

Dehydrogenation of Formic Acid by Heterogeneous Catalysts

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Abstract: Formic acid has recently been considered as one of the most promising hydrogen storage materials. The basic concept is briefly discussed and the research progress is detailedly reviewed on the dehydrogenation of aqueous formic acid by heterogeneous catalysts.

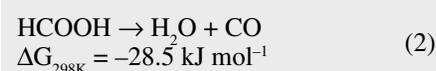
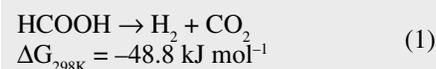
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1. Introduction

With the continuing increase in global energy demand, sustainable and benign energy sources are required to reduce the dependence on fossil fuels, greenhouse gas emissions and other pollutants.^[1,2] Among the various known energy carriers, hydrogen, which has been considered as one of the ultimate energy vectors to connect a host of energy sources to diverse end users for ‘mobile applications’, has been identified as a secure and clean energy carrier.^[3–5] However, safe storage and release of hydrogen are widely known to be challenging for technologies toward the hydrogen-energy-based economy. Some hydrogen storage systems, such as cryogenic liquid/gas containers, high pressure gas containers, porous materials including zeolites, carbon nanotubes, metal–organic frameworks, and so on, suffer from some obstacles in safety (high pressure or low temperature) and efficiency (low volumetric and gravimetric densities of hydrogen).^[6–9] Alternatively, chemical hydrogen storage that involves storing hydrogen in chem-

ical hydrogen storage materials by means of chemical bonds is one of the efficient and safe techniques. Although the solid-state chemical hydrogen storage materials show high hydrogen capacities, some inevitable drawbacks, such as relatively low catalytic activity for releasing H₂, high temperatures required to desorb H₂ and deterioration with successive cycling, severely limit their practical applications.^[10–13] Another promising hydrogen storage process relies on liquid-phase chemical hydrogen storage materials. Recently, in order to conveniently release hydrogen under mild conditions, the search for safe and effective liquid-phase hydrogen storage materials is urgent to meet the required transportation requirements. Hydrolysis of boron-based inorganic chemical hydrides, in particular NH₃BH₃ and N₂H₄BH₃, which have the hydrogen capacities of 19.6 and 15.3 wt%, respectively, has been shown to be a promising hydrogen storage approach.^[14–18] Moreover, due to relatively low toxicity, high energy density and easy handling, organic liquid compounds like methanol and formic acid have received much attention.^[19–24]

Formic acid (FA, HCOOH), a liquid at room temperature containing 4.4 wt% hydrogen, is one of the major products formed during biomass processing and is identified as a nontoxic and convenient hydrogen carrier.^[25] Hydrogen stored in FA can be released *via* a catalytic dehydrogenation reaction (Eqn. (1)). However, carbon monoxide (CO), which is a fatal poison to catalysts of fuel cell, can also be generated through an undesirable dehydration pathway (Eqn. (2)), depending on the pH values of the solutions, catalysts and the reaction temperatures.^[26–28] Only gaseous products (H₂/CO₂) are formed from dehydrogenation of FA (Eqn. (1)), without generation and accumulation of byproducts, endowing itself with an important advantage over other hydrogen carriers, especially for portable use.



Until now, the most widely investigated systems have been homogeneous catalysts for the decomposition of formic acid. Selective dehydrogenation of FA without CO generation using homogeneous catalysts at near-ambient temperature has been reported by Beller, Laurenczy and others.^[29–36] Recently, state-of-the-art heterogeneous catalysts exhibit high catalytic activities near room temperature, yielding high-quality hydrogen without or with low-concentration CO for decomposition of FA.^[24,37]

In this short review the recent advances in the use of FA for chemical hydrogen storage will be discussed with emphasis on its dehydrogenation by heterogeneous catalysts.

2. Development of Heterogeneous Catalytic Dehydrogenation of Formic Acid

The decomposition of FA in the presence of heterogeneous catalysts was reported firstly by Sabatier in 1912.^[38] Since then, this reaction has served as a convenient model reaction to test various theories of catalysis on the surfaces of heterogeneous catalysts.^[39–41] Rienäcker systematically investigated the decomposition of FA vapor over wires of Cu, Ag, Au, CuAu and AgAu alloys under normal pressure.^[42] Compared with the pure metals, the bimetallic alloys exhibited faster reaction rate. Later, Rienäcker *et al.* measured the activity of many types of heterogeneous catalysts, mainly metals and alloys of transi-

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tion metals, such as Fe, Ni, Cu, Pd, Ag, Pt and Au, for the decomposition of FA.^[43–45]

