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

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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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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

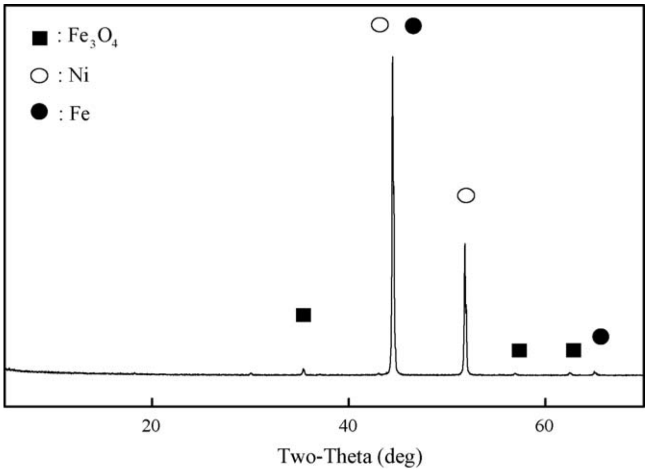

Fig. 1. XRD pattern of the solid residue obtained after hydrothermal reaction (*T*: 250 °C; $NaHCO_3$: 4 mmol; Fe: 24 mmol; Fe/Ni = 1:1; reaction time: 12 h; filling rate: 35%).

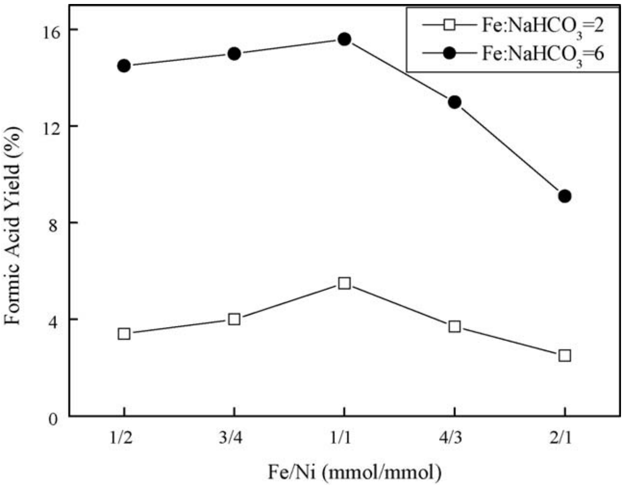

Fig. 2. Effect of Fe/Ni on formic acid yield (*T*: 300 °C; $NaHCO_3$: 1 mmol; Fe: 2 mmol or 6 mmol; reaction time: 120 min; filling rate: 35%).

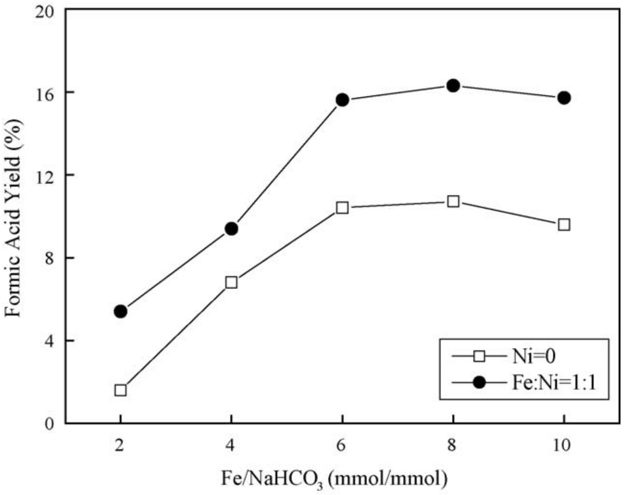

Fig. 3. Effect of Fe and Ni amount on formic acid yield (*T*: 300 °C; $NaHCO_3$: 1 mmol; Fe: 2–10 mmol; reaction time: 120 min; filling rate: 35%).

both Fe amounts and attains its peak level at the Fe/Ni ratio of 1:1. The results indicated that there was an optimal ratio of reductant Fe to catalyst Ni for the hydrothermal conversion of CO_2 into formic acid. When the Fe/Ni ratio increased further, that is, reduced the amount of catalyst, the yield of formic acid decreased gradually maybe due to the insufficient catalyst. On the other hand, when the Fe/Ni ratio is less than 1:1, a decrease in Fe/Ni ratio (or increase of catalyst amount) resulted in a slowly decline of formic acid yield. This may be caused by the further decomposition or conversion of formic acid under excess amount of catalyst Ni.

