

ผลของวิธีการเตรียมต่อสมบัติของตัวเร่งปฏิกิริยา Cu/ZnO ในปฏิกิริยาสตีมีรีฟอร์มมิงของเมทานอล



นายสิราวิชญ์ โชติทรัพย์ยचना

## สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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EFFECT OF PREPARATION METHOD ON THE PROPERTIES OF Cu/ZnO CATALYST  
IN STEAM REFORMING OF METHANOL



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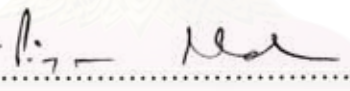
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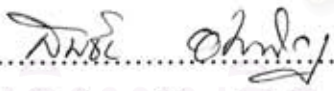
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สิราวิชญ์ โชติทรัพย์ชานา: ผลของวิธีการเตรียมต่อคุณสมบัติของตัวเร่งปฏิกิริยา Cu/ZnO ในปฏิกิริยาสตีมีรีฟอร์มมิ่งของเมทานอล (EFFECT OF PREPARATION METHOD ON THE PROPERTIES OF Cu/ZnO CATALYST IN STEAM REFORMING OF METHANOL) อ.ที่ปรึกษา: ศ. ดร. ปิยะสาร ประเสริฐธรรม, อ.ที่ปรึกษาฯร่วม: รศ.ดร. สมชัย อัครทิวา , 90 หน้า.

งานวิจัยนี้ มุ่งเน้นที่จะศึกษาถึง การสังเคราะห์ตัวเร่งปฏิกิริยาและวิเคราะห์คุณลักษณะของ Cu/ZnO โดยเปรียบเทียบการสังเคราะห์จาก 3 วิธี ได้แก่ วิธีโซลเจล วิธีตกตะกอนร่วม และ วิธีตกตะกอนเนื้อเดียว และศึกษาอัตราส่วนของ Cu ต่อ Zn เท่ากับ 70/30, 50/50 และ 30/70 วิธีโซลเจล ใช้คอปเปอร์อะซิเตด ซิงก์อะซิเตด และ เมทานอลเป็นสารตั้งต้น วิธีตกตะกอนร่วมใช้สารละลายผสมระหว่างคอปเปอร์ไนเตรดกับซิงก์ไนเตรดและ โซเดียมคาร์บอเนต ส่วนวิธีสุดท้าย วิธีตกตะกอนเนื้อเดียว ใช้ยูเรียแทนโซเดียมคาร์บอเนต พบว่าวิธีที่ดีที่สุดคือ วิธีตกตะกอนเนื้อเดียวจากการทดสอบคุณสมบัติทางความว่องไวและค่าการเลือก จากปฏิกิริยาสตีมีรีฟอร์มมิ่งของเมทานอล หลังจากนั้นได้ศึกษาผลของบรรยากาศต่างๆ ในการเผาตัวเร่งปฏิกิริยา Cu/ZnO โดยนำตัวเร่งปฏิกิริยาไปเผาในบรรยากาศต่างๆ ได้แก่ ก๊าซไนโตรเจน ก๊าซออกซิเจน ก๊าซไฮโดรเจน และอากาศ พบว่า ตัวเร่งปฏิกิริยาที่เผาโดยก๊าซไฮโดรเจน มีความว่องไวและค่าการเลือกดีที่สุด และนำตัวเร่งปฏิกิริยาไปวัดคุณลักษณะทางกายภาพและทางเคมี จากเครื่องมือ XRD, BET, N<sub>2</sub>O chemisorption, TG/DTA, TEM และ FT-IR

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ภาควิชา.....วิศวกรรมเคมี  
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ลายมือชื่อนิสิต.....  
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KEY WORD: Cu/ZnO, STEAM REFORMING, HOMOGENEOUS PRECIPITATION, SOL-GEL TECHNIQUE, CO-PRECIPITATION.

SIRAVIT CHODSUBYACHANA: EFFECT OF PREPARATION METHOD ON THE PROPERTIES OF Cu/ZnO CATALYST IN STEAM REFORMING OF METHANOL. THESIS ADVISOR: PROF.PIYASAN PRASERTHDAM, Dr.Ing. THESIS CO-ADVISOR: ASSOC. PROF.SOMCHAI AKARATIWA, D.ENG, 90 pp.

Several methods (sol-gel method, co-precipitation, homogeneous-precipitation) have been comparatively examined for the preparation of binary Cu/ZnO-based catalysts with Cu/Zn molar ratios in 70/30, 50/50 and 30/70 copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) and zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and ethanol were used as precursor for preparation of Cu/ZnO catalyst by sol-gel method. For co-precipitation method were prepared by the addition rate of a mixed copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) and zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) solution with a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution. For homogeneous precipitation method were prepared by urea instead of  $\text{Na}_2\text{CO}_3$  solution. All Cu/ZnO catalysts were applied for the catalytic production of hydrogen by steam reforming of methanol (SRM). Homogeneous precipitation method is preferable for this reaction. Then, study effect of calcination conditions. Cu/ZnO catalysts are calcined by various atmospheres. Gases were used as atmosphere as follows: nitrogen, oxygen, air and hydrogen. Cu/ZnO catalyst was calcined by hydrogen, is the higher activity than the other atmospheres. Physical and chemical properties of Cu/ZnO catalyst were characterized by various techniques including X-ray diffraction (XRD), BET surface area,  $\text{N}_2\text{O}$  chemisorption, Thermal gravimetric and differential thermal analysis (TG/DTA), Transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR).

Department ..... Chemical Engineering.....

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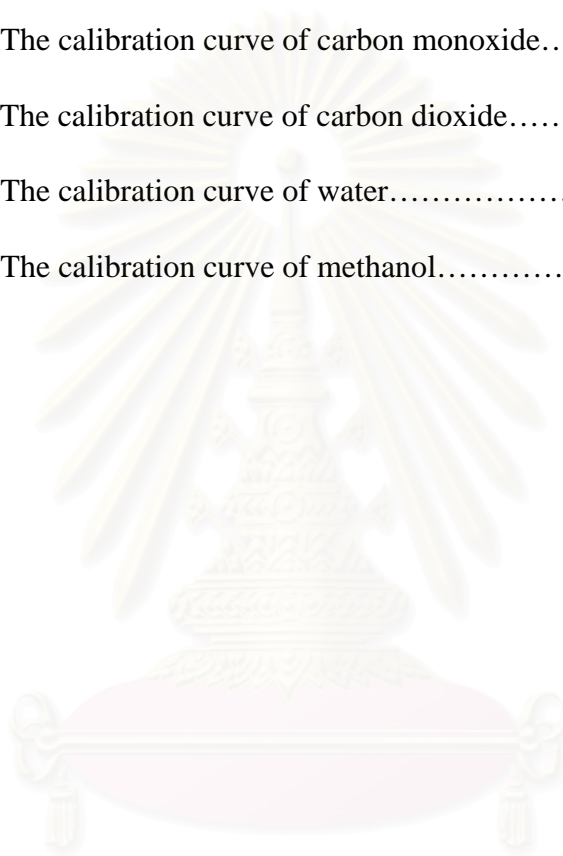


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# CHAPTER I

## INTRODUCTION

At the present, the combustion of hydrocarbon fuels of automobiles is a challenging task. Because large source of the air pollution presence of CO, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> and VOCs. Hydrogen is prophesied to become a major source of energy in the future which can be converted to electricity in proton exchange membrane fuel cells. Fuel cells produce energy at high efficiencies and generate only heat and water as emissions. Therefore, we have used fuel cells for automobiles to reduce air pollutants and abate green house effect. However, hydrogen as an energy source is difficult in storage and distribution. One solution of these problems, hydrogen generate from a suitable liquid fuel of high energy density. The advantages of high energy density are easy availability, safe handing and comfortable storage. One of the most promising sources of hydrogen for fuel cells is methanol (Matter et al. 2004). Consequently, four different processes generate hydrogen as follow: methanol decomposition(Cheng et al. 1998; Matsumura et al. 2000), partial oxidation (Cubeiro and Fierro 1998), steam reforming of methanol (Breen and Ross 1999), and water gas shift (Wainwright and Trimm 1995). Unfortunately, the methanol decomposition, the partial oxidation and the water gas shift produce considerable amount of CO as a by product. So, the steam reforming of methanol can produce the highest hydrogen concentration and low concentration CO, the reformed gas in a fuel cell, even a trace of CO deteriorates the Pt electrode, hence minimizing the risk for coke. Thus, it is likely that steam reforming of methanol is the most suitable process to produce hydrogen from on-board methanol for automobile power source.

A large variety of catalysts for the hydrogen production in fuel cell applications have been reported in the literature (Agrell et al. 2003; Lindstrom et al. 2002; Peppley et al. 1999). Among these, the majority interestingly use Cu/ZnO-based catalyst which is one of the most common metal oxides recognized in various industries (Saito and Murata 2005; Spencer 1999). Due to its good physical and chemical properties, such as catalytic activity, low concentration CO (Shen and Song

2002) and high selectivity, Cu/ZnO has been used in many fields of application the use as catalyst, is used for low pressure methanol synthesis and for the water gas shift.

Cu/ZnO catalyst can be synthesized by different methods, such as co-precipitation (Li and Inui 1996), ion exchange, impregnation (El-Shobaky et al. 1999), gel-oxalate co-precipitation, etc.

In this research, study the effect of preparation from several methods as follow: sol-gel method, homogeneous precipitation and co-precipitation. Compare all of the preparation of binary Cu/ZnO catalysts for the catalytic production of the highest hydrogen by steam reforming of methanol. We have expected diverse methods which enhance copper dispersion on the catalyst surface and improve the catalytic performance about selectivity and activity. The purpose of this work is to study on Cu metal species and ZnO because there is not enough concentration on them, yet.

Last, it is intended to investigate the calcination conditions of these Cu/ZnO catalysts. They are synthesized via homogeneous precipitation, co-precipitation and sol-gel technique.

The objectives of this research are listed as following:

1. To study the effect preparation conditions on chemical and physical properties of Cu/ZnO catalyst in methanol steam reforming for hydrogen production.
2. To investigate the calcination in various atmospheres, using Cu/ZnO as catalyst. Effects of calcinations on activity are also subject to study in this research.

The present thesis is arranged as follows:

Chapter II explains the basic theory about fuel cell and steam reforming reaction such as the general properties of fuel cell and steam reforming, various preparation methods to obtain the Cu/ZnO catalyst.

Chapter III shows experimental systems and procedures for the preparation of Cu/ZnO catalyst by homogeneous precipitation (hp), co-precipitation (cp) and sol-gel technique.

Chapter IV presents the experimental results and discussion

In the last chapter, the overall conclusions of this research and recommendations for the future work are given.



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## CHAPTER II

### LITERATURE REVIEWS

The hydrogen may be supplied directly as a gas from a source outside the system or it may be supplied indirectly, as a hydrogen-rich which is converted to a suitable form in a sub-system associated with fuel cell system. One such indirect source of particular interest is the steam reforming of methanol.

(*Amphlett and Mann 1981*). They showed that in order to get a gas rich in hydrogen and low in carbon monoxide, a poison for many fuel-cell catalyst, temperature about 200°C are required.

(*Amphlett and Mann 1988*). The rate of catalytic decomposition of the methanol in the presence of steam had been studied using a commercial CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>, low temperature shift catalyst from 150-270°C at one atmosphere pressure in a fixed bed reactor. Mole ratio of steam to methanol of 0.66, 1.00 and 1.5 and catalyst mass to molar feed rate ratios of 25 to 1025 kg•s•mol<sup>-1</sup> were utilized. The data were correlated and equations developed to successfully predict methanol conversion and carbon monoxide concentrations in the product gas stream over the temperature range studied

(*Akaratiwa et al. 1994*) Steam reforming of methanol over Cu/ZnO catalysts was investigated. Cu/ZnO catalysts were prepared by conventional co-precipitation method in various molar fraction of Cu ranging from 0 to 100 mole%Cu. The result showed that Cu/ZnO composed of 50-70 mole%Cu exhibited higher activity than other compositions. It also showed that 100% selectivity to carbon dioxide and hydrogen. The dispersion degree of active Cu particle in zinc oxide was a crucial factor contributing to the activity of the reaction. The deactivation of the catalysts was not observed under the test conditions and conversion of methanol increased with temperature. The addition rate of a mixed Cu(NO<sub>3</sub>)<sub>2</sub>/Zn(NO<sub>3</sub>)<sub>2</sub> solution to NaHCO<sub>3</sub> solution in catalyst preparation process also showed some effect on the performance



of catalyst. With a steam/methanol molar feed ratio higher than stoichiometric value, the excess water also can enhance the activity.

(*Jeong et al. 2006*) Hydrogen production by steam reforming of methanol is studied over Cu/Zn-based catalysts (Cu/ZnO, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>). Cu/Zn-based catalysts are derived from hydrotalcite-like precursors prepared by a co-precipitation method. ZrO<sub>2</sub> added to the Cu/Zn-based catalyst enhances copper dispersion on the catalyst surface. Among the catalysts tested, Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> exhibits the highest methanol conversion and the lowest CO concentration in the outlet gas.

According to these researchs, it has explained about Cu/ZnO catalyst, CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst. All of the catalysts are prepared by co-precipitation and precipitation. Next, the research is talked about Zinc oxide (ZnO) which was prepared from sol-gel method.

(*Armelaio et al. 2001*). To achieve a good control over film composition and morphology the sol-gel route was used. The sol-gel synthesis of ZnO nanocrystal embedded in silica has been faced by the gel-derived binary system ZnO-SiO<sub>2</sub>. The dip-coating procedure from alcoholic solution containing tetraethoxysilane (TEOS) and zinc acetate was adopted. Zinc oxide nanograins have been generated in silica by hydrolysis of TEOS and zinc acetate subsequent thermal annealing of the coatings.

(*M.K.Hossain et al. 2003*) Zinc oxide is very useful material for solid state. Zinc oxide is prepared by Sol-gel method. The complete process of synthesis can be divided into three major steps: 1). precursor preparation for zinc acetate solution, 2). colloidal nanoparticles formation by the hydrolysis of the precursor and 3). Formation of nanometric wires and belts from colloidal nanoparticles under controlled conditions. Zinc oxide prepared from zinc acetate sol-gel route is strongly dependent on the temperature, time, pH and concentration of the solution and natural of the catalyst used in hydrolysis step.

(A.Kaddouri *et al.* 2003) Zinc oxide (ZnO) catalysts for ethanol steam reforming were studied so as to elucidate the effect on functionality of the preparation method and of reaction conditions. Total alcohol conversion was obtained at relatively low temperature (450°C) with 78% hydrogen selectivity. The nature of the precursor influences to a significant extent product distribution and stability. The material obtained from zinc acetate dissolved in propionic acid was more selective and less prone to deactivation than the sample prepared from zinc carbonate hydroxide.

Next, we would present about Cu/ZnO and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>, prepared from homogeneous precipitation.

(Shishido *et al.* 2004). Cu/ZnO and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst were prepared by homogeneous precipitation (HP) using urea hydrolysis and were applied for hydrogen production by steam reforming of methanol. The catalysts showed higher activities than those prepared by co-precipitation (CP). The catalysts are good performance due to highly dispersed Cu metal species and to high accessibility of the Cu metal species to methanol and steam.

(Shishido *et al.* 2004). Cu/ZnO and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts with varying Cu/Zn ratio have been prepared by the homogeneous precipitation (hp) method using urea hydrolysis. Steam reforming and oxidative steam reforming of methanol were performed using the hp-Cu/Zn-based catalysts for catalytic production of hydrogen. In both cases, the catalytic activity was well correlated with the surface area of Cu metal and the maximum activity was obtained on the hp-Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst with the Cu/Zn ratio of 1/1. Although a large amount of Cu<sup>+</sup> was detected on the surface of the Cu/Zn-based catalysts after the reduction at 260°C, no obvious correlation was observed between the activity and the surface amount of Cu<sup>+</sup>. The hp-Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst showed a high and stable activity not only for steam reforming but also for oxidative steam reforming of methanol and the latter reaction effectively produced H<sub>2</sub> with a low CO selectivity at a low temperature around 200°C.

## CHAPTER III

### THEORY

#### 3.1 Fuel cell

A fuel cell is an electrochemical energy conversion device similar to a battery, differing in that it is designed for continuous replenishment of the reactants consumed; .etc. it produces electricity from an external supply of fuel and oxygen as opposed to the limited internal energy storage capacity of a battery. Additionally, while the electrodes within a battery react and change as a battery is charged or discharged, a fuel cell's electrodes are catalytic and relatively stable.

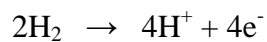
Typical reactants used in a fuel cell are hydrogen on the anode side and oxygen on the cathode side (a hydrogen cell). Usually, reactants flow in and reaction products flow out. Virtually continuous long-term operation is feasible as long as these flows are maintained.

In the archetypal example of a hydrogen / oxygen proton-exchange membrane (or “polymer electrolyte”) fuel cell (PEMFC) (Iojoiu et al. 2006), a proton-conducting polymer membrane, (the electrolyte), separates the anode and cathode sides.

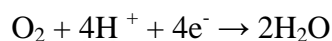
On the anode side, hydrogen diffuses to the anode catalyst where it dissociates into protons and electrons. The protons are conducted through the membrane to the cathode, but the electrons are forced to travel in an external circuit (supplying power) because the membrane is electrically insulating. On the cathode catalyst, oxygen molecules react with the electrons (which have traveled through the external circuit) and protons to form water. In this example, the only product is water vapor and /or liquid water.

Chemistry of a fuel cell (Lafrent et al. 2007).

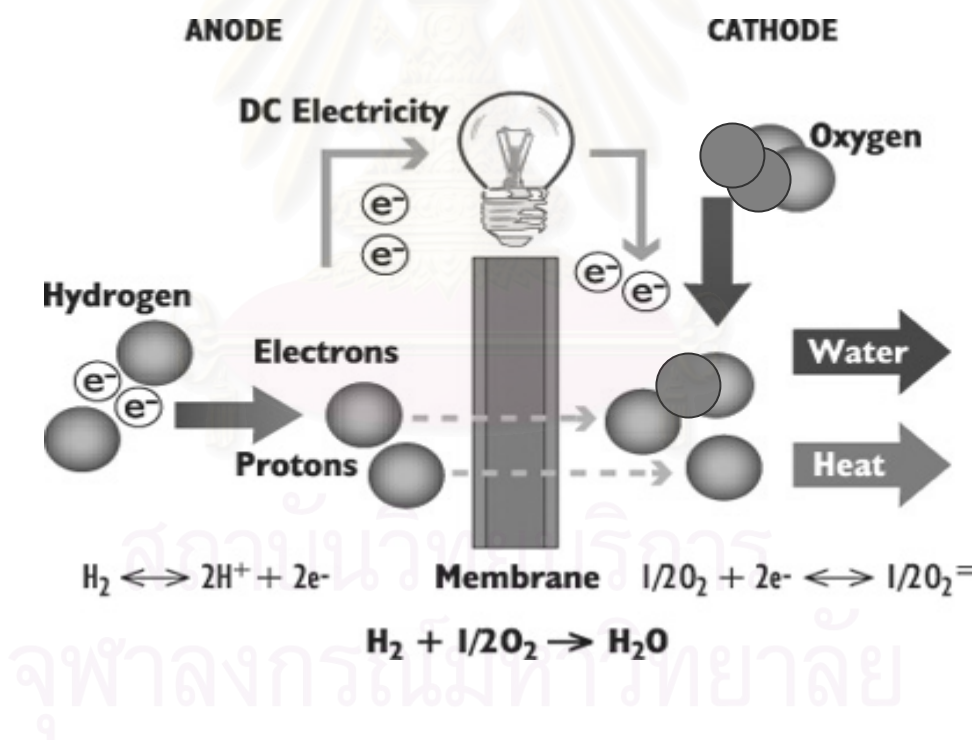
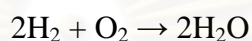
Anode side:



Cathode side:



Net reaction



**Figure 3.1** The chemical reaction of the fuel cell

In addition to pure hydrogen, there are hydrogen-carrying fuels cell for fuel cells, including diesel, methanol and chemical hybrids, the waste product with these types of fuels is carbon dioxide.

