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Formic Acid Synthesis via Biomimetic Autoxidation of Carbon Dioxide and Methane (Biogas and Flare Gas) in Low-Temperature for Carbon Capture and Hydrogen Fuel Carrier Applications

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Abstract. The transition from fossil fuels to renewable energy sources and the utilization of CO_2 through CCU are crucial steps toward energy sustainability. Biogas, a renewable energy source primarily composed of CH_4 and CO_2, holds significant potential in this context. On the other hand, gas flaring continues to contribute to greenhouse gas emissions, yet it also presents an opportunity for utilization. Another challenge in utilizing gaseous fuels lies in their storage and transportation over long distances. This study aims to develop a liquid-phase autoxidation for CH_4 and CO_2 to produce formic acid using synthetic catalysts that mimic the function of the MMO enzyme. Formic acid can act as a future fuel solution due to its role as a liquid hydrogen carrier. In this exploratory study, four types of catalysts based on iron and copper were synthesized. These catalysts were tested in the autoxidation reaction of CH_4 and CO_2 in an ethanol solution at 65°C, followed by condensation at 20°C to obtain a distillate as the product. The results of this study indicate that the Cu,Fe-acetate catalyst exhibits the highest catalytic activity, achieving 6.81 mol HCOOH/kg catalyst·hour with a methane conversion to formic acid of 8.61%. Adding Cu to the Fe-Acetate catalyst increased its catalytic activity by 29.76%. Conversely, adding Cu to Fe-Format decreased catalytic activity by 36.54%.

Keywords: Autooxidation, Biogas, Carbon Capture, Formic Acid, Gas Flaring, Hydrogen Carrier, Renewable Energy

INTRODUCTION

The ongoing decline in global oil production, coupled with rising energy demand, has significantly impacted energy security, leading to increased dependence on fossil fuel imports and widening trade balance deficits. Consequently, there is a growing urgency to reduce reliance on fossil fuels by adopting alternative energy sources. New and Renewable Energy (NRE) holds considerable potential. However, its adoption

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remains limited, primarily due to energy storage and transportation challenges, particularly for locations far from energy production sites. One promising source of bioenergy is biogas, a renewable gas primarily composed of methane (CH_4) and carbon dioxide (CO_2). During the transitional phase toward substituting fossil fuels with renewable energy, gas flaring, which predominantly consists of methane and carbon dioxide, should also be harnessed to support the Net Zero Flaring 2030 initiative. The proposed conversion of gaseous fuel into liquid fuel is in the form of formic acid. Formic acid, when in contact with catalysts (Pd > Pt > Au > Ag), decomposes to produce hydrogen and carbon dioxide (CO_2) at approximately room temperature. Formic acid is also known as a Liquid Organic Hydrogen Carrier (LOHC) (Kawanami *et al*., 2017).

In nature, methanotrophic bacteria provide an interesting model for biogas conversion. These bacteria produce the enzyme Methane Monooxygenase (MMO), which acts as a catalyst to oxidize methane into methanol or formic acid. Inspired by this biological process, this study explores the autoxidation of biogas into formic acid using a synthetic catalyst that mimics the function of MMO. MMO is responsible for transferring oxygen to methane during oxidation, with the enzyme Nicotinamide Adenine Dinucleotide Hydrogenase (NADH) serving as an electron donor. Methane oxidation proceeds through methanol formation, which is further oxidized to formaldehyde by Methanol Dehydrogenase (MDH), with PQQ (pyrroloquinoline quinone) acting as a cofactor. Formic acid is produced by the subsequent oxidation of formaldehyde by Formaldehyde Dehydrogenase (FADH), with Flavin Adenine Dinucleotide (FAD) as the cofactor. Further oxidation of formic acid produces carbon dioxide, regenerating NAD+ for reuse by MMO. There are two types of MMO enzymes, called sMMO and pMMO. Soluble MMO (sMMO) contains iron, and particulate MMO (pMMO) contains copper (Hwang *et al.,* 2014).

Soluble MMO (sMMO) can convert methane to methanol with 100% selectivity, meaning that all methane is converted without any side products. The catalytic activity of sMMO produces 95 moles of methanol per mole of iron per hour, with a catalytic activity of 5.05 $mol/kg_{cat}/h$ at 50 °C using oxygen (O_2) and NADH as the cofactor. However, when hydrogen peroxide (H_2O_2) is used as a substitute for oxygen, the catalytic activity drastically decreases to 0.027 $mol/kg_{cat}/h$ under the same conditions (Dummer *et al*., 2023).

