

การสังเคราะห์ไดเมทิลอีเทอร์แบบอนุกรมิตำจากแก๊สสังเคราะห์บนตัวเร่งปฏิกิริยาคอปเปอร์
ซิงก์ออกไซด์/เฮกแซดเอสเอ็ม-5



นางสาวสุวิทนา เทพพุด

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

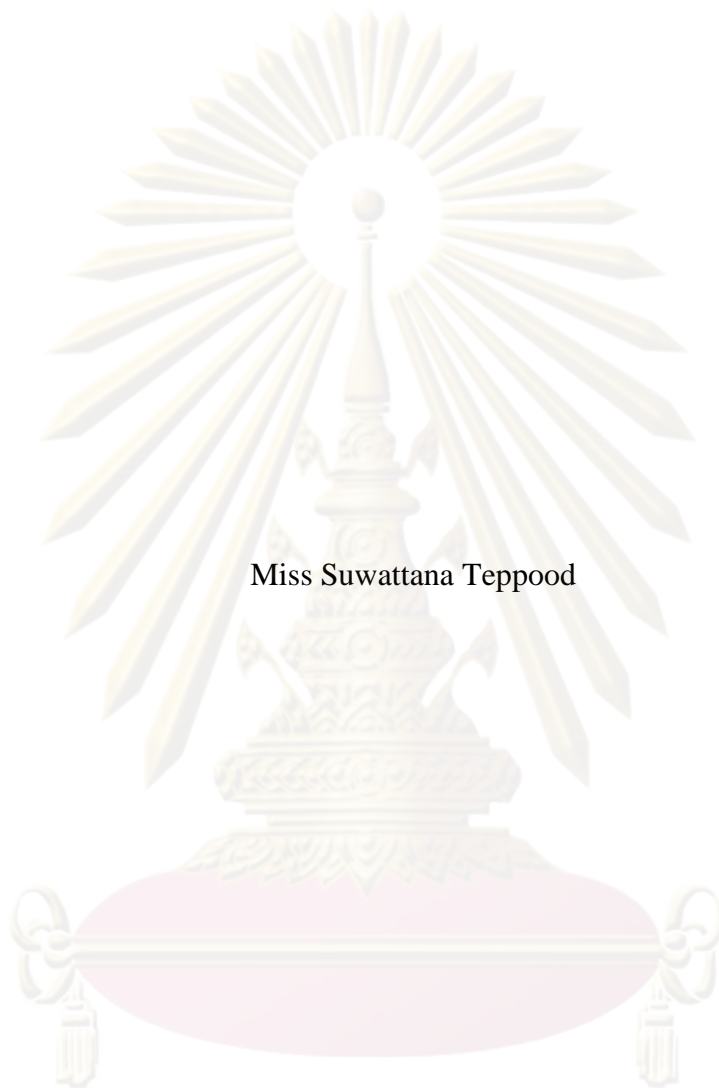
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2552

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

LOW-TEMPERATURE SYNTHESIS OF DIMETHYL ETHER FROM SYNGAS
OVER CuZnO/HZSM-5 CATALYSTS



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ศูนย์วิทยทรัพยากร
A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

จุฬาลงกรณ์มหาวิทยาลัย
Faculty of Science


Chulalongkorn University

Academic Year 2009

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Thesis Title LOW-TEMPERATURE SYNTHESIS OF DIMETHYL
ETHER FROM SYNGAS OVER CuZnO/HZSM-5
CATALYSTS
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สุวิทนา เทพพุด : การสังเคราะห์ไดเมทิลอีเทอร์แบบอุณหภูมิต่ำจากแก๊สสังเคราะห์บน
ตัวเร่งปฏิกิริยาคอปเปอร์ซิงก์ออกไซด์/เฮกแซดเอ็มเอ็ม-5. (LOW-TEMPERATURE
SYNTHESIS OF DIMETHYL ETHER FROM SYNGAS OVER CuZnO/HZSM-5
CATALYSTS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร. ประเสริฐ เรียบร้อยเจริญ, 76 หน้า.

วิธีการสังเคราะห์ไดเมทิลอีเทอร์ (ดีเอ็มอี) แบบใหม่ ที่อุณหภูมิต่ำ (170 องศาเซลเซียส)
จากแก๊สสังเคราะห์ได้ถูกพัฒนาขึ้นเป็นครั้งแรก ด้วยการรวมกันของตัวเร่งปฏิกิริยาผสมระหว่าง
คอปเปอร์ซิงก์ออกไซด์/เฮกแซดเอ็มเอ็ม-5 ซึ่งเป็นตัวเร่งปฏิกิริยาแบบดั้งเดิมสำหรับการสังเคราะห์
ดีเอ็มอี กับเมทานอลซึ่งประพฤติตัวเป็นตัวทำละลายเร่งปฏิกิริยาร่วมกับตัวเร่งปฏิกิริยาแบบ
ดั้งเดิม การเติมเมทานอลเข้าสู่ระบบปฏิกิริยาเป็นกุญแจที่ทำให้การสังเคราะห์ดีเอ็มอีสำเร็จได้ที่
อุณหภูมิต่ำ จากผลการทดลองพบว่า ค่าร้อยละการเปลี่ยนของคาร์บอนมอนอกไซด์มีค่า 30.9
และค่าร้อยละการเลือกเกิดเป็นดีเอ็มอีมีค่าและ 72.5 ที่ภาวะในการสังเคราะห์ดีเอ็มอีแบบ
อุณหภูมิต่ำจากแก๊สสังเคราะห์ คือ อุณหภูมิ 170 องศาเซลเซียส ความดัน 4.0 เมกะปาสคาล
ตัวเร่งปฏิกิริยาหนัก 1 กรัม (อัตราส่วนของคอปเปอร์ซิงก์ออกไซด์/เฮกแซดเอ็มเอ็ม-5 เท่ากับ 2:1
โดยน้ำหนัก) เมื่อใช้เมทานอลปริมาตร 40 มิลลิลิตร เป็นตัวทำละลายเร่งปฏิกิริยา ยิ่งไปกว่านั้น
พบว่า ไม่มีผลิตภัณฑ์ข้างเคียงอื่น รวมทั้งเมทานอลและสารไฮโดรคาร์บอนปะปนในผลิตภัณฑ์
ดีเอ็มอี จึงไม่จำเป็นต้องนำสารผลิตภัณฑ์ที่ได้รับเข้าสู่ขั้นตอนการทำให้บริสุทธิ์ ดังนั้นกระบวนการ
นี้จึงมีศักยภาพในการผลิตดีเอ็มอีที่มีความบริสุทธิ์สูง โดยใช้พลังงานในการผลิตที่ต่ำ และมีโอกาส
นำกระบวนการที่ได้รับการพัฒนาขึ้นนี้ไปใช้ในการผลิตดีเอ็มอีเชิงเศรษฐกิจที่ยั่งยืนในอนาคต

ศูนย์วิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต...สุวิทนา เทพพุด.....
ปีการศึกษา.....2552.....ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก...✓✓✓.....

4972549023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: DIMETHYL ETHER / METHANOL / LOW TEMPERATURE / HZSM-5

SUWATTANA TEPPOOD : LOW-TEMPERATURE SYNTHESIS OF DIMETHYL ETHER FROM SYNGAS OVER CuZnO/HZSM-5 CATALYSTS. THESIS ADVISOR : ASST. PROF. PRASERT REUBROYCHAROEN, Ph.D., 76 pp.

A new dimethyl ether synthesis route from syngas at a low temperature (170°C) has been developed for the first time by the combination of a conventional DME synthesis catalyst (CuZnO/HZSM-5 catalyst) with methanol as a catalytic solvent. The addition of methanol to the reaction system is the key to the success of DME synthesis at this temperature. Indeed, CO conversion of 30.9% and DME selectivity of 72.5% were achieved at 170°C, 4.0 MPa and over a 1 g of catalyst (ratio of CuZnO/H-ZSM-5 = 2:1), when 40 mL of methanol was used as a catalytic solvent. Importantly, no other by-products including methanol and hydrocarbons were observed in the DME product attained, suggesting no significant subsequent purification stages. This process potentially provides a high purity of DME with less energy consumption, and so offers an opportunity of economically viable future sustainable production of DME.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Field of Study:..Petrochemistry and Polymer Science... Student's Signature:..Suwattana
Academic Year:..2009.....Advisor's Signature:..P.L.

ACKNOWLEDGEMENTS

The author would like to express her sincere gratitude to advisor, Asst. Prof. Dr. Prasert Reubroychareon for his encouraging guidance, supervision and helpful suggestion throughout this research. The author is grateful to Prof. Dr. Pattarapan Prasassarakich, Assoc. Prof. Dr. Wimonrat Trakarnpruk, and Asst. Prof. Dr. Chaiyan Chaiya for serving as chairman and members of thesis committee, respectively and for their worthy comments and suggestions. Many thanks are going to technicians of the Department of Chemical Technology, Chulalongkorn University. The author gratefully acknowledges the funding support from The 90th anniversary of Chulalongkorn university fund (Ratchadaphiseksomphot Endowment Fund), Program of Petrochemistry and Polymer Science, PTT Public Company Limited, and National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, NCE-PPAM. Eventually, the author would like to express her gratitude to family members for their love, understanding and great support throughout her study. Also, special thanks are expanded to her friends for friendship, encouragements and cheerful moral support.



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LIST OF ABBREVIATIONS

°C	:	Degree Celsius
Å	:	Angstrom
ml	:	Milliliter
cm	:	Centimeter
nm	:	Nanometer
MPa	:	Mega pascal
%wt	:	Weight percentage
2θ	:	Two-theta angle
GC	:	Gas chromatograph
XRD	:	X-ray diffraction
BET	:	Brunauer Emmett Teller
WGS	:	Water gas shift
ΔH	:	Heat of reaction
(Surf)	:	Surface of catalyst
(a)	:	Active site
(ads)	:	Adsorption
T _{reaction}	:	Reaction temperature
MW	:	Molecular weight

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CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Over the past decade, energy has become a keyword in the affairs of most countries. Nearly 90% of the world's energy comes from petroleum fuels. Petroleum fuels include coal, natural gas and petroleum, which is often called oil. People use petroleum fuels to meet nearly all of their energy needs, such as powering cars, producing electricity for light and heat, and running factories. Petroleum fuels are a popular source of energy because they are considered convenient, effective, plentiful and inexpensive. But a few nations have most of the world's petroleum fuels, a fact that often causes conflicts. However, petroleum fuels are non-renewable resources and are the major drawback of using this fuel that contributes to air and water pollution.

The global community has begun looking for ways to reduce their dependence on petroleum fuels by exploring alternative sources of energy or an alternative fuel. A means of reducing the dependency on petroleum fuels is to use fuels derived from natural gas, biomass or coal such as methane, ethanol, DME, Fischer-Tropsch fuels, biodiesel and biogasoline. These are being researched as alternative fuels. The best candidate of all alternative fuels must be compatible with the proposed energy demand and required technology, environmental and emissions, economics and availability. Compared to some of the other leading alternative fuel candidates (i.e. , methane, methanol, ethanol and Fischer-Tropsch fuels), DME could potentially be an alternative fuel for 21st century due to its major advantages such as environmental friendly, infrastructure, non-petroleum feed stocks, economics and safety [1].

Dimethyl ether (DME) is the simplest ether; with a chemical formula CH_3OCH_3 , colorless gas at ambient temperature and has a sweet ether-like odor. DME is a useful chemical intermediate for production of many important chemicals such as dimethyl sulfate, methyl acetate, light olefins and also used as an environmental friendly aerosol propellant and green refrigerant because of their zero

ozone depletion potential (ODP) and lower globe warming potential (GWP). In view of DME as an alternative fuel, it is a potentially clean fuel for diesel engines due to its high cetane number (>55) and the low emission of CO, NO_x and particulates in its combustion. Moreover, DME can also be a substitute for liquefied petroleum gases (LPG) because its physical properties are similar to LPG, consequently, it may be stored and handled under the same conditions as those of easily transported domestic gases [2]. Traditionally, DME has been produced in a two step processes where syngas is first converted to methanol and followed by methanol dehydration to DME. However, the cost of DME is mainly controlled by the methanol price. Recently, a technology for direct synthesis of DME was developed. DME is directly produced from syngas over a hybrid catalyst, which is composed of a methanol synthesis catalyst consisting of a metallic function (such as CuO, ZnO, Al₂O₃ and Cr₂O₃) and a methanol dehydration catalyst consisting of an acid function (such as γ -Al₂O₃, HZSM-5 or HY zeolites, SAPO₅). The reaction conditions of direct synthesis of DME operated at temperature above 250°C and high pressure of more than 3.0 MPa [3]. Under these severe reaction conditions caused of rapidly deactivated catalyst and high production investment from energy supply in the production process. In terms of DME as a potential clean alternative fuel, much consideration should be given to the production of DME in the large quantities so the production cost becomes important. In previous researches there was almost no literature investigating DME synthesis with considerations on the temperature. Thus, this research was developed to propose a novel process of DME synthesis from syngas at low temperature by using methanol as a liquid solvent over the conventional hybrid catalyst. Furthermore, the effects of temperature, methanol content component and weight ratio of hybrid catalyst on semi-continuous slurry reactor are also studied.

1.2 Objective of Research

To synthesize DME from syngas at low-temperature and investigate the effect of using methanol as a liquid solvent.

1.3 Scope of Research

DME synthesis reaction was performed under low-temperature process in a slurry reactor by using methanol as a liquid solvent.

The experimental procedures were carried out as follows:

1. Survey related literature.
2. Prepare copper zinc oxide (Cu/ZnO) catalysts with Cu/Zn at mole ratio of 1:1.
3. Prepare Cu/ZnO/HZSM-5 catalyst by physical mixing of Cu/ZnO catalyst and HZSM-5 zeolite with different weight ratio.
4. Characterize the prepared catalysts as follows:
 - (A) X-ray diffraction
 - (B) BET surface area
5. Synthesize DME in a semi-continuous type reactor and use syngas ($H_2:CO = 1:1$) as reactant gas.
6. Analyze the gas products by on-line gas chromatograph with detectors as follows:
 - (A) Flame Ionization detector (FID) for DME, methanol and hydrocarbons.
 - (B) Thermal Conductivity detector (TCD) for carbon monoxide and carbon dioxide.
7. Summarize the results and write thesis.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Dimethyl Ether Backgrounds

The current pricing of crude oil has led to seek for non-petroleum based alternative fuels, along with more advanced energy technologies to increase the efficiency of energy use. The most promising alternative fuel will be the fuel that has the greatest impact on society. The major impact areas include greenhouse effect gas emissions, non-petroleum feed stocks, fuel versatility, infrastructure, availability, economics, and safety. Compared to some of the other leading alternative fuel candidates, dimethyl ether (DME) appears to have the largest potential impact on the society, and should be considered as the fuel of choice for eliminating the dependency on petroleum.

DME is gaining worldwide recognition as a multisource, multipurpose clean fuel and chemical feedstock for the 21st century. It is a technically mature, environmentally friendly, and market acceptable alternative fuel. It can be readily produced from natural gas and coal, renewable resources such as biomass and wood, as well as waste matter. It can be used as a clean-burning fuel in a diesel engines, a household fuel (liquefied petroleum gas; LPG) for heating and cooking, a fuel for gas turbines in power generation, a fuel for fuel cells, a feedstock for producing chemicals and oxygenates and a propellant in the aerosols markets. Application of DME as a fuel in various industries has been successfully tested by a number of leading companies. Although studies indicate that DME will become economical when oil prices are at or above a threshold price per barrel, it is clear that recent strides in DME synthesis technology show that it holds tremendous promise with a realistic aspiration to develop into an alternative transportation and domestic fuel. It is apparent that DME production costs will get even lower when its production capacities increase as more and more countries start embracing the idea of utilizing this fuel as a viable

alternative. Feasibility studies on producing DME from syngas have been carried out by NKK Corporation at their 5 ton/day facility and by Haldor Topsoe at their 50 kg/day facility. In addition, commercial plants have been planned under way such as India DME project of 5000 ton/day, DME International Corporation Japan of 2500-4500 ton/day and Japan DME Inc. of 5000 ton/day.

2.2 Properties of Dimethyl Ether [2]

Dimethyl ether (or DME) is the simplest ether having the chemical formula: CH_3OCH_3 . Table 2.1 shows the physical properties and combustion characteristics of DME and related fuels. DME is a colorless gas at ambient temperature, chemically stable, with a boiling point of $-24.9\text{ }^\circ\text{C}$ and its vapor pressure is about 0.6 MPa at $25\text{ }^\circ\text{C}$, DME is easily liquefied. Liquid DME is colorless and its viscosity is 0.12-0.15 kg/m-s, as low as that of propane or butane. It is non-carcinogenic, virtually non-toxic and also non-corrosive in nature. A toxicity study of DME use as propellant to replace fluorocarbons has confirmed that its toxicity is extremely low. DME is decomposed in the troposphere for several hours and has no contribution to the greenhouse effect and ozone layer depletion.

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Table 2.1 Physical properties and combustion characteristics of dimethyl ether and other fuels [2]

	Methane	Methanol	DME	Ethanol	Gasoline	Diesel
Formula	CH ₄	CH ₃ OH	CH ₃ OCH ₃	CH ₃ CH ₂ OH	C ₇ H ₁₆	C ₁₄ H ₃₀
Molecular weight (g mol ⁻¹)	16.04	32.04	46.07	46.07	100.2	198.4
Density (g cm ⁻³)	0.00072	0.792	0.661	0.785	0.737	0.856
Normal boiling point (°C)	-162	64	-24.9	78	38–204	125–400
LHV (kJ cm ⁻³)	0.0346 ^a	15.82	18.92	21.09	32.05	35.66
LHV (kJ g ⁻¹)	47.79	19.99	28.62	26.87	43.47	41.66
Energy (MJ L ⁻¹)	0.037	17.8	20.63	23.1	32.84	33.32
Energy (MJkg ⁻¹)	51.76	22.36	30.75	29.4	47.46	46.94
Carbon Content (wt%)	74	37.5	52.2	52.2	85.5	87
Sulfur content (ppm)	~ 7–25	0	0	0	~ 200	~ 250

The other characteristics of DME as a clean fuel is that it contains no sulfur or nitrogen compounds that are extremely toxic for humans and no corrosive effect on metals. Its calorific value is approximately 65% that of methane (natural gas) and approximately 40% that of methanol. Although DME has a lower calorific value than LPG because of differences in the chemical structure, the density of liquid DME is greater, so that the total calorific value of a tank of DME is approximately 90% of that of a similar tank of LPG. DME has high cetane value, contains oxygen and has a chemical structure that forms carbon-carbon bonds, so that its combustion is not accompanied by black smoke or soot.

