Catalysis Today 194 (2012) 25–29

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic reduction of carbon dioxide into methanol over copper under hydrothermal conditions

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ARTICLE INFO

Article history:
Received 31 January 2012
Received in revised form 16 May 2012
Accepted 10 June 2012
Available online 20 July 2012

Keywords:
Methanol
CO_2
Hydrothermal chemistry
Catalyst
Copper

ABSTRACT

A novel method for the catalytic synthesis of methanol from CO_2 over Cu in the presence of Zn under hydrothermal conditions was investigated. The results showed Cu acts as an active catalyst in conversion of CO_2 into methanol. The methanol yield of 11.4% was achieved at 350 °C for 3 h with Cu 70 mmol, Zn 60 mmol, HCl 2.0 M and water filling 50%. The plausible mechanism for the hydrothermal conversion of CO_2 into methanol was also discussed.

1. Introduction

Global warming caused by the increase in atmospheric CO_2 is threatening human and earth's survival. One of the main scientific and technological challenges facing the humanity is to reduce the concentration of CO_2. Methods for CO_2 reduction are urgently needed to reduce CO_2 emissions and to minimize global warming. The utilization of the CO_2 as a carbon source to produce valuable and useful chemicals could be regarded as the most potential way to solve this problem, and it is attracting more research interests worldwide. A number of research works related to CO_2 utilization, such as methanol, have been reported [1,2].

Methanol is a very important organic chemical because of its wide utilization. Methanol has been often found as an antifreeze, solvent, fuel and as a raw material for production of formaldehyde, flavors, dyes, medicines, gunpowder and also as a common chemical feedstock for acetic acid, methyl *tert*-butyl ether, and chloromethane, etc. [3–6]. In recent years, synthesis of methanol is attracting interest due to the industrial importance, and much attention has been paid to development efficient methods for the synthesis of methanol, such as photochemical reduction [7–11], electrochemical reduction [12–15], and catalytic hydrogenation reduction [16–26]. Although these reactions have proven to be extremely efficient for the synthesis of methanol, most of them have still considerable drawbacks, including the low yield, strict reaction condition, and/or high cost. Therefore, to avoid that, development of a new method to effectively change CO_2 into methanol was increasing demand.

Over the past several decades, CO_2 hydrogenation to methanol is commonly used because of its abundance, low cost, nontoxicity and high potential as a renewable source. It is well known that CO_2 has high thermodynamic stability and low reactivity, no matter what methods are reported for methanol synthesis, the use of catalysts is essential. More importantly, catalytic reduction of CO_2 into methanol has been proved technically feasible. Developing mild methods to catalytically activate CO_2 represents a challenge of both academic and practical importance. Cu-based catalysts like Cu/ZnO or Cu/ZnO/Al_2O_3 have been often utilized for the methanol synthesis from syngas because Cu element was active (Eq. (1)). It is, however, needed to add metal oxides as adsorbed species [16–26]. Recently, hydrothermal treatment in conversion CO_2 or biomass into value-added chemicals has received much attention and become one of the most promising ways of utilizing because of its unique advantages [27–34], such as fast reaction and green solvent. Previously, we and other groups have reported some research results in hydrothermal conversion of CO_2 into value-added chemicals. For example, (1) methane was formed via nickel-catalyzed conversion of CO_2 (Eq. (2)) [35]. (2) CO_2 was reduced to formic acid over Cu in the presence of Fe under hydrothermal conditions (Eq. (3)) [36,37]. Encouraged by these findings above, we thought that CO_2 hydrogenation would be converted to the methanol using transition metal catalysts under hydrothermal conditions.