A study has been conducted to investigate methane oxidation using Fe/ZSM-5 catalysts promoted with copper (Cu). Their study achieved methane conversion into oxygenates with 10% methane conversion, using 27 mg of Fe/ZSM-5 catalyst in a batch reaction at 50 °C for 30 minutes, with 10 mL of water, 0.5 M H_2O_2, and 30.5 bar CH_4. A critical step in preparing the catalyst involved calcination at 550 °C for 3 hours (Hammond *et al*., 2012).

This paper explores an exploratory study on the oxidation of methane and carbon dioxide gases to produce formic acid using oxygen from the air. Oxygen in the air must be converted into superoxide radicals to serve as an oxidant. However, the conversion of oxygen into superoxide radicals has a low equilibrium conversion rate due to the positive Gibbs energy change involved (Wood, 1988). Therefore, a catalyst is required to facilitate the superoxide formation reaction. Transition metals are known to act as electron donors and serve as catalysts. The transition metals present in the MMO enzyme and functioning as active sites are iron (Fe) and copper (Cu). Including copper (Cu) can also accelerate oxidation (Stumm and Lee, 1961).

Based on these considerations, this study aims to achieve continuous autoxidation (oxidation using ambient air) of biogas into formic acid using synthetic catalysts that mimic the function of the MMO enzyme. The proposed liquid-phase autoxidation of biogas is expected to be easily controlled, conducted under mild operating conditions, environmentally friendly, and cost-effective.

METHODOLOGY

The experimental methodology consists of feedstock gas preparation, synthesis of transition metal catalysts mimicking the function of the MMO enzyme, and autoxidation reaction of biogas (CH_4 and CO_2) with air in the liquid phase using a biomimetic MMO enzyme catalyst.

Feedstock Reactant Preparation

The feed used in this reaction is methane and carbon dioxide. Biogas is a suitable feedstock to carry out the autoxidation of methane and carbon dioxide into formic acid.

Biogas production was initiated by constructing a biogas reactor and preparing the substrate required for biogas generation in the primary experiments. The substrate used in the biogas production process consisted of cow manure mixed with water in a 1:2 ratio to achieve a total solid (TS) of 15% and a pH of 7 (Raja and Wazir, 2017). The biogas was generated through anaerobic digestion in a reactor with a working volume of 15 litres. The residence time of the substrate in the reactor was 14 days, with the fresh substrate being introduced daily at a rate of 1 litre.

The schematic of the biogas production reactor is shown in Figure 1.

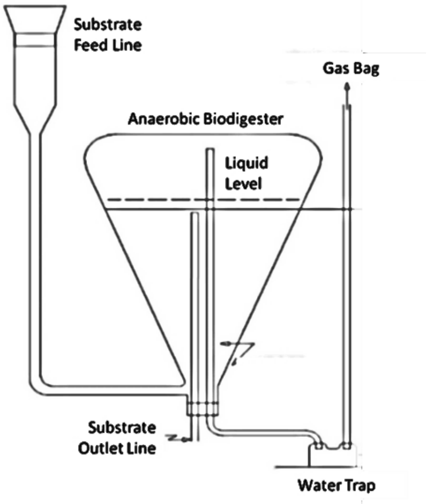


Fig. 1: Anaerobic digestion reactor

Synthesis of Catalysts

In catalyst synthesis, several components are utilized, one of which is the catalyst's active site, consisting of transition metals such as Fe and Cu. These metals are also found in the MMO enzyme (Hwang *et al.*, 2014). The addition of Zn is expected to serve as a structural component in the catalyst and function as superoxide dismutase (SOD) (Engwa, 2018). However, these metals cannot exist independently and must bind with ligands or chelating groups. Carboxylate groups are commonly used ligands as they can provide a stable catalyst structure (Lazou *et al.*, 2023).

Synthesis of Fe-Acetate Catalyst

The Fe-acetate catalyst was synthesized using iron(III) nitrate nonahydrate and zinc nitrate hexahydrate. First, 8.0 grams (0.02 mol) of iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) and 3.0 grams (0.01 mol) of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) were dissolved in 10 ml of deionized water.

