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เทคนิคการเคลือบโดยใช้คาร์บอนไดออกไซด์ที่สภาวะเหนือวิกฤติ

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี   ภาควิชาวิศวกรรมเคมี

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ปีการศึกษา 2549

PREPARATION OF Cu/ZnO AND Cu/TiO$_2$ CATALYSTS VIA DEPOSITION
TECHNIQUE USING CRITICAL CARBON DIOXIDE

Mr. Sorathorn   Wattanamalachai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
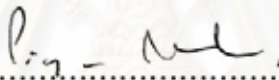Chulalongkorn University
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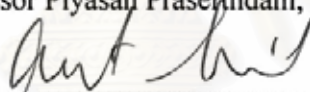
Thesis Title   PREPARATION OF Cu/ZnO AND Cu/TiO$_2$ CATALYSTS
                 VIA DEPOSITION TECHNIQUE USING SUPERCRITICAL
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By   Mr. Sorathorn   Wattanamalachai
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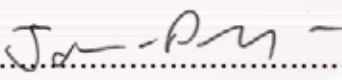Thesis Advisor   Akawat Sirisuk, Ph.D.

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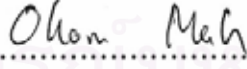
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สรธร วัฒนามาลาชัย : การเตรียมตัวเร่งปฏิกิริยาคอปเปอร์บนซิงค์ออกไซด์และ คอปเปอร์บนไททาเนียด้วยเทคนิคการเคลือบโดยใช้คาร์บอนไดออกไซด์ที่สภาวะเหนือวิกฤติ (PREPARATION OF Cu/ZnO AND Cu/TiO₂ CATALYSTS VIA DEPOSITION TECHNIQUE USING CRITICAL CARBON DIOXIDE) อ. ที่ปรึกษา: ดร.อัครวัต ศิริสุข, 46 หน้า

เราทำการศึกษาวิธีการเตรียมตัวเร่งปฏิกิริยา Cu/ZnO และ Cu/TiO₂ วิธีใหม่โดยการนำคาร์บอนไดออกไซด์ที่สภาวะเหนือวิกฤตมาใช้แทนตัวทำละลายโดยใช้เพื่อละลายสารประกอบของทองแดงแล้วนำไปเคลือบบน ZnO และ TiO₂ ที่ใช้เป็นตัวรองรับ ตัวเร่งปฏิกิริยาทั้งสองประเภทที่เตรียมได้นำไปวิเคราะห์ด้วยเทคนิคต่างๆ เช่น เอ็กซเรย์ดิแฟรคโตมิเตอร์ (XRD) การดูดซับไนโตรเจนทางกายภาพ อินดักทีฟคูเปิลพลาสมาอะตอมมิคอิมิชชันสเปคโตรสโคปี (ICP) และการดูดซับทางเคมีจากนั้น Cu/ZnO และ Cu/TiO₂ ใช้เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาออกซิเดชันของคาร์บอนมอนอกไซด์พบว่าตัวเร่งปฏิกิริยา Cu/ZnO และ Cu/TiO₂ เตรียมจากเทคนิคการเคลือบโดยใช้คาร์บอนไดออกไซด์ที่สภาวะเหนือวิกฤต และเมทานอลจะมีความว่องไวในการเกิดปฏิกิริยาออกซิเดชันของคาร์บอนมอนอกไซด์สูงกว่าตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีการเคลือบฝังเนื่องจากมีการกระจายตัวของทองแดงบนตัวรองรับสูงกว่าจากการใช้คาร์บอนไดออกไซด์ที่สภาวะเหนือวิกฤตแทนตัวทำละลาย ส่วนตัวเร่งปฏิกิริยา Cu/ZnO และ Cu/TiO₂ ที่เตรียมจากเทคนิคการเคลือบโดยใช้คาร์บอนไดออกไซด์ที่สภาวะเหนือวิกฤต และสารประกอบที่มีซัลเฟอร์อยู่ (Cyanex 301) จะมีความว่องไวในการเกิดปฏิกิริยาออกซิเดชันของคาร์บอนมอนอกไซด์ต่ำมาก เนื่องจากตัวเร่งปฏิกิริยาเกิดการเสื่อมสภาพ เพราะสารอินทรีย์ยังคงหลงเหลืออยู่บนตัวรองรับ

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KEY WORD: TITANIUM (IV) OXIDE / ZINC OXIDE / SUPERCRITICAL CARBON DIOXIDE

SORATHORN WATTANAMALACHAI: PREPARATION OF Cu/ZnO AND Cu/TiO$_2$ CATALYSTS VIA DEPOSITION TECHNIQUE USING CRITICAL CARBON DIOXIDE. THESIS ADVISOR: AKAWAT SIRISUK, Ph.D, 46 pp.

A novel method for preparation of Cu/ZnO and Cu/TiO$_2$ catalysts using supercritical carbon dioxide was investigated. Supercritical carbon dioxide was employed as a solvent to dissolve the copper compound. The dissolved compound was then used to deposit the metal on ZnO and TiO$_2$ support. Both ZnO and TiO$_2$ supports were synthesized by a solvothermal method using 1,4-butanediol as a solvent.

The catalysts were characterized by various techniques, including X-ray diffractometer, nitrogen physisorption, inductively-coupled plasma atomic emission spectroscopy, and chemisorption. Cu/ZnO and Cu/TiO$_2$ were then employed as catalysts for oxidation of CO. Both Cu/ZnO and Cu/TiO$_2$ catalysts that were prepared by deposition technique using supercritical carbon dioxide and methanol exhibited higher activities for oxidation of CO than the catalysts that were prepared by incipient wetness impregnation technique. This could be attributed to higher dispersion of copper on the supports brought about by the use of supercritical carbon dioxide. Cu/ZnO and Cu/TiO$_2$ catalysts that were prepared by deposition technique using supercritical carbon dioxide and a sulfer-containing compound, Cyanex 301, exhibited very low activities for oxidation of CO due to poisoning of the catalysts caused by remaining organics on the surface of the catalysts.

Department........Chemical Engineering….. Student's signature....Sorathorn..........

Field of study....Chemical Engineering….. Advisor's signature................

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CHAPTER I

INTRODUCTION

At present, environment and energy saving are hot topics. In catalysis field, there are numerous attempts to develop green processes that produce less waste and consume less energy. Preparation of catalyst usually involves a number of chemicals and solvents, which can become hazardous waste afterwards. A better alternative would be to prepare the catalysts by using non-toxic or environmentally benign chemicals and solvents.

Supercritical carbon dioxide or water has been widely used as a solvent in biochemical or biological application [Jun et al., 2006, Zaidul et al., 2006]. Supercritical fluids possess properties that are intermediate between gases and liquids, which can be adjusted by manipulation of temperature and pressure. The dissolving properties of supercritical fluids have been extensively studied and supercritical CO_2 is the most commonly used as a solvent because it is inexpensive, nontoxic, nonflammable, nonpolluting, and has favorable critical constants ($T_c = 31.1\ ^{o}C$ and $P_c = 7.38$ MPa). To utilize the good dissolving properties of supercritical CO_2, supercritical CO_2 is used to extract heavy metal [Koh et al., 2005].

Several metals, many of which can act as catalysts, can dissolve in supercritical CO_2. Therefore, one might be able to use supercritical CO_2 as a solvent to prepare supported metal catalyst, depending on how well the metal ion can dissolve in supercritical CO_2. Since supercritical CO_2 has a better diffusion inside small pores than water (typical solvent used in preparation of supported metal catalyst), one would expect a better dispersion of active metal on the support.

In this study, we are interested in copper as a metal catalyst. Two types of supports, namely, ZnO and TiO_2, are chosen. Cu/ZnO catalyst is widely employed in oxidation of CO. Several studies have shown that the preparation method of Cu/ZnO catalyst affects the size and dispersion of copper on ZnO support [Mallick et al., 2003]. As a result, these properties could influence the activity and selectivity of

Cu/ZnO catalyst in various reactions [Deraz et al., 2001]. Therefore, preparation of Cu/ZnO catalyst by using supercritical CO_2 as a solvent appears to be a promising method for preparation of the catalyst that may exhibit high performance in the reaction of interest, i.e., CO oxidation.

Objectives of the research:

1. To investigate the deposition of copper on metal oxide support using supercritical carbon dioxide as a solvent.
2. To compare the catalysts prepared using supercritical CO_2 with the ones prepared via incipient wetness impregnation in terms of physical properties and catalytic activities.

The thesis is arranged as follows:

Chapter I is the introduction of this work.

Chapter II presents literature reviews for the extraction of heavy metal using supercritical carbon dioxide and oxidation of CO.

Chapter III presents theory of supercritical fluid and supercritical carbon dioxide.

Chapter IV describes various preparation method for Cu/ZnO and Cu/TiO_2 catalysts and characterization techniques for the catalyst.

Chapter V presents the experimental results and discussion of the research.

In the last chapter, Chapter VI, the overall conclusions and recommendations for the future studies are given.

CHAPTER II

LITERATURE REVIEWS

Koh and coworkers [2005] investigated the synergistic effect of organophosphorus and dithiocarbamate ligands on metal extraction in supercritical CO_2. Cyanex 272 and diethylamine (DEA) were employed as chelating agents to extract Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}. The metal complexes in the original from the amount extracted increase by 10% were insoluble in supercritical CO_2. However, when Cyanex 272 was added, extraction increased by 30%. When both Cyanex 272 and DEA were added extraction increased by 90%. This is because Cyanex 272 was a more effective extractant of metal ions at pH larger than 6, a condition that was achieved by addition of DEA

Liu and coworkers [2001] explored a new strategy for supercritical CO_2 extraction of copper ion using benzoyl acetone as a chelating agent. The suitable condition for copper extraction is 25 MPa, 60 ^{o}C, and ten minutes of extraction time.

Smart and coworkers [1997] extracted of toxic heavy metals using supercritical fluid carbon dioxide dontaining organophosphorus reagents. Chelating agents used are Cyanex 272, Cyanex 301, Cyanex 302, Kelex 100, and D2EHTPA (bis(2-ethylhexyl) monothiophosphoric acid). Cyanex 301 was stable in supercritical $CO_2$and had a better performance in heavy metal extraction than Cyanex 302 because it contained more sulfur substitutes than Cyanex 302 and it gave rise to the highest solubility of copper complex in supercritical CO_2.

Lin and coworkers [2003] studied supercritical fluid extraction of toxic heavy metals and uranium from acidic solutions with sulfur-containing organophosphorus reagents. Cyanex 301 was employed as a chelating agent to extract Cd^{2+}, Cu^{2+}, Pb^{2+}, and Hg^{2+} at 300 atm and 60 ^{o}C in supercritical CO_2. The best extraction was observed for 3%(v/v) Cyanex 301. At a pH less than 2, Cyanex 302 has exhibited very poor extraction efficiency, However pH had no effect on the extraction efficiency of Cyanex 301.

Ning and coworkers [2001] investigated the preparation method for CuO-ZnO-Al$_2$O$_3$ catalyst using oxalate gel-coprecipitation (U8) and ammonium bicarbonate coprecipitation (C9). The reducing temperature for the catalyst prepared via U8 method is 448.3 K, while that for catalyst prepared via C9 method is 436.9 K. The catalyst size of CuO in U8 has smaller than that in C9 and the metal dispersion was also higher for U8. These properties gave rise to higher activity in methanol synthesis for U8

Taylor and coworkers [2003] investigated the preparation and activity of Cu/ZnO catalysts for carbon monoxide oxidation at room temperature. Cu/ZnO catalysts were prepared by co-precipitation method and the ageing time was varied. Aging time affected crystal phase and dispersion of catalysts. The catalyst that was aged for 165 minutes displayed the highest activity. Characterization of catalysts demonstrated that the catalyst with an ageing time of 165 minutes had the smallest crystallite sizes and the highest dispersion. Therefore, the catalyst could adsorb and desorb oxygen very well, resulting in the highest activity.

Deraz and coworkers [2000] studied the surface and catalytic property of Cu/ZnO catalysts. The catalysts were prepared by impregnation method with different loading of Cu ranging from 1% to 20%. The loading of copper had an effect on crystallite size and dispersion of copper, which affected catalyst activities. A loading of 5% Cu displayed the highest activity in CO oxidation because the XRD pattern revealed amorphous phase for 5% Cu/ZnO. At higher copper content, the XRD pattern displayed peaks of copper and a decrease in degree of crystallinity of ZnO phase.

Pillai and coworkers [2006] employed Cu/ZnO and cerium-promoted Cu/ZnO as highly active catalysts for low temperature oxidation of carbon monoxide. Cu/ZnO catalyst was prepared by co-precipitation technique. The role of zinc oxide was to bring about a highly dispersed copper phase, thereby achieving higher activity than CuO catalyst. But cerium decreased activity of the catalyst for CO oxidation because CO bonding on cerium was strong and resulted in the loss of low temperature activity

for CO oxidation. 60% Cu/ZnO displayed the higher activity and complete oxidation of CO at room temperature was achieved.

Manzoli and coworkers [2004] investigated interface species and effect of hydrogen on their amount in CO oxidation on Au/ZnO and Au/TiO$_2$. Au/TiO$_2$ could completely oxidize of CO at low temperature because CO$_2$ desorbed from TiO$_2$ more easily than ZnO. CO adsorbed on Au in the form linear bond or bridge bond, depending on dispersion of Au on support. At high dispersion of Au, CO can absorbed on Au in a linear form, which could desorb more easily than bridge bond form. Therefore, activity of Au/ZnO depended on dispersion of Au on supports.

CHAPTER III

THEORY

3.1 Supercritical fluid

3.1.1 Introduction

A supercritical fluid is any substance at a temperature and pressure above its thermodynamic critical point. It has the unique ability to diffuse through solids like a gas, and dissolve materials like a liquid. Additionally, its density can be changed easily by minor changes in temperature or pressure. These properties make it suitable as a substitute for organic solvents in a process called supercritical fluid extraction. Carbon dioxide and water are the most commonly used supercritical fluids. Above the critical temperature, the densities of the liquid and gas phases become equal and the distinction between them disappears, resulting in a single supercritical fluid phase. In Table 3.1, the critical properties display for compounds commonly used as supercritical fluids.

