CO₂ reduction into formic acid under hydrothermal conditions: A mini review

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Abstract
Converting CO₂, a major component of greenhouse gas in the atmosphere, into value-added fine chemicals is beneficial from environmental and economic aspects. Except for various methods for CO₂ reduction such as thermal catalysis, photocatalysis, electrocatalysis and biological reduction, hydrothermal reduction of CO₂ to organics is becoming a novel and promising strategy. The hydrogen formed in situ from high-temperature water could avoid the serious issues of hydrogen storage and transportation. This paper summarizes the recent advances on CO₂ conversion to formic acid with metal- and biomass-based compounds under hydrothermal conditions mainly focusing on the role of high-temperature water, autocatalysis mechanism of metal reductants, and interfacial catalysis mechanism of metal/metal oxides. The effects of several experimental variables including temperature, reaction time and pH of the solution on formic acid yield are systematically illustrated as well. Finally, future efforts for fundamental researches and industrial applications of hydrothermal CO₂ reduction are discussed.

KEYWORDS
biomass-derived reductants, catalytic mechanism, CO₂ reduction, formic acid, hydrothermal conversion, metallic catalysts
INTRODUCTION

Since the industrial revolution, excessive utilization of fossil fuels (coal, oil and natural gas) had led to a continuous increase of CO\textsubscript{2} concentration in the atmosphere, which caused a series of problems such as the rapid deterioration of the environment, and the serious shortage of the limited fossil resources.\textsuperscript{[1-3]} Nowadays, under the goal of reaching peak carbon dioxide emissions and achieving carbon neutrality, the amount of CO\textsubscript{2} emission is strictly regulated. On the other hand, CO\textsubscript{2} can also be used as a non-toxic, low cost and easily available C\textsubscript{1} source to synthesize highly value-added fine chemicals.\textsuperscript{[4,6]} Formic acid is widely used in rubber, medicine, pesticides, dyes, fuel cells, agriculture and environmental protection and can be generated from CO\textsubscript{2} hydrogenation (CO\textsubscript{2} + H\textsubscript{2} = HCOOH) with the atom's economic efficiency of 100%.\textsuperscript{[7-9]} More importantly, the conversion of CO\textsubscript{2} to formic acid that turns waste into valuable substances could achieve the Sustainable Development Goals related to the energy cycle.

However, due to the thermodynamic stability of CO\textsubscript{2}, the formation of the C−H bond from CO\textsubscript{2} hydrogenation requires efficient catalysts and massive energy input including hydrogen source.\textsuperscript{[10-12]} Apart from gaseous hydrogen, high-temperature water (HTW) could also be served as a hydrogen source. Due to the unique physical and chemical properties of HTW, the in situ hydrogen under hydrothermal conditions (200–400°C, 10–25 MPa) is more active than gaseous H\textsubscript{2}.\textsuperscript{[13-15]} Further, when HTW was applied to in situ hydrogen source, serious problems such as hydrogen transportation and hydrogen storage can be avoided as well.\textsuperscript{[16-18]}

In the past decade, our group had made tremendous efforts on CO\textsubscript{2} hydrogenation to formic acid under hydrothermal conditions and great progress had been achieved in this field.\textsuperscript{[15,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37]} In this review, we systematically summarized the reaction mechanism of CO\textsubscript{2} conversion to formic acid with various metal-based catalysts and biomass-derived reductants including Mn, Fe, Al, Zn, 2-pyrrolidone, hexahexanol, L-alanine and so on. In addition, the effects of experimental conditions such as temperature, reaction time, pH value of water solution and water filling ratio on formic acid yield are reviewed as well. This article aims to provide a detailed insight into the green and novel strategy for CO\textsubscript{2} conversion to formic acid and enrich basic knowledge of catalytic hydrothermal CO\textsubscript{2} hydrogenation for future fundamental researches and industrial applications.

