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## Hydrogen storage in formic acid as a renewable energy source using heterogeneous catalysis

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**Abstract:** One of the most vital chemicals, which is not only found naturally but can also be synthesized in the laboratory, is formic acid (FA). FA is a key byproduct of several second-generation biorefinery processes as well, and it is used in several pharmaceutical and industrial applications. Recently, another significant use of FA that is taking the lead is as a form of fuel. This could either involve reformation, as a possible form of chemical hydrogen storage, or be done without reformation in the form of FA fuel cells, in particular because FA fuel cells are much more effective than other proton-exchange membrane fuel cells. Therefore, FA is a highly useful fuel for applications such as vehicles and portable devices. This review is based on recent developments and processes, showing that FA should become a prominent reversible source for hydrogen storage. Recent developments should permit a cheap and extremely effective source of rechargeable hydrogen fuel cells in the future. This will be possible through the usage of appropriate heterogeneous metal nanoparticle catalysts under ideal reaction conditions. The most significant aspect will be the usage of atmospheric CO<sub>2</sub>, which is a greenhouse gas, to develop FA, as that would help to reduce the quantity of CO<sub>2</sub> in the atmosphere and diminish global warming.

**Key words:** Hydrogen, formic acid decomposition, green chemistry, renewable feedstock, CO<sub>2</sub>, CO

### 1. Introduction

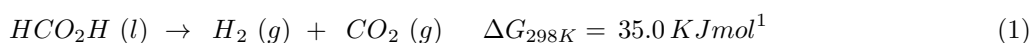
It is common knowledge that nonrenewable fossil fuels will not last indefinitely, and it is important to find alternatives before we run out of them. It is apparent that in the future there will be a major requirement for renewable and secure energy carriers for transportation and other similar applications. Therefore, various energy fields like solar energy, nuclear energy, and lithium ion batteries are being developed at great speeds to counter this issue before it is too late. Hydrogen is one of the vital elements that can be used in several ways, including as an efficient alternative in the future for energy feedstocks. However, hydrogen cannot be depended on as an energy source because of its limitations in storage and transportation. Therefore, numerous research studies are being conducted to discover ways of using hydrogen as a clean fuel and transporting and storing it safely, through newly formed materials that can deliver and store hydrogen cheaply. There are two approaches to dividing it, which are physical or chemical storage [1–9]. If hydrogen has to be stored physically, then it is stored in diatomic molecular form. It can be stored at both high pressures and low temperatures. At high pressure, a closed container is used, and at low temperatures, cryocompression or high-pressure tanks [10] are

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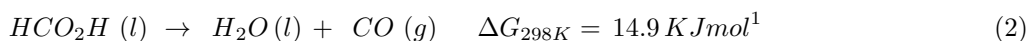
used to absorb it into high-surface-area materials through different carbon materials [11,12], such as zeolites [13], clathrate hydrates [14], or advanced material metal-organic frameworks [15–17]. However, there is an energy gap present between the dehydrogenation and hydrogenation energy levels of these materials and hence they are usually less energy-efficient. During the chemical storing of hydrogen, it is chemically bonded rather than in molecular form. At times, some appropriate higher hydrogen molecules are chosen to effectively emit hydrogen under suitable environmental conditions through a catalytic or noncatalytic process. Formic acid (FA) is also found in natural form, such as in insect bites and bee stings, and it is also a key byproduct of petroleum refining, biomass processing, and numerous industrial organic syntheses. Hydrogen can be conveniently created from the electrolysis of water [18], and it has also been developed by scientists through the atmospheric hydrogenation of  $\text{CO}_2$ , or extracted from industrial waste through appropriate catalysts [19–21]. It is also predicted to become much more useful for hydrogen storage in the near future. The term “useable” or “net capacity” is used to refer to a suitable hydrogen content that can be obtained from a chemical hydrogen storage system in the form of  $\text{H}_2$  [22]. The  $\text{H}_2$  that is produced is effective for the creation of clean power production at low temperatures through the formation of organic hydrogen carriers, which has been well studied, such as carbazole, cycloalkanes, and methanol. However, these have several drawbacks when it comes to being used as hydrogen storage materials: they are toxic, expensive, and not stable enough and they have low levels and low dehydrogenation kinetics, and issues with efficiency during regeneration processes [23,24]. In FA fuel cells, the chemical reaction includes two-electron reductions of  $\text{O}_2$  at the cathode and two-electron direct oxidation of FA at anode. However, there are much more dangerous effects from FA fuel cells, apart from catalyst deactivation and fuel crossover. These include the poisoning of the catalyst when CO moves through an inappropriate route from the dehydration of FA, which can damage 20 ppm of the fuel cell. There have been instances when the active phase of a catalyst is affected by FA corrosion and the FA’s hydrophilicity dehydrates the proton-exchange membrane, leading to a higher cell resistance. Recently, a lot of work and developments have been implemented by a number of researchers in this area to efficiently use FA as a renewable energy source [3,9,25].

