

Recent strategies for enhancing the catalytic activity of CO₂ hydrogenation to formate/formic acid over Pd-based catalyst

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ABSTRACT

The “greenhouse effect” caused by presence of the large amounts of carbon dioxide (CO₂) is becoming extremely serious for the environment. Therefore, it is crucial to advance the progress of practical technologies to minimize the CO₂ emissions. The catalytic CO₂ hydrogenation with hydrogen (H₂) to form formic acid/formate over Pd-based catalysts has been considered as an effective technology to deal with environment and CO₂ emission issues. In the past decades, increasing efforts have been contributed to these fields and significant achievements have been obtained. In this review, the state-of-the-art of Pd-based heterogeneous catalysts for catalytic conversion of CO₂ to formate/formic acid is systematically summarized. First, the key factors associated with catalytic performance are discussed including Pd metal dispersion, electron density of Pd metal and acidity of supports. Second, major achievements on the design of efficient Pd nanometal supported on various materials, mainly metal-organic frameworks (MOFs), carbon materials, silica, zeolites and other porous material, are summarized. Third, the successful strategies applied to maximize catalytic activity of CO₂ conversion by reducing the particle size of Pd, alloying foreign metal with Pd to change the electron density of Pd, as well as anchoring of functional groups were also highlighted. Special attention has been given to the mechanism of the catalytic reaction. Finally, a brief perspective to the challenges and new directions in the development of innovative catalytic materials to achieve high catalytic activity in CO₂ conversion is also proposed, which would be of great interest in realizing carbon-neutrality in near future.

1. Introduction

The massive combustion of fossil fuels during the past three centuries, leads to enormous emission of CO₂ into the atmosphere. As a result, the atmospheric level of CO₂ has reached a value of 415 ppm in comparison to 250 ppm in the past [1,2]. CO₂ is one of the main greenhouse gases, showing a significant impact on climate and environmental changes, such as increase in the heating of our climatic system, sea-level rise and extreme weather conditions, which has attracted substantial awareness from all over the world [3–14]. Therefore, it is critically important to explore practical technologies to reduce CO₂ concentration in the atmosphere. Many efforts have been planned and executed to reduce the level of CO₂, such as by storing CO₂ in deep sedimentary reservoirs, capturing CO₂ by absorption and adsorption as

well as converting CO₂ into value-added chemicals [8,15–21]. Among these technologies, catalytic CO₂ conversion to form fuels and value-added chemicals appears as an effective technical solution because it can not only alleviate global warming caused by overloaded CO₂ in air but can also show new insights in exploring green and renewable energy to replace fossil fuels [22,23].

A wide range of chemicals including methanol, methane, alcohol and other hydrocarbons has been synthesized through catalytic process by using CO₂ as a renewable and abundant carbon feedstock [24–27]. Among these chemicals, formic acid has received considerable attention recently because it is a green energy carrier, which has the advantages of high energy density, low toxicity and remarkable hydrogen content (up to 4.4 wt.%) [28–31]. Importantly, H₂ can be released in a controlled manner through the decomposition of formic acid in the presence of a

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suitable catalyst [4,30]. Moreover, formic acid is also widely used in diversified industries including leather, medical, pesticide and chemical industry [28,29]. Therefore, catalytic hydrogenation of CO₂ and H₂ to formate/formic acid is one of the economically viable strategies for H₂ storage and CO₂ recycling and this reaction is gaining tremendous research interest in the scientific community.

It is well known that CO₂ is one of the most stable and chemically inactive molecules with a linear molecular structure of O=C=O and a high bond energy of 806 kJ mol⁻¹ [17,32]. The major obstacle for catalytic CO₂ conversion is the dissociation of highly stable C=O bonds, which requires a large energy input [33]. Therefore, design of efficient catalytic system is crucial for reducing the high kinetic barriers of CO₂ during the catalytic conversion process.

Until now, various catalytic systems have been obtained, including photocatalytic CO₂ conversion over semiconductor, homogenous catalytic CO₂ conversion over metal complex as well as heterogeneous catalytic CO₂ conversion with metal nanoparticles (NPs) supported on porous materials [34–39]. Among these catalytic systems, the photocatalytic CO₂ conversion to formate/formic acid is regarded as one of the most environmentally friendly and economical approaches without using H₂ gas and high reaction temperature and pressure. However, the selectivity and photocatalytic activity toward formate/formic acid is still very low when compared with thermo-catalysis [40–42]. In contrast, homogeneous catalytic CO₂ reduction over metal complex usually displays high catalytic activity and selectivity [43]. Until now, a series of metal complexes, including noble-metal-based (Pd, Ru, Rh and Ir) metal complexes as well as non-noble-metal-based (Fe, Co, Cu and Ni) metal complexes, have been explored for catalytic CO₂ reduction with relative high TOF (turnover frequency) in range of 20 to 3,500,000 h⁻¹ [44–72]. Despite the outstanding performance of metal complexes, recycling problems, high-cost as well as stability of metal complexes limits their practical application. Alternatively, heterogeneous catalysts, showing good recyclability and remarkable catalytic activity and selectivity, have received considerable research attention. The uniform dispersion of Pd, Au, Ru, and Ir NPs immobilized on porous materials have been designed and fabricated for the synthesis of formic acid/formate from CO₂ and hydrogen [55,73,74]. However, the catalytic activity of those metal NPs supported catalysts usually display lower catalytic performance as compared to the homogeneous counterparts, probably because of the lower metal utilization efficiency.

Among explored heterogeneous catalysts, Pd-based catalyst is one of the most studied metal and usually displays exceptional activity as compared to other transition metals in both hydrogenation of CO₂ to formic acid/formate and dehydrogenation of formic acid/formate to CO₂ and H₂, due to the high stability in the presence of acidic or basic reaction condition as well as high affinity towards H₂ spillover [75–77]. In 1914, Bredig and Carter reported the pioneering work on heterogeneous catalytic conversion of CO₂ to formate/formic acid with Pd black as the catalyst in the presence of KHCO₃ [76]. Unfortunately, Pd black displayed very low activity and poor stability due to their low metal utilization and easy aggregation [78]. Thanks to the advanced equipment for nanomaterial fabrication and characterization as well as constantly improved knowledge of nanotechnology in the past decades, nano-sized Pd particles as well as Pd single atom supported on porous materials have been studied intensively [1]. Indeed, the catalytic activities of nano-sized metal NPs are dramatically enhanced due to the maximized metal utilization as well as unique physical properties arising from the reduced particle size in the adsorption and activation of CO₂. It is well known that the catalytic activities of those Pd-based catalysts are dependent on the size, composition and structure of metal NPs as well as the chemical and physical properties of support [79,80]. Therefore, Pd-based NPs, including monometallic Pd with different size, bimetallic PdAg, PdCu, PdCo and PdNi supported catalysts have been constructed with the aim of tuning the size and electron density of Pd active sites for CO₂ hydrogenation [49,50,81–91]. Indeed, alloying foreign metal with Pd displays higher catalytic activities as compared with their

monometallic Pd counterparts. On the other hand, the physical and chemical properties of supports play important roles in the uniform immobilization and stabilization of Pd species as well as in the adsorption and activation of CO₂ and H₂. Therefore, various porous supports, such as metal-organic framework (MOFs), carbon materials, silica, zeolite as well as other transition metal oxides were employed as supports [44,49,50,85,90,92–94]. The last few years have witnessed impressive progress in the design of efficient Pd-based catalysts for CO₂ conversion through various synthetic methods. Undoubtedly, the interest is continuously increasing. Thus, a review of the recent advances and challenges on design and architecture of Pd-based catalysts for CO₂ conversion to formate/formic acid is of great importance.

Although several review papers have summarized the progress of catalytic CO₂ conversion to a wide range of chemicals as products, including photocatalytic CO₂ conversion, homogenous catalytic CO₂ conversion and electrocatalytic CO₂ conversion [37,42,43,83,90,95]. Little attention has been paid to the heterogeneous conversion of CO₂ to formic acid/formate. Still now, there is a lack of a review paper on systematically summarized Pd-based catalysts for catalytic CO₂ conversion to produce formic acid/formate from the viewpoints of catalyst design and catalytic reaction mechanism. For the aforementioned reasons, in the present review, we mainly concentrated on progress over the last decades in the heterogeneous catalytic CO₂ conversion over Pd-based catalysts to produce formate/formic acid as value-added organic products. This review will start with the fundamentals of catalytic reaction of CO₂ and H₂ to formate/formic acid and discuss the key factors to promote the activity and stability of catalysts towards formic acid/formate, followed by the summary of the explored Pd supported porous material, emphasizing on the role of porous supports. Then, the successful strategies to maximize the catalytic activity of CO₂ conversion over Pd-based catalysts will be introduced. Based on the understanding of the fundamentals and strategies for regulating catalytic activity of CO₂ conversion, a brief perspective on the challenges and future directions in the development of innovative catalytic materials to achieve high catalytic activity in CO₂ conversion is also proposed in the end, which would be of great interest in realizing carbon-neutrality in near future. We sincerely hope that Pd-based catalysts can serve as powerful materials for practical applications.

