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COMMUNICATION

NaHCO₃-enhanced hydrogen production from water with Fe and in-situ highly efficient and autocatalytic NaHCO₃ reduction into formic acid

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We report a highly efficient water splitting for CO₂ reduction into formic acid with a commercially available metal of Fe powder without adding any other catalyst. An excellent formic acid-yield of more than 90% was attained.

Global climate change has stimulated efforts to reduce CO₂ emissions. One approach to addressing this problem is artificial photosynthesis to recycle CO₂ directly into chemical energy by water splitting with solar energy.¹⁻³ However, low conversion efficiencies of solar-to-fuels with the direct use of solar energy are a major bottleneck and it is far from reaching efficiencies close to application. In contrast to direct the use of solar energy, an integrated technology can be expected to have high potential for improving the efficiency of artificial photosynthetic systems. Some integrated technologies have been reported. For example, solar hydrogen production and CO₂ reduction via a two-step water-splitting thermochemical cycle based on metal/metal oxides redox reactions such as Fe/Fe₃O₄ and Zn/ZnO.^{4,5} Also, the electrochemical reduction of CO₂ can be regarded as an a typical integrated technology for improving artificial photosynthetic efficiency because solar electricity could be used.

Hydrothermal reactions have played an important role in the formation of fossil fuel and origin of life in the earth's crust and deep-sea hydrothermal vents,⁶ which involves reduction of CO₂ dissolved in water accompanying hydrothermal alteration of minerals.⁷ Thus, conversion of CO₂ to organics under high temperature and pressure water condition has always been the intensive topics in the field of bio- and geochemistry at deep sea vents,^{8,9} however, there have been very limited number of experiments that demonstrate the formation of organics. In proposed mechanisms of abiotic organic synthesis, the reaction of ferrous iron-bearing minerals with water is considered to generate reducing conditions (H₂).¹⁰ This nature reduction of CO₂ to

hydrocarbon without solar radiation inspired us to study the hydrothermal CO₂ reduction with Fe as a reductant because Fe is a cheap, abundant metallic and redox-active element on the earth, to explore an approach of highly efficient reducing CO₂ linked to global climate change into organic chemicals, but also help to understand the abiotic organic synthesis at deep-sea hydrothermal vents. Previous results showed the formation of formic acid from CO₂ was observed. More interestingly, we also found that the oxidation product, Fe₃O₄, could be reduced into Fe by a biomass-derived chemical of glycerin.¹¹ Accordingly, an integrated technology for improving the efficiency of artificial photosynthetic systems can be also expected by a redox of Fe/Fe_xO_y with biomass.

Formic acid is an important chemical in industry, and has been traditionally employed as a preservative and an insecticide, and is also a useful reducing agent and source of carbon in synthetic chemical industries. Currently, the worldwide capacity for producing formic acid is about 800 kt/a.¹² The demand for formic acid could continue to grow in the future, especially in the context of a renewable energy hydrogen carrier.^{13,14} At present, formic acid is produced from methanol and CO with a strong base. Therefore, formic acid production from greenhouse gases of CO₂ and water remains a topic of significant research.

Although previous research has demonstrated potential of the reduction of CO₂ into formic acid with Fe in water, the yield of formic acid was only less 2% without the addition of catalyst,¹⁵ and therefore further investigation for enhancing the efficiency of water splitting for CO₂ reduction is required.

The enhancement of hydrogen production by Fe oxidation in water should be a key to highly efficient CO₂ reduction with Fe because many unreacted Fe was observed after reactions in previous research. Moreover, if large amount hydrogen can be produced, the surface of Fe₃O₄, a product of Fe oxidation, may be reduced in-situ, to form Fe₃O_{4-x}, and thus make the formed Fe₃O₄ have a highly catalytic activity, leading to an autocatalytic process. Here, we present a simple and highly efficient water splitting for CO₂ reduction into formic acid by enhancing hydrogen production with NaHCO₃ without the addition of any catalyst, and the mechanism of this process is also studied.

First, a series of reactions with Fe in water were conducted by changing wide range reaction parameters including reaction time, temperature, water filling, the size of Fe powder, and the addition of NaOH and NaHCO₃, respectively, to test whether the oxidation of Fe can be enhanced for the hydrogen production in water. Results

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revealed that NaHCO_3 displayed a better performance for producing hydrogen (Table S1, Fig. S5). These observations prompted us to further study the improving role of NaHCO_3 in hydrogen production by examining Fe oxidation in water with changing NaHCO_3 concentration. As shown in Fig. 1, a dramatic enhancement in the conversion of Fe into Fe_3O_4 with the increase in NaHCO_3 concentration was observed, and the conversion of Fe reached 90% with 2 mmol/L NaHCO_3 . The conversion of Fe is defined as the percentage of the amount of oxidized iron divided by the initial iron atom, which was quantified by MDI jade software based on XRD patterns.