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http://dx.doi.org/10.1016/j.cattod.2012.06.013

General methods for catalytic hydrogenation of CO_2 into CH_3OH.

$$CO_2 + H_2 \xrightarrow{\text{Cu-based catalysts}} CH_3OH \qquad (1)$$

Our previous work. Hydrothermal conversion CO_2 into chemicals.

$$CO_2 + H_2O \xrightarrow[\text{Hydrothermal condition}]{\textit{Cat.}\text{ Ni/ Zn reductant}} CH_4 \qquad (2)$$

$$CO_2 + H_2O \xrightarrow[\text{Hydrothermal condition}]{\textit{Cat.}\text{ Cu/ Fe reductant}} HCOOH \qquad (3)$$

This work: Hydrothermal conversion of CO_2 into CH_3OH (first example reported).

$$CO_2 + H_2O \xrightarrow[\text{Hydrothermal condition}]{\textit{Cat.}\text{ Cu/ Zn reductant}} CH_3OH \qquad (4)$$

Scheme 1. Equations.

Here, we focused our attention in the conversion of CO_2 into methanol under hydrothermal conditions (Eq. (4)). In this process, water acts not only as an excellent solvent, but also as a source of hydrogen generated by reduction of metal reductants [38], so it would be advantageous to avoid the use of gaseous hydrogen, which is not easy to obtain with less energy cost, as reducing agent to the reaction system. Among transition metals we investigated, Cu catalyst showed significant activity, which Zn acts as an efficient reductant for methanol formation. Therefore, Zn and Cu, two commercially available and inexpensive metals, were chosen to be a reductant and a catalyst under the hydrothermal reactions. To the best of our knowledge, there has been no example for production of methanol from CO_2 over Cu as a catalyst and Zn as a reductant under hydrothermal reaction conditions (Scheme 1).

2. Experimental

2.1. Experimental materials

In this study, $NaHCO_3$ was used as the source of CO_2 to simplify the experiments. Experiments were conducted using a batch reactor system and the schematic drawing can be found elsewhere [39]. The reactor vessel was made of a piece of stainless steel 316 tubing (9.525 mm (3:8 in.) o.d., 1-mm wall thickness and 120-mm long) with end fittings; one was a Swagelok cap and the other was a valve made by Autoclave Engineers Inc. with a reducing union, providing the inner volume of 5.7 ml.

2.2. Experimental procedure

A typical experimental procedure is as follows. Firstly, the desired amount of different concentrations of HCl solution was loaded into the reactor, then Cu-powder (catalyst), Zn-powder (reductant), $NaHCO_3$ (CO_2 source) were loaded into the reaction chamber in sequence to avoid the quick reaction with HCl and the reactor was sealed. The reactor was put into the salt bath, which had been preheated to the desired temperature (250–350 °C). During the reaction, the reactor was shaken while being kept horizontally to enhance the mixture and heat transfer. After the desired reaction time, the reactor was taken out of the salt bath and put into a cold water bath to quench the reaction. The reaction time was defined as the duration the reactor was kept in the salt bath. Filling ratio was defined as the ratio of the volume of the solution put into the reactor and the inner volume of the reactor.

2.3. Analytical methods

After the reactions, the gas was collected and analyzed by gas chromatography equipped with thermal conductivity detector (GC/TCD). The remaining reaction mixture was filtered, and then the precipitate was dried in isothermal oven at 70 °C for 24 h after washing with distilled water. The liquid sample analyzed with high performance liquid chromatography (HPLC), GC-FID, the precipitate was determined by X-ray diffractometer (XRD).

3. Results and discussion

Initially, we screened the reaction conditions for the hydrothermal conversion of CO_2 into methanol. The reaction was carried out with 2.0 M NaOH at 350 °C for 2 h in the presence of 70 mmol Cu and 60 mmol Zn in H_2O (water filling: 50%). It was found that no methanol formation was observed in the presence of NaOH, while the reaction of CO_2 proceeded to give desired methanol in the presence of HCl. Therefore, we continued to optimize the initially reaction conditions for the formation of methanol from CO_2.

