

ปฏิริยาตีไฮเครชันของเอทานอล บนตัวเร่งปฏิริยาแมงกานีส/อะลูมินา



นางสาวรัตนภรณ์ รัชย์พันธ์

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)  
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)  
are the thesis authors' files submitted through the University Graduate School.

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2558

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

DEHYDRATION OF ETHANOL OVER Mn –  
MODIFIED ALUMINA CATALYST

Miss Rattaporn Rakpan



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Engineering Program in Chemical Engineering  
Department of Chemical Engineering  
Faculty of Engineering  
Chulalongkorn University  
Academic Year 2015  
Copyright of Chulalongkorn University

Thesis Title	DEHYDRATION OF ETHANOL OVER Mn – MODIFIED ALUMINA CATALYST
By	Miss Rattanaorn Rakpan
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Bunjerd Jongsomjit, Ph.D.

---

Accepted by the Faculty of Engineering, Chulalongkorn University in  
Partial Fulfillment of the Requirements for the Master's Degree

..... Dean of the Faculty of Engineering  
(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

..... Chairman  
(Chutimon Satirapipathkul, Ph.D.)

..... Thesis Advisor  
(Associate Professor Bunjerd Jongsomjit, Ph.D.)

..... Examiner  
(Associate Professor Seeroong Prichanont, Ph.D.)

..... External Examiner  
(Ekrachan Chaichana, Ph.D.)

รัตนาภรณ์ รักษ์พันธ์ : ปฏิกริยาดีไฮเดรชันของเอทานอล บนตัวเร่งปฏิกริยาแมงกานีส/อะลูมินา (DEHYDRATION OF ETHANOL OVER Mn – MODIFIED ALUMINA CATALYST) อ.ที่  
 ปรักษาวิทยานิพนธ์หลัก: รศ. ดร.บรรเจิด จงสมจิตร, หน้า.

เอทิลีนถูกนำมาใช้กันอย่างแพร่หลายสำหรับวัตถุดิบในอุตสาหกรรม การผลิตเอทิลีนโดยทั่วไปจะใช้วิธีการแตกสลายทางความร้อนโดยใช้ไอน้ำ ข้อเสียของกระบวนการนี้คืออุณหภูมิที่ใช้ในการผลิตประมาณ 600-1000 องศาเซลเซียส ซึ่งต้องใช้พลังงานที่สูงมาก อีกทั้งวัตถุดิบที่ใช้ในการผลิตเอทิลีนคือสารไฮโดรคาร์บอนเช่น แนฟทา ซึ่งเป็นวัตถุดิบที่มีปริมาณจำกัด วัตถุประสงค์ของการวิจัยนี้เพื่อศึกษาทางเลือกในการผลิตเอทิลีนโดยวิธีดีไฮเดรชันของเอทานอลไปเป็นเอทิลีน ซึ่งเอทิลีนจากกระบวนการนี้เป็นมิตรต่อสิ่งแวดล้อมเพราะใช้เอทานอลเป็นวัตถุดิบที่จะสามารถลดการใช้เชื้อเพลิงฟอสซิล ในงานวิจัยนี้ศึกษาตัวเร่งปฏิกริยาอะลูมินา ถูกเตรียมโดยวิธีโซลโวลเทอร์มอลและถูกวิเคราะห์คุณลักษณะด้วยการกระเจิงรังสีเอ็กซ์ กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด การดูดซับทางกายภาพด้วยไนโตรเจน และการคายแอมโมเนียด้วยการเพิ่มอุณหภูมิแบบตั้งโปรแกรม เปรียบเทียบประสิทธิภาพของแกมมาไคน์อะลูมินาและแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินาในปฏิกริยาการขจัดน้ำของเอทานอลและอุณหภูมิระหว่าง 200 องศาเซลเซียส ถึง 400 องศาเซลเซียส โดยตัวเร่งปฏิกริยาอะลูมินาแสดงให้เห็นถึงการการเปลี่ยนรูปของเอทานอลและความเลือกจำเพาะต่อการเกิดเอทิลีนมากกว่าแมงกานีสบนตัวเร่งปฏิกริยาอะลูมินา ที่อุณหภูมิ 400 องศาเซลเซียส ให้การเปลี่ยนรูปของเอทานอลและความเลือกจำเพาะต่อการเกิดเอทิลีนมากที่สุดทุกตัวเร่งปฏิกริยา ในกรณีของการเปลี่ยนรูปของเอทานอลเรียงลำดับได้โดยอะลูมินา (77.3%) > 0.05 โดยน้ำหนักของแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินา (53.1%) > 0.1 โดยน้ำหนักของแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินา (39.7%) และในกรณีของความเลือกจำเพาะต่อการเกิดเอทิลีนเรียงลำดับได้โดย อะลูมินา (96.8%) > 0.05 โดยน้ำหนักของแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินา (86.7%) > 0.1 โดยน้ำหนักของแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินา (70.5%) อย่างไรก็ตามพบว่าการปรับปรุงอะลูมินาด้วยแมงกานีสจะทำให้ค่าการเลือกเกิดของไดเอทิลอีเทอร์สูงขึ้นที่อุณหภูมิต่ำ ที่อุณหภูมิ 250 องศาเซลเซียส ความเลือกจำเพาะต่อการเกิดไดเอทิลอีเทอร์มากที่สุดเรียงลำดับได้โดย 0.1 โดยน้ำหนักของแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินา (100%) > 0.05 โดยน้ำหนักของแมงกานีสที่เติมบนตัวเร่งปฏิกริยาอะลูมินา (93.0%) > อะลูมินา (82.4%)

ภาควิชา วิศวกรรมเคมี

ลายมือชื่อนิสิต .....

สาขาวิชา วิศวกรรมเคมี

ลายมือชื่อ อ.ที่ปรักษาหลัก .....

ปีการศึกษา 2558

# # 5570940221 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: ETHYLENE, STEAM THERMAL CRACKING, DEHYDRATION, ALUMINA, MANGANESE

RATTANAPORN RAKPAN: DEHYDRATION OF ETHANOL OVER Mn – MODIFIED ALUMINA CATALYST. ADVISOR: ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., pp.

Ethylene is widely used for raw material in industries. Currently, the method to produce the ethylene is steam thermal cracking of hydrocarbons. The weak point of this method is that the reaction temperature is about 600-1000 °C that is very high and hydrocarbons as raw materials are limited quantities such as naphtha. The purpose of this research is to investigate an alternative way of ethylene production. The ethanol dehydration is a novel promising way of ethylene production. The ethylene from this process is environmental friendly because using ethanol as raw material can reduce the utilization of fossil fuel. The catalyst for this reaction is alumina prepared by the solvothermal method and characteristics of catalyst were determined by XRD, SEM, BET and NH<sub>3</sub>-TPD. In this research, we compare performance of  $\gamma$ -  $\chi$  alumina and manganese modified alumina catalyst in ethanol dehydration reaction at various temperatures between 200–400°C. The  $\gamma$ -  $\chi$  alumina catalyst shows high ethanol conversion and high ethylene selectivity more than the manganese-modified alumina catalyst. At 400 °C, the highest ethanol conversion and highest ethylene selectivity were observed for all catalyst. In terms of ethanol conversion, it was in the order of Al<sub>2</sub>O<sub>3</sub> (77.3%)> 0.05Mn/Al<sub>2</sub>O<sub>3</sub> (53.1%)> 0.1Mn/Al<sub>2</sub>O<sub>3</sub> (39.7%) and ethylene selectivity was in order of Al<sub>2</sub>O<sub>3</sub> (96.8%)> 0.05Mn/Al<sub>2</sub>O<sub>3</sub> (86.7%)> 0.1Mn/Al<sub>2</sub>O<sub>3</sub> (70.5%). However, the Mn modification can result in increased diethyl ether (DEE) selectivity at low temperature. At 250 °C, the highest DEE selectivity, was found for 0.1Mn/Al<sub>2</sub>O<sub>3</sub> (100%), while DEE selectivity 0.05Mn/Al<sub>2</sub>O<sub>3</sub> (93.0%)>Al<sub>2</sub>O<sub>3</sub> (82.4%) was observed.

Department: Chemical Engineering Student's Signature .....

Field of Study: Chemical Engineering Advisor's Signature .....

Academic Year: 2015

## ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my advisor Associate Professor Bunjerd Jongsomjit for the continuous support of my study and research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my study.

Besides my advisor, I would like to thank the rest of my thesis committee: Dr. Chutimon Satirapipathkul and Associate Professor Seeroong Prichanont for their insightful comments and encouragement, but also for the hard question, which incited me to widen my research from various perspectives.

I thank my fellow lab mates in for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we have had in the last four years

Last but not the least, I would like to thank my family: my parents and to my sister for supporting me spiritually throughout writing this thesis and my my life in general.

## CONTENTS

	Page
THAI ABSTRACT .....	iv
ENGLISH ABSTRACT.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
TABLES CONTENTS.....	i
FIGURES CONTENTS .....	ii
CHAPTER I.....	1
INTRODUCTION .....	1
1.1 General introduction .....	1
1.2 Research objectives .....	2
1.3 Research scopes .....	2
1.4 Research methodology.....	3
1.5 Research Plan.....	5
CHAPTER II.....	6
THEORY AND LITERATURE REVIEWS .....	6
2.1 Raw material.....	6
2.2 Ethanol dehydration reaction .....	8
2.3 Catalyst .....	11
The mechanism of catalytic dehydration of ethanol is shown in the Figure 2.4 where an acid catalyst protonate the OH group to leave the water molecule. The conjugate base of the catalyst thus formed deprotonates the methyl group, and hydrocarbon rearrangement and form ethylene. ....	11
2.4 Literature reviews .....	15
CHAPTER III .....	17
EXPERIMENTAL.....	17
3.1 Catalyst preparation .....	17
3.2 Catalyst characterization.....	18
3.2.1) <i>X-ray diffraction (XRD)</i> .....	18
3.2.2) <i>Nitrogen physisorption</i> .....	18

	Page
3.2.3) Temperature programmed adsorption (NH <sub>3</sub> -TPD).....	18
3.2.4) <i>Scanning electron microscopy (SEM)</i> .....	19
3.3 Reaction of ethanol dehydration to ethylene .....	19
3.3.1) <i>Chemicals and reagents</i> .....	19
3.4 Reaction of ethanol dehydration reaction to DEE .....	21
Chapter IV.....	22
Results and discussion .....	22
4.1 Catalyst characterization of mixed $\gamma$ - and $\chi$ - Al <sub>2</sub> O <sub>3</sub> and Mn- modified alumina catalysts .....	22
4.2 Catalyst activity of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modified alumina catalyst in ethanol dehydration reaction .....	29
CHAPTER V .....	35
CONCLUSIONS AND RECOMMENDATION .....	35
5.1. Conclusion .....	35
5.2 Recommendation .....	35
.....	36
REFERENCES .....	36
APPENDIX.....	39
APPENDIX A.....	40
CALIBRATION CURVE.....	40
APPENDIX B .....	43
CALCULATION OF CONVERSION AND SELECTIVITY .....	43
APPENDIX C.....	44
CALCULATION OF ACIDITY .....	44
APPENDIX D.....	45
GAS CHROMATOGRAPHY DATA .....	45
APPENDIX E .....	46
Conference proceeding .....	46
VITA.....	47



## TABLES CONTENTS

	Page
<b>Table1:</b> Top industrial ethylene complexes and their location ranked by capacity.....	1
<b>Table 2:</b> Each product from ethanol is occur from many reaction by using catalyst.....	7
<b>Table 3.1</b> Chemicals and the reagents used in the ethanol dehydration reaction.....	19
<b>Table 4.1</b> BET surface area analysis and BJH pore size and volume analysis of Alumina and Mn-modified catalysts.....	23
<b>Table 4.2</b> The amount of acid sites of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modified alumina catalyst.....	25
<b>Table 4.3</b> Ethylene yield in ethanol dehydration at different temperature.....	30
<b>Table 4.4</b> DEE yield in ethanol dehydration at different temperature.....	31
<b>Table 4.5</b> Acetaldehyde yield in ethanol dehydration at different temperature.....	32
<b>Table A.1</b> Conditions in GC-14A.....	38

## FIGURES CONTENTS

	Page
<b>Figure 2.1:</b> Product from ethanol.....	6
<b>Figure 2.2</b> The mechanism of ethanol dehydration reaction to ethylene .....	9
<b>Figure 2.3</b> The mechanism of ethanol dehydration reaction to diethyl ether in $S_{N2}$ .....	11
<b>Figure 2.4</b> Mechanism for the dehydration of ethanol to ethylene.....	12
<b>Figure 2.5</b> The temperature transformation sequence of aluminum hydroxide.....	13
<b>Figure 2.6</b>	
<b>Figure 2.7</b> Most common phases of manganese oxide in air at different temperature.....	15
<b>Figure 3.1</b> Ethanol dehydration system.....	20
<b>Figure 4.1</b> XRD patterns of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modification alumina catalyst.....	22
<b>Figure 4.2</b> The $N_2$ adsorption–desorption isotherms of Alumina and Mn-modified catalysts...	24
<b>Figure 4.3</b> Pore size distribution of Alumina and Mn-modified catalysts.....	24
<b>Figure 4.4</b> TPD profile of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modified alumina catalyst.....	26
<b>Figure 4.5</b> SEM micrograph of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modification alumina catalyst.....	27
<b>Figure 4.6</b> Characteristic dispersion of component of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modified alumina catalyst.....	28
<b>Figure 4.7</b> Ethanol conversion profiles in ethanol dehydration at different temperatures.....	29
<b>Figure 4.8</b> Selectivity profiles of ethylene in ethanol dehydration at different temperature....	30
<b>Figure 4.9</b> Selectivity profiles of diethyl ether (DEE) in ethanol dehydration at different temperature.....	31
<b>Figure 4.10</b> Selectivity profiles of acetaldehyde in ethanol dehydration at different temperature.....	32
<b>Figure 4.11</b> Selectivity of diethyl ether of 0.05 Mn /Al <sub>2</sub> O <sub>3</sub> and 0.1 Mn /Al <sub>2</sub> O <sub>3</sub>	

at 250 °C for 6 hrs.....	33
<b>Figure 4.12</b> %Ethanol conversion of 0.05 Mn /Al <sub>2</sub> O <sub>3</sub> and 0.1 Mn /Al <sub>2</sub> O <sub>3</sub> at 250 °C for 6 h.....	34
<b>Figure A. 1</b> The calibration curve of ethanol.....	39
<b>Figure A. 2</b> The calibration curve of ethylene.....	39
<b>Figure A. 3</b> The calibration curve of acetaldehyde.....	40
<b>Figure A. 4</b> The calibration curve of diethyl ether.....	40
<b>Figure D.1</b> The data result from Gas Chromatography.....	43



# CHAPTER I

## INTRODUCTION

### 1.1 General introduction

Ethylene is a hydrocarbon with the formula of  $C_2H_4$ . It is widely used in many chemical industries. Global demand is large for this compound resulting from the application as a precursor to polymers such as polyethylene, the most common plastic or chemical surfactants such as ethylene oxide or ethylene glycol[1]. True (2012) reported the highest production of ethylene complexes, which is shown in **Table 1** (Rated by their ability tones per year) as biomass steam cracking plant and ethanol to ethylene plants.

