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Catalytic conversion of $NaHCO_3$ into formic acid in mild hydrothermal conditions for CO_2 utilization

Bing Wu, Ying Gao, Fangming Jin *, Jianglin Cao, Yingxun Du, Yalei Zhang

State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science & Engineering, Tongji University, Shanghai, 200092, China

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ABSTRACT

The increasing atmospheric CO_2 level causes global warming and may pose catastrophic effects to the humanity. Among the various options to reduce the CO_2 atmospheric loading, hydrothermal reactions may have a high potential for rapidly and effectively converting CO_2 into useful chemicals. In this study, the hydrothermal conversion of CO_2 into formic acid was carried out by using Fe as a reductant and Ni as a catalyst. The effect of various experimental parameters, e.g., amount of Fe (Ni), Fe/Ni ratio, temperature, reaction time, alkalinity etc. was investigated. Results showed that Ni played a catalytic role in the hydrothermal conversion of CO_2 into formic acid. The highest yield of formic acid of 15.6% was achieved under optimal conditions, i.e., Fe/Ni ratio of 1:1, temperature of 300 °C, reaction time of 120 min, filling rate of 35% and $NaHCO_3$: Fe of 1:6. Additionally, the selectivity of formic acid was more than 98%. It was also found that the hydrothermal conversion could not occur without either the addition of catalyst or the existence of CO_2 when Fe was used as a reductant. The role of CO_2 in the hydrogen production was discussed.

1. Introduction

One of the main scientific and technological challenges facing the humanity in the 21st century is to control the global warming which is caused by the increasing atmospheric CO_2 levels [1,2]. In 2008, the atmospheric concentration of CO_2 is 385 ppm, having increased by 37.5% compared with the pre-industrial level of 280 ppm and still increasing at a rate of 2 ppm per year [3]. The markedly increasing atmospheric CO_2 levels (with most increase occurring in the past 50 years) are due to combustion of large amount of fossil carbon to meet the energy demand of economic growth and civilization of the human society. In the long term, renewable or non-carbon-based energy sources must be exploited to replace fossil fuels in order to reduce the emission of CO_2. However, for the foreseeable future, the annual consumption of fossil fuels is predicted to increase markedly with a corresponding rise in atmospheric CO_2 levels since fossil fuel is currently the main energy source (75%) and the use of renewable or non-carbon energy (e.g., solar, biomass, wind, geothermal, wave and nuclear energy) will not expand that great during the next two or three decades [4]. Even holding atmospheric CO_2 concentration at 550 pm for 2100 is becoming quite impossible, although this level is considered as the threshold limit since it could eventually produce global warming comparable in magnitude but opposite in sign to the global cooling of the last Ice Age as predicted by climate models and paleoclimate data [5,6].

To meet the urgent need of reducing CO_2 atmospheric loading, approaches under consideration can be classified into two groups, namely: (1) reducing the production of CO_2, e.g., increasing energy production efficiency and exploiting/using renewable or non-carbon fuels; (2) implementing innovative technologies for capturing the produced CO_2, then either sequestrating it in spent gas/oil wells, coal beds, saline aquifers or deep ocean, or utilizing it biochemically/chemically as a carbon source to produce useful chemicals [3,4,7,8]. Since the utilization of CO_2 contributes to reducing the atmospheric loading while generating a profit, it is attracting more research interests worldwide. Comparing with biochemical approaches, chemical conversion/utilization of CO_2 is faster and has larger potential for industrial implementation. In consideration of the highly oxidized status and thermodynamically stability of carbon dioxide, its reduction/utilization is always associated with the finding or synthesis of highly reactive metal catalysts. A large amount of research works related to CO_2 utilization and catalytic reduction have been reviewed [2–4,8]. Moreover, a large number of studies have been reported to hydrogenate CO_2 to methanol and further convert methanol to C_1–C_{10} hydrocarbon fuels [9–13]. The hydrogenation of CO_2 to form formic acid, N,N-dimethylformamide (DMF) and methyl formate by using metal-complex-catalysts in supercritical carbon dioxide ($scCO_2$) or its mixture with other cosolvents such as methanol or

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* Corresponding author. Tel.: +86 21 65985792; fax: +86 21 65985792.
E-mail address: fmjin@tongji.edu.cn (F. Jin).