## 2. FA decomposition

The main hindrance in making hydrogen a popular source of fuel cells is due to issues around producing, storing, and transporting it. Rather than transporting hydrogen gas, it would be better to have a chemical  $\text{H}_2$  storage material, or  $\text{H}_2$ -containing material that could be broken in an appropriate environment to release the hydrogen gas. Two standard pathways can be used to break down FA that has 4.4 wt.% hydrogen. The expected reaction from this process would be carbon dioxide and hydrogen (Eq. (1)), and the one producing CO and  $\text{H}_2\text{O}$  (Eq. (2)) would be the undesired side reaction [1–4,6–8].



**Equation 1:** Decomposition of FA to produce  $\text{H}_2$  and  $\text{CO}_2$



**Equation 2:** Decomposition of FA to produce CO and  $\text{H}_2\text{O}$

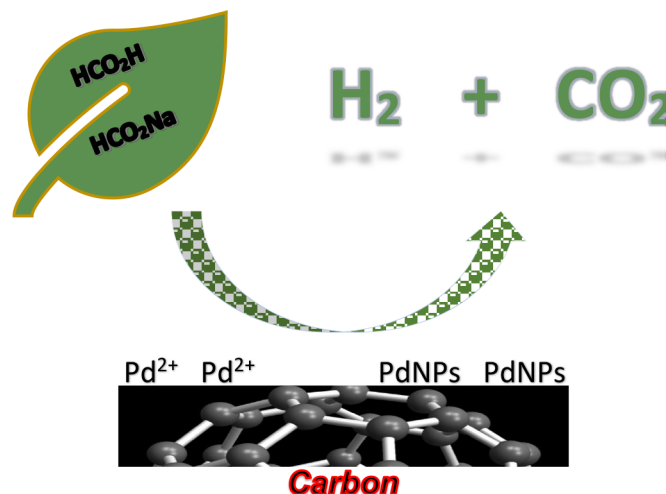
CO-free decomposition of FA is vital for  $\text{H}_2$  storage from the FA. A mixture of  $\text{CO}_2$  and FA acting as a storage system for  $\text{H}_2$  may be a simple idea, but the specific decomposition of FA to  $\text{H}_2$  and  $\text{CO}_2$ , along with the recycling of  $\text{CO}_2$  through a decrease in the existence of  $\text{H}_2$  to FA, can also be attained.  $\text{CO}_2$  is easily

available everywhere at a reasonable price due to its large amount on earth. Hence, a reduction in the release of  $\text{CO}_2$  by decreasing  $\text{H}_2$  turns the  $\text{CO}_2$  into a hydrogen carrier itself. In-depth research has been conducted to discover appropriate catalysts (homo/heterogeneous) that can specifically be used for FA decomposition. However, it is still crucial to gain overall selectivity for FA decomposition through a suitable channel [4,7,26].

