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Ready Hydrothermal Reactions from Carbon Dioxide to Methane

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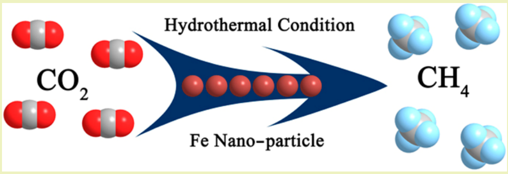
Supporting Information

ABSTRACT:

$$CO_2 + H_2O \xrightarrow[\text{mild hydrothermal condition}]{\text{cat. iron nanoparticles}} CH_4$$



We report that the reduction of carbon dioxide (CO_2) to methane (CH_4) under mild hydrothermal conditions is carried out in the presence of iron nanoparticles. In the reaction, the iron nanoparticles not only act as the reducing agent but also catalyze the reduction of CO_2.

KEYWORDS: *Hydrothermal, CO_2, Nanoparticles, Green chemistry, Reduce*

INTRODUCTION

Nowadays, a shortage of energy is one of the most serious problems related to fossil resources. One of the ways to form a chemical energy carrier from renewable energy is by establishing a reaction to synthesize hydrocarbons from CO_2, which is produced by living organisms as well as by the burning of fossil fuels. A great deal of effort has been explored to convert CO_2 into useful chemicals. Along with this, the reduction of CO_2 to produce organic compounds is one of the most anticipated solutions for the problem of an energy shortage.[1,2] Fischer–Tropsch[3,4] synthesis has excellent performance for the improvement in CO_2 conversion to value-added hydrocarbons at high temperature and/or high pressure. Photo-[5−7] and electro-catalysis[8−10] are high efficiency methods, but they require complex catalysts or special reductants or ultraviolet radiation.

We have developed a feasible method to directly reduce CO_2 to some organic compounds such as phenol, formaldehyde, and carboxylic acids in hydrothermal systems.[11,12] We also notice that all of the materials have a small size effect, even if the change is in a small range.[13−16] When we change the size of catalyst from about 75 μm to about 200 nm, different products are reported.[11,12] We present here a serial study on the hydrothermal reductions of CO_2 to CH_4 in the presense of much smaller iron nanoparticles. The reaction gives the single product CH_4, rather than as a part of products in previously reported systems,[17−19] and uses CO_2 as a gas reagent rather than additional H_2 as in the case for the Al_2O_3-based catalysts.[20,21] An additional advantage for the hydrothermal conversion of CO_2 is the use of iron, which is a widespread and abundant element forming the earth crust, as well as much of our earth's outer and inner core. It is an eco-friendly catalyst in reducing CO_2 as well.

EXPERIMENTAL SECTION

The reactions started with purifying carbon dioxide gas, water, and metal catalyst powder. The results of gas chromatography−mass spectrum (GC-MS) indicated that CO_2 (99.999%) and ultrapure water were free of any organic contamination. Iron nanoparticles with average diameters of 100 nm were prepared by reducing ferrous ion (Supporting Information). The reactions of CO_2 with water in the presence of iron powder as catalysts were carried out using the autoclaves. Iron nanoparticles (5 mmol) and ultrapure water (5 mL) were put into the reactor and sealed. The reactor was pressurized by CO_2 until the pressure was up to 0.14−1.4 MPa. All substrates underwent mild hydrothermal treatments at 80−200 °C for 5−200 h. For changing the source of energy, the autoclave was used to do the experiment using solar thermal collectors. After the reactions, the system was cooled to room temperature, and gaseous products were collected. The final pressure and pH value were about 0.1−1.0 MPa and 5.5, respectively. Gaseous and liquid phase products were analyzed by GC-MS.

RESULT AND DISCUSSION

In gaseous phase, it was quite evident that CH_4 was formed, while the detection of the organic in liquid was below the limitation. The yield of CH_4 increased with an increase in reaction time from 5 to 72 h, as shown in Figure 1A. After 72 h, the yield reached a maximum value of 1.96 mol % and then remained nearly constant. The effect of temperature was also taken into account. The higher the temperature the reaction underwent, the more CO_2 converted to CH_4, as illustrated in Figure 1B. Apparently, CO_2 was more activated under higher temperature, and thus, it was advantageous to be reduced. The higher pressure was also beneficial for the reduction of CO_2. Higher pressure corresponded to more adsorbed CO_2 on the surface of the iron nanoparticles.