In 1950, the decomposition of FA over Ni, Cu and NiCu alloy was systematically investigated.^[46] It was found that the pure Ni showed the highest activity at 253 °C with a gas production rate of 20 mL min⁻¹ cm⁻², whereas information about the purity of the product gas was not given. In 1979, the decomposition of FA on Cu(100) with electron energy loss spectroscopy (EELS) was reported.^[47] A stable layer of formate species was formed at 127 °C, which decomposed to H₂ and CO₂ at 152–227 °C. Then, the adsorption and reaction of FA on the clean and K-promoted Pd (100) surfaces was investigated. It was demonstrated that FA on the clean Pd (100) surface decomposed below –73 °C to give CO and H₂ without formation of surface formate.^[48] However, for the K-promoted Pd (100), the preadsorbed potassium led to HCOOK formation on the Pd surface above 127 °C. The products of the decomposition were H₂ and CO₂ but also CO in equal amounts, which were strongly stabilized by potassium.

Although excellent decomposition activities were achieved in the early works, most studies on the decomposition of FA have been performed in the gas phase, and the reactions require heating above 100 °C.^[39–49] Moreover, these early studies rarely focused on the optimization of hydrogen production. A review of Enthaler *et al.* summarized these early research efforts.^[21] Since the low H₂ selectivity under such conditions and the additional complexity of creating a hydrogen generation device were not sufficient for fuel cell applications, the development of heterogeneous catalysts for liquid-phase FA dehydrogenation is very important. Recent studies of FA as a hydrogen storage material have yielded an increasing amount of dedicated research.^[22–24,28] There have been a number of reports of heterogeneous catalysts for the dehydrogenation of aqueous FA that mainly focus on low-temperature activity and H₂ selectivity (Table 1).

2.1 Monometallic Catalysts

In recent years, several works have been reported on monometallic noble metal nanoparticles (NPs) supported on various materials as the catalysts for dehydrogenation of FA in aqueous solution.^[50–54]

Our group reported the use of Au NPs encapsulated in amine-functionalized silica nanospheres as a stable monometallic nanocatalyst for dehydrogenation of aqueous FA.^[51a] Surprisingly, the amine-functionalized Au@SiO₂ showed high catalytic activities and complete selectivity for decomposition of FA to H₂ and CO₂ at 90 °C. Interestingly, the presence of amine in the silica sphere can make the

Table 1. Heterogeneous catalysts for the dehydrogenation of aqueous formic acid

Catalyst	Temp. [°C]	TOF [h ⁻¹]	CO evolution	Ref.
Pd/C	25	64	No	[50]
Au/ZrO ₂	50	1590 ^a	No	[52]
Pd/MSC-30	50	2623	No	[53]
Pd-B/C	30	1184 ^{a,b}	No	[54]
PdAu/C-CeO ₂	92	227	<140 ppm	[55]
Pd/basic resin	75	820	<5 ppm	[56]
PdAg/basic resin	75	1900	<5 ppm	[56]
Ag@Pd/C	20	125 ^b	No	[64]
	90	626 ^b	84 ppm	[64]
AuPd/ED-MIL-101	90	106	-	[57]
Pd/NH ₂ -MIL-125	32	214	<5 ppm	[58]
AgPd/MIL-101	80	848	No	[59]
Ag ₁₈ Pd ₈₂ @ZIF-8	80	580	No	[60]
Ag _{0.1} Pd _{0.9} /rGO	25	105 ^a	No	[61]
Au@Pd/N-mrGO	25	89 ^a	No	[62]
(Co ₀)Ag _{0.1} Pd _{0.9} /RGO	50	2739	No	[37]
PtRuBiO _x	80	312	No	[74]
PdAuEu/C	92	387	<100 ppm	[75]
Co _{0.30} Au _{0.35} Pd _{0.35} /C	25	80 ^a	No	[76]
CoAuPd/DNA-rGO	25	85 ^a	No	[77]
Ni _{0.40} Au _{0.15} Pd _{0.45} /C	25	12 ^a	No	[78]
PdNi@Pd/GNs-CB	25	150 ^a	No	[73]
MCM41-Si-(CH ₂) ₂ PPh ₂ /Ru-mTPPTS	110	2780	<3 ppm	[81]
Pd-S-SiO ₂	85	719	No	[82]

^aInitial TOF values calculated for the initial stages of the catalytic reactions. ^bThe TOF values calculated based on the surface metal sites.

Au NPs highly active, while the Au NPs supported on silica non-functionalized by amine were inactive for this reaction, which could be assigned to a strong metal-molecular support interaction (SMMSI). It has been demonstrated that the catalysts of Au subnanoclusters (~1.8 nm) dispersed on acid-tolerant ZrO₂ could selectively dehydrogenate the FA-amine mixture.^[52] The reaction, catalyzed by Au/ZrO₂, was highly efficient with a 100% hydrogen selectivity under ambient conditions, and with a high TOF of 1590 h⁻¹ at 50 °C.