Moreover, considering that Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have the same inverse spinel structure and similarity in their d spacing, to further confirm that the oxidation product is Fe_3O_4 , rather than Fe_2O_3 , further identification of Fe_3O_4 from Fe oxidation was conducted by Raman spectroscopy and the results indicated that the oxidation product of Fe was Fe_3O_4 in our system (Fig. S9).

Then, the morphology of solid residue was also examined by SEM to further verify the promotion of NaHCO_3 on Fe oxidation. Many unreacted Fe was observed, but the increase in the NaHCO_3 led to a clear increase in the formation of Fe_3O_4 and the growth of Fe_3O_4 crystal (Fig. S4).

To investigate the role of NaHCO_3 in improving Fe oxidation, the change of oxidative products of Fe with the reaction time was examined at different temperatures. At higher temperatures of 300 °C and 325 °C, only Fe_3O_4 was detected as an oxidative product of Fe, and as shown in Fig. 2, the conversion of Fe into Fe_3O_4 proceeded very quickly in the first 5 min, then became slowly from 5 to 30 min, remained nearly a constant after 90 min. However, at a lower temperature of 275 °C, in addition to Fe_3O_4 , a large number of FeCO_3 was detected in the first 5 min and the amount of FeCO_3 decreased gradually with increasing the reaction time, especially at 5 to 10 min, accompanied with the increase rapidly of Fe_3O_4 . These observations suggest that Fe is oxidized into Fe_3O_4 via FeCO_3 . It has been reported that FeCO_3 can be decomposed into FeO and CO_2 in both air and nitrogen atmospheres at relative high reaction temperature (above 300 °C).¹⁶ According to these results, the mechanism of promoting Fe oxidation with NaHCO_3 can be explained in Scheme 1.

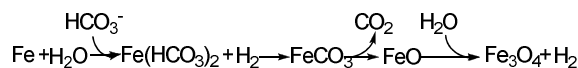
In the presence of HCO_3^- , Fe, NaHCO_3 and water firstly react to produce hydrogen with the formation of $\text{Fe}(\text{HCO}_3)_2$, which then is easily decomposed into FeCO_3 along with CO_2 and H_2O due to the instability of $\text{Fe}(\text{HCO}_3)_2$.¹⁷ Subsequently, FeCO_3 is further

transformed into FeO and CO_2 . Since FeO is extremely unstable in water, FeO is further oxidized into Fe_3O_4 in water with the production of hydrogen.

After confirming the promoting role of NaHCO_3 in hydrogen production from Fe oxidation, the in-situ NaHCO_3 reduction into formic acid with Fe was investigated. As shown in Fig. 3a, similarly to Fe oxidation, the initial NaHCO_3 concentration had a great impact on the yield of formic acid and the yield increased significantly from 32% to 68.3% with increasing NaHCO_3 concentration from 0.3 mmol/L to 1.7 mmol/L. The yield of formic acid is defined as the percentage of formic acid to the initial NaHCO_3 on a carbon basis. The increase of the formic acid yield should be attributed to the enhancement of Fe oxidation in water to supply hydrogen by NaHCO_3 . An examination of pH in the solution indicated that pH of the solution before and after the reactions was 8.3 and about 8.6, respectively, indicating that HCO_3^- existed during the reaction. The moderately alkaline solution caused by the buffer capacity of HCO_3^- leads to both easily oxidization of Fe for producing hydrogen and the formation of formic acid. Thus, the HCO_3^- functions not only for the substrate, but also the pH buffer allowing the reaction to keep activity for long.

In the investigation of the effect of water filling/reaction pressure on Fe oxidation/hydrogen production in water, no significant change was observed (Fig. S6), which is most likely because a higher pressure is not beneficial for the formation of gaseous product of hydrogen ($3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$). However, for CO_2 hydrogenation, no gas product is produced ($2\text{H} + 2\text{HCO}_3^- \rightarrow 2\text{HCOO}^- + \text{H}_2\text{O}$), and thus a higher pressure could be expected to benefit for CO_2 hydrogenation. As expected, the yield of formic acid increased significantly with the increase in water filling, and the highest yield of about 81% was achieved with 60% water filling (Fig. 3a).

