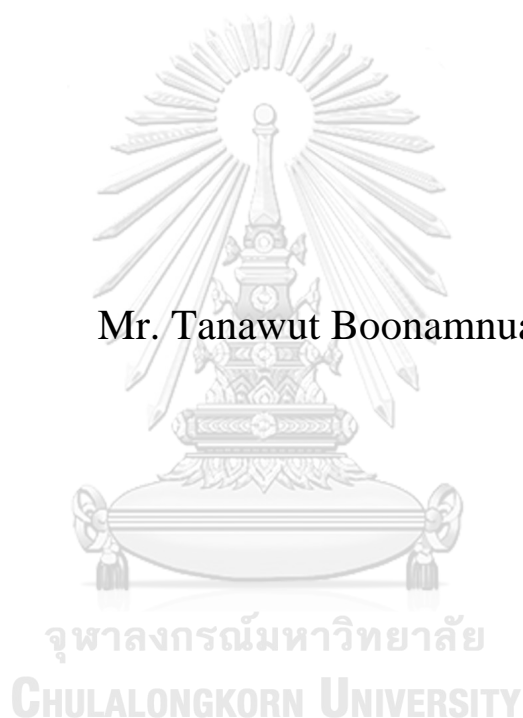# EFFECT OF MOLECULAR SIEVE ADDITION ON METHANOL SYNTHESIS FROM CO$_2$ AND H$_2$ THROUGH ALCOHOL ASSISTED METHOD OVER Cu/ZnO CATALYST

Mr. Tanawut Boonamnuay

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
FACULTY OF ENGINEERING
Chulalongkorn University
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ผลของการเติมโมเลกูลาร์ซีฟที่มีต่อปฏิกิริยาการสังเคราะห์เมทานอลจากคาร์บอนไดออกไซด์และ
ไฮโดรเจนที่มีวิธีการใช้แอลกอฮอล์เป็นตัวช่วยบนตัวเร่งปฏิกิริยาคอปเปอร์ซิงค์ออกไซด์

นายธนวุฒิ บุญอำนวย

Thesis Title	EFFECT OF MOLECULAR SIEVE ADDITION ON METHANOL SYNTHESIS FROM CO_2 AND H_2 THROUGH ALCOHOL ASSISTED METHOD OVER Cu/ZnO CATALYST
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ธนวุฒิ บุญอำนวย : ผลของการเติมโมเลกูลาร์ซีฟที่มีต่อปฏิกิริยาการสังเคราะห์เมทานอลจาก
คาร์บอนไดออกไซด์และไฮโดรเจนที่มีวิธีการใช้แอลกอฮอล์เป็นตัวช่วยบนตัวเร่งปฏิกิริยาคอป
เปอร์ซิงค์ออกไซด์. (EFFECT OF MOLECULAR SIEVE ADDITION
ON METHANOL SYNTHESIS FROM CO_2 AND
H_2 THROUGH ALCOHOL ASSISTED METHOD OVER
Cu/ZnO CATALYST) อ.ที่ปรึกษาหลัก : ภัทรพร คิม

ปฏิกิริยาการสังเคราะห์เมทานอลที่อุณหภูมิต่ำจากคาร์บอนไดออกไซด์และไฮโดรเจนได้ดำเนินการ โดยมีเอทานอล
เป็นตัวทำละลายที่มีส่วนในการเร่งปฏิกิริยา วิธีการใช้แอลกอฮอล์เป็นตัวช่วยนี้ทำให้สามารถลดอุณหภูมิในการสังเคราะห์เมทา
นอลและส่งเสริมให้ผลได้ของเมทานอลดีขึ้น (35.8%) ที่อุณหภูมิดำเนินการ 150 องศาเซลเซียส (ความดัน 5 เมกะพาส
คาล, คอปเปอร์ซิงค์ออกไซด์เป็นตัวเร่งปฏิกิริยา) อย่างไรก็ตาม ก็ยังมีเอทิลอะซิเตทและน้ำเป็นผลิตภัณฑ์ร่วมที่เกิดจากปฏิกิริยา
ซึ่งผลิตภัณฑ์ร่วมเหล่านี้ไปทำให้เกิดเป็นสารผสมอะซิโอโทรปกับเมทานอล ซึ่งส่งผลให้กระบวนการแยกเมทานอลให้บริสุทธิ์
นั้นมีความยุ่งยากซับซ้อนมากยิ่งขึ้น ดังนั้นในงานวิจัยนี้ โมเลกุลาร์ซีฟถูกนำมาใช้ในการดูดซับสารผลิตภัณฑ์ร่วมเหล่านี้ โดย
ทำการศึกษาผลของชนิดโมเลกุลาร์ซีฟที่แตกต่างกัน (3A และ 5A) ซึ่งพบว่า โมเลกุลาร์ซีฟมีส่วนช่วยในการส่งเสริมให้ผล
ได้ของเมทานอลนั้นดีขึ้น โดยที่ผลได้ของเมทานอลจะดีที่สุด (42.6%) เมื่อมีการเติมโมเลกุลาร์ซีฟชนิด 3A เข้ามาช่วยใน
การดูดซับน้ำ นอกจากนี้ยังพบว่าโมเลกุลาร์ซีฟชนิด 5A สามารถที่จะแยกเมทานอลกับเอทิลอะซิเตทให้เมทานอลมีความบริ
สุทธิ์สูงได้ และผลของอุณหภูมิในการดำเนินการก็ยังได้ถูกศึกษาค้นคว้าอีกด้วย พบว่า การลดอุณหภูมิ จะทำให้ผลได้ของเมทา
นอลนั้นลดลง แต่การเลือกเกิดของเมทานอลนั้นเพิ่มขึ้น โดยที่อุณหภูมิที่มีความเหมาะสมที่สุดคือที่ 130 องศาเซลเซียส เป็น
จุดที่ทำให้ผลได้ของเมทานอล (30.6%) และการเลือกเกิดของเมทานอล (มากกว่า 98%) นั้นเป็นที่น่าพอใจ จึงสามารถ
สรุปได้ว่าการควบคุมอุณหภูมิและการใช้โมเลกุลาร์ซีฟสามารถช่วยส่งเสริมผลได้ของเมทานอลและการเลือกเกิดของเมทานอล
ได้

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สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต
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ปีการศึกษา	2563	ลายมือชื่อ อ.ที่ปรึกษาหลัก
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6270110221 : MAJOR CHEMICAL ENGINEERING

Tanawut Boonamnuay : EFFECT OF MOLECULAR SIEVE ADDITION ON METHANOL SYNTHESIS FROM CO_2 AND H_2 THROUGH ALCOHOL ASSISTED METHOD OVER Cu/ZnO CATALYST. Advisor: PATTARAPORN KIM

Low-temperature methanol synthesis from CO_2 and H_2 was carried out using ethanol as catalytic solvent. The alcohol-assisted method reduced synthesis temperature and enhanced methanol yield (35.8%) at 150 ºC (5.0 MPa, Cu/ZnO catalyst). However, ethyl acetate and water were generated as byproducts from the reaction. The byproducts formed azeotrope mixture with methanol and led to a complex product purification. Therefore, in this study, molecular sieves (MS) were introduced to adsorb the byproducts. The effect of different MS (3A and 5A) was studied. It was found that MS helped enhancing methanol yield. The highest methanol yield (42.6%) was obtained when adding MS_3A to adsorb water. The MS_5A could separate methanol and ethyl acetate, providing high methanol purity. The effect of operating temperature was also investigated. When reducing temperature, methanol yield decreased but methanol selectivity significantly increased. The optimum temperature was 130 ºC where the pleasant methanol yield (30.6%) and selectivity (>98%) were obtained. Controlling temperature and using MS could help enhance the yield and selectivity of methanol.

จุฬาลงกรณ์มหาวิทยาลัย

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Field of Study:	Chemical Engineering	Student's Signature	....
Academic Year:	2020	Advisor's Signature	....

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CHAPTER I

INTRODUCTION

1.1 Background

In recent, the rate of emission of carbon dioxide (CO_2) into atmosphere is increasing from human activities such as transportation, the combustion of fuel in industries. CO_2 is one gas which is a cause of greenhouse effect, Heat is contained in the atmosphere leading to the increment of temperature at the earth's atmosphere. Therefore, the trend to mitigate with CO_2 is interesting by many industries. The CO_2 collection and utilization are derived to 2 types. First, it is called "direct CO_2 utilization". CO_2 is used directly without conversion to other chemical products such as in Frozen food industry, Soft drink industry, etc. Another, it is called "CO_2 conversion", that CO_2 is converted to useful chemical products. In this research, CO_2 is converted to an important chemical product like methanol.

Methanol is a necessary chemical in chemical industry because it is a primary feedstock for other chemical products such as formaldehyde, MTBE, Dimethyl ether, acetic acid and other. Moreover, it can also be used as a transportation fuel or be blended with gasoline. The world consumption of methanol is high to 45.5 million tons per year [1]. Normally, methanol is produced from syngas ($CO + H_2$) by steam reforming of fossil fuel, which is an exhausted resource. Therefore, the production of methanol from CO_2 is interesting. Besides reduction of CO_2, it is an alternative way to produce methanol. Moreover, CO_2 is also a renewable resource.

The synthesis of methanol can be conducted from hydrogenation of CO or CO_2 at 250-300°C and 5-10 MPa over Cu-based catalyst that has a reverse water gas shift (RWGS) reaction as parallel reaction as in equations (1.1)-(1.3). In process, the commercial catalyst is $Cu/ZnO/AlO_3$ [2]. Methanol production from direct CO_2 conversion still has a problem that CO_2 hydrogenation is an exothermic reaction, but this reaction needs to operate at high temperature, which is disfavor for the reaction because catalyst is active at this condition and CO_2 is a stable gas [3],[4]. This conflict leads to low CO_2 conversion. To increase methanol yield, high pressure is applied to the process. Therefore, these reasons make this process to an energy intensive process.

Hydrogenation of CO to methanol
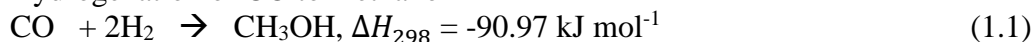
$$CO + 2H_2 \rightarrow CH_3OH, \Delta H_{298} = -90.97 \text{ kJ mol}^{-1} \quad (1.1)$$

Hydrogenation of CO2 to methanol and water

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H_{298} = -49.43 \text{ kJ mol}^{-1} \quad (1.2)$$

Reverse water gas shift reaction

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H_{298} = 41.39 \text{ kJ mol}^{-1} \quad (1.3)$$
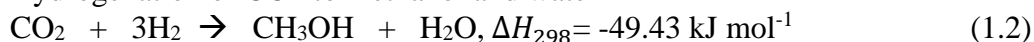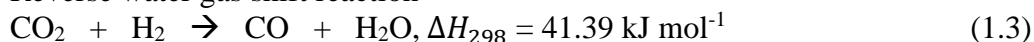
To solve the energy intensive problem, there are many researchers that attempt to decrease the operating conditions [5],[6],[7],[8]. One alternative is "alcohol assisted methanol synthesis" which is initially suggested by Tsubaki [8]. Alcohol is added as catalytic solvent and intermediate in the reaction. It changes reaction pathway and reduces operating conditions (150-170°C and 3-5 MPa). The alcohol assisted methanol synthesis step is suggested as in equations (1.4)-(1.7).

Alcohol assisted methanol synthesis reaction step .

$$CO_2 + 1/2H_2 \rightarrow Cu + HCOOCu \qquad (1.4)$$

$$HCOOCU + ROH \rightarrow HCOOR + CuOH \qquad (1.5)$$

$$HCOOR + 2H_2 \rightarrow ROH + CH_3OH \qquad (1.6)$$

$$CuOH + 1/2H_2 \rightarrow H_2O + Cu \qquad (1.7)$$
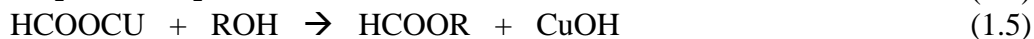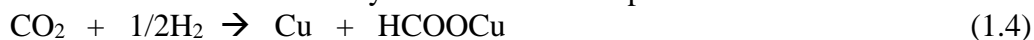
However, this methanol synthesis route still has a problem. Although it can reduce the operating conditions, there are by-products from addition of alcohol. In case ethanol, ethyl acetate will occur as by-product from dehydrogenation of ethanol as in equation (1.8) because this reaction can also be catalyzed by Cu-based catalyst [9],[10]. Moreover, ethyl acetate can react with methanol in transesterification reaction to methyl acetate as in equation (1.9) [11].

Dehydrogenation of ethanol

$$2C_2H_5OH \rightarrow CH_3COOC_2H_5 + 2H_2, \Delta H_{298} = 25.02 \text{ kJ mol}^{-1} \qquad (1.8)$$
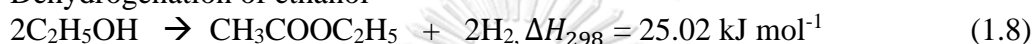
Transesterification of methanol and ethyl acetate

$$CH_3OH + CH_3COOC_2H_5 \rightarrow CH_3COOCH_3 + C_2H_5OH, \Delta H_{298} = -0.195 \text{ kJ mol}^{-1}$$
$$(1.9)$$

These by-products are an azeotropic mixture with methanol. Beside more purification units, it is hard to separate from methanol. 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 [12]. 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 CO_2 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 3A [13]. 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 [14],[15] 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 5A selectively adsorbs methanol, but ethyl acetate is not adsorbed [16]. This presents an opportunity to separate methanol from the byproducts, enhancing methanol selectivity. Up to date, there is no report on the effect of MS in low-temperature methanol synthesis from CO_2/H_2.

With an attempt in enhance both methanol yield and selectivity in alcohol-assisted methanol synthesis, the effect of Molecular sieve (MS) was investigated in this study. The type of MS (3A, 5A, and 3A mixed with 5A) and the ratio of catalyst to MS (1:1 and 2:1) were studied. The effect of operating temperature (100 °C, 130 °C, and 150 °C) was also determined.

1.2 Objective

1. To investigate the effect of molecular sieve addition with Cu/ZnO catalyst on alcohol assisted methanol synthesis

1.3 Scope of research

1. Cu/ZnO catalyst is synthesized by coprecipitation method with controlled pH value (8), precipitating temperature (60 ^{o}C), stirring velocity (600 rpm), and aging time (1 h). After that, precipitating product is calcined at 350 ^{o}C for 3 h. Then, calcined precursor is reduced in H_2 atmosphere at 300 ^{o}C for 3 h.
2. Cu/ZnO catalyst is characterized by techniques including XRD, SEM-EDX, N_2-physisorption, XPS, H_2-TPR and NH_3-TPD.
3. Molecular sieves are activated by heat treatment at 250 ^{o}C for 8 h. After that, they are kept in desiccator.
4. Methanol is produced by alcohol assisted methanol synthesis over Cu/ZnO enhanced by molecular sieves with CO_2:H_2 ratio 1:3 and ethanol as catalytic solvent at various temperature (100-150 ^{o}C) and 5 MPa for 24 h.
5. The effect of molecular sieve type including 3A, 5A and 3A+5A on alcohol assisted methanol synthesis is investigated.
6. The effect of catalyst/adsorbent ratio (2:1, and 1:1) on alcohol assisted methanol synthesis is investigated.

1.4 Expected benefits

1. Able to reduce the CO_2 emission which is a greenhouse gas.
2. Able to convert CO_2 to more valuable products in chemical industry such as methanol.
3. Able to synthesize catalyst which has high catalytic activity for alcohol assisted methanol synthesis.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Theory

2.1.1 Methanol and applications

Methanol is the smallest alcohol organic compound, which has a methyl group bonded with hydroxyl group. The molecular weight of methanol is 32.042 g mol^{-1} with chemical structure, CH_3OH. Physical properties of methanol are listed in Table 1. Methanol is a necessary chemical product from petrochemical industries with several applications. Methanol can be used as feedstock for other compounds, solvent, and fuel. 35% of produced methanol is consumed for formaldehyde production. Another percentage is produced acetic acid, methyl and vinyl acetate, methyl methacrylate, methylamines, methyl tertiary butyl ether (MTBE), fuel additives, and other compounds [1],[17], as present in Figure 1.
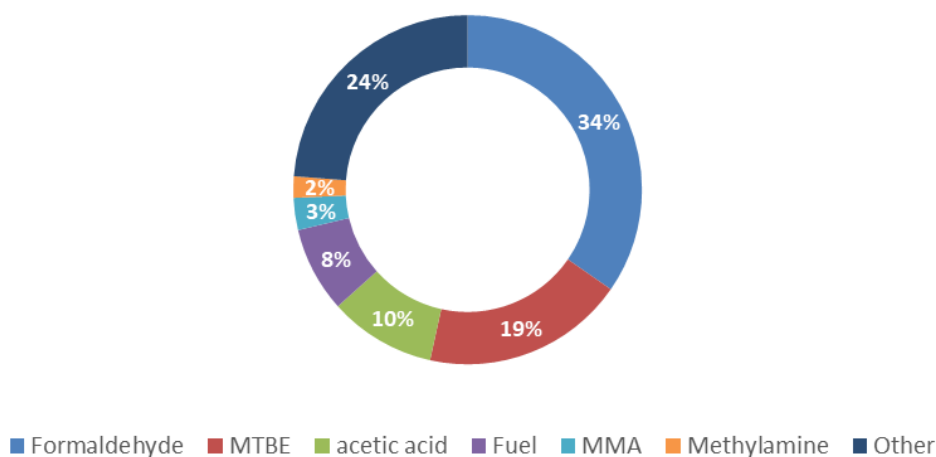
Figure 1 Chemical products from methanol.

Table 1 Physical properties of methanol.

Properties	Value
Molecular weight	32.04 g mol^{-1}
Density	0.791 g ml^{-1} at 25 $^{\circ}$C
Boiling point	64.7 $^{\circ}$C
Melting point	-98 $^{\circ}$C
Viscosity	0.544 cP at 25 $^{\circ}$C
Dielectric constant	33.0 at 20 $^{\circ}$C

In perspective application of methanol as fuel, also fuel additive. Methanol has several advantages for using as fuel. Even though energy density of methanol is 20.1 MJ kg^{-1} lower than gasoline for half (44.3 MJ kg^{-1}) [18], a high value of octane number of methanol suggested it as an appropriate fuel (108 for methanol, 95 for gasoline). The high-octane number means that the combustion is more complete compared to the low-octane number. It leads to reduction of CO and CO_2 emissions [18],[19],[20].

2.1.2 Methanol production

In recently, methanol is produced from synthesis gas or syngas, a mixture of carbon monoxide and hydrogen. Syngas can be produced from variety of feedstock including natural gas, coal, biomass. But it is mainly produced from fossil fuel (natural gas), which is an exhausted resourced. In methanol synthesis technologies, a methanol production process can be derived into 3 sections:
(1.) Synthesis gas production process
(2.) Synthesis gas conversion to methanol
(3.) Methanol purification

As remarked before, about 85% of world methanol production come from natural gas by steam reforming. Therefore, the methanol production process is derived to two step equations.
Steam reforming of methane to syngas
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (2.1)$$
Hydrogenation of CO to methanol
$$CO + 2H_2 \rightarrow CH_3OH \qquad (2.2)$$

The two reactors are required for the two main reactions to produce syngas and methanol. This conventional production will conduct in 4 basic steps, as present in Figure 2. First step, natural gas consists of some components such as sulfur that can poison the catalyst. Catalyst is the key to catalyze reaction. The prevention of deactivation of catalyst is required. Therefore, the purification process of natural gas feed is firstly needed. Second step, treated natural gas is fed into first reactor to react with steam in steam reforming reaction to produce syngas. The effluent of this reaction mainly composes of carbon monoxide and hydrogen. Third step, syngas is passed to a fixed bed reactor over a catalyst bed for methanol synthesis at high temperature and pressure. Liquid methanol is obtained in this step. Fourth step, some of undesirable components occur, and this reaction is not a 100% conversion reaction. The remain reactants need to recycle to the process. Therefore, the last step is methanol purification process to get 99.85 % methanol based on ASTM D-1152/97.