3.1.2 Definition of Supercritical Fluid

A supercritical fluid is a state where matter is compressible and behaves as a gas (i.e., it fills and takes the shape of it container). However, a supercritical fluid has a typical density of liquid (0.1-1 g/ml) and hence its characteristic dissolving ability. Supercritical fluid can also be defined as a heavy gas with a controllable dissolving ability or as a form of matter in which the liquid and gaseous state are indistinguishable.

At a constant pressure, a phase transition takes place at a transition temperature that is a function of pressure. Phase transformation involves enthalpy change. Therefore, in the absence of external influences, two phases can coexist indefinitely at a transition temperature for each pressure. However, only one phase will be stable at such a pressure and a temperature above or below a transition value.

Increasing temperature also varies the pressure at which the liquid and vapor phases coexist on the vapor pressure curve. The increase in vapor pressure is concomitant with the decrease in the difference between the densities of the liquid and gaseous phases. At any given temperature and pressure, the densities of liquid and gas are identical so the two phases are indistinguishable. Above such temperature or pressure, the liquid and gaseous phases exist as a single phase. This region of temperature and pressure above P_c and T_c is called supercritical region.

3.1.3 Solubility in Supercritical Fluid

The process by which a molecule becomes part of a supercritical phase can be described as vaporization because a molecule shifts from a condensed phase to an expanded phase or as dissolution since it involves interactions between solute and solvent. This combined vaporization-dissolution reflects the intermediate nature of the supercritical state.

Interactions between solute and solvent in dense CO_2 increase solubility of naphthalene by a factor of up to 10^4 relative to that one would expect from an ideal gas at 220 atm and 35-55 ^oC**.** In fact, solubility enhancement factor can be as high as 10^{10}. At low pressure, the solubility of naphthalene is determined by its vapor pressure since CO_2 is a relatively ideal gas with no special solvent properties under these conditions. Mole fraction of naphthalene in solution initially decreases with increasing overall pressure. When pressure is raised further, the density of CO_2 increases up to a point where the solubility of naphthalene also starts to increase. When the pressure of CO_2 is close to the critical pressure (72.8 atm), the solubility rises sharply as a result of marked increase in density with pressure. Further increase in pressure gives rise to a small solubility elevation because of a higher density with increasing pressure. At extremely high pressure, the solubility reaches a maximum.

The effect of temperature on solubility is somewhat more complex. Below 60 atm and above 120 atm, the solubility of naphthalene increases as temperature rises. On the other hand, the solubility decreases with increasing temperature at the pressure

between 60 and 120 atm. This phenomenon is commonly known as retrograde vaporization.

As the temperature rises, two competing effects come into play. On the one hand, the vapor pressure of naphthalene increases and so does solubility. On the other hand, the density and dissolving ability of CO_2 decrease, so the solubility tends to decrease as well. Below 60 atm and above 120 atm, the CO_2 density does not depend so heavily on temperature, so an increase in vapor pressure of naphthalene prevails and the solubility rises. At intermediate pressure (60-120 atm), the CO_2 density depends on the temperature and decreases with increasing temperature. As a result, the solubility decreases. At 60 and 120 atm, the two effects cancel each other out, so solubility is essentially independent of the temperature.

3.1.4 Applications of Supercritical fluid

For engineering purposes, supercritical fluids can be regarded as "hybrid solvents" with properties between those of gases and liquids, i.e. a solvent with a low viscosity, high diffusion rates and no surface tension. In the case of supercritical carbon dioxide, the viscosity is in the range of 20–100 μPa·s (0.02-0.1 cP), where liquids have viscosities of approximately 500–1000 μPa·s (0.5-1.0 cP) and gases approximately 10 μPa·s (0.01 cP) for gases. Diffusivities of solutes in supercritical carbon dioxide are up to a factor of 10 higher than in liquid solvents. Additionally, these properties are strongly depend on pressure in the vicinity of the critical point, making supercritical fluids highly tunable solvents. Of the components shown in Table 3.1, carbon dioxide and water are the most frequently used in a wide range of applications, including extractions, dry cleaning, and chemical waste disposal. In polymer systems, ethylene and propylene are also widely used, where they act both as a solvent and as the reacting monomer.

One of the most important properties of supercritical fluids is that their dissolving abilities are a complex function of their pressure and temperature, independent of their density. Therefore, raw materials containing CO_2 soluble products can be selectively extracted or selectively precipitated to obtain ultra-pure

Table 3.1 Critical properties of various solvents (Reid et al., 1987)

Solvent	Molecular weight	Critical temperature	Critical pressure	Density
	g/mol	K	MPa (atm)	g/cm^2
Carbon dioxide (CO_2)	44.01	304.1	7.38 (72.8)	0.469
Water (H_2O)	18.02	647.3	22.12 (218.3)	0.348
Methane (CH_4)	16.04	190.4	4.60 (45.4)	0.162
Ethane (C_2H_6)	30.07	305.3	4.87 (48.1)	0.203
Propane (C_3H_8)	44.09	369.8	4.25 (41.9)	0.217
Ethylene (C_2H_4)	28.05	282.4	5.04 (49.7)	0.215
Propylene (C_3H_6)	42.08	364.9	4.60 (45.4)	0.232
Methanol (CH_3OH)	32.04	512.6	8.09 (79.8)	0.272
Ethanol (C_2H_5OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C_3H_6O)	58.08	508.1	4.70 (46.4)	0.278

products. As a result, this process is the dominant chemical-free technology for the production of decaffeinated coffee, nicotine-free tobacco, and many of the world's best spice extracts.

3.2 Supercritical carbon dioxide

3.2.1 Introduction

Supercritical carbon dioxide refers to carbon dioxide with some unique properties. Carbon dioxide usually behaves as a gas in air or as a solid in dry ice. If both the temperature and pressure are increased, it can adopt properties midway between a gas and a liquid. It behaves like a supercritical fluid above its critical temperature (31.1 ^{o}C) and pressure (73 atm), expanding to fill its container like a gas, but with a density like that of a liquid. Supercritical CO_2 is becoming an important commercial and industrial solvent due to its role in compound extraction as well as its low toxicity and environmental impact. The relatively low temperature of the process

and the stability of CO_2 also allows most compounds to be extracted with little damage or denaturing.

3.2.2 Phase diagram of Supercritical carbon dioxide

Two projections of the phase diagram of carbon dioxide are shown in Figures 3.1 and 3.2. In the pressure-temperature phase diagram (Figure 3.1) the boiling line, which separates the vapor and liquid region and ends in the critical point is observed, At the critical point, the densities of the saturated liquid and vapor phases become equal, resulting in the formation of a single supercritical phase. This phenomena can be observed in the density-pressure phase diagram for carbon dioxide, as shown in Figure 3.2, where the critical point is located at 31.1 ^{o}C and 73 atm (73.8 bar). With increasing temperatures, the liquid-vapor density gap decreases, up to the critical temperature, at which the discontinuity disappears. Thus, above the critical temperature a gas cannot be liquefied by pressure. However, at extremely high pressures the fluid can solidify, as seen at the top of Figure 3.1 By definition, a supercritical fluid is a substance above both its critical temperature and pressure. In a practical sense, the area of interest in supercritical fluids for processing and separation purposes is limited to temperatures in the vicinity of the critical point, where large gradients in the physical properties are observed. The changes near the critical point are not limited to density. Many other physical properties also show large gradients with pressure near the critical point such as viscosity, relative permittivity and solvent strength, which are all closely related to the density. At higher temperatures, the fluid starts to behave like a gas, as can be seen in Figure 3.2. For carbon dioxide at 400 K, the density increases almost linearly with pressure.
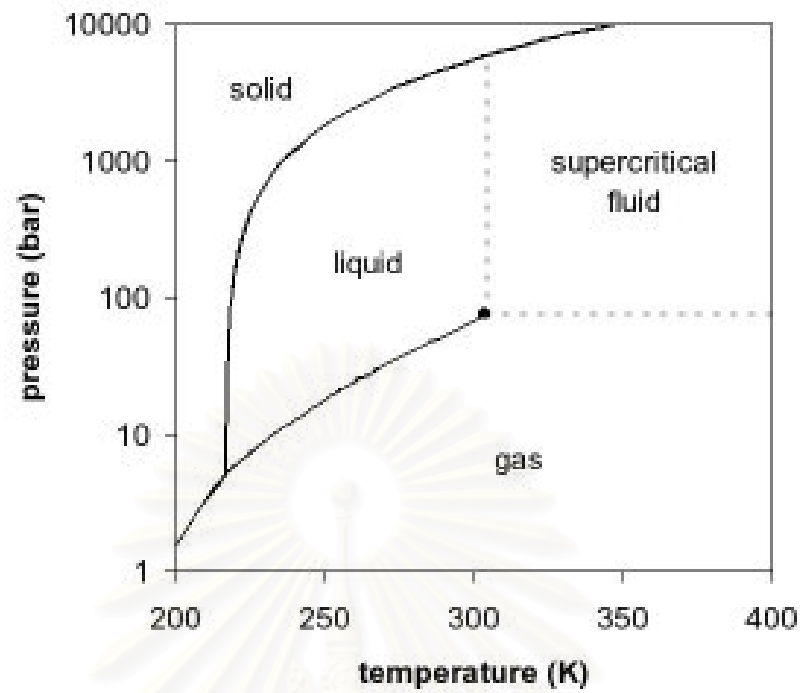
Figure 3.1 Pressure-temperature phase diagram of carbon dioxide
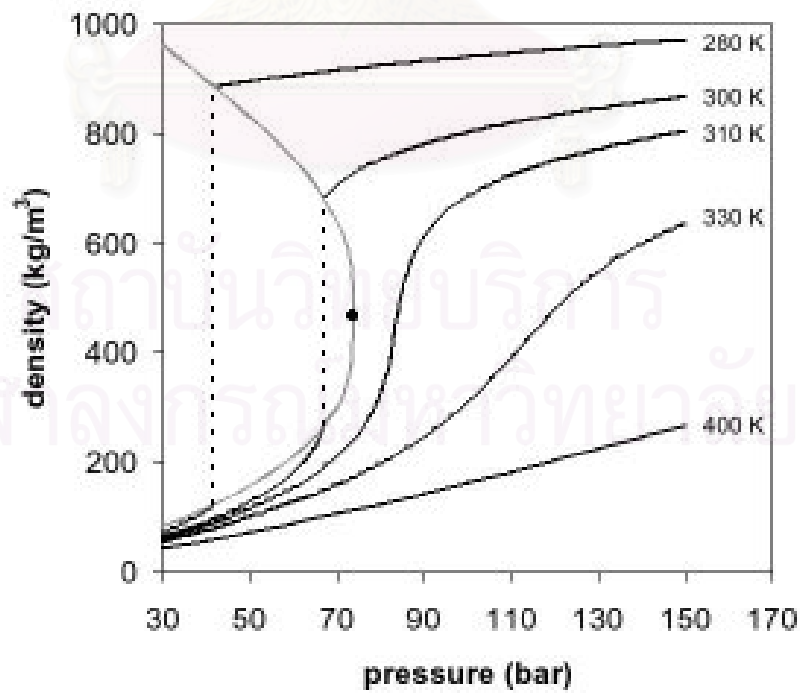
Figure 3.2 Density-pressure phase diagram of carbon dioxide

3.2.3 Applications of Supercritical carbon dioxide

Supercritical carbon dioxide is gaining popularity amongst coffee manufacturers looking to move away from some of the classic decaffeinating solvents of the past; many of which have led to public outcry because of real or perceived dangers related to their use in food preparation. Supercritical CO_2 is forced through the green coffee beans and then sprayed with water at high pressure to remove the caffeine. The caffeine can then be isolated for resale to, for example, cola manufacturers by passing the water through activated charcoal filters or by distillation, crystallization or reverse osmosis. Supercritical carbon dioxide is also becoming a more common process for extracting volatile oils and fragrant compounds from various raw materials that are used in perfumery. The relatively low critical temperature and reactivity of CO_2 allows the fragrant compounds to be extracted without extensive damage or denaturing, which will alter their odor. Supercritical carbon dioxide can be used in cleaning clothes, instead of perchloroethylene or water. Supramics, environmentally beneficial, low-cost substitutes for rigid thermoplastic and fired ceramics, are made using supercritical carbon dioxide as a chemical reagent. The supercritical carbon dioxide in these processes reactes with the alkaline components of fully hardened hydraulic cement or gypsum plaster to form various carbonates. The sole by-product is ultra-pure water. Because supramics consumes and sequesters carbon as stable compounds in useful products, they may serve to reduce carbon that would otherwise be released into the environment. Processes which use supercritical carbon dioxide to produce micro and nano scale particles, often for pharmaceutical uses, are currently being developed. The gas antisolvent process, rapid expansion of supercritical solutions, and supercritical antisolvent precipitation (as well as several related methods) have been shown to process a variety of substances into particles. Supercritical carbon dioxide is also used in the foaming of polymers. Many corporations utilize supercritical carbon dioxide to saturate the polymer with solvent (carbon dioxide). Upon depressurization and heating the carbon dioxide rapidly expands, causing voids within the polymer matrix, i.e., creating a foam. Research is also ongoing at many universities in the production of microcellular foams using supercritical carbon dioxide. Supercritical carbon dioxide is beginning to be used to enhance oil recovery in mature oil fields. Supercritical carbon dioxide is also an important emerging natural refrigerant, being used in new, low carbon

solutions for domestic heat pumps. These systems are undergoing continuous development with the first commercial supercritical carbon dioxide heat pumps being now marketed. The "EcoCute" systems from Japan, developed by consortium of companies including Mitsubishi, develop high temperature domestic water at with small inputs of electric power by moving heat into the system from their surroundings

3.3 Solvothermal method

Solvothermal method employs chemical reactions in organic medium such as methanol [Yin et al., 2003], 1,4 butanediol, or toluene [Chung-Sik Kim, 2003] under self-produced pressures at low temperatures (usually under 250 ^{o}C) inside an autoclave reactor. Generally, but not always, a subsequent thermal treatment is required to crystallize the final material. The solvothermal treatment could be useful to control grain size, particle morphology, crystalline phase, and surface chemistry by regulating the solution composition, reaction temperature, pressure, solvent properties, additives, and ageing time.