2. Key factors of catalytic CO₂ conversion

In order to rationally design Pd-based catalysts for CO₂ hydrogenation to formate/formic acid, it is important to point out the key factors that hinder the catalytic performance. The heterogeneous CO₂ conversion to formic acid/formate is thermodynamically unfavorable due to the change in phase from the gaseous phase (CO₂ and H₂) into liquids product, which requires a great positive change in terms of Gibbs free energy (CO₂(g) + H₂(g) → HCOOH(l), ΔG°_{298K} = 32.9 kJ mol⁻¹) [96]. The most straightforward approach to overcome the thermodynamic limitation is driving the reaction in aqueous phase (such as water, alcohol and ionic liquids). The reaction becomes slightly exothermic due to the solvation effect (CO₂(aq) + H₂(aq) → HCOOH(l) ΔG°_{298K} = -4.0 kJ mol⁻¹) [97]. Furthermore, the hydrogenation of CO₂ becomes more favorable with the addition of base additives into reaction solutions (such as amines, bi/carbonates and hydroxides), which effectively prevents the reverse reactions (the dehydration/dehydrogenation of formic acid) [1]. Undoubtedly, the hydrogenation of CO₂ to formic acid/formate is influenced by many parameters, including the pH of solution, reaction temperature, type of base and the pressure of CO₂ and H₂.

In addition to thermodynamics, the kinetics of heterogeneous CO₂ reduction also have a major impact on the catalytic activity [98]. The interactions of CO₂, H₂ and intermediates with the active sites of catalysts largely determine the catalytic activity [42]. The heterogeneous CO₂ reduction process over solid catalysts mainly involves the adsorption and activation of HC O₃⁻/CO₂ in solution, the adsorption and dissociation of H₂, and the formation and desorption of formate intermediate

over catalysts [91,99–102]. These steps are highly dependent on the number of active sites, the electron density of Pd atom, the interaction forces between chemical molecules and active sites, the transformation rates of $\text{HC O}_3^-/\text{CO}_2$ and H_2 to form formate/formic acid, as well as the pore structure of catalysts for mass transport [1]. Therefore, reducing the size of Pd NPs to expose more surface Pd atom, tuning the electron density of Pd atom as well as anchoring functional groups hold the key to tune the activity of heterogeneous CO_2 reduction. Apart from these factors, the stability of catalysts, especially the stability of Pd atom also play an important role in determining the catalytic activity of CO_2 hydrogenation. As discussed above, hydrogenation of CO_2 into formic acid/formate is usually carried out in alkaline conditions. This requires the catalyst having alkali resistance property. Meanwhile, the Pd NPs always aggregate into large particles or leach into solution during the catalytic reaction process [76]. This suggests that the protection of Pd atoms is also an important factor for achieving high catalytic performance. Up to now, various strategies, including reducing the Pd particle size from nano size to single atom, anchoring functional groups (amines or uncoordinated N as well as other basic functionalities) on supports or Pd NPs, doping Pd NPs with other transition metal atom, confining the Pd NPs within pore or cavity of supports as well as enlargement of surface area were applied for tackling the issues related to catalytic hydrogenation of CO_2 to produce formic acid/formate [1,44,103,104]. With an aim to explore highly active heterogeneous catalysts for industrial applications in the future, the recent advances for these strategies will be systematically elucidated in Section 3 and 4.

3. Pd supported porous catalysts for CO_2 hydrogenation

Porous materials have captivated the attention of scientists in several multidisciplinary areas of research including chemistry and materials science. Their large surface areas, tunable functionalities, size and shape selectivity effects allowed them to be well recognized as support materials in the field of heterogeneous catalysis [105]. Amongst porous solids, organic polymers, zeolites, porous carbon materials and mesoporous silica have been extensively studied because of their remarkable properties like promoting diffusion within the pore spaces and easy surface functionalization. They are often used in conjunction with active metal species (for example Pd) to increase the overall catalytic performance by increasing the number of active sites. They can alter the electronic and geometric structure of metal NPs and increase the interaction of substrate molecules with the active sites to enhance the overall rate of the reaction, as discussed in later subsection. Pd is well known as

the most active metal for CO_2 hydrogenation reaction and the careful selection of appropriate support material can lead to the synergistic enhancement of the catalytic activity (Table 1). Some representative examples exploring the effect of various support materials anchored with Pd NPs will be discussed in this section.

3.1. Porous organic framework supported metal nanocatalysts

Porous organic frameworks have emerged as a promising support material because their properties can be tailored towards specific application based on the preparative procedures. Their remarkable hydrogen storage and CO_2 capture ability prompted researchers to explore their application in CO_2 conversion reactions. Till date, several strategies to incorporate metal NPs within MOF materials have been developed such as impregnation, decomposition, chemical vapor deposition and double solvent method. The MIL-101- NH_2 has free amine groups which assist in the growth of small and uniformly dispersed metal NPs. The unsaturated Cr^{3+} sites can be used to anchor organic amine groups which can further increase the basic sites and hence the CO_2 adsorption capacity of the material. Xu et al. explored the similar approach of the deposition of PdAg bimetallic NPs on triethylenediamine (TEDA) functionalized (1.11 mmol g^{-1}) MIL-101- NH_2 catalyst denoted as PdAg/TEDA-MIL-101- NH_2 [119]. The synthesis strategy for amine group functionalization followed by the impregnation and reduction of PdAg NPs is shown in Scheme 1 [119]. The amine functionalization assisted in the growth of ultra-small metal NPs with a mean diameter of 1.6 nm when compared to 5.4 nm for PdAg/MIL-101- NH_2 . The prepared catalysts displayed type-I isotherm with a specific surface area of $1233 \text{ m}^2 \text{ g}^{-1}$ and large number of micropores in the catalyst. The powder X-ray diffraction (PXRD) peaks for Ag and Pd NPs were not observed implying their smaller size and uniform dispersion on the support. In XPS, the $\text{Cr } 2p_{1/2}$ and $\text{Cr } 2p_{3/2}$ peak in functionalized MOF shifted towards lower binding energy values, probably because of the electron transfer from amine groups to the Cr (III) center. This observation further confirmed the robust interaction between MOF and organic amine groups. The catalytic activity in the CO_2 hydrogenation displayed a turn over number (TON) of 1500 by using 1 M NaHCO_3 solution under pressure condition of 50 bar ($\text{CO}_2/\text{H}_2 = 1/1$) at 70°C for 10 h. The recycling test after fifth cycle displayed 23 % decrease in activity compared to the first cycle catalytic performance. This work can be cited as an example to explore more active catalysts for formic acid production.

The use of poly(ionic liquid)s (PILs) to support highly dispersed Pd

Table 1

The supported Pd catalysts applied for the hydrogenation of CO_2 to formate.

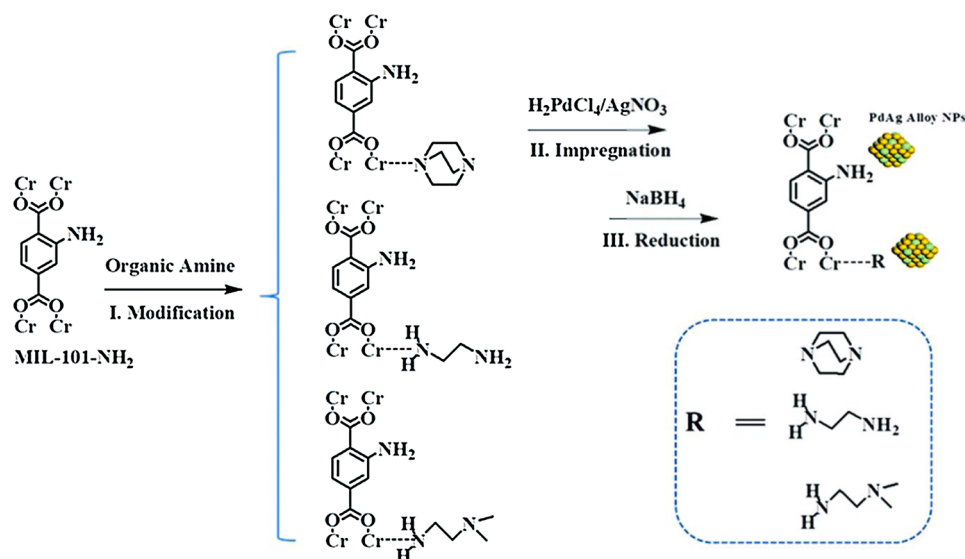
Entry	Catalyst	pH_2/pCO_2 (bar/bar)	Temp. ($^\circ\text{C}$)	Additive	Time (h)	TOF (h^{-1})	TON	Ref.
1	Pd/PIL-2-Tf ₂ N	-/20	80	NaBH_4	1	47,952 ^b	–	[106]
2	Pd/AP-POP	60/60	80	NEt_3	12	–	1279 ^a	[107]
3	Pd/AC	55/-	20	NH_4HCO_3	6	–	1571 ^a	[108]
4	Pd/AC	27.5/-	20	$\text{NH}_2\text{CO}_2\text{NH}_4$	8	–	845 ^b	[109]
5	Pd/r-GO	40/-	100	KHCO_3	32	–	7088 ^b	[110]
6	Pd/C	50/30	40	$[\text{Bmim}][\text{OAc}]$	24	594 ^a	–	[111]
7	$[\text{Pd}(\text{en})_2]\text{Cl}_2$	20/20	80	NEt_3	3 min	–	6860 ^b	[87]
8	Pd/NPMO	10/30	100	KOH	20	108 ^b	–	[74]
9	Pd/g- C_3N_4	25/25	40	–	1.16	1250 ^b	–	[104]
10	Pd/ C_3N_4	25/25	40	–	16	13.3 ^a	–	[112]
11	Pd/g- C_3N_4	25/25	40	NEt_3	24	4.5 ^b	–	[113]
12	Pd/C	25/25	40	NH_4HCO_3	15	–	1769 ^a	[114]
13	Pd/ CeO_2	10/10	40	NaHCO_3	1	746 ^a	–	[115]
14	Pd/chitin	10/10	60	Na_2CO_3	4	257 ^a	–	[116]
15	Pd/u-CN100	35/35	30	–	1	98.9 ^a	–	[117]
16	Pd/ CeO_2	7/7	100	NaHCO_3	1	366 ^a	–	[44]
17	Pd/ ZrO_2	20/20	100	–	1	3000 ^a	–	[118]

TOF = (moles of formate generated)/(Pd on the catalyst_(a,b)* reaction time).

