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CO_2 reduction using hydrothermal method for the selective formation of organic compounds

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The reduction of CO_2 under hydrothermal conditions has been investigated. In typical experiment, Fe-powder, Ni-powder, solvent, and CO_2 have been reacted in a batch-type micro autoclave under hydrothermal conditions for several hours. Methane, formic acid, and hydrogen were generated after treatment in water. With the rise of Ni amount, the methane yield increased while hydrogen and formic acid decreased. It is supposed that Ni has acted as a hydrogenation catalyst. In basic solution, CO_2 was converted to formic acid selectively at 300°C involved with trace of methane. Considering the reduction characteristics of formic acid, the reaction pathway has been discussed. In experiments with the mixture of Fe and Fe_3O_4, trace of methanol was detected at the experiments with less amount of metallic Fe. It is inferred that the control on the effect of reductant is indispensable for oxygenated organic compound formation. Experiment on the effect of water has been conducted using hydrogen. Ethane yield increased with the amount of water, while there was no drastic change in the yield of methane. From these results, it is supposed that the steam reforming reaction of methane was involved in the reduction of CO_2, and effected on the C–C bond formation.

1. Introduction

The "Green-house Effect" is getting to be regarded as a worldwide problem that can cause a series of catastrophic events. To avoid that, CO_2 emission should be reduced as soon as possible. Because of such circumstance, researches dealing with the fixation of CO_2 have attracted much attention. One of that is the disposal of CO_2 into the deep ocean location [1–2] or crust [3], which can be described as a physical fixation. However, such project seems to be difficult to carry on practically because of no economical collateral, even with its technical easiness. On the other hand, the chemical reduction of CO_2 to convert into organic compounds is regarded as one of the most expected solution for that problem. Because such process has large potential to be a new chemical industrial process for producing some of organic compounds, in turn of conventional process using fossil fuels. The most frequently reported one is the catalytic hydrogenation of CO_2. Komada et al. [4] have reported that methane can be produced with high yield by using a Ni-ferrite as a catalyst. Additionally, other oxygenated organic compounds are also synthesized using various metal-based catalysts [5–8]. Moreover, many other methods for the chemical reduction of CO_2 are developed such as electrochemical method [9–11], photochemical method [12], and another catalytic method using a supercritical CO_2 also as a reaction medium [13]. However, there are no examples in the industrial field so far, because of its low yield and/or high cost. To construct the CO_2 reduction process commercially, the higher yield and the selectivity for valuable compounds is important.

To date, the hydrothermal reduction of CO_2 has been investigated from the geological aspect [14, 15], and was discussed with the abiogenic formation of fossil fuels. However, we have been researched on this reaction as a new process for the production of organic compounds. In this process, CO_2 would react with water and reductant.

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The typical reactions using iron as a reductant are as shown below.

$$Fe + H_2O + CO_2 \rightarrow FeCO_3 + H_2 \quad (1)$$

$$3FeCO_3 + H_2O \rightarrow Fe_3O_4 + 3CO_2 + H_2 \quad (2)$$

$$CO_2 + 2H_2O + 3Fe \rightarrow CH_4 + Fe_3O_4 \quad (3)$$

During the reaction, the water acts not only as a solvent, but also as a hydrogen source. The characteristics of this process are comparatively low operation temperature, and no limitation in reductant as far as it reacts with water. Under hydrothermal conditions, the various compounds are easily oxidized by water, and generate hydrogen. Additionally, this hydrogen immediately after the liberation from water, could be expected to be an active hydrogen as a highly effective reductant. In this report, the reduction of CO_2 with hydrothermal method has been studied. This research was especially focused on the effect of Ni and solvent on the product selectivity, and other factors on the formation of various organic compounds.