**Table 1:** Top industrial ethylene complexes and their location ranked by capacity (tons of ethylene produced per year)

Company	Location	Ton/year
<i>Steam-cracking plants</i>	–	–
Formosa Petrochemical Corporation	Mailiao, Taiwan,	2,935,000
Nova Chemicals Corporation	Joffre, Alberta, Canada	2,811,792
Arabian Petrochemical Company	Jubail, Saudi Arabia	2,250,000
ExxonMobil Chemical Company	Baytown, TX, USA	2,197,000
ChevronPhillips Chemical Company	Sweeny, TX, USA	1,865,000
Dow Chemical Company	Terneuzen, Netherlands	1,800,000
Ineos Olefins & Polymers	Chocolate Bayou, TX, USA	1,752,000
Equistar Chemicals LP	Channelview, TX, USA	1,750,000
Yanbu Petrochemical Company	Yanbu, Saudi Arabia	1,705,000
Equate Petrochemical Company	Shuaiba, Kuwait	1,650,000
<i>Ethanol to ethylene plants</i>	–	–
Braskem	Triunfo, Brazil	200,000
Dow Chemical Company	Santa Vitoria, Brazil (under construction)	190,000
Solvay Indupa	Santo Andre, Brazil	60,000

Normally, ethylene is obtained from the steam cracking upon an endothermic reaction requiring high temperatures ( $600^{\circ}C$ - $1000^{\circ}C$ ) [2]. However, at this time with the speedy development and economic process that the demand of ethylene increases, but the crude oils as raw material are unrenewable resource and limit to consume. Therefore, the new alternative way to produce

ethylene instead of crude oil petroleum is considered [3]. The ethanol dehydration is a novel promising way of ethylene production. The process of ethanol dehydration is environmental friendly due to using ethanol as raw material that can reduce the utilization of fossil fuel. Ethanol is generated by fermentation method from renewable and agriculture product, like corn and cassava. These raw materials for ethanol production can be found in Thailand [4].

Ethanol dehydration reaction is endothermic, the optimum reaction temperature is fairly high, starting from 180 °C to 500 °C. The temperature of reaction is considered in the costs of industrial energy. Several researchers have investigated totally different catalysts to increase ethylene yield and lower reaction temperature. Many researchers have reported that use of acid catalyst for ethanol dehydration reaction such as zeolite [5-7], alumina [8] and HZSM-5 zeolite. In this research focus alumina catalyst due to excellent thermal stability, fine particle size, high surface area and inhibit side reaction.

This project is aimed to investigate on using the dehydration of ethanol as an alternative process to thermal cracking for producing ethylene. The purpose of this project is to convert liquid ethanol into ethylene gas using  $\gamma$ - and  $\chi$ -alumina catalysts and Mn-modification alumina catalyst for compare ethanol conversion, yield and selectivity of product.

## 1.2 Research objectives

1. To determine the characteristics and catalytic properties of manganese modified alumina catalysts for ethanol dehydration reaction to ethylene.
2. To investigate the effect of conversion versus time on stream (TOS).

## 1.3 Research scopes

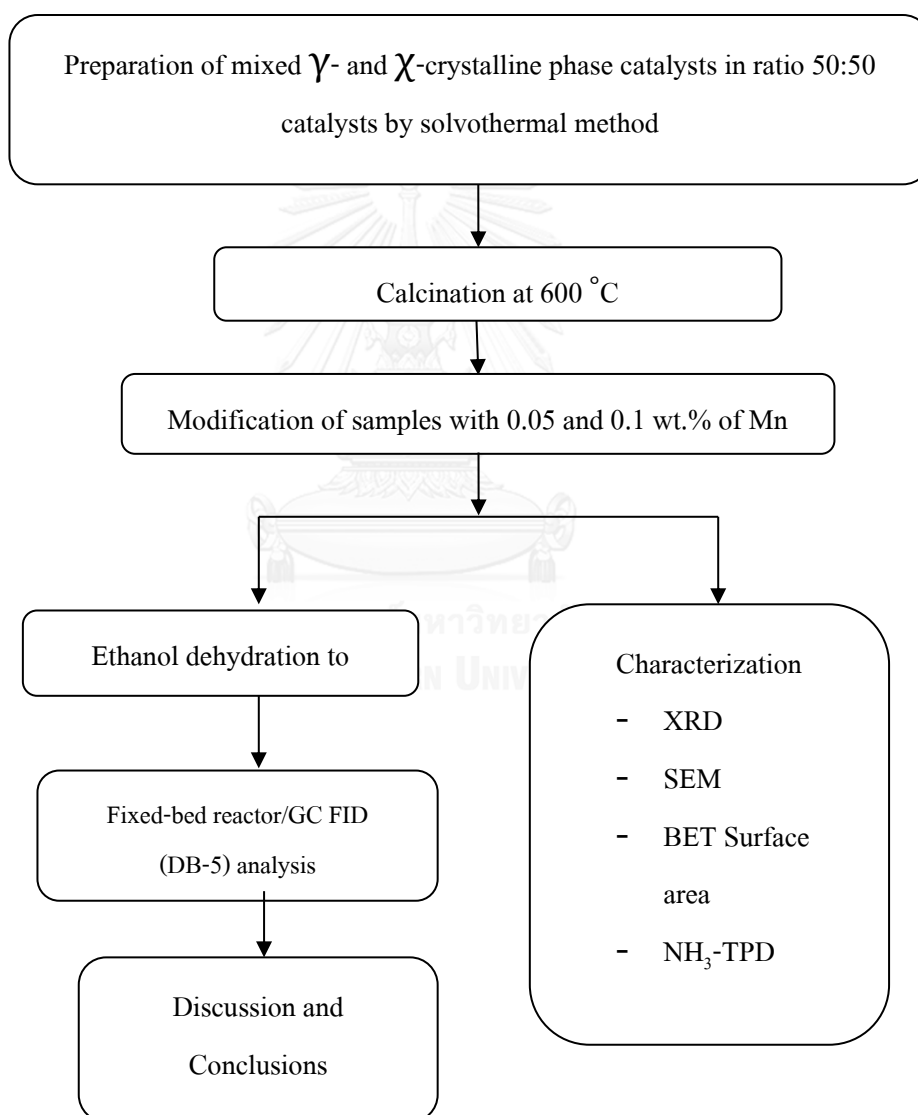
1. Synthesis of the mixed  $\gamma$ - and  $\chi$ -crystalline phase catalysts in 50:50 ratio via solvothermal method.
2. Synthesis of manganese modification on mixed  $\gamma$ - and  $\chi$ -crystalline phase alumina catalysts
3. Investigation amount of loading of manganese at 0.05 and 0.1 wt%
4. Characterization of catalysts with XRD, SEM, BET and  $\text{NH}_3$ -TPD

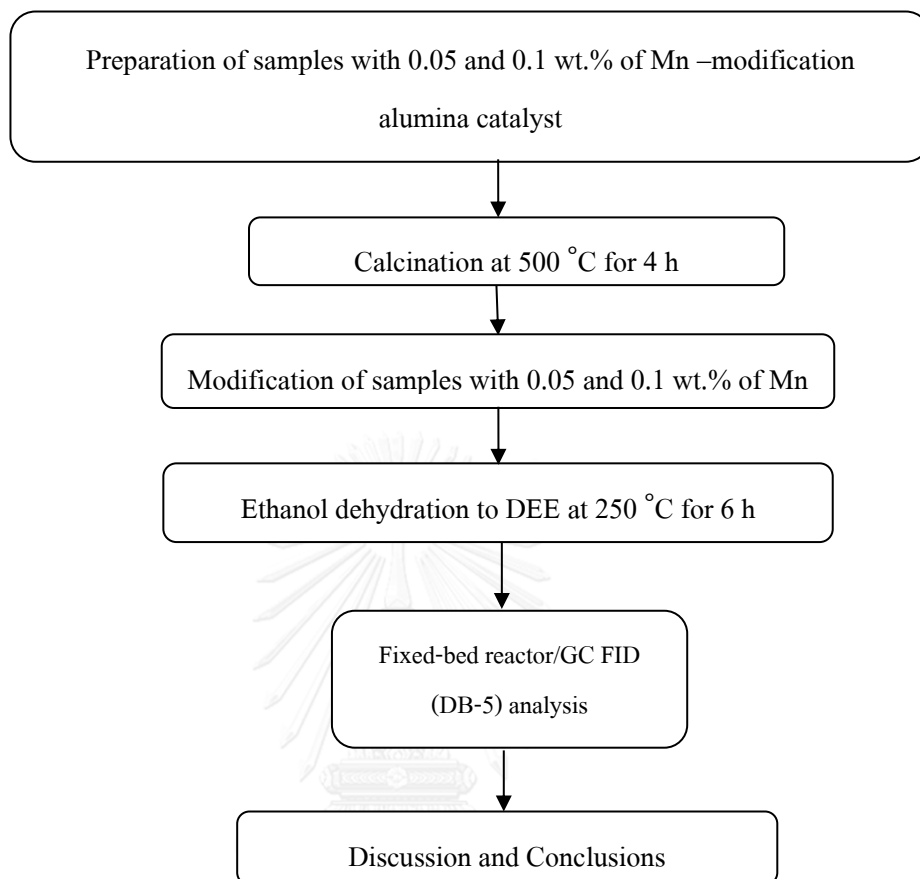
5. Investigation the catalytic performance of all catalysts in ethanol dehydration reaction under atmospheric pressure and various temperatures between 200–400 °C
6. Investigate the effect of conversion versus TOS

#### 1.4 Research methodology

Research methodology is as shown;

**Part I:** Ethanol dehydration to ethylene



**Part II:** Ethanol dehydration to diethyl ether (DEE)

### 1.5 Research Plan

Activities	2014									
	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
The research topic	←→									
Studies related research		←→								
Proposal		←→								

Activities	2015									
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct
Experiment										
- Preparation catalyst	←→									
- Ethanol dehydration reaction				←→						
- Characterization catalyst							←→			
Conclusion									←→	
Conference proceeding							←→			

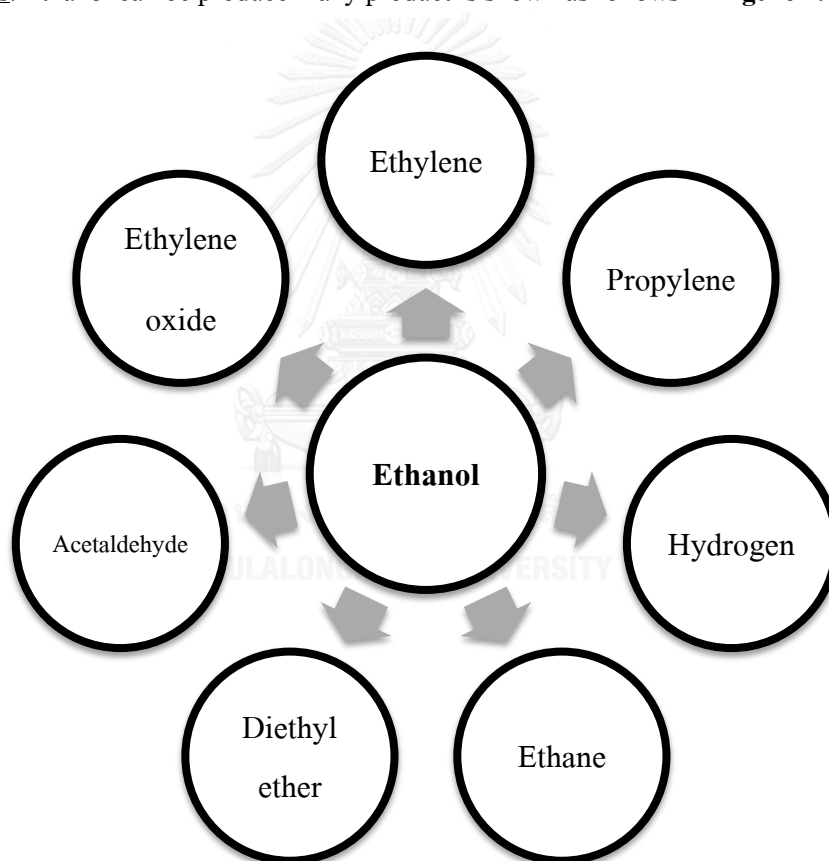


## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Raw material

Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is a clear, colorless liquid. It is also known as ethyl alcohol, grain alcohol, and EtOH. Ethanol has the same chemical formula regardless of whether it is produced from starch- and sugar-based feedstocks, such as corn grain, sugar cane, or from cellulosic feedstocks. Ethanol can be produce many product is shown as follows in **Figure 2.1**



**Figure 2.1:** Product from ethanol

Each product from ethanol is occur from many reaction is shown as follows in **Table 2**

**Table 2:** Each product from ethanol is occur from many reaction by using catalyst

Product	Reaction	Catalyst	Applications
Propylene	Dehydration	-ZSM-5 Zeolite[9] -P-ZSM-5 Zeolite [10] -M-HZSM-5 (M= Sr,Zr,P,Ga,La) [11] -HZSM-5/SAPO-34 [11] -La/P/HZSM-5(Ga) [12] -HZSM-5 vary crystalize size [13]	- Polypropylene [9] - Propylene oxide[9] -Acrylonitrile [14] -Manufacturing plastics [15] -Manufacturing chemical [15]
	Dehydrogenation	-Sc/In <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> [14] -Ni-MCM41[14] -In <sub>2</sub> O <sub>3</sub> -based oxides [15] -Y/CeO <sub>2</sub> [16]	
Ethylene	Dehydration	-HZSM-5 Zeolite -Alumina-based catalyst [17] -WO <sub>3</sub> /ZrO <sub>2</sub> , WO <sub>3</sub> /TiO <sub>2</sub> [18] - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> [19] -H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> [20] - $\gamma$ , $\delta$ , $\theta$ -Al <sub>2</sub> O <sub>3</sub> -Heteropoly acid catalysts	- Ethylene oxide [17] -Polymers ( PE, PET, PVC) [17]
	Steam-cracking	HZSM-5 Zeolite - $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	