Due to endothermic behavior of steam reforming reaction, the high temperature over 800 °C is need for syngas production process. On the contrary, methanol production, which is an exothermic process requires 200-300 °C. Therefore, Heat exchanger networks for effective utilization are necessary parts of the process [21],[22],[23].
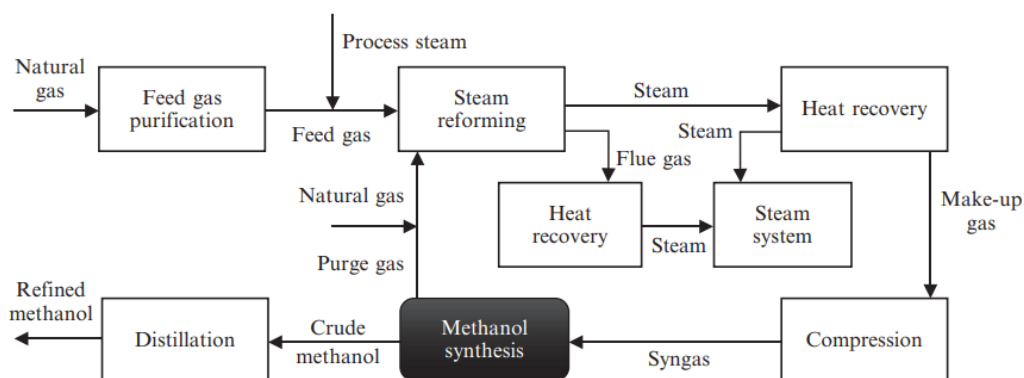
Figure 2 Conventional methanol production.

2.1.3 Methanol production process technologies

In 1923, the German company called Badische Anilin und Soda Fabrik (BASF) firstly developed a metal-based catalytic carbon monoxide hydrogenation to methanol at high pressure. This technology was suggested by both DuPont and the Commercial Solvents Corporation in the United States. It was an initial point of production of methanol in Industrial scale and was the prominent technology for more than 45 years. This process called BASF process is operated at temperature range from 320 ºC to 380 ºC and pressure about 34 MPa [24]. $ZnO-Cr_2O_3$ catalyst is used in this process. The single pass conversion of this process is 12%-15%. Because of high pressure of BASF process, research in that time tried to decrease operating condition.

In 1960s, the Imperial Chemical Industries (ICI) process overcame the BASF process high-pressure process. This ICI process was able to produce methanol in a lower pressure range from 3.5-5.4 MPa and temperature range from 200 ºC to 300 ºC. This was achieved not only by the new more active and selective catalyst ($Cu/ZnO/Al_2O_3$), but also by the improvement of new syngas purification process, which got the more pure syngas (sulfur-chlorine-free syngas) [25],[26]. In recently, the worldwide production of methanol is still mainly based on this ICI process. The schematic of ICI process exhibited as in Figure 3[27].

the Cu/ZnO had a high catalytic activity to produce methanol, but it could not scale up to commercial due to its low cycle life and low thermal stability, mainly caused by poisoning leading to deactivation [28],[29]. These obstacles were solved by promoting of alumina, which improves the stability of Cu/ZnO catalyst and slows the thermal formation of Cu crystallites [30],[31],[32].
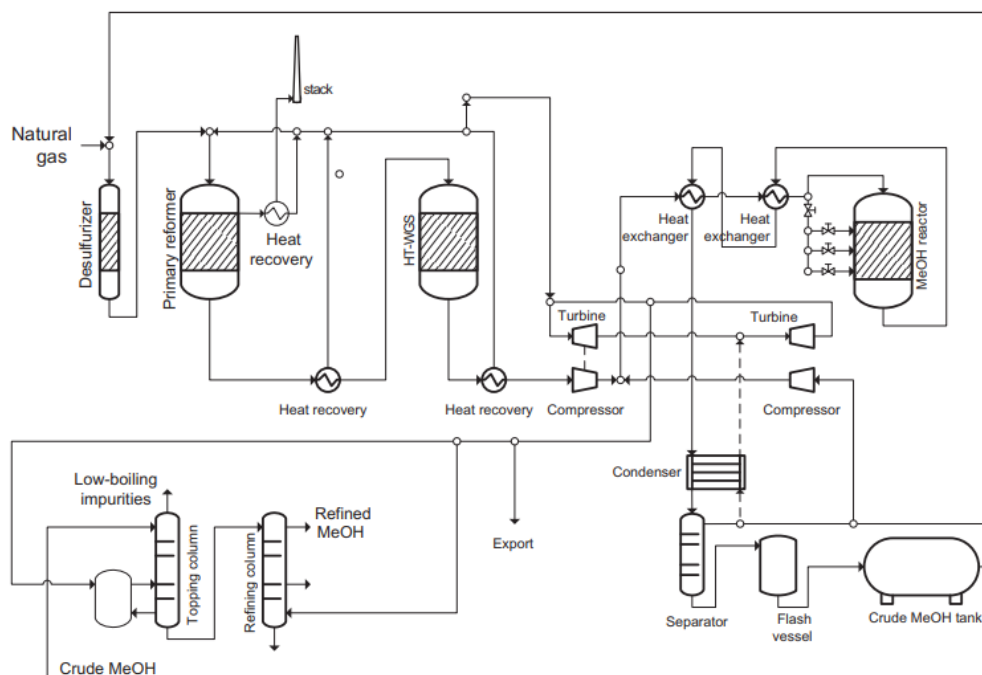
Figure 3 ICI low-pressure methanol process.

The evolution of methanol production process started from BASF high pressure process to ICI low pressure process. The produced methanol capacity was increased about 10^5 ton day^{-1} as shown in Table 2 some difference feedstocks and some difference production methods are reported.

Table 2 Methanol productivity of the main historical industrial process.

Production process	Feedstock	Productivity	Reference
BASF	Syngas	0.07896 ton day^{-1}	[33],[34],[35]
DuPont	Syngas	0.114 ton day^{-1}	[33],[34],[36]
Haldor-Topsφe	Syngas	2400 ton day^{-1}	[37]
ICI	Carbonaceous feedstock	2500 ton day^{-1}	[38]

2.1.4 Methanol synthesis reaction

2.1.4.1 Methanol from syngas

Methanol is commercially acquired from catalytic conversion of syngas. The methanol production process composes of three main reactions: (2.3) Hydrogenation of CO, (2.4) Hydrogenation of CO_2, and (2.5) Water gas shift reaction

Hydrogenation of CO to methanol
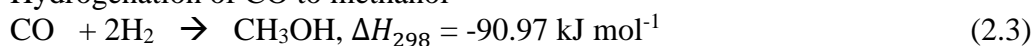
$$CO + 2H_2 \rightarrow CH_3OH, \Delta H_{298} = -90.97 \text{ kJ mol}^{-1} \tag{2.3}$$

Hydrogenation of CO2 to methanol and water

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H_{298} = -49.43 \text{ kJ mol}^{-1} \tag{2.4}$$

Water gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{298} = -41.39 \text{ kJ mol}^{-1} \tag{2.5}$$
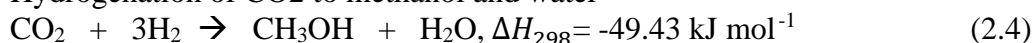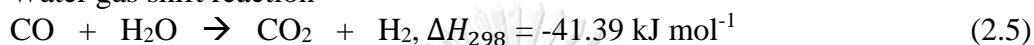
The methanol production process is recommended to operate at low temperature and high pressure due to these exothermic reactions and moles reduction reactions.

2.1.4.2 Methanol from carbon dioxide

Carbon dioxide (CO_2) is a greenhouse gas, which relates to the increment of atmosphere's temperature. Therefore, trend to mitigate with CO_2 is interesting in many industrial fields such as chemical industry, energy industry, and others. One alternative strategy is a CO_2 collection and utilization, which CO_2 is captured and converted to valuable products such as methanol. Using CO_2 for production of methanol is not only a mitigation way of greenhouse gas, but also it is another feedstock, which is a renewable resource. In contrast to syngas, which is produced from an exhausted resource such as natural gas and coal.

There are many benefits when CO_2 is used as a feedstock: It is cheap, plentiful, non-flammable, and non-corrosive compound. In addition, it can be operated in methanol production process from syngas without any adjustment [39].

After all, CO_2 molecule is very stable and unreactive. Due to its high stability ($\Delta G^o = -400 \text{ kJ mol}^{-1}$). It needs sufficient energy to make CO_2 molecule reactive. Therefore, the suitable operating conditions, and a highly active catalyst are required for CO_2 conversion to methanol, because 228 kJ is needed to convert one mole of CO_2 to methanol due to strong carbon-oxygen bonds, and six electrons is required to decrease C^{4+} of CO_2 to C_{2-} of methanol [30].

The catalytic CO_2 hydrogenation to methanol and reverse water gas shift reaction as a parallel reaction are presented in equation (2.6)-(2.7).

Hydrogenation of CO_2 to methanol and water

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H_{298} = -49.43 \text{ kJ mol}^{-1} \tag{2.6}$$

Reverse water gas shift reaction

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H_{298} = 41.39 \text{ kJ mol}^{-1} \tag{2.7}$$
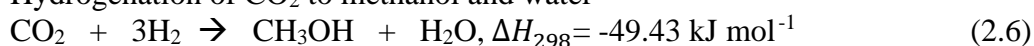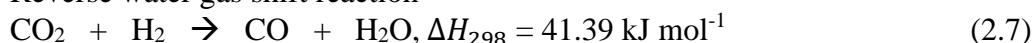
2.1.5 Catalyst for methanol synthesis

The Cu-based catalyst is generally used in industrial methanol production, typically Cu/ZnO/Al$_2$O$_3$ with different composition depending on the manufacturer as present in Table 3. Cu is normally considered as an active site, while a little amount of ZnO is reduced to Zn. Al$_2$O$_3$ is loaded on Cu/ZnO catalyst in order to prevent the sintering of Cu particles and expedite the adsorption and activation of CO, because it has disorganized and imperfect surface [40]. In addition, it is reported that Al^{3+} ions help to enlarge the specific surface area of Cu/ZnO [41].

Table 3 Composition catalyst for methanol production from different manufacturers [42].

Manufacturer	Cu	Zn	Al	Other
ICI	20-35%	15-50%	4-20%	Mg
BASF	38.5%	48.8%	12.9%	Rare earth oxide-5
DuPont	50%	19%	17%	
Haldor Topsϕe	>55%	21-25%	8-10%	
Shell	71%	24%	12%	

Usually, the commercial Cu/ZnO/Al$_2$O$_3$ catalyst is synthesized through coprecipitation technique [43]. For past 10 years of studied about Cu-based catalyst, coprecipitation technique was the highest proportion of methods for Cu-based catalyst synthesis [44] as presented in Figure 4. it might because this method was an inexpensive process compared to other leading to more practical in commercial scale [45]. A coprecipitation process can be shortly explained following Figure 5. The Metal nitrate solutions is used to prepare Cu and Zn precursors, while sodium carbonate is used as precipitating agent. The precipitate precursors are aged, separated, decomposed to get a mixture metal oxide using thermal treatment. After that, catalyst is reduced in H$_2$ atmosphere to transform CuO to Cu.
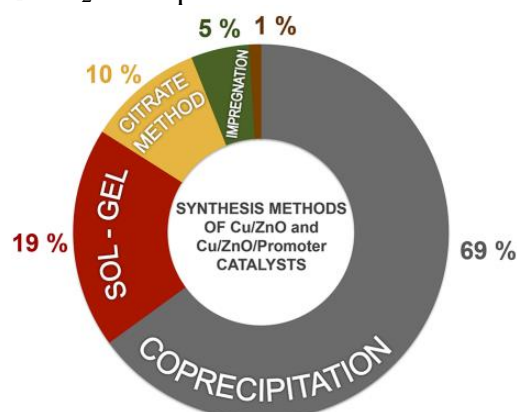
Figure 4 The percentage of several Cu/ZnO and Cu/ZnO/promoter synthesis methods calculated based on the past 10 years publications [44].
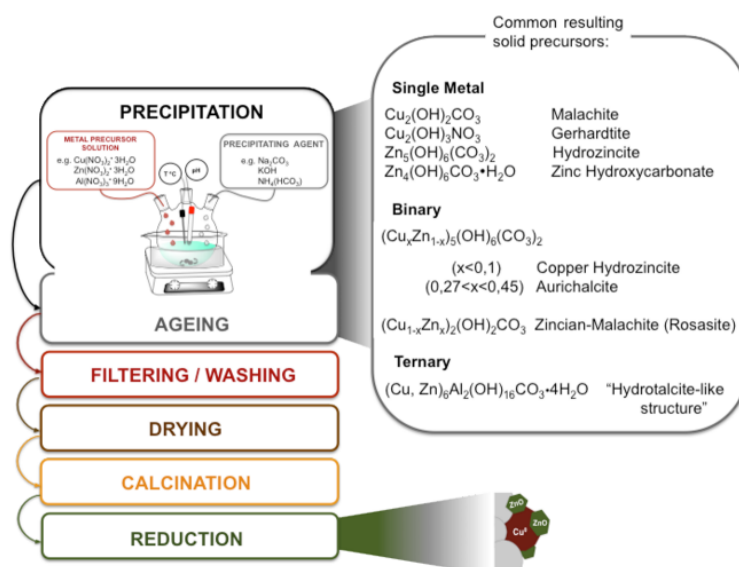
Figure 5 Diagram of coprecipitation process [44].

In industrially, the deactivation of $Cu/ZnO/Al_2O_3$ catalyst is reported that by both poisoning and thermal effects. The impurities in syngas such as sulfur, chloride are very poison to the catalyst. They can accelerate the catalyst sintering. However, the developed technologies in syngas production decreases impurities in order to benefit for catalyst in methanol synthesis. The deactivation by poisoning is eliminated, but the thermal deactivation including thermal sintering and phase segregation remains. It was reported that the sintering of Cu particles occurred after exposing catalyst to a syngas stream. Consequently, the activity decreased down to 60% after 25 h and lost 60% of specific surface area [46]. In addition, the sintering rate of catalyst increase not only by temperature, but also in the present of water.

2.1.6 Molecular sieve

Molecular sieve is one type of zeolite, which is well known as crystalline aluminosilicates compound. It is normally used as adsorbent. Due to the orderly structure of SiO_4 and AlO_4 tetrahedra lattice, it can selectively adsorb molecules of substance that have smaller diameter than the molecular sieve channel. Table 4 presents the diameters of some substance molecules.

Table 4 diameters of some substance molecules [47].

Molecule	Diameter (nm)
Hydrogen (H_2)	0.24
Oxygen (O_2)	0.28
Nitrogen (N_2)	0.30
Carbon dioxide (CO_2)	0.33
Ethane (C_2H_6)	0.44
Hexafluoroethane (C_2F_6)	0.53
Hexachloroethane (C_2Cl_6)	0.68

The popular molecular sieves which are commercial used consist of molecular sieve A type and molecular sieve X type. These molecular sieves have the similar chemical structure, but they have the different crystal structure. If the tetrahedra lattices form a truncated octahedra, the structure of molecular sieve will be A type, while if they form a tetrahedra, structure will be X type, as shown in Figure 6 [48]. The differences of opening channel are from differences of cation inside the molecular sieve. For A type, molecular sieve with sodium cation (NaA) has 0.4 nm opening channel called as "molecular sieve 4A". If sodium cations are replaced by calcium cations (CaA), the molecular sieve will have opening channel at 0.5 nm called "molecular sieve 5A", while replacing with potassium cations (KA) will have 0.3 nm opening channel called "molecular sieve 3A". For X type, molecular sieve with sodium cations (NaX) has 1 nm opening channel, while calcium cations (CaX) has 0.9 nm opening channel. Both of molecular sieve X type are known as "molecular sieve 13X" for NaX and "molecular sieve 10X" for CaX.

Moreover, the selective adsorption property of molecular sieve base on sieve effect, the metal ions also affect to selectivity. Due to the electric charge of these cations, the polar substances strongly interact with cations. Therefore, the higher polar chemicals are favorably adsorbed by molecular sieve.
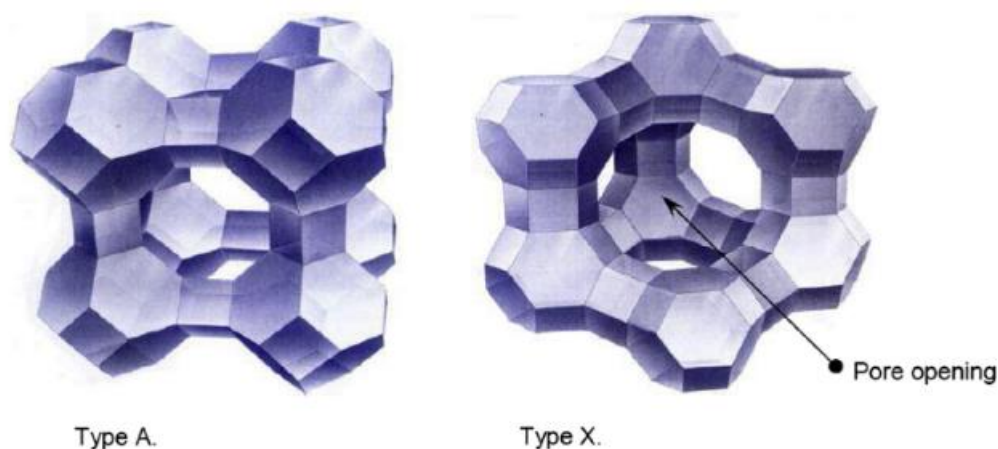
Figure 6 crystal structure of molecular sieve A type and X type.

Normally, molecular sieve 4A is usually used for dehydration of liquids and gases, but molecular sieve 3A is represented for systems, which have CO_2 and H_2S in the systems, to reduce the co-adsorption because sulfur compound, which is formed two gases, can block pores of adsorbent. In addition, molecular sieve 3A is also used for alcohol dehydration.

For molecular sieve 5A and 13X, they are commonly used for desulfurization in Petrochemical industries. Molecular sieve 5A is used for light sulfur adsorption, while 13X is used for heavy and branch sulfur adsorption.

2.2 Literature reviews

Due to CO_2 emission situation in recent, the strategy to converse CO_2 to other chemicals is widely interesting. CO_2 can also be used for methanol production as same as CO by CO_2 hydrogenation, but the conversion of CO_2 is still low. For instance, the equilibrium conversion of CO_2 to methanol at 150 °C and 5 MPa is about 15% [3]. Because this reaction is an exothermic in nature, but it needs to conduct at high temperature due to the high stability of CO_2 gas and reaction rate sufficiency. The low CO_2 conversion leads to large amount of unreacted feed gas. The high capacity of recycle unit is require, resulting in more capital cost [12]. Besides high temperature, and also high pressure (5-10 MPa) is required. These conditions make this process to be an energy intensive process. Therefore, the reduction of operating conditions is an option to mitigate with methanol production process via conventional route.

The new low temperature methanol synthesis called "alcohol assisted methanol synthesis" was initially presented by Tsubaki et al. [8]. ethanol is promoted methanol synthesis leading to can conduct at lower conditions (150-170 °C and 3-5 MPa). This new route mainly composes of 3 steps: (1) CO_2 hydrogenation to formic acid; (2) esterification of formic acid and ethanol to ethyl formate; (3) ethyl formate hydrogenation to methanol and ethanol.

