



Highly efficient water splitting and carbon dioxide reduction into formic acid with iron and copper powder



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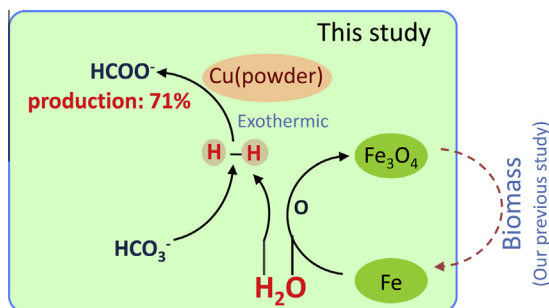
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HIGHLIGHTS

- A highly efficient splitting water to reduce CO₂ into formic acid was presented.
- A simple commercially available Cu and Fe powder can be directed used.
- The highest formic acid production was 71.3%.
- Cu exhibited efficiently catalytic activity and could be used repeatedly.
- Hot water acts not only as a reaction medium but also as a hydrogen source.

GRAPHICAL ABSTRACT



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ABSTRACT

The utilization of CO₂ as a cheap and abundant carbon source to produce useful chemicals or fuels could be regarded as one of the promising ways for sustainable development. The water splitting for CO₂ reduction with solar energy is one of the most potential process, however, a high solar-to-fuel efficiency keeps a great challenge. In this work, a Cu-catalyzed highly efficient and robust method for splitting water to reduce CO₂ into formic acid with a simple commercially available Cu and Fe powder was presented. Results showed that the formic acid production with Cu catalyst was much higher than that without Cu or with Ni catalyst, and an excellent formic acid production of about 71%, which represented the highest formic acid production from CO₂ using Fe reductant to date, was obtained under a mild hydrothermal condition at 300 °C for 2 h. The Cu catalyst was relatively stable and could be used repeatedly without causing a significant change in the formic acid production. A reaction mechanism of the conversion of HCO₃⁻ into formic acid was also proposed. The water splitting for CO₂ reduction with Fe is an exothermic reaction, thus the proposed process may provide a viable method for highly efficient water splitting and CO₂ reduction into value-added chemicals by combining the reduction of Fe_xO_y into Fe with bio-derived chemicals.

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1. Introduction

The utilization of CO₂ as a cheap and abundant carbon source to produce useful chemicals or fuels could be regarded as one of the

promising ways for sustainable development. There have been a large amount of methods for the CO₂ reduction proposed [1–11]. Among these methods, the photochemical reduction of CO₂ is regarded as the most potential process, however, its efficiency is very low [1]. Although the hydrogenation of CO₂ with gaseous hydrogen can produce high reduction products, this method requires either elaborately prepared expensive (or complexes) catalysts or high-purity of hydrogen and also has issues of storage,

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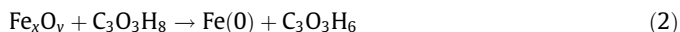
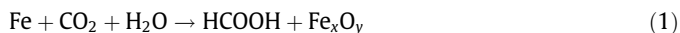
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transportation and safety for the gaseous hydrogen, which are regarded as an energy-intensive process [12].

Hydrothermal reactions have played an important role in the formation of fossil fuels, e.g. the abiotic conversion of dissolved CO₂ into hydrocarbons in Earth's crust [13,14]. 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 the reducing conditions (H₂) through the reaction of ferrous Fe-bearing minerals with water [13,14]. The abiotic synthesis of organics suggests that the highly efficient dissociation of H₂O for reducing CO₂ into organics could be achieved with metals under hydrothermal conditions.

With this in mind, we previously investigated the dissociation of H₂O for reducing CO₂ (or NaHCO₃ as a CO₂ source) to formic acid with metallic iron (Fe) as a reductant in the presence or absence of a nickel (Ni) catalyst [15,16]. In this process with Fe, water is used as a source of hydrogen and Fe is used as the reductant for rapidly producing hydrogen, which then is used to reduce the CO₂ *in-situ*. In such process, water acts as the sole source of hydrogen and also serves as an environmentally benign solvent for the CO₂ reduction. Metal Fe was selected because Fe is one of the most abundant metallic elements in the Earth's crust and can be easily obtained. More importantly, our previous research have found that the iron oxide formed from the oxidation of Fe can be regenerated into Fe again easily by the reaction of iron oxide with bio-derived chemicals such as glycerin, in which lactic acid can be produced [16]. Thus, the cycle of Fe can be achieved when using Fe for the dissociation of H₂O to reduce CO₂ as explained in reactions (1) and (2):