### 3. Heterogeneous catalysts

Initially, FA was decomposed using heterogeneous catalysts that mostly perform in the gas phase through the use of metal, metal oxides, and metal based on oxides or carbon catalysts. The production of hydrogen from the decomposition of FA at low temperatures or in liquid phase has also been examined by researchers. Pd plays a key role in the majority of heterogeneous catalysts that are based on monometallic or bimetallic or trimetallic nanoparticles. One of the main properties of Au:Pd/C is that it forms excellent hydrogen through the decomposition of FA with a base at normal temperature (sodium formate) [27–32]. The classification of activity depending on TOF values is Pd/C < Cu:Pd/C < Ag:Pd/C < Au:Pd/C. The activities of catalytic Ag:Pd/C and Au:Pd/C catalysts have been linked to more variation in Ag, Au, and CO poisoning. In addition,  $\text{CeO}_2(\text{H}_2\text{O})_x$  further enhances the catalytic activity by producing a cationic Pd surface displaying higher activity in the oxidation of CO and methanol decomposition. Moreover,  $\text{CeO}_2(\text{H}_2\text{O})_x$  can also activate the decomposition of FA on the Pd through a more effective channel, in which a lower quantity of poisoning intermediates is formed [33]. Following that, a unique Au and Pd bimetallic catalyst was identified with a Pd:Au core-shell carbon-based nanostructure; its synthesis involved an instantaneous reduction technique without any stabilizer, which acted as a catalyst for  $\text{H}_2$  production through FA decomposition. The catalyst revealed properties such as selectivity, stability, and high activity at low temperature, and it catalytically performed much better than the equivalent monometallic catalysts. Moreover, the gas produced from the decomposition of FA had only 30 ppm of CO and could be directly used in fuel cells. After successful experimentation on the effect of  $\text{CeO}_2$  on the activity of Au:Pd/C and Ag:Pd/C catalysts, other elements were investigated. These catalysts worked steadily for a while at room temperature (RT) and above. Catalytic activity was seen with all of the rare earth metal oxides of Au- and Pd-supported carbon catalysts, which displayed lower activation for the decomposition of FA than Au:Pd/C and Au:Pd:Eu/C. The metal/metal oxide catalysts consisting of Pt, Ru and Bi, presented as PtRuBiOx, are catalyzed by the specific FA dehydrogenation in  $\text{H}_2\text{O}$  at almost ideal temperatures. The activation energy was seen at  $37.3 \text{ kJ mol}^{-1}$  and TOF was  $312 \text{ h}^{-1}$  in the first 60 min of the decomposition. Different core-shell nanoparticles with a metallic inner core and Pd external shell were formed by Tsang et al. From among all the metals, Ag:Pd showed the highest activity during FA decomposition at RT, with the thinnest continuous Pd shell and equivalent Ag and Pd alloy and pure Pd catalysts displaying minimum activity [34,35]. The resulting frequencies per surface Pd site could be compared to homogeneous catalysts at 293 K and 323 K. At 293 K, an equimolar mixture of  $\text{H}_2$  and  $\text{CO}_2$  was consistently formed without any CO; however, CO was seen at temperatures exceeding 323 K. A close link between the catalytic activity and the metal's core work function was also observed, with the highest total difference with the Pd shell work function and consequently the highest energy of adsorption by charge transfer to the shell from the core. This resulted in an excellent activity of the final bimetallic structure for FA decomposition. The minimal range of this “ligand” electronic effect present between two metals caused the highest performance gained for the thinnest Pd layer. Nanomaterial interfaces have also made a major contribution to catalysis, as shown by the in-depth research conducted by Yan et al. into catalytic FA dehydrogenation by utilizing catalysts that have mono/bi/trimetallic nanoparticles with various carbon materials. A less costly Pd/C catalyst can be attained with citric acid for

producing extremely effective CO-free  $H_2$  from  $HCOONa$  at RT (Figure). Citric acid improves the catalytic properties of the resultant Pd/C, which is formed during the development of the Pd nanoparticles on carbon at RT. Ultrafine and completely isolated Au:Pd/N-GO, produced by a facile and green technique, showed higher activity than its alloy or monometallic equivalents towards the production of  $H_2$  from a FA solution at RT. N-mrGO synthesis is both a reducing agent and is supported by benefiting from its average decrease and high dissolving properties. According to another report, Ag:Pd/rGO is an effective catalyst for FA dehydrogenation reaction with full  $H_2$  selectivity, and it has extremely high activity at RT under green conditions. It was also observed by Yan et al. that Au:Pd:Co/C is a stable, cheap, and effective catalyst for the production of CO-free  $H_2$  from FA dehydrogenation at RT. The increased CO stability in the secure nanoalloy structure allows it to be successfully applied in FA dehydrogenation. Au:Pd:Co/C prepared with a lower consumption of noble metals showed 100%  $H_2$  selectivity, maximum activity, and good stability in the production of  $H_2$  from FA with no additive at 298 K. Earlier studies showed the joint catalytic activities of Co:Au:Pd/C and monometallic and bimetallic from Pd, Au, and Co equivalents for development of  $H_2$  from FA decomposition at 298 K in the immediate surroundings. The prepared Co:Au:Pd/C showed enhanced activity compared to bimetallic and monometallic catalysts prepared using the same process. Similarly, carbon-aided extremely homogeneous trimetallic nanoparticles (Au:Pd:Ni/C) are also used as a catalyst for the specific dehydrogenation of FA. This catalyst has also shown high activity and full selectivity for FA dehydrogenation with no additives at RT. Au:Pd:Ni/C had more activity than its monometallic Pd or Ni or Au supported carbon and bimetallic equivalents Pd:Ni, or Au:Pd, or Au:Ni supported carbon, and also a physical mixture of Ni/C, Au/C, and Pd/C under conditions with the same reaction [36–38].