Simultaneously, 10.9 grams (0.08 mol) of sodium acetate trihydrate ($NaOOCCH_3{\cdot}3H_2O$) was dissolved in 8 ml of deionized water and added to the stirring solution. The desired compound precipitated as a solid, which was then filtered using a Buchner funnel and washed three times with a 50:50 (v/v) mixture of deionized water and 95% ethanol. The precipitate was also washed twice with 95% ethanol until the ethanol wash was pale yellow. Finally, the product was air-dried at room temperature, ensuring it was free of nitrate ion.

Synthesis of Cu,Fe-Acetate Catalyst

For the Cu,Fe-acetate catalyst, 8.0 grams (0.02 mol) of iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), 2.7 grams (0.009 mol) of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), and 0.24 grams (0.001 mol) of copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) were dissolved in 10 ml of deionized water. This solution was added to a stirred mixture of 10.9 grams (0.08 mol) of sodium acetate trihydrate ($NaOOCCH_3{\cdot}3H_2O$) in 8 ml of deionized water. The resulting precipitate was filtered, washed three times with a 50:50 (v/v) mixture of deionized water and ethanol, followed by two additional washes with ethanol, then dried at room temperature.

Synthesis of Fe-Formate Catalyst

The Fe-formate catalyst was synthesized by dissolving 8.0 grams (0.02 mol) of iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) and 3.0 grams (0.01 mol) of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) in 10 ml of deionized water. To this stirred solution, 5.44 grams (0.08 mol) of sodium formate (NaOOCH) dissolved in 8 ml of deionized water was added. The precipitate formed was filtered and washed three times with a 50:50 (v/v) mixture of deionized water and ethanol, followed by two washes with ethanol. The product was then air-dried at room temperature, ensuring it was free of nitrate ions.

Synthesis of Cu,Fe-Formate Catalyst

For the Cu,Fe-formate catalyst, 8.0 grams (0.02 mol) of iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), 2.7 grams (0.009 mol) of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), and 0.24 grams (0.001 mol) of copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) were dissolved in 10 ml of deionized water. This solution was added to a stirred solution of 5.44 grams (0.08 mol) of sodium formate (NaOOCH) in 8 ml of deionized water. The precipitate was filtered, washed, and dried following the same procedure as the other catalysts.

Auto-Oxidation of Biogas Reaction

The auto-oxidation of biogas was conducted in a three-neck round-bottom flask containing 200 mL of 95% ethanol and 4 grams of the synthesized catalyst. The mixture was stirred using a magnetic stirrer to ensure homogeneity. The flask was connected to a Liebig condenser and a distillate collection vessel via a Vigreux column, which was insulated with aluminum foil. Two thermometers were positioned to monitor the condenser's flask contents and vapour temperature. The reaction mixture was heated to 65°C using a hot plate, while the condenser vapor temperature was maintained at 45°C. Biogas comprised methane and carbon dioxide, and air was injected slowly at 5:2 directly above the stirrer. The reaction continued until the flask temperature reached 70°C and the vapor temperature in the condenser was 55°C. After the reaction, the distillate was transferred into a clean sample bottle and stored in a refrigerator for further analysis. The reaction equation for the autoxidation of methane

(CH_4) and carbon dioxide (CO_2) in the liquid phase to produce formic acid (HCOOH) is written as follows:

The feed used in this reaction is methane and carbon dioxide. Biogas is a suitable feedstock to carry out the autoxidation of methane and carbon dioxide into formic acid.

$$CH_4 + CO_2 + O_2 \rightarrow 2HCOOH \qquad (1)$$

The parallel chemical process for methane and carbon dioxide oxidation using iron and copper transition metal catalysts to activate oxygen (Stumm and Lee, 1961) is proposed as follows:

Iron-based metal catalyst

$$Fe\ (II) + O_2 \rightleftharpoons Fe\ (III) + O_2^* \qquad (2)$$

Iron-based metal catalyst with copper as a promoter

$$Cu\ (I) + O_2 \rightleftharpoons Cu\ (II) + O_2^* \qquad (3)$$

$$Cu(\ II) + Fe\ (II) \rightleftharpoons Fe\ (III) + Cu(I) \qquad (4)$$

The schematic of the autoxidation reactor is shown in Figure 2.

