# CATALYTIC CONVERSION OF FORMIC ACID TO METHANOL WITH Cu AND Al UNDER HYDROTHERMAL CONDITIONS

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Catalytic conversion of formic acid into methanol was investigated with Cu as a catalyst and Al as a reductant under hydrothermal conditions. It was found that formic acid can be converted into methanol by such means. The highest yield of methanol (30.4%) was attained with a temperature of 300 °C and a reaction time of 9 h. The AlO(OH) formed from Al oxidation may also play a catalytic role in the formation of methanol. This process may provide a promising solution to producing methanol from carbohydrate biomass combined with the process of converting the carbohydrate into formic acid, which is expected to emit no $CO_2$.

*Keywords: Biomass utilization; Catalytic reduction; Methanol; Hydrothermal conditions*

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## INTRODUCTION

One of the main scientific and technological challenges facing humanity in the 21st century is reducing society's dependence on fossil fuels as an energy source. This dependence has led to a serious fuel crisis, effecting environmental sustainability. Taking full advantage of renewable resources is one promising pathway toward meeting future energy demands and reducing greenhouse gas emissions. Conversion of biomass into valuable fuels, as well as into other value-added chemical products, is of considerable interest because it may allow the global carbon system to work harmoniously (Bond et al. 2010; Jin and Enomoto 2011; Kunkes et al. 2008; Zhang et al. 2011). An enzymatic hydrolysis process has traditionally been used for biomass conversion; however, the reaction rate of enzymatic hydrolysis is very slow and the efficiency is low because microorganisms cannot easily and directly degrade biomass. Because of this, the development of an environmentally friendly and highly effective method for converting biomass into useful chemicals is strongly desired.

In recent years, hydrothermal reactions using high temperature water (HTW) as an environmentally friendly reaction medium have received more attention. HTW has unique features compared to ambient liquid water; for example, the ion product ($K_w$) at 250-300 °C is approximately three orders of magnitude greater than that of ambient liquid water, which could help to promote the reactions significantly. In addition, HTW is a source of hydrogen, which can be generated using cheap metals as reductants (Jin and Enomoto 2009; Goto et al. 2004; Peterson et al. 2008; Akiya and Savage 2002; Watanabe et al. 2004). Extensive research on the hydrothermal conversion of organic wastes and biomass has demonstrated that hydrothermal reactions can convert various natural organic materials directly and efficiently into useful chemicals (Jin and Enomoto 2011; Jin et al. 2011; Fang and Fang 2008). We have performed a series of studies on the hydrothermal conversion of biomass into formic acid and other value-added chemicals with considerably high yields (Jin et al. 2008 a, b, 2010, 2011; Wu et al. 2009). The yield of formic acid or formate from glucose under mild hydrothermal conditions can reach as high as 75% (Jin et al. 2008 b). Although formic acid is an important organic chemical in feedstock, the application range of formic acid is limited, and formic acid is difficult to separate from aqueous solutions.

Methanol, an important multipurpose base chemical, has received increasing attention because it is a promising alternative to oil and natural gas with regards to storage, transportation, and use (Olah 2004, 2005, 2009). Compared with formic acid, methanol is easily separated from water and has been a common chemical feedstock for several important chemicals, such as chloromethane, for more than 30 years (Ortelli et al. 2001). The production of methanol from synthesis gas has been widely adopted commercially. However, synthesis gas as raw material for producing methanol is mainly generated from coal gasification or natural gas reforming. Moreover, in this process, it is important to control the considerable methane conversion and coke deposition. Besides, current studies on methanol production from biomass have focused on the conversion of synthesis gas by the biomass gasification and pyrolyzation, which not only need a higher temperature and expensive catalyst, but also will release large amounts of carbon dioxide and by-products (Olah et al. 2009; Hasegawa et al. 2010). Hence, if the formic acid from biomass could be readily and efficiently converted into methanol under mild hydrothermal conditions, then a new process for converting carbohydrate biomass into methanol by a two-step reaction could be achieved. In the two-step reaction, the first-step oxidizes the carbohydrate into formic acid, which then is reduced into methanol in the second-step reaction with the mechanism as follows:

$$C_6H_{12}O_6 + O_2 \rightarrow HCOOH \qquad (1)$$

$$HCOOH + H_2 \rightarrow CH_3OH + H_2O \qquad (2)$$

According to equation 1 and 2 (not stoichiometric), this process could be expected to emit no $CO_2$.

