

Review

Sustainable production of formic acid from biomass and carbon dioxide

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ABSTRACT

Formic acid (FA) is a versatile molecule with widespread applications in both chemical industries and renewable energy fields. However, the commercial manufacture of FA is still based on non-renewable fossil feedstock, and thus alternative methods to obtain FA from renewable resources are highly desirable and attract significant scientific attentions. Biomass represents the largest carbon resource on Earth, and various strategies including acid hydrolysis, wet oxidation and catalytic oxidation have been developing to transform biomass resources into FA with relatively high yield and selectivity. Meanwhile, carbon dioxide (CO₂) as an inexpensive and widely available C1 platform compound, is also a potential resource to produce FA via hydrogenation by different strategies such as chemical, photochemical and electrochemical catalysis. In this review, FA production from biomass resources especially cellulosic biomass will be systematically summarized according to the transformation methods. Following this, recent progresses in the CO₂ valorization to generate FA will be generally illustrated. Finally, the catalytic dehydrogenation of FA to generate hydrogen as a clean and renewable energy fuel will be concisely mentioned since it exemplifies the critical role of FA in future energy restructure tactics.

1. Introduction

Among the 100 most important chemical compounds, formic acid (FA) is the simplest yet strongest organic acid with prominent advantages. It is more eco-friendly, noncorrosive, easily biodegradable, etc. than other organic and inorganic acids, and is broadly applied in agricultures, rubbery, pharmaceuticals, animal feeds, leather and textiles industries [1]. Moreover, it is a frequently-used reductant, green solvent as well as a building block in various chemical syntheses. In 2019, the approximate annual global market for FA is about US\$ 620 million which would maintain a constant increase in the future. Not only being an important chemical commodity, FA is also a key energy carrier/medium which may furnish solutions to the energy crisis and contribute to establishing renewable energy structures [2–4]. It can directly produce or be upgraded into a variety of high-quality fuels including hydrogen (H₂), carbon monoxide (CO), methanol, bio-oils, etc. Especially, FA is regarded as one of the most promising H₂ storage materials with a remarkable volumetric capacity of ~53.4 g/L, equivalent to 4.4 wt% of H₂, which is close to the set value of 5.5 wt% by the US Department of Energy for efficient H₂ storage substances. FA as the energy carrier is crucially beneficial for gaseous fuels to ease the storage and transportation in practical uses, and the dehydrogenation of FA into H₂ has been extensively investigated which can be achieved in a simple, mild and easily-controlled manner. By manipulating the

reaction parameters, FA can be alternatively decomposed into CO and therefore it is also a potential CO storage material. As a result, with its prevalent applications and outstanding virtues, FA is of principal significance to both the modern chemical societies and the energy industries (see Fig. 1).

FA naturally occurs in most ants, some species of bees, and in the atmosphere because of forest emissions. In fact, the name “formic” originates from Latin language *formica* which means ants because it was initially isolated by the distillation of ants. The current industrial production of FA involves a fossil-based, two-step method by first reacting methanol with CO to generate methyl formate which is then hydrolyzed to form FA (see Fig. 2, top). However, large-scale FA production from renewable resources are more preferable to mitigate carbon emission and fight against global warming, as part of a more sustainable human society [5]. So far, persistent endeavors have been made to obtain FA from renewable resources primarily the biomass or CO₂ feedstock [6–9]. Biomass grows based on photosynthesis utilizing solar energy with CO₂ and water as the starting materials. Upon decomposition, the carbon emits back into the atmosphere to close the carbon cycle, in which no extra carbon is released. Biomass represents the largest carbon resource around the world and is considerably decent for chemical syntheses due to the inherently rich functionalities [10–22]. Among the diverse types of biomass, cellulosic biomass with ample hydroxyl groups is inexpensive, readily available and the most

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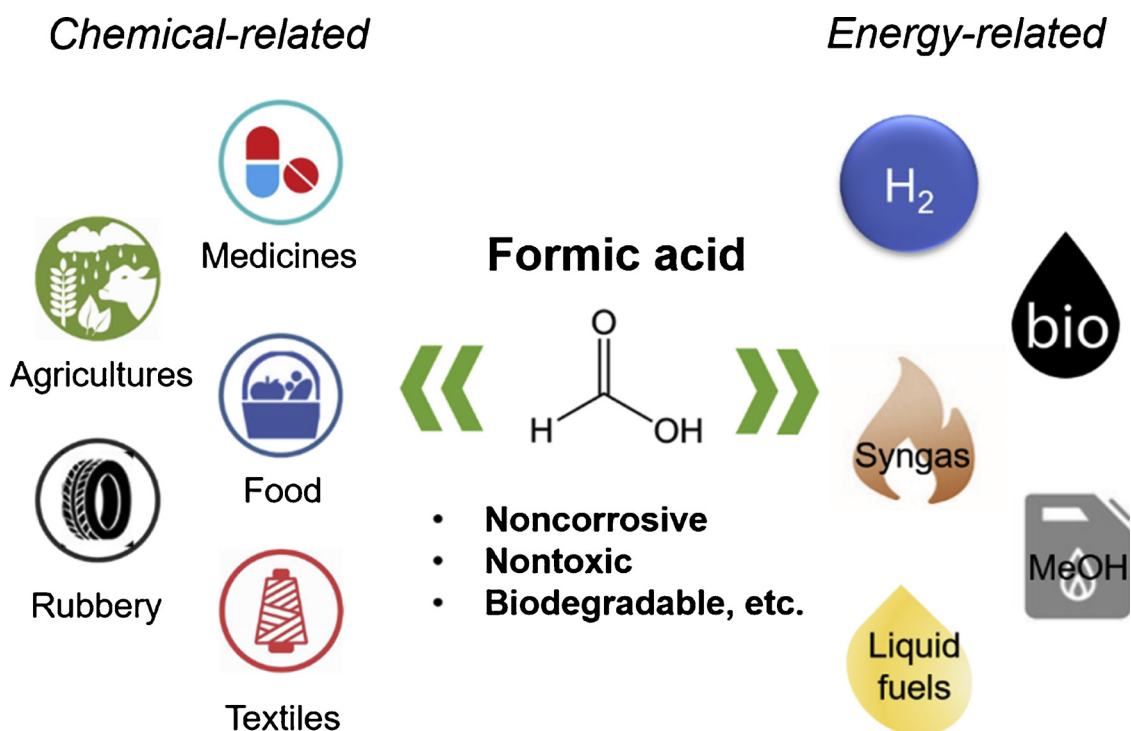
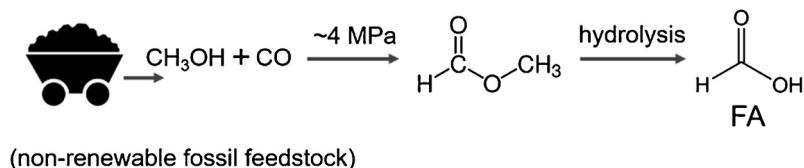


Fig. 1. The wide applications of FA in chemical- and energy-related fields.

Industrial production



Renewable production

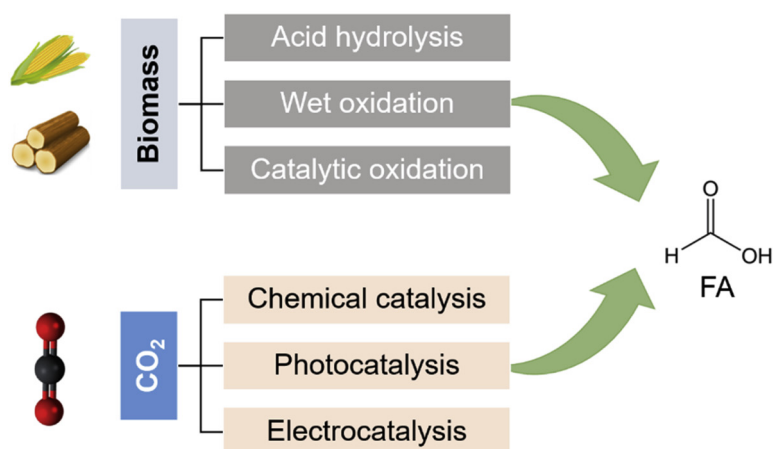


Fig. 2. The current industrial production of FA from non-renewable feedstock (top) and the renewable production of FA from biomass and CO₂ (bottom).

abundant, which is therefore the most studied feedstock to produce FA by exploiting different transformation strategies.

Rather than treating it as a bothersome gas, CO₂ itself can be regarded as a C1 building block chemical for the generation of a series of value-added chemicals and fuels such as FA [23–25]. This CO₂-based

refinery will help mitigate the carbon emission and simultaneously create economic values. Since CO₂ is in the most oxidized state and relatively stable, highly active species or high energy inputs are usually necessary to reduce it, but the conditions can be modified by the rational design and development of catalysts. In fact, the reduction of CO₂

into FA is relatively easier than to other products (methane, etc.) via hydrogenation, and the commonly used reducing agents include H_2 , water, etc. Notably, CO_2 reduction into FA can be realized by chemocatalytic, photocatalytic and electrochemical methods. The reduction efficiency and selectivity are closely relevant to the surface chemistry, nanostructures, electronic states, etc. of the employed catalytic systems. In this review, renewable production of FA using biomass and CO_2 as the feedstock will be the major focus (an overview is provided in Fig. 2, bottom). First, conversion of biomass (mainly cellulosic biomass) into FA by different transformation routes such as hydrolysis, wet oxidation, etc. is illustrated in detail. Next, recent advances in CO_2 reduction into FA by chemical, photochemical and electrochemical methods will be emphasized along with the catalyst optimization tactics. Then, the applications of FA as an energy carrier to produce H_2 will be briefly depicted to showcase its essential role in future hydrogen energy economy. Lastly, the challenges and prospects of renewable FA production will be discussed and summarized.