One exciting result to be noted is that the selectivity of formic acid from CO_2 conversion, defined as the percentage of carbon contained in formic acid to the total organic carbon in the liquid phase, was found to be always larger that 98%. This means that formic acid was almost the only product in the liquid phase, which is favorable to the concentration or separation of formic acid from its aqueous solution in future.

It was also found that the amount of reductant Fe had a significant impact on the formic acid yield. When the amount of Fe increased from 2 to 6 mmol at the optimal Fe/Ni ratio of 1:1, the formic acid yield also increased approximately 3-fold. Therefore, the effect of Fe and Ni amount was further investigated by fixing the Fe/Ni ratio at 1:1 while increasing Fe and Ni from 2 to 10 mmol. Additionally, another set of experiments by using only Fe as a reductant and without addition of any catalysts were also conducted to investigate the catalytic role of Ni. As illustrated in Fig. 3, for both cases, formic acid yields increase linearly with the Fe (or Fe/Ni) amount until the dosage of Fe reaches 6 mmol, and then the formic acid yield levels off. This result suggested that when the addition of reductant Fe approached a certain level, the hydrogen generated from water already exceeded the amount needed to reduce CO_2, and a further increase of reductant is not necessary. Therefore, in the following experiments, we set the ratio of reductant to carbon source of Fe:$NaHCO_3$ at 6:1. The results also showed that even without the addition of catalyst Ni, formic acid was formed and its yield increased with the amount of reductant Fe. However, the existence of catalyst Ni promoted the formic acid formation greatly.

Since the reactor was made of SUS 316, which is an alloy containing Ni, the effect of the reactor material was further studied by using a reactor with Teflon liner. It was found that almost no formic acid was formed in reactions without the addition of catalyst Ni into the Teflon-lined reactor. This result suggested that Ni existing in the SUS 316 reactor material may take part in the catalysis of the hydrothermal conversion of CO_2 or affect the actual Fe/Ni ratio in the reactions. However, due to the temperature limit of Teflon material and the structural limit of the reactor (no gas collection apparatus), all reactions in the Teflon-lined reactors had to be set at not more than 250 °C and no gas samples could be collected. Therefore, in the following hydrothermal reactions, we still use SUS 316 rector unless otherwise stated. Additionally, if only with the addition of Ni and without Fe, no formic acid was formed in the liquid sample either.

3.2. Effect of reaction temperature and time

The effect of temperature on hydrothermal conversion of CO_2 was studied by varying it between 250 and 325 °C. As shown in Fig. 4, the formic acid yield increases linearly with the reaction temperature when no catalysis Ni was added, while for the case of catalyst existence (Fe/Ni = 1:1), the yield of formic acid does not increase further with temperature when the temperature exceeds 300 °C. This result could be possibly caused by the decomposition of the formic acid under the catalysis by Ni or some inhibition effect on the catalyst Ni itself under too much high temperatures. On the other hand, the high temperature is not favorable to the