The last section, a fuel cell uses oxygen and hydrogen to produce electricity. The oxygen required for a fuel cell comes from the air. In fact, in the PEM fuel cell, ordinary air is pumped into the cathode. The hydrogen is not so readily available. However, hydrogen has some limitations that make it impractical for use in most applications. For instance, you do not have a hydrogen pipeline coming to your house, and you cannot pull up to a hydrogen pump at your local gas station.

Hydrogen is difficult to store and distribute, so it would be much more convenient if fuel cells could use fuels that are more readily available. This problem is addressed by a device called a reformer. A reformer turns hydrocarbon or alcohol fuels into hydrogen, which is then fed to the fuel cell. Unfortunately, reformers are not perfect. They generate heat and produce other gases besides hydrogen. They use various devices to try to clean up the hydrogen, but even so the hydrogen that comes out of them is not pure, and this lowers the efficiency of the fuel cell.

Some of the more promising fuels are natural gas, propane and methanol. Many people have natural-gas lines or propane tanks at their house already, so these fuels are the most likely to be used for home fuel cells. Methanol is a liquid fuel that has similar properties to gasoline. It is just as easy to transport and distribute, so methanol may be a likely candidate to power fuel-cell cars.

Pollution reduction is one of the primary goals of the fuel cell. By comparing a fuel-cell- powered car to a gasoline-engine-powered car and a battery-powered car, you can see how fuel cells might improve the efficiency of cars today.

Since all three type of cars have many of the same components (tires, transmissions, etc.), we will ignore that part of the car and compare efficiencies up to the point where mechanical power is generated. Let's start with the fuel-cell car. (All of these efficiencies are approximations, but they should be close enough to make a rough comparison.)

If the fuel cell is powered with pure hydrogen, it has the potential to be up to 80-percent efficient. That is, it converts 80 percents of the energy content of the



hydrogen into electrical energy. But, as we learned in the previous section, hydrogen is difficult to store in a car. When we added a reformer to convert methanol to hydrogen, the overall efficiency drops to about 30 to 40 percents.

Fuel cell still needs to convert the electrical energy into mechanical work. This is accomplished by the motor/inverter is about 80 percents. So we have 30 to 40 percents efficiency at converting methanol to electricity, and 80-percents efficiency converting electricity to mechanical power. That gives an overall efficiency of about 2 to 32 percents.

### 3.2 Sol-gel process

Sol-gel process involves the formation of sol following by that of gel. Sol, which is suspension solid in liquid with particle size ranging from 1 nm to 1  $\mu\text{m}$ , can be obtained by the hydrolysis and partial condensation of a precursor such as an inorganic salt or a metal alkoxide. Further condensation of sol particles into a three-dimensional network produces gel, which is a diphasic material with a solids encapsulating liquid or solvent. Alternatively, gel can be produced by destabilizing the solution of preformed sols. In either case, the materials are referred as aquasol (or aquagel) if water is used as a solvent, and alcosol (or alcogel) if alcohol is used. The encapsulated liquid can be removed from gel by either evaporative drying or drying with supercritical extraction (supercritical drying for short).

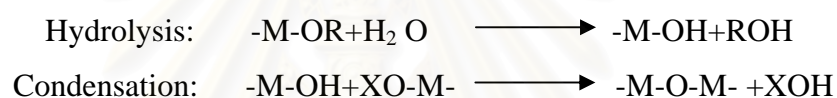
The single most important characteristic of the sol-gel preparation of inorganic materials is its ease of control that translates into the following advantages:

- (i) the ability to maintain high purity (because of purity of starting materials);
- (ii) the ability to change physical characteristics such as pore size distribution and pore volume;
- (iii) the ability to vary compositional homogeneity at a molecular level;
- (iv) the ability to prepare samples at low temperatures;
- (v) the ability to introduce several components in a single step;

(vi) the ability to produce samples in different physical forms;

The four key steps in converting a precursor to a particular product form via sol-gel preparation are: formation of gel, aging of gel, removal of solvent, and heat treatment. The versatility of this preparative approach lies in the number of parameters that can be manipulated in each of these steps.

The precursor in sol-gel preparation can either be a metal salt/alkoxide dissolved in an appropriate solvent or a stable colloidal suspension of preformed sols. Metal alkoxides have been the most extensively used because they are commercially available in high purity and their solution chemistry has been documented. At its simplest level, sol-gel chemistry with metal alkoxides can be described in terms of two classes of reactions:



where X can either be H or R (an alkyl group).

Such a description oversimplifies the overall process because it does not correctly represent the molecular formulas of intermediates and end products, nor does it depict the simultaneous occurrence of the two reactions. However, this oversimplification captures the key phenomenological idea that a three-dimensional gel network comes from the condensation of partially hydrolyzed species. Any parameters that affect either or both of these reactions are thus likely to impact on the properties of the product. In fact, the important variables are the reaction rates of hydrolysis and condensation.

Because hydrolysis and condensation are both nucleophilic displacement reactions, the reactivity of metal alkoxides depends on the positive partial charge of the metal atom and its coordination number. For example, TEOS, which contains small positive partial charge on silicon, is the least reactive among the common alkoxides. In general, the longer and bulkier the alkoxide group attached to a particular metal atom, the less reactive that precursor is in hydrolysis and

condensation. Changing the type of precursor and/or its concentration are thus effective means of controlling the reaction rates.

The amount of water used in sol-gel preparation and the rate by which it is added also influence gel characteristics. The former is usually expressed in terms of the hydrolysis ratio  $h$ , defined as the moles of water per mole of metal alkoxide,  $M(OR)_m$ . There are three specific regions of interest:

- (i)  $h < 1$ : An infinite network seldom forms due to the low functionality of the precursor towards condensation. Because there are few M-OH groups for cross-linking, gelation or precipitation cannot occur when there is no local excess of water.
- (ii)  $1 < h < m$ : Polymeric gels can form.
- (iii)  $h < m$ : Cross-linked polymers, particulate gels, or precipitates can form when an excess of water is added to the alkoxides.

For a given amount of water, another level of control comes from the rate of addition. Common approaches to slowly add water are: using a micropipette, absorbing moisture from a controlled humidity environment, and generating water in the solution with another chemical reaction.

Two other important sol-gel parameters are temperature and type of solvent. Both hot and cold plates are commercially available, which can be used to increase and decrease the reaction rate, respectively. Varying the temperature is most effective when it can alter the relative rate of competing reactions. Solvent can change the nature of an alkoxide through solvent exchange or can affect the condensation reaction directly. It is also possible to prepare gel without solvent as long as another mean, such as ultrasound irradiation, is used to homogenize an otherwise immiscible alkoxide/water mixture.

Using preformed sols instead of metal alkoxides as precursors is an attractive alternative in sol-gel preparation because recent advances in inorganic colloidal dispersions allow some control over the characteristic of the starting sols. Colloidal

suspension of sol particles is often stabilized (i.e. prevented from flocculation) by pH adjustment. Thus, pH of the solution, which can be changed by the addition of either acid or base, is the single most important parameter in obtaining gel from preformed sols. Other parameters that influence gel quality are size and concentration of the starting sol particles.

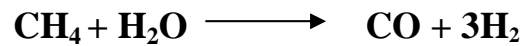
For any of the sol-gel parameters discussed so far, its effect on gel properties can often be observed by an experimental parameter known as gel time. Gel time is defined as the time that the solution undergoes rapid rise in viscosity which is corresponding to the transition from viscous fluid to elastic gel. At the gel point, the solid phase forms a continuous structure that reflects the formation and branching of particles under specific growth condition. This particular phase is important because it is the genesis of structural evolution that takes place in all subsequent processing steps (Ertl et al. 1999). The process starts with the mixing titanium alkoxide with alcohol. Acid aqueous solution is subsequently added to the mixture (Jung 1999). This technique can be adapted by using ultrasonication to aid dispersion, which can result in titania with higher surface area and better thermal stability than titania prepared by using stirring method (Awati et al. 2003). The average crystal size of titania synthesized by this method has been reported to be in the range of 4 – 8 nm with BET surface area in the range of 91-120 m<sup>2</sup>/g, depending on calcination temperature. However the limit of this method is that strong reactivity of alkoxide toward water often results in uncontrolled precipitation.

### **3.3 Steam reforming**

Steam reforming or hydrogen reforming, is a method of producing hydrogen from hydrocarbons. On an industrial scale, it is the dominant method for producing hydrogen. Small-scale steam reforming units are currently subject to scientific research, as way to provide hydrogen to fuel cells.

Steam reforming of natural gas, sometimes referred to as steam methane reforming (Matsumura and Nakamori 2004) is the most common method of producing commercial bulk hydrogen as well as the hydrogen used in the industrial

synthesis of ammonia. It is also the least expensive method. At high temperatures (700–1100°C) and in the presence of a metal-based catalyst, steam reacts with methane to yield carbon monoxide and hydrogen.



Steam reforming of liquid hydrocarbons is seen as a potential way to provide fuel for fuel cells. The basic idea is that for example a methanol tank and a steam reforming unit would replace the bulky pressurized hydrogen tanks that would otherwise be necessary. This might mitigate the distribution problems associated with hydrogen vehicles.

This approach to power generation yields several benefits:

- Steam reforming can utilize CO<sub>2</sub>-neutral liquid hydrocarbon fuels, such as bio-ethanol and bio-diesel, to produce green hydrogen from fuels that can be used during a transition from fossil-based fuels.
- Small scale reformers could be distributed within our current hydrocarbon infrastructure at a relatively low cost, to convert gas stations into hydrogen stations.
- When combined with a fuel cell, such refueling stations could provide backup power to neighborhoods in addition to providing hydrogen for vehicle refueling.

There are also several challenges associated with this technology:

- The reforming reaction takes place at high temperatures, making it slow to start up and requiring costly high temperature materials.
- Sulphur compounds present in the fuel poison certain catalysts, making it difficult to run this type of system from ordinary gasoline. Some new technologies have overcome this challenge, however, with sulfur-tolerant catalyst.



- The carbon monoxide (CO) produced by the reactor poisons the fuel cell, making it necessary to include complex CO-removal systems.

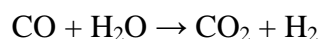
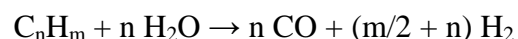
- The thermodynamic efficiency of the process is between 70 and 85% (LHV basis) depending on the purity of the hydrogen product. However, despite these energy losses, the hydrogen product can then be used in an internal combustion engine, typically by a factor of two or more.

- The biggest problem for reformer based systems remains the fuel cell itself, in terms of both cost and durability. The catalyst used in the common polymer-electrolyte-membrane fuel cell, the device most likely to be used in transportation roles, is very sensitive to any leftover carbon monoxide. The membrane is poisoned by the carbon monoxide and its performance degrades.

Even with these problems, the reformer-fuel-cell system is still being researched as a system that will power cars, homes and businesses in the future. An ideal system would be capable of running on existing fuels, such as natural gas or gasoline or diesel, but in the long run a renewable liquid fuel like bio-ethanol or bio-diesel may be preferable. The overall cost of making, transporting and storing the hydrogen fuel is the key issue.

For most hydrocarbons, including methane and temperature in excess of 700°C are necessary. Methanol, however, can be converted at significantly lower temperature (around 350°C).

The chemical reactions that take place:



The produced carbon monoxide can combine with more steam to produce further hydrogen via the water gas shift reaction. The process is endothermic (consumes heat).

The thermodynamic efficiency is more like 30%, not 70-85% as stated. The higher value probably does not take the energy of the steam used, the endothermic heat of reaction and the separation and treatment of the products. Also you have to notice that the CO produced in the first reaction contains a big part of energy of the output: 1 mol of hydrogen contains 68 kcal, 1 mol of CO 67 kcal.

Reaction for product hydrogen:

Steam reforming of methanol:



Decomposition methanol: (Kapoor et al. 2001)



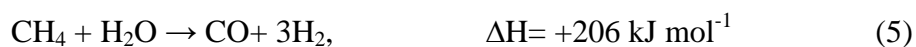
Partial oxidation: (Lindstrom and Pettersson 2002)



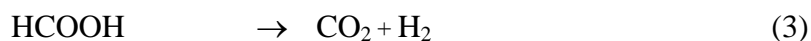
Water gas shift:



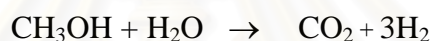
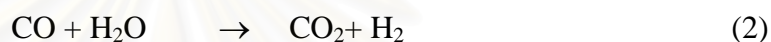
Reforming of methane: (Souza and Schmal 2005)



Mechanism of steam reforming of methanol (Takahashi et al. 1982)



Mechanism of steam reforming of methanol (Jiang et al. 1993)



### 3.4 Preparation of catalyst

#### 3.4.1 Preparation procedures

(i). Multiples precursor contain all the components of the catalysts (Cu and Zn) in suitable proportion, in a strongly dispersed form and uniformly distributed over the whole volume. The precursor may be obtained by co-precipitation, kneading, ion-exchange, and impregnation or leaching of alloys.

(ii). Calcination of the precursor in the air, leading to the decomposition of the primary phase comprised in the precursor (basic carbonates, nitrates, hydroxides, oxalates, citrates, etc.) to the appropriate oxides (CuO and ZnO).

(iii). Reduction of the calcined precursor, most often in the mixture  $\text{H}_2/\text{N}_2$ , during copper oxide is reduced to metallic copper, as zinc oxide does not undergo reduction.

### 3.4.2 Precipitation precursor phases

The original substances in the preparation of binary (Cu, Zn) or ternary (Cu, Zn, Al) precursors are the nitrates of copper, zinc and aluminum: the precipitating agent is  $\text{Na}_2\text{CO}_3$  or a mixture of  $\text{Na}_2\text{HCO}_3$  and  $\text{NaOH}$  or urea. The precipitation of the precursor of the precursor is carried out at an elevated temperature (60-90°C).

There exist three possible variants of precipitation:

(i). simple- the solution of the precipitating agent is added into the solution of metal nitrates, during the precipitation the solution changes from acidic to neutral or weakly basic.

(ii). inverse- the solution metal nitrates is added into the solution of  $\text{Na}_2\text{CO}_3$  ( $\text{NaHCO}_3$ ,  $\text{NaOH}$  and Urea). The solution changes from basic to neutral or weakly basic depending on the proportion and concentrations of the solution.

(iii). mixed- the solution of metal nitrates and  $\text{Na}_2\text{CO}_3$  are added simultaneously into a vessel containing an excess of demineralized water.

By controlling the rate at which the reactants are introduced into the system, pH may be kept constant during the precipitation.

## CHAPTER IV

### EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this work which is divided into four parts. The chemicals and preparation of Cu/ZnO catalyst are shown in section 4.1 and 4.2 respectively. Section 4.3 describes the details of catalyst characterization by various techniques such as X-ray diffraction (XRD), Brunaur-Emmett-Teller (BET), N<sub>2</sub>O chemisorption, Thermal gravimetric and differential thermal analysis (TG/DTA), Fourier transform infrared spectroscopy (FT-IR) and Transmission electron microscopy (TEM). The last part (section 4.4) describes the catalyst evaluation in term of catalytic activity measurement in steam reforming of methanol.

#### 4.1 Materials and Chemicals

The details of chemicals for preparation of Cu/ZnO as follows:

1. Copper nitrate trihydrate, (Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O) from Fluka
2. Zinc nitrate hexahydrate, (Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O) from Fluka
3. Urea, (CO(NH<sub>2</sub>)<sub>2</sub>) from Riedel-deHaën
4. Copper acetate monohydrate, (Cu(CH<sub>3</sub>COO)<sub>2</sub>•H<sub>2</sub>O) from Fluka
5. Zinc acetate dihydrate, (Zn(CH<sub>3</sub>COO)<sub>2</sub>•2H<sub>2</sub>O) from Fluka
6. Acetic acid, (CH<sub>3</sub>COOH) from Carlo erba reagenti
7. Methanol, (CH<sub>3</sub>OH) from Merck
8. Ethanol, (C<sub>2</sub>H<sub>5</sub>OH) from Merck
9. Sodium carbonate, (Na<sub>2</sub>CO<sub>3</sub>) from Ajax finechem

## 4.2 Preparation of Cu/ZnO catalyst

In this work, we have used several methods (sol-gel technique, co-precipitation and homogeneous-precipitation) to synthesize binary Cu/ZnO-based catalysts with Cu/Zn molar ratio in 70/30, 50/50 and 30/70.

For co-precipitation, Cu/ZnO catalyst was prepared by using the addition rate of a mixed copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) 1 M and zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) 1 M solution with a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) 200 ml and ratio Cu/Zn of co-precipitation method shown in table 4.1. The mixture was stirred under magnetic for 90 minutes, while maintaining the pH constant at around 9-10. The precipitates were recovered by filtration, followed by washing with distilled water at ambient temperature to remove all traces of sodium. Drying was carried out in air at  $90^\circ\text{C}$  for 12 h and the final calcinations were performed in air  $300^\circ\text{C}$  for 3 h. The obtained precipitate powders were then milled and sieved and the fraction containing particles of 0.12-0.25 mm were used in the activity measurement.

**Table 4.1** Cu/Zn ratio in preparing catalysts of co-precipitation method.

| Cu/Zn ratios | $\text{Cu}(\text{NO}_3)_2$<br>(ml) | $\text{Zn}(\text{NO}_3)_2$<br>(ml) | $\text{Na}_2\text{CO}_3$<br>(ml) |
|--------------|------------------------------------|------------------------------------|----------------------------------|
| 70/30        | 112                                | 48                                 | 150                              |
| 50/50        | 80                                 | 80                                 | 150                              |
| 30/70        | 48                                 | 112                                | 150                              |



For sol-gel technique (M.K.Hossain and Ghosh 2003), Cu/ZnO catalyst was prepared by using copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) 1 M, zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) 1 M and ethanol were mixed. Those mixtures were refluxed for 1 hour at  $80^\circ\text{C}$ . Then, added acetic acid until pH reaches 3.5. The mixture was dried in air at  $90^\circ\text{C}$  for 3 h and calcined powder in air  $300^\circ\text{C}$  for 3 h. Finally, the precipitate powder were milled and sieved by sieves 40/60 mesh. The Ratio Cu/Zn of sol-gel technique shown in table 4.2.

**Table 4.2** Cu/Zn ratio in preparing catalysts of sol-gel technique.

| Cu/Zn ratios | $\text{Cu}(\text{CH}_3\text{COO})_2$<br>(ml) | $\text{Zn}(\text{CH}_3\text{COO})_2$<br>(ml) | Ethanol<br>(ml) |
|--------------|--|--|-----------------|
| 70/30        | 70   | 30   | 100             |
| 50/50        | 50   | 50   | 100             |
| 30/70        | 30   | 70   | 100             |

Lastly, catalysts were synthesized from homogeneous precipitation method (Shishido et al. 2004), using copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) 1 M and zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) 1 M and urea 1 M solution, mixing under magnetic stirring for 90 minutes at  $90^\circ\text{C}$ . Drying was carried out in air at  $90^\circ\text{C}$  for 12 h. The obtained precipitate powders were then calcined at  $300^\circ\text{C}$  for 3 h, milled and sieved by sieves 40/60 mesh. Then Cu/ZnO catalysts were investigated by activity measurement.

**Table 4.3** Cu/Zn ratios in preparing catalysts of homogeneous precipitation.

| Cu/Zn ratios | Cu(NO <sub>3</sub> ) <sub>2</sub><br>(ml) | Zn(NO <sub>3</sub> ) <sub>2</sub><br>(ml) | CO(NH <sub>2</sub> ) <sub>2</sub><br>(ml) |
|--------------|---|---|---|
| 70/30        | 70  | 30  | 150                                       |
| 50/50        | 50  | 50  | 150                                       |
| 30/70        | 30  | 70  | 150                                       |

### 4.3 Characterization of catalyst

The catalysts were characterized using a variety of techniques, which are briefly outlined below.

#### 4.3.1 X-Ray Diffraction (XRD)

XRD was performed to determine the bulk phase and crystalline size in catalysts by a SIEMENS D5000 X-ray diffractometer using Cu-K<sub>α</sub> radiation with Ni filter in the 2θ range of 20-80 degrees resolution 0.04°.

