INTRODUCTION

Atmospheric CO₂ concentration has increased dramatically in recent decades, resulting in several serious environmental problems such as global warming and climate abnormality.¹ Methods to mitigate these problems have been extensively studied, among which, converting CO₂ into useful chemicals is regarded as one of the most promising technologies since it can not only alleviate the global warming but also utilize CO₂ as a renewable and clean resource.² Traditional CO₂ conversion methods include catalytic hydrogenation,³ electrochemistry,⁴ and photochemistry,⁵ etc. However, catalytic hydrogenation method demands high-pressure gaseous hydrogen as the reductant, which costs huge energy to produce and brings hydrogen transportation, storage, and safety issues. Although photochemical and electrochemical CO₂ reduction methods can utilize water as the hydrogen source and acquire energy from renewable energy sources directly or indirectly, their low-efficiency problems limit the practical application.⁶,⁷ Therefore, developing a highly-efficient CO₂ conversion method with a facile hydrogen source and renewable resources is still an attractive challenge.

Researchers have been inspired by the natural conversion of CO₂ into organics in Earth’s crust and hydrothermal vents,
in which, geochemical redox reaction via the $\text{H}_2\text{CO}_2$ redox couple provides the essential conditions for abiogenic hydrocarbon formation through serpentinization.8-12 Studies on CO$_2$-bearing aqueous fluids with magnetite,12 cobalt-bearing magnetite,13 iron-chromium oxide,14,15 have shown that reduction of CO$_2$ is achieved with metals under hydrothermal conditions. Takahashi et al. have reduced CO$_2$ into formic acid by using Fe and Ni at 330°C under hydrothermal conditions.16 Our recent research has shown that, with the in situ formed hydrogen from the reaction of earth-abundant metals (Fe, Zn, Mg, Al and Mg) as both reductant and catalyst, CO$_2$ can be efficiently reduced into useful chemicals such as acetic acid, formic acid, and methane under hydrothermal conditions.17-21 However, in these methods, metals are oxidized after the reaction and thus regeneration of the metal reductants is required. Therefore, further developing this hydrothermal method for CO$_2$ reduction with renewable materials to replace the metal reductants is needed and attractive.

Biomass is an important and valuable source due to its abundant, clean, renewable, and carbon neutral characteristics.22,23 Our previous study has shown that biomass such as cellulose can demonstrate significant reducing ability for the reduction of CuO to Cu under hydrothermal conditions,24 indicating the feasibility of using biomass or its derivatives as renewable reductants for the CO$_2$ reduction via hydrothermal process.

Moreover, protein-containing biomass wastes are major by-products in industrial biofuel production from lipids, oils, and microalgae.25-27 Also, protein takes quite a proportion in food wastes,28 which provides vast economic and environmental values for its utilization. Thus, developing a suitable and efficient technology for CO$_2$ reduction using protein-containing biomass wastes as potential reductants can provide not only a novel and sustainable way for CO$_2$ reduction but also a new and green strategy for protein-containing biomass waste treatment and utilization. Furthermore, CO$_2$, with a high stability, is generally utilized directly as a reactant in many studies on CO$_2$ reduction, which has the problem of CO$_2$ activation.6 However, CO$_2$ can be easily converted to bicarbonate after being absorbed in alkaline solutions such as NaOH and KOH,29 which is regarded as one promising method to capture CO$_2$ from air.30 Therefore, study on direct reduction of bicarbonate, as a model compound of CO$_2$ in basic solution, is of important meaning for exploring an efficient method of CO$_2$ reduction, and also, there have been many reports of bicarbonate reduction.31-33