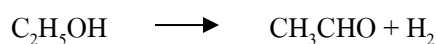
Ethylene oxide	Ethanol oxidation	-Au/Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> [21] -gold-base catalyst [21] -Silver-base catalyst [22] -Copper-base catalyst [22]	-Ethylene glycol [21]
	Ethanol Dehydrogenation	-Copper-base catalyst [21] -silver-base catalyst [22]	
Acetaldehyde	Dehydrogenation	-Alumina-based catalyst [17] - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> [19] -Cu/Al <sub>2</sub> O <sub>3</sub> , Cu/ZnO, Cu/ZrO <sub>2</sub> [23]	Acetaldehyde
Diethyl ether	Dehydration	-HZSM-5 Zeolite -Alumina-based catalyst [17] -WO <sub>3</sub> /ZrO <sub>2</sub> , WO <sub>3</sub> /TiO <sub>2</sub> [18] - $\gamma$ -Al <sub>2</sub> O <sub>3</sub> [19] -Sulfonic-acid catalyst -Heteropoly acid catalysts [24]	Use in gasoline
Hydrogen	Steam reforming	NixWy/SBA15 [25]	

## 2.2 Ethanol dehydration reaction

Ethanol consists of hydroxyl group in molecule. It dehydrated by using acid catalysts. The hydroxyl group is converted to water molecule. After the water molecule is emitted from ethanol molecule, the hydrocarbon rearranges into ethylene or DEE [26]. The reaction temperature used is between 180 to 500°C in gas phase and liquid phase [27]. The chemical equation of ethanol dehydration reaction is shown in equation (1) and (2) as follows;

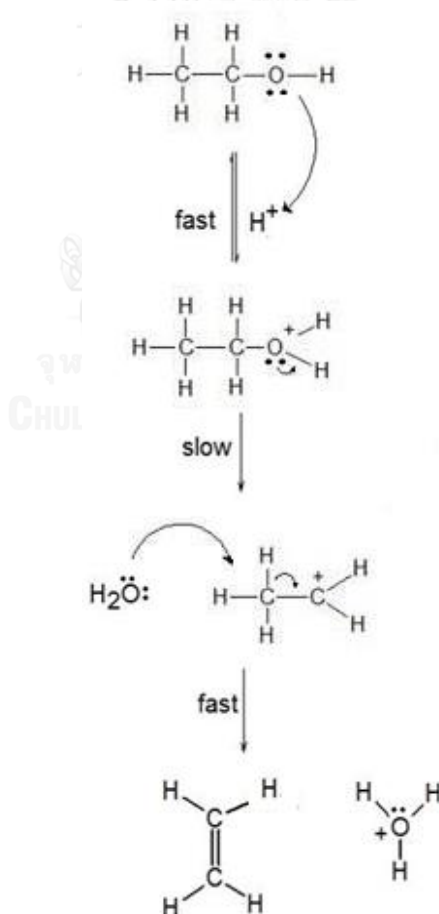


Equation (1) shows that ethanol vaporizes at high temperature to give ethylene in the endothermic reaction. The second step of this reaction depicted in Equation 2 is exothermic as it can take place at low temperature and ethanol is converted to DEE. Acetaldehyde is formed as a by-product as a reaction.



The alternative to produce ethylene is Ethanol dehydration reaction by using acid catalyst due to reaction temperature lower than Steam thermal cracking. As a result the energy cost of production in this reaction is also reduced. According to Nowak and Ziolk (1999), reported the ethanol dehydration reaction required the acid catalyst consisting of the Brønsted acid site on surface of catalyst combining with hydroxyl groups. It generates a water molecule, which is emitted. The mechanism of ethanol dehydration reaction to ethylene is shown as follows in

**Figure 2.2**



**Figure 2.2** The mechanism of ethanol dehydration reaction to ethylene [26]

The **Figure 2.2** reveals that ethanol undergoes elimination reaction type E1 to get converted to ethylene. The E1 reaction is further divided into the following 3 steps:

#### STEP 1: PROTONATION

The leaving group in the ethanol molecule is the OH group. When acid is used as a catalyst, the catalytic proton is added to the oxygen of alcohol to make it a better alcoholic OH group. The lone pair of electrons on the alcoholic oxygen makes it a Lewis base and the step becomes reversible and fast.

#### STEP 2: RATE DETERMINING STEP

The breakage of C-O bond is slow and endothermic. A carbocation intermediate is formed when the leaving group (the water molecule) is lost from the alcohol. The slow speed of this step makes it the rate determining step.

#### STEP 3: C=C REARRANGEMENT

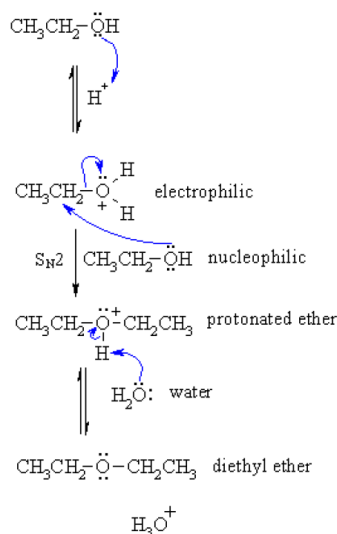
The conjugate base (a water molecule) deprotonates in methyl group leading to the rearrangement of the C=C bond.

However, the production of ethylene requires high temperature. Operating at low temperature occur diethyl-ether in the selective formation but the kinetic reaction is limited and gives slow rate [27]. The bimolecular dehydration generates to form ether by substitution nucleophilic bimolecular reaction ( $S_{N2}$ ). The mechanism of ethanol to diethyl-ether can be described into 3 steps and is shown in **Figure 2.3**.

Step1: The protonation from acid catalyst adds into alcoholic oxygen, which makes a better leaving group. This step is very fast and reversible reaction. The lone pairs on the oxygen make it a Lewis base.

Step2: The other alcoholic oxygen is nucleophile function, which attacks to electrophilic electron. The C-O bond allows the loss of neutral water molecule and creates an oxonium ion intermediate.

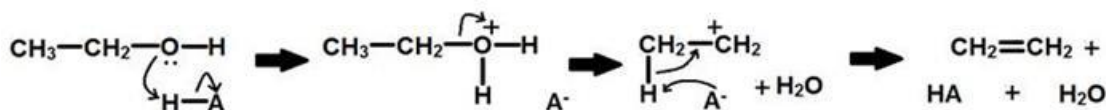
Step3: The protonated ether is removed proton ( $H^+$ ) by molecule of water and rearranges to give the diethyl ether production.



**Figure 2.3** The mechanism of ethanol dehydration reaction to diethyl ether in S<sub>N</sub>2 [28]

## 2.3 Catalyst

The mechanism of catalytic dehydration of ethanol is shown in the Figure 2.4 where an acid catalyst protonate the OH group to leave the water molecule. The conjugate base of the catalyst thus formed deprotonates the methyl group, and hydrocarbon rearrangement and form ethylene.



**Figure 2.4** Mechanism for the dehydration of ethanol to ethylene.

### 2.3.1 Alumina oxide

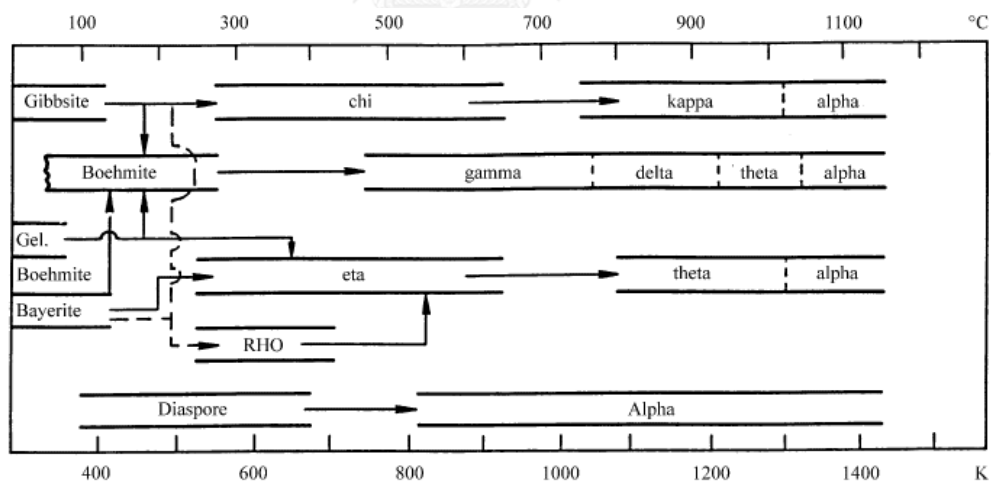
Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) also called alumina is chemical compound made up of oxygen and aluminum molecules in a 2:3 ratio. It acts as a catalyst in dehydration reactions and help form many industrially important products. It is used in the Claus process where it helps to convert Hydrogen Sulfide in its gaseous form (produced as a waste product) elemental sulfur to be utilized in the refineries.

Alumina is formed in many phases, form different types of crystal and possess differing chemical properties in each phase. The phases of  $\text{Al}_2\text{O}_3$  are as follows corresponding the symbols of each phase:

- beta phase ( $\beta\text{-Al}_2\text{O}_3$ )

- Gamma phase ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)
- eta phase ( $\eta$ -Al<sub>2</sub>O<sub>3</sub>)
- chi phase ( $\chi$ -Al<sub>2</sub>O<sub>3</sub>)
- kappa phase ( $\kappa$ -Al<sub>2</sub>O<sub>3</sub>)
- delta phase ( $\delta$ -Al<sub>2</sub>O<sub>3</sub>)
- theta phase ( $\theta$ -Al<sub>2</sub>O<sub>3</sub>)
- Alpha phase ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>)

The properties of each crystal in these phases are different from each other. The reactants (gibbsite, boehmite, and etc.) determine the calcined temperature of reaction and thus determine the crystalline phase. If gibbsite is calcined at a temperature between 280°C to 650°C it will form chi phase of Alumina. The temperature higher than that, i.e. 750°C to 1150°C, results in kappa phase of alumina. Boehmite at 480°C to 780°C calcined temperature forms gamma phase alumina and at 780°C to 920°C form gamma phase of alumina and upon further calcinations at 780°C to 920°C it converts to delta phase. The **Figure 2.5** shows the calcined temperature and reactants that result in formation of different crystalline forms of alumina.



**Figure 2.5** The temperature transformation sequence of aluminum hydroxide

### 2.3.1.1 Advantages of Alumina (Al<sub>2</sub>O<sub>3</sub>) and its usage

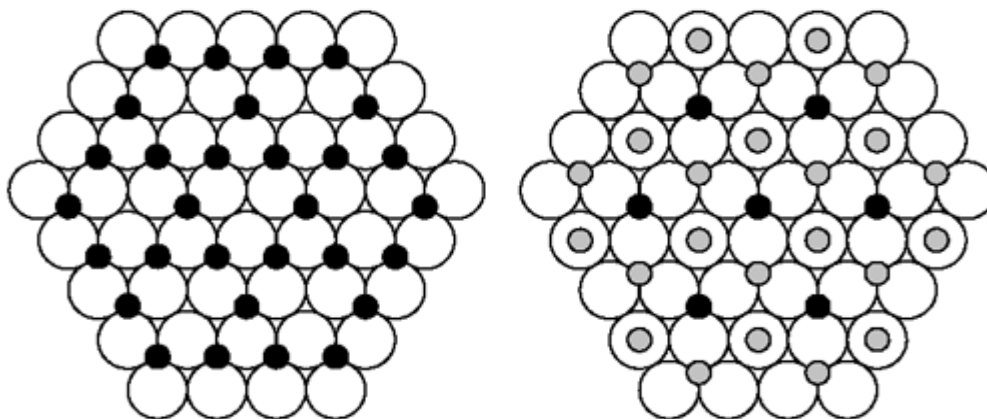
There are many advantages of Al<sub>2</sub>O<sub>3</sub> over other similar type of ceramic materials. The chemical structure and its physical properties make it best catalyst for production of fire bricks,

and IC (integrated circuit) packages. More than 45 million tons of Alumina is produced industrially in the world mainly using bauxite in the Bayer method. More than 1.5 million tons of  $\text{Al}_2\text{O}_3$  is used in the form of raw powder. In addition, more than 5 million tons of  $\text{Al}_2\text{O}_3$  is also produced in different chemical reactions as a residue and it is utilized for a number of purposes. On average about 350,000 tons of  $\text{Al}_2\text{O}_3$  is consumed in Japan alone which is about 20% the global consumption of  $\text{Al}_2\text{O}_3$ .

### 2.3.1.2 Applications of $\text{Al}_2\text{O}_3$

As  $\text{Al}_2\text{O}_3$  is found in many crystalline forms having different chemical and physical properties it has a wide variety of applications. Alpha and Kappa phase alumina for example is used for wear resistant coating due to its chemical property of thermal stability and physical property of hardness. The  $\gamma$  and  $\theta$  phases are used in their metastable phases as crystals or crystal supports due to their chemical property of low surface energy that helps to provide large surface area for catalysis reactions.

The  $\gamma$  phase of alumina is very attractive due to its fine practical size and excellent thermal stability that inhibits the side reaction in chemical reactions. Its structure is shown in **Figure 2.6**. Khomin et al. (2008) used the  $\gamma$ - and  $\chi$ - phase alumina as a catalyst in methanol dehydration. According to them the combined  $\gamma$ - and  $\chi$ - phase has higher acidity than  $\gamma$  alumina and  $\chi$ - phase used separately. The combined form of  $\gamma$ - and  $\chi$ - phase of alumina can be synthesized easily by solvothermal method. A suitable solvent can help to control the size of crystals, structure of grains and their morphological properties at different conditions.



**Figure 2.6** Schematic drawing of the first two layers in the gamma alumina structure. Al ions are black.



### 2.3.2 Modification of $Al_2O_3$

$\gamma$ - phase of alumina has been in use from the earlier studies to convert ethanol to ethylene in the dehydration reaction. But the high temperature of this reaction that is  $450^\circ C$  can yield only 80% of ethylene. Due to the high temperature energy cost of the reaction is very high and yield is less at the same time thus researcher have been in quest to modify alumina by any other suitable catalyst so that the energy cost of reaction can be reduced and yield of ethylene can be increased.