As previously mentioned, DME could be used as a new clean fuel for various fields such as household fuel, transportation, power generation and as LPG. The cetane number of DME is high, thus it can be used in diesel engines. However, modification of fuel injection system is required to maintain stable fuel injection into the engine cylinder. The diesel engine test with DME showed that no black diesel exhaust smoke (particulate matter) was emitted at all, NO_x emissions were much lower than with diesel fuel and fuel consumption as measured by calories was identical to diesel fuel. Furthermore, DME is as easily reformed into hydrogen as methanol, it has a big potential for fuel as fuel cell for automobiles in future. For power generation, gas turbine test with DME was carried out successfully [2].

2.3 Application of Dimethyl Ether

High purity DME is currently used as an aerosol propellant and it also can be used as a clean alternative fuel. A brief description of its applications is given below.

2.3.1 Dimethyl Ether as a Transportation Fuel [2]

The need to develop alternative fuels is motivated by two important issues. First, the important factor is self-reliance in meeting fuel demands, as fossil fuel supply is controlled by a small number of oil exporting countries. Second, the

deleterious effect of fossil fuel combustion on the environment has caused harmful exhaust emission such as nitrogen oxides (NO_x), carbon monoxides, volatile organic compounds, carbon particulates and carbon dioxides which is a greenhouse gas. Use of DME, a cleaner burning oxygenate, has a very positive impact on these problems. Properties of DME are compared with those of diesel in Table 2.2.

Table 2.2 Comparison of dimethyl ether properties with diesel [2]

Property	DME	Diesel
Normal boiling point (°C)	-24.9	180-370
Liquid density (g/cm ³)	0.67	0.84
Ignition temperature (°C)	235	250
Explosion limit (%)	3.4-17	0.60-0.65
Cetane number	55-60	40-55
Net heating value (kcal/kg)	6900	10000

DME has attractive advantage as an ultraclean transportation fuel alternative, most notably as follows:

- DME molecules have no carbon-to-carbon bonds, which diminish the tendency to form solid carbon particulates during combustion.
- DME has a low auto-ignition temperature.
- DME has high cetane number in the range of 55 – 60, compared to about 45 for diesel. Molecular bonds of DME break up to form radicals at reasonable activation energy, which leads to high cetane number.
- The normal boiling point of DME is -24.9°C. This provides fast fuel/air mixture formation, reduces ignition delay, and imparts excellent cold start properties.
- Oxygen content of DME is 35 wt%, which suppress the formation of soot and facilitates smokeless combustion.

- DME qualifies as a renewable fuel, as it can be produced from biomass and wood.

The diesel car market is the biggest prospect for DME because of all the advantages mentioned above. However, it may take some time to establish distribution infrastructures and modification of engine parts. Therefore, DME may be used first for heavy duty fleets such as public buses and trucks. Big diesel car manufacturers like Nissan Diesel, Hino Motors, Isuzu, Mitsubishi Motors in Japan and Volvo in Sweden are actively developing DME-fueled heavy duty fleet cars [2].

2.3.2 Dimethyl Ether as a Household Fuel [4]

DME has the capability to serve as a substitute for LPG as household fuel for heating and cooking purposes, especially in Asian countries such as Japan, China, and India where the demand for LPG is growing. Utilization of DME as a household fuel can also reduce the burden on developing countries that use solid fuels like coal and firewood, which in turn have harmful effects on the environment. DME can be produced indigenously in developing countries by taking advantage of stranded natural gas fields in their vicinity. DME is a clean fuel and the total investment cost would be small because existing LPG infrastructures could be used with minor modification.

DME flame is a visible blue flame similar to that of natural gas, and it can be used in an LPG cooking stove without producing some aldehydes. Its lower explosion limit is higher than that of propane, indicating higher safety than propane in case of leakage. Combustion tests on DME have been conducted with mass-produced household cooking stoves in Japan, and have passed the Japan Industrial Standard combustion test. This study showed that stoves designed to burn city gas (85% methane, 15 % propane) could burn DME well with only an adjustment of the variable air dampers.

2.3.3 Dimethyl Ether for Power Generation [2]

DME is a promising new gas turbine fuel. Roughly speaking, 1 bcf/day of gas, converted into about 20,000 ton per day of DME, can generate about 10,000 MW of power. Utilization of DME for power generation offers tremendous environmental benefits, in term of CO_x , SO_x and NO_x emission. It burns in conventional gas turbines without modifications to the turbine or the combustors. Emissions produced by combustion of conventional fuels in gas turbine include nitrogen oxides, carbon monoxide, unburned hydrocarbons and sulfur oxides. DME produces no sulfur oxide emission, as the fuel is sulfur free. It generates the least amount of NO_x , CO and unburned hydrocarbon as compared with natural gas and distillate and lower CO_2 emissions than the distillates.

NKK Corporation has developed a process for DME production, which will greatly enhance the use of DME in power plants in Asia, especially in Japan, which typically use liquefied natural gas (LNG), LPG, fuel oil and coal. Fuel oil and coal are subject to environmental concerns. A possible solution to circumvent this problem would be to generate DME, which can be shipped and used in more energy-efficient and environmentally conscious manner. Liquefied natural gas and LPG are cleaner burning fuels, albeit at a much higher investment cost. Japan imports LNG, as fuel for electric power generation. Again, it would be economical to import DME produced from natural gas at medium and small-scale gas fields considered too small for LNG development for thermal power generation. The supply source for LPG is limited mainly to the Middle East for countries in Southeast Asia and the Far East. DME can substitute LPG in power generation applications, just like in household applications [4].

2.3.4 Dimethyl Ether for Fuel Cell [5]

Fuel cells can be powered by DME. Daimler Chrysler A.G. has studied the feasibility of using DME as a fuel in a polymer electrolyte membrane (PEM) fuel cell. In Germany, the collaboration with Ballard Power Systems and University of

Technology RWTH Aachen studied the direct oxidation fuel cells by using methanol as fuel. Result showed that using methanol as fuel is hindered by efficiency losses. The effect of methanol fuel crossover oxidation reaction at the cathode is the most significant efficiency loss; the other side effects are the use of parasitic fluid pumps and mild toxicity of methanol vapor. An advantageous finding of the study is that DME is typically not oxidized at the cathode of the fuel cell. This minimizes the unwanted effects of fuel crossover, leading to improved fuel cell efficiencies when compared to direct methanol fuel cells, especially at low to medium current densities.

Researchers at the Electrochemical Engine Center at the Pennsylvania State University have identified additional advantages of using DME as a fuel in PEM fuel cells. It must be noted that DME molecules do not have carbon-carbon double bonds, enabling nearly complete oxidation in low-temperature PEM fuel cells. Also, DME can be stored in high-density liquid phase at modest pressures of around 5 atm, and delivered as a gas-phase fuel in a pump less operation. Therefore, the use of DME can potentially combine the advantage of easy fuel delivery of pressurized hydrogen and the high energy density storage of liquid fuel [6].

2.3.5 Dimethyl Ether as Propellant [2]

DME has been increasingly used as a propellant in aerosol formulations to replace chlorofluorocarbons, which are found to destroy the ozone layer of the atmosphere. DME is nontoxic and easily degrades in the troposphere. Although about 90 % of the major current U.S. aerosol industry uses hydrocarbon-based propellants (mostly isobutene and propane). DME could become a more widely used propellant in the coming years. Several aerosol-based household products include colognes, hair sprays, dyes, personal care mousses, antiperspirants and room air fresheners.

Current suppliers for the DME propellant market include DuPont, Akzo Nobel and Mitsubishi Gas Chemicals. Demeon D, DME-based product from

Akzo Nobel, is used as a propellant in cosmetic formulations, foam blowing and paint or other aerosol sprays.

Dymel[®] A, a product based on DME manufactured by DuPont, is a medium- to high-pressure propellant for general aerosol use, including personal products. It has extremely low toxicity, its lower explosive limit in air is higher than that of propane and isobutene, and it is a chemically stable compound. In aqueous solutions, the propellant is hydrolytically stable over a wide pH range. Dymel[®] A is unique among aerosol propellants in that it has high solubility in both polar and nonpolar solvents. It is completely miscible with most organic solvents and is by itself a very good solvent for many types of polymers, e.g. hair sprays and paint resins. Dymel[®] A has 35 wt% solubility in water, which facilitates formulation of single phase products with large amounts of water and is the only liquefied gas aerosol propellant to do so.

2.3.6. Dimethyl Ether as a Chemical Building Block

DME is an essential intermediate in the synthesis of hydrocarbon from coal or natural gas derived syngas. DME is a building block for the preparation of many important chemicals, including methyl sulfate [7]. First, dimethyl sulfate is an important commercial commodity as a solvent and also as an electrolyte in high-energy-density batteries. Second, lower olefins like ethylene and propylene or downstream products such as gasoline and range boiling hydrocarbons, are produced from syngas using DME as an intermediate [8,9]. Finally, A variety of specialty industrial chemicals such as oxygenates, acetaldehyde, acetic acids, ethylene glycol precursor like 1,2-dimethoxyethane etc. can be formed using DME as a feedstock.

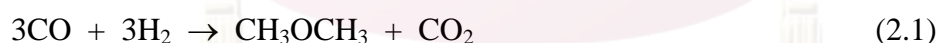
2.4 Dimethyl Ether Synthesis

In the past, traditionally, DME is the by-product of high pressure methanol synthesis and high purity product can be also produced through methanol dehydration.

However, the cost of DME is mainly controlled by methanol price when DME is produced as fuel; the production cost becomes more important than its purity. For this reason, researchers have developed a process for DME synthesis in the vapor phase but suffer from low per-pass conversions. This process has a drawback due to contributing high temperature that directly affects the catalyst life. Synthesis of DME in the gas phase has been studied in detail by Mobil Oil [10, 11]. In general, gas phase DME synthesis processes suffer from the drawbacks of low H₂ and CO conversions per pass, along with low yield and selectivity of DME coupled with a high yield of CO₂. In fact, these processes are typically expensive due to high capital costs for reactors and heat exchangers, and high recycle rates [12, 13].

Therefore, a novel process for producing DME from syngas in a single step has been developed by using an inert liquid as a heat sink for highly exothermic reactions. Heat generated by the exothermic reactions is readily accommodated by the inert liquid medium. This enables the reaction to be run isothermally, minimizing catalyst deactivation, which is commonly associated with the more adiabatic gas phase technologies.

The technology for direct synthesis of DME developed by NKK employs a single step reaction in a slurry phase reactor to synthesize DME from CO and H₂. An overall reaction of DME synthesis from syngas is shown in equation (2.1) below [4].



The equation (2.1) summarizes all of DME direct synthesis from CO and H₂. In practice, the reaction shows from following equations (2.2), (2.3) and (2.4) that occur simultaneously.



The two molecules of methanol synthesized from CO and H₂ in equation (2.2) are dehydrated in equation (2.3) to produce DME. The water produced in equation

(2.3) is recycled as hydrogen in equation (2.4) that is generally called the water-gas shift reaction. It is important to note that the hydrogen produced at the completion of the direct synthesis reaction becomes raw material for the reaction in equation (2.2). In this way, a reaction cycle is formed in which the three reactions consume the by-product in each step. The by-products of the reactions therefore accumulate only to a minimal extent, allowing extremely high conversion efficiency for the total reaction equation (2.1). The equation (2.1) becomes increasingly favorable with increasing pressure, so the reaction is conducted at a pressure of 3 to 7 MPa and temperatures of 250 to 280 °C (basic reaction conditions are 5 MPa and 260 °C).

Additionally, the reaction in equation (2.1) is a highly exothermic reaction that produces 58.8 kcal per mole of DME (approximately 1280 kcal per kilogram of DME). This reaction heat must be removed efficiently from the reactor to maintain a stable temperature and to allow stable control of the DME direct synthesis reaction. Development of using high-pressure DME slurry phase reactor has excellent mixing characteristics and easy control of the reaction temperature. This slurry phase reactor contains a high boiling point solvent (reaction medium) in which fine catalyst particle are mixed. The gases that form the raw materials of the reaction provide strong mixing of the catalyst. This ensures good flow of the gases within the reactor, a very even temperature distribution and ready control of the DME direct synthesis in the presence of the highly exothermic reaction.

2.4.1 The Advantages of Slurry Phase Reactor for Dimethyl Ether Synthesis [14].

A fixed bed is generally used for catalytic reaction. For exothermic reaction such as methanol synthesis, various design ideas are applied to control the temperature in the reactor. The reaction of DME synthesis is highly exothermic, it is more important how to control the reaction temperature than in the case of methanol synthesis, because the higher equilibrium conversion of DME synthesis could give higher reaction heat, and hot spot in the reactor could damage the catalyst. As shown in Figure 2.1, the slurry phase reactor is an apparatus in which the reactant gas forms

bubbles, and chemical reaction takes place during the bubbles rise in the slurry: a solvent containing fine catalyst particles. The heat of the reaction is quickly absorbed by the solvent, which has a large heat capacity, and high heat conductivity. The temperature within the reactor vessel can be easily controlled in order to achieve higher conversion with longer catalyst life. There are fewer restrictions on the shape and strength of the catalyst in the slurry phase reactor than in the fixed bed reactor. However, catalyst particles inside the reactor are surrounded by the solvent so it is required to develop an efficient catalyst.

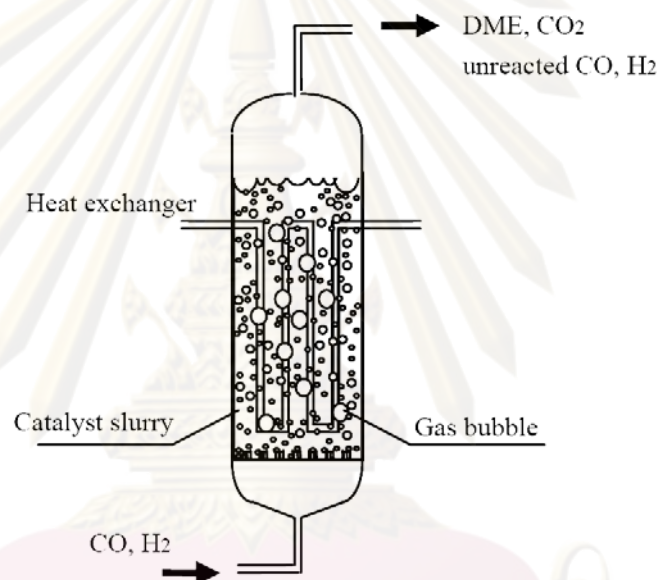


Figure 2.1 Slurry phase reactor for DME synthesis [14]

2.5 Reaction Mechanism

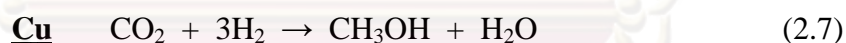
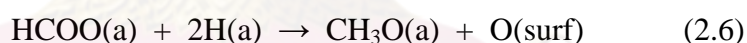
Recently, obtaining DME in a single reaction step using a bifunctional catalyst consist of a metallic function (composed of oxide such as CuO, ZnO, Al₂O₃ and Cr₂O₃) for the synthesis of methanol (methanol synthesis reaction) and of an acid function (such as γ -Al₂O₃, HZSM-5 or HY zeolite and SAPOs) for transforming the methanol into DME (methanol dehydration reaction). The metallic function catalyst and an acid function catalyst are physically mixed to obtain a hybrid catalyst.

For this research, the CuZnO/HZSM-5 hybrid catalyst was chosen to catalyze DME formation reactions. Therefore, the reaction mechanism for synthesis of DME from syngas has been investigated into two mechanisms due to different functions of the hybrid catalyst.

2.5.1 Mechanism of Methanol Synthesis Reaction

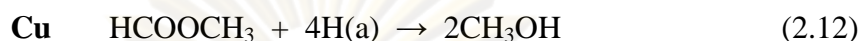
The Cu/ZnO-based has been used successfully for several decades for the production of methanol from syngas therefore the reaction pathway involving the Cu/ZnO-based catalyst is currently accepted. It is assumed that CO₂ is hydrogenated on the Cu sites to yield methanol and water that subsequent gas phase transport from the Cu sites leads to the displacement of relatively stable species from ZnO. However, its mechanism is still not clear and quite different bifunctional mechanism routes were also supposed.

Saussey and Lavalley [15] proposed the following routes:

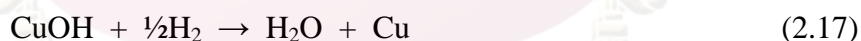
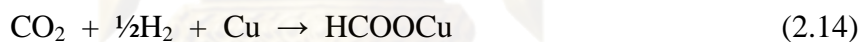


From this mechanism, it is assumed that the gas-phase intermediate is H₂O and methoxy species are hydrated on the ZnO sites. This is consistent with the observation that small amounts of water in the reactant gas feed increase the catalyst activity.

Another group of researchers, Fackley and co-workers [16] proposed a mechanism in which methanol reacts with methanoates on the ZnO to produce methyl methanoate, which ultimately hydrogenated when in contact with copper:



The aim of this research is to develop a new route of low temperature synthesis of DME from syngas. Significant research, in 2003, Reubroycharoen and co-workers [17] has studied a low temperature methanol synthesis by which methanol was synthesized from CO₂ and H₂ using a conventional Cu-based oxide catalyst in an organic alcohol (ROH) as a catalytic liquid medium. The new route can be operated at significantly low temperature and pressure, such as 150-170°C and 30-50 bar. It was assumed that CO₂ and H₂O are utilized as intermediates in the novel pathway. The reaction route is composed of several steps as listed below:



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

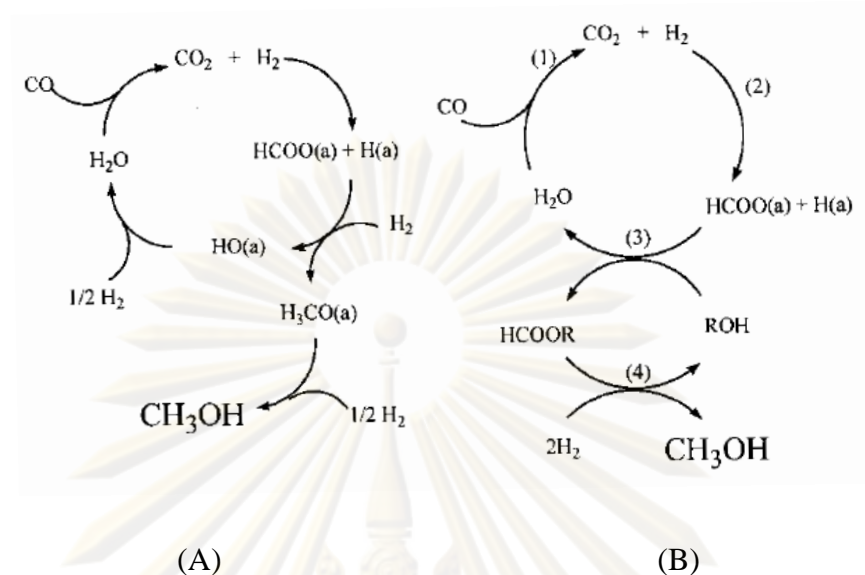


Figure 2.2 Changing the reaction course from a high-temperature ICI process (A) to a new low-temperature route (B) by addition of alcohol [18].