Tsubaki et al. [8] tested that methanol could not be formed at temperature lower than 210 °C without ethanol as assisting solvent. The ethanol was a necessary factor that helped the formation of methanol at this low temperature (150 °C). It was also showed that the increasing ethanol in solvent mixture resulted in more conversion and methanol yield as represented in Figure 7.
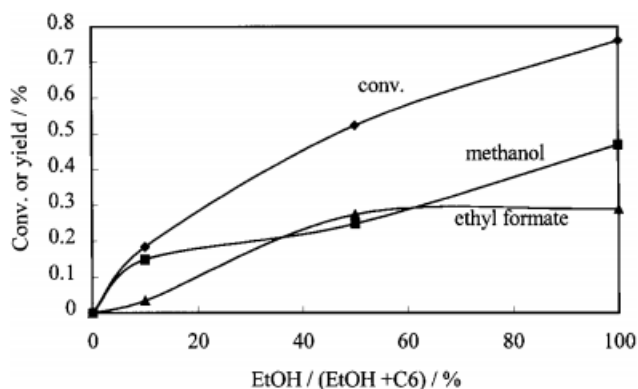
Figure 7 Catalytic activities with varied percentage of ethanol of solvent mixture.

Later, Tsubaki et al. [49] studied effect of alcohol used as promoted solvents, which included primary alcohols, secondary alcohols, and alcohols with similar carbon atom, but different structure as showed in Table 5. For primary alcohol, the result existed conversion decreased when the alcohols were larger molecule. For different structure alcohols, secondary alcohols existed the highest catalytic activities comparing to alcohols with the same carbon atoms. It was believed that factors, which affected to this behavior of alcohols were the electron density and spatial obstacle of alcohols molecule. For instance, the large electron density of iso-butanol should motivate the reaction, but its spatial obstacle acted as barrier for nucleophilic attack leading to low activity. Therefore, secondary alcohols, which had balance of electron density and spatial obstacle, showed the largest activity.

Table 5 Catalytic activities of catalyst with different alcohols on the synthesis of methanol from $CO/CO_2/H_2$.

Solvent	Methanol yield (%)	HCOOR yield (%)	Total conversion (%)	Rate of ROH to feed gas carbon (mol/mol)
none	0	0	0	0
cyclohexane	0	0	0	0
ethanol	10.22	1.13	11.35	12.81
1-propanol	9.27	0.16	9.43	9.94
2-propanol	13.19	10.27	23.46	9.81
1-butanol	8.97	0	8.97	8.16
2-butanol	11.26	10.22	21.48	8.14
iso-butanol	8.19	0	8.19	8.13
t-butanol	5.83	0	5.83	7.96
1-pentanol	7.74	0	7.74	6.91
2-pentanol	3.72	8.09	11.81	6.91
cyclopentanol	6.71	0	6.71	7.08
1-hexanol	7.17	0	7.17	5.96
ethylene glycol	0	0	0	13.40
benzyl alcohol	0	0	0	7.22

The effect of reactant feed composition was also investigated. The result existed that activities increased when the composition of CO_2 in feed gas increased. Pure mixture of CO_2 and H_2 was the highest reaction rate, while reaction rate is low for pure mixture of CO and H_2 as showed in Table 6.

Table 6 Catalytic activities of catalyst with different reactants composition on the synthesis of methanol from $CO/CO_2/H_2$.

expt. no.	CO (bar)	H_2 (bar)	CO_2 (bar)	ethyl formate yield (%)	methanol yield (%)	Total yield (%)
1	10	0	0	0	0	0
2	10	20	0	0.30	0	0.30
3	9.6	18	1.5	0.28	0.15	0.43
4	7.5	18	4.5	0.43	0.17	0.60
5	0	22.5	7.5	0.55	0.40	0.95

After the alcohol assisted methanol synthesis was purposed, there were many researchers studying about catalyst. Cu/ZnO, which was normally synthesized by co-precipitation method, was still used as a catalyst for this reaction. In catalyst synthesis step, there are many parameters that could affect to properties and activities of catalyst. For example, Jeong et al. [50] investigated effect of pH value in catalyst synthesis step, which was varied from 6-10, and found that pH value affected to physiochemical properties of Cu/ZnO including crystallite size of Cu, morphology of catalyst, and surface acidity. The result showed methanol yield trend that increased when the crystallite size of Cu decreased, and strong acidity increased. The optimal pH value in catalyst synthesis step was equal to 8 for this experiment, which showed the finely smallest Cu crystallite size at 11.7 nm and the largest strong acid site at 0.42 mmol NH_3 g_{cat}^{-1}. The catalytic activities of Cu/ZnO with various pH value were plotted and presented in Figure 8.
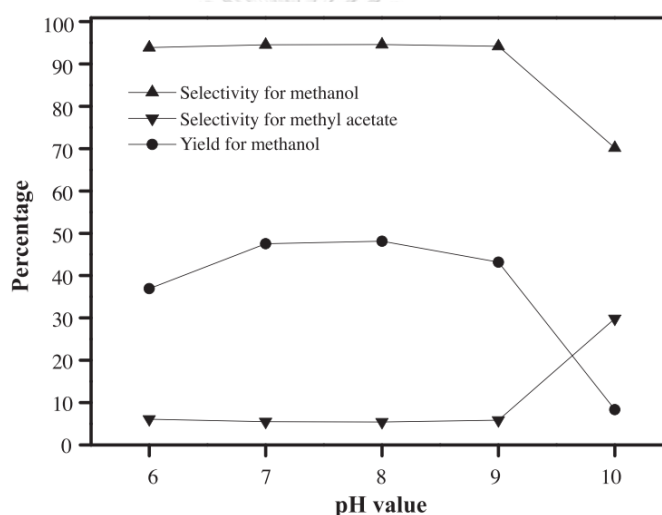
Figure 8 Catalytic activities of Cu/ZnO with different pH values in alcohol assisted methanol synthesis at 150 °C and 5 MPa for 20 h.

Later, Jeong et al. [51] studied another parameter, which is aging times in co-precipitation step from 10 min to 10 h. The changing of aging time showed the changing of catalyst surface morphology follow by the increasing of time. The catalytic activity was different when aging time was changed. It meant that there is a suitable aging time for Cu/ZnO catalyst. In Figure 9, the best catalytic activity exhibited at aging for 5 h in this experiment. In addition, the preferable morphology was reported in this journal as a plate-like structure, which was shown in Figure 10 compared to other morphology of catalyst at other aging times.
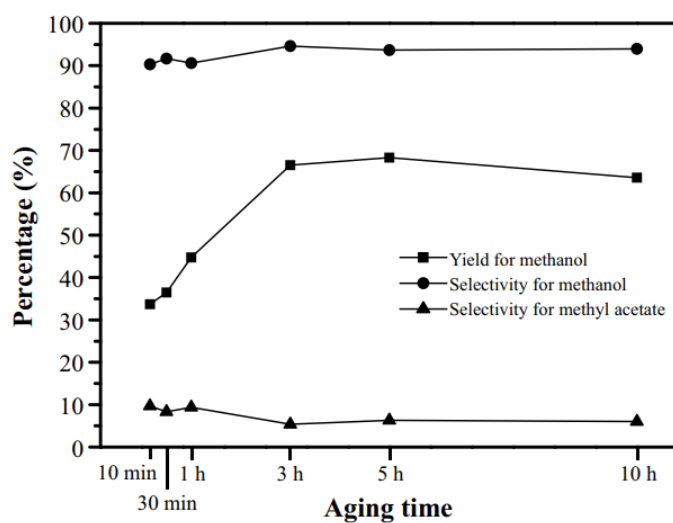
Figure 9 Catalytic activities of Cu/ZnO with different aging times in alcohol assisted methanol synthesis at 150 ºC and 5 MPa for 20 h.

Figure 10 SEM images of the reduced Cu/ZnO_X catalysts prepared with various aging times (X).

Kim et al. [11] studied the effect of copper content of Cu/ZnO catalyst. the copper content (Cu)/ metal content (Cu+Zn) ratios were varied from 0.3 to 0.7. the synthesized catalysts were characterized and tested on alcohol assisted methanol synthesis. Even though the Cu/ZnO catalyst with 0.5 copper content did not exhibit the highest specific surface area, the lowest copper crystallite size, and the highest total acidity as shown in Table 7, the result showed the highest methanol yield (49.5%) when it was used. Therefore, there was other parameter that was important for high methanol yield. the authors believed that the surface morphology of catalyst plays as an important role for high methanol yield. Plate-like structure or aurichalcite was mainly obtained in zinc-rich catalyst (copper content = 0.3, 0.4, and 0.5), while rod-like structure or zincian malachite was mainly observed in copper-rich catalyst (copper content = 0.6 and 0.7). the morphologies of catalyst with various copper contents (0.3 to 0.7) were presented by SEM images in Figure 11. It should be noticed that a little amount of rod-liked structure also occurred in Cu/ZnO catalyst with 0.5 copper content. The authors believed that mixture phase of plate-liked and rod-liked structure was a reason of the highest methanol yield. the reaction pathway as in Figure 12 was also purposed in this journal. Firstly, CO_2 was hydrogenated to active formate species. These formate species rapidly reacted with ethanol to ethyl formate. The ethyl formate was hydrogenated to convert to methanol and returned the ethanol solvent back. It should notice that the dehydrogenation of ethanol to ethyl acetate as a side reaction also was indicated. It was reported that Cu-based catalyst also could catalyze this side reaction. Moreover, by-product such as ethyl acetate can react with methanol to covert to methyl acetate via transesterification reaction.

Table 7 Physical and chemical properties of reduced Cu/ZnO catalysts.

Catalysts	Cu/(Cu+Zn) ratio		S_{BET} (m²/g)	Copper crystallite size (nm)	Total acidity (NH₃ mmol/g_cat)
	ICP	SEM-EDX			
Cu/ZnO_0.7	0.7	0.7	15.0	20.3	0.58
Cu/ZnO_0.6	0.6	0.6	22.3	18.2	0.50
Cu/ZnO_0.5	0.5	0.5	23.8	13.9	0.42
Cu/ZnO_0.4	0.4	0.4	28.2	11.2	0.34
Cu/ZnO_0.3	0.3	0.3	29.3	8.9	0.26
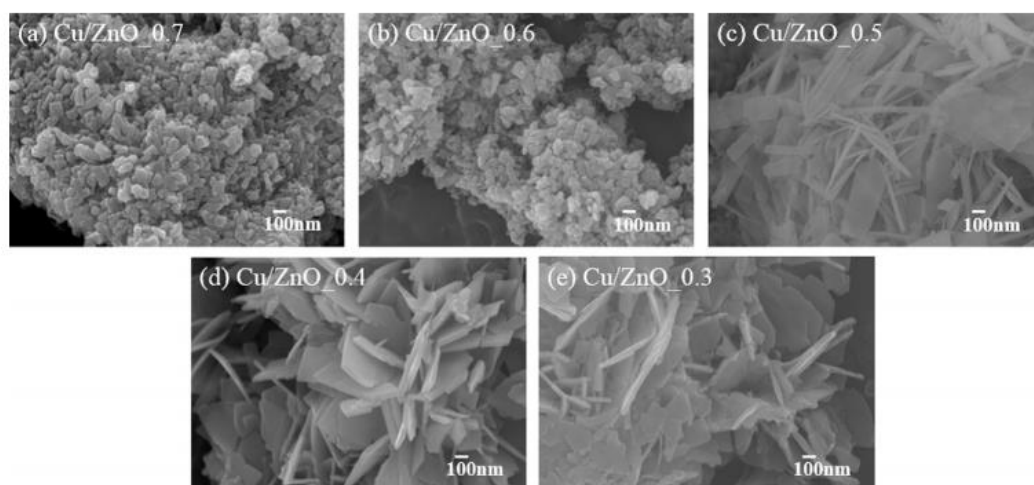
Figure 11 SEM images of Cu/ZnO precipitated precursors.
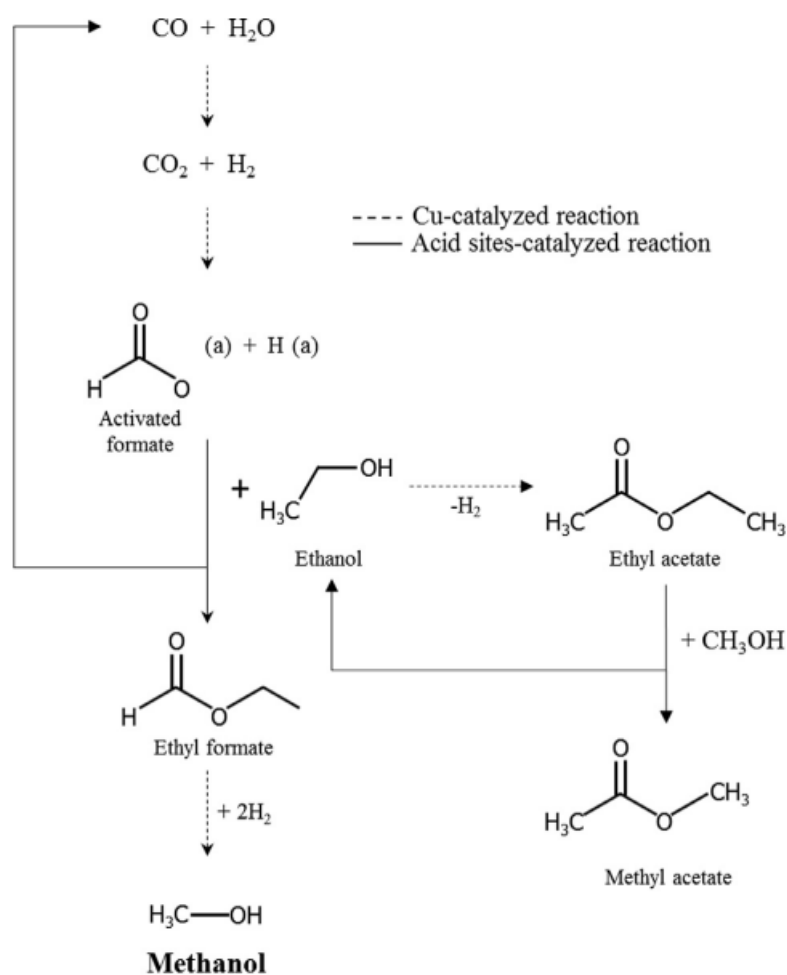
Figure 12 A suggested alcohol assisted methanol synthesis reaction pathway over Cu/ZnO.

Likhittaphon et al. [52] investigated catalyst preparation conditions including precipitation temperature (25-80 °C) and pH value (5-9), and enhanced catalyst synthesis by using ultrasonic assisted precipitation. In case of effect of precipitation temperature, the best characterizations including the smallest Cu crystallite size (5.60 nm), the largest surface area (80.02 m^2 g_{cat}^{-1}), low reduction temperature (351.8 °C), and high surface acidity (0.191 mmol NH_3 g_{cat}^{-1}) were obtained at the precipitation temperature 60 °C. For effect of pH value, the crystallite size decreased with increasing pH value. The higher specific surface area was provided with the smaller crystallite size, and the highest surface area was 90.67 m^2 g_{cat}^{-1} at pH 8. In addition, it also showed the highest acidity (0.224 mmol NH_3 g_{cat}^{-1}) at this pH value. Therefore, these great properties of Cu/ZnO catalyst synthesized at pH value 8 leading to the best catalytic activity (methanol yield equal to 33%). The effect of pH value well corresponded with Jeong et al. [50] that the best catalytic activity was obtained at pH value 8. Another one, the ultrasonic enhanced the Cu/Zn catalyst by decreasing aging time from 1 h to 0.5 h, increasing surface area, increasing surface acidity. Even though the properties of Cu/ZnO catalyst were better, the methanol yield slightly increased to 32% (precipitated at 40 °C) from 31% (precipitated at 60 °C). The ultrasonic assistance only helped to reduce the precipitation temperature. The activities of Cu/ZnO with different synthesis techniques (conventional and ultrasonic assistance) at different precipitation temperature were presented in Figure 13.
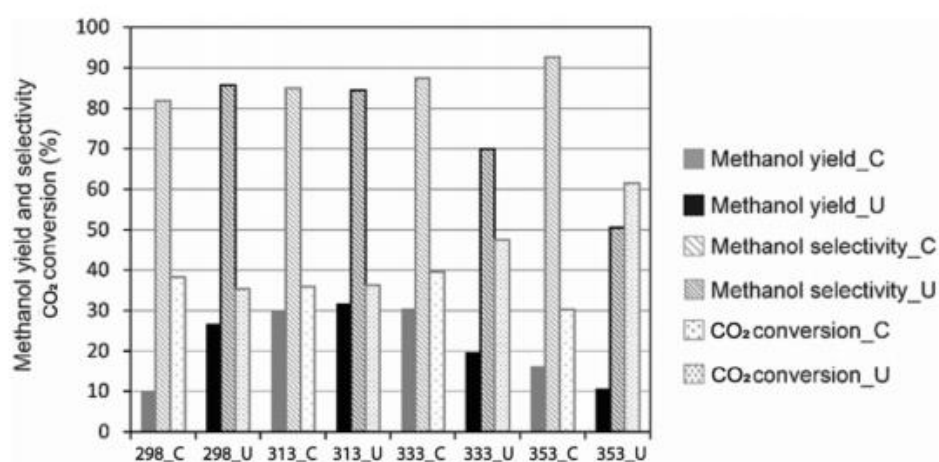
Figure 13 Yield and selectivity of methanol and CO_2 conversion using the catalysts synthesized through a conventional precipitation and ultrasonic assisted precipitation at different temperature (25-80 °C), pH = 7 for all samples.

Some researchers studied the computer modeling of methanol productivity improvement using *in-situ* water adsorption by molecular sieve 4A. Bayat et al. [53] simulated the methanol synthesis reaction from syngas over Cu/ZnO/Al_2O_3 catalyst in gas flowing solids fixed bed reactor (GFSFBR) with continuous regeneration of molecular sieve 4A. the schematic of GFSFBR process was shown in Figure 14.
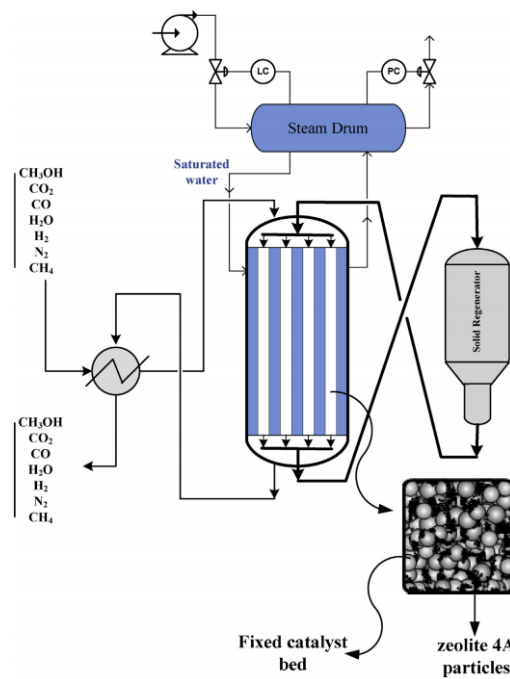
Figure 14 GFSFBR process schematic.