2. Biomass conversion into FA

2.1. Acid hydrolysis of biomass

The conversion of glucose and cellulose under the catalysis of acids would lead to the simultaneous production of the value-added products levulinic acid (LeA) and FA [26]. It is generally recognized that in the presence of an acid, cellulose first undergoes hydrolysis to give oligosaccharides and glucose which are subsequently dehydrated into 5-hydroxymethylfurfural (5-HMF) via glucose isomerization, and then rehydration of 5-HMF happens to afford LeA and FA (see Fig. 3). Hence, in this reaction scheme, the FA is more like a side product and the carbon yield is usually not very high. For example, using 0.1 M sulfuric acid (H_2SO_4), glucose was converted into FA at 180 °C with a carbon yield of ~4.3 % (equivalent to 26 mol%), along with a LeA yield of ~52.5 % [27]. Both Lewis acids and Brønsted acids are effective to catalyze the reaction, which preferably favor the glucose isomerization and the hydrolysis of cellulose/the rehydration of 5-HMF respectively. As a result, the combinational uses of the two types of acid catalysts could be remarkably beneficial. Choudhary et al. reported that the FA yield enhanced to two-fold with the combined use of hydrochloric acid (HCl) and chromium chloride ($CrCl_3$) as the catalyst compared to using $CrCl_3$ alone [28].

Starting from fructose, Yoshida's group has studied the effects of different Brønsted acid species as well as the influence of the acidity in a tube reactor (boasting a very fast heating rate) at 240 °C [29]. The reactions were finished within minutes. Negligible FA was observed in the absence of an acid catalyst. The initial pH at 1.5 resulted in considerably improved FA yield than at pH 2 or pH 2.5, indicating that

sufficient acidity in the aqueous solution promoted FA formation. Among the various acid catalysts employed, the effectiveness to produce FA is in the order: $HCl \approx$ p-toluenesulfonic acid (p-TSA) > H_2SO_4 > phosphoric acid > oxalic acid > citric acid > maleic acid. The highest FA yield was obtained at ~8.5 % using HCl, while the lowest at ~1.5 %. It infers that FA production in water from fructose is favored by strong acid species. Based on the above reports, it is obvious that the acid hydrolysis is not a prevalent method to convert biomass into FA because of the relatively low efficiency. Instead, the acid hydrolysis is generally adopted to produce other chemicals such as 5-HMF and LeA.

2.2. Wet oxidation of biomass

Sub- or supercritical water have been frequently used as a cheap and green solvent for biomass transformations, particularly for acid- and base-catalyzed reactions because water is known to generate protons and hydroxides at high temperatures [30–34]. Early in 1999, short-chain organic acids such as FA, acetic acid (AA), lactic acid (LA), etc. have been identified after glucose conversion in high temperature water (400–600 °C), in which air was acted as the oxidant [35]. It is not difficult to recognize that since the conversion of lignocellulosic biomass into FA involves multiple oxidative steps, the use of a proper oxidant would reasonably stimulate the formation of FA. The prominent advantage of hydrothermal method is the versatility to handle various types of substrates and the high moisture tolerance. Calvo et al. utilized an efficient oxidant hydrogen peroxide (H_2O_2) in the wet oxidation of four different types of organic waste including cellulose, coconut oil solutions, brewery and dairy effluents (except cellulose all the waste contains high percentage of water), under ~300 bar and 400 °C with a reaction time of 5 min [36]. The total yields of organic acids (mainly AA and FA) were averagely less than 15.0 %, because the high temperature and the strong oxidant caused severe decomposition of the liquid organic acids into gaseous products such as CO_2 . The addition of acid or solid catalysts would not solve the issue, whereas the introduction of a base inhibited the decomposition. When 0.5 equivalent (to the substrate) of sodium hydroxide (NaOH) was added into the system, glucose could be converted into FA with a considerably improved yield of about 38.0 % at 250 °C in the presence of H_2O_2 (25 % stoichiometric oxygen).

In addition, Quitain et al. tested the hydrothermal treatment of other organic wastes or the model compounds including domestic sludge, fish waste, glucose and plastic waste (monomers) at 250 ~ 350 °C [37]. A number of short-chain organic acid species were observed in the liquid phase as well as volatile carbon compounds such as CO_2 in the gas phase. In the presence of excessive H_2O_2 , AA was relatively stable and the dominant product in the liquid solution whereas FA

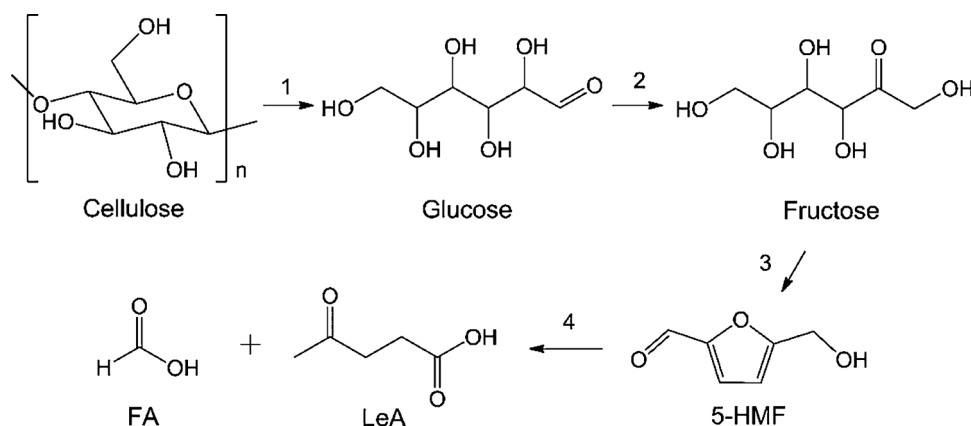


Fig. 3. The reaction scheme of cellulose transformation into FA by acid hydrolysis. Step 2 is favorably promoted by Lewis acid catalysts while Step 1, 3 and 4 by Brønsted acid catalysts.

became unstable and underwent decomposition which agreed with previous studies [35]. The reaction pathway was tentatively proposed that glucose was first degraded into aldehydes/ketones and then oxidized into small organic acids. Apart from the model compound glucose, the raw woody biomass such as cherry and cypress wood samples were also employed as the substrates under hydrothermal conditions with the weak base potassium carbonate (K_2CO_3) as the additive at 280 °C [38]. About 50 wt% of the liquid hydrocarbon products could be obtained but FA was not reported as a product in the system.

Jin's group has undertaken systematic studies on the wet oxidation of cellulosic biomass into FA [39]. The synergy of a base and an oxidant as well as their amounts were essential to realize highly selective FA formation. Excessive supply of H_2O_2 in the reaction was indispensable to facilitate the oxidative cleavage of glucose to boost the FA yield, nonetheless, the overloaded oxidant caused severe decomposition of FA. In concentrated base solutions, FA was shifted into its salt form immediately upon formation becoming more stable under oxidative conditions. Therefore, the co-uses of concentrated base and H_2O_2 led to the high yield of FA that glucose was completely converted at 250 °C within 1 min and the highest FA yield reached 75.0 % with a selectivity of about 95 %. Moreover, the authors assumed that there were two possible pathways for FA production: the α -scission at C1-C2 or C5-C6 position or the β -scission at C2-C3 or C4-C5 position. A control experiment using oxalic acid as the substrate was conducted which afforded low FA yield, and it was speculated that FA was more likely to be produced via the α -scission of glucose instead of β -scission. Following this work, the same group has reported an improved reaction system to selectively convert glucose into FA in 2.5 M NaOH solution at 150 °C, with 80 ~ 85 % FA yield obtained with a reaction time of around 20 min [40].

Very recently, new advancements have been progressed in wet glucose oxidation to generate valuable organic acids. In 2017, Qi's group has unraveled the room temperature conversion of glucose in Ba(OH)₂ aqueous solution into LA with exceedingly high yield of ~95.4 % with a reaction time of 48 h, pointing out the potentials to transform biomass resources under much milder conditions compared to previous literatures [41]. Intrigued by the discovery, a facile, mild and efficient method to convert glucose into FA at room temperature and nearly ambient pressure was developed using H_2O_2 as the oxidant in basic solutions [42]. It was disclosed that common bases including lithium hydroxide (LiOH), NaOH and potassium hydroxide (KOH) were able to activate and prompt glucose conversion at room temperature, whereas the presence of H_2O_2 has impacted on the patterns of oxidative glucose cleavage favoring the FA formation. With a relatively short period of 6 ~ 8 h, glucose was almost quantitatively transformed leading to the highest FA yield of 91.3 % (and a FA selectivity of around ~90 %), which was so far a new record for biomass conversion into FA. Besides, model compound tests were undertaken, and aldehyde species (the formaldehyde, glycolaldehyde and pentose) were identified as the major intermediates to produce FA. It was presumed that the oxidant with increased concentrations has altered the reaction pathways from low-efficient C2-C3 and C3-C4 cleavage to more efficient C1-C2 cleavage pattern (see Fig. 4). The chemical reactions under room temperature and ambient pressure boast distinguished merits such as the minimized energy inputs, inexpensive equipment, safer handling, etc. These works direct attentions to the unveiled chemistry of biomass utilization at room temperature which may stimulate more future research to generate other value-added chemicals in an unexpectedly mild manner.

2.3. Catalytic oxidation of biomass

The catalytic oxidation process engages a specific catalyst (mainly acid catalysts) and an oxidant (normally oxygen (O_2) gas) to catalyze biomass transformation into FA. At present, there were two major types of acid catalysts that widely used in biomass oxidation into FA, namely,

the heteropoly acids (HPAs) and vanadium (V)-based oxidants mainly the $NaVO_3$ salt and the $VOSO_4$ species (as summarized in Table 1). The HPAs represent a group of polyoxo compounds combining hydrogen, oxygen, non-metals and metals. The metal atoms usually V, tungsten (W), molybdenum (Mo), etc. are termed as the addenda atoms while the non-metals normally silica (Si), phosphorous (P), arsenic (As), etc. are termed as the hetero atoms. HPAs have been broadly used in catalytic reactions due to the advantages of low-cost, environmentally benign and multifunctional properties [43–49].