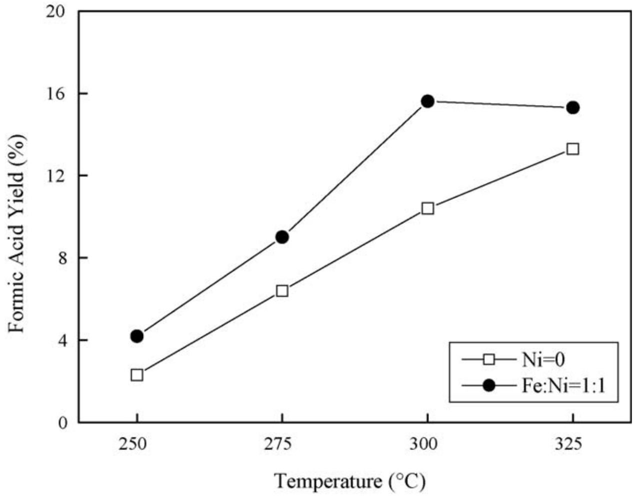

Fig. 4. Effect of reaction temperature on formic acid yield ($NaHCO_3$: 1 mmol; Fe = Ni = 6 mmol; reaction time: 120 min; filling rate: 35%).

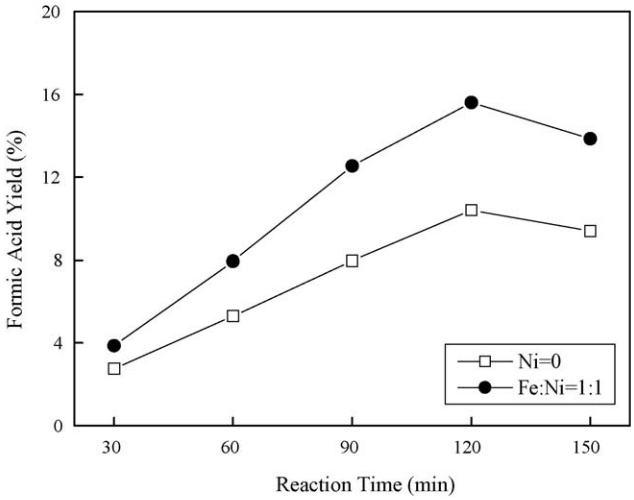

Fig. 5. Effect of reaction time on formic acid yield ($NaHCO_3$: 1 mmol; Fe = Ni = 6 mmol; temperature: 300 °C; filling rate: 35%).

energy saving, therefore, we preferred setting the hydrothermal reaction at a mild temperature of 300 °C in the following studies.

To further explore the change of formic acid yield with reaction time, the yields of formic acid after different reaction time were obtained for the cases of Fe and Fe/Ni, respectively. As shown in Fig. 5, it is evident that an optimal yield of formic acid can be obtained with reaction time of 120 min. Meanwhile, for the same reaction time, Fe/Ni exhibited a higher activity for the formation of formic acid in comparison with only Fe. With Fe/Ni, the yield of formic acid increased from an initial value of 4% to a value of ca. 16% after 120 min and then decreased to ca. 13% after 150 min. The increase in the yield of formic acid during the first 120 min can be attributed to more formic acid produced compared with those decomposed. On the other hand, after 120 min the decomposition of formic acid may be in the ascendant, consequently, the yield of formic acid decreases with further increase of reaction time.

With regard to the decomposition of formic acid, there are two generally agreed pathways: decarboxylation ($HCOOH \rightarrow CO_2 + H_2$) and dehydration ($HCOOH \rightarrow CO + H_2O$) [30–33]. It has been reported that decarboxylation was the favored pathway in the presence of water, while dehydration was dominant in the absence of water [30]. It has also been reported that formic acid decomposed preferentially into CO and H_2O at low temperatures (300 °C) and produced predominantly CO_2 and H_2 at higher temperatures (>380 °C) at 30 MPa and with a residence time of 2 min [31]. In this study, at a temperature of 300 °C and a pressure of ca. 9 MPa with a residence time of 120 min, the decomposition of formic acid should follow the decarboxylation pathway since only CO_2, H_2, trace amount of CH_4 and no CO were detected in the gaseous samples collected after the hydrothermal reactions in the cases of using Ni as a catalyst. Methane may be generated from the further hydrogenation of formic acid with the catalysis of Ni as suggested by Takahashi et al. [21]. The formation and stabilization of the formic acid in this study could be attributed to the weak alkaline conditions with the pH values of the solution measured to be 8.6 and 8.7 before and after the reactions, respectively. The effect of alkalinity on the formation and decomposition of formic acid will be further discussed in the Section 3.3.