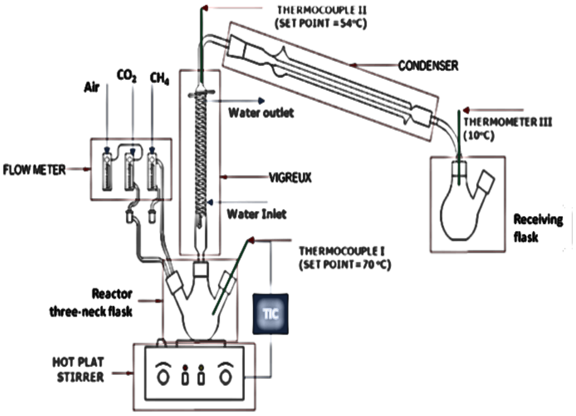


Fig. 2: autoxidation reactor

Experimental Variations

This study is a proof of concept that mimics the MMO enzyme, with the variable under investigation being the variation of four catalysts used in the autoxidation reaction, while the operating conditions (pressure, temperature), reaction time, and volume are kept constant. The effectiveness of each catalyst was evaluated by conducting experiments using four different catalysts: Fe-acetate, Cu,Fe-acetate, Fe-formate, and Cu,Fe-formate. The catalyst concentration remained constant at 2% by weight, and the reaction temperature was maintained at 70°C for 2 hours in all trials.

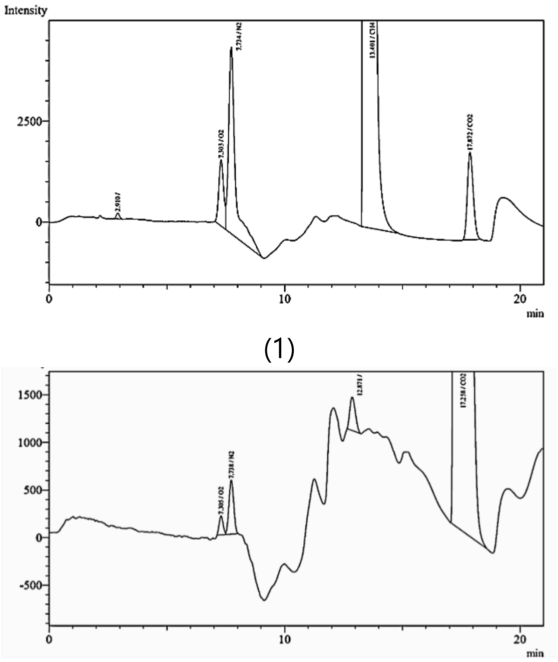
Product Analysis

The distillate obtained from the reaction primarily contained ethyl formate (C_2H_5COOH). The distillate, which contained formic acid, was diluted to a total volume of 1,000 ml using deionized water at a temperature of ≤ 15°C. A 5 ml aliquot of the sample was added to 30 ml of 0.1 N KOH solution and 25 ml of deionized water. A phenolphthalein (PP) indicator was added, and the solution was titrated with 0.1 N HCl until the pink color disappeared, indicating the excess KOH had been neutralized. To quantify the formic acid, bromophenol blue (BPB) indicator was added, and the solution was titrated again with 0.1 N HCl until the color changed to green-yellow, indicating the formic acid concentration.

RESULTS AND DISCUSSION

Feedstock Reactant Preparation

The reactor yielded an average of 5 litres of biogas per day. The limited quantity of biogas produced posed a challenge in conducting the exploratory experiments. To ensure sufficient availability of reactants for the oxidation process, methane (gas fuel) and carbon dioxide gases were synthesized and used in a 1:1 flow rate ratio. Figure 3 presents the gas chromatographic (GC-2014 Shimadzu) analysis of methane and carbon dioxide composition, with the specific breakdown of methane and carbon dioxide detailed in Table 1 and Table 2, respectively.



(1)

(2)

Fig. 3: Gas chromatography (GC) analysis for methane (1) and carbon dioxide (2) gases.

Table 1. Composition of methane (gas)

Component	Retention Time (Minutes)	Concentration (%-V)
O_2	7.303	1.0
N_2	7.734	3.9
CH_4	13.401	93.5
CO_2	17.872	1.6
Others	1.277	0.1

Table 2. Composition of carbon dioxide (gas)

Component	Retention Time (Minutes)	Concentration (%-V)
O_2	7.305	0.3
N_2	7.738	0.9
CH_4	17.258	98.1
CO_2	12.871	0.7
Others	7.305	0.3

Synthesis of Catalysts

Catalyst synthesis was carried out by mimicking the methane monooxygenase (MMO) enzyme, using transition metals Fe and Cu as active centers. Metal sources in the form of nitrate salts ($Fe(NO_3)_3$ and $Cu(NO_3)_2$) were first washed to remove nitrate ions, then complexed with carboxylate ions (acetate and formate) as complexing agents.