2.3.1. HPAs-based catalytic systems

Wasserscheid's group has exploited a homogeneous Keggin-type $H_5PV_2Mo_{10}O_{40}$ catalyst to transform lignocellulosic biomass into FA at a relatively low temperature of 70 ~ 90 °C in water under 30 bar O_2 gas [50]. Glucose was efficiently converted into FA with about 50 % yield, cellulose was seldom transformed (~1 % FA yield), while lignin and hemicellulose were converted with FA yields of 14.0 % and 33.0 % respectively. The reaction pathways were tentatively investigated using various C_2 model compounds and the authors deduced that the reaction might involve different cleavage mechanisms including the previously proposed electron oxygen transfer mechanism [51–53]. Afterwards, the same group has further improved the catalytic system by utilizing p-TSA as an additive [54]. The transformations of crude woody waste were attempted such as beech wood, waste paper, etc., as well as the cyanobacteria algae. The addition of p-TSA has increased the biomass conversion rate and enhanced the FA yield and/or selectivity. The p-TSA additive has induced a general increase in FA yield by 10 ~ 20 %, and the FA yields obtained from beech wood, waste paper and cyanobacteria were 34.8 %, 36.7 % and 39.8 % respectively. Besides, efforts were made to screen the suitable solvents for FA isolation from the aqueous phase after the reaction. In line with these works, the group has then developed a biphasic reaction system with the aqueous reaction phase and the *in-situ* extraction organic layer to boost the FA selectivity and yield [55]. Long-chain primary alcohols were selected as the effective solvent to constantly extract FA from the water phase and shifted the reaction equilibrium towards FA. With the homogeneous $H_8PV_5Mo_7O_{40}$ as the catalyst under 20 bar O_2 gas, a remarkably high FA yield of ~85.0 % was achieved at 90 °C in the biphasic system which was considerably superior to the monophasic systems. The authors have termed the transformation as the OxFA-process and further integrated it with Fischer-Tropsch synthesis (FTS) to generate other fuels (see Fig. 5) [56].

Besides pure O_2 gas, biomass oxidation into FA could be facilitated by using air as the oxidant. Fu's group described glucose and cellulose oxidation into FA by using the $H_5PV_2Mo_{10}O_{40}$ catalyst in water at 100 °C under pressurized air [57]. The acidity of the catalysts was not critical for FA formation, nonetheless, the incorporation of the V metal into the HPAs played a crucial role on FA generation. The use of high-pressure air has efficiently promoted the biomass conversions which exhibited even better performance than that using high pressure O_2 gas. About 52.0 % and 35.0 % FA yields were obtained from glucose and cellulose in the presence of 50 bar air within 3 h. Replacing the pure O_2 gas with inexpensive air would result in an additional decrease in capital costs for the process. Gromov et al. also reported cellulose oxidation into FA under simulated air (20 % O_2 + 80 % N_2) by employing a Co-doped HPA catalyst with the formula of $Co_{0.6}H_{3.8}PV_2Mo_{10}O_{40}$ [58]. The incorporation of Co into the catalyst has led to improved catalytic activity and increased the FA yield by ~10 %. Meanwhile, ball mill pretreatment has been adopted to process cellulose before its transformation, which was an efficient method to deconstruct the crystal structure and facilitate the conversion of biomass resources [59]. Starting from cellulose treated in a planetary ball mill, the FA yield reached ~66.0 % within 5 h.

Another Keggin-type V-substituted phosphomolybdic acid catalyst $H_4PVMo_{11}O_{40}$ was devised to convert cellulose and raw woody biomass into FA under O_2 gas in water [60]. The influence of metal addenda

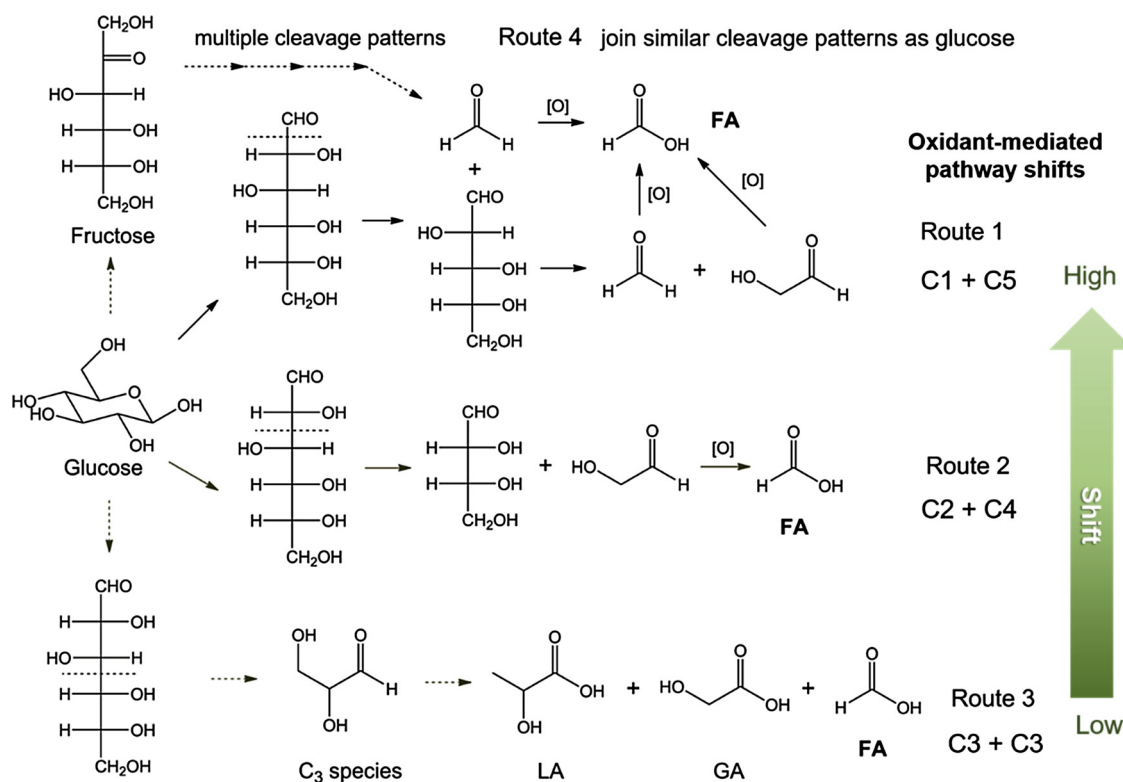


Fig. 4. The proposed reaction mechanisms for room temperature conversion of glucose into FA. Adapted with permission from Ref. [42]. Copyright 2019 the Royal Society of Chemistry.

Table 1

The catalytic oxidation of biomass by various catalysts.

Substrates	Catalysts	T (°C)	t (h)	Additives/co-solvents	Oxidants	FA%	Ref.
Glucose	H ₅ PV ₂ Mo ₁₀ O ₄₀	80	26	–	30 bar O ₂	49.0	[50]
Cellulose	H ₅ PV ₂ Mo ₁₀ O ₄₀	80	26	–	30 bar O ₂	1.0	[50]
Poplar sawdust	H ₅ PV ₂ Mo ₁₀ O ₄₀	80	26	–	30 bar O ₂	11.0	[50]
Cellulose	H ₅ PV ₂ Mo ₁₀ O ₄₀	90	24	p-TSA	30 bar O ₂	18.8	[54]
Beech wood	H ₅ PV ₂ Mo ₁₀ O ₄₀	90	24	p-TSA	30 bar O ₂	34.8	[54]
Waste paper	H ₅ PV ₂ Mo ₁₀ O ₄₀	90	24	p-TSA	30 bar O ₂	36.7	[54]
Cyanobacteria	H ₅ PV ₂ Mo ₁₀ O ₄₀	90	24	p-TSA	30 bar O ₂	39.8	[54]
Glucose	H ₆ PV ₅ Mo ₇ O ₄₀	90	48	1-hexanol, etc.	20 bar O ₂	85.0	[55]
Sucrose	H ₆ PV ₅ Mo ₇ O ₄₀	90	48	1-hexanol, etc.	20 bar O ₂	76.0	[55]
Beech wood	H ₆ PV ₅ Mo ₇ O ₄₀	90	48	1-hexanol, etc.	20 bar O ₂	61.0	[55]
Glucose	H ₅ PV ₂ Mo ₁₀ O ₄₀	100	3	–	50 bar air	52.0	[57]
Cellulose	H ₅ PV ₂ Mo ₁₀ O ₄₀	170	9	–	50 bar air	35.0	[57]
BM cellulose	Co _{0.6} H _{3.8} PV ₂ Mo ₁₀ O ₄₀	160	5	–	20 bar (O ₂ + N ₂)	66.0	[58]
Cellulose	H ₄ PV ₄ Mo ₁₁ O ₄₀	180	3	–	6 bar O ₂	68.0	[60]
Bagasse	H ₄ PV ₄ Mo ₁₁ O ₄₀	180	3	–	6 bar O ₂	61.0	[60]
Hay	H ₄ PV ₄ Mo ₁₁ O ₄₀	180	3	–	20 bar O ₂	54.5	[60]
Cellulose	[MIMPS] ₃ HPMo ₁₁ VO ₄₀	180	1	–	10 bar O ₂	51.3	[62]
Beech wood	K ₅ V ₃ W ₃ O ₁₉	115	72	–	50 bar O ₂	12.5	[63]
Glucose	NaVO ₃	160	1	0.7 wt% H ₂ SO ₄	30 bar O ₂	68.2	[64]
Cellulose	NaVO ₃	160	2	0.7 wt% H ₂ SO ₄	30 bar O ₂	64.9	[64]
Wheat straw	NaVO ₃	160	5 min	2 wt% H ₂ SO ₄	30 bar O ₂	47.0	[65]
Glucose	VOSO ₄	140	3	methanol	20 bar O ₂	75.0	[66]
BM cellulose	VOSO ₄	160	5	ethanol	20 bar O ₂	70.0	[66]

atoms on adjusting FA selectivity was proved significant, which was in accordance with previous studies [61]. Under 6 bar O₂ gas, cellulose was selectively transformed into FA with a yield of 67.8 % at 180 °C. Moreover, the conversion of bagasse and hay were comparably efficient affording the highest FA yields of 61.0 % and 54.5 % respectively. Besides, the H₄PV₄Mo₁₁O₄₀ possessed relatively good stability and recyclability. Based on the model compound tests, C₂ species such as glycolaldehyde, glycolic acid, etc. were more likely the intermediates for FA formation in the reaction system. Apart from HPAs, heteropolyanion-based ionic liquids (ILs) has been designed as the catalysts

for water-phase cellulose oxidation into FA by Liu's group [62]. The synthesized ILs were consisted of the PMo₁₁VO₄₀^{4–} anion and various –SO₃H functionalized cations (the chemical structures of the cations were shown in Fig. 6), which were responsible to catalyze glucose oxidation and cellulose hydrolysis respectively. Most of the ILs displayed better catalytic activity than the H₄PMo₁₁VO₄₀ counterpart. The [MIMPS]₃HPMo₁₁VO₄₀ IL catalyst afforded the highest FA yield of 51.3 % from cellulose at 180 °C under 10 bar O₂ gas compared to the 35.5 % when the HPA counterpart was used. Besides, the IL catalyst has been reused for three times with negligible decrease in FA yield.

