Multifunctional catalyst of Cu/ZnO and molecular sieve for low temperature CO₂ conversion to methanol

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Abstract Carbon dioxide (CO₂) conversion to methanol is a promising way to mitigate CO₂ emission. The Cu/ZnO catalyst applied with molecular sieves was tested on alcohol assisted methanol synthesis at 423 K and 5 MPa. The Cu/ZnO was synthesized by coprecipitation at optimal parameters (precipitation temperature = 333 K, pH = 8) in two different aging time (30min and 1h). The formation of Cu/ZnO was confirmed by XRD technique. The physiochemical properties of Cu/ZnO were analysed by SEM-EDX, N₂-adsorption and desorption, and H₂-TPR. The Cu/ZnO_1h with a longer aging time showed a larger specific surface area (100.58 m²/gcat) and well dispersion. The effect of molecular sieve was investigated. The molecular sieve only adsorbed the target compounds and did not involve as catalyst in the reaction. Methanol yield increased from 8.5% to 33.6% when Cu/ZnO was loaded with molecular sieve 3Å. The adsorption of water shifted the reaction equilibrium toward to more methanol yield. In contrast, when Cu/ZnO with molecular sieve 5Å was used, methanol yield decreased to 4%. It was likely that methanol product was adsorbed by molecular sieve 5Å and was separated from ethyl acetate which is a by-product.

1. Introduction

Now a day, carbon dioxide emission is an important concern. Carbon dioxide as greenhouse gas cause the greenhouse effect that make the atmosphere temperature increasing. Therefore, the strategy of carbon dioxide collection and utilization is now being interested by many industrial fields. One way which can mitigate carbon dioxide emission is the carbon dioxide conversion to high valuable product such as methanol.

Methanol is a primary feedstock of many chemical productions such as formaldehyde, acetic acid, dimethyl ether, dimethyl carbonate, and methyl tertiary butyl ether (MTBE). World consumption of methanol is 65 million tons per year [1]. Normally, methanol can be produced from various methods. Methanol synthesis can be synthesized from syngas (CO+H₂) as in equation (1). Moreover, methanol can be synthesized from CO₂ hydrogenation which is consist of CO₂-rich methanol synthesis and reverse water gas shift reaction as in equation (2)-(3) [2], [3].

\[
\begin{align*}
\text{CO} + 2\text{H}_2 & \rightarrow \text{CH}_3\text{OH} \quad \Delta H_{298} = -90.97 \text{ kJ/mol} \\
\text{CO}_2 + 3\text{H}_2 & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_{298} = -49.43 \text{ kJ/mol} \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298} = 41.39 \text{ kJ/mol}
\end{align*}
\]
The commercial Cu/ZnO catalyst used in methanol synthesis process is active at high temperature 523-573 K. Hydrogenation of CO or CO₂ is a highly exothermic reaction that thermodynamically favors in low temperature range. The equilibrium conversion of CO₂ is therefore low at high synthesis temperature. To increase the equilibrium conversion of CO₂, operations at high pressure 5-10 MPa are required. These conditions result in energy-intensive process. Therefore, the low temperature methanol synthesis method was initially suggested by Tsubaki et al [4], [5]. Alcohol is added as both catalytic solvent and intermediate in alcohol-assisted methanol synthesis. The reaction pathway is changed, presented in equations (4)-(7). The reaction can occur at lower operating temperature and pressure (423-443 K and 3-5 MPa) compared with conventional hydrogenation of CO₂ (523-573 K and 5-10 MPa).

\[
\begin{align*}
\text{CO}_2 + \frac{1}{2}\text{H}_2 & \rightarrow \text{Cu} + \text{HCOOCu} & \quad (4) \\
\text{HCOOCu} + \text{ROH} & \rightarrow \text{HCOOR} + \text{CuOH} & \quad (5) \\
\text{HCOOR} + 2\text{H}_2 & \rightarrow \text{ROH} + \text{CH}_3\text{OH} & \quad (6) \\
\text{CuOH} + \frac{1}{2}\text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{Cu} & \quad (7)
\end{align*}
\]

Even though the alcohol-assisted low-temperature methanol synthesis can occur at lower operating temperature and pressure, there are many by-products occurring in this reaction due to dehydrogenation of alcohol. When ethanol is used as a solvent in this reaction, the dehydrogenation of ethanol forms an ethyl acetate, as presented in equation (8) [6], [7] at same operating temperature during low-temperature methanol synthesis. Moreover, ethyl acetate can react with methanol in transesterification to form methyl acetate, as presented in equation (9) [8].