2.5.2 Mechanism of Methanol Dehydration Reaction

In contrast to methanol synthesis, the catalytic dehydration of methanol to DME has received less attention. Recently, only a few solid acid catalysts, such as γ - Al_2O_3 , silica-alumina and HZSM-5 zeolite have been used as dehydration catalysts for DME synthesis. Among these, HZSM-5 zeolite has been used extensively because of its very high catalytic activity at the optimum reaction temperature [3].

It is well known that an active function of zeolite is composed of two kinds of acid site, Lewis and Bronsted acid site, as shown in Figure 2.3. Both Lewis and Bronsted acidity are involved in the dehydration reaction over acid catalysts, and selectivity control to limit the dehydration of DME to olefins and aromatics requires that the surface acidity not be too high and the reaction temperature be below 300°C [3]. The olefins are generally thought to be produced by a consecutive reaction in which methanol is first converted to DME, which in turn is converted to olefins and aromatics. Reaction mechanisms for DME formation have been proposed by various researchers.

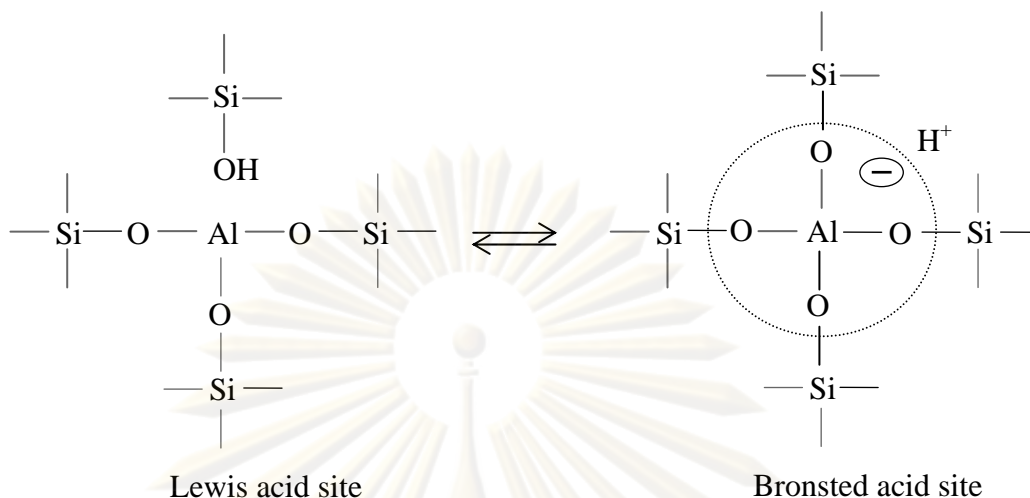
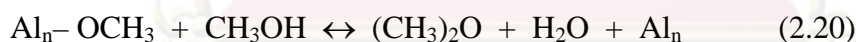


Figure 2.3 Representation of an acidic site in zeolite structure
(silica-alumina framework)

Kubelkova and co-worker [19], proposed the mechanism over Si-Al zeolites that involves protonation of the hydroxyl group and reacts with a gas-phase methanol molecule to form DME at 180-300°C and C₂-C₅ aliphatics and aromatics above 300°C. Furthermore these authors, Lewis acid sites (Al_n-OH), associated with non-skeletal alumina, can also form methoxyls according to the reaction



Bandeira and Naccache [20] proposed a dual acid-base mechanism in which CH₃OH reacts on a Bronsted acid site and another methanol molecule reacts at an adjacent O²⁻ site. Thus a bimolecular Langmuir - Hinshelwood reaction mechanism is proposed according to the following reaction steps:



And reaction in equation (2.24) is the rate limiting step.

In 1997, Corbin and co-workers [21] have reported a reaction mechanism of DME formation via methanol dehydration over solid acid catalyst. The reaction route is presented in Figures 2.4 – 2.7

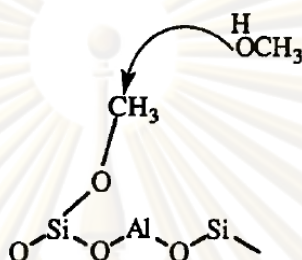


Figure 2.4 Methoxyl species as intermediate [21]

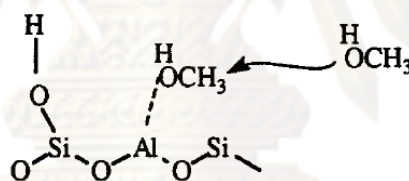


Figure 2.5 DME formation by coordination with Lewis site [21]

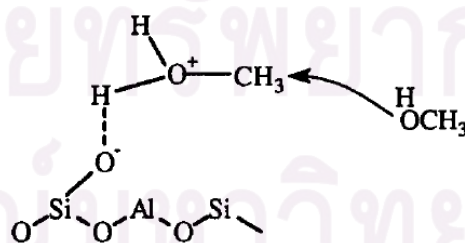


Figure 2.6 DME formation by protonation of hydroxyl group [21]

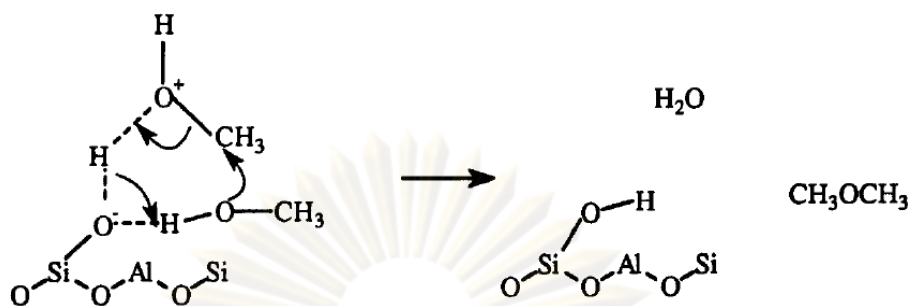


Figure 2.7 Cyclic transition state for DME formation [21]

2.6 Synthesis Gas [22,23]

DME can be produced from natural gas, biomass or other carbon containing materials. Using existing supplies of natural gas combined with current technology, DME can be economically produced on a large scale via synthesis gas. The detail of important reactant, synthesis gas, is reported in this section.

Synthesis gas (or syngas), the third important intermediate for petrochemicals, is the precursor of two big-volume chemicals, ammonia and methanol. It is also an important building block for aldehydes from olefins. The production of syngas is briefly discussed below.

2.6.1 Steam Reforming of Natural Gas

To date, steam reforming of natural gas is the major industrial route to syngas. It is also one of the major processes for manufacturing of H_2 , accounting for about 90% of the world's supply. This reaction is an endothermic, and therefore is carried out in externally fired furnaces. The heat required for this process is obtained by burning a portion of the gas stream. A reaction of steam reforming of natural gas is shown in equation (2.25)



The process uses nickel as catalysts which are normally dispersed on aluminum oxide or magnesium oxide as a support. The concept of a catalyst support derives from the fact that catalytic reactions occur at the surfaces. Figure 2.8 presents an action of a catalyst at its surface.

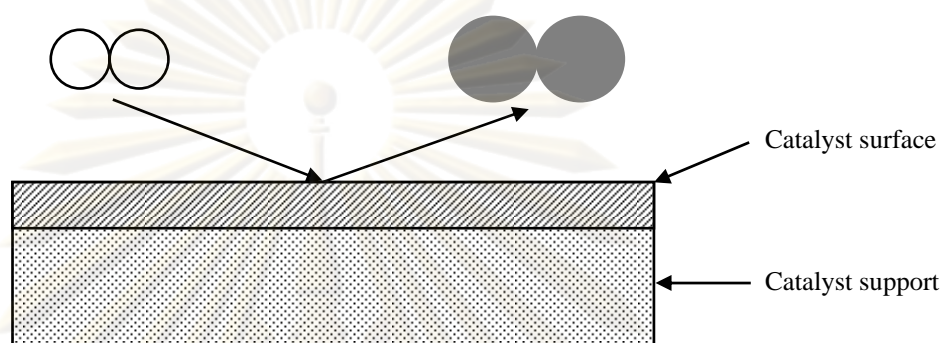
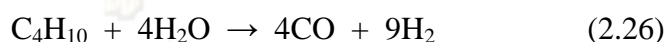


Figure 2.8 The action of a catalyst occurs at the surface; the bulk of the material, which supports the surface, does not have a role in the reaction.

However, two problems are encountered in steam reforming. First, the high temperatures of the reaction can cause sintering of the nickel. As the particles of nickel grow, their surface area decreases, and hence the catalytic activity drops. Second, there is a potential; side reaction of H_2 and CO .

An extension of the steam reforming of natural gas is to use LPG or naphtha as feedstock. The production of syngas from LPG or naphtha is illustrated in the reaction equation (2.26)



A potentially serious problem with the steam reforming of natural gas, LPG or naphtha is that these feedstocks may themselves be in short supply by the early 21st century.

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2.6.2 Coal Gasification [1]

The key feature of steam reforming of natural gas, LPG or naphtha is the reaction of a carbon compound with steam. Indeed, this is a fairly general reaction which could be written as an equation (2.27)



Where the symbol C is taken to mean any source of carbon such as agricultural and forest product wastes, peat, petroleum resids and tar sands. Nevertheless, the most abundant and least expensive source of carbon is coal. Therefore, the prospect of converting coal to syngas is considerate.

As previously mentioned, there are different ways of obtaining syngas. It can be produced by steam reforming or partial oxidation of any hydrocarbon ranging from natural gas to heavy petroleum residues. It can also be obtained by gasifying coal or biomass, because biomass is one of the most abundant renewable resources that can be converted into liquid and gaseous fuels. Therefore, biomass derived from methanol is very attractive and has become an alternative fuel. The composition of syngas derived from biomass is different from that derived from natural gas and coal which consist mainly of H_2 and CO , with a small amount of CO_2 , whereas biomass derived to syngas consists much more of CO_2 .

Theoretically, for DME synthesis, a syngas with hydrogen/carbon monoxide ratio (H_2/CO) of 1.0 is appropriate for DME synthesis. As shown in Figure 2.9 the equilibrium conversion of synthesis gas (CO conversion plus H_2 conversion) calculated at 260°C and 5 MPa for DME synthesis reaction (1) and methanol synthesis reaction (2) as a function of H_2/CO ratio of the synthesis gas. In each reaction, the equilibrium conversion has its maximum peak where H_2/CO ratio corresponds to the stoichiometric value, that is, with H_2/CO ratio of 1.0 for DME synthesis reaction (1) and 2.0 for methanol synthesis reaction (2). The maximum equilibrium conversion for DME synthesis reaction (1) is much higher than that for methanol synthesis reaction (2).

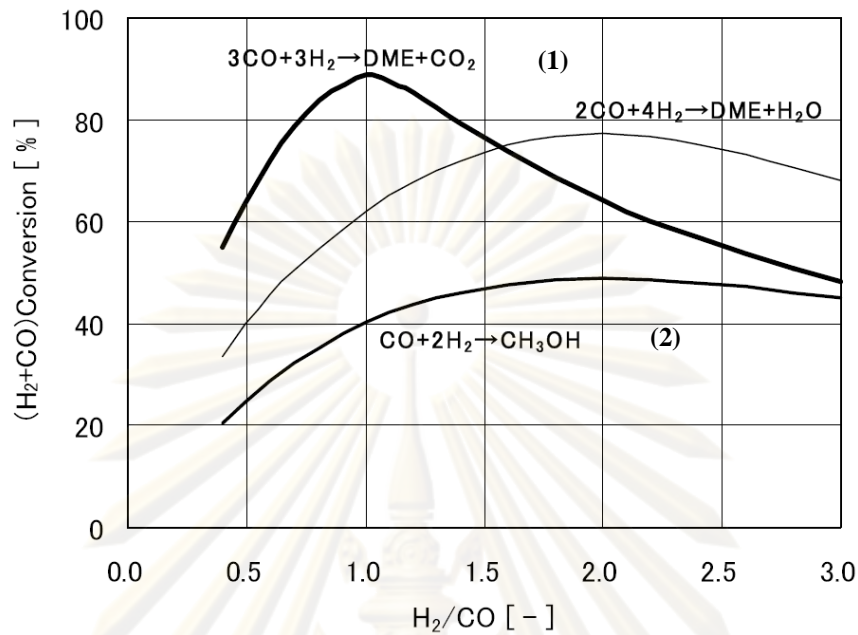


Figure 2.9 Equilibrium conversion of synthesis gas (260 °C, 5 MPa) [14]

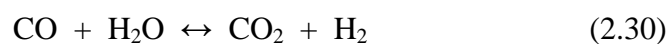
2.7 Dimethyl Ether Synthesis Process Technology

A number of processes have been developed to convert coal or natural gas-based syngas into DME. The prominent ones include those by Haldor Topsoe and NKK Corporation. A brief description of these processes is given below.

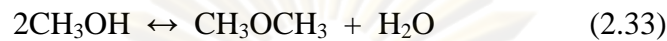
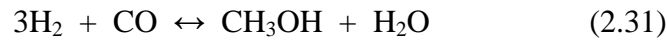
2.7.1 Haldor Topsoe Process [24]

The chemical reactions involved in synthesis of DME from natural gas are as follows:

Reforming:



DME synthesis:



Haldor Topsoe has conducted a considerable amount of research for the purpose of developing DME as a diesel fuel from natural gas. They developed a new process, which is an integrated process from production of methanol from synthesis gas generated from various feed stocks ranging from natural gas to coal and biomass, followed by its subsequent conversion into DME in one single plant. As shown in Figure 2.10, the process consists of the following main steps: synthesis gas preparation, methanol and DME synthesis and final purification unit.

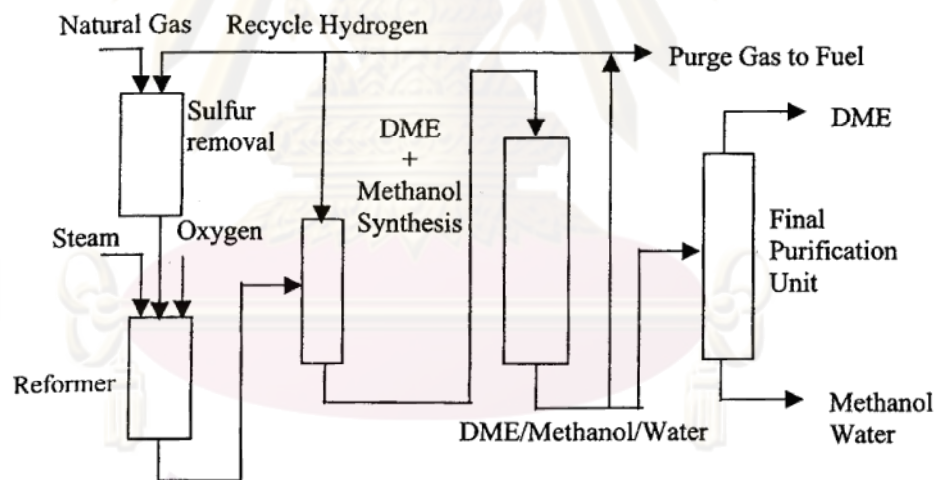


Figure 2.10 Haldor Topsoe technology for DME synthesis [24]

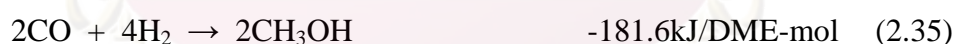
The synthesis gas preparation process uses autothermal reforming (ATR) consisting of a specifically designed burner (CTS burner). In this process, oxygen is added to desulfurize natural gas and steam. The steam to carbon ratio in the ATR is low (as low as 0.6) and the exit temperature is high. This ensures a favorable synthesis gas composition and low methane content. Synthesis of methanol and conversion of methanol into DME takes place in two separate reactors, which

allows both parts of the sequential reaction to be carried out at optimal conditions. Methanol synthesis, which is a more exothermic reaction than DME synthesis, is carried out in a cooled reactor where reaction exothermic is continuously removed. DME synthesis takes place over a proprietary multiple-function methanol/DME catalyst in a loop comprising three adiabatic fixed-bed reactors in series. These have interstate cooling to achieve a high conversion of CO to CO₂. The product mixture of DME/methanol/water is then condensed and separated. The unconverted synthesis gas is split into a recycle stream and a purge stream, which is used as fuel and as hydrogen recycle. DME is purified by distillation in the final purification unit.

2.7.2 NKK Process [14]

Researchers at NKK Corporation have developed a process for DME synthesis from coal-bed methane using a slurry-bed reactor technology, utilizing a proprietary highly active catalyst for producing DME directly from the syngas at high yields. The success of this technology has been demonstrated since 1999.

The reactions and reaction heat concerning DME synthesis are as follows;



On the basis of the operational data, conceptual design and feasibility study will be made for 2500 tons/day-scale commercial plant. As for raw materials, natural gas, coal, bio-mass and so on will be studied. The schematic process flow diagram of 100 tons/day demonstration plant is shown in Figure 2.11.