In addition, the carbon mass balance was calculated for a few samples obtained under the optimal operating conditions for judging the reliability and usefulness of the proposed reaction as a potential CO_2 utilization technology. By combining the carbon in CO_2 and trace methane in the gaseous sample, the organic carbon in formic acid and the inorganic carbon in the residue bicarbonate or carbonate in the liquid solution and comparing it with the initial carbon in $NaHCO_3$ before the reaction, it was found that the carbon mass balance was around 90%.

3.3. Effect of alkalinity

The following discussion is related to the influence of alkalinity on the yield of formic acid with or without adding the catalyst Ni. It has been observed that alkalinity has a great influence on the formation of formic acid [21]. However, it still remains conjectural whether reaction mechanism changes under different alkalinities, consequently, different products are obtained. In the present work, considering the stability of formic acid in alkaline solution, the influence of alkalinity on the stability and yields of formic acid was investigated.

The variation of the formic acid yield with time with or without addition of catalyst Ni is shown in Fig. 6. As shown in the figure, in the case of the addition of Fe, the yield of formic acid increases with the amount of NaOH until 0.2 mmol to attain an optimal formic acid yield of 12.5%, and then decreases gradually with further increase of NaOH. On the other hand, with the same amount of NaOH added, the yields of formic acid in the cases with the addition of Ni catalyst were higher than those without Ni addition, and the yields of formic acid decreased gradually with the increase of NaOH amount. These suggest that although proper alkalinity can stabilize formic acid in the solution, excessive alkalinity is not favorable to the formation of formic acid. This has not been studied by Takahashi et al. although they found that CO_2 was converted to formic acid in alkaline solution under hydrothermal conditions [21].

In addition, the difference in the solution pH values before and after reactions was not observed at initial NaOH amount of 0, 0.2 and 0.6 mmol, respectively. While in the case of initial 1.0 mmol NaOH, a significant increase in solution pH value was observed after reaction. This result suggests that excessive alkali was responsible for the decrease of the yield of formic acid. Thereby, no additional alkali was used in the other experiments in this study.

3.4. Role of CO_2 in hydrogen production

The hydrogen production mechanism was investigated in this study. In particular, we wanted to know if CO_2 had any effect on the hydrogen production. In the absence of CO_2, no hydrogen was produced when using Fe or Ni powder as shown in Table 1. Interestingly, in the presence of CO_2, hydrogen was produced in

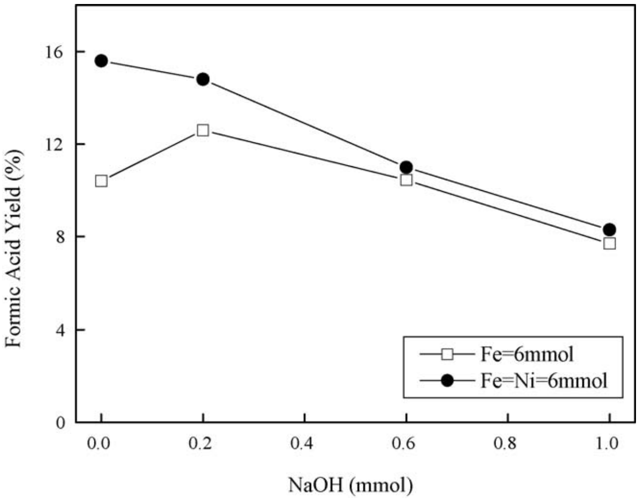

Fig. 6. Effect of alkalinity on formic acid yield ($NaHCO_3$: 1 mmol; Fe = Ni = 6 mmol; temperature: 300 °C; reaction time: 120 min; filling rate: 35%).