2 | THE ROLE OF WATER FOR CO\textsubscript{2} HYDROGENATION IN HYDROTHERMAL CONDITIONS

Water is widely used as a green solvent and its physical and chemical properties would significantly change when rapidly elevating the temperature. The dielectric constant of water decreases from ~78.49 at room temperature to ~34.79 at 200°C, ~20.39 at 300°C and ~14.07 at 350°C. The hydrogen bonds become less persistent, and the HTW possesses the similar property of polar organic solvents, which make the organic compounds and gaseous products completely solvated in HTW.\textsuperscript{[38,39]} As shown in Figure 1a, due to the weak interaction of hydrogen bonds, mass transfer resistance between interfaces would disappear in the supercritical water phase, which can effectively promote heterogeneous reaction rates.\textsuperscript{[40]} Besides, another significant property of HTW is the ion product (K\textsubscript{w}). The value of K\textsubscript{w} is 10^{-14} (mol/kg)^2 at room temperature, which increases to a maximum value of 10^{-11} at about 250°C. The elevated K\textsubscript{w} corresponds to an increased concentration of H\textsuperscript{+} ions, leading to the increase of the rates of any acid-catalysed reactions.\textsuperscript{[41,42]}

During the hydrothermal reduction, the HTW not only served as a green solvent but also a hydrogen donor to provide in situ hydrogen for subsequent hydrogenation. This process had been proved by the isotope labeling experiment in which D in D\textsubscript{2}O would participate in HCO\textsubscript{3}− reduction and was finally transferred to the reduction product acetic acid.\textsuperscript{[14]} Moreover, the existence of molecular H\textsubscript{2}O could also act as a proton acceptor to form the H\textsubscript{2}O\textsuperscript{+} like cation conformation during the transition state of methanol, significantly decreasing the activation energy of methanol oxidation from 378 kJ/mol to 220 kJ/mol. Except for the potential hydrogen source and promoter, water could serve as a reactant to produce hydrogen and alcohol, aldehyde, acid and other oxygen-containing derivatives in the hydrothermal liquefaction of polyethylene to oil.\textsuperscript{[43,44]} Similarly, Guo and Luo et al.\textsuperscript{[45,46]} also found H\textsubscript{2}O in the hydrothermal conditions could directly participate in hydrodenitrogenation reactions of nitrogen-containing heterocyclic substances, in which the oxygen-containing compounds were generated from the interaction with water.

For the hydrothermal reduction of CO\textsubscript{2} to formic acid, previous studies have shown that metals reductants such as Mn, Fe and Al would first interact with H\textsubscript{2}O, generating hydrogen in situ and the corresponding metal oxides.\textsuperscript{[18]} Then, the in situ hydrogen further
reacted with CO\textsubscript{2} to produce formic acid (H\textsubscript{2}O + M \rightarrow M\textsubscript{x}O\textsubscript{y} + H\textsubscript{2} + CO\textsubscript{2} \rightarrow \text{formic acid}), as shown in Figure 1b. Besides, Duo et al.\textsuperscript{19} found the production of in situ hydrogen is highly consistent with the yield of metal oxide Fe\textsubscript{3}O\textsubscript{4}. The in situ hydrogen and Fe\textsubscript{3}O\textsubscript{4} were formed slightly in the initial 10 min, and the reaction rates rapidly increased in the reaction stage from 10 to 30 min. In addition, in situ hydrogen from water splitting had higher activity for CO\textsubscript{2} hydrogenation than the external gaseous H\textsubscript{2}. In terms of thermodynamics, the Gibbs free energy for the formation of formic acid from the hydroxidation between H\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{−} is only \(-7 \text{ kJ/mol}\), which is significantly higher than that of the reaction between HCO\textsubscript{3}\textsuperscript{−} and H atom (\(-399.48 \text{ kJ/mol}\)). According to the control experiment, Lyu et al.\textsuperscript{30} demonstrated that the formation of in situ hydrogen with Mn as reductant under hydrothermal conditions could significantly improve the formic acid yield by 20% compared to that directly inputting high-pressure H\textsubscript{2} into the reaction system.