$\gamma$ -alumina treated with Potassium Hydroxide (KOH) and  $ZnO/Al_2O_3$  was used by Phillips Oil Company (USA) to form ethylene at commercial level. Halcon SD (USA) used  $MgO-Al_2O_3/SiO_2$  based SynDol catalyst for ethylene production. Doheimet *et al.* (2002) succeeded in achieving 97% yield of ethylene from ethanol by using  $Na_2O$ -doped  $Mn_2O_3/Al_2O_3$  at  $300^\circ C$  temperature. Catalytic ability of  $TiO_2$  was investigated by Chen *et al.* (2007) and they modified  $\gamma-Al_2O_3$ . By mixing  $Na_2CO_3$  solution with  $\gamma-Al_2O_3$  in powder form and added  $Ti(SO_4)_2$  and  $Na_2CO_3$  solution.  $SO_4^{2-}$  was eliminated from the reaction by centrifugation and the resultant produced  $TiO_2/\gamma-Al_2O_3$  as a modified catalysis for the reaction helped to increase yield to 99.4% at temperature of  $500^\circ C$ .

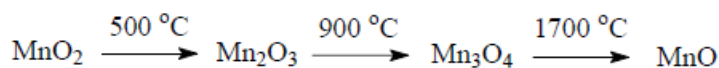
The  $TiO_2/\gamma-Al_2O_3$  catalyst was prepared by mixing commercial  $\gamma-Al_2O_3$  powder with then adding  $Ti(SO_4)_2$  and  $Na_2CO_3$  solution.  $SO_4^{2-}$  was eliminated by washing and centrifugation; then, the material was dried and calcined to produce  $TiO_2/\gamma-Al_2O_3$ . Tests on the catalytic ability resulted in up to 99.4% ethylene selectivity at  $500^\circ C$ . According to Zhang *et al.* (2008) about 90.1% of ethylene is yielded selectively at  $475^\circ C$  using  $\gamma-Al_2O_3$  as a catalyst. With the increase in temperature from  $360^\circ C$  to  $500^\circ C$ , the conversion of ethanol and selectivity of ethylene increased from 75% rate of conversion to 100% and 40% selectivity to 99.4%. Studies also found that decrease from 100% conversion to 93 and 97% selectivity to 96% selectivity with a space velocity increased from  $52\ h^{-1}$  to  $230\ h^{-1}$ . Conversion of Ethanol can be increased from 64% to 88% at  $380^\circ C$  with an increase in ethanol concentration of 10 wt % to 90 wt %, while ethylene selectivity decreased from 94% to 86% at  $380^\circ C$  with the same increase in ethanol concentration. The catalyst deactivated quickly after 400 h of stability testing with temperatures be between  $410$  and  $430^\circ C$ . Although the modification of  $\gamma-Al_2O_3$  has produced much more favorable results

than the original catalyst, the reaction temperature is still high, considering the modern industrial standards. On the other hand, the stability of the modified catalyst is relatively high as compared to other catalysts currently being developed, lasting 400 before deactivating.

### 2.3.2.1 Manganese oxides modified Alumina

Manganese oxide materials are of considerable importance in technological applications including catalysis and rechargeable batteries, due to their outstanding structural flexibility combined with novel chemical and physical properties [29].

Manganese oxides have been widely applied as catalyst in waste water treatment, which are a series of complicated oxides, including MnO, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub> etc.. Porous manganese oxides materials have different structure from micropore to mesopore due to various preparation methods, chemical composition and crystal structure, which concludes its excellent property of cation exchange, molecular adsorption, oxidation, chemical and magnetic reducibility, etc. Therefore, it's widely used in heterogeneous catalysis, toxic wastewater treatment, dye wastewater degradation etc. Manganese element gives rise to a rather complex oxides system, of which the most important phases and their transition temperature in air are given in **Figure 2.7**



**Figure 2.7** Most common phases of manganese oxide in air at different temperature

## 2.4 Literature reviews

Xian Zhang, Rijie Wang, Xiaoxia Yang \*, Fengbao Zhang compare the activity and stability of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, HZSM-5 (Si/Al = 25), silicoaluminophosphate(SAPO-34) and Ni-substituted SAPO-34 (NiAPSO-34) as catalysts in the dehydration of ethanol to ethylene.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 were commercial catalysts. SAPO-34 and NiAPSO-34 molecular sieves had been synthesized with hydrothermal method in the laboratory, characterized with X-ray powder diffraction (XRD), Infrared Spectroscopy (FT-IR), H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) technique and NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) technique. The incorporation of Ni<sup>2+</sup> into the SAPO-34 framework generated in NiAPSO-34 sample was proved by XRD, FT-IR and H<sub>2</sub>-TPR techniques. NH<sub>3</sub>-TPD study had revealed that substitution of Ni<sup>2+</sup> for Al<sup>3+</sup> in the SAPO-34 framework led to increase the weak and moderately strong acid strength

and give rise to weak acid sites. Dehydration of ethanol was carried out over four catalysts and the results showed that conversion of ethanol and selectivity to ethylene decreased in the order HZSM-5 > NiAPSO-34 > SAPO-34 >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. As to the stability of catalyst, NiAPSO-34 and SAPO-34 were better than other two catalysts. Considering the activity and stability of the four catalysts comprehensively, NiAPSO-34 was the suitable catalyst in the dehydration of ethanol.

M.M. Doheim a, S.A. Hanafy a, G.A. El-Shobaky study Pure and Na<sub>2</sub>O-doped Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> solids were prepared by heating pure and NaNO<sub>3</sub>-treated MnCO<sub>3</sub>/Al(OH)<sub>3</sub> mixed solids at 500 °C. The nominal composition of the calcined pure solids was 0.1 Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and the dopant concentration varied between 0.75 and 6 mol% Na<sub>2</sub>O. The obtained results showed that the treatment of the Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system with Na<sub>2</sub>O (3 or 6 mol%) followed by heating at 500 °C led to the formation of the sodium manganese oxide phase. This treatment effected the decrease in the BET surface areas of the treated solids and led to an effective increase in their catalytic activities. The addition of 3 mol% Na<sub>2</sub>O brought about a significant increase in the percentage conversion (dehydration) of both alcohols measured at 300 °C from 22% to 92% and from 40% to 97% for ethanol and isopropanol, respectively

## CHAPTER III

### EXPERIMENTAL

This Chapter explains the detail of experiment that consists of catalyst preparation, catalyst characterization and dehydration reaction of ethanol.

#### 3.1 Catalyst preparation

Mixed  $\gamma$ - and  $\chi$ -crystalline phase alumina catalyst was prepared by the solvolthermal method. Then, Mn was used to modify the mixed phase alumina catalyst by impregnation method.

##### 3.1.1 Chemicals

The chemicals used in the preparation of catalysts are

1. Aluminum isopropoxide AIP (98%) $[(CH_3)_2CHO]_3Al$
2. Toluene (99%) $C_6H_5CH_3$
3. 1-Butanol (99%)  $C_4H_{10}O$
4. Methanol  $CH_3OH$
5. Ultra high purity nitrogen gas (99.99%)
6.  $Mn(CH_3COO)_2$

The AIP supply from Aldrich and toluene, 1-butanol, methanol and  $Mn(CH_3COO)_2$  from Merck.

##### 3.1.2 Synthesis of mixed phase alumina catalysts

Mixed  $\gamma$ - and  $\chi$ -crystalline phase alumina catalyst was prepared by the solvothermal procedure described in [3, 30]. Approximately 25 grams of aluminum isopropoxide (AIP) was suspended in 100 ml of solution mixed (50 ml of toluene and 50 ml of butanol) in test tube, and then in 300 ml autoclave and flushed with nitrogen. In the gap between the test tube and the autoclave wall, additional 30 ml of same solvent was added. The mixture was heated to 300 °C, heating rate was 2.5 °C / minute and holding for 2 h. After that when the mixture was cooled down to room temperature, powder was washed with methanol several times by using a

centrifuge and dried in the air. The powder was calcined in a tube furnace at 600 ° C with a heating rate of 10 ° C / min and held it in air for 6 h.

### *3.1.3 Preparation of Mn-modified mixed phase alumina catalysts*

The Mn-modified mixed phase alumina catalysts were prepared by wet impregnation of Al<sub>2</sub>O<sub>3</sub> with aqueous Mn(CH<sub>3</sub>COO)<sub>2</sub> solution to obtain 0.05 and 0.1 wt.% of Mn (0.05Mn/Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn/Al<sub>2</sub>O<sub>3</sub>). The sample was dried at 110 ° C overnight, and then calcined at 500 ° C for 5 h in air.

## **3.2 Catalyst characterization**

### *3.2.1 X-ray diffraction (XRD)*

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. XRD patterns of the catalysts were determined by the SIEMENS D5000 X-ray diffractometer connected with a personal computer with Diffract ZT version 3.3 programs for fully control of the XRD analyzer. The experiment was carried out by using Cu K<sub>α</sub> radiation source with Ni filter in the 2 $\theta$  range of 20 to 80° with a resolution of 0.02°.

### *3.2.2 Nitrogen physisorption*

Specific surface area and the pore size distribution of catalysts were determined by nitrogen gas adsorption at liquid nitrogen temperature (-196 ° C) using Micromeritics ChemiSorb 2750 Pulse chemisorption System instrument. Before characterization, the sample was thermally treated at 150 ° C for 1 h.

### *3.2.3 Temperature programmed adsorption (NH<sub>3</sub>-TPD)*

The acid properties of catalysts were investigated by temperature programmed adsorption of ammonia (NH<sub>3</sub>-TPD) equipment using Micromeritics chemisorp 2750 Pulse Chemisorption System. In a measurement, a packed quartz wool and 0.1 g of catalyst was loaded in a quartz tube and pretreated at 500 ° C under helium flow. The sample was saturated with 15% NH<sub>3</sub>/He. After that, the physisorbed ammonia was desorbed under helium gas flow about 30 min. Then, the

sample was heated from 40°C to 800 °C at heating rate of 10°C/min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

#### 3.2.4) Scanning electron microscopy (SEM)

Scanning electron microscopy measures the shape and size of the prepared catalyst. The JEOL JSM-35 CF model at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC) is used for this purpose.

### 3.3 Reaction of ethanol dehydration to ethylene

In this research, the ethanol dehydration reaction was tested in gas phase ethanol reaction at atmospheric pressure.

#### 3.3.1) Chemicals and reagents

**Table 3.1** Chemicals and the reagents used in the ethanol dehydration reaction.

Chemicals and Reagents	Supplier
High purity grade hydrogen (99.99%)	TIG
Ultra high purity nitrogen gas (99.99%)	TIG
Argon	TIG
Ethanol	Merck

### 3.3.2) Instruments and apparatus

Figure 3.1 shows the system of the ethanol dehydration

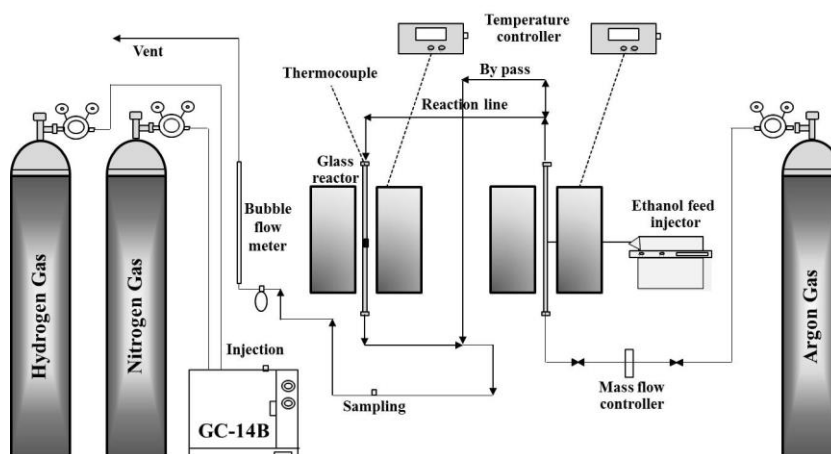


Figure 3.1 Ethanol dehydration system

**Reactor:** The reactor tube has an inner diameter size 0.7 mm and length size 12 cm. It is made from borosilicate glass tube. Ethanol dehydration reaction will occur in this reactor.

**Vaporizer** The vaporizer is made from stainless that use heater to change ethanol in liquid phase to saturated vapor phase under atmospheric pressure by using syringe pump.

**Electrical furnace and heating cable:** The reactor is supported by electrical chamber as heater. The temperature of electrical chamber is controlled via ability of variable voltage electrical device and temperature controller at 190 V. The heating cable is enfolded on outlet reactor line so as to stop the condensation of water dehydrated from reaction.

**Temperature controller:** The temperature controller is connected with thermocouple that attached with reactor and a variable voltage transformer. In this research, the temperature is controlled set point via temperature controller at 200 °C - 400°C

**Gas controlling system:** Argon is employed for carrier ethanol vapor into the reactor. The rate of carrier gas will modify in operation condition via on-off valve, mass flow controller and pressure regulator.

First, liquid ethanol was vaporized at vaporizer. Then, ethanol vapor moved into reactor that had catalyst in tube and occurred ethanol dehydration reaction in this reactor. The dehydration of ethanol was carried out in a fixed-bed continuous flow reactor with an inner diameter 0.7 mm. In the experiment, 0.01 g of a packed quartz wool and about 0.05 g of catalyst

were loaded into the reactor and then the catalyst was pretreated in argon (50ml/min) at 200°C for 1 h under atmospheric pressure. The reaction was carried out in temperature ranging from 200°C to 400°C. The products were analyzed by a Shimadzu GC8A gas chromatograph with FID using capillary column (DB-5) at 150°C.

### **3.4 Reaction of ethanol dehydration reaction to DEE**

The same system in Figure 3.1 was used. For investigation of DEE, the reaction was run by time on steam at 250 °C for 6 h and collected sample every 1 h for monitor ethanol conversion, selectivity of DEE and yield of DEE. In addition, investigate the characteristic of catalyst was determined after run reaction for 6 h.