The concept of GFSFBR was that the syngas as a reactant and molecular sieve 4A as an adsorbent moved pass through a shell and tube reactor, while catalyst bed was fixed in reactor as shown in Figure 15.
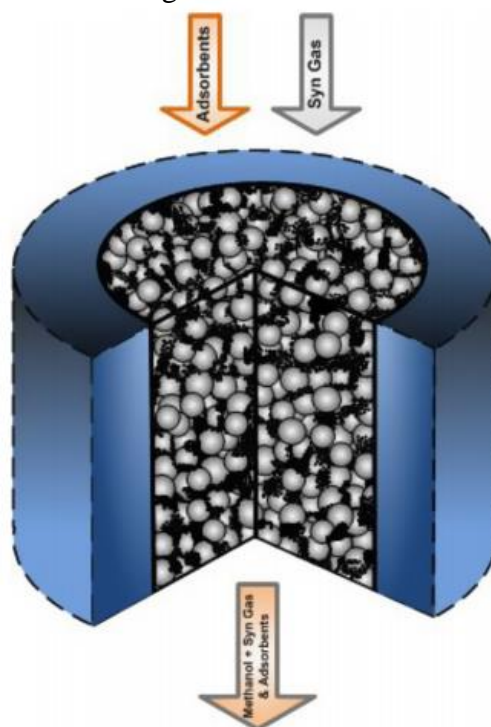
Figure 15 GFSFBR concept for methanol synthesis enhanced by in-situ water adsorption.

the moving of molecular sieve 4A was required, because of the recirculation of fresh molecular sieve and regeneration of saturated molecular sieve. the effect of solids mass flux (molecular sieve) was investigated. The simulation exhibited that production rate of methanol increased with increasing of solids mass flux. The effect of water adsorption in GFSFBR raised the reaction rate (higher production rate at the same reactor length) and methanol as presented in Figure 16a. it should be noted that reverse water gas shift reaction was stimulated toward CO by the effect of water adsorption. the molar flow rates of CO_2 and H_2 decreased as can see in Figure 16c-d, while the CO molar flow rate increased with increasing solids mass flux as in Figure 16b. Consequently, the methanol production rate significantly increased. This computer modelling also was brought to simulate other chemical process such as Fischer-Tropsch synthesis and direct dimethyl ether synthesis that *in-situ* water adsorption enhanced these process to more productivity [54],[55].
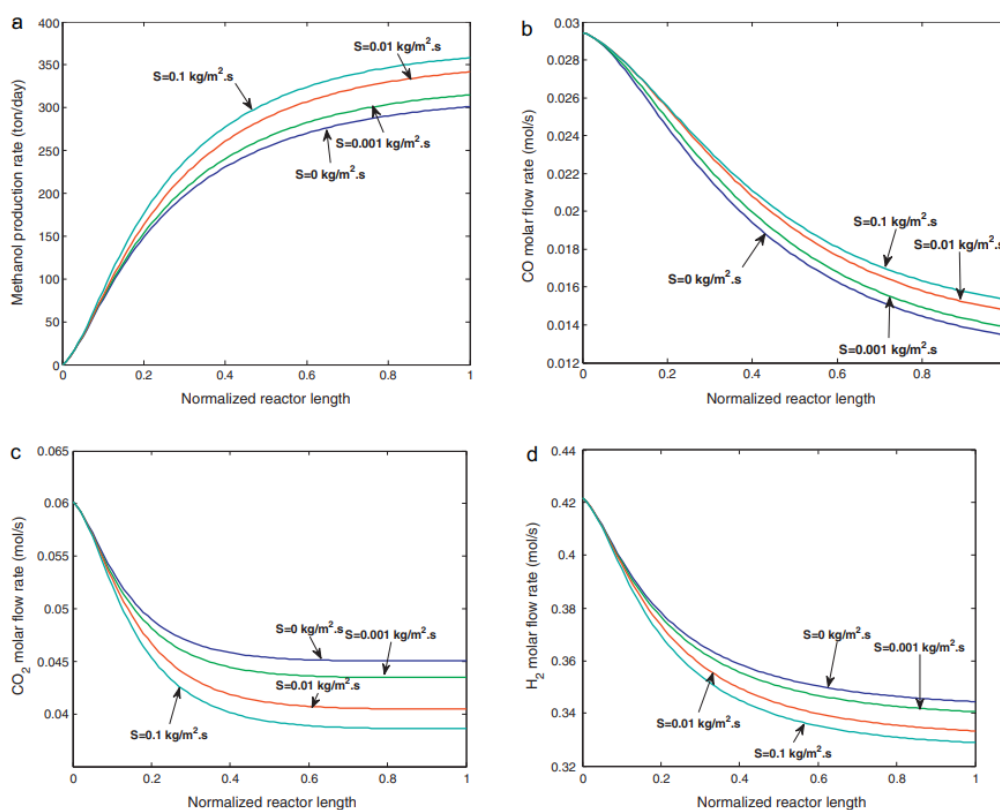
Figure 16 Profiles of (a) methanol production rate, (b) CO, (c) CO_2 and (d) H_2 molar flow rates along GFSFBR for S = 0, 0.001, 0.01, 0.1 kg/m^{2}s.

According to Bayat et al. computer modelling above, the result presented the enhancement effect of water adsorption. Therefore, Nieminen et al. [13] applied this method to the alcohol assisted methanol synthesis by *in-situ* continuous adsorption of water using molecular sieve 3A. Water was known as by-product in reaction that negatively affected the potential of Cu/ZnO catalyst by blocking active site and accelerating the Cu particles sintering. Amounts of molecular sieve 3A were varied in this experiment. the result showed the increment of methanol productivity. In addition, the more adsorbent/catalyst ratio increased, the more methanol productivity was obtained. The highest methanol productivity raised to 54.4 g kg^{-1} h^{-1} from 8.2 g kg^{-1} h^{-1} (20g of Cu/ZnO) when 10g of Cu/ZnO and 40g of molecular sieve 3A were used, as in Figure 17. The authors reported that continuous adsorption of water by molecular sieve 3A made Cu/ZnO catalyst more effective.
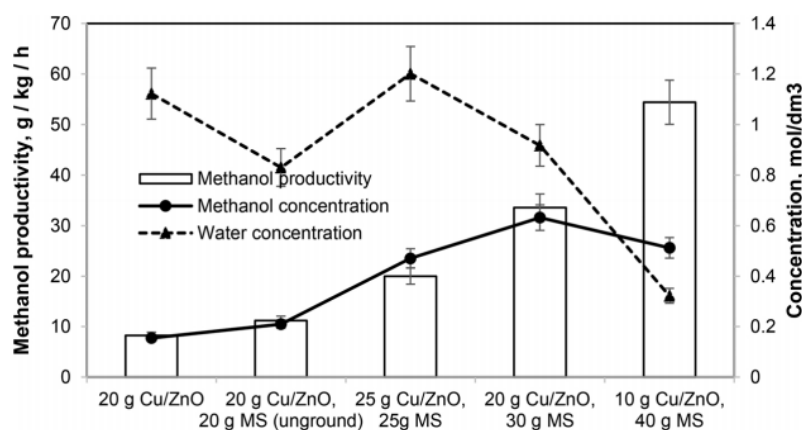
Figure 17 Effect of catalyst and molecular sieve mass on methanol and water formation in 2-butanol. Temperature 180 $^{\circ}$C, feed gas $CO_2:H_2 = 1:3$, total pressure 60 bar.

According to alcohol assisted methanol synthesis, it was known that ethyl acetate was a by-product which existed from dehydrogenation of ethanol. Therefore, the separation of methanol and ethyl acetate was required. Brenner et al. [16] demonstrated molecular sieve 5A as subtractors. To observe what substances were adsorbed by molecular sieve 5A. The result showed that molecular sieve 5A had potential to separate methanol and ethyl acetate by desorption of methanol, while ethyl acetate pass thought it. A list of substances adsorbed by molecular sieve 5A was present in Table 8. On the other hand, a list of substances passing though molecular sieve 5A was presented in Table 9.

Table 8 Chemicals which are perfectly adsorbed by molecular sieve 5A.

Group	Components tested
Normal paraffins (except methane)	Propane, n-Butane, n-Hexane
Normal olefins	Ethylene, Propylene, Hexene-2
Normal alcohols	Methanol, Ethanol, n-Butanol
Aldehydes	Acetaldehyde, Propionaldehyde, Isovaleraldehyde
Acids	Formic acid, Propionic acid

Table 9 Chemicals which passed through molecular sieve 5A.

Group	Components tested
Iso-paraffins	i-Butane, i-Propane, 2,3-Dimethyl butane
Aromatic hydrocarbons	Benzene, Toluene, m-Xylene
Cycloparaffins	Cyclopentane, Cyclohexane
Iso-olefins	i-Butylene, 2-Methyl butadiene-I,3
Esters	Amyl fomiate, Ethyl acetate, Ethyl propionate
Ketones	Acetone, Methyl ethyl ketone, Mesityl oxide
Halogenated hydrocarbons	Methylene chloride, Chloroform
Iso-alcohols	i-Propanol, Methyl butanol
Ethers	Diethyl ether, Di-isopropyl ether
Other components	Carbon monoxide, Oxygen, Nitrogen, Rare gases, Methane, Nitromethane, Carbon disulfide, Dimethyl sulfide, Thiophene

CHAPTER III

EXPERIMENTAL

3.1. Materials and chemicals

Materials and chemicals are listed as follows:
Material
1. 2 pieces of burette
2. 2 pieces of burette clamp stand
3. 2 pieces of 50 ml volumetric flask
4. 1 piece of 100 ml volumetric flask
5. 3 pieces of 50 ml beaker
6. 2 pieces of 100 ml beaker
7. 1 piece of 1000 ml beaker
8. 3 pieces of spoon
8. 1 piece of magnetic stirrer
9. 2 pieces of stirring rod
10. hot plate with temperature control probe
11. pH measuring paper
12. 200 ml reactor with pressure gauge, temperature control probe, propeller
13. Ceramic heater: Maximum temperature 450 ºC
14. Stirrer controller
15. Mass flowmeters
16. cooling water pump

Chemical
1. $Cu(NO_3)_2.3H_2O$ precursor
2. $Zn(NO_3)_2.6H_2O$ precursor
3. Na_2CO_3 precipitating agent
4. Deionized water
5. Ethanol
6. Carbon dioxide
7. Hydrogen
8. Molecular sieve 3A
9. Molecular sieve 5A

3.2. Preparation of catalyst

3.2.1. Preparation of catalyst

Each batch of catalyst synthesis, Cu/ZnO catalyst was synthesized by co-precipitation technique. 40 ml of 1 M copper (II) source solution prepared from copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Sigma-Aldrich, ≥98%) and 39 ml of 1 M zinc (II) source solution prepared from zinc nitrate hexahydrate ($Zn(NO_3)2 \cdot 6H_2O$, Sigma-Aldrich, ≥99%) were mixed as metal precursor solution for synthesis of 5 g Cu/ZnO catalyst with Cu/Zn ratio 1:1, while 1.5 M sodium carbonate (Na_2CO_3, Sigma-Aldrich, ≥99.5%) solution was used as precipitating agent. The precursor and precipitating agent were added drop wise to 600 ml of deionized water which was

stirred by magnetic stirrer. During synthesis, the precipitation temperature, pH-value, and stirring velocity were constantly maintain at 60 $^{\circ}$C, 8 , and 600 rpm, respectively. After completing dropwise of metal precursor solution, the precipitate was aged for 1 h. The precipitate product was washed by deionized water until the electrical conductivity of the washing liquid was lower than 50 μS cm^{-1}. The precipitate solid was spun to separate from slurry using centrifuge (ROTOFIX 18) at 1200 rpm for 2 min. After that, precipitate solid was separated and dried at 110°C overnight. Dried precipitate solid was calcined at 350 $^{\circ}$C for 3 h with ramp rate 5 $^{\circ}$C min^{-1} using furnace (Carbolite, CWF-1100). After that, the calcined CuO/ZnO catalyst was activated to reduce CuO/ZnO to Cu/ZnO. The catalyst was reduced in a fixed bed reactor by passing 60 ml min^{-1} of 50%H$_2$ in N$_2$ through the catalyst bed at 300 $^{\circ}$C for 3 h with the ramp rate at 10 $^{\circ}$C min^{-1}.

3.2.2. Preparation of molecular sieve

3A Molecular sieve (MS_3A) and 5A Molecular sieve MS_5A (Sigma-Aldrich, 8-12 mesh) were crushed using pestle and mortar. The molecular sieve powders with the particle size of 5-55 μm were activated by heat treatment at 250 $^{\circ}$C for 8 h with ramp rate 10 $^{\circ}$C min^{-1} using furnace (Carbolite, CWF-1100).
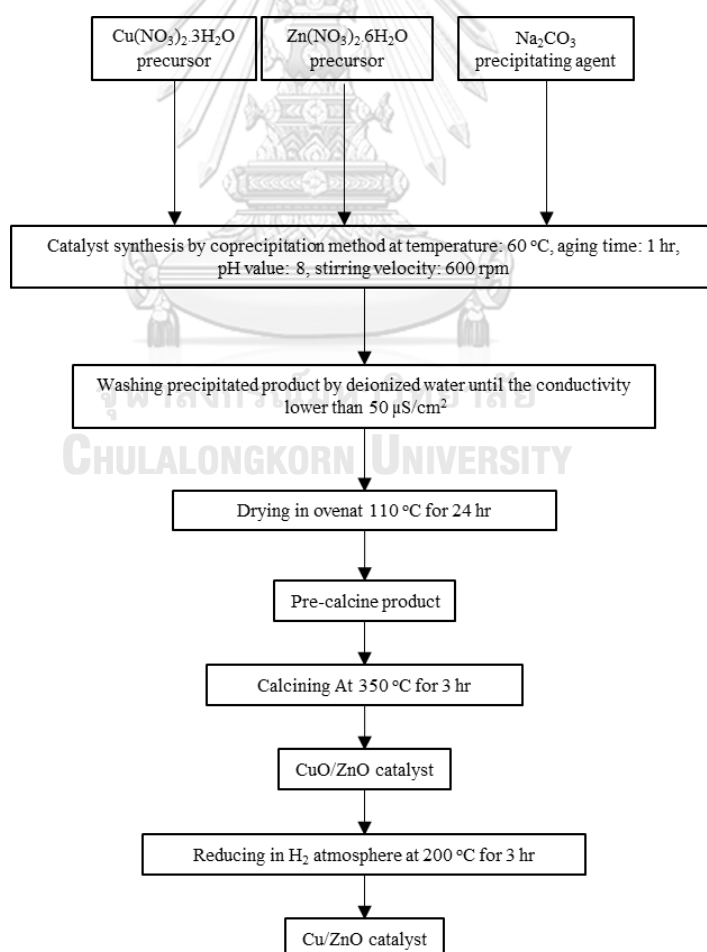
Figure 18 Methodology of preparation of Cu/ZnO catalyst.
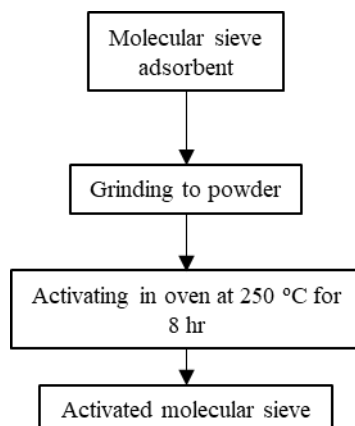
Figure 19 Methodology of preparation of molecular sieves.

3.3. Catalyst characterization

The crystallite phases of catalyst were observed by X-ray diffraction (XRD, Bruker AXS, D8 Advance) using Cu-Kα (λ = 1.5406 Å). The diffraction pattern was scanned from 20° to 80° with scanning rate 2° min⁻¹. After that, Scherrer's equation as exhibited in Eq. (11) was used for calculation of the catalyst crystallite size (d).

$$d = \frac{0.9\lambda}{\beta_{FWHM}\cos(\theta)} \quad (3.1)$$

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

The Brunauer-Emmett-Teller (BET) surface area was measured by nitrogen physisorption (Micromeritics. ASAP 2020). The catalyst morphology and dispersion were observed by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX, Hitachi, S3400N, and EDX, EDAX, Apollo x). X-ray photoelectron spectroscopy (XPS) was analyzed by Kratos, Amicus with Mg kα X-ray source to measure Cu2p using Gaussian fitting.

The reduction temperature was obtained by temperature program of reduction (TPR, Micromeritics, Chemisorb 2750) by packing 0.02 g catalyst in a reactor. Initially, catalyst was dried under 25 ml min⁻¹ flow of N_2 at 250 °C for 1 h. After temperature was decreased to 30 °C, the temperature program was started from 30 °C to 500 °C with ramp rate 10 °C min⁻¹ under 25 ml min⁻¹ flow of 10%H_2/Ar.

The surface acidity of catalyst was measured by ammonia temperature program of desorption (NH_3-TPD, Micromeritics, Chemisorb 2750). Catalyst was packed in quartz reactor. The He flow at 25 ml min⁻¹ was passed through catalyst at 250 °C for 1 h to remove organic impurities. After that, NH_3 adsorption was done at 30 °C for 1 h. Then, the temperature was increased from 30 °C to 600 °C with ramp rate of 10 °C min⁻¹ under 25 ml min⁻¹ flow of He.

3.4. Test of molecular sieve role

The role of MS in alcohol assisted methanol synthesis was investigated. Each type of molecular sieve was tested. The 3g of MS and 60 ml of ethanol were added into the 250 ml autoclave reactor without Cu/ZnO catalyst. A gas mixture of CO_2 and H_2 was fed into the reactor with the ratio of 1:3 until the pressure reached 3.6 MPa. Then, temperature was increased to 150 $^{\circ}$C while pressure raised up to 5.0 MPa at 150 $^{\circ}$C. The reaction was proceeded under vigorous stirring at 600 rpm for 2 h. After that, the liquid product was analyzed by SHIMADZU Nexis GC-2030 gas chromatography with a mid-polar SH-Rtx^{TM}-624 column.