Recently, we successfully prepared well-dispersed ultrafine Pd NPs (2.3 ± 0.4 nm) deposited on nanoporous carbon MSC-30 with a sodium hydroxide-assisted reduction approach. The resultant Pd/MSC-30 exhibited remarkably high catalytic activity and complete selectivity toward dehydrogenation of FA in a FA-sodium formate (SF) system without unwanted CO contamination under mild conditions (Fig. 1).^[53] It is noteworthy that

the TOF reached a value as high as 2623 h⁻¹ at 50 °C. Even at a temperature as low as 25 °C, complete decomposition of FA with a TOF of 750 h⁻¹ can be readily achieved. Very recently, Jiang *et al.* presented an initial report on metalloid-doped Pd NPs (Pd-B) for efficient H₂ production from aqueous FA-SF at ambient conditions, over which the TOF reached 1184 h⁻¹ at 30 °C.^[54] Furthermore, lower coverage of CO on Pd-B/C catalyst as compared to Pd/C was detected by high-sensitivity ATR-IR measurement, correlated with enhanced hydrogen production on the former.^[54]

2.2 Bimetallic Catalysts

It is well known that the addition of a secondary metal can alter not only the electronic properties of the active phase and adsorption behavior, but also the metal dispersion/particle size. Currently, supported Pd-based nanocatalysts have been demonstrated to be active for the

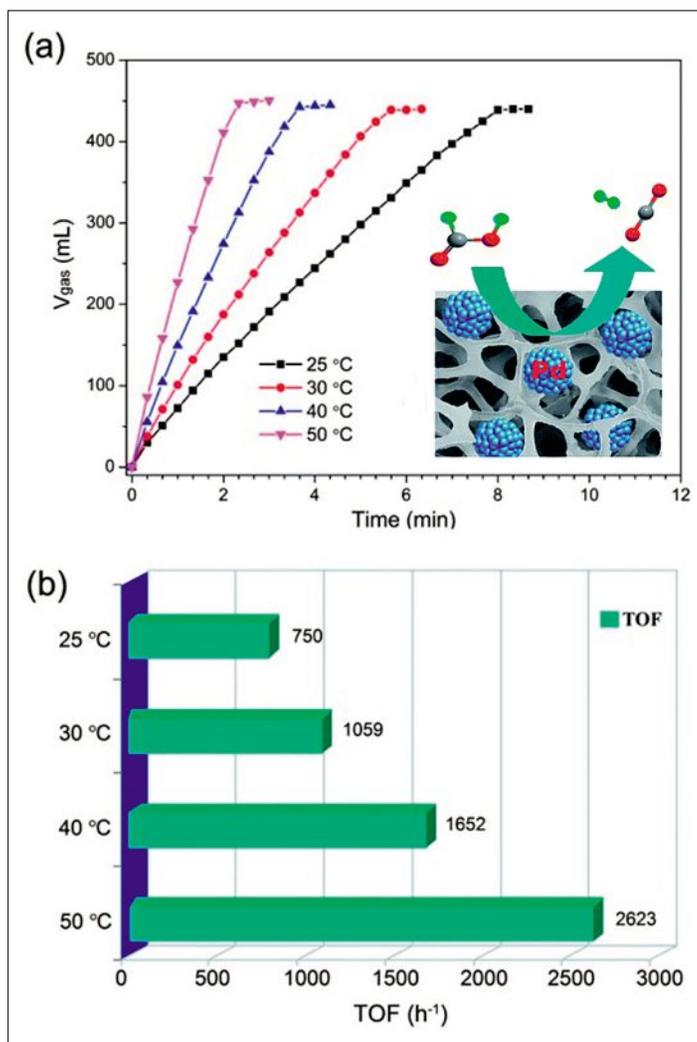


Fig. 1. (a) Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time and (b) corresponding TOF values of H_2 generation for the dehydrogenation of FA-SF (1:1) at different temperatures over Pd/MSC-30 ($n_{\text{Pd}}/n_{\text{FA}} = 0.01$). Reprinted with permission from ref. [53]. Copyright 2014 Royal Society of Chemistry.

the predominant MOFs, by using a simple liquid impregnation method, which exhibit excellent catalytic activity with a TOF value of 580 h^{-1} , and a 100% hydrogen selectivity toward dehydrogenation of FA at $80 \text{ }^\circ\text{C}$.^[60]