The hydrogen source is very important for the reduction of formic acid, and water may be the biggest potential hydrogen source in nature if technology is good enough. Oxidative potential metals have a high potential for producing hydrogen from water. Previous research has revealed that metallic Al can react easily with water to produce large amounts of hydrogen under hydrothermal conditions (Jin et al. 2011). The use of metals as reductants under hydrothermal conditions has the following benefits: (i) unlike stable gaseous hydrogen, the hydrogen produced by the oxidation of metals could be active, which may easily reduce the formic acid into methanol; (ii) the oxidative product of metals may have possibility of catalyzing the reduction of formic acid; and (iii) the problem of $H_2$ storage can be avoided because hydrogen can be produced by the oxidation of metals.

Methanol synthesis over Cu-containing catalysts is a well-researched process (Rozovskii and Lin 2003; Liu et al. 2003), and thus Cu should have high potential for reducing formic acid into methanol under hydrothermal conditions. More importantly, Cu is relatively cheap and easily available. Moreover, previous research has found that Co, W, and Ni have catalytic activity in $CO_2$ reduction (Rozovskii and Lin 2003; Nerlov et al. 2000), and Pd/C can catalyze the reduction of the carboxylic acids to aldehydes or alcohols (Falorni et al. 1999). Thus, the examination of catalytic active of Co, W, Ni and Pd/C for in reduction of formic acid into methanol formation is also needed.

The purpose of the present research, therefore, was to study the catalyzed-reduction of formic acid to methanol in the presence of Al under hydrothermal conditions. The optimum reaction conditions for producing methanol were investigated. The possible mechanism of the reduction of carbohydrate biomass to methanol was also considered.

## EXPERIMENTAL

### Materials

Co, W, Ni, Pd/C (containing 5% metal Pd), Cu, and Al powders, formic acid, HCl, and NaOH if required, were used as test materials. All metal powders except Cu (under 200-mesh in size), formic acid (>99%), HCl, and NaOH were obtained from Sinopharm Chemical Reagent Co., Ltd. The Cu powder (under 200-mesh in size) was obtained from Shanghai-runjie Chemical Reagent Co., Ltd. These reagents were all of analytical grade, and deionized water was used.

### Experimental Procedures

The experiments were performed using a batch reactor consisting of SUS 316 tubing (Jin et al. 2005). Experimental procedures and techniques are described in detail elsewhere (Jin et al. 2003). Briefly, the desired amount of reductant (Al powder), catalyst (Co, W, Ni, Pd/C, and Cu powders) and 2.00 mL of 60 $g{\cdot}L^{-1}$ formic acid aqueous solution were added into the batch reactor occupying 35% of the total reactor volume and then sealed. The reactor was immersed in a salt bath preheated to the desired temperature for the reaction. During the reaction process, the reactor was shaken to fully mix the contents. After the desired reaction time (defined as the elapsed time for which the reactor was kept in the salt bath), the reactor was removed from the salt bath and immersed into a cold water bath. Generally, the pressure with 35% water fill should be the saturated steam pressure at the corresponding temperature, and the saturated steam pressure at 300 °C is 8.6 Mpa. However, a large number of gases was produced in our experiments; thus the real pressure should be higher than the saturated steam pressure. For example, the pressure under the reaction condition with 4.4 mmol Al, 12 mmol Cu at 300 °C was about 12.5 MPa as measured by using a pressure valve.

### Analysis Methods

After the reactions, gas, liquid and solid samples were collected and analyzed using GC-TCD, GC-FID/MS, TOC analyzer, and X-ray diffraction (XRD), respectively. In cases where alkali was added, after filtration and prior to analysis, HCl was used to adjust the pH of the solution to 3. The quantitative estimations of methanol were based on average values obtained from the GC-FID analysis of the three measurements. Gas samples were analyzed with a GC system (HP-5890 Series II), which was equipped with an HP-1 packing column (30 m × 0.25 mm ID) and a TCD detector.

