Dehydration of ethanol to diethyl ether over beta zeolite catalysts

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2018

ดีไฮเดรชันของเอทานอลไปเป็นไดเอทิลอีเทอร์บนตัวเร่งปฏิกิริยาเบต้าซีโอไลต์

นายมนตรี ทัพพลี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2561

Thesis Title	Dehydration of ethanol to diethyl ether over beta zeolite catalysts
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Field of Study	Chemical Engineering
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มนตรี ทัพพลี : ดีไฮเดรชันของเอทานอลไปเป็นไดเอทิลอีเทอร์บนตัวเร่งปฏิกิริยาเบต้าซี
โอไลต์. (Dehydration of ethanol to diethyl ether over beta zeolite
catalysts) อ.ที่ปรึกษาหลัก : ศ. ดร.บรรเจิด จงสมจิตร

งานวิจัยนี้ศึกษาการดีไฮเดรชันของเอทานอลไปเป็นไดเอทิลอีเทอร์โดยใช้ตัวเร่งปฏิกิริยา
เบต้าซีโอไลต์สังเคราะห์ที่มีรูปแบบแตกต่างกันของ Na และรูปแบบผสม Na-H ซึ่งรูปแบบ Na ใน
ตัวเร่งปฏิกิริยาถูกสังเคราะห์ด้วยกระบวนการไฮโดรเทอร์มอล ประกอบด้วยตัวเร่งปฏิกิริยาที่ไม่มี
การเผาและเผา ตัวเร่งปฏิกิริยาที่มีการเผาจะถูกนำมาสังเคราะห์รูปแบบผสม Na-H ด้วยวิธีการ
แลกเปลี่ยนไอออน โดยในการวิจัยเลือกจำนวนครั้งในการและเปลี่ยนไอออนคือ 1 และ4 ครั้ง
ตัวเร่งปฏิกิริยาทั้งหมดจะถูกนำมาตรวจสอบคุณลักษณะด้วยเทคนิคต่างๆ จากนั้นนำตัวเร่ง
ปฏิกิริยามาทดสอบประสิทธิภาพภายใต้ความดันบรรยากาศและอุณหภูมิในช่วง 150-400 องศา
เซลเซียส จากผลการทดลองพบว่าตัวเร่งปฏิกิริยาที่มีการแลกเปลี่ยนไอออน 1 ครั้ง ให้ค่าร้อยละ
ผลผลิตสูงที่สุด 27.3% ที่อุณหภูมิ 250 องศาเซลเซียส เนื่องจากมีพื้นที่ผิวที่มากและมีปริมาณ
ความแรงของกรดแบบปานกลางมากที่สุด ต่อมาได้มีการศึกษาสภาวะที่เหมาะสมในการเปลี่ยนเอ
ทานอลไปเป็นไดเอทิลอีเทอร์ด้วยปัจจัยที่แตกต่างกันเพื่อพัฒนาร้อยละผลผลิตไดเอทิลอีเทอร์ที่
อุณหภูมิต่ำ ปัจจัยที่ทำการศึกษาประกอบด้วยอัตราการไหลของแก๊สต่อน้ำหนักของตัวเร่งปฏิกิริยา
อัตราการไหลของแก๊สไนโตรเจน และความเข้มข้นของเอทานอล จากการทดลองสังเกตว่าการ
ลดลงของอัตราการไหลของแก๊สต่อน้ำหนักของตัวเร่งปฏิกิริยา อัตราการไหลของแก๊สไนโตรเจน
และความเข้มข้นของเอทานอลจะทำให้ค่าร้อยละผลผลิตของไดเอทิลอีเทอร์สูงขึ้นถึง 66.4% ที่
อุณหภูมิ 200 องศาเซลเซียส จากนั้นได้ทำการปรับปรุงตัวเร่งปฏิกิริยาด้วยฟอสฟอรัสหรือ
อิตเทรียมด้วยวิธีการเคลือบฝังเพื่อตรวจสอบคุณสมบัติและประสิทธิภาพของตัวเร่งปฏิกิริยา โดย
พบว่าทำให้พื้นที่ผิวและความแรงของกรดแบบปานกลางลดลงส่งผลให้ค่าร้อยละผลผลิตของได
เอทิลอีเทอร์ต่ำลง จึงสรุปได้ว่าการปรับปรุงด้วยฟอสฟอรัสหรืออิตเทรียมบนตัวเร่งปฏิกิริยาเบต้าซี
โอไลต์จะทำให้ประสิทธิภาพในการผลิตไดเอทิลอีเทอร์ต่ำลง

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
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6070280521 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Beta zeolite / Diethyl ether / Ethanol dehydration / Phosphorus / Yttrium

Montri Thapplee : Dehydration of ethanol to diethyl ether over beta zeolite catalysts. Advisor: Prof. BUNJERD JONGSOMJIT, Ph.D.

The catalytic ethanol dehydration to diethyl ether was investigated using synthesized beta zeolite catalysts having different Na and mixed Na-H form. The Na form in catalyst was synthesized by the hydrothermal process including non-calcined (Na-BEA_N) and calcined (Na-BEA_C) catalysts. The catalysts having different mixed Na-H forms were synthesized under ion-exchange method. In this study, two different cycles were chosen including one cycle (M-BEA_1) and four cycles (M-BEA_4). These catalysts were characterized by various techniques. The catalysts were tested to measure the catalytic activity at atmospheric pressure and the reaction temperature ranged from 150 to 400 °C. The results presented that the M-BEA_1 catalyst exhibited the highest DEE yield of 27.3% at 250 °C due to its large surface area and highest moderate acid site. In addition, the optimal condition was examined by various factors consisting WHSV, carrier gas (N_2) flow rate and ethanol concentration. It was observed that the low WHSV, carrier gas and ethanol concentration gave the highest DEE yield of 66.4% at 200 °C. Furthermore, the M-BEA_1 catalyst was modified with yttrium (Y) or phosphorus (P). It was found that both modifications with Y or P had effect on physical properties and acidity, resulted in decreased surface area and moderate acid site. It can be concluded that the modification of Y or P on beta zeolite catalyst decreased the DEE yield.

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

Academic Year: 2018   Advisor's Signature ....

ACKNOWLEDGEMENTS

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CHULALONGKORN UNIVERSITY

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Thailand is an agricultural country, which has grown many crops such as sugarcane, corn and cassava in all regions of the country. These plants are often used as food and export to other countries. However, the overproduction of those plants that exceed the demand results in lower prices. The government has a policy to help farmers by selling plants to the industry to produce ethanol. Ethanol is the oxygenated chemical compound produced by primary technology using fermentation method of plants from renewable biomass resource for the generation of liquid fuels. Normally, ethanol is mainly used as a biofuel additive by combination with petroleum distillates for transportation fuels such as gasoline and diesel engines. The statistics from Thailand Energy Academy reference shown in Figure 1, revealed that ethanol production capacity is higher than consumption, resulting in oversupply of ethanol and lower prices. It is predicted that the excess ethanol will become available as a used raw material for the production of value-added chemical compounds in the near future.
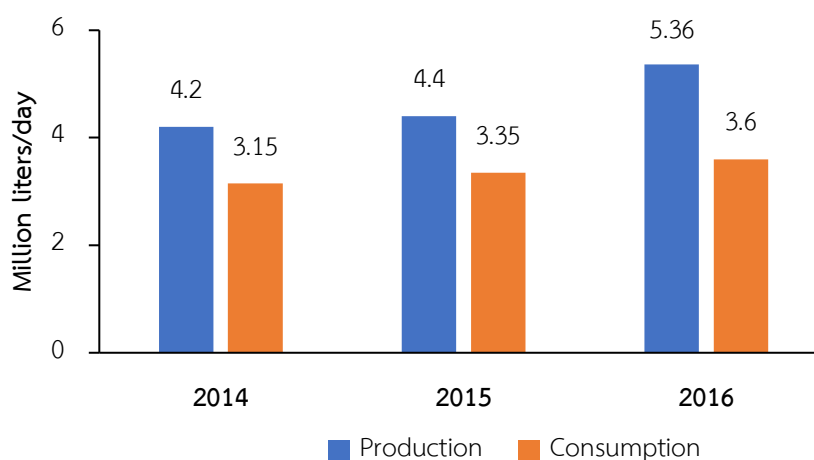
Figure 1 Domestic Ethanol Production and Consumption.

However, we can make the value-added of ethanol by selectively converting it into other chemical products such as diethyl ether, ethylene, acetaldehyde, acetone, acetic acid, etc. [1],[2]. Diethyl ether (DEE) has the potential to open new pathways to produce petrochemicals from non-petroleum feedstock that is an alternative source of clean renewable energy. It is often widely used as a solvent in many industries such as starting fluid for diesel and gasoline engines, general anesthetic during medical procedures and solvent for pharmaceutical industries [3]. Moreover, ethylene is one of the most important olefins that brings increasingly attracting more attention. It has been used as the major feedstock in many petrochemical industries [4]. Basically, ethanol can be converted to DEE and ethylene using catalytic dehydration. The formation of both products depends on the reaction temperature as a main factor. Many studies have been investigated on the correlation between the catalyst properties and catalytic performances in ethanol dehydration. Commercial zeolite catalysts including H-FER, H-MFI, H-MOR, H-BEA, H-Y and H-USY zeolite were investigated. It was found that at lower temperature and higher space velocities, DEE is formed with high yield on H-BEA, which seems to be the best catalyst for DEE synthesis with poor ethylene coproduction [5]. Beta zeolite is one type of zeolite catalysts having high-silica zeolite that is the interesting zeolite for petrochemical reaction because it has porous structures, high thermal stability and large surface area. In addition, the DEE/ethylene selectivity depends on the nature of the active site, where DEE formation being more favored for lower SiO_2/Al_2O_3 ratios. The catalytic performance depends mainly on the acid sites available on the catalyst surfaces. The strong Bronsted acid sites play the main duty for conversion of ethanol to ethylene, while the moderate strength acid sites are responsible to produce DEE [5],[6].