It has been demonstrated that AgPd NPs can be successfully assembled on reduced graphene oxide (rGO), a single-layer carbon material, using a facile co-reduction route, wherein the rGO played a key role as a powerful dispersion agent and distinct support for the nanocatalysts.^[61] The resultant $\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$ exerted 100% H_2 selectivity and exceedingly high activity toward the complete dehydrogenation of FA at room temperature with an initial TOF of 105 h^{-1} . Then, ultrafine (1.8 nm) and well dispersed Au@Pd nanoclusters were supported on a nitrogen-doped mildly rGO (N-mrGO) without any surfactant and additional reducing agent, which exhibited much higher activity (TOF value of 89.1 h^{-1}) than its alloy or monometallic counterparts toward dehydrogenation of aqueous FA without using any additive at room temperature.^[62]

Most recently, we developed a non-noble metal sacrificial approach for the first time to successfully immobilize highly dispersed AgPd NPs on rGO, in which the coprecipitation of $\text{Co}_3(\text{BO}_3)_2$ with AgPd NPs and the subsequent sacrifice by acid etching effectively prevented the primary AgPd particles from aggregation.^[37] Particularly noteworthy is that the resultant ultrafine AgPd nanoparticles exhibited extremely high activity (TOF, 2739 h^{-1} at $50 \text{ }^\circ\text{C}$) for the dehydrogenation of FA to generate hydrogen (Fig. 2). In addition, the resulted catalyst can be recycled by washing with water after each cycle, and the activity remained almost unchanged under the same reaction condition over 5 cycles.

As an alternative to alloys, core-shell NPs that contain an inner core of one or two metal elements and an external shell of the other metal elements have shown some unique physical and chemical properties. PdAu@Au core-shell NPs supported on activated carbon have been firstly investigated, which showed much higher activity and stability compared to the monometallic Au/C and Pd/C catalysts for the liquid phase decomposition of FA at $92 \text{ }^\circ\text{C}$ (Fig. 3), but the specific activity data were not given.^[63] A systematic study has been performed on M@Pd core-shell NPs ($M = \text{Ru}, \text{Rh}, \text{Pt}, \text{Au}$ and Ag).^[64] It has been found that Ag core most effectively promoted the activity of Pd shell, leading to significantly enhanced catalytic properties of the Pd-based catalyst. The resulted Ag@Pd (1:1) NPs displayed significantly enhanced catalytic activity for FA decomposition in comparison with monometallic Pd with the TOF of 626 h^{-1} at $90 \text{ }^\circ\text{C}$.

dehydrogenation of aqueous FA.^[53–64] It has been found that the introduction of Au or Ag additive has a remarkable effect on the stability of the Pd NPs in aqueous media and enhances the catalytic activity.^[55–64] It has been demonstrated that PdAu/C has a unique characteristic of evolving high-quality hydrogen from the catalyzed decomposition of FA in aqueous solution at convenient temperature, which was further improved by the addition of $\text{CeO}_2(\text{H}_2\text{O})_x$.^[55] Compared with the quick deactivation of Pd/C, PdAu/C with particle sizes of $\sim 3.5 \text{ nm}$ (PdAu) produced lower CO contamination at $92 \text{ }^\circ\text{C}$. Furthermore, the moderate activity of PdAu/C was enhanced dramatically by co-deposition of CeO_2 . A maximum TOF of 227 h^{-1} for the PdAu/C- CeO_2 system was obtained at $92 \text{ }^\circ\text{C}$, and further increased to 832 h^{-1} at $102 \text{ }^\circ\text{C}$, which was mainly attributed to an alteration of the electronic properties of the active Pd alloy phase. It has been reported that a basic resin bearing $-\text{N}(\text{CH}_3)_2$ functional groups within its macroporous structure acted as an efficient organic support for the active Pd and PdAg (1:2) NPs, with which high-quality H_2 via FA decomposition in a FA/SF = 9/1 aqueous solution

at convenient temperature was achieved with TOF values of 820 h^{-1} and 1900 h^{-1} , respectively.^[56]

Recently, porous metal-organic frameworks (MOFs), a class of promising hybrid functional materials, have been used as unique host matrices to encapsulate metal NPs within the frameworks by our group, which proved to be an efficient way to prevent the aggregation of metal NPs.^[65–69] We reported the first active MOF-immobilized metal catalyst, AuPd/MIL-101, for complete dehydrogenation of FA in aqueous solution at a convenient temperature.^[57] In order to improve the interactions between metal and MOF support, the electron-rich functional group ethylenediamine (ED) was grafted into MIL-101. The obtained AuPd/ED-MIL-101 (20.4 wt%, Au:Pd = 2.46) exhibited high catalytic activity for dehydrogenation of FA. Using a similar strategy, AgPd and Pd NPs were successfully immobilized in MIL-101 and NH_2 -MIL-125, respectively, and both the resultant composites displayed excellent catalytic activities and selectivities for hydrogen generation from FA.^[58,59] Very recently, highly dispersed AgPd NPs have been immobilized on ZIF-8, one of

