การเปลี่ยนเอทานอลเป็นโอเลฟินส์เบาโดยใช้ตัวเร่งปฏิกิริยามอร์ดิไนต์

นางสาวศิรินภา อานามนารถ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2547

ISBN : 974-17-6423-5

ETHANOL CONVERSION TO LIGHT OLEFINS USING MORDENITE CATALYSTS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2004

ISBN : 974-17-6423-5

Thesis Title ETHANOL CONVERSION TO LIGHT OLEFINS USING MORDENITE CATALYSTS

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Field of Study Petrochemistry and Polymer Science

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ศิรินภา อานามนารถ : การเปลี่ยนเอทานอลเป็นโอเลฟินส์เบาโดยใช้ตัวเร่งปฏิกิริยามอร์ดิไนต์ (ETHANOL CONVERSION TO LIGHT OLEFINS USING MORDENITE CATALYSTS) อาจารย์ที่ปรึกษา: รศ. ดร. วิมลรัตน์ ตระการพฤกษ์; จำนวนหน้า 80 หน้า. ISBN: 974-17-6423-5

ตัวเร่งปฏิกิริยามอร์ดิไนต์ที่มีโลหะ ได้จากการนำมอร์ดิไนต์จากธรรมชาติมากำจัดอะลูมิเนียมด้วยกรดและปรับปรุงสมบัติด้วยการเติมโลหะ ทำการตรวจพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาเหล่านี้ด้วยเทคนิค FT-IR, XRF, XRD และ TGA ใช้ตัวเร่งปฏิกิริยาเหล่านี้ในการศึกษาการเปลี่ยนรูปของเอทานอลและเอทานอลเจือจางไปเป็นโอเลฟินส์เบา ศึกษาถึงปัจจัยต่าง ๆที่มีผลต่อปฏิกิริยา ได้แก่ อุณหภูมิ การเจือจางด้วยน้ำ วิธีการเติมโลหะลงในตัวเร่งปฏิกิริยา การผสมสารเจือจาง (อลูมินา) เพื่อลดปริมาณการใช้ตัวเร่งปฏิกิริยา และปริมาณของตัวเร่งปฏิกิริยา การทดลองในภาวะ ที่อุณหภูมิ 350 องศาเซลเซียส เวลาในการทำปฏิกิริยา 1 ชั่วโมง ความเข้มข้นของเอทานอล 10 เปอร์เซ็นต์ ความเร็วเชิงสเปซ 1 ต่อชั่วโมง และน้ำหนักตัวเร่งปฏิกิริยา 1 กรัม พบว่า ตัวเร่งปฏิกิริยามอร์ดิไนต์/โลหะทุกชนิด ให้เอทิลีนเป็นผลิตภัณฑ์หลัก ที่อุณหภูมิต่ำ (350 องศาเซลเซียส) ให้ความจำเพาะต่อเอทิลีนมากกว่าที่อุณหภูมิสูง (550 องศาเซลเซียส) เมื่อเจือจางเอทานอลด้วยน้ำให้มีความเข้มข้น 10.0 เปอร์เซ็นต์ ให้ความจำเพาะต่อเอทิลีนสูงขึ้น วิธีการเติมโลหะเดี่ยวและโลหะผสมลงในมอร์ดิไนต์มีสองวิธี คือ การแลกเปลี่ยนไอออนในสภาพของแข็ง และวิธีฝังตัว ในตัวเร่งปฏิกิริยามอร์ดิไนต์/โลหะผสมที่ทดสอบ พบว่าตัวเร่งปฏิกิริยามอร์ดิไนต์/เงิน-สังกะสี ซึ่งเตรียมโดยวิธีการฝังตัว ให้ความจำเพาะต่อเอทิลีนสูงสุด (98.0 %) ตัวเร่งปฏิกิริยามอร์ดิไนต์/โลหะผสมทุกชนิด ให้ความจำเพาะต่อเอทิลีนมากกว่าตัวเร่งปฏิกิริยามอร์ดิไนต์/โลหะเดี่ยว สามารถลดปริมาณของตัวเร่งปฏิกิริยาลงได้โดยผสมกับอลูมินา ซึ่งพบว่าความจำเพาะต่อเอทิลีนลดลงเล็กน้อย สำหรับตัวเร่งปฏิกิริยามอร์ดิไนต์/นิกเกิล 1 เปอร์เซ็นต์ ให้ความจำเพาะต่ออีเทนมากที่สุด เนื่องจากความสามารถในการเกิดไฮโดรจิเนชัน เมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยา ความจำเพาะต่อมีเทนเพิ่มขึ้น ตัวเร่งปฏิกิริยามอร์ดิไนต์/โลหะ ที่ศึกษาในงานนี้ให้ประสิทธิภาพใกล้เคียงกับตัวเร่งปฏิกิริยา ZSM-5 นอกจากนี้ ตัวเร่งปฏิกิริยาสามารถนำกลับมาใช้ใหม่ได้

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

ปีการศึกษา 2547 ลายมือชื่ออาจารย์ที่ปรึกษา……….…………

 # # 4672427923: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: MORDENITE / DEALMINATION

SIRINAPA ARENAMNART : ETHANOL CONVERSION TO LIGHT OLEFINS USING MORDENITE CATALYSTS. THESIS ADVISOR : ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D., 80 pp.
ISBN: 974-17-6423-5

Natural mordenite was dealuminated with acid and then modified with metal loading to prepare DM/metal catalysts. The single and mixed metals were loaded onto mordenite using solid state ion exchange and impregnation methods which were characterized by FT-IR, XRF, XRD and TGA techniques. They were used as catalyst for conversion of ethanol and aqueous ethanol to light olefins. Various parameters influencing reaction such as temperature, addition of water into feed, method of metal loading, addition of diluent (alumina) and amount of catalyst were studied. It was found that at 350°C, 1 h, 10% EtOH, WHSV 1 $h^{-1}$and catalyst weight of 1 g, all DM/metal catalysts produced mainly ethylene. At low temperature (350°C) they showed higher selectivity to ethylene than at high temperature (550°C). When diluting ethanol with water to make 10% EtOH, it gave higher selectivity to ethylene. Both seem to give similar product distribution. Among DM/mixed metal catalysts tested, DM/Ag-Zn which prepared by impregnation method gave the highest selectivity to ethylene (98.0%). All DM/mixed metals (DM/Ag-Zn, DM/Mn-Zn, DM/Co-Zn and DM/Fe-Zn) showed a higher ethylene selectivity than DM/single metal (DM/Zn, DM/Rh, DM/Co, DM/Mn, DM/Cu, DM/Fe, DM/Ag and DM/Ni). Amount of catalyst can be reduced by diluting it with alumina. It was found that selectivity to ethylene was slightly decreased. For DM/1%Ni, it showed higher selectivity to ethane due to its hydrogenation ability. Increasing amount of catalysts increased selectivity to methane. The DM/metal catalysts investigated in this work show comparable activity to ZSM-5. In addition, it was shown that the catalysts can be reused.

Field of Study Petrochemistry and Polymer Science Student's signature.
Academic year 2004 Advisor's signature.

ACKNOWLEDGEMENTS

The author wishes to express greatest gratitude to her advisor, Associate Professor Dr. Wimonrat Trakarnpruk, for her advice, assistance and generous encouragement throughout the course of this research. In addition, the author wishes to express deep appreciation to Professor Dr. Pattarapan Prasassarakich, Assistant Professor Dr. Warinthorn Chavasiri and Associate Professor Dr. Vithaya Ruangpornvisuti for serving as the chairman and members of her thesis committee, respectively, for their valuable suggestions and comments.

Appreciation is also extended to Program of Petrochemistry and Polymer Science and the Department of Chemistry, Faculty of Science, Chulalongkorn University for granting financial support to fulfill this study and provision of experimental facilities.

Further acknowledgement is extended to Rayong Olefins Co., Ltd. for GC analysis and her friends for their help and encouragement during her graduate studies. The author wishes to express deep appreciation to Miss Parichat Damrongpong for her help. Finally, the author is very appreciated to her family and her good friends whose names are not mentioned here for their love, assistance and encouragement throughout her entire education. Without them, the author would have never been able to achieve this goal.

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LIST OF ABBREVIATIONS

XRD	X-ray powder diffraction
XRF	X-ray fluorescence spectrometry
BET	Brunauer-Emmett-Teller method
GC	gas chromatography
FT-IR	Fourier-transform infrared spectroscopy
TGA	Thermogravimetric analysis
SBU	secondary building unit
Si/Al	silicon/aluminium ratio
wt	weight
h	hour (s)
°C	degree celsius
kPa.	kilo Pascal
P	pressure
mL	milliliter (s)
V	volume
z	critical compressibility factor
n	mole
J	joule
min	minute (s)
MTO	methanol to olefins
D-MOR	dealuminated mordenite
DM/Me	metal loaded dealuminated mordenite
W_{cat}	weight of catalyst
T_{EtOH}	temperature of ethanol
EtOH	ethanol
SSIE	solid state ion exchange
IMP	impregnation
st.	stretching
ZSM-5	Zeolite Socony Mobil no.5
USY	Ultra stable zeolite Y
MOR	mordenite

LIST OF ABBREVIATIONS (CONT.)

cm^{-1}	unit of wave number
C_1	methane
C_2	ethane
C_2=	ethylene
$C_2\equiv$	acetylene
C_3	propane
C_3=	propylene
C_3=,=	propadiene
$C_3\equiv$,—	methyl acetylene
C_4	*n*-butane
iso-C_4	*iso*-butane
1-C_4=	1-butene
iso-C_4=	*iso*-butene
trans-2-C_4=	*trans*-2-butene
cis-2-C_4=	*cis*-2-butene
1,3-C_4=,=	1,3-butadiene
n-C_5	*n*-pentane
iso-C_5	*iso*-pentane
C_2-C_4 olefins	ethylene-butylene
C_1-C_5 alkanes	methane-pentane

CHAPTER I

INTRODUCTION

Conversion of methanol and ethanol to gasoline and other hydrocarbons has received wide attention these days due to the global energy crisis and the heavy demand for hydrocarbons. Ethanol can be obtained from fermentation of biomass, a renewable agricultural resource. Thailand can produce ethanol from fermentation of molasses, a by-product of the sugar industry. Its concentration is low, which has a high water content (up to 95-wt%). Ethanol is usually separated by distillation. However, purification from 90% to absolute ethanol is particularly energy consuming. If it can be directly converted to hydrocarbons, ethanol can be a very good source for producing hydrocarbons in Thailand.

Both structural and chemical properties of the catalyst as well as various process parameters influence the product distribution. The catalyst acidity, pore size and shape, particle size and the presence of heteroatoms play the major roles in determining activity and selectivity. In general, reductions in contact time, weak acidity, water dilution and modification with suitable promoters can enhance the selectivity to light olefins.

Two ways of modifying the acidity of zeolites were dealumination and cation exchange. Dealuminated and ion-exchanged zeolites were shown to possess higher stability and selectivity than the parent zeolite. The acid properties of zeolites may also affect the catalyst life, because the reaction proceeds on the acid sites.(1) The catalyst life of H-mordenites was improved significantly by dealumination with hydrochloric acid and the temperature of the acid solution.(2)

Advantages of zeolite catlalyst are as follows:(3)

- Crystallinity and therefore precisely defined arrangement of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral.
- Shape selectivity

- Controlled incorporation of acid centers in the intracrystalline surface
- Catalytically active metal ions by ion exchange or impregnation
- Thermally stability (up to 600°C)
- Ability to be regenerated by combustion

In present work, ethanol conversion to light olefins using dealuminated mordenite catalyst loaded with metals were studied. The product and product distribution by catalytic process was investigated. This research was aimed in developing production of light olefins from ethanol. It was expected that the incorporation of transition metal ion into mordenite catalyst will lead to bifunctional catalysts in which metal and acid centers can act simultaneously.

1.1 The objectives of the thesis

1.1.1 To investigate incorporation of single metal and mixed metals into mordenite catalyst for ethanol conversion to light olefins.

1.1.2. To investigate the effect of reaction conditions on ethanol conversion.

1.2 The scopes of the thesis

1.2.1 Study method to introduce metals into mordenite catalyst : solid state ion exchange and impregnation methods.

1.2.2 Characterize the prepared catalysts by following methods:
  - Structure of catalysts by X-ray diffraction (XRD)
  - Amount of metal by X-ray fluorescence (XRF)
  - Surface areas of catalysts by Brunauer-Emmett-Teller (BET) surface area measurement

1.2.3 Investigate the performance of the prepared catalysts on the conversion of ethanol under the following conditions:
  - Atmospheric pressure
  - Reaction temperature 350-550°C
  - Weight hourly space velocity 1.00 h^{-1}
  - Reactant feed: 10.0 %wt and 99.9 %wt ethanol

The product and product distribution were analyzed by gas chromatography.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Zeolites

The name of "zeolite" comes from the Greek words zeo (to boil) lithos (stone).(4) Zeolite is a crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, strontium and barium. These cations can participate in ion-exchange processes and this yields some important properties for zeolites. When the zeolytic cations are protons, the zeolites become a strong solid acid. Such solid acids form the foundations of zeolite catalysis applications including the important fluidized bed catalytic cracking refinery process. Other types of reactive metal cations can also populate the pores to form catalytic materials with unique properties. Thus, zeolites are also commonly used in catalysis which zeolite is often called "shape-selective catalyst".

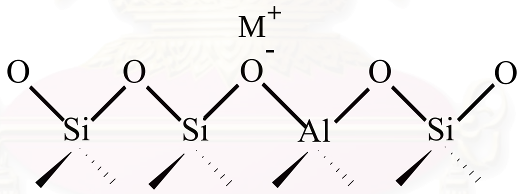


Figure 2.1 The structure of zeolites.

Zeolites may be represented by the general formula

$$\mathbf{M_{x/n}\,[(AlO_2)_x(SiO_2)_y].\ w\ H_2O}$$

Where M is the cation of valance n
w is the number of water molecules

Zeolites have framework (three-dimensional) structures constructed by joining together $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra, each of which contains a silicon or aluminum atom in the center. The oxygen atoms are shared between adjoining tetrahedral, which can be present in various ratios and arranged in a variety of ways. The framework thus obtained contains pores, channels and cages or interconnected void. A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. The secondary building units (SBU’s) consist of 4(S4R), 6(S6R) and 8(S8R)-member ring, 4-4(D4R), 6-6(D6R) and 8-8(D8R)-member double rings and 4-1, 5-1 and 4-4-1 branched rings as illustrated in Figure 2.2.

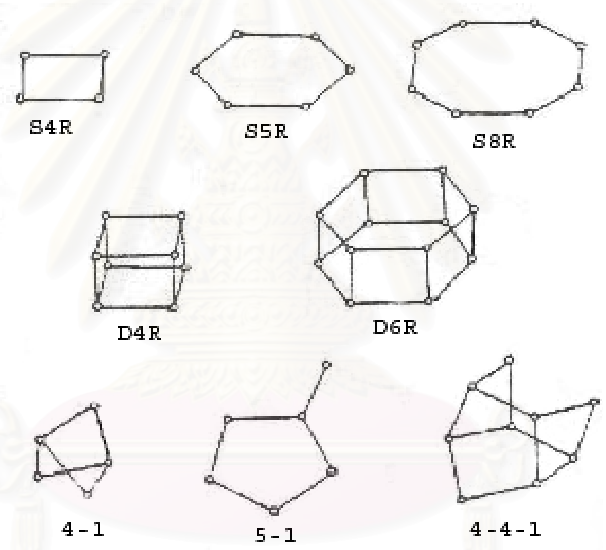


Figure 2.2 Secondary building units found in zeolite structures.

2.2 Zeolite active sites

2.2.1 Acid sites

Classical Bronsted and Lewis acid models of acidity have been used to classify the active sites on zeolites. Bronsted acidity is proton donor acidity, a tridiagonally coordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid.

The increase in Si/Al ratio will increase acidic strength and thermal stability of zeolites. Since the numbers of aluminum in zeolites framework, decrease in Al content is expected to reduce catalytic activity of zeolite. If the effect of increase in the acidic centers, increase in Al content, shall result in enhancement of catalytic activity.

An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxy groups, which is parallel to that of Al. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites.

2.2.2 Generation of acid centers

Protonic acid centers of zeolite are generated in various ways. In high-silica-zeolite they can be made by direct reaction with a mineral acid, giving surface hydroxyl groups the Bronsted acid sites. The thermal decomposition of ammonium exchanged zeolites is preparing hydrogen (or proton) on the zeolite framework. The hydrogen form (acid form) can be generated indirectly by replacing the sodium ion of the zeolite by ammonium ion from an aqueous solution of ammonium chloride or ammonium nitrate and heating above 300°C under vacuum. The bridged OH group across a pair of Si and Al atoms behaves as a classical Bronsted acid. Further thermal treatment at higher temperature results in a loss of water from two nearby hydroxyl groups. This process is called dehydroxylation. The dehydroxylation causes the loss of one oxygen from zeolite framework per water molecule removed, exposing a tricoordinated Al ion, which is an electron-pair acceptor, *i.e.* a Lewis acid site. The formation of these sites is shown in Figure 2.3.

Dealumination is believed to occur during dehydroxylation that may result from the steam generation within the sample. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in Figure 2.4. The framework tetrahedral sites of aluminum are hydrolyzed by steam at elevated temperatures giving aluminum hydroxide phase on the zeolite surface. The hydroxyl groups produced on the tetrahedral are subsequently

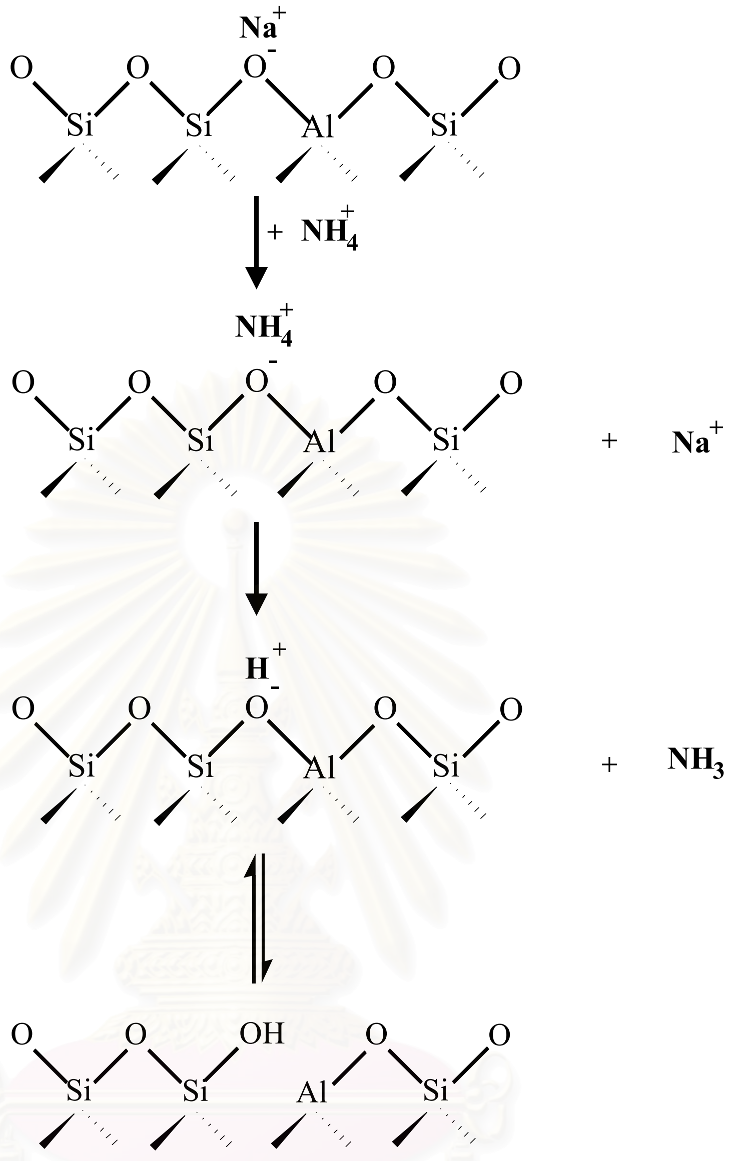


Figure 2.3 Diagram of acid sites in zeolite.

removed during the final calcination procedure and new Si-O-Si linkages are formed. The loss of aluminum from the tetrahedral positions results in the contractionof the unit cell. Dealumination is a major result of hydrothermal treatment of zeolites. Steaming of the zeolites has been found to produce a variety of cations and neutral cations interact with neighboring Bronsted sites to induce the catalytic superacid sites. The new cations have been suggested to function as Lewis acids, which have been considered to induce activity on nearby Brønsted sites as shown in Figure 2.5. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity. If a steam treatment is used for dealumination, the extra framework Al generated stays in the channels. Direct acid treatment is not only dealumination but also removes the extra framework Al. In general, acid extraction of aluminum from the framework usually affects the external surfaces of the crystal.