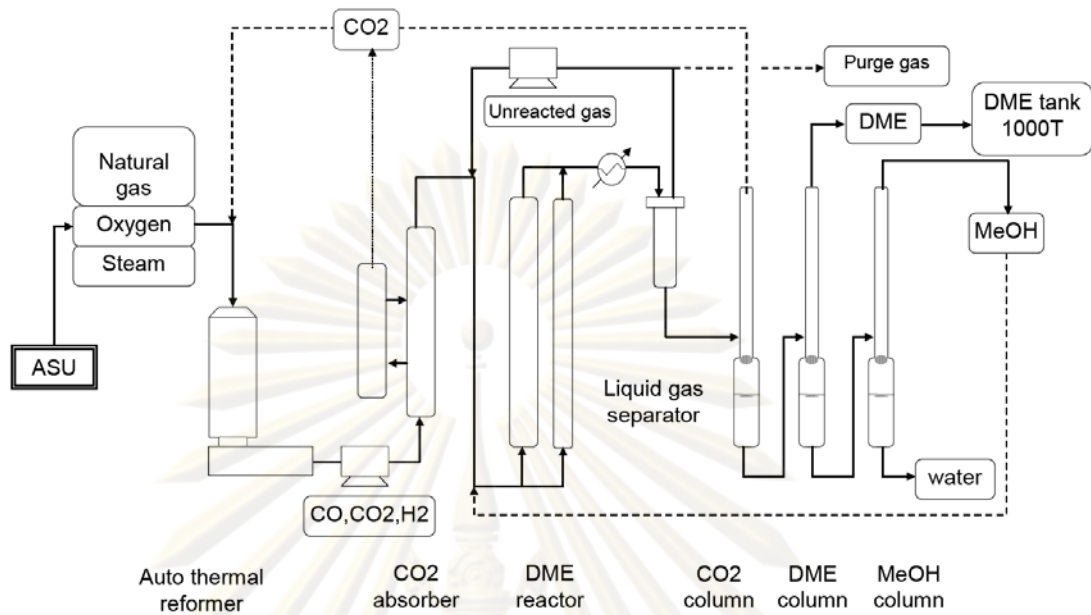


Figure 2.11 Process Flow Diagram of 100 tons/day DME Synthesis Plant [14]

Natural gas is reformed in an auto-thermal reformer at the following conditions: the outlet temperature is 1000-1200°C and the inner pressure is 2.3 MPa with oxygen, steam and carbon dioxide recycled from a carbon dioxide removal unit and a purification unit to give synthesis gas of $H_2/CO=1$. The synthesis gas is cooled, compressed and carbon dioxide is removed by methanol absorption and supplied into the DME synthesis reactor. There are two reactors in parallel; the main reactor is a 2.3 m in inner diameter and 22 m in height, the small reactor is 0.65 m in inner diameter and 28 m in height. The small reactor is equipped to get various engineering data with higher gas velocity conditions. Reaction heat is removed by internal heat exchanger coils to generate steam. The standard reaction condition is temperature: 260 °C and pressure: 5 MPa. The effluent of the reactor is cooled and chilled to separate DME from unreacted gas, which is recycled to the reactor. DME is purified in two distillation columns and stored in pressurized tanks (1,000 tons). The by-product methanol is recycled to the DME synthesis reactor after water removal to be converted into DME.

2.8 Literature Reviews

In 1997, Mingting Xu *et al.* [25] studied the catalytic conversion of methanol to DME over a series of solid-acid catalysts (γ -Al₂O₃, H-ZSM-5, amorphous silica-alumina and titania modified zirconia). All the catalysts are active and selective for DME formation. Water has a strong inhibiting effect of the activity of γ -Al₂O₃, whereas the effect is less significant over H-ZSM-5 (Si/Al = 50). The rate of methanol dehydration decreases with increasing acidity (silica content) over the amorphous silica-alumina catalysts. Although H-ZSM-5 with Si/Al = 25 is the most active among the catalysts tested, the DME selectivity is only 20% at 280°C, a typical temperature used in the syngas-to-methanol process. An amorphous silica-alumina catalyst with 20 wt% silica content (SIRAL20) exhibits the best catalytic performance among those tested at 280°C.

In 2003, Corrie L. Curnes *et al.* [26] prepared and studied several nanoparticulate metal oxides for the catalytic production of methanol from hydrogen and carbon dioxide. ZnO, CuO, NiO and CuO/ZnO catalysts were prepared through sol-gel synthesis. The catalytic production of methanol was studied at various temperatures in a flow reactor. Unlike the CuO catalyst, ZnO and NiO catalysts were active at low temperatures (150-300°C). The CuO sample was found to rapidly reduce to Cu. Copper metal is not active, but small copper particles in a CuO/ZnO matrix are a very active combination.

In 2004, Reubroychareon *et al.* [17] synthesized methanol at low-temperature from CO₂-containing syngas with Cu/ZnO catalyst. The aid of alcohols has been developed in a batch and flow-type semi-batch reactors. The results showed that methanol was synthesized via new reaction route with conventional solid catalyst and the aid of catalytic alcohol at low-temperature from CO₂-containing syngas. The nature of alcohol structure influenced the activity of methanol, 2° alcohol showed the highest activity. By adding 2-butanol in a low-temperature method showed 47.0% conversion and 98.9% selectivity at 443 K and 50 bar.

In 2004, Kompeng Sun *et al.* [27] prepared three series of Pd-modified CuO-ZnO-Al₂O₃-ZrO₂/HZSM-5 catalysts (sequential-precipitating sedimentation (SPS) method, Physical mixing (PM) method, and conventional impregnation (IM) method) compared with CuO-ZnO-Al₂O₃-ZrO₂/HZSM-5 catalysts (co-precipitation sedimentation (CPS) method) for the synthesis of DME for carbon dioxide hydrogenation at low temperature ($T = 200^{\circ}\text{C}$, $P = 3.0\text{ MPa}$, $\text{GHSV} = 1800\text{ h}^{-1}$). The results indicated that the addition of palladium markedly enhanced the DME synthesis and retarded the CO formation. An explanation of this promoting effect of Pd on the DME synthesis could be attributed to the spillover of hydrogen from Pd⁰ to the neighboring phase.

In 2005, Dongsen Mao *et al.* [28] synthesized DME from syngas with magnesium oxide-modified H-ZSM-5 as a dehydration component. The modified H-ZSM-5 zeolites were mixed physically with methanol synthesis components (CuO-Zn-Al₂O₃) to perform the direct synthesis of DME from syngas under pressurized fixed-bed continuous-flow conditions. The hybrid catalysts (1g) were reduced by hydrogen (5 vol% in nitrogen) in situ at 240°C for 6 h. The syngas contained 66% H₂, 30% CO and 4% CO₂. The reaction was performed under the following reaction conditions: 4 MPa, a feed rate of 1500 ml/(hg_{cat}), and a temperature of 260°C. The results indicated that modification of HZSM-5 with a suitable amount of MgO significantly decreased the selectivity for undesigned by-products like hydrocarbons and CO₂ from 9.3 and 37.1% to more than 64%, whereas the conversion of CO was scarcely affected. However, when the MgO contents were equal to or higher than 5 wt%, both the conversion of CO and selectivity of DME decreased, activity for methanol dehydration involved both acidic and basic sites on the MgO modified H-ZSM-5 zeolite.

In 2005, Javier Erena *et al.* [3] studied the effect of operating conditions (time on stream, temperature, pressure and space time) on the conversion of CO and CO₂, selectivity to DME, yield of DME and product distribution in the DME synthesis from H₂, CO and CO₂ in a single reaction step. CO conversion is total at 275°C and 40 bar, with a selectivity to DME of 80% and a yield of DME of 78%, for a space time of 67 (g of catalyst) h/mol of (H₂ + CO) and for a feed made up of H₂/CO = 2/1. Catalyst

deactivation under these conditions is insignificant, even when CO₂ is fed and there is a high water concentration in the medium.

In 2005, Ramos *et al.* [29] studied the direct synthesis of DME (DME) in a continuous high-pressured unit (24 ml min⁻¹, 250°C, 5 MPa). A commercial methanol synthesis catalyst and some solid-acid catalysts (alumina, HZSM-5, tungsten-zirconia and sulfated-zirconia) were used as physical mixtures. One step DME synthesis from syngas can be achieved over physical mixture of a classic methanol catalyst and a solid-acid catalyst. The activity of a solid acid on the methanol dehydration reaction was found to be determined mainly by the number of its more acidic sites. The presence of such acid catalyst to the catalytic system strongly shifts the methanol synthesis reaction, increasing significantly the conversion of CO. It can be concluded that the rate of DME direct synthesis is determined by the acid properties of the dehydrating catalyst.

In 2005, Andres *et al* [30] synthesized DME in a single reaction step, from H₂ + CO and H₂ + CO₂, in a fixed bed reactor on CuO-ZnO-Al₂O₃/γ-Al₂O₃ and CuO-ZnO-Al₂O₃/NaHZSM-5 hybrid catalysts for studying the minimization of catalysts deactivation by coke using the strategy of CO-feeding water. The results indicated that water content in the reaction medium contributed to efficient decreasing the deactivation by coke in both catalysts. However, water also decreased the activity of γ-Al₂O₃ acid function because of its high adsorption capacity on the acid site. Regenerability of the catalysts has been studied in 10 cycles of reaction-regeneration carried out in situ in reactor at 260°C with a mixture of air and helium. It has been observed that γ-Al₂O₃ does not have suitable hydrothermal stability to be used in reaction-regeneration cycles, while CuO-ZnO-Al₂O₃/NaHZSM-5 catalyst had an excellent performance and recovered its kinetic capacity subsequent to 10 reaction-regeneration cycles.

In 2005, Yisheng Tan *et al.* [31] studied an effect of Cu/Zn mole ratio of Cu-based methanol synthesis catalyst and modified Cu-based catalyst with Mn to improve its activity and stability for DME synthesis from syngas in slurry phase. The Cu-based catalyst was prepared by co-precipitation of nitrates of Cu and Zn with

Cu/Zn mole ratio was 5:2, 1:1 and 3:4. The DME yield was improved distinctly from 45.4% to 50.0% with the change of the Cu/Zn mole ratio from 5:2 to 1:1 and reduced to 49.4% with the Cu/Zn mole ratio was 3:4. Obviously, the Cu/Zn mole ratio of 1:1 has the best performance for DME synthesis because an appropriate mole ratio of Cu/Zn. Addition of Mn to the traditional Cu-based catalyst by co-precipitation method can significantly improve stability and activity of catalyst. In the experiment range, 260°C is the optimum operation temperature for DME synthesis over Mn-modified Cu-based catalyst.

In 2006, Jin-Hua Fei et al. [32] studied the effect of copper content on Cu-Mn-Zn/Zeolite-Y catalysts for the synthesis of DME from syngas. Under the reaction condition of 2.0 MPa, 250°C, 1500 h⁻¹ and the mole ratio of H₂/CO = 3/2, the appropriate ratio of Cu/(Cu+Mn+Zn) for catalyst activity was above 0.6, and the conversion of CO and the selectivity of DME reached 78% and 67%, respectively. Increasing copper content in Cu-MnZn/Y catalyst is conducive to enhance its activity for direct synthesis of DME from CO hydrogenation. The content of copper mainly affects the adsorption of CO on the catalyst surface, and the copper reduced from the excess CuO phase is beneficial to the activation of CO at lower temperature.



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In 2006, Shin Dong Kim *et al.* [33] investigated the effect of γ -alumina on the catalytic performance of Na-modified ZSM-5 via the dehydration of methanol to DME. A series of modified ZSM-5 catalysts were prepared with/without γ -alumina and the activity of each catalyst was examined in the dehydration of crude methanol to DME using a fixed-bed reactor at the reaction pressure of 10 atm and LHSV of 10 h^{-1} . The catalyst NaHZSM-5 containing 70% of γ -alumina (NaHZSM-5 (70)) as a binder is active and stable in the conversion of crude methanol to DME. The pure γ -alumina exhibited much lower activity than the ZSM-5 catalysts modified with Na. Even though NaHZSM-5 (70) shows lower DME yield than NaHZSM-5 (0, 30 and 50), NaHZSM-5 (70) has much wider operative temperature range (OTR) than others. NaHZSM-5 (70) has a high stability against coke formation and water for 15 days at 270°C, giving 80% of DME yield. This beneficial effect is ascribed to the adequate dilution of the strong acid sites of ZSM-5 in the γ -alumina matrix.

In 2007, Dingfeng Jin *et al.* [34] prepared a series of zeolite Y modified with rare earth metals (La, Ce, Pr, Nd, Sm and Eu) via ion-exchange for DME synthesis from methanol and syngas. These rare earth metals were encapsulated in the super cage of zeolite Y and resulted in its enhanced acidity. Among them, La-, Ce-, Pr- and Nd- modified zeolite Y exhibited higher activity and stability than pure HY for methanol dehydration to DME. For DME synthesized directly from CO hydrogenation using the dual Cu-Mn-Zn/modified-Y catalysts, Cu-Mn-Zn/La-Y and Cu-Mn-Zn/Ce-HY were more active than Cu-Mn-Zn/pure-HY. The conversion of CO on Cu-Mn-Zn/Ce-HY achieved 77.1% in an isothermal fixed bed reactor at 245°C, 2.0 MPa, $\text{H}_2/\text{CO} = 3/2$ and 1500 h^{-1} .

In 2007, Moradi *et al.* [35] studied the effect of the hybrid catalysts preparation method for direct synthesis of DME from synthesis gas. In hybrid catalyst preparation, sol-gel impregnation has been developed which showed better performance in comparison with the other methods. In this method, a series of catalysts with different contents of alumina have been prepared. The optimum weight ratio for CuO/ZnO/Al₂O₃ catalyst has been found to be about 2:1:5, respectively. The catalysts performance was tested at 240°C, 40 bar and space velocity 1000 $\text{ml/g}_{\text{cat}}\cdot\text{h}$, with the inlet gas composition $\text{H}_2/\text{CO}/\text{N}_2 = 64/32/4$ in a micro slurry reactor.

CHAPTER III

EXPERIMENTAL

3.1 Materials

All chemicals are analytical grade as shown in Table 3.1.

Table 3.1 List of chemicals and sources

Chemicals	Source
Copper (II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$)	Ajax chemicals
Zinc (II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	Qrec
Sodium carbonate (Na_2CO_3)	Ajax chemicals
HZSM-5 zeolite	Tosoh corporation
Methanol (CH_3OH)	Fisher
Paraffin	Fisher
Nitrogen gas (99.9% purity)	Praxair
Hydrogen gas (99.9% purity)	Praxair
5%Hydrogen in nitrogen gas	TIG
2%Oxygen in nitrogen gas	TIG
Standard synthesis gas, $\text{H}_2/\text{Ar}/\text{CO}(48/4/48)$	TIG
Standard synthesis gas, $\text{H}_2/\text{CO}_2/\text{CH}_4/\text{CO}(75/5/10/10)$	TIG

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3.2 Instruments and Equipments

3.2.1 Instruments and Equipments for Catalyst Preparation

1. Peristaltic pump
2. Circulating water bath
3. Mechanical stirrer and impeller
4. pH meter
5. Ultrasonic bath
6. Aspirator pump
7. Desiccator
8. Oven
9. Muffle furnace
10. Mortar
11. Palletized mold set
12. Hydraulic pump
13. Mesh sieve set (25 and 45 mesh sizes)
14. Tube furnace and temperature controller
15. Thermocouple type K
16. Temperature transmitter and indicator
17. Flow meter

3.2.2 Instruments and Equipments for Catalyst Characterization

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

3.2.3 Instruments and Equipments for Dimethyl Ether Synthesis

1. Pressure regulator
2. Mass flow controller
3. Mass flow readout and control equipment
4. Thermocouple type K
5. Band heater and digital temperature controller
6. Pressure gauge
7. Slurry reactor with built in impeller
8. Motor and speed controller

9. Condenser
10. Submersible water pump
11. Back pressure regulator

3.2.4 Instruments and Equipments for Product Analysis

1. Gas chromatograph (GC) (Shimadzu, GC-2014)
2. Methanizer and temperature controller

3.3 Preparation and Characterization of Catalyst

3.3.1 Preparation of CuO/ZnO Catalyst

Copper zinc oxide (Cu/ZnO) catalyst was prepared by co-precipitation method in aqueous solution, 500 mL of copper nitrate and zinc nitrate (each 0.12 M, Cu/Zn mole ratio was 1) [31], and sodium carbonate (0.24 M) were used as precipitant and simultaneously added to 700 mL deionized water under rapid stirred at 65°C and controlled pH range 6.8 to 7.0 and aged overnight under ambient temperature. The precipitate was filtered and washed with 65°C deionized water for eight times to removed sodium residue, then the precipitate was dried at 110 °C for 24 h and finally calcined in air with temperature rate of 3 °C/min. and held at 350 °C for 4 h.

3.3.2 Preparation of Cu/ZnO/HZSM-5 Catalyst

The HZSM-5 zeolite was used as methanol dehydration catalyst. The CuO/ZnO/HZSM-5 catalyst was obtained by physically mixing the methanol synthesis catalyst (CuO/ZnO) and HZSM-5 powder. The obtained hybrid catalyst was grounded, pelletized by compression in the mould at 60 MPa, crushed, screened and collected the particles whose size ranges from 25 to 45 mesh sieve. To activate the

catalyst, the hybrid catalyst particle (CuO/ZnO/HZSM-5) was pretreated with N₂, 30 mL/min, heated from ambient temperature to 110 °C for 1 h and held for 1 h. The reduction was performed by flowing a 5% H₂ in N₂ mixture 30 mL/min, heated up to 220 °C, held for 10 h and cooling to ambient temperature with flowing N₂ 30 mL/min for 6 h followed by passivation of flowing a 2% O₂ in N₂ mixture 5 mL/min for 24 h, as shown in Figure 3.1.

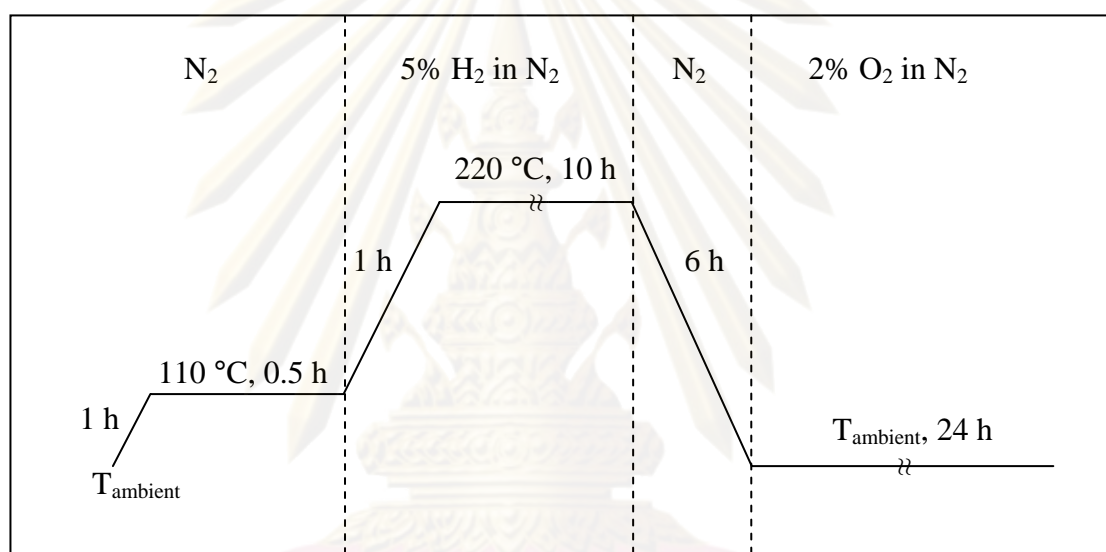


Figure 3.1 Schematic of temperature program for catalyst activation.