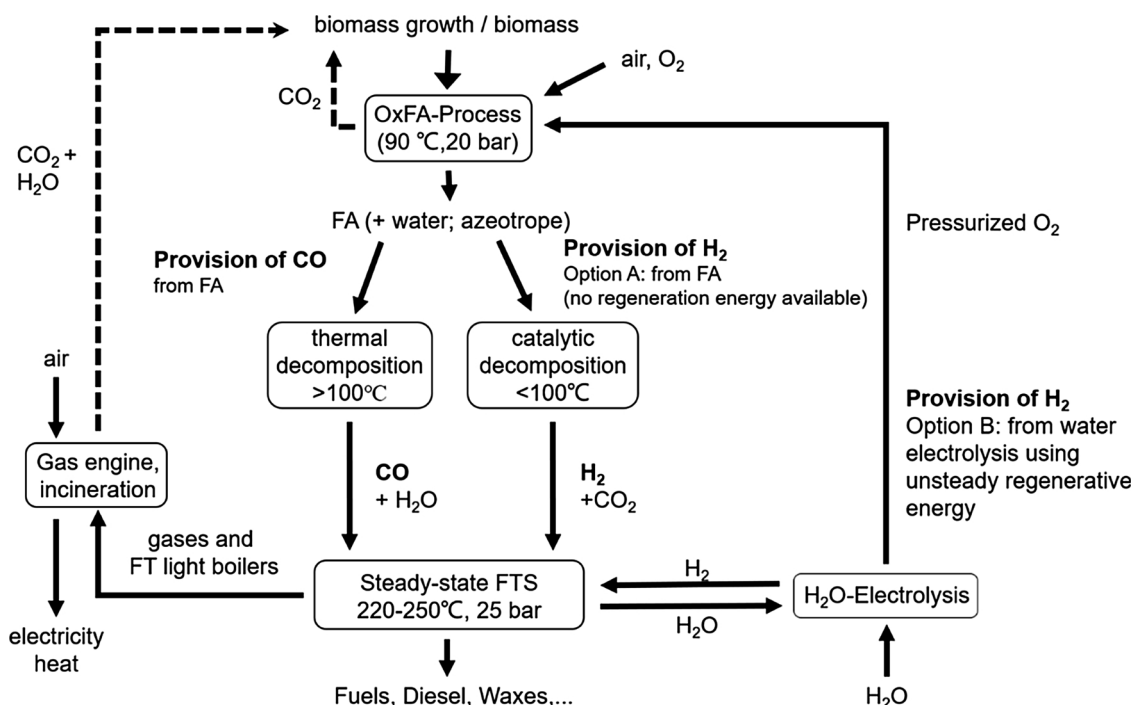


Fig. 5. The diagram of liquid fuel production from biomass by the OxFA-process coupled with FTS. Adapted with permission from Ref. [57]. Copyright 2016 American Chemical Society.

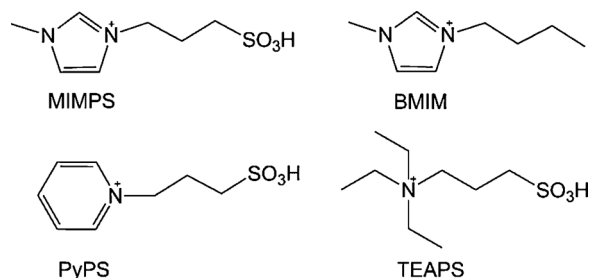


Fig. 6. The chemical structures of the functionalized cations in the ILs to catalyze biomass conversion into FA. Adapted with permission from Ref. [62]. Copyright 2014 the Royal Society of Chemistry.

In contrast to the Keggin-type HPAs, the Lindqvist-type polyoxometalates may show a considerably distinct effect on lignocellulosic biomass conversion into FA. The homogeneous Lindqvist-type $K_5V_3W_3O_{19}$ exhibited satisfactory activity to convert the hemicellulose and lignin components into FA, whereas inefficient to transform cellulose. As a result, it has been employed to produce FA while concurrently fractionate cellulose from raw woody biomass in one step [63]. By adopting the Box-Behnken design of experiments (DoE) to optimize the reaction conditions (see Fig. 7), beech wood has been transformed at 115 °C under 50 bar O₂ gas in water, and the total carbon yield of the products were ~50.0 % with FA yield of 12.5 %. However, the reaction system was less effective to convert the softwood spruce and the green algae *chlorella* with FA yields of 1.6 % and 0.2 % respectively.

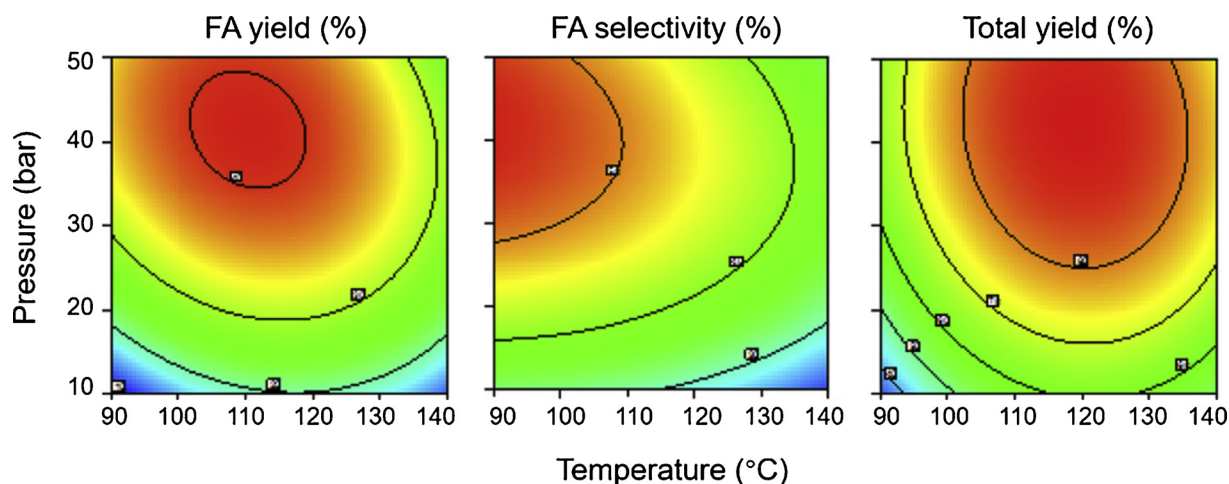


Fig. 7. Parameter optimizations by using the Box-Behnken DoE method. Adapted with permission from Ref. [63]. Copyright 2019 American Chemical Society.

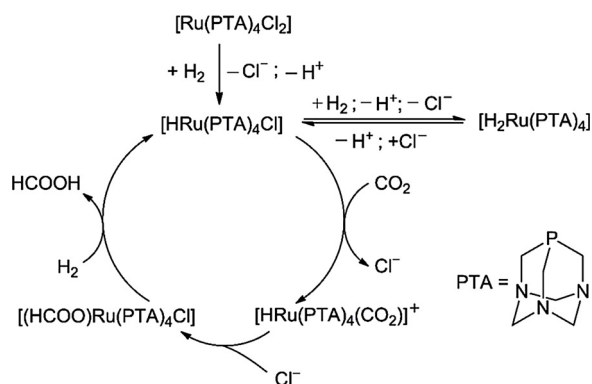


Fig. 9. Proposed catalytic cycle for the hydrogenation of CO₂ using the [RuCl₂(PTA)₄] homogeneous complex.

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transition state energy and favor the H₂ heterolysis. In addition, a new type of Ir catalyst bearing a *N,N'*-diimine ligand was designed to convert CO₂ into FA under base-free conditions [84], and the turnover number (TON) of hydrogenation reached beyond 10,000 at 40 °C under 76 bar pressure in aqueous solutions. Combined the *in-situ* NMR and kinetic study, the rate determining step (RDS) was probably the CO₂ insertion step. Besides, the kinetic isotope effect analysis indicated that water dissociation from the Ir-water complex would impact on the catalytic cycle.

