ORGANIC
LETTERS

2010
Vol. 12, No. 4
649−651

A Mild Hydrothermal Route to Fix Carbon Dioxide to Simple Carboxylic Acids

Chao He, Ge Tian, Ziwei Liu, and Shouhua Feng*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130021, P. R. China

shfeng@mail.jlu.edu.cn

Received November 3, 2009

ABSTRACT

$$CO_2 + H_2O \xrightarrow[\text{hydrothermal condition}]{\text{cat. iron nano-particles}} HCOOH + CH_3COOH$$

The reduction of carbon dioxide (CO_2) under mild hydrothermal conditions was carried out in the presence of iron nanoparticles. In this reaction system, the iron nanoparticles not only act as the reducing agent but also catalyze the reduction of CO_2 to form formic acid and acetic acid.

According to the Intergovernmental Panel on Climate Change (IPCC 2007),[1] the Earth's surface temperature has risen by approximately 0.74 K from 1906 to 2006. The primary contributor to this phenomenon is CO_2 emission from fossil fuel combustion. Presently, the concentration of CO_2, which is the most important anthropogenic greenhouse gas, is increasing faster than at any other time. A great deal of effort has been expended to reduce the concentration of CO_2, among which the chemical reduction of CO_2 to organic compounds is considered as one of the most expected solutions for the "Greenhouse Effect" problem.[2] CO_2 can be transformed from a detrimental greenhouse gas into a valuable, inexhaustible, and eco-friendly carbon source through this process. Many methods to reduce CO_2 have been carried out, such as the catalytic hydrogenation reduction,[3] Fischer−Tropsch synthesis,[4] photochemical reduction,[5] electrochemical reduction,[6] and photoelectrochemical reduction,[7] etc. Because of the poor yields, high cost, or rigorous reaction conditions, the results are still not satisfactory.

The reduction of CO_2 under hydrothermal conditions[8] has attracted more attention in these decades. On one hand, it may be a feasible program to solve the "Greenhouse Effect" problem; on the other hand, it has a plausible implication for the abiotic synthesis of complex organic molecules in the origin of life because the hydrothermal system is considered to be one of the most optimal environments for the origin of life.[9,10] It is reported that nickel−iron alloy can catalyze dissolved HCO_3^- with H_2 to form CH_4 under hydrothermal conditions (200 to 400 °C and 50 MPa).[8a] Formic acid could also be generated in the process of hydrothermal reduction of CO_2 at the effect of Ni-powder

---

(1) *Intergovernmental Panel on Climate Change 2007. Climate Change 2007: The Physical Science Basis*; Cambridge University Press: New York, U.S.A., 2007.

(2) Olah, G. A.; Goeppert, A.; Prakash, G. K. S. *J. Org. Chem.* **2009**, *74*, 487.

(3) (a) Yu, K. M. K.; Yeung, C. M. Y.; Tsang, S. C. *J. Am. Chem. Soc.* **2007**, *129*, 6360. (b) An, X.; Li, J.; Zuo, Y.; Zhang, Q.; Wang, D.; Wang, J. *Catal. Lett.* **2007**, *118*, 264. (c) Gao, L. Z.; Au, C. T. *J. Catal.* **2000**, *189*, 1. (d) Chan, B.; Radom, L. *J. Am. Chem. Soc.* **2006**, *128*, 5322.

(4) Pérez-Alonso, F. J.; Ojeda, M.; Herranz, T.; Rojas, S.; González-Carballo, J. M.; Terreros, P.; Fierro, J. L. G. *Catal. Commun.* **2008**, *9*, 1945.

(5) (a) Usubharatana, P.; McMartin, D.; Veawab, A.; Tontiwachwuthikul, P. *Ind. Eng. Chem. Res.* **2006**, *45*, 2558. (b) Koci, K.; Obalova, L.; Lacny, Z. *Chem. Pap.* **2008**, *62*, 1. (c) Xia, X. H.; Jia, Z. J.; Yu, Y.; Liang, Y.; Wang, Z.; Ma, L. L. *Carbon* **2007**, *45*, 717.

(6) Vladimirov, M. G.; Ryzhkov, Y. F.; Alekseev, V. A.; Bogdanovskaya, V. A.; Otroshchenko, V. A.; Kritsky, M. S. *Origins Life Evol. Biospheres* **2004**, *34*, 347.