3.1. The effect of Cu on methanol yields

First, we carried out the experiments with 2.0 M HCl at 350 °C for 2 h in the presence of 70 mmol Cu and 60 mmol Zn in H_2O (water filling: 50%) to examine the effect of Cu and Zn in hydrothermal reaction. After the hydrothermal reaction, solid residual was analyzed by XRD, as illustrated in Fig. 1. Cu showed no apparent change and still existed in solid samples while Zn was converted into ZnO. Some unknown phases in the precipitates after hydrothermal reaction were also observed. It is just speculative for some unknown phases to be CuO or Cu_2O according to limited experimental data. From the results, it is clarified that Zn acts as a reductant, and Cu has catalytic activity for reduction of CO_2 into methanol as a catalyst.

Effect of Cu amount on the formation of methanol from CO_2 was performed at 350 °C for 2 h with the different ratios of $Zn/NaHCO_3$. The results are shown in Fig. 2. The profile of the reaction of CO_2 monitored by HPLC, indicated that the yield of methanol increased by changing Cu amount from 20 to 70 mmol in all cases. Furthermore, the use of ratio of $Zn/NaHCO_3 = 1:1$ gave higher yield of methanol as compared to ratio of $Zn/NaHCO_3 = 1.5:1$. A small increase on the yield of methanol was observed in the presence of Cu amount from 20 to 40 mmol. Interestingly, the Cu catalyst showed significantly catalytic activity for the methanol production and the yields of methanol increased as Cu amount increased

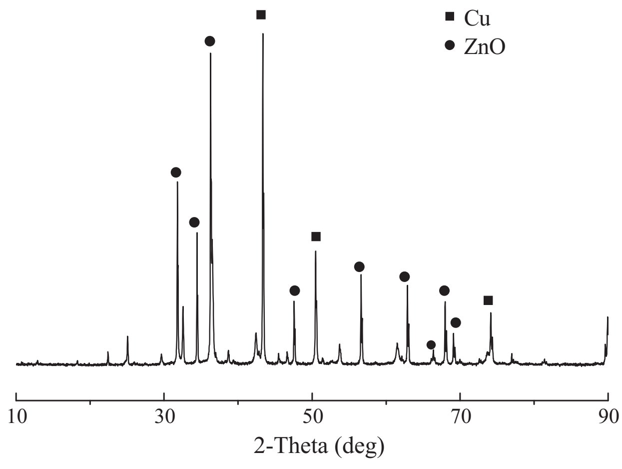

Fig. 1. The XRD pattern of precipitates after hydrothermal reaction (*T*: 350 °C; time: 2 h; Cu: 70 mmol; Zn: 60 mmol; $NaHCO_3$: 40 mmol; HCl: 2.0 M; water filling: 50%).

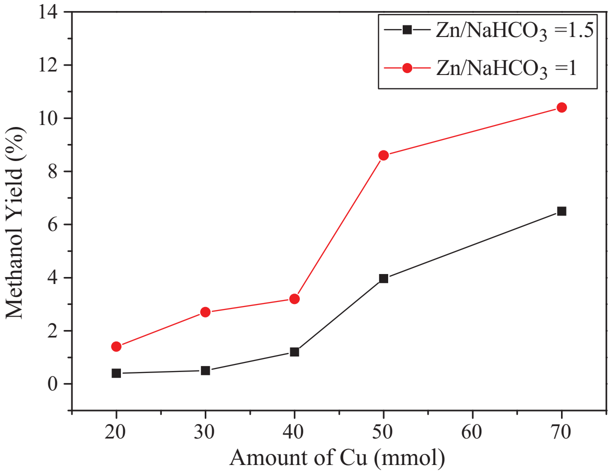

Fig. 2. Effect of amount of Cu on the yields of methanol (*T*: 350 °C; time: 2 h; Zn: 60 mmol; $NaHCO_3$: 40 mmol (or 60 mmol); HCl: 2.0 M; water filling: 50%).

from 40 to 70 mmol to respectively reach the maximum yields of 6.5% and 10.4% for methanol. The highest yield of methanol was obtained at 2 h when Cu (70 mmol) was added in the case of ratio of $Zn/NaHCO_3 = 1:1$.