2. Experimental methods

Experiments were conducted using a batch-type micro autoclave (ca. 48 cm^3) system, lined with Hastelloy-C (Ni-based alloy), and equipped by a high-pressure valve (Fig. 1). A typical experimental procedure is as follows. Pure water (33.6 cm^3), Fe-powder (100 mmol), and Ni-powder (10 mmol) were charged to the reaction chamber, and the reactor was sealed. After air replacement, CO_2 gas (6.4 mmol) was injected into the autoclave through the high-pressure valve at the room temperature. The autoclave was set in the induction heater. Then the initial materials were treated hydrothermally by heating the autoclave to the experimental temperature (300°C) at heating rate of 30°C/min. with constant shaking. After the treatment, autoclave was taken out of the heater, and cooled to the room temperature by air-blower. The gas was collected over saturated salt solution, and analyzed by gas chromatography equipped with thermal conductivity detector (GC/TCD) and flame ionization detector (GC/FID). The remaining reaction mixture was filtered, and then the precipitate was dried in isothermal oven at 110°C for 24h after washing with distilled water. The solution was analyzed with GC equipped with mass spectrometry detector (GC/MS), total organic carbon analyzer(TOC), and GC/FID, and the precipitate was determined by X-ray diffractometer (XRD).

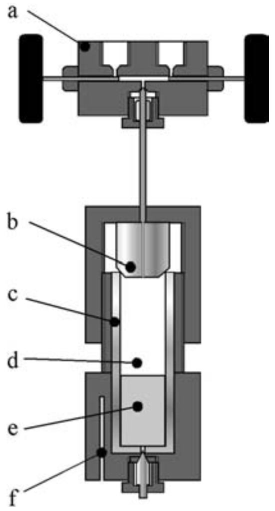

Figure 1 Scheme of micro-autoclave. a: High pressure valve, b: Cone packing (Hastelloy-C), c: Lining(Hastelloy-C), d: Reaction chamber, e: Sample, f: Well of thermocouple.

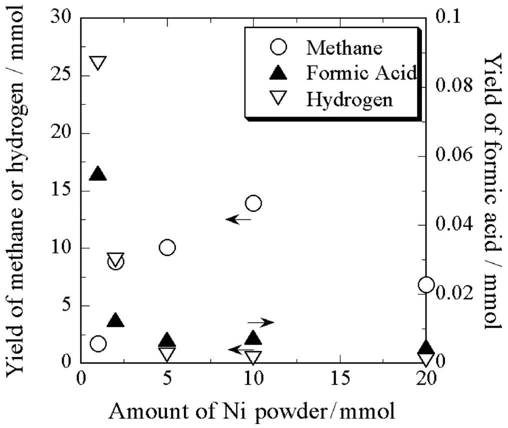

Figure 2 Yield of organic compounds and hydrogen at the different amount of Ni. Fe: 100 mmol, CO_2: 22.5 mmol, Water: 33.6 cm^3 (filling rate: 70%), Temperature: 300°C, Experimental period: 6 h.

3. Results and discussions

3.1. Effect of Ni on the formation of methane and the reaction pathway

It was reported that Ni and Ni containing compounds are active catalyst in the catalytic hydrogenation of CO_2 [4, 16, 17]. Here, we have examined the effect of Ni under hydrothermal condition on the reduction of CO_2. A series of experiments in this section was conducted at 300°C for 6 h using Fe-powder, Ni-powder, water and CO_2 gas. Fig. 2 shows the yield of organic compounds and hydrogen with different amount of Ni-powder. After hydrothermal treatments, methane and hydrogen have mainly generated, with a little amount of formic acid and ethane. Investigation on the precipitates showed that Fe-powder was converted to Fe_3O_4 and $FeCO_3$, while Ni showed no apparent change (Fig. 3). It is clear that hydrogen was formed by the reaction of water and Fe as described in equations (1) and (2). And it is also supposed that Ni did not contributed to the reaction as reactant. As shown in Fig. 2, the methane yield increased with the rise of Ni amount. In contrary, the yield of hydrogen and formic acid decreased with the increasing of the amount of Ni.