2 | MATERIALS AND METHODS

2.1 | Materials

In this research, 2-pyrrolidone was used as the model compound of protein-containing biomass waste. NaHCO$_3$ (99.5%) and 2-pyrrolidone (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. NaH$^{13}$CO$_3$ (99%), H$^{13}$COOH (99%), and CH$_3$$^{13}$COOH (99%) were ordered from Cambridge Isotope Lab., Inc. Gaseous H$_2$ (≥99.999%), CO (≥99.999%), CH$_4$ (≥99.999%), and CO$_2$ (≥99.999%) which were utilized as standard gases for GC-TCD (thermal conductivity detector, Agilent 6890A) qualitative analysis, and N$_2$ (≥99.999%) which was utilized to purify the gas in reactor, were obtained from Shanghai Poly-Gas Technology Co., Ltd. Co powder (200 mesh, ≥99.0%), Ni powder (200 mesh, ≥99.5%), Cu powder (250-300 mesh, ≥99.7%), Cr powder (200 mesh, ≥99.0%), and Mo powder (200 mesh, ≥99.0%) were also purchased from Sinopharm Chemical Reagent Co., Ltd. NiAl (40%-50% Ni basis), and palladium on activated charcoal (Pd/C, 10 wt% Pd) were purchased from Aladdin Industry Corporation. Activated carbon (400 mesh) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All the chemicals were used as received without any further treatment.

2.2 | Experimental procedure

All experiments were conducted in a tubular batch reactor (3/8 inch in diameter and 120 mm length) made of stainless steel (SUS-316) alloy with a Swagelok cap and a gas valve (Autoclave Engineering Inc.) with a reducing union at each end. The inner volume of the reactor was 5.7 mL. Schematic drawing of the experimental setup can be found in our previous report.34 In a typical reaction, desired amount of 2-pyrrolidone, NaHCO$_3$, catalyst, and deionized water were added to the reactor. Subsequently, N$_2$ was introduced into the reactor to replace the remained air in the reactor. Then the reactor was sealed and immersed into a salt bath that had been preheated to desired temperature to initiate the reaction. After the reaction, the reactor was lifted out from the salt bath and placed into a cold water bath immediately to quench the reaction. The reaction time was defined as the duration that the reactor was kept in the salt bath. A water filling rate was used to denote the liquid amount in the reactor, which is defined as the ratio of the liquid volume to the total inner volume of the reactor. Experiments in this research were reproduced for 3 times. The error percentage was no more than 5%.

For examining the stability of Pd/C catalyst, Pd/C catalyst recycling test was conducted. After each cycle, solid sample was collected by washing with deionized water for 5 times and dried in a vacuum oven. Then it was reused in the next run without further purification or regeneration.

2.3 | Analytical methods

After the reactions, gaseous sample was collected through the gas valve at room temperature and was analyzed by a gas chromatography analyzer equipped with a thermal
conductivity detector (GC-TCD, Agilent 6890A) with a TDX-01 column and He as the carrier gas.

Liquid sample was collected after filtering through a 0.22 μm syringe filter and was analyzed by an Agilent 1200 high-performance liquid chromatography (HPLC) analyzer equipped with 2 KC-811 columns (SHODEX) on a tunable ultraviolet/visible (UV/vis) absorbance detector adjusted to 210 nm and a differential refractometer detector. The mobile phase of the HPLC system was a 2 mmol/L HClO4 with a flow rate of 1 mL/min. Liquid samples were also analyzed by a gas chromatography-mass spectrometer (GC–MS, Agilent GC7890A-MS5975C) equipped with an HP-Innowax column (30 m × 0.25 mm × 0.25 μm) for qualification. Metal ions contained in the liquid samples were analyzed by an inductively coupled plasma–atomic emission spectrometry (ICP-AES, Agilent 7700). In reactions with 13C isotope, 13C-nuclear magnetic resonance (13C-NMR) analysis was performed by a Bruker Avance III 400 MHz NMR-spectrometer operated at 100 MHz to determine the concentration of H13COOH. Before the NMR analysis, 100 μL CH313COOH was injected into 400 μL liquid sample as an internal standard.