The reaction parameters were studied as follow:

Semi-Continuous Reaction.

1. The effect of temperature when paraffin is used as a liquid solvent.
2. The effect of mixed liquid solvent system (paraffin and methanol)
3. The effect of methanol is used as a liquid solvent.
4. The effect of methanol content

5. The effect of temperature (160°C, 170°C and 180°C) when methanol is used as a liquid solvent.

6. The effect of weight ratio of CuZnO and HZSM-5 catalyst

7. Catalytic regeneration of CuZnO/HZSM-5 catalyst

3.3.3 Characterization of Catalyst

3.3.3.1 X-ray Diffractometer (XRD)

Structure and crystallite size measurement was performed using an X' Pert Phillips X-ray diffractometer by using $\text{CuK}\alpha$ radiation at an angle of 2θ ranging from 5 to 80 degrees.

Determination of copper oxide crystalline size was evaluated from the full width at half maximum of CuO XRD peak by using Scherrer equation as follows [35]:

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

where K is a unit cell geometry dependent constant

λ is wavelength of the x-ray

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

θ_B is the Bragg angle

3.3.3.2 Surface Area Analyzer (BET)

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

3.4 Dimethyl Ether Synthesis and Characterization of the Reaction Products

3.4.1 Semi-Continuous Dimethyl Ether Synthesis

A semi-continuous dimethyl ether synthesis was used to study the effect of temperature, solvent and catalyst. One gram (1 g) of the catalyst was grounded in liquid solvent and poured into 80 mL reactor. The reactor is connected to the reaction apparatus as shown in scheme 3.2. Prior to the reaction, the system is purged with high-pressure reactant gas ($\text{H}_2/\text{Ar}/\text{CO} = 48/4/48$) using Ar as an internal standard. The reactor pressure is increased to 4.0 MPa and heated to the desired temperature and then the reaction took place by flowing the reactant gas 40 mL/min at the constant stirring speed (1500 rpm) for 15 h. The effluent gases from the reactor were passed through the water-cooled condenser and analyzed the on-line gas products as described in section 3.4.2

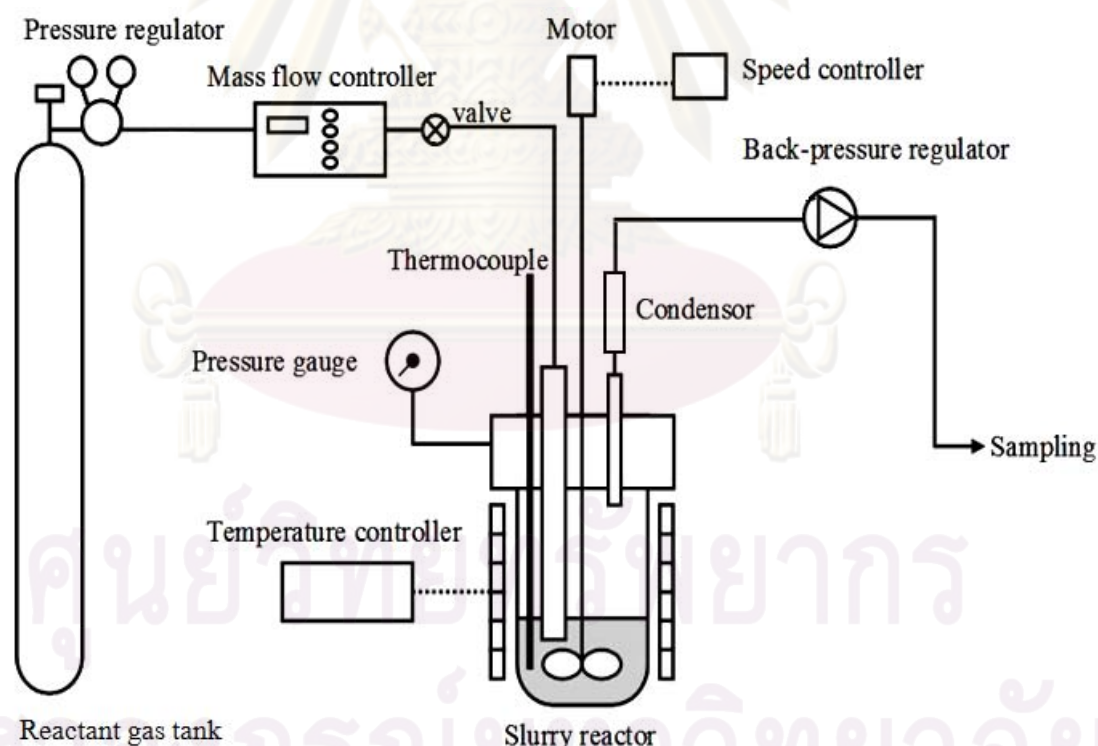


Figure 3.2 Schematic of apparatus for dimethyl ether synthesis reaction.

3.4.2 Analysis of the Reaction Products

The effluent gases were analyzed by an on-line Shimadzu GC-2014 gas chromatograph by two types of detector.

(A) Thermal Conductivity detector (GC-TCD) equipped with the Unibead-C column.

CO conversion was calculated as follows:

$$\text{CO}_{\text{conversion}} (\%) = 100 \times \frac{(R_{\text{CO/Ar},0} - R_{\text{CO/Ar},1})}{R_{\text{CO/Ar},0}} \quad (3.2)$$

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

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

(B) Flame Ionization detector (GC-FID) equipped with the Porapak-Q column and methanizer.

Selectivity was calculated as follows:

$$P_i \text{ selectivity} (\%) = 100 \times \frac{P_i \text{ mole}}{\sum P_i \text{ mole}} \quad (3.3)$$

where P_i is liquid product i

Yield was calculated as follows:

$$\text{Yield} (\%) = \frac{\text{CO}_{\text{conversion}} \times P_i \text{ selectivity}}{100} \quad (3.4)$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Cu/ZnO/HZSM-5 Catalyst

An important factor that affects the activity of catalyst is its surface area so it is normally desirable for the catalyst to have a high surface area. Jun *et al* [36] prepared catalysts mesoporous Cu/ZnO by sol-gel technique that was used for methanol synthesis from syngas. Results showed that its catalytic activity of Cu/ZnO-based catalyst for the methanol synthesis is strongly dependent on the surface area because larger surface area can improve the dispersion of copper.

Table 4.1 presents the surface properties of CuOZnO, HZSM-5 and CuO ZnO/HZSM-5 catalysts. The CuOZnO prepared by co-precipitation method has surface area and pore volume of $61.3 \text{ m}^2\text{g}^{-1}$ and $0.23 \text{ cm}^3\text{g}^{-1}$, respectively. For HZSM-5 zeolite, methanol dehydration catalyst, its surface area and pore volume are $273.2 \text{ m}^2\text{g}^{-1}$ and $0.11 \text{ cm}^3\text{g}^{-1}$, respectively. In addition, CuOZnO/HZSM-5, DME synthesis catalyst was physically mixed between CuOZnO and HZSM-5 with weight ratio of 2:1. This catalyst has average surface area and pore volume of $131.5 \text{ m}^2\text{g}^{-1}$ and $0.18 \text{ cm}^3\text{g}^{-1}$, respectively. From the results, the CuOZnO/HZSM-5 catalyst clearly has surface area proportional to the weight ratio between CuOZnO and HZSM-5 catalyst therefore the physical mixing method has less effect of the loss of overall surface area of catalyst.

Table 4.1 The textural properties of catalyst

	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	V_{p}^{b} ($\text{cm}^3 \text{g}^{-1}$)
CuOZnO	61.3	0.23
HZSM-5 ^c	273.2	0.11
CuOZnO/HZSM-5 ^d	131.5	0.18

Note ^a BET surface area

^b Average pore volume

^c Calcined at 500 °C

^d The weight ratio of CuOZnO/HZSM-5 = 2:1

As previously mention, methanol synthesis catalyst prepared by co-precipitation method of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. After calcination, CuOZnO was obtained but the actual active species that have a role in catalyzing the reaction should be the Cu/ZnO that is received after the H_2 reduction step. Confirming this expectation by XRD pattern is illustrated in Figure 4.1.

The XRD patterns of the catalysts are shown in Figure 4.1. The unreduced catalyst and reduced catalyst are represented as BR (before H_2 reduction) and AR (after H_2 reduction), respectively. From the diffraction line of BR, there are peaks ascribed only to CuO ($2\theta = 35.6^\circ, 38.8^\circ$ and 49.0°) [37]. The identical peaks ascribed to ZnO was observed at about $2\theta = 32.5^\circ, 34.5^\circ, 36.5^\circ, 56.5^\circ, 63.0^\circ$ and 68.0° [37]. The last species presented in XRD pattern of BR is HZSM-5, there are peaks at about $2\theta = 7.9^\circ, 8.8^\circ, 23.0^\circ, 23.5^\circ, 23.9^\circ$ and 24.4° [38]. In conclusion, all the species detected in the diffraction lines of BR certainly exhibits the diffraction lines of CuO, ZnO and HZSM-5. In the case of AR, the catalyst not only presents diffraction line of CuO, ZnO and HZSM-5 but also exhibits a new peaks which located at about $2\theta = 43.5^\circ, 51.2^\circ$ and 74.3° , which are assigned to Cu [39]. However, the diffraction peaks of CuO were still observed after H_2 reduction due to the effect of passivation by

O₂. The only Cu metal is located at the surface of catalyst granules are transformed to CuO after passivation. Meanwhile, ZnO and HZSM-5 peaks are kept almost unchanged after H₂ reduction, indicating that both are not reduced during the reduction process.

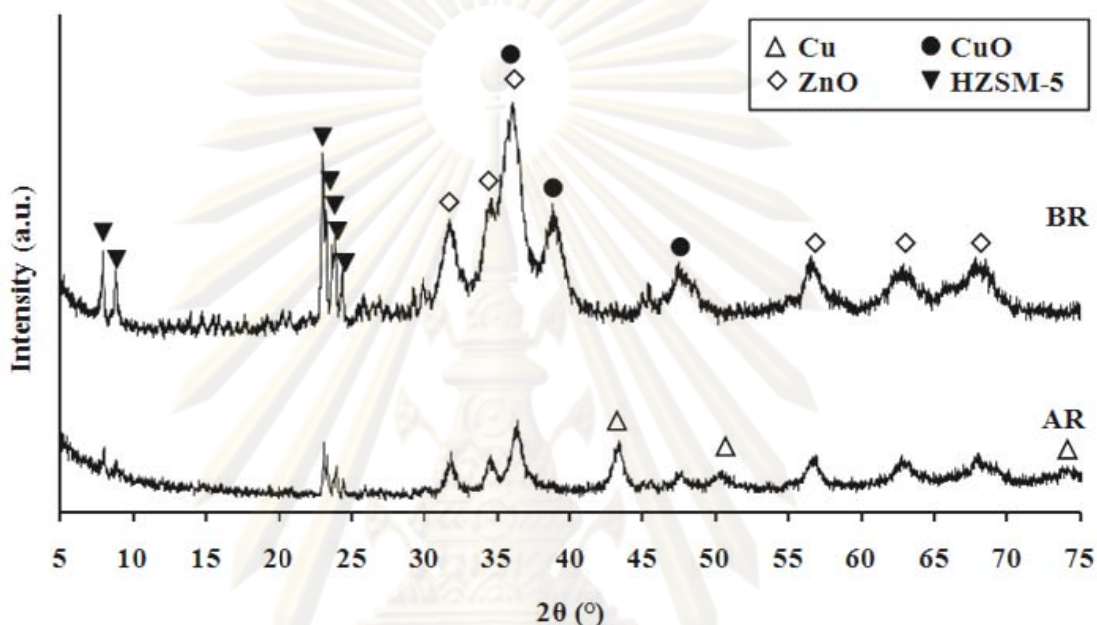
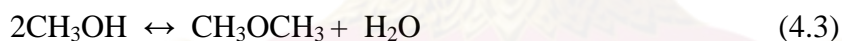
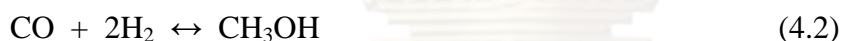
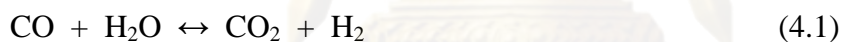


Figure 4.1 The X-ray diffraction patterns of Cu/ZnO/HZSM-5 catalyst; BR as catalyst before H₂ reduction and AR as catalyst after H₂ reduction.

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4.2 Effect of Temperature on the Semi-Continuous Dimethyl Ether Synthesis; Paraffin as Liquid Solvent.

Traditionally, production of DME in single step from syngas is usually operated at high temperature since limiting of Cu-based catalyst, in methanol synthesis reaction, showed quite low activity at low temperature. The one step synthesis DME from syngas includes four important reactions such as water gas shift reaction in equation (4.1), CO hydrogenation reaction in equation (4.2), methanol dehydration reaction in equation (4.3) and overall reaction in equation (4.4). Clearly, the reaction in equation (4.1) and (4.2) took place over methanol synthesis catalyst while the reaction in equation (4.3) is catalyzed by acidic catalyst, conventional Cu/ZnO was used as methanol synthesis catalyst and HZSM-5 was used as acidic catalyst in this study. Therefore, it is inevitable that the activity of methanol synthesis catalyst will influence the result of DME synthesis because methanol formation has been believed to be the rate limitation step among the series of reactions.



In this experiment, DME synthesis from syngas using liquid paraffin as liquid solvent in slurry reactor with various temperature (260°C, 200° and 170°C) was studied. The CO conversion and the time on stream change for DME synthesis with Cu/ZnO/HZSM-5 catalyst during 15 hours and reaction temperature = 260°C, 200° and 170°C is shown in Figure 4.2. From the result of the reaction temperature at 260°C, within initial reaction time of 0-6 hours, CO conversion increased and got the maximum conversion at 6 hours (about 67% CO conversion). After 6 hours of the reaction, the CO conversion slightly dropped and became stable at about 40% conversion. It implied that DME synthesis got into equilibrium of reaction. The possible reason for high CO conversion at the initial time was due to high CO

consumption in the water gas shift (WGS) reaction in equation (4.1) and methanol synthesis reaction in equation (4.2).

At the reaction temperature of 200°C, CO conversion was gradually increased at initial reaction time (0-5 h) and became stable at about 14% conversion which is much lower than the conversion of the reaction at temperature = 260°C because the decreasing temperature directly affected the activity of the catalyst. Also, at the reaction temperature of 170°C, the reaction exhibited almost no conversion of CO (about 1% CO conversion).

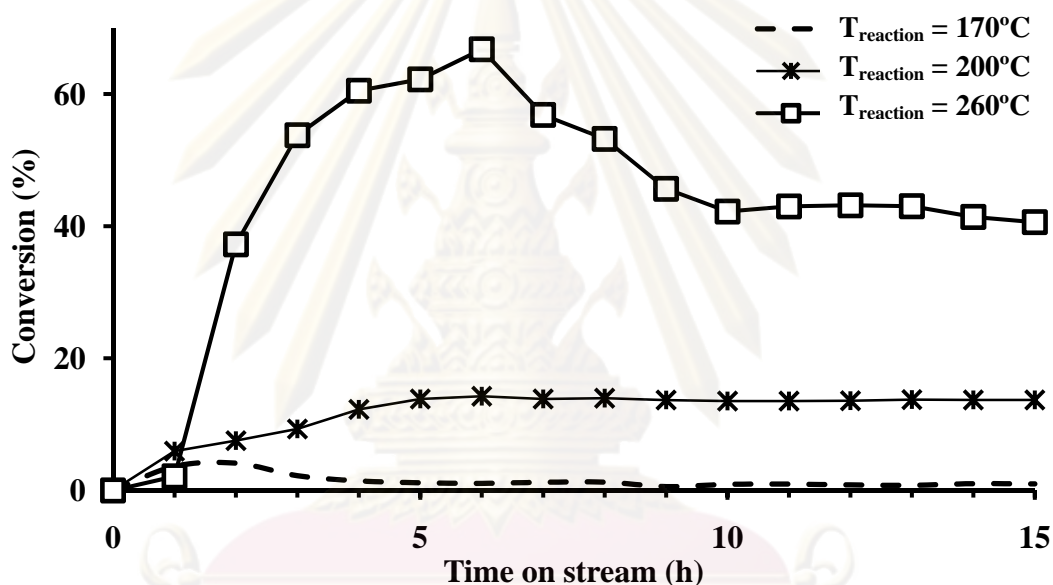


Figure 4.2 Variations of CO conversion (%) with time on stream for DME synthesis in semi-continuous reactor by a various temperatures of reaction. Conditions; $H_2/Ar/CO = 48/4/48$; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; paraffin = 20 mL; reactant gas flow rate = 40 mL/min.

At 170°C of reaction temperature, DME could not synthesize from syngas over Cu/ZnO/HZSM-5 catalyst by using paraffin as liquid solvent and also showed low CO conversion as the result of a catalyst performance at low temperature (170°C). The reducibility is also a key parameter to assess catalyst performance which illustrated in Figure 4.3.