We have proposed the possible reaction mechanism for the formation of methane. Similar to our previously suggested formation mechanisms for phenol and carboxylic acids,[11,12] the iron nanoparticles acted as both reducing and catalytic agents. Part of the iron nanoparticles reacted with water to generate

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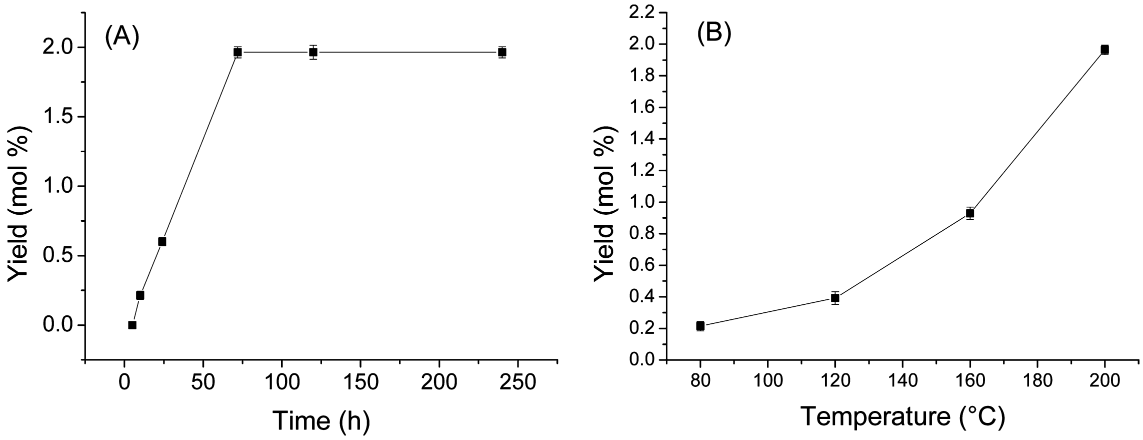
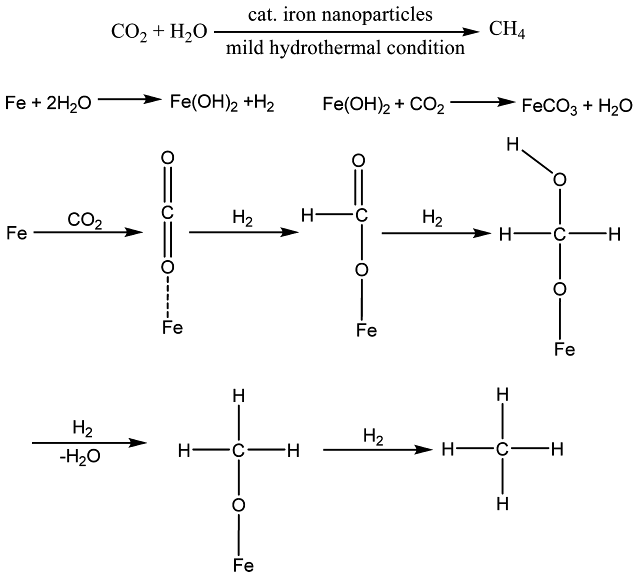


Figure 1. (A) Kinetic curve of hydrothermal production of CH_4 in the presence of iron nanoparticles with 100 nm diameters. (B) Yields of CH_4 at different temperatures.

Scheme 1. Proposed Mechanism of Methane Formation



H_2, and simultaneously, part of the iron nanoparticles absorbed and reduced the dissolved CO_2 molecules by attacking of H_2 on and at the surface of iron nanoparticles. Finally, methane was formed. In order to study the catalytic effect of the iron nanoparticles, we conducted comparison experiments, e.g., H_2 gas as a feedstock was introduced into the CO_2–H_2O system without iron nanoparticles. According to the experimental procedure mentioned above, methane was not detected in the gaseous phase nor liquid phase. The formation reaction for methane is as indicated in Scheme 1.