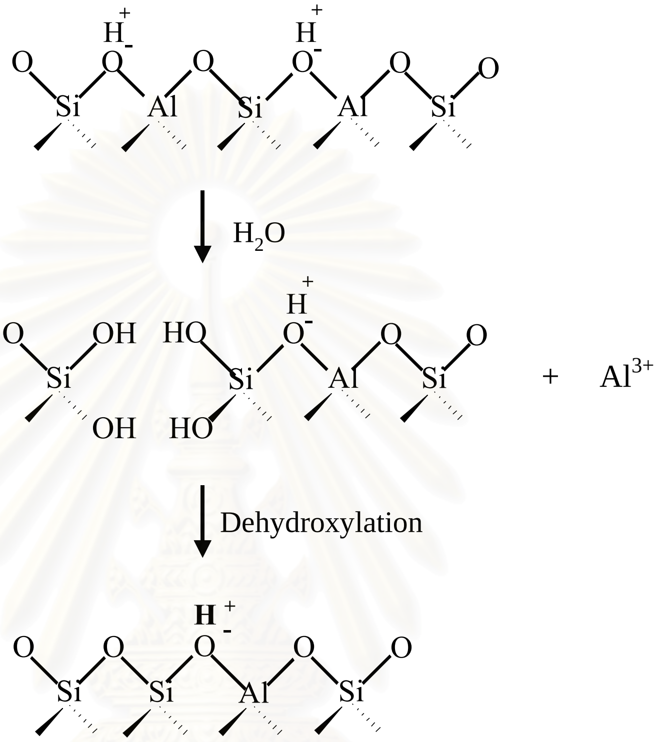


Figure 2.4 Steam dealumination process in zeolite.

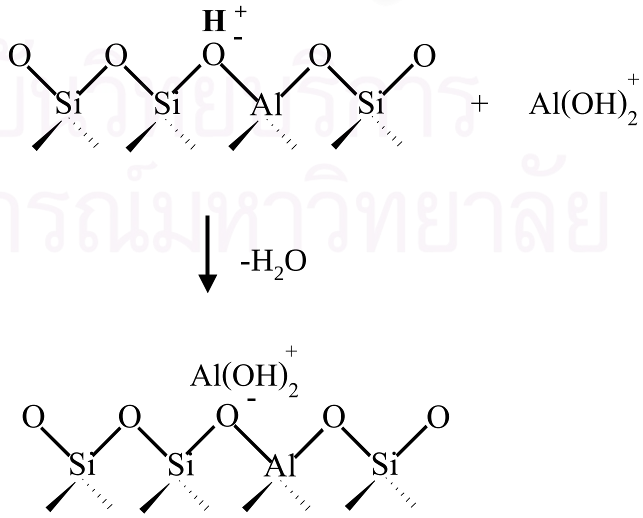


Figure 2.5 The enhancement of the acid strength of OH groups.

2.3 Shape selectivity

Many reactions involving carbonium intermediates are catalyzed by acidic zeolites. With respect to a chemical standpoint the reaction the reaction mechanisms are not fundamentally different with zeolites or with any other acidic oxides. The shape selectivity characteristics of zeolites influence their catalytic phenomena by three modes; reactant shape selectivity, product shape selectivity and transition state shape selectivity. These types of selectivity are illustrated in Figure 2.6.

Reactant selectivity results from the limited diffusibility of some of the reactants, which effectively enter and diffuse inside crystal pore structure of the zeolites. Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reactions. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect arising from local environment around the active site, the rate constant for a certain reaction mechanism is reduced of the shape required for formation of necessary transition state is restricted.

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and can pass through openings, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

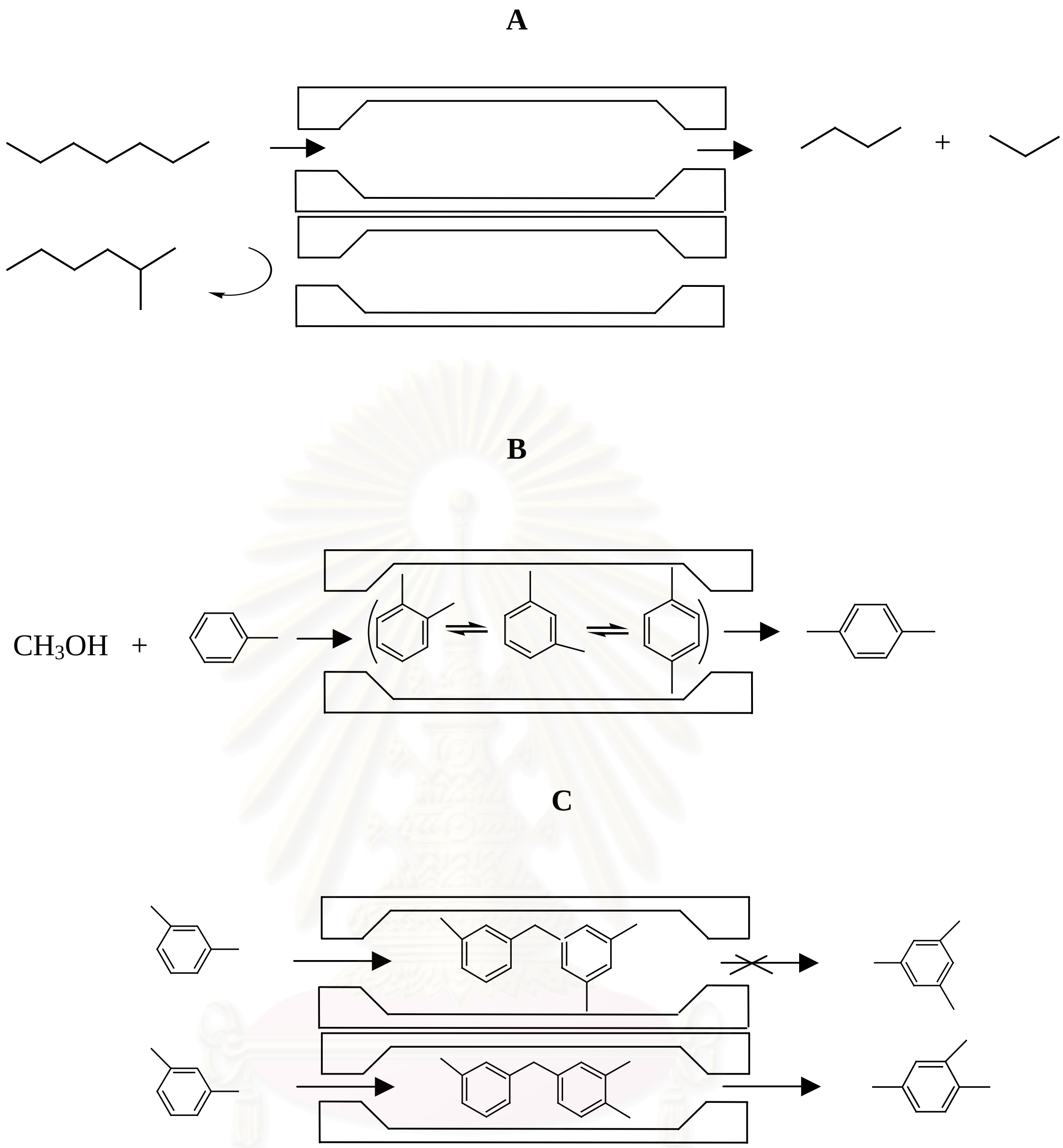
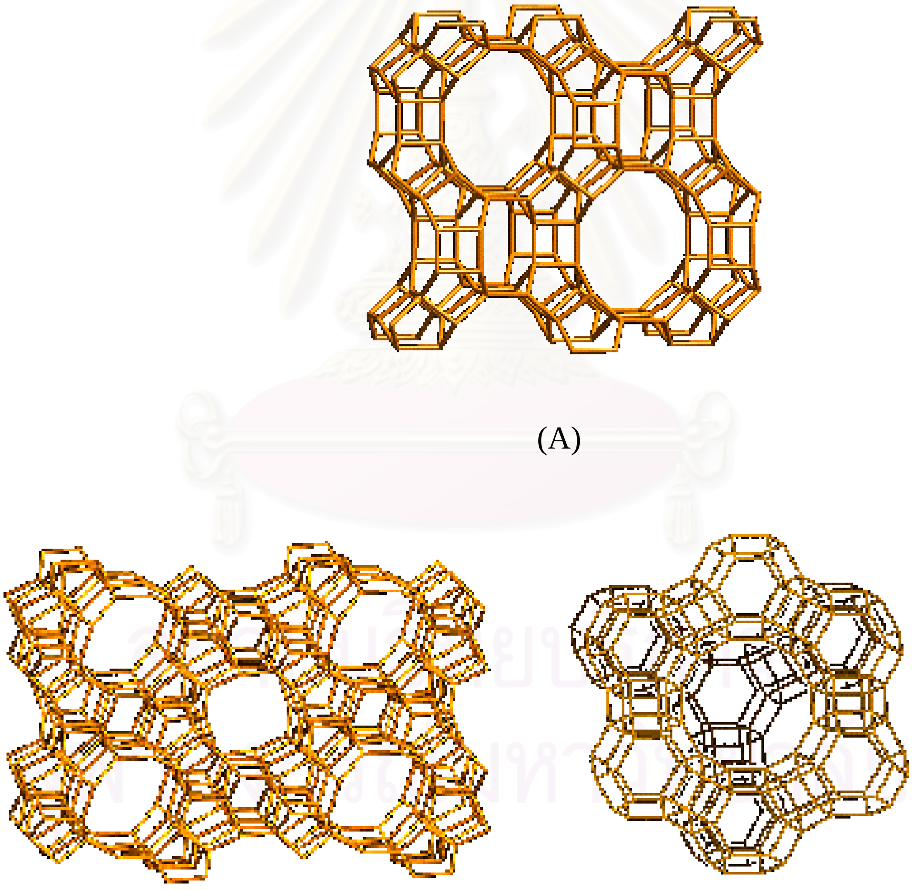


Figure 2.6 Three types of selectivity in zeolite: (A) Reactant selectivity (B) Product selectivity (C) Transition-state selectivity.

2.4 Structure and chemical composition of zeolite mordenite

An alternative formula for mordenite is Na_8 $[(AlO_2)_8$ $(SiO_2)_{40}].24H_2O$, which represents the range of possible cation occupancies of channels in the aluminosilicate framework. This framework is made from complex chains of 5-membered rings composed of SiO_4 and AlO_4 tetrahedra. These rings are cross-linked by 4-tetrahedra rings, to form twisted 12-tetrahedra rings around nearly cylindrical channels parallel to the c-axis. Aluminium is enriched in the 4-tetrahedra rings. Mordenite forms either from hydrothermal alteration, or from lower temperature transformation, of volcanic glasses. Mordenite-like phases include dachiardite, epistilbite, ferrierite and bikitaite. Mordenite is a large-pore zeolite having an orthorhombic crystalline structure. The strurctrue consists of chains that are crosslinked by the sharing of neighboring oxygens. The main cage has two exits, through two eight-member rings. The main channel parallel c axis with dimensions of 6.7 × 7.0 Å (12-member ring) and are linked by small channels parallel to b axis with 2.9 × 5.7 Å (8-member ring). ZSM-5 has pore aperture of 10-member ring and pore diameter of 0.56 nm. USY has larger pore diameter (0.74 nm) than mordenite and ZSM-5 as shown in Figure 2.7.



(A)

(B) (C)

Figure 2.7 (A) Mordenite, a large-pore zeolite. (B) ZSM-5. (C) USY.

2.5 Structure and structure modification

There are three structural aspects: the basic arrangement of the individual structural units in space, which defines the framework topology; the location of charge-balancing metal cations; and the channel-filling material, which is water, as the zeolite is formed. After the water is removed, the void space can be used for adsorption of gases, liquids, elements, and many other substances. Modern tools such as X-ray crystallography have provided a very detailed description of many structures.

2.6 Olefins process

Olefins found as by-products of the cracking of petroleum, are the most important source of industrial olefins. Cracking may be accomplished with or without a catalyst, but if a catalyst is not used considerably, higher temperatures are required. Olefins are produced from steam cracking of hydrocarbons such as ethane, propane, butane, naphtha and gas oil in tubular coils installed in externally fired heaters. Due to uncertainty of oil prices, depression of product prices, over capacity of olefins facilities, and oversea competition, the olefins industry has struggled to maintain minimum cost and process flexibility. During the past decades, various research and developmental work were pursued to find processes using alternative and providing cost advantages.

2.7 Ethanol

Ethanol or ethyl alcohol has been described as one of the most exotic synthetic oxygen containing organic chemicals because of its unique combination of properties as a solvent, a germicide, a beverage, an antifreeze, a fuel, a depressant, and especially because of its versatility as a chemical intermediate for other organic chemicals.

Ethanol under ordinary conditions is a volatile, flammable, clear, colorless liquid. Its odor is pleasant, familiar, and characteristic, as is its taste when it is suitably diluted with water. The physical and chemical properties of ethyl alcohol are primarily dependent upon the hydroxyl group. This group imparts polarity to the molecule and also gives rise to intermolecular hydroxyl bonding. A summary of physical properties of ethanol is presented in Table 2.1.

The energy crisis of the early seventies may have generated renewed interest in ethanol fermentation. Ethanol can be derived by fermentation processes from any material that contains sugar. The many and varied raw materials used in the manufacture of ethanol via fermentation are conveniently classified under three types of agricultural raw materials: sugar, starches, and cellulose materials. Sugar (from sugar cane, sugar beet, molasses, and fruit) can be converted to ethanol directly. Starches (from grains, potatoes) must first be hydrolyzed to fermentable sugars by the action of enzymes from malt of molds. Cellulose (from wood, agricultural residues, waste sulfite liquor from pulp and paper mills) must likewise be converted to sugar generally by the action of mineral acids.

Dehydration of ethanol has been affected over a variety of catalysts among the synthetic and naturally occurring aluminas, silica-alumina, and activated alumina. Operating space velocity is chosen to ensure that the two consecutive reactions go to completion, avoiding the need to recover and recycle unreacted ethanol. The dehydration is endothermic, and temperature is a critical operating parameter: high temperature produce aldehydes and low temperatures, ethers. The catalyst is usually regenerated with steam and air every few weeks to remove carbon deposits.

$$2C_2H_5OH \longrightarrow CH_3CH_2OCH_2CH_3 + H_2O$$

$$CH_3CH_2OCH_2CH_3 \longrightarrow 2C_2H_4 + H_2O$$

Scheme 2.1 Ethanol dehydration.

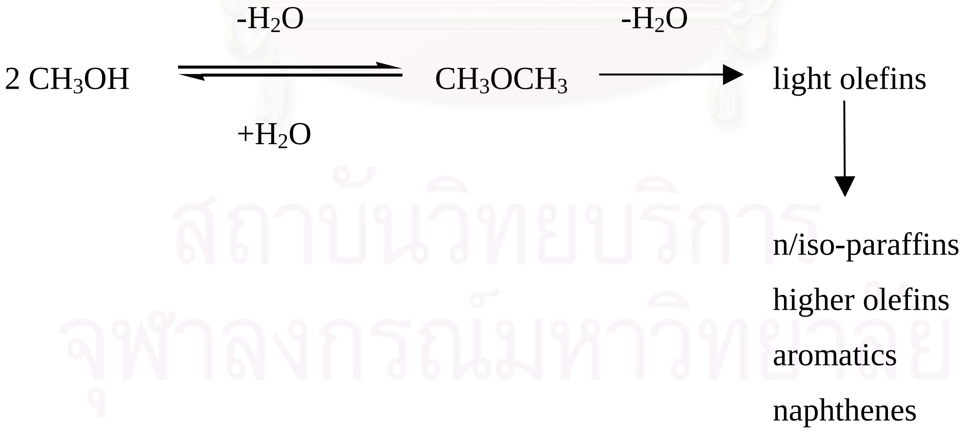
Table 2.1 Physical properties of ethanol (5)

Property	Value
freezing point, °C	-114.1
normal boiling point, °C	+78.32
critical temperature, °C	243.1
critical pressure, kPa	6383.48
critical volume, L/mol	0.167
critical compressibility factor, z, in PV = znRT	0.248
density, g/mL	0.7893
refractive index	1.36143
$\Delta n_D/\Delta t$, 20-30°C, per °C	0.000404
surface tension, at 25°C, mN/m (= dyn/cm)	231
viscosity, at 20°C, mPa.s (= cP)	1.17
solubility in water, at 20°C	Miscible
heat of vaporization, at normal boiling point, J/g	839.31
heat of combustion, at 25°C, J/g	29676.69
heat of fusion, J/g	104.6
flammable limits in air	
lower, vol %	4.3
upper, vol %	19.0
autoignition temperature, °C	793.0
flash point, closed-cup, °C	14
specific heat, at 20°C, J/(g °C)	2.42
thermal conductivity, at 20°C, W/(mK)	0.170
dipole moment, liq at 25°C, Cm	5.67×10^{-30}
magnetic susceptibility at 20°C	0.734×10^{-6}
dielectric constant at 20°C	25.7

2.8 Methanol to olefins

The methanol is converted to either gasoline (methanol-to-gasoline, MTG) or olefins (methanol-to-olefin, MTO), depending on the catalyst and/or can be blended with gasoline.(6) The commercial MTG reaction runs at temperatures around 400°C and a methanol partial pressure of several bars and uses a ZSM-5 catalyst. These are the optimal conditions for converting the olefins that form within the catalyst into paraffins and aromatics. However, the product mixture consists of about 40% light olefins. A number of attempts were made to selectively form light olefins from methanol, not only on medium pore zeolites but also on small-pore zeolites. By adjusting the reaction condition (rising the temperature to 500°C) as well as the catalyst applied, one can increase dramatically the olefin yield. This discovery led to the development of the MTO process, which generates mostly propylene and butylene, with high-octane gasoline as a byproduct. However, the catalyst can be modified in such a way that even more ethylene is produced.

The main reaction steps of methanol conversion to hydrocarbons can be summarized as follows:



Scheme 2.2 The main reaction steps of methanol conversion to hydrocarbons.

Methanol is first dehydrated to dimethyl ether. The equilibrium mixture is then converted to light olefins. In the last step of this scheme, the light olefins react to form paraffins, aromatics, naphthenes and higher olefins by hydrogen transfer, alkylation and polycondensation. It was proposed that the intermediate in the dehydration of methanol to dimethyl ether over solid acid catalysts is a protonated surface methoxy, which is subjected to a nucleophilic attack by methanol. The subsequent conversion of light olefins to paraffins, aromatics, naphthenes and higher olefins, which proceeds via classical carbenium ion mechanisms with concurrent hydrogen transfer, is well known from hydrocarbon chemistry in acid media. However, the second step that represents the initial C-C bond formation from the C_1 reactants, has been the topic of an extensive discussion throughout the years.

2.9 Ethanol to olefins

Ethylene is the key product in the reaction and the general pathway for production of different hydrocarbons has been shown to be as follows:(7)

$$C_2H_5OH \longrightarrow C_2H_4 \longrightarrow C_2H_{2n} \longrightarrow \text{paraffins} + \text{primary aromatics}$$

$$\text{primary aromatics} \xrightarrow{\text{isomerization / dealkylation}} \text{secondary aromatics}$$

Scheme 2.3 The main reaction steps of ethanol conversion to hydrocarbons.

It has been shown before that all aromatic and non-aromatic products can be starting from ethylene and the formation of paraffins and aromatics from olefins occurs simultaneously. The formation of aromatics can be explained by a scheme similar to that proposed for methanol conversion.