Solid sample after the reaction was washed with deionized water for 5 times and dried in a vacuum oven before further analysis. X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance XRD analyzer equipped with a Cu Kα radiation source at a scan rate of 0.1°/s. X-ray photoelectron spectroscopy (XPS, EXCALAB 250) with a monochromatic Al Kα source (1486.6 eV) was conducted to observe the valence states of solid samples. Specimen for XPS analysis were washed with deionized water for 5 times and dried in a vacuum oven after the reaction and before the XPS analysis. The obtained XPS spectra were calibrated by aligning with the C 1s peak. Transmission electron microscopy (TEM, JEOL JEM-2100) was conducted to observe the microscopic particle shape and size of catalysts. Samples for TEM analysis were ultrasonically dispersed in ethanol and then suspended on a copper grid before the analysis. Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) mesopore were determined by static nitrogen adsorption-desorption technique on a BET analyzer (Autosorb-iQ-TPX, Quantachrome, USA). Samples for BET analysis were pretreated at 523 K under vacuum for 6 hours. Thermogravimetric analysis (TGA, Mettler-Toledo) was conducted to determine the Pd loading of Pd/C under the following operational conditions: 3-5 mg powder sample heated from 50°C to 700°C in dynamic air atmosphere (30 mL/min) with a heating rate of 30°C/min.

2.4 Definition

Formate yield in this research was defined as the molar ratio of the carbon in the produced formate to the carbon in the initial NaHCO₃ [Eqn (1)].

\[
\text{Yield\%} = \frac{C \text{ in formate, mmol}}{C \text{ in initial NaHCO₃, mmol}} \times 100\%
\]  

3 RESULTS AND DISCUSSION

3.1 Confirmation of HCO₃⁻ reduction with 2-pyrrolidone

Our preliminary experiment has demonstrated that Spirulina (a typical microalga) and bovine serum albumin (BSA, a typical protein contained in the microalgae) are unstable and easy to decompose to various nitrogen-containing ring compounds under hydrothermal conditions. Specifically, N-containing heterocyclic rings were generated substantially when Spirulina or BSA reacted solely in high-temperature water (Figure 1). On the other hand, when NaHCO₃ was added to the reaction, the quantity of N-containing heterocyclic rings decreased tremendously, and quantitative formic acid was generated in the reaction. These results suggest that the addition of NaHCO₃ leads to a decomposition of N-containing ring compounds and promotes the formic acid production. To further study the production of formic acid from the reaction of NaHCO₃ with biomass, 2-pyrrolidone was selected as a representative of the nitrogen-containing ring compounds since it has similar structure to those of nitrogen-containing ring compounds derived from Spirulina and it is relatively low-cost and commercially available.

Subsequently, reaction of 2-pyrrolidone in the presence and absence of NaHCO₃ under hydrothermal conditions was examined. Results showed that peaks of propanol, hydroxylbutyric acid, N-propyl-2-pyrrolidone, and 2-pyrrolidone

![FIGURE 1 GC-MS chromatograms of aqueous samples of Spirulina or bovine serum albumin (BSA) reacting with or without NaHCO₃ (1.2 mol/L NaHCO₃, 0.75 mol/L BSA, 0.28 g Spirulina, 2 h, 300°C, 50% water filling rate)](image-url)
were observed in the GC-MS spectrum (Figure S1), and only a broad peak of 2-pyrrolidone was observed in the HPLC spectrum of the liquid sample after the reaction of 2-pyrrolidone (Figure S2). Interestingly, with the addition of NaHCO₃, a clear formation of formate together with a trace amount of propionate was detected after the reaction (Figure S2). Based on the initial HCO₃⁻ concentration and the produced formate concentration, a formate yield of 7.4% was obtained. Then, gaseous products after the reaction of 2-pyrrolidone with NaHCO₃ were collected and analyzed by GC-TCD, and the result showed that only CO₂ was detected (Figure S3). To assure the formate production was from the HCO₃⁻ rather than the 2-pyrrolidone, experiments of 2-pyrrolidone reacting with NaH¹³CO₃ were conducted. The NMR analysis of the liquid product revealed that an apparent peak of H¹³COOH in ¹³C-NMR spectra was generated (Figure S4). The yield of H¹³COOH was determined to be 7.6% by using CH₃¹³COOH as an internal standard. This yield is almost the same as that obtained by using normal NaHCO₃ as the starting material. These results indicate that the formate is produced from the HCO₃⁻. Thus, using 2-pyrrolidone as the reducing agent for the bicarbonate reduction to formate is feasible.