3.4 Oxidation of carbon monoxide

Carbon monoxide (CO) - a colorless, odorless, flammable, toxic gas - is produced by steam reforming or partial oxidation of carbonaceous materials. It was discovered by Lassonne in 1776 by heating a mixture of charcoal zinc oxide.

Carbon monoxide burns readily in air or oxygen. Ignition temperature is 644-658 ^{o}C, respectively. Mixtures of carbon monoxide and air are flammable over a wide range of composition at atmospheric pressure. The oxidation of CO, the reaction of carbon monoxide with oxygen to form carbon dioxide, occurs readily at a temperature above 650 ^{o}C. However, the reaction has been found to be catalyzed at lower temperatures by many metal support catalyst such as Cu/ZnO, Cu/TiO_2, Cu/Al_2O_3, Au/ZnO, Au/TiO_2, and Au/Al_2O_3.

CHAPTER IV

EXPERIMENTAL

Synthesis of zinc oxide and titanium dioxide using solvothermal methods and deposition of copper on such supports are explained in this chapter.

4.1 Chemical

1. Zinc acetate ($Zn(CH_3COO)_2$), 99.99%, available from Sigma-Aldrich.
2. Titanium isopropoxide ($C_{12}H_{28}O_4Ti$), 97%, available from Sigma-Aldrich.
3. Copper chloride ($CuCl_2$), 99.5%, available from Carlo Erba.
4. 1, 4-butanediol (1,4-BG,$HO(CH_2)_4OH$, 99.99%, available from Sigma-Aldrich.
5. Methanol (CH_3OH), available from Merck.
6. Cyanex 301 or bis(2 ,4 ,4 -trimethyl pentyl) dithiophosphinic acid, from Cyatec.

4.2 Equipment

4.2.1 Autoclave reactor

The schematic diagram of the equipment used to prepare zinc oxide and titanium dioxide is show in figure 4.1 and mainly consisted of an autoclave reactor. The autoclave reactor is displayed in Figure 4.2. The reactor has the following features.

- Made from stainless steel
- Volume of 1000 cm^3
- Inside diameter of 10 cm
- Maximum temperature of 350 ^{o}C
- Pressure gauge in the range of 0 – 140 bar
- Relief valve used to prevent runaway reaction
- Iron jacket used to reduce the volume of autoclave from 1000 to 300 cm^3
- Test tube used to hold the reagents and solvent
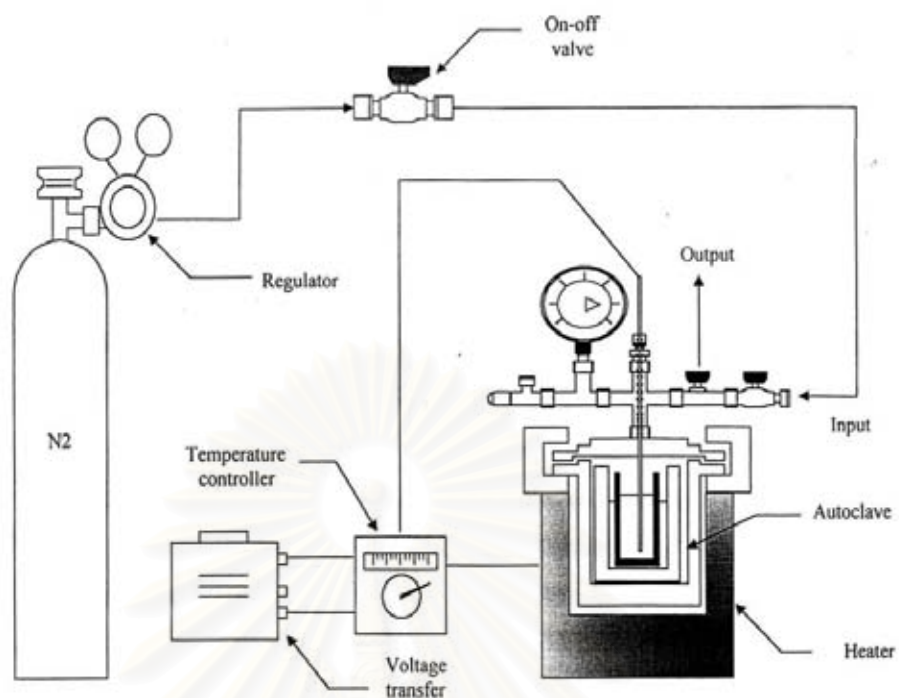
Figure 4.1 Schematic diagram of the reaction equipment for preparation of support.
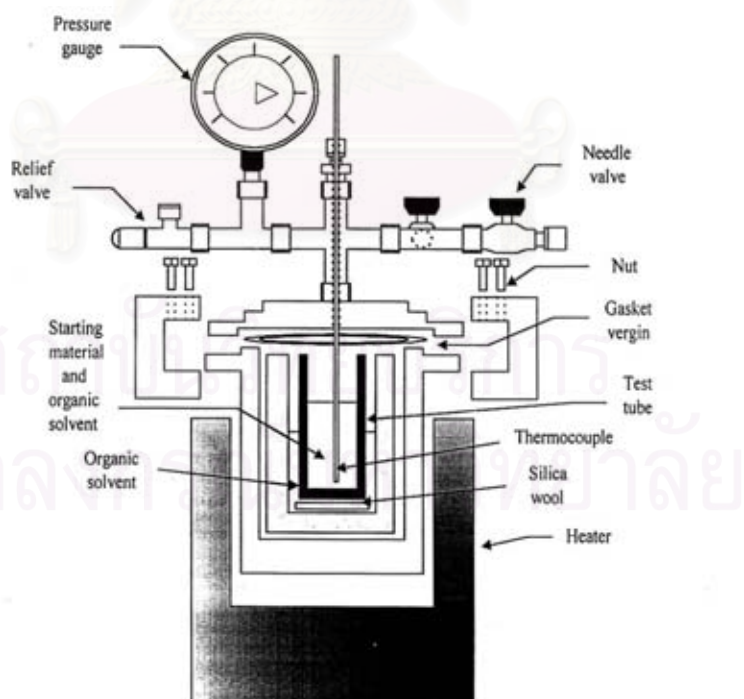
Figure 4.2 Autoclave reactor.

4.3 Experimental Procedures

4.3.1 *Preparation of ZnO support*

First, 15 g of zinc acetate was dissolved in 100 ml of 1,4-butanediol in a test tube. Then the test tube was set in an autoclave reactor. In the gap between the test tube and the autoclave wall, one added 30 ml of 1,4-butanediol. The autoclave was heated to 200 °C at a rate of 2.5 °C/min and was held at this temperature for two hours. The resulting powder was then cooled and was washed repeatedly with methanol.

4.3.2 *Preparation of TiO$_2$ support*

First, 15 g of titanium isopropoxide was dissolved in 100 ml of 1,4-butanediol in a test tube, which was then set in an autoclave reactor. In the gap between the test tube and the autoclave wall, one added 30 ml of 1,4-butanediol. The autoclave reactor was heated to 300 °C at a rate of 2.5 °C/min and was held at this temperature for two hours. The resulting powder was then cooled and is washed repeatedly with methanol.

4.3.3 *Deposition of copper*

Copper chloride was mixed with 3 ml of methanol (for deposition technique using supercritical carbon dioxide and methanol or SCCO$_2$-Me) or a solution of equivolume Cyanex 301 and methanol (for deposition technique using supercritical carbon dioxide and Cyanex 301 or SCCO$_2$-Cy). The copper-containing mixture and support was then placed in a high pressure reactor vessel, which was connected to a high-pressure CO$_2$ delivery system (see Figure 4.3). Carbon dioxide was fed to the reactor at 60°C and 30 MPa and was kept in the chamber for 20 minutes. After that, vent valve was opened and CO$_2$ was released from the reactor. The resulting powder was dried at 110 °C and calcined at 350 °C for six hours.
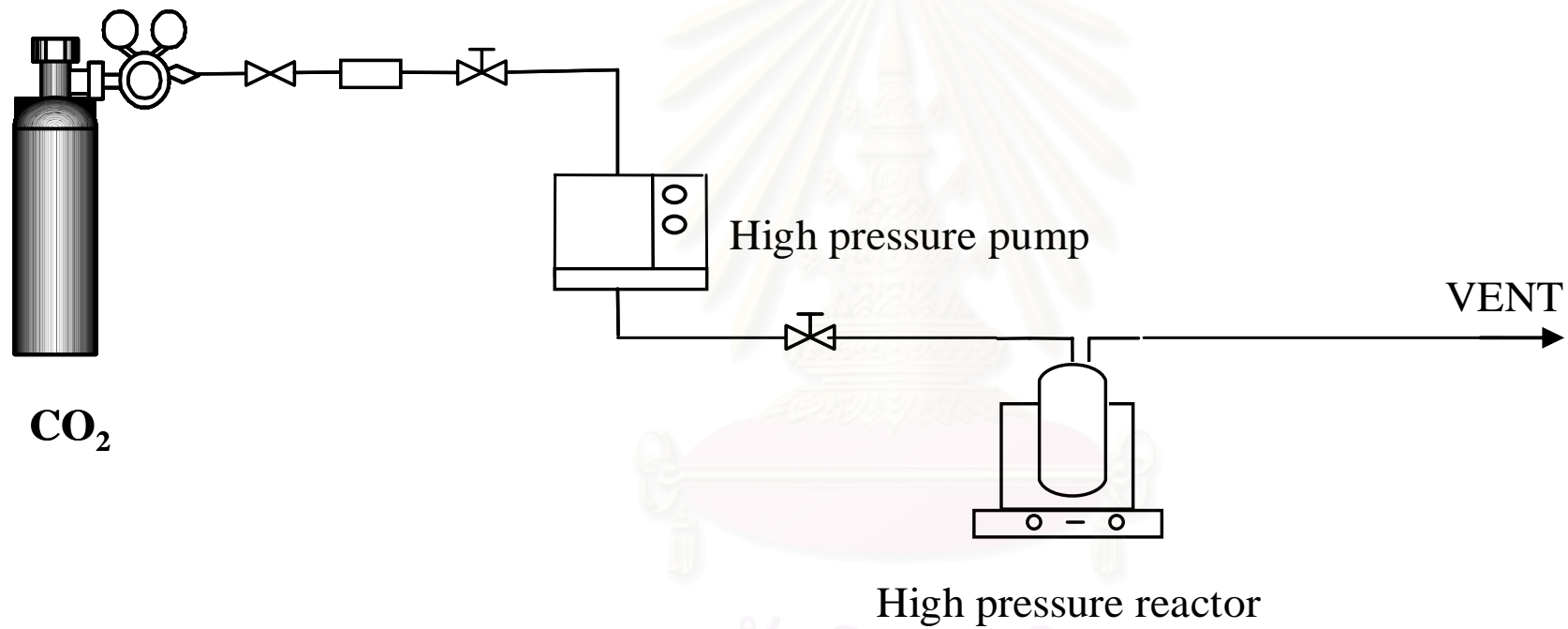
Figure 4.3 Schematic diagram of a system used for deposition of copper on the support using supercritical carbon dioxide

4.3.4 *Measurement of catalytic activity*

Measurement of catalytic activity was performed at atmospheric pressure in a fixed-bed reactor consisting of a pyrex tube and a coaxially-centered thermocouple with its tip located in the middle of the bed (see Figure 4.4).

Prior to each experiment, the catalyst was reduced in situ at 400 ºC in stream of 10% H_2/He for one hour. After that, hydrogen was removed by purging with Helium for another hour prior to activity measurements. To produce the reactant mixture, two streams (i.e. 1% CO/He and 2% O_2/He) were combined and fed to the reactor mixture.

The catalytic activity measurements were performed at atmospheric pressure in a tubular reactor of 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 two Shimadzu gas chromatographs (GC). One GC was equipped with a thermal conductivity detector (TCD) while the other was equipped with a flame ion cation detector. Helium was used as the carrier gas and separation of the constituents in the other GC with FID was achieved using molecular sieves 5A column (3 m × 3 mmØ). Molecular sieves 5A were used to analyze N_2, CO, O_2, H_2 and other hydrocarbons. The other GC contained Porapak QS column (3 m×3 mmØ), were used to analyze H_2O, O_2 and CO_2
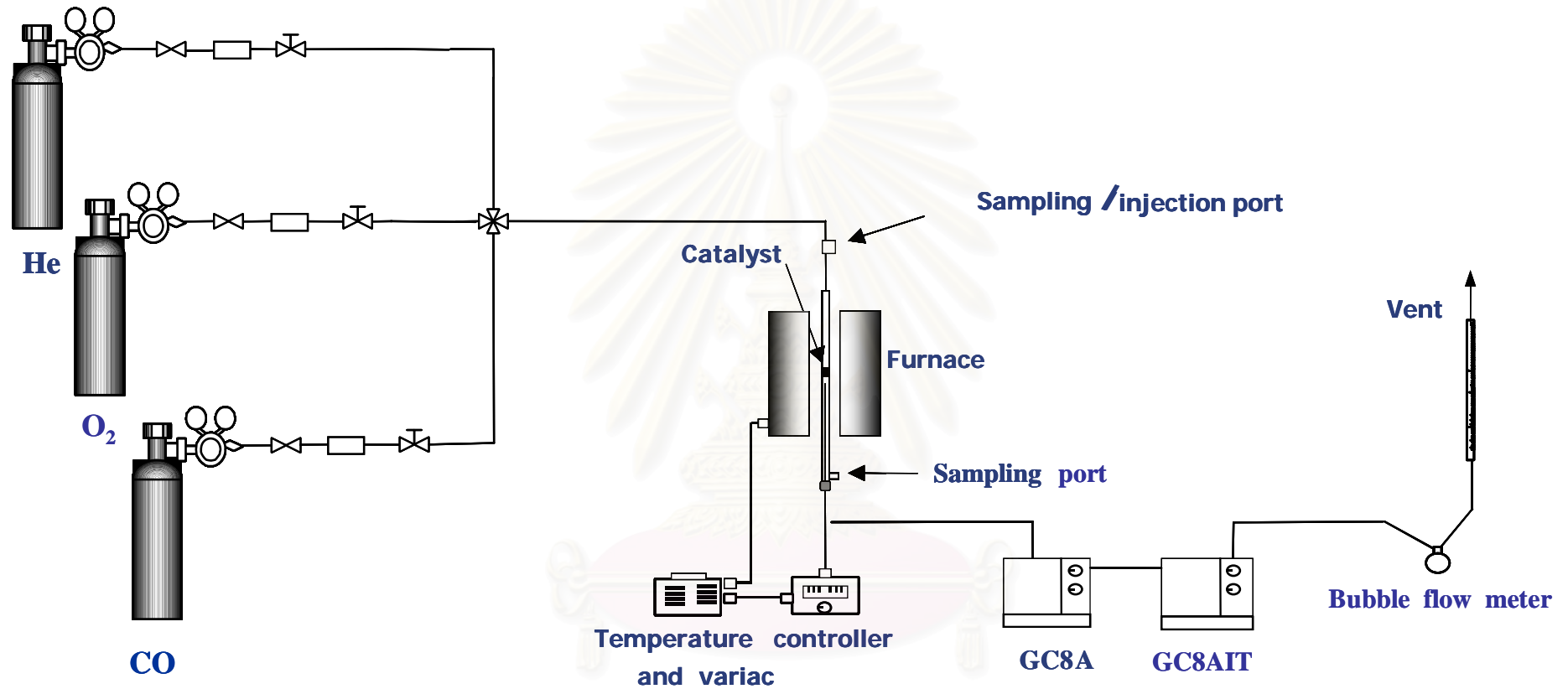
Figure 4.4 Schematic diagram of a reactor system employed for oxidation of CO experiment

4.4 Characterization of catalysts

4.4.1 *X-ray diffractometry (XRD)*

X-ray diffractometry is performed using a SIEMENS D5000 X-ray diffractometer connected. The measurement was carried out using CuKα radiation with Ni filter. The scan range is between 2θ values of 10° to 80° with a resolution of 0.04^o.