Usually the formation of ethoxy groups is the main intermediate step in forming olefins.(8) Surface ethoxy groups are converted to ethylene. The possible mechanisms of diethyl ether and ethylene formation were shown in Figures 2.8 and 2.9.

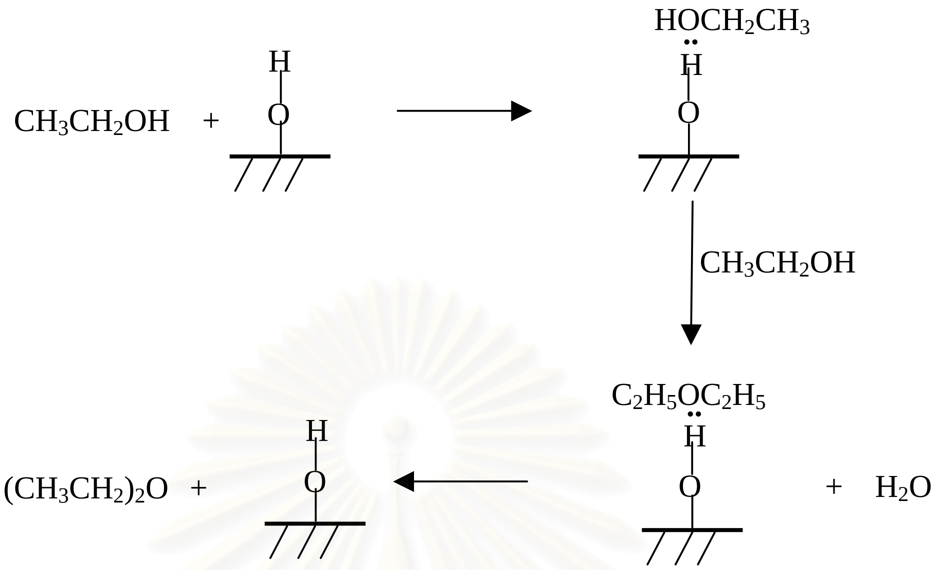


Figure 2.8 The formation of diethyl ether.

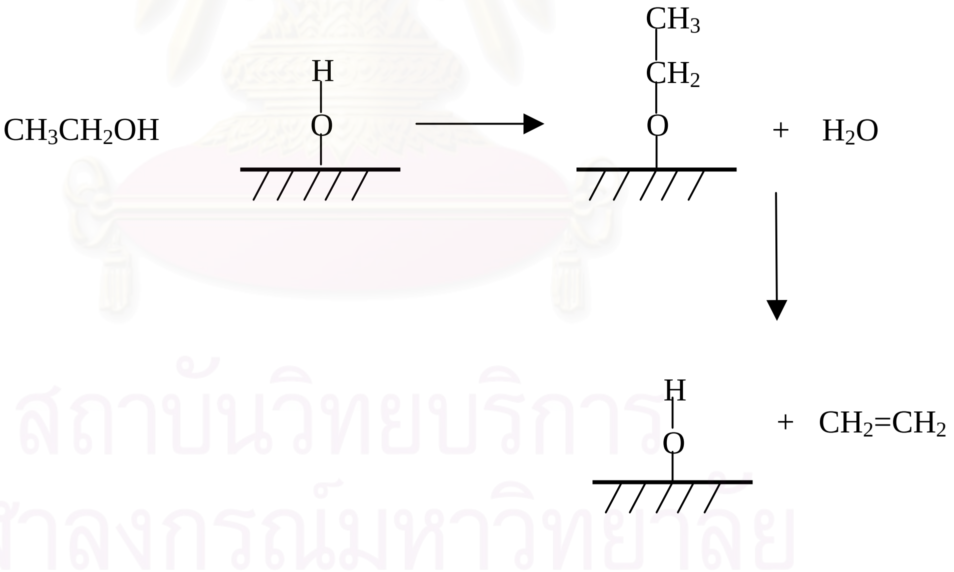
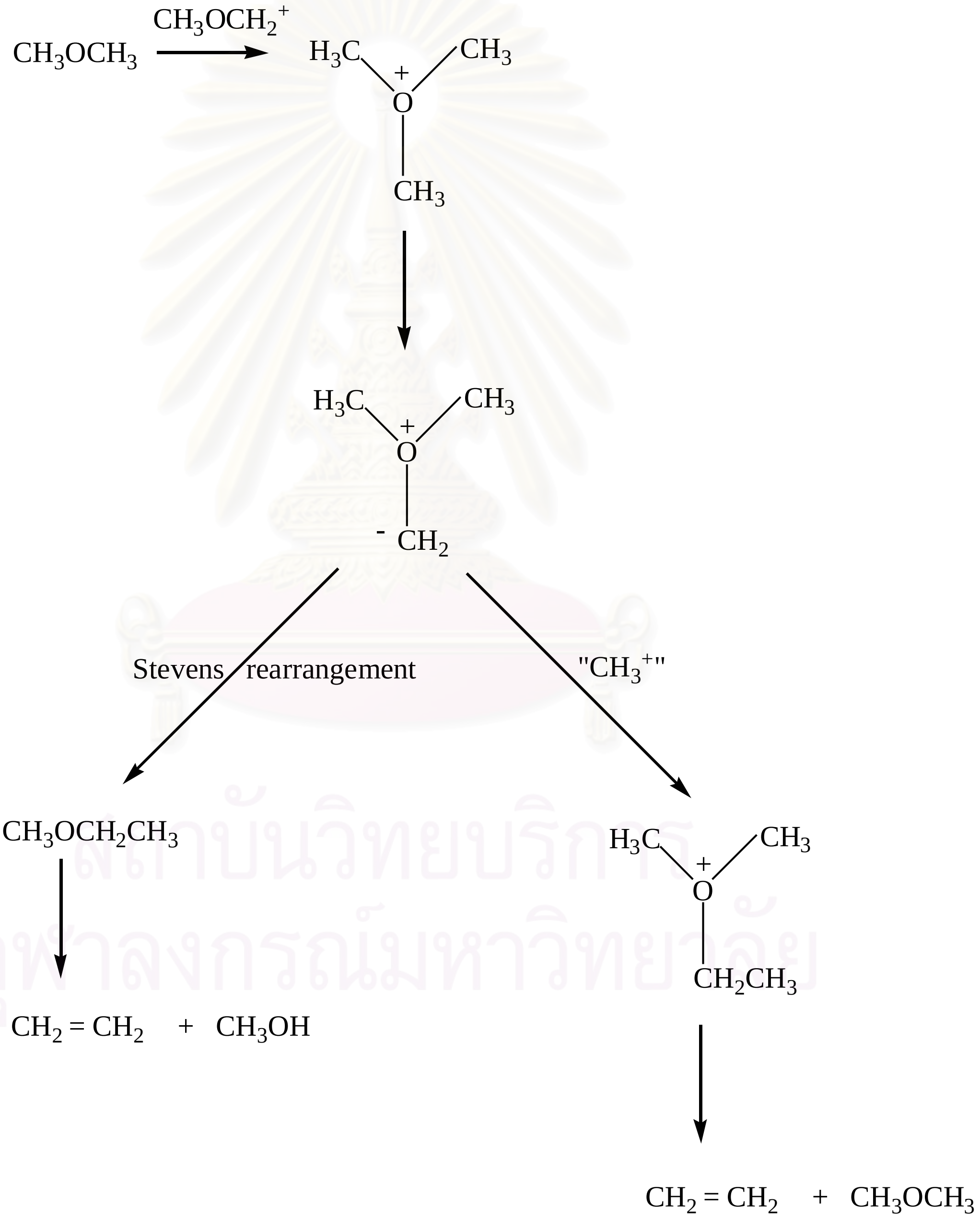


Figure 2.9 The formation of ethylene.

2.10 Mechanism of methanol conversion

2.10.1 The oxonium ylide mechanism

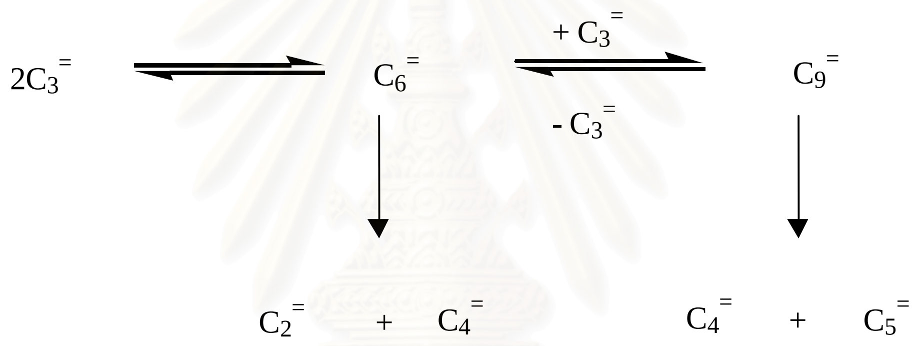
Froment *et al.*(9) postulated that dimethyl ether interacts with a Bronsted acid site of the solid catalyst to form a dimethyl oxonium ion, which reacts further with another dimethyl ether to form a trimethyl oxonium ion. This trimethyl oxonium ion is subsequently deprotonated by a basic site to form a surface associated dimethyl oxonium methyl ylide species. The next step is either an intramolecular Stevens rearrangement, leading to the formation of methyl ethyl ether, or an intramolecular methylation, leading to the formation of the ethyl dimethyl oxonium ion as shown in Scheme 2.4.



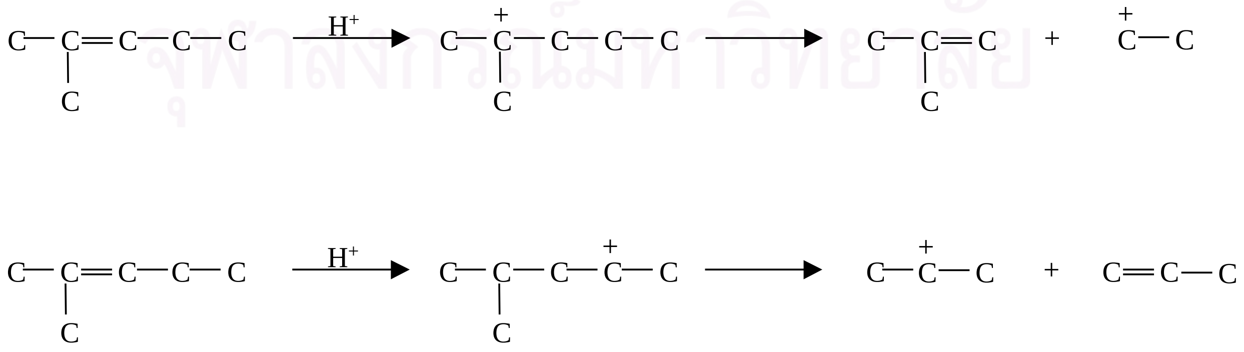
Scheme 2.4 Oxonium ylide mechanism.

2.10.2 Carbenium ion intermediate

Fougerit *et al.*(10) found C_3-C_7 olefins were primary products from the direct transformation of dimethyl ether and methanol. The C_6-C_7 alkenes were transformed by cracking with the formation of the products from carbenium ion intermediates. Hexene was transformed to propylene and butylene + ethylene. Propylene, butylene and pentene was mainly transformed through successive oligomerization and cracking steps as shown in Scheme 2.5. The formation of ethylene requires very unstable carbenium ions as intermediates. The cracking of isohexanes results from n-hexene isomerization as shown in Scheme 2.6. The formation of the other products, which involve more stable intermediates, was much more favoured.

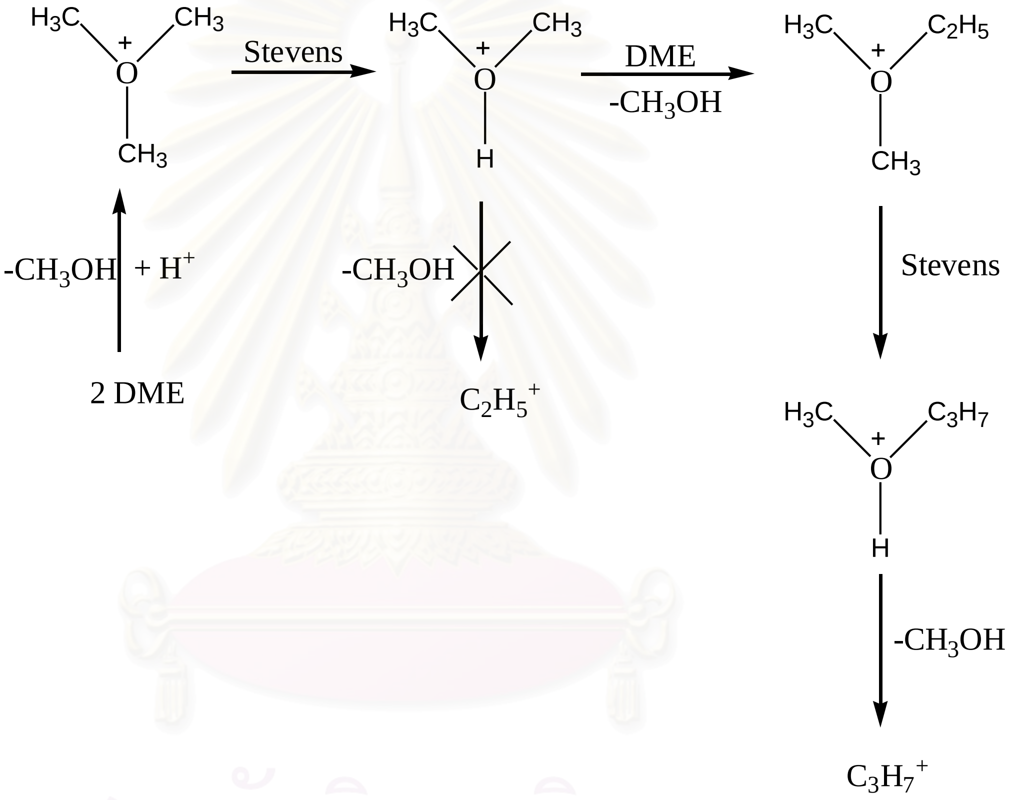


Scheme 2.5 The oligomerization and cracking steps.



Scheme 2.6 The cracking of isohexanes.

It can be proposed that the formation of the ethyl dimethyloxonium ions, its Stevens rearrangement and the formation of an isopropyl carbenium ion would be much faster than the formation of the very unstable ethyl carbenium ion as shown in Scheme 2.7. It should be emphasized that the Stevens rearrangment occurs through ylide intermediates. In the rearrangement of the ethyl dimethyloxonium ion, the ylide intermediate $(CH_2)O(CH_3)CH_2CH_3$ should be favoured in comparison to $(CH_3)O(CH_3)CHCH_3$ because of the higher acidity of the hydrogen of the methyl group as shown in Figure 2.10.



Scheme 2.7 The formation of isopropyl carbenium ion

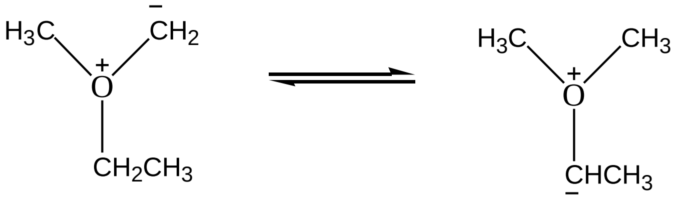


Figure 2.10 Delocalization of ethyl dimethyloxonium ion.

2.11 Literature reviews

2.11.1 Ethanol conversion

In 1982, Oudejans *et al.*(11) studied the conversion of ethanol over zeolite H-ZSM-5 in the presence of water. Above 272°C up to 50-wt% of aromatics were found while at lower temperatures dehydration and oligomerization predominate. Water added to the feed appears to increase the yield of aromatic. A low space velocity results in a high selectivity for aromatics whereas at high space velocity dehydration becomes more important. Water was assumed to decrease the rate of deactivation. Dealiminated zeolite H-Y and dealuminated H-mordenite show only dehydrative activity while dealuminated H-mordenite deactivated rapidly.

In 1987, Mao *et al.*(12) studied the conversion of ethanol to ethylene using ZSM-5/Zn, ZSM-5/Zn-Mn compared to ZSM-5 catalysts at temperature 400°C. Such an unusual selectivity of ethanol to ethylene was observed with ethanol mixed with other C_1-C_4 alcohols or in aqueous solutions. In both cases, ZSM-5 zeolite gave much lower yields in ethylene.

In 1990, Nguyen *et al.*(13) reported the conversion of aqueous ethanol over ZSM-5 (Si/Al = 21) and Asbestos-ZSM (Si/Al = 26) zeolites. Diethyl ether was found as a reaction intermediate at reaction temperatures below 260-270°C for both zeolites. Below 260-270ºC, the two-step pathway with diethyl ether as the intermediate coexists with the direct conversion- to-ethylene route. Above 260-270ºC, the one step path for the direct-conversion-to-ethylene predominates.

In 1997, Talukdar *et al.*(7) studied the conversion of aqueous ethanol to hydrocarbons over HZSM-5 catalyst (Si/Al = 206 and 40) at temperature 400-500°C. The yield and products distribution were influenced by catalyst-binder (alumina) composition, dilution of feed and the Si/Al ratio of the catalyst. Light olefins can be obtained in good yield at high temperature, in the absence of binder, with diluted feed and higher Si/Al ratio.

In 1990, Chaudhuri *et al.*(14) studied ethanol conversion over HZSM-5. Ethanol was converted to a mixture of higher aliphatic and aromatic hydrocarbons. A strong non-linear dependence of activity and selectivity upon the concentration of strong Bronsted acid sites in HZSM-5 exists. For HZSM-5 containing less than one proton per unit cell, it was not observed an appreciable concentration of hydrocarbons larger than ethylene. Ethanol was converted completely to hydrocarbons. Water had only little effect upon the rate or the selectivity of the reaction. The concentration of strong Bronsted acid sites increases the activity. Presence of non-protonated hydrocarbon molecules at vicinal strong Bronsted acid sites may be important for the formation of higher hydrocarbons.

In 2002, Aunalom et *al.*(15) reported the conversion of ethanol to ethylene on modified ZSM-5 zeolites containing iron metal. The catalysts were prepared by either ion exchange or gel preparation method. The optimum condition of reaction temperature, the percentage of Fe loading and GHSV were 600°C, 5% by weight and 2000 h^{-1}, respectively. The main products were ethylene and diethyl ether. The selectivity to ethylene was 83 %. Decreasing space velocity of ethanol from 6000 h^{-1} to 2000 h^{-1} resulted in the increase of selectivity to ethylene. The catalyst prepared by ion exchange method has higher ethylene selectivity than that prepared by gel preparation method.

In 2002, Aguayo *et al.*(16) studied variables in the transformation of aqueous ethanol into hydrocarbons on an HZSM-5 zeolite. The catalyst was prepared by agglomerating the HZSM-5 zeolite (15%wt) with bentonite (30%wt) and using fused alumina as an inert diluent. Ethylene was formed directly by ethanol dehydration which occurs on weak acid sites, whereas the subsequent reaction steps requir sites of higher acid strength. Below 400°C the catalyst was stable under regeneration cycles.

In 2003, Mohamed *et al.*(17) studied the transformation of ethanol on Fe ion-exchanged mordenite, which prepared in the solution and solid states at temperature of 200-400°C. Ethane and methane were found as major products, as well as acetaldehyde and acetone. The reaction activity increased with increasing reaction temperature and Fe content. In solid state ion-exchange method selectivity to ethane is 75.9%.

2.11.2 Methanol conversion

In 1993, Marchi *et al.*(2) studied the conversion of methanol to light olefins over dealuminated mordenite at 480°C. The feed was methanol-water (30%-70%wt). The rapid deactivation by coke was observed. The reduction of the number of strong acid sites led to a lower deactivation by coke and a higher selectivity to light alkenes. Decreasing the partial pressure of methanol and the addition of water to the feed led to higher yields of light alkenes and less coke deposition. Water competed with alkenes and aromatics for the Lewis and Br∅nsted acid sites.