**Figure.** FA decomposition using Pd/C with citric acid at RT.

The as-synthesized Pd/SiO<sub>2</sub> and Pd@SiO<sub>2</sub> catalysts contain maximum catalytic activities compared to Pd NPs supported on commercial silica at ambient temperature. Moreover, it has been found that the Pd nanoparticles' surface groups of silica support interactions are significant in catalytic functioning. A strong metal-molecular support interaction is the closely linked joint influence of surface molecular groups on silica to the metal surface, which could introduce new approaches to developing high-activity heterogeneous catalysts that are either less active or inactive metal catalysts. The nanoparticles of Pd on mesoporous carbon nitride were synthesized by Cai et al. and found to be extremely effective Mott–Schottky photocatalysts for FA

dehydrogenation. The improved enrichment of Pd nanoparticles using an electron transferring charge that works at the interface of the Mott–Schottky contact caused excellent catalytic performance by the catalyst. Similarly, Pd/CN catalytic performance has higher magnitudes than Pd/C. A basic resin bearing a  $N(CH_3)_2$  functional group within its macroreticular structure acted as an effective organic support for active Pd nanoparticles that produce high-quality  $H_2$  through FA ( $HCOOH$ ) decomposition at ambient temperature. The kinetic isotope effect and physicochemical characterization showed the development of both small Pd nanoparticles and joint action by the  $N(CH_3)_2$  groups within the resins that are vital to attaining an effective catalytic performance. This catalyst has various benefits, such as having an easy workup process, being additive-free, and having higher catalytic activity, compared to conventional inorganic supports, and it can curb the unwanted CO formation of  $<5$  ppm. Hence, it is a perfect hydrogen vector for proton-exchange membrane fuel cells' industrial applications. In addition, the basic resin support also offered Pd:Ag nanocatalyst from an aqueous solution of a mixture of  $PdCl_2$  and  $AgNO_3$ . The existence of Ag atoms was crucial for the catalytic activities involved in  $H_2$  production from FA and displayed higher performance than the pure Ag and Pd catalysts. A sodium hydroxide-assisted reduction approach has been used to synthesize the extremely scattered Pd NPs on nanoporous carbon MSC-30. NaOH was useful for properly distributing ultrafine Pd on MSC-30. The catalyst's performance was greatly improved by both the support of metal interaction and the high dispersion of NPs. Percent  $H_2$  selectivity and notably high activity was shown by this catalyst for FA decomposition by heterogeneous catalyzation at 323 K. The ready catalyst's activity could be compared with the most active homogeneous catalysts and heterogeneous catalysts at convenient temperatures. Preparations of Au and Pd in a mesoporous organometallic framework were shown by Xu et al. to be effective FA decomposition catalysts for hydrogen production. There are coordinative unsaturated  $Cr^{3+}$  centers in MIL-101. For better interactions between metal precursors and the MIL-101 support, ED-MIL-101 is made by implanting MIL-101 with electron-rich ethane-1,2-diamine (ED) [39–42].

ED-MIL-101 showed a better immobilization of small metal nanoparticles. Within the Au and Pd immobilized in the MOFs, Au:Pd/MIL-101 and Au:Pd/ED-MIL-101 show the active MOF-immobilized metal catalysts for converting FA to hydrogen under ambient conditions. Ag:Pd immobilizing into MIL-101 for catalytic FA dehydrogenation was examined by Dai et al. The highest catalytic activity among all Ag:Pd:MIL-101 catalysts with various compositions of Ag and Pd was shown to be the Ag:Pd/MIL-101 catalyst for FA conversion to  $H_2$ . Also, Yamashita et al. used the photocatalytically active organometallic framework MIL-125 and its equivalent oamine-functionalized  $NH_2$ -MIL-125 to stop Pd through ion-exchange deposition procedures. High catalytic activity was seen when using the Pd- $NH_2$ -MIL-125 catalyst for  $H_2$  production from FA at convenient temperatures as compared to Pd-MIL-125 and other Ti-related porous materials. The key factors involved in the high catalytic activity included the MOF functionalization and small-sized NPs. Moreover, the photoassisted deposition process proved to be more efficient than the process of small and very dispersed NP production within the MOF structure [43–45].