4.4.2 *Specific surface area and pore volume measurement*

Specific surface area and pore volume was measured by nitrogen physisorption technique. The sample cell that contained 0.3 gram of sample is placed into a degas port of Micromeritics ASAP 2020. After completion of the degassing step, the cell is transferred to the analytical port of the same equipment. Specific surface area was calculated using a BET analysis while pore volume is calculated using a BJH method.

4.4.3 *Active site measurement*

The specific surface area of Cu^0 on the catalysts was determined by nitrous oxide (N_2O) chemisorption. The reaction with nitrous oxide allows one to measure metal surface area for both pure and supported copper catalyst. This method was based on the reaction of nitrous oxide molecule on a copper surface, which produce one nitrogen molecule according to the reaction:

$$N_2O \text{ (g)} + 2Cu^0 \text{ (s)} \longrightarrow N_2 \text{ (g)} + (Cu\text{-}O\text{-}Cu) \text{ (s)} \qquad (1)$$

where subscript s denotes surface species.

Surface area of copper can be determined using the amount of N_2O consumed during the measurement. Prior to each measurement, the catalyst was reduced under hydrogen flow of 10 ml/min at 400 °C for one hour. After the reaction period, helium

was employed to purge the system for 8-10 minutes to ensure that no hydrogen remained in the system. The temperature was reduced from 400 °C to 90 °C and remained at 90 °C during nitrous oxide reaction. Known volume of nitrous oxide is injected into helium stream through injection port of a gas chromatograph and pass over the catalyst. The volume of nitrous oxide is fed in 1 ml and the amount of catalyst packed in the reactor varies, depending on its estimated surface area of copper. The configuration of a thermal conductivity detector enables both nitrous oxide and nitrogen to be detected. The column used is a Porapak Q column (see Figure 4.5).

4.4.4 *Inductively-coupled plasma atomic emission spectroscopy (ICP-AES)*

Copper content is measured using Perkin Elmer Optical Emission Spectrometer Optima 2100 DV. To digest the sample, the catalyst was mixed with ammonium sulfate and sulfuric acid. The mixture was then stirred and heat at 80 °C over night. After the catalyst was completely digested, the solution is diluted to a volume of 100 ml
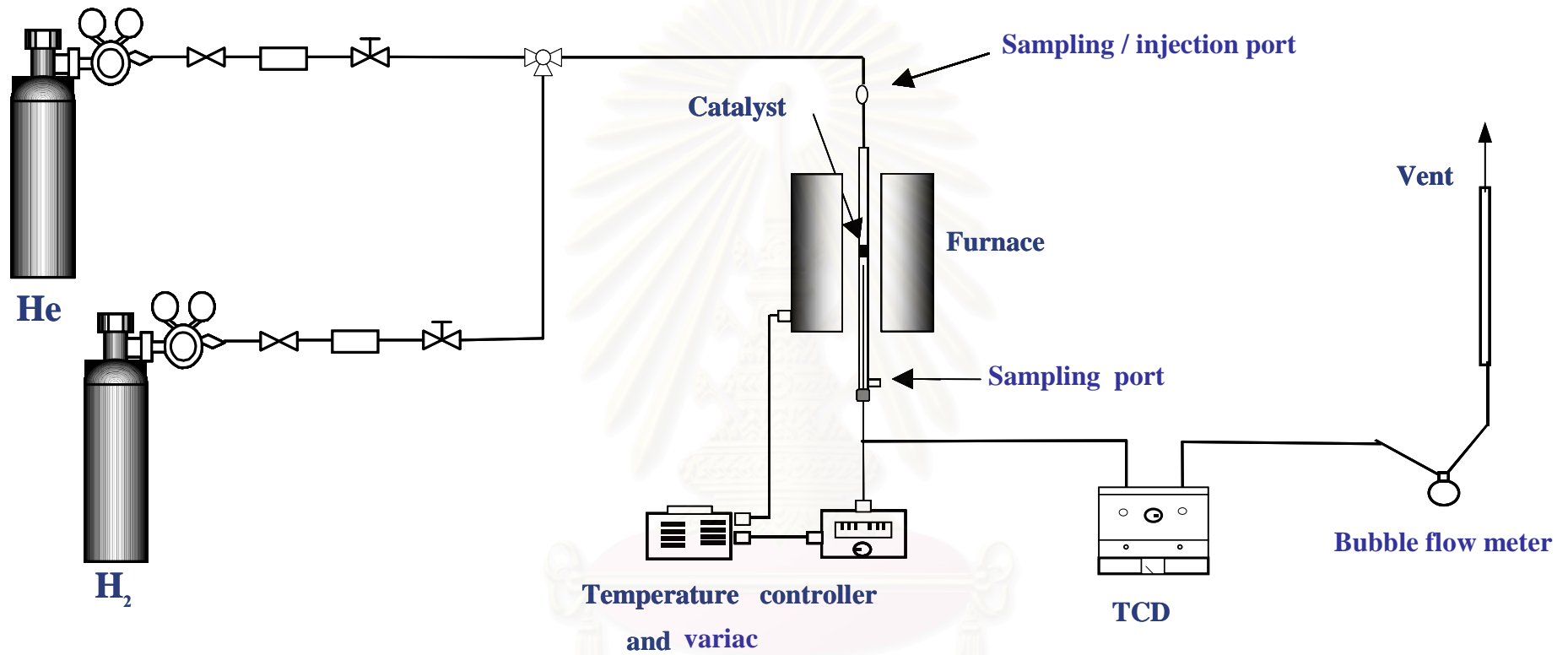
Figure 4.5 Schematic of diagram of a system employed for nitrous oxide chemisorption

CHAPTER V

RESULTS AND DISCUSSION

5.1 Characterization of Cu/ZnO Catalysts

5.1.1 *Crystal phase*

The result from XRD analysis of Cu/ZnO catalysts prepared by incipient wetness impregnation method, deposition technique using supercritical carbon dioxide and methanol and deposition technique using supercritical carbon dioxide and Cyanex 301 are displayed in Figures 5.1 to 5.3, respectively. Inspection of the diffractograms revealed that zinc oxide existed as a hexagonal form. The strong intensity of diffraction peaks indicated that the products possessed high crystallinity. We observed peaks corresponding to CuO in Cu/ZnO catalysts that were prepared by incipient wetness impregnation technique at high percentage of copper, i.e., 10% and 20% (see Figure 5.1). This finding was in good agreement with work done by Nars and coworker [2001], in which peaks corresponding of CuO were observed in Cu/ZnO samples that had copper content higher than 5%. However, the peaks corresponding to CuO were not detected in any Cu/ZnO catalysts that were prepared using supercritical carbon dioxide (see Figures 5.2 and 5.3). the absence of the peaks corresponding to CuO in there samples suggested that either the crystallite size of metal on the support was too small or dispersion of metal on the support was high. [Komandur et al. 2007]

5.1.2 *Specific surface area and pore structure*

Specific surface areas and pore size information of catalysts were determined from nitrogen adsorption isotherms and were displayed in Table 5.1. Cu/ZnOcatalysts had comparable specific surface area, pore volumes, and average pore size, regardless of preparation technique.
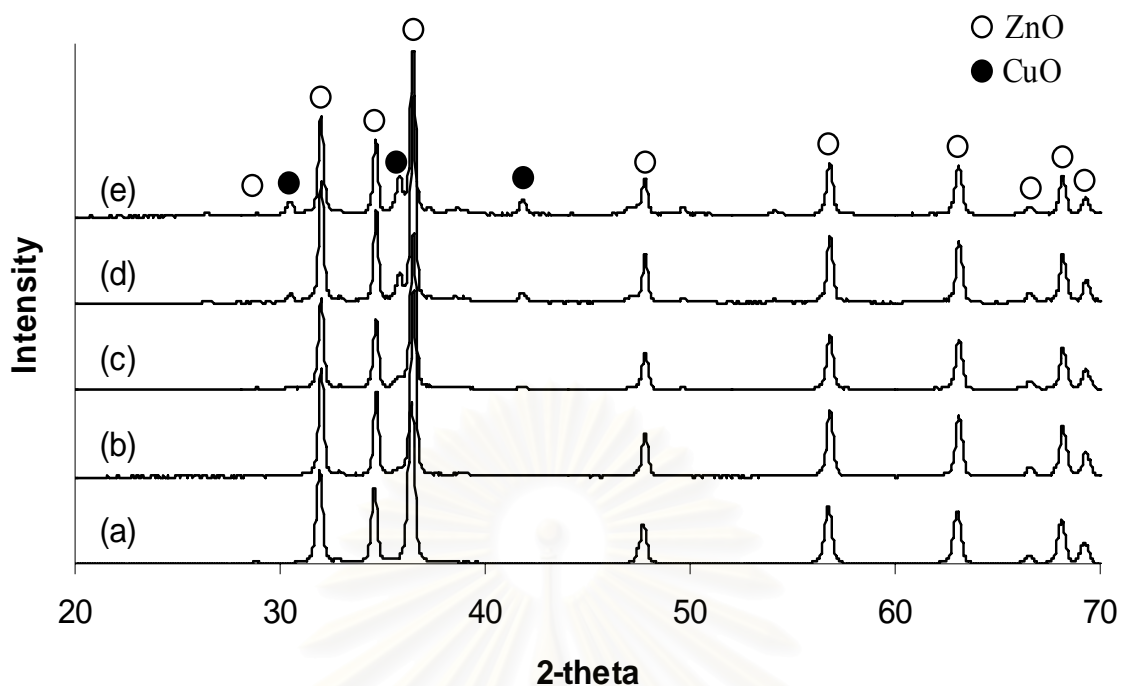
Figure 5.1 XRD patterns of Cu/ZnO catalysts prepared by incipient wetness impregnation method at copper contents of (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.
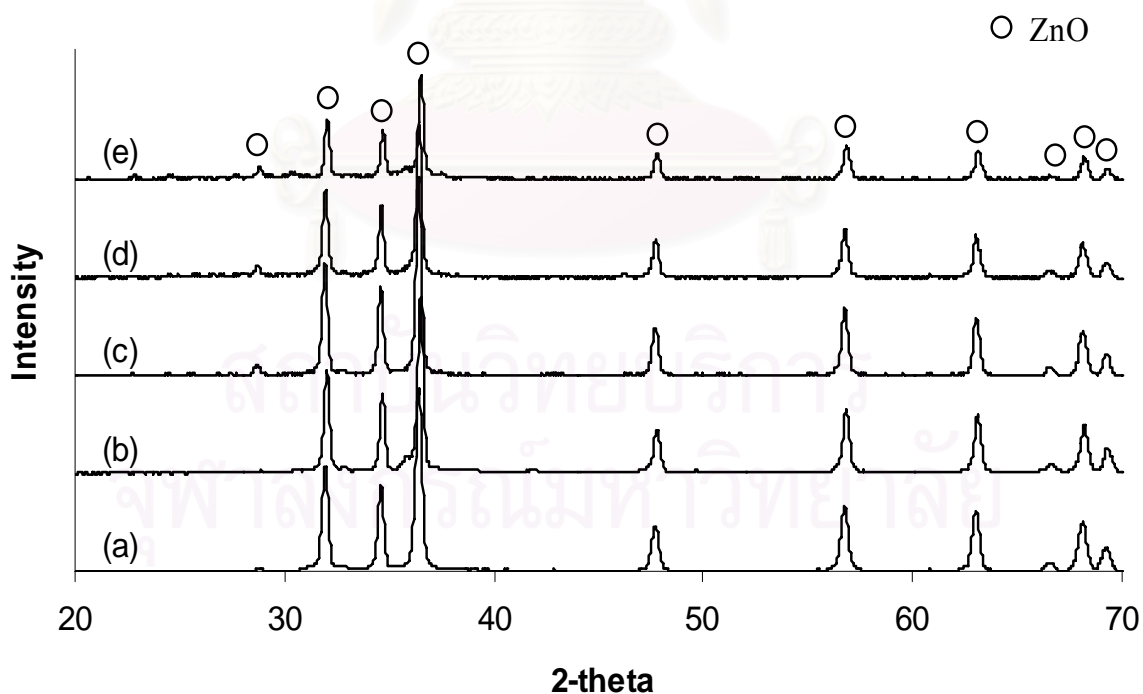
Figure 5.2 XRD patterns of Cu/ZnO catalysts prepared by deposition technique using supercritical carbon dioxide and methanol at copper contents of (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.
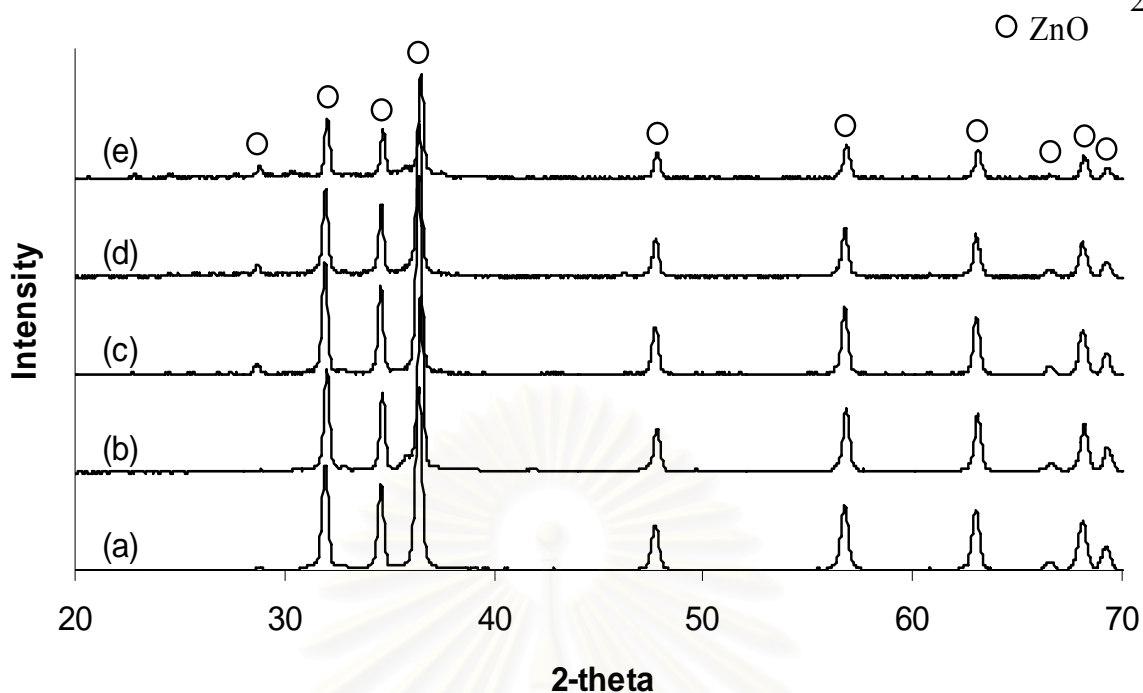
Figure 5.3 XRD patterns of Cu/ZnO catalysts prepared by deposition technique using supercritical carbon dioxide and cyanex 301 at copper contents of (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.