3.2 Optimizing reaction conditions for the formate yield

Since formate can be effectively produced from the reaction of 2-pyrrolidone with HCO₃⁻, effect of different reaction parameters on the formate yield was studied to optimize the reaction condition and to promote the formate yield. Figure 2 illustrates the formate yield obtained at various concentrations of 2-pyrrolidone and NaHCO₃. It can be seen that increasing the 2-pyrrolidone concentration from 0.25 to 1 mol/L significantly improved formate yield from 3.7% to 8.0%. This is probably because higher 2-pyrrolidone concentration provided stronger reduction condition, which then promoted the conversion of NaHCO₃ to formate. However, the formate yield reached a plateau when the 2-pyrrolidone concentration exceeded 1 mol/L, indicating that a reaction equilibrium was reached (Figure 2A). On the other hand, increasing the NaHCO₃ concentration could also enhance the formate yield when the NaHCO₃ concentration was lower than 1.2 mol/L (Figure 2B). However, unlike the effect of 2-pyrrolidone, the formate yield dropped to 6% of when the NaHCO₃ concentrations further increased to 1.8 mol/L. Since the absolute formate concentration ascended incessantly with the NaHCO₃ concentrations, the decrease in the formate yield is probably attributed to the relatively insufficient amount of 2-pyrrolidone.

Then, effect of reaction time and temperature on formate yield was examined, and the results are shown in Figure 3. Formate yield was negligible at 250°C and only a 2% formate yield was obtained at 275°C. When the temperature exceeded 300°C, formate yield increased remarkably with the reaction
temperature, indicating higher temperature is advantageous to the bicarbonate conversion into formate. The reaction time also had an obvious effect on the formate yield, especially in the case of at high reaction temperature. At 350°C, the formate yield increased from 14% at 30 minute to 20% at 150 minute.

In our previous studies, it has been found that water filling rate has a significant effect on the hydrothermal reduction of bicarbonate to formate with metal reductants (Zn, Fe etc.), which is attributed to that the increasing water filling rate leads to an increase in the in situ produced hydrogen pressure and then enhances the bicarbonate reduction. Thus, effect of water filling rate on formate yield with 2-pyrrolidone as the reductant was subsequently investigated. It should be noted that increasing water filling rate would generally lead to a decrease in the reactant concentration in the solution. Thus, the amount of NaHCO₃ and 2-pyrrolidone were increased simultaneously in the study of the water filling rate to maintain a constant reactant concentration. Results revealed that formate yield was relatively stable when water filling rate increased from 30% to 55% (Figure S5), indicating that the water filling rate had a negligible effect on the formate production from NaHCO₃. This result is different from our previous research, in which, the water filling rate has a significant effect on the formate yield from bicarbonate when using metal reductants. This suggests that the reaction mechanism using the 2-pyrrolidone as the reductant is different from that using the metals as the reductant.

### Table 1: Formate yields from the reaction of NaHCO₃ and 2-pyrrolidone with different catalysts

| Entry | Catalyst | Formate yield (%) |
|-------|----------|-------------------|
| 1     | –        | 7.4               |
| 2     | Co       | 5.1               |
| 3     | Ni       | 7.8               |
| 4     | Pd/C     | 17.8              |
| 5     | Pd/Cᵇ    | 30                |
| 6     | Activated carbon | 7.6          |
| 7     | Cu       | 6.1               |
| 8     | Cr       | 13.9              |
| 9     | NiAl     | 6.0               |
| 10    | Mo       | 6.9               |

*Reaction conditions: 1.2 mol/L NaHCO₃, 0.75 mol/L 2-pyrrolidone, 0.1 g catalysts, 50% water filling rate, 2 h, 300°C.  
*Temperature: 350°C.