## Chapter IV

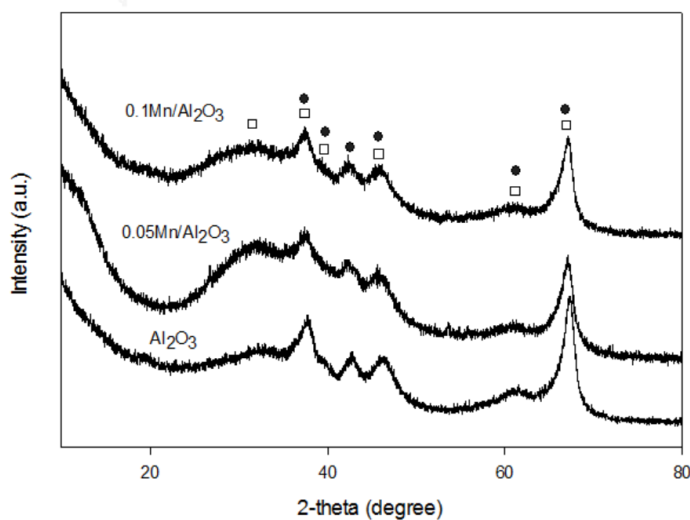
### Results and discussion

Chapter IV explains the results and discussion of the effect of mixed  $\gamma$ - and  $\chi$ - $\text{Al}_2\text{O}_3$  catalysts and manganese modification of alumina catalysts for ethanol dehydration reaction to ethylene and DEE. The characteristics of catalyst were investigated by X-ray diffraction (XRD), temperature programmed adsorption ( $\text{NH}_3$ -TPD), nitrogen physisorption and scanning electron microscopy (SEM). All Catalyst were tested in ethanol dehydration reaction to measure the ethanol conversion and product selectivity.

#### 4.1 Catalyst characterization of mixed $\gamma$ - and $\chi$ - $\text{Al}_2\text{O}_3$ and Mn- modified alumina catalysts

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

XRD was used to identify the structure of catalyst. From **Figure 4.1**, XRD patterns indicated the presence of  $\gamma$ - crystalline ( $32^\circ$ ,  $37^\circ$ ,  $39^\circ$ ,  $45^\circ$ ,  $61^\circ$  and  $66^\circ$ ) and  $\chi$ -crystalline ( $37^\circ$ ,  $40^\circ$ ,  $43^\circ$ ,  $46^\circ$ ,  $60^\circ$  and  $67^\circ$ ) phases of alumina [31]. After Mn was modified onto the alumina catalyst, no peaks of Mn species were observed. This is suggested that Mn species was highly dispersed.



**Figure 4.1** XRD patterns of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modification alumina catalyst; (□) gamma-alumina, (●) chi-alumina

#### 4.1.2 Nitrogen physisorption

The BET (Brunauer, Emmett and Teller) surface areas were analyzed by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer to identify the total specific surface area in  $\text{m}^2/\text{g}$  unit. The BJH analysis can find pore size and specific pore volume by using adsorption-desorption isotherms as shown in **Figure 4.2** The Bet surface, pore volume and pore size diameter of all catalysts as shown in **Table 4.1** The pore diameter (D) is divided into three categories; macropores ( $D > 50 \text{ nm}$ ), mesopores ( $2 \text{ nm} < D < 50 \text{ nm}$ ) and micropores ( $D < 2 \text{ nm}$ ) [32]. Therefore, the pore size distribution curve of all catalysts shows mesopores as shown in **Figure 4.3**.

**Table 4.1** BET surface area analysis and BJH pore size and volume analysis of Alumina and Mn-modified catalysts

Sample	BET surface area	Pore volume	Pore size diameter
	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$P_v$ ( $\text{cm}^3/\text{g}$ )	$P_d$ (nm)
$\text{Al}_2\text{O}_3$	200	0.69	8.26
0.05Mn/ $\text{Al}_2\text{O}_3$	243	0.54	6.16
0.1Mn/ $\text{Al}_2\text{O}_3$	213	0.58	7.11

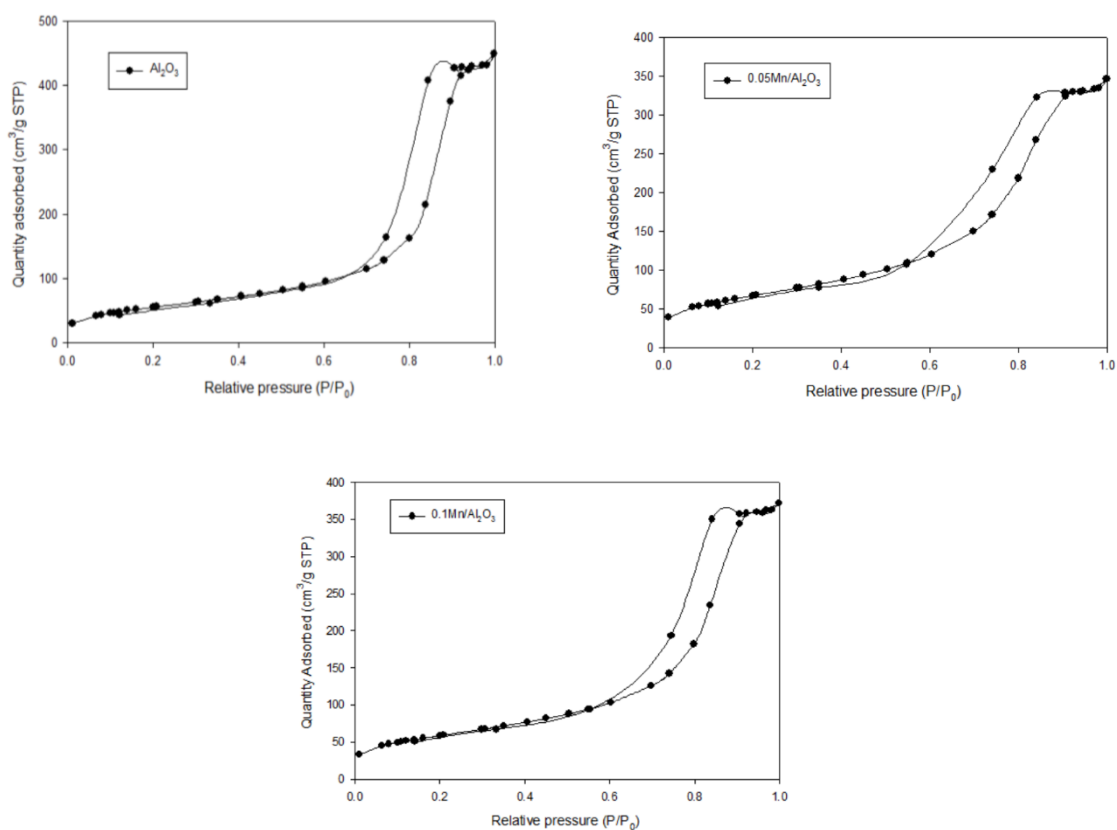


Figure 4.2 The  $N_2$  adsorption–desorption isotherms of Alumina and Mn-modified catalysts

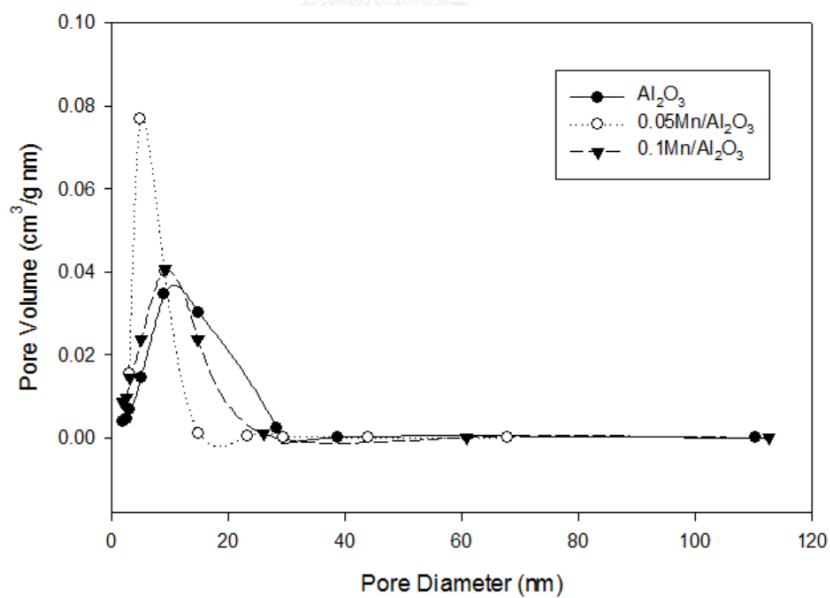


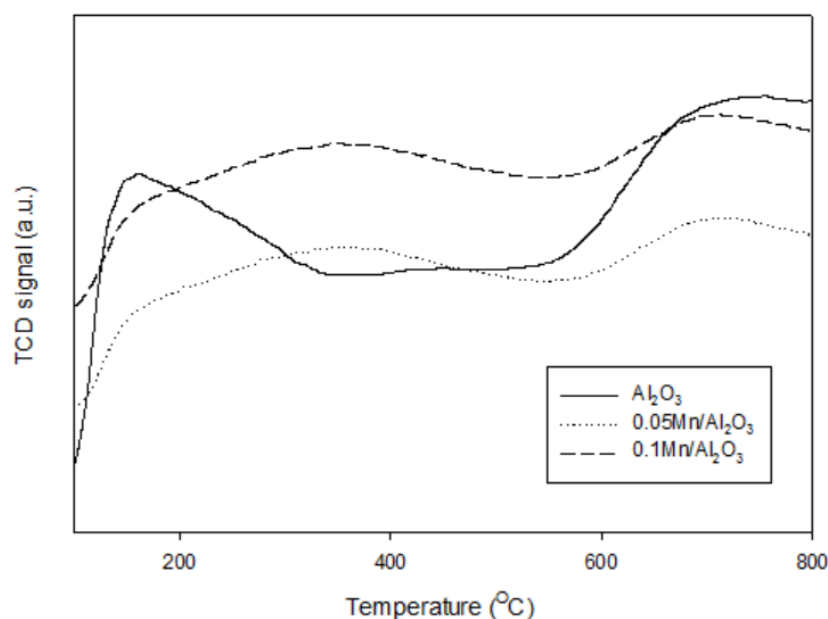
Figure 4.3 Pore size distribution of Alumina and Mn-modified catalysts

#### 4.1.3 Temperature programmed adsorption (NH<sub>3</sub>-TPD)

NH<sub>3</sub>-TPD is used to measure the characteristic of surface acidity of catalysts. The higher desorption temperature refer to more strong acid sites, corresponding to amount of NH<sub>3</sub> desorbed from the acid sites of catalyst as shown in **Table 4.2**. The NH<sub>3</sub> profiles of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modified alumina catalyst are shown in **Figure 4.4**. From TPD profile of each catalyst, it consist of two peaks. Total acidity is divided into two parts of acidic sites; weak acid sites and medium to strong acid sites. The amounts of weak acid sites and medium to strong acid sites were analyzed at 100-220°C and 220-800°C respectively.

**Table 4.2** The amount of acid sites of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modified alumina catalyst

Sample	NH <sub>3</sub> desorption ( $\mu\text{mol NH}_3/\text{g cat.}$ )		Total acidity ( $\mu\text{mol NH}_3/\text{g cat.}$ )
	Weak acid sites	Medium to strong acid sites	
	(100-220°C)	(220-800°C)	
Al <sub>2</sub> O <sub>3</sub>	340.9	551.9	892.9
0.05Mn/Al <sub>2</sub> O <sub>3</sub>	420.6	297.4	718.1
0.1Mn/Al <sub>2</sub> O <sub>3</sub>	430.2	288.1	718.3

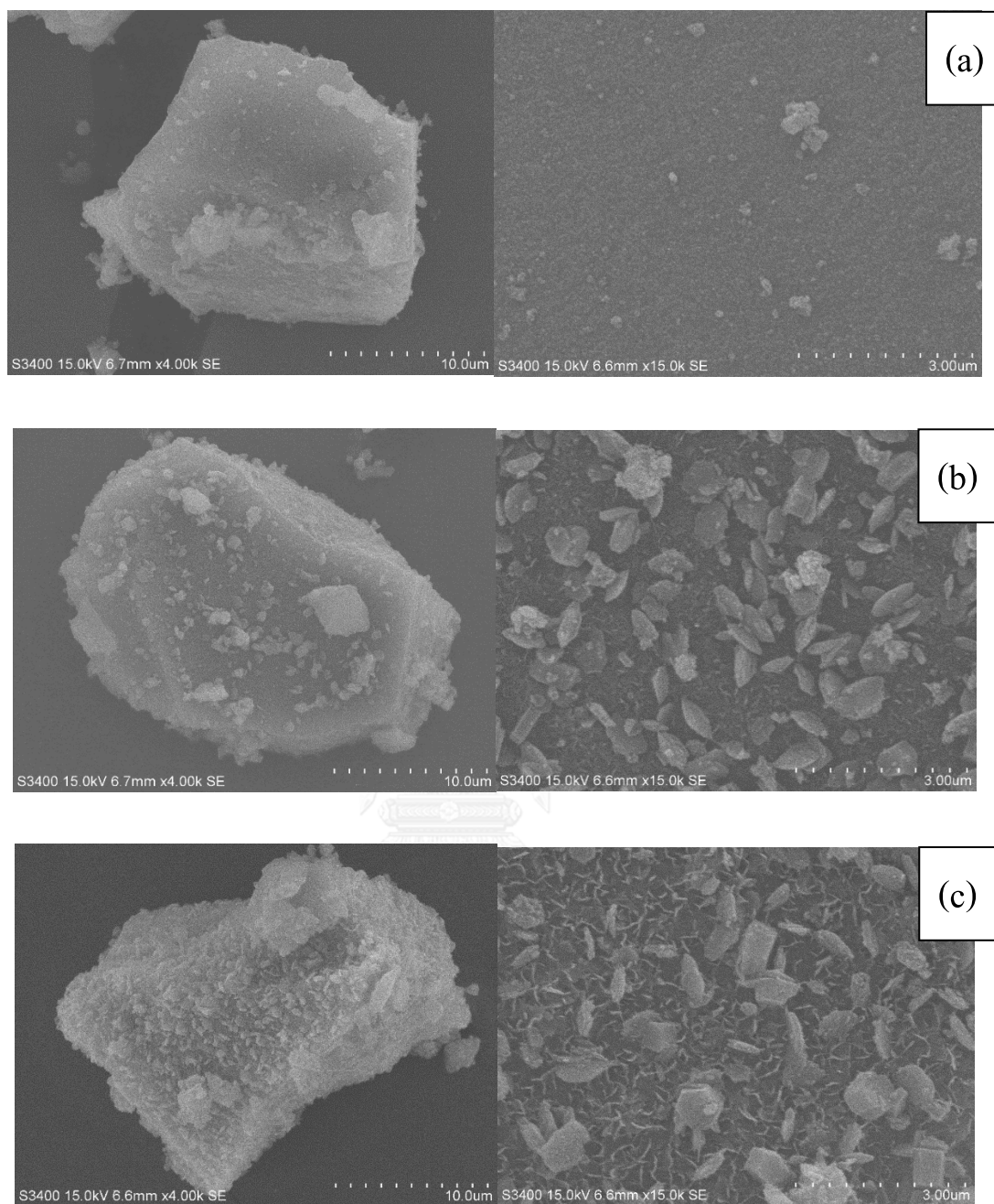


**Figure 4.4** TPD profile of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modified alumina catalyst

Table 4.1 summarizes the amount of acidity of each catalyst. It was found that the total acidity decreased with manganese loading. The weak acid sites referred to the amount of  $\text{NH}_3$  desorption in the range from 340.9-420.6  $\mu\text{mol NH}_3/\text{g cat}$ . The 0.1Mn/ $\text{Al}_2\text{O}_3$  exhibited the highest weak acid sites among other samples. For the medium to strong acid sites, all sample exhibited the amount of  $\text{NH}_3$  desorption in the range from 297.4-551.9  $\mu\text{mol NH}_3/\text{g cat}$ . The medium to strong acid sites was in order of  $\text{Al}_2\text{O}_3 > 0.05 \text{ Mn}/\text{Al}_2\text{O}_3 > 0.1 \text{ Mn}/\text{Al}_2\text{O}_3$