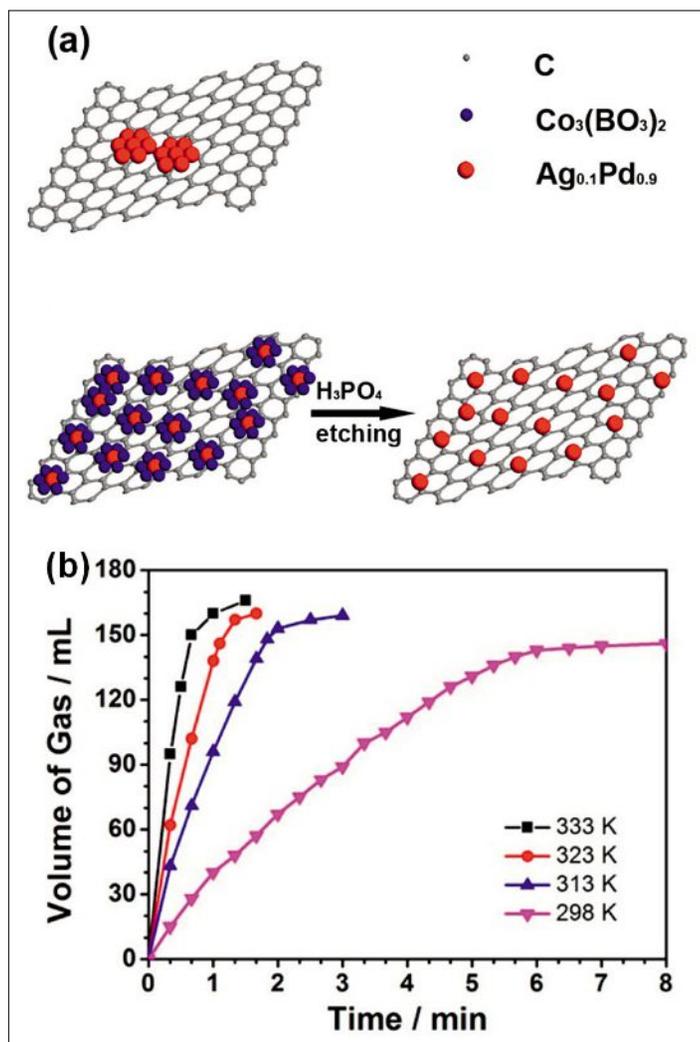


Fig. 2. (a) Schematic illustration of immobilization of AgPd NPs on RGO by a non-noble metal sacrificial approach and (b) volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA over $(\text{Co}_0)_{0.08}\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{RGO}$ (molar ratio of Co:Ag:Pd = 0.08:0.1:0.9) at different temperatures ($n_{\text{Ag-Pd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$). Reprinted with permission from ref. [37]. Copyright 2015 American Chemical Society.

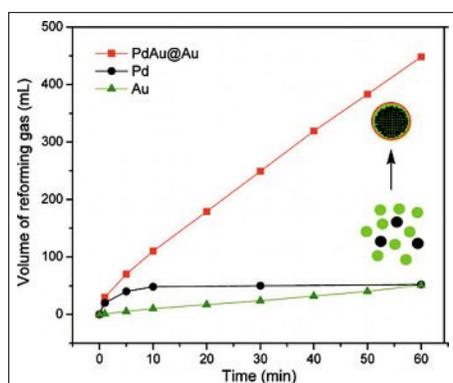


Fig. 3. Volume change of reforming gas with time for 60 mg of the synthesized PdAu@Au catalyst in 5 mL of solution containing 6.64 M FA and 6.64 M SF at 92 °C. Reprinted with permission from ref. [63]. Copyright 2010 American Chemical Society.

Up to now, almost all of the heterogeneous catalysts reported for FA dehydrogenation contain noble metals, such as Pd, Pt, Ag and Au, which severely restricts their practical applications due to their high costs and limited resources. On the other hand, for FA dehydrogenation, non-noble

metals are easily etched by acidic FA solution, whereas, when they are incorporated into the noble metals with the alloy or core-shell structure, their stabilities under acidic condition might be enhanced.^[70–72] PdNi@Pd/graphene nanosheets (GNs)-carbon black (CB) were prepared *via* a substitution reaction between PdNi/GNs–CB and PdCl_4^- in aqueous solution, which exhibited enhanced catalytic activity and cycle stability toward FA dehydrogenation.^[73]

2.3 Trimetallic Catalysts

An interesting trimetallic system composed of Pt, Ru and Bi oxide has been reported, where the Bi-oxide was co-impregnated on an activated carbon carrier rather than serving as catalyst support, since no activity was found in PtRu without Bi-oxide for FA dehydrogenation.^[74] The resultant PtRuBiO_x could catalyze selective dehydrogenation of FA in aqueous solution with a low activation energy of 37.3 kJ mol⁻¹ and a TOF of 312 h⁻¹ in the first hour at 80 °C. The promotion effects of three rare earth elements (REs) (Dy, Eu and Ho) on the activity of PdAu/C catalyst systems toward the decomposition of FA have been investigated in detail.^[75] It was found that