In 1996, Benito *et al.*(18) studied effect of Si/Al ratio and of acidity of H-ZSM-5 zeolites on the product of methanol conversion. It has been determined that alkenes (ethylene, propylene and butylenes) were the first reaction product, the amount of each depending on the Bronsted/Lewis ratio and on acid site density. The formation of olefins of higher molecular weight as the Si/Al ratio of the catalyst increases, explained on the basis of a mechanism of propagation of oxonium ions.

In 1997, Jarallah *et al.*(19) studied effect of metal impregnation on the activity, selectivity using a high silica MFI zeolite for methanol conversion to light alkenes at 400°C. The silicalite zeolite was impregnated with metal nitrates of Ag, Ca, Cd, Cu, Ga, In, La and Sr. Incorporation of La and Ag led to an improvement in light alkene selectivity by 18% and 14% respectively. Incorporation of the metal atoms within the catalyst pores could also lead to slight reduction in the catalyst active life-on-stream as a result of coke deposition.

In 1998, Nishi *et al.*(20) studied formation of multi-branched-chain aliphatics in methanol conversion over modified mordenites. The influences of zeolite pore structure, dealumination and Na ion exchange on the product distribution were observed. The selectivity to multi-branched-chain aliphatics on H-form mordenite was higher than ZSM-5 and Y zeolites. The dealumination to mordenite suppressed the formation of aromatics and coke by decreasing the density of strong acid sites. The basic sites generated by Na ion exchange would promote the formation of side chains, which results in higher selectivity of multi-branched-chain aliphatics.

In 1998, Canizares *et al.*(21) studied Ni and Pd supported on H-mordenite catalysts. The isomerization of n-butane was used as a test reaction for the activity of the catalysts. The results show no difference between two loading methods: ion exchange and impregnation when Ni is used. At low Ni content isomerization was improved because more butenes were formed. However, high Ni content led to a decrease in its selectivity to isobutane. A very different behavior was found with Pd/HM catalysts. Pd was present as small particles in the ion-exchange method, but formed cluster in the impregnation method. Higher conversion and isobutane selectivity were obtained for the impregnated catalysts.

In 1999, Lucke *et al.*(22) studied coupled methanol hydrocarbon cracking (CMHC) reaction with liquid hydrocarbons as well as gaseous hydrocarbons as the co-feed. CMHC reaction was carried out using methanol (99.8%) and liquid (e.g. n-butylene, n-decane, n-hexane, cyclohexane), as feedstocks. The production of olefins depended on the type of hydrocarbon co-feed. Butylene or olefins mixture gave better olefins yield and higher methanol conversion.

In 1999, Kolboe *et al.*(23) studied the conversion of methanol to hydrocarbons over H-beta zeolite catalysts at 400ºC. The experiments were carried out at a methanol pressure of about 150 mbar, using a WHSV of 0.8 or 7.2 h^{-1}. At WHSV = 0.8 h^{-1} the methanol conversion was still 30% after 16 h on stream. Ethylene, propylene, propane, isobutane, hexamethylbenzene and some pentamethylbenzene were the dominant products. Methane was not only initially a minor product, but with progressive catalyst deactivation it became a major product.

In 1999, Fougerit *et al.*(10) studied the conversion of a dimethyl ether-water mixture into hydrocarbon using dealuminated mordenite catalyst (Si/Al ratio = 80) at 530ºC. A dimethyl ether-water mixture was chosen instead of methanol in order to limit thermal effects due to the exothermic of the transformation of methanol to dimethyl ether. The main products were methanol, C_1-C_{12} hydrocarbons. The C_3-C_7

alkenes were primary products. Ethylene was obtained from secondary cracking of C_3-C_7 alkenes products. Propane was formed from Stevens rearrangement of oxonium ions and higher alkenes from methylation of propylene. Aromatics were rapidly alkylated by dimethyl ether or methanol. Methane was formed directly from dimethyl ether or methanol, but also from the demethylation of polymethylbenzenes and of coke molecules.

In 2003, Franklin *et al.*(24) studied the influence of the degree of substitution of the cobalt and manganese ions into AlPO-18 structure. The conversion of methanol to light olefins (MTO) was investigated at 350°C. The activity for methanol conversion increased with metal content up to 2 atom% after 2 h on stream. These catalysts show good stability after regeneration, suggesting that there is no leaching of the active metal centers.

In 2004 Wu *et al.*(25) studied conversion of methanol to light olefins over SAPO-34 catalyst. The feed of methanol (20 mol%) and water (80 mol%) was shown to be the most optimum feed. The optimum reaction temperature was at 400°C. Higher temperatures led to faster catalyst deactivation while lower temperatures led to higher selectivities to $CO+CO_2$ and CH_4, but lower methanol conversion.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals used were analytical grades, and obtained as listed in Table 3.1:

Table 3.1 Chemicals and suppliers

Chemicals	**Suppliers**
Aluminium oxide	Merck, Germany
Ammonium chloride	Fluka Chemie A.G., Switzerland
Cobalt chloride hexahydrate	Fluka Chemie A.G., Switzerland
Cupric chloride 2.5 hydrate	J.T. Baker, USA.
Ethanol	Merck, Germany
Iron (III) chloride anhydrous	Merck, Germany
Hydrochloric acid	Merck, Germany
Manganese sulfate monohydrate	Fluka Chemie A.G., Switzerland
Nickel nitrate hexahydrate	CARLO ERBA,
Rhodium trichloride	BHD Laboratory, England
Silver nitrate	Merck, Germany
Sodium form mordenite (Si/Al = 5)	Malaysia
Rhodium chloride monohydrate	BHD Laboratory, England
Ultra high purity nitrogen gas (99.99%)	Thai Industry Gas Co., Ltd., Thailand
Ultra high purity hydrogen gas (99.99%)	Thai Industry Gas Co., Ltd., Thailand
Ultrastable zeolite Y (USY)	The PQ Corporation, Japan
Zeolite Socony Mobil no.5 (ZSM-5)	Japan
Zinc chloride	BHD Laboratory, England

3.2 Equipment and apparatus

Oven and furnace

The catalysts were preliminary dried at 100°C in a Memmert UM-500 oven and further calcined at 550°C in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

Catalytic apparatus

The catalytic apparatus assembled in laboratory comprises a quartz tubular reactor of 10-mm. inner diameter. Catalytic apparatus were shown in Figures 3.1. Ethanol and water were fed as liquids by using syringe pump (No.15). Ethanol gas was carried by the nitrogen through a catalyst bed (No.7) set in a catalytic reactor (No.5) contained inside a furnace (No.8).

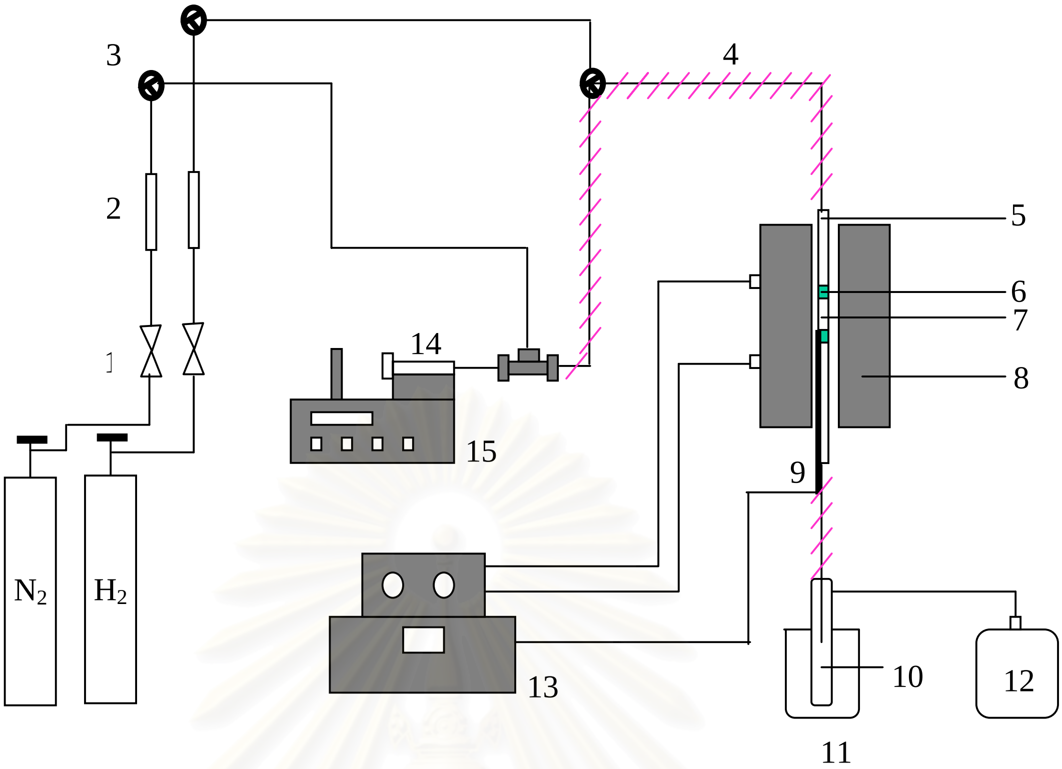


Figure 3.1 Schematic diagram of the reaction apparatus

1 = needle valve, 2 = flow controller, 3 = three-way valve,
4 = heater cable, 5 = tubular reactor, 6 = quartz wool,
7 = catalyst, 8 = electric furnace, 9 = thermocouple,
10 = cold trap, 11 = dry ice-acetone bath, 12 = Tedlar bag,
13 = temperature programmed controller,
14 = syringe, 15 = syringe pump.

In addition, for some experiments in this work, another route for the ethanol supply was by heating ethanol using water bath (shown in Fig. 3.2, No. 17 below).

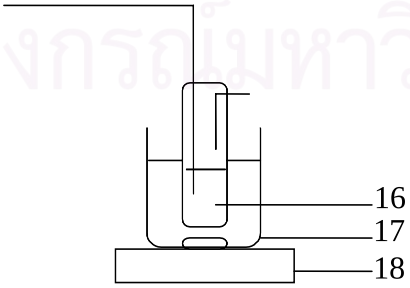


Figure 3.2 Ethanol supply

16 = ethanol container, 17 = water bath, 18 = heater.

3.3 Characterization methods

3.3.1 Fourier-transform infrared spectroscopy (FT-IR)

Fourier-transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer. The samples were made into a KBr pellet. Infrared spectra were recorded between 400 to 4000 cm^{-1} in transmittance mode.

3.3.2 X-ray powder diffraction (XRD)

The XRD of catalysts were obtained on Rigaku, DMAX 2002/Ultima Plus. X-ray diffraction is used to obtain information about the structure and composition. Common compounds can be identified using tabulations of reference patterns.

3.3.3 X-ray fluorescence spectrometry (XRF)

Silicon (Si), aluminum (Al) in the catalysts were determined using a SISONS instrument ARL 8410 X-ray fluorescence spectrometer.

3.3.4 Thermogravimetric analysis (TGA)

Thermogravimetric measurements were performed on a TA instrument thermogravimetric analyzer (SDT 2960) at the heating rate of 10°C/min under nitrogen atmosphere.

3.3.5 Nitrogen adsorption (Brunauer-Emmett-Teller method, BET)

BET specific surface area of the catalysts was carried out using a Quantachrome Autosorb-1 nitrogen adsorptometer. The principle is by adsorption of a particular molecular species from a gas or liquid onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample.

3.3.6 Gas chromatography (GC)

Hydrocarbon gases were analyzed using a HP-6890 (Hewlett Packard) gas chromatography with Carbowax Porasite column, Chromosorb column, Carbowax column, Carbopak B column, Hayesep Q, Hanesep T column, Molecular Sieve 5A column, Hanesep Q column and Molecular Sieve 13X column. The arrangement of columns is shown in Figure 3.3. The condition used for GC is in Table 3.2.

Table 3.2 Conditions used in GC

	Front Inlet	Back Inlet
Detector	FID	TCD
Carrier gas	Hydrogen	Helium
Flow rate (cm^3/min)	19.5	22
Detector temperature (°C)	170	150

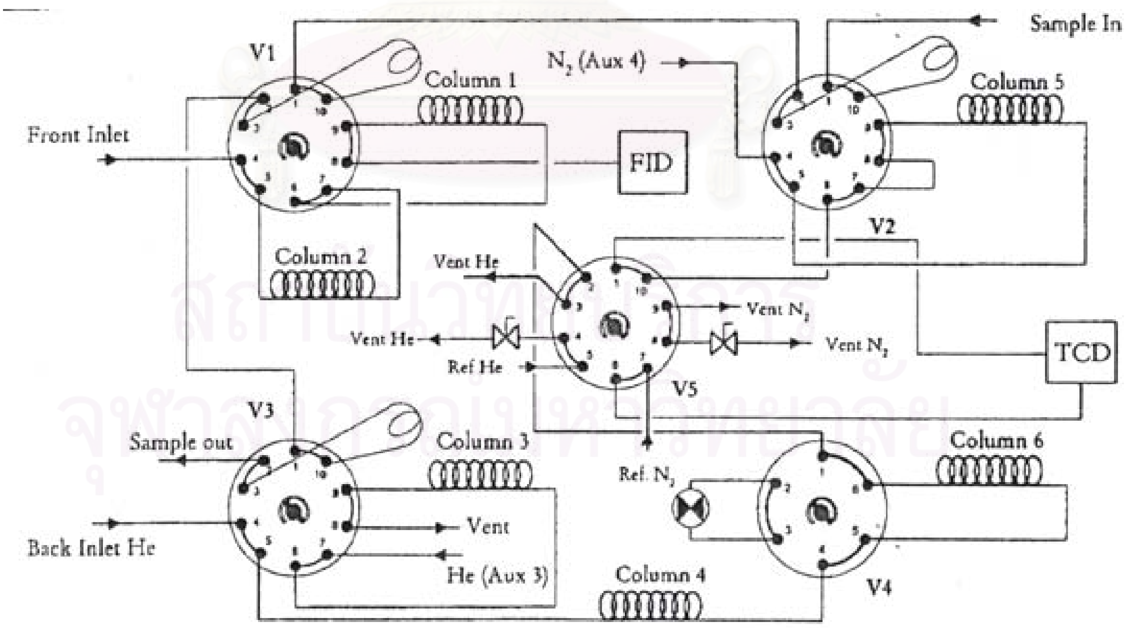
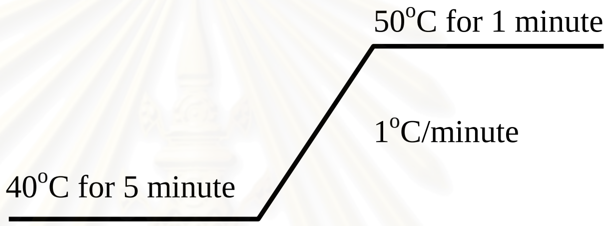


Figure 3.3 Arrangement of columns in GC

Liquid products were performed using a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25μm film thickness) DB-1 capillary column. The condition used for the determination of %conversion of Ethanol was set as follows:

Carrier gas : Nitrogen
Carrier gas pressure : 40 kPa
Detector temperature : 220 °C
Injection temperature : 220 °C
Programmed temperature :



3.4 Preparation of acidic mordenite (H-MOR) (1)

Na-MOR (40.0 g) was mixed with 500 mL of 0.05 M ammonium chloride solution and boiled with stirring for 24 h. The ammonium-form mordenite obtained was separated from the solution by centrifugation (3700 rpm, 30 min) and washed several times with deionized water until no chloride observed by precipitating with 0.1 M silver nitrate solution. The sample was dried at 100ºC and calcined in a muffle furnace at 550ºC for 5 h.

3.5 Preparation of dealuminated mordenite (D-MOR)

H-MOR (1.0 g) and 20 mL of 8.0 M HCl solution were added to the reflux distillation set up. The mixture was heated using an oil bath at 80ºC for 5 h. The solids were separated from the solution by centrifugation (3700 rpm, 30 min) and washed several times with deionized water until no chloride observed. The resulting solid was dried at 100°C and calcined in a muffle furnace at 550ºC for 5 h. It was characterized using XRD and XRF techniques.

3.6 Preparation of metal loaded catalysts

Two methods of metal loading were done. The metal salts used are: zinc chloride, manganese sulfate monohydrate, cobalt chloride hexahydrate, rhodium chloride monohydrate and nickel nitrate hexahydrate.

A. Solid state ion exchange

The D-MOR and metal salt (1% by wt) were mixed in a mortar and calcined in a muffle furnace at 550ºC for 5 h. The second metal salt (1% by wt) was mixed with DM/metal and then calcined in a muffle furnace at 550ºC for 5 h.

B. Impregnation

Solution of metal salt (1 mL) was dropped onto D-MOR (1g) in plastic bottle and shaked for 30 min., then calcined in a muffle furnace at 550ºC for 5 h. The second metal salt solution (1% by wt) was mixed with DM/metal and then calcined in a muffle furnace at 550ºC for 5 h.

3.7 Preparation of pellet catalysts

The catalysts were pressed towards a 0.7-mm thick self-supporting wafer using a stainless steel of a 13-mm inner diameter, in the similar manner to making KBr samples for IR measurement. The hydraulic press with pressing force of 5 tons was held on the catalyst wafer for 5 min. The catalyst wafer was crushed into tiny pellets of approximate size of 2 x 2 x 0.7 mm^3

3.8 Catalytic activity tests of the mordenite catalysts

The catalysis was carried out in an apparatus shown in Figure 3.1. The catalyst (1.0 g) was loaded into a quartz tubular reactor and held in place by a plug of quartz wool, the catalyst portion was covered with small amount of quartz wool. The gas lines were stainless steel tubing wrapped in the heating tape. The height of the catalyst portion was 25 mm. The catalyst was activated by flowing with N_2 (10 mL/min) or reduced by flowing with H_2 (10 mL/min) at 500ºC for 1 h. The ethanol was fed using syringe pump to mix with nitrogen at a constant WHSV of 1.0 h^{-1} (which was correspond to a gas flow of 10.0 mL/min). The feed was passed from the top through the catalyst. After a given time, the gaseous products were collected into a Tedlar bag and analyzed for hydrocarbon components using GC. For the liquid products, they were trapped in a Dewar cooled with dry ice/acetone. It was found many kinds of hydrocarbons in the gaseous products while in the liquid product, only ethanol was detected (determined by GC).

In this work, blank test was performed without catalyst in the reactor, at the same condition used in this work. The result showed that liquid trapped in the Dewar contained only ethanol. Therefore, it was concluded that percent conversion of the reaction was 100.

Parameters affecting the reaction were studied as follows:

A. Effect of metal loaded

The effect of single and mixed metals loaded onto mordenite was studied. Metals used are: Zn, Rh, Co, Mn, Cu, Fe, Ag, Ni

B. Effect of temperature

The reaction were performed at different temperatures: 350, 450 and 550ºC.

C. Effect of ethanol concentration

Different ethanol concentration, 10.0 and 99.9% was used for ethanol conversion.

D. Effect of activation and reduction

The catalysts were activated with N_2 at 500°C for 1 h or reduction with H_2 at 500°C for 1 h and were investigated their activity.

E. Effect of metal loading methods

Two different methods of metal loading: solid state ion exchange and impregnation, were compared.

F. Effect of dilution and amount of metal

The alumina (0.5 g) was packed at upper zone of the reactor tube and DM/metal (0.5 g) was packed at lower zone. It was tested catalytic activity.

In the other experiment, varying amount of metal in the catalyst (namely Zn and Ni) was compared between 1 % and 5% (by wt) using impregnation method.

G. Other catalysts

Three types of zeolites were compared: D-MOR, ZSM-5 and USY.

3.9 Catalyst regeneration

Catalyst was run repeatedly and regenerated by calcination at 550ºC for 2 h.

3.10 Determination of coke deposition on the catalysts

The coke deposited on the catalysts was determined by the difference in mass before and after calcinations. The used catalysts were dried in an oven at the temperature of 100ºC for 2 h and calcined in a muffle furnace at 550ºC for 2 h. The coke amount was determined using Equation below.

$$\%\ \text{wt.coke} = \frac{(W_{af} - W_{be})}{W_{af}} \times 100$$

When, W_{af} = Weight of the used catalyst after calcination

W_{be} = Weight of the used catalyst before calcination

CHAPTER IV

RESULTS AND DISCUSSION

In this work, D-MOR was obtained by refluxing H-MOR with 8.0 M HCl. Then metal loading on the D-MOR was performed using two different methods (solid state ion exchange or SSIE and impregnation or IMP methods). The resultant catalysts were characterized by FT-IR, XRD, XRF and BET techniques.