5.1.3 *Copper content*

The amount of copper on Cu/ZnO catalyst was determined using inductively coupled plasma atomic emission spectroscopy and the results are shown in Table 5.2. Catalyst prepared by incipient wetness impregnation had higher copper content than catalysts prepared by two deposition techniques using supercritical carbon dioxide because some copper was dissolved in supercritical carbon dioxide and was carried out of reactor without being deposited on support. Further more, the copper contents of the Cu/ZnO catalysts prepared by the two deposition techniques with supercritical carbon dioxide ($SCCO_2$-Me and $SCCO_2$-Cy) were comparable.

Table 5.1 Specific surface area and pore structure information of Cu/ZnO catalysts

SAMPLE	SPECIFIC SURFACE AREA (m^2/g)			PORE VOLUME (cm^3/g)			AVERAGE PORE SIZE (Å)		
	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy
2% Cu/ZnO	11	9	15	0.06	0.06	0.05	206	249	194
5% Cu/ZnO	8	7	11	0.08	0.06	0.06	298	282	211
10% Cu/ZnO	7	6	9	0.05	0.04	0.05	218	177	153
20% Cu/ZnO	7	8	5	0.04	0.03	0.05	192	136	244

Table 5.2 Copper content for Cu/ZnO catalysts

SAMPLE	COPPER CONTENT (%)		
	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy
2 % Cu/ZnO	2.1	1.9	1.8
5 % Cu/ZnO	4.5	4.3	4.2
10 % Cu/ZnO	9.5	9.1	9.1
20 % Cu/ZnO	20.0	18.7	18.4

5.1.4 *Active sites and metal dispersion*

Active sites were measured by chemisorption using nitrous oxide (N_2O) and the results were listed in Table 5.3. The number of active sites grew larger as the copper loading increase for all Cu/ZnO catalysts. Cu/ZnO catalysts that were prepared using supercritical carbon dioxide, i.e., $SCCO_2$-Me and $SCCO_2$-Cy, possessed comparable numbers of active sites, which were significantly greater (7%-54%) than Cu/ZnO catalysts that were prepared by incipient wetness impregnation technique. After we measured the number of active sites on the catalyst, metal dispersion for copper on ZnO could be calculated according to a procedure described in Appendix A. the results for metal dispersion for Cu/ZnO catalyst were shown in Table 5.4. As the copper loading was increased copper dispersion became less because a grater amount of copper was deposited on the surface of ZnO while the surface area remained essentially the same. Cu/ZnO catalysts that were prepared using supercritical carbon dioxide, i.e., $SCCO_2$-Me and $SCCO_2$-Cy, possessed comparable dispersion of copper on ZnO. Nevertheless, $SCCO_2$-Me and $SCCO_2$-Cy had significantly grater copper dispersion (27%-61%) than Cu/ZnO catalysts that were prepared using incipient wetness impregnation technique. These results may be attributed to the ability of supercritical carbon dioxide that could diffuse into pores of the support better than water

Table 5.3 Result from active site measurements for Cu/ZnO catalysts

SAMPLE	ACTIVE SITE (X 10^{-18} sites)		
	IMPREG	$SCCO_2$-Me	$SCCO_2$-Cy
2% Cu/ZnO	0.47	0.50	0.57
5% Cu/ZnO	0.78	1.20	1.20
10% Cu/ZnO	1.02	1.42	1.29
20% Cu/ZnO	1.77	2.09	2.19

Table 5.4 Dispersion of copper on Cu/ZnO catalysts

SAMPLE	COPPER DISPERSION (%)		
	IMPREG	$SCCO_2$-Me	$SCCO_2$-Cy
2% Cu/ZnO	2.04	2.78	3.17
5% Cu/ZnO	1.83	2.90	2.95
10% Cu/ZnO	1.13	1.66	1.50
20% Cu/ZnO	0.93	1.18	1.24

5.2 Characterization of Cu/TiO$_2$ Catalysts

5.2.1 *Crystal phase*

The result from XRD analysis of Cu/TiO$_2$ catalysts prepared by incipient wetness impregnation method, deposition technique using supercritical carbon dioxide and methanol and deposition technique using supercritical carbon dioxide and Cyanex 301 are displayed in Figures 5.1 to 5.3, respectively. Inspection of the diffractograms revealed that titanium dioxide existed as anatase form. The strong intensity of diffraction peaks indicated that the products possessed high crystallinity. We observed peaks corresponding to CuO in Cu/TiO$_2$ catalysts that were prepared by incipient wetness impregnation technique at high percentage of copper, i.e., 10% and 20% (see Figure 5.4). This finding was in good agreement with work done by Nars and coworker [2001], in which peaks corresponding of CuO were observed in Cu/TiO$_2$ samples that had copper content higher than 5%. However, the peaks corresponding to CuO were not detected in any Cu/TiO$_2$ catalysts that were prepared using supercritical carbon dioxide (see Figures 5.5 and 5.6). The absence of the peaks corresponding to CuO in the samples suggested that either the crystallite size of metal on the support was too small or dispersion of metal on the support was high. [Komandur et al., 2007]
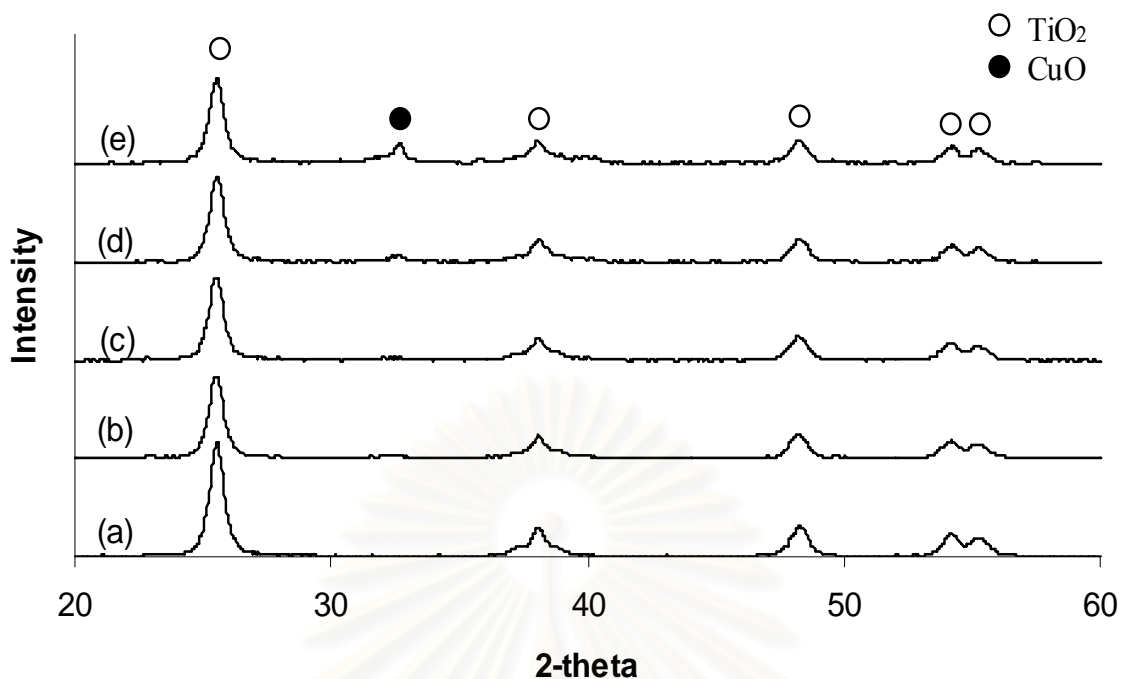
Figure 5.4　XRD patterns of Cu/TiO$_2$ catalysts prepared by incipient wetness impregnation method at copper contents of (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.
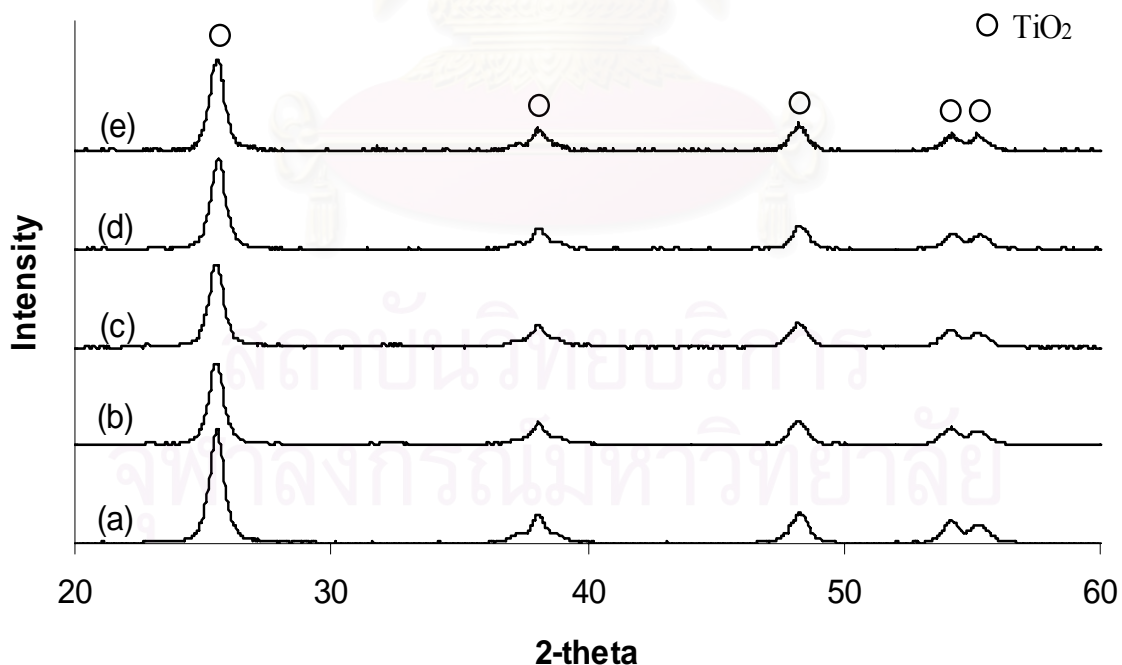

Figure 5.5　XRD patterns of Cu/TiO$_2$ catalysts prepared by deposition technique using supercritical carbon dioxide and methanol at copper contents of (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.
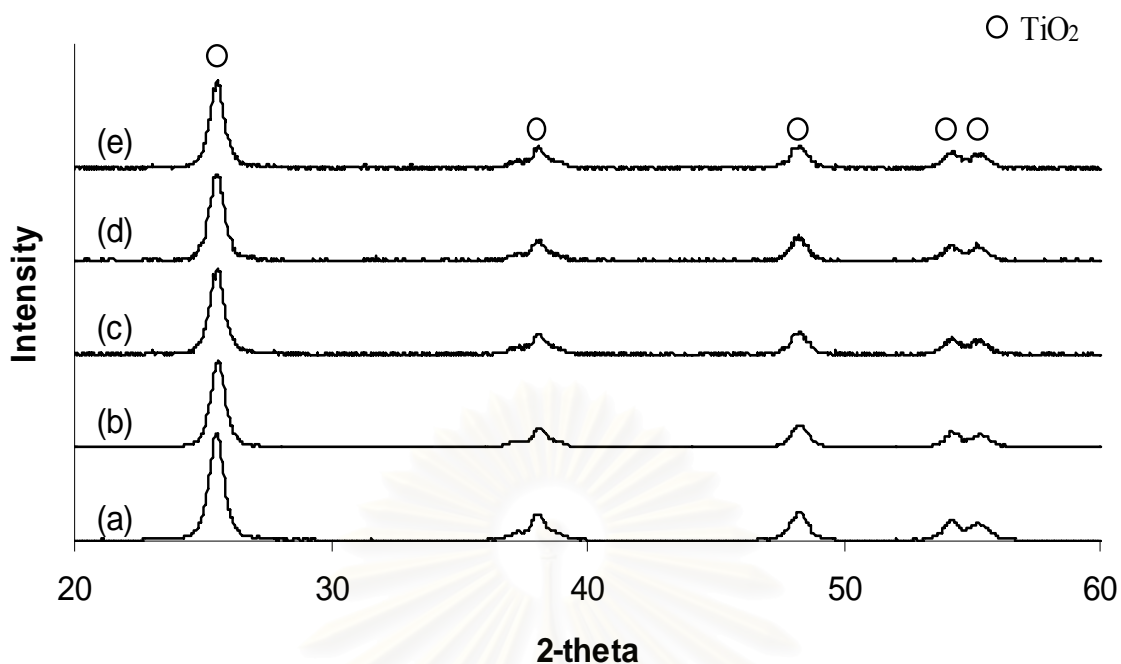
Figure 5.6   XRD patterns of Cu/TiO$_2$ catalysts prepared by deposition technique using supercritical carbon dioxide and cyanex 301 at copper contents of (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.

