ABSTRACT: The utilization of CO₂ as a cheap and abundant carbon source to produce useful chemicals or fuels, has been regarded as one of the promising ways to reduce CO₂ emissions and minimize the green-house effect. Previous studies have demonstrated that CO₂ (or HCO₃⁻) can be efficiently reduced to formic acid with metal Fe under hydrothermal conditions without additional hydrogen and any catalyst. However, the pathways and kinetics of the autocatalytic CO₂ reduction remain unknown. In the present work, the reaction kinetics were carefully investigated according to the proposed reaction pathways, and a phenomenological kinetic model was developed for the first time. The results showed that the hydrothermal conversion of HCO₃⁻ into formic acid with Fe can be expressed as the first-order reaction, and the activation energy of HCO₃⁻ is 28 kJ/mol under hydrothermal conditions.

1. INTRODUCTION

Due to the increasing demand for energy and consumption of fossil fuels, the level of CO₂ atmosphere has raised at a faster rate, which leads to a series of problems in the environment and ecological balance.¹⁻³ In recent years, a great deal of focus has been expended to reduce the CO₂ concentration in the atmosphere, such as photosynthesis, electrochemical and biochemical technology, and so on.⁴⁻⁷ Among these methods, artificial photosynthesis is regarded as one of the most promising methods for solar energy technologies.⁸ However, there are still many challenges in the direct conversion of CO₂ using solar energy, such as the low conversion efficiency and product selectivity. Recently, the catalytic reduction of CO₂ with hydrogen has attracted increasing attention due to its commercial feasibility.⁹⁻¹¹ Nevertheless, high purity hydrogen and noble metal catalysts (Ir, Ru, Rh, etc.) are usually needed in the reduction process, leading to high energy consumption and cost.¹²,¹³ Therefore, the development of an alternative method for the feasible reduction of CO₂ is highly desirable.

Hydrothermal chemistry has played an important role in the formation of fossil fuels and origin of life in the earth’s crust and deep-sea hydrothermal vents.¹⁴⁻¹⁶ The abiotic synthesis of organics suggests that highly efficient dissociation of H₂O and the subsequent reduction of CO₂ into organics could be achieved with metals under hydrothermal conditions. In the abiotic synthesis of organics, the generally inferred pathway involves the reduction of CO₂ dissolved in water that accompanies the hydrothermal alteration of minerals, in which a primary role for the minerals is to generate H₂ through the reducing conditions as the reaction of ferrous Fe-bearing minerals with water.¹⁷,¹⁸ Recently, Jin’s group has developed a new strategy for the hydrothermal reduction of CO₂ with various zero-valent metals, such as Fe, Zn, and Mn, and it was found that formic acid was the main product from reduction of CO₂.¹⁹⁻²² As an important chemical, formate can serve as the raw material for the environmentally friendly road de-icer.²³ Furthermore, the dehydrogenation of formic acid can proceed easily under mild conditions.²⁴ Therefore, as an excellent hydrogen storage carrier, formic acid can play an important role in the future context of a hydrogen energy economic picture.

Although previous research has demonstrated the potential of the autocatalytic reduction of CO₂ into formic acid with zero-valent metal Fe under hydrothermal conditions, few studies have been focused on investigating the comprehensive pathways and reaction kinetics in CO₂ reduction. In this work, the detection and distribution for all products from the autocatalytic hydrothermal reduction of CO₂ were conducted, and then, based on these results, a possible reaction network and a quantitative model for the kinetics of hydrothermal carbon dioxide reduction were developed. Considering that HCO₃⁻ is the product of CO₂ captured from waste streams by
basic solution, NaHCO₃ was used as the CO₂ source. Simultaneously, the application of NaHCO₃ can also simplify the experimental procedure and ensure the accuracy of carbon amount.