\[
\begin{align*}
2\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + 2\text{H}_2, \Delta H_{298} = 25.02 \text{ kJ/mol} & \quad (8) \\
\text{CH}_3\text{OH} + \text{CH}_3\text{COOC}_2\text{H}_5 & \rightarrow \text{CH}_3\text{COOCH}_3 + \text{C}_2\text{H}_5\text{OH}, \Delta H_{298} = -0.195 \text{ kJ/mol} & \quad (9)
\end{align*}
\]

In Khunathorncharoenwong et al. work, the simulation of alcohol assisted methanol synthesis process was done and compared with the conventional methanol synthesis process. Effect of separation method is studied in the work [9]. The result shows that the profitability index of the process is still lower than that of the conventional process mainly due to the cost involving in purification process. Even though the cost of supplied energy in reaction part decreases and CO₂ conversion per pass increases, the cost of product purification increases due to by-product formation. The work concludes that catalyst development and product purification can play important role. Therefore, the strategy to improve catalyst which can increase methanol productivity or improve product purification part in alcohol assisted methanol synthesis is needed for further development.

There is a report on enhancing the methanol productivity in alcohol assisted low temperature methanol synthesis by adsorption of water with molecular sieve 3Å [10]. The result shows that the catalyst is most effectively utilized, when the larger amount of molecular sieve is used. This adsorbent is popular for hydration of many organic compounds such as alcohols, ethers, and esters [11], [12] because of the constant size pore lead to selectively adsorb water molecules which are smaller than its pore size. It is also reported that molecular sieve 5Å selectively adsorbs methanol [13], but ethyl acetate is not adsorbed [14]. Therefore, these adsorbents could be applied in this study.

In this study, ethanol is used in the alcohol assisted methanol synthesis because the better catalytic activity than other 1-alcohols [5], [1]. Molecular sieve 3Å can adsorb water to enhance the reaction. Molecular sieve 5Å is reported that selectively adsorbs methanol. It might be used to separate methanol and by-product such as ethyl acetate. Therefore, effect of addition of molecular sieve was investigated.
2. Experimental

2.1. Preparation of catalyst
First, The Cu/ZnO catalyst was synthesized by Co-precipitation method that Copper(II)nitrate (Cu(NO₃)₂·3H₂O, Sigma-Aldrich, ≥98%) and Zinc(II)nitrate (Zn(NO₃)₂·6H₂O, Sigma-Aldrich, ≥99%) were used as precursors with Cu/Zn ratio at 1 and Sodium carbonate (Na₂CO₃, Sigma-Aldrich, ≥99.5%) was a precipitating agent. 1M copper(II)nitrate solution, 1M zinc(II)nitrate solution and 1.5M sodium carbonate solution were prepared by dissolution the solid materials in water as solvent. The volumes of each solution were calculated for 5g of catalyst. Then, all solutions were added dropwise into 600ml deionized water which was stirred by magnetic stirrer. After completing addition of precursors solutions, the precipitation was allowed to proceed for 30 min and 1 h at controlled temperature (333.15 K), Stirred velocity (600 rpm), and pH value (8). The precipitated product was washed by deionized water in order to remove sodium ion until the electrical conductivity was below 50 μS/cm². and then centrifuged to separate the precipitated product from slurry. After that, the precipitated products were dried at 383.15 K for 24 h and calcined in air at 623.15 K for 1 h with heating rate of 10 K/min. In this step, the last product is CuO/ZnO catalyst.

2.2. Preparation of molecular sieve
The molecular sieve 3Å (Sigma-Aldrich, 8-12 mesh) and molecular sieve 5Å (Sigma-Aldrich, 8-12 mesh) were used in this study. First, the adsorbent was crushed by pestle and mortar to powder and sieved to 150-400 μm. Then, it was activated by heat treatment at 523.15 K for 8 hr with heating rate of 10 K/min in order to eliminate adsorbed water in molecular sieve pore. After that, the treated molecular sieve was kept in a desiccator.