Therefore, the purpose of this study was to examine three parts. First, synthesis of catalysts, which is synthesized beta zeolite catalysts by the hydrothermal process followed by ion-exchanged method to obtain different Na and mixed Na-H form. Secondly, optimum conditions to produce DEE from ethanol will be investigated. Finally, modification of catalyst with yttrium or phosphorus will be conducted. The catalytic performance was evaluated via ethanol dehydration in the gas phase using a fixed-bed flow microreactor.

1.2 OBJECTIVE

1.2.1 To study the effect of different form in beta zeolite catalysts including Na form synthesized by the hydrothermal process and mixed Na-H form synthesized under ion-exchange conditions in ethanol dehydration.

1.2.2 To compare catalytic performance between calcined and non-calcined catalysts in ethanol dehydration.

1.2.3 To study the optimum condition to convert ethanol to diethyl ether in dehydration.

1.2.4 To study the influence of catalyst modification with yttrium and phosphorus that affect the catalytic performance in ethanol dehydration.

1.3 RESEARCH SCOPE

1.3.1 The Na form in beta zeolite was synthesized by hydrothermal process.

1.3.2 The calcined catalyst was prepared under air flow condition.

1.3.3 The beta zeolite catalysts having different mixed Na-H forms were synthesized under ion-exchange conditions that two different cycles were chosen including one cycle and four cycles.

1.3.4 The synthesized beta zeolite catalysts were characterized with X-ray diffraction (XRD), N_2 physisorption (BET and BJH), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (SEM-EDX) and temperature programmed desorption (NH_3-TPD).

1.3.5 All of catalysts were investigated for the catalytic performance by ethanol dehydration at atmospheric pressure and the reaction temperature ranging from 150 to 400 °C.

1.3.1 Choose the appropriate catalyst that gives the best activity in converting ethanol to DEE via ethanol dehydration.

1.3.2 The suitable condition was optimized by various factors including space velocity (WHSV=3.1, 6.3 and 11.4 h^{-1}), N_2 flow rate (900, 1800 and 3600 ml/h) and ethanol concentration (1.7 x 10^{-4} and 3.5 x 10^{-4} g_{EtOH}/ml) at optimal temperature in dehydration.

1.3.3 Determining the most suitable condition, which gives the best value of DEE yield in ethanol dehydration.

1.3.4 Modification of appropriate catalyst with transition metal such as yttrium and/or phosphorus were investigated in ethanol dehydration reaction at atmospheric pressure and reaction temperature ranging from 150 to 400 °C.

1.3.5 Comparing the performance of unmodified and modified catalysts that gives the best activity in ethanol dehydration.

1.4 RESEARCH MEDTHODOLOGY

Part 1: Investigation the different of Na form and mixed Na-H form in beta zeolite catalyst.

```
        ┌────────────────────────────────────────────────┐
        │  Synthesis of beta zeolite catalysts by hydrothermal  │
        └────────────────────────────────────────────────┘
```

Synthesis of beta zeolite catalysts by hydrothermal

Non-calcined catalyst

Calcined catalyst (Na form)

Synthesis Mixed Na-H form under ion-exchange

One cycle

Four cycles

Catalyst testing

Catalyst characterization

Ethanol dehydration at atmospheric pressure and reaction temperature ranging from 150 to 400 °C

XRD   BET   NH$_3$-TPD   SEM-EDX

Compare four catalysts that give the best activity in dehydration

Discuss and conclude result of catalyst characterization

Choose the appropriate catalyst to use in part II

Part 2: Investigation the suitable condition by various factors in ethanol dehydration.

```
┌─────────────────────────────────────────┐
│    Use the appropriate beta zeolite catalyst   │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│       Investigation the suitable condition      │
│              by various factors                │
└─────────────────────────────────────────┘
```

Space velocity (WHSV), h^{-1}	N_2 flow rate, ml/h	Ethanol concentration, g_{EtOH}/ml

3.1	6.3	11.4	900	1,800	3,600	1.7×10^{-4}	3.5×10^{-4}

```
┌─────────────────────────────────────────┐
│         Test in ethanol dehydration at        │
│      atmospheric pressure and reaction        │
│   temperature ranging from 150 to 400 °C      │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│        Discuss and conclude result of         │
│            the suitable condition             │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│         Choose the suitable condition         │
│            to use in part III                 │
└─────────────────────────────────────────┘
```

Part 3: Investigation the influence of modification catalyst with yttrium or phosphorus.

1.5 THESIS GANTT CHART

Tasks	2018 (Year 1)												2019 (Year 2)					
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6
Literature review	▓	▓	▓	▓														
Decide research topic					▓													
Decide methodology						▓												
Preliminary reaction test							▓											
Prepare the catalysts Part I								▓	▓									
Characteriza-tion catalysts Part I										▓	▓							
Conduct research Part I											▓	▓						
Analyse data Part I												▓	▓					
Conduct research Part II														▓	▓			
Analyse data Part II																▓		
Prepare the catalysts Part III																▓		
Characteriza-tion catalysts Part III																▓	▓	
Conduct research Part III																▓	▓	
Analyse data Part III																	▓	▓

1.6 BENEFITS

1.6.1 The obtained appropriate form of mixed Na-H in beta zeolite catalyst for ethanol dehydration.

1.6.2 The obtained optimum condition for the production of DEE by catalytic ethanol dehydration.

1.6.3 The influence of Y or P modified on beta zeolite catalysts for dehydration of ethanol to DEE had been reported.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 BACKGROUND

This section represented the fundamental concept and theoretical information related to the catalytic dehydration.

2.1.1 Dehydration of ethanol

Nowadays, renewable energy is interesting to people all over the world due to non-renewable energy is running out. Ethanol is a popular renewable energy that is used as a raw material for converting into other chemical compounds.

Basically, there are two competitive pathways during catalytic dehydration of ethanol. Ethanol can be converted into ethylene at high temperature, which is an endothermic reaction, while DEE is generated at lower temperature via an exothermic reaction as shown in both reactions. (1) and (2) [7].

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad \Delta H_{298} = +44.9 \frac{kJ}{mol} \quad (1)$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \quad \Delta H_{298} = -25.1 \frac{kJ}{mol} \quad (2)$$
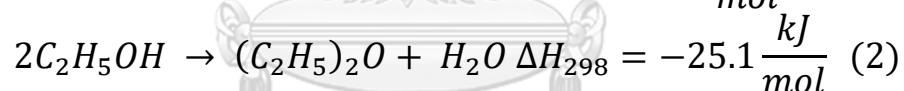
For the research of mechanism on surface catalyst via the ethanol dehydration can be described as shown in Figure 2. The mechanism on the surface zeolite is essentially the same as alumina catalyst. It can be observed that the dehydration to ethylene occurs through two paths, which direct one by ethoxy groups cracking and the serial one composed of DEE by reaction of an ethoxy group with undissociated ethanol and sequent cracking of DEE on the acid sites. Water is the byproduct of equations (1) and (2) that at low reaction temperature, it can be assumed that the surface of catalyst is largely hydroxylated. Consequently, the active site can be assumed to be formed by active hydroxyl groups.

In summary, it can divide the mechanism into 3 steps as follows:

Step A: This step corresponds to reaction (3), the production of ethoxy groups by desorption of water.

$$C_2H_5OH_{(g)} + Si(OH^-)Al \leftrightarrow Si(C_2H_5O^-)Al + H_2O_{(g)} \quad (3)$$

Ethanol   Hydroxy group   Ethoxy group   Water

Step B: This step forms ethylene through a considerably irreversible elimination mechanism as presented in reaction (4).

$$Si(C_2H_5O^-)Al \rightarrow Si(OH^-)Al + H_2C = CH_{2(g)} \quad (4)$$

Ethoxy group   Hydroxy group   Ethylene

Step C: This step as a parallel way with step B. The gas phase ethanol generates DEE in a reversible way as shown in reaction (5).

$$Si(C_2H_5O^-)Al + C_2H_5OH_{(g)} \leftrightarrow (C_2H_5)_2O_{(g)} + Si(OH^-)Al \quad (5)$$

Ethoxy group   Ethanol   DEE   Hydroxy group

In fact, the adsorption of DEE can crack by the sequence step C and step B to produce ethylene, too. As mentioned, step B is faster than step C when the conversion and reaction temperature is high, but the reverse is actual at lower conversion and temperature [8].