Four types of catalysts were prepared: Fe-acetate, Fe-formate, Cu;Fe-acetate, and Cu;Fe-formate (Figure 4). The resulting precipitates were filtered and dissolved in ethanol, which served as both the reaction solvent and a trapping agent for formate ions to form ethyl formate. Since ethyl formate has a lower boiling point (54 °C), product separation becomes more efficient.

The precipitates retained on the filter paper were considered to meet the criteria as ready-to-use catalysts for the autoxidation of biogas into formic acid.

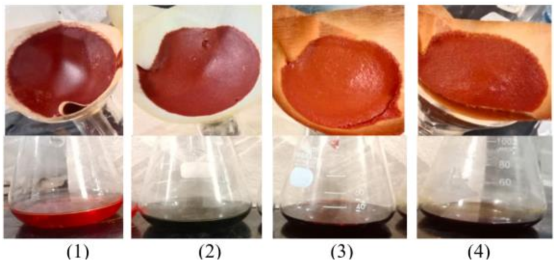


Fig. 4: (1) Fe-Acetate; (2) Cu,Fe-Acetate; (3) Fe-Formate; (4) Cu,Fe-Formate

Auto-Oxidation of Biogas Reaction

The auto-oxidation of biogas was carried out in the liquid phase, where methane, carbon dioxide, and oxygen gases were injected into a three-neck round-bottom flask containing a catalyst dissolved in ethanol. The reaction occurred at 70°C, and the catalyst solution was maintained at this temperature for 2 hours. The oxygen used in the process was sourced from ambient air at the research site. The composition of the air was analyzed using gas chromatography (GC), and the results are presented in Figure 5 and Table 3.

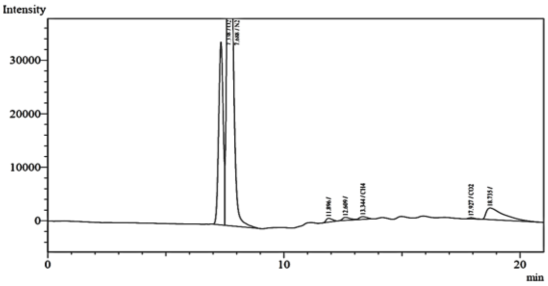


Fig. 5: GC analysis for air at the research site.

Table 3. Composition of air

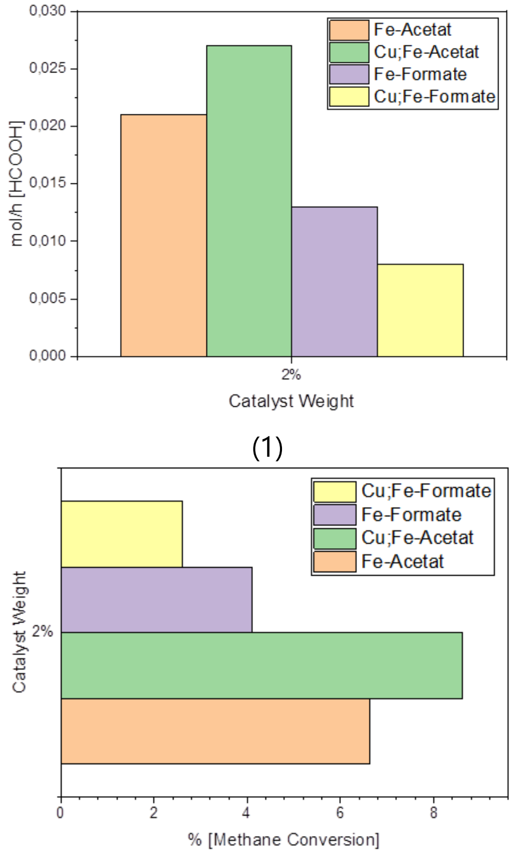
Component	Retention Time (Minutes)	Concentration (%-V)
O_2	7.338	22.8
N_2	7.688	69.5
CH_4	13.344	0.6
CO_2	17.927	0.0
Others	43.240	7.2

