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Hydrothermal Reactions from Carbon Dioxide to Phenol

Ge Tian, Chao He, Yan Chen, Hong-Ming Yuan, Zi-Wei Liu, Zhan Shi, and Shou-Hua Feng*[a]

Carbon dioxide, originating from the combustion of fossil fuel, is the most important greenhouse gas contributing to global warming.[1–5] To further elucidate this topic, which is of worldwide interest, and achieve the goals of carbon dioxide emission reduction and utilization, extensive research has been carried out to convert carbon dioxide gas into other materials, ideally industrial chemicals. The predominant methods proposed to transform carbon dioxide into chemicals and fuels are photo- and electrocatalysis.[6,7] Furthermore, the formation of abiogenic hydrocarbons by the reduction of carbon dioxide was believed to occur under hydrothermal conditions involving Fischer–Tropsch reactions and the serpentinization of ultramafic rocks.[8,9] In most cases, the products of this process were methanol, methane, and/or formate, which are all C1 chemicals.

In our previous studies, we reported the hydrothermal conversion of carbonates into phenol[10] and, further, into peptides.[11] Because studying the chemical utilization of carbon dioxide gas is significant for environmental purposes, our current study aims to confirm that carbon dioxide gas follows the mechanism of carbonate conversion and determine if carbon dioxide gas reacts with water under hydrothermal conditions. We have found that carbon dioxide gas can be converted into phenol by ecofriendly catalysts and under mild hydrothermal conditions.

Our study on the reactions of carbon dioxide with water in the presence of iron powder is based on well-established hydrothermal methods.[12] We began with purified carbon dioxide gas, water, and metal catalyst powders in a reactor. GC-MS results indicated that no organic compound could be detected in the purified carbon dioxide gas starting material (99.999 %) (Supporting Information, Figure S1). The metal powders, water, and reactor system used in this experiment were purified according to the treatment procedures reported earlier and free of organic contamination.[11] In a specific experiment, 560 mg (10 mM) of purified iron powder was mixed with water in a glass-liner Endeavor Catalyst Screening System (ECSS) with a filling capacity of 50 % in a total volume of 20 mL. Carbon dioxide gas was injected into the ECSS, increasing the inside pressure to 1.4 MPa. The system was heated at 200 °C for 120 h. The final pressure and pH of the system after cooling to room temperature were 1.0 MPa and 5.5, respectively. Product analysis was carried out with GC-MS (Figure S2). A mass spectrum of the solution after reaction showed the formation of phenol, consistent with its standard mass spectrum (Figure S3), according to:

$$CO_2 + H_2O \rightarrow C_6H_5OH \qquad (1)$$

We monitored the change of the iron powder after the reaction. After reaction, 1 wt % Fe^{2+} was proven to be present in the solution by inductively coupled plasma (ICP) analysis. Thus, a possible oxidization mechanism of iron under the hydrothermal conditions is proposed:

$$Fe + H_2O \rightarrow Fe^{2+} + H_2 \qquad (2)$$

In addition to iron, other metals and zeolites were used under the same reaction conditions. These materials, including Al, Zn, Co, and Ni powders, Fe_3O_4, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}-modified ZSM-5, MCM-41, MCM-48, H-beta and Na-Y zeolites, did not result in significant phenol formation, although trace amounts of phenol were obtained in the presence of Co and Ni powders. The possible role of oxygen in this reaction was studied and both the products and the yield remained unchanged with changing oxygen concentration.

Kinetic studies were carried out in this system. Figure 1 shows a kinetic curve for the hydrothermal production of phenol. The yield was obtained by comparing the peak area of the product with a calibration curve of peak area as a function of concentration (Figure S4). In the first 10 h of reaction, the yield of phenol increased slowly. With the increasing of reaction time from 10 to 120 h, the phenol yield increased rapidly. This is typical of a self-catalytic reaction, with a short induction

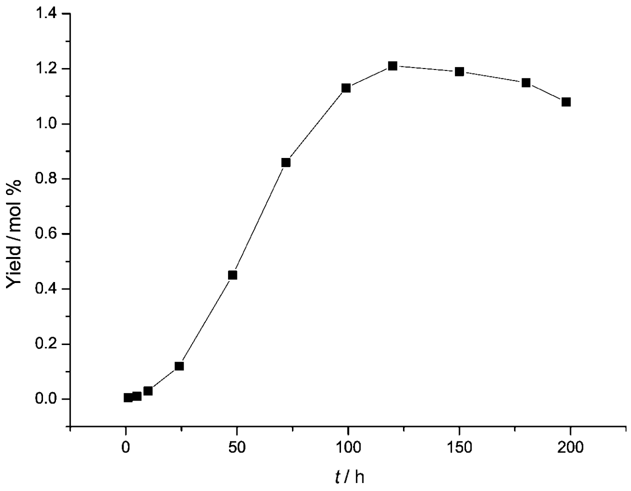

Figure 1. Kinetic curve for the hydrothermal production of phenol.