Except for using metals for hydrogen production under hydrothermal conditions, it was found that more than 70% of hydrogen yield was achieved by the gasification of biomass-derived compound ethylene glycol at 256°C for 2 h.\textsuperscript{47} Our studies also showed the formation of in situ hydrogen from water splitting with glycerol as a reducing agent.\textsuperscript{48,49}

3 | REACTION MECHANISM OF HYDROTHERMAL REDUCTION OF CO\textsubscript{2} INTO FORMIC ACID

In section 2, we had illustrated that the HTW would play as both hydrogen source and promoter. Previous researches had already proved that CO\textsubscript{2} cannot be reduced to formic acid in pure hydrothermal conditions even at a temperature of 300°C,\textsuperscript{50} which emphasized the necessity of additional catalysts or reductants. In this section, we would discuss the reaction mechanism of CO\textsubscript{2} reduction to formic acid with several metals as reductant (red elements in Figure 2) and catalysts (blue elements in Figure 2) as well as the biomass-derived reductants.
3.1 Autocatalysis mechanism of CO2 reduction to formic acid with metals

When metals such as Mn, Fe and Al were used to reduce CO2, an autocatalysis mechanism with the generation of in situ hydrogen is applied to explain the formation of formic acid under hydrothermal conditions.

3.1.1 Fe

Yamasaki et al.50 first studied the synthesis of formic acid by CO2 hydrogenation under hydrothermal conditions with Fe as a reductant. The results showed that CO2 is difficult to be reduced if only Fe was present, while a trace amount of formic acid (less than 1 mmol/L) is detected in the presence of the Fe−Fe3O4 mixture, indicating that the redox state of Fe would highly affect this hydrogenation process. The low yield of formic acid was supposed to be attributed to the difficulty of Fe oxidation to produce in situ hydrogen for hydrogenation. After that, Duo et al.19 found the HCO3− (CO2 source) hydrogenation to formate with Fe occurred through an autocatalysis mechanism. First, Fe was rapidly oxidized to Fe3O4 by H2O with the generation of in situ active hydrogen. Next, Fe3O4 was further reduced to Fe3O4-x where the in situ hydrogen and C=O of HCO3− were simultaneously adsorbed. Finally, formic acid was created from the attack of in situ hydrogen to C=O bond in HCO3− as shown in Figure 3. Besides, they also pointed out that in the process of hydrothermal conversion of CO2 to formic acid with Fe as reductant, different kinetic reaction stages existed: (1) only 8.5% of formic acid was produced within 10 min; (2) the formic acid yield explosively increased to 42% from 10 to 90 min; and (3) the reaction reaches equilibrium after 90 min to form a ‘S’ shape kinetic curve in the whole reaction scale. What’s more, such a ‘S’ shape trend was further explained with X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM) characterization: (1) in the initial 0−10 min, in situ hydrogen and oxygen vacancy-containing compound Fe3O4-x were massively created; (2) in the medium term (10−90 min), Fe3O4-x effectively catalysed HCO3− reduction by in situ hydrogen, and (3) formic acid yield reaches the maximum value gradually before equilibrium. This is a typical feature of autocatalysis reaction in which the ‘induction period’ occurred earlier than the ‘rapid reaction’ stage. In addition, Jin et al.51 developed a kinetic reaction modelling to describe the pathway from HCO3− to formic acid with Fe as reductant under hydrothermal conditions. The fitting results showed that the activation energy of hydrothermal HCO3− reduction to formic acid (21 kJ/mol) is much lower than that of the earlier kinetic modelling work on conventional hydrogenation, which needs to overcome the 68 kJ/mol energy barrier. Besides, numerous reports demonstrated that conversion of HCO3− to formic acid follows the first-order reaction model in a wide temperature range from 225 to 375°C.19,51,52,53