2. RESULTS AND DISCUSSION

2.1. Product Distribution. First, a series of experiments were conducted to investigate the distribution of products from the reduction of NaHCO₃ in water with Fe as a reductant. From Figure 1, it was shown that formic acid was the main liquid product. A little amount of acetic acid was also detected after 600 s of reaction time. With the increase of the temperature, the conversion of HCO₃⁻ significantly increased from 30 to 50 mol %, similarly with the trend for the yield of formic acid. However, the yields of gas products remained steady without significant change.

The analysis of the gas samples by gas chromatography/thermal conductivity detection (GC/TCD) showed that H₂, CO₂ and a trace amount of CO were produced at a reaction time of 600 s. In Table 1, it is obviously seen that the hydrogen was the main product in gas products, which was mainly from the decomposition of H₂O. Only a trace amount of CO was produced after the reaction. With the increasing temperature, the ratio of carbon dioxide was first decreased and then increased, which means that the decomposition of products such as formic acid and acetic acid appeared at higher temperatures.

| temperature (°C) | H₂ (wt %) | CO₂ (wt %) | CO (wt %) |
|------------------|-----------|------------|-----------|
| 250              | 90        | 9.1        | 0.9       |
| 300              | 91        | 7.9        | 1.1       |
| 350              | 91        | 8.4        | 0.6       |

2.2. Effect of Reaction Time and Temperature. A series of experiments were carried out to investigate the effect of residual time and temperature on hydrothermal conversion of HCO₃⁻ by varying the time from 0 to 600 s and the reaction temperature from 250 to 350 °C with the same amount of Fe (12 mmol), respectively. As shown in Figure 2a, it was suggested that the yield of formic acid has shown a rapid increase with the increase of reaction time in 180 s at 250 and 300 °C, while the yield of formic acid increased linearly further with the reaction time over 300 s in all test temperatures. For the temperature at 350 °C, the yield of formic acid increased rapidly at all set reaction times. However, the trend of acetic acid yield was in contrast to that of formic acid. In Figure 2b, it was observed that the yield of acetic acid increased first from 0 to 600 s and dropped a little in 600 s at 350 °C. With regard to the decomposition of acetic acid, the decarboxylation pathway existed under hydrothermal conditions. It has also been reported that acetic acid decomposed preferentially into CO₂ and H₂ at a temperature of 325 °C and a pressure of 350 bars. The possible reason for the decreasing yield of acetic acid is that the decarboxylation of acetic acid dominated gradually and exceeded the formation rate of acetic acid with increasing temperature.

2.3. Effect of the Fe Amount. To further examine the effect of the hydrogen amount on the yield of product distribution, the effect of the initial Fe amount was also investigated at 350 °C. In Figure 3, it is shown that the yield of formic acid, acetic acid, and gas products all improved in the set reaction time (600 s) with the increase of the amount of Fe from 2 to 12 mmol. The high formic acid yield can be obtained without adding any other catalysts, which may be caused by several factors. First, being a closed system, when the H₂ amount was increased, the total gas amount and pressure increased; this caused the increase of H₂ partial pressure and the solubility of H₂ in the liquid phase. If the H₂ concentration was increased, the reaction rate of HCOO⁻ also increased as per Le Chatelier’s principle. The same effect can be achieved by increasing the pressure by reducing the empty volume of the reactor, which was shown by Roman-Gonzalez et al. The second reason may be that Fe₃O₄ formed in hydrothermal conditions acted as a catalyst, which corresponds to the previous study. In Section 3.2, it is also suggested that with the increase of temperature, Fe improved the formation of formic acid. It is possible that higher temperatures are favorable for the formation of Fe₃O₄.