TON = (produced moles of formate) / (moles of Pd_(a,b)).

^a the total amount of Pd in the catalyst.

^b the amount of surface Pd, it was calculated using the following equation: $\text{Pd}_{\text{surface}} = \text{Pd}_{\text{total}} * \text{Dispersion} = \text{Pd}_{\text{total}} / d$ (average size).



Scheme 1. Synthesis strategy and structural representation of PdAg encapsulated on amine functionalized MIL-101-NH₂. Adapted with permission from ref [119]. Copyright 2021 The Royal Society of Chemistry.

NPs was reported to investigate the CO₂ hydrogenation reaction [106]. The PILs are the polymer of ionic liquids, comprising of dications and hydrophobic anions (bis(trifluoromethanesulfonyl)amide, Tf₂N⁻), which can stabilize metal NPs by strong metal-support interactions. Their synthesis procedure doesn't involve the use of templates and organic solvents and can easily be recycled after the reaction. PILs have been reported to alter the electronic structure of Pd NPs to increase the catalytic activity, however, the low chemical activity and selectivity prompts the preparation of highly active heterogeneous catalysts. 1 wt % of Pd immobilized on PIL-2-Tf₂N had uniform distribution of Pd NPs with a particle size of 3.6 ± 0.9 nm. These highly dispersed Pd NPs displayed a TOF of 47,952 h⁻¹ over 1%Pd/PIL-2-Tf₂N in 0.88 M NaBH₄ aqueous solution under 20 bar pressure of CO₂ at 80 °C for 1 h. The plausible mechanism was proposed, and the enhanced catalytic activity was attributed to the synergistic metal-support interactions in the hydrogenation reaction.

Another striking example of employing porous organic polymer (POP) support material for Pd NPs immobilization was reported by Shao and coworkers [107,120]. The basic functionality involving pyridine and amide group-based POPs was employed to generate electron rich Pd species on the surface, designated as Pd/AP-POP. The presence of basic sites and electron rich Pd sites assisted in the CO₂ activation during hydrogenation reaction, further confirmed by CO chemisorption and XPS analysis. During CO₂ hydrogenation to formate reaction, a TON of 1279 was obtained with reaction conditions of 80 °C for 12 h under pressure condition of 80 bar (CO₂/H₂ = 1/1). This performance was much inferior when compared with other reference catalysts, Pd/C₃N₄ (694) and Pd/AC (302). This work can be referred as an example for tuning the electronic state of active sites by the careful modification of support material to promote the catalytic reaction.

3.2. Porous carbon supported metal nanocatalyst

Until 2015 most of the reported reversible hydrogen storage systems were homogeneous which created the problem of separation and regeneration of catalysts. Su et al. reported the liquid phase bicarbonate/formate hydrogen storage system using Pd/activated carbon-based catalysts [108]. Authors investigated the use of several Pd supported materials for example, Al₂O₃, CaCO₃ and BaSO₄ but activated carbon (AC) support displayed superior catalytic performances. All catalysts contained 5 wt % of Pd NPs and purchased from Sigma-Aldrich®. The hydrogenation of bicarbonate is a complicated gas-liquid-solid

multiphase reaction, and it was speculated that the dispersion of hydrogen is the rate determining step because of its low solubility in aqueous medium. Being hydrophobic in nature, the activated carbon can store hydrogen within the porous channels or on the surface by the spill over from Pd NPs. The localization of higher amounts of hydrogen on the carbon surface can attribute to its active catalytic performance. Furthermore, the presence of larger number of active Pd sites were formed on the activated carbon surface in comparison to other oxide supports. The effect of increasing the temperature of the reaction was studied in which higher reaction temperatures increases the rate of hydrogenation but decreases the equilibrium yield of the reaction from 95 % to 50 %. A TOF of 782 h⁻¹ for the hydrogenation of NH₄HCO₃ was obtained at H₂ pressure of 27.5 bar and 1578 h⁻¹ for the dehydrogenation of ammonium formate with an initial nitrogen pressure of 1 bar at 80 °C.

The same research group extended the approach of hydrogenating ammonium carbonate to formate species in 70 wt % ethanolic solution under 27.5 bar H₂ pressure and Pd/AC nanocatalyst [109]. This strategy involves the conversion of industrial intermediates, generated during the production of urea or carbon capture techniques, into value-added formate species. For example, ammonium carbamate (NH₂CO₂NH₄) and ammonium carbonate ((NH₄)₂CO₃) are formed when ammonia reacts with CO₂ as shown in Eq. (1) and (2).



It was interesting to observe the significant higher hydrogen efficiency of these two salts in comparison to NaHCO₃ and Na₂CO₃ at higher ethanol: water ratio as shown in Fig. 1 [109]. The difference in the formate yield was dependent on the type and ratio of solvent used in the reaction. The NaHCO₃ gave highest formate yield in pure water while the same reaction formed no products when anhydrous ethanol was used as the solvent because of decreased solubility of NaHCO₃ in ethanol. The superior yields of ammonium carbamate and ammonium carbonate in ethanol was due to the formation of ethyl carbonate ions, however, these ions tend to become less stable when the proportion of water was increased in the solvent. This observation was further studied by ¹³C NMR spectroscopic studies which revealed the formation of ethyl carbonate ions attributing to the superior hydrogenation efficiency.

The continuing efforts in the design and synthesis of carbon-based nanocatalysts for rechargeable hydrogen battery was explored by uti-

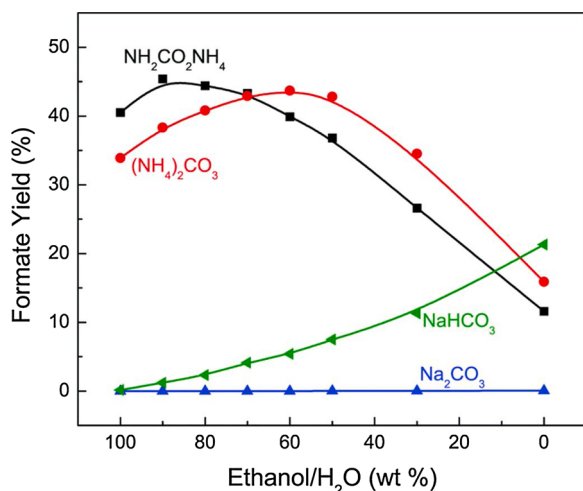


Fig. 1. Effect of solvent in the CO₂ hydrogenation reaction using derived salts. Reaction conditions: 0.1 g Pd/AC (5 wt %) dispersed in 20 mL solvent (ethanolic aqueous) containing 0.5 M salts at 20 °C for 1 h with initial 25 bar H₂. Adapted with permission from ref [109]. Copyright 2015 Royal Society of Chemistry.

lizing graphite oxide nanosheets as the robust support material for Pd NPs deposition [110]. The key factors for achieving exceptional hydrogen storage/release efficiency are the optimization of the combination of metal and support material for creating metal-support synergistic interaction. For example, the reduced graphite oxide (r-GO) provides microstructural properties to firmly anchor Pd NPs and acts as an efficient and robust catalyst for practical applications. The anchoring of Pd NPs in the absence of capping or stabilizing agents was rarely reported till then. The Pd/r-GO was prepared by impregnation followed by NaBH₄ reduction with Pd NPs average diameter of 2.4 ± 0.1 nm. The metal-support interaction effects were studied in depth and analyzed that r-GO facilitated the formation of highly strained Pd nanocrystals which are responsible for the superior catalytic performances in the hydrogenation of KHCO₃ to potassium formate (PF). At much lower H₂ pressure of 40 bars, TON of 7088 was obtained at 100 °C [110]. This catalyst was also reported to be active in the dehydrogenation of PF (TOF = 11,299 h⁻¹) and hence making the system viable for reversible and controlled hydrogen storage for sustainable energy supply in the near future.