#### 4.3.2 Brunauer Emmet-Teller (BET Surface Area)

The BET surface area of samples was measured by N<sub>2</sub> absorption-desorption, with nitrogen as the adsorbate using a Micromeritics ASAP 2000 instrument. The powders were first outgases at 200°C for 1 h prior to N<sub>2</sub> absorption-desorption.

### 4.3.3 N<sub>2</sub>O decomposition

The specific Cu<sup>0</sup> surface areas of the catalysts were measured by nitrous oxide (N<sub>2</sub>O) chemisorption, using a method similar to the one described by Chinchén et al. (1987). The reaction with nitrous oxide is able to measure metal surface area for both pure and support copper catalyst. This method is based on nitrous oxide molecule on a copper surface which is accompanied by the liberation of one nitrogen molecule according to the reaction:



where the subscript s signifies surface atom.

By quantifying the amount of consumed N<sub>2</sub>O, a measurement of the Cu<sup>0</sup> surface area can be obtained. Prior to reaction with nitrous oxide, each catalyst was reduced in hydrogen (10 ml/min) at 250°C for 1 hour. At the end hydrogen period, hydrogen was substituted by helium passing over the catalyst at the reduction temperature for 8-10 min to ensure that all hydrogen was accumulated in the system. The temperature of catalyst sample was decreased from 250°C to 90°C and maintained at 90°C for nitrous oxide reaction. Certain volumes of nitrous oxide were injected into helium stream through injection port of gas chromatograph and pass over the catalyst. The volume of nitrous oxide was fed in 1 ml and the amount of catalyst was packed in the reactor ranging from 0.10 to 0.15 g which depends on their estimated copper surface area. The configuration of the thermal conductivity detector (TCD) enables both the nitrous oxide peaks and the nitrogen peak to be determined. Nitrogen and nitrous oxide are separated on the Porapak Q column.

The flow diagram of nitrous oxide reaction that was used to measure copper surface area was shown in Figure 4.1

#### 4.3.4 Thermogravimetric and differential thermal analysis (TG/DTA)

Thermal gravimetric and differential thermal analysis (TG/DTA), was applied to determine the true metal loading and to analyze the thermal properties of supported, were determined by using TG/DTA analysis on a SDT Q600 instrument. Between 10 and 13 mg of sample was used for each experiment. The rate of temperature increase was 5 °C/min to heat from 35 to 300 °C with input nitrogen (25 ml/min<sup>-1</sup>). The temperature of catalyst sample was decreased from 300°C to 100°C and then hydrogen flow (25 ml min<sup>-1</sup>) with a heating rate of 2 °C min<sup>-1</sup> from 100°C to 305°C, using Al<sub>2</sub>O<sub>3</sub> as a reference.

#### 4.3.5 Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FTIR) was used to detect the functional groups on the surface of Cu/ZnO-based catalysts, were determined by using a Nicolet 6700 infrared spectrometer. For adsorption experiments pressed disks of pure catalyst powders were used. Spectra obtained in a FTIR spectrometer were corrected for slope and baseline and then expanded in absorbance. The spectra were recorded at wavenumber between 400 and 4000 cm<sup>-1</sup>.

#### 4.3.6 Transmission electron microscopy (TEM)

Morphology and structure of the catalysts was investigated by Transmission Electron Microscopy (TEM) model TECNAI 20 TWIN model 200kv at the Center of Nanoimaging (CNI) Mahidol University.

### **4.4 Reaction study in steam reforming of methanol**

Catalytic experiments were performed at atmosphere pressure in fixed-bed reactor consisting of a Pyrex tube, a coaxially centered thermocouple with its tip located in the middle of the bed.

Prior to each experiment, the catalyst was reduced in situ at 250°C in stream of 10% H<sub>2</sub>/He for 1 h. At the end hydrogen period, hydrogen was removed by purging with Helium for another hour prior to activity measurements to produce the reactant mixture, streams containing CH<sub>3</sub>OH and H<sub>2</sub>O were combined. The CH<sub>3</sub>OH containing stream was produced by passing Helium flowing at 50 ml/min through a CH<sub>3</sub>OH saturator maintained at 0°C. Another stream of He flowing at 50 ml/min was passed through a H<sub>2</sub>O saturator held at 35°C was fed to the DRIFTS cell. The two streams were mixed and the resulting gas containing 5% CH<sub>3</sub>OH and 7.5% H<sub>2</sub>O, (balance Helium) was fed to the reactor. A premixed CH<sub>3</sub>OH and H<sub>2</sub>O (1:1.5 mol) stream was fed to the reactor.

The catalytic activity measurements were performed at atmospheric pressure in a 5 mm I.D. Approximately 30 mg of the catalyst was placed in a glass wool plug inside the reactor. The reactor was then placed in a furnace. The temperature of the reactor was measured using a thermocouple contacting the catalyst bed and controlled using temperature controller connected to the furnace. The catalysts were pretreated using conditions described in the previous section. The reactor was then brought to the desired temperature in order to measure the catalytic activity.

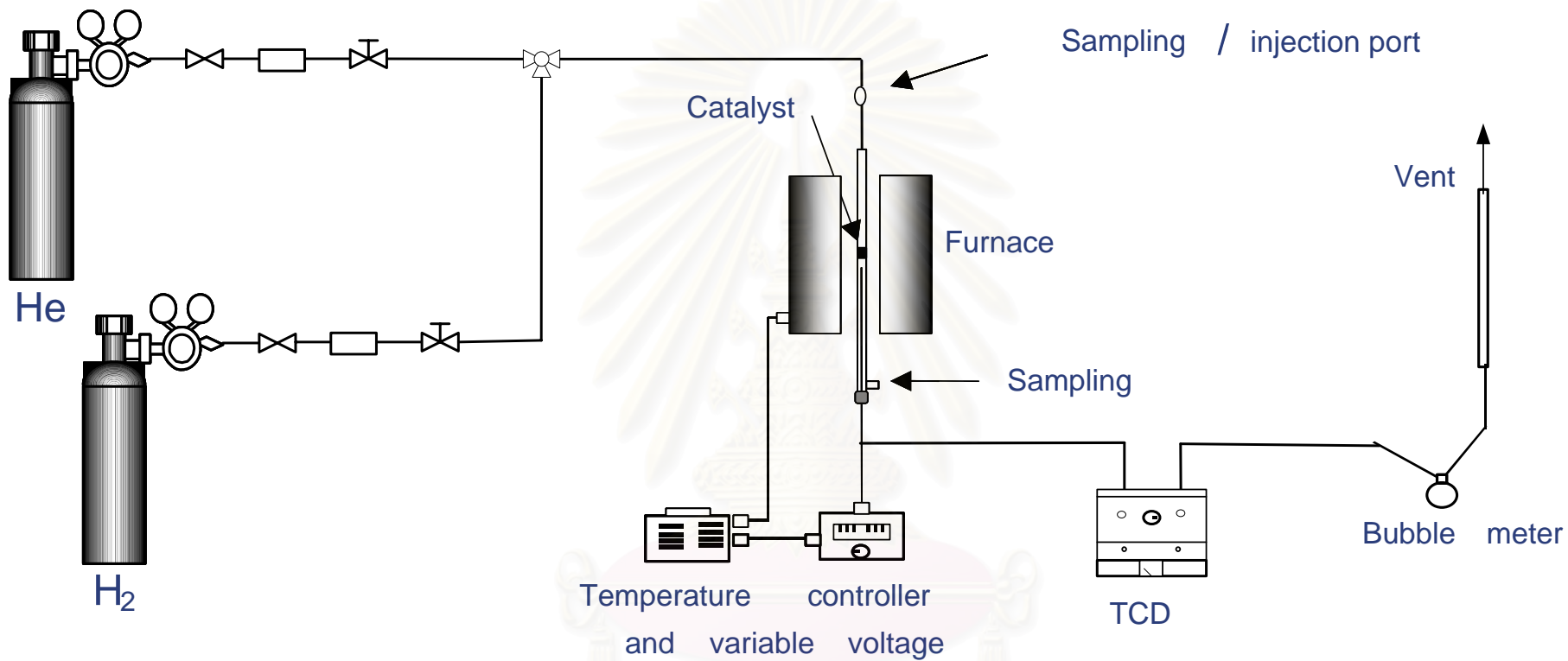
The product gas composition was analyzed on-line by a Shimadzu gas chromatograph (GC). The GC was equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas and separation of the constituents was achieved using molecular sieves 5A column (3 m × 3 mmØ). Molecular sieves 5A were used to analyze N<sub>2</sub>, CO, O<sub>2</sub>, H<sub>2</sub> and other hydrocarbons. Another GC packs Porapak QS column (3 m × 3 mmØ). Helium was carrier gas and Porapak QS were used to analyze H<sub>2</sub>O, O<sub>2</sub>, CH<sub>3</sub>OH and CO<sub>2</sub>. Table 4.3 shows operation conditions of SRM.

The flow diagram of steam reforming of methanol reaction that was used to measure activity was shown in Figure 4.2

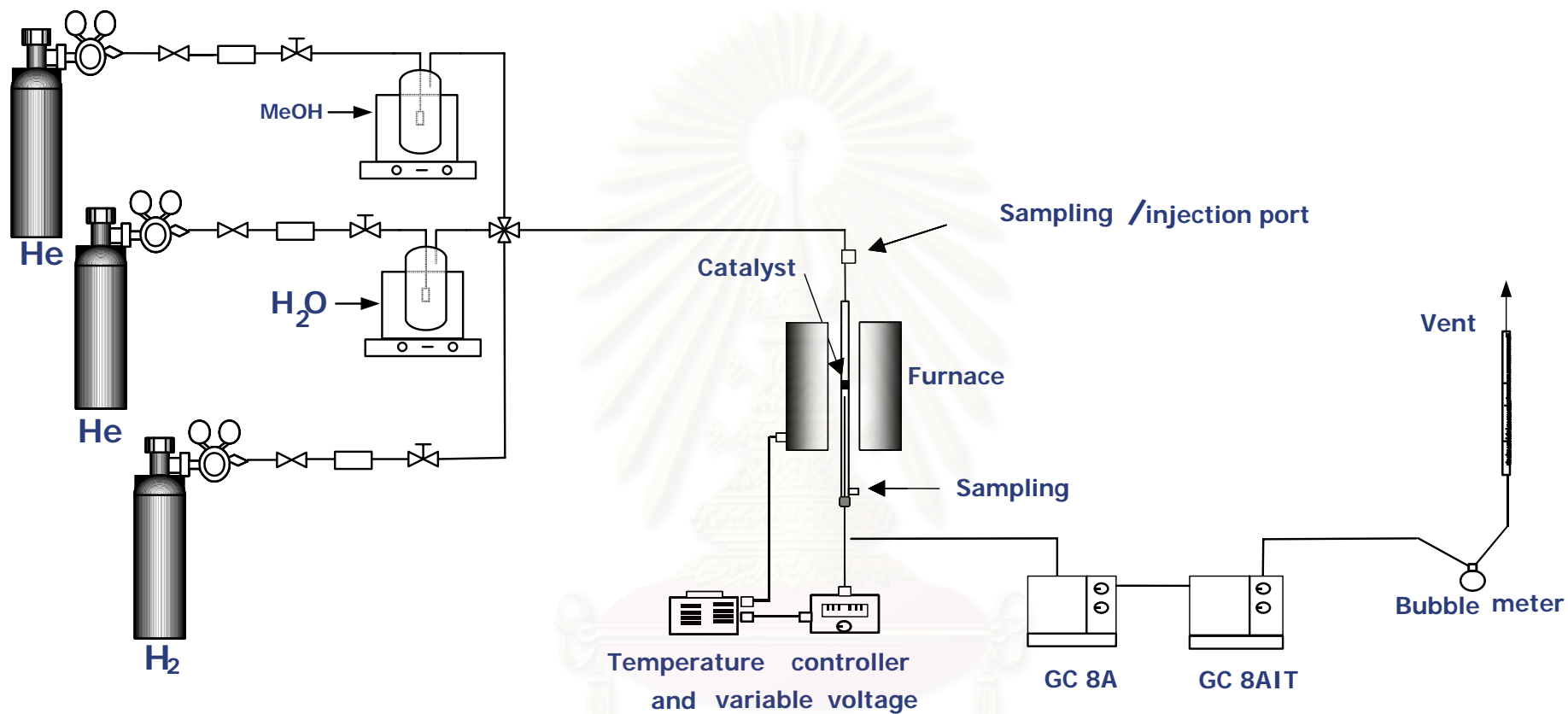
**Table 4.4** Operating conditions of gas chromatograph for steam reforming of methanol.

| Gas Chromatograph               | SHIMADZU TCD GC 8AIT  | SHIMADZU TCD GC 8A                                |
|---------------------------------|---|---|
| Detector                        | TCD   | TCD   |
| Packed column                   | Porapak QS  | Molecular sieve 5A                                |
| Carrier gas                     | Ultra high purity He  | Ultra high purity He                              |
| Carrier gas flow rate (ml/min)  | 30  | 30  |
| Injector temperature (°C)       | 120   | 120   |
| Detector temperature (°C)       | 120   | 120   |
| Initial column temperature (°C) | 120   | 120   |
| Initial holding time (min)      | -   | -   |
| Programmed rate (°C/min)        | -   | -   |
| Final column temperature (°C)   | 120   | 120   |
| Final holding time (min)        | -   | -   |
| Current (mA)                    | 90  | 80  |
| Analyzed gas                    | CH <sub>3</sub> OH,H <sub>2</sub> O,CO <sub>2</sub> ,O <sub>2</sub> | H <sub>2</sub> ,CO,O <sub>2</sub> ,N <sub>2</sub> |





**Figure 4.1** A schematic of nitrous oxide system



**Figure 4.2** A schematic of steam reforming of methanol system

## CHAPTER V

### RESULTS AND DISCUSSIONS

In preliminary experiments, the study was conducted so as to investigate the physical and chemical properties of Cu/ZnO-based catalyst. These Cu/ZnO catalysts were synthesized by several methods (homogeneous precipitation, co-precipitation and sol-gel techniques), various Cu/Zn molar ratios are 70/30, 50/50 and 30/70. The catalytic properties were evaluated using steam reforming of methanol. The results in this chapter are divided into two main parts. The first part describes the characteristics of Cu/ZnO consisting of various preparation methods (section 5.1). The catalytic properties and activities of Cu/ZnO (section 5.2). The other parts describe the characteristics of the synthesized Cu/ZnO catalyst, calcined by various atmospheric conditions (hydrogen, air, oxygen and nitrogen) (section 5.3) and the catalytic properties and activities of Cu/ZnO (section 5.4).

#### 5.1 Synthesis of Cu/ZnO catalyst

##### 5.1.1 Properties of Cu/ZnO catalyst

###### 5.1.1.1 X-ray diffraction (XRD)

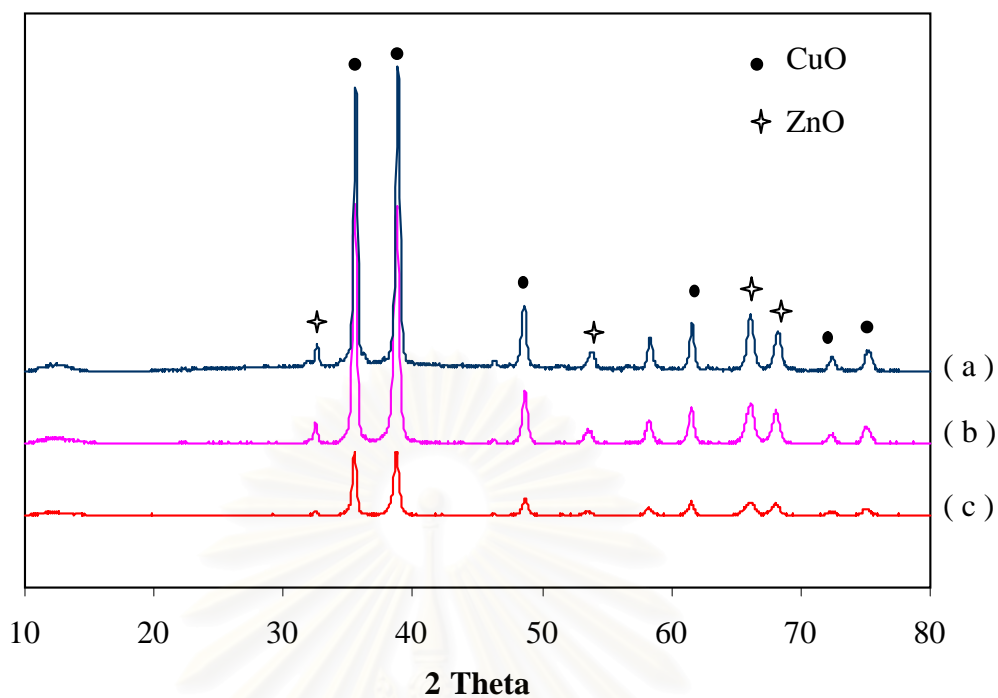
Bulk crystal structure and chemical phase composition of a crystalline material can be detected by diffraction of an X-ray beam as a function of the angle of the incident beam. The measurements were carried out at the diffraction angles ( $2\theta$ ) between 10 and 80°. Broadening of the diffraction peaks were used to estimate crystallite diameter from Scherrer Equation.

The XRD patterns of Cu/ZnO catalysts were prepared by several methods (homogeneous precipitation (HP), sol-gel techniques and co-precipitation (CP)) and are illustrated in Figure 5.1, 5.2 and 5.3. Most peaks are identified as the diffraction lines of CuO species, only small peaks is assigned to ZnO.

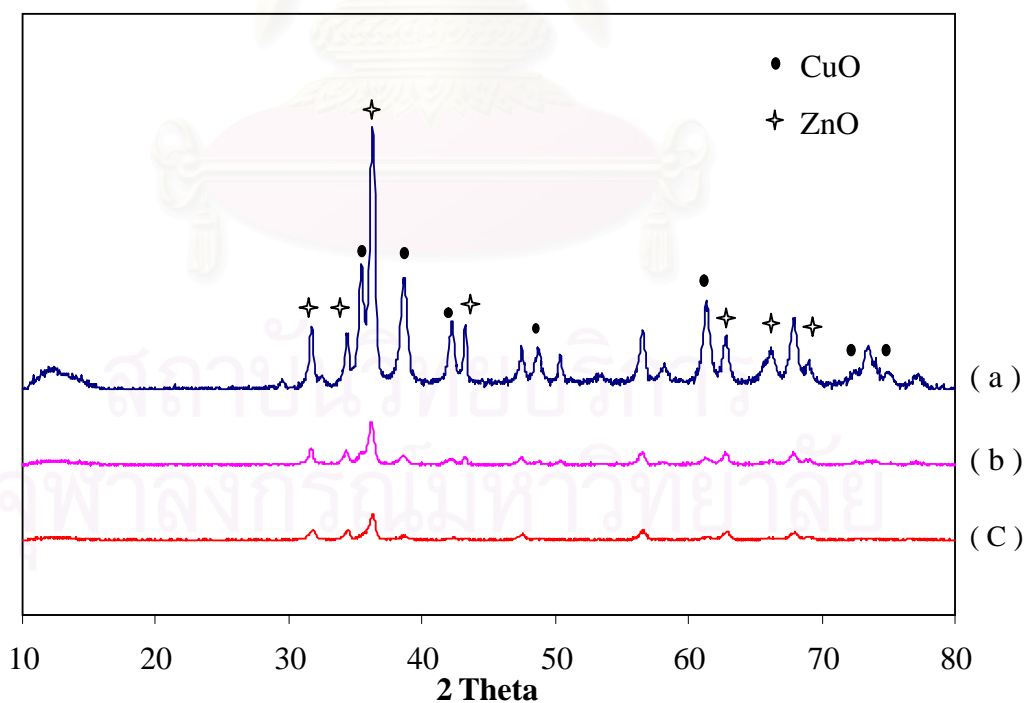
CuO crystal size of hp-Cu/ZnO is about 22-32 nm, cp-Cu/ZnO is about 8-18 nm and sol-gel Cu/ZnO is around 24 nm. The CuO crystal size of several preparation methods are the same size and smaller. Copper species was reduced by hydrogen, the peaks assigned to metallic Cu appears, instead of CuO species and shown in Figure. 5.2

The XRD patterns of the Cu/ZnO prepared by homogeneous precipitation, sol-gel technique and co-precipitation method in the calcined state are shown in Figure 5.1, 5.2 and 5.3 respectively. The XRD characteristic peaks for CuO at  $2\theta$  of ca.  $38.84^\circ$  and less so at  $35.6$ ,  $48.68$ ,  $61.68$ ,  $72.68$  and  $75.56^\circ$  (Ning et al. 2001) were observed only for the catalysts prepared by homogeneous precipitation method. The average CuO crystallite sizes on Cu/ZnO catalyst was calculated from the full width at half maximum of the XRD peak at  $38.84^\circ$ ,  $2\theta$  using Scherrer's equation (Klug and Alexander) to be 22-32 nm.