In order to put together the benefits of GNs and CB, Zhang et al. produced well-dispersed Ni and Pd developed on a GNS/CB. Surprisingly, Ni and Pd loaded on a carbon black graphene nanosheet showed higher activity for the decomposition of FA in aqueous media at RT than on Ni and Pd. Moreover, Pd has been used to change the Ni surface of Ni and Pd into a unique Pd:Ni:Pd catalyst to enhance catalytic stability and activity. Graphene nanosheet carbon black is a new type of carbon can be effective in dispersing, anchoring, and promoting active nanocatalysts in the long term for optimization and improvement in catalysts' efficiency in FA formation as a hydrogen storage material. Little work has been done on the decomposition

of FA by heterogeneous catalysts of Au, although it was first highlighted in 2009 by Ojeda and Iglesia that Au-related heterogeneous catalysts can form FA dehydrogenation in the gas phase at convenient temperatures. Well-dispersed Au species present on the  $\text{Al}_2\text{O}_3$  showed HCOOH decomposition with metal-time yields, i.e. rates per Au atom, larger than groups of Pt on  $\text{Al}_2\text{O}_3$  at 353 K. HCOOH dehydrogenation occurs either through a H-assisted formate decomposition method or by orderly cleavage of O-H and C-H bonds and H-atom recombination on remote areas. Xu et al. reported the first liquid phase FA dehydrogenation by a monometallic Au catalyst. Au nanoparticles encased in amine functionalized silica nanospheres served as an active catalyst for  $\text{H}_2$  formation in aqueous FA. It was noted that the FA dehydrogenation reaction is inactive for unsupported forms or Au/ $\text{SiO}_2$  with no amine functional group. Therefore, it is vital to have a mine in the silica sphere Au activity as a strong metal molecular support interaction is required. Bi et al. presented a low and specific FA/amine mixture for dehydrogenation with highly dispersed subnanometric Au on acid-tolerant  $\text{ZrO}_2$  as catalysts. At convenient temperatures, the catalytic reactions worked effectively and selectively without producing any extra byproduct such as CO. A unimolecular process with novel amine-assisted formate decomposition at the Au/ $\text{ZrO}_2$  interface was aided by HD production and the basic kinetic isotope effects were measured from HCOOD or DCOOH dehydrogenation. Subnanometric Au extra activity on FA activation is suitable for advanced Au research by setting the distributed Au. Trimetallic Pd:Ni:Ag nanoparticles were synthesized by Yurderi et al. with various metal ratios, and their bimetallic and monometallic (Ag, Ni, and Pd) equivalents helped in activating carbon through simple and reproducible wet-impregnation. After that, a simultaneous reduction procedure was used without any stabilizer at RT. All the ready composites were used as heterogeneous catalysts for FA formation in mild reaction conditions. The results of trimetallic Pd:Ni:Ag supported carbon show the dehydrogenation of FA with high conversion and high selectivity. Moreover, the highly stable Ag:Pd:Ni nanoparticles would not agglomerate, leach, or poison CO, making trimetallic Pd:Ni:Ag supported carbon a reusable catalyst; this catalyst maintained its essential activity even after being used five times in FA decomposition with full selectivity under mild conditions. Ag:Pd:Ni catalyzed the dehydrogenation of FA at various temperatures and the activation parameters and a proposed relevant method for Ag:Pd:Ni/C FA dehydrogenation was presented [46]. Lately, a budding boron-doped Pd nanocatalyst (B:Pd/C) was discovered that improved hydrogen production at RT from FA formate solutions at a high rate [47–50].... The wet chemical reduction of  $\text{NaBH}_4$  and dimethylamineborane was used to synthesize Pd supported carbon and boron and Pd supported carbon catalysts with a Pd loading of 5 wt.% (Table). To avoid any boron doping, HCOONa was used as a reducing agent for Pd supported carbon-HCOONa synthesis.

#### 4. Conclusion

This short review is mainly based on the future use of FA as a renewable energy source. Along with that, there has been a focus on using different procedures to generate FA and future opportunities of reproducing it from the greenhouse gas  $\text{CO}_2$ . This review has attempted to give an idea of the current developments occurring in this research field, as several papers have been published annually by chemical, physical, and material scientists. Therefore, with the continuous publications taking place, it was not possible to include all the research in the review, and because of space limitations, only selected papers have been focused on. Due to this, the first part of review focused on the current advancements in the decomposition of FA reactions that are catalyzed by heterogeneous catalysts, with or without the base and other additives. For higher catalytic performance, C-H bonds of formate anion should be activated, as this is considered to be a rate-limiting step. The majority of the heterogeneous catalytic processes and selectivity/activity of heterogeneous catalytic dehydrogenation of FA