Then, the effect of Fe amount on CO_2 reduction was investigated under the optimized reaction conditions in hand. As shown in Fig. 3b, the formic acid yield was dramatically improved with increasing Fe amount. Considering the pressure limitation of the reactor used in this study, experiments with a higher Fe amount was not conducted. To further examine the effect of the Fe amount, experiments with a lower concentration of 0.7 mmol/L NaHCO_3 were conducted, and the yield of formic acid reached up to 92%.



Scheme 1 The possible pathway of Fe oxidation in the presence of HCO_3^- .

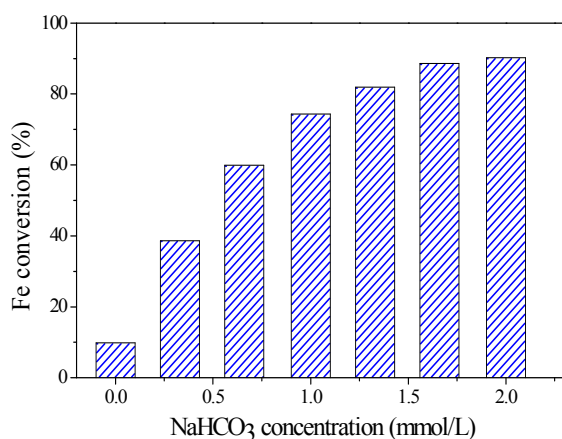


Fig. 1 The conversion of Fe into Fe_3O_4 with the change of NaHCO_3 concentration (300 °C, 2 h, 12 mmol Fe).

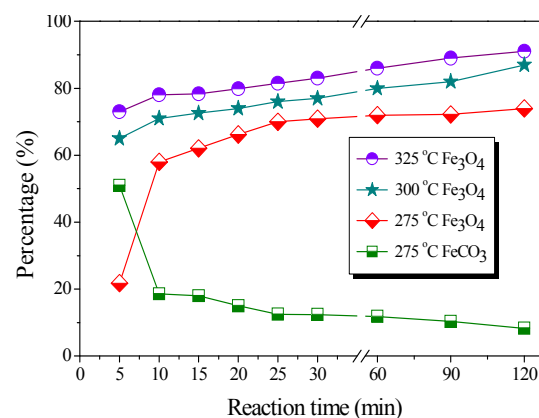


Fig. 2 Effects of reaction time and reaction temperature on Fe oxidation (2 mmol/L NaHCO_3 , 12 mmol Fe).

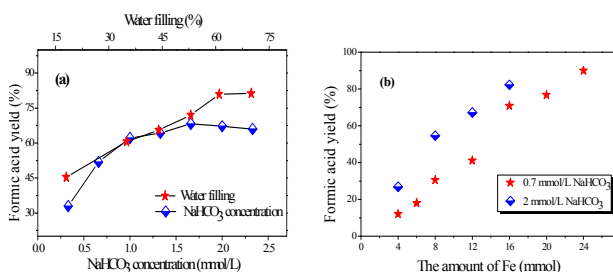


Fig. 3 Effect of NaHCO₃ concentration, water filling and the amount of Fe on the yield of formic acid (300 °C, 2 h, a: 12 mmol Fe for NaHCO₃ concentration; 1 mmol/L NaHCO₃ for water filling).

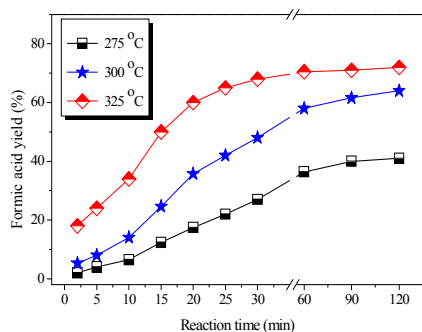


Fig. 4 Effects of reaction time and reaction temperature on formic acid yield (2 mmol/L NaHCO₃, 12 mmol Fe).

Fig. 4 shows a kinetic curve of the formic acid production. At the beginning of the reaction, the yield of formic acid increased slowly, and then increased rapidly with the increase in the reaction time. Finally, no significant change in formic acid was observed. Furthermore, CO₂ reduction proceeded efficiently at 300 °C and 325 °C and a high formic acid yield of 40%-60% was achieved in the first 30 min, indicating that a higher temperature is favorable for the production of formic acid.

