Original Paper

Fundamental Study on the Reduction of Carbon Dioxide to Methanol/Ethanol Using a Cyclic Fenton Reaction

Fumiya YAMAGISHI¹, Chiharu TOKORO²*, Daisuke HARAGUCHI¹ and Toshiaki MURATA³

¹Graduate School of Creative Science and Engineering, Waseda University, Tokyo 169-8555, Japan
²Faculty of Science and Engineering, Waseda University, Tokyo 169-8555, Japan
³Mitsui Zosen Plant Engineering, Inc., Chiba 261-7130, Japan

Abstract
Conversion of carbon dioxide to useful chemicals or fuels has become an active area of research. However, most methods used in these studies need expensive or precious reagents, such as hydrogen or rare metals. The objective of this study is the reduction of carbon dioxide to organic compounds using a cyclic Fenton reaction that uses only inexpensive reagents. We achieved carbon dioxide reduction to methanol and ethanol using this reaction at ambient temperatures and pressures. The Fenton reaction was promoted by the repetitive addition of H₂O₂ and Fe(II) salts, resulting in the synthesis of methanol/ethanol and formic/acetic acids from carbon dioxide saturated water. In addition, it was found that H₂O₂ and Fe(II) in a molar ratio of 1 or 2 is optimal for the reaction as this increase the generation of ⋅OH.

The catalytic effects of magnetite, pyrite, sodium hypophosphite and copper sulfate were also investigated in the reduction of carbon dioxide to acetic acid. All reagents acted as a catalyst, and the concentration of TOC and acetic acid was increased. The highest concentration of acetic acid was achieved with the addition of copper sulfate. This enhanced the generation of H⋅ or H⁻ as Cu(II) forms more stable complexes with oxalic acid than Fe(II)/Fe(III), meaning more free Fe(II)/Fe(III) ions were present in the solution.

Key words: Fenton reaction, Carbon dioxide, Alcohol synthesis, Hydroxyl radical, Catalyst

1. Introduction
It is well known that carbon dioxide in the atmosphere is a major contributor to recent global warming and climate change¹. Therefore, conversion of CO₂ to useful chemicals or fuels is one of the most ambitious ways to control large-scale emissions of CO₂. The catalytic reduction of CO₂ with H₂ to form renewable energy sources, such as methanol, has received considerable attention. Tominaga and co-workers reported the production of Cl containing compounds by CO₂ hydrogenation using [Ru₃(CO₁₂)]/KI mixtures as catalysts⁶⁻⁷. Several researchers have developed other catalysts for CO₂ reduction⁸⁻⁹. Recently, Stephan and co-workers have developed the concept of “frustrated Lewis pairs (FLPs)”¹⁰⁻¹² and have applied these to the room temperature reduction of CO₂ to methanol. Hare and co-workers have also reported homogeneous conversion of CO₂ to methanol by non-metal catalysts¹³.

On the other hand, the Fenton reaction has been widely studied for the oxidization of many hazardous organic pollutants to form harmless compounds, such as CO₂, water and inorganic salts¹⁴⁻¹⁶. Fenton reagents consist of hydrogen peroxide (H₂O₂) and Fe(II) salts, which are inexpensive, safe, easy to handle and environmentally friendly. The Fenton chain reaction produces the hydroxyl radical (⋅OH), one of the most powerful oxidants, as shown in Table 1¹⁴⁻¹⁶. Reduction of Fe³⁺ to Fe²⁺ (the second equation in Table 1) is several orders of magnitude slower than the oxidation of...
Fe$^{2+}$ to Fe$^{3+}$ (the first equation in Table 1), and so this is the rate-limiting step.

We report herein the reduction of CO$_2$ to formic acid/acetate acid and methanol/ethanol by a cyclic Fenton reaction under ambient conditions. This study is inspired from our experimental detection of a small amount of short-chain fatty acid produced during the oxidative decomposition of persistent organic pollutants. The objective of this study was systematic investigation to identify the effect of the molar ratio of H$_2$O$_2$/Fe on the production of formic acid/acetate acid and methanol/ethanol. Moreover, we also investigated the effect of some catalysts, namely magnetite, sodium hypophosphite, copper sulfate and pyrite, on the CO$_2$ reduction in a cyclic Fenton reaction under the same conditions.

