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ที่มีปริมาณคาร์บอนไดออกไซด์มาก



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METAL OXIDE CATALYSTS FOR METHANOL SYNTHESIS  
FROM CO<sub>2</sub>-RICH SYNGAS



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ศูนย์วิทยทรัพยากร  
A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

จุฬาลงกรณ์มหาวิทยาลัย  
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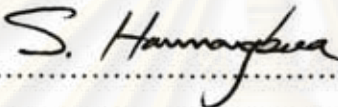
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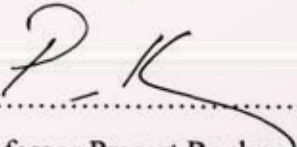
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ชานากานต์ ภูวพิทยานนท์ : ตัวเร่งปฏิกิริยาโลหะออกไซด์สำหรับการสังเคราะห์เมทานอลจากแก๊สสังเคราะห์ที่มีปริมาณคาร์บอนไดออกไซด์มาก. (METAL OXIDE CATALYSTS FOR METHANOL SYNTHESIS FROM CO<sub>2</sub>-RICH SYNGAS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร. ประเสริฐ เรียบร้อยเจริญ, 75 หน้า.

การพัฒนาตัวเร่งปฏิกิริยาโลหะออกไซด์สำหรับการสังเคราะห์เมทานอลจากแก๊สสังเคราะห์ที่มีปริมาณคาร์บอนไดออกไซด์มากเป็นฟังก์ชันหนึ่งของกระบวนการเตรียมตัวเร่งปฏิกิริยาซึ่งได้ถูกศึกษาโดยการเติมโลหะ เช่น เซอร์โคเนียมและแพลเลเดียม อัตราส่วนโดยโมลคอปเปอร์ต่อซิงค์ วิธีการเตรียมตัวเร่งปฏิกิริยา ปริมาณการเติมโลหะ ตัวทำละลายแอลกอฮอล์ ตัวรองรับ เกลือของสารเริ่มต้น ปริมาณคาร์บอนไดออกไซด์ในแก๊สสังเคราะห์ และการเติมโลหะที่มีต่อความว่องไวของตัวเร่งปฏิกิริยาโลหะออกไซด์พื้นฐาน กระทำปฏิกิริยาภายใต้ภาวะกระบวนการอุณหภูมิต่ำในปฏิกรณ์แบบปั่นกววนโดยอาศัยแอลกอฮอล์เป็นตัวทำละลายเร่งปฏิกิริยาร่วม อัตราส่วนโดยโมลคอปเปอร์ต่อซิงค์เป็นหนึ่งในแสดงความว่องไวที่ดีที่สุด ที่อุณหภูมิ 170 และ 200 องศาเซลเซียสด้วย 0.5%wt Zr/Cu/ZnO ซึ่งเตรียมด้วยวิธีการตกตะกอนร่วมเป็นตัวเร่งปฏิกิริยาที่ให้ผลดีที่สุด 0.5%wt Zr-Cu/ZnO ซึ่งเตรียมด้วยวิธีการตกตะกอนร่วมและการฝังตัวเป็นตัวเร่งปฏิกิริยาที่ให้ผลดีสำหรับการสังเคราะห์เมทานอลด้วยแก๊สสังเคราะห์ที่มีคาร์บอนไดออกไซด์มาก 0.5%wt Pd-Cu/ZnO ช่วยปรับปรุงความว่องไวการปฏิกิริยาได้เช่นเดียวกันโดยเฉพาะอย่างยิ่งเมื่อกระทำปฏิกิริยาเป็นระยะเวลายาวนาน การบริโภคปริมาณไฮโดรเจนมากของตัวเร่งปฏิกิริยา Pd-Cu/ZnO นำมาซึ่งความสามารถในการรีดิวซ์สูงเพื่อเพิ่มความว่องไว เมื่อใช้ 2-โพรพานอลเป็นตัวกลางในการทำปฏิกิริยาพบว่าให้การเปลี่ยนคาร์บอนรวมสูงสุด ตัวรองรับซิงค์ออกไซด์แสดงบทบาทเพื่อส่งเสริมความว่องไวต่อการก่อรูปไฮโดรเจนชั้นของคาร์บอนมอนอกไซด์ Cu/ZnO ซึ่งเตรียมจากสารเริ่มต้นอะซิเตทแสดงความว่องไวสูง เมื่อใช้ตัวเร่งปฏิกิริยา Cu/ZnO ในการสังเคราะห์เมทานอลแบบกะจากแก๊สสังเคราะห์ที่มีปริมาณคาร์บอนไดออกไซด์มากเป็นผลให้การเปลี่ยนคาร์บอนรวมลดลงเนื่องจากการเสื่อมสภาพของตัวเร่งปฏิกิริยาจากคาร์บอนไดออกไซด์และน้ำ แก๊สสังเคราะห์ที่มีปริมาณคาร์บอนไดออกไซด์สูงถึง 10 เปอร์เซ็นต์ พบว่า 0.5%wt Zr-Cu/ZnO สามารถส่งเสริมว่องไวและความเสถียรโดยเพิ่มการไฮโดรเจนชั้นของคาร์บอนไดออกไซด์และยับยั้งการเกิดน้ำขึ้นในระบบปฏิกิริยา



สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต.....

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# # 497 22635 23 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE  
 KEYWORDS: METHANOL SYNTHESIS / CO<sub>2</sub> / SYNGAS / METAL OXIDE /  
 METAL-DOPED Cu/ZnO

CHANAKARN PUWAPITAYANON : METAL OXIDE CATALYSTS  
 FOR METHANOL SYNTHESIS FROM CO<sub>2</sub>-RICH SYNGAS. ADVISOR :  
 ASST. PROF. PRASERT REUBROYCHAROEN, Ph.D., 75 pp.

Development of metal oxide catalysts for methanol synthesis from CO<sub>2</sub>-rich syngas as a function of catalyst preparation process has been carried out by using metal doping such as Zr and Pd. Activity of metal oxide catalysts were investigated in terms of catalyst molar ratio, preparation methods, metal-doped content, alcohol solvent, support, salt precursor, CO<sub>2</sub>-containing syngas and metal doping. Reactions were performed under low temperature process in a slurry reactor by using alcohols as a catalytic solvent. Molar ratio of Cu/Zn = 1 exhibited the highest activity. At 170 and 200 °C, 0.5%wt Zr/Cu/ZnO prepared by co-precipitation method was the most effective catalyst. 0.5%wt Zr-Cu/ZnO prepared by co-precipitation-impregnation method was an effective catalyst for methanol synthesis with CO<sub>2</sub>-rich syngas. 0.5%wt Pd-Cu/ZnO also improved catalytic activity especially for long period of reaction time. High hydrogen consumption of Pd-Cu/ZnO catalyst brought in high reducibility to increase activity. The highest total carbon conversion was found by using 2-propanol as reaction medium. ZnO support played a role to promote activity form CO hydrogenation. Cu/ZnO formulated from acetate precursor showed high reactivity. Using of Cu/ZnO catalyst for batch methanol synthesis from CO<sub>2</sub>-rich containing syngas resulted in decreasing total carbon conversion due to the catalyst deactivation by CO<sub>2</sub> and water. Up to 10%CO<sub>2</sub> containing syngas, 0.5%wt Zr-Cu/ZnO promoted activity and stability by increasing CO<sub>2</sub> hydrogenation and suppressed water formation in the reaction system.

Field of Study:..Petrochemistry and Polymer Science... Student's Signature:   
 Academic Year..2008..... Advisor's Signature: 

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ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

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**LIST OF ABBREVIATIONS**

°C	:	Degree celsius
Å	:	Angstrom
ml	:	Milliliter
cm	:	Centimeter
nm	:	Nanometer
min	:	Minute
h	:	Hour
g	:	Gram
mg	:	Milligram
MPa	:	Mega pascal
% wt	:	Weight percentage
CH <sub>3</sub> OH	:	Methanol
HCOOC <sub>3</sub> H <sub>7</sub>	:	2-propyl methanoate
H <sub>2</sub>	:	Hydrogen
Ar	:	Argon
CO	:	Carbon monoxide
CO <sub>2</sub>	:	Carbon dioxide
Cu	:	Copper
CuO	:	Copper oxide
Zn	:	Zinc
ZnO	:	Zinc oxide
Cr <sub>2</sub> O <sub>3</sub>	:	Chromium oxide
Zr	:	Zirconium
Pd	:	Palladium

2 $\theta$	:	Two-theta angle
GC	:	Gas chromatograph
XRD	:	X-ray diffraction
BET	:	Brunauer Emmett Teller
TPR	:	Temperature program reduction
WGS	:	Water gas shift
$\Delta H$	:	Heat of reaction
(Surf)	:	Surface of catalyst
(a)	:	Active site
(ads)	:	Adsorption
T <sub>reaction</sub>	:	Reaction temperature
MW	:	Molecular weight



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# CHAPTER I

## INTRODUCTION

### 1.1 Statement of Problem

Recently, the world-wide energy crisis is driven by the cost and availability of fossil fuel which is non-renewable resource. Thailand has limited domestic fuel oil production and imports make up a significant portion of the country's oil consumption. It is crucial to find supplementary sources of alternative energy to replace over-dependence on oil and use existing technological science to transform its most abundant agricultural biomass resource into potentially highly profitable alternative energy and environmental friendly fuel. Methanol has been considering as an alternatively clean transportation fuel, and energy storage. It is a very important raw material that is widely used in the chemical industry including organic synthesis, dye, medicine, dope, and defense. It is not only a basic substance in  $C_1$  chemistry but is also a potential clean fuel. It can be directly used as an octane promoter or indirectly converted to dimethyl ether (DME) or gasoline [1]. For the past, methanol was originally produced by the destructive distillation of wood (wood alcohol) for charcoal production but currently methanol synthesis route has been produced syngas (or synthesis gas) that mainly contain two part of hydrogen ( $H_2$ ) and one part of carbonmonoxide (CO) along with small amount of carbondioxide ( $CO_2$ ).

Commercially, the methanol is run mostly on the conventional Cu/ZnO-based catalyst, synthesized from syngas which its production based on gasification process of hydrocarbon compounds such as coal, petroleum and biomass. Biomass is a renewable feedstock for syngas because it is an alternative energy resource, domestically produced that can be reduced or stabilize fuel imports, so biomass derived to methanol is very attractive and become futuristically competitive fuel. The composition of syngas derived from biomass is different from that derived from natural gas and coal which consist mainly of  $H_2$  and CO, with a small amount of  $CO_2$ , whereas biomass derived to syngas consists much more of  $CO_2$ . Therefore, the composition of biomass-derived syngas is not favorable for methanol synthesis under

the conventional method. For the past researches, there was only a small amount of literature proposed at investigating for methanol synthesis using biomass-derived syngas and there are many alternative way to modify the conventional methanol synthesis catalysts which contains metal oxide components. Thus, in this research was investigated the methanol synthesis from CO<sub>2</sub>-rich syngas that was imitated from biomass-derived syngas by developed the metal oxide catalysts, concern in catalyst preparation using different metal-doped catalyst and compositions. Additionally, the effect of supported catalyst precursor, alcohol solvent, catalyst component, and catalyst preparation methods are also studied.

### **1.2 Objective of Research**

To study process conditions and develop the metal oxide catalysts which are suitable for methanol synthesis from CO<sub>2</sub>-rich syngas.

### **1.3 Scope of Research**

Methanol synthesis reaction was performed under low-temperature (170 - 200 °C) process in a slurry reactor by using alcohols as a catalytic solvent. Catalysts were be prepared by two different techniques:

1. Co-precipitation method for single, binary, and ternary component catalysts.
2. Co-precipitation-impregnation method for ternary component catalysts.

The experimental procedures were carried out as follows:

1. Survey literature
2. Prepare copper zinc oxide (Cu/ZnO) catalysts from different Cu/Zn mole ratio.



3. Prepare copper zinc oxide (Cu/ZnO) catalysts from different salt precursors: nitrate, acetate, and chloride precursors.
4. Prepare zirconium-doped Cu/ZnO, palladium-doped Cu/ZnO, copper chromium oxide (Cu/Cr<sub>2</sub>O<sub>3</sub>), and unsupported copper catalysts.
5. Synthesize methanol in a semi-continuous-type and use 5%CO<sub>2</sub>-syngas as reactant gas.
6. Synthesize methanol in a batch-type and use CO<sub>2</sub>-rich syngas (5 - 15% CO<sub>2</sub> content) as reactant gas.
7. Characterize the prepared catalysts as follows:
  - (A) X-ray diffraction
  - (B) BET surface area
  - (C) Temperature program reduction
8. Analyze the gas and liquid products by gas chromatograph.
9. Summarize the results and write thesis.



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## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Methanol Backgrounds

Methanol is one of the largest volume commodity chemicals produced in the world. It has drawn keen attention a number of times in the chemical and energy industry which plays an important role in C<sub>1</sub> chemistry. It has been used in variety of applications, which can be divided into three categories: feedstock for other chemicals, fuel use, and other direct uses as a solvent, antifreeze, inhibitor, or substrate [1]. Beside the use in chemical manufacture, it is also regarded as one of the most promising alternative clean automobile fuel not based on petroleum. Due to the fast global development, the global environmental problems caused by vehicles which release sulfur oxide, nitrogen oxide, and aromatic compound are the world issues.

Methanol (or methyl alcohol) is a clear, colorless, and volatile liquid, giving off a mild alcoholic odor at room temperature. It is polar, acid-base neutral, and generally considered non-corrosive. It is miscible with water and most organic solvents and is capable of dissolving many inorganic salts. Anhydrous methanol is hygroscopic, toxic to human beings but is not considered particularly harmful to the environment [1]. Methanol has been considering as an alternatively clean transportation fuel and energy storage since the crisis in 1970 [2]. The energy crisis and environmental problems have played significant roles as a driving force of the use of methanol as clean transportation fuel. It can be directly used as an octane promoter or indirectly converted to gasoline by methanol-to-gasoline (MTG) process. Because of no undesirable emissions and nitrogen oxides, sulfur oxide after burn, it is considered as an environmental friendly fuel. More recently, the development of the fuel cell vehicles where methanol is used as H<sub>2</sub> resources makes it most outstanding chemicals as energy for the future [3].

From the past, methanol was originally produced by the destructive distillation of wood (wood alcohol) for charcoal production. Currently, it is mainly produced from synthesis gas [4]. The first commercial synthetic methanol from synthesis gas raw material was produced for a number of years, making at high- pressure process with using zinc oxide/chromium oxide catalyst. In the 1960s, ICI made improvements on the use of the copper-based catalyst. They discovered copper/zinc oxide catalyst, allowing for milder operating conditions called the development of the low-pressure process, led to permitting the more economical synthesis conditions [5]. This low-pressure process is now the major synthesis technology. More details of methanol synthesis will be reviewed in the section below.

## **2.2 Synthesis gas [4,6]**

Synthesis gas (or syngas), the third important intermediate for petrochemicals, is the precursor of two big-volume chemicals, ammonia and methanol. It is also an important building block for aldehydes from olefins. The catalytic hydroformylation reaction (Oxo reaction) is used with many olefins to produce aldehydes and alcohols of commercial importance. Syngas generally refers to a mixture of carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide varies according to the type of feed, the method of production, and the end use of the gas. During World War II, when it was used to produce alternative hydrocarbon fuels using Fischer Tropsch technology. The syngas mixture was produced then by gasifying coal. The mixture was used for producing a liquid hydrocarbon mixture in the gasoline range using Fischer-Tropsch technology. Although this route was abandoned after the war due to the high production cost of these hydrocarbons, it is currently being used in South Africa, where coal is inexpensive [4].

As mentioned above, there are different sources for obtaining syngas. It can be produced by steam reforming or partial oxidation of any hydrocarbon ranging from natural gas to heavy petroleum residues. It can also be obtained by gasifying coal or biomass. Due to biomass is one of the most abundant renewable resources that can be converted into liquid and gaseous fuels. Therefore, biomass derived to methanol is

very attractive and become alternative fuel. The composition of syngas derived from biomass is different from that derived from natural gas and coal which consist mainly of  $H_2$  and  $CO$ , with a small amount of  $CO_2$ , whereas biomass derived to syngas consists much more of  $CO_2$ . Theoretically, a syngas with a  $H_2/CO$  ratio of 2.0, which is appropriate for methanol synthesis, can be obtained by adjusting certain gasification parameters. However, the differences between the actual data and theoretical results are substantial. Moreover, economical aspects must be considered for practical processes. In most cases, biomass-derived syngas is a  $CO_2$ -rich syngas, which can be tailored in the downstream process by water gas shift reaction, by methane reforming, by  $CO_2$  removal, or by supplying  $H_2$  to readjust its composition before entering into the synthesis loop. However, the capital cost for syngas generation made in this way will be very high [6].

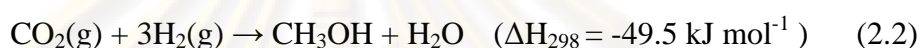
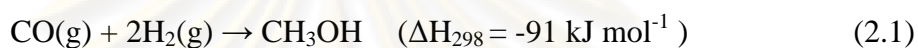
### **2.3 Methanol Synthesis [7,8]**

Today, methanol is commercially produced from the hydrogenation of synthesis gas. Prior the use of synthesis gas, “wood distillation” was the only process to produce methanol. The beginning of commercial methanol synthesis was in 1923 by BASF. BASF chemists in Leuna, Germany, produced methanol from synthesis gas at high pressure. This process is known as “high-pressure process” which operates at pressure of 250-300 bar and temperature of 593-723 K. The major catalyst was zinc oxide/chromium oxide ( $ZnO/Cr_2O_3$ ) catalyst. This process also required high temperature due to its low catalytic activity. Even though its activity was low, this catalyst was highly tolerant to poison in synthesis gas. The synthesis gas production was based on German coal which contained chlorine and sulfur. This process was widely used for long periods (about 45 years) until the more efficiently catalyst was developed by ICI.