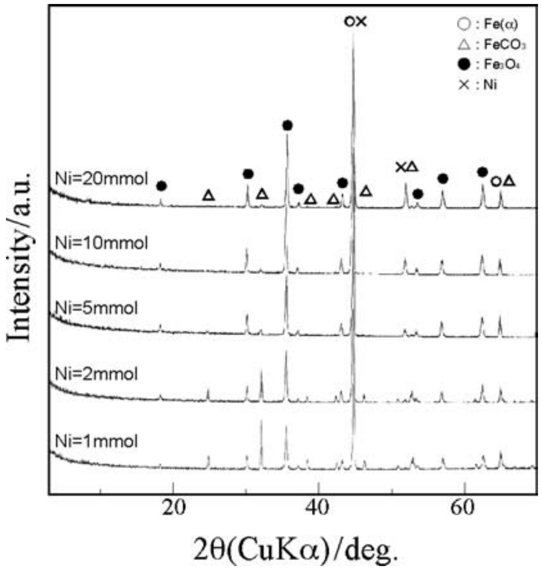

Figure 3 XRD pattern of precipitates after hydrothermal treatment with different amount of Ni. Conditions same as described in Fig. 2.

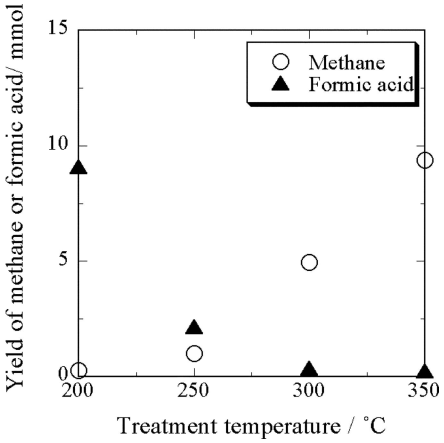

Figure 4 Formic acid decomposition in the hydrothermal conditions with Ni. Formic acid: 10 mmol, Fe: 100 mmol, Ni: 10 mmol, Water: 33.6 cm^3 (filling ratio: 70 %), Experimental period: 2 h.

At the experiment with less amount of the Ni (1 mmol), methane yield was small, even with a much amount of generated hydrogen. Thus, it is clear that formed molecular hydrogen did not react easily with CO_2 under the experimental condition. From this fact, it can be assumed that generated hydrogen reacted effectively with CO_2 by the addition of Ni. And this lead the high yield conversion of CO_2 to methane. From this behavior of hydrogen, it can be supposed that, as shown in Fig. 3, Ni has acted as a hydrogenation catalyst during the reaction. This assumption can also be confirmed by the fact that Ni showed no change in its chemical state after the reaction. On the contrary, the formic acid yield has decreased with the Ni increase, at the same time methane was increased. This is supposed that the reductive decomposition of formic acid into methane has been occurred. With this assumption, it is suggested that formic acid is an intermediate for methane formation during the hydrothermal reduction of CO_2.

To clarify the role of formic acid, the reductive characteristics of it under hydrothermal conditions have been investigated. Experiments have been conducted under same conditions as before, but the formic acid was used instead of CO_2. Fig. 4 shows the yield of methane and soluble organic carbon at different temperature after treatment. In the solution, formic acid was dominant, and trace of methanol and acetic acid were also detected. Thus, the organic carbon in solution can be regarded as a contribution of formic acid. With experimental temperature increased, the yield of soluble organic compounds has been decreased, while the amount of methane increased. And the yield of methane has reached to 94% at 350°C based on the initial amount of formic acid, with the assumption of a reaction shown below.

$$HCOOH + 3H_2 \rightarrow CH_4 + 2H_2O \qquad (4)$$

From this, the formic acid is reduced to form methane under hydrothermal condition with Ni. Considering the former results with CO_2, It was assumed that formic acid is the intermediate during the methane formation from CO_2 in the hydrothermal conditions. Thus, CO_2 is firstly reduced into formic acid, and subsequently methane is generated through the reduction of formic acid by the reaction (4) under hydrothermal conditions.