Generally, catalysts are needed in the traditional CO₂ hydrogenation. However, a high formic acid yield can be obtained without adding any other catalyst in the present study, suggesting that some intermediates such as FeCO₃ or Fe₃O₄ may act as a catalyst. For test this assumption, reactions with gaseous hydrogen (H₂) as a substitute for Fe were conducted in the presence of FeCO₃ or Fe₃O₄. As shown in Table 1, no significant change in the yield of formic acid with commercial Fe₃O₄ or FeCO₃ (entries 3 and 9) was observed compared to those without FeCO₃ or Fe₃O₄ (entry 2). Interestingly, however, the formic acid yield with the collected Fe₃O₄ after the reaction was higher (entry 4) than that with commercial Fe₃O₄ or FeCO₃, particularly for wet Fe₃O₄ collected after the reaction (entry 5), indicating catalytic activity of the Fe₃O₄ collected after the reaction in the reduction of CO₂ into formic acid. Although formic acid yield with gaseous hydrogen in the presence of wet Fe₃O₄ collected increased, the yield was lower than those with Fe. These results suggest the activity of the hydrogen produced in-situ at high-temperature water with Fe may be higher than that of gaseous hydrogen in the reduction of CO₂. The study with this line is now in progress.

To explore the catalytic mechanism of collected Fe₃O₄, we analyzed chemical composition and valence states on the collected and commercial Fe₃O₄ by XPS. As shown in Fig. 5, both of collected and commercial Fe₃O₄ have two peaks at 710.5 eV and 724.6 eV

Table 1 Effect of additives of Fe₃O₄ or FeCO₃ on the formic acid yield^a

Entry	NaHCO ₃ concentration (mmol/L)	H ₂ (MPa)	Additives	Yield (%)
1	2	2		2.3
2	2	6		2.6
3	2	6	Commercial Fe ₃ O ₄	0.6
4	2	6	Collected dry Fe ₃ O ₄	4.5
5	2	6	Collected wet Fe ₃ O ₄	14.3
6	2	-		0
7	-	-	Commercial FeCO ₃	0
8	2	-	Commercial FeCO ₃	1.7
9	2	6	Commercial FeCO ₃	2.9

^a300 °C, 2 h.

corresponding to the binding energies of Fe 2p_{1/2} and Fe 2p_{3/2}, respectively,^{18,19}. Table 2 lists the ratio of Fe²⁺ and Fe³⁺ of collected and commercial Fe₃O₄. The Fe²⁺/Fe³⁺ ratio of the collected Fe₃O₄ was 0.89:0.11, which is apparently higher than the theoretical ratio of Fe₃O₄ (0.33:0.67), suggesting in-situ reduction of Fe³⁺ into Fe²⁺ on the surface of Fe₃O₄, which should be caused by the hydrogen formed from Fe oxidation due to the enhance in Fe oxidation with NaHCO₃. Moreover, a lower Fe²⁺/Fe³⁺ ratio (0.22:0.78) of commercial Fe₃O₄ than the theoretical ratio was observed, which can be explained the oxidation of Fe²⁺ into Fe³⁺ in the air. Similar results were also observed in XPS spectroscopies of the commercial Fe₃O₄, in which a weak satellite peak of Fe 2p_{3/2} for Fe³⁺ at 718.7 eV (Fig. 5a) was observed.

The spectrum of O 1s of the collected and commercial Fe₃O₄ can be fitted to three peaks at different BEs Oa (529.7eV), Ob (531.3 eV), Oc (533.2 eV), and the O 1s spectra are displayed in Fig. 5d. The Oa, Ob and Oc peaks are usually attributed to O²⁻ in the Fe₃O₄ structure, to oxygen of OH groups on the Fe₃O₄ surface, and to chemisorbed or dissociated oxygen on the surface of the Fe₃O₄, such as -CO₃/-HCO₃, adsorbed H₂O or adsorbed O₂, respectively.^{19,20} Table 3 lists

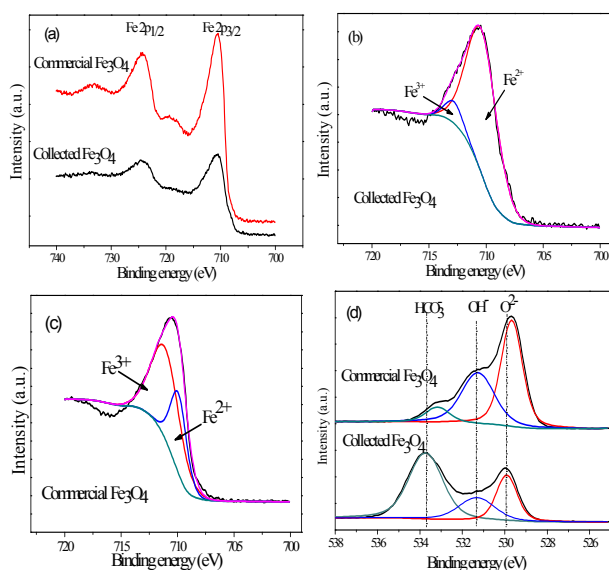


Fig. 5 X-ray photoelectron spectroscopies of collected and commercial Fe₃O₄: (a) Fe 2p, (b) commercial Fe₃O₄ 2p_{3/2}, (c) collected Fe₃O₄ 2p_{3/2} and (d) O1s.