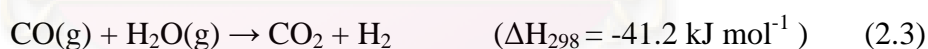
In 1966, ICI have made the shift in methanol synthesis by introducing the new methanol synthesis. The copper/zinc oxide-based catalyst allowed the much lower operating pressure and higher catalytic activity. This catalyst was very active but easily deactivated by sulfur. The synthesis gas production based on coal was shift to

that based on hydrocarbon such as methane, naphtha by streaming reforming process. The ICI process is well known as “low-pressure process” operating at pressure of 35-55 bar and temperature of 473-573 K. The beginning of low-pressure process is the end of high-pressure process due to its high efficiency. Until now, Cu/ZnO-based catalysts are still the most active catalyst for the commercial methanol synthesis.

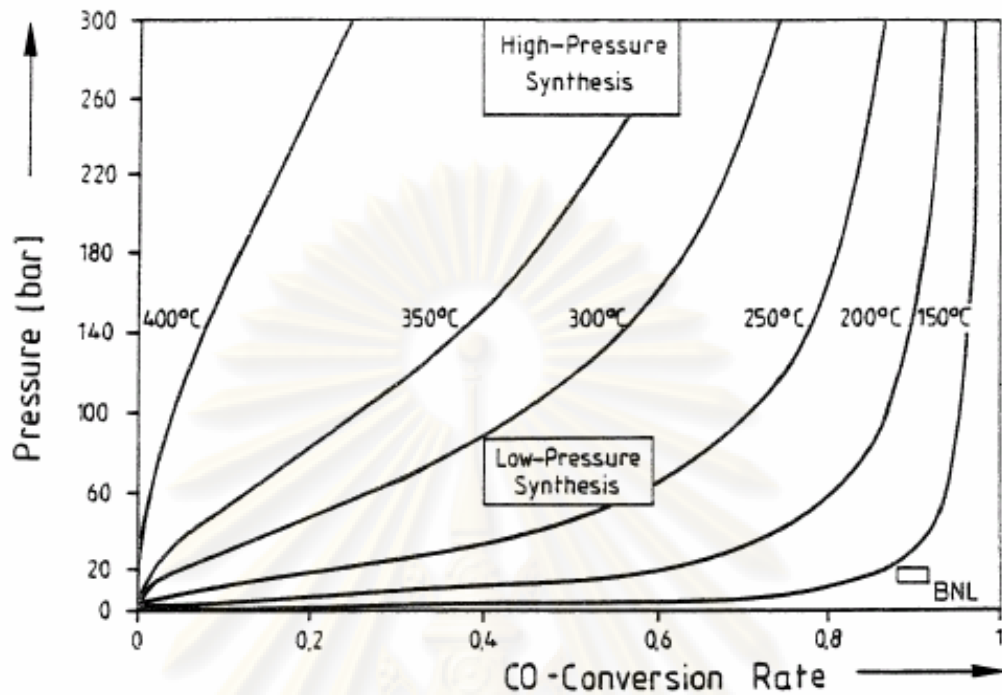
Methanol synthesis from syngas involves the following reaction of carbon oxide with hydrogen to produce methanol:



Both of above reactions are hydrogenation of carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). Both reactions are a moderately exothermic reaction and result in the reduction in volume. Thus, the methanol synthesis is more favored at low-temperature and high-pressure reaction in the thermodynamic point of view. The reactions are promoted by use of catalysts. Simultaneously, reaction (2.3) is the water gas shift (WGS) reaction, occurs as a sub-reaction in conventional processes, consuming water from reaction (2.2):



Combination of the WGS reaction results in a strong driving force, which dramatically increases the syngas conversion. Many research projects have been carried out to illustrate the role of CO<sub>2</sub> in methanol formation and reaction mechanism that will be addressed in the following sections. A new possible way of methanol synthesis directly from biomass-derived syngas, which the syngas is rich in CO<sub>2</sub>, directly to methanol, is recently attracted much interest.

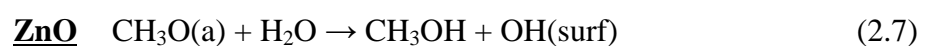
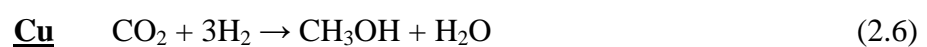
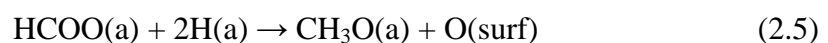
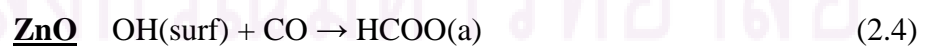


**Figure 2.1** Methanol synthesis equilibrium based on  $H_2/CO = 2$  [9].

#### 2.4 Reaction Mechanism [8]

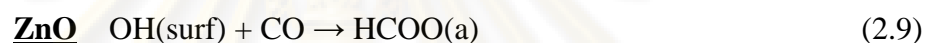
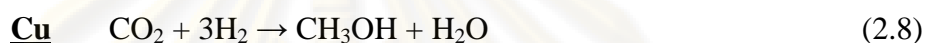
The mechanism of methanol synthesis has been extensively investigated for nearly 4 decades. The reaction pathway involving the copper-based catalyst is still a topic of intensive debate. For a bifunctional mechanism of Cu/ZnO catalyst is currently accepted. It is assumed that  $CO_2$  is hydrogenated on the Cu sites to yield methanol and water that subsequent gas phase transport from the Cu sites leads to the displacement of relatively stable species from ZnO. However, its mechanism is still not clear and quite different bifunctional mechanism routes were also supposed.

Saussey and Lavalley [10] proposed the following routes:



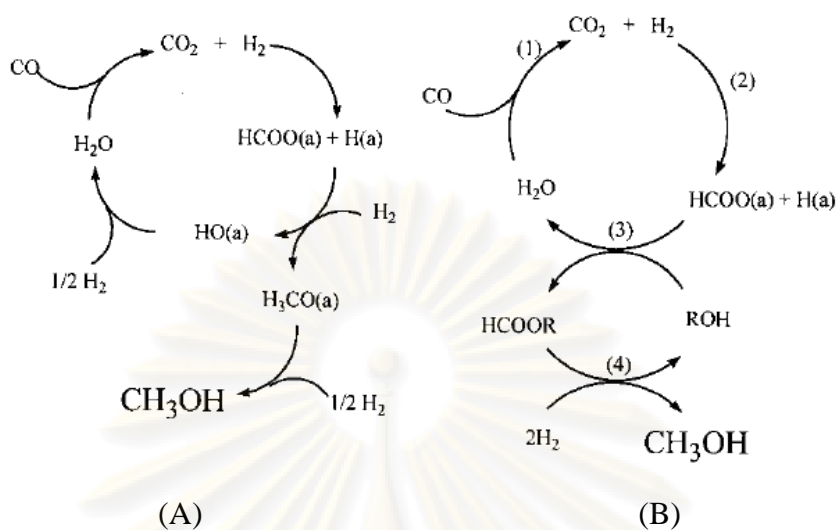
From this mechanism, it is assumed that the gas-phase intermediate is H<sub>2</sub>O and methoxy species are hydrated on the ZnO sites. This is consistent with the observation that small amounts of water in the reactant gas feed increase the catalyst activity.

Fackley and co-workers [11] proposed another mechanism in which methanol reacts with methanoates on the ZnO to produce methyl methanoate, which ultimately hydrogenated when in contact with copper:



On the other hand, Tsubaki co-workers [12] altered the traditional reaction path to a low temperature using an organic alcohol (ROH) as the catalytic liquid medium. The new route can use CO<sub>2</sub>-containing syngas and can be operated at significantly low temperature and low pressure, such as 150-170 °C and 30-50 bar. It was assumed that carbondioxide and water are utilized as intermediates in the novel pathway. The reaction route is composed of several step as listed below:





**Figure 2.2** Changing the reaction course from a high-temperature ICI process (A) to a new low-temperature route (B) by addition of alcohol [12].

Copper represents the catalytic site of Cu-based catalysts. ROH is the accompanying alcohol which is cycled during the reaction. Involvement of alcohol in the reaction changes the reaction route from (A) to (B) as shown in Figure 2.2.

## 2.5 Catalyst and Process Technology

Developments to improve methanol synthesis are therefore composed of elements of catalyst system improvements and process system improvements.

### 2.5.1 Zinc Oxide/Chromium Oxide Catalyst [1]

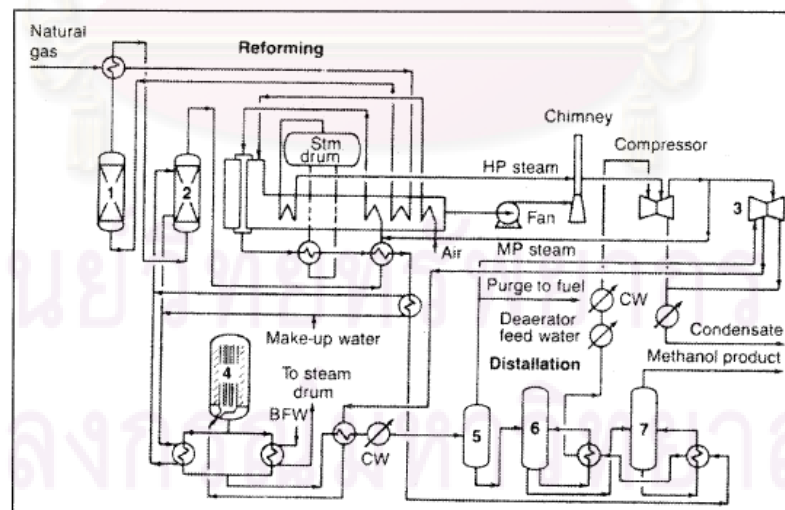
Originally, industrial synthesis of methanol was over ZnO/Cr<sub>2</sub>O<sub>3</sub> catalyst that was operated under high-pressure of about 350 bar and temperatures up to about 450 °C. Although this catalyst was highly stable to poison such as sulfur, chlorine containing in synthesis gas, because of its low activity due to a tendency to promote the exothermic methanation reaction under the certain reaction. It was no longer used



after the introduction of low-pressure synthesis and the highly active copper-based catalyst was developed.

### 2.5.2 Copper/Zinc Oxide Catalyst [1,13]

Cu/ZnO catalyst is well known to be active for methanol synthesis from syngas containing few amount of CO<sub>2</sub>. It can be damaged by sulfur and chlorine in syngas. Thus, it was not commercialized until 1960s by ICI low-pressure plant (gas-phase synthesis) because desulfurization process of syngas was developed. As its high activity, the methanol synthesis was operated at high temperature (200-300 °C). Under the reaction condition, one-pass conversion of the process using H<sub>2</sub>-rich syngas (H<sub>2</sub>/CO = 5) from natural gas steam reforming resource. The process diagram of ICI low-pressure methanol synthesis from natural gas is shown in Figure 2.3. The theoretical one-pass conversion is limited to limited to 15–25% due to the thermodynamic limitation of the highly exothermic reaction. The recycle of unreacted syngas is necessary to enhance the syngas conversion. Furthermore, The higher conversion will be achieved by lowering the reaction temperature which is of the thermodynamic favor will greatly lower the cost of production.



**Figure 2.3** The ICI low-pressure methanol synthesis process from natural gas: (1) desulfurization, (2) saturator (for producing process steam), (3) synthesis loop circulator, (4) reactor, (5) heat exchanger and separator, (6) column for light ends recovery, (7) column for water removal [4].

### 2.5.3 Other Catalyst Innovation [1,8]

Recent advancement in catalyst development has led to some promising catalysts not based on Cu/ZnO. These may be classified into five types: intermetallic copper/thorium (Cu/Th), copper/lanthanides (Cu/La), Pt group on silica, Raney Copper and homogeneous catalysts. It should be pointed out here that some of these potential catalysts are active at low temperature. This would permit high conversions of syngas in a single pass and reduce or eliminate costly gas recycling.

Even the industrial copper/zinc/aluminium-based catalysts have been modified to achieve higher productivity or longer catalyst life. At the present, the key to methanol synthesis is to innovate the efficient catalyst. These may be summarized as 4 categories for the catalyst development:

#### 2.5.3.1 Active site

Copper still remains as an important active catalyst component, even though the nature of the active site is yet to be fully understood. It is generally accepted that the coordination, chemisorption, and activation of carbon monoxide and the homogeneous splitting of hydrogen take place on  $\text{Cu}^0$  or  $\text{Cu}^+$  and that the heterogeneous splitting of hydrogen takes place on ZnO. However, different opinions on the nature and valence of copper sites still exist. Some researchers noted that metallic Cu atoms were uniformly active for methanol synthesis. The activity of the catalyst is directly proportional to the surface area of metallic Cu and methanol is formed on a metallic Cu surface of a Cu-based catalyst. Similarly, there was a report suggested that the catalytic activity of a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> ternary catalyst for carbon dioxide hydrogenation increases with an increase in the metallic copper surface area, reached a maximum, and then decreased at a Cu/ZnO molar ratio.

On the condition of absence of active copper catalyst, a catalyst promoted by silver and gold oxides also possessed a high activity for methanol

formation. This means that the above noble metals could adjust the electronic properties of their oxides and thus modify the nature of the active centers, which results in surface oxygen vacancies.

### 2.5.3.2 Support effect

An appropriate support not only provides a good configuration but also must have some function in modulating the interactions between the primary components of the catalyst and promoter. In addition, the basicity/acidity characteristics of the catalyst can also be affected. Metal oxides are the more common supports used for the preparation of a methanol synthesis catalyst. Their properties greatly affect the catalyst activity as a result of the aspects mentioned in the previous section. Of all metal oxides ZnO, ZrO<sub>2</sub>, and SiO<sub>2</sub> are the most typical materials used as supports in methanol synthesis catalysts.

Zinc oxide is a good hydrogenation catalyst that activates hydrogen. Hydrogen spillover from Cu to ZnO occurs very rapidly from a partially oxidized Cu surface. Moreover, the hydrogen atoms were trapped at surface defects or at interstitial sites of ZnO, but they were not held too strongly. This means that a possible role of ZnO might serve as a reservoir to provide H atoms for subsequent hydrogenation of adsorbed reaction intermediates. The ZnO support may optimize the dispersion of the Cu particles and stabilize many active sites by attenuating the unavoidable agglomeration of Cu particles, which takes place during a long-term operation, and by restraining Cu particles to be poisoned by feed gas impurities.

Zirconia has also been investigated as a promoter or support for the methanol synthesis catalyst. It is a strong and thermal-resistant material, which is a very promising catalyst support because it bears high stability under reducing or oxidizing atmospheres. It was observed that catalytic activity using ZrO<sub>2</sub> as the support is better than that using Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and other materials. On the other hand,

CuO can be uniformly dispersed on a ZrO<sub>2</sub> surface, forming a specific interface that might be favorable for the methanol synthesis reaction.

### 2.5.3.3 Promoter effect

Since methanol synthesis on a Cu-based catalyst is a structurally sensitive reaction, it is useful to modify its performance using various promoters, which could improve the activity, selectivity, or stability of the catalyst.

Chromia in a skeletal copper catalyst could prevent the rearrangement of Cu sites and improve the pore structure and active surface of the catalyst. An important observation is that loading chromia on skeletal copper can partially inhibit the reverse water gas shift reaction, improving the bulk activity and selectivity for methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> and accelerating simultaneously the reduction of CuO species.

Palladium-doped copper catalyst showed a promotion effect similar to that of Chromia and positively prevented the rearrangement of Cu species. In addition, the formation of a special intersurface or surface defects between Cu and ZnO might contribute to the fast adsorption and high stability effects of a highly dispersed Cu/ZnO structure.

Zirconia also acts as a favorable promoter in methanol synthesis as explained previously. The dissolution of zirconium ions in a copper catalyst results in the presence of a new copper oxide phase and promotes the formation of Cu<sup>+</sup> ions, which enhances the activity of the catalyst for methanol synthesis at low temperatures and pressures. Addition of ZrO<sub>2</sub> improves the surface area of Cu species and adjusts the ratio of Cu<sup>+</sup>/Cu<sup>0</sup> in the surface, increasing specifically CO conversion.

Other elements such as B, Ga, Co, and Mg were also used as copper-based catalyst promoters in methanol synthesis. They can modify the physical-chemical properties just like the above elements. Recently, many researchers are

engaged in searching for new promoters to improve the performance of the methanol synthesis catalyst.

#### **2.5.3.4 Catalyst preparation method**

Methanol synthesis catalysts are structurally sensitive. The differences in preparation methods as well as pretreatment conditions showed remarkable influences on the structure of the catalysts, ultimately affecting the catalytic performance. Catalyst preparation methods were extensively reviewed as follows:

##### **2.5.3.4.1 Co-precipitation Methods**

Co-precipitation methods are the most widely used methods to prepare copper-based catalysts. Generally, the considerable factors of this technique are:

**(A) Effect of the Reaction Conditions.** There are many parameters of precipitation strongly affect the performance of a CuO-ZnO-based catalyst such as Cu/Zn ratio, pH value, composition of precipitates, and temperature. These can play an important role during the preparation of the optimum catalyst precursor.

**(B) Effect of the Precipitation Species.** The catalysts prepared by using different precipitator agents gave different shapes. For example, using sodium carbonate as a precipitator, the catalyst cannot exclude the sodium ions, which remain in the catalyst, reducing the total Cu surface area and activity of the catalyst.

**(C) Solvent Effect.** The effects of different solvents on the texture and morphology of the catalyst are ascribed to their surface tension, viscosity, and dielectric constant.

#### **2.5.3.4.2 Other Preparation Methods**

The most common way to prepare metal-supported catalysts, the impregnation technique, can also be used to synthesize methanol catalysts. The characteristics of the impregnated catalysts are determined by the precursor used and the impregnation conditions.

#### **2.5.3.4.3 Pretreatment Effect**

The structure and catalytic performance of the catalysts also depends on calcination and subsequently reduction. The lower heating rate of calcination benefits the formation of fine particle size catalysts.

The reduction is necessary to obtain optimum catalyst performance. It is exothermic, which could accelerate the agglomeration of surface active sites. The lower reduction temperature is beneficial for improving copper dispersion and activity for the methanol synthesis and that using methanol as the reducing agent is better than using hydrogen.