But ethylene take place, at low temperature, with a coherent path via DEE formation and cracking (DEE cracking) as shown in reaction (6).

$$(C_2H_5)_2O_{(g)} \leftrightarrow H_2C = CH_{2(g)} + C_2H_5OH_{(g)} \quad (6)$$

DEE   Ethylene   Ethanol

Figure 2 Schematics of the ethanol dehydration on surface catalyst [8].

2.1.2 Catalyst

Catalyst is a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed in the reaction. The catalyst offers an alternative pathway, which the catalyzed reaction has lower activation energy (E_a) than the uncatalyzed reaction. Therefore, a fraction of molecules will be able to react faster via this catalyzed pathway than they could without the catalyst at the same temperature as shown in Figure 3 [9].

Traditionally, the field of catalysis is divided into three areas: heterogeneous, homogeneous, and enzyme catalysis. Heterogeneous catalysts are present in a phase different from that of the reactants; normally, the reactants are in the gas or liquid phase, whereas the catalyst is a solid material. Heterogeneous catalysts have the good property that after reaction they are easily separated from the reactants and products.

This is an important reason why heterogeneous catalysts are often preferred in industry [10].
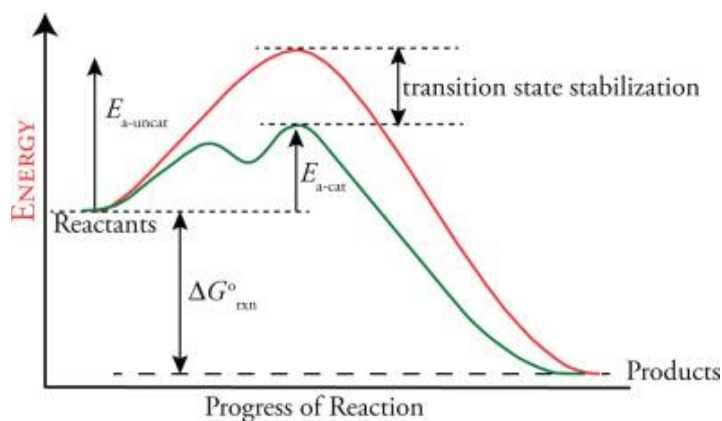
Figure 3 Energy Diagram for a Catalyzed and an Uncatalyzed Reaction.

2.1.3 Zeolites

Zeolites are crystalline material which hydrated aluminosilicates. Their structure is a framework depend on an exceedingly connecting three-dimensional network of SiO_4 and AlO_4 tetrahedra joined to each other by sharing oxygen atoms [11]. In addition, zeolites find wide use as ion-exchange agents, catalysts, and molecular filters in a range of industrial processes. The word "zeolite" comes from the Greek for "boiling stone" due to the early observation that zeolites release water when heated [12]. Furthermore, as their compositions are not fixed, they are examples of nonstoichiometric compounds. The ordinary crystallographic unit cell formula of a zeolite is given as:

$$M_{x/m}[(AlO_2)_x(SiO_2)_y].z\,H_2O$$
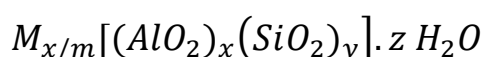
where, M substitues the non framework of metal cation, m is its charge, z is the number of water molecules and x and y are integers such that y/x ≥ 1. The exhibition enclosed in the square brackets presents the anionic framework composition [13].

2.1.4 Beta zeolite

Beta zeolite is a large-pore material with the SiO_2/Al_2O_3 ratio of beta zeolite is generally larger than 10, low-Al microporous material that properties an intergrowth of two or more polymorphs comprising a three-dimensional, 12-membered ring channel system represented in Figure 4. Many studies have been attempted to the synthesis of commercially important beta zeolite due to it is of great industrial interest as an excellent catalyst for various reactions [14]. The industrial interest in beta zeolites is due to a combination of several favorable properties, including high surface area, good ion-exchange capability, strong acidity, and high thermal and hydrothermal stability. It is well known that the acid-base properties of a zeolite are influenced greatly by the content of silicon and aluminum in its framework. Therefore, adjusting the chemical composition of zeolite beta may be a way to obtain a zeolite material with stronger acidity [15]. Moreover, the activity of zeolite is measured by the strength of acid sites, the amount of approachable Bronsted acid sites per unit cell, which are relative to the tetrahedrally coordinated Al content in the zeolite framework. Therefore, the SiO_2/Al_2O_3 ratio of beta zeolite performs an main role in defining its catalytic activity and lifetime of the zeolite catalyst.

The high Al content in zeolite that is low SiO_2/Al_2O_3 ratio generally has high quantity of acid sites, but a zeolite will lead to high coke formation rate, which results in quick catalyst deactivation [16],[17].
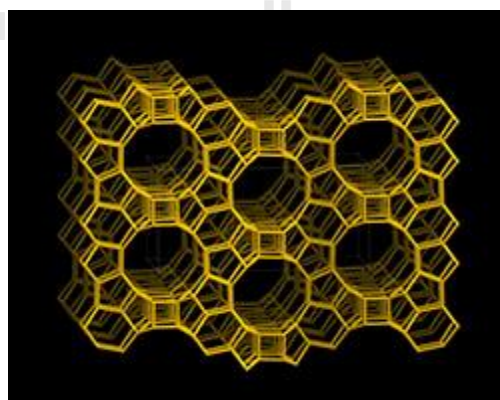
Figure 4 Beta zeolite structure.

2.1.5 Ion-exchange method

Ion exchange is an intrinsic property of most zeolites. The most common application of ion- exchange here is the synthesis of ammonium forms of zeolites to the generation of acidic catalysts. Upon calcination of the ammonium zeolite, ammonia is driven off, leaving behind the acidic form of the zeolite, where protons reside at the ion exchange sites as demonstrated in Figure 5 [18]. Which can be described the method as follows:

a) The ammonium solution was added to create ammonium exchange by ion-exchange method.

b) Na^+ was exchanged by NH_4^+ to produces the NH_4^+ form.

c) The NH_3 compound was decomposed by calcination to create an acid site (H^+ form).

d) The acid form c) is in equilibrium with the form d) that is a silanol group close to tricoordinate aluminium.
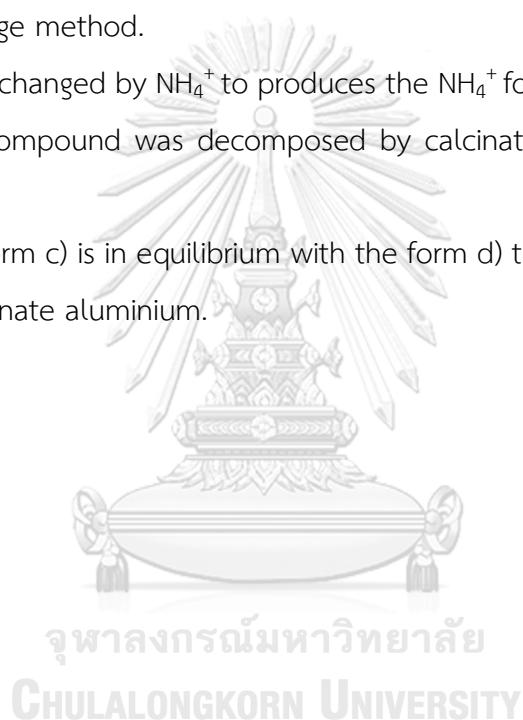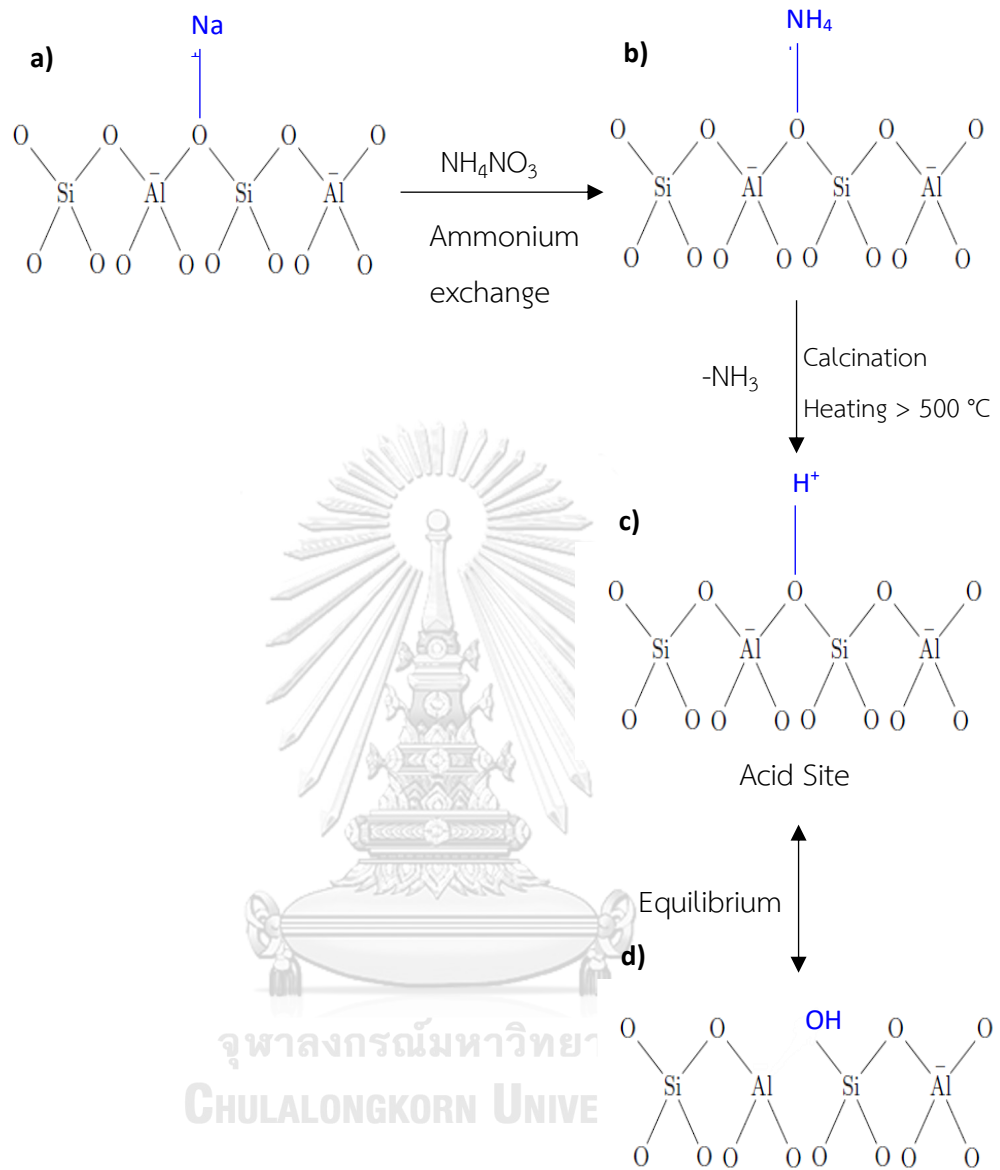
Figure 5 Diagram of the ion-exchange of a zeolite framework.