Apart from the noble metal complexes, non-noble metal catalysts were also employed. An iron (Fe(II))-based pincer complex was synthesized to catalyze the reduction of sodium bicarbonate (NaHCO₃) and CO₂ in basic solutions at relatively low pressure which exhibited comparable activity with noble metal-based complexes [85]. Starting from NaHCO₃ feedstock, FA (as sodium formate) was formed with 32.0 % yield at 80 °C under ~8 bar H₂ gas in water/tetrahydrofuran (THF) (10:1) solvent. Starting from CO₂ gas with the addition of NaOH as an

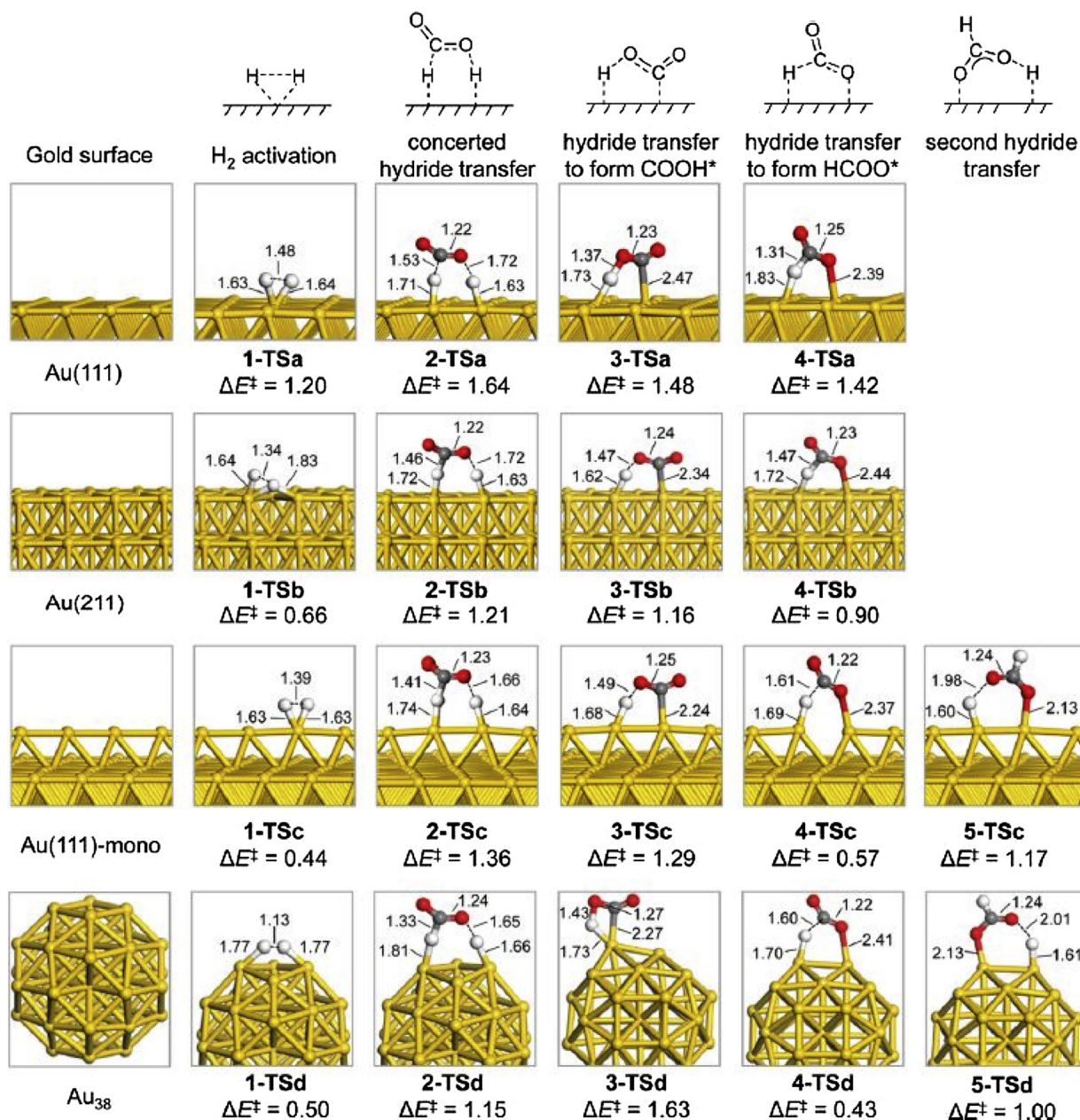


Fig. 10. The hydride transfer pathways for CO₂ hydrogenation on different Au surfaces. Reprinted with permission from Ref. [97]. Copyright 2017 American Chemical Society.

absorbent, a high FA yield of 53.2 % could be achieved under similar conditions. Afterwards, a highly stable and efficient Fe complex was developed [86], which could transform NaHCO_3 into FA at about 100 °C under 60 bar H_2 gas with a notably high yield of ~80 % and a TON of > 7500. Nonetheless, the FA yield from CO_2 was relatively low of 16.7 % with a TON of ~2000. *In-situ* NMR experiments were conducted to understand the reaction mechanisms and a catalytic cycle was proposed. Cobalt (Co)-based homogenous catalyst such as the $\text{Co}(\text{dmpe})_2\text{H}$ (dmpe is 1,2-bis(dimethylphosphino)ethane) was also utilized for this reaction under relatively mild conditions [87]. An organic base was added into the THF solvent to facilitate the reduction of CO_2 , and the TON could reach 9400 at room temperature under 20 bar H_2 gas. Later on, a Co homogeneous complex with pincer ligands was synthesized and the cationic complex coordinated with lithium triflate was identified as an effective catalyst for CO_2 reduction [88]. A high TON was realized at about 30,000 at 45 °C in acetonitrile (ACN) with the addition of 1,8-diazabicycloundec-7-ene (DBU) after a reaction time of 16 h. In the field of homogeneous-catalyzed CO_2 reduction, there are several excellent reviews that can be referred to [89–93].

3.1.2. Heterogeneous catalysis

Heterogeneous catalysts are also widely used for FA production from CO_2 [94]. Preti et al. have utilized a heterogeneous gold/titanium oxide (Au/TiO_2) catalyst to promote CO_2 reduction by H_2 with the addition of the triethylamine (NEt_3) base [95]. CO_2 and H_2 (1:1) were charged into an autoclave to 180 bar and the reaction happened at 40 °C. A cyclic continuous reaction process was established by pumping the gas when the pressure dropped to 130 bar, and the catalyst displayed a good stability in a period of 37 days. Negligible side products were detected except for the FA/ NEt_3 adduct while small amount of CO was identified as a by-product in the gas phase. Besides, an amine-exchange method was exploited to separate the FA product with an overall recovery yield of about 83 %. The support was proved crucial in the reaction system because unsupported Au NPs aggregated easily and quickly lost the catalytic activity. Later on, the support effect of Au NPs-catalyzed CO_2 hydrogenation has been studied by using three types of unsupported Au NPs and seven different types of supported Au NPs including Au/TiO_2 , $\text{Au}/\text{aluminum oxide}$ (Al_2O_3), $\text{Au}/\text{zinc oxide}$ (ZnO), etc. [96] The reaction was conducted with a H_2/CO_2 mixture of 40 bar at 70 °C for 20 h in organic solvent with the NEt_3 additive. Among various catalysts, $\text{Au}/\text{Al}_2\text{O}_3$ exhibited the best performance due to the synergistic effects of the $\text{Au}(0)$ NPs and the basic sites on the support to facilitate the heterolytic H_2 dissociation. The mechanisms and effect of Lewis base in the Au-catalyzed CO_2 hydrogenation have been also investigated by using the first principle calculations [97]. Various Au surfaces were able to couple with the Lewis base such as NH_3 which facilitated the dissociation of H_2 (see Fig. 10). The proton transfer from NH_4^+ species to HCOO^* species to form FA was significantly favored and eased the CO_2 hydrogenation.

Supported Ru catalysts were also efficient for CO_2 hydrogenation. A series of Ru/TiO_2 with different metal loadings were synthesized by a micro-emulsion protocol, and low loading of Ru NPs was beneficial to stimulate the FA formation from CO_2 using H_2 as the reductant in aqueous solution at 80 °C with the NEt_3 additive [98]. Mori et al. have developed the layered double hydroxide (LDH)-supported single atom Ru catalyst to reduce CO_2 into FA at 100 °C with H_2 under 20 bar in basic aqueous solutions (NaHCO_3 , NaOH or KOH as the additives) [99]. The schematic illustration of the Ru/LDH was shown in Fig. 11. The single atom Ru species were surrounded by the $-\text{OH}$ ligands which were orderly arranged on the LDH surface with electron donating ability, and the vicinity of the Ru center provided active sites for CO_2 adsorption which could be adjusted by varying the ratio of metal ions in the LDH support. The simultaneous electron donating ability and CO_2 adsorption capacity have enhanced the catalytic activity for CO_2 hydrogenation. In addition, Ru NPs/hydroxalite (HT) was fabricated by a co-precipitation method [100], in which the HT acted both as a support

and a soft solid base. The H_2/CO_2 gas mixture was used as the substrates and the reactions were examined in methanol/water solvent at a temperature range of 40–100 °C and a pressure range of 10–100 bar, with no external base added. The parameters were systematically optimized, and the highest TON could reach 11389 under optimal conditions. Ru(II) was observed as the active species for CO_2 hydrogenation in which the water and the hydrides have promoted the CO_2 activation in the catalytic cycle. The as-synthesized Ru/HT catalyst has been recycled for seven runs with negligible loss of activity. Palladium-nickel (PdNi) nanoalloys supported on carbon nanotubes (CNTs)-graphene composite were constructed to catalyze CO_2 hydrogenation by H_2 gas in water without the addition of a base under mild conditions of 40 °C and 50 bar pressure [101]. The bimetallic nanoalloys exhibited superior catalytic activity than the monometallic counterparts due to the synergistic effects between Pd and Ni. Meanwhile, the carbon composites as the support enhanced the dispersion of the PdNi nanoalloys and improved the stability of the catalyst.

Yan's group has synthesized a series of supported Pd catalysts which displayed excellent performances for CO_2 hydrogenation into FA. Various metal oxides were tested as the support and the optimized Pd/ TiO_2 was identified as the most efficient [102]. The Pd supported on different metal oxides promoted CO_2 reaction with similar pathways, but the RDS could be distinct. Besides the support effect, the crystal phase of the metal oxides also affected the catalytic activity [103]. For example, tetragonal phase ZrO_2 was superior to the monoclinic ZrO_2 as the support for Pd NPs to reduce CO_2 into FA. In line with these works, a catalytic system of Pd-CoO bimetallic NPs/mesoporous silica nanospheres (MSNs) were prepared by a simple ligand-protected strategy [104], which has been highlight by *Nature Catalysis* [105]. The catalyst exhibited high activity for CO_2 hydrogenation into FA (among the top-level reported) and was stable after five runs (structures unchanged and activity negligibly dropped).

The heterogeneous non-noble metal NPs-catalyzed CO_2 reduction have been relatively less studied. Peng et al. have studied the mechanisms of CO_2 hydrogenation on heterogeneous Ni(110) and Ni(111) surfaces by DFT calculations [106,107]. On the Ni(110) surface, the surface H^* species was able to transform the CO_2 into the formate product, whereas further reduction of formate into FA was more difficult and highly active subsurface H^* species were required. On the Ni(111) surface, the formate intermediate was much more favorable than the carboxyl intermediate for CO_2 reduction. Nonetheless, it was similar that the subsequent hydrogenation of formate into FA was challenging and involved the subsurface H^* species, in which the formate possessed the unidentate structure and fast converted to the bidentate form. Copper (Cu)-based heterogeneous catalysts have been widely used in CO_2 hydrogenation but in most cases methanol was formed as the major product and FA sometimes identified as a by-product [108], and relevant reviews can be found elsewhere [109–111].