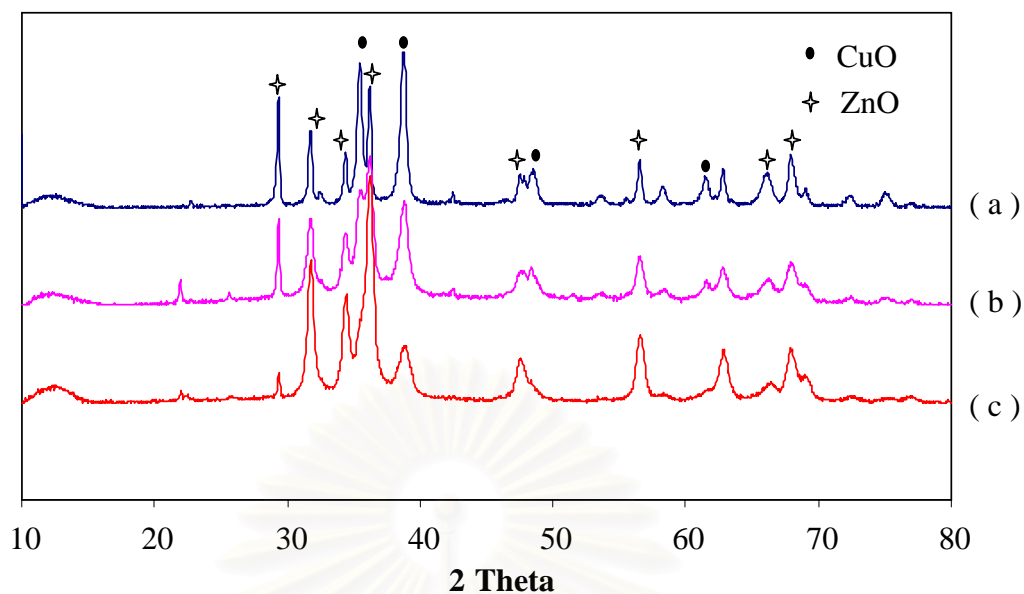
The catalysts prepared by sol-gel technique, it was found that CuO was indicated by XRD characteristic peaks at  $2\theta = 35.48$ ,  $38.72$ , and  $42.32^\circ$  (Agrell et al. 2003). The average CuO crystallite size was calculated to be 24 nm. For co-precipitation method, CuO was signified by XRD peaks at  $2\theta = 35.52$ ,  $38.76$ ,  $48.72$  and  $61.76^\circ$  (Agrell et al. 2001). The average CuO crystallite size was about 8-18 nm.



**Figure 5.1** XRD patterns of Cu/ZnO catalyst prepared by homogeneous precipitation. ( a ) hp-Cu/ZnO (70/30), ( b ) hp-Cu/ZnO (50/50) and ( c ) hp-Cu/ZnO (30/70).



**Figure 5.2** XRD patterns of Cu/ZnO catalyst prepared by sol-gel technique. ( a ) sol-gel Cu/ZnO (70/30), ( b ) sol-gel Cu/ZnO (50/50) and ( c ) sol-gel Cu/ZnO (30/70).



**Figure 5.3** XRD of Cu/ZnO catalyst prepared by co-precipitation.

( a ) cp-Cu/ZnO (70/30), ( b ) cp-Cu/ZnO (50/50) and  
( c ) cp-Cu/ZnO (30/70).

#### 5.1.1.2 BET surface area

The most common procedure for determining surface area of a solid is based on adsorption and condensation of nitrogen at liquid nitrogen temperature using static vacuum procedure. This method is also called BET (Brunauer Emmett Teller) method.

BET surface areas of Cu/ZnO catalysts were determined by N<sub>2</sub> physisorption technique and are shown in Table 5.1. The N<sub>2</sub> adsorption-desorption. It is indicated that the BET surface areas of all the Cu/ZnO catalysts range of 2 to 20 m<sup>2</sup>/g. Cu/ZnO catalyst prepared by homogeneous precipitation method is the smallest surface areas.

Moreover, BET surface area suggest that building of Cu/ZnO catalysts are crystalline structure due to surface area of catalysts are small.



**Table 5.1** Surface area of Cu/ZnO catalysts prepared by different methods.

| <b>Cu/Zn Ratios</b> | <b>BET surface area (m<sup>2</sup>/g)</b> |                |           |
|---------------------|---|----------------|-----------|
|                     | <b>CP</b>                                 | <b>Sol-gel</b> | <b>HP</b> |
| <b>70/30</b>        | 3.6                                       | 2.5            | 1.4       |
| <b>50/50</b>        | 12  | 6.0            | 3.5       |
| <b>30/70</b>        | 22.3                                      | 10.0           | 5.6       |

#### 5.1.1.3 N<sub>2</sub>O decomposition

Cu surface areas of the catalysts were measured by nitrous oxide (N<sub>2</sub>O) chemisorption (Chinchen et al. 1987). The amounts of N<sub>2</sub>O chemisorption on the catalysts reduced at 250°C. The reaction with nitrous oxide is able to measure metal surface area for both pure and support copper catalyst. Table 5.2 shows active sites of Cu/ZnO catalysts synthesized by different methods. Cu/ZnO catalysts composed of 70 mol% of Cu are higher active sites than Cu 50 mol% and 30 mol% (Akaratiwa et al. 1994), (Shishido et al. 2004). Cu/ZnO catalysts prepared by homogeneous precipitation method, which are the highest active sites of the other methods (sol-gel technique and co-precipitation), indicating that Cu atom are the active species. This may elucidated that for catalysts with low copper content the active sites will decrease, whereas for higher copper content the active sites will increase. From table 5.2, it was found the active sites depend on the amount of copper loading.

**Table 5.2** Cu surface area of Cu/ZnO catalysts prepared by different methods.

| <b>Cu/Zn Ratios</b> | <b>Active sites*10<sup>19</sup> (molecule Cu/g cat)</b> |                |           |
|---------------------|---|----------------|-----------|
|                     | <b>hp</b>   | <b>sol-gel</b> | <b>cp</b> |
| <b>70/30</b>        | 1.68  | 1.44           | 1.29      |
| <b>50/50</b>        | 1.41  | 1.25           | 1.08      |
| <b>30/70</b>        | 0.97  | 0.86           | 0.74      |

## 5.2 The catalytic activities of Cu/ZnO catalyst in steam reforming of methanol.

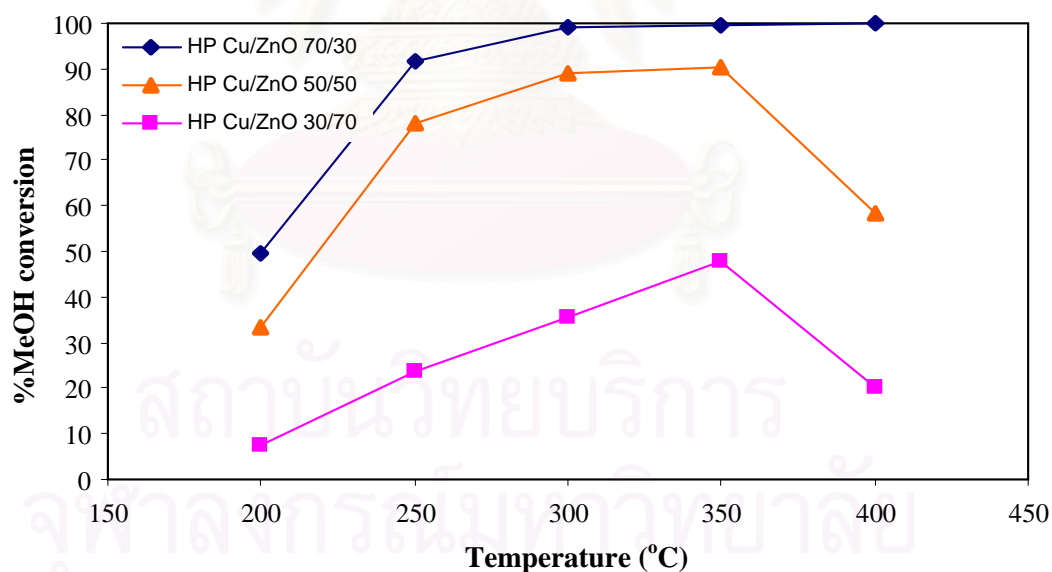
The performance of the catalysts in steam reforming of methanol was defined in terms of methanol conversion and selectivity towards carbon dioxide. Methanol conversion is identified as moles of methanol converted with respect to methanol in the feed.

In order to study the effect of reaction temperature on the performance of catalyst, Cu/ZnO catalysts were used to test over a temperature range of 200 to 400°C. Under this test condition, hydrogen and carbon dioxide were the major products of the reaction.

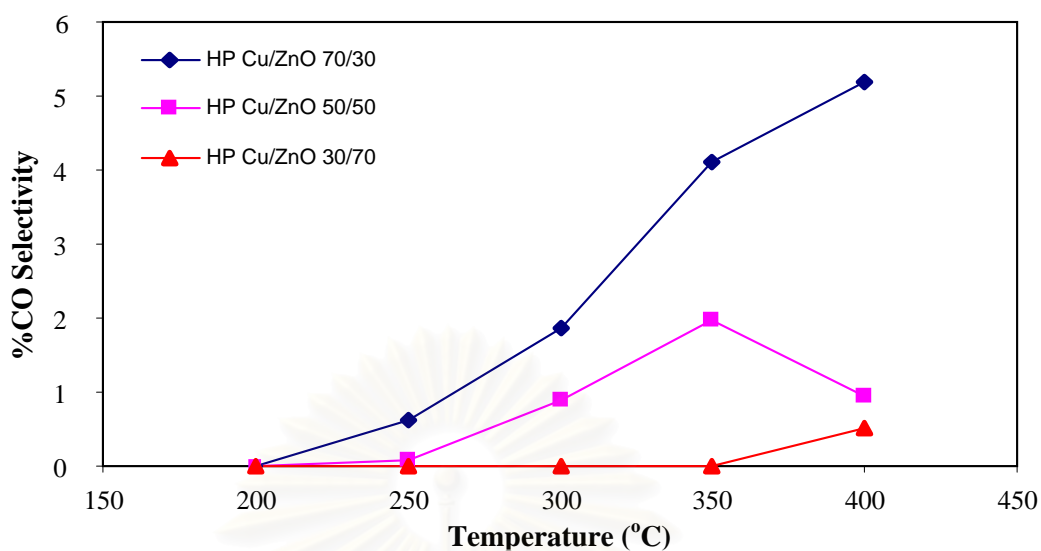
Figure 5.4, illustrates that the methanol conversion increase with increasing temperature over Cu/ZnO catalyst prepared by homogeneous precipitation method with Cu/Zn molar ratios in the range of 30/70 to 70/30. The result shows clearly that Cu/ZnO the performance of catalyst was affected by the compositions of catalysts in all of preparation conditions. Catalyst composed of 70 mol% of Cu, the conversion of methanol was nearly 100% at 350°C, while Cu/Zn ratios 50/50 and 30/70 the maximum conversion of methanol at the same temperature were equal to 87%, 40%

respectively, indicating that Cu atom are the active species for this reaction. With increase the Cu content the methanol conversion increase. Moreover, catalysts Cu/Zn ratios 50/50 and 30/70 decrease conversion of methanol at 400°C, while catalyst Cu/Zn ratio 70/30 reaches to 100% methanol conversion at the same temperature. It is remarkable that the total conversion of methanol could be achieved over the Cu/ZnO catalyst (70/30) at a relatively temperature of 400°C.

Furthermore, CO selectivity is shown in Figure 5.5. Because of carbon monoxide, Pt electrode of fuel cell was deteriorated. Catalyst synthesized by homogeneous precipitation method, Catalysts ratios 70/30, 50/50 and 30/70 the CO selectivity were equal to 5%, 1% and 0.5% at 400°C, respectively. The CO selectivity increases with increasing reaction temperature.



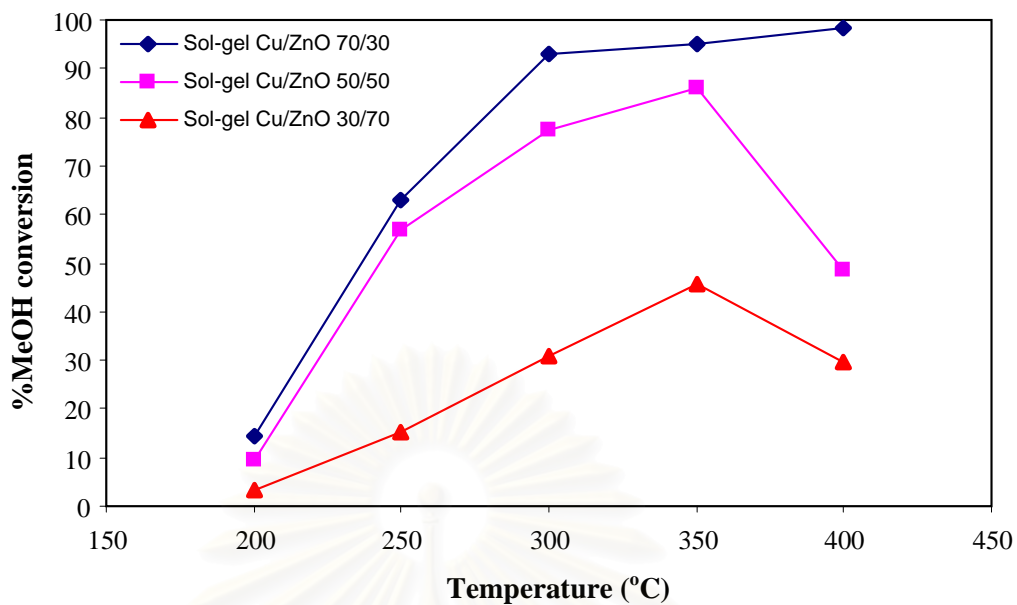
**Figure 5.4** Catalytic activity of Cu/ZnO catalyst prepared by homogeneous precipitation method.



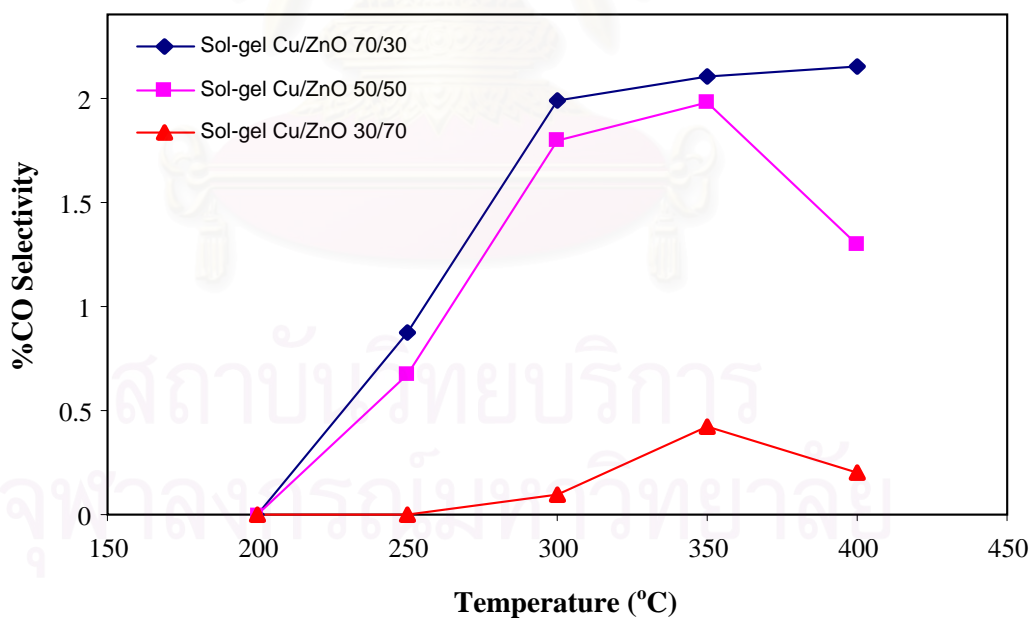
**Figure 5.5** CO selectivity of Cu/ZnO catalyst synthesized by homogeneous precipitation method.

Catalysts also prepared by sol-gel technique. Figure 5.6, shows that the methanol conversion of Cu/Zn ratio 70/30, which is the highest of the other molar ratios. It can be seen that methanol conversion and CO selectivity increase with increasing reaction temperature, as methanol is converted almost completely into hydrogen and carbon dioxide at 400°C. In addition to, catalysts consist of Cu 50 and 30 mol%, have higher conversion of methanol at 350°C. Conversion of methanol decrease at 400°C, it was speculate that catalyst occurs sintering this reaction temperature.

As shown Figure 5.7, CO selectivity is observed to be less than 2% over Cu/ZnO catalyst (70/30) in the temperature range of 200-400°C. Cu/ZnO catalysts have ratios of Cu/Zn 50/50 and 30/70, showing lower CO selectivity.



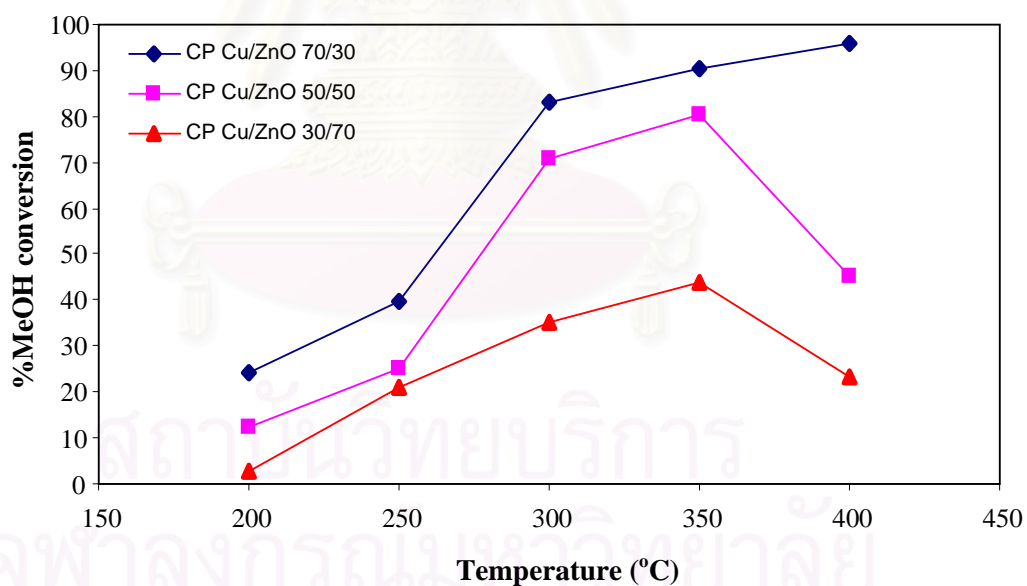
**Figure 5.6** Catalytic activity of Cu/ZnO catalyst synthesized by sol-gel technique.