2.1.6 Yttrium properties

Yttrium is a chemical composition with atomic number 39 and symbol Y. It is a silvery metallic transition metal chemically same as the lanthanides and has often been grouped as a "rare earth element". Yttrium is a mild, silver metallic, gleaming and highly crystalline transition metal in group 3. As forecasted with periodic trends, it is few electronegative than its predecessor in the group, scandium (Sc), and less electronegative than the next member of period 5, zirconium (Zr); as well, it is more electronegative to its beneficiary in its group, lanthanum (La), being closer in electronegativity to the later lanthanides due to the lanthanide retraction. Yttrium is the first of d-block element in the fifth period. The essential physical properties of Yttrium is reported in Table 1 [19].

Table 1 Yttrium properties.

Properties	Specification
Group, Period, Block	3, 5, d
Atomic number, mass	39, 88.91 g/mol
Appearance	Silvery white
Phase	Solid
Density near r.t.	4.472 g/cm^3
Melting point	1,526 ℃
Boiling point	2,930 ℃

Yttrium oxide (Y_2O_3) or yttria is very wide range of important applications. its properties include chemical stability, high thermal stability, low thermal expansion and high thermal conductivity. However, Bonne M. et al. [20] reported that the addition of small amount of Y_2O_3 seems to increase not only the basicity but also the acidity of ZrO_2. It presents basic site, after addition to the oxide, the surface basicity of the material increases. Furthermore, addition of Y_2O_3 into ZrO_2 lattice will make some vacancies that generate acid sites and increase the general acidity of the material. In addition, the modification of Y_2O_3 affects the inhibition of sintering mechanism and increase the catalytic activity.

2.1.7 Phosphorus properties

Phosphorus is a chemical element with symbol P and atomic number 15. It has several allotropes that exhibit strikingly different properties. The two most common allotropes are white phosphorus and red phosphorus. Most production of phosphorus-bearing material is for agriculture fertilizers. For this purpose, phosphate minerals are converted to phosphoric acid. The important physical properties of Phosphorus is reported in Table 2 [21].

Table 2 Phosphorus properties.

Properties	Specification
Group, Period, Block	15 , 3 , p
Atomic number, mass	15, 30.97 g/mol
Appearance	Colorless, yellow, scarlet, red, violet, black
Phase	Solid
Density near r.t.	white: 1.823 g/cm^3
	red: $\approx$ 2.2–2.34 g/cm^3
	violet: 2.36 g/cm^3
	black: 2.69 g/cm^3
Melting point	44.25 ℃
Boiling point	280.15 ℃

Phosphoric acid catalysts have been industrially used for many processes. P-modified catalysts also exhibited very high catalysts stability due to their improved coke resistance properties. Moreover, the mainly properties of P indicate that the strong acid sites are being changed by the addition of P by generating mostly weak acid sites [22].

2.2 LITERATURE REVIEW

The section of literature review describes previous research on the catalyst for ethanol dehydration. A variety of research have studied with different type catalysts, which summarize the results in advantages and disadvantages of each catalyst. This information can lead to further development of the catalyst efficiency in dehydration reaction.

The dehydration of alcohol to ether or to ethylene is known from about the 13th and 18th centuries, respectively. In 1797 four Dutch chemists including Bondt, Deiman, Pacts van Troostwijk, and Lauwerenburgh discovered the catalytic dehydration of alumina on alcohol (at that occasion they introduced the name "olefin") [23].

In 1923, Robert N. Pease et al. [24] studied the dehydration of ethanol on alumina catalyst. The result shown that ethylene are formed by alcohol at 275 and 300 °C, the amount of ethanol decomposed attains a maximum corresponding to about 65% of conversion, whereas at 350 °C the reaction goes to complete dehydration to form ethylene. The ether decomposes promptly when the temperature above 275 °C.

In 1998, Kito-Borsa T., et al. [25] investigated the catalytic activity of Resin-based catalysts (sulfonated polystyrene resin that Dow Chemical and HCR-W2) and a sulfonated polystyrene resin with a fluorinated carbon backbone (Du Pont and Nafion NR50) and γ-alumina catalysts. The result indicated that Resin-based catalysts fail to pay the conversion while γ-alumina catalyst gives a better performance in dehydration of ethanol to DEE.

In 2007, Varisli D. et al. [26] studied dehydration of ethanol in the temperature ranging of 140-250 °C with three different heteropolyacid catalysts including tungstophosphoricacid (TPA), silicotungsticacid (STA) and molybdophosphoricacid (MPA). It can be seen that TPA gives high the ethylene yield of 75% at 250 °C. On the other hand, DEE is the main product at temperatures lower than 180 °C. The trend of catalyst activity was obtained as STA>TPA>MPA, STA showed

the highest activity in ethanol dehydration because its higher number of protons and stability in the temperature over 180 °C. Besides, parallel routes for the production of ethylene and DEE some decrease of catalyst activity in the presence of water vapor with TPA catalyst.

In 2008, Zhang D. et al. [27] studied A series of phosphorus (P) modified HZSM-5 catalysts with P loading of 1.9-5.1 wt% were prepared impregnation. It was found that modification of phosphorus decreased strong acid site but increased weak acid site in catalyst. Over the catalyst with 3.4 wt% P, the main product is ethylene at 300-440 °C, due to after P modification presence of weak acid sites in catalyst.

In 2010, Varisli D. et al. [28] reported the catalyst activity of synthesized W–silicate-based catalyst (TRC-92) in ethanol dehydration. As a result, this catalyst is a highly stable solid acid catalyst, with having pore size between meso and macrospores material. Such a pore structure allows easier move of the reactant molecules to the active sites of the catalyst. The highest of DEE selectivity showed at 200 °C in dehydration of ethanol, while ethylene selectivity approached to 100% over 200 °C.

In 2011, Nair H. et al. [29] investigated the mechanism of metal oxide (VOx, MoOx, and WOx) on silica-supported catalysts in dehydration of ethanol. The main point presented that DEE formation ability of the metal oxide is related to the electronegativity of the active metal atom.

In 2013, Rahmanian A. et al. [30] predicted using software program in the effect of ethanol flow rate (WHSV= 0.59-2.96 h^{-1}) on aluminum phosphate-hydroxyapatite catalyst via liquid phase ethanol dehydration. Due to ethanol flow rate is a main factor because it directs the contract time of the reactants and products on the catalyst bed. The results showed that the DEE yield and DEE selectivity increased with increasing the flow rate of ethanol at temperature upper than 350 °C. Moreover, the optimal conditions of ethanol flow rate of 0.17ml.min^{-1} (WHSV=1.01 h^{-1}), 200 bar and 340 °C, the DEE yield, DEE selectivity, ethanol conversion, and liquid selectivity obtained above 75%, 96%, 78%, and 97%, respectively.

In 2015, Phung T.K. et al. [8] investigated the catalytic conversion of ethanol and DEE over alumina (A), zeolites (MFI, FER and USY), silica-alumina (SA) and MgO/Al$_2$O$_3$ (MgA). It indicated that the acid of catalysts like alumina, zeolites and silica-alumina are active in the temperature range 180-300 °C for dehydration of ethanol to DEE and to ethylene. The conversion trend at 300 °C, MFI (98.3%) > USY (83.8%) > A (55.9%) > SA (52.1%) > MgA (0.1%). In addition, this research studied the effect of space velocities showed that at lower space velocities the DEE selectivity falls in favour of ethylene selectivity.

