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Reduction of CO_2 with water splitting hydrogen under subcritical and supercritical hydrothermal conditions

Yuqian Chen, Zhenzi Jing*, Jiajun Miao, Yi Zhang, Junjie Fan

Key Laboratory of Advanced Civil Engineering Materials, Ministry of Education, Tongji University, 4800 Cao'an Road, Shanghai 201804, China

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ABSTRACT

Hydrothermal conversion of CO_2 into organic chemicals in the presence of Fe and Ni powder under subcritical and supercritical hydrothermal conditions has been carried out, and the results showed that H_2 could be obtained from water splitting under hydrothermal condition. According to Fe_3O_4 formation, the reaction temperature seemed to influence the generation of H_2, and H_2 could be formed largely at supercritical condition especially at 425 °C. The formic acid could be produced from CO_2 reduction, and the reaction temperature had a great effect on the formic acid yield. The increase in temperature could improved the formic acid yield, however higher temperature (≥275 °C) seemed to exert a minus influence on the formic acid yield due to decomposition of formic acid. The decomposition of formic acid became quick from 350 °C, and the results showed that the formic acid was decomposed into methane at higher temperature (350 °C).

Introduction

Carbon dioxide (CO_2) is one of the highest contributions to the greenhouse effect, and on the other hand CO_2 is a cheap and nontoxic building block for single carbon source chemistry as well [1]. As such, CO_2 conversion has become one of the most important research areas, and many studies, therefore, have been developed for the CO_2 reductions, such as electrochemical reduction [2], catalytic hydrogenation reduction [3], chemical reduction [4], and chemical vapor deposition [5]. The CO_2 hydrogenation with gaseous hydrogen is currently considered to be the most commercially feasible method, however, it requires either expensive catalysts or high-purity hydrogen, and in addition there also exist a great challenge for its storage and transport. Reduction of CO_2 can lead to various products such as carbon materials (carbon nano-tubes and carbon spheres) [4,5], organic carbonates (methanol, formic acid and acetic acid) [6,7], and syngas [8]. Among these, formic acid and methane hold a central position because they are both important feedstock for the manufacture of everyday chemicals [9].

From the perspective of thermodynamics, it is difficult to reduce CO_2 into useful chemicals due to its stable carbon-bearing molecules, unless a large energy input or a high energy substrate such as hydrogen (H_2) is used [10].

According to oceanic serpentinization occurred at relatively high temperatures (200–400 °C) [11], the hydrogen (H_2)

* *Corresponding author*. Tel./fax: +86 21 6958 0264.
E-mail address: zzjing@tongji.edu.cn (Z. Jing).
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can produce through water splitting, during which olivine is converted to serpentine and magnetite, while released Ni is deposited as Ni_3Fe [12], showing that the H_2 could be obtained from water splitting under hydrothermal condition with the existence of Fe and Ni. This further suggests that CO_2 might be reduced hydrothermally into useful chemicals in situ with the H_2 split from H_2O. The work [13] also showed that Ni could be used as catalyst for the synthesis of organic compounds from CO_2.

The transition metals were found to have a capability of promoting the split of H_2O into H_2, and then reducing CO_2 under hydrothermal conditions, e.g., the methane was obtained hydrothermally at temperature of 300 °C [14]. In the hydrothermal reduction of CO_2, the high-temperature water acts not only as a reaction medium or solvent, but also as a hydrogen source generated by reduction of metal reductants [7]. Compared with hydrogenation method, hydrothermal reduction would be advantageous to avoid the use of gaseous hydrogen, thus it is currently regarded as one of the most feasible methods for CO_2 reduction.

To date, the hydrothermal reductions of CO_2 were carried out under subcritical conditions, and few studies seemed to deal with supercritical conversion. The objective of this study is to reduce CO_2 into formic acid and/or methane with H_2 split from H_2O under subcritical and supercritical hydrothermal conditions, and compare the CO_2 reduction behaviors between subcritical and supercritical hydrothermal treatment.