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[a] Dr. G. Tian, C. He, Dr. Y. Chen, Prof. H.-M. Yuan, Z.-W. Liu, Prof. Z. Shi, Prof. S.-H. Feng
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry
College of Chemistry, Jilin University
Changchun 130012 (PR China)
Fax: (+86) 431-85168624
E-mail: shfeng@mail.jlu.edu.cn

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period and fast formation reaction after the induction period. In the short induction period, some compounds (formaldehyde, formic acid, and others) are formed that further catalyze the reaction. At this stage several organic molecules could be identified by GC-MS, including the main product phenol and trace amounts of formic acid and formaldehyde. After 120 h, the phenol yield reached a maximum value of 1.21 mol% according to carbon dioxide, and then remained nearly constant. The final product was phenol.

In the past decade, organic syntheses starting from carbon dioxide have also been studied.[13,14] The production of phenol from solid carbon dioxide reduced by Fe_3O_4 in supercritical state was reported.[15] In comparison, our hydrothermal approach is highly selective under lower temperature and pressure. As an insight into the origin of life, it would be important to prove that the reactions of carbon dioxide with water proceed hydrothermally. In this process, dissolved carbon dioxide chemisorbs onto the surface of iron atoms, and the reduction of carbon dioxide is closely related to the oxidation of iron atoms.[10] Therefore, we believe that this process consists of a catalysis reaction and a redox reaction of carbon dioxide. The reactions take place much more efficiently with the use of iron powder than with cobalt and nickel powder, under the same reaction conditions. This is consistent with the relatively large redox potential of iron in group VIIIB: Fe -0.44 V, Co -0.277 V, and Ni -0.25 V. Because iron is the most abundant metallic, redox-active element on Earth, the iron powder catalyst is ecofriendly, abundant, and easily prepared.

Based on the observation of the final product phenol and intermediate formic acid and formaldehyde in the hydrothermal reactions, we conclude that the reaction mechanism from carbon dioxide to phenol does follow the mechanism proposed previously.[10] At the first stage of the reaction, the iron metal reacts with water, producing H_2 and Fe^{2+}. Meanwhile, the dissolved CO_2 molecules are adsorbed onto the surface of the iron powder. Upon attack of H_2, CO_2 is reduced to form formaldehyde and formic acid. The complicated processes involves two simple types of reactions: oxidative coupling and rearrangement reactions. Further research on the reaction mechanism and kinetics will be performed to provide more information for a more efficient catalyst. As a source of hydrogen, water is necessary in this reaction, whereas the ratio of carbon dioxide to water has little effect on the reduction of carbon dioxide. The conversion of carbon dioxide into phenol becomes an alternative to the existing electrochemical and biotic techniques to reuse the greenhouse gas carbon dioxide. The decreasing carbon dioxide pressure and accumulation of the product phenol restrict the further conversion of carbon dioxide into phenol. Therefore, we conducted a constant-pressure experiment, continuously supplying enough carbon dioxide, and the results showed an increasing tendency for the phenol yield. We believe that this simple process can be repeated to reach an industrial level by gradually collecting phenol.

Our study on the hydrothermal reaction of carbon dioxide to phenol is a basic study for carbon dioxide fixation, and provides a possible route to produce complicated aromatic chemicals directly from a greenhouse gas. The conversion process is consistent with almost all principles of green chemistry. It is a single-step process under mild conditions, uses ecofriendly catalysts, avoids the separation of products, and avoids the use of any harmful solvent. Most importantly, carbon dioxide is used as a feedstock to produce very useful chemicals.

Experimental Section

In a typical experimental procedure, 560 mg (10 mM) Fe powder (Sinopharm Chem. Reagent Co.; calcined at 500 °C for 3 h in N_2 (99.99% flow) was mixed with 8 mL of pure water and then added into a glass liner in the ECSS (Argonaut Technologies, Inc.) with a filling capacity of 50%. After cycling carbon dioxide gas into the glass liner twice, to drive out the air in it, carbon dioxide was injected into the ECSS up to a pressure of 1.4 MPa. The mixture was stirred at 600 rpm and subjected to hydrothermal treatment at 200 °C for 1–200 h, and then rapidly cooled to room temperature. The final pressure inside the ECSS after reaction was 1.0 MPa. The entire process was under controlled by software.

The products were identified by GC-MS. Data were recorded on a TRACE MS GC-MS (Finnigan Co.). Temperatures: column, 80 °C for 1 min, then increased to 280 °C at 20 °C min^{-1}, final temperature 280 °C. Sample volume: 1 μL. Column type: HP-5 ms. MS: EI source.

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