To test this assumption, the X-ray diffraction (XRD) patterns of the solid residues obtained at different temperatures are shown in Figure 4. In our previous research, we indicated that Fe first reacts with CO₂ and H₂O to form FeCO₃, which then loses CO₂ to form Fe₃O₄. In addition, the existence of HCOO⁻ also accelerated the Fe oxidation in water to produce hydrogen. Simultaneously, Fe₃O₄ is reduced in situ, leading to the formation of more active sites on the surface of Fe₃O₄. The formed hydrogen and HCOO⁻ are activated on the Fe₃O₄-x surface. This suggested that the more the Fe is oxidized to Fe₃O₄ under hydrothermal conditions, the more the surface of Fe₃O₄-x and the amount of H₂ could be acquired, improving the reduction of HCOO⁻.

2.4. Kinetic Modeling for the Hydrothermal Reduction of HCOO⁻. Based on the above experimental data, the reaction network for hydrothermal reduction of HCOO⁻ was investigated in the present work, which differs from that offered recently for isothermal hydrothermal reduction of bicarbonate concentration at subcritical temperatures. In Figure 5, the reaction network is proposed, which includes a primary pathway which shows that the reversible reaction appeared between bicarbonate concentrate and formate, a secondary pathway through two stages of tandem reaction for...
the conversion of bicarbonate into acetate, and the final pathway that allows for gas formation from bicarbonate, formate, and acetate.

Mathematica 10.2 was employed to solve the system of ordinary differential equations and simultaneously estimate the $A_i$ (Arrhenius pre-exponential factors) and $E_i$ (activation energies) of hydrothermal $\text{HCO}_3^-$ reduction by minimizing the sum of squared residuals (SSR) as shown in eq 1.

$$\text{SSR} = \sum_i \sum_m (x_i(t) - x_{i,m}(t))^2$$  

The first-order-rate law was postulated to describe the kinetics for each pathway, which corresponded with Chiang et al. and then coupled them with the batch reactor design equation, as shown below in eqs 5–8. The subscripts on each mass fraction, $x_i$ and $k_i$, referred to the yields of each product fraction and the rate constants for pathways (liquids = $\text{HCO}_3^-$, $\text{FA} = \text{formic acid}$, $\text{AA} = \text{acetic acid}$, $G = \text{gas}$). The temperature profiles of the proxy reactors for each set point temperature were fitted using power series models and incorporated directly into the model to give the reactor temperature as a function of time. Additionally, we have assumed that all reactions take place in a single fluid phase.

$$\frac{dx_k}{dt} = -(k_1 + k_3 - k_2)x_k$$  

$$\frac{dx_{\text{FA}}}{dt} = k_1x_k - (k_2 + k_4 + k_5)x_{\text{FA}}$$  

$$\frac{dx_{\text{AA}}}{dt} = k_4x_{\text{FA}} - k_6x_{\text{AA}}$$  

$$\frac{dx_G}{dt} = k_7x_k + k_9x_{\text{FA}} + k_{10}x_{\text{AA}}$$

In Table 2, we describe the kinetics parameters and optimized Arrhenius parameters for the hydrothermal reduction of $\text{HCO}_3^-$. It was determined that the activation energy for formation of formic acid from $\text{HCO}_3^-$ during
hydrothermal conditions is about 28 kJ/mol, which is similar with the results from the range determined previously for decomposition of acids. 32 It was indicated that the kinetic constant for formic acid is significantly increasing with the temperature, which is consistent with the results from our experiments. The earlier kinetics modeling work on conventional hydrogenation of CO 2 provided an opportunity for comparison of these activation energies (80 kJ/mol), which are higher than our results from hydrothermal reduction. 33

However, the activation energy of acetic acid from formic acid is about 72 kJ/mol, which is the rate-determining step to limit the formation of acetic acid. The activation energies for the gasification of acetic acid are also comparable to activation energies reported by Belsky et al. for the decarboxylation of acetic acid and its derivatives (71–178 kJ/mol). 34

According to the determined the kinetic parameters based on the results of experiments, the correlation between the model calculations and the experimental data for the hydrothermal reduction of HCO₃⁻ at different temperatures and times are displayed in Figure 6. The model accurately describes the trends in the data and provides the species concentrations within experimental errors. From Figure 6a–c, it was also illustrated that the proposed reaction network and optimized Arrhenius parameters could capture the trends in the observed product yields for all three set point temperatures, which is also consistent with the first-order-rate law as postulated.