**Figure 5.7** CO selectivity of Cu/ZnO catalyst prepared by sol-gel technique.

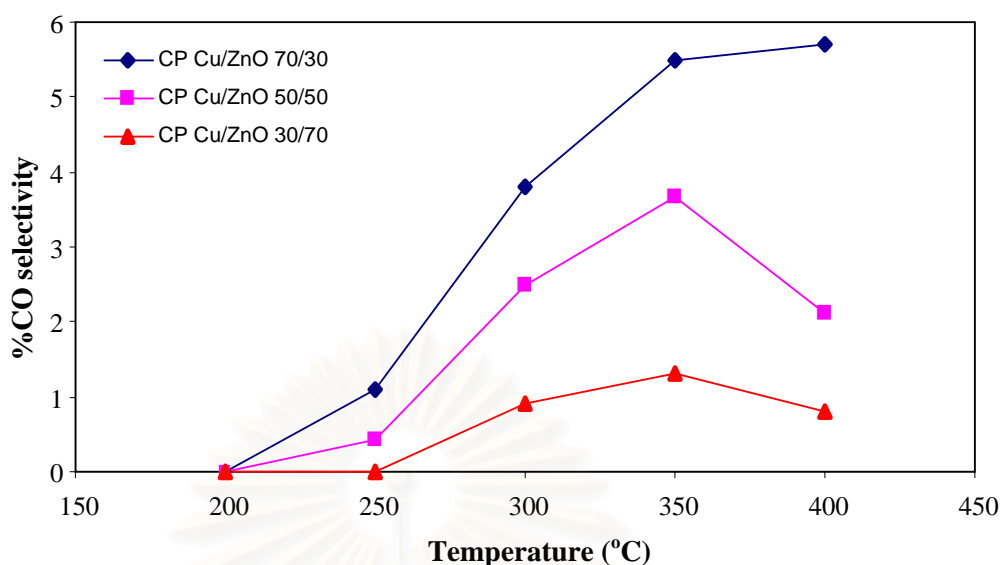
Next, Cu/ZnO catalyst, with which vary Cu contents, synthesized by co-precipitation method. Figure 5.8, shows that catalysts compose of Cu 70, 50 and 30 mol%. These results clearly confirm that the maximum activity was attained at Cu content of 70 mol% in all of ratios. The methanol conversion increased with increase reaction temperature. Catalysts consist of Cu 50 and 30 mol%, decreased conversion of methanol at high temperature. This performance is the same reason as catalyst prepared by sol-gel technique.

Production of CO, which has a detrimental effect for fuel cells, was more than 5% in catalyst ratio 70/30, shown in Figure 5.9. CO selectivity of co-precipitation method is the higher than other methods.



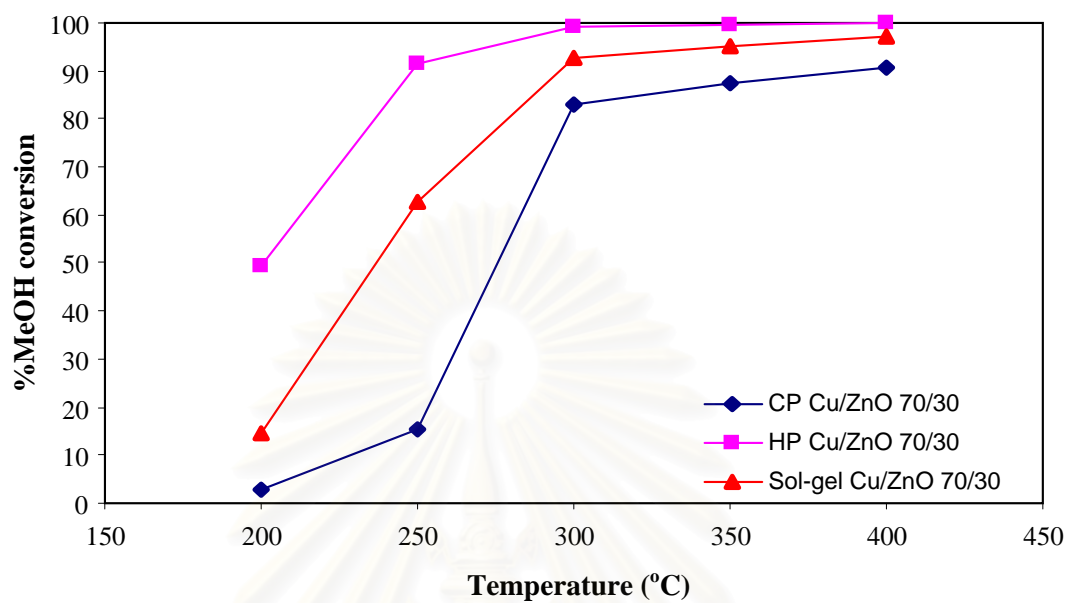
**Figure 5.8** Catalytic activity of Cu/ZnO catalyst prepared by co-precipitation.





**Figure 5.9** CO selectivity of Cu/ZnO catalyst prepared by co-precipitation.

Figure 5.10 compares the steam reforming of methanol activities for the three catalyst prepared by different methods. Note that all three catalysts show similar behavior, with the major differences being temperature. The Cu/ZnO catalyst prepared by homogeneous precipitation, the conversion value of methanol was nearly 100% at 350 °C. Cu/ZnO catalyst synthesized by sol-gel technique, reaching to 92% methanol conversion at 350 °C. Cu/ZnO catalyst prepared by co-precipitation method, is lower conversion of methanol of 80% at the same temperature. At lower temperature reactions, especially at 250°C, catalyst prepared by homogeneous precipitation displays much higher activity as compared with sol-gel technique and co-precipitation, methanol conversion is up to 63%. It was found Cu/ZnO catalyst was prepared by homogeneous precipitation, exhibits the higher activity than other methods for steam reforming of methanol. It is clear that the preparation methods have a significant influence on the performance of the catalyst for hydrogen production from steam reforming of methanol. These results imply that the highly active Cu/ZnO catalyst prepared by homogeneous precipitation can effectively exhibit high conversion for steam reforming methanol.



**Figure 5.10** Comparison catalytic activity of Cu/ZnO catalysts prepared by different methods.

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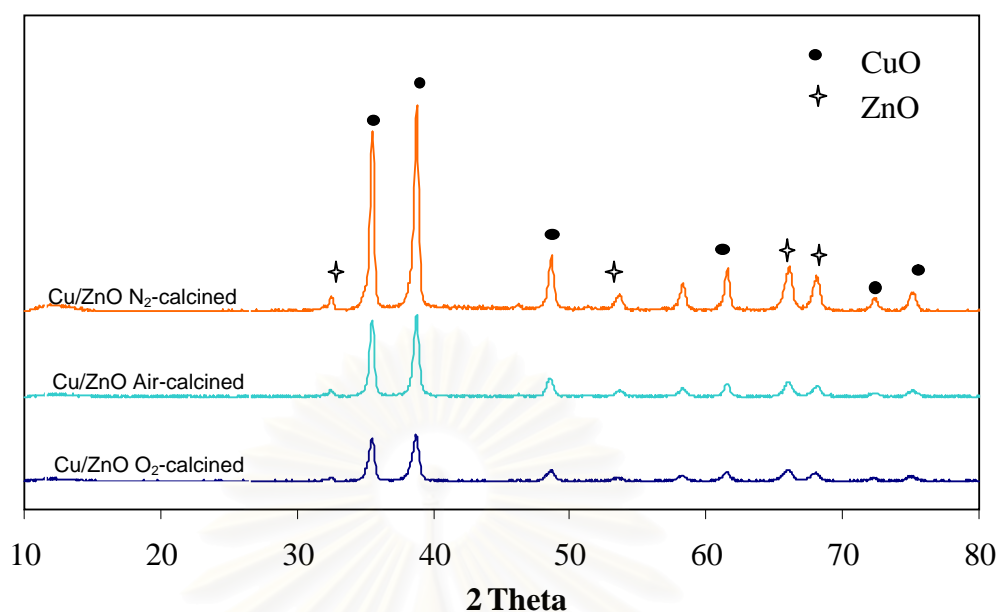
### 5.3 Effect of calcination conditions of Cu/ZnO catalysts.

This section describes Cu/ZnO catalyst, calcined by various atmospheric conditions (hydrogen, air, oxygen and nitrogen). Cu/ZnO catalyst prepared by homogeneous precipitation method, which was chosen to investigate affect of various atmospheric conditions. Cu/ZnO catalyst (50/50) is selected in this section, because it is lower CO selectivity than catalyst content Cu 70 mol%. Carbon dioxide has a harmful effect for fuel cell.

#### 5.3.1 Properties of Cu/ZnO catalyst calcined by various conditions.

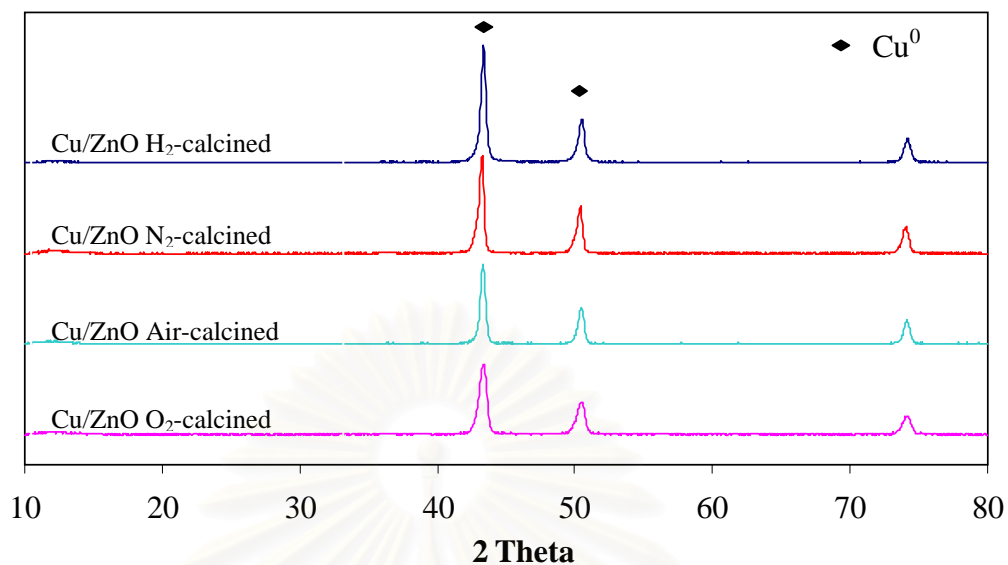
##### 5.3.1.1 X-ray diffraction (XRD)

The precursor structure was determined by XRD. Figure 5.11 illustrates the XRD (X-ray diffraction) patterns of precursors prepared by homogeneous precipitation method. The XRD characteristic peaks for CuO at  $2\theta$  of ca. 38.76 and less so at 35.56, 48.68, 61.6, 72.68 and 75.35° (Yao et al. 2006). It is shown in Figure 5.11 that all calcined precursors the Cu/ZnO catalyst do not contain any detectable crystalline ZnO, suggesting that the particles of ZnO are either amorphous in phase or very small crystals that could not be detected by XRD. From comparison of the diffraction peaks of CuO in these catalysts, one can find that the diffraction peaks of CuO for catalyst is calcined by nitrogen, is much sharp and higher as compare of those catalysts calcined by air and oxygen. The mean crystal sizes of CuO are estimated by using the Scherrer equation. The CuO crystal size of catalyst calcined by nitrogen, is about 27.96 nm, while those of catalysts calcined by air and of catalyst calcined by oxygen are lower, are about 25 and 21 nm, respectively.



**Figure 5.11** XRD patterns of Cu/ZnO catalyst calcined by various conditions (before reduction).

To establish a correlation between the catalytic performance and the active phase, XRD patterns of the catalysts after the reduction were recorded and are shown in Figure 5.12. It was found that only diffraction peaks corresponding to metallic Cu are identified at  $2\theta \approx 43^\circ$  (Yao et al. 2006), demonstrating metallic copper is the active species of the resent Cu/ZnO catalyst for steam reforming of methanol reaction. Assuming that Cu particles were spherical, the average copper metal crystalline sizes were estimated from the full width at half maximum (FWHM) of Cu diffraction lines. The calculation results reveal a copper particles size of catalyst calcined by hydrogen, is about 27 nm as compared to catalyst calcined by nitrogen (26.59 nm), catalyst calcined by air (24.4 nm) and catalyst calcined by oxygen (24.1 nm).



**Figure 5.12** XRD patterns of Cu/ZnO catalyst calcined by various conditions (after reduction).

### 5.3.1.2 BET surface area

Table 5.3 shows BET surface area of the binary Cu/ZnO varies atmospheric conditions. One can see that the BET surface area nearly  $1 \text{ m}^2/\text{g}$ . These results illustrate clearly that Cu/ZnO catalysts are crystalline structure. BET surface area of Cu/ZnO catalyst could not affect for steam reforming of methanol reaction.

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**Table 5.3** Surface areas of Cu/ZnO catalysts calcined by various conditions.

| <b>Cu/ZnO catalyst</b>        | <b>BET surface area (m<sup>2</sup>/g)</b> |
|-------------------------------|---|
| <b>H<sub>2</sub>-calcined</b> | 0.9                                       |
| <b>N<sub>2</sub>-calcined</b> | 0.8                                       |
| <b>Air-calcined</b>           | 1.0                                       |
| <b>O<sub>2</sub>-calcined</b> | 0.7                                       |

### 5.3.1.3 N<sub>2</sub>O decomposition

It is known in the literature that methanol conversion over copper based catalysts during the steam reforming reaction greatly depends on the status copper, such as the dispersion and metal surface area. General catalyst is higher copper dispersion, showing better performance in methanol steam reforming. It is interesting for metallic copper to studies in this part. The metallic copper surface area obtained from N<sub>2</sub>O decomposition Table 5.4 demonstrates the surface area of metallic copper.

It was found that Cu/ZnO catalyst calcined by hydrogen, exhibits the highest active sites. From Table 5.4 indicate that atmospheric calcination have affect with Cu/ZnO catalyst.



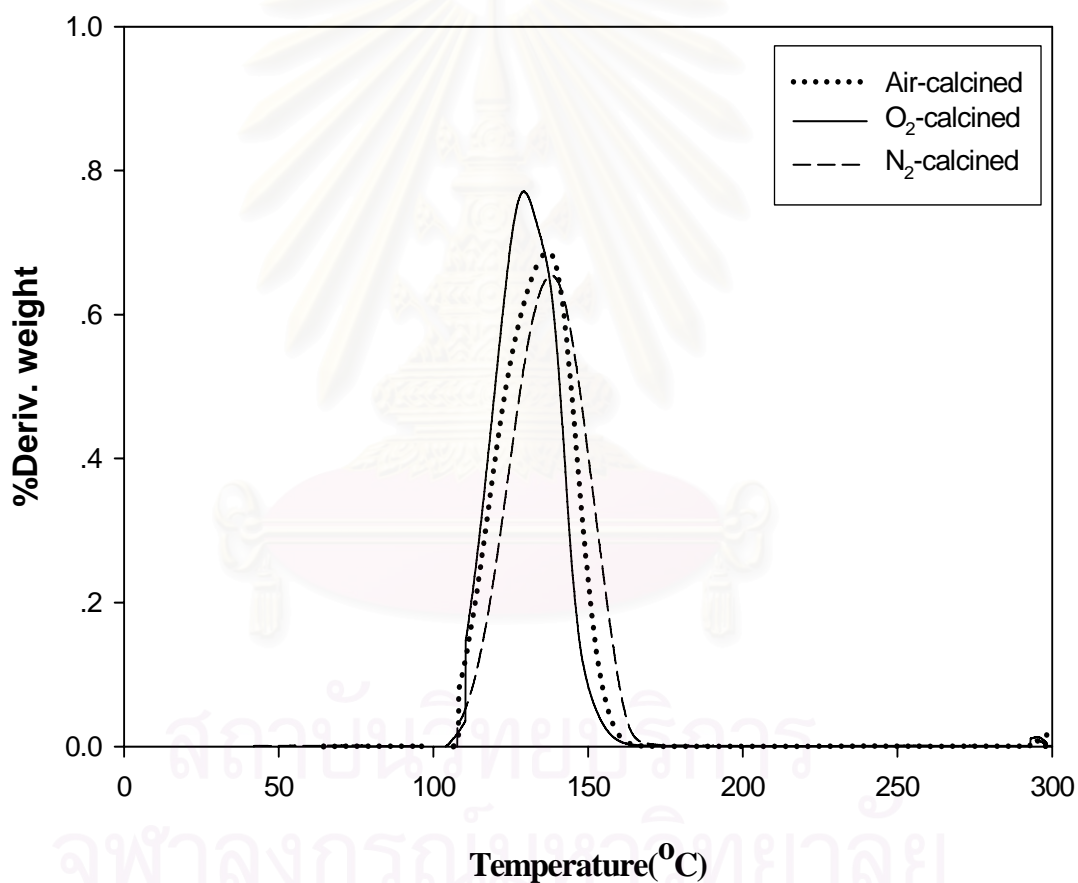
**Table 5.4** Cu surface area of Cu/ZnO catalysts calcined by various conditions.

| <b>Cu/ZnO catalyst</b>        | <b>Active sites*10<sup>19</sup> (molecule Cu<sup>0</sup>/g cat)</b> |
|-------------------------------|---|
| <b>H<sub>2</sub>-calcined</b> | 1.44  |
| <b>N<sub>2</sub>-calcined</b> | 0.62  |
| <b>Air-calcined</b>           | 0.38  |
| <b>O<sub>2</sub>-calcined</b> | 0.13  |

#### 5.3.1.4 Thermogravimetric and differential thermal analysis (TG/DTA)

The amount of copper in each state (Cu<sup>2+</sup>, Cu<sup>1+</sup> and Cu<sup>0</sup>) was determined by Thermal gravimetric and differential thermal analysis (TG/DTA). The TG/DTA thermodiagrams for the obtained Cu/ZnO catalyst are shown in Figure 5.13, which is to the reduction profiles of the Cu/ZnO catalysts calcined by various atmospherics. According to the TG analysis results, mass of the catalysts are calcined by various atmospherics (hydrogen, nitrogen, air and oxygen). The TG/DTA analysis shows the reduction of Cu/ZnO catalyst. All of the profiles show one main reduction peak, presumably due to the reduction of crystalline CuO, with a shoulder to the main peak identifiable at a lower temperature. This shoulder may be due to the reduction of amorphous or highly dispersed copper oxide species (Gunter et al. 2001). The Cu/ZnO catalyst was calcined by atmospheric oxygen, displaying the lowest reduction peak at 131°C. The Cu/ZnO catalyst was calcined by atmospheric air, which has a reduction peak at 136°C, and the Cu/ZnO catalyst was calcined by atmospheric nitrogen, required higher temperature of 138°C to attain a maximum copper oxide

reduction rate. From these results, the Cu/ZnO catalyst was calcined by atmospheric oxygen, which facilitates the reduction of copper oxide, and the Cu/ZnO catalyst was calcined by atmospheric nitrogen, which is hardly reduction, whereas the metallic copper surface area measurements of Cu/ZnO calcined by atmospheric nitrogen, is higher active sites. The results suggest agglomeration of CuO in calcination with nitrogen atmosphere has more effectively for methanol conversion than reduction temperature. Therefore, the agglomeration of CuO makes large CuO crystal size. The surface of agglomerated CuO is easier to access than that normal CuO.