3.1.2 Mn

To investigate the mechanism of hydrothermal conversion of CO2 to formic acid with Mn, XRD characterization showed that only Mn and a trace amount of Mn(OH)2 were detected in the initial 10 min of reaction, indicating that Mn has not been fully oxidized. In the reaction period of 10 to 120 min, a strong MnO signal appeared and the Mn signal gradually disappeared.30 Those results are consistent with the yield of in situ hydrogen, which was produced slowly at the beginning of 10 min and then formed rapidly from 10 to 120 min, suggesting MnO is active for generating the in situ hydrogen. According to the kinetic fitting results, there are two different kinetic reaction stages in the catalytic hydrothermal hydrogenation of CO2 to formate with the metal Mn. The rate constants were −0.0007, −0.0055 and −0.0226 k/h at 275, 300 and 325°C, respectively, in the initial reaction time (0−10 min). The rate constants rapidly elevated to −0.0007, −0.0055 and −0.0226 k/h at the corresponding temperatures when batch holding time extend to 10−120 min. Those results suggest that some active intermediate formed during the second kinetic reaction stage to promote yielding formic acid from HCO3−. Detailed analysis revealed that Mn was first oxidized to Mn(OH)2, which is dehydrated and transformed into MnO. According to those experimental results, the autocatalysis mechanism was also applied for Mn-based hydrothermal CO2 reduction to
formic acid, as described in Figure 4. First, zero-valent Mn directly interacted with H$_2$O to form the reactive intermediate where HCO$_3^-$ was adsorbed and activated. Then, electronegative H in the intermediate would attack the C atom of HCO$_3^-$ to generate C−H by nucleophilic substitution with OH being desorbed from Mn to generate HCOO$^-$. 

3.1.3 | Al

When using Al as a reductant, H−Al−OH intermediate species was first formed from the interaction between Al and H$_2$O as shown in Figure 5. Then, electronegative H attacked the carbon centre of HCO$_3^-$, forming a bond with carbon as a transition state. Finally, the OH$^-$ species left, forming HCOO$^-$ through an SN$_2$-like mechanism.$^{22}$ The calculated energy profile showed that the H−Al−OH species was more stable (with respect to Al + H$_2$O) by 31.96 kcal/mol and the energy of the transition state is larger (with respect to Al + H$_2$O) by 18.18 kcal/mol, suggesting that this reaction would easily take place under mild hydrothermal conditions.$^{24}$ More specifically, the Al−O distance of H−Al−OH was shortened to 1.718 Å from 2.079 Å of the initial state. As a result, OH$^-$ would be closer to Al, promoting the formation of Al−H. Besides, the existence of this metal hydride (Al−H) was also be confirmed by electron analysis, in which the Mulliken charge of H was transformed from positive in the initial state to negative in the final state. The transition state calculation illustrated the antibonding interaction between Al and H of the Al−H species with the adsorption of HCO$_3^-$, suggesting the cleavage of the Al−H bond and the formation of new C−H. Those advantages lead to a 64% yield of formic acid at 300°C and 2 h with Al as reductant under hydrothermal conditions. The kinetic analysis showed that the activation energy of HCO$_3^-$ reduction to HCOO$^-$ was relatively low (50.6 kJ/mol).

3.2 | Interfacial catalytic mechanism of metal/metal oxide for CO$_2$ reduction to formic acid