3.2. The effect of HCl concentration on methanol yields

To examine the effect of concentration of HCl on yield of methanol, experiments were carried out by varying HCl concentration from 0 to 3 M at 350 °C for 2 h in the presence of 50 mmol Cu and 60 mmol Zn. The results are shown in Fig. 3, the yield of methanol remarkably increased as the concentration of HCl increased from 0 to 2.0 M. Between the HCl concentration of 0.5 M and 1.2 M, the yield of methanol was almost constant. The yield respectively reached a maximum value of 4.2% for methanol at an HCl concentration of 2.0 M. The yield was decreased drastically with the further increase of HCl concentration after attaining a peak level at the concentration of 2.0 M. Probably, it is because of the catalyst deactivation caused by chlorine. It has been reported that a trace of chlorine can lead to a great loss of the activity of Cu-based catalyst [5]. The optimum HCl concentration was 2.0 M to achieve the maximum yield of methanol from CO_2. The present study indicated that HCl concentration had a greater effect on the yield of methanol under hydrothermal conditions.

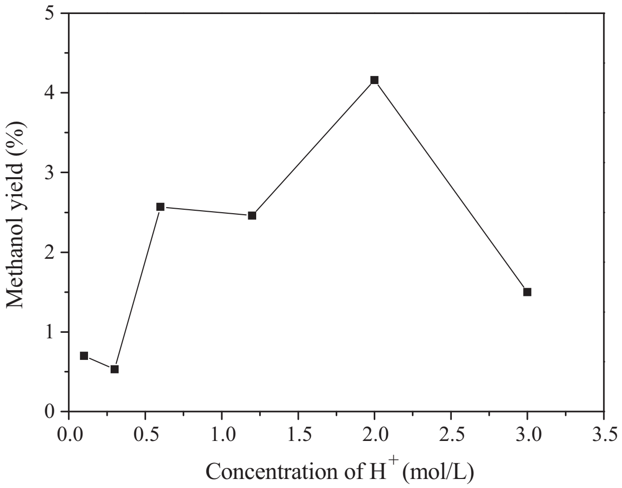

Fig. 3. Effect of concentration of HCl on the yield of methanol (*T*: 350 °C; time: 2 h; Cu: 50 mmol; Zn: 60 mmol; $NaHCO_3$: 40 mmol; water filling: 50%).

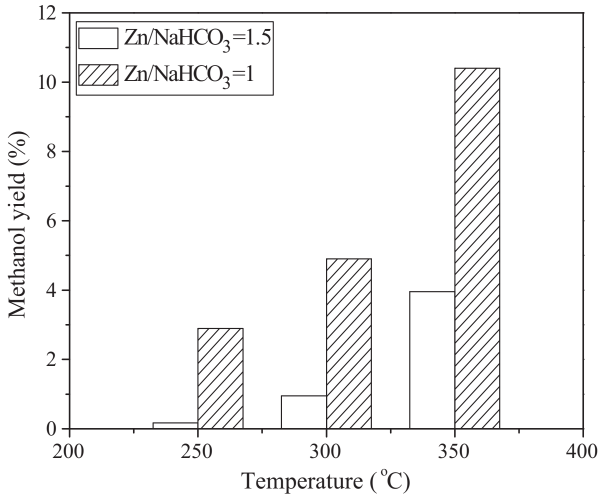

Fig. 4. Effect of temperature on the yield of methanol (time: 2 h; Cu: 50 mmol; Zn: 60 mmol; $NaHCO_3$: 40 (or 60) mmol; water filling: 50%; HCl: 2.0 M).

3.3. The effects of reaction temperature and time on methanol yields

It is known that CO_2 has high thermodynamic stability and low reactivity. Therefore, high reaction temperature is favorable to conversion of CO_2. Experiments were performed to examine the effect of reaction temperature on the yields of methanol from CO_2 at different reaction temperatures from 250 to 350 °C for 2 h. The results in Fig. 4 showed that the yields of methanol remarkably increased as the temperature increased from 250 to 350 °C. The reaction temperature was 350 °C to achieve the maximum value of 10.4% methanol from CO_2, respectively. In addition, in the case of ratio of $Zn/NaHCO_3$, the ratio of $Zn/NaHCO_3 = 1:1$ gave higher yield of methanol as compared to ratio of $Zn/NaHCO_3 = 1.5:1$. It means that large amount of $NaHCO_3$ can improve the yield of methanol under hydrothermal conditions.