3.2. Selective formation of formic acid under basic conditions

Experiment using K_2CO_3 as a CO_2 source has been conducted. Other initial materials were same as described in

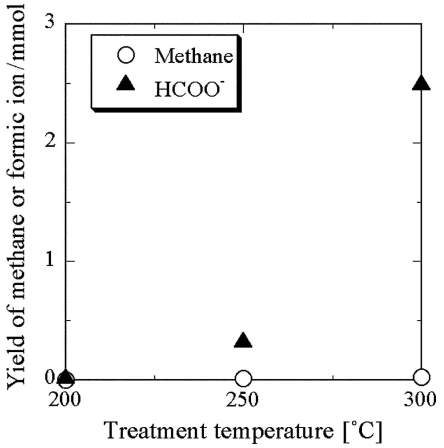

Figure 5 Yield of organic compounds in basic solution at different temperature. K_2CO_3: 10 mmol, Fe: 100 mmol, Ni: 10 mmol, Water: 33.6 cm^3 (filling rate: 70 %), Experimental period: 2 h.

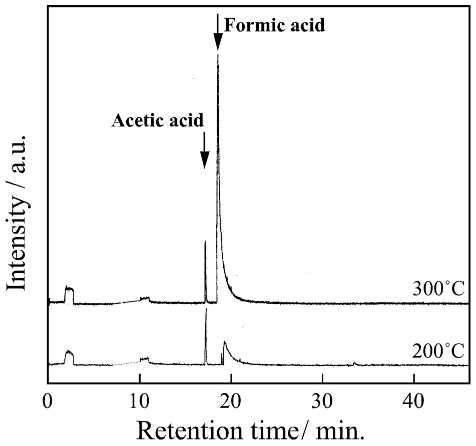

Figure 6 Gas chromatogram of the residual solution certified with mass spectroscopy. Conditions same as described in Fig. 5.

former section. The initial pH of the solution was 11.24 due to the hydrolysis of the carbonate. Fig. 5 shows the effect of temperature on the yield of generated organic compounds. It was certified with GC/MS that the formic acid was the main product in the solution after treatment (Fig. 6). As shown in Fig. 5, formic acid was generated selectively with trace of methane, and its yield increased with treatment temperature increasing. In former section, it was clarified that formic acid easily decomposes into methane in hydrothermal reduction with neutral solvent. Though, formic acid was remained with little amount of methane formed in basic solution. It is obvious that formic acid is ionized to the HCOO- form in basic solvent. Considering these, it is supposed that the formic acid has been stabilized by the ionization to HCOO- in basic solution, and then the further reduction of formic acid into methane has been inhibited.

3.3. Reaction with mixture of Fe and Fe_3O_4

Experiments using the mixture of Fe and Fe_3O_4 were also conducted. In this section, initial ratio of Fe and Fe_3O_4 was described as Fe(0). This indicates the ratio of metallic iron in all of the iron atoms, and was calculated as below.

$$\mathrm{Fe(0)} = \frac{\mathrm{Fe}}{\mathrm{Fe} + {}^{1}\!/_{3}\mathrm{Fe_3O_4}} \tag{5}$$

Fig. 7 shows the yield of gaseous product with different Fe(0). Fe_3O_4 did not show clear effect as a reductant because yield were affected only by Fe(0). Though, in the liquid phase, trace methanol was detected at the experiment with Fe(0) = 50, 10%. This methanol generation may be due to some interaction between Fe_3O_4 and Fe or hydrogen. In the case when CO_2 was completely reduced, all the CO_2 would be converted to methane. However, after hydrothermal treatment with low Fe(0), the methanol has remained. According to these facts, it is supposed that Fe_3O_4 acted as some suppressive factor on the effect of reductant to avoid further reduction. From this point of view, it is inferred that the control of reductive effect of reductant is indispensable for the synthesis of some kind of oxygenated organic compounds, such as alcohol and aldehyde.

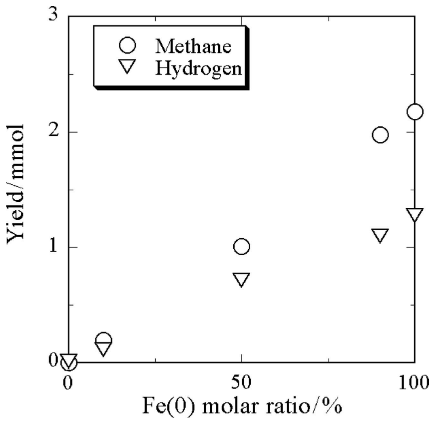

Figure 7 Yield of methane and hydrogen from CO_2 reduction with mixture of Fe and Fe_3O_4. CO_2: 6.4 mmol, Ni: 10 mmol, Water: 33.6 cm^3(filling ratio: 70%), total Fe atom: 100 mmol, Temperature: 300°C, Experimental period: 1 h.