4.1 Characterization of the dealuminated mordenite

The dealuminated mordenite and metal-mordenites were characterized using many techniques as follows.

4.1.1 Fourier-transform infrared spectroscopy (FT-IR)

The FT-IR spectra of D-MOR, DM/Zn and DM/Mn-Zn in Figure 4.1 and summarized in Table 4.1.

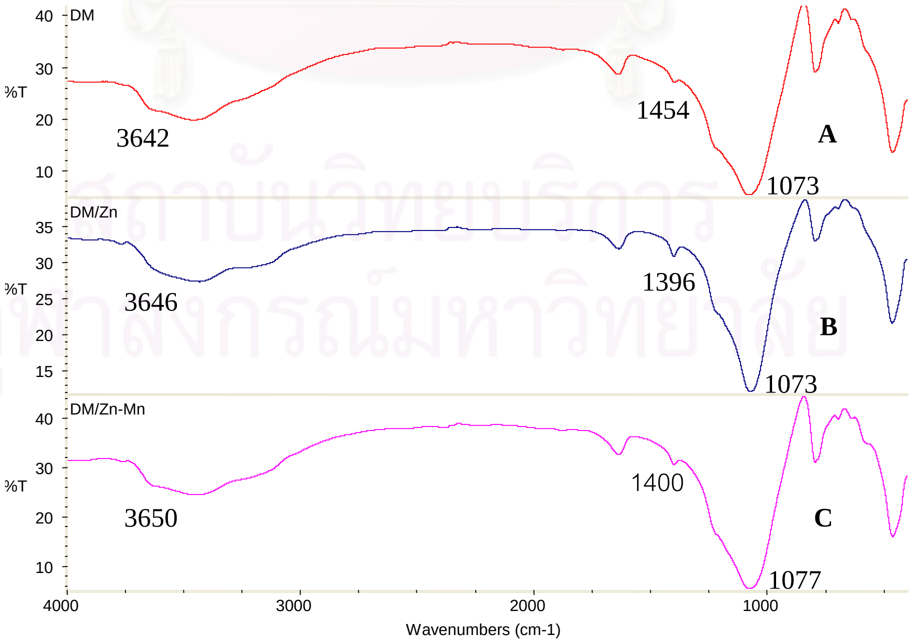


Figure 4.1 FT-IR spectra of (A) D-MOR, (B) DM/Zn and (C) DM/Mn-Zn

Table 4.1 The assignment for the FT-IR spectra of D-MOR, DM/Zn and DM/Mn-Zn

Wave number (cm^{-1})			**Assingment**
D-MOR	**DM/Zn**	**DM/Mn-Zn**	
3642	3646	3650	O-H stretching
1397	1396	1400	O-H bending
1073	1073	1077	Si-O stretching

The FT-IR spectrum of D-MOR shows characteristic absorption peaks of mordenite, O-H stretching at 3642 cm^{-1}, O-H bending at 1397 cm^{-1} and Si-O stretching at 1073 cm^{-1}.(35) After loading metal onto the mordenite, it was found that the O-H bending vibration appeared at 1396 and 1400 cm^{-1}. The shift to higher frequency (1077 cm^{-1}) of the Si-O stretching vibration also indicated that metal ions were coordinated.(36)

4.1.2 X-ray powder diffraction (XRD)

The XRD patterns of D-MOR, DM/Zn and DM/Mn-Zn were shown in Figure 4.2.

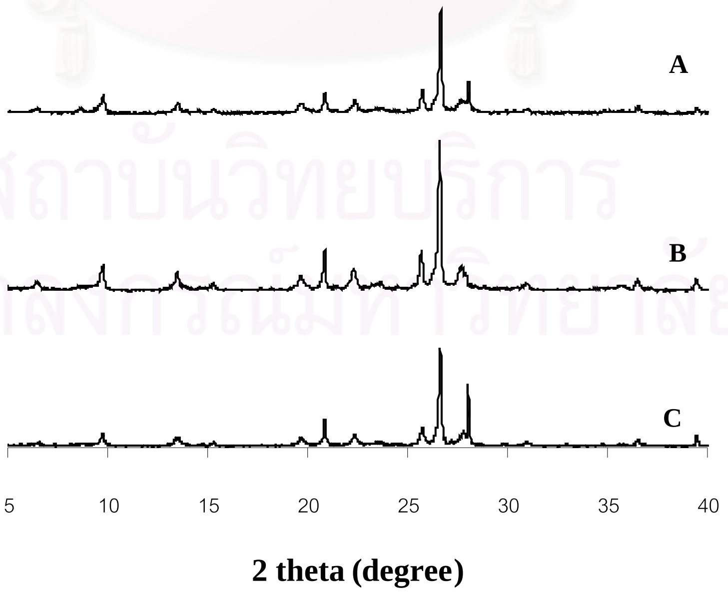


Figure 4.2 X-ray diffractograms of (A) D-MOR , (B) DM/Zn and (C) DM/Mn-Zn.

The XRDs patterns after metal loading did not show any change in mordenite structure. This was in good agreement with the previous report that the structure of the H-MOR after acid treatment with 6 M HCl solution did not change.(38)

4.1.3 X-ray fluorescence spectrometry (XRF) and nitrogen adsorption (Brunauer-Emmett-Teller method, BET)

Si/Al ratios in catalysts were determined by XRF and surface area was determined by BET, as seen in Table 4.2.

Table 4.2 Si/Al ratio by XRF and BET

Catalysts	Si/Al mol ratio	BET surface area (m^2/g)
Na-MOR	5.66	79
D-MOR	26.90	244
DM/Mn-Zn	24.91	165

After dealumination of Na-MOR catalyst, the XRF results showed that Si/Al ratio of D-MOR was increased (from the original 5.66). This was due to the leaching of aluminium from the framework of mordenite when refluxing with hydrochloric acid. It was reported that dealumination helps increase the olefin.(2)

When loaded with metal, DM/Mn-Zn gave similar Si/Al mole ratio (24.91) to D-MOR. D-MOR was shown to have higher surface area than Na-MOR due to hydrochloric acid leaching which eliminated aluminium from mordenite framework. The introduction of mesopores in mordenite could provide the accessibility of reactant into the active site.(37)

After loading metal, the surface area of the DM/metal catalyst was decreased. It might be due to metal oxide deposition into the mordenite pores. The results are similar to the previous report, a reduction of the volume and re-distribution of pore sizes after metal modifications of the silicalite was observed.(19)

As it was always reported that catalytic activity was affected by acidity of the catalyst. Therefore, it should be mentioned that there was a report on the study of acidity of mordenite.(38) By temperature programmed desorption of ammonia (NH_3-TPD) for the H-MOR which was treated with 1 M HCl solution for 3 h at 120ºC, the NH_3-TPD profiles presented two types of acid sites: weaker acid sites (the desorbed ammonia peak at temperature 180ºC) due to Bronsted acidity and stronger acid sites (the desorbed ammonia peak at 430ºC) due to Lewis acidity.

The optimal conditions were studied by varying type of metal loaded, temperature, metal loading methods, ethanol concentration and amount of metal.

4.2 Catalytic activity tests of the metal mordenite catalysts

4.2.1 Effect of type of metal loaded

Ethanol conversion and gas product distribution were investigated using single and mixed metals loaded into D-MOR catalysts by using solid state ion exchange method. The results were shown in Tables 4.3 and 4.4.

Table 4.3 Gas product distribution using single metal loaded mordenites

Product distribution (% mol)	**DM/Zn**	**DM/Mn**	**DM/Co**
C_1	2.2	1.6	3.2
C_2	0.7	1.8	3.4
C_2=	93.5	86.7	71.3
C_3	0.6	3.4	10.6
C_3=	2.2	4.2	5.4
C_2-C_4 =	96.2	91.7	78.1
C_1-C_5	3.7	8.2	21.7
%Coke	5.1	5.3	4.9

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 2 h, T_{EtOH} = 50°C, 99.9% EtOH, temperature 450°C.

It was found that all catalysts show high % selectivity to ethylene in the following order: DM/Zn > DM/Mn > DM/Co.

The result corresponded to previous report, AlPO-18/Mn gave better catalytic activity than AlPO-18/Co for conversion of methanol to hydrocarbons.(26) SAPO-34/Mn showed higher C_2-C_4 selectivity compared to SAPO-34/Co.(27) For the selectivity, ZSM-5/Zn was reported to show high ethanol conversion (99%) and selectivity to ethylene (82%) for 100% EtOH at 400°C. Zn ions substituted acid sites of catalyst by stabilizing the aluminium sites and prevented destruction of the zeolite crystallinity. (12) Zinc metal did not adsorb ethylene.(40) It gave selectivity to ethylene higher than other alcohols (methanol, propanol and butanol).(5, 36)

Amount of coke deposited on D-MOR and DM/metal catalysts at 450°C shown in Table 4.3 were similar.

Table 4.4 Ethanol conversion and gas product distribution using mixed metals loaded mordenites (SSIE)

Product distribution (% mol)	**DM/Mn-Zn**	**DM/Mn-Co**
C_1	13.1	13.2
C_2	2.3	3.3
C_2=	81.0	78.8
C_3	0.2	0.8
C_3=	2.9	3.1
C_2-C_4=	84.3	82.5
C_1-C_5	15.5	17.4
%Conversion	100	100
Yield of gas product (% wt.)	79.5	80.9
Yield of liquid product (% wt.)	18.0	16.4
%Coke (%wt of catalyst)	2.5	2.7

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, T_{EtOH} = 50°C, 99.9% EtOH, temperature 450°C.

The liquid product was used to determine %conversion as used in other work.(29) From GC chromatogram of the liquid product, no ethanol was detected, therefore, % conversion was 100 in all experiments.

The selectivity of DM/Mn-Zn catalyst in ethanol conversion was not different from that of DM/Mn-Co. Both catalysts show selectivity to ethylene. However, the composition of product is in between those of single metals. It was reported that the incorporation of Zn and Mn into ZSM-5 (ZSM-5/Mn-Zn) led to very selective catalysts for the ethanol dehydration.(12) The proposed mechanism of ethanol dehydration was shown in Figure 4.3. Ethanol was adsorbed on hydroxyl groups of the zeolite. The ethylene product was resulted from the conversion of ethoxy group.

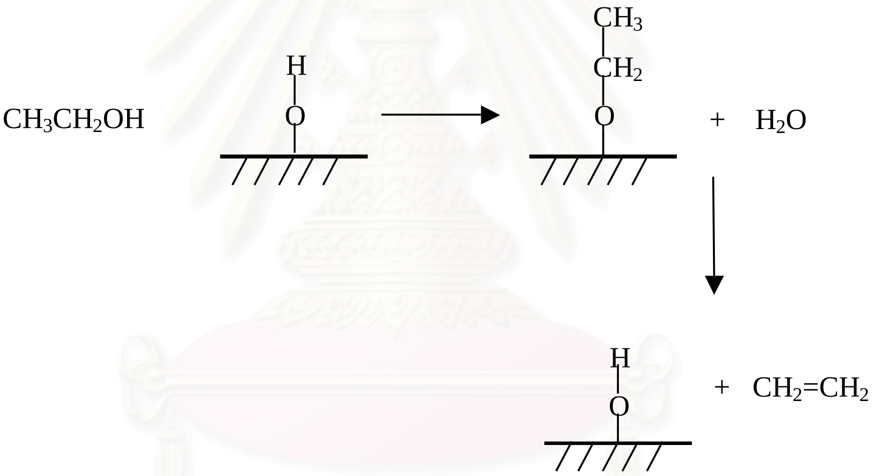


Figure 4.3 The mechanism of ethylene formation.

4.2.2 Effect of temperature

To investigate the effect of temperature on ethanol conversion, tests were performed using DM/Mn-Zn (SSIE) catalyst, which was activated with N_2 at 500°C for 1 h. The result was shown in Table 4.5.

Table 4.5 Ethanol conversion and gas product distribution using activated DM/Mn-Zn (SSIE) at various reaction temperatures

Product distribution (% mol)	**Temperature (°C)**		
	350	**450**	**550**
C_1	2.3	13.1	77.9
C_2	1.0	2.3	6.9
C_2=	94.9	81.0	14.6
C_3	0.3	0.2	0.1
C_3=	1.0	2.9	0.4
C_2-C_4=	96.2	84.3	15.1
C_1-C_5	3.6	15.5	84.8
%Conversion	100	100	100
Yield of gas product (% wt.)	72.3	79.5	93.4
Yield of liquid product (% wt.)	23.4	18.0	4.6
%Coke (%wt of catalyst)	4.3	2.5	2.1

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, T_{EtOH} = 50°C, 99.9% EtOH.

It can be seen that the highest selectivity to ethylene was obtained at 350°C. The selectivity to ethylene was decreased with increasing temperatures. At 550°C the selectivity to methane was increased, this might be due to the competitive cracking of hydrocarbon.

It was reported that increasing temperature led to simultaneous decomposition of methanol producing methane, H_2, and CO.(25) It was also reported that at a high temperature, the oligomers crack into smaller molecules.(7) In the literature, formation of methane was increased due to the decomposition of methanol over SAPO-34 at 500°C.

It was also reported that the selectivity to ethylene from ethanol conversion reached a maximum value at 300°C using H-MOR (Si/Al=10) and decreased with increasing temperature because ethylene was changed further to others hydrocarbons.(5)

4.2.3 Effect of ethanol concentration

Ethanol conversion and gas product distribution using ethanol concentration of 99.9% and 10.0% over DM/Mn-Zn catalyst prepared by solid state ion exchange (SSIE) method at 350°C were compared in Table 4.6.

Table 4.6 Ethanol conversion and gas product distribution using activated DM/Mn-Zn (SSIE) at 350°C with different ethanol concentrations

Product distribution (% mol)	**99.9% EtOH**	**10.0% EtOH**
C_1	2.3	trace
C_2	1.0	trace
C_2=	94.9	97.0
C_3	0.3	0.2
C_3=	1.0	2.1
C_2-C_4=	96.2	99.5
C_1-C_5	3.6	0.3
%Conversion	100	100
%Coke (%wt of catalyst)	4.3	2.5

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, T_{EtOH} = 50°C.

trace was < 0.05 % mol of product distribution

The results show that 10.0% EtOH provided the higher selectivity to ethylene than 99.9% EtOH. These results corresponded with previous report that the activity of the dealuminated mordenites and the selectivity to light alkenes can be improved by decreasing the partial pressure of the methanol and adding water to the feed.(41)

For comparison, it was reported that ZSM-5/Mn-Zn gave high selectivity to ethylene and 100% conversion for all ethanol concentrations (25% - 100%) at 400°C.

In this work, diluted ethanol (10% EtOH) exhibited higher selectivity to ethylene than 100% EtOH. This could be explained that water competed with light alkenes for the Bronsted and Lewis acid sites. The adsorption of water on these acid centers reduced their strength, concentration and the probability of their interaction with hydrocarbons. As a consequence, the conversion of light olefins into oligomers, aromatics and coke decreased. (12)

In this work, % coke when using 10% EtOH is lower than using 99.9% EtOH. Deactivation by coke is attenuated as the water content in the reaction medium increases.(16)

4.2.4 Effect of activation and reduction

Ethanol conversion and gas product distribution were compared between DM/Mn-Zn catalyst which was activated at 500°C with N_2 and DM/Mn-Zn catalyst which was reduced at 500°C with H_2 at reaction temperature 350°C. The results were shown in Table 4.7.

Table 4.7 Ethanol conversion and gas product distribution using activated catalyst and reduced catalyst, DM/Mn-Zn (SSIE) at 350°C

Product distribution (% mol)	Activated	Reduced
C_1	2.6	0.6
C_2	0.6	1.7
C_2=	95.2	96.4
C_3	0.1	0.1
C_3=	1.1	1.1
C_2-C_4=	96.6	97.6
C_1-C_5	3.4	2.3
%Conversion	100	100
Yield of gas product (% wt.)	43.7	36.0
Yield of liquid product (% wt.)	54.8	62.5
%Coke (%wt of catalyst)	1.4	1.5

Condition: $W_{cat} = 1.0$ g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

In this work, the catalysts were activated under nitrogen gas, which removes gas from the catalysts.(17) Another way to activate the catalyst is by reduction with hydrogen gas. It appeared that selectivity to ethylene was slightly increased when using reduced catalyst.(28) Therefore, for the next experiments, reduced catalysts were used.

4.2.5 Effect of metal loading method

In this work, two methods for the preparation of the catalysts were compared solid state ion exchange method and impregnation method. They were used to prepare DM/single metal (Zn, Mn, Co). The results are shown in Table 4.8.

Table 4.8 Ethanol conversion and gas product distribution using reduced single metal catalysts prepared by SSIE and IMP at 350°C

Product Distribution (% mol)	**D-MOR**	**DM/Zn**		**DM/Co**		**DM/Mn**	
		SSIE	**IMP**	**SSIE**	**IMP**	**SSIE**	**IMP**
C_1	45.1	0.2	0.1	0.2	0.1	0.1	0.1
C_2	7.5	trace	0.8	1.9	1.6	2.3	1.4
C_2=	46.2	96.0	96.6	89.7	94.7	86.3	94.3
C_3	0.1	0.2	0.2	2.2	0.6	3.7	0.9
C_3=	0.4	2.0	1.8	3.8	2.2	4.8	2.4
C_2-C_4=	46.9	99.5	98.7	94.4	97.4	92.2	97.2
C_1-C_5	52.8	0.4	1.2	5.3	2.5	7.4	2.6
%Conversion	100	100	100	100	100	100	100
Yield of gas product (% wt.)	55.5	41.5	N.D.	46.2	54.2	N.D.	N.D.
Yield of liquid product (% wt.)	43.4	56.1	N.D.	50.9	45.3	N.D.	N.D.
%Coke	1.0	2.4	1.8	2.7	0.5	2.1	1.9

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH.
N.D.= not determined

The highest selectivity to ethylene was found in the DM/Zn catalyst which prepared by the solid state ion exchange method (97.2%). The order in selectivity to ethylene was DM/Zn > DM/Co ~ DM/Mn. These results corresponded to selectivity order obtained when using reaction temperature at 450°C in Table 4.3.

For the catalysts prepared by the impregnation method, the order in selectivity to ethylene was DM/Zn > DM/Co ~ DM/Mn.

For D-MOR, the selectivity to ethane is higher than that of DM/metal. This can be explained by the acid strength of D-MOR, which is higher than DM/metal catalysts.

In the literature, the product on CoSAPO-34 was reported to be C_2-C_4 olefins, the total C_2-C_4 olefins reached maximum at around 6 h. Thereafer, both ethylene and propylene in the product decreased systematically and fell below 1% at 36 h.

The MnSAPO-34 showed double activity in comparison with CoSAPO-34, although, the total conversion to C_2-C_4 olefins remained the same.

As seen in the above results that the DM/Zn catalyst shows highest selectivity to ethylene, therefore this was used for the incorporation of second metal, Mn, using both SSIE and IMP methods and its activity was investigated, shown in Table 4.9.

Table 4.9 Ethanol conversion and gas product distribution using reduced DM/Mn-Zn at 350°C

Product distribution (% mol)	**SSIE method**	**IMP method**
C_1	0.6	0.5
C_2	1.7	0.9
C_2=	96.4	97.3
C_3	0.1	0.1
C_3=	1.1	1.1
C_2-C_4=	97.6	98.5
C_1-C_5	2.3	1.5
%Conversion	100	100
Yield of gas product (% wt.)	36.0	39.0
Yield of liquid product (% wt.)	62.5	59.1
%Coke	1.5	1.8

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

For DM/Mn-Zn, it was found that impregnation method gave higher selectivity to ethylene than the solid state ion exchange method. Therefore, for other metals (metal = Rh, Cu, Fe, Ag and Ni) loaded onto the mordenite, the impregnation method was chosen for the loading of both single and mixed metals. The results are shown in Tables 4.10-4.11.