**3.3 | NaHCO₃ reduction into formate with 2-pyrrolidone on Pd/C catalyst**

Although the reduction in NaHCO₃ into formate was successfully achieved by reacting with 2-pyrrolidone, the formate yield was relatively low. Thus, various transient metals as catalysts were screened to enhance the formate yield. As summarized in Table 1, among all the tested catalysts, only Pd/C and Cr powder exhibited a positive effect on promoting the formate yield, and the formate yields obtained at 300°C on Pd/C and Cr were 17.8% and 13.9%, respectively. In addition, an optimum formate yield of 30% was successfully obtained by increasing the reaction temperature to 350°C in the presence of Pd/C. Figure S6 showed the XRD pattern of Pd/C before and after the reaction. Diffraction peaks centered at 27° and 32° were probably related to the carbon support, and diffraction peak at 42° was related to Pd metal (Pd⁰, 111). BET measurements showed that the surface area of Pd/C were 731.1 and 726.3 m² g⁻¹ before and after the reaction (Table S1). The pore volume of Pd/C before and after the reaction were 0.64 and 0.61 cm³ g⁻¹, respectively. The Pd loading of Pd/C (determined by the TGA analysis) were 11.6% before the

**FIGURE 4** Transmission electron microscopy (TEM) images of Pd/C before reaction (A), Pd/C after the 1st recycling reaction (B), Pd/C after the 2nd recycling reaction (C), and Pd/C after the 3rd recycling reaction (D), overlaid figures are particle size distribution of Pd (0.75 mol/L 2-pyrrolidone, 1.2 mol/L NaHCO₃, 0.1 g Pd/C, 50% water filling rate, 2 h, 300°C)
reaction and 11.5% after the reaction (Table S1, Figure S7). These results indicated that Pd/C had no obvious change after the reaction. Then, the morphology of Pd/C before the reaction was analyzed by TEM. From Figure 4A, well-distributed nano-sized Pd particles can be clearly observed and the mean particle size was determined to be 3.3 ± 0.7 nm based on the TEM results. Although Pd/C is a well-known catalyst for the CO₂ reduction and Pd is generally regarded as the active site, to confirm the active site of Pd/C, reaction using activated carbon to replace Pd/C was performed. Result showed the formate yield obtained with the activated carbon was almost the same to that obtained without Pd/C (Table 1, Entries 1 and 6). These results evidenced that the active component for promoting the formate yield was the Pd in the Pd/C.

To further determine the stability of the Pd/C catalyst in the conversion of NaHCO₃ to formate, Pd/C after the reaction was recovered and reused in the NaHCO₃ reduction reactions for 3 cycles. Results showed that the formate yield was relatively stable after 3 cycles (Figure 5). To confirm whether Pd leaching was occurred after the reaction, ICP analysis of the liquid sample was conducted. No Pd was detected in the solution, indicating that the leaching of Pd was negligible. Then, particle size distributions of Pd/C after each cycle were compared by TEM analysis. Results showed the particle sizes of Pd before the reaction and after 3 cycles were almost the same (Figure 4). Subsequently, to explore the catalytic mechanism of Pd/C, Pd/C before and after each cycling reactions were subjected to XPS analysis. As shown in Figure 6, 2 elementary peaks at 335.8 eV and 341.0 eV corresponding to the binding energies of Pd 3d⁵/₂ and Pd 3d³/₂ were detected from the spectrum of original Pd/C. The binding energy of Pd⁰ before the reaction and after used for 3 cycles displayed no shifts, indicating that the Pd kept a stable chemical state during the reaction.