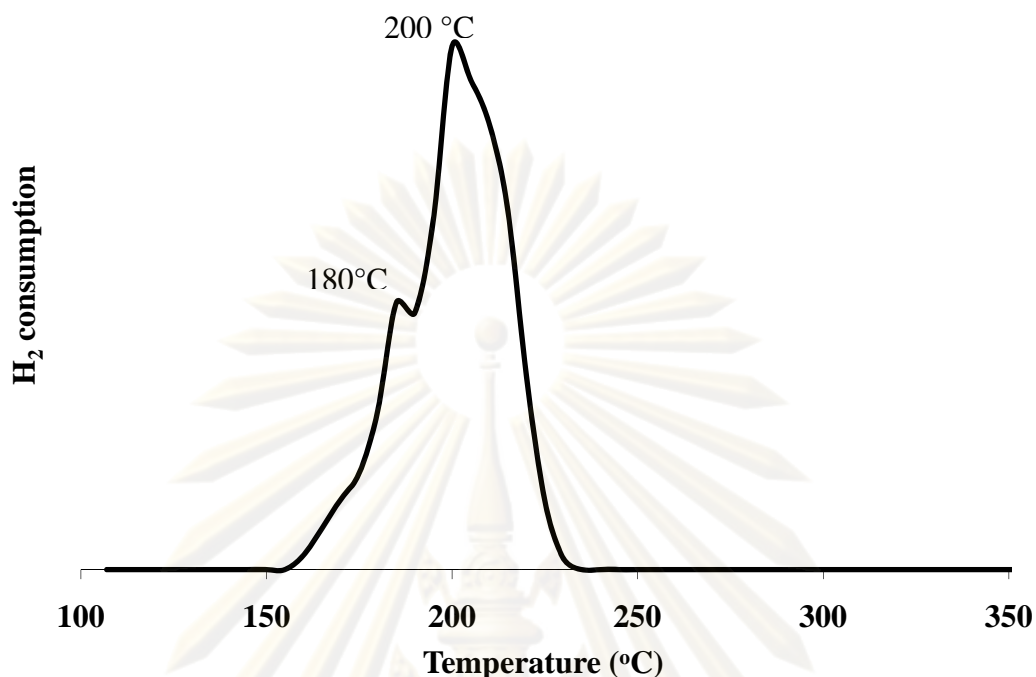


Figure 4.3 Temperature programmed reduction (TPR) profiles on CuZnO/HZSM-5

The CuZnO/HZSM-5 catalysts showed two reduction peaks for TPR curve. The CuZnO/HZSM-5 catalyst exhibited two different reduction peaks at about 180-200°C, which are known as the reduction of CuO. A peak around 200°C was observed as a main peak together with a pre-tail peak around 180°C. The larger area of the peak at high temperature than that at low temperature was indicative of well-crystallized CuO species [40]. It was found that CuO was reduced by hydrogen in two steps from TPR profiles: the Cu₂O phase was reduced in the first step from Cu²⁺ into Cu⁺ and the CuO phase was reduced in the second step from Cu⁺ into Cu⁰ [41,42]. Obviously, the reduction of copper species took place at around 180-200°C. It indicated that the catalyst had less active at 170°C. The result of its restriction directly influenced on the methanol synthesis reaction which could not occur at low temperature and was the cause of almost no CO conversion at 170°C.

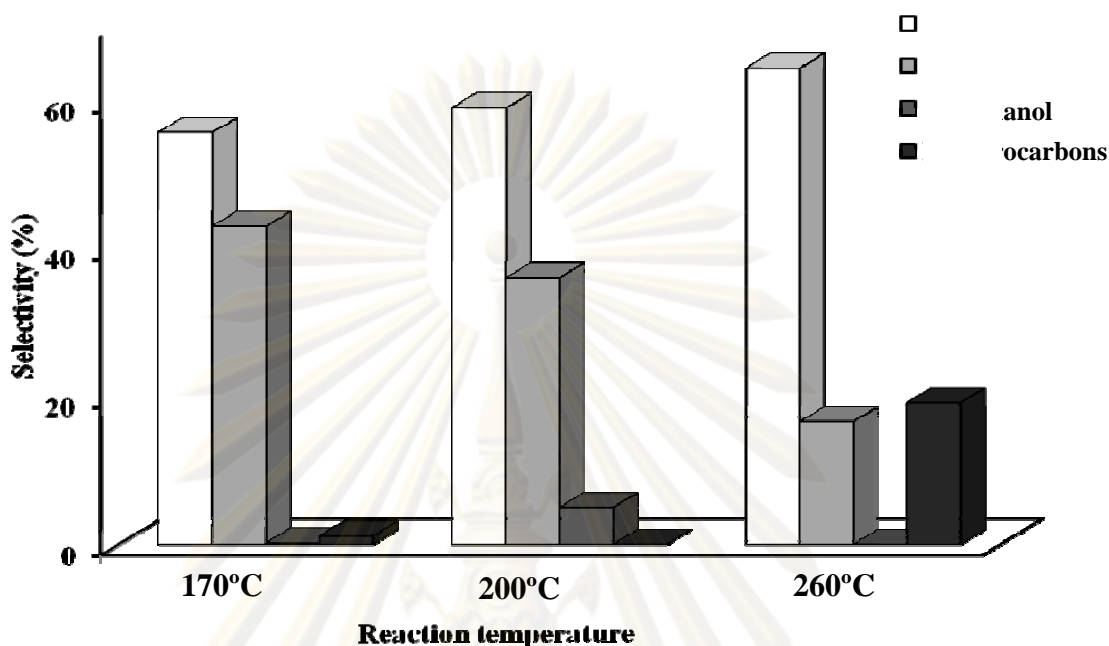
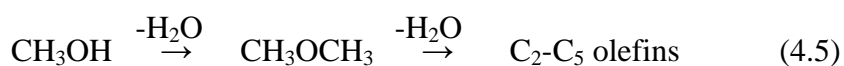


Figure 4.4 Effect of reaction temperature on selectivity of products for DME synthesis in semi-continuous reactor at 15 hours. Conditions; H₂/Ar/CO = 48/4/48; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; paraffin = 20 mL; reactant gas flow rate = 40 mL/min.

The selectivity of products for DME synthesis with various temperatures is presented in Figure 4.4. Results are considered into two significant cases. First, the selectivity of DME at reaction temperatures of 260°C, 200 °C and 170°C are about 64%, 59% and 56%, respectively. The high reaction temperature promoted the high DME selectivity because HZSM-5 had a very high catalytic activity at the optimum reaction temperature (below 300°C). Second, the selectivity of hydrocarbons at the reaction temperature of 260°C, 200°C, and 170°C are about 19%, 0% and 1%, respectively. However, the selectivity of hydrocarbons of reaction temperature of 260°C is too high (about 19%) which is probably influenced from the strongly catalysis of HZSM-5 solid acid catalyst. The reaction of methanol over acid catalysts can lead to the formation of hydrocarbons in addition to DME. The general reaction scheme given by Ton V. W. Janssens [43] can be outlined as follows:



Concisely, DME synthesis from syngas actually could not proceed at reaction temperature = 170°C in liquid paraffin as a solvent because the results exhibited almost no CO conversion. The CO conversion and DME selectivity were directly depended on temperature and implied that an increasing temperature led to increased CO conversion. At higher temperature of reaction, the methanol dehydration proceeded at relatively high rate and the total reaction rate was not controlled by thermodynamic of methanol synthesis reaction but by the kinetics of methanol dehydration reaction. It should be noted that the higher selectivity to hydrocarbons at higher temperature of reaction thus the side reaction in equation (4.5) led to dehydrated DME to small molecules of hydrocarbons over HZSM-5 catalyst which has a good activity at high temperature.



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4.3 Effect of Liquid Solvent System on CO Conversion

In a slurry reactor, solvent becomes important function to remove heat formation from the exothermic reaction as methanol synthesis. The fact that, in the slurry reactor, the reactant gas forms bubbles and chemical reaction takes place during the bubbles rise in the slurry; a solvent containing fine catalyst in the slurry reactor than fixed bed reactor, conventional reactor for DME synthesis. Nevertheless, as catalyst particles are surrounded by the solvent, it is required to develop on efficient catalyst.

As previously reported, developing DME synthesis from syngas at low temperature with conventional hybrid catalyst was investigated under a concept of novel methanol synthesis at low temperature was proposed by Reubroycharoen and co-worker [17]. A new reaction route of methanol synthesis at low temperature with Cu/ZnO catalyst was used in a batch and flow-type semi-batch reactor by addition of alcohols. The use of alcohols as catalytic solvents realized methanol synthesis at 443 K (170°C) with formate as an intermediate.

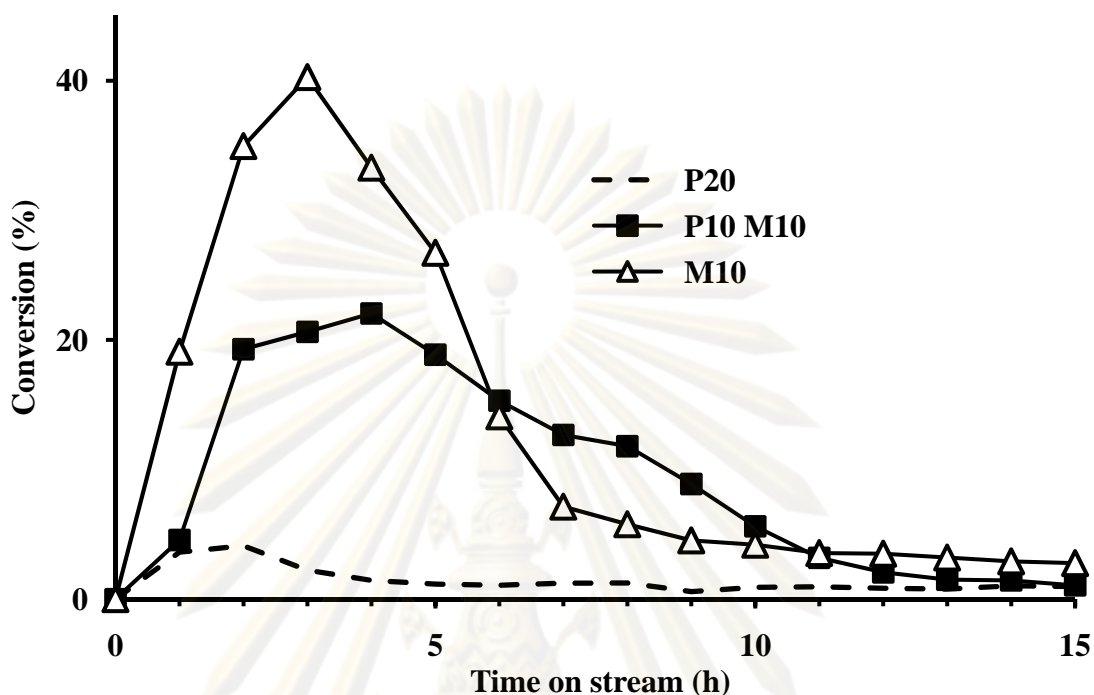
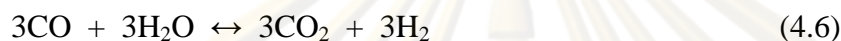


Figure 4.5 Variations of CO conversion (%) with time on stream (h) for DME synthesis in semi-continuous reactor by a various liquid solvent systems. Conditions; $H_2/Ar/CO = 48/4/48$; temperature = $170^\circ C$; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; reactant gas flow rate = 40 ml/min. P20 = paraffin 20 mL, P10 M10 = paraffin 10 mL and methanol 10 mL, M10 = methanol 10 mL.

As shown in Figure 4.5, DME synthesis of syngas over conventional catalyst could not take place at reaction temperature of $170^\circ C$ which has conversion of only about 1% after 15 hours of reaction. The CO conversion data at 15 hours of reaction is chosen because the CO conversion became constant value at 12 hours of reaction and still remained for 3 hours ago. It implied that DME synthesis got into equilibrium of reaction or steady state so the CO conversion at this reaction should be a good representative data for semi-continuous synthesis. Therefore, development of DME synthesis at low temperature over common hybrid catalyst was studied by adding methanol as a solvent in a slurry reactor. The results showed that CO conversion of paraffin 20 mL, paraffin 10 mL mixed with methanol 10 mL and methanol 10 mL are about 1%, 1% and 3% at 15 hours of reaction time.

The addition of methanol into paraffin influences the dimethyl ether synthesis preceded at low temperature (170°C). For paraffin 10 mL and methanol 10 mL mixer, in the initial reaction time shows high CO conversion due to the existence of methanol. After 10 hours of reaction, the CO conversion slightly dropped until almost no conversion that was probably because the methanol was running low. Therefore, methanol could be used as catalytic liquid medium. It was co-catalyst with Cu/ZnO for methanol synthesis reaction. The novel process of production of DME at low temperature was proposed as four reaction steps.

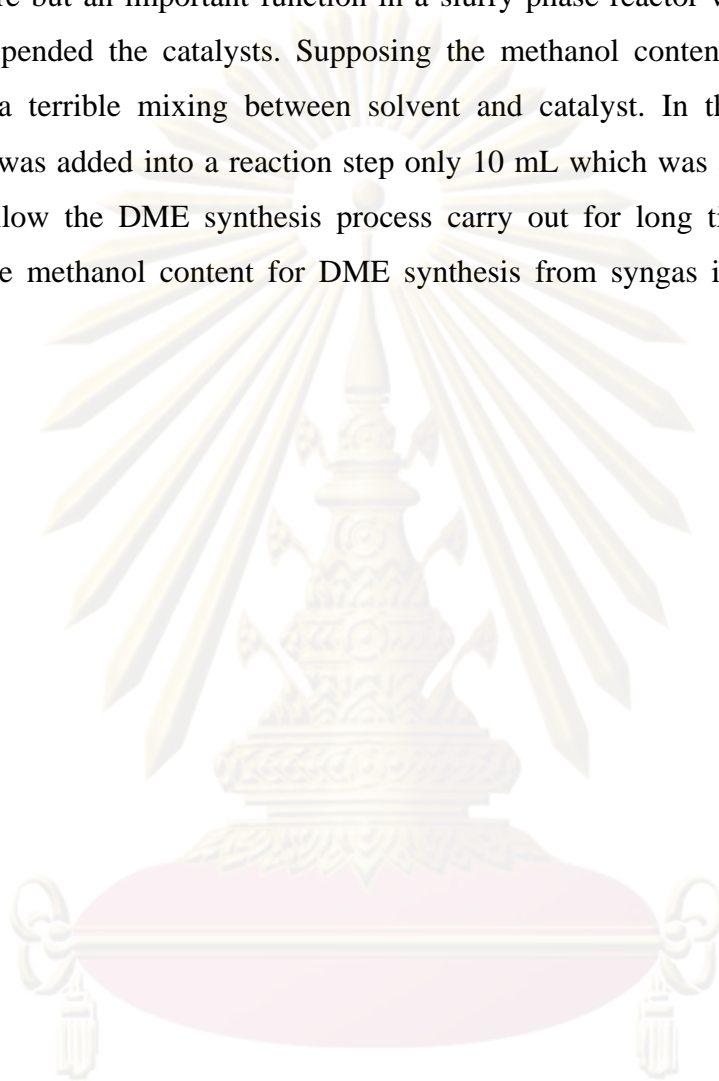


The equation (4.6) was the water-gas shift reaction, then a formation of methyl formate from an esterification of methanol (4.7). After that, the hydrogenation of methyl formate led to the formation of methanol (4.8). Another reaction was the dehydration of methanol to form DME (4.9). Finally, the overall DME synthesis reaction followed as in equation (4.10). Therefore, a new process for DME synthesis from syngas at low temperature was realized when methanol was added as catalytic liquid solvent.

However, comparing the CO conversion of the mixed system and the paraffin free system, the CO conversion of paraffin free system was higher than the mixed system because methanol could not dissolve in liquid paraffin and formed methanol droplets that resulted in low catalytic activity. Substitution of paraffin by methanol could not affect significantly the selectivity for DME but can reduce the hydrocarbon formation that was a by-product from DME synthesis.

Nevertheless, Calculation of obtained methanol content from equations (4.6) to (4.8) realized the obtained methanol content was 2.39 mL when 2400 mL/h of

reactant gas ($\text{CO}/\text{H}_2 = 1:1$) and 10 mL of methanol was added into the reaction. Although the addition of methanol directly assisted DME formation step at low temperature but an important function in a slurry phase reactor was a liquid solvent which suspended the catalysts. Supposing the methanol content was too low that cause of a terrible mixing between solvent and catalyst. In this experiment, the methanol was added into a reaction step only 10 mL which was a small content that did not allow the DME synthesis process carry out for long time. Therefore, the appropriate methanol content for DME synthesis from syngas is studied in a next issue.



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4.4 Effect of Methanol Content on Dimethyl Ether Synthesis.

The aim of this section is to study the effect of methanol content on DME synthesis over conventional Cu/ZnO/HZSM-5 catalyst. Figure 4.6 shows the CO conversion with various methanol contents for semi-continuous DME synthesis at 15 hours of reaction time.

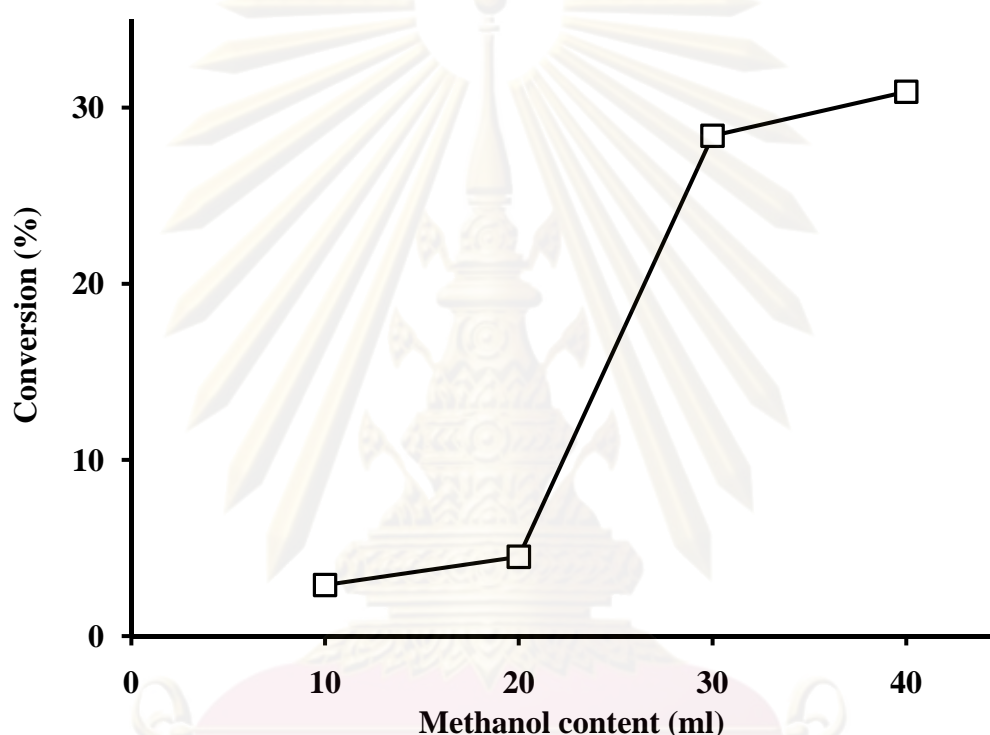


Figure 4.6 Effect of methanol content on the CO conversion (%) for DME synthesis in semi-continuous reactor at 15 hours. Conditions; $H_2/Ar/CO = 48/4/48$; temperature = $170^\circ C$; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; reactant gas flow rate = 40 mL/min.