REs could reduce the activation energy of this reaction and PdAuEu/C showed the highest catalytic activity for the dehydrogenation of FA with a TOF of 387 h⁻¹ at 92 °C among the REs-promoted PdAu/C catalysts.^[75]

A non-noble metal-based trimetallic Co_{0.30}Au_{0.35}Pd_{0.35} nanoalloy catalyst supported on carbon has been used for dehydrogenation of aqueous FA at 25 °C.^[76] The initial TOF and final conversion for the decomposition of FA could reach a high value of 80 h⁻¹ and 91%, respectively, without any extra additive at room temperature. In order to enhance the catalytic performance, their research efforts were further directed to changing the types of both non-noble and noble metals and the supports, and controlling the particle distribution, size and configuration.^[77,78]

2.4 Other Catalysts

As an interesting alternative to deposited metal NPs, the immobilization of high performance homogeneous catalysts represents a promising step toward the combination of excellent catalytic performance of homogeneous catalysts and reusability of heterogeneous systems. Laurency and co-workers immobilized their highly active Ru(II)-meta-trisulfonated triphenylphosphine (TPPTS)^[79] on various supports by polymer immobilization, ion exchange and physical adsorption, all of which exerted high initial activities although gradual deactivation was observed.^[80] In a follow-up study, they prepared a series of heterogenized catalysts by the reaction of the Ru(II)-mTPPTS dimer and silica functionalized with diphenylphosphine groups *via* alkyl chains.^[81] The optimized catalytic system, MCM41-Si-(CH₂)₂PPh₂/Ru-mTPPTS, exerted much higher activity and stability compared to those of the homogeneous catalyst with a TOF of 2780 h⁻¹ at 110 °C. The dehydrogenation of FA over single-atom Ru and Pd on mercapto-functionalized SiO₂ supports in an aqueous FA-SF solution has been investigated.^[82] After multiple catalyst cycles, the obtained Pd-S-SiO₂ gave a TOF over 719 h⁻¹ at 85 °C. Moreover, cheap sulfate salts could accelerate the reaction rate by 30–70%, which is attractive for practical applications.

Recently, several metal oxides have been demonstrated to be active catalysts for photocatalytic dehydrogenation of FA.^[83–85] TiO₂ nanorods photocatalytically decomposed an aqueous FA solution, over which more than 80% of the FA could be decomposed within 45 min.^[84] A Cu₂O photocatalyst selectively decomposed FA into CO₂/H₂ in the presence of visible light.^[85] However, these studies need a source for radiation and a diluted aqueous solution, which hinder practical applications of this approach.

3. Conclusions

Formic acid has recently been identified as an environment-friendly hydrogen storage material not only due to its easy storage and non-toxicity but also because of its sole gaseous products (H_2/CO_2) by dehydrogenation. Furthermore, CO_2 can be hydrogenated back to formic acid using catalysts under mild conditions, depicting a CO_2 -neutral hydrogen storage cycle.^[24,34] In recent years, the rapid development of high performance catalysts has opened up the opportunity to fully make use of these advantages. A large number of highly active and robust heterogeneous catalysts, which could selectively decompose aqueous FA to H_2 and CO_2 at convenient temperature, have been reported. In addition, intensive efforts have been made to investigate and develop cost-effective non-noble metal catalysts, which is important for implementation of hydrogen storage as a global energy solution. Nevertheless, up to now, the described catalyst systems and techniques are designed still for small-scale processes. Further research efforts are required to make progress especially for mobile applications.