### **2.5.4 Gas Phase Technologies [7,14]**

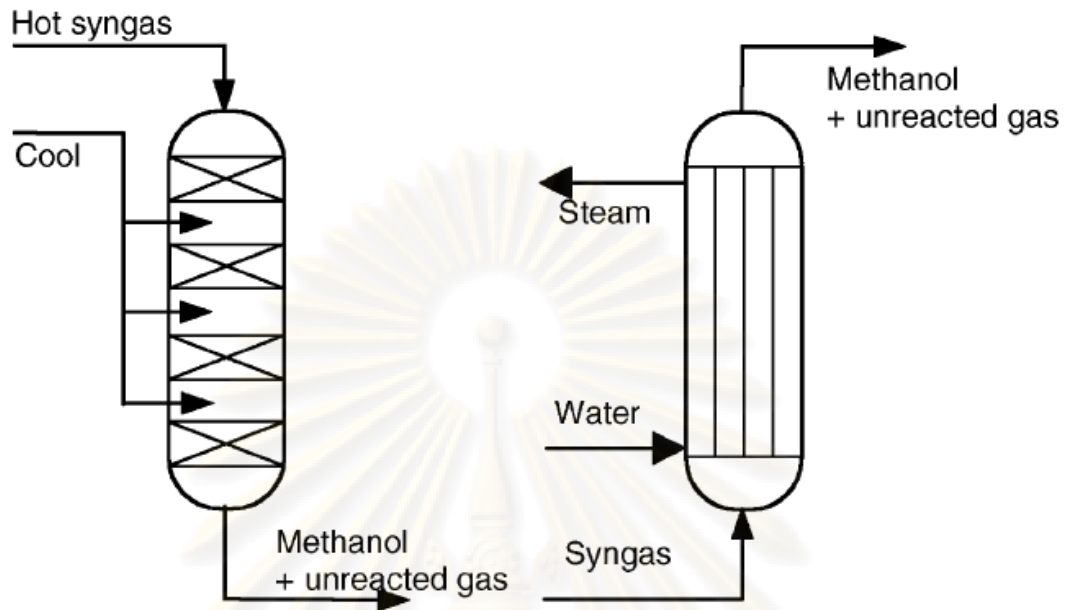
#### **2.5.4.1 Fixed Bed Converter**

Methanol is produced by the hydrogenation of carbon oxides over a Cu/Zn/Al catalyst. The synthesis reactions are exothermic and give a net decrease in molar volume. Therefore, the equilibrium is favoured by high pressure and low temperature. During production, heat is released and has to be removed to maintain optimum catalyst life and reaction rate. The catalyst deactivates primarily because of loss of active copper due to physical blockage of the active sites by large by-product molecules, poisoning by halogens or sulphur in the synthesis gas, and sintering of the

copper crystallites into larger crystals. Conventional methanol reactors use fixed beds of catalyst pellets and operate in the gas phase. Two reactor types predominate in plants built after 1970. The ICI low pressure process is an adiabatic reactor with cold unreacted gas injected between the catalyst beds (Figure 2.3, left). The subsequent heating and cooling leads to an inherent inefficiency, but the reactor is very reliable and therefore still predominant. The Lurgi system (Figure 2.3, right), with the catalyst loaded into tubes and a cooling medium circulating on the outside of the tubes, allows near-isothermal operation. Conversion to methanol is limited by equilibrium considerations and the high temperature sensitivity of the catalyst. Temperature moderation is achieved by recycling large amounts of hydrogen rich gas, utilizing the higher heat capacity of H<sub>2</sub> gas and the higher gas velocities to enhance the heat transfer. Typically, a gas phase reactor is limited to about 16% CO gas in the inlet to the reactor, in order to limit the conversion per pass to avoid excess heating.

#### **2.5.4.2 Fluidized Bed Converter**

A project attempting to lower methanol production costs by using new technology to expand the scale of methanol production facilities was started in 1993 by the New Energy and Industrial Technology Development Organization (NEDO) and the Petroleum Endowment Center (PEC) in Japan. The fluidized bed methanol synthesis converter takes in synthesis gas from the bottom, by which grains of copper/zinc oxide catalyst having a mean diameter of 50-60 μm are fluidized. The heat of reaction is removed by cooling pipes. A special feature of the system is that the reaction heat can be collected as high-pressure steam. Whereas the conventional process requires the operating temperature to be changed in accordance with the degeneration of the catalyst, the fluidized bed process allows supply and exchange of catalyst during operation, making possible constant and stable operation.



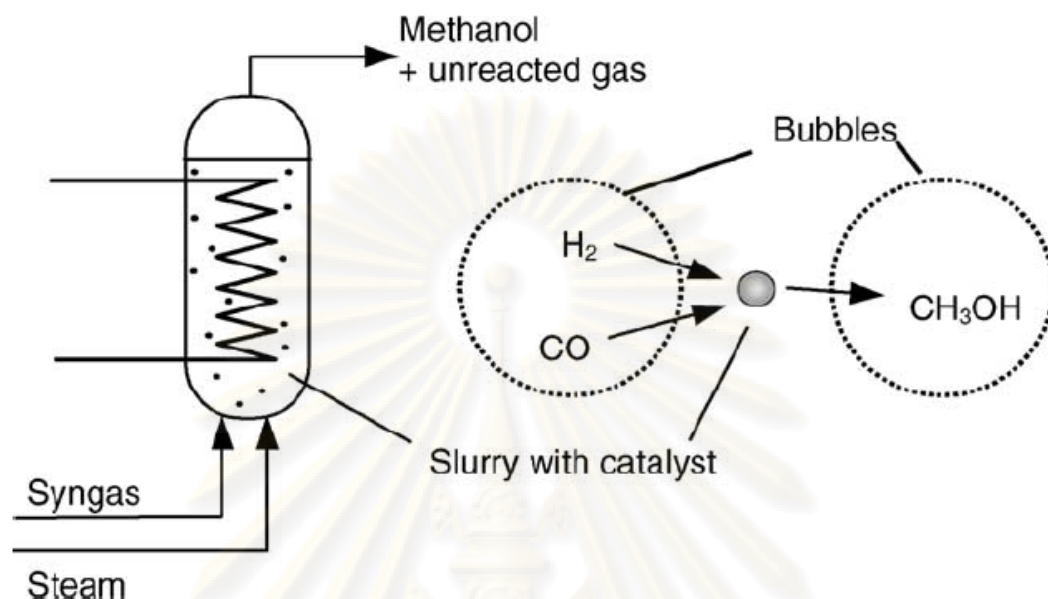
**Figure 2.4** Methanol reactor types: quench (left) and steam raising (right) [14].

## 2.5.5 Liquid Phase Technologies [7,14]

### 2.5.5.1 LPMEOH™ by Air Products and Chemicals, Inc.

In Figure 2.4, the liquid-phase reactor, the mineral oil acts as a temperature moderator and heat removal medium. The heat of reaction is efficiently transferred from the catalyst surface to boiling water in an internal tubular heat exchanger through the mineral oil medium. The temperature control enables the reactor to process synthesis gas that is rich in carbon oxides. In liquid phase processes heat transfer between the solid catalyst and the liquid phase is highly efficient, thereby allowing high conversions per pass without loss of catalyst activity. This allows a much higher conversion rate and the number of recycle passes required is greatly reduced. Whereas, the gas phase process typically uses 5:1 recycle ratio, the liquid phase process operates fine with ratios of 1:1 to 2:1. Conversion per pass depends on reaction conditions, catalyst, solvent and space velocity. Experimental results show 15–40% conversion for CO rich gases and 40–70% CO for balanced and H<sub>2</sub> rich gases.





**Figure 2.5** LPMEOH reactor with detail of reaction [14].

### 2.5.5.2 Liquid phase research by BNL.

Brookhaven National Laboratory (BNL) has developed a methanol synthesis process (believed to go via methyl formate) that operates at lower pressures than usual ( $< 5\text{MPa}$ ) and low temperature (active as low as  $100\text{ }^\circ\text{C}$ ). The process operates as a homogenous liquid phase system and claims conversion rates in excess of 90% in one pass, so high that the synthesis gas recycling is not needed. The low pressure operation, along with the inertness of the catalyst to  $N_2$  also allows partial oxidation of natural gas by air, eliminating the need for air separation during synthesis gas manufacture. The research initially used a catalyst based on  $Ni(CO)_4$  but recent research, conducted by Amoco, has resulted in a new catalyst complex in which Ni is ligated with a general formula,  $NiL_x(CO)_y$ . This catalyst avoids the problems caused by the toxicity of  $Ni(CO)_4$  and is safe and convenient to handle whilst being just as active. A further benefit is that the new catalyst is not as sensitive to  $CO_2$  and  $H_2O$  so that, by adding a co-catalyst, it may be possible to avoid synthesis gas pretreatment and allow the  $CO_2$  and  $H_2O$  to pass straight through the methanol synthesis reaction.

### 2.5.5.3 Co-current Synthesis of Methanol/Methyl formate Process.

Researchers at the Pittsburgh University have developed a co-current slurry phase process, which operates under relatively mild conditions (100-200 °C), similar to the BNL approach. The reaction scheme involves carbonylation of methanol to methyl formate, followed by hydrogenolysis of methyl formate to two molecules of methanol, the net result being the reaction of H<sub>2</sub> with CO to give methanol. Up to 90% conversion per pass and 98% selectivity to methanol were obtained. The use of temperatures above 170 °C at a pressure of 50 bar were reported to result in methyl formate being the limiting reactant. Latter is a severe limitation and reason why this process was never scaled up.

## 2.6 Literature Reviews

In 1989, Lee *et al.* [15] studied the effects of water and CO<sub>2</sub> on the metal content and chemical constitution of the methanol synthesis. It has been shown that the presence of CO<sub>2</sub> promotes the leaching of metals from the catalyst. It has also been observed that the presence of CO<sub>2</sub> leads to the formation of rosasite ((CuZn)<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>). These results have been statistically analyzed. The effects of temperature, pressure, and CO<sub>2</sub> on the amount of metals leached out from the catalyst as well as the extent of formation of ((CuZn)<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>) have been determined.

In 2003, Reubroycharoen *et al.* [16] studied a new reaction route of methanol synthesis at low temperature from CO<sub>2</sub>-containing syngas with Cu/ZnO catalyst and the aid of alcohols has been developed in a batch and a flow-type semi-batch reactors. The use of alcohols as catalytic solvents realized methanol synthesis at 443K with formate as an intermediate. The activity of methanol synthesis depends on types and structures of alcohols. Among all alcohols, secondary alcohol exhibited the highest activity. With the aid of 2-butanol, the one-pass 47.0% conversion and 98.9% selectivity were achieved at a mild condition, 443K and 50 bar.

In 2004, Huang *et al.* [17] studied the effects of chromium, zinc and cobalt additives on the properties of skeletal copper catalysts for the reactions of methanol synthesis, water gas shift and methanol steam reforming. Small amounts of  $\text{Cr}_2\text{O}_3$  were found to significantly enhance the activity for the water gas shift reaction. The presence of ZnO on the surface of skeletal copper was shown to greatly enhance methanol synthesis, suggesting that very active Cu-ZnO sites were created. ZnO also enhanced the activity for both the water gas shift and methanol steam reforming reactions. On the other hand, addition of Co additive reduced the activity of skeletal Cu to the extent that more than 1.1%wt Co additive on the surface resulted in negligible activity for the water gas shift reaction. The reason for the different performance with the Co additive is thought to be the reduction of surface CoO to metallic cobalt under the reducing conditions of catalyst pretreatment and reaction. Temperature programmed reduction (TPR), titration with  $\text{N}_2\text{O}$ , and CO chemisorption measurements support this reasoning. This investigation of the role of additives in methanol steam reforming and the water gas shift reactions provides support for a recently proposed pathway for methanol steam reforming reaction over Cu catalysts via a formaldehyde or methyl formate intermediate.

In 2004, Zeng *et al.* [18] studied catalytic promoting effects of eleven different alcohols, as reaction medium, on the synthesis of methanol from feed gas of  $\text{CO}/\text{CO}_2/\text{H}_2$  on Cu/ZnO solid catalysts. Added alcohol altered the reaction route to realize a low-temperature synthesis method where formate intermediate was produced from esterification reaction, then it was hydrogenated to methanol. Many alcohols showed catalytic promoting effect for methanol formation at temperature as low as 433 K remarkably lower than that in the present industrial ICI process.

In 2005, Yin *et al.* [19] studied the characteristics of methanol synthesis from biomass-derived syngas in a high pressure microreactor with a commercial Cu/ZnO/ $\text{Al}_2\text{O}_3$  catalyst. Four model bio-syngases with different  $\text{H}_2/\text{CO}/\text{CO}_2/\text{N}_2$  ratios, which were configured according to the results of biomass gasification, were used in the studies. The effect of temperature, pressure, and space velocity on the space-time yield and selectivity of methanol was explored. The sensitivity analysis of the yield and selectivity of methanol with different  $\text{H}_2/(\text{CO} + \text{CO}_2)$  and  $\text{CO}_2/\text{CO}$  ratios was

investigated. Results show that both yield and selectivity of methanol are affected by the operating parameters, and optimum conditions exist within the tested range. The yield of methanol is sensitive to the  $H_2/(CO + CO_2)$  ratio, whereas the selectivity of methanol is more sensitive to the  $CO_2/CO$  ratio. It is concluded that the yield of methanol from the syngas derived from air-steam gasification is lower than that from catalytic gasification, whereas the selectivity of methanol is the reverse. With a partial removal of  $CO_2$ , both yield and selectivity of methanol can be improved.

In 2006, Yang *et al.* [20] studied methanol synthesis method from  $CO_2$ -rich syngas by  $ZrO_2$ -doped CuZnO catalyst which prepared by successive-precipitation method was investigated by ICP-AES, BET, TEM, XRD, EXAFS,  $H_2$ -TPR and  $CO/CO_2$  hydrogenation. The active phase of copper in CuZnO catalyst prepared by co-precipitation method was well-crystallized. The presence of  $ZrO_2$  led to a high copper dispersion, which was distinctive from CuZnO. Though the activity for carbon monoxide hydrogenation was little lower than that of CuZnO catalyst,  $ZrO_2$ -doped CuZnO catalyst showed much higher activity and selectivity towards methanol synthesis from carbon dioxide hydrogenation. Moreover,  $ZrO_2$ -doped CuZnO catalyst showed high performance for methanol synthesis from  $CO_2$ -rich syngas.

In 2006, Zhang *et al.* [21] studied the effect of palladium on the performance of Cr/ZnO catalyst for the synthesis of methanol from synthesis gas. The methanol synthesis catalysts based on Cr/ZnO or supported palladium showed more stability. The catalyst Pd-Cr/ZnO containing Pd of 1 wt.% showed a high activity and selectivity for methanol synthesis from syngas. It was assumed that the role of Pd in the promotion effect was attributed to the promotion of hydrogen activation due to hydrogen spreading over the neighboring phase through a hydrogen-spillover mechanism. This process leads a more reduced state for the catalyst surface that may further facilitates hydrogenation of CO into methanol. Catalyst containing more than 2 wt.% Pd markedly produced more hydrocarbons although its activity for conversion of CO was high. High content of palladium would result in low dispersion and large particle size of palladium metal. Low dispersion of palladium impaired synergic effect

between Pd and Cr/ZnO. Also, CO can be catalytically hydrogenated to methane over surface of palladium metal with large particle size.



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## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

All chemicals are analytical grade as shown in Table 3.1.

**Table 3.1 List of chemicals and sources**

Chemicals	Source
Copper (II) nitrate hydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ )	Ajax chemicals
Copper (II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ )	Ajax chemicals
Copper (II) acetate hydrate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ )	Ajax chemicals
Zinc (II) nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )	Qrec
Zinc (II) chloride ( $\text{ZnCl}_2$ )	Ajax chemicals
Zinc (II) acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ )	Ajax chemicals
Chromium (II) nitrate hexahydrate ( $\text{Cr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )	Ajax chemicals
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	Ajax chemicals
Zirconyl nitrate hydrate ( $\text{ZrN}_2\text{O}_7 \cdot n\text{H}_2\text{O}$ )	Fluka
Palladium nitrate dihydrate ( $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ )	Fluka
Methanol ( $\text{CH}_3\text{OH}$ )	Fisher
Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )	BDH
2-Propanol	Fisher
Hexanol	Ajax chemicals
Ethylene glycol	Ajax chemicals
Glycerol	Ajax chemicals
Nitrogen gas (99.9% purity)	Praxair
Hydrogen gas (99.9% purity)	Praxair

**Table 3.1 List of chemicals and sources (continued)**

Chemicals	Source
5%Hydrogen in nitrogen gas	TIG
2%Oxygen in nitrogen gas	TIG
Carbon dioxide (99.9% purity)	Praxair
Standard synthesis gas, H <sub>2</sub> /Ar/CO/CO <sub>2</sub> (61.5/3/30.5/5)	TIG
Standard synthesis gas, H <sub>2</sub> /Ar/CO <sub>2</sub> (73/3/24)	TIG
Standard mixed gas, H <sub>2</sub> /Ar/CO (65/3/32)	TIG

### 3.2 Instruments and Equipments

#### 3.2.1 Instruments and Equipments for Catalyst Preparation

1. Peristaltic pump
2. Circulating water bath
3. Mechanical stirrer and impeller
4. pH meter
5. Ultrasonic bath
6. Aspirator pump
7. Dessicator
8. Oven
9. Muffle furnace
10. Mortar

11. Palletized mold set
12. Hydraulic pump
13. Mesh sieve set (25 and 45 mesh sizes)
14. Tube furnace and temperature controller
15. Thermocouple type K
16. Temperature transmitter and indicator
17. Flow meter

### **3.2.2 Instruments and Equipments for Catalyst Characterization**

1. X-ray diffractometer (XRD) (Bruker, D8 AXS Advance)
2. Surface area and porosity analyzer (Micromeritics, ASAP 2020)
3. Gas chromatograph (GC) (Shimadzu, GC-2014)
5. Tube furnace and temperature controller
6. Thermocouple type K
7. Temperature transmitter and indicator
8. Mass flow controller
9. AC transformer
10. Mass flow readout and control equipment