In 2015, Phung T.K. et al. [31] reported the catalytic activity on different ratio of SiO$_2$/Al$_2$O$_3$ catalysts including A, SA5, SA30, SA87 and S by ethanol dehydration. The result showed that DEE selectivity at low conversion follows the trend selectivity: A > SA5 > SA30 > SA87 > S, observed that DEE formation being more favored for lower SiO$_2$/Al$_2$O$_3$ ratios.

In 2015, Phung T.K. et al. [5] investigated commercial H-FER, H-MFI, H-MOR, H-BEA, H-Y and H-USY zeolite samples, and alumina and silica alumina for comparison. The result indicated that Protonic zeolites are more active than silica alumina and alumina in converting ethanol into DEE and ethylene that presence of Bronsted acidic bridging hydroxyl groups only in the zeolite cavities. At lower temperature and higher space velocities, DEE is formed with high yield over of 70% at 180-200 °C on H-BEA zeolite.

In 2017, Said A.E.-A.A. et al. [6] reported the effect of phosphotungstic acid loading (0.5–40 wt/wt%) on γ-Alumina catalyst for the ethanol dehydration to DEE. It found that 20 wt% PWA exhibits 99% of DEE selectivity because the monolayer generation of WO$_3$ on the support. Furthermore, the duty of Bronsted acid site strength on the catalytic performance was investigated. The result observed that the catalytic performance of ethanol dehydration depends mostly on the acid sites accessible on the surfaces of catalyst, so the strong Bronsted acid sites show the main duty for change ethanol to ethylene. But the moderate acid sites created with WO$_3$ were

responsible for change ethanol to DEE with selectivity of 99% at lower temperature of 190 °C.

In 2018, de Oliveira T.K.R. et al. [32] investigated the dehydration reaction over impregnation of Cu and Fe on ZSM-5 zeolite. The result found that Fe on ZSM-5 not changed the acidity of ZSM-5 but reduced the crystallization of the catalyst. While, Cu changed the acidity of ZSM-5 and favored formation of DEE with moderate strength acid sites of Cu/ZSM-5. The generation of DEE is favored at temperatures between 180-200 °C over the Cu/ZSM-5 catalyst.

From all previous researches, they show using a variety of catalysts for ethanol dehydration. However, beta zeolite has an interesting property in this reaction such as the acidity, strength acid site, physical properties and chemical properties. Therefore, the synthesis of zeolite was chosen in this research to study the various factors that affect the performance of the catalyst. In addition, the modification of catalyst and the optimum conditions were investigated for better efficiency in converting ethanol to DEE.

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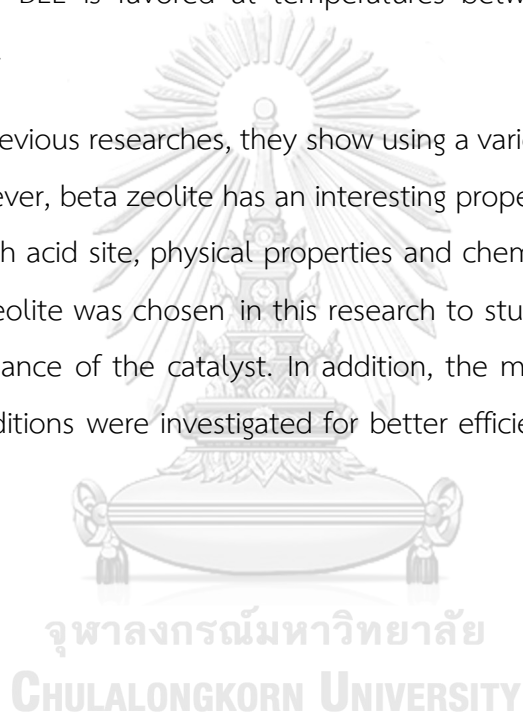
CHAPTER 3

EXPERIMENTAL

This section explained the information in experimental part including synthesis the beta zeolite catalysts by hydrothermal process and ion-exchange method, study of the appropriate conditions, modification catalyst with yttrium and phosphorus by incipient wetness impregnation method, catalyst characterization including X-ray diffraction (XRD), N_2 physisorption (BET and BJH), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (SEM-EDX), and temperature programmed desorption (NH_3-TPD) and catalyst testing in ethanol dehydration.

3.1 PREPARATION OF CATALYST

3.1.1 Synthesis of beta zeolite

Beta zeolite catalyst was synthesized by hydrothermal process using tetraethylammoniumhydroxide solution (TEAOH) 40% in H_2O, sodium chloride, potassium chloride, silica nanopowder, sodium hydroxideand sodium aluminate as shown in Table 3.

The synthesis of catalyst following procedures described by Camblor M.A. et al. [33]. First, 89.6 g TEAOH (40%) was mixed with 0.53 g sodium chloride, 1.44 g potassium chloride and 59.4 g in distilled water. After that added 29.54 g silica and stirred until homogenized. The solution was mixed with 0.33 g sodium hydroxide, 1.79 g sodium aluminate and 20.0 g water and stirred to give a thick gel. Then, it was transferred to an autoclave and the zeolite was crystallized at 135 °C for 20 h with agitation at 60 rpm. The obtained crystal product was centrifuged at 10,000 rpm for 15 min for each cycle, washed with distilled water until pH~9 and dried at 110 °C for overnight in oven to obtain the non-calcined catalyst (Na-BEA_N).

Table 3 The chemical used in synthesis of beta zeolite catalyst.

Chemical	Formula	Supplier
tetraethylammoniumhydroxide solution (TEAOH) 40% in H2O	$(C_2H_5)_4N(OH)$	Aldrich
sodium chloride	NaCl	Emsure
potassium chloride	KCl	Riedel-de Haën
silica nanopowder	SiO_2	Aldrich
sodium hydroxide	NaOH	Emsure
sodium aluminate	$NaAlO_2$	Sigma-aldrich

3.1.2 Synthesis of Na and mixed Na-H form in beta zeolite catalyst

The Na form in beta zeolite was synthesized by using non-calcined catalyst through calcined under air flow at 550 °C for 6 h with heating rate of 5 °C/min to decompose the organic template and to generate the channels in the crystals which is called Na-BEA_C catalyst.

The different mixed Na-H forms were synthesized under ion-exchange method using 1M ammonium nitrate as demonstrated in Table 4 with the v/w ratio of 20 ml NH_4NO_3/g cat. under continues agitation at 70 °C for 2 h/cycle. In this study, two different cycles were chosen including one cycle (M-BEA_1) and four cycles (M-BEA_4). Next, the ion-exchange sample were washed with deionized water, filtered, dried in oven at 110 °C for overnight and calcined under air flow at 550 °C for 6 h with 5 °C/min of the heating rate to drive off the unstable components that NH_3 and NO_x. The one and four cycles in ion-exchange method are called M-BEA_1 and M-BEA_4 catalysts.

Table 4 The chemical used in synthesis of Na and mixed Na-H form in beta zeolite catalyst.

Chemical	Formula	Supplier
85% Phosphoric acid	H_3PO_4	Merck

3.1.3 Synthesis of modified Y on beta zeolite catalyst

The loading of 0.5 wt% Y on beta zeolite catalyst was prepared by incipient wetness impregnation method. Yttrium (III) nitrate hexahydrate as presented in Table 5 was used as a precursor of Y. Before adsorption, the beta zeolite catalyst was dried in oven at 110 °C for overnight in order to remove adsorbed water on the surface and it was determined the amount of desired solution in the total pore volume of catalyst. Then, the catalyst was impregnated with the Y precursor solutions. After that, the mixture was gradually dried in an oven at 110 °C to remove excess water until the catalyst was almost dried. Finally, it was calcined under air flow at 450 °C for 3 h with 5 °C/min of the heating rate to obtain the modified Y on beta zeolite catalyst (0.5Y/M-BEA_1).

Table 5 The chemical used in synthesis of modified Y on beta zeolite catalyst.

Chemical	Formula	Supplier
Yttrium (III) nitrate hexahydrate, 99.9%	$Y(NO_3)_3 \cdot 6H_2O$	Aldrich

3.1.4 Synthesis of modified P on beta zeolite catalyst

The loading of 5 wt% P on beta zeolite catalyst was prepared by incipient wetness impregnation method. Phosphoric acid (H_3PO_4) as shown in Table 6 was used as a precursor of P. Before adsorption, the beta zeolite catalyst was dried in oven at 110 °C for overnight in order to remove adsorbed water on the surface and it was determined the amount of desired solution in the total pore volume of catalyst. Then, the catalyst was impregnated with the phosphoric acid precursor solutions. After that, the mixture was gradually dried in an oven at 110 °C to remove excess water until the catalyst was almost dried. Finally, it was calcined under air flow at 550 °C for 4.5 h with 5 °C/min of the heating rate to obtain the modified P on beta zeolite catalyst (5P/M-BEA_1).

Table 6 The chemical used in synthesis of modified Y on beta zeolite catalyst.

