Partial Oxidation of Methane by Fenton Reaction 
under Hydrothermal Environment

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Methanol is an important industrial material for the production of medicines, fuels, and resins. Methanol is generally synthesized under catalyst by reacting CO and H2 through steam reforming of methane. This process is, however, energy consuming. Hence, a direct methanol synthesis method, which is less energy consuming, should be developed. The authors conducted flow-type partial oxidation of methane using the Fenton reaction under hydrothermal conditions for the direct synthesis of methanol from methane. Parameter variation included reaction temperatures of 100-250 °C, reaction times of 2-31 s, and initial H2O2/CH4 molar flow rate ratios of 0.5-2.0. The methane conversion using the Fenton reaction was higher than that of the catalyst-free conversion at temperatures of less than 200 °C. The methane conversion reached the highest value of 6.04% at T = 200 °C, τ = 31 s, and H2O2/CH4 = 2.0. Hence, it can be concluded that the Fenton reaction prompted the formation of hydroxyl radicals, reactive species. However, the methane conversion by the Fenton reaction decreased rapidly at T = 250 °C, resulting in a lower conversion value than that of the catalyst-free reaction.

Key Words
Methane hydrothermal oxidation, Fenton reaction, methanol formation

1. Introduction

Methanol is an important industrial material for the production of medicines, fuels, and resins. It is generally synthesized using catalysts by reacting CO and H2 through steam reforming of methane. This process, however, requires multistep reactions and high temperatures, resulting in large energy consumption. Therefore, less-energy-consuming processes such as direct methanol production through partial oxidation of methane is a promising technology.

Recently, researchers applied the Fenton reaction for methane oxidation. Eqs. (1) and (2) define the Fenton reaction.

\[
\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{+} + \cdot\text{OOH} + \text{H}^+ \quad (1)
\]

For example, Savage et al. examined a batch-type hydrothermal oxidation of methane. They used O2 as an oxidant and conducted the reaction between 349 and 448 °C for 180-540 s. They achieved methane conversion rates of 0.01-6.0%, where methanol yields ranged from 0.01% to 0.69%. In addition, Sato et al. examined a flow-type hydrothermal oxidation of methane. They used H2O2 as an oxidant and conducted the reaction at 400 °C for 29-109 s. This group achieved methane conversion rates of 0.51% to 3.30%, where the methanol yields ranged from 0.17% to 0.75%.

Other researchers have applied the Fenton reaction for methane oxidation. Eqs. (1) and (2) define the Fenton reaction.

\[
\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{+} + \cdot\text{OOH} + \text{H}^+ \quad (1)
\]

\[
\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{+} + \cdot\text{OOH} + \text{H}^+ \quad (2)
\]
Cu^+ + H_2O_2 → Cu^{2+} + ·OH + OH \hspace{1cm} (2)

The Fenton reaction generates hydroxyl radicals, the strongest oxidant of all reactive oxygen species; copper ions are the catalyst and H_2O_2 is a reactant in this reaction. Wei et al. \cite{wei11} applied the Fenton reaction for methane oxidation using a bubble tower reaction apparatus at room temperature. On the other hand, Kometani et al. \cite{kometani12} reported that Eq. (1) normally becomes a rate-determining step and the Fenton reaction is rather slow at ambient conditions because Cu^{2+} is more stable than Cu^+ under these conditions. Under hydrothermal conditions, Cu^{2+} becomes relatively unstable, resulting in an acceleration of the Fenton reaction since the hydration structure of ions and physical properties (dielectric constant and ionic product) of water change. In fact, chlorophenol oxidation tests of the Fenton reaction under hydrothermal conditions \cite{kometani13} showed higher reactivity. There are, however, few reports on the partial oxidation of methane using the Fenton reaction under hydrothermal conditions.