### 3.2.3 Instruments and Equipments for Methanol Synthesis

1. Pressure regulator
2. Mass flow controller
3. Mass flow readout and control equipment
4. Thermocouple type K
5. Band heater and digital temperature controller
6. Pressure gauge
7. Slurry reactor with built in impeller
8. Motor and speed controller
9. Condenser
10. Submersible water pump
11. Cooled trap
10. Back pressure regulator

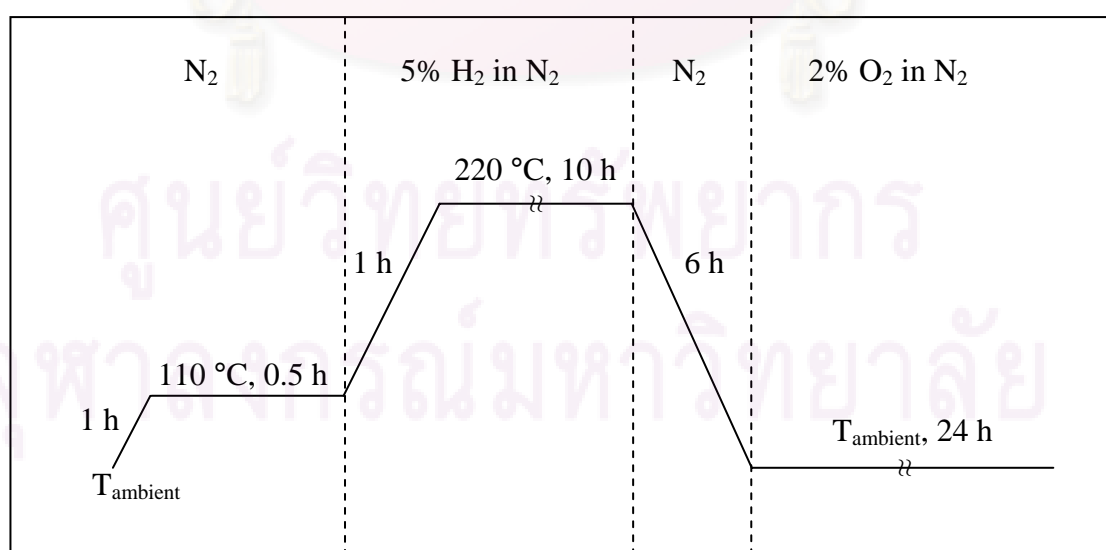
### 3.2.4 Instruments and Equipments for Product Analysis

1. Gas chromatograph (GC) (Shimadzu, GC-2014)
2. Methanizer and temperature controller
3. Centrifuge
4. Auto-pipette

### 3.3 Preparation and characterization of catalyst

#### 3.3.1 Preparation of catalyst

Copper zinc oxide (Cu/ZnO) catalyst was prepared by co-precipitation method in aqueous solution. Used 600 mL of copper nitrate and zinc nitrate (each 0.21 M, Cu/Zn mole ratio was 1), and sodium carbonate (0.47 M) used as precipitant were simultaneously added to 600 mL deionized water under rapid stir at 65 °C and controlled pH range 8.3 to 8.5 and aged overnight under ambient temperature. The precipitate was filtered and washed for 5 times with 65 °C deionized water, then dried the precipitate at 110 °C for 24 h followed by calcination in air with temperature rate 3 °C/min and held at 350 °C for 1 h. The obtained solid oxide was grounded, pelletized by compression in the mould at 60 MPa, crushed, screened and collected the particle which size between 25 to 45 mesh sieve. To activate the catalyst, the solid oxide particle (CuO/ZnO) was pretreated with N<sub>2</sub>, 30 mL/min, heated from ambient temperature to 110 °C for 1 h and held for 1 h. The reduction was performed by flowing a 5% H<sub>2</sub> in N<sub>2</sub> mixture 30 mL/min, heated up to 220 °C, held for 10 h and cooling to ambient temperature with flowing N<sub>2</sub> 30 mL/min for 6 h followed by passivation of flowing a 2% O<sub>2</sub> in N<sub>2</sub> mixture 5 mL/min for 24 h, as shown in figure 3.1.



**Figure 3.1** Schematic of temperature program for catalyst activation.

For the metal-doped Cu/ZnO catalysts (denoted as M/Cu/ZnO) prepared by co-precipitation method, the catalysts were prepared by adding the metal nitrate into copper nitrate and zinc nitrate aqueous solution and then precipitating using the same method as described above.

For metal-doped catalysts (denoted as M-Cu/ZnO) prepared by co-precipitation-impregnation method, the catalysts were prepared by impregnating the metal nitrate on the calcined CuO/ZnO, then drying and calcining by the same method as described above.

For all experiments, Cu/ZnO which prepared from nitrate precursor was used as an fundamental catalyst and 2-propanol was used as an fundamental catalytic solvent. The reaction parameters were studied from two sections as follow:

**(A) Semi-continuous Reaction.**

1. The effect of Cu/Zn mole ratio of the Cu/ZnO catalyst. (0.5-2 mole ratio)
2. The effect of metal-doped catalyst preparation method of Zr-doped Cu/ZnO catalyst. (co-precipitation and co-precipitation-impregnation)
3. The effect of metal-doped content on catalyst of zirconium-doped Cu/ZnO and palladium-doped Cu/ZnO catalysts. (0-1% wt Zr and Pd-doped Cu/ZnO)
4. The effect of alcohol (2-propanol, hexanol, ethylene glycol, glycerol, and mixed alcohol of 2-propanol and hexanol (1:1) as catalytic solvent.
5. The effect of support of copper-based catalyst. (Cu/ZnO, Cu/Cr<sub>2</sub>O<sub>3</sub> and unsupported Cu)
6. The effect of Cu/ZnO catalyst precursor. (copper and zinc complex of nitrate, acetate, chloride and salt)

**(B) Batch Reaction.**

1. The effect of CO<sub>2</sub>-rich syngas. (5,10, and 15% CO<sub>2</sub>-syngas)

## 2. The effect of zirconium-doped Cu/ZnO.

### 3.3.2 Characterization of catalyst

#### 3.3.2.1 X-ray Diffractometer (XRD)

Structure and crystallite size measurement was performed using a Bruker D8 AXS Advance X-ray diffractometer by using  $\text{CuK}\alpha$  radiation at an angle of  $2\theta$  ranged from 20 to 80 degrees.

Determination of copper oxide crystalline size evaluated from the full width at half maximum of CuO XRD peak by using Scherrer equation as follows [22]:

$$\text{Crystalline size (nm)} = \frac{K\lambda}{\beta_{1/2} \cos\theta_B} \quad (3.1)$$

where K is a unit cell geometry dependent constant

$\lambda$  is wavelength of the x-ray

$\beta_{1/2}$  is the full-width-half-max of the peak

$\theta_B$  is the Bragg angle

#### 3.3.2.2 Surface area analyzer

Textural properties of the catalysts were determined using a Micromeritics ASAP 2020 surface area porosity analyzer. The catalyst weight was about 100 mg and weighed exactly after pretreatment at 200 °C for 4 h before each measurement. Determination of specific surface area of the catalysts were obtained respectively using the BET calculation method.

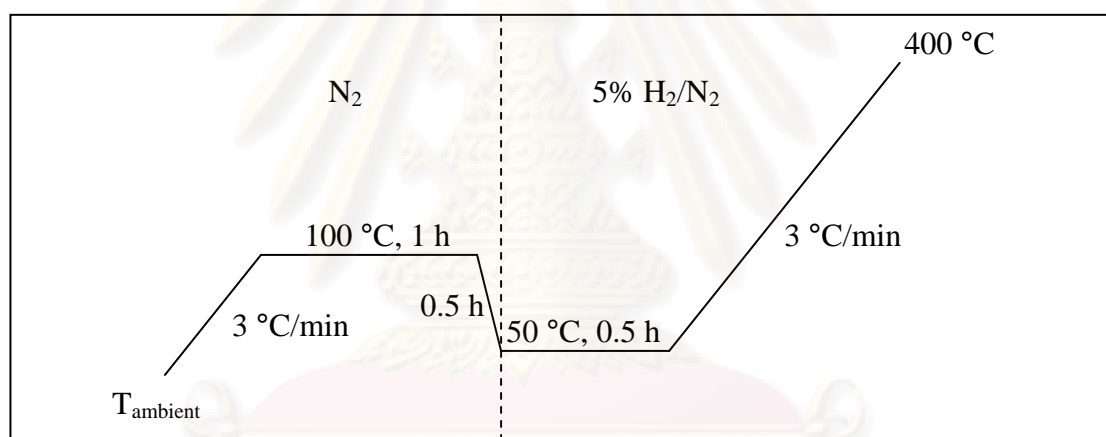
#### 3.3.2.3 Temperature Program Reduction (TPR)

The temperature program reduction was performed to determine the reducibility of the catalysts. The TPR were carried out in a fixed-bed quartz tube with a set of tube furnace and temperature controller. The pretreatment was performed by flowing a  $\text{N}_2$  20 mL/min over 50 mg of calcined catalyst, heated from ambient temperature to 100 °C, kept for 1 h to removed the adsorbed water and other

contaminants followed by cooling to 50 °C and kept for 0.5 h. The reducing gas containing 5% H<sub>2</sub> in N<sub>2</sub> was passed over the calcined catalyst at a flow rate of 20 mL/min with the heating rate of 3 °C/min up to the 400 °C as shown in figure 3.2. The effluent gas was passed over a silica gel to trap the generated water and analyzed by an on-line Shimadzu GC-2014 gas chromatograph thermal conductivity detector (GC-TCD) equipped with the Unibead-C column.

Determination of percentage of copper reduction of catalyst was calculated as follows:

$$\text{Reduction degree (\%)} = 100 \times \frac{\text{mole of H}_2 \text{ consumption}_{\text{measured}}}{\text{mole of H}_2 \text{ consumption}_{\text{calculated}}} \quad (3.2)$$



**Figure 3.2** Schematic of temperature program for pretreatment and reduction reaction.

### 3.4 Methanol synthesis and characterization of the reaction products

#### 3.4.1 Semi-continuous methanol synthesis

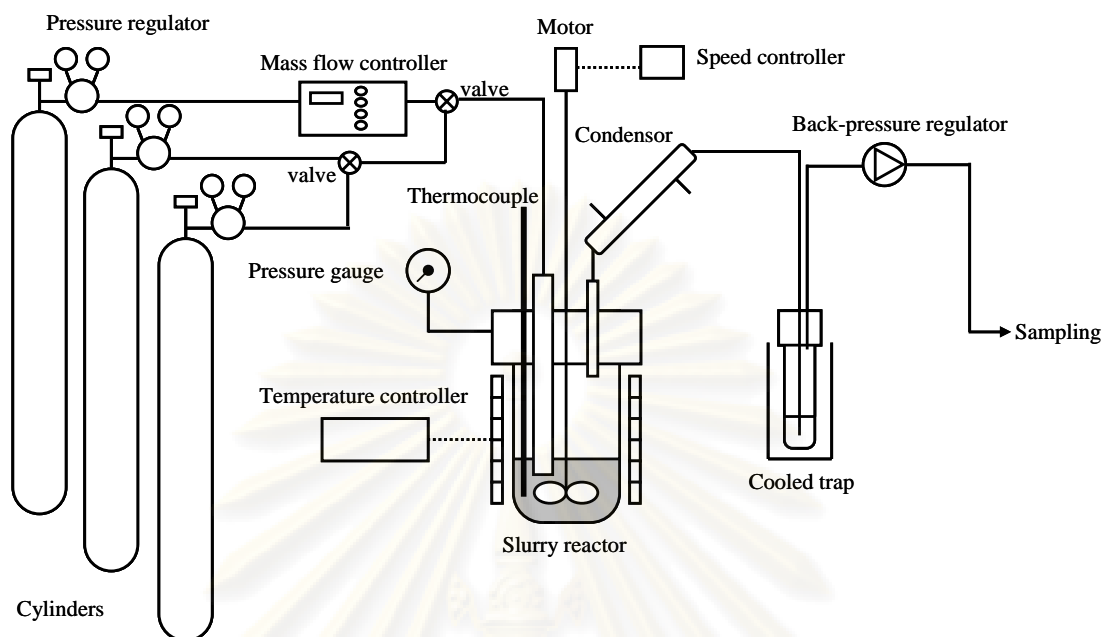
A semi-continuous methanol synthesis was used to study the effect of catalyst, alcohol solvent, reaction time and reaction temperature. 3 g of the catalyst was grounded in 25 mL of alcohol and poured into 80 mL reactor. 10 mL of alcohol was poured in liquid trap. Connected reactor and liquid trap to the reaction apparatus as

shown in scheme 3.3, Prior to the reaction, purging the system with high-pressure reactant gas ( $\text{H}_2/\text{Ar}/\text{CO}/\text{CO}_2 = 61.5/3/30.5/5$ ) which Ar was employed as an internal standard), increasing the reactor pressure to 50 bar, heating the reactor to the desired temperature, then the reaction took place by flowing the reactant gas 20 mL/min at the constant stirring speed (1260 rpm) for 20 h. The effluent gases from the reactor were pass through the water-cooled condenser and the ice-cooled trap of liquid product to prevent solvent escaping and analyzed the on-line gas products which described in section 3.4.3 (A). After completion of the reaction, the reactor was cooled down to the ambient temperature then liquid from the reactor and the cooled trap was collected for liquid products characterization which described in section 3.4.3 (B).

### 3.4.2 Batch methanol synthesis

A batch methanol synthesis was used to study the effect of metal-doped catalyst and quantity of  $\text{CO}_2$  in reactant gas which contain component of  $\text{H}_2$ , Ar, CO and  $\text{CO}_2$  (5, 10 and 15 %  $\text{CO}_2$  in syngas which  $\text{H}_2:\text{CO}$  molar ratio was 2:1). 1 g of the catalyst was grounded in 20 mL of 2-propanol, poured into 80 mL reactor and closed the reactor. The system was purged by the reactant gas then the initial reactor pressure was increased to 30 bar. The reaction took place at the reaction temperature of 170 °C and the constant stirring speed of 1260 rpm for 2 h. After completion of the reaction, the reactor was cooled down to the ambient temperature. The effluent gases and the liquid in the reactor were analyzed in the similar way which described in section 3.4.3.

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**Figure 3.3** Schematic of apparatus for methanol synthesis reaction.

### 3.4.3 Analysis of the reaction products

#### 3.4.3.1 Gas products

The effluent gases were analyzed by an on-line Shimadzu GC-2014 gas chromatograph thermal conductivity detector (GC-TCD) equipped with the Unibead-C column.

Determination of CO, CO<sub>2</sub>, and total carbon conversion were calculated as follows [23]:

$$\text{CO}_{\text{conversion}} (\%) = 100 \times \frac{(R_{\text{CO/Ar},0} - R_{\text{CO/Ar},1})}{R_{\text{CO/Ar},0}} \quad (3.3)$$

$$\text{CO}_{2\text{conversion}} (\%) = 100 \times \frac{(R_{\text{CO}_2/\text{Ar},0} - R_{\text{CO}_2/\text{Ar},1})}{R_{\text{CO}_2/\text{Ar},0}} \quad (3.4)$$

$$\text{Total carbon conversion} (\%) = \left( \text{CO}_{\text{conversion}} \times \frac{A}{A+B} \right) + \left( \text{CO}_{2\text{conversion}} \times \frac{B}{A+B} \right) \quad (3.5)$$

where  $R_{\text{CO/Ar},0}$  is the ratio of peak area of CO to that of Ar in reactant gas

$R_{\text{CO/Ar},1}$  is the ratio of peak area of CO to that of Ar in post-reaction gas

$R_{\text{CO}_2/\text{Ar},0}$  is the ratio of peak area of CO<sub>2</sub> to that of Ar in reactant gas

A and B are concentration of CO and CO<sub>2</sub> in reactant gas

### 3.4.3.2 Liquid products

The liquid from the reactor and the cooled trap were firstly dropped with 0.2 mL of ethanol as an internal standard, particularly, the reactor liquid was centrifuged to separate the suspended catalyst then analyzed by an on-line Shimadzu GC-2014 gas chromatograph flame ionization detector (GC-FID) equipped with the Poropak-Q column and methanizer.

Determination of selectivity and yield were calculated as follows [23]:

$$P_i \text{ selectivity (\%)} = 100 \times \frac{P_i \text{ mole}}{\sum P_i \text{ mole}} \quad (3.6)$$

$$P_i \text{ yield (\%)} = 100 \times \frac{P_i \text{ selectivity}}{\text{total carbon conversion}} \quad (3.7)$$

where  $P_i$  is liquid product i

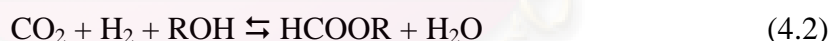
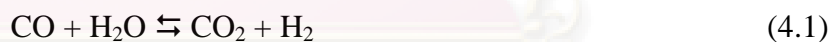


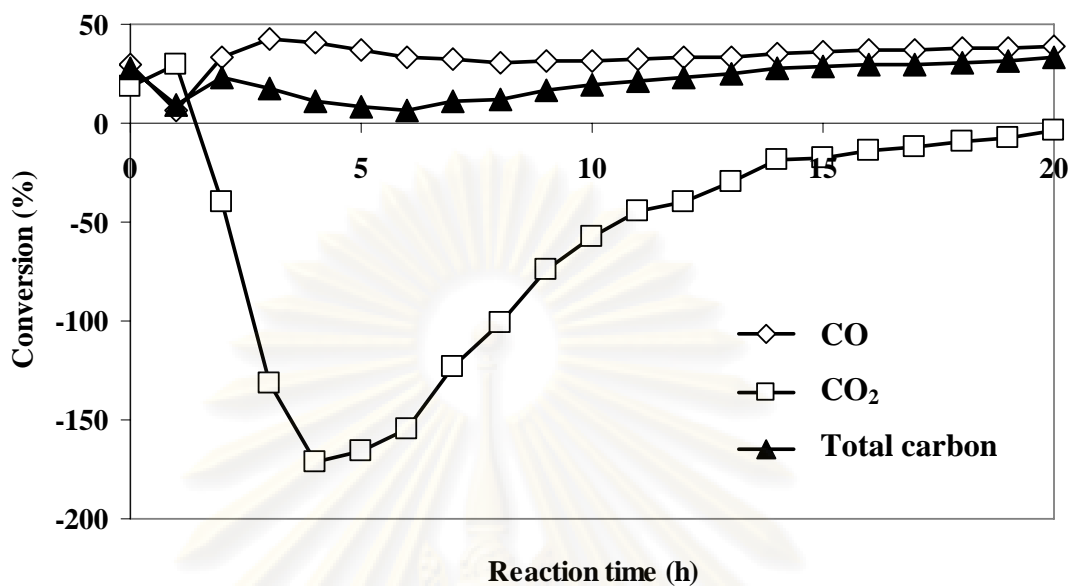
## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Effect of Conversion on The Semi-continuous Methanol Synthesis

The time-on-stream and conversion change was shown for the continuous reaction of methanol synthesis with Cu/ZnO catalyst during 20 h as Figure 4.1. In the initial reaction time (0-4 h), CO conversion increased due to water gas-shift (WGS) reaction in (4.1) [13,16], lead to the excess of CO<sub>2</sub> formed which affected to total carbon conversion also dropped. After 5 hours of the reaction, CO<sub>2</sub> conversion tended to increase as CO<sub>2</sub> reacted with alcohol and formed ester intermediate component of methanol. Until 15 hours of reaction, total carbon conversion also gradually increased and became stable at about 33% conversion. It implied that methanol synthesis got into equilibrium of reaction. CO<sub>2</sub> conversion was negative in the whole reaction time, suggesting a rapid rate of WGS reaction, particularly at the initially step of reaction and then, CO<sub>2</sub> converted to methanol via reactions (4.2)-(4.3) [16,23].



