)}₂], various alkyl dimethylamines with longer alkyl chains showed a higher degree reaction rate promotion. However, high decomposition rates (TOF = 21 h^{−1}) were also observed by using triethylamine.^[19,89] Among all examined catalysts in the different reaction conditions, the decomposition of formic acid in a 5HCOOH/2NEt₃ mixture over a catalyst prepared in situ from RuBr₃·xH₂O and three equivalents of PPh₃ after pretreatment in DMF at 80 °C for 2 h, yielded an initial TOF of 3630 h^{−1} at 40 °C, which is the best performance for formic acid decomposition reported so far.^[19] Another catalyst, [RuCl₂(PPh₃)₃], also gave an excellent activity with a TOF of 2688 h^{−1} under the same conditions.^[21] Because of the high activity of the catalyst, hydrogen was selectively released at room temperature from formic acid and no CO was detected as a byproduct. The authors also performed the experiments to clearly show that hydrogen generated from formic acid under their conditions can be directly used in fuel cells without CO pre-removal. Table 2 summarizes some Ru-based homogeneous catalysts for the decomposition of formic acid. Very recently, Beller et al. developed an active and stable system applicable for the direct use in fuel cells, which was studied in batch and continuous modes for up to

Table 2. Decomposition of 5HCO₂H/2NEt₃ in the presence of Ru/PPh₃ catalysts under conditions: preformed 5HCO₂H/2NEt₃ adduct (5.0 mL), 3 equivalents PPh₃ at 40 °C, 3 h; catalyst pretreated at 80 °C for 2 h in DMF (1.0 mL).^[19]

Ru precursor	n_{Ru} [μmol]	$V_{\text{gas,2h}}$ [mL] ^[a]	TON (2 h) ^[b]
[RuCl ₂ (PPh ₃) ₃]	5.95	260	891
RuCl ₃ ·xH ₂ O ^[c]	5.95	202	691
RuBr ₃ ·xH ₂ O ^[d]	5.30	230	882
RuBr ₃ ·xH ₂ O ^[d]	17.1	1154 ^[e]	1375 ^[e]
[RuCl ₂ (<i>p</i> -cymene)] ₂	6.05	22	73
[RuCl ₂ (<i>p</i> -cymene)] ₂	19.0	47	50
[Ru(<i>p</i> -cymene)] ₂	5.97	13	44
[RuCl ₂ (benzene)] ₂	5.95	106	3361
[RuCl ₂ (benzene)] ₂	19.4	324	340
[RuCl ₂ (benzene)] ₂	29.8	450	308
[RuCl ₂ (C ₁₀ H ₁₆) ₂] ^[f]	5.99	47	159
Ru(methylallyl) ₂ cod	5.96	20	68
Ru(acac) ₃	5.93	1.1	3.9
RuCl ₂ (bipy) ₂	5.96	0.2	0.85

[a] Measured by gas burette (H₂/CO₂ = 1:1). [b] The value of TON (3 h) is near to TON (2 h). [c] The same results have been obtained with 3.5 equivalents of PPh₃. [d] 3.4 equivalents PPh₃. [e] After 20 min: 1015 mL, TOF 3630 h⁻¹. [f] [RuCl₂(C₁₀H₁₆)₂]₂ = dichlorobis(μ-chloro)-bis[(1,2,3,6,7,8-η)-2,7-dimethyl-2,6-octadien-1,8-diy]-diruthenium(IV).

two months. The optimized catalyst system containing *N,N*-dimethyl-*n*-hexylamine with a catalyst generated in situ from (benzene)ruthenium dichloride dimer [RuCl₂(benzene)]₂ and six equivalents of 1,2-bis(diphenylphosphino)ethane (dppe), reached, at room temperature, a total TON of approximately 260 000, with an average TOF of about 900 h⁻¹.^[97] They also found that visible light significantly accelerated and controlled the ruthenium-catalyzed generation from formic acid in the presence of amines.^[98]

Almost at the same time, Laurency et al. reported the reaction of [Ru(H₂O)₆]²⁺ or commercial RuCl₃·xH₂O with *meta*-trisulfonated triphenylphosphine (TPPTS) to yield a hydrophilic ruthenium-based catalyst, which was catalytically active for the decomposition of formic acid.^[20,96] Formic acid was catalyzed to gradually decompose over Ru^{II} species with a low rate at room temperature. With increased temperatures, the reaction rate became much higher (TOF = 670 h⁻¹ at 120 °C). At all reaction temperatures, the conversion was higher than 90% and the catalyst remained active, even after one year in solution. During the reaction, the generated pressure of the H₂/CO₂ mixture typically ranges from 1 to 220 bar (1 bar = 10⁵ Pa), whereas the catalytic activity was not restrained, even up to 750 bar. No CO in the generated gases at 100 °C was detected by FTIR spectroscopy (detection limit of 3 ppm); therefore the gas mixture from the decomposition of formic acid with this catalyst may be suitable for fuel cell applications. Under the consideration of the practical application, the authors designed a continuous system, in which the generated gases were released at a rate that maintained a constant pressure inside the reactor. It could be used directly in combustion or electrical devices and avoided technical problems owing to pressure drops that occur with high pressure cylinders because hydrogen can be

generated to give a constant pressure. More recently, they have also proposed a detailed mechanistic study by the optimization of the reaction conditions.^[96] They identified several intermediates by multinuclear NMR spectroscopy, which led to a tentative reaction mechanism consisting of two competitive catalytic cycles involving a monohydride ruthenium complex [RuH(tppts)₂(H₂O)₃]⁺ as a common intermediate.