In this study, we conducted flow-type hydrothermal partial oxidation of methane by the Fenton reaction. The parameter variations for this investigation included reaction temperatures of 100-250 °C, reaction times of 2-31 s, and initial H_2O_2/CH_4 molar flow rate ratios of 0.5-2.0.

2. Experimental

2.1 Procedure

Fig. 1 shows the flow-type apparatus used in this work. Methane (99.5% CH_4, 0.42% CO_2 Otaki Industries) was enclosed in a methane feeding vessel (0.98L Toyo Koatsu) with a front pressure regulator (YR5062 Yamato Industries). Distilled water was supplied using high-pressure metering pump P4 (NP-KX-540 Nihon Seimitsu Kagaku) to the bottom of the methane-feeding vessel. Distilled water displaced the enclosed methane, which results in constant feeding of highly pressurized methane. Furthermore, distilled water was also supplied using metering pump P3 (LC-10ADvp Shimadzu) and added to the methane gas stream. Then, 35 vol% H_2O_2 aq. solution and anhydrous copper sulfate were diluted with distilled water. After that, the two solutions were supplied using metering pumps P1 and P2, respectively.

The liquid, which includes methane and water, was heated with a microheater (HM-30 Yamari Industries). H_2O_2 aq. was also heated with a microheater (HM-30 Yamari Industries). Preheating tubes for these fluids were SUS316 (1.76 mm i.d.). Preheating temperatures of the liquid, which includes methane and water, were controlled between 200 and 500 °C, depending on the subsequent reaction temperature. The preheating temperature of H_2O_2 aq. was fixed at 120 °C to prevent thermal decomposition. The supplying tube for CuSO_4 aq. was HasteloyC276 (1.76 mm i.d.). CuSO_4 aq. was not heated since the solubility of CuSO_4 in water decreases rapidly at higher temperatures, which leads to CuSO_4 deposition. Each supplying fluid was mixed by a crossing at the reactor inlet.

The deposition of Cu(OH)_2 and CuO and flow channel plugging are some of the problems faced when flow-type reactors are used to conduct the Fenton reaction. Therefore, we installed a vertical reactor and a solid separator at the reactor outlet. The reactor was heated with a microheater (HM-30 Yamari Industries). We measured the surface
temperature of the reactor both at the inlet and outlet. The heater regulated the temperature difference between these two points within 10 °C. The inner temperature of the cell at the outlet was measured and controlled within 5 °C of the target temperatures.

At the reactor outlet, the effluent was cooled down with a water-cooled double-pipe heat exchanger. The reaction pressure was controlled using a back pressure regulator (TESCOM). The effluent was separated into gas and liquid streams in a separator. The gas flow rate was measured by collecting the effluent gas with a gas sampling pack at a fixed time.

2.2 Analytical Chemistry

Hydrogen, oxygen, methane, and CO were analyzed with a GC-TCD (GC-8A Shimadzu, column: Molecular Sieve, carrier gas: helium). CO2 was analyzed using a GC-TCD (GC-8A Shimadzu, column: Porapack Q, carrier gas: helium).

The total organic carbon contents (TOC) were analyzed with a TOC analyzer (TOC-V CPH Shimadzu). The methanol product was analyzed with a GC-FID (GC-14B Shimadzu, column: TC-BOND Q, carrier gas: helium). Formic acid was analyzed using an anion chromatograph (nonsupresser, column: IC N-424, detector: CD20 DIONEX). The Cu2+ concentration of the effluent liquid was analyzed using UV-vis spectrometry (UV-1850 Shimadzu).

In addition, it was assumed that the components of the effluent liquid were methanol, formaldehyde, and formic acid, which are the products of partial oxidation of methane.

Therefore, the formaldehyde yield was calculated as follows:

\[
\text{formaldehyde yield (\%)} = \text{TOC yield (\%)} - \text{methanol yield (\%)} - \text{formic acid yield (\%)}
\]

2.3 Experimental Conditions.

Parameter variations included reaction temperatures of 100-250 °C, reaction times of 2-31 s, and initial H2O2/CH4 molar flow rate ratios of 0.5-2.0. We fixed the reaction pressure to 25 MPa, inlet methane concentration to 1.0 wt%, and CuSO4/CH4 molar flow rate ratio to 0.01.