3.1.3. Hydrothermal conversion of CO_2 into FA

Hydrothermal process in general describes chemical reactions that undertaken in super- or subcritical fluids such as water at high temperature and pressure [112–114]. The process was initially adopted for crystal synthesis, whereas extended to biomass and CO_2 conversions due to its outstanding advantages including low dielectric constant, the relatively large polarity, increased ion concentrations, etc. [115] As a result, hydrothermal process may furnish a green, rapid and efficient method to hydrogenate CO_2 into FA with the aid of a proper reductant and a catalyst that could be either homogeneous or heterogeneous. Takahashi et al. have demonstrated the reduction of CO_2 gas in water at 200 °C under 20 bar pressure with Fe powder as the reductant and Ni powder as the catalyst in a continuous system [116]. The FA production rate was about 240 $\mu\text{mol}/\text{h}$ at the reaction time of 1 h. Afterwards, Jin's group investigated the reduction of NaHCO_3 into FA using various zero-valent metals under hydrothermal conditions, in which water was the hydrogen source [117]. H_2 gas was generated from the zero-valent

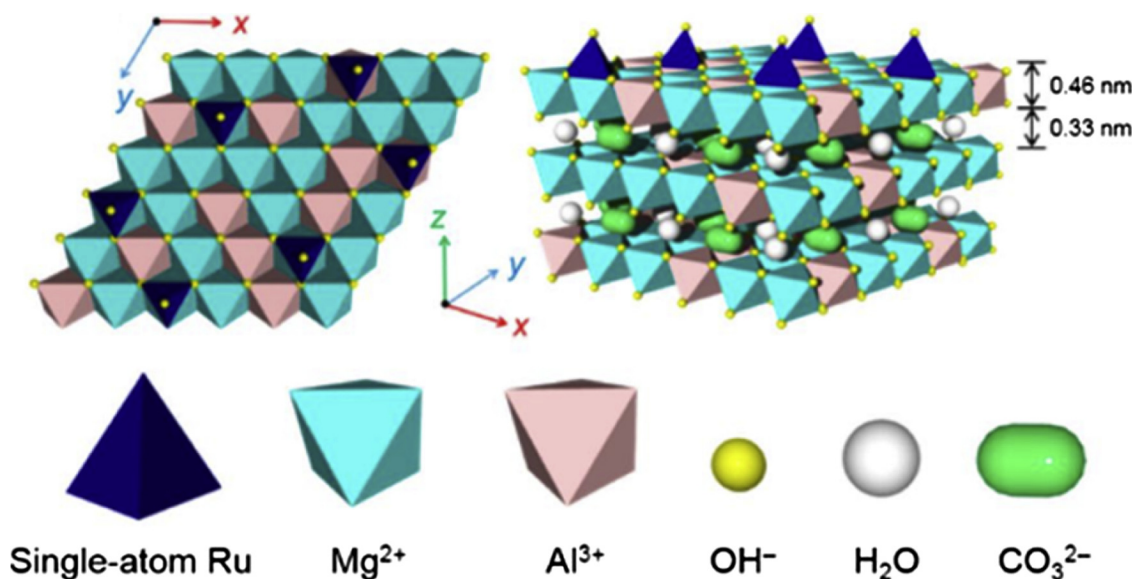


Fig. 11. The schematic illustration of Ru/LDH catalysts.

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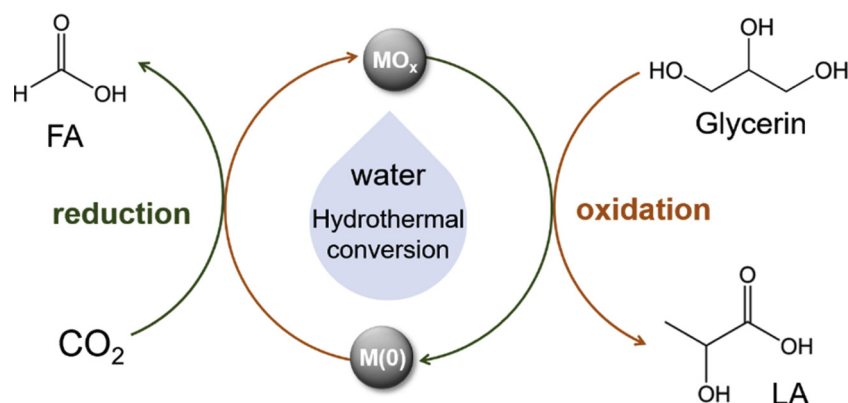


Fig. 12. CO₂ utilization with biochemicals as reductants via metal/metal oxide redox cycles.

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metals such as Fe, Zn, *etc.* in subcritical water at 300 °C, providing a reducing atmosphere for NaHCO₃ reduction into FA. The addition of Ni or Cu as a catalyst usually led to further enhanced FA yield. However, without additional catalysts, the Al metal promoted FA formation with a high yield of 62.8 % under optimal conditions. The X-ray diffraction (XRD) data showed that the metal reductants such as Fe have been completely oxidized into Fe₃O₄ after the reaction, which confirmed that the metals were the reducing agent. Ideally, the spent metals could be easily recovered by treating with glycerin to transform back into the zero-valent states under hydrothermal conditions, achieving a reusable cycle (see Fig. 12).

Following the work, the same group has tested manganese (Mn) powder to realize the reaction without the addition of a catalyst [118]. A remarkably high FA yield was obtained of about 75 % from NaHCO₃ with 98 % selectivity. It was found that the substrate NaHCO₃ assisted the dissociation of water to produce H₂. Besides, a quick color change of the solid residues was noticed from green to brown, indicating the oxidation of Mn powder during the reaction. Indeed, the species of Mn (OH)₂, MnO and Mn₃O₄ were detected on XRD analysis which explained the possible evolution route of the Mn reductant. In addition, the MnO species was proved catalytically active to facilitate the reduction. Hence, the Mn powder acted as both the reducing agent and the catalyst in the reaction system. Apart from commercial metal powders, the waste Al-can strip was utilized as a reductant [119]. Up to

~65 % FA yield could be reached from NaHCO₃ under hydrothermal conditions at 300 °C, meanwhile, the Al(OH)₃ product with a surface area of around 129.3 m²/g was formed from the Al waste, which could be potentially used as ceramics, catalysts, absorbents, *etc.* As a result, the work not only exempted the valorization of CO₂ for valuable chemicals but also contributed to waste management.

Non-metallic, organic compounds can also be employed as the reducing agent for CO₂ reduction. For example, isopropanol played a similar role as the metal reductants to convert NaHCO₃ into FA in water at 300 °C with the highest yield of ~70 % [120]. After the reaction, the isopropanol was transformed to acetone which is also a value-added product. Glycerin as a reductant has also been investigated, in which the ratio of NaHCO₃/glycerin and the temperature were the critical factors to the reaction [121]. Particularly, the FA yield was rather low of ~17 % at 260 °C whereas the yield jumped to ~82 % at 300 °C, which infers that the reduction was efficient at beyond 300 °C possibly because the H₂ evolution effectively occurred at this temperature. The glycerin was converted into the high-value chemical LA after the reaction, which pointed out the possibilities of co-utilization of CO₂ and biomass-derived compounds or even raw biomass in one step. To verify the assumption, hexanehexol was first utilized as a model compound to reduce NaHCO₃ under similar hydrothermal conditions [122], and FA was obtained with about 80 % yield within only 1 h. Afterwards, the raw biomass microalgae, waste plastics, *etc.* have been successfully

Table 2Hydrothermal conversions of CO₂ into FA by using various reductants/catalysts.

Substrates	Catalysts	Reductants	T (°C)	t (h)	FA (%)	Ref.
CO ₂	Ni	Fe	200	1	240 μmol/h	[116]
NaHCO ₃	–	Al	300	2	62.8	[117]
NaHCO ₃	Cu	Fe	300	2	48.0	[117]
NaHCO ₃	–	Mn	325	1	75.0	[118]
NaHCO ₃	AlO(OH)	Al	300	2	65.0	[119]
NaHCO ₃	–	Isopropanol	300	2.5	70.0	[120]
NaHCO ₃	–	Glycerin	300	1.5	82.0	[121]
NaHCO ₃	–	Hexanehexol	300	1	80.0	[122]
NaHCO ₃	Ni ₃ S ₂	H ₂ S	300	2	67.3 %	[123]
NaHCO ₃	–	Microalgae	325	2	9.8	[124]
NaHCO ₃	–	Waste plastic	300	8	16.0	[125]

adopted as the reductants to hydrogenate NaHCO₃ into FA with satisfactory yields under hydrothermal conditions [123–125]. An overview of CO₂ hydrothermal conversions into FA was displayed in Table 2.

3.2. Photo- and electro-chemical reduction of CO₂ into FA

Photocatalytic reduction of CO₂ is a strategy to exploit solar energy to promote the chemical transformation by a photocatalyst usually a semiconductor [126–129]. The semiconductor has a low-energy valence band (VB) and a high-energy conductive band (CB) with a band gap in between (E_g), upon light irradiation when the $h\nu > E_g$, the electron in VB could be excited into the CB with a hole left in VB (see Fig. 13a). In this way, an electron-hole pair normally called the charge carrier is formed which functioned as the active sites for reductive and oxidative reactions. To improve the photocatalytic activity, the targets are to increase the light harvesting capacity, suppress the recombination of the charge carriers, promote the charge transfer to the surface species and enhance the CO₂ adsorption on the catalyst surfaces.