Chemical	Formula	Supplier
Phosphoric acid (85%)	H_3PO_4	Merck

3.2 CHARACTERIZATION OF CATALYST

3.2.1 X-ray diffraction (XRD)

The catalysts were characterized using a SIEMENS D-5000 X-ray diffractometer with Cu K_α (λ = 1.54439 Å). It was applied to identify the crystalline phases of the catalysts. The spectra were scanned in the range 2θ of 10 to 50°.

3.2.2 N₂ physisorption (BET and BJH)

Micromeritics ASAP2000 automated system was consumed to determine of BET surface area, average pore size diameter and isotherms type of catalysts.

3.2.3 Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (SEM-EDX)

Hitashi mode S-3400N was used to investigate the morphology of catalysts. Micrographs were taken at the accelerating voltage of 30 kV and magnification ranging from 1,000 to 10,000 and the resolution of 3 nm. The SEM was performed using the secondary scattering electron (SE) mode. The elemental distribution mapping of catalysts was determined by using Link Isis series 300 program Energy dispersive X-ray spectroscopy.

3.2.4 Temperature programmed desorption (NH₃-TPD)

Micromeritics chemisorp 2750 pulse chemisorption system was performed to measure the acid properties of the catalysts. In the measurement, 0.05 g of catalyst was packed in a U-tube glass with 0.03 g of quartz wool and pretreated at 500°C under helium flow for 1 h. Then, the sample was saturated with 15% of NH₃/He and the physisorbed ammonia was desorbed under helium gas flow after saturation.

The sample was heated from 40 °C to 500 °C at a heating rate of 10 °C /min to desorb the chemisorbed NH_3.

3.3 STUDY OF THE APPROPRIATE CONDITIONS

The study of the appropriate conditions for ethanol dehydration by using the appropriate beta zeolite catalyst was divided into three factors. First, the factor of space velocity including various the weight hourly space velocity (WHSV) of 3.1, 6.3 and 11.4 h^{-1} were performed. Each WHSV was investigated in catalytic ethanol dehydration. Secondly, the factor of carrier gas (N_2) flow rate that including 900, 1,800 and 3,600 ml/h were investigated in catalytic ethanol dehydration by controlled a constant ethanol flow rate. Third, the factor of ethanol concentration including 1.7 x 10^{-4} and 3.5 x 10^{-4} g_{EtOH}/ml were investigated in catalytic ethanol dehydration by controlled a constant N_2 flow rate.

3.4 ETHANOL DEHYDRATION TESTING

The dehydration reaction of ethanol in gas phase was performed in a fixed-bed continuous flow microreactor, made from a borosilicate glass with an inside diameter of 10 mm and a length of 49.5 cm. In the experiment, 100 mg of catalyst was packed with quartz wool in the middle of microreactor and catalyst was removed the impurity from the surface by pretreating with nitrogen with 60 ml/min at 200 °C for 1 h. After that, the ethanol was fed into a microreactor at atmospheric pressure and the reaction temperature ranging from 150 to 400 °C. Finally, main product (DEE) and other products were detected and analyzed by a Shimadzu GC8A gas chromatograph with flame ionization detector (FID) using capillary column (DB-5). The chemical, operating condition of gas chromatograph and schematic of ethanol dehydration are reported in Tables 7, 8 and Figure 6, respectively.

Table 7 The chemical used in dehydration reaction.

Chemical	Formula	Supplier
99 wt % Ethanol	C_2H_5OH	Merch
UHP Nitrogen gas 99.99 %	N_2	Linde

Table 8 The operating conditions of gas chromatograph.

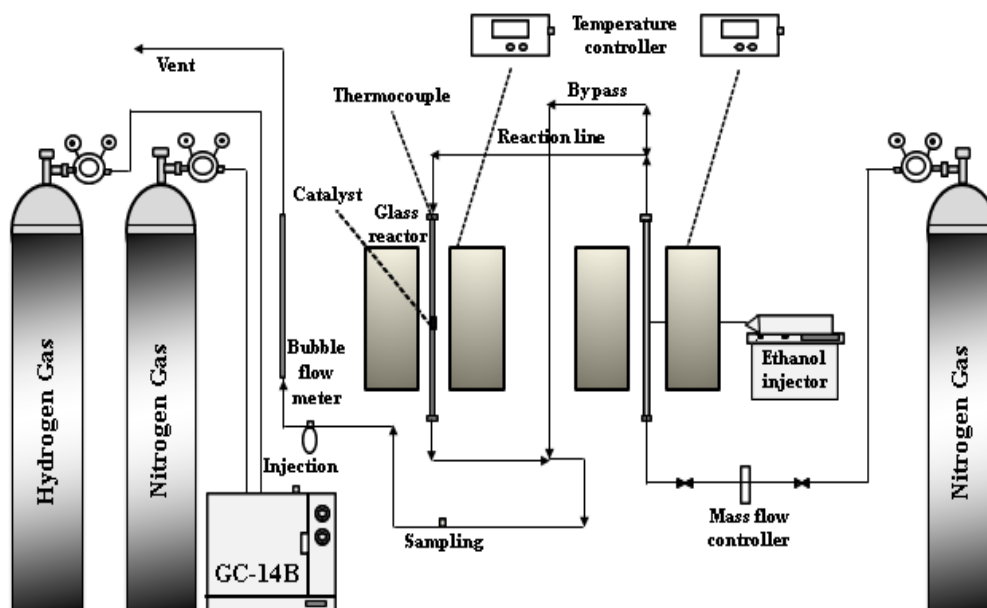| Gas Chromatograph	Shimadzu GC 14-A
Detector	FID
Capillary column	DB-5
Temperature of column	Initail 40 ºC
	Final 40 ºC
Carrier gas	Nitrogen gas
	Hydrogen gas
Temperature of detector	150 ºC
Tempurature of injector	150 ºC
Time analysis	8 min

Figure 6 Schematic of the ethanol dehydration reaction.

CHAPTER 4
RESULTS AND DISCUSSION

In this chapter, the analytical instruments and testing the dehydration were used to discuss the identification of the prepared beta zeolite with various forms in the structure of the catalyst, which lead to different properties. The different properties of the catalyst will result in different ability to catalyze the dehydration reaction. However, with understanding the reaction mechanism deeply, we can improve the operating condition in order to obtain the maximum value of DEE yield and use the most cost-effective resources. This chapter is divided into three parts. The first part describes the effect of catalytic preparation with different forms, consisting of Na and mixed Na-H using calcination and ion-exchanged methods. The second part summarizes the results of the dehydration reaction test to find the optimal condition for DEE production, which is divided into 3 factors including space velocity (WHSV), N_2 flow rate and ethanol concentration. The final part describes modified catalysts with P and Y that affect the physical and chemical properties in the catalyst. All results will be concluded about the appropriate form in beta zeolite catalyst, working conditions and the influence of catalyst modification to produce DEE better.

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PART 1: INVESTIGATION THE DIFFERENT OF Na FORM AND MIXED Na-H FORM IN BETA ZEOLITE CATALYST

4.1 CATALYTIC ACTIVITY OF DIFFERENT FORM IN BETA ZEOLITE CATALYSTS

The beta zeolite catalysts including Na and mixed Na-H form in catalyst were investigated the catalytic activity. The synthesized catalyst was characterized by various techniques to compare the properties of the catalyst. The different forms in beta zeolite catalyst were tested the performance by dehydration reaction.

4.1.1 Characterization of synthetic beta zeolite catalysts with the different of Na and mixed Na-H form

The Na form in beta zeolite is synthesized through the hydrothermal process under autoclave at 135 °C for 20 h without calcination and calcination in the air flow at 550 °C for 6 h to obtain the non-calcined and the calcined catalysts, respectively. The amounts of different mixed Na-H form in catalysts are generated by the ion-exchange method with different cycles, including one and four cycles. The physical properties of different form in catalysts are identified by X-ray diffraction (XRD), N_2 physisorption (BET and BJH), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (SEM-EDX) and temperature programmed desorption (NH_3-TPD).
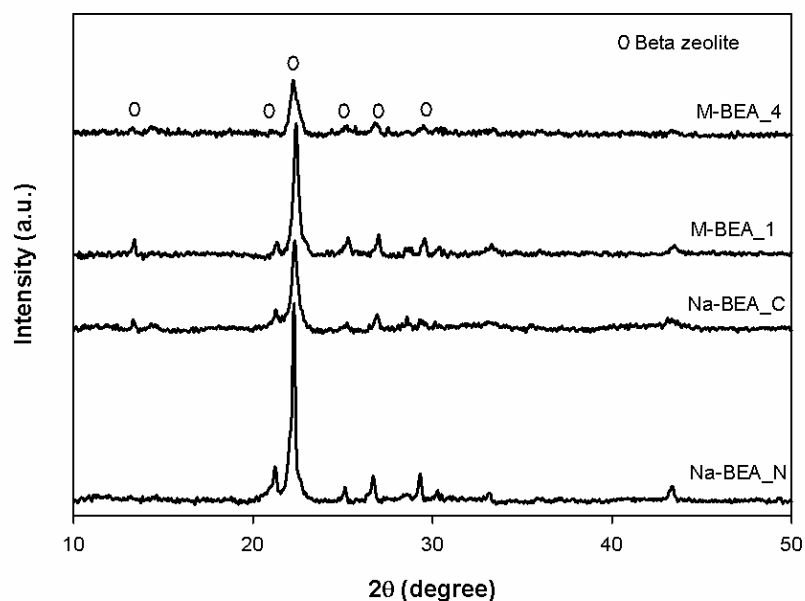
4.1.1.1 X-ray diffraction (XRD)

Figure 7 XRD patterns of different form in beta zeolite catalysts.