An Agilent 6890 gas chromatograph with a flame ionization detector was used for the quantification of methanol. The initial oven temperature of the gas chromatograph was kept at 40 °C for 1 min and was increased at a rate of 7 °C/min to 110 °C. This temperature was held for 1 min and was then increased at a rate of 35 °C/min to 220 °C. The samples were separated on a DB-WAX capillary column using nitrogen as the carrier gas. GC/MS analyses were performed with an HP 5890 Series II GC equipped with a HP-INNOWAX capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness) and a 5898 B mass spectrometer. HPLC analyses were performed on an RSpak KC-811 (SHODEX) column with a UV detector (210 nm).

Solid samples were washed with deionized water several times, dried in air, and then characterized by XRD (D/MAX2550, Rigaku, and Bruker D8 Advance) using Ni filtered Cu Kα radiation at an acceleration voltage of 40 KV and an emission current of 100 mA for D/MAX2550 and 40 mA for Bruker D8 Advance. The step scan covered an angle range of 5 ° to 70 ° (2θ), at a rate of 10 °/min for D/MAX2550, Rigaku and 1.2 °/s for Bruker D8 Advance.

## RESULTS AND DISCUSSION

### Effects of Different Types of Catalyst

First, the catalytic effects of Co, W, Ni, Pd/C, and Cu for the conversion of formic acid into methanol were tested at 300 °C for 3 h with 4.4 mmol of Al used as a reductant. The methanol yield was defined as the percentage of methanol to initial formic acid on a carbon basis. As shown in Fig. 1, the methanol yield was 11.4% in the case of Cu powder, while the methanol yields were almost zero in the case of Co and W. For a lower yield of methanol with Pd/C, a possible explanation may be that it was due to a lower amount of Pd/C. Thus, a further experiment with 0.2 g Pd/C was conducted. Although the yield of methanol increased to 1.9%, this yield still was much lower than that with Cu. These results showed that the Cu exhibited higher activity for the formation of methanol. The solid residue that remained after the reactions with the addition of Cu powder was characterized by XRD. After the reaction, almost all of the copper still existed in the form of pure metal, and only a small amount was oxidized into $Cu_2O$. On the other hand, Al was not detected, but AlO(OH), which should be the oxidation product of Al, was detected; hence, Cu and Al played catalytic and reductive roles in the reduction of formic acid into methanol, respectively.

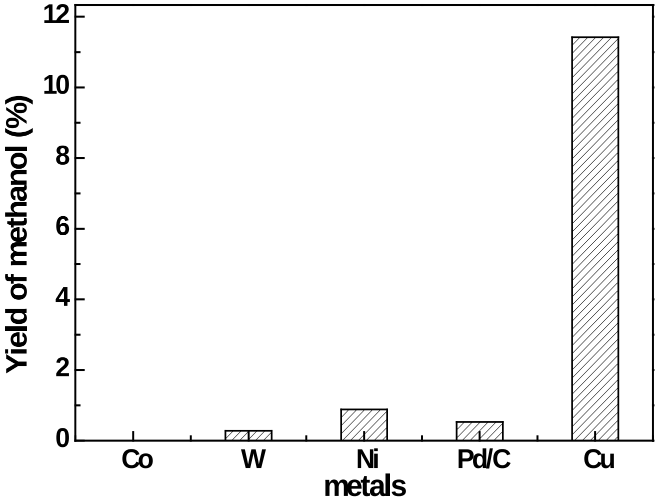

**Fig. 1.** Effect of different types of catalyst on the conversion of formic acid into methanol (Al: 4.4 mmol, Co, W, Ni, and Cu: 12 mmol, Pd/C: 0.1 g, temperature: 300 °C, time: 3 h)