### 3.4 Mechanism of NaHCO₃ reduction into formate with 2-pyrrolidone

Liquid samples after the reduction of HCO₃⁻ with 2-pyrrolidone at different reaction times were further analyzed by GC-MS to identify the reaction intermediates to determine the reaction mechanism. As shown in Figure 7, no products were detected in the first 5 minutes. After 10 minutes, a trace amount of hydroxyl-butyric acid was detected, suggesting the hydrolysis and deamination of 2-pyrrolidone was the first reaction step. To verify the deamination of 2-pyrrolidone, liquid sample after the reaction at 2 hours was further analyzed by ion chromatography, and a generation of 0.35 mol/L ammonia in the liquid sample was confirmed. At 30 minutes, in Figure 7,
production of propanol was identified, which was probably derived from the decarboxylation of hydroxyl-butyric acid since decarboxylation reaction is ready to occur under hydrothermal conditions, especially when Pd catalyst exists.41 From 30 minute to 120 minute, hydroxyl-butyric acid, propanol and formate increased incessantly, accompanied by the appearance and increase in nitrogen-containing compounds.

In our previous studies of hydrothermal reduction in bicarbonate to formate with isopropanol,42 it has been found that alcoholic hydroxyl group can be used as an effective reductant for bicarbonate reduction. Thus, the propanol produced during the presented reaction probably acted as the active reductant for the bicarbonate reduction. To confirm this assumption, reaction of propanol (0.75 mol/L) with NaHCO₃ (1.2 mol/L) at 300°C for 2 hours under hydrothermal conditions was conducted, and a 13.7% formate yield was successfully obtained after the reaction. This result evidenced that propanol was acted as the reductant during the conversion of bicarbonate to formate. It should be noted that the formate yield obtained with propanol as the reductant was higher than that obtained with 2-pyrrolidone (7.4%) at the same reaction condition, which is probably because various side reactions occurred when 2-pyrrolidone was used and thus led to a decrease in the formate yield. In addition, we also tested the propanol reaction with NaHCO₃ in the presence of Pd/C at the same reaction condition, and a 22% formate yield was obtained. It has been reported that Pd is a common catalyst for CO₂ or HCO₃⁻ reduction since CO₂ and HCO₃⁻ can be adsorbed onto the Pd surface, which decreases the reaction energy barrier.43-46 Thus, the Pd/C in the presented research probably acted as the similar role.

Based on the above results, a possible reaction mechanism of 2-pyrrolidone reducing NaHCO₃ was proposed in Scheme 1. First, 2-pyrrolidone is hydrolyzed and deaminated into hydroxyl-butyric acid under hydrothermal condition. Then, propanol is derived via the decarboxylation of hydroxyl-butyric acid under alkaline condition. The produced propanol subsequently reduces bicarbonate to formate on Pd surface, while the propanol itself is oxidized to propionaldehyde. Finally, propionaldehyde reduces another bicarbonate ion to formate, while itself being oxidized to propionate. Therefore, the net effect of this reaction is 1 mol HCO₃⁻ was converted to 1 mol formate with 1 mol 2-pyrrolidone.

## CONCLUSION

In this study, a novel method of using 2-pyrrolidone as a renewable reductant to reduce NaHCO₃ into formate on various catalysts was studied. Among all the tested catalysts, Pd/C exhibited the optimum performance for promoting the formate yield, and an optimal formate yield of 30% was successfully obtained. During the hydrothermal reaction, 2-pyrrolidone was decomposed to various different compounds, in which, propanol was determined to be the active reducing agent and hydrogen source for the bicarbonate reduction to formate. Based on these research results, a reaction mechanism of the 2-pyrrolidone reduction of bicarbonate to formate was also proposed. This study provides new insights of utilizing nitrogen-containing organic compounds as a renewable hydrogen source for the reduction of NaHCO₃, and would probably create a new method for utilizing protein-containing biomass for NaHCO₃ conversion.
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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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