The average diameter of the residual solids that were collected from the reactor after the reactions is the same as that of the solids before the reactions (Figure 2A,B), but the residual solids are the mixture of iron and ferrous carbonate. The iron powder was separated by magnet, and the residual solids were identified as ferrous carbonate by powder X-ray diffraction (XRD). It was obvious that part of the CO_2 reacted with water and iron powder to form ferrous carbonate under the hydrothermal conditions. To prove the iron nanoparticles are the catalyst in the system, we used two experiments where one was without any catalysts in the system and the other was in the presence of ferrous carbonate as the catalysts under the same condition. We did not find any organic compounds in the gaseous phase nor in the liquid phase in the above two experiments.

In summary, we have conducted mild hydrothermal reactions from CO_2 to CH_4 in the presence of iron nanoparticles 100 nm in diameter and have characterized the reaction process through its gas and solid products. The ready CO_2 conversion process follows the main principles of green chemistry, e.g., one-step process under mild condition, ecofriendly catalyst, no toxicity to human health and environment, solar as the source of energy, and no organic solvents. The work will help the utilization of CO_2 in the future.

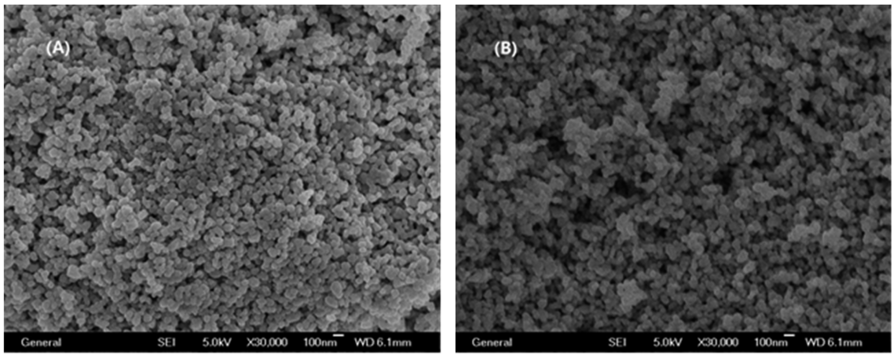


Figure 2. Low-magnification scanning electron microscopy (SEM) images of 100 nm diameter iron nanoparticles before (A) and after hydrothermal reactions (B).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on the method of the catalyst, GC-MS characterization, and calibration curve of methane. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Quadrelli, E. A.; Centi, G.; Duplan, J.-L.; Perathoner, S. Carbon dioxide recycling: Emerging large-scale technologies with industrial potential. *ChemSusChem* **2012**, *4* (9), 1194−1215.

(2) Jin, F.; Zeng, X.; Jing, Z.; Enomoto, H. A potentially useful technology by mimicking nature-rapid conversion of biomass and CO_2 into chemicals and fuels under hydrothermal conditions. *Ind. Eng. Chem. Res.* **2012**, *51* (30), 9921−9937.

(3) Visconti, C. G.; Lietti, L.; Tronconi, E.; Forzatti, P.; Zennaro, R.; Finocchio, E. Fischer−Tropsch synthesis on a Co/Al_2O_3 catalyst with CO_2 containing syngas. *Appl. Catal., A* **2009**, *355* (1−2), 61−68.

(4) Taran, Y. A.; Kliger, G. A.; Sevastianov, V. S. Carbon isotope effects in the open-system Fischer−Tropsch synthesis. *Geochim. Cosmochim. Acta* **2007**, *71* (18), 4474−4487.

(5) Hoffmann, M. R.; Moss, J. A.; Baum, M. M. Artificial photosynthesis: Semiconductor photocatalytic fixation of CO_2 to afford higher organic compounds. *Dalton Trans.* **2010**, *40* (19), 5151−5158.