2.3. Characterization of catalyst and molecular sieve
The Cu/ZnO catalyst’s crystallite phases were investigated by X-ray diffraction (XRD, Bruker AXS, D8 Advance) using Cu-Kα (λ = 1.5406 Å). The XRD pattern of catalyst was scanned 2θ from 20 to 80° with a scanning rate of 2°-min⁻¹. Then, the Cu/ZnO catalyst’s crystallite size (d) was determined using Scherrer’s equation as presented in equation (10).

\[ d = \frac{0.9λ}{β_{FWHM}\cos(θ)} \]  

where, λ is wavelength of X-ray, β_{FWHM} is the full width for the half-maximum (FWHM) intensity peak, and θ is the diffraction angle.

The surface morphology of catalyst and metal dispersion on support were observed by Scanning electron microscopy-energy dispersive spectroscopy (SEM, Hitachi, S3400N, and EDX, EDAX, Apollo x) image. The Brunauer-Emmett-Teller (BET) surface area of catalyst was determined using nitrogen adsorption-desorption (Micromeritics, ASAP 2020). The reduction temperature of catalyst was characterized with Temperature Program of Reduction (TPR, Micromeritics, ChemiSorb 2750) by adding catalysts in a flow reactor. First, catalysts were heated to 523.15 K in N₂ atmosphere to dry the sample. After that, the temperature was programmed from 303.15 K to 773.15 K with heating rate of 10 K-min⁻¹ under 25 ml/min flow of 10%H₂/Ar.
2.4. Alcohol assisted methanol synthesis
About 3 g of CuO/ZnO catalyst and 3 g of treated molecular sieve were loaded into reactor. The synthesized catalysts were firstly metal oxide form. Therefore, reduction of CuO/ZnO to Cu/ZnO was required. H2 gas was passed to a reactor with controlled volumetric flow to be 30 ml/min by mass flow controller. After that, the reactor temperature was raised to reduction temperature (473.15 K) with heating rate 2 K/min and hold at this temperature for 3 h. Only CuO was reduced at this temperature because ZnO could not be reduced at temperature below 573.15 K [15], [16]. The reduced form of Cu/ZnO catalyst was still in the reactor. 50 ml ethanol as catalytic solvent was added into the reactor. After that, CO2 and H2 were compressed into the reactor with CO2 and H2 at the molar ratio 1:3, controlled using mass flow controllers until the pressure of reactor reached 3.6 MPa. The temperature was ramped up to 423.15 K while the pressure was increased to 5 MPa at 423.15 K during the heating process. Vigorous stirring was applied at 1000 rpm for 24 h.
After the reaction was complete, the reactor was left to cool down to room temperature. The liquid product was collected. The SHIMADZU Nexis GC-2030 gas chromatography with a flame ionization detector (FID) was used to analyse the composition of liquid product. A mid-polar SH-RtxTM – 624 column was used. Helium gas was used as carrier gas and was fed with flowrate 1.88 ml/min. the product was analysed in temperature program mode with an initial temperature 323.15 K then raised up to 503.15 K. After that, the composition of product was determined using the external standard method. Finally, the conversion of CO2, yield of methanol, and selectivity of methanol were calculated by equation (11)-(13).

\[
%\text{CO}_2 \text{ conversion} = \frac{\text{Mole of converted CO}_2}{\text{Mole of feeding CO}_2} \times 100 \quad (11)
\]

\[
\text{Yield of methanol} = \frac{\text{Mole of methanol product}}{\text{Mole of feeding CO}_2} \times 100 \quad (12)
\]

\[
\text{Selectivity of methanol} = \frac{\text{Mole of methanol product}}{\text{Mole of all products}} \times 100 \quad (13)
\]

3. Result and discussion
3.1 Catalyst characterization
In catalyst preparation step, the catalyst was initially aged for 30 min in coprecipitation step. The synthesized catalyst was tested in alcohol assisted methanol synthesis and was characterized. The result showed low catalytic activity. Jeong et al. [17] reported that aging time in coprecipitation step significantly affected to catalytic activity of Cu/ZnO catalyst. Cu/ZnO with aging time 5 h exhibited the highest catalytic activity, but there are some researches still aged the catalyst for 1 h [1], [8]. Therefore, the effect of aging time in catalyst preparation is still uncertain. In this work, aging time of 1 h was selected.