In section 3.1, we had discussed that the metal oxidizes and in situ hydrogen would simultaneously be formed from the interaction between metal reductants (Mn, Al, Fe) and water. Except for the autocatalysis mechanism for hydrothermal CO$_2$ reduction to formic acid, we found the metal/metal oxide interface is also active for catalysing CO$_2$ hydrogenation to formic acid.$^{18,23,24,28,29,35}$ Ye et al.$^{29}$ found that the formic acid yield could be improved to 48.4% with the coexistence of Zn (23% yield with Zn existed alone) and ZnO under hydrothermal conditions. The formation of H−ZnO−H from the chemisorption of H$_2$ should be responsible for the production of formic acid, as the yield of formic acid was only 13% with ZnO and gaseous H$_2$. Those results suggest that the in situ formed Zn/ZnO interface is the real active site for CO$_2$ reduction to formic acid. Combining with density functional theory (DFT) calculation results that zinc hydride species (Zn−H) plays a crucial role for CO$_2$ hydrogenation,$^{54}$ the proposed catalytic mechanism of synergetic Zn/ZnO interface can be described as shown in Figure 6. Zn was firstly oxidized to ZnO in the water to produce in situ hydrogen, which was then adsorbed on the oxygen vacancies of the Zn/ZnO interface. Next, formate and H$_2$O were, respectively, formed by nucleophilic attack of the H$^-$ on bicarbonate ion with combination between cationic proton and leaving hydroxyl group in HCO$_3^-$. In addition to Zn/ZnO interface, Wang et al.$^{13}$ found that H$_2$ and HCO$_3^-$ were separately adsorbed on the Co$^0$ and Co$^{6+}$ site where the attack of active H on HCO$_3^-$ generated HCOO$^-$ based on DFT calculation and catalyst characterization. They also pointed out that the in situ formed metal/metal oxide interface could be attributed to the oxidation-reduction equilibrium on the catalyst surface between the oxidation effect of HTW and the reduction effect of H$_2$ and high H$_2$ pressure would suppress the formation of CoO. Wan et al.$^{55}$ also showed that the mixed-valence metal sites and oxygen vacancies were capable of heterolysis of H$_2$ and adsorption of CO$_2$. 

![Figure 4](image-url) Proposed mechanism of reaction of CO$_2$ to formic acid with Mn as reductant$^{30}$

![Figure 5](image-url) Proposed SN$_2$-like mechanism for the formation of HCOO$^-$$^{22}$
3.3 Multi-metallic catalysis for hydrothermal reduction of CO₂ to formic acid

The multi-metallic catalysis usually involves a synergistic effect due to the interaction of different metal components, which could significantly improve the catalytic activity and expand their function scale compared to the single-metal catalyst.56,57 As discussed in section 3.2, the Zn/ZnO interface was the active site for converting CO₂ into formic acid under hydrothermal conditions29; however, the study by Zhong et al.35 showed that 81% yield of formate production could be achieved when adding additional Ni into Zn/ZnO at 225°C for 2 h that is equal to the same formate yield (80%) required 300°C when only Zn/ZnO existed. XPS, XRD and HRTEM characterization results indicate the additional Ni could inhibit Zn oxidation and create more Zn/ZnO active sites as well as the oxygen vacancies at Zn/ZnO interface to increase formate yield. When Fe was used as a reductant, the formic acid production was slightly improved from 13% to 16% with additional Ni at 300°C for 2 h.21 Zhong et al.25 also found that the formic acid yield increased linearly with the Cu/Fe ratio from 1 to 2 and decreased when increasing Cu/Fe ratio further as excessive Cu would lead to formic acid decomposition. The highest
Formic acid yield 71.3% was obtained at 300°C for 2 h with Cu/Fe = 1. Besides, formic acid yield raised from 2.8% with Cu powder to 26.9% with Cu-Al alloy and further to 77.2% with skeletal CuAlZn at 200°C for 2 h. A possible reaction mechanism for hydrogenation of bicarbonate to formic acid using skeletal CuAlZn as catalyst was proposed as shown in Figure 7. Bicarbonate ion was absorbed on the surface of CuAlZn catalyst, and H₂ was absorbed simultaneously to form a metal hydride intermediate. The adsorbed H attacked the activated HCO₃⁻ to form formic acid with the loss of H₂O.

### 3.4 Hydrothermal reduction of CO₂ to formic acid with biomass-derived reductants

Considering that biomass stores solar energy and contains various reductive groups such as hydroxyl, aldehyde, amino, it can be used as an ideal reductant to reduce CO₂ theoretically. We found that a large amount of hydrogen is generated from both glycerol gasification and water splitting during hydrothermal glycerol conversion to lactic acid. These results further indicate that biomass is reductive under hydrothermal conditions, and the hydrogen could be produced from both biomass and water decomposition for efficient in situ hydrothermal reduction of CO₂.