The auto-oxidation of biogas was carried out in the liquid phase, with the reaction occurring in an ethanol solution containing the dissolved catalyst. Consequently, only the reactants soluble in the catalyst solution actively participated in the reaction. On the other hand, the challenge lies in the low solubility of methane and CO_2 in alcoholic solvents (García-Aguilar *et al.*, 2011). The solubility of the gases in ethanol was estimated by simulations using Aspen HYSYS V.14 software. Based on the gas composition entering the reactor, the flow rates of methane, carbon dioxide, and air were 0.1 LPM, 0.1 LPM, and 0.5 LPM, respectively. It should be noted that air, not pure oxygen, was used as the oxidizing agent. Table 4 presents the composition of the reactants entering the reactor and those dissolved in the solution.

This study explored variations in both catalyst type and catalyst loading. Four types of catalysts were tested: Fe-acetate, Cu,Fe-acetate, Fe-formate, and Cu,Fe-formate. In each experiment, the catalyst weight was set at 2% of the total reaction volume for each type. The objective of these experiments was to evaluate the effectiveness of each catalyst in the auto-oxidation of biogas into formic acid, assess the influence of catalyst type and the addition of copper as a promoter on the rate of formic acid production. The experimental results are illustrated in Figure 6.

Table 4. Composition of the entering reactants and those dissolved

Component	Gas Inlet (mol/h)	Gas Outlet (mol/h)
CH_4	0.233	0.158
CO_2	0.241	0.192
O_2	0.278	0.036



(1)

(2)

Fig. 6: Produced formic acid (1) and methane conversion (2).

Based on the results, it was observed that the Fe-acetate catalyst produced formic acid at a rate of 0.021 mol/h. When copper (Cu) was added as a promoter to form the Cu,Fe-acetate catalyst, the formic acid production rate increased to 0.027 mol/h, representing a 29.76% improvement. Indicates that adding Cu enhances the catalytic activity of Fe-acetate in formic acid production. In contrast, the Fe-formate catalyst generated formic acid at a rate of 0.013 mol/h, but when Cu was added to form Cu,Fe-formate, the production rate decreased to 0.008 mol/h, reflecting a 36.54% reduction. Therefore, the Cu addition has a detrimental effect on the catalytic performance of Fe-formate.

These findings align with the observations by Stumm and Lee, which demonstrated that adding Cu positively impacts oxidation activity, leading to increased production of the desired oxygenate products, as seen with the Cu,Fe-acetate catalyst. Adding Cu strengthened the oxidation process, thereby increasing formic acid production. However, the behavior differs for catalysts based on formate complexes. In the case of Fe-formate, the formic acid yield decreased after adding Cu. This is attributed to the difference in the stability between acetate and formate complexes. The Fe-acetate complex is more stable, whereas Fe-formate is more prone to oxidation, leading to the formation of Fe_2O_3 (precipitate) and CO_2. The presence of Cu accelerates the formation of Fe_2O_3, thereby reducing the number of active sites for formic acid production and decreasing catalytic efficiency.

The conversion of dissolved methane to formic acid for each catalyst—Fe-acetate, Cu,Fe-acetate, Fe-formate, and Cu,Fe-formate—was 6.64%, 8.61%, 4.11%, and 2.61%, respectively. These results clearly show that adding Cu to Fe-acetate significantly improves the conversion of methane into formic acid. In Contrast, adding Cu to Fe-formate leads to a decline in catalytic performance.

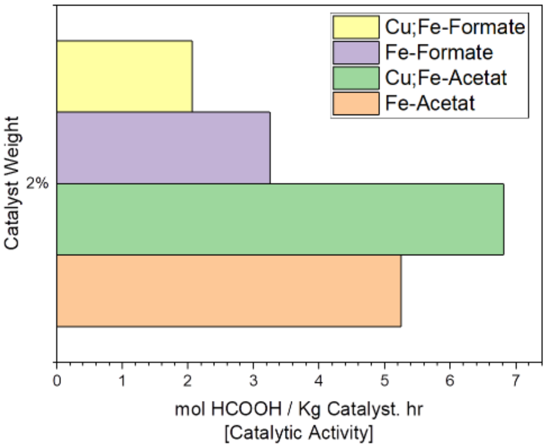


Fig. 7: Catalytic activities of autoxidation carbon dioxide and methane into formic acid

The catalytic activity, expressed in mol HCOOH produced per kilogram of catalyst per hour, for Fe-acetate, Cu,Fe-acetate, Fe-formate, and Cu,Fe-formate was 5.25 $mol/kg_{cat}/h$, 6.81 $mol/kg_{cat}/h$, 3.25 $mol/kg_{cat}/h$, and 2.06 $mol/kg_{cat}/h$, respectively. These results show that Cu,Fe-acetate exhibited the highest catalytic activity, followed by Fe-acetate. Adding Cu to Fe-acetate increased the catalyst's activity, while adding Cu to Fe-formate decreased its efficiency.

