

Formation of Organic Compounds by the Hydrothermal Reduction of CO₂

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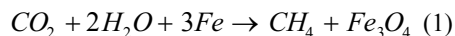
The reduction of carbon dioxide under hydrothermal conditions using Fe compound reductant has been investigated. In this paper, the effect of solvent, reductant, and water amount on the selectivity for the generated organic compound have been focused. In typical experiment, Fe powder, Ni powder, solvent, and CO₂ were reacted in batch-type micro autoclave under hydrothermal condition for several hours. In alkaline solution, CO₂ has been reduced to formic acid selectively at 300 °C, involved with a trace amount of methane. Based on the reduction characteristics of formic acid, the reaction pathway has been discussed for the reduction of CO₂ under hydrothermal conditions. Experiments with the mixture of Fe and Fe₃O₄ as a reductant were also carried out. A trace amount of methanol was detected at the experiment with low metallic iron ratio, though the yield of methane was accompanied with the amount of Fe. The effect of water has also been investigated with the experiment in vapor phase using hydrogen. Ethane yield increased with the amount of water, meanwhile no drastic change in the yield of methane. Ethane was not detected in the water free treatment. From these results, it is presumed that the steam reforming reaction of methane has been involved during the reduction of CO₂, and affected on the C-C bond formation.

1. Introduction

Recently, the utilization of CO₂ has attracted much attention because of its increasing emission and the possibility to cause the global warming [1-2]. Under the circumstance, many researchers have focused on the chemical reduction of CO₂ to synthesize the organic compounds, as one of the most promising solution for that problem. Because chemical CO₂ reduction has large potential to be a new chemical industrial process for producing some of organic compounds, which have been produced commercially using fossil fuels in conventional process. Komada et al. [3] have reported that the high methane yield of 30 % has been obtained with Ni-ferrite catalyst during the catalytic hydrogenation of CO₂. Additionally, other researches focusing on the formation of oxygenated organic compounds using various metal-based catalysts have also been reported about the hydrogenation method [4-7]. On the other hand, many other methods for the reduction of CO₂ have been reported such as electrochemical method [8-10], photochemical method [11], and method using supercritical CO₂ also as a reaction medium [12].

Nevertheless, there is no example applied in the industrial field so far, because of low yield and/or high cost of the process. In order to build up the CO₂ reduction process in commercial base, high yield and selectivity for valuable compounds are indispensable.

Authors have previously reported the novel method for the reduction of CO₂ under hydrothermal condition [13]. In this process, CO₂ react with water and reductant to be reduced to the organic compounds. The typical reaction using iron as a reductant is shown in (1).



Water act not only as a solvent but also as a hydrogen source during the reaction. The characteristics of this process are comparatively low operation temperature, and no limitation of reductant to the extent that it react with water. Such feature may be superior in diminishing the environmental load occurred by the process operation.

In this report, the reduction of CO₂ using the hydrothermal method has been studied, especially

focused on the effect of solvent on the product selectivity, and other factors on the formation of organic compounds.

2. Experimental Method

Experiments were conducted using a batch-type micro autoclave (ca. 48 cm³) system, lined with Hastelloy-C, and equipped with a high-pressure valve (Fig.1). A typical procedure was as follows. Water (33.6 cm³), Fe-powder (100 mmol), and Ni-powder (10 mmol) were charged to the reaction chamber. After air replacement, CO₂ gas (6.4 mmol) was charged into the autoclave through the high-pressure valve at room temperature. Autoclave was sealed and set in the induction heater. Then the initial materials were treated under hydrothermal conditions by heating the autoclave to the experimental temperature (300 °C) with constant shaking. After heating, autoclave was taken out of the heater, and cooled to the room temperature by air-blower. The generated gas was collected over saturated salt water, and analyzed with GC/FID and GC/TCD. The remaining reaction mixture was filtered, and the precipitate was dried in the isothermal oven on 110 °C for 24 hours. The collected solution was analyzed with GC/MS and GC/FID, and the precipitate was determined by XRD.

3. Results and Discussion

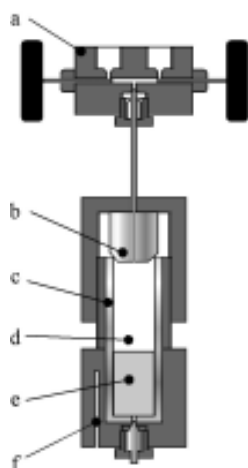


Fig.1 Scheme of micro-autoclave
a: high pressure valve, b: cone packing (Hastelloy-C), c: lining (Hastelloy-C), d: reaction chamber, e: sample, f: well of thermocouple.