The reaction times \( \tau \) were varied by arranging the length of the reactor and flow rate of the pumps. The reaction times were defined as:

\[
\tau = \frac{V_R}{G_w + \left( \frac{G_{\text{CH}_4}}{\rho_{\text{CH}_4}} + \frac{G_{\text{H}_2\text{O}_2}}{\rho_{\text{H}_2\text{O}_2}} + \frac{G_{\text{CuSO}_4}}{\rho_{\text{CuSO}_4}} \right)}
\]

where \( V_R \) is the volume of reactor (cm³), \( G \) is the mass flow rate (g/s) of each material, and \( \rho \) is the density (g/cm³) of each material at the given conditions. The density of H2O2, aq. and CuSO4, aq. was approximated with the density of water. Each \( \rho \) was acquired from Ref. (14).

The following equations define the methane conversion, product yield, product selectivity, and carbon balance:

\[
\text{Methane conversion, } \chi_{\text{CH}_4} (\%) = \frac{F_1 + F_4 + F_5 + F_6}{F_1} \times 100 \quad (4)
\]

\[
\text{Yield, } Y_i (\%) = \frac{F_i}{F_1} \times 100 \quad (5)
\]

\[
\text{Selectivity, } S_i (\%) = \frac{Y_i}{\chi_{\text{CH}_4}} \times 100 \quad (6)
\]

\[
\text{Carbon balance (\%) = } \frac{F_2 + F_3 + F_4 + F_5}{F_1} \times 100 \quad (7)
\]

In Eqs. (4)-(7), \( F_i \) is the flow rate of the reactant or product in mol/s. \( F_6 \) was calculated by subtracting molar flow rate equal to 0.42 mol% of CO2 existing in the CH4 cylinder from molar flow rate of CO2 measured actually.

3. Results and Discussion

3.1 Temperature and methane solubility

Fig. 2 shows the methane solubility in water at 25 MPa as a function of temperature; the data displayed in Fig. 2 has been sourced from Ref. (15). The methane solubility in Fig. 2 ranges from 0.218 to 0.546 wt% at temperatures of 100-250 °C. The inlet methane concentration in this work was set to 1.0 wt%, which is higher than the saturation solubility of methane in all experiments. This means that methane and water enter the reactor in a gas-liquid multiphase flow.

Hydroxyl radicals, the reactive species of our study, may be formed in the aqueous phase. Hydroxyl radicals are unstable with a life span of less than 1 ms. This indicates that hydroxyl radicals do not transfer to the gas phase and oxidize gaseous methane. Therefore, it can be assumed that methane dissolved in the aqueous phase of the gas-liquid multiphase is mainly oxidized by hydroxyl radicals. This implies that the methane concentration associated with the
reaction is the concentration in the aqueous phase, which is near the saturation solubility under the given conditions.

3.2 Products of hydrothermal partial oxidation of methane using the Fenton reaction.

Table 1 lists the experimental conditions and results. The methane conversion rate ranged from 0.08% to 6.04% and the methanol yield ranged from 0.01% to 0.20%. The carbon balance was between 81.8% and 119.5%. The major reaction products were methanol, formic acid, and CO₂; CO and hydrogen by-products were negligible in all experiments.

Most researchers 3) ~ 7) examined catalyst-free hydrothermal oxidation of methane. In these studies, formic acid has never been detected as a product. On the other hand, experiments of methane oxidation using the Fenton reaction 2) 8) ~ 11) detected formic acid as a product. Besides, Hammond et al. 2) proposed a reaction model, in which hydroxyl radicals oxidized methane, resulting in the formation of formic acid. This suggests that methane oxidation by the Fenton reaction and hydroxyl radicals generates formic acid. In this work, the formation of formic acid was confirmed. Thus, it can be concluded that hydroxyl radicals contributed to methane oxidation through the Fenton reaction, so that methane traced different reaction passes from catalyst-free hydrothermal oxidation.