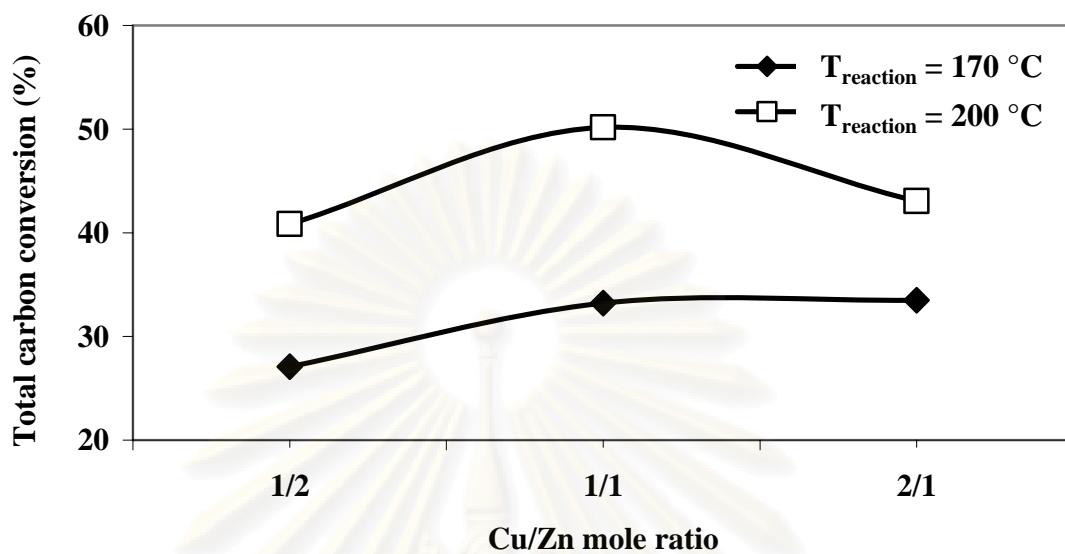


**Figure 4.1** Variations of conversions with time on stream for methanol synthesis in semi-continuous reactor.  $H_2/Ar/CO/CO_2 = 61.5/3/30.5/5$ ; temperature = 170 °C; pressure = 50 bar; Cu/ZnO (Cu/Zn=1) = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

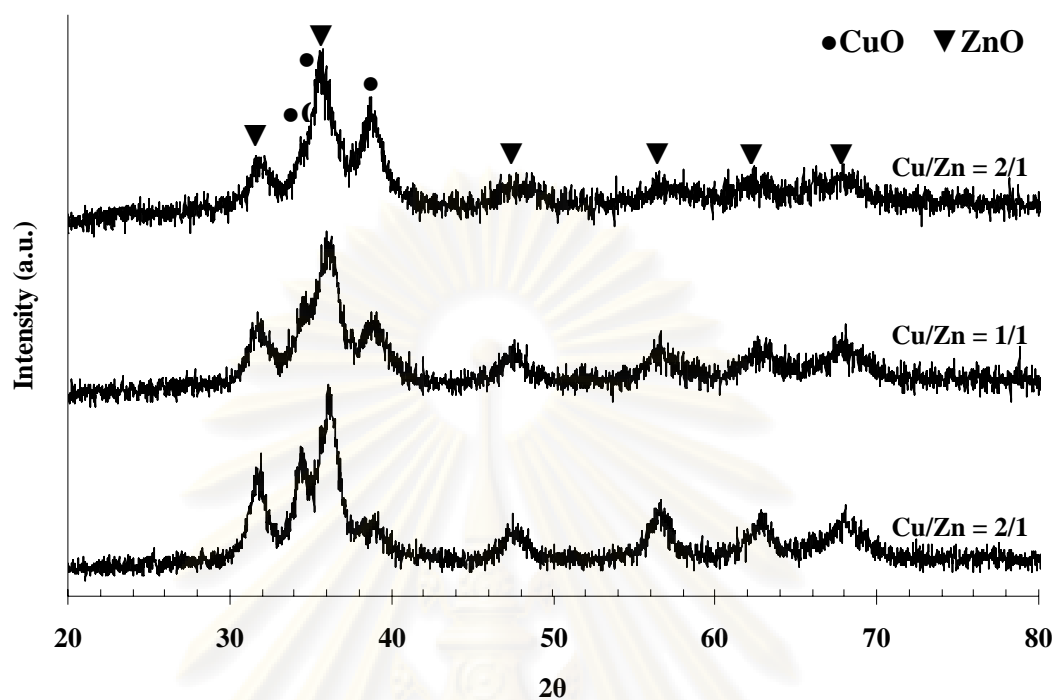
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#### 4.2 Effect of Copper Zinc Mole Ratio on Cu/ZnO catalyst

The effect of Cu/Zn mole ratio of Cu/ZnO catalyst on the total carbon conversion illustrates in Figure 4.2. The mole ratio used in this study were 1/2, 1/1 and 2/1. At reaction temperature of 170 °C, the mole ratio of Cu/Zn equaled to 1/1 and 2/1 showed the approximate total carbon conversion of 33.22% and 33.47% respectively. At temperature reaction of 200 °C, the mole ratio of Cu/Zn equaled to 1/1 clearly exhibited the highest total carbon conversion (50.19%). These indicated that the Cu/ZnO catalyst prepared at Cu/Zn mole ratio equaled to 1/1 exhibited the good activity for methanol synthesis. Figure 4.3 presents the XRD patterns of Cu/ZnO catalysts with different Cu/Zn mole ratio. The sharpest CuO peak of Cu/ZnO catalyst which Cu/Zn mole ratio equaled to 2/1 implied high crystallinity and high active sites of copper [24]. In order to confirm the change in the particle size of the metal due to Cu/Zn mole ratio, the particle sizes of catalysts were calculated by Scherrer equation with full-width at half maximum (FWHM) from XRD peak corresponding to CuO and their results were shown in Table 4.1. Nevertheless small CuO crystalline size was obtained at lower Cu/Zn mole ratio that influenced to the increase of catalyst surface area. While large CuO crystalline size of higher Cu/Zn mole ratio ensured higher concentration of copper active sites and methanol productivity values, but conversions were limited by equilibrium of methanol synthesis reaction. The optimum CuO crystalline size and copper content of catalyst could bring about the highest total carbon conversion for methanol synthesis. Therefore, mole ratio of Cu/Zn equaled to 1/1 was chosen to be a fundamental Cu/ZnO catalyst and this mole ratio entirely used for Cu-based catalysts in this study.



**Figure 4.2** Effect of Cu/Zn mole ratio on methanol synthesis in semi-continuous reactor.  $\text{H}_2/\text{Ar}/\text{CO}/\text{CO}_2 = 61.5/3/30.5/5$ ; pressure = 50 bar; Cu/ZnO = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.



**Figure 4.3** Comparison of X-ray diffraction patterns on Cu/Zn mole ratio of Cu/ZnO catalysts.

**Table 4.1** Effect of Cu/Zn mole ratio on CuO crystalline size

Cu/Zn mole ratio	CuO crystalline size (nm)	Total carbon conversion (%)
1/2	2.49	40.86
1/1	4.24	50.19
2/1	8.73	43.06

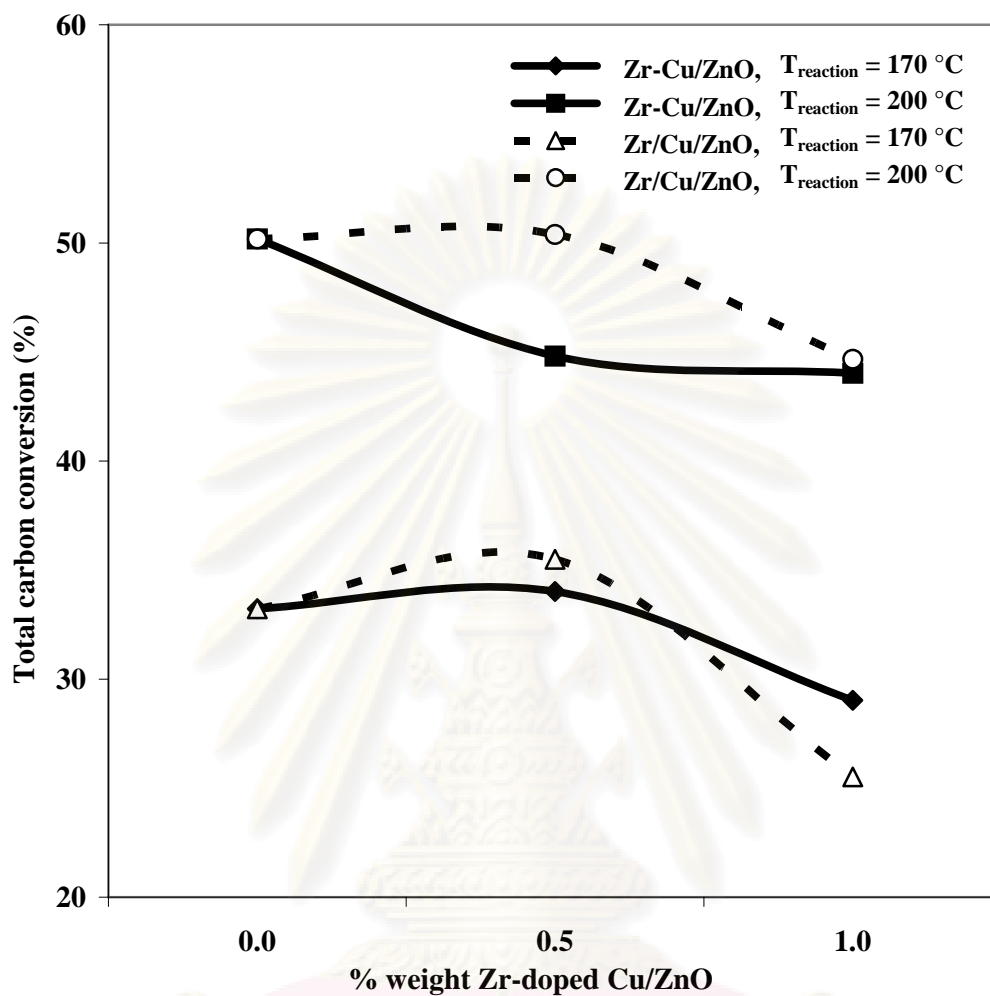
Conditions:  $\text{H}_2/\text{Ar}/\text{CO}/\text{CO}_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; temperature = 200 °C; pressure = 50 bar; Cu/ZnO = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

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### 4.3 Effect of Metal-doped on Cu/ZnO catalyst

#### 4.3.1 Effect of Zirconium-doped Content and Preparation Method on Cu/ZnO catalyst

Many researchers reported the promoting action of zirconium oxide on the activity of Cu/ZnO catalysts in the methanol synthesis from CO<sub>2</sub>, by improving the dispersion and stability of copper. Furthermore, doping Zr on the Cu/ZnO catalyst possessed higher activity, selectivity and long life [20]. In this work, the effects of zirconium content and preparation method on Zr-doped Cu/ZnO were investigated. Figure 4.4 shows variation of conversion when catalysts were prepared by two different methods, co-precipitation method (Zr/Cu/ZnO) and co-precipitation-impregnation method (Zr-Cu/ZnO). At reaction temperature of 170 and 200 °C, the total carbon conversion of 0.5%wt Zr/Cu/ZnO was higher than that of Cu/ZnO. Moreover, total carbon conversion decreased when Cu/ZnO contained more than 0.5%wt Zr. Even though promoter improved the catalyst stability, the excess amount of promoter tended to decrease the catalyst activity due to loss of copper surface area [17].



**Figure 4.4** Effect of zirconium-doped content and catalyst preparation on methanol synthesis in semi-continuous reactor.  $\text{H}_2/\text{Ar}/\text{CO}/\text{CO}_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

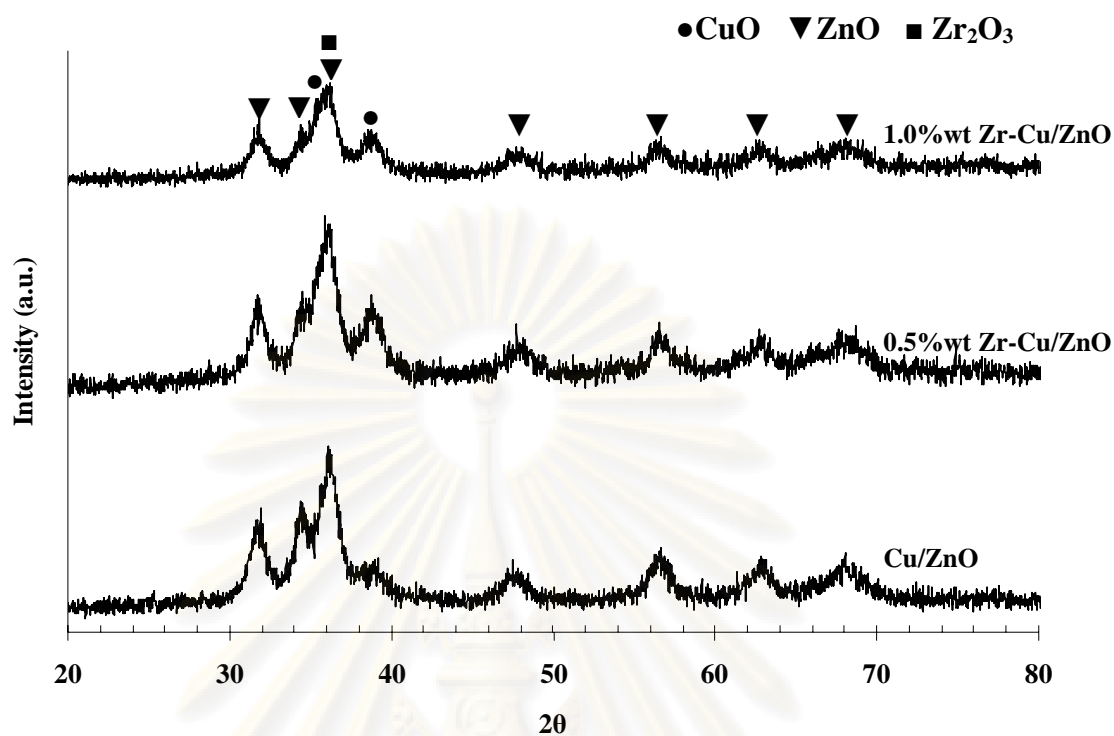
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Cu/ZnO catalysts with different zirconium content were used to examine methanol synthesis. Figure 4.5 shows the XRD patterns of Cu/ZnO catalysts during the zirconium-doping. CuO peak of 0.5%wt Zr-Cu/ZnO was sharper than 1.0%wt Zr-Cu/ZnO. It marked that the content of 0.5%wt Zr well-dispersed on Cu/ZnO catalyst. The CuO crystalline size of calcined catalysts was considered together with total carbon conversion as shown in Table 4.2. The catalyst containing 0.5%wt Zr displayed the slightly increase CuO crystalline size with a little higher total carbon conversion than undoped-metal Cu/ZnO. Catalyst contained 1.0%wt Zr save smaller lower CuO crystalline size and lower in total carbon conversion than that contained 0.5%wt Zr. Recommendation, high zirconium content might cause low zirconium dispersion in Cu/ZnO impaired synergic effect between Zr and Cu/ZnO. As a result, Cu/ZnO containing 0.5%wt Zr was the optimum Zr-doped content for methanol synthesis.



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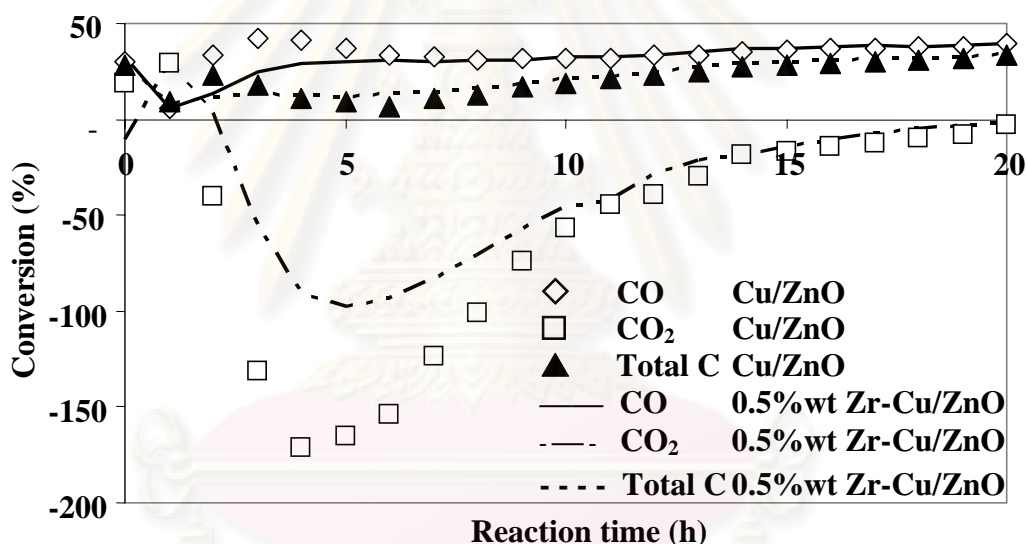
**Figure 4.5** Comparison of X-ray diffraction patterns on different zirconium-doped content on Cu/ZnO catalysts.