A simple and efficient catalytic system for CO₂ hydrogenation was reported over Pd/C based catalysts using ionic liquids (ILs) as the solvent (Fig. 2a) [111]. The Pd/C based catalyst displayed porous structure with a very tiny Pd NPs size of 1.7 nm. The N₂ physisorption analysis showed the integration of both mesopores and micropores in the catalyst. ILs are made of organic cations and inorganic anions with low vapor pressure and special H-bonding interaction amongst ions. Their specific properties can be tailored by the careful selection of anions and cations

for the formation of ILs. For example, for CO₂ hydrogenation reaction, the use of pyrimidine and azolate based ILs are well reported to increase the efficiency of the reaction. This is possible via the activation of CO₂ due to the presence of electronegative sites with nitrogen and oxygen atoms. In this report, [bmim] [OAc] (1-butyl-3-methylimidazolium acetate) was used as the IL solvent in the absence of basic conditions [111]. The role of IL involves the capture and activation of CO₂ to form a carbene intermediate and also changing the electronic properties of Pd to improve the catalytic activities, as studied by NMR analysis. A TON of 594 was obtained at 40 °C with a formic acid generation rate of 233.5 mmol · g⁻¹ h⁻¹. Based on the observations obtained via NMR analysis, a plausible reaction pathway was proposed as shown in Fig. 2b [111]. The process initiates with the proton extraction from the C2 position of [bmim]⁺ to form a carbene intermediate which can capture CO₂ to form a carboxylate intermediate. The gaseous H₂ is activated by the Pd NPs dispersed in the IL to form Pd-H species followed by carboxylate intermediate protonation to generate FA and regenerate IL and Pd NPs.

A unique structural electrocatalyst of Pd@TiO₂ NPs supported on single walled carbon nanohorns (SWCNHs) were prepared for the direct reduction of CO₂ to formic acid [121]. The small sized Pd NPs of 1.5 nm are protected in the phase of TiO₂ supported on high surface area nano-carbon. The catalyst could electrochemically activate the CO₂ to form formic acid at zero overpotential values in the aqueous phase. The release of hydrogen via FA dehydrogenation was also possible making it as an ideal hydrogen storage/release system.

3.3. Zeolite and mesoporous silica-supported metal nanocatalysts

Zeolites are microporous support materials with ordered channels and excellent thermal stability. They are suitable to accommodate guest molecules within their matrix to achieve superior catalytic and thermal properties. The ultra-small sub-nanometer sized Pd-Mn clusters immobilized in the silicalite-1 zeolite was prepared by the hydrothermal synthesis method [87]. A ligand-protected method was employed in which [Pd(en)₂]Cl₂ and (Mn-TEPA)Cl₂ were used as precursors to prepare bimetallic nanoclusters under hydrothermal conditions at 170 °C for 3 days. The electron rich Pd species formed by the synergistic bonding between Pd-Mn clusters led to the CO₂ hydrogenation rate of 2151 mol_{formate}mol_{Pd}⁻¹ h⁻¹ at 80 °C. The density functional theory (DFT) findings showed the synergistic bonding between Pd and Mn forms a compact structure and passivated Pd active sites to prevent the strong binding of the intermediates formed during the FA decomposition.

The catalytic reaction between CO₂ and H₂ to produce formate/formic acid has a Gibbs free energy change, $\Delta G^\circ = 32.9$ kJmol⁻¹ at ambient temperature conditions. The use of suitable base in the reaction media or its modification with the catalyst surface is one of the several strategies to overcome the thermodynamic barrier of the hydrogenation reaction. Many researchers have reported the use of N-heterocyclic carbenes, carbon nitride and amine functionalized porous silica materials as the source for introducing basic sites in the catalyst. Mesoporous

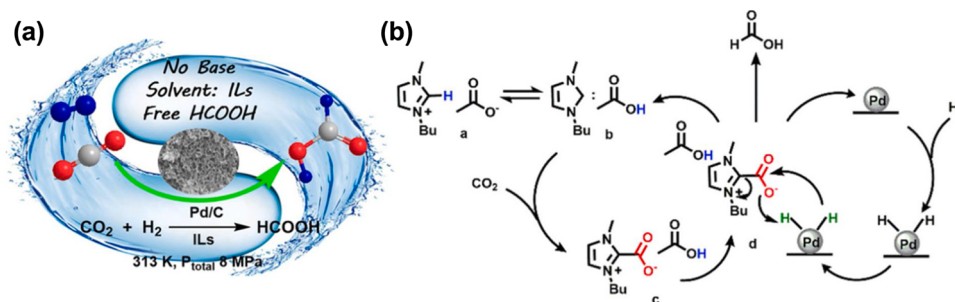


Fig. 2. (a) Schematic illustration of employing Pd/C catalysts for CO₂ hydrogenation in IL solvent (b) Plausible reaction mechanism for the FA generation. Adapted with permission from ref [111]. Copyright 2019 American Chemical Society.

organic silica materials can be easily modified with basic functional groups, however, the introduction of active sites without the use of polymer or capping agents is still challenging. Recently, Vinod et al. has reported a design strategy to synthesize nitrogen-modified periodic mesoporous organosilica (NPMO) by utilizing N-containing tris-organosilane precursor and tetraethyl orthosilicate (TEOS) as the silica source (Scheme 2) [74]. The active Pd sites were introduced by impregnation and chemical reduction with NaBH₄ in the absence of surfactant species. The presence of nitrogen in the silica acted as a pseudo ligand for the stabilization of Pd NPs due to its strong interaction with N atoms in the framework. A TOF of 108 h⁻¹ was obtained for the formate synthesis under 40 bar (CO₂/H₂ = 1/3) at 100 °C. Under identical conditions, Pd NPs immobilized on SBA-15 displayed a TOF of 9.4 h⁻¹. However, increasing the temperature from 100 °C to 150 °C, the structural deformation in the framework and the aggregation of Pd NPs was observed.

3.4. Metal nanocatalysts supported by other porous materials

The Pd NPs with a particle size of 1.7 nm immobilized on mesoporous graphitic carbon nitride (mpg-C₃N₄) were investigated for the reversible chemical hydrogen storage system [103]. A 10 wt % of Pd NPs was loaded onto mpg-C₃N₄ by a simple impregnation followed by H₂ reduction method without any polymer or stabilizing agents. The mpg-C₃N₄ can assist in the CO₂ capture and activation that can react with H₂ to form formic acid using triethylamine as a base and pressure of 40 bar at 100 °C. The FA production was dependent on the reaction conditions such as total pressure and temperature as enlisted in Table 2 [103]. The Pd/mpg-C₃N₄ catalyst displayed catalytic activity two times higher than the commercial Pd/C catalyst due to the higher affinity of mpg-C₃N₄ towards CO₂.

Another similar approach of utilizing C₃N₄ as a support material to deposit Pd NPs was reported by Park et al. due to the higher affinity of C₃N₄ towards CO₂ [104]. The g-C₃N₄ was prepared by the pyrolysis of cyanamide at 550 °C followed by Pd NPs deposition using palladium nitrate solution and hydrazine reduction. The direct synthesis of formic acid from the hydrogenation of CO₂ was explored under neutral conditions without adding any additives at 40 °C under pressure of 50 bar (H₂/CO₂ = 1/1). The prepared catalyst displayed a yield of 306.7 μmol mol_{Pd}⁻¹ s⁻¹ over 1.4 wt % Pd deposited on g-C₃N₄. The same research group has reported a lower yield of 120 μmol mol_{Pd}⁻¹ s⁻¹ when PdNi bimetallic NPs were deposited on carbon nanotube (CNT) which shows the efficacy of using C₃N₄ as the support material [86]. The catalyst also displayed excellent recycling ability up to seven cycles which can prove

Table 2
CO₂ hydrogenation over Pd/mpg-C₃N₄^a.

Entry	Pressure ^b (bar)		Temp. (°C)	Formic acid ^c (mmol)
	CO ₂	H ₂		
1	20	20	100	1.74
2	13	27	100	1.70
3	27	13	100	1.22
4	20	20	150	3.62
5	13	27	150	4.74
6	10	30	150	4.26
7	5	35	150	3.44
8 ^d	13	27	150	2.05
9 ^e	13	27	150	n.d.

^a 50 mg of Pd/mpg-C₃N₄ dispersed in 10 mL of D₂O and 2.5 mL of triethylamine and the mixtures were continuously stirred for 24 h.

^b Pressure at 25 °C.

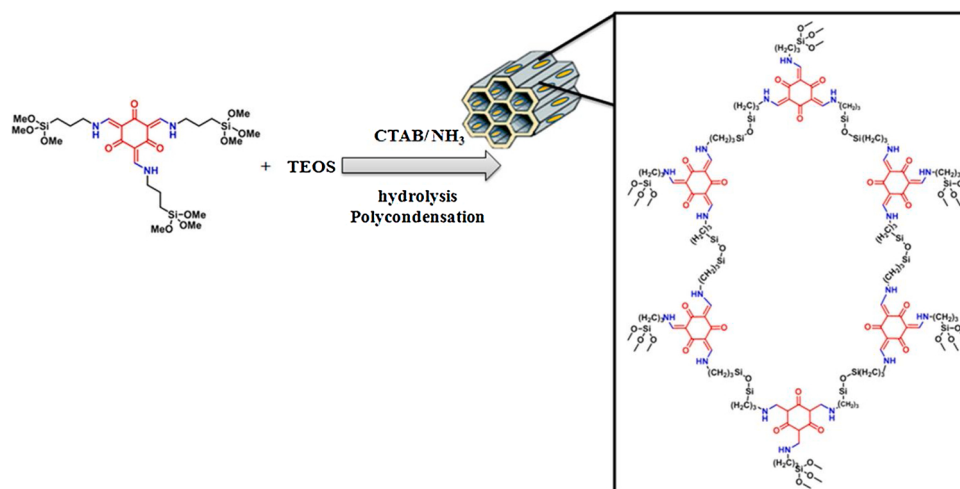
^c Analysis by ¹H-NMR and the internal standard is acetone.