Yang et al. systematically studied the process of HCO₃⁻ reduction to formic acid using amino group-based substance 2-pyrrolidinone under hydrothermal conditions as shown in Figure 8. γ-aminobutyric acid was first formed from the ring-opening reaction of 2-pyrrolidinone and reacted with one molecule HCO₃⁻ to produce formic acid. During the reaction, the 2-pyrrolidone could also be oxidized by imine cation intermediate to produce primary oxidation product hydroxylamine, which would reduce another molecule of HCO₃⁻ to formic acid with the formation of secondary oxidation product oxime. In addition, oxime continuously reduced one molecular of HCO₃⁻ to formic acid and was converted to nitro eventually. Notably, the above-mentioned oxidation processes proceeded rapidly under hydrothermal conditions. After the formation of a nitro compound, nitrobutyric acid is formed through intramolecular attack or nucleophilic attack of OH⁻ to γ-hydroxybutyric acid in an alkaline reaction system where the free NO₂⁻ reacts with NH₄⁺ to form N₂ to complete the whole reaction. Moreover, they found that substitutional groups on −NH₂ oxidation could have a steric effect on the production of formate from HCO₃⁻. The benzene containing amino-based substance like L-lysine had a weaker ability for HCO₃⁻ reduction with only 19.2% yield of formate, which was even less than a half of the yield (51.2%) with glycine as reductant. DFT calculation revealed that the steric hindrance had a negative impact on the dehydrogenation of the amino group, in which 2.53 eV energy barrier for rate-determining step of L-lysine was required that is significantly higher than the value of 1.5 eV for glycine. Except for the amino group, Yang et al. found hydroxyl-based compound can also reduce HCO₃⁻ to formate, in which 80% yield of formate was obtained with hexanehexol as a reductant under 300°C hydrothermal condition for 1 h.

### 4 Effects of Reaction Variables

In this section, we discuss the impact of several experimental variables including temperature, water filling ratio.
and the pH value of the solution on CO₂ reduction under hydrothermal conditions.

4.1 | Temperature and Reaction Time

Yu et al. had reported that formic acid would be completely decomposed under hydrothermal conditions of 371°C within 34 s, demonstrating that there should be a proper temperature range for yielding formic acid from HCO₃⁻. The optimum temperature and reaction time conditions for the yield of formic acid with various catalysts and reductants are summarized in Table 1. For most metal-based catalysts, the preferable condition for producing formic acid is 300°C and 2 h; however, a higher temperature (350°C) and longer reaction time (2.5 h) were required for the biomass-derived 2-pyrrolidinone case, suggesting that the amino group has a relatively lower reducing effect compared to metal compounds. The temperature would directly impact the ion product and dielectric constant of HTW, which is highly related to its oxidation capacity for metal oxidation. Duo et al. investigated the influence of temperature and reaction time on Fe oxidization through the XRD characterization. The results showed that the Fe₃O₄ signal gradually intensified from 5 to 120 min. Particularly, a weak signal of FeCO₃ intermediate was detected at 275 and 300°C and disappeared at 350°C. At a higher temperature of 350°C, only H₂ and some CH₄ were detected, demonstrating that formic acid would be decomposed into CH₄ at a higher temperature, which is consistent with thermodynamics analysis (CH₄; \( \Delta G^0 = -50.72 \text{ kJ/mol} \); HCOOH; \( \Delta G^0 = -372.3 \text{ kJ/mol} \)).

4.2 | Water filling ratio and pressure

The hydrothermal CO₂ hydrogenation was conducted in a closed system, and a large amount of in situ H₂ would be generated during this process; thus, the water filling ratio would directly affect the reaction pressure. At 325°C, the yield of formic acid increased linearly from 61% to 76% with increasing water filling ratio from 35% to 55% over Mn catalyst. In addition, experiments conducted with HCO₃⁻ and Cu at 300°C for 120 min demonstrated that the formic acid yield increased from 16% to 63% when changing the water filling from 20% to 55%. Those results suggested that the yield of formic acid is directly related to the pressure of the system. Two possible mechanisms might decipher this observation: (1) more CO₂ would be adsorbed on the metal surface under higher pressure to promote the activation of CO₂ on metal catalysts; and (2) CO₂ reduction by in situ H₂ is a volume diminution reaction, so higher pressure would facilitate reaction in the direction of H₂ consumption according to Le Chatelier’s principle. Similarly, when Fe was used as a reductant under hydrothermal conditions, the yield of formic acid also improved from 37.5% to 59.0% with the water filling ratio changing from 35% to 55%. However, the oxidation degree of Fe is maintained at 65%, indicating that the pressure rather than the number of Fe/Fe₃O₄ catalytic centre is responsible for the enhanced activity when changing the water filling ratio.