2. Experiments

2.1. Standards and reagents

All chemicals and solution used in this study were analytical grade and were purchased from Wako Chemicals, Inc., Japan. The 0.83 M of FeSO$_4$ solution was prepared from FeSO$_4$. 7H$_2$O. All experiments were conducted at 25°C.

2.2. Varied H$_2$O$_2$/Fe molar ratio experiments

First, 1 L of the initial solution was prepared from 1.7 mM H$_2$SO$_4$ under CO$_2$ gas injection at 40 mL/min, with an initial pH adjusted to 2.5 ± 0.1. Every 5 min, a small amount of 0.83 M FeSO$_4$ solution and 7.8 M NaOH were added alternately, and 2 mM H$_2$O$_2$ was added before each addition of FeSO$_4$. This alternate supply of H$_2$O$_2$, FeSO$_4$ and NaOH was repeated five times for each batch. The amount of FeSO$_4$ solution added to each batch was determined to achieve a target final molar ratio of H$_2$O$_2$: Fe(II) of 1 to 7. The amounts of H$_2$O$_2$, FeSO$_4$ and NaOH added are listed in Table 2. The concentration of formic/acetate acid, methanol and ethanol in the solutions were analyzed as described in the analysis section.

2.3. Catalytic experiments

As with the experiments varying the H$_2$O$_2$/Fe molar ratio, 1 L of initial solution was prepared from 1.7 mM H$_2$SO$_4$ under CO$_2$ gas injection at 40 mL/min, with an initial pH adjusted to 2.5±0.1. The catalyst was added to reach a concentration of the key element of 4 mmol, and the catalysts and their key elements are showed in the Table 3.

Every 5 min, a small amount of 0.83 M FeSO$_4$ solution and 7.8 M NaOH were added alternately, and 2 mM H$_2$O$_2$ was added before each addition of FeSO$_4$. This alternate supply of H$_2$O$_2$, FeSO$_4$ and NaOH was repeated five times for each batch. Using the results of varying the H$_2$O$_2$/Fe molar ratio, the H$_2$O$_2$/Fe molar ratio was fixed at 2, in which each addition of 0.83 M FeSO$_4$ solution was set to 1.2 mL and each addition of NaOH was 0.2 mL. After the experiments, the total organic carbon (TOC) and the concentration of formic/acetate acid and H$_2$O$_2$ in the solutions were analyzed as described in the analysis section.

2.4. Analysis methods

2.4.1. TOC analysis

TOC was measured using a TOC analyzer (Shimadzu TOC-V). Samples were pre-treated to pH < 2.0 with 2 M HCl to remove any inorganic carbon formed during the oxidation reaction. After that, TOC was analyzed immediately, without any storage.

It was also confirmed that CO and H$_2$ gases were not detected using a gas detector tube (Gastec No. 1LC (1–30 ppm) for CO and Gastec No.30 (0.5–2.0%) for H$_2$).

Table 1 Schemes and kinetic constants for the homogeneous Fenton chain reactions

| Reaction                                      | $k$ (M$^{-1}$s$^{-1}$) |
|-----------------------------------------------|----------------------|
| Fe$^{2+}$ + H$_2$O$_2$→Fe$^{3+}$ + ·OH + OH$^-$ | ≈70                  |
| Fe$^{3+}$ + H$_2$O$_2$→Fe$^{2+}$ + HO$_2$ + H$^+$ | 0.001–0.01           |
| ·OH + H$_2$O$_2$→HO$_2$ + H$_2$O              | 3.3 × 10$^7$         |
| ·OH + Fe$^{3+}$→Fe$^{2+}$ + OH$^-$           | 3.2 × 10$^7$         |
| Fe$^{2+}$ + HO$_2$→Fe$^{3+}$ + O$_2$H$^+$    | ≤2 × 10$^7$          |
| Fe$^{2+}$ + HO$_2$ + H$^+$→Fe$^{3+}$ + H$_2$O | 1.2 × 10$^5$         |
| 2HO$_2$→H$_2$O$_2$+O$_2$                      | 8.3 × 10$^5$         |

Table 2 Amounts of Fenton reagents added

| H$_2$O$_2$/Fe | H$_2$O$_2$ | Fe(II) | 25%NaOH |
|---------------|------------|--------|---------|
| Molar ratio   | Concentration | [mM]   | Additive | [mL]    |
|               |             |        |          |
| 1             | 10.0        | 2.0    |          |         |
| 2             | 5.00        | 1.0    |          |         |
| 3             | 3.33        | 0.67   |          |         |
| 4             | 10.0        | 2.50   | 0.50     |         |
| 5             | 2.00        | 0.40   |          |         |
| 6             | 1.67        | 0.33   |          |         |
| 7             | 1.43        | 0.29   |          |         |