First, X-ray diffraction technique is used for confirmation of formation of Cu/ZnO catalyst. The XRD pattern of catalyst exhibited peak of CuO (111) at 20 = 39°, ref. JCPDS 45-0937 and ZnO (101) at 20 = 36°, ref. JPDS card no. 79-0206, respectively for both Cu/ZnO with aging time 30 min and Cu/ZnO with aging time 1 h as shown in Figure 1. The Scherrer’s equation was used for calculation of crystallite sizes which were reported in Table 1. The crystallite sizes of both Cu/ZnO did not show significantly different value, but it slightly decreased when aging time increased. The BET surface areas of both Cu/ZnO which were investigated by N2-adsorption and desorption well corresponded with crystallite sizes that small crystallite size showed high BET surface area. Consequently, the BET surface area of Cu/ZnO with aging time 1 h (100.58 m²/gcat) was higher than another one (81.66 m²/gcat).
In temperature program of reduction (TPR), both CuO/ZnO had low reduction temperature (approximately 473 K) comparing with pure bulk CuO that had to be reduced at 613.15 K [18], [19]. The ZnO as a support helped the dispersion of Cu particle leading to great reducibility or low reduction temperature [20].

**Table 1.** Crystalline size, Specific surface area and reducing temperature of the synthesized catalyst.

| Catalyst            | Crystalline size (nm) | Specific surface area (m²/gcat) | Reducing temperature (K) |
|---------------------|-----------------------|---------------------------------|--------------------------|
|                     | CuO                  | ZnO                             |                          |
| CuO/ZnO_30min       | 5.27                 | 7.23                            | 81.66                    | 476.95                   |
| CuO/ZnO_1h          | 5.16                 | 6.85                            | 100.58                   | 472.65                   |

SEM images of both CuO/ZnO were investigated the crystalline morphology of CuO/ZnO as present in Figure 2. Both CuO/ZnO exhibited a mix crystallite phase of rod-like structure, plate-like structure, and irregular shape. Some authors reported that a rod-like structure as zincian malachite (Cu,Zn)2(OH)2CO3) [8] was a relevant precursor [21], [22]. In the other hand, some authors reported that a plate-like structure as aurichalcite (Cu,Zn)5(OH)6(CO3)2 was a phase in zinc-rich sample [8] and was a precursor for active Cu/ZnO catalyst [23], [24].
3.2 Catalytic activity of catalyst

Both catalytic activities of Cu/ZnO catalysts were tested on alcohol-assisted methanol synthesis reaction at 423.15 K and 5 MPa with ethanol as solvent for 24 h. The result showed that methanol yield of Cu/ZnO with aging time 1 h was 8.5% higher than Cu/ZnO with aging time 30 min. The high specific surface area and well dispersed catalyst provided more catalytic activity.

Figure 2. SEM image of synthesized catalyst: (a) CuO/ZnO_30min (b) CuO/ZnO_1h.
Table 2. %CO₂ conversion, methanol selectivity, and methanol yield of Cu/ZnO catalysts.

| Catalyst       | %CO₂ conversion | Methanol selectivity | Methanol yield |
|----------------|-----------------|----------------------|---------------|
| Cu/ZnO_30min   | 8.3%            | 55.7%                | 4.6%          |
| Cu/ZnO_1h      | 18.4%           | 46.1%                | 8.5%          |

3.3 Effect of addition of molecular sieve

In this experiment, the effect of addition of molecular sieve was investigated including molecular sieve 3Å and molecular sieve 5Å. These adsorbents are crystalline aluminosilicates compound which are a 3-dimension network of alumina and silica tetrahedra [25]. The orderly orientation of molecular sieve has an advantage leading to uniform pore size. Therefore, molecular sieves selectively adsorb molecules that are smaller than their pore size. The different cations in molecular sieve crystal structure lead to different pore size of molecular sieve 3Å (pore size 3Å, potassium ions) and 5Å (pore size 5Å, calcium ions) [26]. The surface morphology of molecular sieve were shown in Figure 3.

![SEM images of molecular sieves](image)

**Figure 3.** SEM images of molecular sieves (a) molecular sieve 3Å (b) molecular sieve 5Å.

The role of molecular sieves was expected to only to adsorb target compounds and did not involve as catalyst in the reaction. To prove this, 2g of molecular sieves were tested on alcohol assisted methanol synthesis with ethanol as solvent at 423 K and 5 MPa for 2 hr. The catalytic activities of molecular sieves on this reaction were shown in Table 3. The result showed that molecular sieves could not catalyze the carbon dioxide hydrogenation to methanol, both molecular sieve 3Å (MS 3Å) and molecular sieve 5Å (MS 5Å). Therefore, this result confirmed that Cu/ZnO catalyst acted as catalyst and molecular sieves acted as adsorbent in this reaction.