In contrast, the water filling ratio had little impact on formic acid yield when biomass-derived reductants were used for CO₂ hydrogenation as shown in Figure 9. Yang et al. found the yield of formic acid always maintained at ~7% even the water filling ratio raised to 45% when using 2-pyrrolidinone as a reductant. The same phenomenon also occurred when amino-based reductant L-alanine was used to generate formic acid from hydrothermal CO₂ reduction, in which the formic acid yield is near ~45% even though Pt/γ-Al₂O₃ was added to promote this process.

4.3 | pH and HCO₃⁻ concentration

Five forms of CO₂ exist in the aqueous phase, including CO₂(aq), CO₃²⁻(aq), H₂CO₃(aq), HCO₃⁻(aq) and CO₂⁺(aq). The corresponding distribution of carbon species in water at different pHs is shown in Figure 10A. Notably, the solubility of different CO₂ forms has a relatively huge gap. In this section, we explored the impact of pH value on CO₂ reduction under hydrothermal conditions. A series of control experiments were conducted and the results showed that only 0.2% formic acid was formed when gaseous CO₂ was directly used as the carbon source. Adding NaOH to
Enhance the dissolution of gaseous CO$_2$ in water improved the yield of formic acid to 5.5%. In contrast, when HCO$_3^-$ was used as a carbon source, a 43% yield of formic acid was observed. Those results indicated that formic acid is generated mainly from HCO$_3^-$ instead of CO$_2$ and the yield is highly related to the solubility of CO$_2$ in water. Furthermore, part of HCO$_3^-$ would be converted to Na$_2$CO$_3$ at higher alkaline pH, resulting in the decrease of formic acid yield. Such a volcano-type relationship existed between the yield of formic acid and HCO$_3^-$ concentration as shown in Figure 10C. The optimum HCO$_3^-$ concentration for producing formic acid is generally around 1 mol/L. These results suggest that a relatively higher concentration of HCO$_3^-$ could facilitate producing more formic acid. However, a continuous increase in the initial concentration of HCO$_3^-$ would inhibit formic acid formation probably due to the decomposition of formic acid under higher pressure in the closed reactor.

### 4.4 Stability of catalysts under hydrothermal conditions

Considering that the hydrolysis of HCO$_3^-$ would increase solution alkalinity, the effect of HCO$_3^-$ concentration on the yield of formic acid was investigated. The volcano-type relationship also existed between the yield of formic acid and HCO$_3^-$ concentration as shown in Figure 10C. The optimum HCO$_3^-$ concentration for producing formic acid is generally around 1 mol/L. These results suggest that a relatively higher concentration of HCO$_3^-$ could facilitate producing more formic acid. However, a continuous increase in the initial concentration of HCO$_3^-$ would inhibit formic acid formation probably due to the decomposition of formic acid under higher pressure in the closed reactor.