We also compared the yield of each product from experiment and the yield data from the predicted model in Figure 7. It displays a plot that compares the experimental and predicted product yields, in which the circles represent data from temperatures with long reaction time (0–20 min), triangles represent data from the amount of 14 mmol Fe, and squares represent data from 275 °C. It has been shown that the predicted data are almost below the diagonal. Though our perfection may not be fitted together to predict the product

| rate constant | pathway                      | $k_{250°C}$ (min⁻¹) | $k_{300°C}$ (min⁻¹) | $k_{350°C}$ (min⁻¹) | ln A     | $E_i$ (kJ/mol) |
|---------------|-----------------------------|----------------------|---------------------|---------------------|---------|--------------|
| $k_1$         | liquids $\rightarrow$ formic acid | 0.00817              | 0.0143              | 0.0230              | 1.63    | 28           |
| $k_2$         | formic acid $\rightarrow$ solids | 0.00290              | 0.00657             | 0.0131              | 3.58    | 41           |
| $k_3$         | liquids $\rightarrow$ gas    | 0.00022              | 0.000859            | 0.00269             | 7.21    | 68           |
| $k_4$         | formic acid $\rightarrow$ acetic acid | 7.04 × 10⁻⁶     | 2.98 × 10⁻⁵         | 0.0001              | 4.69    | 72           |
| $k_5$         | formic acid $\rightarrow$ gas | 3.08 × 10⁻⁷          | 1.84 × 10⁻⁵         | 8.22 × 10⁻⁶         | 5.47    | 89           |
| $k_6$         | acetic acid $\rightarrow$ gas | 1.12 × 10⁻⁹          | 9.76 × 10⁻⁹         | 6.02 × 10⁻⁸         | 4.22    | 108          |

Figure 6. Experimental (points) and model calculated yields (continuous curves) for the hydrothermal reduction of HCO₃⁻ at set point temperatures (a) 250, (b) 300, and (c) 350 °C with different reaction times (0–600 s).
yields from reduction of CO\textsubscript{2}, it was a true prediction to an extrapolation to a reaction regime with limited parametrization.

3. EXPERIMENTAL SECTION

3.1. Materials. Zero-valence metal Fe powders (325-mesh size) were obtained from Aladdin Chemical Reagent, and NaHCO\textsubscript{3} (used as a CO\textsubscript{2} source) was obtained from Sinopharm Chemical Reagent Co., Ltd. All other reagents were commercially available from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the study. The reactions were conducted by 316 stainless-steel Swagelok tube fittings with an internal volume of approximately 5.7 mL.

3.2. Reactors and Hydrothermal Reduction Procedure. In a typical experimental procedure, the desired amount of NaHCO\textsubscript{3} (2 mmol), Fe powder, and deionized water was loaded in a batch reactor to occupy 35% of the total reactor volume. After loading, the reactor was immersed in a salt bath, which has been preheated at the set point temperatures of 250, 300, and 350 °C. It took the time at which the reactor reached its isothermal temperature as \( t = 0 \). While the reactors remained in the salt bath for an additional 0–600 s, the reactors were removed from the salt bath and cooled in a cold-water bath to quench the reactions. Then, the gas products were initially collected into a TCD for analysis, and the liquid and solid samples were separated through the filter membrane (0.22 μm filter film) for analysis, respectively. Liquid samples were analyzed by high-performance liquid chromatography (HPLC) (Agilent Technologies 1200 system), GC–flame ionization detector/mass spectrometry (Agilent 6890 gas chromatographs with a mass spectrometer), and a total organic carbon (TOC) analyzer (Shimadzu TOC 5000A). Solid residues were analyzed by XRD (Bruker D8 Advance X-ray diffractometer). All the experiments were conducted three times to force the influence of systematic errors.