Table 4.10 Ethanol conversion and gas product distribution using reduced single metal catalysts prepared by IMP at 350°C

Product distribution (% mol)	**DM/Rh**	**DM/Cu**	**DM/Fe**	**DM/Ag**	**DM/Ni**
C_1	2.4	trace	0.1	trace	0.7
C_2	0.0	1.5	1.2	2.1	62.5
C_2=	96.5	92.4	91.5	85.6	35.4
C_3	trace	1.4	1.8	4.1	0.3
C_3=	0.4	3.1	3.8	5.2	0.1
C_2-C_4=	97.7	96.3	96.2	91.9	36.3
C_1-C_5	2.4	3.6	3.6	7.9	63.6
%Conversion	100	100	100	100	100
Yield of gas product (% wt.)	48.9	57.8	25.0	65.8	64.3
Yield of liquid product (% wt.)	49.9	40.9	73.7	33.4	35.1
%Coke	1.2	1.2	1.2	0.7	0.6

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

The order in selectivity to ethylene was: DM/Rh > DM/Cu ~ DM/Fe > DM/Ag > DM/Ni.

In the literature, methanol conversion using 1% Rh/Al_2O_3 was reported to produce a lot of ethylene (60%) at low temperatures (400-450°C) but this has disappeared completely at 650°C.(29)

For ZSM-5/Fe catalyst, the result revealed that it gave high selectivity to light olefins. (42), which corresponds to our result, DM/Fe catalyst gave ethylene selectivity of 91.5%.

For DM/Ni, it can be seen that very low %ethylene was obtained. However, high selectivity to ethane (62.5%) was resulted which will be discussed later. In the literature, it was reported that 1%Ni/Al_2O_3 at 700°C produced hydrogen without ethylene.(29)

As seen in Table 4.8 above that the DM/Zn catalyst showed better results than other catalysts, therefore it was chosen for the incorporation of the second metal: Ag, Mn, Co, Fe and their activities were compared in Table 4.11.

Table 4.11 Ethanol conversion and gas product distribution using reduced mixed metal catalysts prepared by IMP at 350°C

Product distribution (% mol)	**DM/Ag-Zn**	**DM/Mn-Zn**	**DM/Co-Zn**	**DM/Fe-Zn**
C_1	0.1	0.5	0.1	0.2
C_2	0.3	0.9	0.6	0.3
C_2=	98.0	97.3	96.9	96.9
C_3	0.1	0.1	0.1	0.1
C_3=	1.3	1.1	1.9	2.1
C_2-C_4=	99.5	98.5	99.1	99.3
C_1-C_5	0.4	1.5	0.8	0.6
%Conversion	100	100	100	100
Yield of gas product (% wt.)	36.3	39.0	27.8	45.3
Yield of liquid product (% wt.)	61.6	59.1	69.3	52.8
%Coke	2.0	1.8	2.9	1.8

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH

It was found that all mixed metal catalysts show a little higher selectivity to ethylene compared with the DM/Zn catalyst. This can be regarded as synergistic effect, as was reported in the literature that the bimetallic catalysts (Cr+Pt/HZSM-5) exhibited better activity and selectivity than single metal for propane and cyclohexane conversions. (28)

4.2.6 Effect of dilution and amount of metal

In order to decrease amount of catalyst to save cost, experiments were carried out by diluting the catalyst with alumina. The results are shown in Table. 4.12.

Table 4.12 Ethanol conversion and gas product distribution using dilutent (alumina) and various amount of catalyst at 350°C

Product distribution (% mol)	**Al_2O_3**	**DM/ Zn**	**Al_2O_3**	**DM/ Ag**	**Al_2O_3**	**DM/ Ag-Zn**	**Al_2O_3**
			DM/ Zn		**DM/ Ag**		**DM/ Ag-Zn**
C_1	12.6	0.1	3.2	trace	9.2	0.1	8.1
C_2	12.8	0.8	0.1	2.1	0.9	0.3	0.3
C_2=	73.4	96.6	95.7	85.6	83.8	98.0	90.8
C_3	trace	0.2	0.1	4.1	1.5	0.1	trace
C_3=	0.2	1.8	0.8	5.2	3.1	1.3	0.6
C_2-C_4=	74.0	98.7	96.6	91.9	87.7	99.5	91.6
C_1-C_5	25.6	1.2	3.4	7.9	12.2	0.4	8.4
%Conversion	100	100	100	100	100	100	100
Yield of gas product (% wt.)	50.4	N.D.	34.2	65.8	54.5	36.3	22.6
Yield of liquid product (% wt.)	46.8	N.D.	61.4	33.4	40.9	61.6	73.6
%Coke	3.0	1.8	4.6	0.7	4.6	2.0	3.9

Condition: W_{cat}/W_{Al2O3} = 1/1 (1.0 g), WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH.

It can be seen that Al_2O_3 alone shows % selectivity to ethylene lower than other catalysts (73.4%).

It could be explained that the chemisorption of olefins on an aluminosilicate catalyst proceeds by a mechanism similar to that in Figure 4.4. The dehydration proceeds by mechanism involving the action of an acid and a basic center of Al_2O_3.(3)

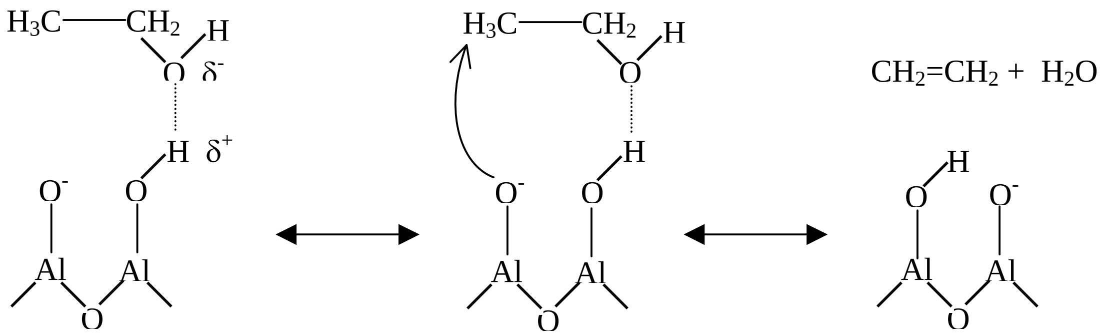


Figure 4.4 Mechanism of gas-phase dehydration of ethanol on aluminium oxide

The order in selectivity to ethylene of DM/metal was: DM/Ag-Zn ~ DM/Zn > DM/Ag.

When the ethanol feed was passed through an upper zone of alumina and a lower zone of catalyst, the order in selectivity to ethylene of Al_2O_3-DM/metal was changed to: Al_2O_3-DM/Zn > Al_2O_3-DM/Ag-Zn > Al_2O_3-DM/Ag. %Conversion was not decreased. This means that amount of catalyst can be decreased by diluting it with alumina.

From the previous experiments, the catalysts loaded with 1%metal were used. In order to see effect of metal amount on product distribution, 5% metal catalyst (DM/5%Zn) was prepared and tested. The results were shown in Table 4.13.

Table 4.13 Ethanol conversion and gas product distribution using reduced DM/Zn catalysts at 350°C

Product distribution (% mol)	**DM/1%Zn (1.0g)**	**DM/5%Zn (1.0g)**
C_1	0.1	13.3
C_2	0.8	trace
C_2=	96.6	84.7
C_3	0.2	0.1
C_3=	1.8	1.8
C_2-C_4=	98.7	86.6
C_1-C_5	1.2	13.4
%Conversion	100	100
Yield of gas product (% wt.)	66.2	71.0
Yield of liquid product (% wt.)	31.9	24.1
%Coke	1.8	4.5

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH.

From the results, % selectivity to ethylene was decreased when the amount of metal loading of catalyst was increased from 1%Zn to 5%Zn. This result could be explained by the agglomerization of metal.

In the case of coke formation, DM/5%Zn gave higher %coke than DM/1%Zn , this can be due to increased amount of zinc metal.

Next, in the case of 1%Ni catalyst, which gave high selectivity to ethane as mentioned above (in Table 4.10), higher amount of Ni loaded onto the dealuminated mordenite was investigated, the results were shown in Table 4.14.

Table 4.14 Ethanol conversion and gas product distribution using reduced DM/Ni catalysts at 350°C

Product distribution (% mol)	**DM/1%Ni (1.0 g)**	**DM/5%Ni (1.0 g)**
C_1	0.7	97.4
C_2	62.5	trace
C_2=	35.4	trace
C_3	0.2	0.1
C_3=	0.1	trace
C_2-C_4=	36.3	2.6
C_1-C_5	63.6	97.4
%Conversion	100	100
Yield of gas product (% wt.)	64.3	53.6
Yield of liquid product (% wt.)	35.1	42.3
%Coke	0.6	3.8

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH.

The results show that at 1%Ni, the catalyst gave selectivity to ethane whereas at 5% Ni, the catalyst showed high selectivity to methane.

It was reported in the literature that 5%Ni on Al_2O_3 produced a substantial amount of methane at temperature of 750°C.(30) In addition, SAPO-34/Ni with large concentration of nickel was also reported that extra-framework nickel caused formation of methane in the methanol to olefin reaction.(32)

On the reduction with hydrogen gas, metallic Ni was formed on the mordenite. This corresponds to the previous report.(31) The adsorption of ethylene product on Ni is associative, especially in the presence of hydrogen. The ethylene double bond opens, forming two σ bonds to neighboring Ni atoms and giving the ethane structure.(3) The possible mechanism of ethane formation was shown in Figure 4.5.

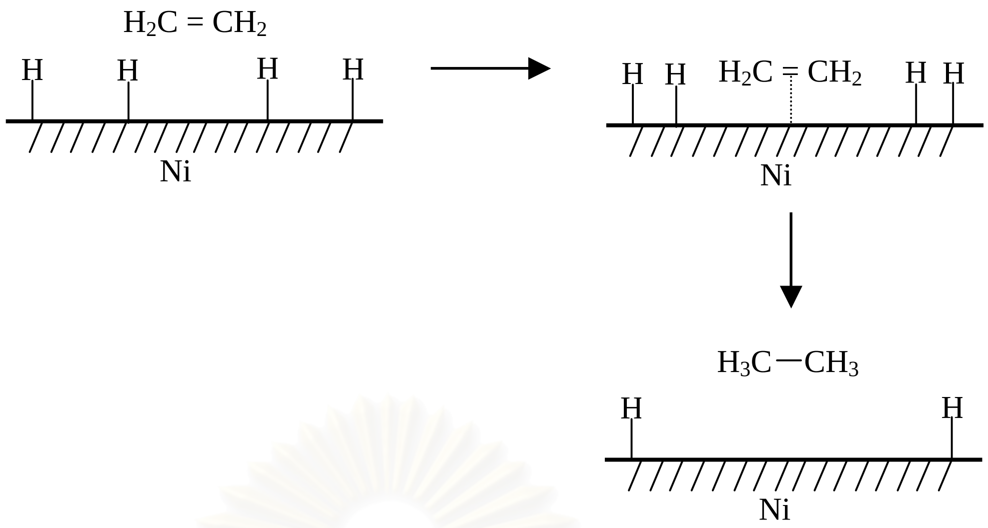


Figure 4.5 Mechanism of hydrogenation of ethylene.

4.2.7 Other catalysts

In order to compare and also to search for other zeolite catalysts, besides mordenite studied in this work, ZSM-5 and USY were tested. The results were shown in Table 4.15.

Table 4.15 Ethanol conversion and gas product distribution using zeolites at 350°C

Product distribution (% mol)	**D-MOR**	**ZSM-5**	**USY**
C_1	45.1	0.2	0.2
C_2	7.5	trace	3.3
C_2=	46.2	98.7	50.6
C_3	0.1	0.1	31.4
C_3=	0.4	0.9	5.3
C_2-C_4=	46.9	99.7	57.0
C_1-C_5	52.8	0.2	42.9
%Conversion	100	100	100
%Coke	1.0	0.4	1.6

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH.

From the results it can be concluded that product distribution depended on type of zeolites. For the catalysts tested in this section, % ethylene decreased in the following order: ZSM-5 > USY > D-MOR.

ZSM-5 gave higher % ethylene which corresponded to the reported result in the literature.(12) In contrast, the USY gave higher propane selectivity (31.4%) than D-MOR due to its larger pore window. It should be pointed out that the ZSM-5 catalyst exhibits a remarkable resistance to deactivation by coke (0.4%) which corresponded to the literature.(43)

4.3 Catalyst regeneration

After the reaction, the catalyst was calcined to remove coke. It was reused at the same condition as for fresh catalyst. The result was shown in Table 4.16.

Table 4.16 Ethanol conversion and gas product distribution using fresh and reused DM/Zn catalyst at 350°C

Product distribution (% mol)	**Fresh**	**Reused 2 times**	**Reused 7 times**	**Reused 8 times**
C_1	0.1	2.8	6.7	25.2
C_2	0.8	1.2	13.2	trace
C_2=	96.6	95.7	79.2	73.4
C_3	0.2	trace	trace	0.1
C_3=	1.8	0.2	0.3	0.8
C_2-C_4=	98.7	98.8	79.8	74.5
C_1-C_5	1.2	1.2	20.0	25.4
%Conversion	100	100	100	100
%Coke	1.8	N.D.	N.D.	1.3

Condition: W_{cat} = 1.0 g, WHSV= 1.0 h^{-1}, time on stream = 1 h, 10.0% EtOH.
N.D.= not determined

For the deactivation study on the catalysts, it was found that the selectivity to ethylene of the spent catalyst was decreased with number of times use.

The use of dilute ethanol might contribute to the reduction of coke formation, resulting in the decrease in the catalyst deactivation.(16) After 7-8 times of use, the selectivity to methane was increased.

4.4 Coke formation

In the determination of coke formed on the catalysts after use, the thermogravimetric (TG) technique was used the TG is shown in Figure 4.6.

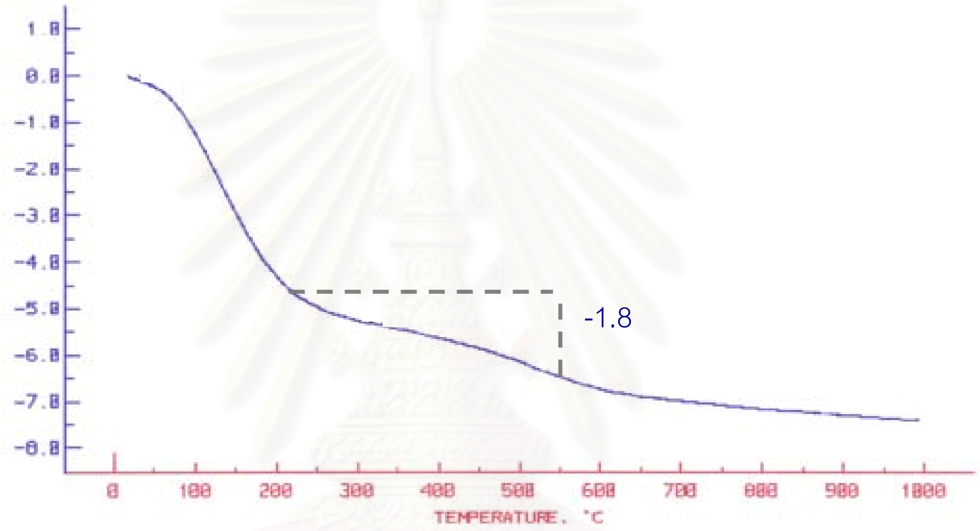


Figure 4.6 The thermogravimetric curve of DM/1%Zn (IMP).

1.8% coke was obtained from TG technique which corresponds to the result obtained by the method of calcination at 550ºC (1.8% coke) in Table 4.16.

CHAPTER V

CONCLUSION AND SUGGESTIONS

The conversion of ethanol and aqueous ethanol to light olefins over dealuminated mordenite (D-MOR) catalyst were investigated. The hydrogen-form mordenite (H-MOR) was prepared by reflux distillation of Na-MOR (Si/Al ratio of 5.66) with ammonium chloride solution followed by calcination. Then, H-MOR was leached out aluminium using 8.0 M HCl to obtain D-MOR. The resultant catalysts were characterized by FT-IR, XRD, XRF, BET and TGA techniques. FT-IR spectra showed that metal loaded onto dealuminated mordenite were coordinated. From XRD technique, there was no destruction of the mordenite structure. The Si/Al ratio of the D-MOR determined by XRF technique, increased to 26.90.

Ethanol conversion was studied on D-MOR and DM/metal. The product distributions were influenced by temperature, dilution of the feed, metal loading method, amount of catalyst and addition of alumina,. Lower temperature (350ºC) led to higher selectivity to ethylene while higher temperature (550ºC) led to selectivity to methane. The selectivity to ethylene can be obtained and increased using ethanol with added water (10% EtOH). Deactivation by coke was decreased as the water content was increased.

Two methods of metal loading: impregnation (IMP) or solid state ion exchange (SSIE) were used for the loading of both single metal and mixed metals (Zn, Rh, Co, Mn, Cu, Fe, Ag and Ni) onto the D-MOR. The catalysts from both methods showed similar trend of product distribution. The DM/single metal and DM/mixed metals showed selectivity to ethylene with small quantities of other olefins. DM/Zn (preapred by SSIE and IMP methods) gave high selectivity to ethylene (97.2% and 96.6%, respectively). DM/Ag-Zn (IMP) led to an improvement in ethylene selectivity (98.0%). Compared with the DM/Zn catalyst which gave ethylene selectivity of 96.6%, it was found that all mixed metals catalysts: DM/Ag-Zn (98.0%), DM/Mn-Zn (97.3%), DM/Co-Zn (96.9%) and DM/Fe-Zn (96.9%) catalysts showed a little higher selectivity to ethylene.

In addition, it was found that alumina can be used as diluent in order to decrease amount of catalyst. The diluted catalysts: Al_2O_3-DM/Zn, Al_2O_3-DM/Ag and Al_2O_3-DM/Ag-Zn showed slight decrease in ethylene selectivity than the non-diluted catalysts.

When increasing amount of metal loading onto the mordenite from 1% to 5% wt, the experimental results revealed that for DM/5%Zn catalyst, the selectivity to methane was increased while the selectivity to ethylene was decreased, compared to the DM/1%Zn.

Interesting results were observed for DM/Ni which were different from other metal catalysts . DM/1%Ni gave highest % selectivity to ethane due to hydrogenation of ethylene product whereas DM/5%Ni gave highest % selectivity to methane (97.4%) as main product.

Two other zeolites, ZSM-5 and USY were also studied. At the condition tested in this work, ZSM-5 gave higher selectivity to ethylene than D-MOR and USY. It might be due to higher acidity of ZSM-5. USY gave high selectivity to propane, this is due to its larger pore than ZSM-5 and D-MOR. However, the results obtained from this work showed that % selectivity to ethylene using DM/Zn and DM/mixed metals were comparable to that from ZSM-5. Finally, the catalysts can be reused.

Suggestions

From the results in this work, further work shall be done follows:

1. Optimize the reaction condition to get selectivity to other light olefins,

2. Using methanol as feed to get selectivity to other light olefins for industrial demand.

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APPENDICES

APPENDIX A

Effect of metal loaded

Table A-1 Ethanol conversion and gas product distribution using single metal loaded mordenite at 450°C

Product distribution (% mol)	**DM/Zn**	**DM/Mn**	**DM/Co**
C_1	2.17	1.59	3.22
C_2	0.66	1.81	3.36
$C_2=$	93.49	86.74	71.34
$C_2\equiv$	trace	trace	trace
C_3	0.62	3.35	10.56
$C_3=$	2.17	4.19	5.44
$C_3=,=$	trace	trace	trace
$C_3\equiv$,—	trace	trace	trace
C_4	0.04	0.19	0.75
iso-C_4	0.18	1.13	3.38
1-$C_4=$	0.07	0.12	0.18
iso-$C_4=$	0.24	0.40	0.63
trans-2-$C_4=$	0.10	0.14	0.26
cis-2-$C_4=$	0.08	0.11	0.20
1,3- $C_4=,=$	0.01	0.01	0.01
n- C_5	0.00	0.01	0.05
iso- C_5	0.03	0.13	0.41
$C_{5=}/C_{6+}$	0.12	0.10	0.19
C_2-C_4 olefins	96.15	91.71	78.07
C_1-C_5 alkanes	3.72	8.20	21.73
Coke (% wt. of catalyst)	5.14	5.32	4.86

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 2 h, T_{EtOH} = 50°C, 99.9% EtOH.