3.4. Effect of water on the organic compound formation

To clarify the effect of water, CO_2 reduction experiments over Ni-powder have been conducted under water-free and steam conditions. In this section, the iron was not used, and hydrogen gas was injected as an alternative reductant before the CO_2 pressurization, so as to H_2/CO_2 ratio becomes 3. Fig. 8 shows the yield of hydrocarbon with different vapor saturation ratio. The main product

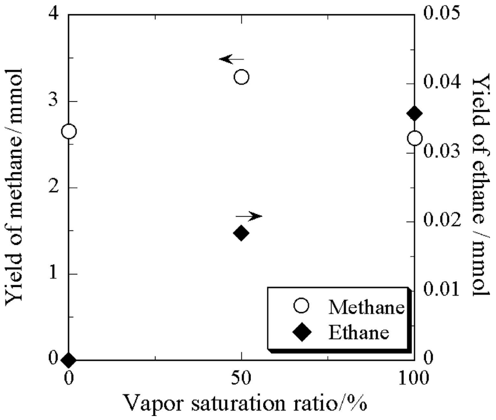

Figure 8 Effect of water content on the yield of hydrocarbons during the gas-phase hydrogenation of CO_2 over Ni-powder. CO_2: 6.4 mmol, H_2: 19.2 mmol, Ni: 10 mmol, Temperature: 300°C, Experimental period: 1 h.

was methane, involved with a little amount of ethane. Also propane was detected only at the experiment with vapor saturation ratio = 100 %. No other organic compound was detected in all the experiment in this section. As shown in Fig. 8, the vapor saturation ratio affected to the yield of methane and/or ethane. Especially, ethane was synthesized almost proportionally to the vapor saturation ratio. In water-free experiment, ethane was not detected. Therefore, it is supposed that water should have some effect on the C–C bond formation. While, from the relationship between vapor saturation ratio and ethane yield, it is more reasonable to regard water as a reactant than as a reaction medium. From these facts, it can be presumed that the steam reforming of methane may be involved in the CO_2 reduction. The steam reforming of methane is one of the partial oxidation reactions of methane, and can be described as below.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (6)$$

This reaction (6) occurs on some metallic catalysts including Ni. Jin et al. have reported [18] that during the steam reforming of methane over Ni/Al_2O_3 catalyst, an active carbon specie, which are free from hydrogen and oxygen atoms, was generated on the catalyst surface as an intermediate. In our study, it is assumed that similar carbon species might be occurred, and they have acted as an active specie for the C–C bond formation on the surface of catalyst.

4. Conclusions

1. It was found that CO_2 is difficult to be reduced without any catalytic effect under hydrothermal conditions at 300°C. However, CO_2 was converted into methane with high yield by the addition of Ni. It is clarified that Ni has acted as an active hydrogenation catalyst. Formic acid has been easily reduced at 300°C with Ni. The reaction pathway is supposed that CO_2 is reduced into the methane accompanied with the formic acid formation as an intermediate.
2. Formic acid was formed selectively at the basic conditions up to 300°C, in consequence of its stability in the form of HCOO-.
3. In Fe-Fe_3O_4 mixture system with Ni, the methanol occurred slightly with less amount of metallic iron, while methane was formed in accordance with the amount of metallic iron. In consideration of the oxidation-reduction states of carbon compounds, it is supposed that Fe_3O_4 has affected on the reductant as some suppressive factor, and the methanol was generated.
4. In the gaseous phase reaction with hydrogen, the ethane was formed in proportional to the water content. It was supposed that the steam reforming reaction of methane, was involved in this reaction. And some active carbon species during this reaction is assumed to have contributed to the C–C bond formation.

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