As shown in Figure 4.6, the CO conversion increases as methanol content increases. At 15 hours of reaction time, the CO conversion (%) of each condition is 2.9, 4.5, 28.4 and 30.9, respectively.

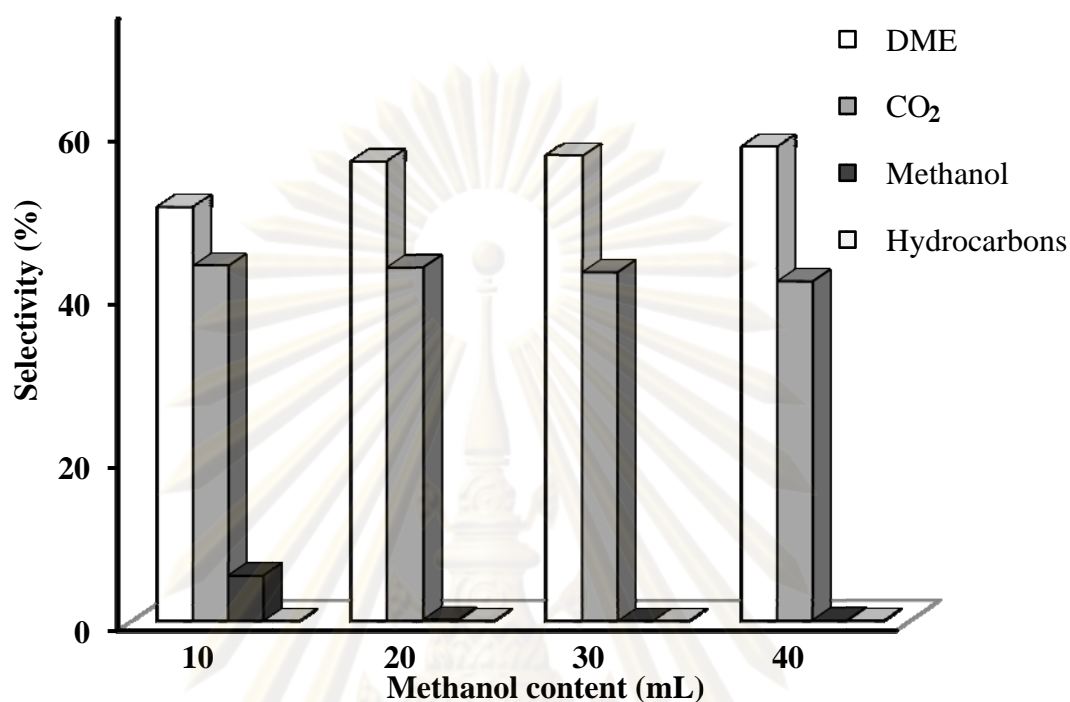


Figure 4.7 Effect of methanol content on selectivity of products for DME synthesis in semi-continuous reactor at 15 hours. Conditions; $H_2/Ar/CO = 48/4/48$; temperature = $170^\circ C$; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; reactant gas flow rate = 40 mL/min.

From Figure 4.7, selectivity of DME with various methanol contents was 50.8%, 56.4%, 57.1% and 58.2%, respectively. Therefore, the methanol content did not directly affect on selectivity of DME.

Concisely, comparison of DME synthesis between a conventional process (paraffin was used as liquid solvent) and a proposed process (methanol was used as liquid solvent) in cases of CO conversion (%) and DME yield (%) was shown in Figure 4.8. The CO conversion (%) and DME yield (%) of a conventional process was 0.9 and 0.5, respectively, while a proposed process was 30.9 and 22.4, respectively. Obviously, both of the CO conversion and DME yield of a proposed process exhibited higher value than a conventional process because of an effect of adding methanol. The optimum methanol content used as solvent in a slurry reactor which was chosen for further study was 40 mL.

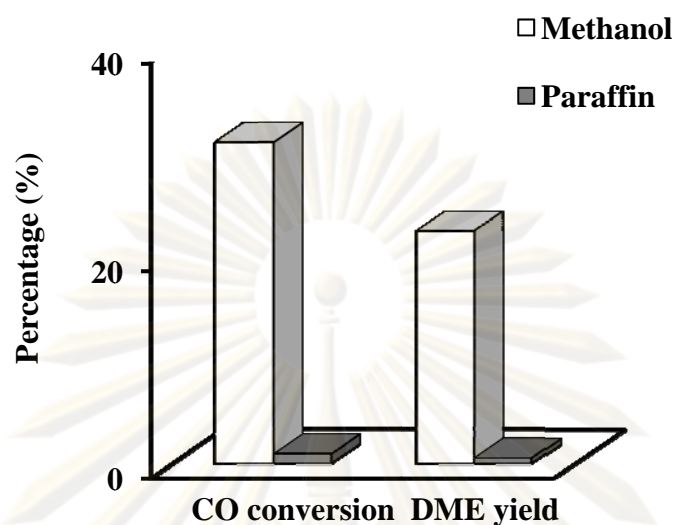


Figure 4.8 Comparison of DME synthesis between a conventional process (paraffin was used as liquid solvent) and a proposed process (methanol was used as liquid solvent) Conditions; $H_2/Ar/CO = 48/4/48$; temperature = $170^\circ C$; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; reactant gas flow rate = 40 mL/min.

4.5 Effect of Reaction Temperature on Dimethyl Ether synthesis; Methanol as Liquid Solvent

Figure 4.9 presents CO conversion change and time on stream for semi-continuous DME synthesis over Cu/ZnO/HZSM-5 catalyst with the various reaction temperatures. Results were reported that the conversion at reaction temperatures of $160^\circ C$, $170^\circ C$ and $180^\circ C$ at the end of reaction (15 hours) are about 15%, 31% and 4%., respectively. At the reaction temperature of $180^\circ C$, the CO conversion showed slight increase with increase in initial reaction time, after that it dropped a little and became constant after only 3 hours of reaction before declining rapidly after 12 hours of reaction time. Although the reaction temperature of $180^\circ C$ really exhibited the highest conversion but stability of reaction was poor. The reaction stability was an appearance of reaction which showed constant value of CO conversion through reaction time. The poor reaction stability at $180^\circ C$ was the cause of its CO conversion

rapidly dropped at 12 hours of reaction, before 15 hours which was the end of reaction time. However, at 12 hours, the CO conversion slightly increased before rapidly declined because the added methanol was probably running low and nearly terminated from the reaction. Therefore, the gas–solid (reactant–catalyst) could directly contact together. After the added methanol was already lost from the reaction, the CO conversion suddenly dropped due to lack of catalytic-solvent (methanol). On the other hand, at the reaction temperature 160°C, the reaction could take place and showed good reaction stability (CO conversion had been constant for along reaction time) but the conversion was low. The DME synthesis at 170°C from syngas was an optimum temperature when methanol was used as liquid solvent.

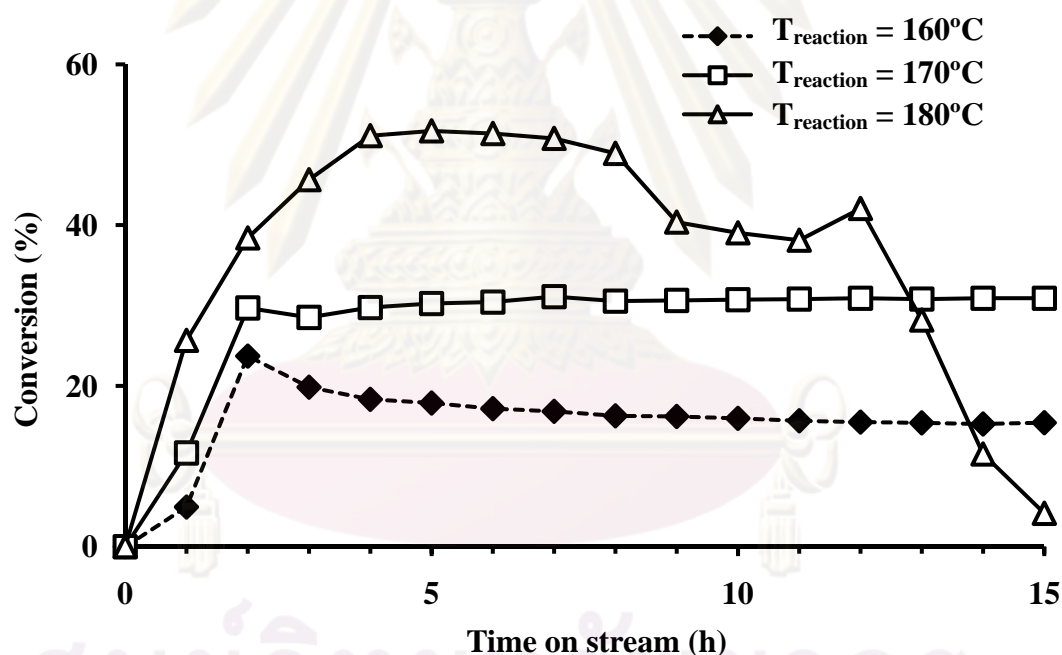


Figure 4.9 Variation of CO conversion (%) for DME synthesis in semi-continuous reactor by a various reaction temperatures in methanol. Conditions; $H_2/Ar/CO = 48/4/48$; pressure = 4.0 MPa; catalyst (CuZnO/HZSM-5 = 2:1) = 1 g; methanol = 40 mL; reactant gas flow rate = 40 mL/min.

As results shown in Table 4.2, DME selectivity at the reaction temperatures of 160°, 170° and 180°C are 68.3%, 72.5% and 84.9%, respectively. The DME selectivity at 180°C shows the highest selectivity which is affected by the higher temperature. In the case of hydrocarbons selectivity, result at the reaction temperatures of 160°, 170° and 180°C are 11.8%, 0% and 13.2%, respectively.

Table 4.2 Effect of temperature on DME synthesis

Temperature (°C)	Conversion (%)	Selectivity (%)				DME yield (%)
		DME	CO ₂	CH ₃ OH	Hydrocarbons	
160	15.1	68.3	19.8	11.8	0.1	10.3
170	30.9	72.5	27.3	0.1	0.0	22.4
180	4.1	84.9	1.9	0.0	13.2	3.5

Reaction conditions; H₂/Ar/CO = 48/4/48; temperature = 170°C; pressure = 4.0 MPa; catalyst (Cu/ZnO/HZSM-5 = 2:1) = 1 g; methanol = 40 mL; reactant gas flow rate = 40 mL/min; at 15 hours of reaction.

Therefore, at 180°C is not suitable for a reaction temperature because a severe reaction takes place which was not only influenced by a catalyst that had lost its ability but also leads to reaction stability that was not constant and the high formation of hydrocarbons.

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4.6 Effect of Ratio of CuZnO/HZSM-5 Catalyst (wt:wt) on Dimethyl Ether Synthesis

As shown in Figure 4.10, an effect of various ratio of CuZnO/HZSM-5 catalyst (wt:wt) on DME synthesis was studied. CuZnO/HZSM-5 with the ratio of 1:2, 1:1, 2:1, 3:1 and 4:1 exhibited the conversion at 15 hours as 4.3%, 24.4%, 30.9%, 24.6% and 13.3%, respectively. The CuZnO/HZSM-5 with ratio of 2:1 had the highest CO conversion. Reasonable explanation of this result should be the optimize content of methanol synthesis catalyst (Cu/ZnO) led to a well occurring of methanol synthesis reaction. However, in the case of too much of methanol synthesis catalyst presented low CO conversion because of an unbalanced reaction. The low content of methanol dehydration catalyst (HZSM-5) influenced to the right toward reaction less happen.

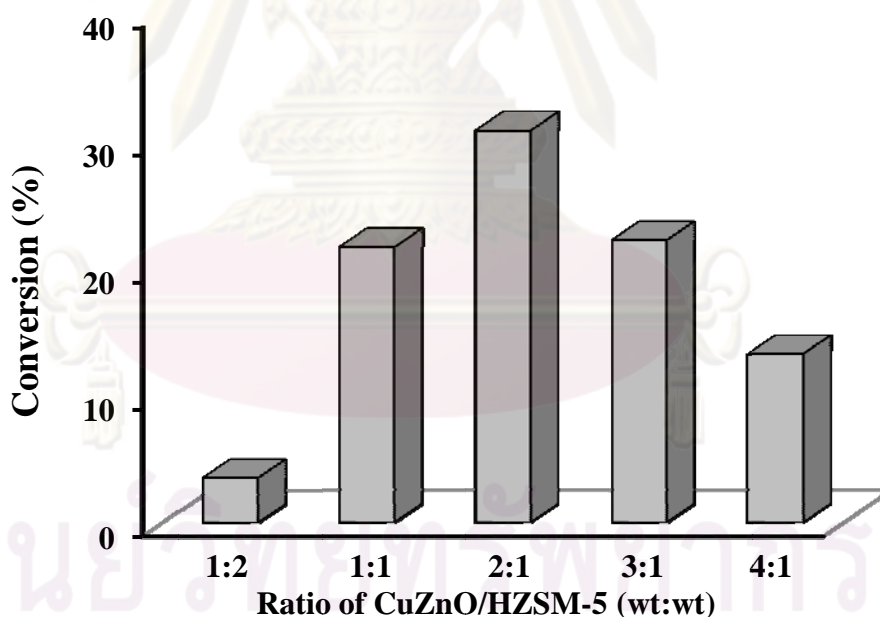


Figure 4.10 Effect of ratio of CuZnO/HZSM-5 (wt:wt) on the CO conversion (%) for DME synthesis in semi-continuous reactor at 15 hours. Conditions; $H_2/Ar/CO = 48/4/48$; pressure = 4.0 MPa; catalyst = 1 g; methanol = 40 mL; reactant gas flow rate = 40 mL/min.

Effect of weight ratio of CuZnO/HZSM-5 (wt:wt) on DME yield was presented in Figure 4.11. The CuZnO/HZSM-5 with ratio of 1:2, 1:1, 2:1, 3:1 and 4:1 showed DME yield (%) at 15 hours as 3.7, 17.9, 22.4, 15.7 and 8.9, respectively.

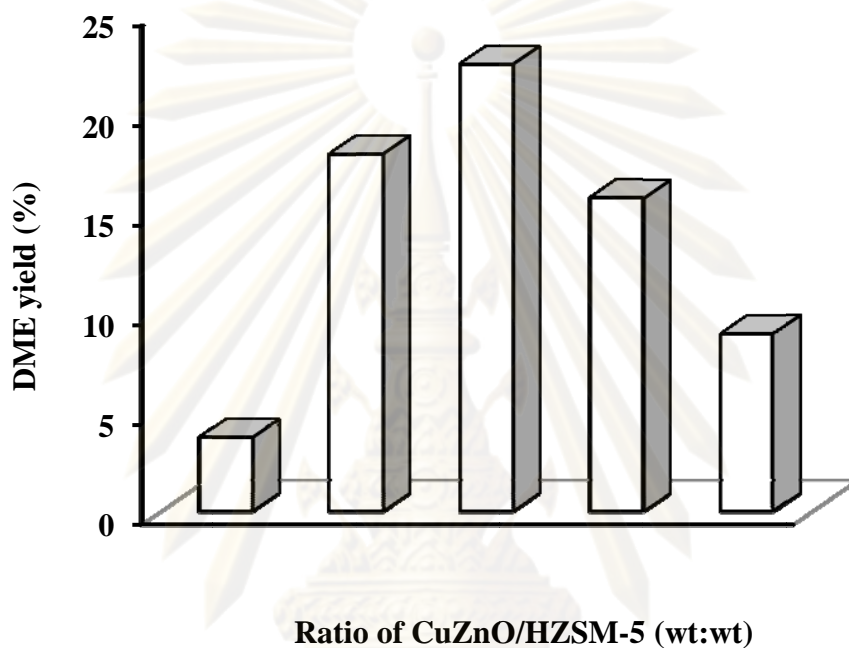


Figure 4.11 Effect of weight ratio of CuZnO/HZSM-5 on DME yield of DME synthesis in semi-continuous reactor at 15 hours. Conditions; $H_2/Ar/CO = 48/4/48$; pressure = 4.0 MPa; temperature = 170°C; catalyst = 1 g; methanol = 40 mL; reactant gas flow rate = 40 mL/min.

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Selectivity of products was exhibited in Table 4.3. The CuZnO/HZSM-5 with ratio of 1:2, 1:1, 2:1, 3:1 and 4:1 showed DME selectivity (%) as 88.1, 73.7, 72.5, 70.5 and 67.5, respectively. Clearly, the ratio of methanol synthesis catalyst (CuZnO) and methanol dehydration catalyst (HZSM-5) importantly affect on DME selectivity. The lower DME selectivity was obtained when the higher methanol synthesis catalyst. A partial methanol content could not transform to DME because of the low content HZSM-5.

Table 4.3 Effect of the weight ratio of CuZnO/HZSM-5 on DME synthesis

Ratio of CuZnO/HZSM-5	Conversion (%)	Selectivity of products (%)				Yield of DME (%)
		CO ₂	DME	CH ₃ OH	Hydrocarbons	
1:2	88.1	11.1	88.1	0.2	0.0	3.7
1:1	73.7	26.3	73.7	0.0	0.0	17.9
2:1	72.5	27.3	72.5	0.1	0.0	22.4
3:1	70.5	27.9	70.5	1.6	0.0	15.7
4:1	67.5	22.4	67.5	9.6	0.0	8.9

Reaction conditions: H₂/Ar/CO = 48/4/48; temperature = 170°C; pressure = 4.0 MPa; catalyst = 1 g; methanol = 40 mL; flow rate = 40 mL/min; reaction time = 15 hours.

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4.7 Catalytic Regeneration of CuZnO/HZSM-5 Catalyst on Dimethyl Ether Synthesis

The time on stream and various conversions (%) of DME synthesis over CuZnO/HZSM-5 compared with regenerated catalyst as R-Cu/ZnO/HZSM-5 were shown in Figure 4.12. CO conversion of Cu/ZnO/HZSM-5 and R-Cu/ZnO/HZSM-5 are about 30% and 3%, respectively. The CO conversion of the fresh Cu/ZnO/HZSM-5 is much higher than the R-Cu/ZnO/HZSM-5 catalyst.