Quantitative estimation of formic acid and acetic acid was based on the average value from the HPLC analysis, which was analyzed by the HPLC analyzer equipped with two Shodex RS\textsubscript{pak} KC-811 columns in series and a refractive index detector. The mobile solvent of the HPLC was HClO\textsubscript{4} (2 mmol/L) on a flow rate of 1.0 mL/min and holding 30 min. The yield of acids was defined as the percentage of formic acid or acetic acid and the initial NaHCO\textsubscript{3} on a carbon basis as follows in eqs 6, 7:

\[
Y_{FA} = \frac{C_{FA}}{C_S} \times 100 \text{ mol %}
\]

\[
Y_{AA} = \frac{2C_{AA}}{C_S} \times 100 \text{ mol %}
\]

where \( C_{FA}, C_{AA}, \) and \( C_S \) are the amounts of carbon in formic acid, acetic acid, and the initial NaHCO\textsubscript{3} added to the reactors.

For gas products, a 15 ft stainless steel column, as Carboxen 1000 (Supelco), was employed to separate each component in the gas phase sample, which used Ar as the carrier gas (15 mL/min). The programmed temperature of the column was first held at 40 °C for 5 min, followed by heating at a rate of 20 °C/min until it reached 220 °C and held for 10 min, which has a total of 24 min for the run time. To quantify the amount of gas, the high-pressure valve of the reactor was connected to a sampling valve attached to an Agilent Technologies model 6890N GC equipped with a TCD. The calibration curve relates the mole fraction, \( y_i \), and the peak area for each component. The molar yield, \( n_i \), of each component was subsequently calculated from the mole fractions of each compound detected in the gas chromatograph using eq 8, which was determined by the moles of N\textsubscript{2} from air in the reactor using the ideal gas law.

\[
n_i = \frac{Y_i}{y_i} \times n_{N_2}
\]

4. CONCLUSIONS

In this work, a kinetic study was conducted for the first time to investigate the distribution of products from the autocatalytic hydrothermal reduction of HCO\textsubscript{3}\(^-\) using zero-valent metal Fe, and the pathways were proposed. The rate constants, activation energy, and frequency factors were calculated according to the Arrhenius equation, which is consistent with the first-order-rate law as postulated. The activation energy for the formation of formic acid from HCO\textsubscript{3}\(^-\) reduction is about 28 kJ/mol, which is much lower than that in the earlier kinetic modeling work on conventional hydrogenation of CO\textsubscript{2}. The present study is helpful for providing a promising perspective to show the pathways and phenomenological kinetics of hydrothermal reduction of carbon dioxide.

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The article was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes
The authors declare no competing financial interest.

Acknowledgments
The authors thank the financial support of the National Natural Science Foundation of China (grant no. 31801321), the Shanghai Sailing Program (grant no. 19YF1436300), and the Natural Science Foundation of Shanghai (grant no. 18ZR1428100).

References

(1) Li, K.; An, X.; Park, K. H.; Khausisheh, M.; Tang, J. A critical review of CO2 photocatalysis: Catalysts and reactors. Catal. Today 2014, 224, 3–12.

(2) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Raney Ni-Sn catalyst for H2 production from biomass-derived hydrocarbons. Science 2003, 300, 2075–2077.

(3) Lal, R. Sequestration of atmospheric CO2 in global carbon pools. Energy Environ. Sci. 2008, 1, 86–100.

(4) Aresta, M.; Dibenedetto, A. The contribution of the utilization option to reducing the CO2 atmospheric loading: research needed to overcome existing barriers for a full exploitation of the potential of the CO2 use. Catal. Today 2004, 98, 455–462.

(5) Hoffert, M. I.; Covey, C. Deriving global climate sensitivity from palaeo-climate reconstructions. Nature 1992, 360, 573–576.