TiO₂-based semiconductors are inexpensive, abundant and environmentally friendly which represent the most widespread photocatalysts [130–132]. Cu-doped TiO₂ NPs were synthesized by a solvothermal strategy which inserted the Cu(II) ion into the TiO₂ crystal lattices to mitigate the E_g value and therefore extended the light absorption range [133]. The FA yield of ~26 μmol/g/h was achieved in water with sodium sulfide as a sacrificial reagent from CO₂ at room temperature under UV-rich irradiations. Metal disulfides have been also employed for photocatalytic reduction of CO₂ due to their strong light absorption capacity. SnS₂ atomic layers with different oxidation degrees were fabricated on the SnO₂ support to disclose the role of surface

oxygen species [134]. The energy band structure and the schematic illustration of the SnS₂/SnO₂ composite were shown in Fig. 14. The COOH* species was probed by the *in situ* FTIR analysis as an important intermediate and pointed to be the rate-determining step by DFT calculations. The localized surface oxygen domains promoted the electron-hole separation and stabilized the COOH* species to diminish the activation energy barrier.

Recently, the ternary metal chalcogenides of (Mo-Bi)S_x/mesoporous CdS have been designed for the photochemical reduction of CO₂ into FA [135]. At room temperature, the highest rate of FA generation was about 208 μmol/g/h in IL-ACN solvent mixture under visible light irradiation in the presence of triethanolamine (TEOA). The as-synthesized (Mo-Bi)S_x/CdS catalyst possessed an average diameter of around 50 nm, in which the MoS_x species favored the hydrogen evolution and the BiS_x was effective to active CO₂ for its reduction. The synergistic effects between the uniformly dispersed (Mo-Bi)S_x and the CdS support were also critical to promote FA formation. The use of imidazolium-based ILs as a co-solvent was because the ILs have strong interactions with CO₂ and would reduce the energy barrier of the reaction. In the reaction system, FA was the only organic product with H₂ as the side product which would make the purification process simpler.

The metal organic frameworks (MOFs) are a class of heterogeneous hybrid crystalline materials with advantages of synthetic tunability and extraordinary structural properties [136–138]. By the rational design and development of the metal clusters and the organic linkers in the structure, photoactive MOFs could be generated to efficiently catalyzed the photoreduction of CO₂ into FA. In fact, due to their unique structures, the MOFs were able to localize electrons on separated positions and thus assisted to inhibit the recombination of the electron-hole pairs. A Zr-based MOF with a homogeneous Ru(cptpy)₂ complex (bis(4'-(4-carboxyphenyl)-terpyridine)Ru(II)) in the backbone was fabricated to promote the photocatalytic reduction of CO₂ into FA [139]. The Ru complex was obtained by a slow evaporation procedure, and then the Ru complex was mixed with the precursor ZrOCl₂·8H₂O in DMF solvent. By introducing a small amount of FA as the additive, the mixtures were heated at 120 °C for 2 days to afford the red-color MOF material (named as AUBM-4). The crystal structure of AUBM-4 have been thoroughly examined and the stability was tested by soaking it in aqueous and organic solvent for one week. Negligible changes were observed of its crystal structure. Under visible light irradiation, the AUBM-4 facilitated FA formation from Na₂CO₃ with a rate of 366 μmol/g/h in ACN solvent with TEOA as the additive, which was higher than that of previously reported MOF catalysts such as NH₂-UIO-66(Zr), NNU-28, PCN-222, etc. The AUBM-4 have been recycled and reused in four consecutive runs. No significant change in FA yield was noticed and the structure remained similar as indicated by the characterization analyses, which

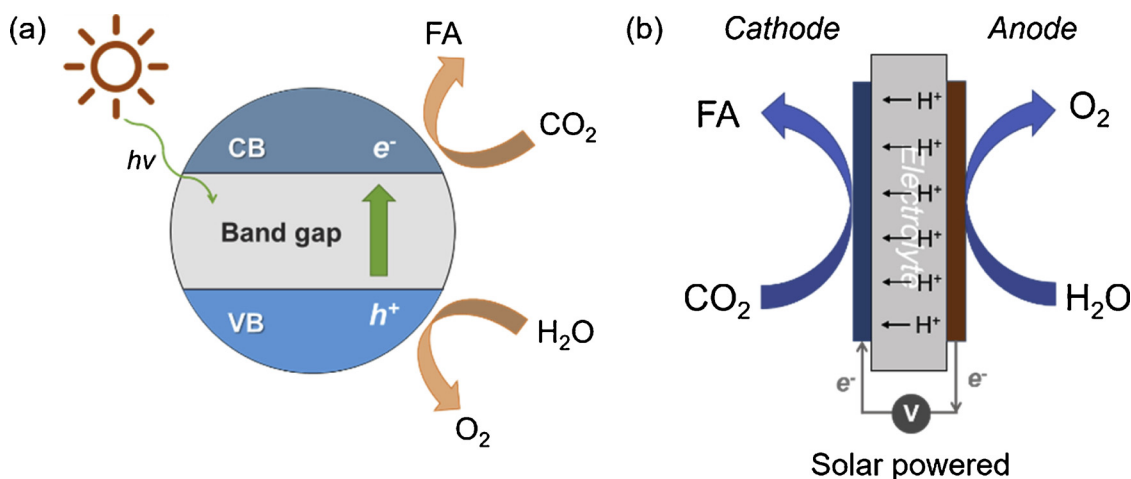


Fig. 13. Schematic illustration of (a) photochemical reduction of CO₂ and (b) electrochemical reduction of CO₂.

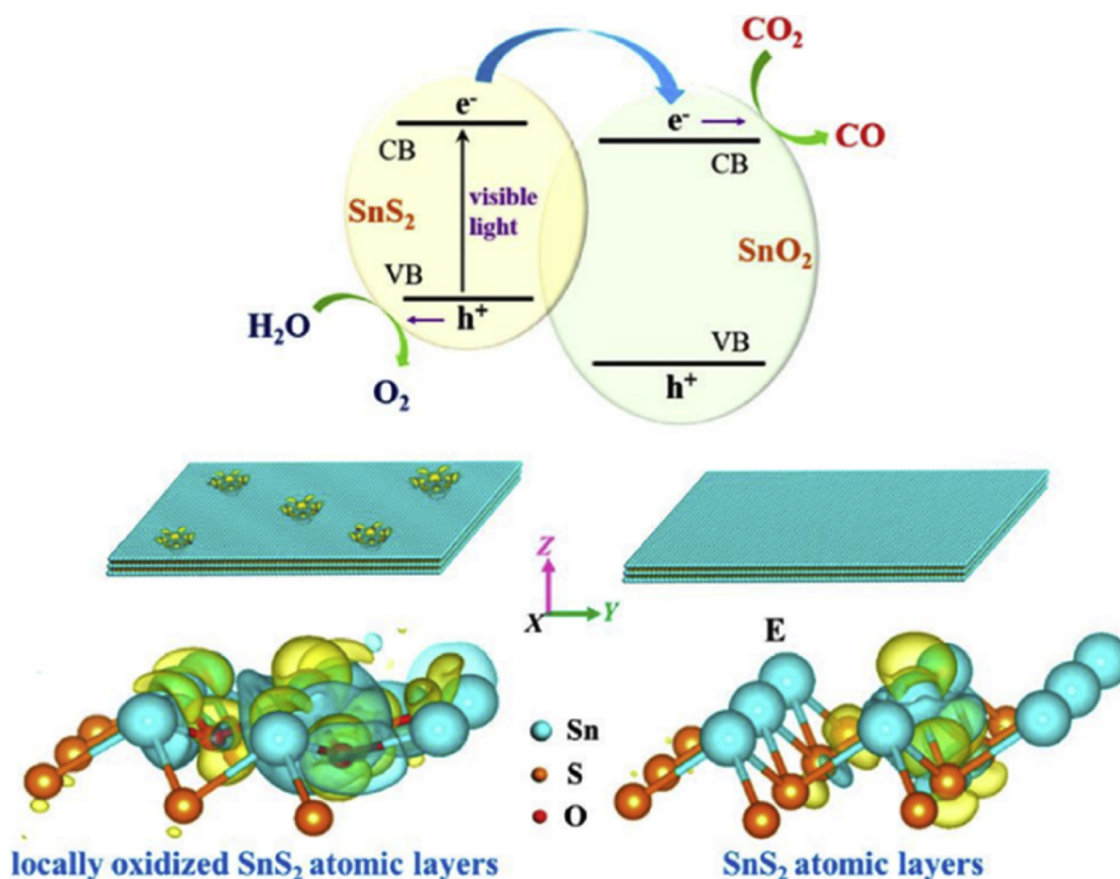


Fig. 14. The energy band structure and the schematic illustration of the $\text{SnS}_2/\text{SnO}_2$ composite. Reprinted with permission from Ref. [134]. Copyright 2017 American Chemical Society.

suggested the relatively good stability of the MOF catalyst. The mechanisms were proposed based on the experimental results and the DFT calculations. More studies on the photoreduction of CO_2 by MOFs into a variety of gas and liquid fuels are provided elsewhere [140–142].

The electrochemical reduction of CO_2 is an indirect way to utilize the solar energy to produce fuels (see Fig. 13b). Ideally, the electricity is sustainable that generated by photovoltaic cell or other techniques. Usually, the electrochemical reduction of CO_2 occurred at the inter-surface of the electrodes. The redox potential of $\text{CO}_2/\text{CO}_2^{\cdot-}$ is approximately -1.9 V vs. the standard hydrogen electrode (SHE) in water which is rather negative. As a result, the fabrication of catalytic layers onto the electrodes are required for efficient and selective CO_2 reduction. The catalytic species can be homogeneous metal complexes and heterogeneous metal films that anchored on the surfaces of the electrodes where a suitable potential is applied. Cu and CuO-based electrodes are the most widely used heterogeneous species to reduce CO_2 into CO, FA, methanol, etc. The progresses in electrochemical reduction of CO_2 has been summarized by a plethora of exceptional reviews and thus will not be expanded on herein [143–146]. For the photoelectro- and electro-chemical reduction of CO_2 into FA, metal-free catalysts were also adopted to promote the reactions. Carbon-based conducting polymers such as polypyrrole (PPy) and polyaniline (PAN) were employed for the electroreduction, due to the merits of low-cost, highly conductive, relatively stable and adjustable. For instance, Aydin et al. utilized a PPy-based electrode to reduce CO_2 into FA at pressurized conditions and room temperature [147]. The FA yield was improved with increased pressure and shorter electrolysis time. The PAN electrode has been used to hydrogenate CO_2 in methanol solvent at ambient condition [148]. FA and AA were formed as the main products. Recent reviews on this topic can be found elsewhere [149,150].