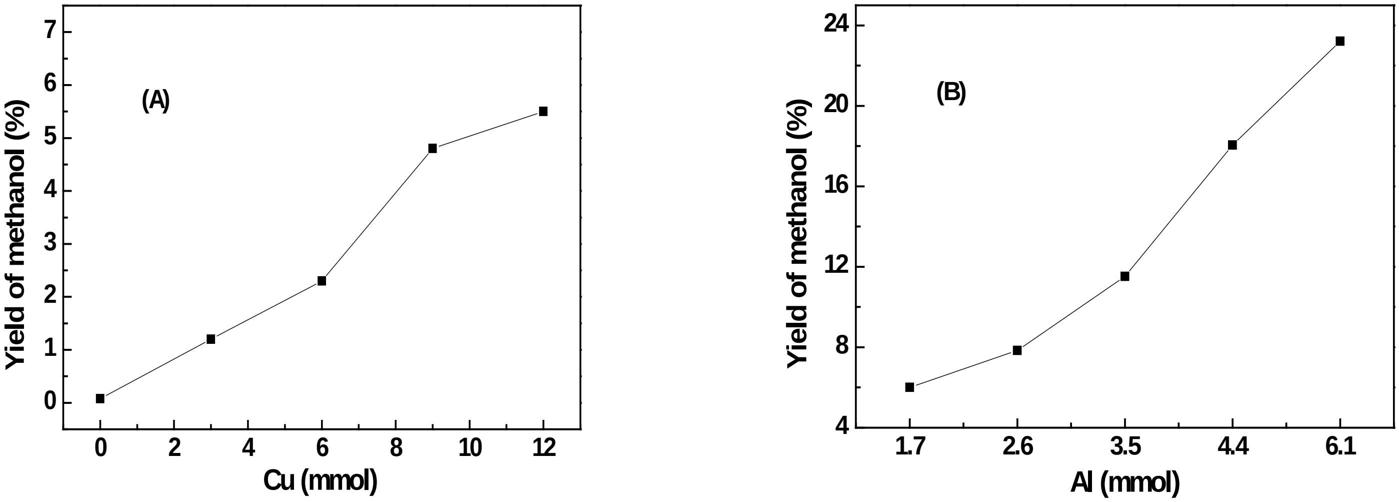

**Fig. 2.** Effect of the amount of Cu (A) and Al (B) on methanol yield ((A): temperature: 300 °C, time: 3 h, (B): Cu: 12 mmol, temperature: 300 °C, time: 5 h)

## Effects of the Amount of Cu and Al

The effects of the amounts of Cu and Al on the methanol yield were investigated. Fig. 2a shows the variation in the yield of methanol with Cu in dosages of 0, 3, 6, 9, and 12 mmol at 300 °C for 3 h. As illustrated in Fig. 2a, in the absence of Cu, the methanol yield was close to zero; however, the methanol yield increased linearly with an increase in the amount of Cu powder, and when the Cu amount reached 12 mmol, the yield of methanol reached 5.5%. These results indicate that the conversion of formic acid into methanol is facilitated by an increase in the amount of Cu in the hydrothermal reactions.

In the subsequent experiments, the amount of Cu catalyst was set at 12 mmol. Figure 2b shows the effect of the amount of Al on the yield of methanol by fixing the amount of Cu at 12 mmol for 5 h at 300 °C. The methanol yield increased greatly with an increase in the amount of Al. The maximum yield increase was 23.2% at 6.1 mmol of Al. When the amount of Al increased from 2.6 to 6.1 mmol, the methanol yield increased approximately 3-fold. This indicates that the amount of Al has a significant impact on the formation of methanol; however, Al in excess of 4.4 mmol produced too much gas. For safety precautions, the amount of Al was set to 4.4 mmol in subsequent experiments.

### Effect of pH Value

Further experiments were conducted to investigate the influence of the solution pH value on the methanol yield with and without the addition of acid or alkali. As shown in Table 1, in the case of 0.3 pH adjusted with HCl, the yield of methanol significantly decreased to 1.6%, and residual of formic acid was only 0.09%. Analyses for the gas sample indicated the presence of a great amount of $H_2$, $CO_2$, and a little CO, which suggest that most of the formic acid was decomposed into $CO_2$ and $H_2$ at a low pH. In addition, it has been reported that a trace amount of chlorine can lead to a great loss in Cu-based catalyst activity (Liu et al. 2003); thus, the decreases in the yield of methanol at the low pH were probably due to catalyst deactivation caused by the chlorine. On the other hand, NaOH was also used to adjust the pH of the solution to 12.3. In this case, the yield of methanol was 0.4%, and the residual of formic acid after the reaction increased to 60.9%. These results suggest that strongly alkaline concentrations also do not facilitate the conversion of formic acid into methanol. As discussed later, formic acid may first decompose into $H_2$, $CO_2$, and CO in the formation of methanol. $HCOO^-$ is stabilized and difficult to reduce or decompose (Takahashi et al. 2006). Thus, this may be the reason why the residual of formic acid significantly increased and the yield of methanol decreased at a high pH. In addition, no other organic products in liquid samples were detected by GC-MS. Similarly, the products in gas sample mainly were $H_2$, $CO_2$, and a little CO, but the amount of these gas products were much lower than that at pH 0.3. These results indicate that acid or alkali were responsible for the decrease in the yield of methanol; hence, further experiments investigating the effect of the reaction temperature and time were conducted in the absence of acid or alkali.