5.2.2 *Specific surface area and pore structure*

Specific surface areas and pore size information of catalysts were determined from nitrogen adsorption isotherms and were displayed in Table 5.5. All Cu/TiO$_2$ catalysts had comparable specific surface areas, pore volumes, and average pore size, regardless of preparation technique. But Cu/TiO$_2$ catalysts that were prepared using SCCO$_2$-Me technique possessed slightly lower specific surface areas, pore volumes, and average pore size than the other two types of Cu/TiO$_2$ catalysts.

5.2.3 *Copper content*

The amount of copper on Cu/TiO$_2$ catalyst was determined using inductively coupled plasma atomic emission spectroscopy and the results are shown in Table 5.6. Catalyst prepared by incipient wetness impregnation had higher copper content than catalysts prepared by two deposition techniques using supercritical carbon dioxide because some copper was dissolved in supercritical carbon dioxide and was carried out of reactor without being deposited on support.

Table 5.5 Specific surface area and pore structure information of Cu/TiO$_2$ catalysts

SAMPLE	SPECIFIC SURFACE AREA (m^2/g)			PORE VOLUME (cm^3/g)			AVERAGE PORE SIZE (Å)		
	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy
2% Cu/TiO$_2$	83	67	75	0.37	0.28	0.32	129	118	121
5% Cu/TiO$_2$	77	63	70	0.35	0.25	0.31	128	108	125
10% Cu/TiO$_2$	70	56	65	0.30	0.23	0.29	119	107	128
20% Cu/TiO$_2$	62	41	51	0.25	0.19	0.24	116	113	136

Table 5.6 Copper content for Cu/TiO$_2$ catalysts

SAMPLE	COPPER CONTENT (%)		
	IMPREG	SCCO$_2$-Me	SCCO$_2$-Cy
2 % Cu/TiO$_2$	1.8	1.7	1.7
5 % Cu/TiO$_2$	4.5	4.6	4.5
10 % Cu/TiO$_2$	11	10.5	10.3
20 % Cu/TiO$_2$	21	18.9	18.7

Further more, the copper contents of the Cu/TiO_2 catalysts prepared by the two deposition techniques with supercritical carbon dioxide ($SCCO_2$-Me and $SCCO_2$-Cy) were comparable.

5.2.4 *Active sites and metal dispersion*

Active sites were measured by chemisorption using nitrous oxide (N_2O) and the results were listed in Table 5.7. The number of active sites grew larger as the copper loading increase for all Cu/TiO_2 catalysts. Cu/TiO_2 catalysts that were prepared using supercritical carbon dioxide, i.e., $SCCO_2$-Me and $SCCO_2$-Cy, possessed comparable numbers of active sites, which were significantly greater (23%-80%) than Cu/TiO_2 catalysts that were prepared by incipient wetness impregnation technique. After we measured the number of active sites on the catalyst, metal dispersion for copper on TiO_2 could be calculated according to a procedure described in Appendix A. the results for metal dispersion for Cu/TiO_2 catalyst were shown in table 5.8. As the copper loading was increased copper dispersion became less because a grater amount of copper was deposited on the surface of TiO_2 while the surface area remained essentially the same. Cu/TiO_2 catalysts that were prepared using supercritical carbon dioxide, i.e., $SCCO_2$-Me and $SCCO_2$-Cy, possessed comparable dispersion of copper on TiO_2. Nevertheless, $SCCO_2$-Me and $SCCO_2$-Cy had significantly grater copper dispersion (36%-83%) than Cu/TiO_2 catalysts that were prepared using incipient wetness impregnation technique. These results may be attributed to the ability of supercritical carbon dioxide, that could diffuse into pores of the support better than water

Table 5.7 Result from active site measurements for Cu/TiO_2 catalysts

SAMPLE	ACTIVE SITE (X 10^{-18} sites)		
	IMPREG	$SCCO_2$-Me	$SCCO_2$-Cy
2% Cu/TiO_2	0.67	1.00	0.84
5% Cu/TiO_2	1.00	1.80	1.70
10% Cu/TiO_2	1.76	2.35	2.33
20% Cu/TiO_2	2.36	2.94	2.90

Table 5.8 Dispersion of copper on Cu/TiO_2 catalysts

SAMPLE	COPPER DISPERSION (%)		
	IMPREG	$SCCO_2$-Me	$SCCO_2$-Cy
2% Cu/TiO_2	3.39	6.21	5.22
5% Cu/TiO_2	2.35	4.10	3.90
10% Cu/TiO_2	1.69	2.36	2.34
20% Cu/TiO_2	1.19	1.64	1.62

5.3 Measurement of catalytic activity for oxidation of carbon monoxide

5.3.1 *Cu/ZnO Catalysts*

Prior to each activity measurement, Cu/ZnO catalyst was reduced under hydrogen atmosphere at 400 ^{o}C for one hour. The activity of Cu/ZnO catalyst was measured at a temperature ranging from 100 ^{o}C to 500 ^{o}C. Figures 5.7 and 5.8 display the catalytic activities as a function of temperature for Cu/ZnO catalysts that were prepared by incipient wetness impregnation technique and deposition technique using supercritical carbon dioxide and methanol respectively. From Figure 5.7, the activities of the catalysts were in the following order.

10% Cu/ZnO > 20% Cu/ZnO > 5% Cu/ZnO > 2% Cu/ZnO

On the other hand, the activities of the catalyst prepared by $SCCO_2$-Me technique were in the following order.

20% Cu/ZnO > 10% Cu/ZnO > 5% Cu/ZnO > 2% Cu/ZnO

Then we plotted conversion of CO at 250 ^{o}C vs. number of active sites for both Cu/ZnO catalysts (see Figure 5.9). For Cu/ZnO catalysts that were that prepared by $SCCO_2$-Me technique, the conversion of CO increased as the number of active sites increase. This finding suggested that oxidation of CO over Cu/ZnO catalysts that were prepared by $SCCO_2$-Me technique was a structure-insensitive surface reaction [Barnes et al., 2001]. However, since the activities of Cu/ZnO catalyst that were prepared by incipient wetness impregnation did not follow the same trend, we concluded that oxidation of CO on these catalysts was not a structure-insensitive surface reaction.
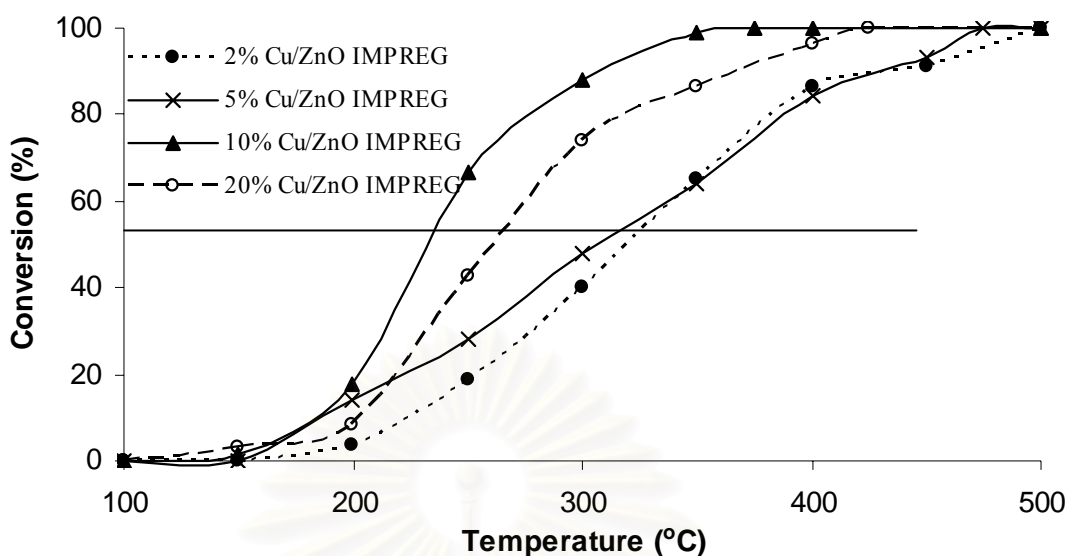
Figure 5.7   Activity of Cu/ZnO catalysts prepared by incipient wetness impregnation method on oxidation of CO as a function of temperature.
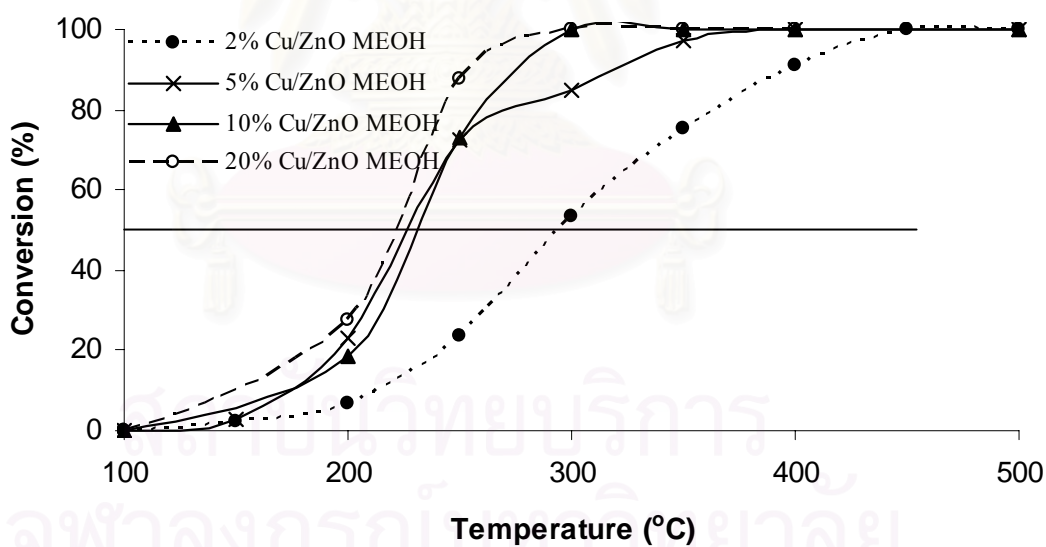

Figure 5.8   Activity of Cu/ZnO oxide catalysts prepared by deposition technique using supercritical carbon dioxide and methanol for oxidation of CO as a function of temperature.
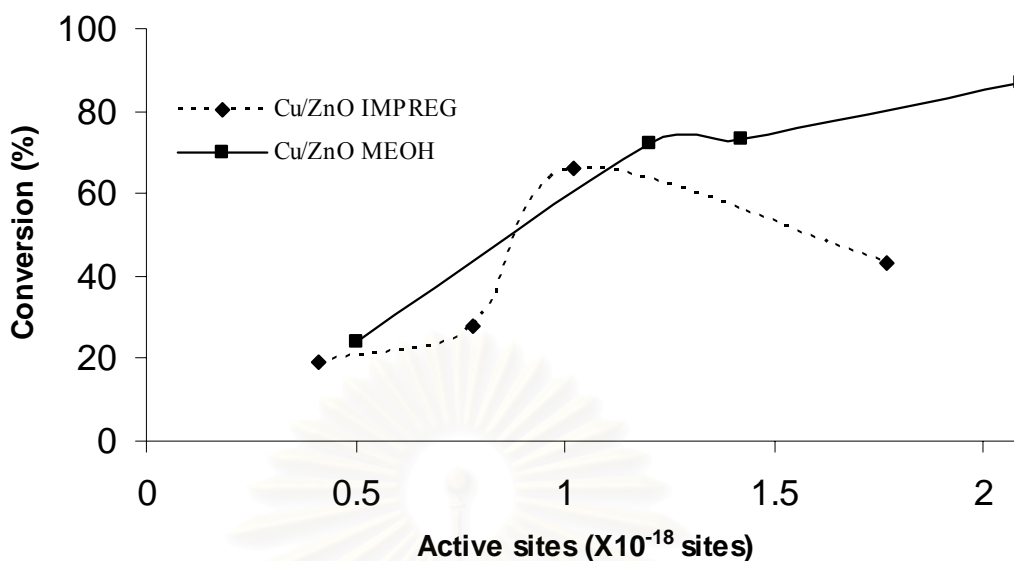
Figure 5.9   Conversion of CO at 250 $^{\circ}$C for Cu/ZnO catalysts as a function of number of active sites

Next, we determined the light off temperature for each catalyst from the temperature at which 50% conversion of CO was achieved When we compared the activities (in term of light off temperature) of Cu/ZnO that were prepared by the two techniques (as shown in Figure 5.10), the active sites of Cu/ZnO catalyst were prepared by SCCO$_2$-Me technique were higher than those of Cu/ZnO catalysts that were prepared by incipient wetness impregnation technique at similar copper content. These higher activities could be a consequence of higher dispersion of copper on ZnO obtained from the use of supercritical carbon dioxide.
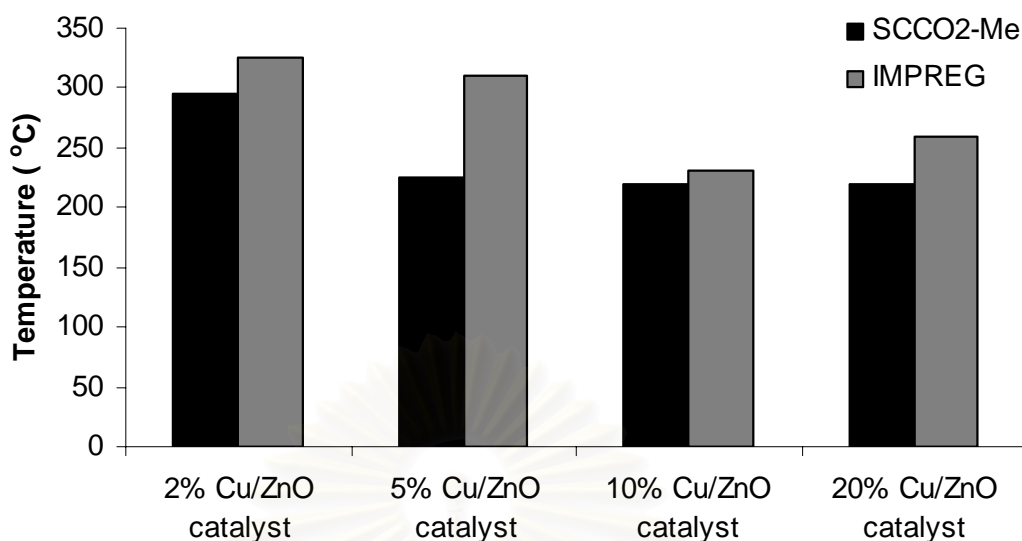
Figure 5.10   Comparison of light off temperature at various copper contents for Cu/ZnO catalysts that were prepared by incipient wetness impregnation technique and deposition technique using supercritical carbon dioxide and methanol.