(7) (a) Zhang, X. V.; Martin, S. T.; Friend, C. M.; Schoonen, M. A. A.; Holland, H. D. *J. Am. Chem. Soc.* **2004**, *126*, 11247. (b) Barton, E. E.; Rampulla, D. M.; Bocarsly, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 6342.

(8) (a) Horita, J.; Berndt, M. E. *Science* **1999**, *285*, 1055. (b) Takahashi, H.; Kori, T.; Onoki, T.; Tohji, K.; Yamasaki, N. *J. Mater. Sci.* **2008**, *43*, 2487. (c) Takahashi, H.; Liu, L. H.; Yashiro, Y.; Ioku, K.; Bignall, G.; Yamasaki, N. *J. Mater. Sci.* **2006**, *41*, 1585. (d) Tian, G.; Yuan, H.; Mu, Y.; He, C.; Feng, S. *Org. Lett.* **2007**, *9*, 2019.

(9) Corliss, J. B.; Dymond, J.; Gordon, L. I.; Edmond, J. M.; von Herzen, R. P.; Ballard, R. D.; Green, K.; Williams, D.; Bainbridge, A.; Crane, K.; van Andel, T. H. *Science* **1979**, *203*, 1073.

(10) Martin, W.; Baross, J.; Kelley, D.; Russell, M. J. *Nat. Rev.* **2008**, *6*, 805.

10.1021/ol9025414

and Fe-powder.[8b,c] Since Fe is abundant and widespread, which accounts for 5.0 wt % of the Earth's crust, it is used as catalyst widely in the reduction of CO_2, and it could have played an important role in prebiotic synthesis. In our previous work, we also used Fe as catalyst to synthesize phenol from the hydrothermal reaction of carbonate with water.[8d] Our group has concentrated tremendous efforts on the reduction of CO_2 under hydrothermal conditions. Herein, we described a mild hydrothermal route from CO_2 to simple carboxylic acids in the presence of iron nanoparticles.

The reactions of CO_2 with water in the presence of iron nanoparticles were carried out using the Endeavor Catalyst Screening System (Argonaut Technologies, Inc.). Iron nanoparticles were prepared by reducing ferrous ion (Supporting Information). The result of gas chromatography−mass spectroscopy (GC−MS) indicated that CO_2 (99.999%) and ultrapure water were free of any organic contamination. We put the iron nanoparticles and ultrapure water into a reactor, sealed it, and then pressurized it to 0.14−1.4 MPa by CO_2 gas. The mixture was subjected to a hydrothermal treatment at 80−200 °C for 5−200 h. After the reaction, the pH value of the mixture was 5.5. The product was identified by GC−MS.

It is quite evident that formic acid and acetic acid were formed after the hydrothermal reduction of CO_2, when the mass spectra of the products were compared to that of standard substance (Supporting Information, Figures S1 and S2). As shown in Figure 1, the yields of formic acid and acetic acid increase with the increase of reaction time, reaching the maximum value after 72 h, and then remain nearly constant. The yields of formic acid and acetic acid are 8.5 and 3.5 mmol·L^{-1}, respectively.

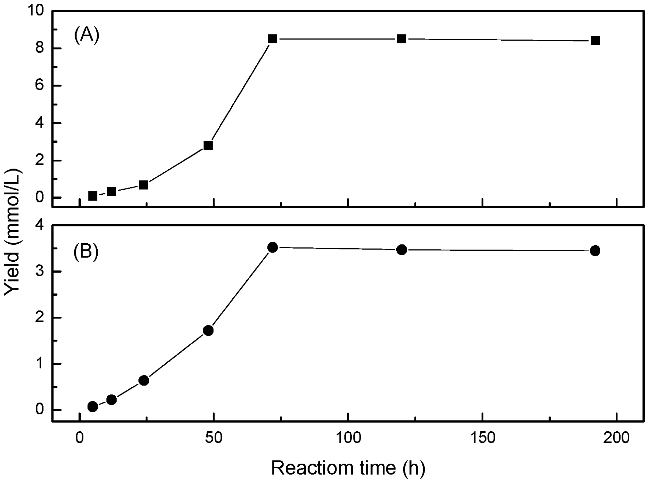


Figure 1. Kinetic curve of the hydrothermal production of formic acid (A) and acetic acid (B). Water: 6 mL. CO_2: 1.4 MPa. Fe: 5 mmol. Temperature: 200 °C.