Table A-2 Ethanol conversion and gas product distribution using mixed metals loaded mordenite at 450°C

Product distribution (% mol)	**DM/Mn-Zn**	**DM/Co-Mn**
C_1	13.08	13.19
C_2	2.28	3.30
C_2=	80.99	78.83
C_2≡	0.05	0.02
C_3	0.15	0.75
C_3=	2.94	3.13
C_3=,=	0.00	0.00
C_3≡,—	0.00	0.00
C_4	0.01	0.05
iso-C_4	0.01	0.08
1-C_4=	0.07	0.10
iso-C_4=	0.09	0.17
trans-2-C_4=	0.07	0.11
cis-2-C_4=	0.06	0.09
1,3- C_4=,=	0.10	0.06
n- C_5	0.00	0.00
iso- C_5	0.00	0.00
$C_{5=}/C_{6+}$	0.09	0.12
C_2-C_4 olefins	84.32	75.17
C_1-C_5 alkanes	15.54	24.71
Yield of gas product (% wt.)	79.47	80.86
Yield of liquid product (% wt.)	18.00	16.38
Coke (% wt. of catalyst)	2.51	2.74

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, T_{EtOH} = 50°C, 99.9% EtOH.

Effect of temperature

Table A-3 Ethanol conversion and gas product distribution using activated (with N_2 at 500°C for 1 h) DM/Mn-Zn at various reaction temperatures

Product distribution (% mol)	**Temperature (°C)**		
	350	**450**	**550**
C_1	2.30	13.08	77.89
C_2	0.99	2.28	6.90
C_2=	94.87	80.99	14.63
$C_2\equiv$	0.00	0.05	0.01
C_3	0.29	0.15	0.06
C_3=	1.05	2.94	0.45
C_3=,=	0.00	0.00	0.00
$C_3\equiv$,—	0.00	0.00	0.00
C_4	0.03	0.01	0.00
iso-C_4	0.03	0.01	0.00
1-C_4=	0.06	0.07	0.01
iso-C_4=	0.08	0.09	0.01
trans-2-C_4=	0.08	0.07	trace
cis-2-C_4=	0.06	0.06	trace
1,3- C_4=,=	0.03	0.10	0.02
n- C_5	0.00	0.00	0.00
iso- C_5	0.00	0.00	0.00
$C_{5=}/C_{6+}$	0.11	0.09	0.01
C_2-C_4=	94.79	84.32	15.12
C_1-C_5—	5.11	15.54	84.85
Yield of gas product (% wt.)	72.3	79.47	93.40
Yield of liquid product (% wt.)	23.4	18.00	4.55
Coke (% wt. of catalyst)	4.32	2.51	2.09

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, T_{EtOH} = 50°C, 99.9% EtOH.

Effect of ethanol concentration

Table A-4 Ethanol conversion and gas product distribution using activated DM/Zn-Mn (SSIE) at 350°C with different ethanol concentrations

Product distribution (% mol)	**99.9% EtOH**	**10.0% EtOH**
C_1	2.30	trace
C_2	0.99	trace
C_2=	94.87	97.04
C_2≡	0.00	0.00
C_3	0.29	0.24
C_3=	1.05	2.11
C_3=,=	0.00	0.00
C_3≡,—	0.00	0.00
C_4	0.03	0.03
iso-C_4	0.03	0.03
1-C_4=	0.06	0.05
iso-C_4=	0.08	0.17
trans-2-C_4=	0.08	0.08
cis-2-C_4=	0.06	0.06
1,3- C_4=,=	0.03	trace
n- C_5	0.00	0.00
iso- C_5	0.01	trace
$C_{5=}/C_{6+}$	0.11	0.17
C_2-C_4 olefins	94.79	99.51
C_1-C_5 alkanes	5.11	0.31
Coke (% wt. of catalyst)	4.32	2.50

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, T_{EtOH} = 50°C.

Effect of activation and reduction

Table A-5 Ethanol conversion and gas product distribution using activated catalyst and reduced catalyst, DM/Mn-Zn (SSIE) at 350°C

Product distribution (% mol)	**Activated**	**Reduced**
C_1	2.64	0.55
C_2	0.63	1.66
C_2=	95.24	96.36
$C_2\equiv$	0.00	0.00
C_3	0.10	0.06
C_3=	1.09	1.10
C_3=,=	0.01	0.01
$C_3\equiv$,—	trace	0.02
C_4	0.00	0.00
iso-C_4	0.01	0.01
1-C_4=	0.06	0.02
iso-C_4=	0.11	0.06
trans-2-C_4=	0.03	0.04
cis-2-C_4=	0.02	0.03
1,3- C_4=,=	0.01	0.01
n- C_5	0.00	0.00
iso- C_5	0.00	0.00
$C_{5=}$/C_{6+}	0.04	0.07
C_2-C_4 olefins	96.56	97.65
C_1-C_5 alkanes	3.39	2.30
Yield of gas product (% wt.)	43.66	35.95
Yield of liquid product (% wt.)	54.82	62.50
Coke (% wt. of catalyst)	1.40	1.48

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Effect of metal loading method

Table A-6 Ethanol conversion and gas product distribution using reduced single metal catalysts prepared with SSIE and IMP at 350°C

Product distribution (% mol)	**D-MOR**	**DM/Zn**		**DM/Co**		**DM/Mn**	
		SSIE	**IMP**	**SSIE**	**IMP**	**SSIE**	**IMP**
C_1	45.10	0.19	0.10	0.20	0.14	0.11	0.12
C_2	7.49	trace	0.83	1.88	1.58	2.26	1.39
C_2=	46.23	97.16	96.56	89.67	94.71	86.34	94.32
$C_2\equiv$	0.10	0.00	0.00	0.00	0.00	0.00	0.00
C_3	0.14	0.18	0.23	2.21	0.60	3.73	0.90
C_3=	0.38	2.05	1.78	3.82	2.21	4.75	2.38
C_3=,=	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_3\equiv$,—	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_4	0.05	0.01	0.01	0.17	0.03	0.24	0.04
iso-C_4	0.06	0.03	0.03	0.73	0.10	0.92	0.17
1-C_4=	0.10	0.04	0.09	0.14	0.07	0.16	0.08
iso-C_4=	0.11	0.12	0.19	0.43	0.22	0.52	0.25
trans-2-C_4=	0.07	0.06	0.05	0.20	0.10	0.24	0.11
cis-2-C_4=	trace	0.04	0.04	0.15	0.07	0.19	0.08
1,3- C_4=,=	trace	0.01	0.01	trace	trace	trace	trace
n- C_5	trace	trace	trace	0.02	trace	0.02	trace
iso- C_5	trace	0.01	0.01	0.13	0.01	0.16	0.03
$C_{5=}/C_{6+}$	0.17	0.11	0.09	0.26	0.13	0.34	0.14
C_2-C_4 olefins	46.90	99.49	98.72	94.41	97.39	92.20	97.21
C_1-C_5 alkanes	52.83	0.41	1.20	5.34	2.48	7.45	2.65
Yield of gas product (% wt.)	55.53	41.46	N.D.	46.25	54.24	N.D.	N.D.
Yield of liquid product (%wt.)	43.40	56.08	N.D.	50.88	45.29	N.D.	N.D.
Coke (% wt. of catalyst)	1.03	2.35	1.82	2.71	0.46	2.08	1.88

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Table A-7 Ethanol conversion and gas product distribution using reduced DM/Mn-Zn at 350°C

Product distribution (% mol)	**SSIE method**	**IMP method**
C_1	0.55	0.50
C_2	1.66	0.89
C_2=	96.36	97.29
$C_2\equiv$	0.00	0.00
C_3	0.06	0.07
C_3=	1.10	1.07
C_3=,=	0.01	trace
$C_3\equiv$,—	0.02	trace
C_4	0.00	0.00
iso-C_4	0.01	trace
1-C_4=	0.02	0.02
iso-C_4=	0.06	0.05
trans-2-C_4=	0.04	0.03
cis-2-C_4=	0.03	0.02
1,3- C_4=,=	0.01	trace
n- C_5	0.00	0.00
iso- C_5	0.00	0.00
$C_{5=}/C_{6+}$	0.07	0.05
C_2-C_4 olefins	97.64	98.48
C_1-C_5 alkanes	2.29	1.47
Yield of gas product (% wt.)	35.95	39.03
Yield of liquid product (% wt.)	62.50	59.13
Coke (% wt. of catalyst)	1.48	1.75

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Table A-8 Ethanol conversion and gas product distribution using reduced single metal catalysts prepared with IMP at 350°C

Product distribution (% mol)	**DM/Rh**	**DM/Cu**	**DM/Fe**	**DM/Ag**	**DM/Ni**
C_1	2.42	0.05	0.09	0.03	0.71
C_2	trace	1.52	1.19	2.13	62.49
C_2=	96.48	92.42	91.45	85.56	35.42
C_2≡	0.00	0.00	0.00	0.00	0.00
C_3	trace	1.38	1.79	4.13	0.31
C_3=	0.36	3.12	3.79	5.18	0.07
C_3=,=	0.82	trace	trace	trace	trace
C_3≡,—	0.00	0.00	0.00	0.00	0.00
C_4	trace	0.10	0.10	0.29	0.01
iso-C_4	trace	0.46	0.38	1.13	0.04
1-C_4=	0.01	0.11	0.14	0.17	0.79
iso-C_4=	0.01	0.35	0.46	0.55	0.02
trans-2-C_4=	trace	0.14	0.18	0.24	0.01
cis-2-C_4=	0.01	0.11	0.13	0.19	0.01
1,3- C_4=,=	0.03	trace	trace	0.01	trace
n- C_5	trace	0.01	0.01	0.02	trace
iso- C_5	trace	0.08	0.08	0.16	0.01
$C_{5=}/C_{6+}$	0.16	0.15	0.21	0.22	0.06
C_2-C_4 olefins	97.71	96.26	96.15	91.90	36.32
C_1-C_5 alkanes	2.42	3.59	3.64	7.88	63.57
Yield of gas product (% wt.)	48.91	57.85	25.02	65.83	64.27
Yield of liquid product (% wt.)	49.88	40.90	73.68	33.44	35.07
Coke (% wt. of catalyst)	1.22	1.19	1.17	0.67	0.58

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Table A-9 Ethanol conversion and gas product distribution using reduced mixed metal catalysts prepared with IMP at 350°C

Product distribution (% mol)	**DM/Ag-Zn**	**DM/Mn-Zn**	**DM/Co-Zn**	**DM/Fe-Zn**
C_1	0.06	0.50	0.10	0.17
C_2	0.26	0.89	0.58	0.31
C_2=	98.05	97.29	96.91	96.89
C_2≡	0.00	0.00	0.00	0.00
C_3	0.12	0.07	0.13	0.13
C_3=	1.26	1.07	1.93	2.14
C_3=,=	0.00	0.00	0.00	0.00
C_3≡,—	0.00	0.00	0.00	0.00
C_4	0.00	0.00	0.00	0.00
iso-C_4	0.01	trace	0.01	0.01
1-C_4=	0.03	0.02	0.04	0.03
iso-C_4=	0.10	0.05	0.13	0.14
trans-2-C_4=	0.03	0.03	0.04	0.05
cis-2-C_4=	0.02	0.02	0.04	0.03
1,3- C_4=,=	trace	trace	trace	0.01
n- C_5	0.00	0.00	0.00	0.00
iso- C_5	0.00	0.00	0.00	0.00
$C_{5=}/C_{6+}$	0.05	0.05	0.08	0.07
C_2-C_4 olefins	99.50	98.48	99.10	99.29
C_1-C_5 alkanes	0.44	1.47	0.83	0.64
Yield of gas product (% wt.)	36.31	39.03	27.83	45.30
Yield of liquid product (% wt.)	61.55	59.13	69.27	52.80
Coke (% wt. of catalyst)	2.00	1.75	2.87	1.75

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Effect of dilution catalyst

Table A-10 Ethanol conversion and gas product distribution using dilutent (alumina) and various amount of catalyst at 350°C

Product distribution (% mol)	**Al_2O_3**	**DM/ Zn**	**Al_2O_3**	**DM/ Ag**	**Al_2O_3**	**DM/ Ag-Zn**	**Al_2O_3**
			DM/ Zn		**DM/ Ag**		**DM/ Ag-Zn**
C_1	12.64	0.10	3.20	0.03	9.25	0.06	8.11
C_2	12.82	0.83	0.09	2.13	0.90	0.26	0.24
C_2=	73.44	96.56	95.73	85.56	83.83	98.05	90.85
C_2≡	0.16	trace	trace	trace	trace	trace	trace
C_3	0.02	0.23	0.06	4.13	1.54	0.12	0.04
C_3=	0.18	1.78	0.77	5.18	3.14	1.26	0.57
C_3=,=	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_3≡,—	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_4	0.06	0.01	trace	0.29	0.09	trace	trace
iso-C_4	0.03	0.03	0.01	1.13	0.35	0.01	trace
1-C_4=	0.13	0.09	trace	0.17	0.11	0.03	0.06
iso-C_4=	0.10	0.19	0.05	0.55	0.36	0.10	0.08
trans-2-C_4=	0.08	0.05	0.03	0.24	0.14	0.03	0.02
cis-2-C_4=	0.04	0.04	0.02	0.19	0.10	0.02	0.01
1,3- C_4=,=	trace	0.01	trace	0.01	trace	trace	trace
n- C_5	trace	trace	trace	0.02	trace	trace	trace
iso- C_5	trace	0.01	trace	0.16	0.06	trace	trace
$C_{5=}/C_{6+}$	0.29	0.09	0.03	0.22	0.13	0.05	0.02
C_2-C_4 olefins	73.98	98.72	96.60	91.90	87.68	99.50	91.59
C_1-C_5 alkanes	25.57	1.20	3.37	7.88	12.19	0.44	8.39
Yield of gas product (% wt.)	50.37	N.D.	34.23	65.83	54.47	36.31	22.63
Yield of liquid product (% wt.)	46.78	N.D.	61.38	33.44	40.93	61.55	73.59
Coke (% wt. of catalyst)	2.99	1.82	4.61	0.67	4.62	2.00	3.92

Condition: W_{cat} = 1.0 g, W_{cat}/W_{Al2O3} = 1/1 (1.0 g), WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Effect of amount of catalyst

Table A-11 Ethanol conversion and gas product distribution using reduced DM/Zn catalysts at 350°C

Product distribution (% mol)	**DM/1%Zn (1.0g)**	**DM/5% Zn (1.0g)**
C_1	0.10	13.32
C_2	0.83	0.00
C_2=	96.56	84.73
C_2≡	0.00	0.00
C_3	0.23	0.06
C_3=	1.78	1.76
C_3=,=	0.00	0.00
C_3≡,—	0.00	0.00
C_4	0.01	trace
iso-C_4	0.03	trace
1-C_4=	0.09	0.02
iso-C_4=	0.19	0.05
trans-2-C_4=	0.05	0.02
cis-2-C_4=	0.04	0.02
1,3- C_4=,=	0.01	trace
n- C_5	0.00	0.00
iso- C_5	0.01	trace
$C_{5=}/C_{6+}$	0.09	0.03
C_2-C_4 olefins	98.72	86.60
C_1-C_5 alkanes	1.20	13.37
Yield of gas product (% wt.)	66.20	71.02
Yield of liquid product (% wt.)	31.89	24.06
Coke (% wt. of catalyst)	1.82	4.51

Condition: W_{cat} = 1.0 g or W_{cat}/W_{Al2O3} = 1/1 (1.0 g), WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Effect of amount of catalyst

Table A-12 Ethanol conversion and gas product distribution using reduced DM/Ni catalysts at 350°C

Product distribution (% mol)	**DM/1%Ni (1.0 g)**	**DM/5%Ni (1.0 g)**
C_1	0.71	97.35
C_2	62.49	trace
$C_2=$	35.42	trace
$C_2\equiv$	0.00	0.00
C_3	0.31	trace
$C_3=$	0.07	0.05
$C_3=,=$	0.00	0.00
$C_3\equiv,$—	0.00	0.00
C_4	0.01	0.00
iso-C_4	0.04	0.00
1-$C_4=$	0.79	2.57
iso-$C_4=$	0.02	trace
trans-2-$C_4=$	0.01	0.00
cis-2-$C_4=$	0.01	0.00
1,3- $C_4=,=$	0.00	0.00
n- C_5	0.00	0.00
iso- C_5	0.01	trace
$C_{5=}/C_{6+}$	0.06	0.03
C_2-C_4 olefins	36.32	2.62
C_1-C_5 alkanes	63.57	97.35
Yield of gas product (% wt.)	64.27	53.56
Yield of liquid product (% wt.)	35.07	42.29
Coke (% wt. of catalyst)	0.58	3.79

Condition: W_{cat} = 1.0 g, or W_{cat}/W_{Al2O3} = 1/1 (1.0 g), WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Other catalysts

Table A-13 Ethanol conversion and gas product distribution using various catalysts at 350°C

Product distribution (% mol)	**D-MOR**	**ZSM-5**	**USY**
C_1	45.10	0.15	0.24
C_2	7.49	trace	3.33
C_2=	46.23	98.66	50.62
C_2≡	0.10	trace	trace
C_3	0.14	0.06	31.45
C_3=	0.38	0.86	5.26
C_3=,=	0.00	0.00	0.00
C_3≡,—	0.00	0.00	0.00
C_4	0.05	0.01	1.92
iso-C_4	0.06	0.01	5.44
1-C_4=	0.10	0.03	0.17
iso-C_4=	0.11	0.06	0.58
trans-2-C_4=	0.07	0.03	0.23
cis-2-C_4=	trace	0.03	0.16
1,3- C_4=,=	trace	0.02	trace
n- C_5	trace	trace	0.08
iso- C_5	trace	0.01	0.40
$C_{5=}/C_{6+}$	0.17	0.04	0.13
C_2-C_4 olefins	46.90	99.70	57.01
C_1-C_5 alkanes	52.83	0.24	42.86
Yield of gas product (% wt.)	55.53	56.98	19.58
Yield of liquid product (% wt.)	43.40	42.60	78.88
Coke (% wt. of catalyst)	1.03	0.40	1.62

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

Catalyst regeneration

Table A-14 Ethanol conversion and gas product distribution using fresh and reused DM/Zn catalyst at 350°C

Product distribution (% mol)	Fresh	Reused 2 times	Reused 7 times	Reused 8 times
C_1	0.10	2.82	6.67	25.20
C_2	0.83	1.16	13.20	0.00
$C_2=$	96.56	95.67	79.22	73.36
$C_2\equiv$	trace	0.02	0.10	0.04
C_3	0.23	0.03	0.04	0.11
$C_3=$	1.78	0.24	0.29	0.79
$C_3=,=$	trace	0.02	trace	0.20
$C_3\equiv,$—	0.00	0.00	0.00	0.00
C_4	0.01	trace	0.03	trace
iso-C_4	0.03	trace	0.02	0.04
1-$C_4=$	0.09	0.01	0.09	0.06
iso-$C_4=$	0.19	trace	0.06	0.05
trans-2-$C_4=$	0.05	0.01	0.06	0.05
cis-2-$C_4=$	0.04	0.01	0.03	0.03
1,3- $C_4=,=$	0.01	trace	trace	trace
n- C_5	0.00	0.00	0.00	0.00
iso- C_5	0.01	trace	trace	trace
$C_{5=}/C_{6+}$	0.09	0.01	0.19	0.07
C_2-C_4 olefins	98.72	95.96	79.75	74.53
C_1-C_5 alkanes	1.20	4.01	19.95	25.35
Yield of gas product (% wt.)	66.20	N.D.	N.D.	40.45
Yield of liquid product (% wt.)	31.89	N.D.	N.D.	58.27
Coke (% wt. of catalyst)	1.82	N.D.	N.D.	1.26

Condition: W_{cat} = 1.0 g, WHSV = 1.0 h^{-1}, time on stream = 1 h, 10.0%EtOH.