Figure 5.11 display a comparison of activities of 20% Cu/ZnO catalysts that were prepared by the three techniques. Very low activities for oxidation of CO were observed for 20% Cu/ZnO catalyst that was prepared by deposition technique using supercritical carbon dioxide and Cyanex 301. These low activities could be attributed to poisoning of catalyst by the presence of organic chemical (i.e., Cyanex 301) on the surface. To ascertain this, thermogravimetic analysis (TGA) was performed for the three samples. The results from TGA were displayed in Figure 5.12. The weight losses for 20% Cu/ZnO catalysts that were prepared by incipient wetness impregnation technique and SCCO$_2$-Me technique became constant after the temperature exceeded 500 °C. However, the weight loss for 20% Cu/ZnO catalyst that was prepared by SCCO$_2$-Cy technique decreased steadily even when the temperature exceeded 800 °C. This result suggested that organic chemical remained on the surface of the catalyst.
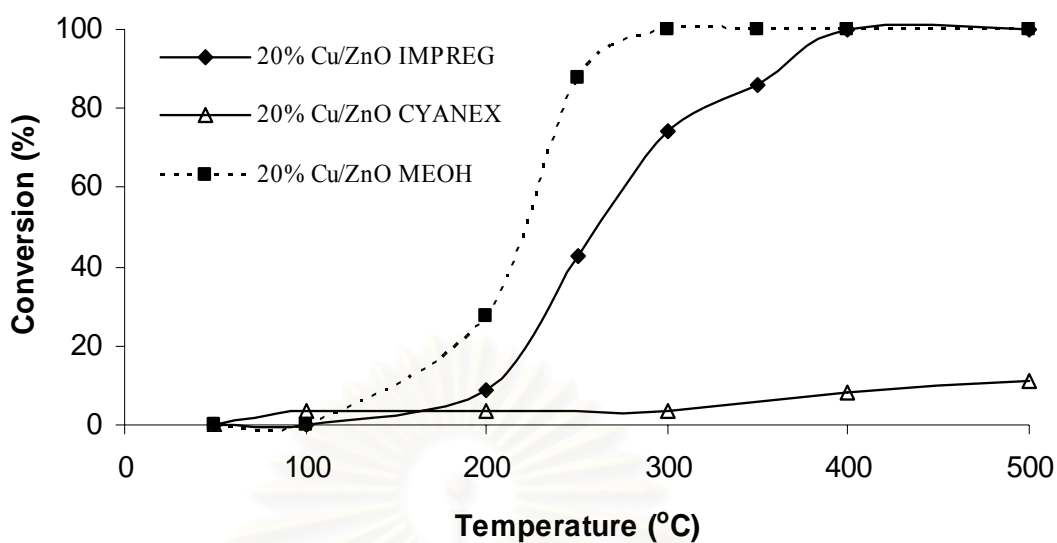
Figure 5.11 Activity of 20% Cu/ZnO catalysts prepared by the three different techniques as a function of temperature.
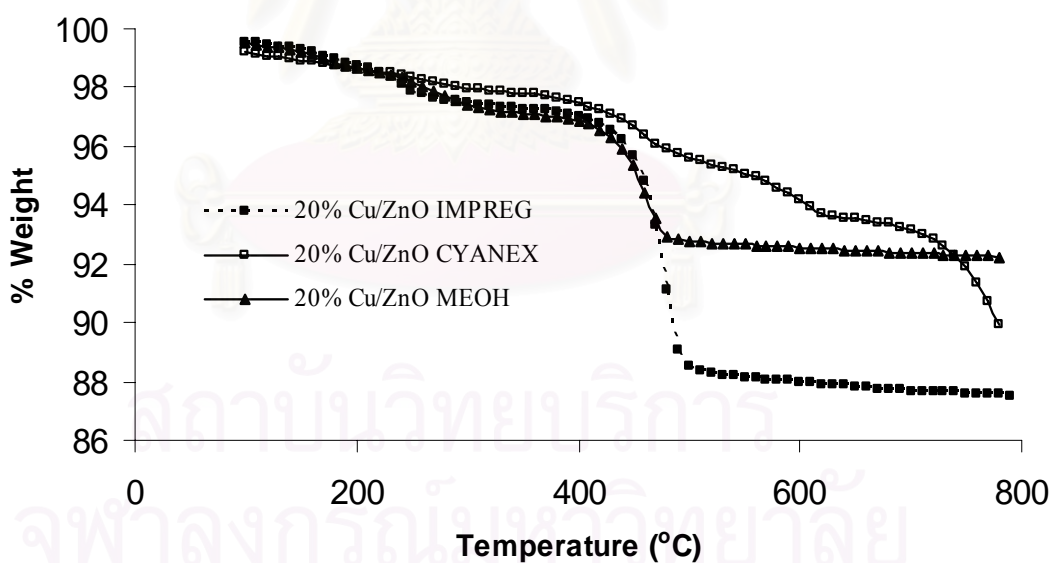

Figure 5.12 Results from thermogravimetric analysis of 20% Cu/ZnO catalysts that were prepared by the three different techniques.

5.3.2 *Cu/TiO$_2$ Catalysts*

Prior to each activity measurement, Cu/TiO$_2$ catalyst was reduced under hydrogen atmosphere at 400 ^{o}C for one hour. The activity of Cu/TiO$_2$ catalyst was measured at a temperature ranging from 50 ^{o}C to 250 ^{o}C. Figures 5.13 and 5.14 display the catalytic activities as a function of temperature for Cu/TiO$_2$ catalysts that were prepared by incipient wetness impregnation technique and deposition technique using supercritical carbon dioxide and methanol respectively. From Figure 5.13, the activities of the catalysts were in the following order.

5% Cu/TiO$_2$ > 2% Cu/TiO$_2$ > 10% Cu/TiO$_2$ > 20% Cu/TiO$_2$

On the other hand, the activities of the catalyst prepared by SCCO$_2$-Me technique were in the following order.

5% Cu/TiO$_2$ > 2% Cu/TiO$_2$ > 10% Cu/TiO$_2$ > 20% Cu/TiO$_2$

Then we plotted conversion of CO at 125 ^{o}C vs. number of active sites for both Cu/TiO$_2$ catalysts (see Figure 5.15). For Cu/TiO$_2$ catalysts that were that prepared by incipient wetness impregnation technique, the activity of the catalysts decreased as the number of active sites increased. This behavior suggested that the oxidation of CO those Cu/TiO$_2$ catalysts were a structure-sensitive surface reaction. For Cu/TiO$_2$ catalysts that were prepared by SCCO$_2$-Me technique, the activities of the catalysts remained steady and did not change as the number of active sites increased. This behavior suggested that the oxidation of CO over these Cu/TiO$_2$ catalysts was also a structure-sensitive surface reaction [Barnes et al., 2001].

When we compared the activities (in term of light off temperature) of Cu/TiO$_2$ that were prepared by the two techniques (as shown in Figure 5.16), the active sites of Cu/TiO$_2$ catalyst were prepared by SCCO$_2$-Me technique were higher than those of Cu/TiO$_2$ catalysts that were prepared by incipient wetness impregnation technique at the similar copper content. These higher activities could be a consequence of higher dispersion of copper on TiO$_2$ obtained from the use of supercritical carbon dioxide.
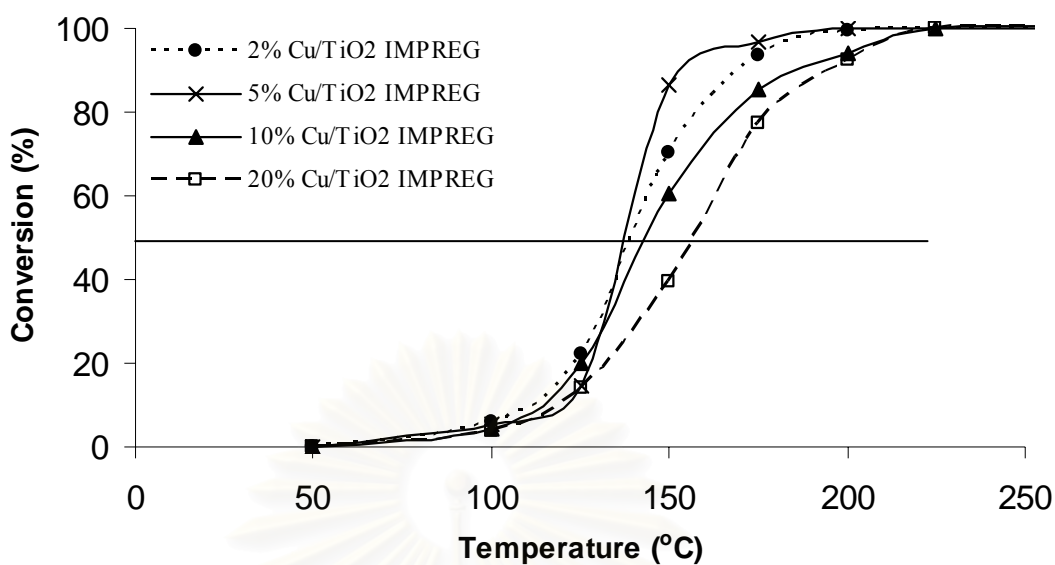
Figure 5.13 Activity of Cu/TiO₂ catalysts prepared by incipient wetness impregnation method on oxidation of CO as a function of temperature.
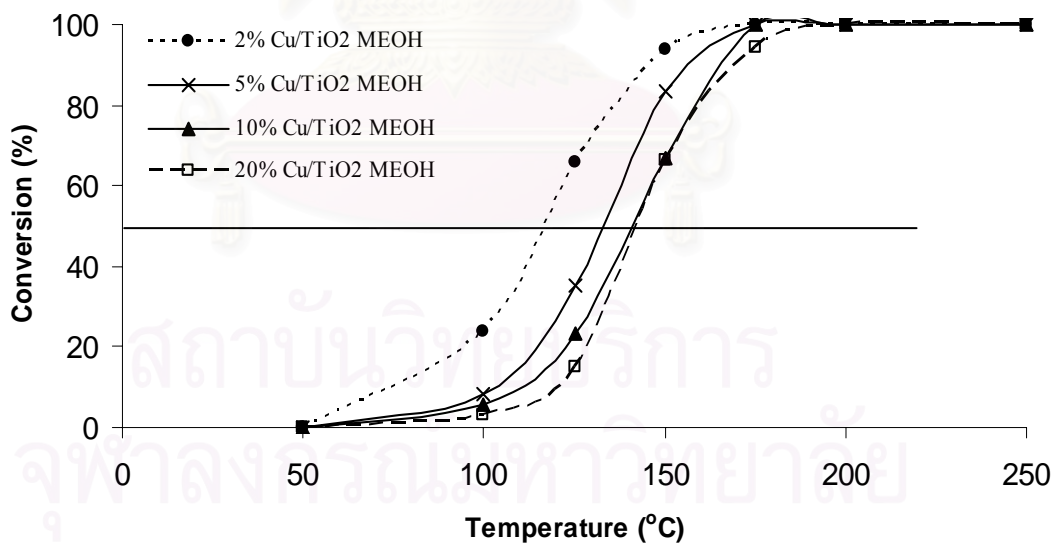