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- [1] J. O. M. Bockris, *Science* **1972**, *176*, 1323.
- [2] G. W. Crabtree, M. S. Dresselhaus, M. V. Buchanan, *Phys. Today* **2004**, *57*, 39.
- [3] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353.
- [4] S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, *Catal. Today* **2007**, *120*, 246.
- [5] H. M. Chen, C. K. Chen, R.-S. Liu, L. Zhang, J. Zhang, D. P. Wilkinson, *Chem. Soc. Rev.* **2012**, *41*, 5654.
- [6] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353.
- [7] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127.
- [8] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem., Int. Ed.* **2008**, *47*, 3966.
- [9] W. Liu, Y. H. Zhao, Y. Li, Q. Jiang, E. J. Lavernia, *J. Phys. Chem. C* **2009**, *113*, 2028.
- [10] W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283.
- [11] J. Graetz, *Chem. Soc. Rev.* **2009**, *38*, 73.
- [12] Z. Huang, T. Autrey, *Energy Environ. Sci.* **2012**, *5*, 9257.
- [13] B. Peng, J. Chen, *Energy Environ. Sci.* **2008**, *1*, 479.
- [14] Q.-L. Zhu, D.-C. Zhong, U. B. Demirci, Q. Xu, *ACS Catal.* **2014**, *4*, 4261.
- [15] C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279.
- [16] J. Hannauer, O. Akdim, U. B. Demirci, C. Geantet, J.-M. Herrmann, P. Miele, Q. Xu, *Energy Environ. Sci.* **2011**, *4*, 3355.
- [17] U. B. Demirci, P. Miele, *Energy Environ. Sci.* **2011**, *4*, 3334.
- [18] J. Li, Q.-L. Zhu, Q. Xu, *Chem. Commun.* **2014**, *50*, 5899.
- [19] M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller, *Nature* **2013**, *495*, 85.
- [20] R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, *Nat. Chem.* **2013**, *5*, 342.
- [21] S. Enthaler, J. von Langermann, T. Schmidt, *Energy Environ. Sci.* **2010**, *3*, 1207.
- [22] M. Graseaman, G. Laurenczy, *Energy Environ. Sci.* **2012**, *5*, 8171.
- [23] B. Loges, A. Boddien, F. Gärtner, H. Junge, M. Beller, *Top. Catal.* **2010**, *53*, 902.
- [24] Q. Zhu, Q. Xu, *Energy Environ. Sci.* **2015**, *8*, 478.
- [25] S. Ott, *Science* **2011**, *333*, 1714.
- [26] F. Joo, *ChemSusChem* **2008**, *1*, 805.
- [27] S. Sato, T. Arai, T. Morikawa, K. Uemura, T. M. Suzuki, H. Tanaka, T. Kajino, *J. Am. Chem. Soc.* **2011**, *133*, 15240.
- [28] M. Yadav, Q. Xu, *Energy Environ. Sci.* **2012**, *5*, 9698.
- [29] C. Fellay, N. Yan, P. J. Dyson, G. Laurenczy, *Chem.-Eur. J.* **2009**, *15*, 3752.
- [30] Y. Himeda, *Green Chem.* **2009**, *11*, 2018.
- [31] T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.* **2010**, *39*, 81.
- [32] A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 8924.
- [33] A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science* **2011**, *333*, 1733.
- [34] J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* **2012**, *4*, 383.
- [35] A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* **2008**, *1*, 751.
- [36] B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem., Int. Ed.* **2008**, *47*, 3962.
- [37] Y. Chen, Q.-L. Zhu, N. Tsumori, Q. Xu, *J. Am. Chem. Soc.* **2015**, *137*, 106.
- [38] P. Sabatier, A. Mailhe, *Compt. Rend.* **1912**, *152*, 1212.
- [39] J. M. Trillo, G. Munuera, J. M. Criado, *Catal. Rev.* **1972**, *7*, 51.
- [40] M. R. Columbia, P. A. Thiel, *J. Electroanal. Chem.* **1994**, *369*, 1.
- [41] K. Tamaru, *Appl. Catal. A* **1997**, *151*, 167.
- [42] G. Rienäcker, *Z. Anorg. Allg. Chem.* **1936**, *227*, 353.
- [43] G. Rienäcker, N. Hansen, *Z. Anorg. Allg. Chem.* **1956**, *285*, 283.
- [44] G. Rienäcker, J. Volter, *Z. Anorg. Allg. Chem.* **1959**, *302*, 299.
- [45] G. Rienäcker, H. Mueller, *Z. Anorg. Allg. Chem.* **1968**, *357*, 255.
- [46] D. A. Dowden, P. W. Reynold, *Discuss. Faraday Soc.* **1950**, *8*, 184.