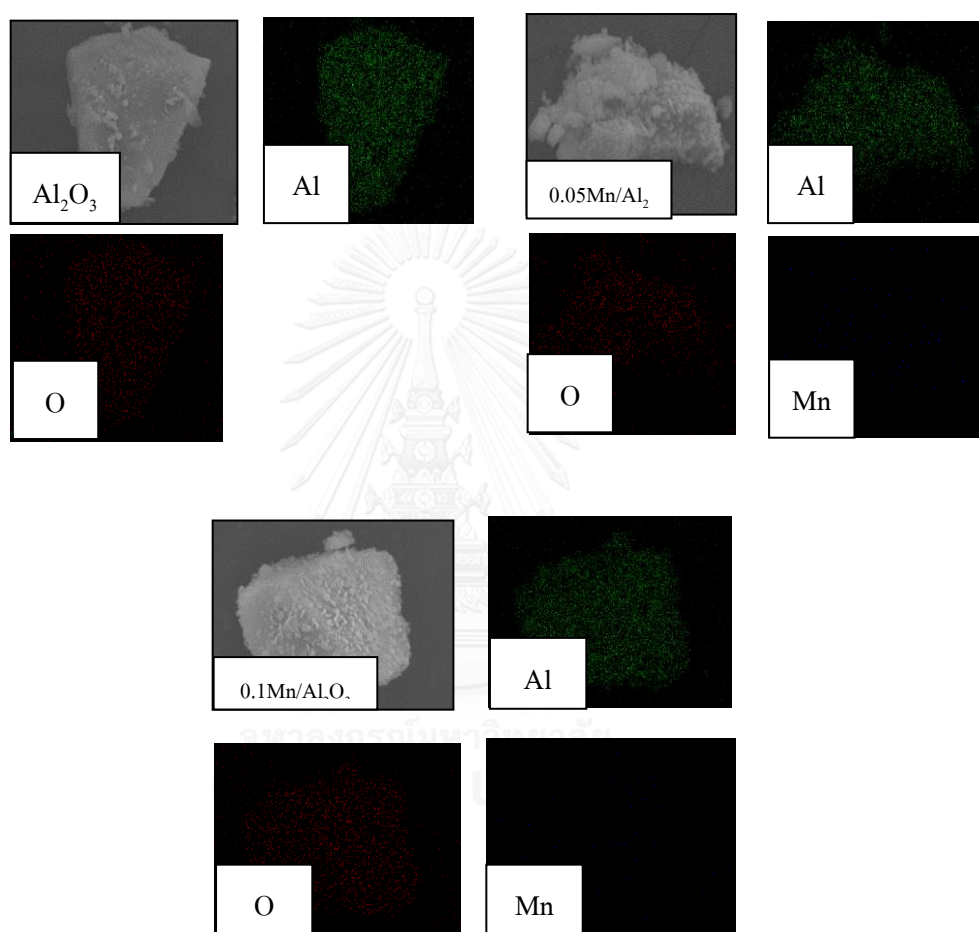
#### 4.1.4 Scanning Electron Microscopy

The morphologies of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modified alumina catalyst are shown in **Figure 4.5** measured by Scanning Electron Microscopy (SEM). From SEM image, was found fine particle in unmodified catalyst on the other hand modified catalyst was found particle accumulate on surface catalyst which is consistent with XRD result in **Figure 4.1**. The Mn-modified alumina catalyst did not show the XRD peak of Mn due to high dispersion.



**Figure 4.5** SEM micrograph of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modification alumina catalyst; (a)  $\text{Al}_2\text{O}_3$  (b)  $0.05\text{Mn}/\text{Al}_2\text{O}_3$  (c)  $0.1\text{Mn}/\text{Al}_2\text{O}_3$

**Figure 4.6** shows elemental dispersion of all catalysts (Al, O and Mn). The results show that all component were well dispersed. The Mn component that add in catalyst exhibited good dispersion.

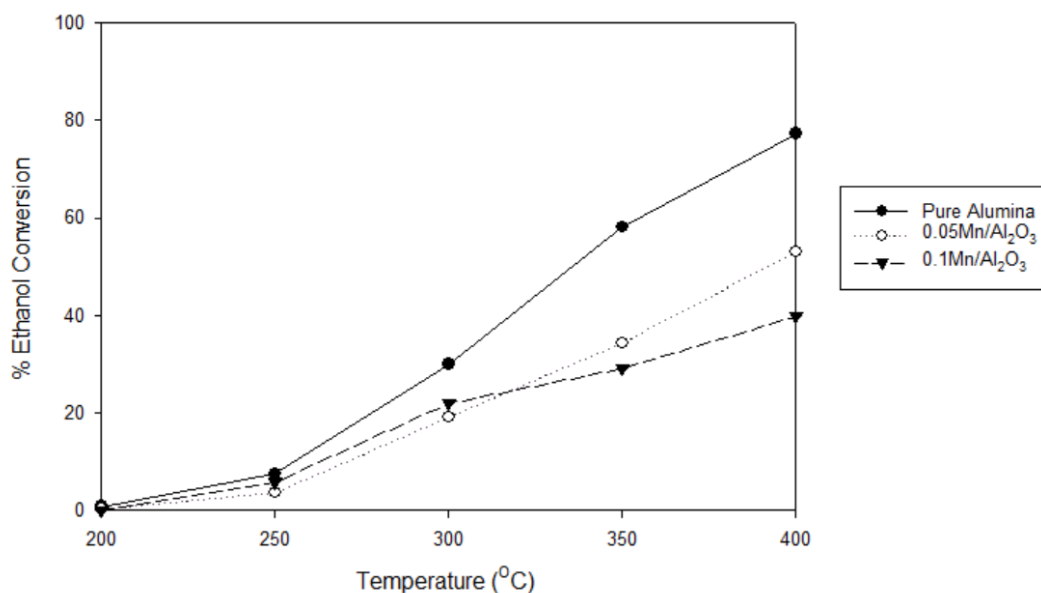


**Figure 4.6** Characteristic dispersion of component of mixed  $\gamma$ - and  $\chi$  alumina catalyst and Mn-modified alumina catalyst

## 4.2 Catalyst activity of mixed $\gamma$ - and $\chi$ alumina catalyst and Mn-modified alumina catalyst in ethanol dehydration reaction

### 4.2.1 Ethanol dehydration to ethylene

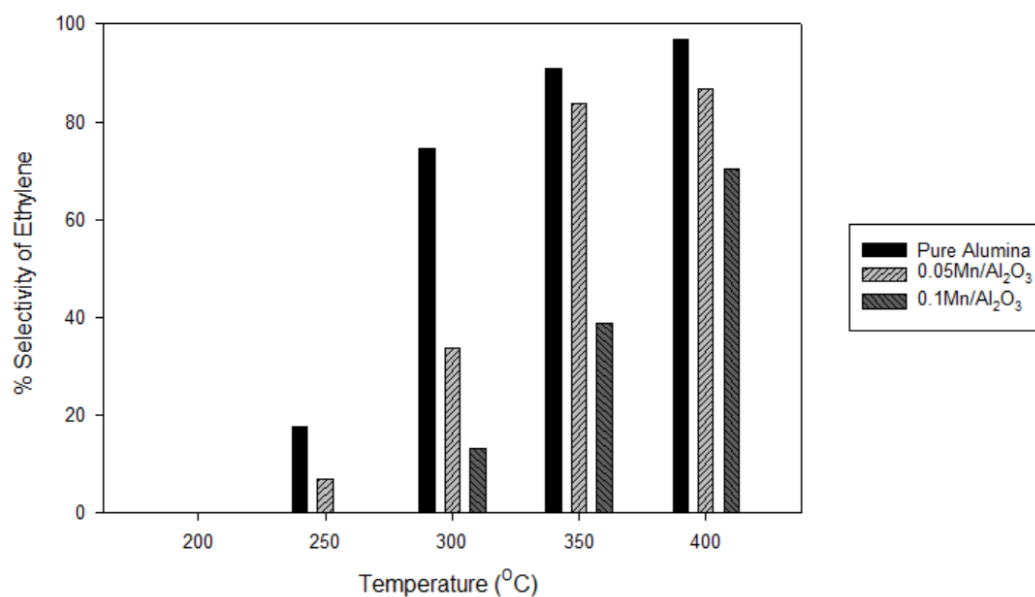
The catalytic activity depends on the reaction temperature. All catalysts were measured upon the catalytic performance in ethanol dehydration reaction under temperature between 200 to 400 °C. The results of catalytic activity were reported in terms of conversion and selectivity versus temperature profile. The products of ethanol dehydration reaction are ethylene, diethyl ether and acetaldehyde.



**Figure 4.7** Ethanol conversion profiles in ethanol dehydration at different temperatures

From the **Figure 4.7**, when increase reaction temperature the ethanol conversion increases for all catalyst. It reveals that the unmodified alumina shows the highest ethanol conversion followed by 0.05 Mn/Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn/Al<sub>2</sub>O<sub>3</sub>, respectively.



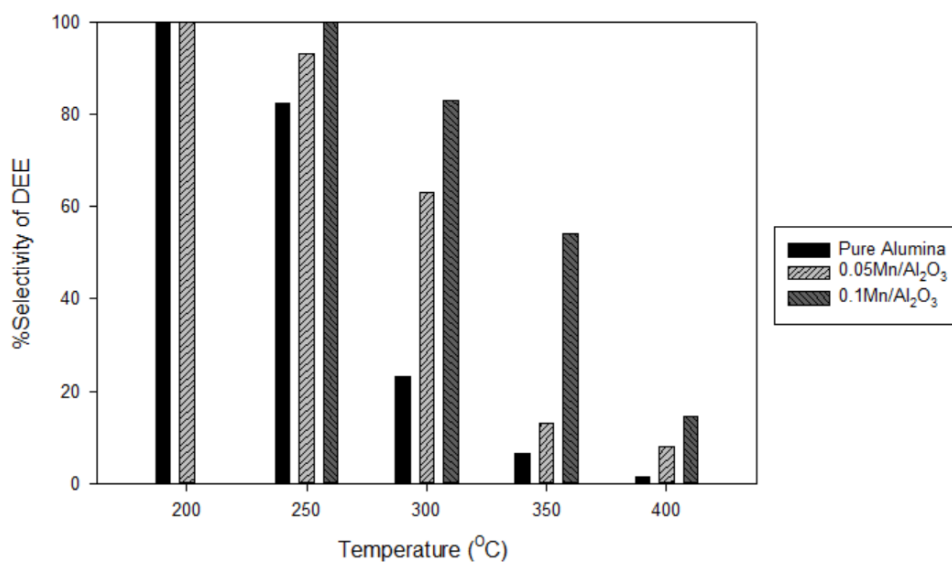


**Figure 4.8** Selectivity profiles of ethylene in ethanol dehydration at different temperature

**Table 4.3** Ethylene yield in ethanol dehydration at different temperature

Catalyst	Ethylene yield (%)				
	200 °C	250 °C	300 °C	350 °C	400 °C
Al <sub>2</sub> O <sub>3</sub>	0.0	1.3	22.3	52.7	74.9
0.05Mn/Al <sub>2</sub> O <sub>3</sub>	0.0	0.3	6.5	28.8	46.1
0.1Mn/Al <sub>2</sub> O <sub>3</sub>	0.0	0.0	2.9	11.3	28.0

From **Figure 4.8**, it shows the selectivity profiles of ethylene in ethanol dehydration at different temperature. It was found that selectivity of ethylene increased with increasing reaction temperature for all catalysts. It reveals that the unmodified alumina shows the highest for selectivity of ethylene followed by 0.05 Mn/Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn/Al<sub>2</sub>O<sub>3</sub>, respectively. For manganese-modified alumina catalyst, when increase manganese loading, selectivity of ethylene decreases. Ethylene yield was the highest when using Al<sub>2</sub>O<sub>3</sub> (74.9% at 400 °C), 0.05 Mn/Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn/Al<sub>2</sub>O<sub>3</sub>, respectively as shown in **Table 4.3**

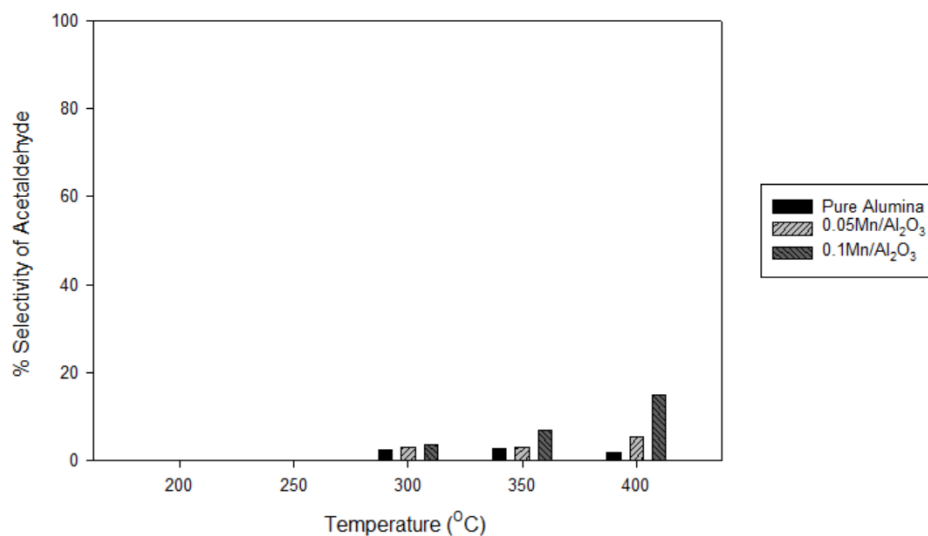


**Figure 4.9** Selectivity profiles of diethyl ether (DEE) in ethanol dehydration at different temperature

**Table 4.4** DEE yield in ethanol dehydration at different temperature

Catalyst	DEE yield (%)				
	200 °C	250 °C	300 °C	350 °C	400 °C
Al <sub>2</sub> O <sub>3</sub>	0.8	6.1	6.9	3.7	1.1
0.05Mn/Al <sub>2</sub> O <sub>3</sub>	0.2	3.3	12.0	4.5	4.2
0.1Mn/Al <sub>2</sub> O <sub>3</sub>	0.0	5.8	18.2	15.7	5.8

From **Figure 4.9**, it shows selectivity of DEE in ethanol dehydration at different temperature. It was found that selectivity of DEE was high at low temperature for all catalysts. It was found that DEE selectivity increased when increased manganese loading, but DEE yield was low as shown in **Table 4.4** due to lower temperature. The DEE yield highest at 300 °C with 0.1Mn/Al<sub>2</sub>O<sub>3</sub> catalyst (18.2%).