3.3 Difference of methane conversion between catalyst-free and Fenton reactions.

Fig. 3 shows the dependence of the methane conversion on reaction temperatures when using a catalyst-free or the Fenton reaction. The results of the catalyst-free experiment, where no CuSO₄ aq. was supplied, are acquired

| Reactor | Temp (°C) | Time (s) | H₂O₂/CH₄ (molar ratio) | CuSO₄/CH₄ (molar ratio) | X(CH₄) (%) | Yield (%) | CH₃OH | HCOOH | HCHO | CO₂ | CH₃OH | HCOOH | HCHO | CO₂ | Carbon Balance (%) |
|---------|-----------|----------|------------------------|------------------------|------------|-----------|-------|-------|------|-----|-------|-------|------|-----|------------------|
| 100     | 31        | 0.5      | 0.01                   | 0.60                   | 0.06       | 0.04      | 0.45  | 0.05  |
| 150     | 31        | 0.5      | 0.01                   | 1.83                   | 0.17       | 0.37      | 1.12  | 0.16  |
| 200     | 31        | 0.5      | 0.01                   | 1.77                   | 0.03       | 0.41      | 0.59  | 0.75  |
| 250     | 31        | 0.5      | 0.01                   | 0.85                   | 0.03       | 0.25      | 0.25  | 0.51  |
| 100     | 31        | 1.0      | 0.01                   | 0.63                   | 0.06       | 0.06      | 0.47  | 0.04  |
| 150     | 31        | 1.0      | 0.01                   | 2.29                   | 0.20       | 0.51      | 1.39  | 0.19  |
| 200     | 31        | 1.0      | 0.01                   | 2.32                   | 0.05       | 0.80      | 0.53  | 0.95  |
| 250     | 31        | 1.0      | 0.01                   | 0.90                   | 0.02       | 0.06      | 0.17  | 0.66  |
| 100     | 31        | 2.0      | 0.01                   | 0.35                   | 0.04       | 0.00      | 0.29  | 0.03  |
| 150     | 31        | 2.0      | 0.01                   | 4.48                   | 0.07       | 1.56      | 1.15  | 1.70  |
| 200     | 31        | 2.0      | 0.01                   | 6.04                   | 0.05       | 1.62      | 0.61  | 3.75  |
| 250     | 31        | 2.0      | 0.01                   | 0.25                   | 0.03       | 0.02      | 0.03  | 0.18  |
| 100     | 8         | 1.0      | 0.01                   | 0.19                   | 0.07       | 0.02      | 0.30  | 0.00  |
| 150     | 8         | 1.0      | 0.01                   | 1.92                   | 0.19       | 0.44      | 1.09  | 0.20  |
| 200     | 8         | 1.0      | 0.01                   | 2.12                   | 0.04       | 0.62      | 0.75  | 0.70  |
| 250     | 8         | 1.0      | 0.01                   | 0.81                   | 0.02       | 0.01      | 0.36  | 0.62  |
| 100     | 2         | 1.0      | 0.01                   | 0.08                   | 0.06       | 0.00      | 0.02  | 0.00  |
| 150     | 2         | 1.0      | 0.01                   | 0.91                   | 0.11       | 0.08      | 0.70  | 0.01  |
| 200     | 2         | 1.0      | 0.01                   | 1.49                   | 0.05       | 0.55      | 0.50  | 0.38  |
| 250     | 2         | 1.0      | 0.01                   | 0.82                   | 0.01       | 0.11      | 0.27  | 0.43  |
| 150     | 8         | 0.5      | 0.01                   | 1.11                   | 0.11       | 0.13      | 0.76  | 0.10  |
| 150     | 8         | 2.0      | 0.01                   | 2.26                   | 0.16       | 0.59      | 1.02  | 0.49  |
| 150     | 2         | 0.5      | 0.01                   | 0.80                   | 0.11       | 0.04      | 0.64  | 0.00  |
| 150     | 2         | 2.0      | 0.01                   | 1.15                   | 0.10       | 0.15      | 0.78  | 0.12  |
from Ref. (16). Under the catalyst-free conditions, the methane conversion rate simply increased with the reaction temperature. Three reasons were considered responsible for this increasing trend. First, the increase of methane reactivity with increasing temperature. Second, increase in methane solubility with increasing temperature. Lastly, the increment of the amount of hydroxyl radicals formed via H2O2 thermal decomposition at higher temperatures. Eq. (8) depicts the thermal decomposition of H2O2 \(^{17}\).