The effect of temperature was also taken into account. As shown in Figure 2, the yield of formic acid increases obviously with the increase of temperature, while the yield of acetic acid increases less. The total conversion of CO_2 increases as the temperature increases. We think that at higher temperature H_2 is produced more and faster, which provides a stronger reducing environment and promotes the conversion of CO_2.

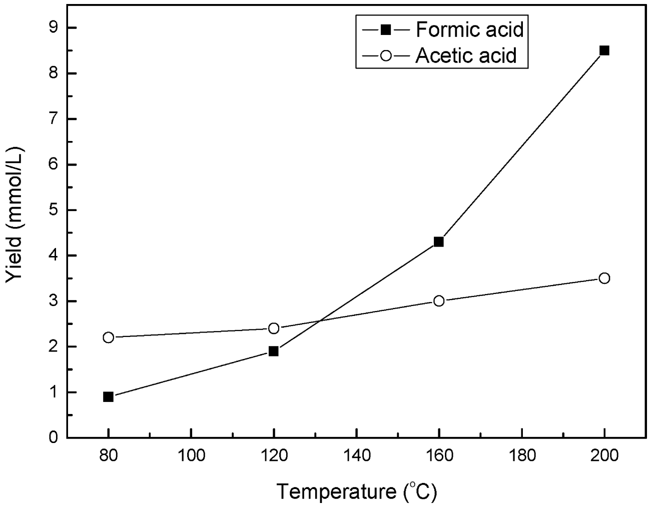
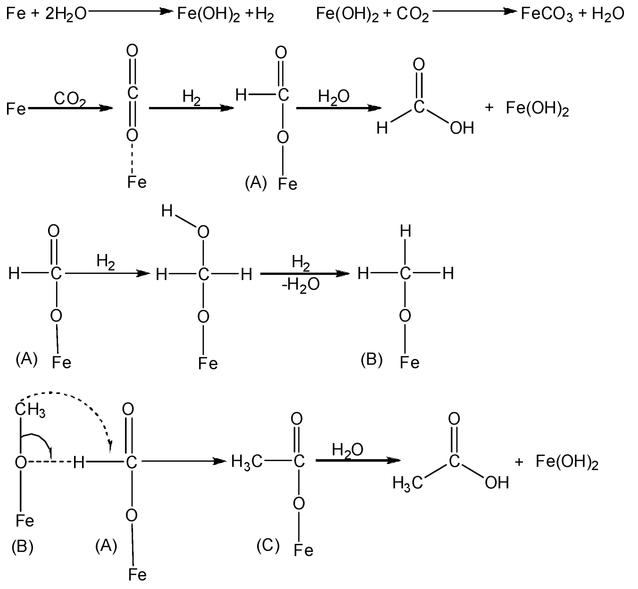


Figure 2. Yields of formic acid and acetic acid at different temperatures. Water: 6 mL. CO_2: 1.4 MPa. Fe: 5 mmol. Reaction time: 72 h.

Higher CO_2 pressure can increase the yield of formic acid because more CO_2 is adsorbed and a more active center is formed at the surface of the iron nanoparticles. The volume of water has little effect on the conversion of CO_2.

On the basis of the result of the reaction, we proposed a possible reaction mechanism of formic acid and acetic acid formation. Scheme 1 illustrates the main process of the reaction

Scheme 1. Proposed Mechanism for the Formation of Formic Acid and Acetic Acid in the Presence of Nano Fe under Hydrothermal Conditions



(see details in Supporting Information, Scheme S1). At the first stage of the reactions, the iron nanoparticles reacted with water, producing H_2. Meanwhile, the dissolved CO_2 molecule was adsorbed at the surface of the iron nanoparticles. At the attack of H_2, CO_2 was reduced to intermediate A, which was hydrolyzed to formic acid. Intermediate A continued reacting with H_2, generating intermediate B. At last, intermediate A and intermediate B reacted to form intermediate C, which was hydrolyzed to acetic acid.