Table 1
Hydrogen production in the presence or absence of CO_2.[a]

Entry	Metal	$NaHCO_3$ [mmol]	Total gas [ml][c]	CO_2 [ml]	H_2 [ml]
1	Ni	0	0	0	0
2	Ni	1	0	0	0
3	Fe	0	0	0	0
4	Fe[b]	0	0	0	0
5	Fe	1	50	2	48
6	Fe	2	80	2	75
7	Fe	3	100	4	90

[a] Reaction conditions: 300 °C, 120 min, Fe = 6 mmol, pH of the initial solution was 8.3–9.0.

[b] pH of the initial solution was adjusted to about 9 with NaOH.

[c] Volume of total gas was measured at room temperature of 20 ± 1 °C and pressure of 1 atm.

substantial quantities with the addition of Fe, the increase in the initial CO_2 amount led to an increase in the hydrogen production (Table 1 runs 5–7). To understand the mechanism of the hydrogen production, the solid residue after the reaction was analyzed by X-ray diffraction. Almost no iron oxides but mainly Fe was detected in the absence of CO_2, while Fe_3O_4 was detected in the presence CO_2 (Fig. 7), clearly indicating that CO_2 contributed to the oxidation of Fe. Thus, it is reasonable to suggest that the hydrogen production mechanism using Fe could be as follows:

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \quad (1)$$

$$3FeCO_3 + H_2O \rightarrow Fe_3O_4 + H_2 + 3CO_2 \quad (2)$$

Fe first reacts with CO_2 and H_2O to form $FeCO_3$, which then loses CO_2 to form Fe_3O_4. However, no $FeCO_3$ was detected. An experiment with the addition of Fe was conducted within a very short reaction time of 5 min to test if $FeCO_3$ was decomposed after a longer reaction time of 2 h. There was no $FeCO_3$ detected in the solid residue by XRD either (Fig. 8). To further confirm whether $FeCO_3$ was produced, we conducted an experiment using a Fe and Mg mixture at Fe:Mg mole ratio of 1:1 as reductants in the presence of CO_2. The reason for using the Fe and Mg mixture was that we found only $Mg(OH)_2$ was detected in the experiment using Mg as a reductant in the presence of CO_2. If $MgCO_3$ could be found in the experiment using the mixture of Fe and Mg, it should provide an evidence for the formation of $FeCO_3$ in the experiment using Fe probably according to following reactions.

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \quad (4)$$

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \quad (5)$$

$$Mg(OH)_2 + FeCO_3 \rightarrow MgCO_3 + Fe(OH)_2 \quad (6)$$

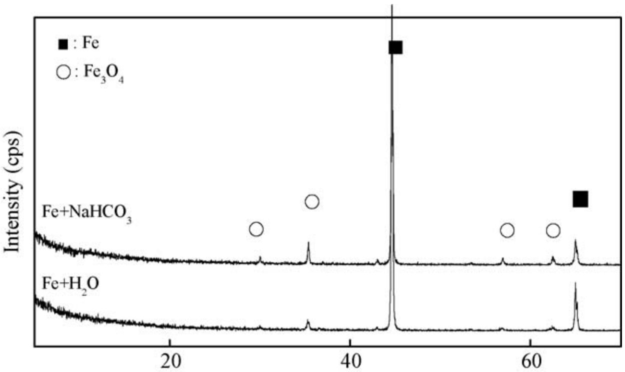

Fig. 7. XRD patterns of the solid residues with or without CO_2 ($NaHCO_3$: 1 mmol; Fe = 6 mmol; temperature: 300 °C; reaction time: 120 min; filling rate: 35%).