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water has also been reported [14]. It should be noted that hydrogen gas has been used as a reductant in most of the reported studies, while hydrogen is currently produced by reforming of hydrocarbons which is an energy-intensive process. Therefore, in this study, a hydrothermal method was proposed to convert CO_2 into formic acid under mild conditions by using Fe as a reductant and Ni as a catalyst with water acting not only as a reaction media but also as a hydrogen source.

Hydrothermal reactions have played an important role in the formation of fossil fuels, e.g., conversion of dissolved CO_2 into hydrocarbons abiotically in the earth's crust [15,16] and have shown high potential for rapid conversion of a wide range of biomass into value-added products [17–20]. Hydrothermal processes simulating the natural phenomena of abiotic synthesis of hydrocarbons from CO_2 would be expected to have high potential to quickly and efficiently convert CO_2 into organics. In this study, transition metals Fe and Ni were chosen to be a reductant and a catalyst in the hydrothermal reactions, respectively, in consideration of their readily availability and low cost. Additionally, Ni or alloy of Ni and Fe can catalyze the conversion of CO_2 into methane [15,16,21]. Although Takahashi et al. [21] have reported that CO_2 can be converted into CH_4 in hydrothermal conditions with Fe as a reductant and Ni as a catalyst, they did not specify the formation and selectivity of formic acid from CO_2. Furthermore, they did not investigate the role of CO_2 in the hydrothermal reduction either. Formic acid is an important organic chemical. For example, calcium formate has been used as a leather tanning agent, a concrete cure accelerator, or an additive in the animal feed industry. In addition, formic acid in its Na/Ca salt form has been proposed as an environmentally friendly road de-icer [22,23]. More importantly, recent research has demonstrated that formic acid has the potential to power fuel cells for electricity generation and automobiles [24–26].

In this study, we focused on the conversion of CO_2 into formic acid by changing experimental parameters, such as temperature, time, amount of Fe and Ni and the ratio of Fe/Ni. Also, the role of CO_2 in the hydrothermal CO_2 conversion was discussed.

2. Experimental

In this study, $NaHCO_3$ was used as a CO_2 resource to simplify handling. The reason was that in our previous study, it had been found the repeatability of the experimental results was not good in the case of using gaseous CO_2 probably due to the small volume of the reactor and the difficulty in controlling the amount of CO_2 introduced into the reactor precisely just through adjusting a pressure regulator. On the other hand, CO_2 can be easily dissolved in the alkaline aqueous solution especially under high temperatures and pressures. Therefore, even gaseous CO_2 was used as a reactant, it would be dissolved into the alkaline aqueous solution and equilibriums among CO_2, H_2O, HCO_3^-, CO_3^{2-} and OH^- would be attained under the hydrothermal conditions similar to those of the $NaHCO_3$ aqueous solution in this study. Therefore, it is reasonable to use $NaHCO_3$ as a CO_2 source in this study and the results could be applied to the utilization of atmospheric CO_2 to form formic acid under similar hydrothermal conditions.