\[
\text{H}_2\text{O}_2 \rightarrow 2\cdot\text{OH} \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2 \quad (8)
\]

A rapid increase in temperature at the reactor prompts the formation of strong oxidants, hydroxyl radicals. The amount of radicals formed increases with increasing temperature, which contributes to a higher methane conversion rate. Ref. (16) reported these considerations for methane oxidation under thermal decomposition of H2O2.

When the Fenton reaction was utilized, different results were obtained. The methane conversion rates observed are higher than those under catalyst-free conditions at temperatures of less than 200°C. Not only the thermal decomposition of H2O2 but also the Fenton reaction probably generated hydroxyl radicals. However, methane conversion rates decreased rapidly at T = 250°C, resulting in a lower conversion value than that of the catalyst-free reaction. The authors assume that the cause of this behavior is that the Fenton reaction at higher temperatures results in reduced generation of hydroxyl radicals. Murcia-Lopez et al. \(^{18}\) reported the initial methane oxidation using the Fenton reaction as displayed in Eq. (9).

\[
\text{CH}_4 + \cdot\text{OH} \rightarrow \text{CH}_3\cdot + \text{H}_2\text{O} \quad (9)
\]

In this present work, Eq. (9) is regarded as the initial reaction. Thus, lower amounts of hydroxyl radicals could lead to lower methane conversion rates. In addition, formic acid selectivity, as displayed in Table 1, shows lower values at T = 250°C. As stated above, hydroxyl radicals oxidize methane, which results in the formation of formic acid. This means that lower formic acid selectivity at T = 250°C implies lower amounts of hydroxyl radicals. Therefore, we concluded that hydroxyl radical concentration decreased at higher temperatures, decreasing the methane conversion.

Furthermore, two factors that reduce hydroxyl radicals at higher temperatures should be noted. First, the suppression of the Fenton reaction caused by the loss of copper ions occurs. Generally, heating of CuSO4 aq. solutions generates Cu(OH)\(_2\), through hydrolysis. More heating then generates CuO through a dehydrated condensation reaction. We confirmed such phenomena by measuring both inlet and outlet Cu\(^{2+}\) concentrations in the reactor. Fig. 4 shows outlet Cu\(^{2+}\) concentration/inlet Cu\(^{2+}\) concentration as a function of reaction temperature. This result clearly indicates that the ratio of the loss of Cu\(^{2+}\) in the reactor increased with increasing temperature. This also shows the loss of catalytic activity of Cu\(^{2+}\) under conditions of higher temperatures, which would result in the suppression of the Fenton reaction. However, it should be noted that this is not the only factor that causes the decrease of hydroxyl radicals at higher temperatures.