With such concept, a highly efficient reduction of CO₂ with Fe is crucial in the reaction (1). However, previous research on the reduction of CO₂ with Fe as a reductant showed that the formic acid production was very low (below 10%) without the addition of catalyst [15]. Therefore, further research with the use of catalyst is required to improve efficient reduction of CO₂. In general, noble metals such as Pd, Pt, Rh and Au can act as a high catalytic activity in the CO₂ hydrogenation, but noble metals are expensive. Thus, our research interest focused on the development of cheap and highly active metal catalyst. Among candidate cheap metal catalysts, Ni exhibited a lower catalytic activity in hydrothermal reduction of CO₂ into formic acid with Fe [17] and the formic acid production was limited to only about 16% [15]. Then, we turned our attention to the next candidate of cheap metal Cu, because the study on the activity of Cu for catalyzing CO₂ reduction is limited. We found that Cu showed a much higher catalytic activity than Ni catalyst in the conversion of CO₂ into formic acid. These new findings are reported in this paper, mainly including (1) the examination of the catalytic activity of Cu, (2) the investigation of the reaction characteristic and design of the optimum conditions to obtain high formic acid production, (3) the investigation of the mechanism of the reactions involved.

2. Experimental

In this study, NaHCO₃ was used as the source of CO₂ to simplify the operation and to allow for an accurate quantification of CO₂ [15]. The reagents NaHCO₃ powder (99.5%), Fe powder (200-mesh, 98%) and Cu powder (200-mesh, 99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. A standard reagent formic acid (puriss. p.a., ~98%, Fluka) was used for quantitative analysis. In this research, three types of reactors

(Reactor I, II and III) were used. Reactor I and II were made of stainless steel with an inner volume of 5.7 mL and 42 mL respectively, and Reactor III was a Teflon-lined stainless steel reactor with an inner volume of 28 mL. The schematic drawing of these reactors can be found elsewhere [18–20]. The Reactor I was made of a piece of SUS-316 stainless steel tubing (9.525 mm (3/8 in.) o.d., 1-mm wall thickness and 120 mm long) with end fittings; one fitting was a Swagelok cap and the other was a valve made by Autoclave Engineers Inc. with a reducing union, providing an inner volume of 5.7 mL. The pressure limit of the Reactor I is 20 MPa. A typical experimental procedure using Reactor I was as follows. Pure water, Fe powder, Cu powder, and NaHCO₃ were added to the reaction chamber, and then the reactor was sealed. After that, the reactor was put into a salt bath which had been preheated to required reaction temperature (250–325 °C). After the desired reaction time, the reactor was taken out from the salt bath and put into a cold-water bath (20 °C) to quench the reaction. The reaction time was defined as the duration of the reactor was kept in the salt bath. The water filling was defined as the ratio of the volume of the solution put into the reactor to the inner volume of the reactor. Reactor II with an inner volume of 42 mL and a pressure limit of 50 MPa was also used to further examine the effect of the initial amount of the starting materials on the formic acid production. The reactor was heated to the desired temperature by an induction heating furnace. The induction heating furnace was swayed (20 times min⁻¹) during experiments. The reaction time was defined as the duration time when the reactor was kept in the induction heating furnace at the desired temperature. After a desired reaction time, the reactor was removed from the induction heating furnace and air-cooled by an electric fan. Reactor III with a Teflon-lined inner was also used to further study the iron conversion mechanism. The details of this reactor has been described elsewhere [20]. If there is no specific explanation, all the experiments were carried out in the Reactor I.

After the reactions, the gas was collected and analyzed by a Hewlett-Packard model 5890 Series II gas chromatograph equipped with a thermal conductivity detector (GC/TCD). The liquid samples were filtered (0.22 μm filter film) and then analyzed by a UV-detector (210 nm) equipped Agilent 1200 high-performance liquid chromatography (HPLC) with one Shodex RSpak KC-G and two RSpak KC-811 columns using 2 mmol L⁻¹ HClO₄ solution flowing solvent. An Agilent 7890 gas chromatography–mass spectrometry (GC–MS) equipped with 5985C inert MSD with triple-axis detector was also used to investigate other possible chemicals in liquid phase. The remaining reaction mixture was filtered, and the precipitate was dried in an isothermal oven (50 °C) for 24 h after washing with distilled water. Then it was determined by X-ray diffractometer (XRD) using a Bruker D8 Advance X-ray Diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å, scanning rate: 0.02° s⁻¹, 2θ ranges: 10–80°). The morphologies of the Cu before and after the reactions were examined with a scanning electron microscope (SEM, Philips XL30 D6716). The specific surface area of the particles was determined by nitrogen sorption experiments on an ASAP2010 instrument (Micromeritics, USA). The samples were degassed at 160 °C for 2 h under vacuum prior to the adsorption measurements.

3. Results and discussion

3.1. Catalytic activity of Cu in the reduction of NaHCO₃ into formic acid

To examine the catalytic activity of materials other than Ni in the hydrothermal reduction of CO₂ into formic acid, the productions of formic acid in the presence of different materials such as Cu, Co, ZnO, Al₂O₃, Fe₂O₃, SiO₂ and active carbon, were examined

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