The differences in catalytic activity can be explained by the stability of the catalyst structures and the influence of Cu addition. For acetate-based catalysts, adding Cu accelerates the activation of oxygen into superoxide radicals, which are essential for the oxidation of reactants to formic acid. This contributes to an increase in catalytic efficiency, as evidenced by the difference in activity between Fe-acetate and Cu,Fe-acetate.

Conversely, in formate-based catalysts, the formate complex tends to degrade more easily, forming iron oxide (Fe_2O_3), especially when Cu is added, which further accelerates the oxidation of the formate to carbon dioxide. As a result, the catalytic activity decreases, as observed in the comparison between Cu,Fe-formate and Fe-formate.

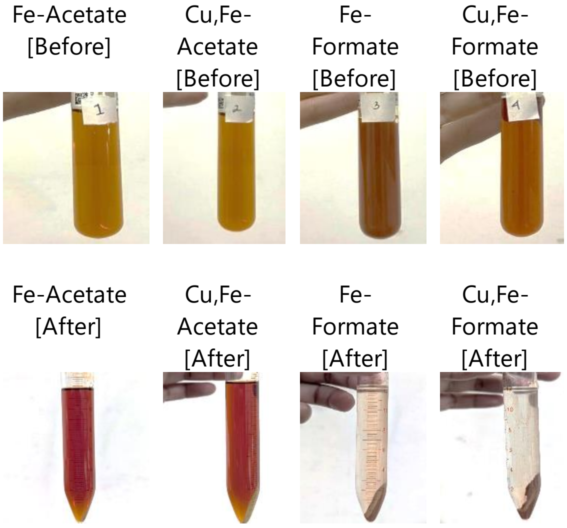


Fig. 8: Qualitative documentation of the catalyst (before and after being used in the auto-oxidation reactions)

Qualitative documentation of the catalysts used in the auto-oxidation process revealed that formate-based catalysts generated more precipitation than acetate-based ones. This precipitate formation indicates iron(III) oxide (Fe_2O_3) production.

When formate-based catalysts are involved in the reaction, they tend to undergo oxidation more readily, forming Fe_2O_3 and carbon dioxide as by-products. In contrast, acetate-based catalysts demonstrate greater stability during the reaction, reducing the likelihood of precipitate formation. The presence of precipitate diminishes the amount of transition metal available in the liquid phase as active sites, thereby negatively impacting catalytic activity and the overall efficiency of the reaction, as fewer catalyst sites are available to interact with dissolved reactants in the liquid phase.

CONCLUSION

Catalysts based on Fe-acetate and Cu,Fe-acetate demonstrated significantly higher catalytic activity compared to those based on Fe-formate and Cu,Fe-formate. The catalytic activity of Fe-acetate was measured at 5.25 mol HCOOH/kg catalyst per hour, while the addition of Cu to form Cu,Fe-acetate increased the activity to 6.81 mol HCOOH/kg catalyst per hour, representing a 29.76% enhancement. In contrast, the activity of Fe-formate, which was 3.25 mol HCOOH/kg catalyst per hour, decreased to 2.06 mol HCOOH/kg catalyst per hour when Cu was added to form Cu,Fe-formate, marking a reduction of 36.54%.

The methane-to-formic acid conversion for Fe-acetate was 6.64%, whereas the addition of Cu to form Cu,Fe-acetate increased the conversion to 8.61%. For the formate-based catalysts, methane conversion for Fe-formate was 4.11%, but after Cu was added to form Cu,Fe-formate, the conversion dropped to 2.61%.

Adding Cu to acetate-based catalysts enhanced the oxidation of methane and CO_2, leading to increased formic acid production. Conversely, adding Cu to formate-based catalysts resulted in a decline in catalytic activity, as the formation of precipitates reduced the number of active sites available for the reaction.

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