(6) Hoffert, M. I.; Caldeira, K.; Benford, G.; Crisswell, D. R.; Green, C.; Herzig, H.; Jain, A. K.; Kheshgi, H. S.; Lackner, K. S.; Lewis, J. S.; Lightfoot, H. D.; Manheimer, W.; Mankins, J. C.; Mauel, M. E.; Perkins, L. J.; Schlesinger, M. E.; Volk, T.; Wigley, T. M. L. Advanced technology pathways to global climate stability: energy for a greenhouse planet. Science 2002, 298, 981–987.

(7) He, R.; Hu, B.; Zhong, H.; Jin, F.; Fan, J.; Hu, Y. H.; Jing, Z. Reduction of CO2 with H2S in a simulated deep-sea hydrothermal vent system. Chem. Commun. 2019, 55, 1056–1059.

(8) Omae, I. Aspects of carbon dioxide utilization. Catal. Today 2006, 115, 33–52.

(9) Sahibzada, M.; Chadwick, D.; Metcalfe, I. S. Hydrogenation of carbon dioxide to methanol over palladium-promoted Cu/ZnO/Al2O3 catalysts. Catal. Today 1996, 29, 367–372.

(10) Borodko, Y.; Somorjai, G. A. Catalytic hydrogenation of carbon oxides—a 10-year perspective. Appl. Catal., A 1999, 186, 355–362.

(11) Tominaga, H.; Nagai, M. Density functional study of carbon dioxide hydrogenation on molybdenum carbide and metal. Appl. Catal., A 2005, 282, 5–13.

(12) Inui, T.; Kitagawa, K.; Takeguchi, T.; Hagiwara, T.; Makino, Y. Hydrogenation of carbon dioxide to C1–C7 hydrocarbons via methanol on composite catalysts. Appl. Catal., A 1993, 94, 31–44.

(13) Nam, S.-S.; Kim, H.; Kishan, G.; Choi, M.-J.; Lee, K.-W. Catalytic conversion of carbon dioxide into hydrocarbons over iron supported on alkali ion-exchanged Y-zeolite catalysts. Appl. Catal., A 1999, 179, 155–163.

(14) Jessop, P. G.; Leitner, W. Chemical Synthesis Using Supercritical Fluids; Wiley-VCH, 1999; p 358.

(15) Horita, J.; Berndt, M. E. Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. Science 1999, 285, 1055–1057.

(16) McCollom, T. M.; Seewald, J. S. A reassessment of the potential for reduction of dissolved CO2 to hydrocarbons during serpentinization of olivine. Geochim. Cosmochim. Acta 2001, 65, 3769–3778.

(17) Takahashi, H.; Liu, L. H.; Yashiro, Y.; Ioku, K.; Bignall, G.; Yamashita, N.; Kori, T. CO2 reduction using hydrothermal method for the selective formation of organic compounds. J. Mater. Sci. 2006, 41, 1585–1589.

(18) Fu, Q.; Sherwood Lollar, B.; Horita, J.; Lacrampe-Couloume, G.; Seyfried, W. E. Abiogenic formation of hydrocarbons under hydrothermal conditions: Constraints from chemical and isotope data. Geochim. Cosmochim. Acta 2007, 71, 1982–1998.

(19) Wu, B.; Gao, Y.; Jin, F.; Cao, J.; Du, Y.; Zhang, Y. Catalytic conversion of NaHCO3 into formic acid in mild hydrothermal conditions for CO2 utilization. Catal. Today 2009, 146, 405–410.

(20) Lu, L.; Zeng, X.; Yun, J.; Wei, F.; Jin, F. No Catalyst Addition and Highly Efficient Dissociation of H2O for the Reduction of CO2 to Formic Acid with Mn. Environ. Sci. Technol. 2014, 48, 6003–6009.