^d Reference sample: 10 % commercial Pd/C.

^e Reference sampler: mpg-C₃N₄.

to be pivotal for the practical applications.

The same type of the catalyst Pd/g-C₃N₄ was explored by Mondelli et al. to fine-tune the carrier defects in g-C₃N₄ in order to enhance the catalytic activity and stability of the material for CO₂ hydrogenation reaction [122]. The post synthetic modifications of g-C₃N₄ to tune the basic properties were C-enrichment, hard templating and thermal exfoliation techniques to form carbon nitride with increased number of edge sites. The calcination of dicyandiamide at high temperatures of 823 K with a ramp rate of 2.3 K min⁻¹ for 4 h yielded bulk carbon nitride (BCN). The mesoporous carbon nitride (MCN) was obtained by treating a mixture of cyanamide and SiO₂ in water at 373 K to completely evaporate the water followed by calcining at similar conditions as mentioned above for BCN. The obtained brownish-yellow powder was then treated with NH₄HF₂ solution for 48 h to remove the silica template and form MCN. The thermal treatment of BCN at 773 K under static air conditions formed exfoliated carbon nitride (ECN). Amongst the BCN (bulk), MCN (mesoporous) and ECN (exfoliated) carbon nitride, ECN was found to be more efficient in generating large number of edge defects in the support. Furthermore, the optimization of reaction conditions with respect to the loading of the Pd amount, reaction time, temperature and pressure, led to the 20-fold enhancement in the CO₂ hydrogenation catalytic activity. As shown in Fig. 3 [122], the optimum temperature and pressure was chosen to be 50 bar and 40 °C. Although the activity is higher at 70 bar due to the increase in the solubility of both the gaseous reactants, the use of 50 bar was selected to minimize



Scheme 2. Synthetic strategy for N-modified periodic mesoporous silica (NPMO) through hydrolysis and polycondensation under basic conditions. Adapted with permission from ref. [74] Copyright 2020 American Chemical Society.

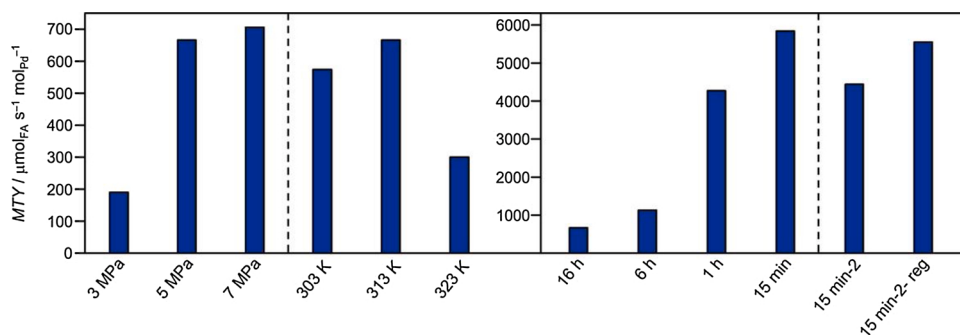


Fig. 3. Metal time yield (MTY) of FA to study the effect of pressure, temperature, reaction time and recycling tests with and without regeneration over 2Pd/ECN-1 h. Reproduced with permission from ref [122]. Copyright 2018 Wiley-VCH.

the energy consumption which is preferable for practical application. The stability tests were carried out on 2Pd/ECN (2.0 wt % Pd) catalyst and found that the morphology and basicity are preserved with no leaching and sintering of the metal NPs.

4. Strategies for enhancing the catalytic activity of CO₂ hydrogenation

4.1. Design of single atom catalysts

Single atom catalysts with uniform, isolated and spatially separated active sites, bridges the advantages of heterogeneous and homogeneous catalysts for organic transformation reactions. Single atom catalysts generally display excellent catalytic activity and considerable high stability as compared with their heterogeneous counterparts due to maximized metal utilization and a large number of active metal sites, showing great potential as an alternative of homo- and heterogeneous catalyst [123–125].

Numerous approaches have been proposed in the architecture of single atom catalysts for CO₂ conversion, and Ir, and Ru atoms anchored on various porous supports were fabricated and reported with high catalytic activity and selectivity toward formic acid/formate production [126,127]. The employed porous supports such as organic polymers, MOFs as well as layered materials, are always featured by high surface area, a large number of metal binding sites as well as considerable amounts of basic groups for CO₂ adsorption [104,128–131]. For instance, Tshuma et al. has reported the synthesis of two-dimensional isostructural MOF with Pd (II) active sites (Pd@Mg:JMS-2 and Pd@Mn:JMS-2) prepared by using 2,2'-bipyridine-4-4'-dicarboxylate (bpd) as ligand and Mg/Mn ions as metal center [83]. The as-prepared samples were further treated to remove the residual organic molecules in pore structure. Then, the catalytic activities of treated MOFs were investigated by catalytic CO₂ hydrogenation to produce formate. The reaction for the CO₂ reduction to generate formate over treated samples in the presence of base under certain temperature and pressure is shown in Eq. (3).



Several test reactions were carried out to find the optimum conditions such as appropriate base, temperature and pressure conditions in order to achieve the highest turnover number (TON) values, as KOH, 100 °C and 50 bar (CO₂/H₂ = 1:4), respectively. After 24 h of reaction, the activated MOFs displayed TON values of 7272 and 9808 over Pd@Mg:JMS-2 and Pd@Mn:JMS-2, respectively. The findings suggest that Pd incorporation within the MOF increased the catalytic activity by two times when compared with Pd complex species. The superior performance with MOF was attributed to the presence of open metal sites which can enhance the adsorption of CO₂ and H₂ gases before catalysis. Furthermore, the presence of active sites is incorporated within the pores of the MOF and not on the surface, which was demonstrated by

thiol poisoning experimental studies. When bulky benzylmercaptan and 2-mercapto-ethanol was used in the reaction to poison the Pd sites, 2-mercapto-ethanol which is smaller and can easily penetrate the pores decreased the TON by 60 % in comparison to bulky benzylmercaptan (20 % inhibition). Furthermore, the catalyst stability was investigated by various characterizations. The results suggested that the physical properties of the recycled MOFs were retained after catalytic reactions. It was concluded that the catalytic performance of homogeneous catalyst can be significantly increased by anchoring homogeneous catalysts within the framework MOFs. The design and development of such Pd-based catalysts is necessary with the aim to increase the efficiency of the reaction and find an alternative of expensive Ir- and Ru-based catalysts. Up to now, very few studies have focused on the construction of single Pd atom supported catalysts for the application of formic acid/formate production from CO₂. However, due to the maximized metal utilization and exceptional catalytic performance of single atom catalysts, single Pd atom supported on MOFs, COFs or other porous materials bearing metal anchoring sites would be a new research direction in the near future.

4.2. PdM bimetallic catalysts

It is well known that the geometric and electronic properties of Pd plays a vital role in achieving high catalytic activity of CO₂ hydrogenation. The most common strategy is to tailor the geometric and electronic properties of Pd NPs through alloying or by forming a core-shell structure with a second transition metal, which has lower electronegativity as compared with Pd. As a result, the electron density of Pd changed by transfer of charge due to the difference in electronegativity of two metals leading to the enhancement of Pd catalytic performance. For example, PdAg, PdNi, PdCu, PdMn NPs with alloy or core-shell structures have been developed, and the improved catalytic activity of bimetallic catalysts was observed as compared with monometallic Pd counterparts. For example, Yan and co-workers have synthesized a novel catalyst, Pd_xCo_{1-x} bimetallic NPs encapsulated inside the channels of mesoporous silica nanospheres (Pd_xCo_{1-x}@MSN) via a one-pot ligand protected synthetic route [49]. The size of Pd_xCo_{1-x} bimetallic NPs with different Pd/Co molar ratios are in the range of 1.7–1.9 nm. In order to elucidate the electronic properties of catalyst, XPS (X-ray photoelectron spectroscopy) was applied. The Pd 3d_{5/2} XPS spectra of Pd_{0.8}Co_{0.2} supported sample displays two peaks at 335.2 and 340.5 eV, the two peaks are shifted to lower binding energies as compared with metallic Pd supported samples, which suggested the generation of electron-rich Pd sites after alloying with Co. This result is further confirmed by X-ray absorption and in situ CO-DRIFT (Diffuse reflectance infrared Fourier transform) measurements, where a small edge shifted to lower energy in Pd K-edge XANES (X-ray absorption near-edge structure) profile of Pd_{0.8}Co_{0.2}@MSN sample and stronger bridging-adsorbed CO peaks shifted to lower wavenumber in FTIR spectra of CO adsorbed on Pd_{0.8}Co_{0.2}@MSN were observed as compared to spectra of metallic Pd