**Table 4.2** Effect of zirconium-doped content on Cu/ZnO catalyst for methanol synthesis.

% wt Zr	CuO crystalline size (nm)	Total carbon conversion (%)
0.0	4.24	33.22
0.5	4.92	34.01
1.0	4.67	29.02

Conditions: H<sub>2</sub>/Ar/CO/CO<sub>2</sub> = 61.5/3/30.5/5; reaction time = 20 h; temperature = 170 °C; pressure = 50 bar; Zr-Cu/ZnO = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

Figure 4.6 presents the comparison of 0.5%wt Zr-Cu/ZnO and Cu/ZnO catalysts. Although their CO, CO<sub>2</sub>, and total carbon conversions of both catalysts were close together to the end of reaction time, the higher CO<sub>2</sub> formation (negative in conversion) in the initial of reaction of Cu/ZnO could deactivate the catalyst. The negative CO<sub>2</sub> conversion value was low in the initial of reaction time when methanol synthesis catalyzed by Zr-Cu/ZnO. This implied that zirconium not only reduced deactivation of Cu/ZnO catalyst from CO<sub>2</sub> in the reactant gas but also assisted to convert CO<sub>2</sub> to methanol. It could be concluded that Zr-Cu/ZnO was the effective catalyst for synthesized the methanol with CO<sub>2</sub>-rich syngas.



**Figure 4.6** The comparison of 0.5% wt Zr-Cu/ZnO and Cu/ZnO catalysts on variation conversions of methanol synthesis in semi-continuous reactor. H<sub>2</sub>/Ar/CO/CO<sub>2</sub> = 61.5/3/30.5/5; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

Table 4.3 shows the effect of different catalyst preparation of zirconium-doped Cu/ZnO catalysts on conversions and selectivities for methanol synthesis. At the reaction temperature of 200 °C, both Zr/Cu/ZnO and Zr-Cu/ZnO showed higher CO and total conversion than that of 170 °C as the activity of catalyst increased with temperature. At the reaction temperature of 170 °C, total carbon conversion of 0.5% wt Zr/Cu/ZnO was closed to 0.5% wt Zr-Cu/ZnO but 0.5% wt Zr/Cu/ZnO clearly showed higher activity than 0.5% wt Zr-Cu/ZnO at the reaction temperature of 200 °C. The reason for the different performance between Zr/Cu/ZnO and Zr-Cu/ZnO could be referred to the preparation method. Catalyst prepared by co-precipitation method showed a well-dispersion of Zr on the copper phase while that prepared by impregnation dispersed the Zr only on the Cu surface. The optimum amount of 0.5% wt Zr/Cu/ZnO resulted in maximum CO and total carbon conversion. In addition, higher temperature reaction slightly affected to methanol selectivity by increasing both methanol product and 2-propyl methanoate intermediate.

**Table 4.3 Effect of different catalyst preparation of zirconium-doped Cu/ZnO catalysts on conversions and selectivities for methanol synthesis**

Catalyst	T <sub>reaction</sub> (°C)	Conversion (%)			Selectivity (%)	
		CO	CO <sub>2</sub>	Total carbon	CH <sub>3</sub> OH	HCOOC <sub>3</sub> H <sub>7</sub>
Cu/ZnO		39.19	-3.26	33.22	100.00	0.00 <sup>a</sup>
0.5% wt Zr/Cu/ZnO	170	44.07	-16.84	35.49	100.00	0.00 <sup>a</sup>
0.5% wt Zr-Cu/ZnO		39.98	-2.44	34.01	100.00	0.00 <sup>a</sup>
Cu/ZnO		63.17	-28.99	50.19	99.42	0.58
0.5% wt Zr/Cu/ZnO	200	62.79	-25.25	50.39	99.66	0.34
0.5% wt Zr-Cu/ZnO		59.59	-45.35	44.81	99.24	0.76

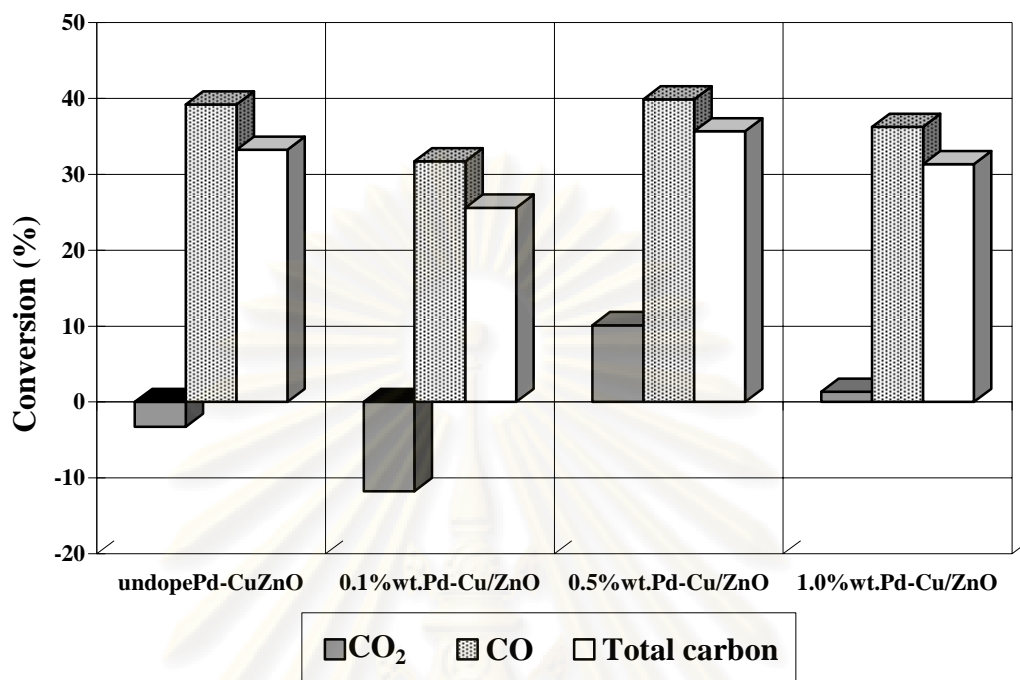
Conditions: H<sub>2</sub>/Ar/CO/CO<sub>2</sub> = 61.5/3/30.5/5; reaction time = 20 h; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

<sup>a</sup> cannot detected: no HCOOC<sub>3</sub>H<sub>7</sub> formation or too small amount of HCOOC<sub>3</sub>H<sub>7</sub>

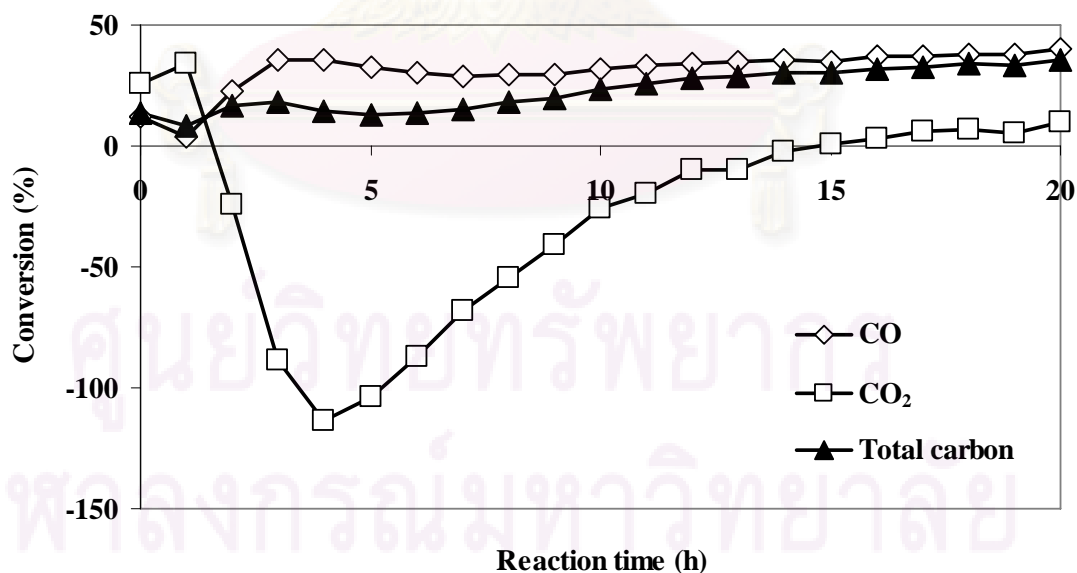
### 4.3.2 Effect of Palladium-doped on Cu/ZnO Catalyst

The palladium-doping for methanol synthesis showed a promotion effect similar to zirconium. In figure 4.7, no positive effect of Pd-doping was observed when Cu/ZnO contained Pd lower than 0.1%wt. The conversions tended to increase by increasing Pd-doping on Cu/ZnO catalyst from 0.1 to 0.5%wt while it tended to decrease by increasing Pd-doping on Cu/ZnO catalyst from 0.5 to 1.0%wt. Too little palladium content might cause low palladium dispersion in Cu/ZnO or excess palladium content might cause large palladium particle that resulted in low palladium dispersion. The low palladium dispersion impaired synergic effect between Pd and Cu/ZnO. As a result, Cu/ZnO containing 0.5%wt Pd was the optimum Pd-doped content because it improved activity of Cu/ZnO catalyst by increasing CO and CO<sub>2</sub> conversion. Moreover, the positive CO<sub>2</sub> conversion ascribed to the high rate of hydrogenation.

At the end of reaction time, conversions inclined to increase to higher value as shown in Figure 4.8, indicated that reaction was not at equilibrium. Thus the conversions will increase for longer reaction time.



**Figure 4.7** Effect of doping palladium on Cu/ZnO catalyst for methanol synthesis in semi-continuous reactor.  $H_2/Ar/CO/CO_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; temperature = 170 °C; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

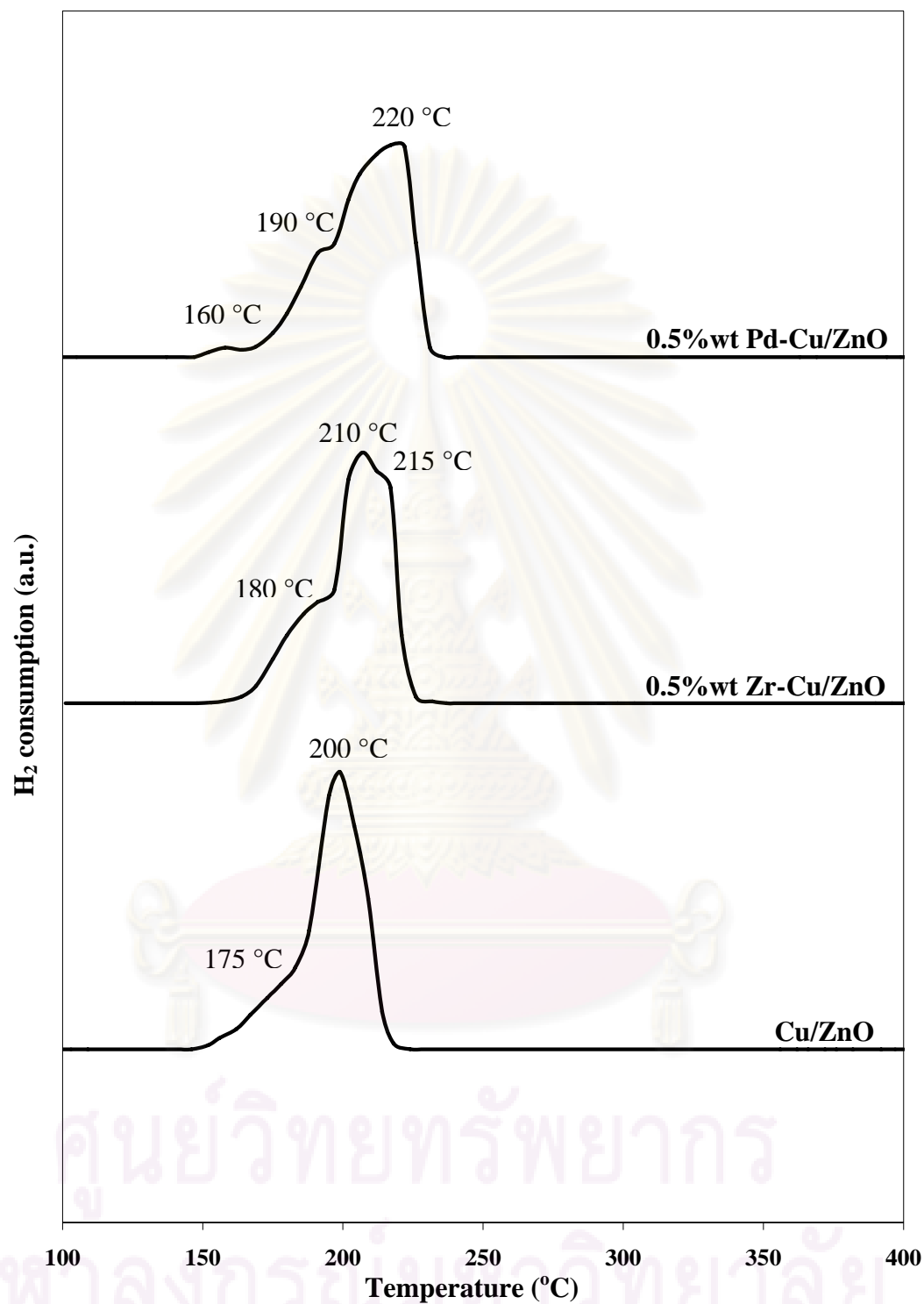


**Figure 4.8** Effect of 0.5% wt Pd-Cu/ZnO catalyst on the variations of conversions for methanol synthesis in semi-continuous reactor.  $H_2/Ar/CO/CO_2 = 61.5/3/30.5/5$ ; temperature = 170 °C; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

### 4.3.3 Reducibility of Metal-doped on Cu/ZnO Catalyst

Although the CuO crystalline size is an important factor for determining catalytic activity, the reducibility is also a key parameter to assess catalyst performance. Furthermore, the different metal-doped Cu/ZnO catalysts were affected to their reducibility, illustrated in Figure 4.9. The catalysts showed two or three reduction peaks for each TPR curve, the peak temperature of which varied depending on different metal doping. The Cu/ZnO catalyst exhibited two different reduction peaks between 150 °C and 250 °C which are assigned to the reduction of copper species. A peak around 200 °C was observed as a main peak together with a pre-tail peak around 175 °C. The larger area of the peak at high temperature than that at low temperature was indicative of well-crystallized CuO species [20]. It was found that CuO was reduced by hydrogen in two stepwise from TPR profiles: the Cu<sub>2</sub>O phase was reduced in the first step from Cu<sup>2+</sup> into Cu<sup>+</sup> and the CuO phase was reduced in the second step from Cu<sup>+</sup> into Cu<sup>0</sup> [25,26].

At high temperature, the metal-doped Cu/ZnO catalysts exhibited higher H<sub>2</sub> consumption than the Cu/ZnO catalyst. For Zr and Pd doping, the reduction peaks shifted towards higher temperature, possibly due to a size growth of CuO crystals as shown in Table 4.4 [25]. Simultaneously, high H<sub>2</sub> consumption of metal-doped catalysts brought in high reducibility that could be a factor for exhibiting higher catalytic activity. It could be induced from the nature of strong interactions of well-dispersed metal-doped particles on Cu-ZnO as the 0.5%wt Zr-Cu/ZnO catalyst. The intensity of the pre-tail and main peaks were reduced around 180 and 210 °C respectively. In addition, it appeared a shoulder peak at the somewhat high temperature of 215 °C. The 0.5%wt Pd-Cu/ZnO catalyst also slightly enhanced the activity. Pd plays a role in counteracting the inhibition by water that could be explained by hydrogen spillover which moderates the [Cu(metal) + H<sub>2</sub>O ⇌ CuO(ads) + H<sub>2</sub>] redox [28], resulting in the highest reduction degree. It was firstly reduced to palladium metal at 160 °C, which meant that palladium stayed as metal on the CuO. During the CuO reduction, Pd metal plays a role by increasing the reduction of CuO to Cu metal [27].



**Figure 4.9** Temperature programmed reduction (TPR) profiles on different metal-doped on Cu/ZnO catalysts.

**Table 4.4 Effect of metal-doped Cu/ZnO catalysts on reducibility and total carbon conversion for methanol synthesis**

Catalysts	CuO crystalline size (nm)	Reduction degree (%)	Total carbon conversion (%)
Cu/ZnO	4.24	75.34	33.22
0.5% wt Zr-Cu/ZnO	4.92	79.64	34.01
0.5% wt Pd-Cu/ZnO	4.89	83.25	35.67

Conditions:  $H_2/Ar/CO/CO_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

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#### 4.4 Effect of Alcohol Solvent on Methanol Synthesis

The effect of different alcohol solvents was also studied as it not only was reaction medium but also participated in the reaction of methanol synthesis catalytically [23]. Figure 4.10 shows the effect of each alcohol on the conversion. For comparison, the results were separated into three cases. The first case focused on alcohol with the same number hydroxyl group (-OH group) but different structure. At reaction temperature of 170 °C, 2-propanol exhibited higher total carbon conversion than 1-hexanol. It could be concluded that the catalytic activity of secondary alcohol as 2-propanol was high due to the high electron density in its oxygen atom assisted to accelerate the reaction. On the other hand, large molecular volume of higher alcohol as 1-hexanol became an obstacle in nucleophilic attack, so esterification rate was slow [18,23]. At reaction temperature of 200 °C, total carbon conversion of 1-hexanol was close to 2-propanol.