X-ray diffraction instrument was used to determine the identification phase and the crystallinity of zeolite beta with different form in catalysts. The peaks indicate the characteristics of zeolite phase with a BEA type structure appearing at $2\theta = 13.4°$, $21.5°$, $22.6°$, $25.4°$, $27.0°$ and $29.7°$ [33],[34],[35]. Figure 7 shows the phase patterns of synthesized catalysts having 2θ positions corresponding to the reference database, thus confirmed that all catalysts were beta zeolite structure.

4.1.1.2 N$_2$ physisorption (BET and BJH)

The physical adsorption of N$_2$ gas was used as a probe molecule to analyze the specific surface area, pore size diameter and pore volume of the catalyst as shown in Table 9. The BET surface area of a Na form indicated that the calcined catalyst (Na-BEA_C) has a higher surface area than the non-calcined (Na-BEA_N) catalyst while its pore size diameter was lower because of the calcination decomposes the organic template and generate the channels in the crystals structure of the catalyst. The mixed Na-H form showed that one cycle in the ion-exchange method (M-BEA_1) exhibited a higher surface area than four cycles (M-BEA_4), but its pore size diameter was lower.

A comparison between the Na and mixed Na-H form concluded the M-BEA_1 exhibited the highest the surface area (392.4 m^2/g).

Moreover, Figure 8 shows the isotherm graph of different form in beta zeolite catalysts that demonstrated an isotherm type of the materials, according to the International Union of Pure and Applied Chemistry (IUPAC) classification by analyzing at a constant temperature (liquid N$_2$=-196 °C). The Na and mixed Na-H form shown the isotherm characteristic between type 1 and 4 (appeared the hysteresis loop), represented the typical of solid materials with micropores and mesopores [36].

Table 9 BET surface area, pore size diameter and pore volume of different form in beta zeolite catalysts.

Catalysts	BET surface area[a], S$_{BET}$ (m²/g)	Pore size diameter[b] (nm)	Pore volume[c] (cm³/g)
Na-BEA_N	15.8	8.1	0.03
Na-BEA_C	235.7	5.4	0.04
M-BEA_1	392.4	4.4	0.05
M-BEA_4	195.8	4.1	0.03

[a] calculated from BET method

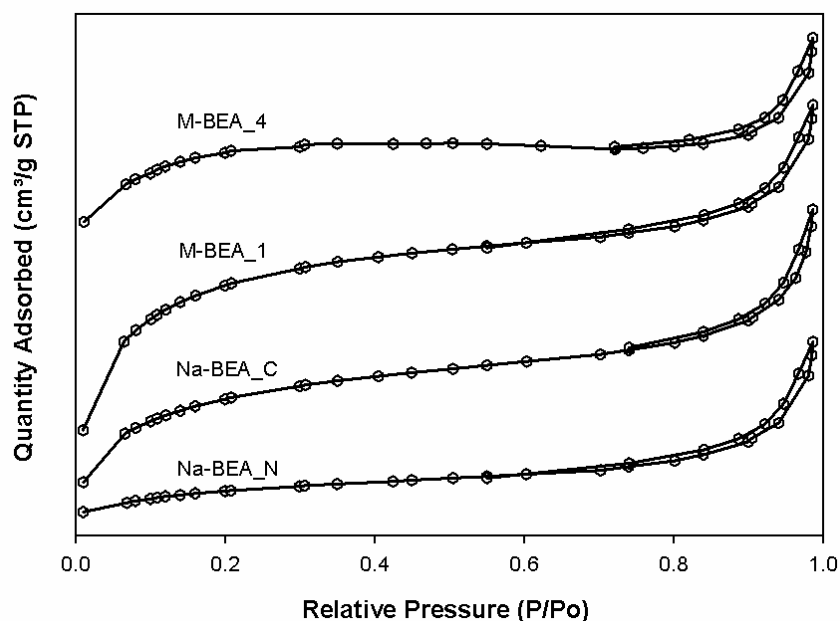[b,c] calculated from BJH adsorption and desorption method

Figure 8 Isotherm graph of different form in beta zeolite catalysts.

4.1.1.3 scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (SEM-EDX)

SEM technique was used to characterize the surface of the material (surface roughness). The morphology on the surface of catalysts is shown in Figure 9. It was observed that the particle shapes of all catalyst (Na and mixed Na-H form) are mostly spherical (round ball) and partially irregular [37].

In addition, Figures 10, 11, 12 and 13 are shown the elemental mapping of oxygen, silicon, aluminium and sodium (O, Si, Al and Na) on surface catalyst. It indicated that all elements are well dispersed on the catalyst surface.

Besides, the quantity of elements distribution in weight and atom percent are shown in Table 10. The ratio of Si/Al in weight and atom percent increased with the catalyst through the calcination and ion-exchange method while, the quantity of Na elements decreased.
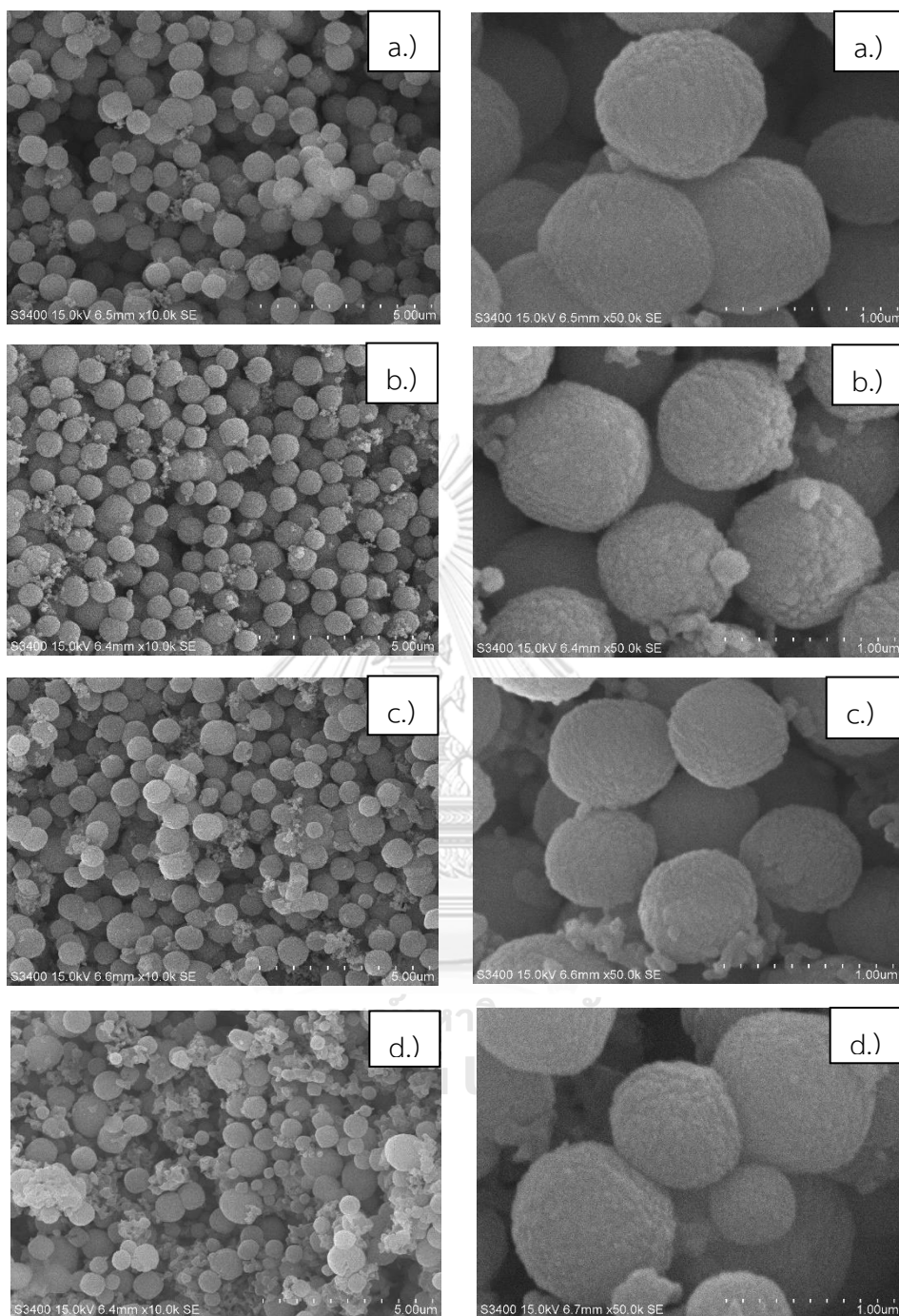
Figure 9 SEM micrographs of different form in beta zeolite catalysts a.) Na-BEA_N,
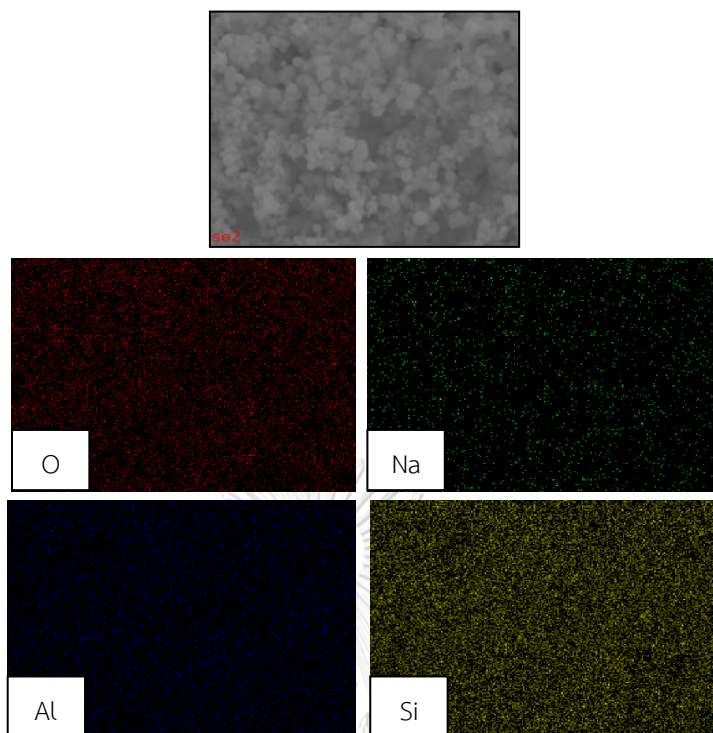b.) Na-BEA_C, c.) M-BEA_1 and d.) M-BEA_4.
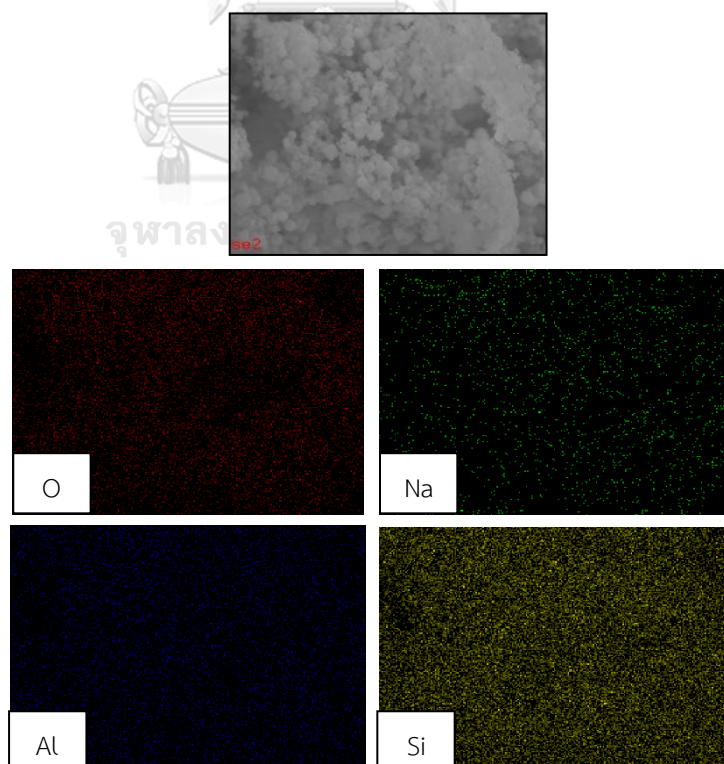
Figure 10 SEM-EDX mapping of Na-BEA_N catalyst.