Three series of experiments have been conducted for each purpose.

3.1. Selective Formation of Formic Acid under Basic Conditions

Experiments using K₂CO₃ as a carbon source have been conducted. Other initial materials were same as described in former section. The initial pH of the solution was 11.24 due to the hydrolysis of the carbonate. Fig.2 shows the effect of temperature on the generated organic compounds. As shown in this figure, formic acid was generated selectively with a trace amount of methane, and its yield increased with treatment temperature increasing. In our previous paper, it was clarified that formic acid is easily decomposed into methane by the hydrothermal reduction in neutral solvent (Fig.3). The decomposition of formic acid has also been studied by the Kyoto University group [14-15]. They have treated formic acid under hydrothermal condition without a reductant, and clarified that formic acid is decomposed into CO and CO₂ reversibly. From these facts, the reaction pathway for the methane formation from CO₂ under hydrothermal condition has been suggested as follows. Firstly, CO₂ is converted to the formic acid with the generated hydrogen. Then, the formed formic acid decomposes into CO and CO₂ subsequently. Finally, CO is reduced into methane with the activated hydrogen on the surface of Ni. It is well known that CO is easily reduced to methane with the attendance of hydrogen over the

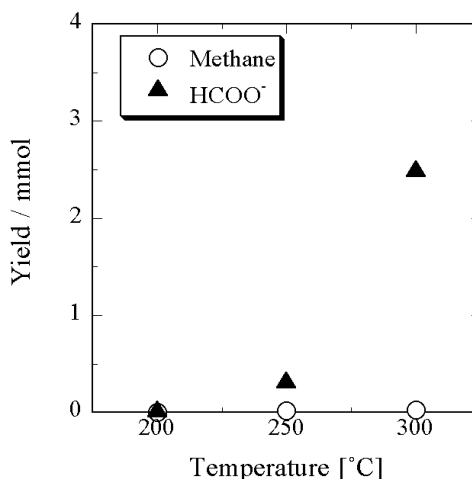


Fig.2 Yield of organic compounds in basic solution at different temperature. K₂CO₃: 10 mmol, Fe: 100 mmol, Ni: 10 mmol, Water: 33.6cm³ (filling rate 70 %), Experimental period: 2 h.

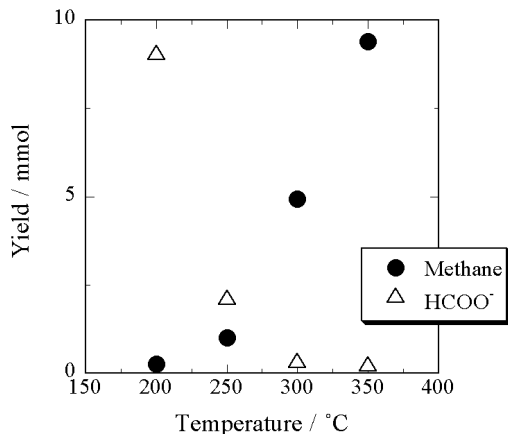


Fig.3 Formic acid decomposition in the hydrothermal reduction with Ni. Formic acid: 10 mmol, Fe: 100 mmol, Ni: 10 mmol, Water: 33.6 cm³ (filling ratio: 70 %), Experimental time: 2 h.

corresponding metal catalyst, including Ni. Meanwhile, the selective formation of formic acid as shown in Fig.2 can be explained by the ionization of formic acid in alkaline solvent. It is supposed that generated formic acid has been ionized into HCOO⁻ during the treatment in alkaline solvent. HCOO⁻ ion is suggested not to decompose into other substrate. Thus it is supposed that the further reduction of formic acid into methane has been inhibited.

3.2. Reaction with Mixture of Fe and Fe₃O₄ Experiments using the mixture of Fe and magnetite, in place of Fe, have been carried out. In this section, initial ratio of Fe and Fe₃O₄ was described as Fe(0), which indicates the ratio of metallic iron in the experiment and was calculated as below.

$$Fe(0) = \frac{Fe}{Fe + \frac{1}{3}Fe_3O_4} \quad (2)$$

Fig.4 shows the yield of gaseous product with different Fe(0). The yield of the methane and hydrogen were affected by Fe(0). Therefore, it is supposed that Fe₃O₄ has no clear effect as a reductant. In contrast, trace methanol was detected in the liquid phase at the experiment with Fe(0) to be 50, 10 %. This generation may be due to some interaction between Fe₃O₄ and Fe or hydrogen. In