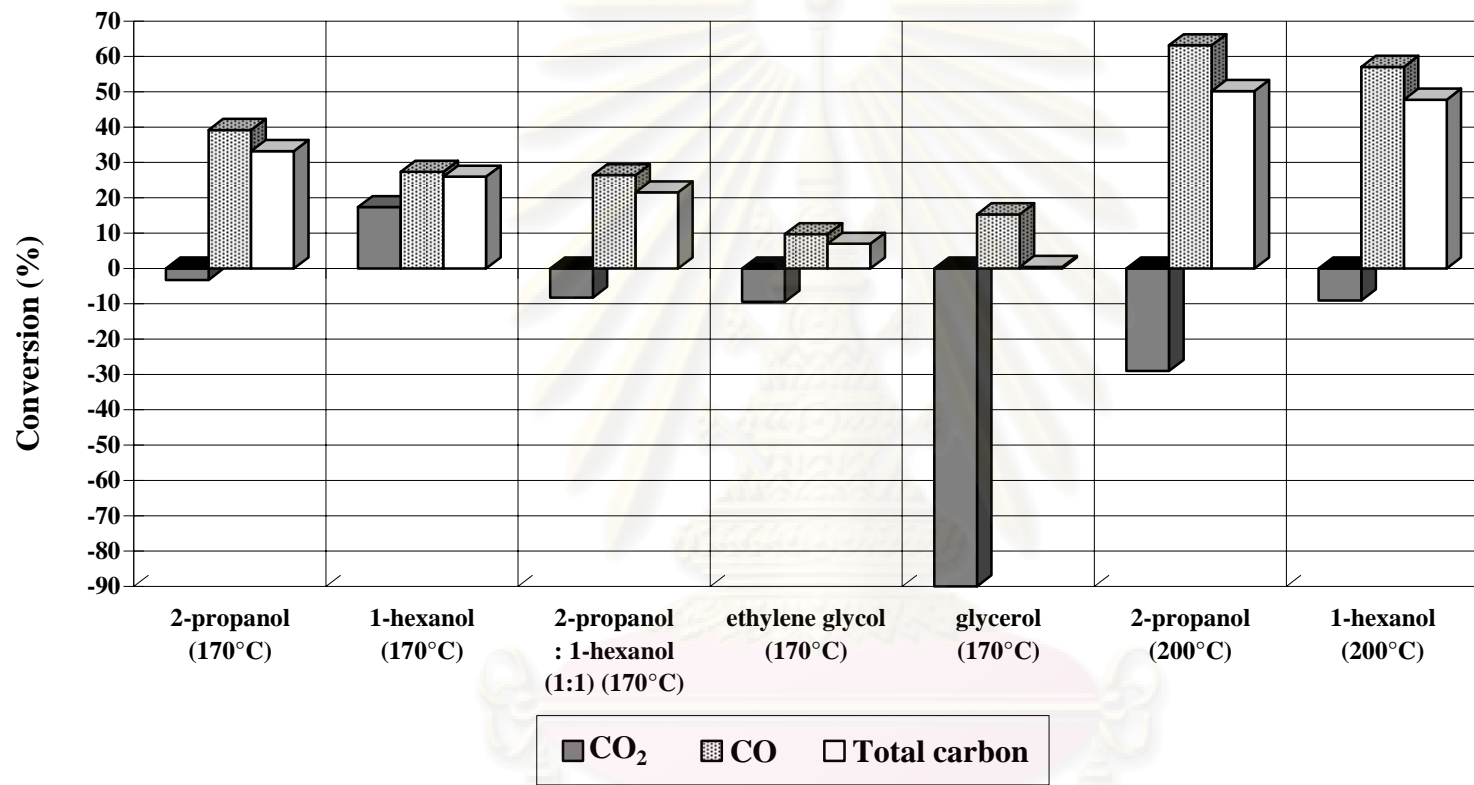
The second case focused on the mixed alcohol between 2-propanol and 1-hexanol (1:1 by volume). The lower conversions by using mixed alcohol solvent could be explained relatively to the vapor pressure of alcohol solvent. At 170°C, vapor pressure of 1-hexanol (1.45 bar) is much lower than that of 2-propanol (13.89 bar). This implied that the amount of 2-propanol in liquid phase is much lower than that of 1-hexanol when using at the same level. Moreover, the amount of each alcohol in vapor phase was not changed when the amount of alcohol solvent was reduced in mixed alcohol system. Thus, decreasing the solvent amount by using mixed alcohol would greatly reduce the amount of 2-propanol in liquid phase as its high vapor pressure, leading to lower the conversions of mixed alcohol system. This exhibition was corresponding with the results of Tsubaki *et al.* that the conversion of reactant and the yield of methanol decreased with decreasing the amount of alcohol solvent added in the reaction mixture [12].

The last case concerned the comparison of number of hydroxyl group in alcohol molecule as 2-propanol, ethylene glycol, and glycerol were selected as the alcohol with different hydroxyl group. Although increasing number of hydroxyl group caused to increasing conversion by increasing chance of esterification, the results was

different in this work. 2-propanol which its molecule has only one hydroxyl group showed the highest conversion due to its small alcohol molecule [22,29]. Moreover, high viscosity of ethylene glycol and glycerol was another condition, that affected to catalyst dispersion in slurry reaction did not well. Then the conversions were low.



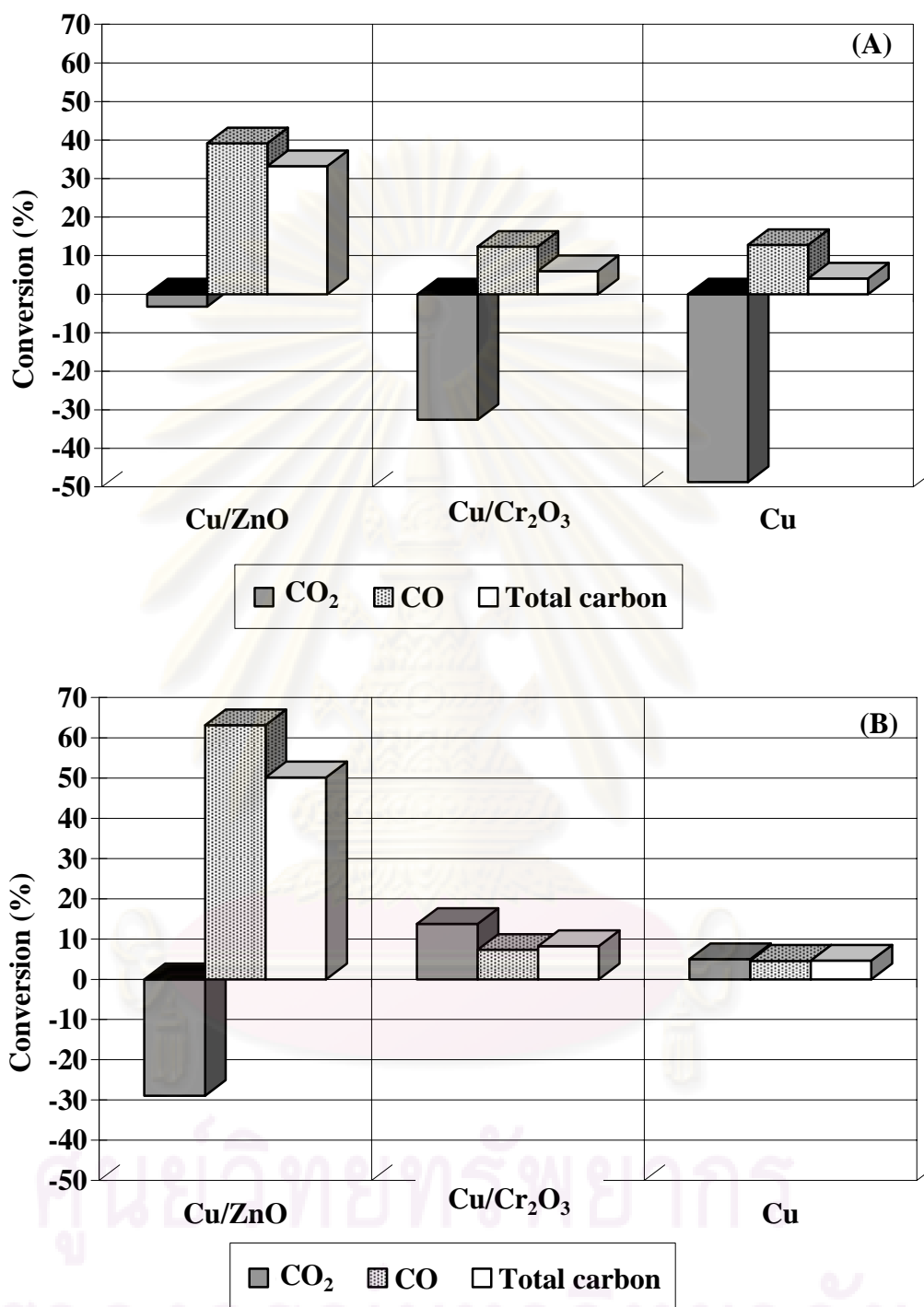
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**Figure 4.10** Effect of alcohol solvent on methanol synthesis in semi-continuous reactor.  $H_2/Ar/CO/CO_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; pressure = 50 bar; Cu/ZnO = 3 g; alcohol = 25 ml; flow rate = 20 ml/min.

#### 4.5 Effect of Supported Catalyst

Copper was known to be the major in catalyst for methanol synthesis. With the aid of good support, catalysts should have an open structure with high specific surface area leading to effectively increase in the degree of dispersion of active sites [30]. There by, Cu-based catalyst was considered as one of the most promising catalysts. The supports used in this study were ZnO, Cr<sub>2</sub>O<sub>3</sub> and unsupported Cu. In Figure 4.11, the methanol synthesis performed by Cu/ZnO catalyst showed the highest CO and total carbon conversions indicated that ZnO was a significant support for methanol synthesis. Remarkably, the role of ZnO support in a Cu-based catalyst was to disperse Cu particles and stabilize active sites by decreasing the unavoidable agglomeration of Cu particles, suggesting that ZnO itself promoted the methanol synthesis activity from CO hydrogenation [8,31]. On the contrary, both Cu/Cr<sub>2</sub>O<sub>3</sub> and unsupported Cu showed poor conversions. Because the activity of Cu/Cr<sub>2</sub>O<sub>3</sub> was rather low at low temperature reaction. Thus Cu/Cr<sub>2</sub>O<sub>3</sub> catalyst could increase conversion, preferably activated to CO<sub>2</sub> hydrogenation when the reaction temperature was increased (200 °C) as shown in Figure 4.11 (B). Lacked of the aid of support, unsupported Cu showed low conversion, because this catalyst had low dispersion resulted in loss of the active copper site.



**Figure 4.11** Effect of supported catalyst for methanol synthesis in semi-continuous reactor.  $H_2/Ar/CO/CO_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; pressure = 50 bar; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min; (A) temperature = 170 °C and (B) temperature = 200 °C.

#### 4.6 Effect of Catalyst Salt Precursors

It is known, that the preparation method is one of the promising ways to control the catalysts properties. In this relation, the state of the metal-metal oxides catalyst significantly depended on the nature of their corresponding precursors [32]. Therefore, the effect of different copper and zinc compounds used as precursors for co-precipitation of Cu/ZnO catalysts was investigated with respect to structure, textural properties, and catalytic activity. Table 4.5 displays BET surface area, CuO crystalline size and total carbon conversion of different copper and zinc salt precursors. The increasing in total carbon conversion of the catalysts prepared by nitrate, acetate and chloride salt precursors did not correlate to their textural properties. As shown in Figure 4.12, their BET surface area, average pore volume and average pore size of were close to each other. However the conversion of CO, CO<sub>2</sub>, and total carbon decreased in the following order: acetate > chloride ~ nitrate. This result indicated that reactivity of Cu/ZnO catalyst formulated from acetate precursor was high.

Additionally, different metal salt precursor etc. nitrate, acetate, chloride, and carbonate anions were removed during the calcination step, revealed different structure formation of CuO crystalline size which significantly improved interface between their particles. Kim *et al.* reported that the crystallinity of CuO would exert an influence on the reactivity of catalyst. Therefore, the higher reactivity is expected at the lower crystallinity [24]. The calcined catalysts was characterised by XRD and their result was shown in Figure 4.13. Comparing the XRD patterns of nitrate, chloride, and acetate precursors, the catalysts showed a little different crystallinity of CuO peak. Meanwhile CuO crystalline size of acetate and chloride salt precursors was close to nitrate salt precursor (as shown in Table 4.5).

**Table 4.5 Total carbon conversion, CuO crystalline size and textural properties of Cu/ZnO catalysts prepared from different salt precursor**

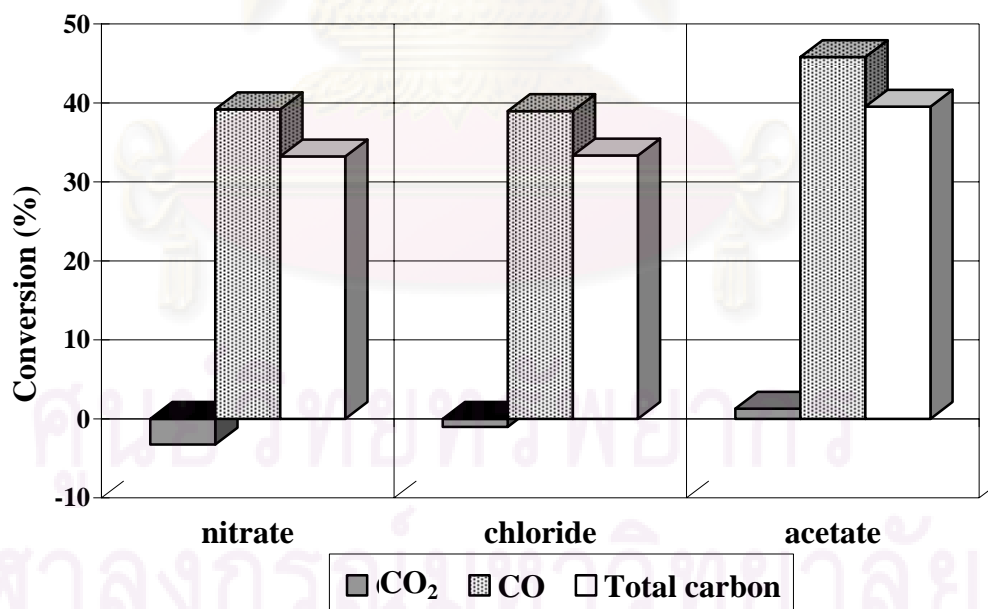
Cu and Zn salt precursors	Total carbon	CuO	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{P}}^{\text{b}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{p}}^{\text{c}}$ ( $\text{\AA}$ )
	conversion	crystalline size			
	(%)	(nm)			
nitrate	33.22	4.24	38.06	0.19	187
chloride	33.34	4.46	42.40	0.15	112
acetate	39.53	5.26	47.90	0.20	144

Conditions:  $\text{H}_2/\text{Ar}/\text{CO}/\text{CO}_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; pressure = 50 bar; temperature = 170 °C; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.

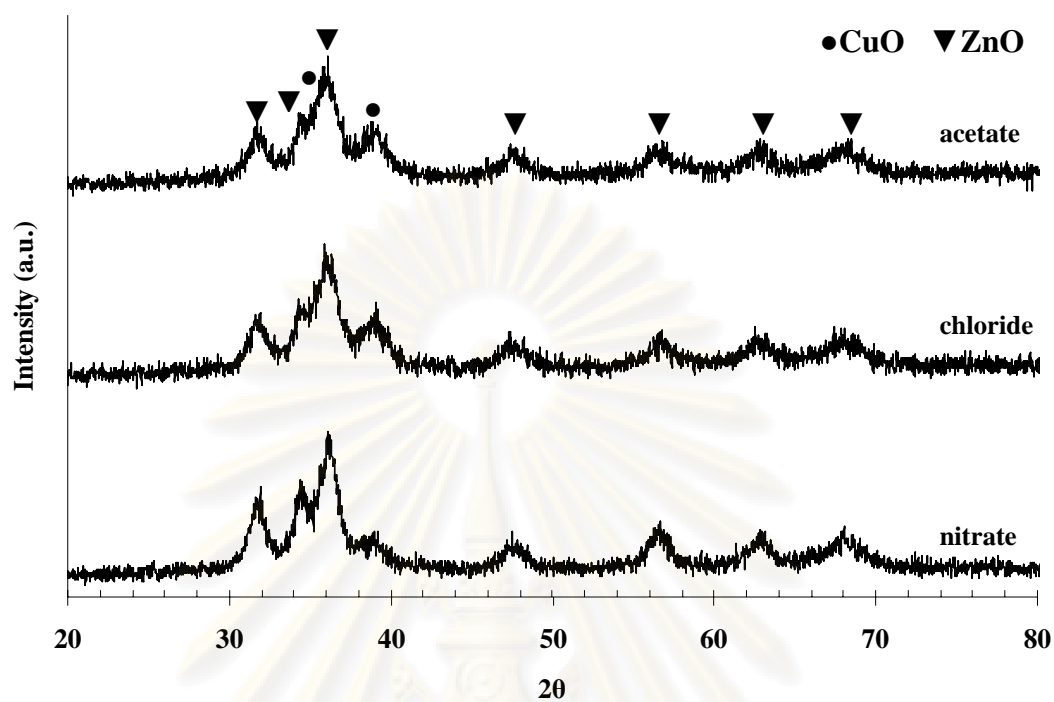
<sup>a</sup> BET surface area.

<sup>b</sup> Average pore volume.

<sup>c</sup> Average pore size.