The second factor is that formed CuO might capture the hydroxyl radicals. As stated above, the heating of CuSO4 aq. solutions generally forms Cu(OH)\(_2\) or CuO. Considering this general theory and the trend depicted in Fig. 4, it is expected that the amount of formed CuO increases at higher temperatures. In addition, Hammond et al. \(^{2}\) implied based on electron paramagnetic resonance and experimental results that CuO could capture hydroxyl radicals. Hence, it can be inferred that the effect of capturing the hydroxyl radicals was elevated at higher temperatures, which results in lower methane conversion rates. Consequently, two factors that reduce methane conversion might compete with three factors that increase it, resulting in a maximum methane conversion rate between 150 and 200°C.

### 3.4 Effect of temperature, reaction time, and H\(_2\)O\(_2\)/CH\(_4\) ratio for methane conversion.

Fig. 5 shows the variation of methane conversion vs. reaction time at each H\(_2\)O\(_2\)/CH\(_4\) ratio. Methane conversion exhibits its maximum point between 150 and 200°C even at different H\(_2\)O\(_2\)/CH\(_4\) ratios, showing the higher values in higher H\(_2\)O\(_2\)/CH\(_4\) ratios. As a result, the highest conversion rate of 6.04% was obtained at T = 200°C and H\(_2\)O\(_2\)/CH\(_4\) = 2.0. We can assume that the formed amount of hydroxyl radicals via the Fenton reaction and thermal decomposition of H2O2 became greater with increasing H\(_2\)O\(_2\)/CH\(_4\) ratios.

Fig. 6 shows the variation of methane conversion vs.
reaction time and temperature. At $T = 100^\circ C$, methane oxidation proceeded even at $\tau = 31$ s. In the case of $T = 150$-200$^\circ C$, methane oxidation appears to be almost completed at $\tau = 31$ s. At $T = 250^\circ C$, an increase in methane conversion ceased after $\tau = 2$ s. This indicates that the Fenton reaction is completed more quickly with increasing temperature.

3.5 Effect of temperature, reaction time, and H$_2$O$_2$/CH$_4$ ratio for methanol yield.

Fig. 7 shows the variation of methanol yield vs. reaction temperature at each H$_2$O$_2$/CH$_4$ ratio. Methanol yield reached the highest value at $T = 150^\circ C$ regardless of the H$_2$O$_2$/CH$_4$ ratio. This result indicates that $T = 150^\circ C$ is the optimal temperature for the partial oxidation of methane and formation of methanol.

Fig. 8 displays the variation of methanol yield vs. reaction time at each H$_2$O$_2$/CH$_4$ ratio. When H$_2$O$_2$/CH$_4$ was 2.0, the methanol yield reached a maximum at $\tau = 8$ s. Hence, it can be inferred that excess H$_2$O$_2$ not only promotes methane oxidation but also causes undesirable excessive oxidation of methanol. When H$_2$O$_2$/CH$_4$ was less than 1.0, the methanol yield simply increased with increasing $\tau$, reaching the highest values at $\tau = 31$ s. This result indicates that the combination of H$_2$O$_2$/CH$_4$ ratio of less than 1.0 and relatively long reaction times is effective for the formation of methanol.

4. Conclusion

This study examined the flow-type hydrothermal partial oxidation of methane using the Fenton reaction. The parameter variation for this study included reaction temperatures of 100-250$^\circ C$, reaction times of 2-31 s, and initial H$_2$O$_2$/CH$_4$ molar flow rate ratios of 0.5-2.0. As a result, methane conversion rates ranged from 0.08% to 6.04% and methanol yields ranged from 0.01% to 0.20%.

Methane conversions using the Fenton reaction surpassed the values of catalyst-free reactions at temperatures of less than 200$^\circ C$. This is probably because the Fenton reaction increased the amount of formed hydroxyl radicals. However, the methane conversion rate decreased rapidly at 250$^\circ C$, resulting in a lower value than that achieved with the catalyst-free reaction. Two factors may be responsible for this behavior. First, the suppression of the Fenton reaction by the loss of copper ions with
increasing temperature, and second, the capturing of hydroxyl radicals by increasingly formed CuO.

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