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Hydrothermal processing of metal based compounds and carbon dioxide for the synthesis of organic compounds

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Abstract Reservation of carbon-based resources including fossil fuel is an important issue for futuristic development. As a possible carbon resource, we had proposed a process for the reduction of CO_2 by hydrothermal method. In the process, CO_2, aqueous solvent, and reductant are to react under hydrothermal condition, to generate organic compounds. In this report, the extension of the process to continuous-type process has been focused. For the experiments, newly developed continuous-type equipment was used. Metallic materials such as carbon steel cutting chaff was treated at 200 °C, 2.0 MPa under the constant flow of CO_2 gas and solvent, with or without the hydrogenation catalyst, Ni. During the experimental period, reaction gas and liquid are collected successively. The samples are analyzed with GC and TOC. In treatment without Ni powder, organic compound was detected in neither reaction gas nor solution, while the occurrence of CO was confirmed. On the other hand, in the experiment with Ni powder additionally, formic acid was generated. It has been confirmed that the reaction process proceeds even in the continuous-type treatment including the catalytic effect of Ni.

Introduction

Fossil fuels is one of the most important resources for the energy and/or materials production, especially in the industrial field. Although, it is widely accepted that the fossil fuels are the limited resources on earth. In such circumstance, it is predicted that such resources can be depleted in several decades. The depletion of them, especially petroleum oil, may cause the short supply of energy, and/or the problems in the production of materials such as plastics. Thus, it is important to develop other organic resources.

In these decades, the chemical reduction of CO_2 to organic compounds has attracted much attentions. Such process can produce organic feedstock using CO_2 as the carbon source, in change for the fossil fuels. One of the most popular methods is the catalytic hydrogenation of CO_2. Komada et al. [1] have reported that methane could be produced with high yield by using a Ni-ferrite catalyst and hydrogen. Other group reported [2, 3] the synthesis of oxygenated organic compounds using various metal-based catalysts. While, many other methods for the chemical reduction of CO_2 are being investigated such as electrochemical method [4, 5], photochemical method [6], and another catalytic method using a supercritical CO_2 also as a reaction medium [7]. Though, there are no examples in the industrial field so far, because of its low yield and/or

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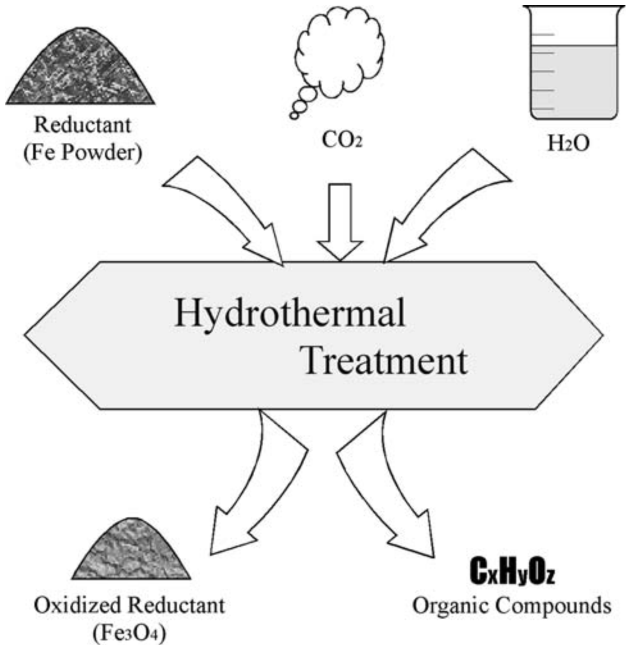

Fig. 1 Schematic process flow of the hydrothermal reduction of CO_2

high cost. To develop the CO_2 reduction as commercially available process, higher yield and the selectivity for valuable compounds is important.

The reduction of CO_2 under hydrothermal conditions has been investigated from the geological aspect so far [8]. Such reports has been focused on the abiogenic formation of fossil fuels. The authors have proposed on this reaction as a novel process for the production of organic compounds [9]. In this process, CO_2 react with water and reductant. This process was conceptually described in Fig. 1.

In the reaction, the water acts not only as a solvent, but also as a hydrogen source. The characteristics of this process are relatively low operation temperatures, and wide variety of the reductant. Under hydrothermal conditions, the various compounds are easily oxidized by water, and generate hydrogen. Additionally, this. hydrogen immediately after the liberation from water molecule, could be expected to be a highly effective reductant as an active hydrogen. In previous publication [9], the reaction pathway for the formation of methane and formic acid has been investigated. For the commercialization, the development of continuous treatment and the investigation of the reductant with low cost is inevitable. In this report, a novel flow-type equipment for the continuous treatment under hydrothermal conditions has been developed. And the reduction of CO_2 has been studied from the viewpoint of recycling by using iron-based waste as a model compound.