**Figure 4.12** Effect of catalyst salt precursors on Cu/ZnO for methanol synthesis in semi-continuous reactor.  $\text{H}_2/\text{Ar}/\text{CO}/\text{CO}_2 = 61.5/3/30.5/5$ ; reaction time = 20 h; temperature = 200 °C; pressure = 50 bar; temperature = 170 °C; catalyst = 3 g; 2-propanol = 25 ml; flow rate = 20 ml/min.



**Figure 4.13** Comparison of X-ray diffraction patterns on Cu/ZnO catalysts prepared from different salt precursors.

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#### 4.7 Effect of CO<sub>2</sub>-rich Syngas on Methanol Synthesis

Syngas dominantly employed in the commercial scale synthesis of methanol could be produced from biomass gasification which generated biomass-derived H<sub>2</sub>-deficient and CO<sub>2</sub>-rich syngas. Biomass gasification has been gaining more attention for methanol synthesis due to their application for renewable energy sources [33]. However, copper-based catalysts are sensitive to a variety of deactivation factors. As well known the Cu/ZnO catalyst was deactivated under the atmosphere of CO<sub>2</sub> and water [20]. Remarkably, drawback of low temperature methanol synthesis in liquid phase process was the trace amount of carbon dioxide and water in the feed gas or reaction system, deactivated the catalyst soon [34]. Moderate concentrations of CO<sub>2</sub> from syngas produced water in the reverse WGS reaction which in turn acted as an inhibitor of the active metal sites of the catalyst [35]. As shown in Table 4.6, CO<sub>2</sub>-rich contained syngas impaired total carbon conversion due to the formation of excess water which caused the decreasing in CO conversion and methanol product. The decreasing of CO conversion from WGS reaction resulted in the decreasing negative CO<sub>2</sub> conversion. Furthermore, methanol synthesis could not perform by using high CO<sub>2</sub> and H<sub>2</sub> (syngas no. 4) as feed gas. Cu/ZnO catalyst displayed slight total carbon conversion because it was severely deactivated by high content of CO<sub>2</sub>. Moreover, CO<sub>2</sub> partly converted to CO from reverse WGS reaction product.

**Table 4.6 Effect of CO<sub>2</sub> content in syngas reactant on methanol synthesis for catalytic Cu/ZnO in batch reactor**

Syngas No.	Syngas composition (% mole)				Conversion (%)		
	H <sub>2</sub>	Ar	CO	CO <sub>2</sub>	CO	CO <sub>2</sub>	Total carbon
1	61.5	3.0	30.5	5.0	38.18	-141.74	12.84
2	58.5	2.7	28.8	10.0	27.58	-49.90	7.61
3	55.3	2.5	27.2	15.0	15.12	-15.47	4.25
4	73.0	3.0	0.0	24.0	0.00	0.09	0.09

Conditions: H<sub>2</sub>/CO = 2; reaction time = 2 h; initial pressure = 30 bar; temperature = 170 °C; Cu/ZnO = 1 g; 2-propanol = 20 ml.

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#### 4.8 Effect of Metal-doped Cu/ZnO on Methanol Synthesis from CO<sub>2</sub>-rich Syngas

To improve the life of the Cu/ZnO catalyst, it is essential to add a suitable promoter to increase its stability because Cu/ZnO catalyst is not so active for the CO<sub>2</sub>-rich syngas. The water formed as a by-product, from both methanol synthesis and the reverse WGS side reaction also had an inhibitory effect on the active copper metal by a great loss of the catalyst activity. The performance of catalyst could be improved by doping Zr on the Cu/ZnO catalyst. The effect of Zr-doped Cu/ZnO on conversions was showed in Table 4.7. At 5 and 10 %CO<sub>2</sub> containing syngas, total carbon conversions of 0.5%wt Zr-Cu/ZnO were higher than that of Cu/ZnO. The result implied that Zr-doping improved catalytic activity under concentration up to 10%CO<sub>2</sub> containing syngas. This evidence supported that doping small amount of zirconium as a promoter on Cu/ZnO catalyst increased CO<sub>2</sub> hydrogenation and suppressed water formation to prevent the agglomeration of copper and zinc sites. Eventually, adding of 15%CO<sub>2</sub> in syngas inclined to the lowest conversions for the 0.5%wt Zr-Cu/ZnO catalyst.

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**Table 4.7 Effect of zirconium-doped Cu/ZnO on conversions in methanol synthesis from CO<sub>2</sub>-rich syngas reactant in batch reactor**

Catalyst	CO <sub>2</sub> content in syngas (% mole)	Conversion (%)		
		CO	CO <sub>2</sub>	Total carbon
Cu/ZnO	5	38.18	-141.74	12.84
	10	27.58	-49.90	7.61
	15	15.12	-15.47	4.25
0.5% wt Zr-Cu/ZnO	5	36.49	-122.82	14.05
	10	27.29	-39.49	10.53
	15	16.37	-23.12	2.34

Conditions: H<sub>2</sub>/CO = 2; reaction time = 2 h; initial pressure = 30 bar; temperature = 170 °C;  
Catalyst = 1 g; 2-propanol = 20 ml.

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## CHAPTER V

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

In this study, Cu/ZnO was selected as fundamental metal oxide catalyst for methanol synthesis from CO<sub>2</sub>-rich syngas to perform the reaction under low temperature process in a slurry reactor. Activities of fundamental metal oxide catalysts were investigated in terms of catalyst mole ratio, preparation methods, metal doping, metal-doped content, alcohol solvent, support, salt precursor, and CO<sub>2</sub>-containing syngas in semi-batch methanol synthesis. Modification of metal oxide catalysts was done by doping zirconium in batch methanol synthesis from CO<sub>2</sub>-rich syngas.

For semi-batch methanol synthesis from 5%CO<sub>2</sub>-containing syngas, Cu/Zn equaled to 1 was a suitable mole ratio for Cu/ZnO catalyst. The catalyst preparation process has been carried out by two different methods. At 170 and 200 °C, 0.5%wt Zr/Cu/ZnO prepared by co-precipitation preparation method was the most effective catalyst. Zirconium was well-dispersed in the copper phase. While that prepared by impregnation method dispersed the zirconium only on the Cu surface. 0.5%wt Zr-Cu/ZnO prepared by co-precipitation-impregnation preparation method was an effective catalyst for synthesized with CO<sub>2</sub>-rich syngas by assist to convert CO<sub>2</sub> to methanol. Over 0.5%wt Zr doping caused in the reduction of the copper surface area resulted in decreasing total carbon conversion. 0.5%wt Pd-Cu/ZnO was the optimum content that improved catalytic activity for longer period of reaction time. Catalytic activity of 2-propanol was the highest because this secondary alcohol has high electron density in its oxygen atom to accelerate the reaction. Furthermore, esterification reaction could occur easily due to its small molecule. Cu/ZnO catalyst had the highest activity by the aid of ZnO support promoted CO hydrogenation in the methanol synthesis. Cu/ZnO prepared from acetate salt precursor showed high activity.

High CO<sub>2</sub> content resulted in the decrease of catalyst activity caused by trace of CO<sub>2</sub> and water. Metal-doped Cu/ZnO was expected to overcome the drawback of

low-temperature methanol synthesis from CO<sub>2</sub>-rich syngas in terms of catalyst deactivation. Up to 10%CO<sub>2</sub> containing syngas, 0.5%wt Zr-Cu/ZnO was the most active catalyst that it could improve activity and stability by increasing CO<sub>2</sub> hydrogenation and suppress water formation. The high performance of Zr doping was ascribed to the favored emergence of enhancement of active sites and to the high hydrogen spillover on the catalyst.

## 5.2 Recommendation

For future research work, methanol synthesis from CO<sub>2</sub>-rich syngas in semi-continuous reactor should be firstly investigated. In addition, other modification of metal oxide catalysts for CO<sub>2</sub> hydrogenation should be studied to further CO<sub>2</sub>-rich syngas methanol synthesis in low temperature process. Since, methanol synthesis by biomass-derived syngas might be a promising practical way for methanol production for commercial scale.

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**APPENDICES**

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## Appendix A

### Examined Calculation for Preparation of 1%wt Zr-Cu/ZnO

1% wt Zr-Cu/ZnO was prepared by co-precipitation-impregnation method

*Basis* 10 g of CuO/ZnO (mol ratio of Cu/Zn = 1)

#### 1<sup>st</sup> step: Co-precipitation

CuO 1 mol = Cu 1 mol, ZnO 1 mol = Zn 1 mol

CuO ( MW = 79.55 ) 1 mol = 79.55 g, ZnO ( MW = 81.39 ) 1 mol = 81.39 g

Total wt = g CuO + g ZnO = 79.55 + 81.39 = 160.94 g

weight fraction of CuO = 79.55 / 160.94 = 0.49428

weight fraction of ZnO = 81.39 / 160.94 = 0.50572

*Basis* 10 g of CuO/ZnO

Therefore weight of CuO = 0.49428 × 10 = 4.9428 g

weight of ZnO = 0.50572 × 10 = 5.0572 g

CuO mole used = 4.9428 × 79.55 = 0.0621 mole

ZnO mole used = 5.0572 × 81.39 = 0.0621 mole

1 mole CuO = 1 mole Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O

1 mole ZnO = 1 mole Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O

Therefore,

weight of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O ( MW = 232.59, Assay = 0.99 )

= 0.0621 × 232.59 / 0.99 = 14.5979 g

weight of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O ( MW = 297.47, Assay = 0.98 )

= 0.0621 × 297.47 / 0.98 = 18.8605 g

Total mole used = 0.0621 + 0.0621 = 0.1243 mol

The use of Na<sub>2</sub>CO<sub>3</sub> ( MW = 105.99, Assay = 1.00 )

= 0.1243 × 105.99 / 1.00 = 13.1714 g

For pH control in range 8.3 - 8.5, Na<sub>2</sub>CO<sub>3</sub> must used > 13.1714 g

Therefore, from the experiment, weight of Na<sub>2</sub>CO<sub>3</sub> ~ 20 g

#### 2<sup>nd</sup> step: Impregnation

*Basis* 3.4500 g of CuO/ZnO ( mol ratio Cu/Zn = 1, MW = 160.94 )

Mol ratio of Cu/ZnO = 1, MW = 144.94

So, weight of Cu/ZnO =  $3.4500 \times 144.94 / 160.94 = 3.1070$  g

Catalyst :1%wt Zr-Cu/ZnO

So, Zr weight ratio =  $1 / 99 = 0.0101$

Therefore Zr ( MW = 91.22 ) =  $3.1070 \times 144.94 / 91.22 = 0.000344$  mole

$\text{N}_2\text{O}_7\text{Zr}$  1 mole = Zr 1 mole

Therefore,

weight of  $\text{N}_2\text{O}_7\text{Zr}$  ( MW = 231.23 )

=  $0.000344 \times 231.23 = \underline{0.0796}$  g



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## Appendix B

### Examined Calculation of Reaction Products

Data from the use of catalyst: 1% wt Zr-Cu/ZnO,  $T_{\text{reaction}} = 200\text{ }^{\circ}\text{C}$

Determination of CO, CO<sub>2</sub>, and total carbon conversion.

**Table B-1 CO/Ar and CO<sub>2</sub>/Ar of reactant gas**

time	Area					
	H <sub>2</sub>	Ar	CO	CO <sub>2</sub>	CO/Ar	CO <sub>2</sub> /Ar
1	2226	5977	56894	9943	9.52	1.66
2	2229	5886	57002	10400	9.68	1.77
3	2150	5790	56878	10095	9.82	1.74
				<b>AVG</b>	9.68	1.72

H<sub>2</sub>/Ar/CO/CO<sub>2</sub> = 61.5/3/30.5/5

**Table B-2 Determination of CO, CO<sub>2</sub>, and total carbon conversion of gas products**

Hr.	Area						%Conversion		
	H <sub>2</sub>	Ar	CO	CO <sub>2</sub>	CO/Ar	CO <sub>2</sub> /Ar	CO	CO <sub>2</sub>	Total carbon
0	2192	6361	57470	7160	9.03	1.13	6.62	34.74	10.58
1	2170	6136	56367	7888	9.19	1.29	5.05	25.45	7.92
2	2133	5827	50726	10657	8.71	1.83	10.02	-6.05	7.76
3	2278	5889	43929	13961	7.46	2.37	22.90	-37.47	14.40
4	2381	6204	37108	17778	5.98	2.87	38.18	-66.17	23.48
5	2329	6548	33917	21424	5.18	3.27	46.46	-89.72	27.28
6	2257	7265	32479	23625	4.47	3.25	53.79	-88.56	33.74
7	2337	8181	32984	26126	4.03	3.19	58.33	-85.17	38.12
8	2252	8825	33855	27484	3.84	3.11	60.35	-80.59	40.50
9	2182	9633	35524	28429	3.69	2.95	61.88	-71.13	43.15
10	2182	10377	36946	29045	3.56	2.80	63.20	-62.29	45.53
11	2186	10921	38143	29721	3.49	2.72	63.90	-57.80	46.76
12	2180	11145	38863	30064	3.49	2.70	63.96	-56.41	47.01
13	2116	11470	39712	30248	3.46	2.64	64.21	-52.92	47.72
14	2095	11515	40379	30803	3.51	2.68	63.76	-55.11	47.01
15	2075	11790	41243	29764	3.50	2.52	63.84	-46.38	48.32
16	2057	11622	41440	29812	3.57	2.57	63.15	-48.74	47.39
17	2153	11475	41897	29857	3.65	2.60	62.26	-50.87	46.33
18	2124	11408	42715	29018	3.74	2.54	61.30	-47.50	45.98
19	2185	11231	42960	29200	3.83	2.60	60.46	-50.76	44.80
20	2097	11125	43498	27887	3.91	2.51	59.59	-45.35	44.81

Determination of selectivity and yield.

**Table B-3 Determination of selectivity and yield of liquid products**

Liquid	Reactor		ColdTrap	
		Area		Area
C <sub>2</sub> H <sub>5</sub> OH (g)	0.158		0.158	
C <sub>2</sub> H <sub>5</sub> OH (C-mmol)	6.86	1024586	6.86	4749341.1
CH <sub>3</sub> OH (C-mmol)	295.49	44139458	0.00	
HCOOC <sub>3</sub> H <sub>7</sub> (C-mmol)	0.694735	415105.6	1.82	1258404.1
		Selectivity		Yield
CH <sub>3</sub> OH (%)		99.16		44.43
HCOOC <sub>3</sub> H <sub>7</sub> (%)		0.84		0.38

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**Table B-4 Conversions and conditions of semi-continuous<sup>a</sup> methanol synthesis**

Catalyst	Catalyst mole ratio	Catalyst salt precursor	Solvent	Conversion (%)		
				CO	CO <sub>2</sub>	Total carbon
<i>T<sub>reaction</sub> = 170°C</i>						
Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	39.19	-3.26	33.22
Cu/ZnO	Cu/Zn: 1/2	nitrate	2-propanol	31.36	1.04	27.09
Cu/ZnO	Cu/Zn: 2/1	nitrate	2-propanol	39.48	-3.15	33.47
Cu/Cr <sub>2</sub> O <sub>3</sub>	Cu/Cr: 1/1	nitrate	2-propanol	12.36	-32.57	6.03
Cu	Cu: 1	nitrate	2-propanol	12.78	-48.74	4.12
Cu/ZnO	Cu/Zn: 1/1	chloride	2-propanol	38.97	-1.01	33.34
Cu/ZnO	Cu/Zn: 1/1	acetate	2-propanol	45.80	1.28	39.53
Cu/ZnO	Cu/Zn: 1/1	nitrate	1-hexanol	27.37	17.37	25.97
Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol/ 1-hexanol :1/1 <sup>b</sup>	26.40	-8.28	21.52
Cu/ZnO	Cu/Zn: 1/1	nitrate	ethylene glycol	9.68	-9.42	6.99
Cu/ZnO	Cu/Zn: 1/1	nitrate	glycerol	15.36	-90.53	0.45
0.5% wt Zr/Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	44.07	-16.84	35.49
1.0% wt Zr/Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	30.42	-4.45	25.51
0.5% wt Zr-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	39.98	-2.44	34.01
1.0% wt Zr-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	34.74	-5.87	29.02
0.1% wt Pd-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	31.72	-11.74	25.60
0.5% wt Pd-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	39.86	10.13	35.67
1.0% wt Pd-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	36.27	1.35	31.35
<i>T<sub>reaction</sub> = 200°C</i>						
Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	63.17	-28.99	50.19
Cu/ZnO	Cu/Zn: 1/2	nitrate	2-propanol	52.78	-31.87	40.86
Cu/ZnO	Cu/Zn: 2/1	nitrate	2-propanol	55.25	-31.29	43.06
Cu/Cr <sub>2</sub> O <sub>3</sub>	Cu/Cr: 1/1	nitrate	2-propanol	7.34	13.78	8.25
Cu	Cu: 1	nitrate	2-propanol	4.59	5.00	4.65
Cu/ZnO	Cu/Zn: 1/1	nitrate	1-hexanol	57.05	-9.06	47.74
0.5% wt Zr/Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	62.79	-25.25	50.39
1.0% wt Zr/Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	56.70	-28.79	44.66
0.5% wt Zr-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	59.59	-45.35	44.81
1.0% wt Zr-Cu/ZnO	Cu/Zn: 1/1	nitrate	2-propanol	56.71	-33.36	44.02

<sup>a</sup>Semi-continuous conditions: H<sub>2</sub>/Ar/CO/CO<sub>2</sub> = 61.5/3/30.5/5; reaction time = 20 h; pressure = 50 bar; catalyst = 3 g; solvent = 25 ml; flow rate = 20 ml/min.

<sup>b</sup>by volume.



## VITA

Miss Chanakarn Puwapitayanon was born on July 15, 1983 in Chiangrai, Thailand. She graduated with a Bachelor's degree of Engineering, majoring in Petrochemicals and Polymeric Materials, Faculty of Engineering and Industrial Technology, Silpakorn University in 2005. She has continued her study in Master's degree, majoring in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2005 and finished her study in 2008.

### **Presentation Experience**

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Oral presentation from The 6<sup>th</sup> PSU Engineering Conference (PEC-6) which organized by Faculty of Engineering, Prince of Songkla University in the topic of "Metal Oxide Catalysts for Methanol Synthesis from CO<sub>2</sub>-rich Syngas".

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