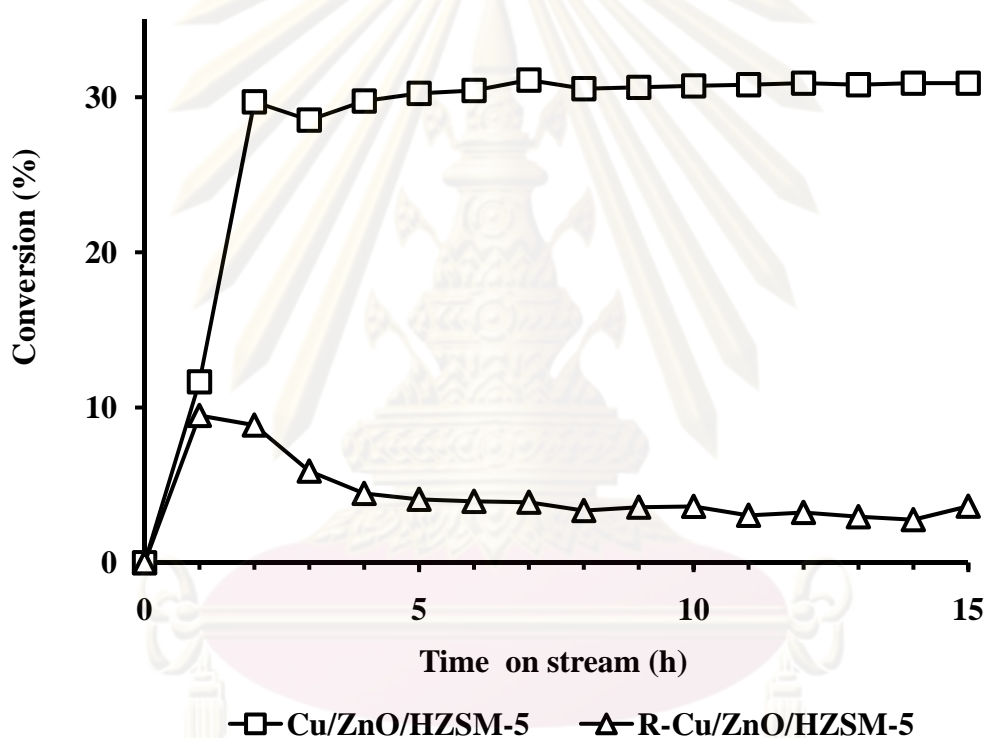


Figure 4.12 Variations of conversion (%) with time on stream for DME synthesis in semi-continuous reactor over Cu/ZnO/HZSM-5 and R-Cu/ZnO/HZSM-5 catalyst. Conditions; $H_2/Ar/CO = 48/4/48$; temperature = $170^\circ C$; pressure = 4.0 MPa; catalyst = 1 g; paraffin = 20 mL; reactant gas flow rate = 40 mL/min.

Selectivity of products is shown in Table 4.4. DME selectivity of CuZnO/HZSM-5 is higher than that of the R-Cu/ZnO/HZSM-5. Methanol selectivity of the CuZnO/HZSM-5 is lower than that of the R-Cu/ZnO/HZSM-5.

Table 4.4 Comparing an effect of CuZnO/HZSM-5 and R-Cu/ZnO/HZSM-5 on DME synthesis

Catalyst	Conversion (%)	Selectivity (%)				DME yield (%)
		DME	CO ₂	CH ₃ OH	Hydrocarbons	
Cu/ZnO/HZSM-5	30.9	72.5	27.3	0.1	0.0	22.4
R-Cu/ZnO/HZSM-5 ^a	3.2	68.2	19.5	12.4	0.0	2.2

Reaction conditions: H₂/Ar/CO = 48/4/48; temperature = 170°C; pressure = 4.0 MPa; catalyst = 1 g; methanol = 40 mL; flow rate = 40 mL/min.; reaction time = 15 hours

^a Regenerated Cu/ZnO/HZSM-5

Comparing the XRD patterns of CuZnO/HZSM-5 in various states was shown in Figure 4.13. A difference between diffraction peak of catalyst before and after reaction, peaks of Cu disappeared but ZnO and HZSM-5 still existed. This result reveals the metal Cu species were transform to original (before H₂ reduction step) forms that was CuO. After that catalyst was regenerated by H₂ reduction step and used for catalyze reaction again. The diffraction peaks shows small peaks of Cu. However, the diffraction peaks of ZnO became stronger slightly and high peaks of Cu appeared after reaction with the crystalline size was 31.37 nm (as shown in Table 4.5). It means the crystal grains of Cu increased greatly and agglomeration occurred on the catalyst surface, weakening the synergistic effect between Cu and ZnO and decreasing the catalytic activity and stability.

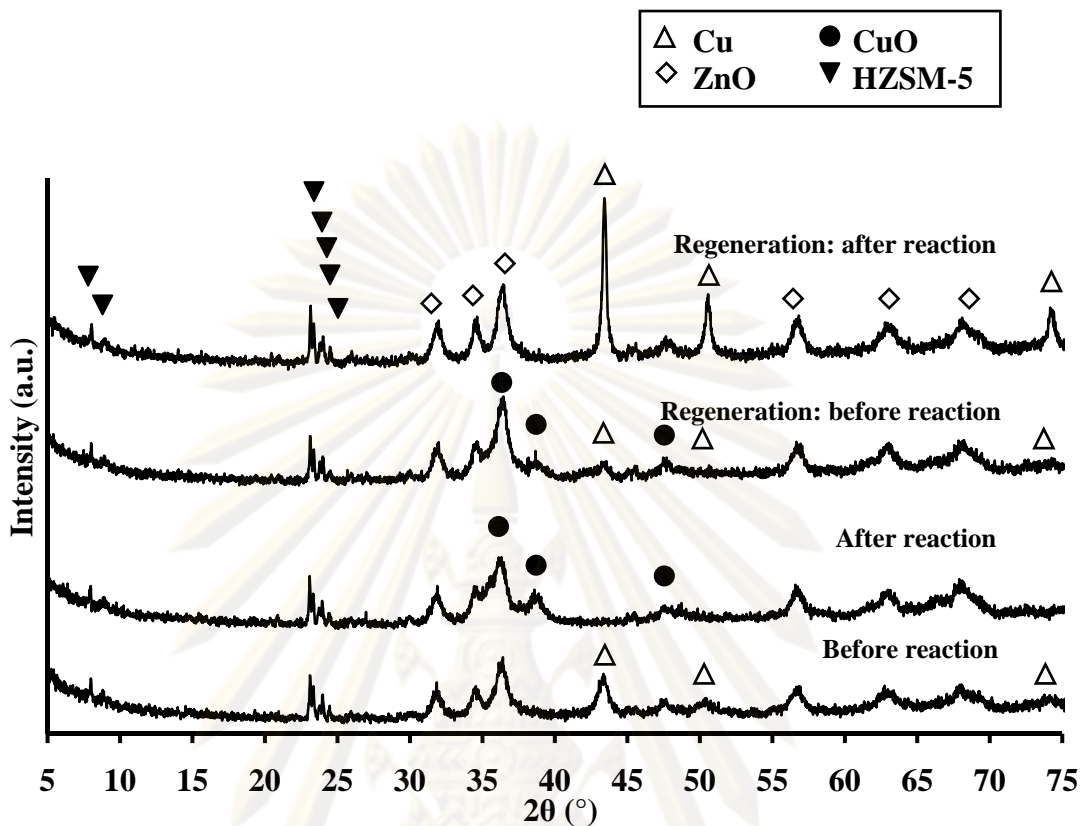


Figure 4.13 The X-ray diffraction patterns of CuZnO/HZSM-5 catalyst in various states.

Kim *et al.* reported that the crystallinity of catalyst would exert an influence on the reactivity of catalyst. Therefore, the higher reactivity is expected at the lower crystallinity [44]. Cu crystalline size of catalyst with various states was reported in Table 4.5. The Cu crystalline size of catalyst at each state (before reaction, regeneration: before reaction and regeneration: after reaction) was 10.97, 12.68 and 31.37 nm, respectively. Clearly, the Cu crystalline size of the regenerated catalyst exhibited a higher crystallinity (12.68 nm) than the fresh catalyst (10.97 nm) therefore the difference of their crystallinity importantly influenced on their activity.

Table 4.5 Effect of catalytic regeneration of CuZnO/HZSM-5 catalysts on crystalline size and CO conversion for DME synthesis

Catalysts	Cu crystalline size (nm)	CO conversion (%)
Before reaction	10.97	30.9
Regeneration: before reaction	12.68	3.6
Regeneration: after reaction	31.37	0.0

Reaction conditions: H₂/Ar/CO = 48/4/48; temperature = 170°C; pressure = 4.0 MPa; catalyst = 1 g; methanol = 40 mL; flow rate = 40 mL/min.; reaction time = 15 hours.

However, this experiment has some drawbacks due to a restriction of semi-continuous process. The catalyst was taken out of reactor and was crushed, heated again and again. Therefore, its structure probably was destroyed and showed poor activity.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, CuZnO/HZSM-5 catalyst was selected as hybrid catalyst for dimethyl ether synthesis from syngas to perform reaction at low temperature by adding methanol as catalytic solvent.

Mole ratio for Cu/Zn of 1 was proper as methanol synthesis catalyst. For conventional process, paraffin as liquid solvent, the higher reaction temperature, the higher the CO conversion. However, the selectivity to hydrocarbon was high. The result revealed the catalytic activity of HZSM-5 was increased when reaction temperature increased. Partial content of DME was transformed to hydrocarbon. Meanwhile at reaction temperature 170°C, the reaction could not proceed. Adding a little content of methanol into reaction system assisted an increasing of CO conversion at low temperature. Methanol could potentially change the reaction pathway to allow DME formation at low temperature. The concept of study was to use methanol as catalytic solvent. In addition, 40 ml of methanol exhibited the best results both of CO conversion and DME selectivity. Indeed, the DME synthesis reaction proceeds though reaction time due to suitable methanol content. The effect of ratio of CuZnO/HZSM-5 (wt:wt) catalyst was also studied. The weight ratio of CuZnO/HZSM-5 of 2:1 was proper for DME synthesis at low temperature with addition of methanol as catalytic solvent. Obviously, the ratio of methanol synthesis catalyst (CuZnO) and methanol dehydration catalyst (HZSM-5) importantly affect on DME selectivity. The lower DME selectivity was obtained when the higher methanol synthesis catalyst. A partial methanol content could not transform to DME because the low content of HZSM-5. Finally, the CO conversion of regenerated CuZnO/HZSM-5 was less than that of fresh catalyst.

Concisely, DME synthesis from syngas was successfully synthesized at low temperature by addition of methanol as catalytic solvent. CO conversion of 30.9% and DME selectivity of 72.5% were achieved with an optimum reaction conditions as follow; component of syngas as $H_2/Ar/CO = 48/4/48$; temperature = $170^\circ C$; pressure = 4.0 MPa; catalyst (Cu/ZnO/HZSM-5 = 2:1)= 1 g; liquid solvent as methanol = 40 ml; flow rate = 40 mL/min.

5.2 Recommendation

For future research works, DME synthesis from syngas in semi-continuous reactor should be further investigated. The other modification of metal oxide catalysts for improving its activity at low temperature should be studied for the first issue. However, the reduction of methanol content should be investigated. Finally, catalytic regeneration process of catalyst should be improved for production of DME synthesis in a commercial scale.

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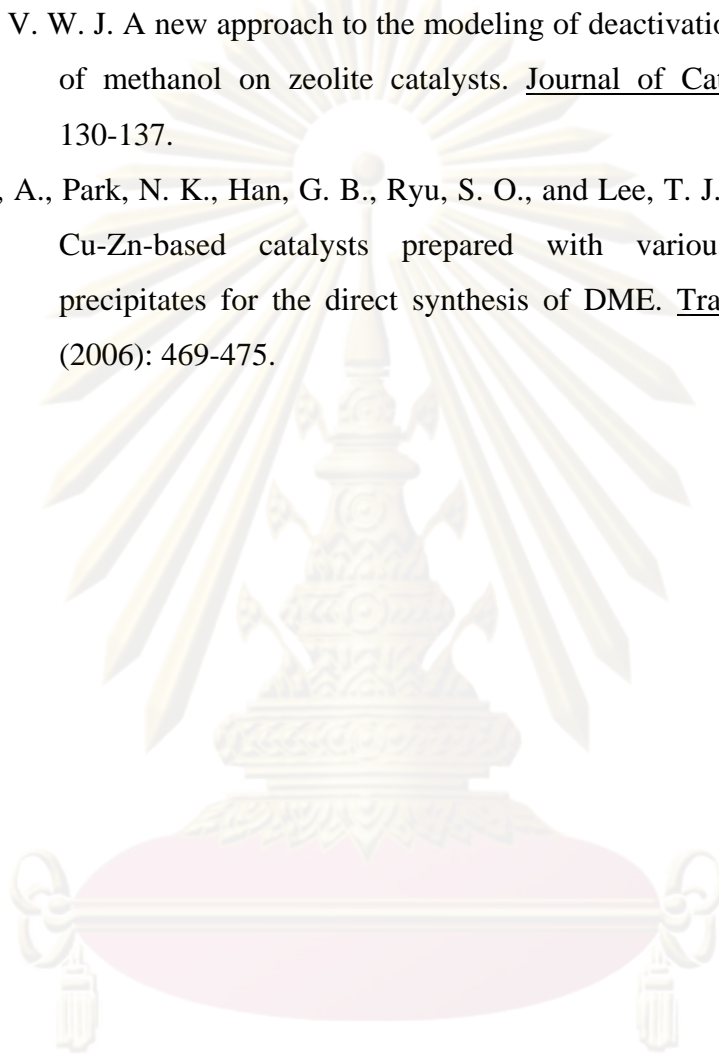
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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



APPENDICES

ศูนย์วิทยทรัพยากร
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Appendix A

Examined Calculation for Preparation of Cu/Zn = 1

Cu/Zn = 1 was prepared by co-precipitation method

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

Co-precipitation

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

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

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

weight fraction of CuO = $79.55 / 160.94 = 0.49428$

weight fraction of ZnO = $81.39 / 160.94 = 0.50572$

Basis 10 g of CuO/ZnO

Therefore weight of CuO = $0.49428 \times 10 = 4.9428$ g

weight of ZnO = $0.50572 \times 10 = 5.0572$ g

CuO mole used = $4.9428 \times 79.55 = 0.0621$ mole

ZnO mole used = $5.0572 \times 81.39 = 0.0621$ mole

1 mole CuO = 1 mole $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$

1 mole ZnO = 1 mole $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Therefore,

weight of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (MW = 232.59, Assay = 0.99)

= $0.0621 \times 232.59 / 0.99 = \underline{14.5979}$ g

weight of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MW = 297.47, Assay = 0.98)

= $0.0621 \times 297.47 / 0.98 = \underline{18.8605}$ g

Total mole used = $0.0621 + 0.0621 = 0.1243$ mol

The use of Na_2CO_3 (MW = 105.99, Assay = 1.00)

= $0.1243 \times 105.99 / 1.00 = 13.1714$ g

For pH control in range 6.8 – 7.0, Na_2CO_3 must used > 13.1714 g

Therefore, from the experiment, weight of $\text{Na}_2\text{CO}_3 \sim \underline{18.50}$ g

Appendix B

Examined Calculation of Reaction Products

Data from the use of catalyst : weight ratio of Cu/ZnO:HZSM-5=2:1, $T_{\text{reaction}} = 170\text{ }^{\circ}\text{C}$

Determination of CO conversion.

Table B-1 CO/Ar of reactant gas

time	Area			CO/Ar
	H ₂	Ar	CO	
1	1095.8	5579.1	61674.2	11.05451
2	1270.6	7139.1	79265.8	11.10305
3	1249.5	7125.4	79234.5	11.12001
4	1261.8	7161.7	79344.2	11.07896
5	1266.6	7111.4	79247.0	11.14366
6	1264.3	7119.4	79152.1	11.11780
			AVG	11.10300

H₂/Ar/CO/ = 48/4/48

Table B-2 Determination of CO conversion of gas products

Hr.	Area				CO/Ar	% CO Conversion
	H ₂	Ar	CO	CO ₂		
0	825.30	4440.3	40623.2	2441.4	9.148751	17.6
1	1339.8	6583.4	50661.5	15896.0	7.695340	30.7
2	1304.5	6250.3	52815.7	19370.7	8.450106	23.9
3	1295.4	6093.0	52561.0	17376.1	8.626457	22.3
4	1300.1	5918.7	48372.9	19591.8	8.172893	26.4
5	1292.7	5817.4	47188.7	20505.1	8.111648	26.9
6	1294.6	5753.7	46754.1	20866.8	8.125919	26.8
7	1297.1	5676.0	46337.9	20713.8	8.163830	26.5
8	1210.9	5180.2	42225.6	18771.7	8.151346	26.6
9	1264.2	5556.1	45398.6	20503.5	8.170947	26.4
10	1248.8	5496.5	44817.7	20800.3	8.153862	26.6
11	1281.8	5409.5	43978.8	20536.5	8.129920	26.8
12	1279.9	5335.1	43222.5	20609.7	8.101535	27.0
13	1269.0	5349.9	43632.7	20231.1	8.155797	26.5
14	1259.1	5379.6	43890.8	20129.9	8.158748	26.5
15	825.30	4440.3	40623.2	2441.40	9.148751	26.5

Determination of selectivity and yield.

Table B-3 Determination of selectivity and yield of products^a

Products	Reactor	
		Area
CO ₂ (%)	8.044065	271891296.5
CH ₃ OCH ₃ (%)	24.22241	21182284.9
CH ₃ OH (%)	3.428518	575701.9
Hydrocarbons (%)	0.215263	625522.8
	Selectivity	Yield
CO ₂ (%)	22.4	5.94
CH ₃ OCH ₃ (%)	67.5	17.89
CH ₃ OH (%)	9.5	2.52
Hydrocarbons (%)	0.6	0.16

^aSemi-continuous conditions: H₂/Ar/CO = 48/4/48; reaction time = 15 h; pressure = 4.0 MPa; catalyst = 1 g; solvent = 40 ml; flow rate = 40 ml/min.

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Publication

Prasert, R., Suwattana, T., Tharapong, V., Chaiyan, C., Suchada, B., and Noritatsu, T. A Novel, Low Temperature Synthesis Method of Dimethyl Ether Over Cu-Zn Catalyst Based on Self-Catalysis Effect of Methanol. Topic in Catalysis (2009) 52:1079–1084.

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