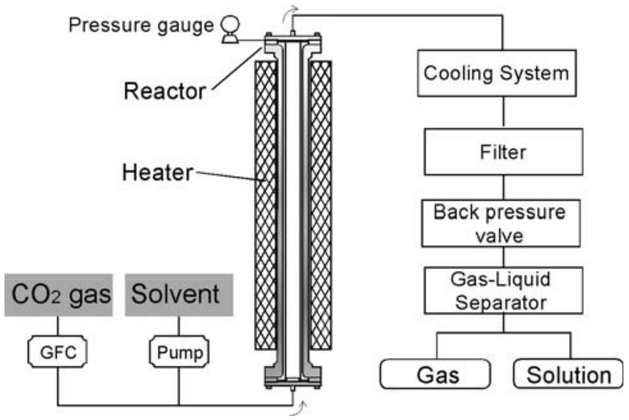

Fig. 2 Illustration of the equipment for the three-phase continuous hydrothermal treatment

Flow-type equipment

Development of flow-type equipment

Figure 2 shows the schematic illustration of newly-developed flow-type equipment for the hydrothermal treatment. This equipment can be divided roughly into three parts. Those are the flow-controlling devices, reactor, and post-treatment instruments. In the first part, a mass flow controller and a quantitative solvent pump were equipped for the regulation of pressurized CO_2 gas and solvent, respectively. In experiments, fluid is introduced into the bottom of the reactor with constant flow rate. The reactor, a second part of whole equipment, has been fabricated of stainless steel lined with PTFE, to avoid the corrosion and unexpected attendance of the reactor materials to the reaction. The length was 1,000 mm and the inner diameter was 27 mm including the lining thickness (ca. 3 mm). Four electric furnaces are fixed with the reactor for the control of temperature-set region. The solid substrates such as reductants were supposed to be settled inside the reactor before the treatment. At the place where the solid substrates are settled, the reaction involving three-phase substrates occur under hydrothermal conditions. The pressure gauge has been connected with the reactor directly for the monitoring of the fluid pressure. The fluids through the reaction would be exhausted from the top side of the reactor. At the post-treatment region, those fluid is cooled down, filtrated, regulated the pressure, and separated into the gaseous and liquid phase under atmospheric pressure.

Heating characteristics

The heating characteristics for the equipment have been examined. For the precise measurement of temperature distribution inside the reactor, a stainless steel tube has been equipped to the reactor, one end of that has been sealed. The reactor has been filled up with distilled water and pressurized to 2 MPa. Then, the heaters were turned on. Temperature distribution inside the reactor was measured by moving the thermocouple inside the stainless tobe. The temperature distribution inside the reactor during the heating step, and the equilibrium temperature has been illustrated in Fig. 3. As shown in the figure, temperature differences inside the reactor, compared with that in equilibrium state, have reached to ±5 °C after 1 h. At the equilibrium condition, temperature for upper half of the reactor has been stabilized between 197 °C and 202 °C. From these facts, the heating period for reaction experiment was adjusted at 1 h.

Experimental procedure

Experiments has been conducted with two kind of reductant. As a preliminary test, 0.1 mol of Fe reagent powder (Wako Pure Chemical, ca.400 μm) has been used. 0.01 mol/l HCl aqueous solution was adopted as a solvent. Experimental procedure is as follows. Firstly, reductant powder was settled inside the reactor with PTFE tube, mesh, and glass filter, as the reductant would be placed at corresponding temperature region of the reactor. Then, solvent was introduced to the reactor to be pressurized, and back-pressure valve was controlled to adjust the pressure at 2.0 MPa. Solvent injection was stopped, and heaters were turned on to heat the reactor. After 1 h elapsed, the injection of the solvent and CO_2 gas have been started at 6.0 mL/min and 70 NmL/min. This moment was defined as a start time of the reaction. As given time elapsed, the effluent reaction gas and solution have been collected. After treatment, the residual solution and solid substrate inside the reactor were recovered. Samples were analyzed with TOC, GC, and XRD.