**Table 1.** Effect of pH Value on Methanol Yield

| pH Value | 0.3 | 1.3 | 12.3 |
|---|---|---|---|
| Yield of Methanol (%) | 1.6 | 11.3 | 0.4 |
| Residual of Formic Acid (%) | 0.09 | 0.12 | 60.9 |
| * Cu: 12 mmol, Al: 4.4 mmol, T: 300 °C, time: 3 h | | | |

### Effect of Reaction Temperature and Reaction Time

Figure 3a shows the variations in the yield of methanol as a function of reaction temperature from 250 to 325 °C with 12 mmol of Cu and 4.4 mmol of Al for 7 h. As illustrated in Fig. 3a, the increases in the reaction temperature led to a significant increase in the yield of methanol; however, the yield of methanol sharply decreased when the temperature exceeded 300 °C. Thus, the use of a reaction temperature above 300 °C should be avoided to obtain a high yield of methanol. This result is possibly caused by the decomposition of methanol under the catalysis by Cu or some inhibition effect on the catalyst Cu itself under too high a temperature. As shown in Fig. 3b, the yield of methanol drastically increased with an increase in the reaction time until the reaction time reached 7 h; from 7 h to 9 h, the methanol yield continued to increase but only slightly. As the reaction time was further increased, the yield of methanol decreased rapidly. The decrease in methanol after 9 h may be attributed to the decomposition of methanol. The gas samples of experiments for reaction time of 9 h and 12 h were analyzed, respectively. The results indicated that the amount of gas increased from 1.64 mmol for 9 h to 1.85 mmol for 12 h. Furthermore, we conducted a methanol decomposition experiment with methanol (20 g/L) at 300 °C for 2 h. As a result, the residue methanol was 18.9%, and a large amount of $H_2$, $CO_2$, and little CO in the gas sample were detected. No other organic products were detected.

In addition, the carbon mass balance was calculated for the experiment with the highest yield of methanol. By examining the carbon in $CO_2$ and trace CO in the gas sample, the organic carbon in methanol and unconverted formic acid, and the inorganic carbon in the bicarbonate or carbonate in the liquid solution, it was found that the carbon mass balance was around 95%, and formic acid decomposition into $CO_2$ was predominant.