**Figure 4.10** Selectivity profiles of acetaldehyde in ethanol dehydration at different temperature

**Table 4.5** Acetaldehyde yield in ethanol dehydration at different temperature

Catalyst	Acetaldehyde yield (%)				
	200 °C	250 °C	300 °C	350 °C	400 °C
Al <sub>2</sub> O <sub>3</sub>	0	0	0.7	1.6	1.3
0.05Mn/Al <sub>2</sub> O <sub>3</sub>	0	0	0.6	1.0	2.9
0.1Mn/Al <sub>2</sub> O <sub>3</sub>	0	0	0.8	2.0	6.0

Acetaldehyde is formed as a by-product from dehydrogenation reaction (side reaction). **From Figure 4.10**, the results show that selectivity of acetaldehyde increases with increasing the manganese loading and acetaldehyde yield was low as shown in **Table 4.5**. The catalyst without modification of manganese consisted of acid sites that act as active phase on surface. While the Mn-modified catalyst, acid sites and metal (manganese) sites were obtained. Metal sites in catalyst act as the catalyst for the dehydrogenation of ethanol to acetaldehyde.

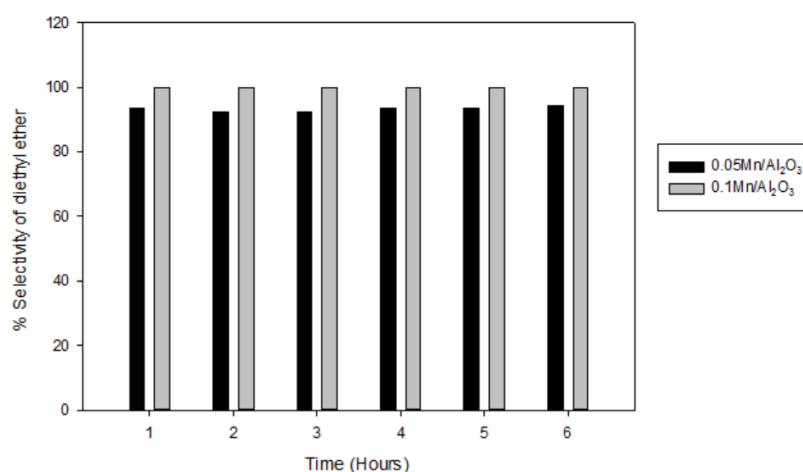
From the investigation of the catalytic performance of all catalysts in ethanol dehydration reaction under atmospheric pressure and various temperatures between 200–400 °C, it was found that the Mn-modified catalyst exhibited the high selectivity of DEE than unmodified catalyst as

shown in **Figure 4.4**. From the result, the highest selectivity of DEE is condition at 250 °C. So the next part will focus on the effect of catalyst activity and time on stream for manganese-modified alumina catalyst at 250 °C.

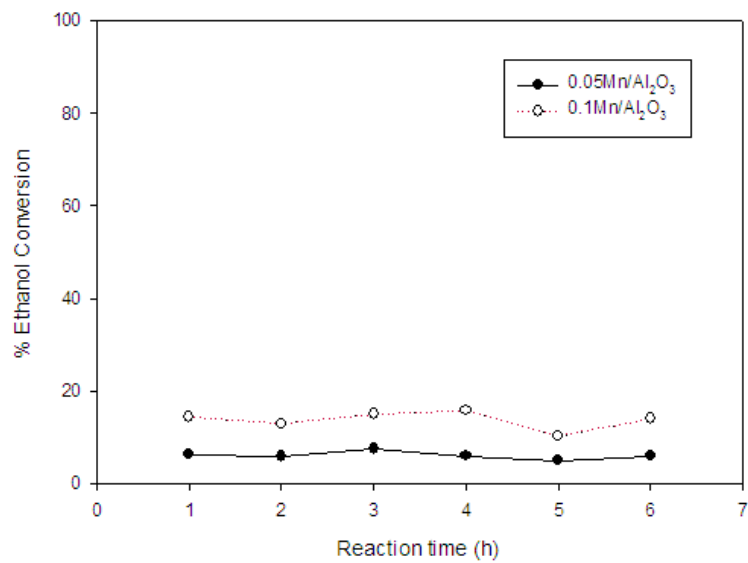
#### 4.2.2 Ethanol dehydration to DEE

Ethanol can be converted through a dehydration process to produce diethyl ether (DEE), which is an excellent compression – ignition fuel with higher energy density than ethanol. DEE has long been known as a cold start aid for engines but little is known about using DEE as a significant component in a blend or as a complete replacement for diesel fuel [33].

In this part the effect of catalyst activity and time on stream for manganese-modified alumina catalyst at 250 °C for 6 h was investigated. From **Figure 4.11** % selectivity of DEE of 0.05 Mn /Al<sub>2</sub>O<sub>3</sub> sample is lower than 0.1 Mn /Al<sub>2</sub>O<sub>3</sub> and stability of both catalyst are quite similar.



**Figure 4.11** Selectivity of diethyl ether of 0.05 Mn /Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn /Al<sub>2</sub>O<sub>3</sub> at 250 °C for 6 hrs.



**Figure 4.12** %Ethanol conversion of 0.05 Mn /Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn /Al<sub>2</sub>O<sub>3</sub> at 250 °C for 6 h.

From **Figure 4.12** shows %Ethanol conversion of 0.05 Mn /Al<sub>2</sub>O<sub>3</sub> and 0.1 Mn /Al<sub>2</sub>O<sub>3</sub> at 250 °C for 6 h. are stable so the catalyst still activate.

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATION

Chapter V summarizes the characteristics and catalyst activity of  $\gamma$ - $\chi$  alumina catalyst and manganese-modified alumina catalyst.

#### 5.1. Conclusion

The product of ethanol dehydration is ethylene, diethyl ether and acetaldehyde. At high temperature, the main product is ethylene, while at low temperature, the main product is diethyl ether. The ethylene formation is favored by medium to stronger acid sites, whereas diethyl ether requires only weak acid sites. Manganese loading results in decreased ethanol conversion and selectivity to ethylene, but increased selectivity of diethyl ether. The highest ethanol conversion and highest ethylene selectivity were observed for all catalyst at 400 °C. In terms of ethanol conversion, it was in the order of  $\text{Al}_2\text{O}_3$  (77.3%) > 0.05Mn/ $\text{Al}_2\text{O}_3$  (53.1%) > 0.1Mn/ $\text{Al}_2\text{O}_3$  (39.7%) and ethylene selectivity was in order of  $\text{Al}_2\text{O}_3$  (96.8%) > 0.05Mn/ $\text{Al}_2\text{O}_3$  (86.7%) > 0.1Mn/ $\text{Al}_2\text{O}_3$  (70.5%). However, the Mn modification can result in increased diethyl ether (DEE) selectivity at low temperature. At 250 °C, the highest DEE selectivity, was found for 0.1Mn/ $\text{Al}_2\text{O}_3$  (100%), while DEE selectivity 0.05Mn/ $\text{Al}_2\text{O}_3$  (93.0%) >  $\text{Al}_2\text{O}_3$  (82.4%) was observed.

#### 5.2 Recommendation

The result activity of Mn modification low yield of DEE at low temperature so should be study increase activity at low temperature by using chemical promoter for DEE production.

## REFERENCES

1. <http://en.wikipedia.org/wiki/Ethylene>.
2. J. Bedia, R.B., J. Rodriguez-Mirasol and T. Corderoj. , *Ethanol dehydration to ethylene on acid carbon catalysts*. Applied Catalysis B: Environmental, 2011: p. 103, 302-310.
3. A. Takahashi, W.X., I. Nakamura, H. Shimada and T. Fujitani, *Effects of added phosphorus on conversion of ethanol to propylene over ZSM-5 catalysts*. Applied Catalysis A: General 2012: p. 423– 424, 162– 167.
4. Denise Fan, D.-J.D.a.H.-S.W., *Ethylene formation by catalytic dehydration of ethanol with industrial consideration*. Materials, 2012.
5. Bedia, J., Barrionuevo, R., Rodriguez-Mirasol, J., and Cordero, T. , *Ethanol dehydration to ethylene on acid carbon catalyst*. Applied Catalysis B. Environmental 103, 2011: p. 302-310.
6. Lu, J., Liu, Y., and Li, N. , *Fe-modified HZSM-5 catalysts for ethanol conversion into light olefins*. Journal of Natural Gas Chemistry, 2011: p. 423-427.
7. Ouyang, J., Kong, F., Su, G., Hu, Y., and Song, O., *Catalytic conversion of bio-ethanol to ethylene over La-modified HZSM-5 catalysts in a bioreactor*. Catalysis letters 132, 2009: p. 64-74.
8. Zotov, R.A., Molchanov, V.V., Volodin, A.M., and Bedilo, A.F., *Characterization of the active sites on the surface of Al<sub>2</sub>O<sub>3</sub> ethanol dehydration catalysts by EPR using spin probes*. Journal of Catalysis 278, 2011: p. 71-77.
9. Atsushi Takahashi, W.X., Qiang Wu, Teruyuki Furukawa, Isao Nakamura, Hiromichi Shimada, Tadahiro Fujitani, *Difference between the mechanisms of propylene production from methanol and ethanol over ZSM-5 catalysts*. Appl. Catal. A, 2013: p. 380-385.
10. Atsushi Takahashi, W.X., Isao Nakamura, Hiromichi Shimada, Tadahiro Fujitani, *Effects of added phosphorus on conversion of ethanol to propylene over ZSM-5 catalysts*. Appl. Catal. A, 2012: p. 162- 167.
11. Chao Duan, X.Z., Rui Zhou, Yuan Hua, Li Zhang, Jie Chen, *Comparative studies of ethanol to propylene over HZSM-5/SAPO-34 catalysts prepared by hydrothermal synthesis and physical mixture*. Fuel Processing Technology 108, 2013: p. 31-40.
12. Yoshiyasu Furumoto, N.T., Yusuke Ide, Masahiro Sadakane, Tsuneji Sano, *Conversion of ethanol to propylene over HZSM-5(Ga) co-modified with lanthanum and phosphorous*. Appl. Catal. A, 2012: p. 137- 144.
13. Tao Meng, D.M., Qiangsheng Guo, Guanzhong Lu, T, *he effect of crystal sizes of HZSM-5 zeolites in ethanol conversion to propylene*. Catalysis Communications 21, 2012: p. 52-57.
14. Iwamoto, M., *Selective catalytic conversion of bio-ethanol to propene :A review of catalysts and reaction pathways*. Catalysis Today 242, 2015: p. 243-248.

15. Masakazu Iwamoto, S.M., and Masashi Tanaka, *Direct and Selective Production of Propene from Bio-Ethanol on Sc-Loaded In<sub>2</sub>O<sub>3</sub> Catalysts*. Chemistry a European Journal.
16. Fumitaka Hayashi, M.T., Dongmei Lin, Masakazu Iwamoto, *Surface structure of yttrium-modified ceria catalysts and reaction pathways from ethanol to propene*. Journal of Catalysis 316 2014: p. 112-120.
17. A.P. Kagyrmanova\*, V.A.C., V.N. Korotkikh, V.N. Kashkin, A.S. Noskov, *Catalytic dehydration of bioethanol to ethylene: Pilot-scale studies and process simulation*. Chemical Engineering Journal 2011: p. 188- 194.
18. Thanh Khoa Phung, L.P.H., Guido Busca, *Conversion of ethanol over transition metal oxide catalysts: Effect of tungsta addition on catalytic behaviour of titania and zirconia*. Appl. Catal. A: Gen. 489, 2015: p. 180-187.
19. Leandro Martinsa, D.C., Peter Hammera, Teresita Garetto, Sandra H. Pulcinella, Celso V. Santillia, *Efficiency of ethanol conversion induced by controlled modification of pore structure and acidic properties of alumina catalysts*. Appl. Catal. A: Gen. 398, 2011: p. 59-65.
20. Matachowski, A.D., E. Lalik, M. Ruggiero-Mikołajczyk, D. Mucha, J. Kryściak-Czerwenka, *Efficient dehydration of ethanol on the self-organized surface layer of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> formed in the acidic potassium tungstophosphates*. Appl. Catal. A: Gen. 469, 2014: p. 290- 299.
21. M.J. Lippits, B.E.N., *Direct conversion of ethanol into ethylene oxide on gold-based catalysts Effect of CeO<sub>x</sub> and Li<sub>2</sub>O addition on the selectivity*. Journal of Catalysis 274, 2010: p. 142-149.
22. M.J. Lippits \*, B.E.N., *Direct conversion of ethanol into ethylene oxide on copper and silver nanoparticles Effect of addition of CeO<sub>x</sub> and Li<sub>2</sub>O*. Catalysis Today 154, 2010: p. 127-132.
23. Dezhi Gao, Y.F., Hengbo Yin, Aili Wang a, Tingshun Jiang, *Coupling reaction between ethanol dehydrogenation and maleic anhydride hydrogenation catalyzed by Cu/Al<sub>2</sub>O<sub>3</sub>, Cu/ZrO<sub>2</sub>, and Cu/ZnO catalysts*. Chemical Engineering Journal 233, 2013: p. 349-359.
24. Walaa Alharbi, E.B., Elena F. Kozhevnikova, Ivan V. Kozhevnikov, *Dehydration of ethanol over heteropoly acid catalysts in the gas phase*. Journal of Catalysis 319, 2014: p. 174-181.
25. Dongjin Kim, B.S.K., Bong-Ki Min, Misook Kang, *Characterization of Ni and W co-loaded SBA-15 catalyst and its hydrogen production catalytic ability on ethanol steam reforming reaction*. Applied Surface Science 332 2015: p. 736-746.
26. Vijay V. Bokade, G.D.Y., *Heteropolyacid supported on montmorillonite catalyst for dehydration of dilute bio-ethanol*. Applied Clay Science, 2011: p. 263-271.
27. Varisli, D.D., T.; Dogu, G. , *Ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropolyacid catalysts*. Chem. Eng. Sci, 2007: p. 5349-5352.
28. Alcohols, D.a.T.,  
<http://www.mhhe.com/physsci/chemistry/carey/student/olc/ch15synthesisethers.html> .
29. Thackeray, M.M., Solid State Chem, 1997.