Another experiment, with the concept of recycling, was conducted using 70 g of carbon steel (S-45C) cutting chaffs as the reductant, with or without Ni powder (Wako Pure Chemical, 150 μm). The cutting chaff were washed twice with acetone and dried before treatment, to remove remaining cutting oil. Experimental procedure is fundamentally same as the preliminary one, except reductant, and solvent changed to distilled water.

Results and discussions

An experiment using a small amount of Fe powder has been conducted. Figure 4 shows the yield of hydrocarbons at the corresponding experimental time. As shown, methane, ethane, ethylene, and propylene generation have been confirmed. The yield of hydrocarbons decreased as the reaction time elapsed. No other organic compounds such as

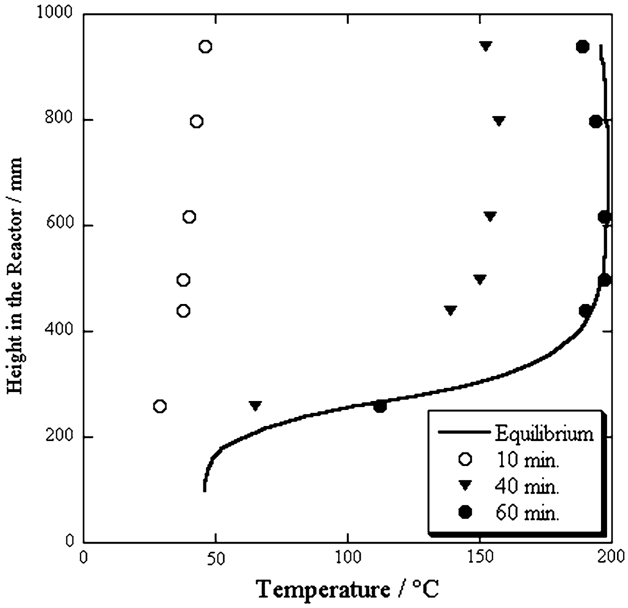

Fig. 3 Temperature characteristics for at the heating period and the equilibrium. Pressure: 2.0 MPa, distilled water: 6.0 mL/min., CO_2 gas: 70 NmL/min

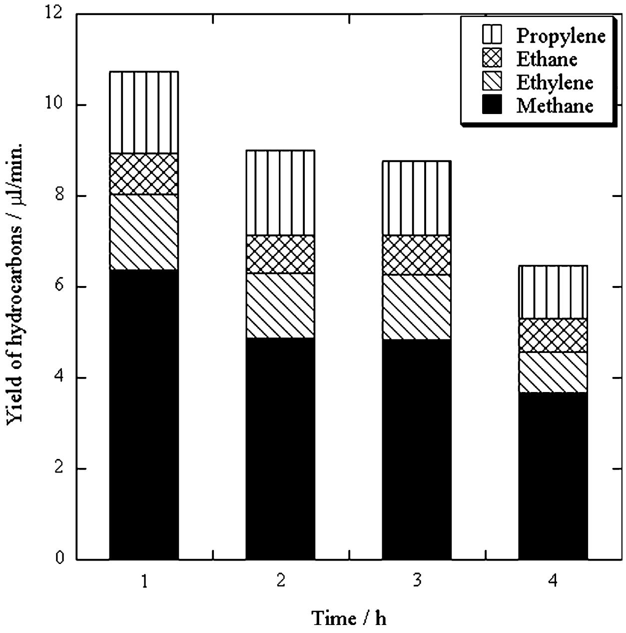

Fig. 4 Yield of hydrocarbons from the hydrothermal treatment of Fe powder and CO_2. Temperature: shown as Fig. 3, Pressure: 2.0 MPa, Fe powder: 5.6 g, CO_2 gas: 70 NmL/min (3.1 mmol/min), 0.01 mol/L HCl solution: 6.0 mL/min