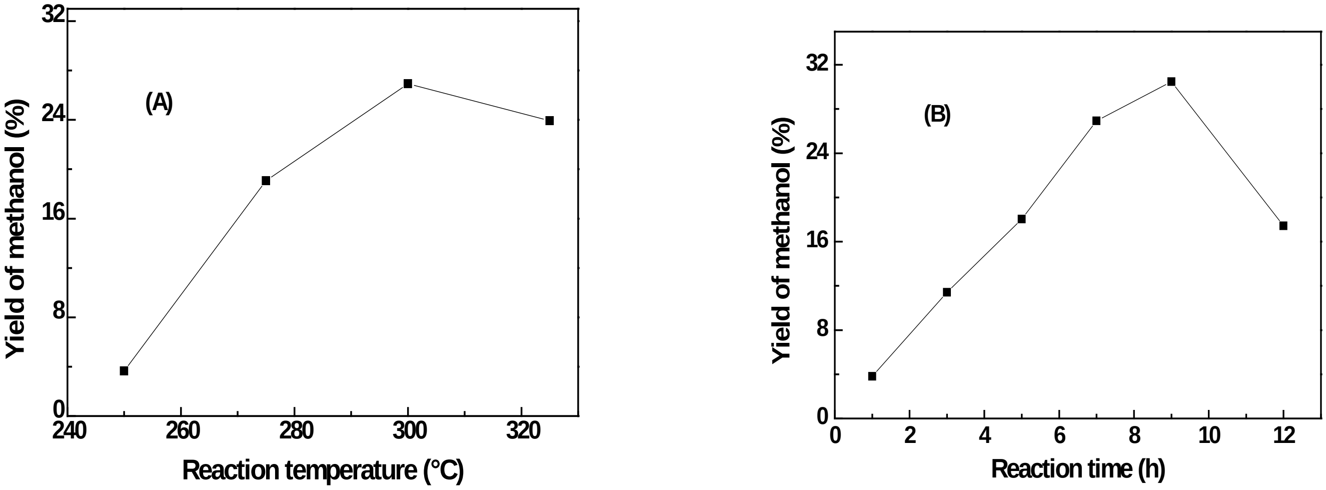

**Fig. 3.** Effect of reaction temperature (a) and reaction time (b) on methanol yield ((a): Cu: 12 mmol, Al: 4.4 mmol, time: 7h, (b): Cu: 12 mmol, Al: 4.4 mmol, temperature: 300 °C)

## Mechanism and Discussion

The reaction pathways for methanol formation from formic acid will be considered as follows. There may be two possible reaction paths: the first reaction path supposes that formic acid is directly reduced into methanol by hydrogen released from the water due to the oxidization of Al; the second path suggests that methanol is synthesized from $H_2$, $CO_2$, and CO that decomposed from the formic acid. If the first reaction mechanism is responsible, then the yield of methanol would increase with a decrease in formic acid; however, the shorter experiments, which had reaction times between 10 to 120 min with 12 mmol of Cu and 4.4 mmol of Al at 300 °C, indicated that the residual formic acid decreased dramatically with increasing reaction time; however, the yield of methanol was very low (seen in Fig. 4). Consequently, the first pathway may not be the predominant reaction. With regard to the second path, it is generally known that two alternative reactions can occur: decarboxylation ($HCOOH \leftrightarrow CO_2+H_2$) and dehydration ($HCOOH \leftrightarrow CO + H_2O$) (Takahashi et al. 2006; Yu and Savage 1998; Akiya and Savage 1998; Broll et al. 1999; Yagasaki et al. 2002). It has been reported that decarboxylation is the favored pathway in the presence of water, while dehydration is dominant in the absence of water (Akiya and Savage 1998). Therefore, the reaction path of the formation of methanol may involve synthesis by gases decomposed from formic acid. To confirm the decomposition of formic acid, the byproducts $H_2$, $CO_2$, and CO were detected in the gas samples.

As shown in Table 2, the amount of $CO_2$ that decomposed from formic acid was much higher than the amount of CO at all reaction times. Besides, it can be seen from Table 2 that the change in $CO/CO_2$ ratio from 10 to 30 min clearly increased. This may be attributed to the reverse water gas shift (RWGS) reaction. Previous research has demonstrated that the RWGS reaction occurs in hydrothermal reaction (Waldner and Vogel 2005) and many other processes using copper rich with alumina as a support (Wang et al. 2011) whenever $CO_2$ and $H_2$ are present in a reaction mixture (Xu and Moulijn 1996).

$$CO_2 + H_2 = CO + H_2O \quad \Delta H_{298K} = 41.2\ kJ \cdot mol^{-1} \tag{3}$$

Moreover, RWGS reaction is an endothermic reaction, and thus high temperature would facilitate the formation of CO.

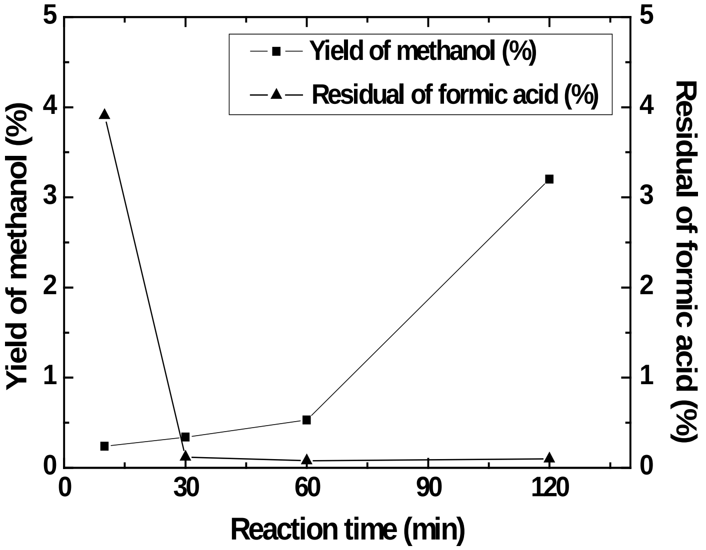

**Fig. 4.** Effect of shorter reaction time on methanol yield and residual of formic acid (Cu: 12 mmol, Al: 4.4 mmol, temperature: 300 °C)