Table 3. %CO₂ conversion, methanol selectivity, and methanol yield of molecular sieves.

|        | %CO₂ conversion | Methanol selectivity | Methanol yield |
|--------|-----------------|----------------------|---------------|
| MS 3Å  | 0               | 0                    | 0             |
| MS 5Å  | 0               | 0                    | 0             |
In this study, Cu/ZnO with aging time 1h was chosen for the reaction test. The alcohol-assisted methanol synthesis over 3g of Cu/ZnO catalyst without an adsorbent was tested with ethanol as promoted solvent at 423 K and 5 MPa. Addition of ethanol promoted reaction to occur at lower operating conditions. Ethanol play an important role as catalytic solvent and intermediate in this reaction leading to change of reaction pathway. The result showed that methanol yield was 8.5 % under this condition. Next, the 3g of molecular sieve 3Å was applied with 3g of Cu/ZnO catalyst in this reaction. Methanol yield significantly increased from 8.5% to 33.6%. This result could be explained by Le Chatelier’s principle. Water is also a product in the overall methanol synthesis from carbon dioxide hydrogenation. The disappearance of water helped shifting the equilibrium of reaction toward more products. Moreover, water was a by-product that can block active site of the catalyst and accelerate the sintering of Cu particles [27]. Therefore, the removal of water helped improving catalytic activity. Finally, 3g of molecular sieve 5Å was applied with 3g of Cu/ZnO catalyst. The result showed the lowest methanol yield 3.7% when compared with other samples even if the weight of Cu/ZnO catalyst was fix in every experimental batch. It was implied that methanol was adsorbed by molecular sieve 5Å.

| Table 4. %CO₂ conversion, methanol selectivity, and methanol yield of Cu/ZnO catalyst with molecular sieves. |
|---------------------------------------------------------------|
| %CO₂ conversion | Methanol selectivity | Methanol yield |
| Cu/ZnO          | 18.4%         | 46.1%        | 8.5%          |
| Cu/ZnO_MS 3Å    | 62.3%         | 53.9%        | 33.6%         |
| Cu/ZnO_MS 5Å    | 34.5%         | 10.8%        | 3.7%          |

It should be noted that ethyl acetate was formed from ethanol by dehydrogenation of ethanol. This by-product increased when the temperature overshoot to 433-443 K occurred during the experimental batch which molecular sieves were used. The reason of temperature overshoots might be the nature of adsorption that it was an exothermic reaction.

However, the adsorption of methanol by molecular sieve 5Å could not guarantee that methanol can be separated from ethyl acetate. The desorption of molecular sieve 5Å after used in reaction should be further studied. Moreover, in case of 5Å molecular sieve, separation of methanol instead by-product might not be the great option when commercial scale is considered because methanol capacity can be larger than by-product. Both capital and operating cost relating adsorbent material and regeneration unit. The selective adsorbent of by-product such as ethyl acetate should be further investigated.

4. Conclusion
CuO/ZnO catalysts were successful synthesis by coprecipitation. The Cu/ZnO with aging time 1 h showed higher catalytic activity because high surface area (100.58 m²/gcat) and well dispersion on ZnO support. It was selected to use in studying effect of addition of molecular sieve. The role of molecular sieves as adsorbents was proved by testing on alcohol assisted methanol synthesis reaction without Cu/ZnO. Methanol yields of both molecular sieve 3Å and molecular sieve 5Å were 0%. The results confirmed that molecular sieve could not catalyse this reaction. The alcohol assisted low temperature methanol synthesis was improved by addition of molecular sieve. Molecular sieve 3Å was applied with Cu/ZnO catalyst to enhance the methanol yield. Addition of molecular sieve 3Å showed that the methanol yield was improved from 8.5% to 33.6%. Disappearance of water shifted the reaction equilibrium toward to more methanol and unblocked active site. Methanol yield decreased to 3.7% when molecular sieve 5Å was applied with Cu/ZnO catalyst. It was implied that methanol was separated from ethyl acetate.
Acknowledgement
The acknowledgment is made to Malaysia-Thailand Joint Authority (MTJA), Research Cess Fund and Thailand Science Research and Innovation (TSRI). T. Boonamnuay thanks the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for the student scholarship support. P. Kim-Lohsoontorn thanks to “Research Chair Grant” National Science and Technology Development Agency (NSTDA).

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