The stability of the catalyst is another crucial standard for evaluation, which is more related to the subsequent industrial application. In this section, we discuss the robustness of metal catalysts for CO$_2$ hydrogenation under hydrothermal conditions. Generally, hydrothermal methods were widely used for synthesizing materials; however, some metal oxides are not stable enough under harsh hydrothermal conditions, in which the γ-Al$_2$O$_3$ can be easily deactivated at 225°C for 12 h due to the collapse of pore structure and the decrease of the specific surface area of γ-Al$_2$O$_3$. Besides, bare γ-Al$_2$O$_3$ was rehydrated in hot water (200°C) and completely converted into crystalline boehmite within 10 h with a significant loss of a surface area. By contrast, in the hydrothermal CO$_2$ reduction, metal catalysts including Cu, Pd/C, Pd$_{0.5}$Cu$_{0.5}$/C and Ni displayed relatively high stability, during which the fluctuation of formic acid yield is less than 5% after 3−5 times recovery for all the tested metals, as shown in Figure 11. More specifically, Cu and Pd/C maintained their activity.
at 300°C and 2-h condition, and the catalytic activity for bimetallic catalyst Pd$_0.5$Cu$_0.5$/C was still kept after for 5 times reused times at 180°C for even 16 h. Additionally, scanning electron microscope (SEM) and XRD results showed the morphology and crystallinity of reused catalyst had no obvious change after the reaction, while only a slight content of aggregation of metal particles was observed by TEM characterization, further indicating the relative stability of catalyst for hydrothermal CO$_2$ reduction.

**5 | CONCLUSIONS AND PERSPECTIVES**

This article systematically summarized the reaction mechanism of CO$_2$ hydrogenation to formic acid with various catalysts or reductants under hydrothermal conditions and the effect of experimental parameters including temperature, reaction time, pH value and water filling ratio on the yield of formic acid. The major conclusions in this review can be described as follows:

- For reductants Mn and Fe, an autocatalytic mechanism was applied for the reduction of CO$_2$ to formic acid under hydrothermal conditions, during which metal—H formed from the interaction between the oxidation products (MnO and Fe$_3$O$_4$) and water as the active sites. The HCOO$^-$ was formed by the attack of the active H on metal—H intermediate to C in HCO$_3$-. The in situ hydrogen generated from HTW has higher activity than the external gaseous hydrogen for CO$_2$ hydrogenation.
- The effect of the water filling ratio on formic acid yield is moderate when biomass-derived reductants were used for CO$_2$ reduction. In contrast, water filling has a considerable impact on the metal-based catalytic reaction system. The 300°C and 2 h are the optimum experimental conditions for formic acid formation in most cases since higher temperature and longer reaction time would lead to formic acid decomposition under hydrothermal conditions.
- Among the five forms of CO$_2$ (CO$_2$ (g), CO$_2$ (l), H$_2$CO$_3$(aq), HCO$_3^-$ (aq) and CO$_3^{2-}$ (aq)) in water, formic acid is mainly generated from HCO$_3^-$. The in situ mechanical strength of supporter to make active components highly dispersed on the catalyst surface. Some advanced and functional catalysts, such as MOFs, COFs, and single-atom catalysts could be applied to innovate the hydrothermal field.

Developing low-cost metal catalysts and biomass-derived reductants is an economic and practical way to achieve CO$_2$ reduction to formic acid. However, the inefficient activity and robustness of those catalysts might be the major obstacle for industrial application. Besides, a fundamental understanding of the mechanism of those catalytic reactions is lacking in the current stage, and the following suggestions are raised for this concern.

- In the catalytic mechanism and kinetic research, a more detailed kinetic reaction modelling for the conversion from CO$_2$ to formic acid needs to be developed to determine the specific rate-determining step during hydrothermal reactions.
- It is not clear about the interactions between C$_1$ compounds (reactant and intermediates) and catalyst surface so far, thus in situ and operando characterization methods, such as XRD, XPS, and DRIFTS, are necessary to obtain a deep understanding of the structure—catalysis relationship.
- Modifying the acidity, pore size, pore volume, and mechanical strength of supporter to make active components highly dispersed on the catalyst surface. Some advanced and functional catalysts, such as MOFs, COFs, and single-atom catalysts could be applied to innovate the hydrothermal field.
- DFT calculation is a promising approach to help reveal the catalytic mechanism at an atomic level and screen the optimized catalysts. Also, the DFT calculation may be promising to predict some important hydrothermal reactions at extreme conditions that occur at the natural process but could not be simulated at the laboratory.
- The combination of bimetallic synergistic effects with other strategies such as strong metal–support interactions, confinement effects, surface acidity—basicity, and mobility of oxygen species are promising approaches to create more active and robust CO$_2$ hydrogenation catalysts.

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