In the reaction system, the iron nanoparticles not only act as a reducing agent but also catalyze the reduction of CO_2. As shown in Figure 3, the diameter of the particles was about 200 nms. The highly active iron nanoparticles reacted rapidly with water to form H_2, whose formation was confirmed by igniting. After the reaction, the unreacted iron was separated by magnet, and the residual solid was collected and then checked by powder X-ray diffraction (XRD). The result of XRD showed that the solid was ferrous carbonate (Figure 4). It is concluded that a great part of the iron nanoparticles was converted to ferrous carbonate after the hydrothermal reaction. The production of H_2 and ferrous carbonate also confirmed the suggested mechanism.

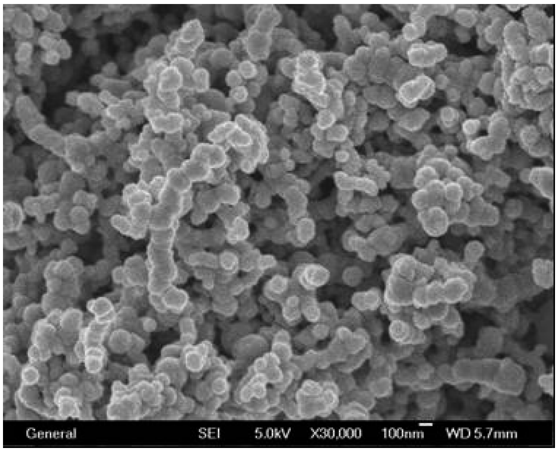


Figure 3. Low-magnification scanning electron microscopy (SEM) images of the prepared iron nanoparticles.

The products of this reaction are formic acid and acetic acid instead of phenol obtained in our previous work.[8d] We think the amount of rapid formation of H_2 plays an important role in the selectivity of the product. At the beginning of the reaction, more H_2 was generated from the reaction of the iron nanoparticles with water than from the reaction of iron powder with water, which provided a stronger reducing environment. Each adsorbed CO_2 molecule formed an active reaction center, which was reduced by H_2 to form formic acid and acetic acid under this environment.

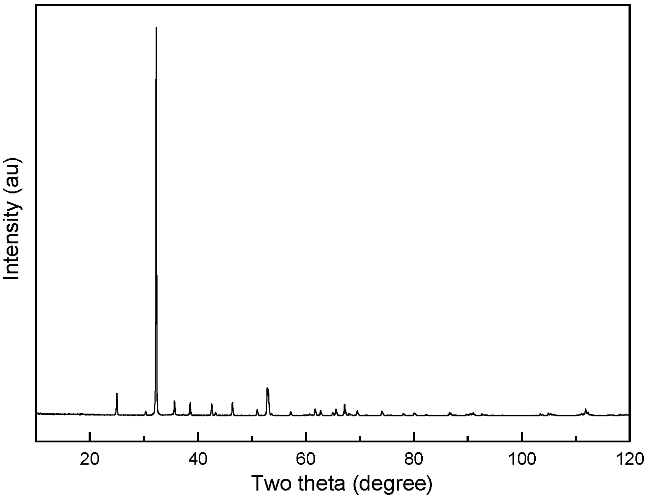


Figure 4. XRD pattern of the residual solid after removal of unreacted iron by a magnet.

Compared to other reported methods of the reduction of CO_2, the characteristics of this reaction system are as follows: first, the catalyst, Fe powder, is widespread and prepared readily. Second, the reaction is carried out under lower pressure and temperature, which is readily accessible. Third, we do not need to add additional H_2 as reducing agent to the reaction system because H_2 is autogenously generated in the reaction. Fourth, water as the source of hydrogen is necessary in this reaction, and it does not impede the formation of the organic matter.

In summary, we demonstrate a mild hydrothermal route for reducing CO_2 to formic acid and acetic acid with the catalytic effect of iron nanoparticles. The present work is a basic study for CO_2 fixation, and it will provide a possible way to reduce the concentration of CO_2 and to mitigate the “Greenhouse effect” after further research.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 20631010 and 90922034).

Supporting Information Available: Experimental procedure, the preparation method of the catalyst, GC−MS characterization, calibration curves of formic acid and acetic acid for GC−MS and method of calculation for the yields, and detailed mechanism for the formation of formic acid and acetic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9025414