supported samples. The catalytic activities of samples were evaluated in NaHCO₃ (1 M, 20 bar H₂) solution at 100 °C. Among all tested samples, Pd_{0.8}Co_{0.2}@MSN exhibited the highest catalytic activity. The HCOONa generated over Pd_{0.8}Co_{0.2}@MSN reaches up to 408 mol_{FA}mol_{Pd}⁻¹ h⁻¹, corresponding to the TOF of 777 h⁻¹, which is about nearly 2 times of Pd@MSN (Fig. 4a) [49]. The catalytic stability of Pd_{0.8}Co_{0.2}@MSN was studied and the activity of Pd_{0.8}Co_{0.2}@MSN remains unchanged even after 5 cycles (Fig. 4b) [49], suggesting the high catalytic stability of Pd_{0.8}Co_{0.2}@MSN. In addition, the catalytic activity of Pd_{0.8}Co_{0.2}@MSN can be further enhanced under optimized the reaction conditions, the best catalytic activity was obtained under the pressure of 20 bar (H₂/CO₂ = 1/1) and 2 mL of 1.5 M KHCO₃ solution at 100 °C. The authors concluded that the enhanced catalytic efficiency can be attributed to the formation of electron-enriched Pd surfaces in facilitating the hydrogenation of bicarbonate.

It is widely accepted that the distribution of PdM bimetallic NPs is also an important factor in affecting the catalytic activity. Till date, several strategies have been developed to incorporate bimetallic PdM NPs on various porous supports bearing basic groups with an aim to promote the distribution of PdM NPs and enhance the adsorption and activation of CO₂. For example, our group reported the hydrogen storage/production system by CO₂ hydrogenation to form formic acid and dehydrogenation of formic acid to release H₂ over Pd₁Ag₂ NPs encapsulated within the zeolitic imidazolate framework (ZIF-8) [90]. The catalyst was prepared by “bottle around ship” approach in which PdAg NPs were loaded onto the ZIF-8 core followed by an additional layer of ZIF-8 as illustrated in Fig. 5a [90]. The growth of ZIF-8 core was carried out by using 2-methylimidazole (Hmin) and Zn²⁺ as the organic linker and connecting center, respectively. The prepared MOF was then loaded with PVP-stabilized PdAg NPs followed by an additional layer of ZIF-8 to form ZIF-8@Pd₁Ag₂@ZIF-8. The pre-synthesized 0.5 mL of PdAg NPs (9.4 μmol) was added during the synthesis which gave the metal loading of 2.98 % by ICP analysis. The average size of PdAg alloy NPs, which was well distributed between by ZIF-8 (zeolitic imidazolate framework) shell and ZIF-8 core, was measured to be 2.8 nm. The chemical states of the Pd and Ag was examined by spectroscopic methods. The Fourier transform (FT) of k³-weighted extended X-ray absorption fine structure (EXAFS) data at the Pd K-edge and Ag K-edge of Pd₁Ag₂ alloy solution, Pd foil and Ag foil suggested that the electron density of Pd species in Pd₁Ag₂ was enhanced due to the transfer of charge from Ag to Pd. Fig. 5 (b) displays the catalytic activities over different ratios of PdAg NPs where the optimum ratio of Pd:Ag was found to be 1:2 in order to achieve the superior catalytic activity, much higher than that of unsupported PdAg NPs and ZIF-8@Pd@ZIF-8 without Ag alloying [90]. The enhanced catalytic activity can be associated with the electron rich Pd sites and the presence of basic sites in ZIF-8, which assisted in the synergistic enhancement of the catalytic activity in the formation of FA and H₂. This study successfully demonstrated the significance of core-shell nanostructure in order to prevent the aggregation of metal NPs and hence achieve the superior catalytic performances by alloy NPs.

Apart from alloy distribution, the effect of alloy structure on the catalytic activity of bimetallic PdM supported catalysts has also been studied by Yamashita lab [49]. The authors prepared a series of PdAg NPs supported TiO₂ with precise control of the surface-exposed Pd atoms, including Ag@Pd/TiO₂ with little Pd atoms exposed on the surface of alloy NPs, PdAg/TiO₂ with Pd atom randomly distributed in the alloy NPs and Pd@Ag/TiO₂ with most Pd exposed on the surface of alloy NPs. The catalytic activities of those PdAg NPs supported on TiO₂ were investigated for CO₂ hydrogenation to formate at 100 °C for 24 h in the presence of NaHCO₃ under 20 bar H₂/CO₂ (1/1). Among the tested catalysts, Pd@Ag/TiO₂ displayed the highest TON of 14389, much higher than that of Pd/TiO₂, Ag@Pd/TiO₂ and PdAg/TiO₂. The improved catalytic performance of Pd@Ag/TiO₂ can be attributed to the electron-enriched Pd atoms generated by alloy effect as well as high density of surface-exposed Pd atoms in promoting the rate determining reduction step of the adsorbed HC O₃⁻ species. The recent works related to the design and synthesis of PdM alloy NPs for the application of catalytic CO₂ conversion to produce formic acid/formate are summarized in Table 3 [49,50,81,82,84–91,132–134]. On the basis of previous studies, it can be concluded that the alloy particle distribution, the electronic density of Pd atom, the density of surface-exposed Pd atoms play an important role in the catalytic activity of PdM bimetallic catalyst for hydrogenation of CO₂ to formic acid/formate. These works will stimulate further research into the fabrication of bimetallic or multi-metallic Pd based catalyst for catalytic CO₂ conversion.

4.3. Functional group modified catalysts

In the last decades, numerous modification methods have been explored to tune the chemical and physical properties of catalysts, and the most widely used method is anchoring of the functional groups on the support or active sites. Numerous studies have demonstrated that tuning the interfacial properties of catalysts have extremely important positive effects to enhance their catalytic activity and selectivity. In the case of CO₂ hydrogenation to formic acid/formate, nitrogen containing or amine groups anchored basic supports (such as amine/nitrogen functionalized MOFs, N-containing carbon materials and organic polymers) are frequently employed as supports for catalyst fabrication due to their high affinity towards efficient CO₂ capturing. Most of these materials can be obtained by in-situ preparation methods, in which amine/N functionalized organic compounds are used as starting materials or building blocks. The pre-synthetic methods to obtain the functionalized supports as well as the role of basic functionalities are discussed in section 3, so it will not be discussed in this section. Apart from pre-synthetic methods for anchoring functional group, amine groups anchored on porous materials by post-synthetic methods are alternative to those N-containing or amine functionalized materials.

Inspired by enzymic catalysis, Zhao and co-workers employed three different surfactants for the synthesis of interfacially cross-linked reverse micelles to engineer the environment surrounding Pd NPs

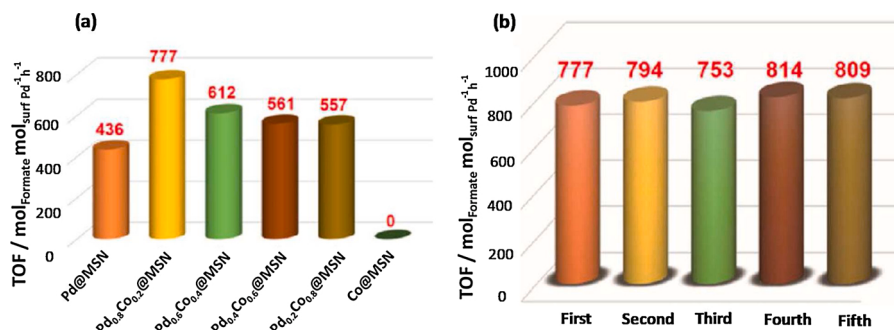


Fig. 4. Catalytic activity of Pd_xCo_{1-x}@MSN (a) and stability tests (b) of the Pd_{0.8}Co_{0.2}@MSN for NaHCO₃ hydrogenation. Adapted with permission from ref [49]. Copyright 2019 Wiley-VCH.

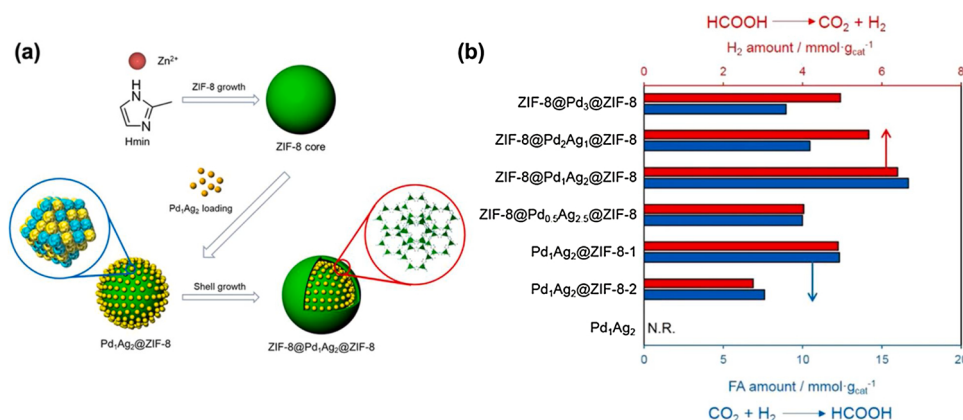


Fig. 5. (a) schematic illustration of the synthesis of ZIF-8@PdAg@ZIF-8 and (b) comparison of catalytic activities for CO₂ hydrogenation (blue) and FA dehydrogenation (red) over prepared catalysts. Adapted with permission from ref [90]. Copyright 2019 Nature.