30. J.Lu, Y.L.a.N.L., *Fe-modified HZSM-5 catalysts for ethanol conversion into light olefins*. Natural Gas Chemistry, 2011: p. 423-427.
31. Khom-in, J., Prasertdam, P., Panpranot, J., and Mekasuwandumrong, O. , *Dehydration of methanol to dimethyl ether over nanocrystalline Al<sub>2</sub>O<sub>3</sub> with mixed  $\gamma$ - and  $\chi$ -crystalline phase*. Catalysis Communications 9, 2008: p. 1955-1958.
32. Radovic, L.R., Chemistry & Physics of Carbon, 2004. **29**.
33. [http://shodhganga.inflibnet.ac.in/bitstream/10603/27287/6/06\\_chapter%201.pdf](http://shodhganga.inflibnet.ac.in/bitstream/10603/27287/6/06_chapter%201.pdf).



# APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย  
CHULALONGKORN UNIVERSITY

## APPENDIX A

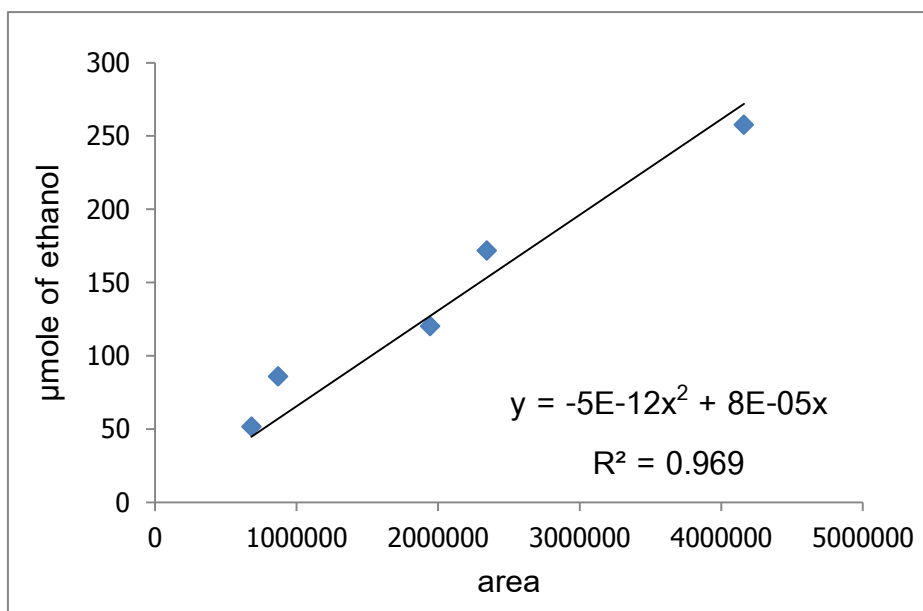
### CALIBRATION CURVE

Appendix A showed the calibration curves for calculation of composition of reactant and products in ethanol dehydration reaction that consist of as shown in **Figures A.1-A.4**. The reactant is ethanol and the main product is ethylene. The other products are DEE and acetaldehyde.

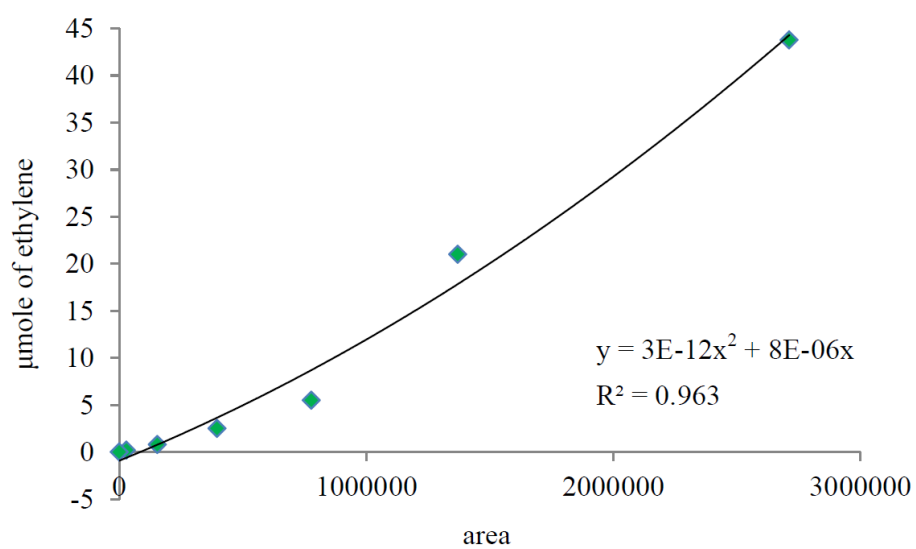
The concentration of reactant and products were analyzed by the gas chromatography Shimadzu model 14A, capillary column DB-5 of flame ionization detector (FID). The used conditions in GC are presented in **Table A.1**.

**Table A.1** Conditions in GC-14A

Parameters	Condition
Width	5
Slope	100
Drift	0
Min. Area	300
T.DBL	1000
Stop time	12 min.
Atten	2
Speed	3
Method	Normalization
SPL.WT	100
IS.WT	1



**Figure A. 1** The calibration curve of ethanol



**Figure A. 2** The calibration curve of ethylene

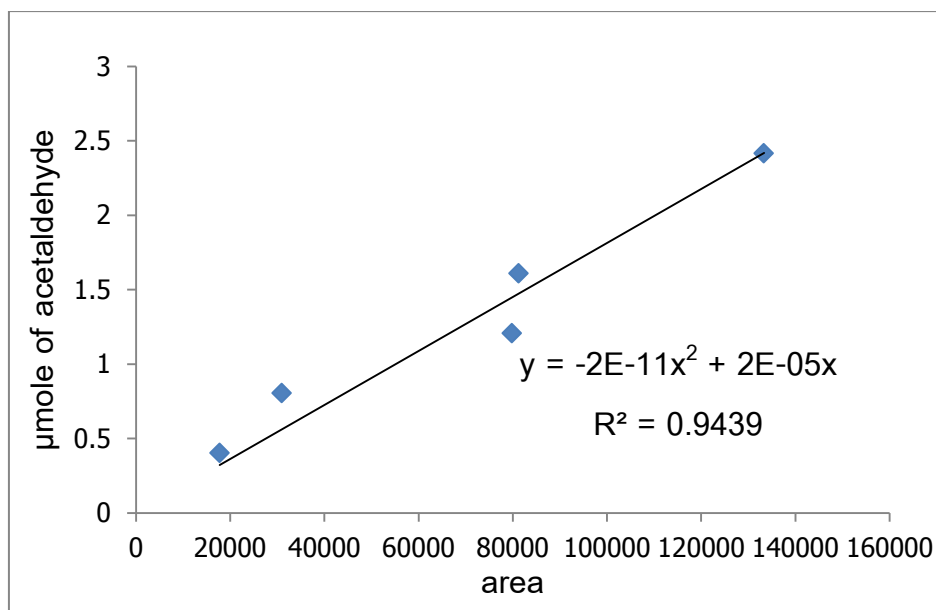


Figure A. 3 The calibration curve of acetaldehyde

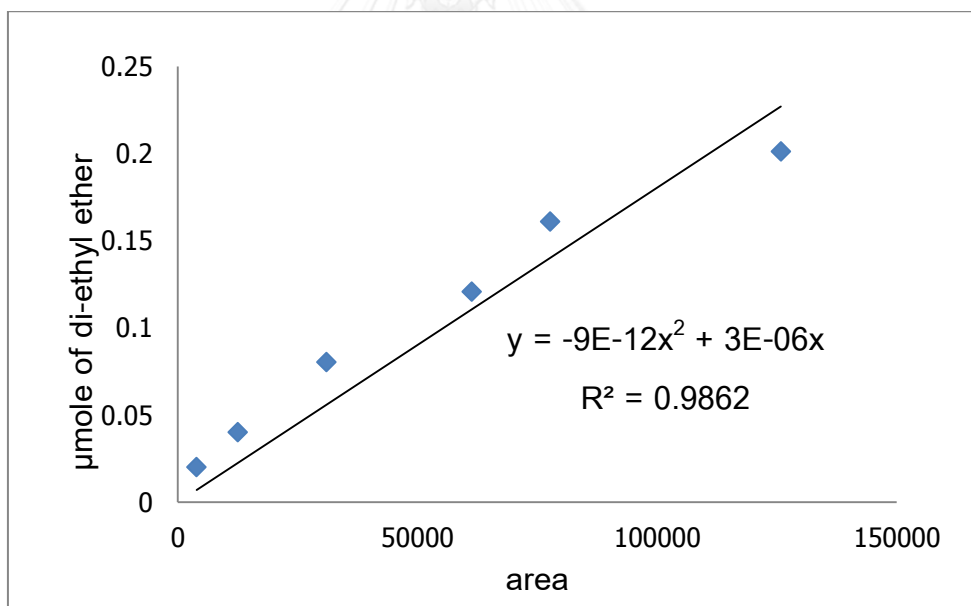


Figure A. 4 The calibration curve of diethyl ether

## APPENDIX B

### CALCULATION OF CONVERSION AND SELECTIVITY

The catalyst activity for the ethanol dehydration reaction was considered in term of ethanol conversion and selectivity of products.

Ethanol conversion calculate as equation

$$\% \text{ conversion} = \frac{\text{Moles of reacted ethanol}}{\text{Moles of fed ethanol}} \times 100$$

Selectivity of product calculate as equation

$$\% \text{ selectivity} = \frac{\text{Moles of each product}}{\text{Total moles of product}} \times 100$$

where: product in ethanol dehydration reaction is only ethylene, acetaldehyde and diethyl ether

Neglect other component that low composition

Yield of product calculate as equation

$$\begin{aligned} \% \text{ yield of each product} \\ = \text{ethanol conversion} \times \text{selectivity of each product} \times 100 \end{aligned}$$

## APPENDIX C

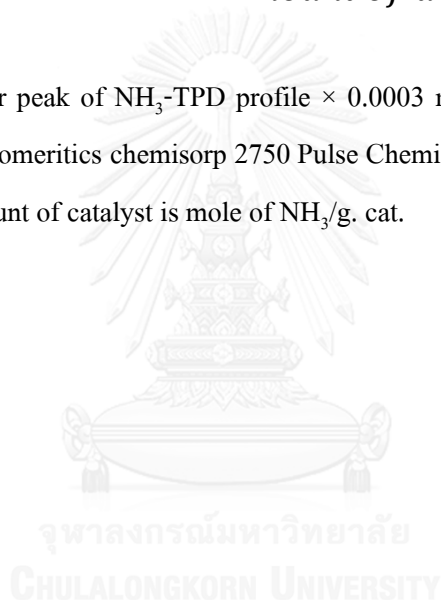
### CALCULATION OF ACIDITY

The amount of acid site was represented for acidity of catalyst. In this research, the acidity was measured by NH<sub>3</sub>-TPD technique, which amount of TCD signal versus temperature as follows:

$$\text{Amount of catalyst} = \frac{A}{\text{Amount of dry catalyst (g)}}$$

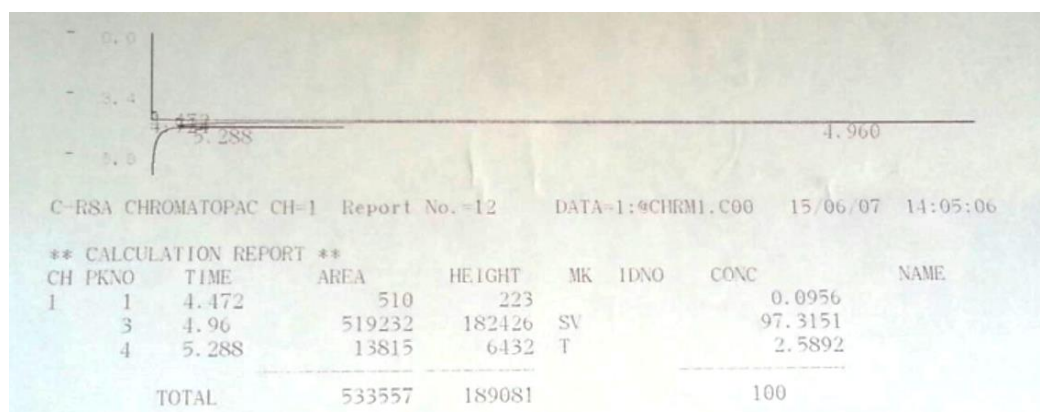
where: - A is area under peak of NH<sub>3</sub>-TPD profile × 0.0003 mole of NH<sub>3</sub> desorption based on calibration curve of micromeritics chemisorp 2750 Pulse Chemisorption System.

- The unit of amount of catalyst is mole of NH<sub>3</sub>/g. cat.



## APPENDIX D

## GAS CHROMATOGRAPHY DATA



**Figure D.1** data result from Gas Chromatography

From the **Figure D.1** shows the result from GC. The time at 4.9 is ethanol, time at 4.4 is ethylene and time at 5.2 is DEE.



## APPENDIX E

### Conference proceeding

#### Proceeding

Rattanaporn Rakpan and Bunjerd jongsomjit, “Dehydration of Ethanol over Mn-modified Alumina Catalyst” Proceeding of the 1<sup>st</sup> national conference TECHCON 2015, Bangkok, Thailand, July 11 2015.



## VITA

Miss Rattanaporn Rakpan was born on April 2nd, 1989 in Samutprakarn province, Thailand. I graduated the bachelor's degree in chemical technology department, faculty of science, Chulalongkorn University (CU) in May 18, 2011. I continued to study master's degree in chemical engineering department, faculty of engineering, Chulalongkorn University (CU) in May 2012.