Figure 5.14 Activity of Cu/TiO₂ oxide catalysts prepared by deposition technique using supercritical carbon dioxide and methanol for oxidation of CO as a function of temperature.
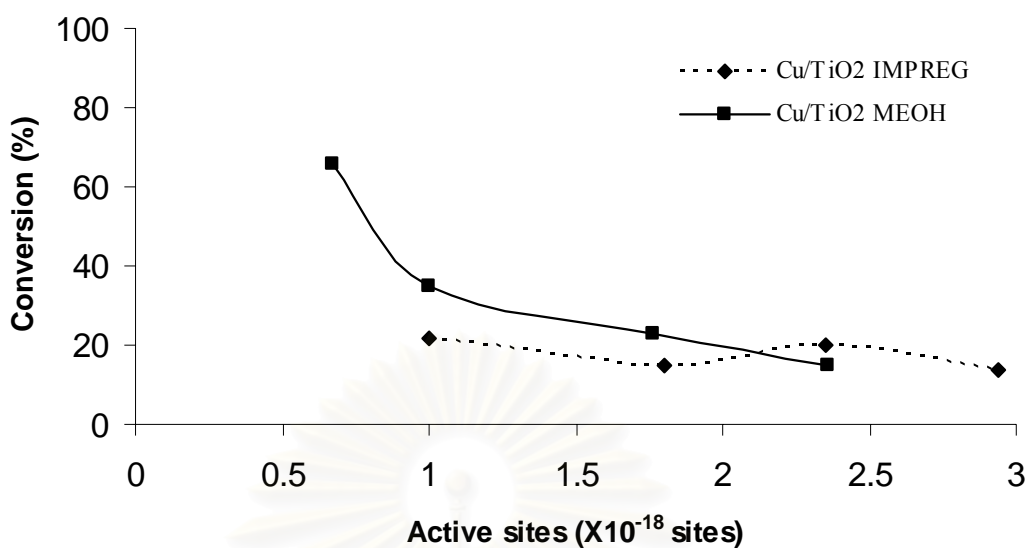
Figure 5.15 Conversion of CO at 125 °C for Cu/TiO$_2$ catalysts as a function of number of active sites
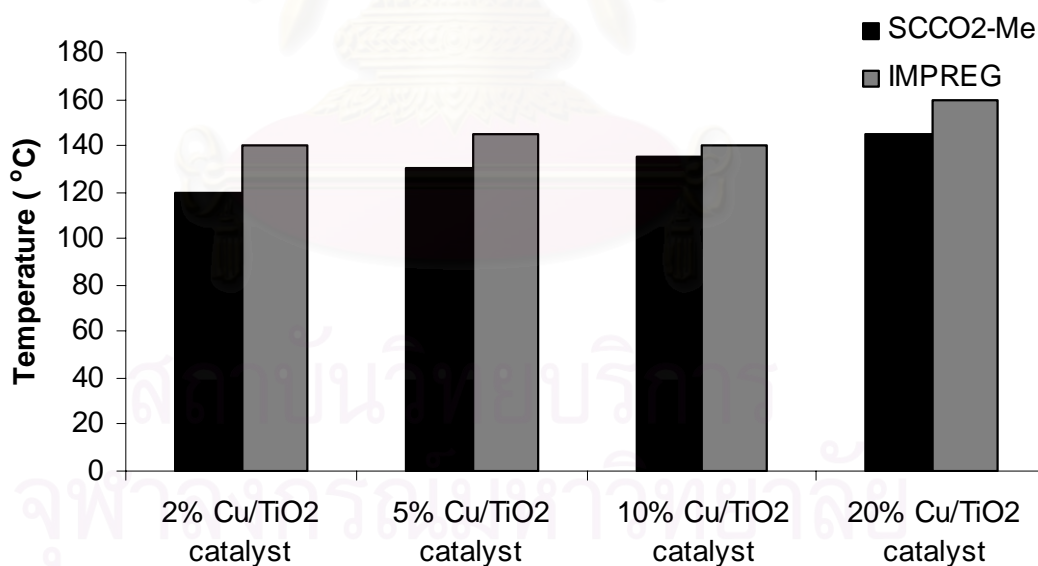

Figure 5.16 Comparison of light off temperature at various copper contents for Cu/TiO$_2$ catalysts that were prepared by incipient wetness impregnation technique and deposition technique using supercritical carbon dioxide and methanol.

Figure 5.17 display a comparison of activities of 20% Cu/TiO_2 catalysts that were prepared by the three techniques. Very low activities for oxidation of CO were observed for 20% Cu/TiO_2 catalyst that was prepared by deposition technique using supercritical carbon dioxide and Cyanex 301. There low activities could be attributed to poisoning of catalyst by the presence of organic chemical (i.e., Cyanex 301) on the surface. To ascertain this, thermogravimetic analysis (TGA) was performed for the three samples. The results from TGA were displayed in Figure 5.18. The weight losses for 20% Cu/TiO_2 catalysts that were prepared by incipient wetness impregnation technique and $SCCO_2$-Me technique became constant after the temperature exceeded 600 ^{o}C. However, the weight loss for 20% Cu/TiO_2 catalyst that was prepared by $SCCO_2$-Cy technique decreased steadily even when the temperature exceeded 800 ^{o}C. This result suggested that organic chemical remained on the surface of the catalyst.
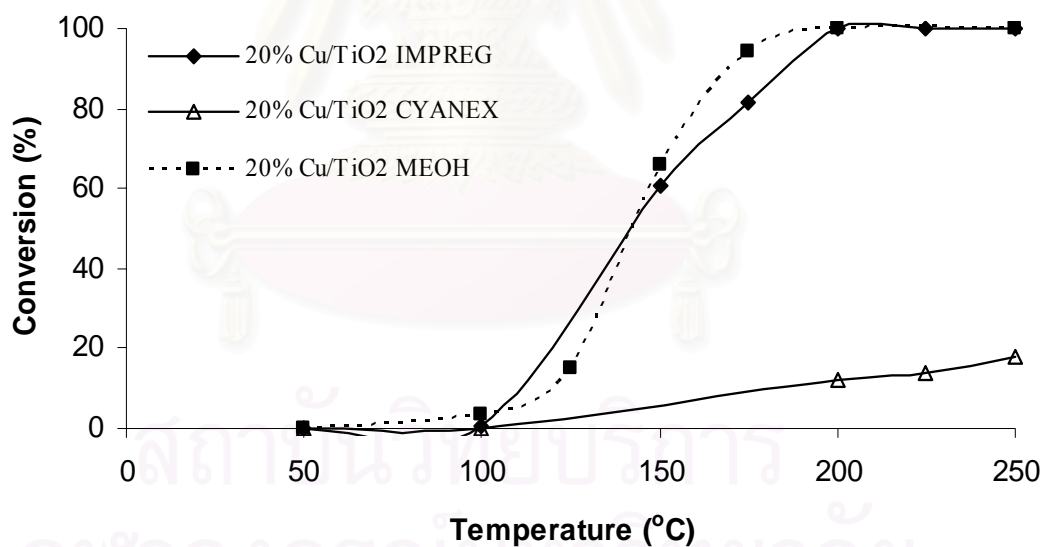

Figure 5.17   Activity of 20% Cu/TiO_2 catalysts prepared by the three different

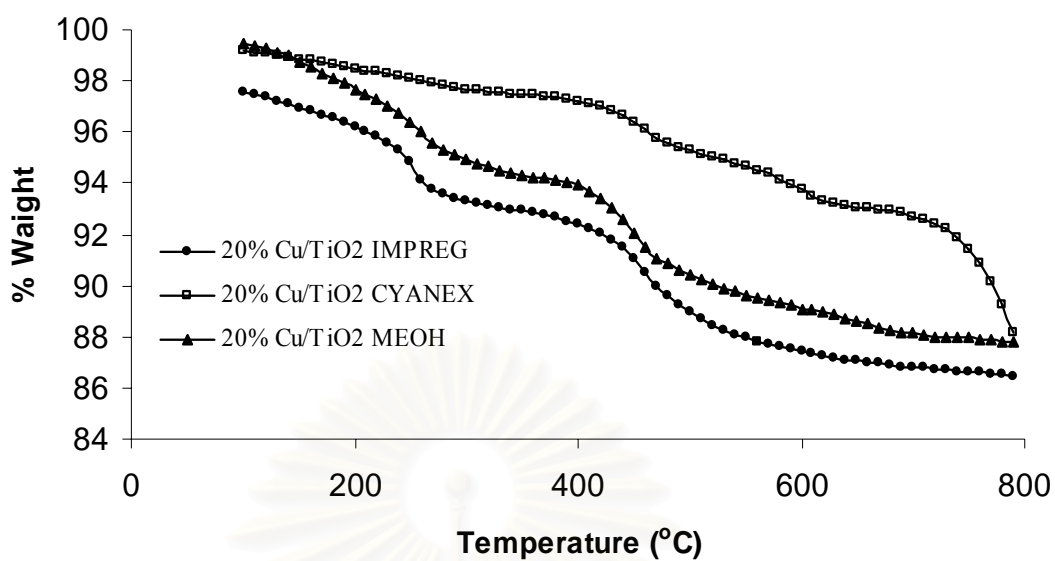   techniques as a function of temperature.

Figure 5.18   Results from thermogravimetric analysis of 20% Cu/TiO$_2$ catalysts that were prepared by the three different techniques.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

In this study, properties of Cu/ZnO and Cu/TiO$_2$ catalysts prepared by deposition technique using supercritical carbon dioxide were investigated. The conclusions of the study are summarized as follows:

1. Cu/ZnO and Cu/TiO$_2$ catalysts that were prepared by deposition technique using supercritical carbon dioxide and methanol exhibited higher activities for CO oxidation than the catalysts prepared by incipient wetness impregnation technique due to higher dispersion of copper on the supports obtained from the use of supercritical carbon dioxide.
2. The oxidation of CO over Cu/ZnO catalysts that were prepared by SCCO$_2$-Me technique was a structure-insensitive surface reaction while the reaction over Cu/TiO$_2$ catalysts was a structure-sensitive surface reaction.

6.2 Recommendations for future studies

1. Employ Cu/ZnO and Cu/TiO$_2$ catalysts that were prepared by deposition technique using supercritical carbon dioxide in other reactions such as water gas shift and steam reforming of methanol.

2. Investigated the activity of the oxidation of CO using the catalyst on a support that was prepared by a sol-gel method.

REFERENCES

C. S. Kim, B. K. Moon, J. H. Park, S. T. Chung, and S. M. Son. Synthesis of nanocrystalline TiO2 in toluene by a solvothermal route. Journal of Crystal Growth 254(3-4) (2003): 405.

I.S.M. Zaidul, N.A. Nik Norulaini, A.K. Mohd Omar, and R.L. Smith Jr. Supercritical carbon dioxide (SC-CO2) extraction of palm kernel oil from palm kernel. Journal of Food Engineering 79 (2007): 1007–1014.

J. Liu, W. Wang, and G. Li. A new strategy for supercritical fluid of copper ions. Talanta 53 (2001):1149–1154.

J. Yu, Y.-F. Liu, A.-Y. Qiu, and X.-G. Wang. Preparation of isoflavones enriched soy protein isolate from defatted soy hypocotyls by supercritical CO_2. LWT-food science and technology 40 (2007): 800–806.

K. Mallick and M. S. Scurrell. CO oxidation over gold nanoparticles supported on TiO_2 and TiO_2-ZnO: catalytic activity effects due to surface modification of TiO_2 with ZnO. Applied Catalysis A 253 (2003): 527–536.

K. V.R. Chary, D. Naresh , V. Vishwanathan, M. Sadakane, and W. Ueda. Vapour phase hydrogenation of phenol over Pd/C catalysts:A relationship between dispersion, metal area and hydrogenation activity. Catalysis Communications 8 (2007): 471–477

M. Koh,K. Park, D. Yang, H. Kim, and H. Kim. The synergistic effect of organophosphorus and dithiocarbamate ligands on metal extraction in supercritical CO_2. The Korean Chemical Society 26(3) (2005): 423-427.

M. Manzoli, A. Chiorino, and F. Boccuzzi. Interface species and effect of hydrogen on their amount in the CO oxidation on Au/ZnO. Applied Catalysis B 52 (2004): 259–266.

N.-A. M. Deraz. Surface and catalytic property of Cu/Zn mixed oxide catalysts. Colloids and Surface A 190 (2001): 251–260.

N. G. Smart, T. E. Carleson, S. Elshani, S. Wang, and C. M. Wai. Extraction of toxic heavy metals using supercritical fluid carbon dioxide dontaining organophosphorus reagents. Industrial & Engineering Chemistry Research 36 (1997): 1819-1826.R. Barnes, I. M. Abdelrehim, and T. E. Madey. KMC

Simulations of Structure Sensitive Catalytic Reactions. Topics in Catalysis 14 (2001): 53

S. H. Taylor, G. J. Hutchings, and A. A. Mirzaei. The preparation and activity of copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation. Catalysis Today 84 (2003): 113–119.

S. Yin, Y. Fujishiro, J. H. Wu, M. Aki, and T. Sato. Synthesis and photocatalytic properties of fibrous titania by solvothermal reactions. Journal of Materials Processing Technology 137(1-3) (2003): 45.

U. R. Pillai, S. Deevi. Copper-zinc oxide and ceria promoted copper-zinc oxide as highly active catalysts for low temperature oxidation of carbon monoxide. Applied Catalysis B 65 (2006): 110–117.

W. Ning, H. Shen and H. Liu. Study of the effect of preparation method on CuO-ZnO-Al2O3 catalyst Applied Catalysis A. 211 (2001): 153–157.

Y. Lin, C. Liu, H. Wu, H. K. Yak and C. M. Wai. Supercritical fluid extraction of toxic heavy metals and uranium from acidic solutions with sulfur-containing organophosphorus reagents. Industrial & Engineering Chemistry Research 42 (2003): 1400-1405.

APPENDIX A

CALCULATION OF Cu DISPERSION

Let the weight of copper used from ICP   =   W   g

Molecular weight of Cu   =   63.543   g/mol

Amount of molecule per mol   = 6.02×10^{23} molecule/mol

Amount of active site of Cu   =   A   molecule

% Dispersion of Cu   = $[A/((w/63.543) \times 6.02 \times 10^{23})] \times 100$
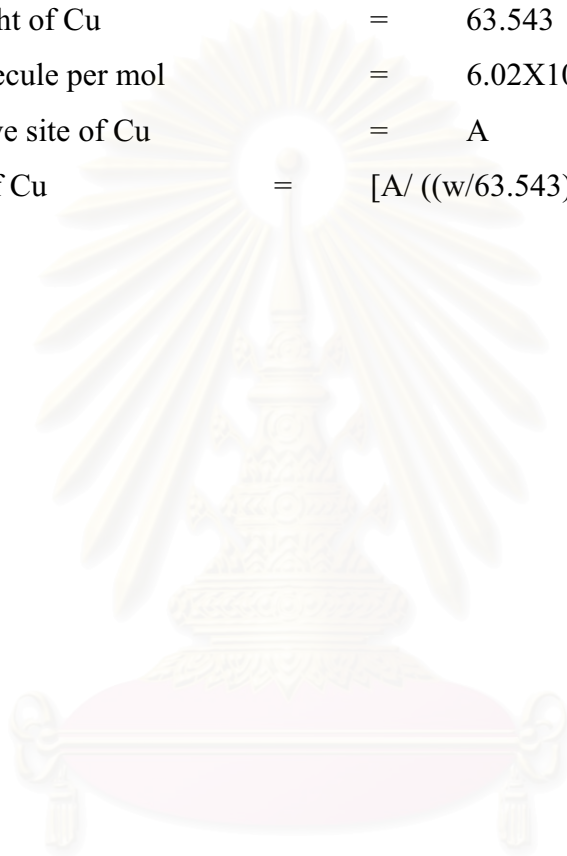
VITA

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