APPENDIX B

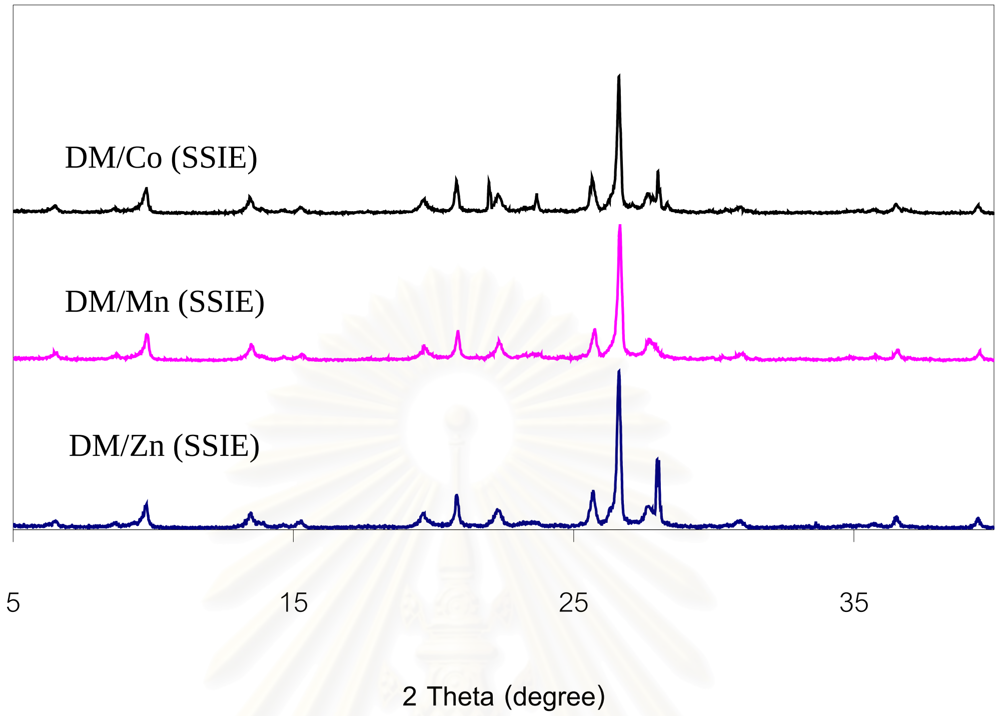

Figure B-1 X-ray diffractograms of DM/single metal.

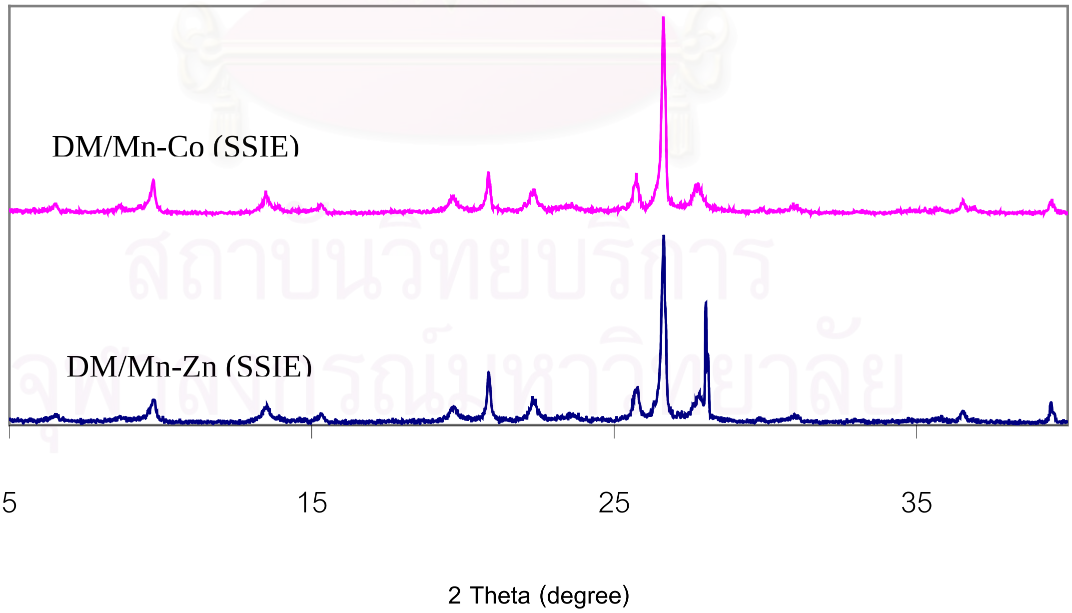

Figure B-2 X-ray diffractograms of DM/mixed metals.

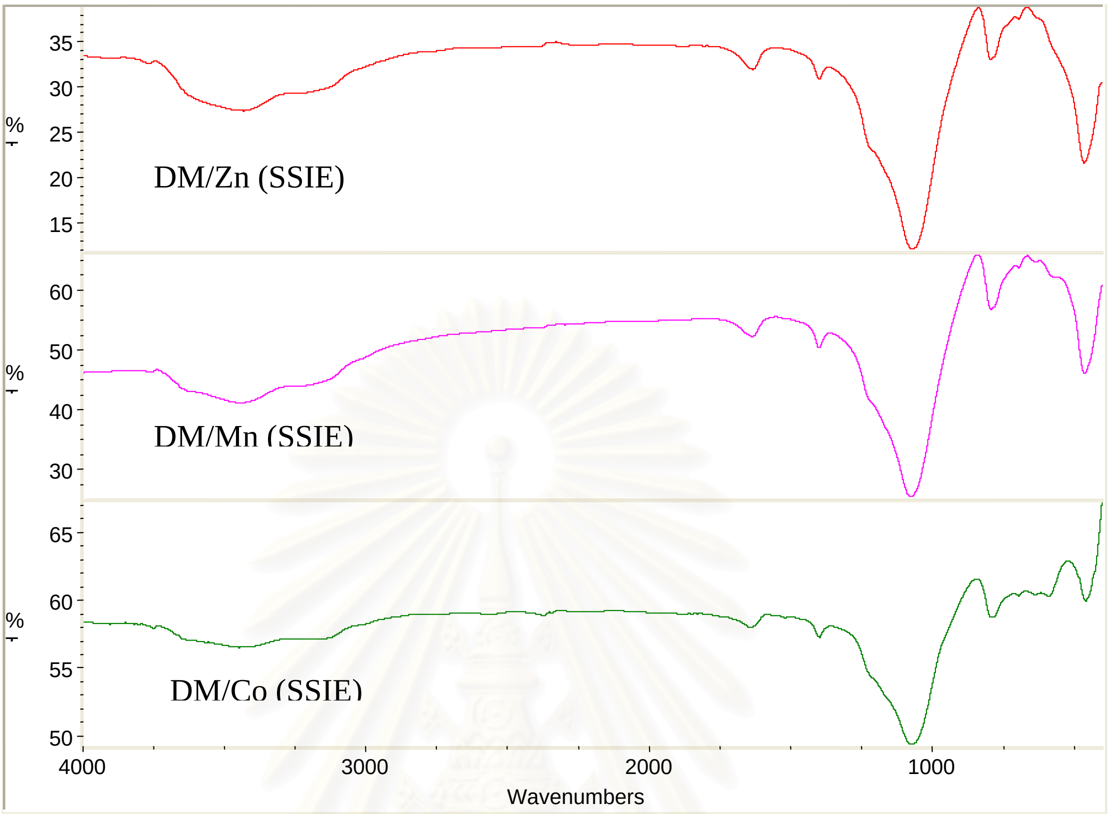

Figure B-3 FT-IR spectra of DM/ single metal.

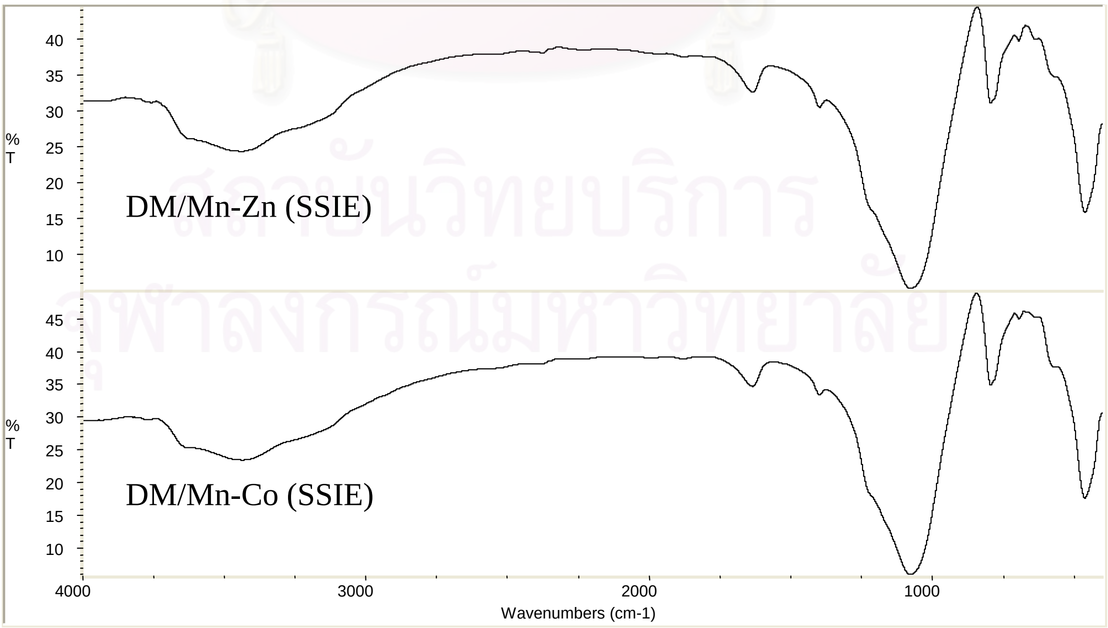

Figure B-4 FT-IR spectra of DM/ mixed metals.

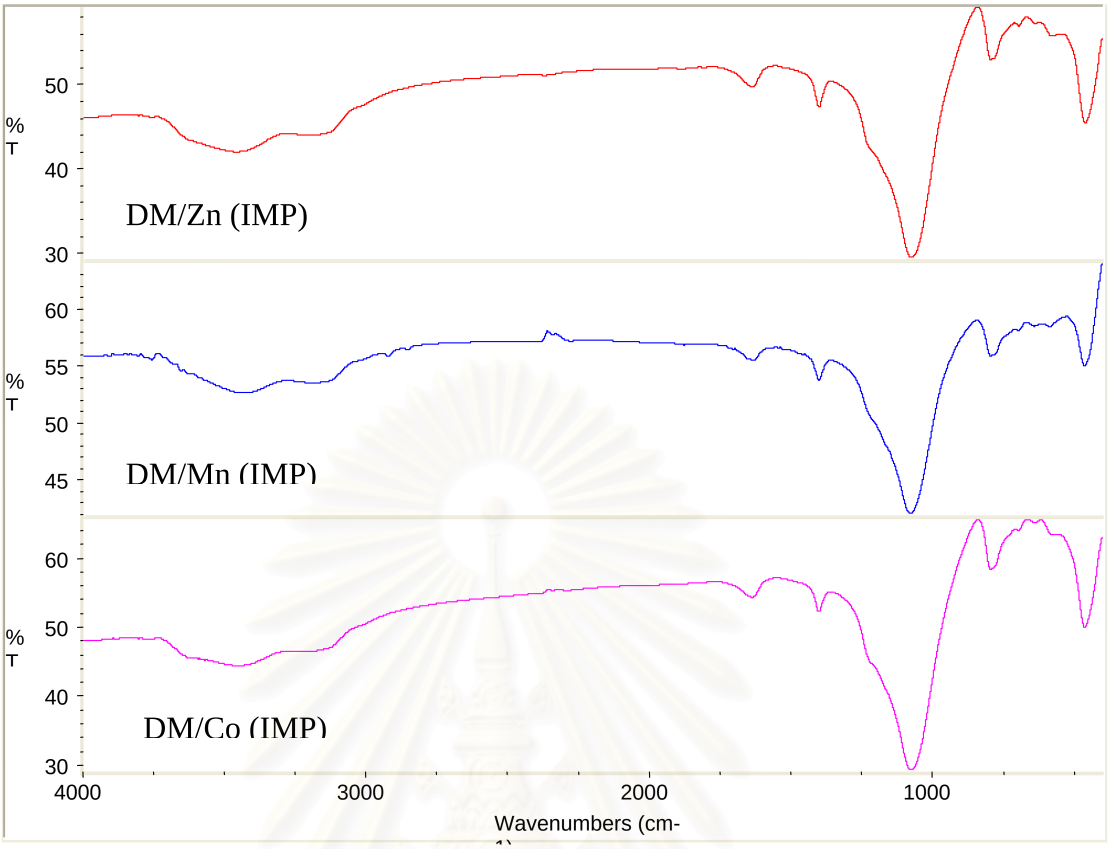

Figure B-5 FT-IR spectra of DM/ single metal.

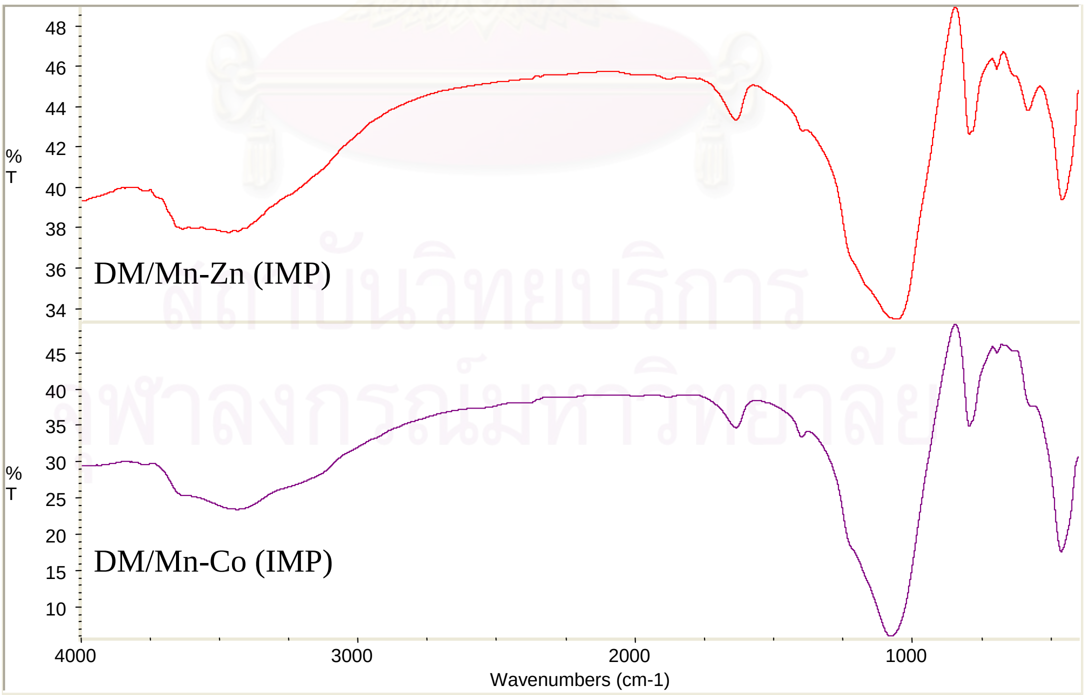

Figure B-6 FT-IR spectra of DM/ mixed metals.

APPENDIX C

C-1 Calculation of liquid product and gas product

Example Products obtained from activated catalyst DM/Mn-Zn in Table 4.7

wt. of feeding ethanol = 1.0000 g.
wt. of liquid product = 0.5482 g.
wt. of coke = 0.0119 g.

$$\%\text{Yield of liquid product (wt.\%)} = \frac{\text{wt. of liquid product} \times \%\text{conv.}}{\text{wt.ethanol}}$$

$$\%\text{Yield of liquid product} = \frac{0.5482 \times 100}{1.0}$$

$$= 54.82\ \%$$

$$\%\text{Yield of gas product (wt.\%)} = \frac{(\text{wt.feeding ethanol} - \text{wt.liquid product} - \text{wt.Coke}) \times \%\text{conv.}}{\text{wt. ethanol}}$$

$$\%\text{Yield of gas product} = \frac{(1.0-0.5482-0.0119) \times 100}{1.0}$$

$$= 43.66\ \%$$

APPENDIX D

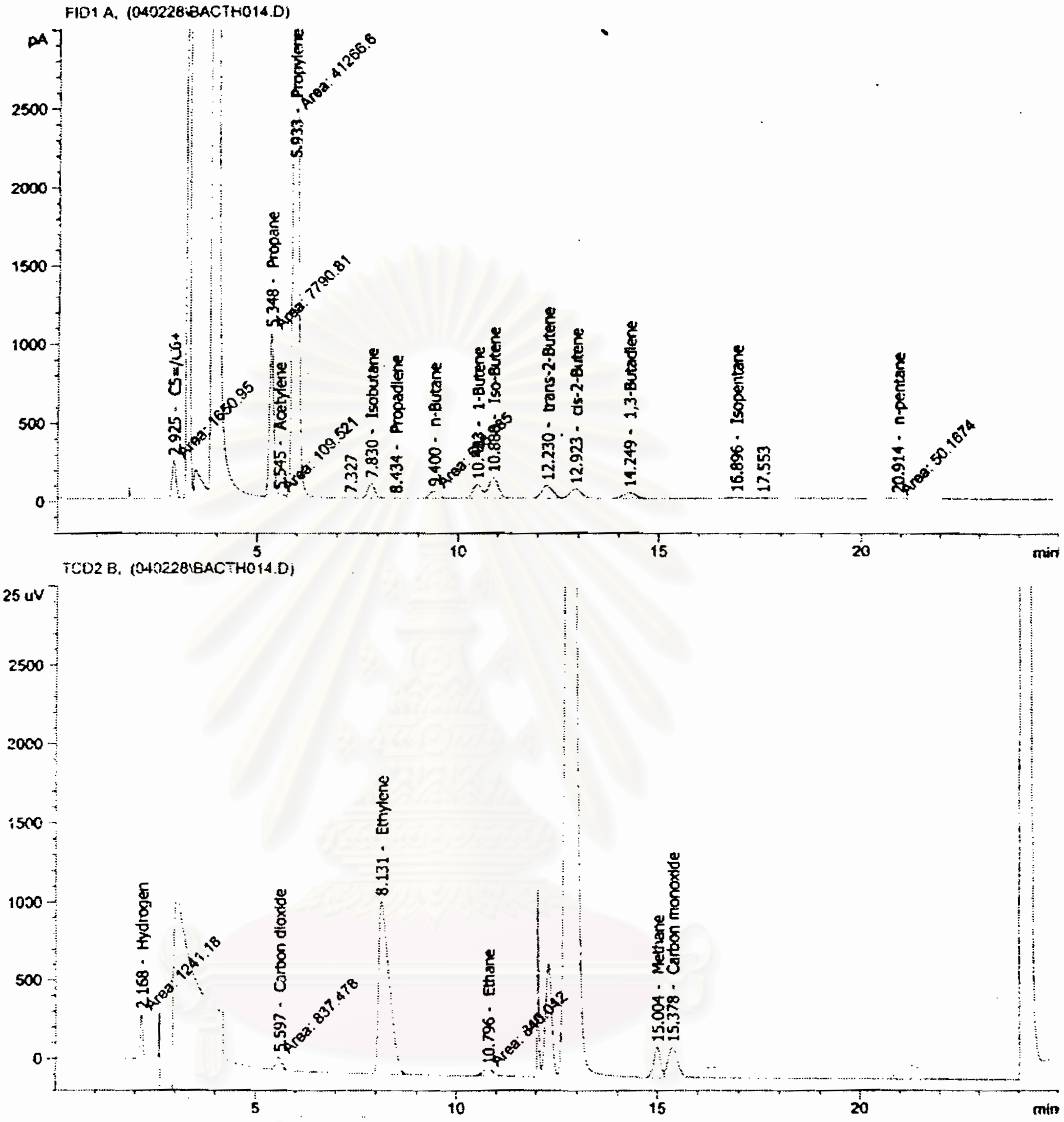

Figure D-1 A gas chromatogram of gas product of DM/Mn-Co from Table 4.4.

VITAE

Miss Sirinapa Arenamnart was born on December 21, 1978 in Chanthaburi. She received the B. Sc. Degree in Chemistry at Kasetsart University in 2000. Since then, she has been a graduate student studying in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University.

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