3.5 The performance test of alcohol-assisted methanol synthesis

2.6 g of Cu/ZnO catalyst with different molecular sieve type (3A, 5A, and 3A+5A) and different catalyst/adsorbent ratio (1:1-2:1) were loaded in 250 ml autoclave reactor. the 60 ml liquid ethanol were added into reactor after loading solid. The 360 ml min^{-1} of CO_2 and H_2 mixture with CO_2:H_2 ratio 1:3 was fed to reactor. Each batch was proceeded at 150 $^{\circ}$C, 5 MPa, except in section 3.3.4 effect of operating conditions. There are some experimental batches, which conducted at other conditions (150 $^{\circ}$C, 3.5 MPa and 130 $^{\circ}$C, 5 MPa). The reaction was proceeded under vigorous stirring at 600 rpm for 24 h. After reaction completed, the reactor was cooled down by 10 $^{\circ}$C cooling supply water. Gas outlet was directly connected to SHIMADZU Nexis GC-2030 gas chromatography with a mid-polar SH-Rtx^{TM}-624 column. Gas effluent was firstly analyzed using thermal conductivity detector (TCD), while flame ionization detector (FID) was used for liquid effluent. Helium was used as carrier gas with flowrate 1.88 ml min^{-1}. Product was analyzed in temperature scanning mode from 50 $^{\circ}$C to 230 $^{\circ}$C. Finally, methanol yield, and selectivity were calculated by Eq.(3.2)-(3.3).

$$\text{Yield of methanol} = \frac{\text{Mole of methanol product}}{\text{Mole of feeding } CO_2} \times 100 \qquad (3.2)$$

$$\text{Selectivity of methanol} = \frac{\text{Mole of methanol product}}{\text{Mole of all products}} \times 100 \qquad (3.3)$$
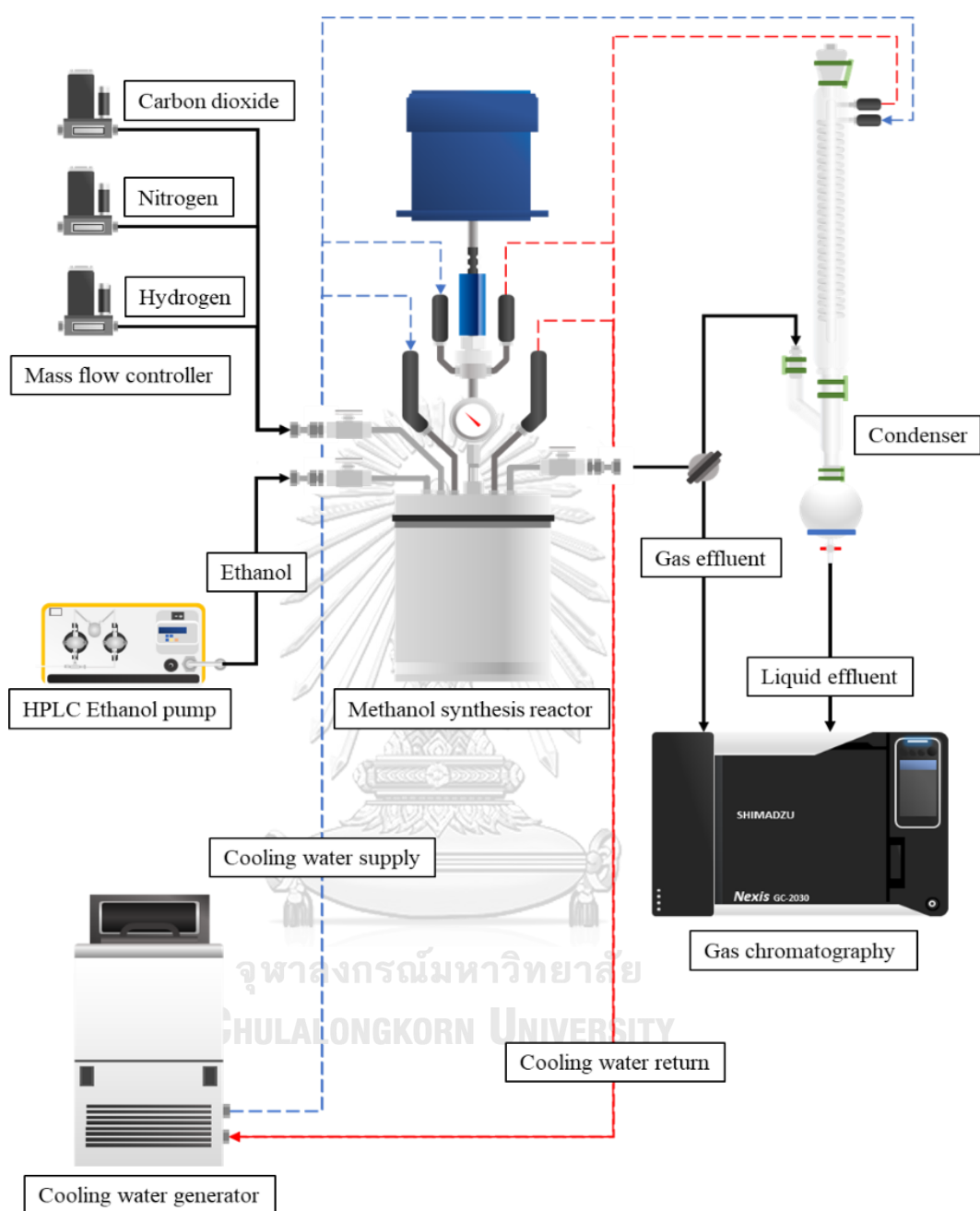
Figure 20 Schematics of Alcohol assisted methanol synthesis reactor.

CHAPTER IV

RESULT AND DISCUSSION

4.1. Catalyst characterization

The X-ray diffraction was used to identify the successful synthesis of the catalyst. both non-reduced catalyst (CuO/ZnO) and reduced catalyst (Cu/ZnO) were analyzed. The XRD patterns of were represent in Figure 21, corresponding to the previous study [11, 50-52]. For CuO/ZnO, the two major peaks of CuO and ZnO were observed (for CuO (111) at $2\theta = 39^o$, JCPDS card no. 45-0937, and for ZnO (101) at $2\theta = 36^o$, JCPDS card no. 79-0206). The main peaks were used for calculation of the catalyst crystallite size by Scherrer's equation. The synthesized catalyst had rather small crystallite size. It was reported that slow heating rate in calcination results in a smaller crystallite size of a catalyst. Moreover, the dispersion of Cu in catalyst and methanol formation rate increases when low heating rate in calcination is applied [56]. In present study, the heating rate of 5 ^{o}C min^{-1} was used in the calcination. Specific surface area of catalyst was carried out by N_2-physisorption. These results are presented in Table 10. Relatively lower specific surface area was obtained in present study when compared to our previous work, likely due to a slower heating rate.

After CuO/ZnO was reduced by passing 50% H_2/N_2 through catalyst at 300 ^{o}C for 3 h, the main Cu (111) peak existed at $2\theta = 43.2^o$, while CuO (111) peak disappeared. This indicated that catalyst was completely reduced from CuO to Cu, which corresponding to the XPS characterization result. In XPS result, the shift of Cu 2p3/2 peak was observed, but it could not absolutely confirm that the oxidation state of reduced catalyst was Cu^0 because the binding energy of both Cu^0 and Cu^{1+} were rather similar at about 932 eV [57]. To clarify this doubt, the XRD pattern of Cu/ZnO was used. The results obtained from the XRD pattern supported to the XPS spectra that the reduction of CuO/ZnO to Cu/ZnO was complete.
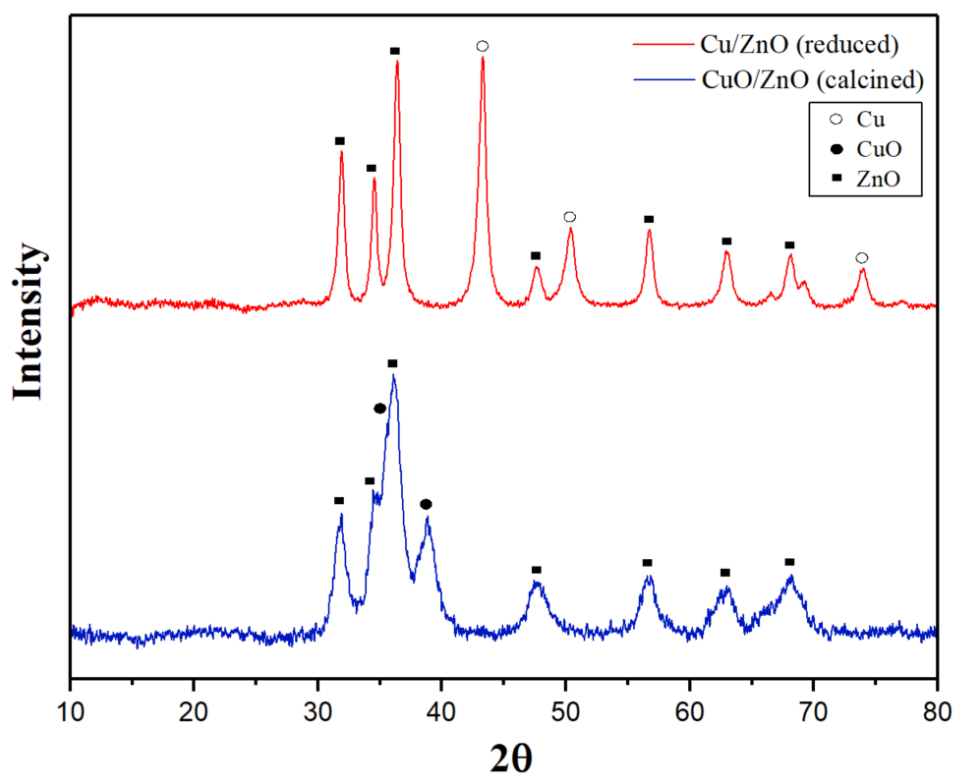
Figure 21 The XRD pattern of both calcined CuO/ZnO catalyst and reduced Cu/ZnO catalyst.

Table 10 Catalyst crystallite size and specific surface area of calcined CuO/ZnO catalyst.

Catalyst	Catalyst crystallite size (nm)		Specific surface area (m^2/g$_{cat}$)	Ref.
	CuO (111)	**ZnO (101)**		
CuO/ZnO	1.03	1.02	66.16	this work
CuO/ZnO	5.56	6.08	90.67	[52]

The morphology of the catalyst was observed by the SEM-EDX. During the precipitation, the color changing of mother liquor was observed, attributing to the formation of hydroxyl carbonate crystalline such as aurichalcite $[(Cu,Zn)_5(OH)_6(CO_3)_2]$, zincian malachite $[(Cu,Zn)_2(OH)_2CO_3]$, and malachite $[Cu_2CO_3(OH)_2]$ [9, 58, 59], which are precursors for the catalyst synthesis. As shown in Figure 22(a)-(b), the mixture crystallite phase of rod-liked structure, plate-liked structure and irregular shape were observed. There is unclear about the desirable catalyst structure. It was reported that rod-like structure or zincian malachite was a desirable precursor [60, 61], while plate-like structure or aurichalcite was also reported to provide high activity of Cu/ZnO catalyst [62, 63]. Kim et.al reported that a mixture of needle-like and plate-like structure led to superior performance in Cu/ZnO [10]. In this study, the SEM images exhibited successful synthesis of the desirable phases which were a mixture of rods and plate structure. In addition, the Cu/Zn ratio was confirmed by the element mapping obtained from the EDX analysis as shown in Figure 22(c)-(d). The mapping showed that the metals dispersed well, indicating the ratio of Cu to Zn at 1:1.
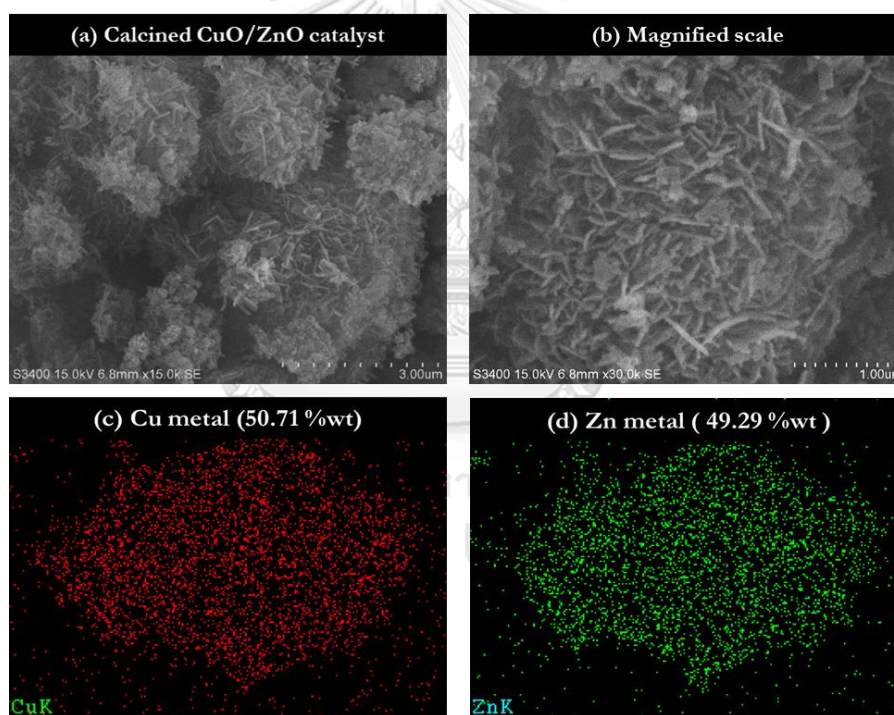
Figure 22 The SEM-EDX images of (a) calcined CuO/ZnO catalyst and (b) the magnified scale (c) Cu element mapping (d) Zn element mapping.

The reduction of catalyst was investigated by the TPR in H_2 atmosphere. In Figure 23, the reduction was derived in two steps following the two peaks, which were indicated as α peak (179.4 °C), and β peak (197.7 °C). It was reported that the first peak can be assigned to changing in the oxidation state of Cu^{2+} to Cu^{1+}, and the second peak is changing from Cu^{1+} to Cu^0 [64]. The calcined CuO/ZnO catalyst showed rather low reducing temperature that can contribute to be good reducibility and metal dispersion [65]. Therefore, the reduction temperature of CuO/ZnO catalyst was lower than that of the bulk CuO (340 °C) [66-68].
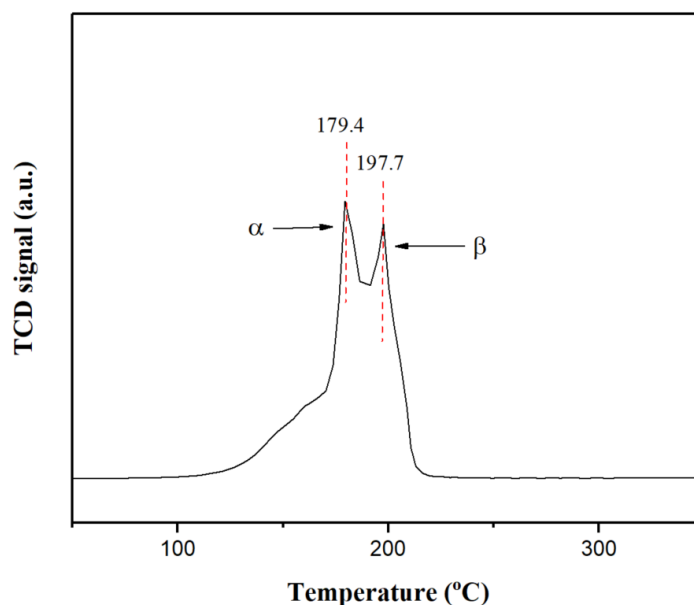
Figure 23 The H$_2$-TPR profile of calcined CuO/ZnO catalyst

The acidic property of catalyst was determined. It was reported that the pH-value during catalyst precipitation significantly affects the catalyst activity [50, 52]. Therefore, the pH-value of 8 was constantly controlled during the catalyst precipitation. Moreover, it was indicated that quantity of strong acid site on catalyst surface significantly affects methanol yield [50]. Weak, medium and strong acid site were classified by the NH$_3$-TPD. The temperature ranges of 60-170 °C, 190-310 °C and 310-575 °C were corresponded to weak, medium and strong acid site, respectively. The quantity of the acid sites is presented in Table 11, compared to literature. It should be noted that precipitating temperature is different between this work (60 °C) and literature (70 °C) and it might be the cause of different acidity in catalyst.

Table 11 Acid property of synthesized Cu/ZnO catalyst

Catalyst	Acidity (mmol NH$_3$/g$_{cat}$)				Ref.
	Weak site	**Medium site**	**Strong site**	**Total**	
Cu/ZnO	0.013	0.013	0.20	0.23	This work
Cu/ZnO	0.036	0.022	0.18	0.23	[52]
Cu/ZnO	0.08	0.14	0.42	0.64	[50]

The catalyst reduction was confirmed by the oxidation state of Cu particles. The binding energy was measured by the XPS. Both non-reduced and reduced catalyst were tested. The oxidation state of Cu particles was measured by considering the Cu $2p_{3/2}$ peaks (Cu^0 = 932.2 eV and Cu^{2+} = 933.0 eV)[57]. In this study, the CuO/ZnO was a catalyst in a metal oxide form. The oxidation state of Cu particle exhibited only peak of Cu^{2+} at 935 eV as shown in Figure 24a. When this CuO/ZnO catalyst was reduced to Cu/ZnO catalyst, the copper metal was an active site for methanol synthesis in temperature range 200-300 ^oC [64]. The catalyst reduction was conducted in a fixed bed reactor by passing 50%vol H_2/N_2 through catalyst at 300 ^oC for 3 h. For Cu/ZnO catalyst, the weak satellite was not observed. The shift of the peak position to 932 eV was noticed after reduction. It indicated that the catalyst was completely reduced from Cu^{2+} to Cu^0 as presented in Figure. 24b. The necessary of reduction process was presented in section 4.3. The result from this study shows that the reduced Cu/ZnO could provide much higher methanol yield comparing to non-reduced CuO/ZnO.
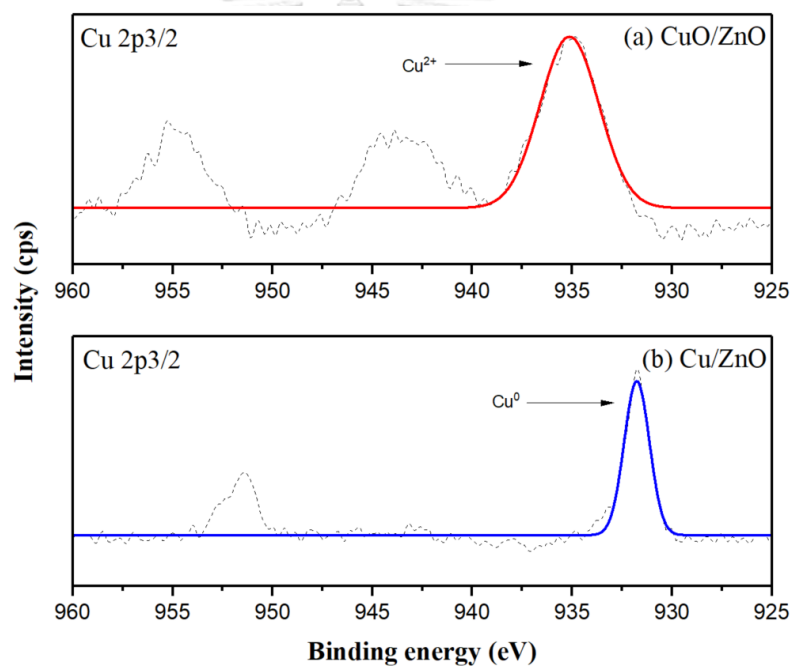
Figure 24 XPS spectra of Cu particles in (a) non-reduced CuO/ZnO, and (b) reduced Cu/ZnO.

4.2. The role of molecular sieve (MS)

MS has a uniform pore size, which is controlled by the cation in the crystal structure (3Å pore size for K ions, and 5Å pore size for Ca ions) [69]. The surface morphology of MS in this study was shown in Figure 25.
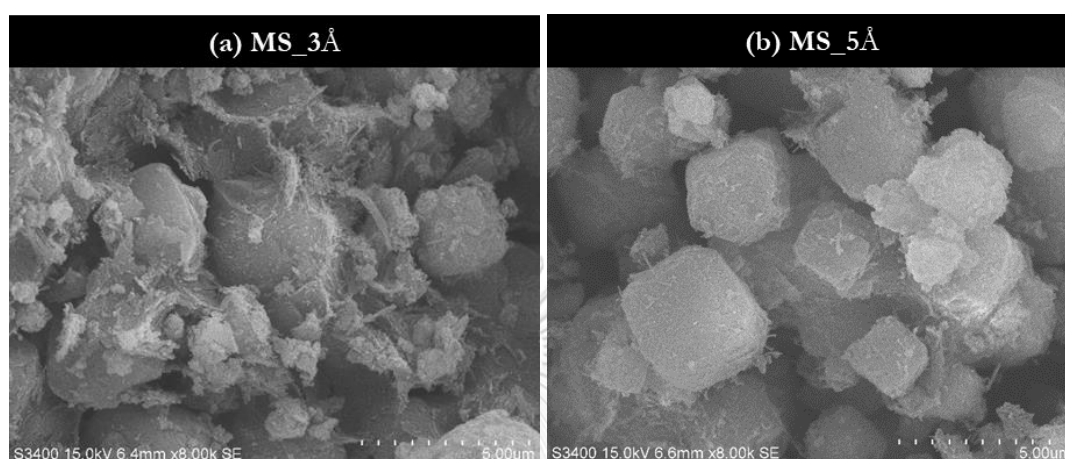
Figure 25 SEM images of molecular sieves (a) MS_3A (b) MS_5A.

To confirm the role of MS in alcohol-assisted methanol synthesis, the MS_3A and MS_5A were tested under the reaction conditions without Cu/ZnO catalyst (150 ᵒC, 5.0 MPa, CO_2:H_2 of 1:3). The results proved that both MS_3A and MS_5A could not catalyze the reaction. As can be seen in Table 12, the methanol yield and selectivity were 0% without catalyst. The MS only acted as adsorbent in this reaction. Due to the pore size, MS_3A selectively adsorbs water while MS_5A can adsorb methanol, ethanol and water.