(21) Jin, F.; Moriya, T.; Enomoto, H. Oxidation reaction of high molecular weight carboxylic acids in supercritical water. Environ. Sci. Technol. 2003, 37, 3220–3231.

(22) Jin, F.; Gao, Y.; Jin, Y.; Zhang, Y.; Cao, J.; Wei, Z.; Smith, R. L., Jr. High-yield reduction of carbon dioxide into formic acid by zero-valent metal/metal oxide redox cycles. Energy Environ. Sci. 2011, 4, 881–884.

(23) Kang, P.; Zhang, S.; Meyer, T. J.; Brookhart, M. Rapid selective electrocatalytic reduction of carbon dioxide to formate by an iridium pincer catalyst immobilized on carbon nanotube electrodes. Angew. Chem., Int. Ed. 2014, 53, 8709–8713.

(24) Tedsree, K.; Li, T.; Jones, S.; Chan, C. W. A.; Yu, K. M. K.; Bagot, P. A. J.; Marquis, E. A.; Smith, G. D. W.; Tsang, S. C. E. Hydrogen production from formic acid decomposition at room temperature using a Ag–Pd core–shell nanocatalyst. Nat. Nanotechnol. 2011, 6, 302–307.

(25) Watanabe, M.; Inomata, H.; Smith, R. L., Jr.; Araí, K. Catalytic deamination of acetic acid with zirconia catalyst in supercritical water. Appl. Catal., A 2001, 219, 149–156.

(26) Bang, S. S.; Johnston, D. Environmental Effects of Sodium Acetate/Formate Deicer, Ice Shear. Arch. Environ. Contam. Toxicol. 1998, 35, 580–587.

(27) Roman-Gonzalez, D.; Moro, A.; Burgoa, F.; Pérez, E.; Nieto-Márquez, A.; Martín, Á.; Bermejo, M. D. 2Hydrothermal CO2 conversion using zinc as reductant: Batch reaction, modeling and parametric analysis of the process. J. Supercrit. Fluids 2018, 140, 320–328.

(28) Du, J.; Jin, F.; Wang, Y.; Zhong, H.; Lyu, L.; Yao, G.; Hua, Z. NaHCO3-enhanced hydrogen production from water with Fe and in situ highly efficient and autocatalytic NaHCO3 reduction into formic acid. Chem. Commun. 2016, 52, 3316–3319.

(29) Zhong, H.; Yao, H.; Du, J.; Yao, G.; Jin, F. Pd/C-catalyzed reduction of NaHCO3 into CH3COOH with water as a hydrogen source. Catal. Today 2016, 274, 28–34.

(30) Luo, L.; Sheehan, J. D.; Dai, L.; Savage, P. E. Products and kinetics for isothermal hydrothermal liquefaction of soy protein concentrate. ACS Sustainable Chem. Eng. 2016, 4, 2725–2733.

(31) Chiang, C.-L.; Lin, K.-S.; Chuang, C.-H.; Yu, J. K. Direct synthesis of formic acid via CO2 hydrogenation over Cu/ZnO/Al2O3 catalyst Author links open overlay panel Journal of Cleaner Production. J. Cleaner Prod. 2018, 172, 1957–1977.

(32) Yu, J.; Savage, P. E. Decomposition of formic acid under hydrothermal conditions. Ind. Eng. Chem. Res. 1998, 37, 2–10.

(33) Suh, H.-W.; Schmeier, T. J.; Hazziri, N.; Kemp, R. A.; Takase, M. K. Experimental and Computational Studies of the Reaction of Carbon Dioxide with Pincer-Supported Nickel and Palladium Hydrides. Organometallics 2012, 31, 8225–8236.

(34) Belsky, A. J.; Maiella, P. G.; Brill, T. B. Spectroscopy of Hydrothermal Reactions 13. Kinetics and Mechanisms of Decarboxylation of Acetic Acid Derivatives at 100–260 °C under 275 bar. J. Phys. Chem. A 1999, 103, 4253–4260.