Table 3 Types and concentrations of catalysts

| Catalyst          | Key element | Concentration of key element [mmol] |
|-------------------|-------------|-------------------------------------|
| Magnetite         | Fe(III)     |                                     |
| Sodium hypophosphite | P(I)      | 4.0                                 |
| Copper sulfate    | Cu(II)      |                                     |
| Pyrite            | Fe(II)      |                                     |
2.4.2. IC analysis

The concentrations of formic and acetic acid were analyzed using ion chromatography (IC, Dionex DX ICS-90) equipped with an Ion Pac AS25S column (150 mm long). Aqueous solutions of 3.0 mM Na$_2$CO$_3$ were used as eluent and maintained at a flow rate of 1.0 mL/min and operated in isocratic mode. The peaks were detected at 4.12 and 3.73 min (±0.2) of retention time for formic acid and acetic acid, respectively. For the chromatographic analysis, 10 ml samples were treated with Dionex Onguard II Ba/Ag/H to remove SO$_4^{2-}$ and Fe, and filtered through a 0.2 μm membrane filter (Advantec) before injecting the sample into the column.

2.4.3. GC-MS analysis

The concentrations of methanol and ethanol were determined by GC-MS analysis using an Agilent 6890GC-5973MSD system (Agilent Technologies, Wilmington, DE, U.S.A.) with an HP7694 headspace auto sampler (Agilent Technologies). 10 mL of sample was injected into a HP7694 headspace auto sampler (Agilent Technologies, Wilmington, DE, U.S.A.) with an Agilent 6890GC-5973MSD system (Agilent Technologies, Wilmington, DE, U.S.A.) with an HP7694 headspace auto sampler (Agilent Technologies). 10 mL of sample was injected into a 20 mL headspace vial. Static headspace equilibration was achieved at 60°C over 5 min while shaking the vial. Injection of 1.0 μL of headspace gas was performed using a heated (150°C) gastight syringe (10.0 μL) in split mode (1/50 split ratio) at 200°C (split/splitless inlet temperature). Separation was performed on a 60 m × 0.25 mm i.d. × 1.00 μm df Inertcap Aquatic column (GL Sciences). The carrier gas was helium at a constant flow rate of 1.0 mL/min. The column temperature program had a 2 min hold at 40°C; then an increase at 4.00°C/min to 80°C; then an increase at 25°C/min to 180°C.

The MS operating conditions were as follows; ion source and transfer line temperatures 150 and 230°C, respectively. The instrument was tuned in EI positive mode using perfluorotributylamine (FC-43) according to the manufacturer’s recommendations in order to achieve the maximum sensitivity. Parameters such as automatic gain control (AGC) and the multiplier (1588V, 53667 gain) were set by automatic tuning. The electron energy was 69.9 eV and the emission current was 34.6 A.

2.4.4. H$_2$O$_2$ analysis

The concentration of H$_2$O$_2$ was determined with an absorptiometer (Hach DR 5000) using the Mutarotase-GOD method. 0.02 mL of the samples were collected every 5 min (before adding FeSO$_4$ and NaOH), and added to 3.0 mL of Glucose C2. After reaction for 15 min at room temperature, these samples were measured by absorptiometer at a wavelength of 505 nm. When sodium hypophosphite was used as catalyst, H$_2$O$_2$ could not be measured because of interference from the phosphorus.

3. Results and Discussion

3.1. Relation between H$_2$O$_2$/Fe final molar ratio and generation of organic compounds

Figure 1 shows that CH$_3$OH and C$_2$H$_5$OH were detected along with small amounts of formic and acetic acids. We believe this is the first process involving the reduction of CO$_2$ to CH$_3$OH and C$_2$H$_5$OH using only Fe(II) salts and H$_2$O$_2$ under ambient conditions. As shown in Figure 1, the highest concentrations of CH$_3$OH and C$_2$H$_5$OH were achieved when the final molar ratios of H$_2$O$_2$ and FeSO$_4$ were 1 or 2. Moreover, oxalic acid was also detected by IC analysis in H$_2$O$_2$/Fe final molar ratio of 1 or 2, but the quantity could not be determined because of the interference by the SO$_4^{2-}$ peak. This can be explained stoichiometrically from the reactions of ·OH generation and Fe$^{3+}$ reduction by H$_2$O$_2$ (the first and second equations in Table 1). That is, in an ideal situation, equimolar amounts of Fe$^{2+}$ and H$_2$O$_2$ react to form Fe$^{3+}$ and ·OH and any remaining Fe$^{3+}$ and H$_2$O$_2$ react to form Fe$^{2+}$.