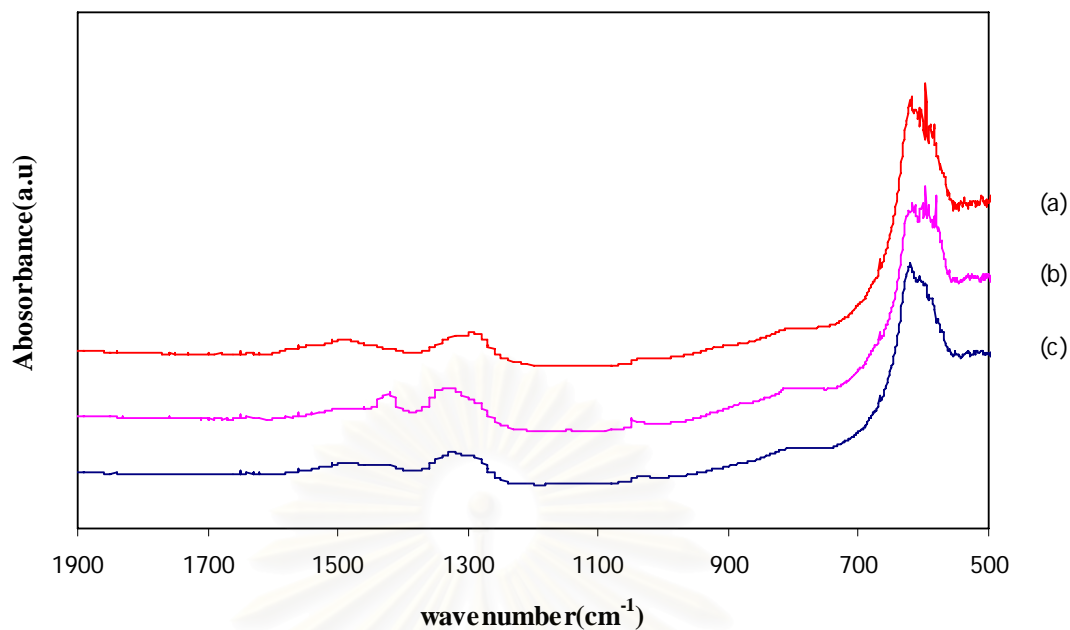


**Figure 5.13** TG/DTA thermodiagrams for the Cu/ZnO catalyst calcined by various conditions.

### 5.3.1.5 Fourier transform infrared spectroscopy (FT-IR)

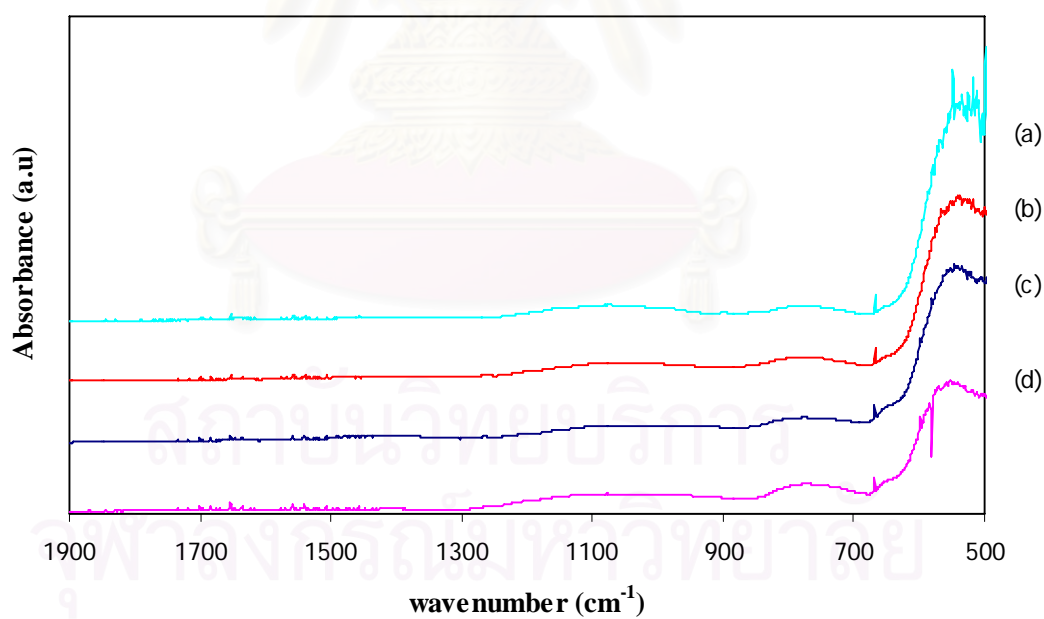
FT-IR analysis was carried out at room temperature, in an attempt to identify any intermediate adsorbed. FT-IR is well established as an analytical technique for functional group analysis. The results of Cu/ZnO catalysts are shown in Figure 5.14 and Figure 5.15, respectively. It should be noted that wavenumber of around 1300 and 1480  $\text{cm}^{-1}$  are assigned as the vibrational stretching bands of organic compound, while wavenumber at around 524  $\text{cm}^{-1}$  correspond to the stretching vibration of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  around 534  $\text{cm}^{-1}$  (Nagase et al. 1999). According to the FT-IR analysis, all distant bands of the Cu/ZnO catalysts were calcined by various conditions.

According to Figure 5.15, the Cu/ZnO catalysts are reduced by hydrogen. It was found that wavenumber of around 1300 and 1480  $\text{cm}^{-1}$  disappeared. Therefore, it is confirmed that the wavenumber around 1300 and 1480  $\text{cm}^{-1}$  are organic compound. The broad adsorption band was present at the wavenumber around 1500-1600  $\text{cm}^{-1}$ , which relates to stretching vibration of nitrate species. In this study the nitrate species was not observed.



**Figure 5.14** FT-IR of Cu/ZnO catalyst calcined by various conditions

- (a) Cu/ZnO air-calcined, (b) Cu/ZnO O<sub>2</sub>-calcined and  
(c) Cu/ZnO N<sub>2</sub>-calcined.

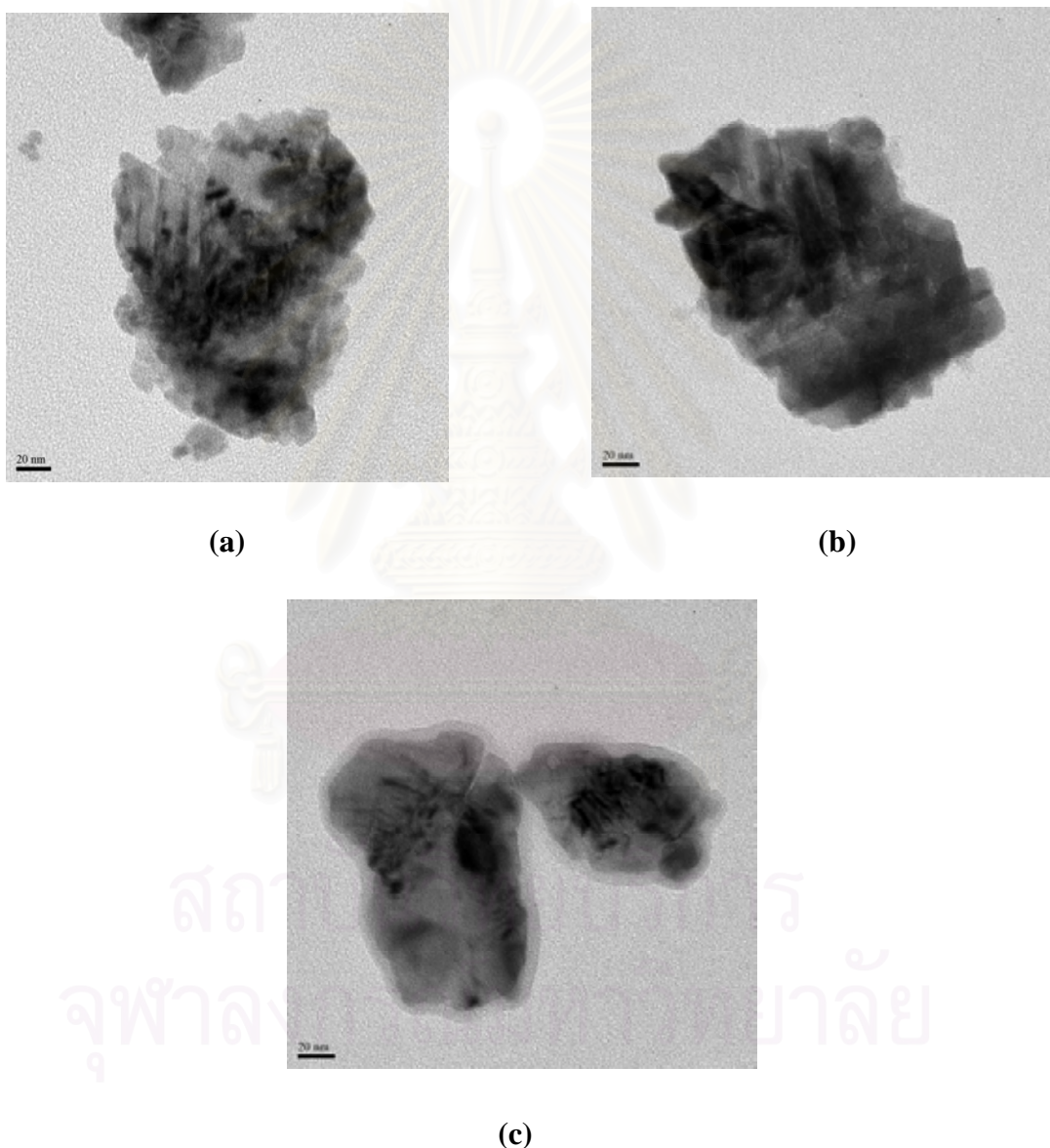


**Figure 5.15** FT-IR of Cu/ZnO catalyst catalyst calcined by various conditions

- (a) Cu/ZnO H<sub>2</sub>-calcined, (b) Cu/ZnO air-calcined, (c) Cu/ZnO  
N<sub>2</sub>-calcined and (d) Cu/ZnO O<sub>2</sub>-calcined.

### 5.3.1.6 Transmission electron microscopy (TEM)

TEM micrographs were taken so as to physically measure the size of the copper oxide and /or copper clusters, using Transmission Electron Microscopy (TEM) model TECNAI 20 TWIN model 200kv. TEM micrographs of Cu/ZnO catalysts were calcined by various conditions are shown in Figure 5.16



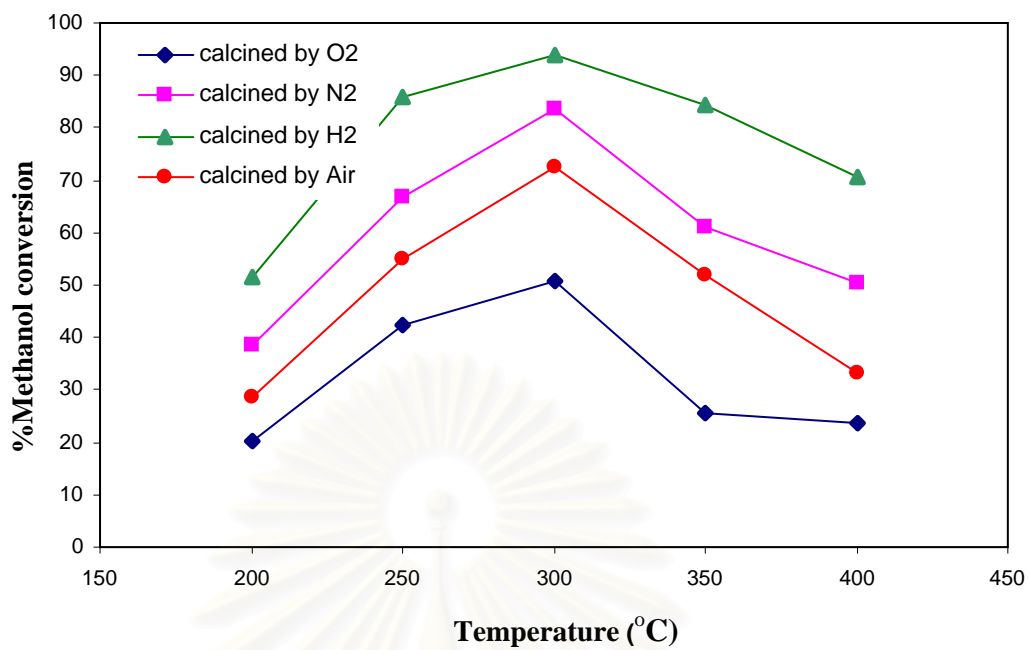
**Figure 5.16** TEM micrographs of (a) Cu/ZnO N<sub>2</sub>-calcined (b) Cu/ZnO Air-calcined and (c) Cu/ZnO O<sub>2</sub>-calcined. Magnification = 80,000x.

It was found that the Cu/ZnO catalyst prepared by homogeneous precipitation, calcined by various conditions, made catalyst (Cu/ZnO N<sub>2</sub>-calcined, Cu/ZnO Air-calcined and Cu/ZnO O<sub>2</sub>-calcined) had no significantly difference in the TEM images.

#### **5.4 The catalytic activity of Cu/ZnO catalyst calcined by various conditions.**

The effect of reaction temperature on the catalytic performance of Cu/ZnO catalysts is calcined by different conditions of calcination, illustrating in Figure 5.17. Note that all four catalysts show similar behavior. All of Cu/ZnO catalysts are higher methanol conversion at 300°C. Particularly, Cu/ZnO catalyst calcined by hydrogen, is very efficient in the steam reforming of methanol reaction, due to a higher metallic copper surface area. Moreover, catalytic activity decreased conversion of methanol over 350°C. Cu/ZnO catalysts were calcined by atmospheric nitrogen, air and oxygen. Atmospheric nitrogen caused crystalline size of Cu/ZnO catalyst, which had large crystalline size than Cu/ZnO catalysts calcined from atmospheric air and atmospheric oxygen. Consequently, catalytic activity of catalyst calcined by atmospheric nitrogen, showing high activity. This catalytic activity of steam reforming of methanol relates to X-ray diffraction XRD and N<sub>2</sub>O decomposition. Therefore, it confirmed that crystalline size of Cu influenced to activity of steam reforming of methanol. It was speculated that Cu active species was clustered, when calcined by various conditions. According to N<sub>2</sub>O decomposition, it was anticipated that hydrogen atmosphere clustered Cu active species more than the other atmospheres.





**Figure 5.17** Catalytic activity of Cu/ZnO catalyst calcined by various calcination conditions.

## CHAPTER VI

### CONCLUSIONS AND RECOMMADATIONS

#### 6.1 Conclusions

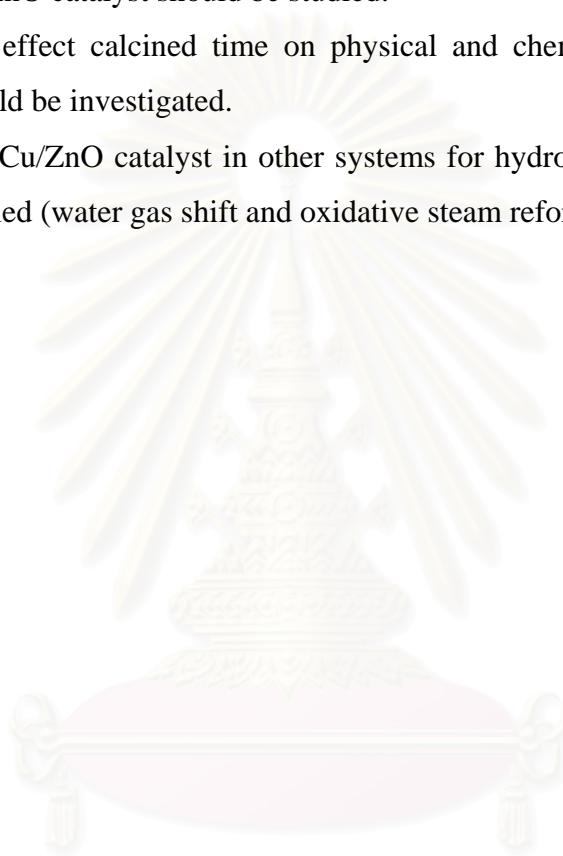
In this research, the various synthesis methods of Cu/ZnO catalysts and the calcination conditions on Cu/ZnO catalysts were investigated. The Cu/ZnO catalysts, synthesized using the homogeneous precipitation, co-precipitation and sol-gel technique were studied. A number of conclusions may be summarized as follows:

1. From N<sub>2</sub>O decomposition, it indicated that the high active sites of Cu/ZnO catalysts synthesized by various methods, which are high catalytic activity.
2. From figure 5.1, it showed that Cu/ZnO catalyst (Cu/Zn = 70/ 30) is the highest catalytic activity of the other ratios (Cu/Zn = 50/50 and 30/70) on steam reforming of methanol.
3. The homogeneous precipitation method is the best for the Cu/ZnO catalysts from this work for hydrogen production by steam reforming methanol. The high activities of the catalysts prepared by homogeneous precipitation method may be due to the highly copper metallic particles.
4. The calcination conditions of Cu/ZnO catalyst in diverse atmospheres, the atmospheres consist of N<sub>2</sub>-calcined, Air-calcined, O<sub>2</sub>-calcined and H<sub>2</sub>-calcined. In this study, the catalysts were calcined by hydrogen, is the highest catalytic activity.

## 6.2 Recommendations

From this experiment, we have expected to improve activity Cu/ZnO catalyst for hydrogen production. Recommendations for the future work are the following.

1. The effect of treatment of nitrous oxide on physical and chemical of Cu/ZnO catalyst should be studied.
2. The effect calcined time on physical and chemical of Cu/ZnO catalyst should be investigated.
3. The Cu/ZnO catalyst in other systems for hydrogen production should be applied (water gas shift and oxidative steam reforming of methanol etc.)



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**APPENDICES**

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## APPENDIX A

### CALCULATION FOR CATALYST PREPARATION

The calculation shown below is for Cu/ZnO catalyst.

Reagent: 1. Copper nitrate trihydrate,  $(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})$

Molecular weight = 241.63

2. Zinc nitrate hexahydrate,  $(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$

Molecular weight = 297.48

3. Sodium carbonate,  $(\text{Na}_2\text{CO}_3)$

Molecular weight = 105.99

Calculation for Cu/ZnO catalyst

$\text{Cu}(\text{NO}_3)_2$  1 M 50 ml

$\text{Zn}(\text{NO}_3)_2$  1 M 50 ml

$\text{Na}_2\text{CO}_3$  1 M ? ml



- Solution 1000 ml  $\text{Cu}(\text{NO}_3)_2$  1 mol

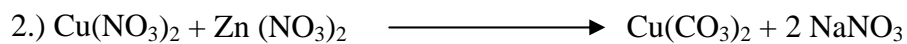
Solution 50 ml  $\text{Cu}(\text{NO}_3)_2$   $\frac{(50\text{ml})(1\text{mol})}{1000\text{ml}} = 0.05 \text{ mol}$

- 1 mol of  $\text{Cu}(\text{NO}_3)_2$  exactly react  $\text{NaNO}_3$  1 mol

0.05 mol of  $\text{Cu}(\text{NO}_3)_2$  exactly react  $\text{NaNO}_3$   $\frac{(0.05\text{mol})(1\text{mol})}{1\text{mol}} = 0.05 \text{ mol}$

- 1 mol  $\text{NaNO}_3$  1000 ml

0.05 mol  $\text{NaNO}_3$   $\frac{(1000\text{ml})(0.05\text{mol})}{1\text{mol}} = 50 \text{ ml}$



Because ratio Cu : Zn equal to 1 : 1

Cu(NO<sub>3</sub>)<sub>2</sub>     50 ml

Zn (NO<sub>3</sub>)<sub>2</sub>     50 ml

NaNO<sub>3</sub>            50 ml

Then, we use solution NaNO<sub>3</sub> = 50 +50 +50 = 150 ml

Calculation weight of Cu/ZnO

- CuO 1 mol has weight 79.546 g

CuO 0.05 mol has weight 79.546\*0.05 = 3.9773 g

- ZnO 1 mol has weight 81.37 g

CuO 0.05 mol has weight 81.37\*0.05 = 4.0685 g

Then, weight of Cu/ZnO = 3.9773+4.0685 = 8.045 g



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## APPENDIX B

### CALCULATION OF THE CRYSTALLITE SIZE

#### Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size was calculated from the half-height width of the diffraction peak of XRD pattern using the Debye-Scherrer equation.

From Scherrer equation:

$$D = \frac{\kappa \lambda}{\beta \cos \theta} \quad (\text{B.1})$$

- where
- D = Crystallite size, Å
  - K = Crystallite-shape factor = 0.9
  - $\lambda$  = X-ray wavelength, 1.5418 Å for CuK $\alpha$
  - $\theta$  = Observed peak angle, degree
  - $\beta$  = X-ray diffraction broadening, radian

The X-ray diffraction broadening ( $\beta$ ) is the pure width of a powder diffraction free from all broadening due to the experimental equipment.  $\alpha$ -Alumina is used as a standard sample to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening ( $\beta$ ) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta = \sqrt{B_M^2 - B_S^2} \quad (\text{B.2})$$

- Where
- $B_M$  = The measured peak width in radians at half peak height.
  - $B_S$  = The corresponding width of the standard material.