4. The dehydrogenation of FA to produce H_2 fuel

A salient advantage and potential application of FA is its role as a H_2 energy carrier to solve the storage issue for gas fuels, ease the transportation and improve the safety of using H_2 as a fuel. The dehydrogenation of FA is a reverse reaction of CO_2 hydrogenation, and many of the catalysts that catalyzed the CO_2 hydrogenation into FA are also able to promote FA dehydrogenation. A common side reaction is the FA dehydration into water and CO which should be avoided to favor H_2 fuel generation. Besides, it is desirable that the release of H_2 from FA happens under mild conditions with high efficiency to favor its practical uses. For these purposes, various homogeneous and heterogeneous catalysts have been developed to achieve the mild, selective and effective dehydrogenation of FA.

Ir-based complexes have been frequently used to catalyze this reaction. Celaje et al. have reported the facile and selective dehydrogenation of neat FA (no solvent was needed) by a Ir complex catalyst (as shown in Fig. 15, 1) with a base as the co-catalyst [151]. The base co-catalyst could nonspecifically be NaOH, KOH or Na_2CO_3 , etc. The catalytic system was robust with relatively high moisture and air tolerance. Furthermore, since the Ir complex and co-catalyst appeared at the bottom of the reactor after the reaction, the catalytic system could be simply reused for more than 50 times by recharging the reactor without catalyst regeneration. The conversion rate of FA could reach $\sim 97\%$ at 90°C with a TON beyond 66,000. Besides, the system was also highly selective with trace amount of CO detected, which was formed probably via a thermal, non-catalytic step. The mechanisms of FA dehydrogenation have been studied in detail by using model reactions, kinetic studies and isotope labelling analyses. A plausible way for catalyst initiation and an active species were proposed (as shown in Fig. 15). Iguchi et al. synthesized a variety of water-soluble

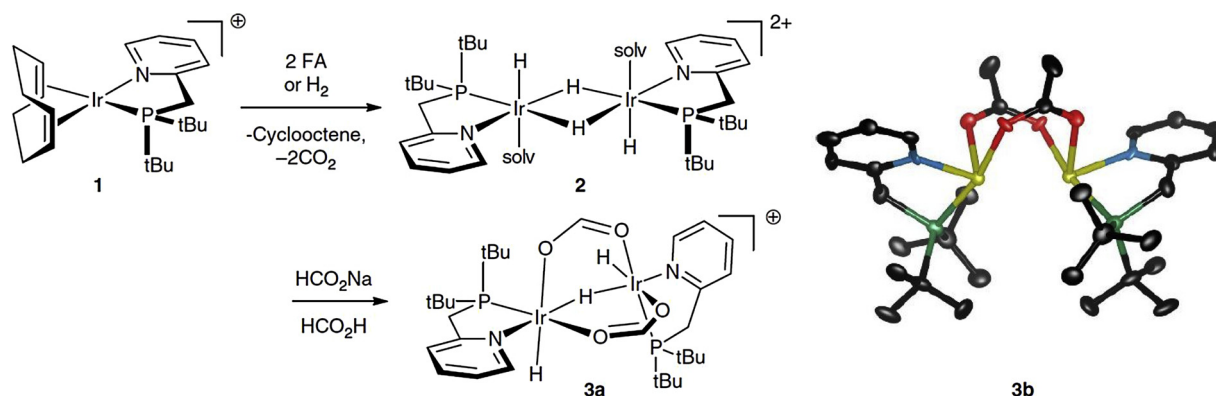


Fig. 15. Catalyst initiation and molecular structure of active catalyst homologue 3b. Reprinted with permission from Ref. [151]. Copyright 2016 Springer Nature.

pentamethylcyclopentadienyl Ir (Cp*Ir) complexes to dehydrogenate FA [152]. The Ir catalyst with 1,10-phenanthroline-4,7-diol as the ligand exhibited good activity and durability to convert aqueous FA solution into H₂ gas at about 60 °C with a TON as high as 203,000. More importantly, the water solubility of the Ir complex depended on the pH and precipitated at the end of the reaction that could be easily recycled by filtration. In this way, the catalyst has been reused for 10 times without significant loss of activity. Following the work, the ligand effect on Cp*Ir complexes was investigated by the same group [153], which revealed that the stability of the catalysts was associated with the pyridine moiety in the ligand and Ir complexes with the pyridyl-imidazole ligand was the most active and stable.

Heterogeneous catalysts usually the supported metal NPs were adopted for FA dehydrogenation. Noble metal NPs such as Au, Pd, etc. were more often used, and the supports include carbon, metal oxides, MOFs, zeolites, etc. Liu et al. demonstrated the efficient dehydrogenation of highly concentrated FA solution (nearly pure FA) at 50 °C by using a Schiff base functionalized Au NPs that anchored on the SiO₂ support (Au@Schiff-SiO₂) without any additives [154]. The synergy between the electron-rich Au NPs and the protonated Schiff base was believed to be the major reason for the high activity. Cao's group developed a Pd NPs/CN catalyst to promote FA dehydrogenation in aqueous solution at room temperature [155]. The conversion rate of FA was almost quantitative and the catalytic system was capable of both the FA dehydrogenation and its reverse reaction. The N-doped carbon hybrid support was obtained by using a controllable chitosan-based pyrolysis method. The pyridinic-N was identified as a main species to interact with the Pd NPs which enhanced the catalytic activity. In line with this work, Pd/N-doped carbon support was reported by using the dicyandiamide as a nitrogen source, which also displayed improved activity for FA dehydrogenation [156]. Besides, the catalytic system was integrated with a fuel cell to demonstrate the practical applications of FA-based H₂ generation in the energy field. The performances of Pd NPs on different zeolite supports including H-BETA, H-Y and H-ZSM-5 were studied by García et al. [157]. The zeolites were able to interact with FA molecules and facilitated the activation, and the porous structure of zeolites were found crucial for FA dehydrogenation. Among the employed zeolite support, the H-BETA exhibited the best catalytic activity because of its high porosity and high surface area. In addition, Wang et al. prepared a novel material of ultra-small Pd clusters (~1.8 nm) on the nanosized silicalite-1 zeolite by a hydrothermal method [158]. The Pd clusters were well dispersed within the channels of the porous support and displayed high activity to dehydrogenate FA into H₂ gas. Besides, the catalysts boasted excellent recyclability and stability.

Ke et al. disclosed a bimetallic core-shell AgPd catalyst supported on MIL-100(Fe) to produce H₂ from FA in aqueous solution at room temperature without additives [159]. The supported catalyst displayed a higher catalytic activity and generated H₂ almost two-fold as that by

unsupported catalyst, which infers the significance of support effect. In addition, Wen et al. reported a core-shell AuPd NPs supported on UiO-66(Zr_{100-x}Ti_x) to facilitate FA dehydrogenation under visible light irradiation at room temperature [160], in which the localized surface plasmon resonance effect and the doped amine functionality in the MOFs were crucial to the boosted catalytic activity. Jiang's group has fabricated a AuPd-MnO_x/(ZIF-8)-rGO composite by a wet chemical strategy to catalyze FA dehydrogenation at room temperature [161]. The reasons for the high catalytic activity were ascribed to the modified Pd electronic states, the small size, high dispersion as well as the positive support effect. A feature review has been published by the group introducing their relevant works on the synthesis of heterogeneous catalysts for FA dehydrogenation [162].

5. Challenges and outlook

In the past decade, the conversion of biomass into FA has remarkably developed with prominent outcomes. The efficiency of the transformation is not any more a major challenge, and many of the catalytic systems can result in highly selective conversion of glucose into FA. Some works exploited powerful catalysts can even directly transform raw woody biomass such as waste paper into FA with relatively satisfactory yields. In particular, a room-temperature transformation strategy has been put forward very recently which has solved the issues such as considerable energy consumption and expensive equipment of previous transformation processes. However, so far, there is still not an integrated system that simultaneously meet all the requirements for industrialization. That is, the catalytic system with high efficiency and low energy costs may suffer from product purification problem, whereas the processes with easy separation could be expensive and energy-intensive. As a result, the major challenge is to establish an economically feasible procedure boasting the features of low-cost, easy product separation, facile handling and catalyst recycling. Future efforts are necessary to disclose cheap and stable catalysts preferably that promotes the reaction in acidic aqueous solutions to enable simple FA separation, and mild reaction conditions are also targeted. For example, the HPAs boast high structural variability and the properties can be finely adjusted to adapt to varied biomass applications. Hence, there is still a huge potential to explore and engineer novel HPA catalysts for more efficient, inexpensive and versatile biomass valorization processes, and eventually to push the FA production from biomass resources into an industrial scale.

At present, CO₂ reduction into FA is often not energy efficient. Since CO₂ is rather thermally and kinetically stable, its transformations generally require considerable energy inputs. If the energy consumed exceeds the energy generated, the utilization is not plausible. As a result, the CO₂ valorization should be coupled with renewable energy supplies such as solar power or solar-driven electric power. Moreover,

the catalyst design and development are significant to diminish the activation energy barriers to improve the conversion efficiency and selectivity. Compared to the chemocatalytic hydrogenation of CO₂, photochemical or photoelectrochemical reduction methods normally generate FA in lower yields in which the rational design of catalysts is more important. Besides, simple, inexpensive and recyclable catalysts are desirable to reduce the capital costs. The process engineering and optimization are of paramount values for the wide application of the CO₂ reduction techniques. Overall, the two sustainable routes for FA production, namely from biomass or CO₂, have the specific advantages and disadvantages. The biomass route is more developed and approaching the practical applications. Particularly, the catalytic oxidation of biomass by HPAs could achieve high yield, high selectivity and easy product separation from sugars or raw biomass resources at relatively low temperature and pressure, which in this regard is superior to the hydrolysis and wet oxidation. The reduction of CO₂ into FA is still challenging at current stage, which may involve expensive catalytic systems, or energy-intensive conditions (high pressure and temperature). As a result, low-cost catalysts and solar-driven conversions are preferable. In the future, collaborative endeavors from chemists, engineers, governors, etc. are indispensable to produce value-added chemicals such as FA from renewable resources such as biomass and CO₂, which will promote the low-carbon sustainable development of the modern industries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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