Table 3

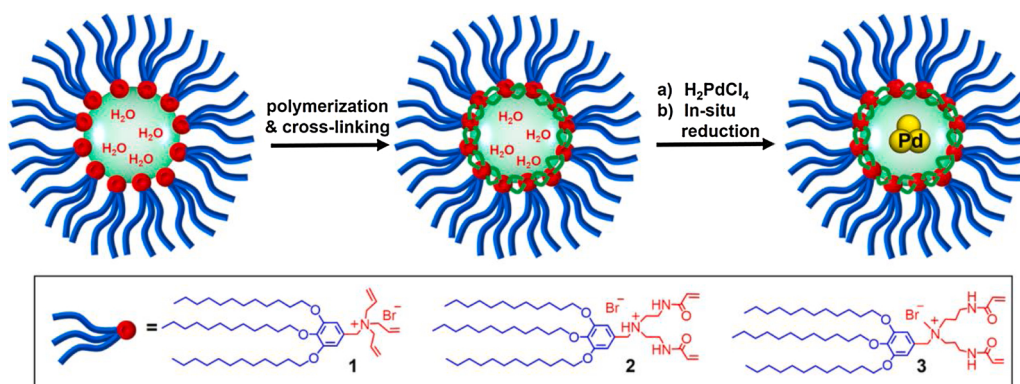
PdM bimetallic catalysts for CO₂ hydrogenation to formic acid/formate.

Entry	Catalyst	pH ₂ /pCO ₂ (bar/bar)	Temp.(° C)	Additive	Time (h)	TOF (h ⁻¹)	TON	Ref.
1	PdAg/TiO ₂	10/10	100	NaHCO ₃	24	–	748	[50]
2	PdAg/amine-MSC	10/10	100	NaHCO ₃	24	–	839	[89]
3	PdAg/NPs	20/20	40	–	24	–	241	[81]
4	PdNi/CNT-GR	25/25	40	–	15	–	6.4	[86]
5	PdAg@NMHCS-0.6–500	10/10	100	NaHCO ₃	24	–	2750	[88]
6	Pd ₂ Cu _{1.4} -N@MHCS	10/10	100	NaHCO ₃	24	–	1432	[132]
7	Pd ₂ Ag ₈ -P@MHCS	10/10	100	NaHCO ₃	24	–	2680	[82]
8	PdAg-PEI@HMOS	10/10	100	NaOH	22	125	2754	[84]
9	PdAg/TiO ₂ @ZIF-8	10/10	100	NaHCO ₃	6.0	–	913	[133]
10	Pd-Cu/ZnO/Al ₂ O ₃	50/10	150	–	10 min	38.15	–	[85]
11	Pd _{0.8} Co _{0.2} @MSN	10/10	100	KHCO ₃	–	1824	–	[49]
12	PdAg/SBA-15-amine-5	10/10	100	NaHCO ₃	24	–	874	[134]
13	PdAg/amine-RF10	10/10	100	NaHCO ₃	24	867	–	[91]
14	Pd@Ag/TiO ₂	10/10	100	NaHCO ₃	24	14 839	–	[50]
15	PdMn0.6@S-1	20/20	80	NaOH	–	2151	–	[87]
16	ZIF-8@PdAg@ZIF-8	10/10	100	NaHCO ₃	24	1191	–	[90]

(Pd@ICRM) for hydrogenation of bicarbonate and CO₂ [135]. The Pd NPs were confined within the hydrophilic core of the micelles bearing amine groups as illustrated in Scheme 3 [135]. The as-prepared Pd@ICRM was applied for catalytic CO₂ reduction. It was found that the head group of the employed surfactant plays an important role in affecting the catalytic performance of Pd@ICRM. Quaternary ammonium-based catalyst (Pd@ICRM3) displayed higher affinity towards bicarbonate adsorption. The catalytic activity of Al₂O₃-doped Pd@ICRM(3) displayed a TON of 580 in the 1,4-dioxane/D₂O (3/2) mixtures at ambient temperature and 40 bar H₂ for 8 h, which is higher than that of Pd@ICRM(1) and Pd@ICRM(2), whereas the tertiary

amine-based catalyst Pd@ICRM(2) performed well in CO₂ hydrogenation as compared with Pd@ICRM(3), gave a TON of 250 in the 1,4-dioxane/water (3/2) mixtures under 40 bar CO₂ and 40 bar H₂ for 20 h. The high catalytic activity of these catalysts can be attributed to the reversible formation of carbamate and subsequent diffusion to metallic Pd core.

In addition to decorating basic functionalities around Pd NPs, N functionalities anchored on porous supports have also been reported for CO₂ hydrogenation. Various basic molecules with N functionalities have been utilized as modifiers for the development of amine-functionalized supports with the aim of improving the catalytic activity. For example,



Scheme 3. Schematic illustration of the preparation of Pd@ICRM. Adapted with permission from ref [135]. Copyright 2017 American Chemical Society.

phenylamine-grafted SBA-15 has been synthesized by post-modification method [134]. The as prepared supports were subsequently used to support tiny PdAg NPs by a simple impregnation method. Indeed, the catalytic activity significantly improved after phenylamine modification, giving a TON of 874 after 24 h in a 1.0 M NaHCO₃ solution under 20 bars (H₂: CO₂ = 1:1). The enhancement can be explained due to the relative weak basicity of phenylamine moderating the interactions with formate for the stabilization of adsorbed formate and enhancing the HC O₃⁻/CO₂ adsorption. Inspired by this work, tiny PdAg NPs with an average diameter of 1.2 nm supported on phenylamine-functionalized mesoporous carbon were prepared (PdAg/amine-MSC) for CO₂ hydrogenation [89]. A TON of 839 was obtained over PdAg/amine-MSC after 24 h in a 1.0 M NaHCO₃ solution under 20 bar (H₂: CO₂ = 1:1). It is well known that leaching of functional group and active metal sites often occurs during the catalytic reaction process. In order to solve the leaching problems, a novel catalyst (PdAg-PEI@HMOS), hollow mesoporous silica spheres encapsulated PdAg NPs as active metal and poly (ethyleneimine) as amine moieties were prepared [84]. As a result, a total TON of 2754 in 22 h was obtained in a 0.1 M NaOH solution under 20 bar (H₂: CO₂ = 1: 1). The catalytic stability was evaluated by continuously running for five cycles, the catalytic activity of fifth cycle did not decrease, and a total TON of 13,700 in five cycles was obtained, demonstrating the high catalytic activity and stability of PdAg-PEI@HMOS. These works clearly demonstrated that anchoring N functionalities on supports by pre-synthetic or post- synthetic methods can not only improve the adsorption of CO₂/HC O₃⁻, but also plays important roles in the fabrication of tiny PdM metal NPs and facilitating the rate-determining step of CO₂ hydrogenation to formate, leading to enhanced catalytic performance.

4.4. The plausible mechanism for CO₂ hydrogenation to formic acid/formate

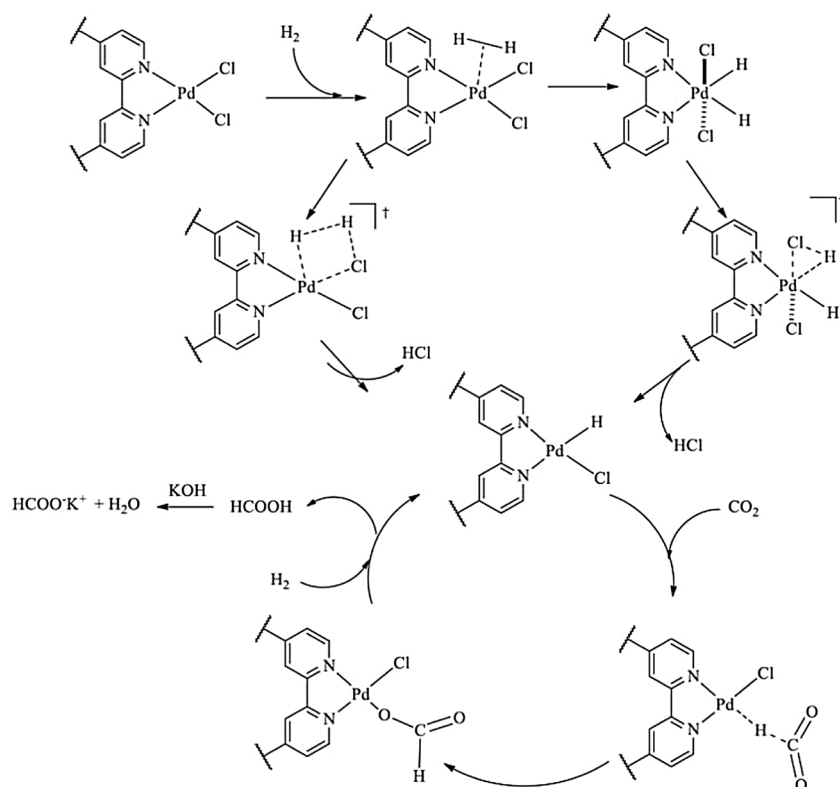
Catalytic hydrogenation of CO₂ to formic acid/formate is a

complicated gas-liquid-solid multiphase involved reaction. Several steps such as the dissolution of CO₂ and H₂ in liquid phase, the adsorption and activation of CO₂ and H₂, and the cleavage of H₂ to form Pd-H hydride intermediates, as well as the reduction of HC O₃⁻/CO₂ to form formate-Pd intermediates and the desorption of formate. Therefore, various catalysts and catalytic systems have been developed to promote these fundamental steps. Therefore, understanding the catalytic reaction mechanism would be helpful for the design of highly efficient catalyst in near future. However, only a few studies have paid attention on the deep understanding of catalytic reaction mechanism. In this section, two typical reaction mechanisms are discussed.