**Table.** Catalytic activities of different types of catalysts for the decomposition of FA.

Catalyst	T (°C)	Reagent	TOF (h <sup>-1</sup> )		$\Delta G$ (KJ/mol)	Ref.
			Initial	2 h		
Ag <sub>18</sub> Pd <sub>82</sub> @ZIF-8	80	FA (1.5 M)/sodium formate (0.5 M)	580		51	[53]
	100	FA		32.4		
10 wt.% Pt	100	FA		43	64	[54]
Pd/C	30	FA (0.2 M)/sodium formate (1.8 M)		228.3	–	[55]
PtRuBiO <sub>x</sub>	80	FA (1.15 M)	312		37	[56]
Pd–Ag/C	92	FA (9.94 M)/sodium formate (3.33 M)	22		115	[33]
Pd–Au/C	92	FA (0.5 M)	45		138.6	
Pd <sub>IMP</sub> /CNF	30	FA (0.5 M)	563.2	28.4		[57]
Pd <sub>SI</sub> /CNF	30	FA (0.5 M)	979.1	27.5		
Pd <sub>SI</sub> /AC	30	FA (0.5 M)	240.5	26.2		
Pd/C	21	FA (1.33 M)	18	15		[58]
Pd/C	30	FA (1.33 M)	48	53.7		
Pd/C (citric acid)	25	FA				[59]
Au <sub>41</sub> Pd <sub>59</sub> /C	50	FA (1 M)	230			[48]
Ag@Pd (1:1)	35	FA		28 ± 2		
Ag@Pd (1:1)	50	FA		30		
Ag/Pd alloy (1:1)	20	FA				[60]
Ag <sub>42</sub> Pd <sub>58</sub>	50	FA (1 M)	382			
Pd–MnO <sub>x</sub> /SiO <sub>2</sub> -NH <sub>2</sub>	20	FA (0.265 M)	140	22 ± 1		[61]
Pd–MnO <sub>x</sub> /SiO <sub>2</sub> -NH <sub>2</sub>	50	FA (0.265 M)	1300	61.9		
Ag <sub>0.1</sub> Pd <sub>0.9</sub> /rGO	25	FA	105	-		[62]
(Pd <sup>0</sup> /CeO <sub>2</sub> )	25	FA (1.5 M)/sodium formate (13.4 M)	1400	-		[63]
			2040	-		
Ag <sub>0.25</sub> Pd/WO <sub>3</sub>	50	FA (1.5 M)/sodium formate (12 M)	683	-	45.7	[64]

processes are based on the size, morphology, surface, and distribution states of NPs, capping agents, and catalyst supports for bimetallic and trimetallic counter elements. Smaller particles are known to be better catalysts for large surface areas; however, they can be quickly aggregated because of high surface energy and so induce low activity. This is why an appropriate capping agent or support is needed to disperse NPs to minimize aggregation without deactivating the NPs' surfaces through a strong connection with the capping agent or support. During the dehydrogenation of FA, unsupported Pd catalysts are inactive because of the aggregation of nanoparticles and the formation of a poisoned surface by carbon monoxide upon decomposition of FA. Immobilization of Pd on/in graphene or carbon or ceria or zirconia or silica supports produces better activity with higher selectivity for FA dehydrogenation. These supports are useful for metal dispersion and the catalytic oxidation of CO at the metal support interface, thus avoiding catalyst deactivation by CO poisoning. Also, in bimetallic forms, the second part, such as Au or Ag, aids in halting the production of CO through FA decomposition. This results in FA dehydrogenation with higher activity and selectivity. Density functional theoretical methods have been used to gain a better understanding of the approach involved in the decomposition of FA on the surface. Some catalyst systems actively work on both FA dehydrogenation and carbon dioxide hydrogenation under different reaction conditions, thus giving a chance for the charge or discharge of H<sub>2</sub> fuel cells that are similar to other rechargeable batteries. As stated in the third part of this review, these reversible catalyst systems were used by



Beller et al. to create some rechargeable hydrogen batteries. Apart from the many other benefits of FA-based H<sub>2</sub> storage, for advancements in practical applications more work needs to be done to form cheap, effective, and reversible catalysts. Moreover, the formation of photocatalysts for both processes (fixation and the evolution of H<sub>2</sub> to/from HCO<sub>2</sub>H) that use sustainable/renewable energy resources is required [27,51,52].

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