**Example:** Calculation of the crystallite size of Cu/ZnO

$$\begin{aligned} \text{The half-height width of peak} &= 0.465^\circ \text{ (from the figure B.1)} \\ &= (0.465 \times \pi) / 180 \\ &= 0.00811 \text{ radian} \end{aligned}$$

The corresponding half-height width of peak of  $\alpha$ -alumina (from the  $B_s$  value at the  $2\theta$  of  $38.6^\circ$  in figure B.2) = 0.0038 radian

$$\begin{aligned} \text{The pure width, } \beta &= \sqrt{B_M^2 - B_s^2} \\ &= \sqrt{0.00811^2 - 0.0038^2} \\ &= 0.006942 \text{ radian} \end{aligned}$$

$$B = 0.006942 \text{ radian}$$

$$2\theta = 38.6^\circ$$

$$\theta = 19.3^\circ$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\begin{aligned} \text{The crystallite size} &= \frac{0.9 \times 1.5418}{0.0069 \cos 19.3} = 223.9 \text{ \AA} \\ &= 22.3 \text{ nm} \end{aligned}$$

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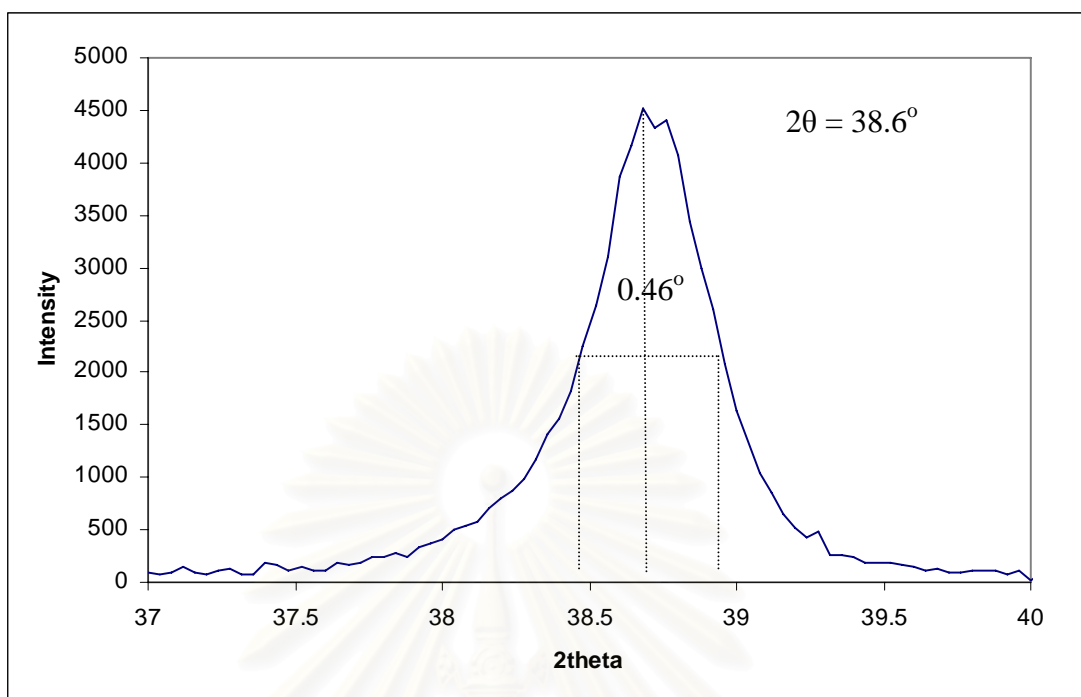


Figure B.1 The diffraction peak of Cu/ZnO for calculation of the crystallite size.

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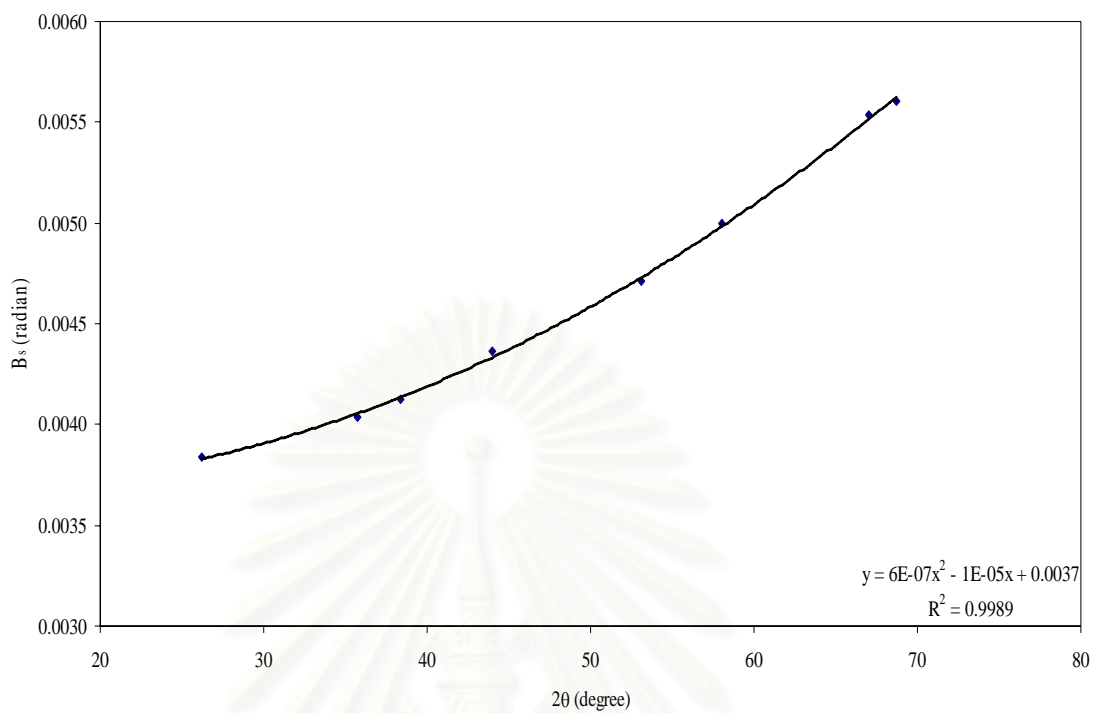


Figure B.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using  $\alpha$ -alumina as a standard.

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## APPENDIC C

### CALCULATION OF COPPER METAL ACTIVE SITE ON CATALYST

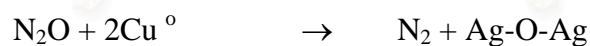
|   |   |  |       |
|---|---|--|-------|
| The weight of catalyst used                         | = | w  | g.    |
| Area of N <sub>2</sub> O peak afte adsorption       | = | A  | unit. |
| Average area of 1ml. standard N <sub>2</sub> O peak | = | B  | unit. |
| Amounts of N <sub>2</sub> O asorbed on catalyst     | = | $\sum(B-A)$                                    | unit. |
| Volume of N <sub>2</sub> O adsorbed on catalyst     | = | $[\sum(B-A)/B] \times 1$                       | ml.   |
| Volume of gas 1 mole at 30°C                        | = | $1.243 \times 10^6$                            | ml.   |
| Mole of N <sub>2</sub> O asorbed on catalyst        | = | $[[\sum(B-A)/B] \times [1/1.243 \times 10^6]]$ |       |

1 mole is  $6.02 \times 10^{23}$  molecule

Then, molecule of N<sub>2</sub>O adsorbed on catalyst

$$= 8.045 \times 10^{-7} \times [\sum(B-A)/B] \times 6.02 \times 10^{23}$$

1 molecule of N<sub>2</sub>O reacts with 2 molecule of silver metal as the equation



$$\text{Metal active site} = 4.84 \times 10^{17} \times [\sum(B-A)/B]/w \text{ molecule of Cu}^0/\text{g.cat}$$

## APPENDIX D

### CALIBRATION CURVES

This appendix showed the calibration curves for calculation of composition of reactant and products in steam reforming of methanol. The reactants are methanol and water. The products are hydrogen, carbon dioxide and carbon monoxide.

The thermal conductivity detector (TCD), gas chromatography Shimadzu modal 8AIT was used for analyzing the concentration of methanol, water and carbon mono oxide by using Parapak Q column. The other TCD, gas chromatography Shimadzu modal 8A was used for analyzing the concentration of hydrogen, carbon dioxide by using Molecular sieve 5A.

Mole of reagent in y-axis and area, which was reported by gas chromatography, in x-axis is exhibited in the curves. The calibration curves of methanol, water, hydrogen, carbon dioxide and carbon monoxide.

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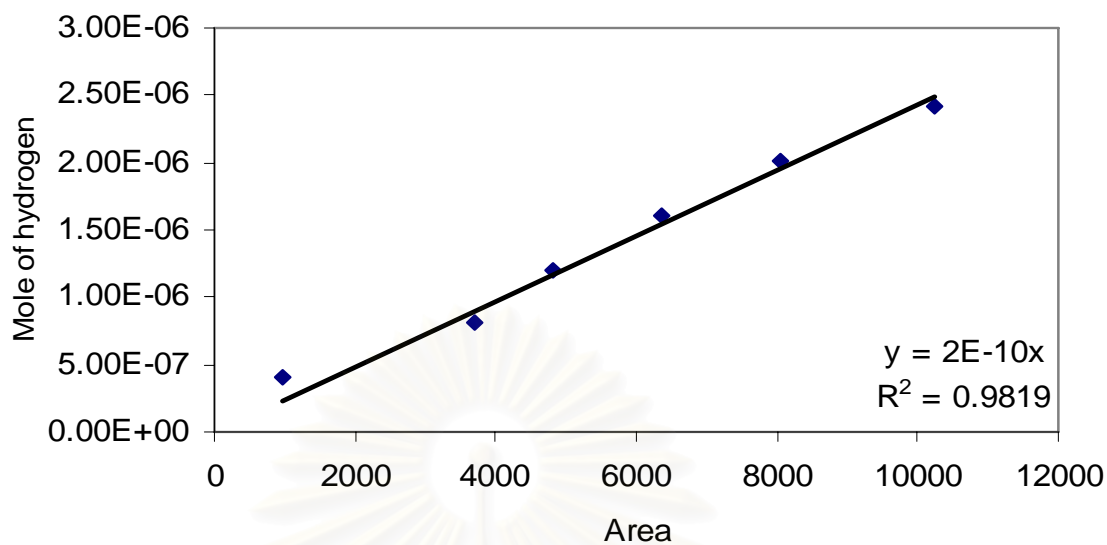


Figure D.1 The calibration curve of hydrogen.

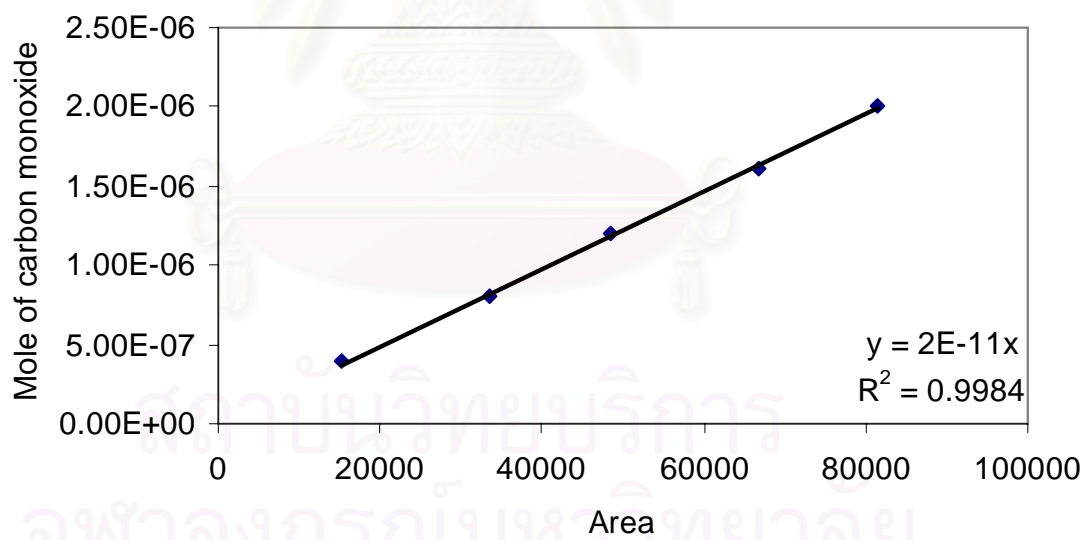


Figure D.2 The calibration curve of carbon monoxide.



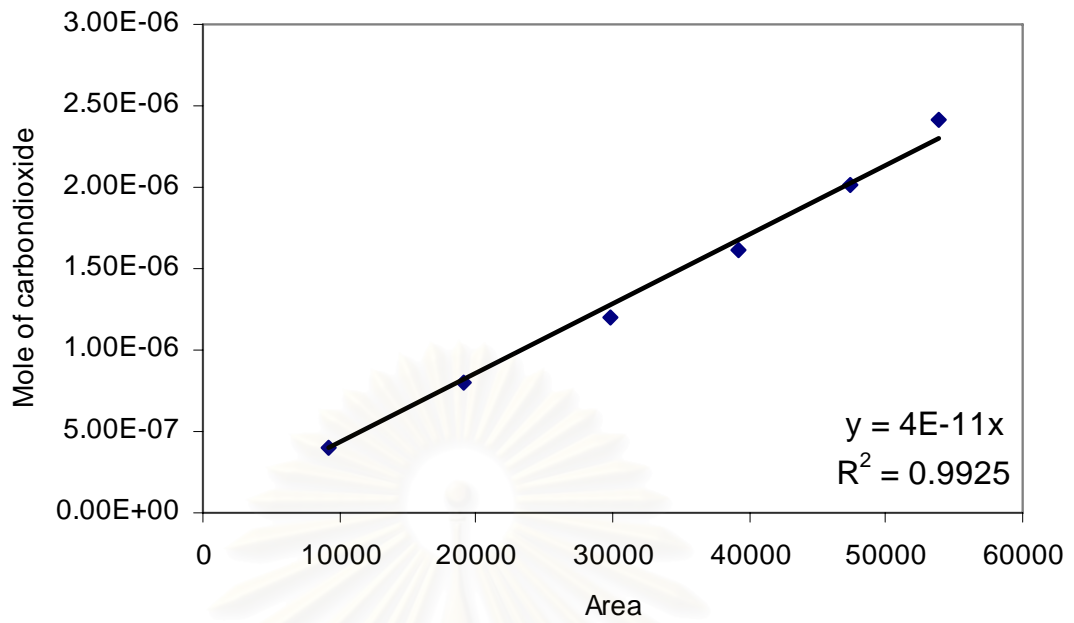


Figure D.3 The calibration curve of carbon dioxide.

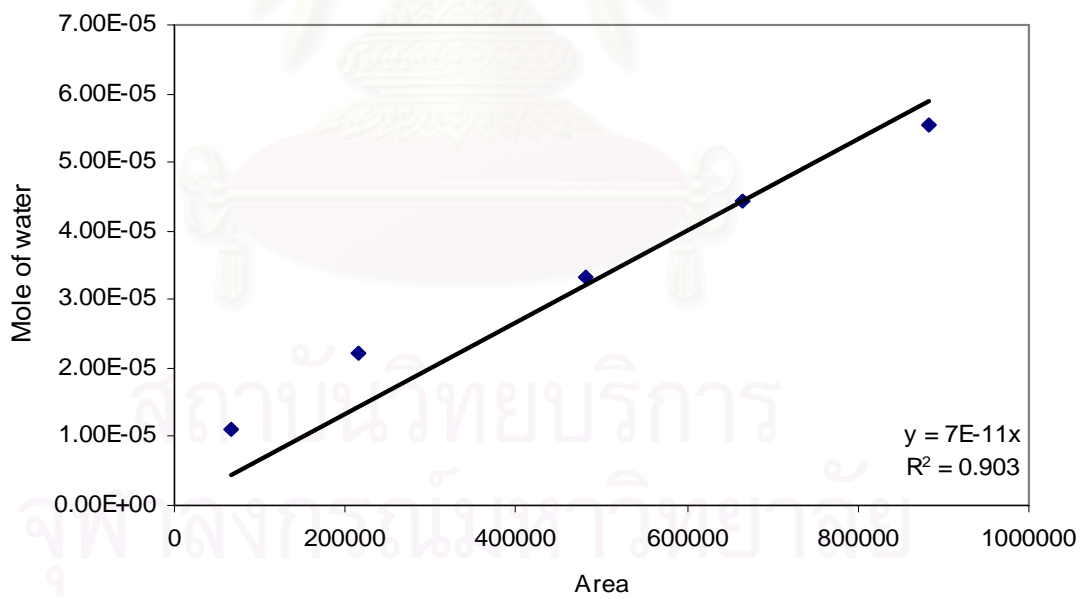


Figure D.4 The calibration curve of water.

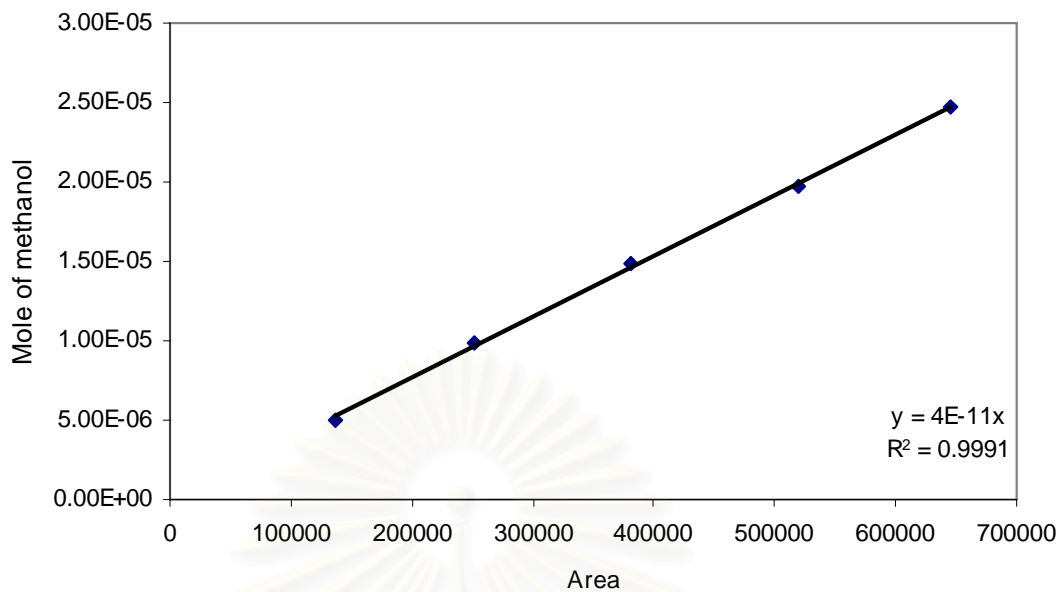


Figure D.5 The calibration curve of methanol.