Although the detailed mechanism of this process is not well understood, the reduction pathway from CO$_2$ to CH$_3$OH can be explained by assuming the presence of atomic hydrogen (H·) in the solution. This H· would be generated from H$_2$O oxidation by ·OH attack. It is known that H· can act as both an oxidant for Fe$^{2+}$ ions and reductant for Fe$^{3+}$ ions. When Fe$^{2+}$ ions are oxidized by H·, a hydride ion (H$^-$) is produced as follows:

![Fig. 1 Relationship between methanol/ethanol and formic/acetic acid generation and the final molar ratio of H$_2$O$_2$/Fe](image-url)
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\[ \text{Fe}^{2+} + \text{H} \rightarrow \text{Fe}^{3+} + \text{H}^+ \]  
\[ \text{Fe}^{3+} + \text{H} \rightarrow \text{Fe}^{2+} + \text{H}^+ \]  

Lundstöm and co-workers reported that the rate constants for reactions (1) and (2) are $1.3 \times 10^7$ and $1.0 \times 10^8 \text{M}^{-1}\text{s}^{-1}$, respectively. These rates are more rapid than the rate of $\cdot \text{OH}$ generation shown in Table 1.

Although, the CO$_2$ molecule in the solution as a whole is non-polar, the oxygen atoms are partially negatively charged and the carbon atom is partially positively charged, because the electronegativity of oxygen (3.5) is larger than that of carbon (2.5). The fact that HCOOH was detected suggests that $\text{H}^+$ acted as an electrophile to the partial negative oxygen atom in the CO$_2$ molecule and $\text{H}^+$ acted as a nucleophile to the partial positive carbon atom.

\[ \text{CO}_2 + \text{H}^+ + \text{H}^+ \rightarrow \text{HCOOH} \] \hspace{1cm} (3)

An additional reaction between the carbon-oxygen double bond in HCOOH and the H$^+$/H$^-$ ions would, in a similar way, generate formaldehyde.

\[ \text{HCOOH} + \text{H}^+ + \text{H}^+ \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \] \hspace{1cm} (4)

Because CH$_3$OH was detected in this study, the carbon-oxygen double bond in CH$_2$O must have again reacted with H$^+$ and H$^-$ ions.

\[ \text{CH}_2\text{O} + \text{H}^+ + \text{H}^+ \rightarrow \text{CH}_3\text{OH} \] \hspace{1cm} (5)

This conversion from HCOOH to CH$_3$OH must have been more rapid than from CO$_2$ to HCOOH because only a small amount of HCOOH was detected, as shown in Figure 1.

Moreover, the further reaction from CH$_3$OH to C$_2$H$_5$OH can be explained by assuming the presence of the methyl anion (CH$_3^-$) in the solution. CH$_3^-$ is known theoretically to be a strong nucleophile\(^{20,21}\). As CH$_3$COOH was detected in this study, this suggests that the CH$_3^-$ acted as a nucleophile towards the partial positively charged carbon atom in CO$_2$, as seen from the HCOOH generation by H$^+$.

\[ \text{CO}_2 + \text{CH}_3^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} \] \hspace{1cm} (6)

The CH$_3$COOH would convert to C$_2$H$_5$OH via acetaldehyde, as with the HCOOH conversion to CH$_3$OH.

\[ \text{CH}_3\text{COOH} + \text{H}^- + \text{H}^+ \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \] \hspace{1cm} (7)

\[ \text{CH}_3\text{CHO} + \text{H}^- + \text{H}^+ \rightarrow \text{C}_2\text{H}_5\text{OH} \] \hspace{1cm} (8)

There are likely to be other types of reaction pathway in addition to these, because oxalic acid and the other intermediates or byproducts could have been present in solution. The detailed mechanism for CO$_2$ reduction to CH$_3$OH and C$_2$H$_5$OH via this process will be the subject of future work.