Table 2 The ratio of Fe²⁺ and Fe³⁺ for collected and commercial Fe₃O₄

	Peak position (ev)		Atomic ratio (%)	
	Fe 2p _{3/2}	Satellite	Fe 2p _{3/2}	Fe ²⁺ / Fe ³⁺
Collected Fe ₃ O ₄	724.1	-	710.6	89 / 11
Commercial Fe ₃ O ₄	724.1	718.6	710.6	22 / 78

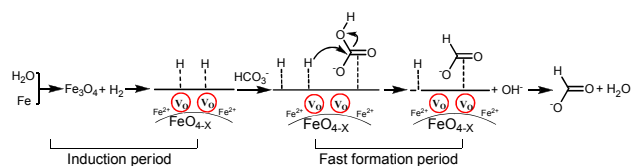
Table 3 Relative intensity of Oa, Ob, and Oc peaks of the O1s spectrum of collected and commercial Fe₃O₄

	Peak binding energy (ev)			Relative intensity (%)		
	Oa	Ob	Oc	Oa	Ob	Oc
Collected Fe ₃ O ₄	529.9	531.4	533.8	33.3	19.7	47.0
Commercial Fe ₃ O ₄	529.7	531.3	533.2	54.7	30.6	14.8

the relative intensity of Oa, Ob, and Oc peaks of the O1s spectrum for collected and commercial Fe₃O₄. Compared to commercial Fe₃O₄, the relative intensity of Oa peak of collected Fe₃O₄ decreased, indicating the formation of the more oxygen vacancies. Meanwhile, the relative intensity of the Oc peak of collected Fe₃O₄ was stronger than that of commercial Fe₃O₄, suggesting the adsorption of more HCO₃⁻ on the surface of collected Fe₃O₄. More Fe²⁺ on the Fe₃O₄ surface should provide the active sites for CO₂ reduction.

According to XPS analysis and the kinetic curve (Fig. 2 and 4), water splitting for CO₂ reduction with Fe in water should be a typical of a self-catalytic reaction including a short induction and fast formation period. In the short induction period during the initial 5-10 min, hydrogen and Fe₃O₄ with more oxygen vacancies (Fe₃O_{4-x}) are formed. Then, the formed Fe₃O_{4-x} acts as a catalyst in the reduction of HCO₃⁻ into formic acid and thus leads to an quick increase in formic acid yield within 10- 30 min. Finally, the reaction comes to an equilibrium stage. Thus, the profile of formic acid formation shows a sigmoidal-like curve. With these experimental results, a tentative mechanism of dissociating water for the conversion of HCO₃⁻ to formic acid with Fe is postulated in Fig. 6. Initially, Fe is oxidized into Fe₃O₄ in water with the help of HCO₃⁻ to produce a large amount of hydrogen, which simultaneously reduce in-situ Fe₃O₄ to lead to the more active sites on the surface of Fe₃O₄ (Fe₃O_{4-x}). Subsequently, the formed hydrogen and HCO₃⁻ are activated by adsorbing on the Fe₃O_{4-x} surface, and then the activated H on the Fe₃O_{4-x} surface attacks to C=O, followed by the leaving of hydroxyl group of HCO₃⁻. Finally, formate is formed along with H₂O. Although the detailed studied are needed, the proposed auto-catalytic role of Fe₃O_{4-x} formed at hydrothermal reducing conditions in this study may provide some useful experimental data for understanding abiotic organic synthesis at deep-sea hydrothermal vents.

In summary, we have developed a highly efficient water splitting for reducing CO₂ into formic acid with a general Fe powder in hot water without adding any other catalyst. An excellent formic acid yield of 92% was obtained. In this process, HCO₃⁻ is found to play a key role in enhancing Fe oxidation in water to produce hydrogen,

**Fig. 6** Proposed mechanism of reduction of HCO₃⁻ into formate with Fe.

and the mechanism of autocatalytic reduction CO₂ involves the formation of Fe₃O_{4-x} by in-situ reducing Fe₃O₄ with the formed hydrogen. The exact mechanism of this water splitting for CO₂ reduction is under further investigation. The present study provides a potential approach to highly efficient reducing atmospheric CO₂ linked to global climate change into organic chemicals, but also can provide some experimental data for further understanding the abiotic organic synthesis at deep-sea hydrothermal vents.

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