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## APPENDIX E

### CALCULATION OF VAPOR PRESSURE

Antione equation :

$$\ln P = A - B / ( T + C ) \quad (1)$$

Define:            P = vapor pressure

A, B, C = constant value

T = temperature, (K)

Table E.1 Constant value of substance for calculation vapor pressure.

| Substance | A       | B       | C      |
|-----------|---------|---------|--------|
| Methanol  | 7.89750 | 1474.08 | 229.13 |
| Water     | 18.3036 | 3816.4  | -46.13 |

For methanol, substitute in Antione equation

$$\begin{aligned} \ln P &= 7.8975 - 1471.08 / ( (273+0) + 229.13) \\ &= 3.6963 \end{aligned}$$

$$= 40.2998 \text{ mmHg}$$

$$\text{Pressure from tank} = 15 \text{ psig} = 775.725 \text{ mmHg}$$

$$\text{Volume of methanol} = 40.2998 / 775.725$$

$$= 5.20 \%$$

## APPENDIX F

### DATA OF STEAM REFORMING OF METHANOL

**Table F.1** Data of Empty reactor.

| Area    | Water    | Methanol |
|---------|----------|----------|
| 1       | 85134    | 101349   |
| 2       | 91238    | 105794   |
| 3       | 85816    | 107217   |
| Average | 87396    | 104787   |
| Mole    | 6.12E-06 | 4.19E-06 |

**Data of methanol:**

**Table F.2** Data of methanol of Cu/ZnO (30/70) catalyst prepared by homogeneous precipitation.

| Temperature<br>(°C) | Area  |   | Average | %conversion |
|---------------------|-------|---|---------|-------------|
|                     | 1     | 2 |         |             |
| 200                 | 97155 | 0 | 97155   | 7.28        |
| 250                 | 79738 | 0 | 73738   | 23.9        |
| 300                 | 67640 | 0 | 67640   | 35.45       |
| 350                 | 54618 | 0 | 14618   | 47.88       |
| 400                 | 93124 | 0 | 93124   | 20.33       |

**Table F.3** Data of methanol of Cu/ZnO (50/50) catalyst prepared by homogeneous precipitation.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 69705 | 64781 | 97155   | 33.48       |
| 250                 | 22817 | 23868 | 73738   | 78.23       |
| 300                 | 7915  | 9791  | 67640   | 88.91       |
| 350                 | 11623 | 11645 | 14618   | 90.45       |
| 400                 | 93124 | 53266 | 93124   | 58.48       |

**Table F.4** Data of methanol of Cu/ZnO (70/30) catalyst prepared by homogeneous precipitation.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 55602 | 50151 | 52876.5 | 49.54       |
| 250                 | 8936  | 8577  | 8756.5  | 91.64       |
| 300                 | 0     | 1446  | 723     | 99.31       |
| 350                 | 0     | 500   | 250     | 99.76       |
| 400                 | 0     | 0     | 0       | 100.00      |

**Table F.5** Data of methanol of Cu/ZnO (30/70) catalyst prepared by sol-gel technique.

| Temperature<br>(°C) | Area   |       | Average | %conversion |
|---------------------|--------|-------|---------|-------------|
|                     | 1      | 2     |         |             |
| 200                 | 105000 | 98000 | 101500  | 3.14        |
| 250                 | 88871  | 89056 | 88964   | 15.10       |
| 300                 | 72000  | 72569 | 72285   | 31.02       |
| 350                 | 58560  | 55000 | 56780   | 45.81       |
| 400                 | 71003  | 72000 | 71502   | 31.76       |

**Table F.6** Data of methanol of Cu/ZnO (50/50) catalyst prepared by sol-gel technique.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 95000 | 94562 | 94781   | 9.55        |
| 250                 | 45871 | 44256 | 45064   | 57.00       |
| 300                 | 22000 | 25236 | 23618   | 77.46       |
| 350                 | 14560 | 15000 | 14780   | 85.90       |
| 400                 | 42000 | 45000 | 43500   | 58.49       |

**Table F.7** Data of methanol of Cu/ZnO (70/30) catalyst prepared by sol-gel technique.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 83667 | 95521 | 89594   | 14.50       |
| 250                 | 38806 | 38885 | 38846   | 62.93       |
| 300                 | 7503  | 7502  | 7503    | 92.84       |
| 350                 | 5252  | 5253  | 5252    | 94.99       |
| 400                 | 2100  | 2000  | 2100    | 98.00       |

**Table F.8** Data of methanol of Cu/ZnO (30/70) catalyst prepared by co-precipitation.

| Temperature<br>(°C) | Area   |       | Average | %conversion |
|---------------------|--------|-------|---------|-------------|
|                     | 1      | 2     |         |             |
| 200                 | 112687 | 91287 | 101987  | 2.67        |
| 250                 | 82563  | 82563 | 82563   | 21.21       |
| 300                 | 68987  | 66523 | 67755   | 35.34       |
| 350                 | 59263  | 58259 | 58761   | 43.92       |
| 400                 | 80563  | 80063 | 80313   | 23.36       |



**Table F.9** Data of methanol of Cu/ZnO (50/50) catalyst prepared by co-precipitation.

| Temperature<br>(°C) | Area   |        | Average  | %conversion |
|---------------------|--------|--------|----------|-------------|
|                     | 1      | 2      |          |             |
| 200                 | 129311 | 139311 | 134311   | 12.18       |
| 250                 | 109390 | 108843 | 109116.5 | 28.66       |
| 300                 | 43100  | 45300  | 44200    | 71.10       |
| 350                 | 25386  | 35036  | 30211    | 80.25       |
| 400                 | 78000  | 78500  | 78250    | 48.84       |

**Table F.10** Data of methanol of Cu/ZnO (70/30) catalyst prepared by co-precipitation.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 81265 | 82171 | 81718   | 22.01       |
| 250                 | 65567 | 65403 | 65485   | 37.51       |
| 300                 | 19449 | 16269 | 17859   | 82.96       |
| 350                 | 0     | 9977  | 9977    | 90.48       |
| 400                 | 5000  | 5077  | 5077    | 95.69       |

**Table F.11** Data of methanol of Cu/ZnO catalyst calcined by nitrogen.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 78775 | 78756 | 78765.5 | 39.84       |
| 250                 | 33780 | 53200 | 43490   | 66.78       |
| 300                 | 24292 | 24546 | 24419   | 81.35       |
| 350                 | 52317 | 52264 | 52290.5 | 60.06       |
| 400                 | 60326 | 68373 | 64349.5 | 50.85       |

**Table F.12** Data of methanol of Cu/ZnO catalyst calcined by air.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 84943 | 63580 | 74261.5 | 28.53       |
| 250                 | 45110 | 48444 | 46777   | 54.98       |
| 300                 | 26085 | 31324 | 28704.5 | 72.38       |
| 350                 | 41558 | 58568 | 50063   | 51.82       |
| 400                 | 60999 | 78090 | 69544.5 | 33.07       |

**Table F.13** Data of methanol of Cu/ZnO catalyst calcined by oxygen.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 78775 | 78756 | 78765.5 | 39.84       |
| 250                 | 33780 | 53200 | 43490   | 66.78       |
| 300                 | 24292 | 24546 | 24419   | 81.35       |
| 350                 | 52317 | 52264 | 52290.5 | 60.06       |
| 400                 | 60326 | 68373 | 64349.5 | 50.85       |

**Table F.14** Data of methanol of Cu/ZnO catalyst calcined by hydrogen.

| Temperature<br>(°C) | Area  |       | Average | %conversion |
|---------------------|-------|-------|---------|-------------|
|                     | 1     | 2     |         |             |
| 200                 | 63548 | 63580 | 63564   | 51.45       |
| 250                 | 18322 | 19528 | 18925   | 85.55       |
| 300                 | 8396  | 7261  | 7828.5  | 94.02       |
| 350                 | 20304 | 20626 | 20465   | 84.37       |
| 400                 | 36832 | 39832 | 38332   | 70.72       |

## APPENDIX G

### DATA OF N<sub>2</sub>O DECOMPOSITION

Data of Cu surface area:

**Table G.1** Data of Cu surface area of Cu/ZnO (70/30) catalyst prepared by homogeneous precipitation.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 22201             | 8556        | 13702.5              |
| 22316             | 7719        | 14539.5              |
| Average = 22258.5 | 5133        | 17125.5              |
|                   | 4127        | 18131.5              |
|                   | 7807        | 14451.5              |
|                   | 7532        | 14726.5              |
|                   | 7675        | 14583.5              |

Weight catalyst = 0.1009 g

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**Table G.2** Data of Cu surface area of Cu/ZnO (50/50) catalyst prepared by homogeneous precipitation.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 21458             | 8556        | 13702.5              |
| 21819             | 7719        | 14539.5              |
| Average = 21638.5 | 5133        | 17125.5              |
|                   | 4127        | 18131.5              |
|                   | 7807        | 14451.5              |
|                   | 7532        | 14726.5              |
|                   | 7675        | 14583.5              |

Weight catalyst = 0.1011 g

**Table G.3** Data of Cu surface area of Cu/ZnO (30/70) catalyst prepared by homogeneous precipitation.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 26163             | 13793       | 12733.5              |
| 26890             | 10903       | 15623.5              |
| Average = 21638.5 | 13566       | 12960.5              |
|                   | 14109       | 12417.5              |

Weight catalyst = 0.1013 g

**Table G.4** Data of Cu surface area of Cu/ZnO (70/30) catalyst prepared by sol-gel technique.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 22595             | 9179        | 12842.5              |
| 21448             | 9179        | 12842.5              |
| Average = 22021.5 | 8531        | 13490.5              |
|                   | 7571        | 14450.5              |
|                   | 12411       | 12598.33             |
|                   | 12158       |                      |
|                   | 13226       |                      |

Weight catalyst = 0.1014 g

**Table G.5** Data of area of Cu/ZnO (50/50) catalyst prepared by sol-gel technique.

| Standard Area   | Sample area | Std area-Sample area |
|-----------------|-------------|----------------------|
| 21514           | 12413       | 9306                 |
| 21924           | 10748       | 10971                |
| Average = 21719 | 8203        | 13516                |
|                 | 8293        | 13426                |
|                 | 11819       | 9900                 |
|                 | 12201       | 9518                 |

Weight catalyst = 0.1018 g

**Table G.6** Data of area of Cu/ZnO (30/70) catalyst prepared by sol-gel technique.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 21909             | 12079       | 9492.5               |
| 21234             | 9068        | 12503.5              |
| Average = 21571.5 | 13142       | 8429.5               |
|                   | 13370       | 8201.5               |

Weight catalyst = 0.1012 g

**Table G.7** Data of Cu surface area of Cu/ZnO (70/30) catalyst prepared by co-precipitation.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 21097             | 10088       | 12278.5              |
| 23636             | 8792        | 13574.5              |
| Average = 22366.5 | 11625       | 10741.5              |
|                   | 11633       | 10733.5              |
|                   | 12256       | 12875.3              |
|                   | 13338       |                      |
|                   | 13032       |                      |

Weight catalyst = 0.1011 g



**Table G.8** Data of Cu surface area of Cu/ZnO (50/50) catalyst prepared by co-precipitation.

| Standard Area   | Sample area | Std area-Sample area |
|-----------------|-------------|----------------------|
| 20113           | 10170       | 10245                |
| 20717           | 9970        | 10445                |
| Average = 20415 | 11302       | 9113                 |
|                 | 11706       | 8709                 |
|                 | 12736       | 7679                 |

Weight catalyst = 0.1009 g

**Table G.9** Data of Cu surface area of Cu/ZnO (50/50) catalyst prepared by co-precipitation.

| Standard Area   | Sample area | Std area-Sample area |
|-----------------|-------------|----------------------|
| 20054           | 12807       | 7482                 |
| 20524           | 12037       | 8252                 |
| Average = 20289 | 12118       | 8171                 |
|                 | 16939       | 3350                 |
|                 | 15987       | 4302                 |

Weight catalyst = 0.1017 g

**Table G.10** Data of Cu surface area of Cu/ZnO catalyst calcined by hydrogen.

| Standard Area   | Sample area | Std area-Sample area |
|-----------------|-------------|----------------------|
| 22114           | 17922       | 4299                 |
| 22328           | 17743       | 4478                 |
| Average = 22221 | 16468       | 5753                 |
|                 | 15769       | 6452                 |
|                 | 15172       | 7049                 |
|                 | 12379       | 9842                 |
|                 | 10323       | 11898                |
|                 | 8547        | 13674                |
|                 | 22019       | 202                  |
|                 | 20964       | 1257                 |
|                 | 20909       | 1312                 |

Weight catalyst = 0.1004 g

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**Table G.11** Data of Cu surface area of Cu/ZnO catalyst calcined by nitrogen.

| Standard Area   | Sample area | Std area-Sample area |
|-----------------|-------------|----------------------|
| 24962           | 21332       | 3485                 |
| 24672           | 21025       | 3792                 |
| Average = 24817 | 19876       | 4941                 |
|                 | 19503       | 5314                 |
|                 | 19048       | 5769                 |
|                 | 18782       | 6035                 |
|                 | 23685       | 1132                 |
|                 | 23691       | 1126                 |

Weight catalyst = 0.1002 g

**Table G.12** Data of Cu surface area of Cu/ZnO catalyst calcined by air.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 69449             | 66318       | 2574.5               |
| 68336             | 68141       | 751.5                |
| Average = 68892.5 | 67780       | 1112.5               |
|                   | 65893       | 2999.5               |
|                   | 68619       | 273.5                |
|                   | 68410       | 482.5                |

Weight catalyst = 0.1001 g

**Table G.13** Data of Cu surface area of Cu/ZnO catalyst calcined by oxygen.

| Standard Area     | Sample area | Std area-Sample area |
|-------------------|-------------|----------------------|
| 31265             | 32123       | 255.5                |
| 33492             | 30834       | 1544.5               |
| Average = 32378.5 | 30365       | 2013.5               |
|                   | 30332       | 2046.5               |
|                   | 31945       | 433.5                |
|                   | 31501       | 877.5                |
|                   | 31068       | 1310.5               |

Weight catalyst = 0.1004 g

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## APPENDIX H

### LIST OF PUBLICATIONS

1. Siravit Chotisubadchana, Piyasan Prasertdam and Somchai Akaratiwa  
“The effect of preparation method on the properties of Cu/ZnO catalyst in steam reforming of methanol for hydrogen production”, Regional Symposium on Chemical Engineering, Singapore, December 3-5, 2006.



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# The effect of preparation method on the properties of Cu/ZnO catalyst in steam reforming of methanol for hydrogen production

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## ABSTRACT

Several methods (sol-gel method, co-precipitation, homogeneous-precipitation) have been comparatively examined for the preparation of binary Cu/ZnO-based catalysts with Cu/Zn molar ratio in 70/30, 50/50 and 30/70 copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) and zinc acetate ( $\text{zinc}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and ethanol were used as precursor for preparation of Cu/ZnO catalyst by sol-gel method. For co-precipitation method were prepared by the addition rate of a mixed copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) and zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) solution with a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution. For homogeneous precipitation method were prepared by urea instead of  $\text{Na}_2\text{CO}_3$  solution. All Cu/ZnO catalyst were applied for the catalytic production of hydrogen by steam reforming of methanol (SRM). Physical and chemical properties of Cu/ZnO catalyst were characterized by various techniques including X-ray diffraction (XRD), BET surface area,  $\text{N}_2\text{O}$  chemisorption, and scanning electron micrograph (SEM).

## INTRODUCTION

Cu/ZnO catalyst has been recognized as one of the most important steam reforming of methanol. Its steam reforming of methanol activity is enhanced because it is high dispersion Cu. Cu/ZnO catalysts can be synthesized by many techniques. In this work, sol-gel method, co-precipitation, and homogeneous-precipitation, which have been used to preparation catalyst. Those methods have been proved in our preliminary work to result in Cu/ZnO with activity for steam reforming of methanol. Cu/ZnO catalyst have been used to product hydrogen, but hydrogen is difficultly in storage and transportation. One solution of these problem is hydrogen generate form a suitable liquid fuel of high energy density. The advantages of high energy density, easy availability, safe handling and storage are now making methanol one of the most promising sources of hydrogen. The steam reforming of methanol can produce the highest hydrogen concentration and low concentration CO, hence minimizing the risk problems for coke. In this work, we have compared Cu/ZnO catalysts, which have been prepared by sol-gel method, co-precipitation and homogeneous-precipitation, which will improve Cu/ZnO catalyst formulations and preparation procedures for the highest hydrogen.

## MATERIALS AND METHODS

Cu/ZnO catalysts were synthesized according to procedures described in detail in our previous work [1,2]. Copper acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) and zinc acetate ( $\text{zinc}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and ethanol were used as precursor for preparation of Cu/ZnO catalyst by sol-gel method. Those mixture were refluxed for 1 hour at 80 °C. For co-precipitation method were prepared by the addition rate of a mixed copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) and zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) solution with a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) under magnetic stirring for 90 minutes. For homogeneous precipitation method were prepared by urea under magnetic stirring for 90 minutes at 90 °C. The obtained Cu/ZnO catalysts were then calcined at 300°C for 3 h. The characterization of powder included X-ray diffraction (XRD), scanning electron microscope (SEM), surface area measurement via BET method and  $\text{N}_2\text{O}$  chemisorption.

For the steam reforming of methanol experiments, 3 mg of Cu/ZnO catalyst was reduced at 250°C for 1 hour. The steam reforming of methanol reaction was initiated by mixing the reactant between methanol and water. This reaction of the Cu/ZnO catalysts obtained is evaluated by using temperature of reaction at 200-350 °C.

## RESULTS AND DISCUSSION

The XRD analysis of the obtained powder confirmed that the product was Cu/ZnO catalyst phase without contamination from others. The crystallite size of all samples calculated from the Scherrer equation was approximately 4 nm, regardless of the solvent employed during method synthesis. Surface area of all Cu/ZnO catalyst was also found to be roughly equal (c.a. 3-20 m<sup>2</sup>/g). XRD analysis suggested that the product synthesized in different method had different degree of crystallinity. Cu/ZnO catalyst prepared by homogenous-precipitation method, which showed sign of very high crystallinity, was suggested to be a collection of Cu single crystals. On the contrary, for Cu/ZnO catalyst was synthesized by sol-gel method and co-precipitation, which indicated remaining crystallinity phase was observed, but their crystallinity were lower than crystallinity of Cu/ZnO catalyst prepared by homogenous-precipitation method.

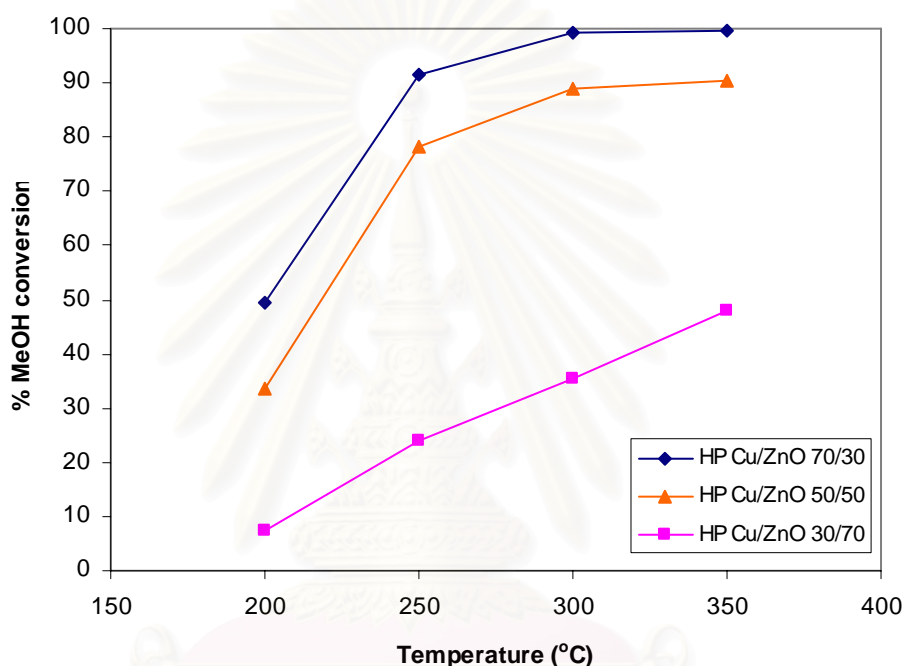


Figure 1. Activity and selectivity for steam reforming of methanol over Cu/ZnO catalysts.

According to figure 1, steam reforming of methanol experiments confirms that type of ratio between copper oxide and zinc oxide influences the catalytic activity of the obtained Cu/ZnO catalyst. It was found that Cu/ZnO composed of 70 mole% Cu exhibited higher activity than other compositions. The result from the steam reforming of methanol was increased conversion of methanol with increasing temperature. Above all, it is quite clear that Cu/ZnO synthesized in homogenous-precipitation method has high catalytic activity.

## CONCLUSION

Cu/ZnO catalyst can be synthesized via the homogenous-precipitation method. Moreover, crystallinity of the obtained Cu/ZnO catalyst depend upon synthesized method. Consequently, steam reforming of methanol activity of Cu/ZnO is greatly affected. Cu/ZnO were prepared by those methods show potential for the productive hydrogen.

## REFERENCE

- [1] Shishido, T., Y. Yamamoto, et al. (2004).. Active Cu/ZnO and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by homogeneous precipitation method in steam reforming of methanol." *Applied Catalysis A : General* 263: 249-253.
- [2] M.K.Hossain, S. C. Ghosh, et al. (2003). . *Growth of zinc oxide nanowires and nano belts for gas sensing applications*. *Microelectronics*. Pathumthani, Asian institute of technology.



## VITA

Mr. Siravit Chodsubyachana was born on June 10, 1982 in Bangkok, Thailand. I received the Bachelor's Degree in Chemical Engineering from Department of Chemical Engineering, Faculty of Engineering, Mahanakorn University of Technology in November 2005, entered the Master of Engineering in Chemical Engineering at Chulalongkorn University in June, 2005.



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