Table 12 Alcohol-assisted methanol synthesis at 150ᵒC and 5.0 MPa with Cu/ZnO catalyst and MS

Adsorbent and catalyst	%Methanol yield	%Methanol selectivity
MS_3A	0.0%	0.0%
MS_5A	0.0%	0.0%
CuO/ZnO	13.9%	77.7%
Cu/ZnO	35.8%	87.9%

4.3. Alcohol assisted methanol synthesis

In this section, Cu/ZnO catalyst was mixed with MS for alcohol-assisted methanol synthesis when ethanol was used as the catalytic solvent in all experimental. Each experimental batch was carried out for 24 h. After that, the reactor was cooled down using cooling water circulation system. The gas effluent and liquid effluent were collected and analyzed by gas chromatography. The composition of product was calculated based on internal standard method where methanol yield and selectivity were calculated by Eq. (11)-(12).

4.3.1 The effect of MS type

The catalytic activities of Cu/ZnO catalyst with different MS types on alcohol assisted-methanol synthesis were investigated at 150 °C, 5 MPa. The 2.6g Cu/ZnO catalyst with 1.3g MS was used. The non-reduced catalyst (CuO/ZnO) also was tested in this experiment. The results showed that Cu/ZnO catalyst provided the higher methanol yield (35.8%) than CuO/ZnO catalyst (13.9%). It was reported that the methanol yield increased with increased Cu metallic surface area [68]. Therefore, the reduction was significant step to activate the catalyst. Ethyl acetate was detected as the byproduct in this experiment, but not methyl acetate. This contrasted to the work of Kim et al. [11] who reports the detection of methyl acetate. Although, it is still unclear the conditions of methyl acetate formation, it was reported that ZnO, which was basicity catalyst, can catalyze transesterification of ethyl acetate with methanol to form methyl acetate. Therefore, ZnO morphology as well as the catalyst preparation parameters might be the cause of the different results.

As presented in Figure 26, the addition of MS enhanced methanol yield. The highest methanol yield was obtained (42.6%) when the MS_3A was added. Due to the pore size, MS_3A selectively adsorbs water. As described earlier, water can poison the catalyst by blocking the active site. Removing of water during the reaction significantly enhanced methanol yield. Consider the pore size, the MS_5A can adsorb methanol, ethanol, and water. It also promoted methanol yield by decreasing the concentration of methanol and water during the reaction, shifting the reaction toward to more product. However, the methanol yield (38.5%) did not increase as much as in the case of MS_3A. This was likely due to adsorption capacity. Methanol and ethanol were also competing adsorbed with water. Consequently, the MS_3A was more effective to enhance methanol yield. The combination of MS_3A and MS_5A exhibited the performance (methanol yield = 40.2%) in the middle between in case of MS_3A and MS_5A.

4.3.2 The effect of catalyst/MS ratio

The effect of the ratio of catalyst to MS (2:1 and 1:1) was investigated. The amount of Cu/ZnO was fixed at 2.6g while the amount of MS was varied. The result showed that increasing MS amount decreased the methanol yield for both cases of MS_3A and MS_5A, as shown in Figure 26. This result was contrary to the work of Nieminen et al. [13] who reports that the methanol productivity increases with the larger amount of MS. The reduction of methanol yield could relate to the obstruction of MS on the catalyst. The MS was proved not to participate as a catalysis in the reaction (section 4.2.). Therefore, too high amount of MS could block the catalyst site and hinder the reactant/catalyst collision. Consequently, the methanol yields were even lower than the Cu/ZnO catalyst without MS.
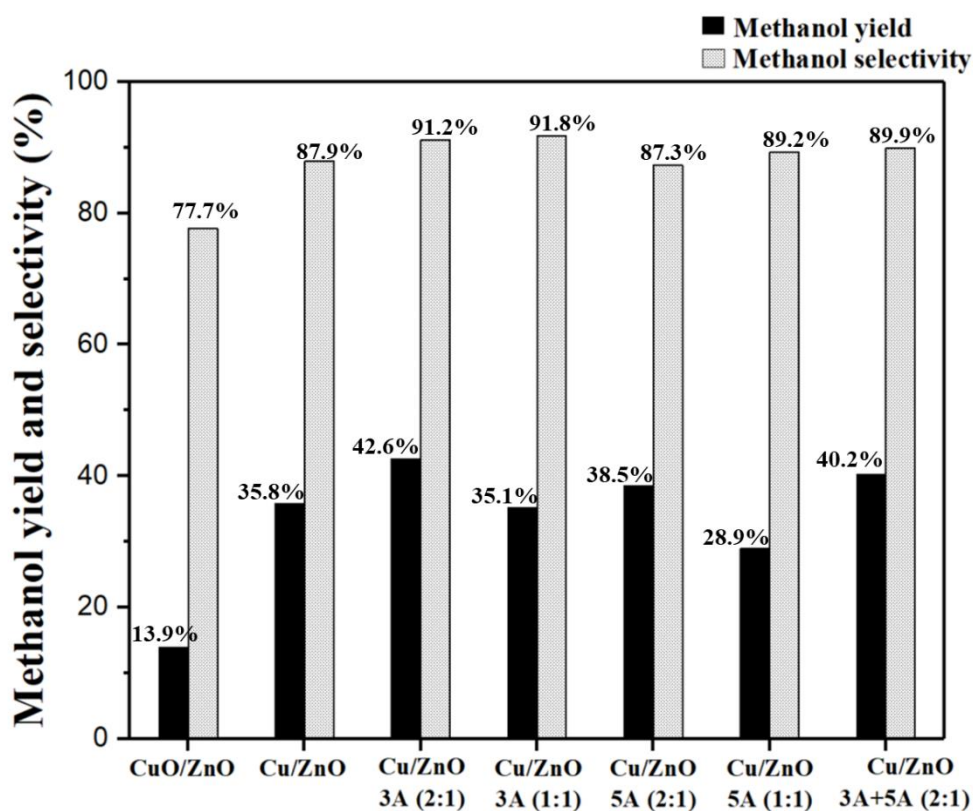
Figure 26 Catalytic activities of Cu/ZnO catalyst with different molecular sieve types on alcohol assisted methanol synthesis at 150 ^{o}C, 5 MPa.

4.4. The desorption of MS_5A

The 5A MS was added into the reactor (both MS_5A and MS_3A+MS_5A), aiming to adsorb the methanol product. Therefore, desorption of methanol from MS_5A must be done in order to measure the methanol yield. The liquid effluent was collected and analyzed by gas chromatography as the sampling 1 after cooling down the reactor to room temperature while the sampling 2 was done after the desorption, as presented in Figure 27. After collecting the sampling 1, the liquid product and solids (catalyst and adsorbent) was heat to 130 ^{o}C to vaporize the liquid product and desorb the MS. The 30 ml min^{-1} of N$_2$ gas flow as carrier gas was passed through the reactor to carry the vaporized product to the condenser, which cooled by 10°C cooling water circulation. The composition of liquid effluent at condenser was then analyzed by gas chromatography as the sampling 2. The different methanol content of sampling 1 and sampling 2 was the net adsorbed methanol in MS. The result showed that the MS_5A selectively adsorbed methanol while only slight amount of ethyl acetate was adsorbed as presented in Table 13. The adsorbed methanol was 95.8%-96.8% while the adsorbed ethyl acetate was 3.2%-4.2%. This result proved that methanol could be separated from ethyl acetate by using 5A. Although MS_5A could provide high purity methanol up to more than 95%, the methanol uptake was small (2.4-3.9%) and methanol yield did not significantly increased. Moreover, the absorption of water and ethanol by MS_5A should be further studied.
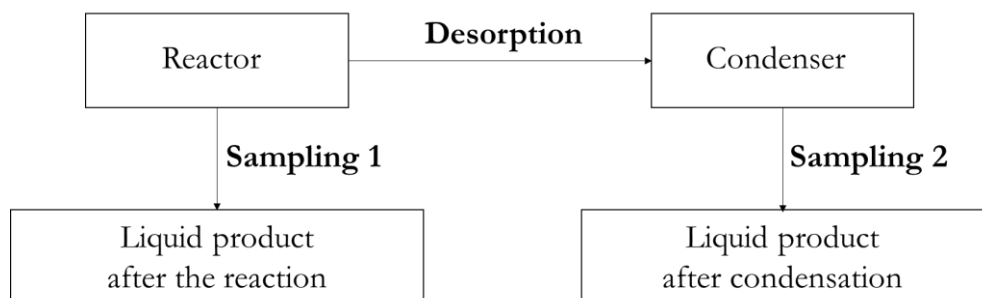
Figure 27 Schematic drawing of the desorption of MS-5A.

Table 13 Methanol yields before and after desorption of molecular sieve 5A.

Step	%Methanol yield	%adsorbed methanol[a]	%adsorbed ethyl acetate[b]
Cu/ZnO_MS 5A			
Sampling 1	37.0%		
Sampling 2	38.5%		
Net adsorbed methanol	3.9%	96.8%	3.2%
Cu/ZnO_MS 3A + MS 5A			
Sampling 1	39.3%		
Sampling 2	40.2%		
Net adsorbed methanol	2.4%	95.8%	4.2%

[a] Percentage of methanol in the mixture of methanol/ethyl acetate, which was adsorbed by MS_5A
[b] Percentage of ethyl acetate in the mixture of methanol/ethyl acetate, which was adsorbed by MS_5A

4.5. Effect of operating temperature

Alcohol-assisted methanol synthesis was conducted under different operating conditions. According to the literatures, low-temperature methanol synthesis has been done at a typical condition at temperature of 150 $^{\circ}$C and pressure of 5.0 MPa [11, 50-52]. To our knowledge, the operating temperature lower than 150 $^{\circ}$C has not been reported elsewhere. Therefore, the effect of temperature range between 100-150 $^{\circ}$C is interesting. As mentions before, the dehydrogenation of ethanol to ethyl acetate is an endothermic reaction. Therefore, decreasing temperature resulted in lower ethyl acetate yield. Although decreasing temperature also positively affects thermodynamics since CO_2 hydrogenation to methanol is an exothermic reaction, the lower temperature led to the lower rate of reaction. This trade-off between higher purity methanol and lower methanol yield is of interest in term of optimum operating condition. Therefore, the effect of temperature was investigated in this study.

As shown in Figure 28 , the activity of Cu/ZnO catalyst on alcohol-assisted methanol synthesis was carried out at various temperatures including 100 $^{\circ}$C, 130 $^{\circ}$C, and 150 $^{\circ}$C when pressure was maintained at 5 MPa. The result corresponded to what was described earlier. The methanol selectivity was higher when the temperature decreased. The 100% methanol selectivity was gained at operating temperature of 100 $^{\circ}$C, but the methanol yield decreased to only 3.6% due to insufficiency of reaction rate. Therefore, 100 $^{\circ}$C was not a suitable temperature for this reaction. At 130 $^{\circ}$C, even though the methanol yield decreased to 30.6% (130 $^{\circ}$C) from 35.8% (150 $^{\circ}$C), the methanol selectivity was rather high (>98%). Therefore, operating temperature of 130oC can be an optimum operating temperature in this study.

Another concerned factor was the solubility of CO_2 in the catalytic solvent which is ethanol in this study. CO_2 and H_2 were still in gas phase, while main ethanol was compressed by high pressure into liquid phase under these conditions (5 MPa, 130 $^{\circ}$C). The Cu/ZnO was in solid phase. Gas reactants needed to contact catalyst which was submerged under ethanol. Therefore, some factors, which could affect to the activity of catalyst, were considered. Stirring rate was used as high as possible to avoid effect of mass transfer limitation. It was known that the solubility of CO_2 in ethanol decreased with increasing temperature was increased [70]. Therefore, if solubility of CO_2 in ethanol would significantly affect the formation of methanol, the methanol yield should decrease with increasing of temperature. The result turned out in opposite side of the assumption above. It indicated that reaction rate was the most influential factor affecting the reaction when compared with the CO_2 solubility and the thermodynamic equilibrium.
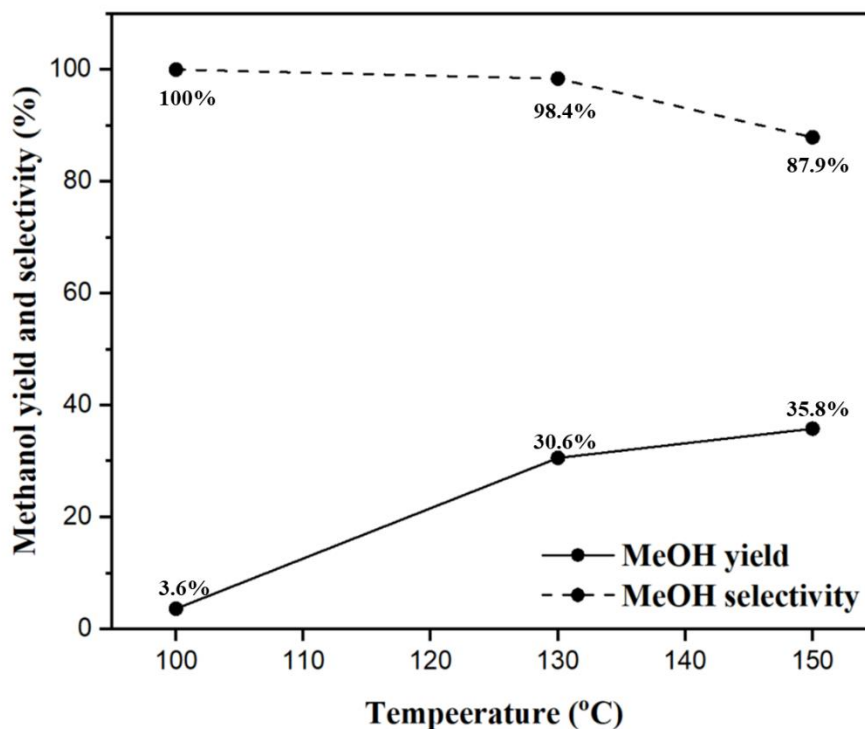
Figure 28 Catalytic activities of Cu/ZnO catalyst at different operating temperature (100 °C, 130 °C, and 150 °C), pressure 5 MPa.

The MS_3A and MS_5A were introduced at the reaction temperature of 130 °C comparing to typical condition (150 °C). It was found that the effect of MS on the reaction 130 °C was less than that at 150 °C. The methanol yields slightly increased to 33.4% when MS were applied at operating temperature of 130 °C, as can be seen in Figure 29, although the adsorption on MS was reported to increase as decreasing temperature [71, 72]. The methanol formation rate mainly depends on the reaction temperature. Therefore, methanol yield decreased with decreasing temperature although the adsorption ability increased.
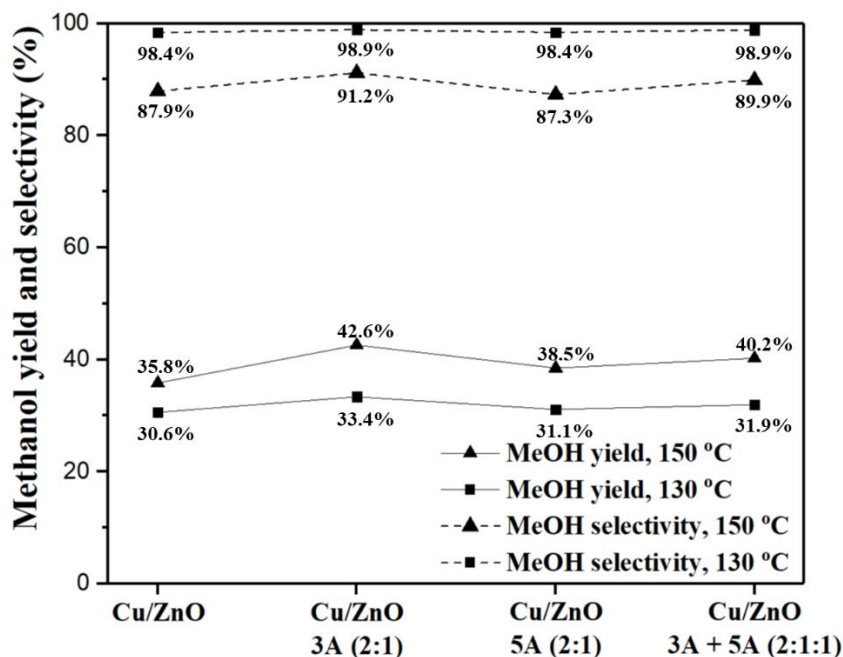
Figure 29 Catalytic activities of Cu/ZnO catalyst with different molecular sieve on alcohol assisted methanol synthesis at 130 °C and 150°C, 5 MPa.

The result showed that MS_3A could enhance methanol yield from 30.6% to 33.4% which was a good option in the experiment. However, considering a large-scale commercial production, it might not be a suitable option. This experiment was carried out in a batch system. The continuous system should be further investigated as a future work. Moreover, the adsorption capacity should be considered. Therefore, the regeneration of MS is inevitable in a real process. The specially designed reactor is required for MS transporting from the reactor to a regeneration unit with less effect on the reaction. For example, Bayat et al. suggested a modelling called "Gas flowing solid fix bed reactor (GFSFBR)" at which MS is applied with methanol synthesis reactor [53].

Another option, the development of catalyst which has better catalytic activity under this operating condition can be an alternative choice when the complex reactor system is not required. Complication from MS regeneration can be eliminated.

To sum up, methanol selectivity significantly increased with a few amounts of ethyl acetate formed at 130 °C. This benefits the methanol synthesis in purification process, leading to simpler separation unit as represent in Figure 30 when compared with the low-methanol selectivity system [12]. However, the techno-economic analysis under should be further carried out to realize the new process feasibility.
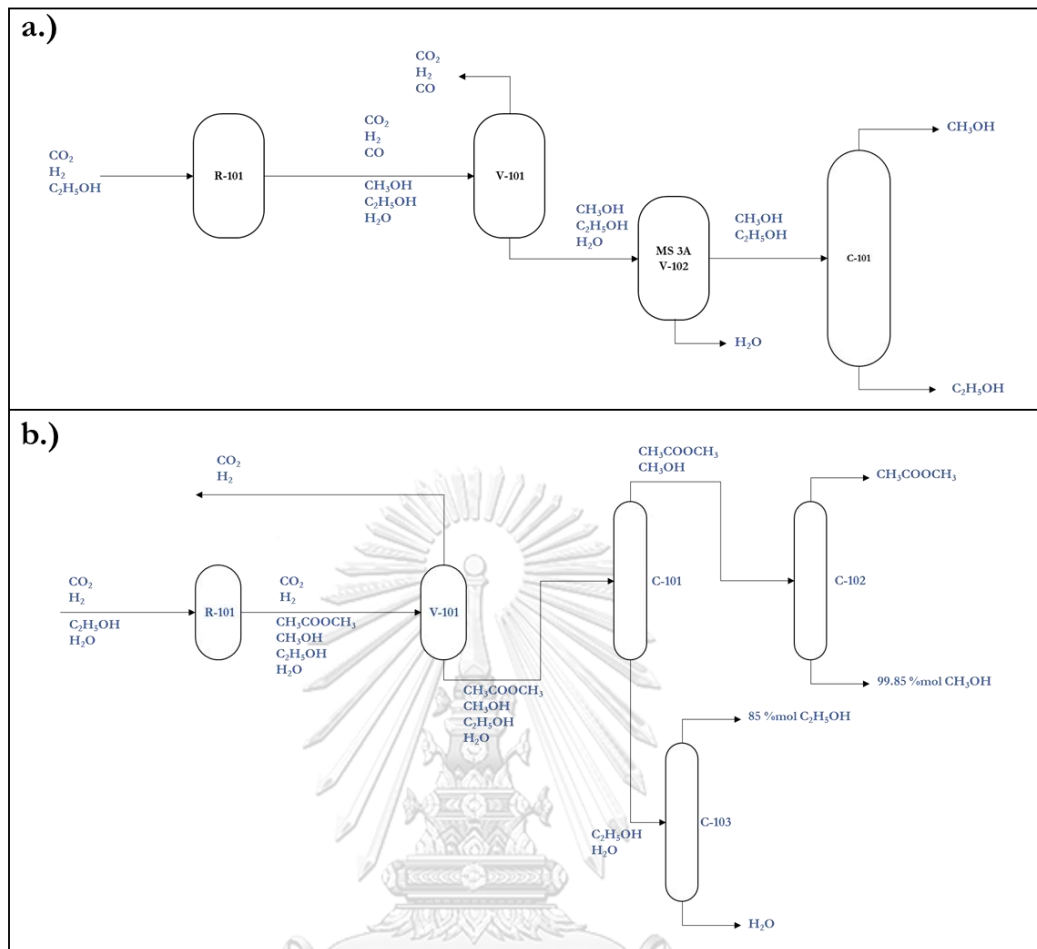
Figure 30 purification process of a.) methanol without ethyl acetate as by-product, and b.) methanol with ethyl acetate as by-product

CHAPTER V

CONCLUSION

5.1. Conclusion

The effect of MS on alcohol-assisted methanol synthesis was investigated. The catalyst was Cu/ZnO, prepared by co-precipitation based on optimal temperature, pH-value, and aging time. Ethanol was used as the catalytic solvent in the reaction enabled methanol to be synthesized from CO_2 and H_2 at low temperature (150°C, 5.0 MPa), providing methanol yield and selectivity of 35.8% and 87.9 %, respectively. However, ethyl acetate and water were generated as byproduct of the reaction and formed azeotrope mixture with methanol product. In this study, it was found that controlling temperature and using MS could help enhance the yield and selectivity of methanol.