Experiments were performed by changing the reaction time from 1 to 6 h with Cu 70 mmol, Zn 60 mmol and HCl 2.0 M at 350 °C to examine the effect of reaction time. Variation of the yields of methanol is shown in Fig. 5. The time profile of the reaction of CO_2

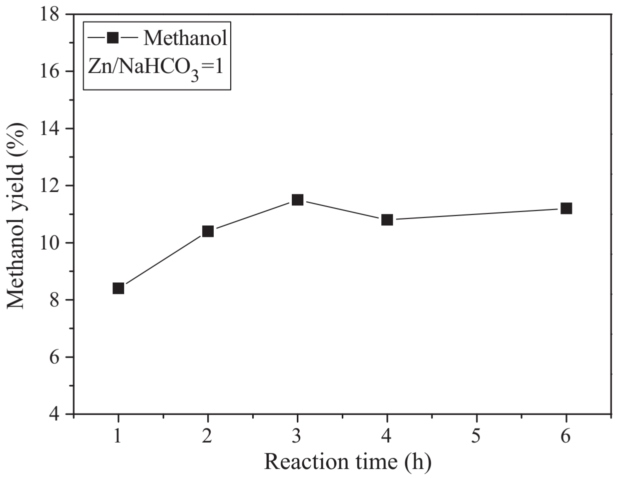

Fig. 5. Effect of reaction time on the yield of methanol (*T*: 350 °C; Cu: 70 mmol; Zn: 60 mmol; $NaHCO_3$: 40 (or 60) mmol; water filling: 50%; HCl: 2.0 M).

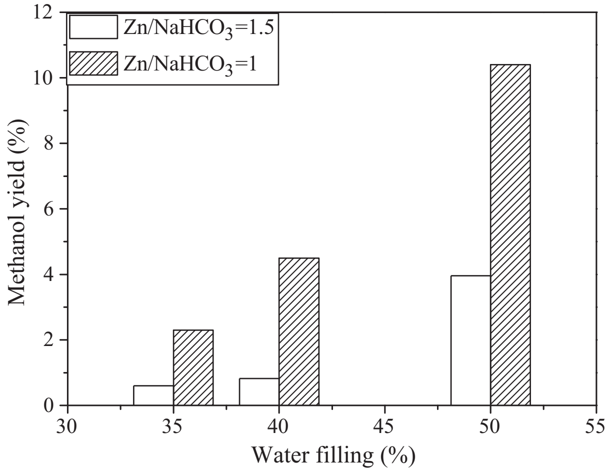

Fig. 6. Effect of water filling on the yield of methanol (*T*: 350 °C; Cu: 70 mmol; Zn: 60 mmol; $NaHCO_3$: 40 (or 60) mmol; HCl: 2.0 M).

indicated that the yields increased with reaction time increased in the first 3 h. The highest yield of methanol, 11.4%, was obtained when the reaction time was 3 h. The yield of methanol had a small change and decreased a little from 3 to 4 h. The formation of methanol reached to plateau after 4 h and the yield did not almost increase significantly even at a prolonged reaction time. Therefore, longer reaction time influenced little for the yield of methanol.

3.4. *The effect of water filling on methanol yields*

The effect of filling rate on the yield of methanol was also investigated at different water filling from 35% to 50% for 3 h when ratio of $Zn/NaHCO_3$ is 1:1 and 1.5:1. As shown in Fig. 6, the yields of methanol increased as the water filling increased from 35% to 50% in all cases. In the case of ratio of $Zn/NaHCO_3 = 1.5:1$, the yield of methanol increased from 0.6% (water filling: 35%) to 3.96% (water filling: 50%). The optimum water filling was 50% to achieve the maximum value of 11.4% methanol from CO_2. The ratio of $Zn/NaHCO_3 = 1:1$ showed higher yield than that of ratio of $Zn/NaHCO_3 = 1.5:1$.