The schematic drawing of the experimental set-up can be found elsewhere [27,19]. In a typical hydrothermal experiment, the desired amount of $NaHCO_3$ (CO_2 source), reductant (Fe powder), catalyst (Ni powder) if required and 2.00 ml deionized water, were loaded in a batch reactor to occupy 35% the total reactor volume. All metal powder was of 200-mesh size. The batch reactor was 3/8 in. stainless steel SUS 316 tubing with fittings (Swagelok, SUS 316) sealed at each ends. The reactor had a total length of 120 mm, wall thickness of 1 mm and an inner volume of 5.7 ml. After loading, the reactor was immersed in a salt bath, which had been filled with $NaNO_3$ and KNO_3 salts mixed at a ratio of ca. 1:1 and preheated to the desired temperature (250–300 °C). During the reaction, the reactor was shaken while being kept horizontally to enhance the mixture and heat transfer. After the preset reaction time (30–120 min), defined as the elapsed time during which the reactor was kept in the salt bath, the reactor was removed from the salt bath to quench in a cold-water bath. The controlled experiments to examine the effect of the reactor wall (SUS 316) on reactions were conducted in a Teflon-lined reactor. These experiments were carried out only at 250 °C due to the temperature limit of Teflon material.

After the reactions, the liquid, gaseous and solid samples were collected for analysis, respectively. Liquid samples were analyzed by HPLC, GC-FID/MS and TOC analyzer, gaseous samples by GC-TCD, and solid residues by X-ray diffraction. Quantitative estimation of formic acid was based on the average value obtained from the HPLC analysis of at least three samples with the relative errors always less than 10% for all experiments.

The state of formic acid in the reaction mixture may be sometimes neutral acid and sometimes formate, in particular in the presence of additional NaOH. Thus, the pH of the solution was adjusted to 6–7 with sulfuric acid before the quantitative analysis of formic acid with HPLC. Moreover, since the flowing solvent in the HPLC was 2 mM $HClO_4$ aqueous solution, it would result in the conversion of formate into formic acid under the acid conditions.

3. Results and discussion

3.1. Effect of Fe (Ni) amount and Fe/Ni ratio

The XRD patterns of the solid residue obtained from the hydrothermal reactions to convert CO_2 with the addition of Fe and Ni powder confirmed the reductive and catalytic role of Fe and Ni, respectively. As shown in Fig. 1, after the reaction, Ni still exists in the form of pure metal while Fe is oxidized into Fe_3O_4. The catalytic roles of Ni or Ni containing compounds on the hydrogenation of CO_2 have also been reported in literature [15,28,29].

The effect of Fe and Ni amount and Fe/Ni ratio were studied by fixing Fe amount at 2 mmol or 6 mmol, respectively, while varying Fe/Ni ratio between 1/2 and 2/1 with the addition of 1 mmol $NaHCO_3$ at the temperature of 300 °C, the reactor filling rate of 35% and the reaction time of 120 min. As illustrated in Fig. 2, formic acid yield, defined as the percentage of formic acid to the initial $NaHCO_3$ based on the carbon basis, shows the similar trends for

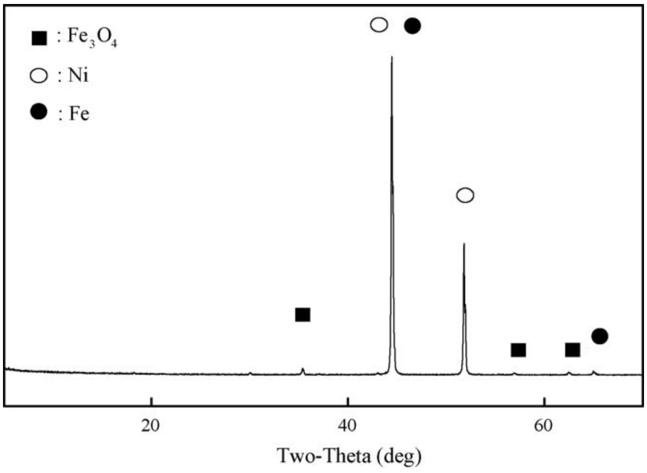

Fig. 1. XRD pattern of the solid residue obtained after hydrothermal reaction (*T*: 250 °C; $NaHCO_3$: 4 mmol; Fe: 24 mmol; Fe/Ni = 1:1; reaction time: 12 h; filling rate: 35%).