The key points of this study are summarized as follows:

The MS (3A and 5A) was used to adsorb the byproduct during the reaction in this study. It was found that MS acted only as adsorbent. MS_3A adsorbed water while MS-5A could adsorb methanol. The test of MS under the reaction condition without Cu/ZnO showed 0% methanol yield.

Mixing MS with Cu/ZnO enhanced the methanol yield for all cases (MS_3A, MS_5A, and MS_3A mixed MS_5A). However, the best methanol yield (42.6%) was obtained when MS_3A was applied. The reaction was promoted by the adsorption of water.

The ratio of catalyst to MS (2:1 and 1:1) affected the methanol synthesis. The lower methanol yields were obtained when the amount of MS increased at constant amount of Cu/ZnO catalyst.

This result proved that methanol could be separated from ethyl acetate by using MS_5A. The adsorbed methanol was 95.8%-96.8% selectivity while the adsorbed ethyl acetate was 3.2%-4.2%. However, although high purity methanol could be absorbed, the methanol uptake was low (2.4-3.9%) and methanol yield was not significantly increased.

The operating temperatures were also varied. The lower temperature (150 °C -> 130 °C -> 100 °C) decreased methanol yield but increased methanol selectivity. The optimum temperature of 130 °C provided rather high methanol selectivity (>98%) although methanol yield decreased to 30.6%. When MS was applied with Cu/ZnO under the reaction at 130°C, 5.0 MPa, methanol yield only slightly increased.

5.2 Recommendation

1. The effect of stirring rate should be concerned. In this experiment, the used stirring rate is 600 rpm. It should be tested that this speed is high enough to be free from mass transfer limitation. To make confirm that there is no mass transfer limitation to the activities of catalyst. Higher stirring rate is required. However, 600 rpm is the maximum stirring rate of the reactor in this study. For further work, the reactor can be modified to accommodate higher stirring speed.

2. Detailed study on molecular sieve desorption should be carried out. The size of catalyst and molecular sieve should be different for separation purpose. The catalyst should be smaller than molecular sieve because catalyst is a necessary part for reaction which is highly sensitive to surface area of catalyst. However, the adsorption capacity of a molecular sieve also drops in a larger particle size. This is a tradeoff between catalysis activity and adsorption ability. A proper ratio of catalyst to molecular sieve size should be determined.

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APPENDIX

A.1. Preparation of solutions

The solutions, which were used in catalyst synthesis, included Copper nitrate solution, Zinc nitrate solution and Sodium carbonate solution. The precursors and precipitating agent were provided from Sigma-Aldrich. The specification of solutions was represented in Table 14.

Table 14 Specification of precursors and precipitating agent solutions.

Chemical	Molecular weight (g)	Purity(%wt)	Concentration (Molar)
$Cu(NO_3)_2 \cdot 3H2O$	241.6	98.0%	1 M
$Zn(NO_3)_2 \cdot 6H2O$	297.4	99.0%	1 M
Na_2CO_3	106.0	99.5%	1.5 M

$$\frac{g(\%purity)}{M_w} = \frac{CV}{1000}$$

Where:

g	=	Weight of chemical (g)
%purity	=	Percentage purity of chemical (%wt)
Mw	=	Molecular weight of chemical (g)
C	=	Concentration of solution (Molar)
V	=	Volume of solution (ml)

In coprecipitation of Cu/ZnO catalyst, the solid precursor was prepared by the reaction between precursor solutions and precipitating agent solution as in equation (a)-(b).

$Cu(NO_3)_2$ (aq) + Na_2CO_3 (aq) → $CuCO_3$ (s) + $2NaNO_3$ (aq)(a)
$Zn(NO_3)_2$ (aq) + Na_2CO_3 (aq) → $ZnCO_3$ (s) + $2NaNO_3$ (aq)(b)
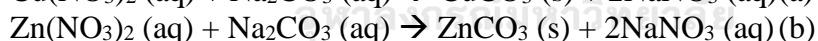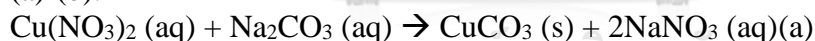
Each catalyst synthesis batch, 5g of Cu/ZnO catalyst was desired with Cu:Zn ratio = 1:1. Amount of each metal was 2.5 g. Therefore, amount of each required chemical was calculate as following:

Amount of required copper nitrate $= \dfrac{2.5 \text{ g x } 241.5 \text{ g}}{63.55 \text{ g x } 0.98\%wt}$ = 9.7 g

Amount of required zinc nitrate $= \dfrac{2.5 \text{ g x } 297.4}{65.38 \text{ g x } 0.99\%wt}$ = 11.6 g

To determine used volume of each solution, weights of each metal source were converted to mole. After that the required volumes were calculated from the concentration of solution as mentioned above.

Mole of required copper nitrate $= \dfrac{9.7 \text{ g}}{241.5 \text{ g}}$ = 0.0401 mole

Mole of required zinc nitrate $= \dfrac{11.6 \text{ g}}{297.4 \text{ g}}$ = 0.0386 mole

Volume of required copper nitrate $= \dfrac{0.0401 \text{ mole} \times 1000 \text{ ml}}{1 \text{ mole}}$ = 40.1 ml

Volume of required zinc nitrate $= \dfrac{0.0386 \text{ mole} \times 1000 \text{ ml}}{1 \text{ mole}}$ = 38.6 ml

From equation (a)-(b):
mole of required sodium carbonate   = 0.0401 + 0.0386   = 0.0787 mole
,but purity was 99.5%wt. the actual required mole   = 0.0791 mole

Volume of required sodium carbonate $= \dfrac{0.0791 \text{ mole} \times 1000 \text{ ml}}{1.5 \text{ mole}}$ = 52.73 ml

As mentions above, the required information for synthesis of 5g Cu/ZnO catalyst was summarized in Table 15.

Table 15 information about quantities of chemicals for synthesis of 5g Cu/ZnO catalyst.

Chemical	Required weight (g)	Concentration (Molar)	Required volume (ml)
$Cu(NO_3)_2 \cdot 3H_2O$	9.7	1 M	40.1
$Zn(NO_3)_2 \cdot 6H_2O$	11.6	1 M	38.6
Na_2CO_3	8.4	1.5 M	52.73

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A.2. Crystallite size calculation from Scherer's equation

$$d = \frac{0.9\lambda}{\beta_{FWHM}\cos(\theta)}$$

Where:

d	= Crystallite size (nm)
λ	= Wavelength of X-ray (Cu-Kα, λ = 1.5406 Å)
β_{FWHM}	= The full width for the half-maximum (FWHM) intensity peak
θ	= The diffraction angle

The crystallite size of each element could be calculated from the main peak of metal in XRD pattern of CuO/ZnO catalyst. In case of the main peak of CuO (111) was located at 2θ = 39o (JCPDS card no. 45-0937), while main peak of ZnO (101) was at 2θ = 36o (JCPDS card no. 79-0206) as indicated in Figure 31. After that, parameters of each peak were obtained. The calculated crystallite size of CuO and ZnO were 1.03 nm and 1.02 nm, respectively.
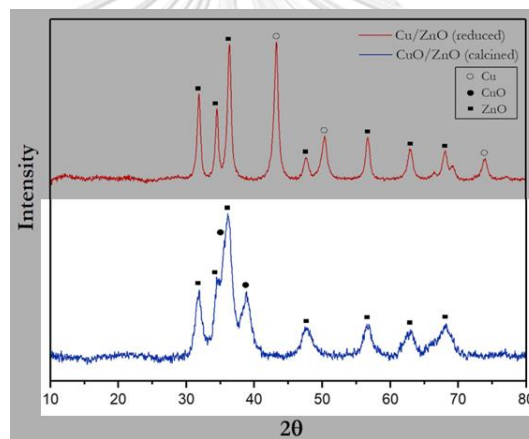
Figure 31 The XRD pattern of calcined CuO/ZnO catalyst (blue line).

A.3. Calibration curve information

A.3.1.Liquid effluents

a). MeOH calibration at 0.05%-1%

$y = 0.0185045852x - 0.0002833284$
$R^2 = 0.9986251248$

b). MeOH calibration at 1%-40%

$y = 0.0142433516x + 0.0047380065$
$R^2 = 0.9958792048$

c). MeOH calibration at 40%-100%

$y = 0.0082666837x + 0.1767423460$
$R^2 = 0.9997506786$
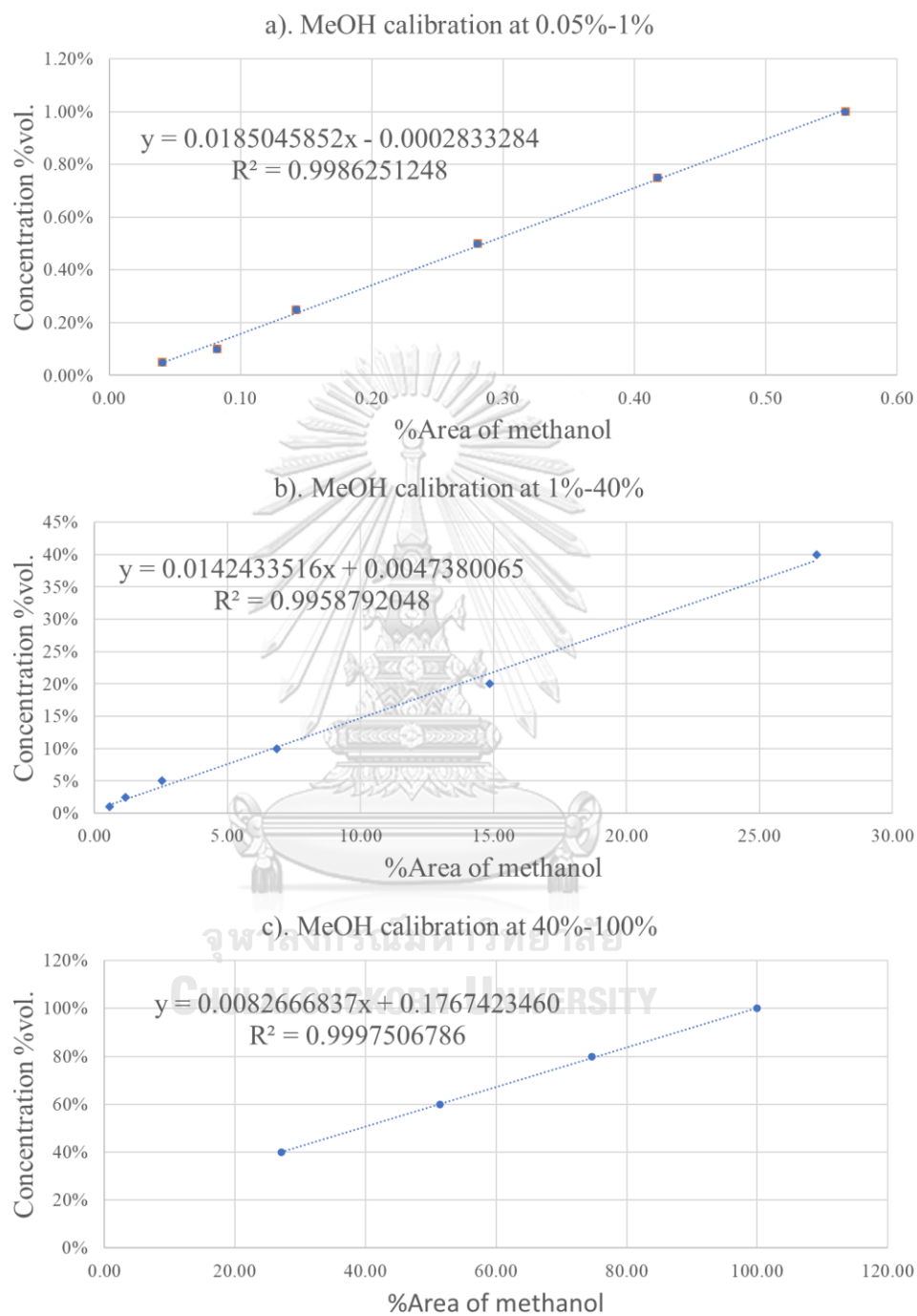
Figure 32 Calibration curve of methanol depended on concentration range
a). 0.05%-1%, b). 1%-40%, and c). 40%-100%.

EtAc calibration at 0.1%-1%
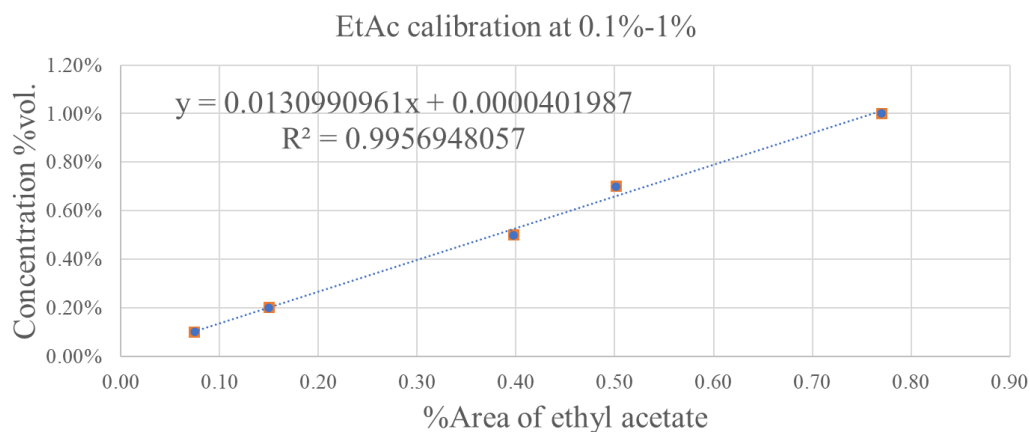
Figure 33 Calibration curve of ethyl acetate at concentration range 0.1%-1%.

Calibration curve equation for amount of products calculation.
Methanol:
For y = 0.05%-1%,
y [concentration, %vol] = 0.0185045852x [%area of methanol] - 0.0002833284
For y = 1%-40%
y [concentration, %vol] = 0.0142433516x [%area of methanol] + 0.0047380065
For y = 40%-100%
y [concentration, %vol] = 0.0082666837x [%area of methanol] + 0.1767423460

Ethyl acetate:
For x = 0.1%-1%
y [concentration, %vol] = 0.0130990961x [%area of ethyl acetate] + 0.0000401987

Table 16 Raw data of standards methanol for calibration curve establishing.

Methanol raw data for calibration curve establishing					
Concentration	Area of MeOH	Area of EtOH	%Area of MeOH	%Area of EtOH	AVG %Area MeOH
MeOH 0.05%	6045	14899348	0.041	99.959	0.04
	5614	14038965	0.04	99.96	
	4461	11056111	0.04	99.96	
	2370	6102784	0.04	99.96	
	5395	13654741	0.04	99.96	
	4560	11555390	0.04	99.96	
	8276	19174693	0.043	99.957	
	4338	11221190	0.04	99.96	
MeOH 0.1%	13280	16002763	0.083	99.917	0.08
	13425	15947221	0.084	99.916	
	2401	2832659	0.084	99.916	
	4498	5465986	0.082	99.918	
	12270	14977597	0.082	99.918	
	9113	11171773	0.082	99.918	
	11576	14236642	0.081	99.919	
	7804	9623448	0.081	99.919	
	11276	14000280	0.08	99.92	
MeOH 0.25%	23672	15726756	0.15	99.85	0.14
	20543	15076088	0.14	99.86	
	19995	14412396	0.14	99.86	
	20520	15044190	0.14	99.86	

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Table 17 Raw data of standards methanol for calibration curve establishing (cont.).

Methanol raw data for calibration curve establishing

Concentration	Area of MeOH	Area of EtOH	%Area of MeOH	%Area of EtOH	AVG %Area MeOH
MeOH 0.5%	43726	15502904	0.281	99.719	
	39007	13847444	0.281	99.719	
	42118	15028388	0.279	99.721	0.28
	46397	16487738	0.281	99.719	
MeOH 0.75%	60140	14288121	0.419	99.581	
	39274	9299072	0.421	99.579	
	65231	15619555	0.416	99.584	0.42
	57920	13776238	0.419	99.581	
	61123	14754435	0.413	99.587	
MeOH 1%	88130	15140673	0.579	99.421	
	60690	10825283	0.558	99.442	
	87085	15532389	0.558	99.442	
	96289	16546114	0.579	99.421	
	57300	10286434	0.554	99.446	0.56
	59732	10704616	0.555	99.445	
	60846	10919443	0.554	99.446	
	80993	14666236	0.549	99.451	
MeOH 2.5%	202938	16848572	1.190	98.810	
	111590	9342608	1.18	98.82	
	185157	15632180	1.171	98.829	1.17
	201503	17058455	1.167	98.833	
	152391	12977543	1.161	98.839	
MeOH 5%	430343	16151429	2.595	97.405	
	422553	16263473	2.532	97.468	
	298537	11491702	2.532	97.468	
	207454	7976539	2.535	97.465	
	347317	13477818	2.512	97.488	2.53
	376325	14615460	2.51	97.49	
	189318	7355621	2.509	97.491	
	232729	9041647	2.509	97.491	
	437509	16964343	2.514	97.486	
MeOH 10%	933722	12649415	6.874	93.126	
	873344	11930583	6.821	93.179	
	833412	11321234	6.857	93.143	6.85
	967932	13202479	6.831	93.169	
MeOH 20%	2063961	11620393	15.083	84.917	
	1987983	11459852	14.783	85.217	14.86
	1838445	10646953	14.725	85.275	

Table 18 Raw data of standards methanol for calibration curve establishing (cont.).

Methanol raw data for calibration curve establishing

Concentration	Area of MeOH	Area of EtOH	%Area of MeOH	%Area of EtOH	AVG %Area MeOH
MeOH 40%	1985092	5113654	27.964	72.036	27.15
	2833073	7653993	27.015	72.985	
	3647874	9932538	26.861	73.139	
	3352771	9183901	26.744	73.256	
MeOH 60%	5983664	5463462	52.272	47.728	51.37
	4994925	4793294	51.03	48.97	
	3562056	3450871	50.793	49.207	
MeOH 80%	8363319	2214404	79.065	20.935	74.68
	5707688	2130582	72.818	27.182	
	2135818	1112839	72.15	27.85	
MeOH 100%	9070067	0	100	0	100.00
	11417304	0	100	0	
	9609159	0	100	0	

Table 19 Raw data of standards ethyl acetate for calibration curve establishing.