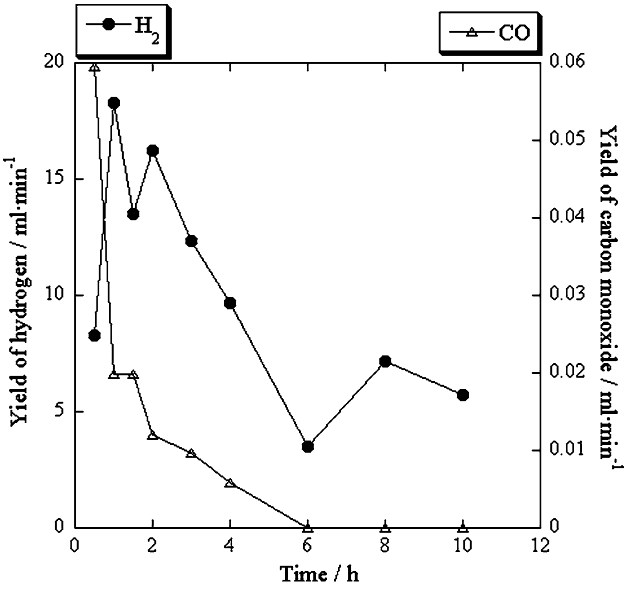

Fig. 5 Yield of hydrogen and carbon monoxide from the hydrothermal treatment of carbon steel cutting chaff and CO_2. Temperature: shown as Fig. 3, Pressure: 2.0 MPa, carbon steel cutting chaff: 70 g, CO_2 gas: 70 NmL/min (3.1 mmol/min), distilled water: 6.0 mL/min

carboxylic acid have been detected. The conversion ratio of CO_2 was calculated about 0.016%. It is supposed that the small amount of reductant consumed caused this low reaction rate, as well as the system under continuous system. In the hydrothermal reduction of CO_2 without catalyst, a nascent hydrogen, which is supposed unstable, is suggested as a driving force of the reaction. Thus, the reaction is supposed to have occurred at very near place beside the reductant. Two facts shown above have been supposed to lead the short contact time. Thus, the conversion of CO_2 remained at those low values. It is noteworthy that unsaturated hydrocarbons were generated in comparable amount to the saturated ones.

Experiments using the cutting chaff as reductants have been conducted. Without Ni powder, no organic compounds were detected in both of the reaction gases and solutions. Only the hydrogen and carbon monoxide were found as product. Figure 5 shows the yield of hydrogen and carbon monoxide with the reaction time. This may be because of the low specific surface area of the reductant. For more effective reaction of the hydrogen and CO_2, another experiment was conducted with the Ni powder as a hydrogenation catalyst. From this treatment, formic acid was found in the reaction solution. Figure 6 shows the yields of formic acid and the hydrogen. The yield of both compounds decreased with the reaction time elapsed. Though the formation of formic acid is confirmed only at the experiment with Ni powder, the yield of hydrogen is almost same with or without Ni powder. This suggest that the Ni powder had acted as a hydrogenation catalyst which let the hydrogen react with CO_2 effectively. In these experiment, hydrocarbon was not confirmed, while the preliminary experiment formed some hydrocarbons. The reason for this difference is suggested because the particle size of the reductant in preliminary experiment was enough small, for fast and constant hydrogen generation. To recycle the Fe-based waste material, the particle size might be fatal.

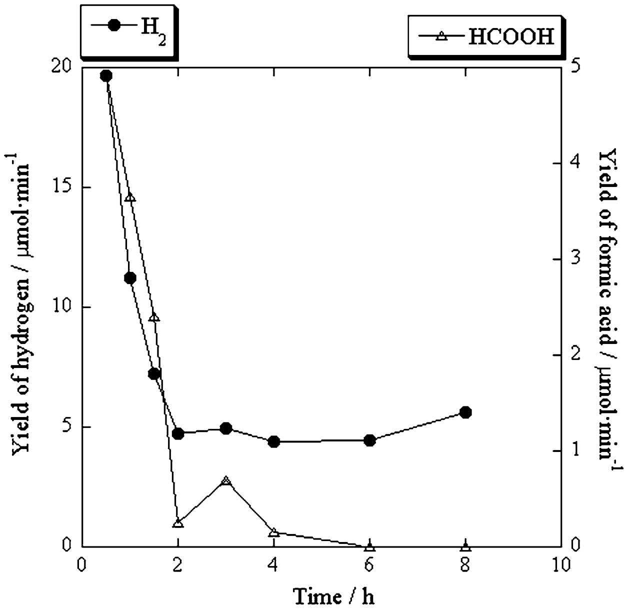

Fig. 6 Yield of hydrogen and carbon monoxide from the hydrothermal treatment of carbon steel cutting chaff and CO_2 with Ni powder. Temperature: shown as Fig. 3, Pressure: 2.0 MPa, carbon steel cutting chaff: 70 g, Ni powder: 7.5 g, CO_2 gas: 70 NmL/min (3.1 mmol/min), distilled water: 6.0 mL/min

Conclusions

A novel flow-type equipment for the continuous treatment of CO_2 has been developed. With that equipment, three phase substrates can be treated under hydrothermal conditions at the same time. The hydrothermal reduction of CO_2 using the equipment has been investigated. By the addition of Ni powder, the formation of formic acid has been observed.

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