- [47] B. A. Sexton, *Surf. Sci.* **1979**, *88*, 319.
- [48] F. Solymosi, I. Kovacs, *Surf. Sci.* **1991**, *259*, 95.
- [49] M. Ojeda, E. Iglesia, *Angew. Chem., Int. Ed.* **2009**, *48*, 4800.
- [50] Z.-L. Wang, J.-M. Yan, H.-L. Wang, Y. Ping, Q. Jiang, *Sci. Rep.* **2012**, *2*, 598.
- [51] a) M. Yadav, T. Akita, N. Tsumori, Q. Xu, *J. Mater. Chem.* **2012**, *22*, 12582; b) M. Yadav, A. K. Singh, N. Tsumori, Q. Xu, *J. Mater. Chem.* **2012**, *22*, 19146.
- [52] Q.-Y. Bi, X.-L. Du, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *J. Am. Chem. Soc.* **2012**, *134*, 8926.
- [53] Q.-L. Zhu, N. Tsumori, Q. Xu, *Chem. Sci.* **2014**, *5*, 195.
- [54] K. Jiang, K. Xu, S. Zou, W.-B. Cai, *J. Am. Chem. Soc.* **2014**, *136*, 4861.
- [55] X. Zhou, Y. Huang, W. Xing, C. Liu, J. Liao, T. Lu, *Chem. Commun.* **2008**, 3540.
- [56] K. Mori, M. Dojo, H. Yamashita, *ACS Catal.* **2013**, *3*, 1114.
- [57] X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita, Q. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 11822.
- [58] M. Martis, K. Mori, K. Fujiwara, W.-S. Ahn, H. Yamashita, *J. Phys. Chem. C* **2013**, *117*, 22805.
- [59] H. Dai, N. Cao, L. Yang, J. Su, W. Luo, G. Cheng, *J. Mater. Chem. A* **2014**, *2*, 11060.
- [60] H.-M. Dai, B.-Q. Xia, L. Wen, C. Du, J. Su, W. Luo, G.-Z. Cheng, *Appl. Catal. B* **2015**, *165*, 57.
- [61] Y. Ping, J.-M. Yan, Z.-L. Wang, H.-L. Wang, Q. Jiang, *J. Mater. Chem. A* **2013**, *1*, 12188.
- [62] Z.-L. Wang, J.-M. Yan, H.-L. Wang, Y. Ping, Q. Jiang, *J. Mater. Chem. A* **2013**, *1*, 12721.
- [63] Y. Huang, X. Zhou, M. Yin, C. Liu, W. Xing, *Chem. Mater.* **2010**, *22*, 5122.
- [64] K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith, S. C. E. Tsang, *Nat. Nanotechnol.* **2011**, *6*, 302.
- [65] H.-L. Jiang, Q. Xu, *Chem. Commun.* **2011**, 47, 3351.
- [66] A. Dhakshinamoorthy, H. Garcia, *Chem. Soc. Rev.* **2012**, *41*, 5262.
- [67] H. R. Moon, D.-W. Lim, M. P. Suh, *Chem. Soc. Rev.* **2013**, *42*, 1807.
- [68] Q.-L. Zhu, Q. Xu, *Chem. Soc. Rev.* **2014**, *43*, 5468.
- [69] A. Aijaz, Q. Xu, *J. Phys. Chem. Lett.* **2014**, *5*, 1400.
- [70] M. Watanabe, K. Tsurumi, T. Mizukami, T. Nakamura, P. Stonehart, *J. Electrochem. Soc.* **1994**, *141*, 2659.
- [71] E. Antolini, J. R. C. Salgado, E. R. Gonzalez, *J. Power Sources* **2006**, *160*, 957.
- [72] V. Mazumder, M. Chi, M. N. Mankin, Y. Liu, O. n. Metin, D. Sun, K. L. More, S. Sun, *Nano Lett.* **2012**, *12*, 1102.
- [73] Y.-I. Qin, J. Wang, F.-Z. Meng, L.-M. Wang, X.-B. Zhang, *Chem. Commun.* **2013**, *49*, 10028.
- [74] S.-W. Ting, S. Cheng, K.-Y. Tsang, N. van der Laak, K.-Y. Chan, *Chem. Commun.* **2009**, 7333.
- [75] X. Zhou, Y. Huang, C. Liu, J. Liao, T. Lu, W. Xing, *ChemSusChem* **2010**, *3*, 1379.
- [76] Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng, Q. Jiang, *Angew. Chem., Int. Ed.* **2013**, *52*, 4406.
- [77] Z.-L. Wang, H.-L. Wang, J.-M. Yan, Y. Ping, S.-I. O, S.-J. Li, Q. Jiang, *Chem. Commun.* **2014**, *50*, 2732.
- [78] Z.-L. Wang, Y. Ping, J.-M. Yan, H.-L. Wang, Q. Jiang, *Int. J. Hydrogen Energy* **2014**, *39*, 4850.
- [79] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem., Int. Ed.* **2008**, *47*, 3966.
- [80] W. Gan, P. J. Dyson, G. Laurenczy, *React. Kinet. Catal. Lett.* **2009**, *98*, 205.
- [81] W. Gan, P. J. Dyson, G. Laurenczy, *ChemCatChem* **2013**, *5*, 3124.
- [82] Y. Zhao, L. Deng, S.-Y. Tang, D.-M. Lai, B. Liao, Y. Fu, Q.-X. Guo, *Energy Fuels* **2011**, *25*, 3693.
- [83] J. Farias, E. D. Albizzati, O. M. Alfano, *Catal. Today* **2009**, *144*, 117.
- [84] H. J. Yun, H. Lee, J. B. Joo, W. Kim, J. Yi, *J. Phys. Chem. C* **2009**, *113*, 3050.
- [85] S. Kakuta, T. Abe, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2707.