(6) Usubharatana, P.; McMartin, D.; Veawab, A.; Tontiwachwuthikul, P. Photocatalytic process for CO_2 emission reduction from industrial flue gas streams. *Ind. Eng. Chem. Res.* **2006**, *45* (8), 2558−2568.

(7) Takeda, H.; Ishitani, O. Development of efficient photocatalytic systems for CO_2 reduction using mononuclear and multinuclear metal complexes based on mechanistic studies. *Coord. Chem. Rev.* **2010**, *254* (3−4), 346−354.

(8) Saveant, J. M. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chem. Rev.* **2008**, *108* (7), 2348−2378.

(9) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels. *Chem. Soc. Rev.* **2009**, *38* (1), 89−99.

(10) Rakowski, D. M.; Dubois, D. L. Development of molecular electrocatalysts for CO_2 reduction and H_2 production/oxidation. *Acc. Chem. Res.* **2009**, *42* (12), 1974−1982.

(11) Tian, G.; Yuan, H. M.; Mu, Y.; He, C.; Feng, S. H. Hydrothermal reactions from sodium hydrogen carbonate to phenol. *Org. Lett.* **2007**, *9* (10), 2019−2021.

(12) He, C.; Tian, G.; Liu, Z.; Feng, S. A mild hydrothermal route to fix carbon dioxide to simple carboxylic acids. *Org. Lett.* **2010**, *12* (4), 649−651.

(13) Martinez-Perez, M. J.; de, M. R.; Carbonera, C.; Martinez-Julvez, M.; Lostao, A.; Piquer, C.; Gomez-Moreno, C.; Bartolome, J.; Luis, F. Size-dependent properties of magnetoferritin. *Nanotechnology* **2010**, *21* (46), 465707/1−465707/14.

(14) Guisbiers, G. Size-dependent materials properties toward a universal equation. *Nanoscale Res. Lett.* **2010**, *5* (7), 1132−1136.

(15) Lian, J.; Liang, Y.; Kwong, F.-l.; Ding, Z.; Ng, D. H. L. Template-free solvothermal synthesis of ZnO nanoparticles with controllable size and their size-dependent optical properties. *Mater. Lett.* **2012**, *66* (1), 318−320.

(16) Belle, C. J.; Bonamin, A.; Simon, U.; Santoyo-Salazar, J.; Pauly, M.; Begin-Colin, S.; Pourroy, G. Size dependent gas sensing properties of spinel iron oxide nanoparticles. *Sens. Actuators, B* **2011**, *160* (1), 942−950.

(17) Pan, J.; Wu, X.; Wang, L.; Liu, G.; Lu, G. Q.; Cheng, H.-M. Synthesis of anatase TiO_2 rods with dominant reactive {010} facets for the photoreduction of CO_2 to CH_4 and use in dye-sensitized solar cells. *Chem. Commun.* **2011**, *47* (29), 8361−8363.

(18) Xi, G.; Ouyang, S.; Ye, J. General synthesis of hybrid TiO_2 mesoporous "french fries" toward improved photocatalytic conversion of CO_2 into hydrocarbon fuel: A case of TiO_2/ZnO. *Chem.—Eur. J.* **2011**, *17* (33), 9057−9061.

(19) Takahashi, H.; Kori, T.; Onoki, T.; Tohji, K.; Yamasaki, N. Hydrothermal processing of metal based compounds and carbon dioxide for the synthesis of organic compounds. *J. Mater. Sci.* **2008**, *43* (7), 2487−2491.

(20) Jacquemin, M.; Beuls, A.; Ruiz, P. Catalytic production of methane from CO_2 and H_2 at low temperature: Insight on the reaction mechanism. *Catal. Today* **2010**, *157* (2010), 462−466.

(21) Gnanamani, M. K.; Shafer, W. D.; Sparks, D. E.; Davis, B. H. Fischer−Tropsch synthesis: Effect of CO_2 containing syngas over Pt promoted $Co/\gamma\text{-}Al_2O_3$ and K-promoted Fe catalysts. *Catal. Commun.* **2011**, *12* (11), 936−939.