### 3.2. The effect of the catalyst

Figure 2 shows a comparison between several catalysts that were used to promoting the CO$_2$ reduction to formic/acetic acid. The concentration of TOC is also shown in Figure 2. In this figure, the concentration of formic/acetic acid is represented as carbon base, so that the concentration of formic/acetic acid can be compared with TOC directly.

As shown in Figure 2, the total carbon concentration of formic/acetic acid is smaller than that of TOC, which suggests other organic compounds, such as methanol/ethanol and oxalic acid and formaldehyde/acetaldehyde, were produced in the cyclic Fenton reaction. In addition, the concentration of formic acid was considerably smaller than the concentration of acetic acid or TOC, which suggests the generation rate of formic acid by equation (3), was slower than the decomposition rate of formic acid in equation (4).

Furthermore, the concentration of acetic acid and TOC increased when any catalyst was added. The highest concentration of acetic acid and TOC was achieved with copper sulfate. To discuss the mechanism of the CO$_2$ reduction involving a catalyst, the oxidation-reduction potentials (ORP) and the concentration of H$_2$O$_2$ were measured, and the results are shown in Figure 3 and 4. Figure 3 shows sodium hypophosphite enhanced the reducing conditions of the solution. These reducing conditions would promote the reduction of Fe(III)
as shown in the second equation of Table 1 and resulted in the promotion of CO$_2$ reduction. On the other hand, the other reagents made the conditions slightly oxidizing. This means all catalysts except for sodium hypophosphite promoted the oxidation of Fe(II) as shown in equation (1). In this case, generation of ⋅OH would be promoted at the beginning of the cyclic Fenton reaction, followed by the generation of H⋅ and CO$_2$ reduction.

As shown Figure 4, the amount of H$_2$O$_2$ consumption was higher with catalysts than that without catalyst. The consumption of H$_2$O$_2$ after each addition of FeSO$_4$ was higher when magnetite or pyrite was used as the catalyst. This result suggests the increase in both the oxidation of Fe(II) and reduction of Fe(III) as shown in the first or second equation of Table 1, which agrees with the result of ORP in Figure 3.

Although copper sulfate was the most effective reagent for CO$_2$ reduction, the amount of H$_2$O$_2$ consumed was no higher than the other catalysts. These results suggest that copper sulfate did not merely promote the Fe(II) oxidation. Oxalic acid is often formed during the Fenton reaction and can inhibit the oxidative decomposition of persistent organic pollutants. In general, Cu(II) forms more stable complexes with oxalic acid than Fe(II) or Fe(III) as shown in Table 4. This means Cu(II) preferentially complexes to the oxalic acid and this increases the amount of free Fe(II)/Fe(III) ions in solution. Promotion of CO$_2$ reduction by copper sulfate would be obtained from increase of free Fe(II)/Fe(III) ions in the solution and hence the consequent promotion of formation of H · or H$^{-}$ shown in equations (1) and (2).

4. Conclusions

The reduction of CO$_2$ to methanol/ethanol by a cyclic Fenton reaction was examined to determine the optimum H$_2$O$_2$/Fe molar ratio and catalyst. We confirmed methanol/ethanol and formic/acetic acid were produced during the cyclic Fenton reaction. The production of methanol/ethanol and formic/acetic acid was highest when final molar ratios of H$_2$O$_2$ to Fe(II) were 1 or 2, which was in agreement with the theoretical value from the stoichiometric analysis.

When magnetite, pyrite, sodium hypophosphite or copper sulfate were used as the catalyst, the production of TOC and acetic acid was increased. In the case of magnetite or pyrite, the generation of ⋅OH was enhanced by the promotion of Fe(II) oxidation, followed by the promotion of CO$_2$ reduction. For sodium hypophosphite, ⋅OH was enhanced by the promotion of Fe(III) reduction, followed by the promotion of CO$_2$ reduction. Finally, copper sulfate enhanced the generation of H or H$^{-}$ by increasing the free Fe(II)/Fe(III) ions in the solution by reducing the oxalic acid concentration and thus promoting the CO$_2$ reduction.

Table 4 Complex formation constants of Cu(II), Fe(II) or Fe(III) with oxalic acid

|        | log β₁ | log β₂ | log β₃ | t [°C] |
|--------|--------|--------|--------|--------|
| Cu$^{2+}$ | 4.84   | 9.21   | —      | 25     |
| Fe$^{2+}$ | 3.05   | 5.15   | —      | 25     |
| Fe$^{3+}$ | 7.53   | 13.64  | 18.49  | 25     |
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