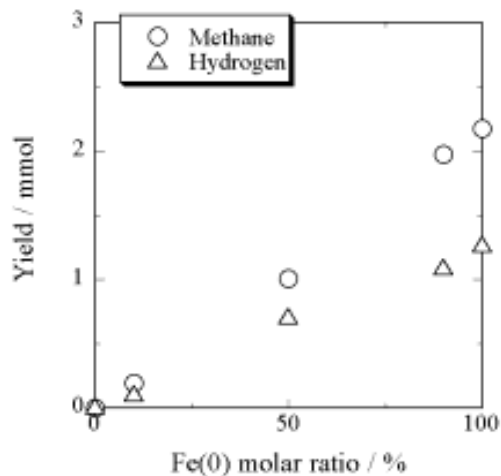


Fig.4 Yield of methane and hydrogen from CO₂ reduction with mixture of Fe and Fe₃O₄. CO₂: 6.4 mmol, Ni: 10 mmol, water: 33.6 cm³ (filling ratio: 70 %), total Fe atom: 100 mmol, Temperature: 300 °C, Experimental period: 1 h.

case that CO₂ is reduced completely, all CO₂ would be converted to methane. Though, methanol has been remained, after hydrothermal treatment with low Fe(0). From these results, it is supposed that Fe₃O₄ has acted as some suppressive factor on the effect of reductant to avoid further reduction. From this point of view, it is inferred that controlling the reductive effect of Fe is indispensable for the synthesis of oxygenated organic compounds, such as alcohol or aldehyde.

3.3. Effect of Water on the Organic Compounds Formation

To clarify the effect of water, CO₂ reduction with hydrogen and Ni powder has been studied in gaseous phase with different amount of water. In this section, no Fe compound was used. As an alternative reductant, hydrogen gas was injected before the CO₂ pressurization, in order for H₂/CO₂ ratio to be 3. Fig.5 shows the yield of hydrocarbon with different vapor saturation ratio. The main products were methane involved with ethane. Additionally, propane was also detected at the experiment with vapor saturation ratio to be 100%. No other organic compound was detected. As shown in Fig.5, vapor saturation ratio affected to the yield of methane and ethane. Especially, ethane was synthesized approximately proportionally to the vapor saturation ratio. Ethane was not detected in the liquid phase. Thus, it is supposed that water has some effect on the C-C

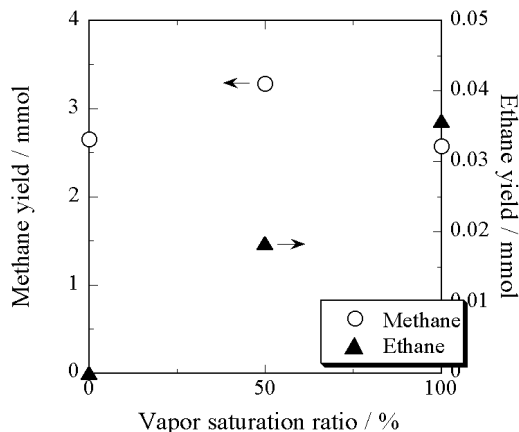
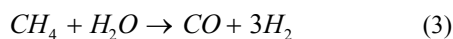


Fig.5 Effect of water content on the yield of organic compounds. Methane: circle(open), Ethane: triangle (close), CO₂: 6.4 mmol, H₂: 19.2 mmol, Ni: 10 mmol, Temperature: 300 °C, Experimental period: 1 h.

bond formation. Furthermore, 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 results, it can be presumed that the steam reforming of methane has been involved in the C-C bond formation. Steam reforming of methane is one of the partial oxidation reactions using water. Its whole reaction can be described as eq. (3).



This reaction (3) occurs over several kind of metallic catalysts including Ni. Jin et al. have reported [16] that an adsorbed carbon specie was generated on the catalyst surface as an intermediate, during the partial oxidation of methane over Ni/Al₂O₃ catalyst. In our study, it is assumed that similar carbon specie has been occurred, to be an intermediate for the C-C bond formation on the surface of catalyst with water.

4. Conclusions

The hydrothermal reduction of CO₂ has been investigated, and following fact has been clarified.

(1) The selective formation of formic acid has been achieved in basic solution. The reason for this selectivity is supposed that the formic acid has been stabilized in the form of HCOO⁻.

(2) By controlling the reductive effect of Fe, methanol has been formed.

(3) In the experiment in gaseous phase, the yield of ethane has been increased by increasing the water content. From this fact, it was supposed that the steam reforming reaction of methane has been occurred simultaneously with the reduction of CO₂.

References and Notes

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