**Table 2.** Effect of Shorter Reaction Time on Gas Productions

| Reaction Time (min) | 10 | 30 | 60 | 120 |
|---|---|---|---|---|
| The Amount of $CO_2$ (mmol) | 1.46 | 1.41 | 1.35 | 1.34 |
| The Amount of CO (mmol) | 0.11 | 0.55 | 0.52 | 0.47 |
| * Cu: 12 mmol, Al: 4.4 mmol, temperature: 300 °C | | | | |

Figure 5 shows the schematic diagram for a hypothetical mechanism of the conversion of formic acid into methanol. According to this scheme, the formic acid first decomposed into $H_2$ and $CO_2$, and then, $CO_2$ was adsorbed onto the surface of the Cu and further associated with the hydrogen generated from water to form methanol. Finally, to complete the catalytic cycle, methanol was removed from the surface of the Cu. Moreover, the AlO(OH) may also play a catalytic role in the formation of methanol. To further confirm whether AlO(OH) played a catalytic role, an experiment was conducted that fixed the amount of Cu at 12 mmol for 3 h at 300 °C using 4.4 mmol of Fe as a reductant. Under these conditions, no methanol could be detected. Hence, AlO(OH) may have a synergetic effect with Cu as a catalyst on the formation of methanol in the reactions. Although further investigation is needed, considering that the role of CO in the synthesis of methanol by $H_2$, CO, and $CO_2$ over ZnO is to reduce ZnO to $ZnO_{1-x}$ (Kurtz et al. 2005; Liu et al. 2003), which is active for reduction of $CO_2$, and the reducing capacity of CO is generally superior to $H_2$, we are proposing that CO decomposed from formic acid may activate the AlO(OH).

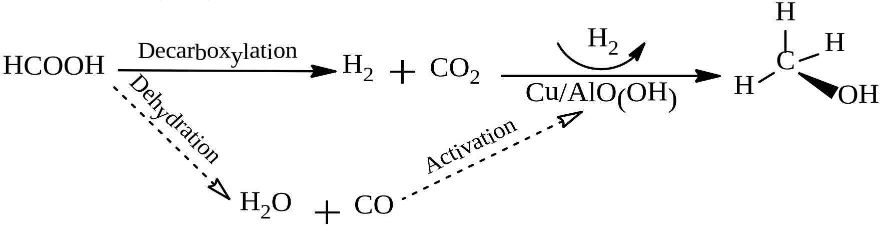

**Fig. 5.** The hypothetical mechanism schematic diagram of the conversion of formic acid into methanol

In the traditional hydrogenation of $CO_2$ catalyzed by Cu, the catalyst usually needs special and complicated treatment to form a specific structure and to obtain increased catalytic activity (Wang et al. 2010); however, in the present research, an as-received catalyst of Cu was directly used without any prior treatment and showed good catalytic activity in the conversion of formic acid into methanol. Although further studies are needed to provide direct evidence, this phenomenon probably occurs because high-temperature water activates the surface of Cu, which leads to an increase in surface defects and hence, makes the adsorption of $CO_2$ onto the surface of Cu possible and easy.

## CONCLUSIONS

1. Formic acid can be converted into methanol under mild hydrothermal conditions using Cu as a catalyst in the presence of Al. Through the investigation of various experimental parameters, it was found that the highest yield of methanol (30.4%) was attained under optimal conditions of 300 °C, a reaction time of 9 h, 12 mmol of Cu,

and 4.4 mmol of Al. This process may provide a promising solution to producing methanol from carbohydrate biomass combined with the process of converting carbohydrate into formic acid to meet the urgent need for atmospheric $CO_2$ reductions.
2. Methanol is probably formed primarily by the Cu-catalyzed synthesis of $H_2$ and $CO_2$ from the decomposition of formic acid.
3. The addition of acid or alkali was not favorable for the conversion of formic acid into methanol.
4. AlO(OH) may also play a catalytic role in the formation of methanol.

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