The plausible mechanism for the hydrogenation of CO₂ and H₂ to form formate over single atom Pd (II) MOFs was proposed as shown in Scheme 4 [83]. At first, H₂ gets activated to form Pd-dihydride intermediate which gets converted into active Pd-hydride complex after the elimination of HCl. The addition of CO₂ into the active Pd-hydride complex via associative addition formed the formate complex that dissociates into the formate species. Many researchers have also investigated the role of amino functional groups in enhancing the rate of CO₂ capture and hydrogenation reaction. For example, when the effect of primary, secondary and tertiary amines was studied, the secondary amine displayed the highest TOF values. This was attributed to the better electron donation ability of secondary amines and hence it can enhance the reaction activity to a great extent. The optimal electron donation effect of amines was also found to be the highest amongst other functional groups including nitrile and thiol groups. The use of polymers with amino functional groups has also been reported to facilitate the capture of CO₂ to ultimately enhance the rate of reaction.

5. Conclusions and future perspectives

The use of CO₂ to generate fuels and value-added chemicals i.e., formic acid, is a promising strategy to mitigate the effects arising from global warming and serious environmental concerns. It has been proven



Scheme 4. Plausible mechanism for the catalytic CO₂ conversion to formate at Pd (II) site. Reproduced with permission from ref [83]. Copyright 2020 American Chemical Society.

that catalytic conversion of CO₂ is a powerful alternative to produce renewable fuels and chemicals. However, CO₂ is a thermally and kinetically stable molecule and hence its reduction into value added chemicals generally require significant amounts of energy for example high pressure and temperature conditions. Therefore, the design of catalysts should be carried out to reduce the activation energy barriers to achieve efficient conversion efficiency. Furthermore, the engineering and optimization of the reaction conditions are crucial to obtain stable and recyclable catalysts which can reduce the total capital costs.

In this review article, we have presented the recent strategies and advancements to increase the catalytic activity of CO₂ hydrogenation reaction by studying the support effect, geometrical and electronic properties of the active metal, alloy effect, creation of heterojunction, focusing mainly on the design of Pd-supported catalyst. The chemical methods to reduce the size of active Pd metal, anchoring of basic functional groups and discussion of mechanistic cycle was outlined. In CO₂ hydrogenation reaction, the key factors affecting the kinetics of the reaction are the adsorption of CO₂ on the support and H₂ on the active sites followed by the reaction at metal-support interface. Some of the most active catalysts for CO₂ hydrogenation that were identified and discussed in this article are Pd/AP-POP with a TON = 1279 (80 °C, 80 bar (CO₂:H₂, 1:1), 12 h), Pd/Mn:JMS-2 (TON = 9808, 100 °C, 24 h, 50 bar (CO₂:H₂ = 1:4)), Pd/r-GO (hydrogenation of KHCO₃, TON = 7088, 100 °C, 40 bar) and PdAg-PEI@HMOS (TON = 2754, 100 °C, 22 h, 20 bar (CO₂:H₂ = 1:1)). The catalytic conversion of CO₂ can be increased by raising the temperature of the reaction, however increasing the temperature beyond 350 °C can favor the reverse water gas shift reaction (RWGS). It has been widely reported that introducing the basic sites and oxygen vacancies in the catalyst can increase the adsorption and activation of CO₂.

Although several reports have discussed the methods of CO₂ valorization, significant advancements are still necessary to design more active and stable catalysts for their implementation in practical applications. The activation and capture of CO₂ technologies needs to be developed in a way to be able to produce large amounts of pure CO₂. The existing techniques to separate CO₂ from industries such as sorption by using chemical solvents are very expensive. The innovative methods to produce green H₂ should be developed simultaneously in order to make the cycle of CO₂ valorization more sustainable. The hydrogen generation process should not create CO₂ emissions to reduce the overall CO₂ emission in the hydrogenation process. Formic acid is a potential candidate for hydrogen storage applications because of its non-toxicity, easy-handling and transportation. Although the 4.4 wt % of H₂ in FA is less than other hydrogen storage materials but its high density of 1.22 gcm⁻³ generates a high volumetric H₂ content of 1.77 kWhL⁻¹. This is in accordance with the 2025 target set by the U.S. Department of Energy with a usable energy density from H₂ of 1.3 kWhL⁻¹. Therefore, research efforts in the direction to improve the efficiency of formate synthesis will lead to its usage as an alternative liquid fuel. The synthesis of not only sustainable but also the selective formation of H₂ without any side products (CO, CH₄ and CH₃OH) is essential for its application as a fuel as the presence of CO (even in ppm concentration) can poison the catalytic active sites. In addition, the CO₂ to formate synthesis process may further lead to the development of low temperature synthesis of other value-added chemical fuels such as methanol under mild reaction conditions. The formate synthesis by solar-driven conversion is another sustainable approach towards enhancing the efficiency of the process using renewable source of energy. Presently, very few reports have explored the photocatalytic hydrogenation of CO₂ to FA. Very recently, Zhang et al. has reported for the first time the hydride transfer reduction of CO₂ on hydrogenated TiO₂ [136]. The hydride-like species generated on TiO₂ directly participated in the CO₂ reduction to facilitate the C-H bond formation and hence the generation of formic acid. The photocatalytic reduction of CO₂ in water (also known as 'artificial photosynthesis') would be the ultimate option to increase the prospects of carbon recycling. The electrocatalytic conversion of CO₂ has also been reported

by many researchers. The catalytic process (catalytic, electrocatalytic and photocatalytic) and reaction conditions have a significant impact on the type of product formation. For example, photocatalytic approach mainly forms the FA as the main product however, only trace of FA is produced in electrocatalytic process.

The design of bimetallic and alloy catalysts has been reported to furnish higher TOF values for the reversible hydrogen storage reaction and therefore there is a need for more efficient catalysts that are selective for hydrogen release. The recent advancements in the synthesis of single atom catalysts (SACs) can be a promising approach to prepare highly selective catalyst. For example, SACs anchored on MOFs or COFs as support materials can offer uniform dispersion of active sites with respect to geometrical and electronic properties. The desired properties for a breakthrough in catalytic performance involve low cost, abundance, better storage capacity and an ability to charge and discharge quickly. It has been widely reported that the presence of basic sites and oxygen vacancies can synergistically enhance the rate of CO₂ conversion reaction by increasing the adsorption and activation of CO₂. This has to be explored in detail by in-situ techniques that can assist in revealing the mechanistic pathway to understand the initial C—O bond breaking and C—C bond formation. The synergistic mechanism for the existence of multiple active sites and the deactivation of the catalyst after reaction needs to be investigated by operando techniques. The spectroscopic techniques that are being used till now involves the use of in-situ FTIR or DRIFT analysis techniques that doesn't include the effect of solvent used in the reaction. As discussed above, the use of solvent plays an important role in achieving the superior catalytic yields because of solubility and stability of intermediate species. Therefore, the use of in-situ attenuated total reflection infrared (ATR) spectroscopy including the effect of solvent under temperature and pressure conditions can assist in the realistic understanding of the mechanistic pathway.

We hope that the results summarized in this report will assist in the better understanding of the design of catalysts that are available at the current stage of chemistry and will further promote scientific discussions towards design of greener catalytic processes. The development of competitive technologies can play a key role in moving forward towards a carbon neutral society, ultimately leading to a lower carbon footprint. We hope that with continuous and collaborative efforts from academics and industrialists, innovative and practical strategies will be developed utilizing research expertise across multidisciplinary areas across catalysis, theoretical simulations and advanced material synthesis and characterization to promote the sustainable production of value-added chemicals and fuels.

CRediT authorship contribution statement

Priyanka Verma: Writing- Original draft, review & editing. **Siyuan Zhang:** Writing – review & editing. **Shengnan Song:** Writing – review & editing. **Kohsuke Mori:** Supervision, Revision & Suggestions. **Yasutaka Kuwahara:** Supervision, Revision & Suggestions. **Meicheng Wen:** Writing- Original draft, review & editing. Funding acquisition. **Hiromi Yamashita:** Supervision, Revision & Suggestions. **Taicheng An:** Supervision, Revision & Suggestions.

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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