5.2 Heterogeneous catalytic decomposition

The first work on the heterogeneous catalysis for the decomposition of formic acid by catalysts of Pd-Au alloy wires was reported in 1957,^[101] and followed by using Pd/C as a catalyst.^[102,103] After this, the heterogeneously catalyzed HCOOH decomposition received little attention. Very recently, Ojeda and Iglesia reported that well-dispersed Au species (Au/Al₂O₃), which were undetectable by transmission electron microscopy (TEM), dehydrogenate HCOOH with much higher metal-time yields than Pt clusters (Pt/Al₂O₃) at 343–383 K.^[104] The Arrhenius plot for HCOOH decomposition showed that the activation energies in the zero-order kinetic regime were 53 ± 2 and 72 ± 4 kJ mol⁻¹ on Au and Pt, respectively. In Beller's work, they also tried alternative heterogeneous catalysts, including Pd/C, Fe₂O₃/silica, and nano-Fe₂O₃, but obtained less success compared to the Ru-based complex catalysts.^[21] Xing et al. developed Pd-Au and Pd-Ag alloys supported on carbon and overcame the poisoning and steadily evolved high-quality hydrogen from the decomposition of formic acid at low temperatures (Figure 4a).^[105] They also found that the activities of Pd-Au/C and Pd-Ag/C can be markedly enhanced by the co-depo-

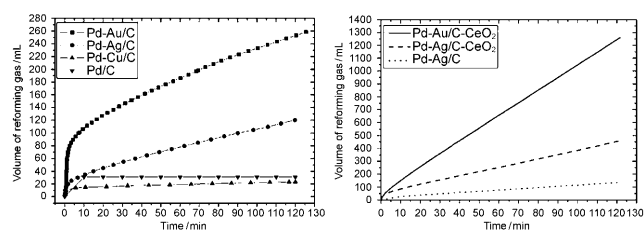


Figure 4. a) The output volume of reforming gas (H₂+CO₂) during 2 h with Pd-M/C (30 mg, 20 wt % Pd, $n_{\text{Pd}}/n_{\text{M}}=3:1$, M = Cu, Ag and Au), respectively, at 92 °C and formic acid (9.94 M)-sodium formate (3.33 M) solution (5.00 mL). b) The output volume of reforming gas at 92 °C with formic acid (9.94 M)-sodium formate (3.33 M) solution (5.00 mL). PdAu/C–CeO₂ (60 mg, 10 wt % Pd), 50 % CeO₂, $n_{\text{Pd}}/n_{\text{Au}}=1:1$ (solid line); PdAg/C–CeO₂ (60 mg, 10 wt % Pd), 50 % CeO₂, $n_{\text{Pd}}/n_{\text{Ag}}=1:1$ (dashed line); PdAg/C (30 mg, 20 wt % Pd), $n_{\text{Pd}}/n_{\text{Ag}}=1:1$ (dotted line). Reprinted with permission from Ref. [105].

sition with CeO₂ (Figure 4b). At 92 °C, the catalytic activities of Pd-Au/C–CeO₂ or Pd-Ag/C–CeO₂ (60 mg, 10 wt % Pd, 50 wt % CeO₂, $n_{\text{Pd}}:n_{\text{Au/Ag}}=3:3$) are 10.3 and 3.4 times, respectively, of that of Pd-Ag/C (30 mg, 20 wt % Pd, $n_{\text{Pd}}:n_{\text{Ag}}=3:3$). The TOFs of Pd-Au/C–CeO₂ and Pd-Ag/C–CeO₂ are 227 and 76 h⁻¹, respectively. The reaction rate for Pd-Au/C–CeO₂ became extremely fast (>6000 mL min⁻¹ g, TOF up to 832 h⁻¹) by only elevating the temperature by 10 °C, which showed high potential for transportable applications.

Although there are only limited reports on the decomposition of formic acid, the current results have already showed that HCOOH could be a promising candidate for hydrogen storage. Developments of more effective catalysts, especially separable heterogeneous catalysts, for the selective decomposition of formic acid are expected.

6. Summary

All the liquid-phase chemical hydrogen storage materials reviewed above containing relatively high hydrogen contents have the potential to be used as hydrogen sources suitable for portable fuel cells. However, each of them has its own merits and drawbacks. The materials and systems presented herein can effectively work under mild conditions (even at room temperature) with suitable catalysts compared to the organic hydrogen generating (for example, various cyclohexane derivatives and alcohols as feedstock) and thermolysis systems of solid-state chemical hydrogen storage materials, which usually need high temperature reforming or decomposition processes. The easy recharging and the availability of the current infrastructure of liquid fuels for recharging as well as the only production of nitrogen/carbon dioxide, which does not need recycling, besides hydrogen, of hydrous hydrazine and formic acid as hydrogen storage materials, are extraordinary advantages over NaBH₄ and NH₃BH₃. In addition, hydrous hydrazine could be more promising because its byproduct, nitrogen, is more environmentally benign compared to formic acid with lower hydrogen content, which produces carbon dioxide during hydrogen generation. Recent research efforts have greatly improved the hydrogen generation temperature and the reaction kinetics in these systems. However, for practical applications in portable electric devices, limitations are still pending, such as, cost, catalyst deactivation, regeneration of byproducts, and control of the reaction kinetics. We are looking forward to further developments of these systems in the future.

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