Experimental

In this research, $NaHCO_3$ was the source of carbon to simplify the operation and to control the amount of CO_2 precisely. In fact, CO_2 capture usually uses alkaline solution to dissolve CO_2, for which the solution of CO_2 in alkaline aqueous (exist equilibriums among CO_2, H_2O, HCO_3^-, CO_3^{2-} and OH^-) is very similar to $NaHCO_3$ aqueous solution. $NaHCO_3$ (99.5%), Fe (98.0%) and Ni (99.5%) obtained from Sinopharm Chemical Reagent Co. Ltd, China, were used as test materials. Experiments were carried out in a batch autoclave made of SUS316 stainless steel with an internal volume of 50 ml. Firstly, the desired amount of 20 mmol $NaHCO_3$ (the CO_2 source), 120 mmol reductant (Fe powder), 120 mmol catalyst (Ni powder), and 17.5 ml deionized water were added to occupy 35% of the reaction volume. Then the sealed autoclave was heated in an oven until setting temperature, kept the temperature for 2 h, and cooled to room temperature in the oven naturally.

After the reactions, the liquid samples were filtered (0.22-μm-filter film) and then analyzed by a tunable absorbance detector (VWD) 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} $HClO_4$ solution flowing solvent. The columns were maintained at 50c. The fluent containing 2mMHClO4 was applied at a flow rate of 1 mL/min. The UV detector used was set at 210 nm. The remaining reaction mixture was filtered, and the precipitate was dried in oven at 80 °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 ($\lambda = 1.5406$ Å, scanning rate: 0.1° s^{-1}, 2θ ranges: 25°–70°).

Results and discussion

Effect of temperature on the generation of H_2

A serious of experiments which the temperature ranged from subcritical to supercritical hydrothermal condition (200 °C–425 °C) at 25 °C intervals were made to investigate effect of temperature on the reduction of $NaHCO_3$.

The precipitates were investigated by XRD (Fig. 1). The peak at 2θ = 32° corresponding to $FeCO_3$ was observed at 200 °C which suggested that added Fe has converted $NaHCO_3$

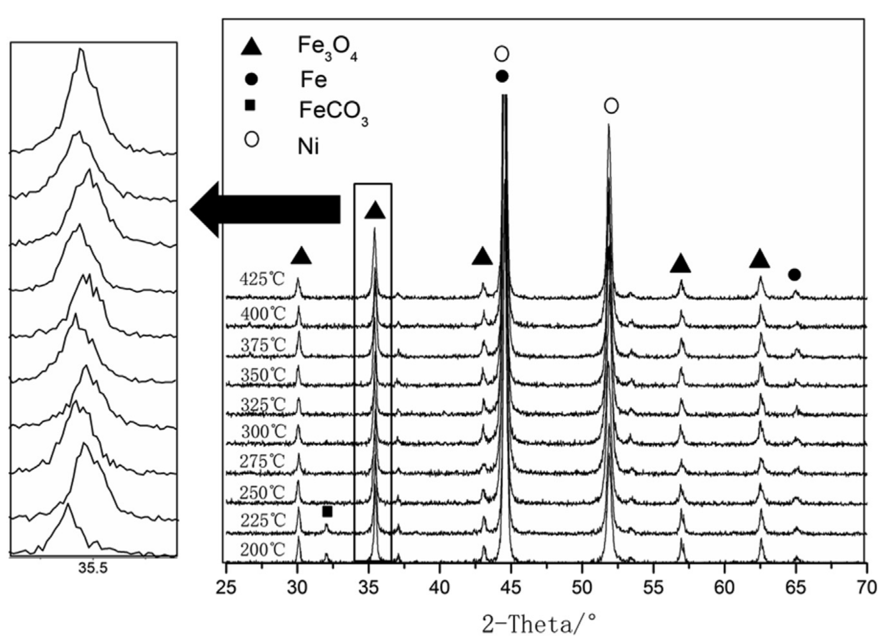

Fig. 1 – XRD pattern of the precipitates after hydrothermal reaction ($NaHCO_3$: 20 mmol, Fe: 120 mmol, Ni: 120 mmol, Deionized water: 17.5 ml, Filling ratio: 35%, Temperature: 200°C–425 °C, Experimental period: 2 h).