Ethyl acetate raw data for calibration curve establishing

Concentration	Area of EtAc	Area of EtOH	%Area of EtAC	%Area of EtOH	AVG %Area EtAc
EtAc 0.1%	10765	14944308	0.072	99.928	0.07
	9198	12179827	0.075	99.925	
	7380	9855397	0.075	99.925	
	7501	9931648	0.075	99.925	
	7457	9854768	0.076	99.924	
EtAc 0.2%	27794	18733573	0.15	99.85	0.15
	17020	10946611	0.16	99.84	
	38591	27507508	0.14	99.86	
	15965	10681889	0.15	99.85	
	13922	8852035	0.16	99.84	
	17021	11582221	0.15	99.85	
	15805	10771944	0.15	99.85	
EtAc 0.5%	38162	9343192	0.41	99.59	0.40
	40355	9949443	0.4	99.6	
	34659	8839269	0.39	99.61	
	39863	10164775	0.39	99.61	

Table 20 Raw data of standards ethyl acetate for calibration curve establishing (cont.).

Ethyl acetate raw data for calibration curve establishing					
Concentration	Area of EtAc	Area of EtOH	%Area of EtAC	%Area of EtOH	AVG %Area EtAc
EtAc 0.7%	74981	14689342	0.5	99.5	0.50
	90967	18349799	0.49	99.51	
	68552	13523813	0.5	99.5	
	8871	1699734	0.52	99.48	
	55714	11128596	0.5	99.5	
	77116	15458601	0.5	99.5	
	62291	11675792	0.53	99.47	
	70864	15105787	0.47	99.53	
EtAc 1%	89005	10685556	0.83	99.17	0.77
	103263	13468569	0.76	99.24	
	102869	13666984	0.75	99.25	
	103710	13978861	0.74	99.26	

A.3.2. Gas effluents
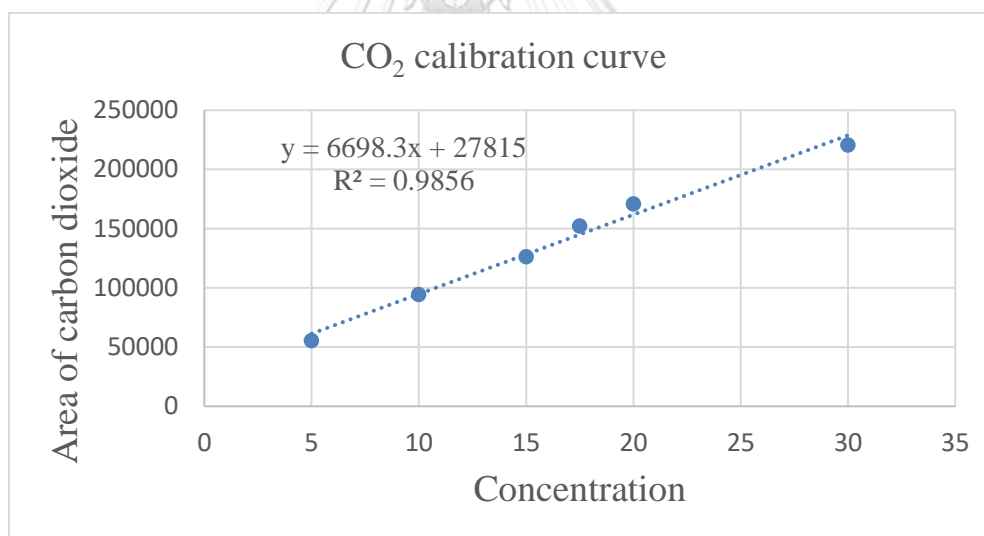
Figure 34 Calibration curve of carbon dioxide at concentration range 5%-30% (old calibration curve).
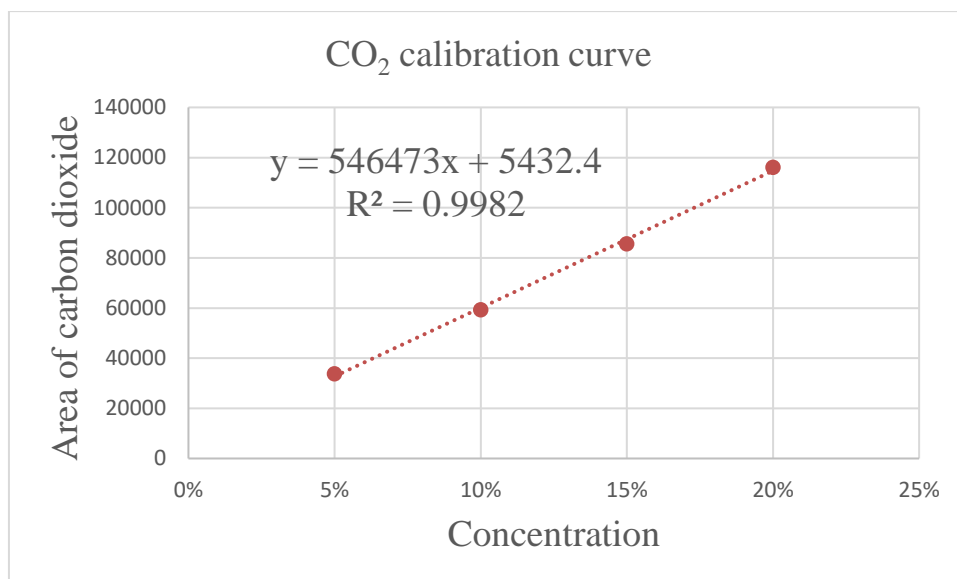
Figure 35 Calibration curve of carbon dioxide at concentration range 5%-20% (new calibration curve).

CO_2 calibration curve equation
For experiment that was tested before 1st January 2021,
y [Area of carbon dioxide] = 6698.3x [Concentration] + 27815

For experiment that was tested after 1st January 2021,
y [Area of carbon dioxide] = 546473x [Concentration] + 5432.4

Table 21 Raw data of standards carbon dioxide for calibration curve establishing (old calibration curve data).

Carbon dioxide raw data for calibration curve establishing		
Concentration	**Area of CO$_2$**	**AVG Area CO$_2$**
5%	50091	55463.8
	65330	
	57396	
	53507	
	50995	
10%	90505	94459.7
	99876	
	92998	
15%	124266	126286
	128306	
17.5%	153164	152344
	151524	
20%	167655	170933
	164911	
	180234	
30%	220486	220486

Note: the old CO2 calibration curve was used for experiment that was tested before 1st January 2021

Table 22 Raw data of standards carbon dioxide for calibration curve establishing (new calibration curve data).

Carbon dioxide raw data for calibration curve establishing		
Concentration	**Area of CO$_2$**	**AVG Area CO$_2$**
5%	34473	33828
	33535	
	33476	
10%	59502	59362
	59616	
	58968	
15%	84442	85623
	86524	
	85903	
20%	116462	116153.3
	116400	
	116246	
	115505	

Note: the new CO$_2$ calibration curve was used for experiment that was tested after 1st January 2021

A.4. Activity calculation

The activity parameters including yield of methanol, and selectivity of methanol were calculated following equations below, respectively.

$$\text{Yield of methanol} = \frac{\text{Mole of methanol product}}{\text{Mole of feeding CO2}} \times 100$$

$$\text{Selectivity of methanol} = \frac{\text{Mole of methanol product}}{\text{Mole of all products}} \times 100$$

Example: yield of methanol calculation
Experiment: 2.6g Cu/ZnO at 150 $^{\circ}$C, 5 MPa
The liquid effluent was collected for analysis by gas chromatography technique. A few amounts of liquid effluent (about 0.2 µl) were injected into GC 3-4 times. The area of chemicals was represented below.

Chemicals	Area 1	Area 2	Area 3	Area 4	Average
MeOH	151712	148133	153085	148377	150326.75
EtOH	16147759	15894917	16362592	15977076	16095586
EtAc	73041	74122	73995	72458	73404

The area of each chemical was averaged. After that, the percentage of each chemical in solution was calculated.

Chemicals	Average	%Area
MeOH	150326.75	0.921158357
EtOH	16095586	98.6290434
EtAc	73404	0.449798243

The percentage of methanol area was 0.92%. Therefore, the calibration curve equation for concentration range (1%-40%) was chosen for calculation
y [concentration, %vol] = (0.0142433516x [%area of methanol]+ 0.0047380065)x100
y [concentration, %vol] = (0.0142433516 x (0.921158357) + 0.0047380065)x100
y [concentration, %vol] = 1.786 %vol

1.786 % The final liquid effluent volume was 55 ml.
Total methanol volume   = 55 ml x 1.786 %vol = 0.98 ml

After the total methanol volume was carried out, the mole of methanol was calculated (density of methanol = 0.792 g ml^{-1}, molecular weight of methanol = 32 g mol^{-1})

$$\text{Weight of total methanol} = \frac{0.792\ g}{cm^3} \times 0.98\ ml = 0.78\ g$$

$$\text{Mole of total methanol} = \frac{0.78\ g}{32\ g\ mol^{-1}} = 0.0243\ \text{mole}$$

The mole of CO_2 feeding was calculated using ideal gas law.

$$PV = nRT$$

Where:

P	=	Pressure (Pa)	
V	=	Volume of gases (m^3)	
n	=	Mole of gases (mole)	
R	=	The gas constant	= 8.314 Pa m^3 mol^{-1} K^{-1}
T	=	Temperature (K)	

System: pressure = 5 x 10^6 Pa, reactor volume = 250 x 10^{-6} m^3, liquid volume = 60 x 10^{-6} m^3, temperature = 150 ^oC, and CO_2:H_2 molar ratio = 1:3

Therefore,

Mole of CO_2 feeding $= \dfrac{(5 \ x \ 10^6 \ Pa) \ x \ ((250-60) \ x \ 10^{-6} m^3)}{4 \ x \ (8.314 \frac{Pa \ m^3}{mol \ K}) \ x \ (273+150 \ K)} = 0.0675$ mole

Therefore, yield of methanol $= \dfrac{0.0243 \ mol}{0.0675 \ mol}$ x 100 $= 36\%$

Example: selectivity of methanol calculation

Experiment: 2.6g Cu/ZnO at 150 ^oC, 5 MPa

According to example: yield of methanol calculation, the mole of methanol was 0.0243 mole. For mole of ethyl acetate, the calculation was similar to how to find mole of methanol except the calibration curve. Finally, the percentage of ethyl acetate area (0.59 %vol) was obtained.

Total ethyl acetate volume = 55 ml x 0.59 %vol = 0.32 ml

After the total methanol volume was carried out, the mole of methanol was calculated (density of methanol = 0.902 g ml^{-1}, molecular weight of methanol = 88 g mol^{-1})

Weight of total methanol $= \dfrac{0.902 \ g}{cm^3}$ x 0.32 ml = 0.293 g

Mole of total methanol $= \dfrac{0.293 \ g}{88 \ g \ mol^{-1}}$ = 0.00334 mole

Therefore,

Selectivity of methanol $= \dfrac{0.0243 \ mol}{0.0243 \ mol + 0.00334 \ mol}$ x100 = 87.9%

The summary of methanol yield and selectivity of all experiment was represented in Table 23 below.

Table 23 Summary of methanol yield and selectivity of all experiment.

Temp. (°C)	Exp. Batch	Remain Liq. volume	Average %area MeOH	Average %area EtAc	%Vol	Total MeOH volume	weight MeOH (g)	mole MeOH	mole EtAc	mole CO_2 feeding	MeOH yield	MeOH selectivity
150	CuO/ZnO	55	0.389	0.363	0.00692	0.381	0.301	0.0094	0.0027	0.068	13.9	77.7
	Cu/ZnO	55	0.921	0.450	0.0178	0.982	0.778	0.024	0.0033	0.068	35.8	87.9
	Cu/ZnO+3A(2:1)	55	1.158	0.376	0.0212	1.168	0.925	0.029	0.0028	0.068	42.6	91.2
	Cu/ZnO+5A(2:1)	55.5	1.002	0.505	0.0190	1.056	0.836	0.026	0.0038	0.068	38.5	87.3
	Cu/ZnO+3A5A	56	1.051	0.405	0.0197	1.103	0.874	0.027	0.0031	0.068	40.2	89.9
	Cu/ZnO+3A(1:1)	55	0.897	0.285	0.0175	0.963	0.763	0.024	0.0021	0.068	35.1	91.8
	Cu/ZnO+5A(1:1)	57	0.644	0.306	0.0139	0.793	0.628	0.020	0.0024	0.068	28.9	89.2
130	Cu/ZnO	55	0.786	0.0451	0.0159	0.876	0.694	0.022	0.00036	0.071	30.6	98.4
	Cu/ZnO+3A	57	0.845	0.0320	0.0168	0.956	0.757	0.024	0.00027	0.071	33.4	98.9
	Cu/ZnO+5A	53	0.847	0.0465	0.0168	0.891	0.706	0.022	0.00035	0.071	31.1	98.4
	Cu/ZnO+3A5A	56	0.814	0.0319	0.0163	0.915	0.724	0.023	0.00026	0.071	31.9	98.9
100	Cu/ZnO	55	0.126	0	0.00205	0.113	0.089	0.0028	0.00	0.077	3.6	100

A.5. Carbon balance calculation

$$\% \text{ Carbon balance} = \frac{\text{Mass C}_{\text{inlet}} - \text{Mass C}_{\text{outlet}}}{\text{Mass C}_{\text{inlet}}} \times 100$$

From the reaction, source of inlet carbon was carbon dioxide only. Ethanol was not considered because it was not used as reactant in this reaction.

Therefore, T^T

$$\text{Mass C}_{\text{inlet}} = \text{C in } CO_2 \text{ feeding}$$

Methanol was a product from CO_2

Therefore,

$$\text{Mass C}_{\text{outlet}} = \text{C in methanol} + \text{C from } CO_2 \text{ remaining}$$

In section A.4., mole of CO_2 feeding and methanol of all experiment were reported in Table 23. The mass of carbon was calculated (molecular weight of carbon = 12). The mass of carbon from CO_2 feeding and methanol was represented in Table 24

Table 24 Mass of carbon from CO_2 feeding and methanol

Temp. (ºC)	Exp. Batch	mole C feeding [CO2] (mol)	mass C feeding [CO₂] (g)	mole MeOH (mol)	mass C [MeOH] (g)
150	CuO/ZnO	0.068	0.815	0.0094	0.113
	Cu/ZnO	0.068	0.815	0.0243	0.292
	Cu/ZnO+3A(2:1)	0.068	0.815	0.0289	0.347
	Cu/ZnO+5A(2:1)	0.068	0.815	0.0261	0.314
	Cu/ZnO+3A5A	0.068	0.815	0.0273	0.328
	Cu/ZnO+3A(1:1)	0.068	0.815	0.0238	0.286
	Cu/ZnO+5A(1:1)	0.068	0.815	0.0196	0.236
130	Cu/ZnO	0.071	0.851	0.0217	0.260
	Cu/ZnO+3A	0.071	0.851	0.0237	0.284
	Cu/ZnO+5A	0.071	0.851	0.0220	0.265
	Cu/ZnO+3A5A	0.071	0.851	0.0226	0.272
100	Cu/ZnO	0.077	0.919	0.0028	0.034

Example: mole of unreacted CO_2 calculation (old calibration curve)
Experiment: 2.6g Cu/ZnO at 150 $^{\circ}$C, 5 MPa

Mole of CO_2 remaining was calculated by using CO_2 calibration curve. Gas effluent was analyzed by GC

Exp.	Chemical	Area
Cu/ZnO 150°C	CO_2	116511
		114596
		107625
		103468
		94273
		90059
AVG area		**104422**

Percentage of CO_2 in gas effluent was determined by using CO_2 calibration curve

y [Area of carbon dioxide] = 6698.3x [Concentration] + 27815

(104422) = 6698.3 x[Concentration] + 27815

x[Concentration] = (104422-27815)/6698.3*100

x[Concentration] = 11.4%

After that, the ideal gas equation was used to find mole of CO_2.

Conditions after running reaction

Remaining liquid volume = 55 ml

Final pressure = 4.23 MPa at 150 $^{\circ}$C

Mole of CO_2 remaining $= \dfrac{11.4}{100} x \dfrac{(4.23 \ x \ 10^6 \ Pa) \ x \ ((250-55) \ x \ 10^{-6} m^3)}{(8.314 \frac{Pa \, m^3}{mol \, K}) \ x \ (273+150 \ K)} = 0.027$ mole

Therefore,

% Carbon balance $= \dfrac{0.027 + 0.024}{0.068} x \ 100 = 75.3\%$

Example: mole of unreacted CO_2 calculation (new calibration curve)
Experiment: 2.6g Cu/ZnO at 130 °C, 5 MPa
Mole of CO_2 remaining was calculated by using CO_2 calibration curve. Gas effluent was analyzed by GC

Exp.	Chemical	Area
Cu/ZnO 130°C	CO_2	64079
		64370
		64737
		65163
AVG area		**64587.25**

Percentage of CO_2 in gas effluent was determined by using CO_2 calibration curve

y [Area of carbon dioxide] = 546473x [Concentration] + 5432.4

(64587.25) = 546473 x[Concentration] + 5432.4

x[Concentration] = (64587.25-5432.4)/546473*100

x[Concentration] = 10.8%

After that, the ideal gas equation was used to find mole of CO_2.

Conditions after running reaction

Remaining liquid volume = 55 ml

Final pressure = 2.73 MPa at 24 °C

Mole of CO_2 remaining $= \frac{10.8}{100} x \frac{(2.73 \ x \ 10^6 \ Pa) \ x \ ((250-55) \ x \ 10^{-6} m^3)}{(8.314 \frac{Pa \ m^3}{mol \ K}) \ x \ (273+24 \ K)} = 0.023$ mole

Therefore,

% Carbon balance $= \frac{0.023 + 0.022}{0.071} x \ 100 = 63.5\%$

It should be note that % carbon balance was not precise because some CO_2 also converted to CO through reverse water gas shift reaction. the CO calibration curve should be established further to determine mole of formed CO. if mole of CO was considered in calculation, the precise % carbon balance would be achieved.

% Carbon balance for all case was reported in Table 25.

Table 25 % Carbon balance for all experiments.

Temp. (°C)	Exp. Batch	mass C feeding [CO₂]	Average area of CO₂	% CO₂	Remaining Liq. Volume (ml)	Final pressure (Mpa)	Final temp. (°C)	mass C [unreacted CO₂] (g)	mass C [MeOH] (g)	% Carbon balance
150	CuO/ZnO	0.815	122410	14.12	55	4.59	150	0.036	0.113	66.8
	Cu/ZnO	0.815	104422	11.44	55	4.23	150	0.027	0.292	75.3
	Cu/ZnO+3A(2:1)	0.815	102591	11.16	55	4.16	150	0.026	0.347	80.5
	Cu/ZnO+5A(2:1)	0.815	94769	9.99	55.5	2.50	30	0.019	0.314	66.9
	Cu/ZnO+3A5A	0.815	48470	7.88	56	2.58	26	0.016	0.328	63.6
	Cu/ZnO+3A(1:1)	0.815	125795	14.63	55	4.27	150	0.035	0.286	86.1
	Cu/ZnO+5A(1:1)	0.815	117128	13.33	57	4.62	150	0.034	0.236	78.7
130	Cu/ZnO	0.851	64587	10.82	55	2.73	24	0.023	0.260	63.5
	Cu/ZnO+3A	0.851	54058	8.90	57	2.73	25	0.019	0.284	60.0
	Cu/ZnO+5A	0.851	67498	11.36	53	2.76	24	0.025	0.265	66.4
	Cu/ZnO+3A5A	0.851	57665	9.56	56	2.76	24	0.021	0.272	61.2
100	2.6g Cu/ZnO	0.919	77658	13.22	55	3.70	27	0.038	0.034	53.6

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