4. Proposed mechanism for catalytic conversion of CO_2 into methanol in the presence of Cu

After reaction, the gas samples were collected for analysis by using GC–TCD. The experimental results are shown in Table 1. Only H_2 and CO_2 were detected in gas samples, and almost no CO and CH_4 was detected, which indicated that the reactions concerning CO and CH_4 did not occur. Compared with the two experiments, CO_2 was nearly used up in experiment 1.

The mechanism for methanol synthesis from CO_2/H_2 has been proposed by a number of researchers. For example, Fisher and Bell [40,41], have investigated the $Cu/ZrO_2/SiO_2$ catalysts by in situ infrared spectroscopy and suggested Cu supported on zirconia is exceptionally active for methanol synthesis from CO_2. Therefore, the addition of zirconia to Cu/SiO_2 progressively enhances the activity of the catalyst for methanol synthesis from CO_2. Liu [5] reported that ZnO can act synergistically with Cu to catalyze the synthesis of methanol, and ZnO was a good hydrogenation catalyst that activates hydrogen by heterogeneous splitting. According to these findings, the proposed path of reduction of CO_2 into methanol with Cu in the presence of Zn under hydrothermal conditions is illustrated in Fig. 7. Initially, CO_2 is adsorbed on ZnO, and subsequent undergoes stepwise hydrogenation to methoxide species, with atomic hydrogen being supplied by spillover from Cu. The final step is the hydrolysis of methoxide groups on ZnO to obtain methanol along with H_2O produced as a co-product of methanol formation.

Table 1
The percentage of H_2 and CO_2 for gas samples after the reactions.

	Experiment 1[a]	Experiment 2[b]
H_2	0.98	0.73
CO_2	0.031	0.253

[a] With reductant and catalyst.
[b] Without reductant and catalyst.

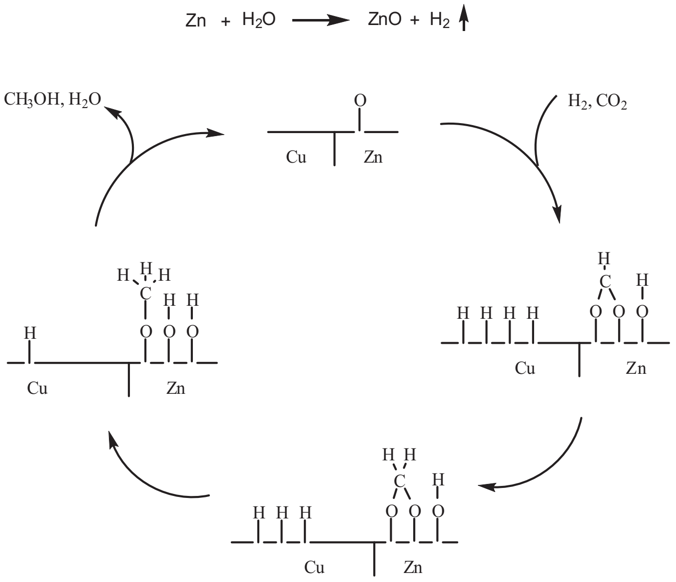

Fig. 7. Plausible mechanism for the formation of methanol from CO_2 over Cu.

5. Conclusions

A new chemical process for the conversion of CO_2 into methanol using Zn as a reductant and Cu as a catalyst in mild hydrothermal conditions has been developed. The effect of various experiment parameters was studied and the methanol yield of 11.4% was obtained at 350 °C for 3 h with Cu 70 mmol, Zn 60 mmol, water filling of 50% and HCl 2.0 M. The proposed mechanism for the formation of methanol from CO_2 under hydrothermal conditions was investigated. The present study is not only helpful for future practical application in controlling the global “Green-house Effect”, but also useful for alternative fuels or carbon resources.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21077078), the National High Technology Research and Development Program of China (863 program; No. 2009AA063903), The Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

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