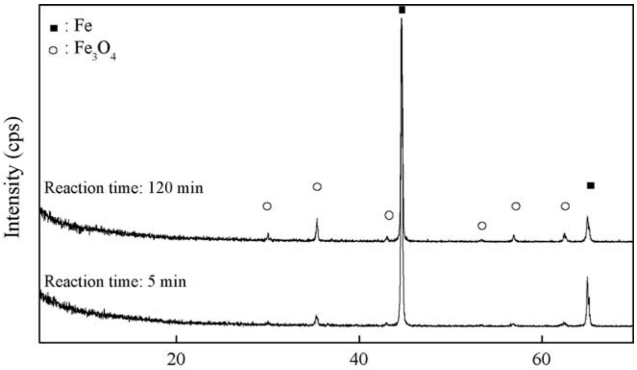

Fig. 8. XRD patterns of solid residues at different reaction time ($NaHCO_3$: 1 mmol; Fe = 6 mmol; temperature: 300 °C; filling rate: 35%).

As expected, $MgCO_3$ was detected in the experiment using the mixture of Fe and Mg (Fig. 9). Furthermore, the production of hydrogen did not seem to be from the decomposition of the catalytically formed formic acid into CO_2 and H_2, since if so, the produced CO_2 and H_2 should be in same amount, while in the gaseous samples in this study, almost no CO_2 was detected (Table 1). Moreover, if the hydrogen was coming from the decomposition of the formic acid, the amount of it could not be so large since the total amount of formic acid was little. Therefore, the mechanism proposed was reasonable. According to this mechanism, clearly, CO_2 played a catalytic role for improving hydrogen production from water. To our knowledge, the catalytic effect of CO_2 in hydrogen production from water has not been reported by others.

In conclusion, formic acid was formed through the hydrogenation of CO_2 as follows:

$$CO_2 + H_2 \rightarrow HCOOH \quad (7)$$

The overall reaction of formic acid formation from CO_2 using Fe as a reductant at 300 °C could be expressed as:

$$3Fe(s) + 4CO_2(g) + 4H_2O(l) \rightarrow Fe_3O_4(s) + 4HCOOH(l) - 80.45\,\mathrm{KJ/mol} \quad (8)$$

where the reaction heat was estimated based on the enthalpy difference between the products and reactants at 25 °C and their heat capacity variation with temperatures from 25 to 300 °C. The hydrogenation of CO_2 was an exothermic reaction according to our estimation.

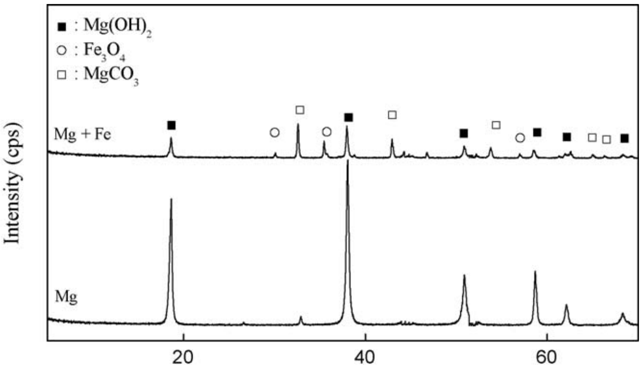

Fig. 9. XRD patterns of solid residues with Mg or Mg/Fe ($NaHCO_3$: 4 mmol; Mg = Fe = 4 mmol; temperature: 250 °C; reaction time: 12 h; filling rate: 35%; Teflon-lined reactor).

4. Conclusions

Carbon dioxide was successfully converted into formic acid under mild hydrothermal conditions using Fe as a reductant and Ni as a catalyst. The selectivity of formic acid from CO_2 conversion was found to be more than 98%. Through the investigation of various experimental parameters, it was found that the highest yield of formic acid of 15.6% was attained 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. The role of CO_2 in the hydrogen generation in the hydrothermal CO_2 conversion was investigated. It was fount that CO_2 promoted the hydrogen production and a mechanism was proposed. This hydrothermal conversion of CO_2 under mild conditions may provide a promising solution to meet the urgent need of reduction of the atmospheric CO_2 loading.

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