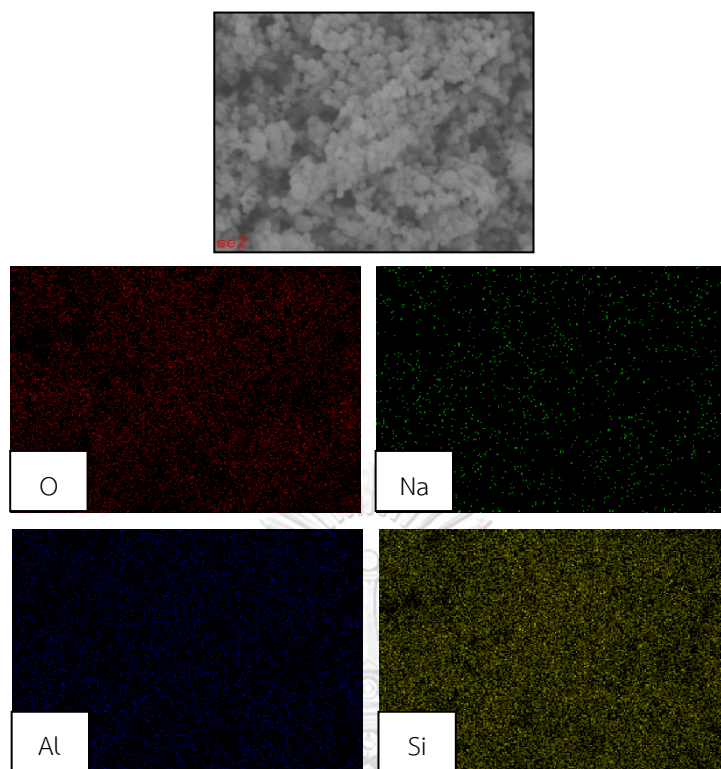**Figure 11** SEM-EDX mapping of Na-BEA_C catalyst.

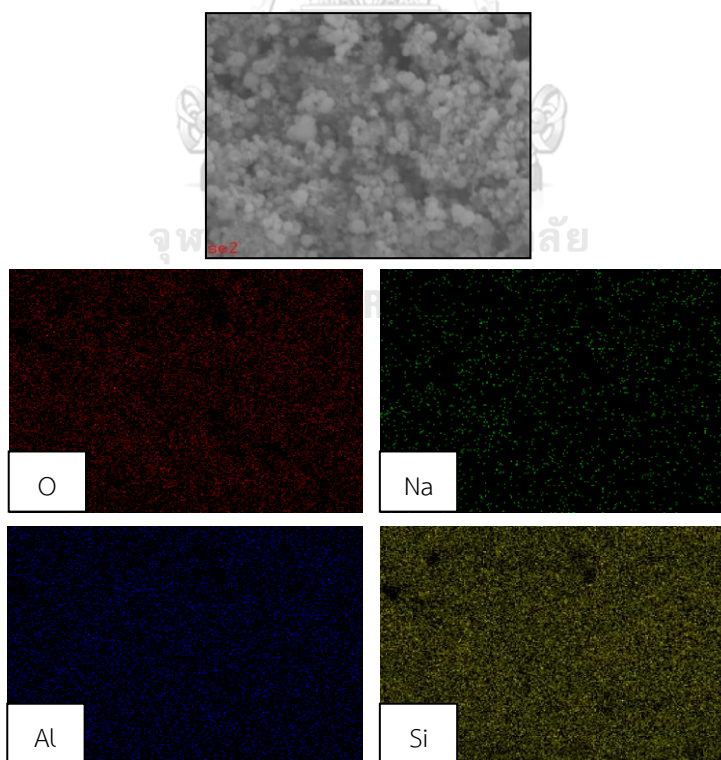**Figure 12** SEM-EDX mapping of M-BEA_1 catalyst.

Figure 13 SEM-EDX mapping of M-BEA_4 catalyst.

Table 10 Element distribution in weight and atom percent of different form in beta zeolite catalysts.

Catalysts	Element distribution									
	% weight					% Atom				
	Al	Si	O	Na	Si/Al	Al	Si	O	Na	Si/Al
Na-BEA_N	8.7	51.3	38.2	1.8	5.9	7.0	39.6	51.7	1.7	5.7
Na-BEA_C	8.9	54.4	35.0	1.7	6.1	7.3	42.8	48.3	1.7	5.9
M-BEA_1	6.7	52.0	40.8	0.5	7.8	5.3	39.6	54.6	0.5	7.5
M-BEA_4	6.3	51.5	41.9	0.3	8.1	5.0	39.1	55.7	0.3	7.8

4.1.1.4 temperature programmed desorption (NH$_3$-TPD)

NH$_3$ TPD technique was used NH$_3$ gas as a probe molecule to allow the number of acid sites (Acidity) and acid strength. The ability of the active site in a catalytic dehydration reaction depends on the acidity and strength of acid site as a function with the temperature. At a higher temperature it exhibited a higher acid strength affecting the activity for catalyzed reactions. The NH$_3$ TPD profiles of catalyst having different forms are shown in Figure 14. It can be divided the strength of acid site according to desorption peaks into three groups, which are the temperature below 200 °C, between 200-400 °C and above 400 °C indicating the acid site as a weak, moderate and strong, respectively.

The amount of acid site per mass catalyst and specific surface area was measured by integration of ammonia desorption peak via Fityk program as shown in Table 11. The results presented that the non-calcined catalyst (Na-BEA_N) has the highest total acidity, but it is not the amount of active site due to the acidity that is partially measured from acidic templates in the synthesis of beta zeolite catalyst. When comparing the different form in catalysts, it was observed that the mixed Na-H form (M-BEA_1) has the highest moderate acid site.
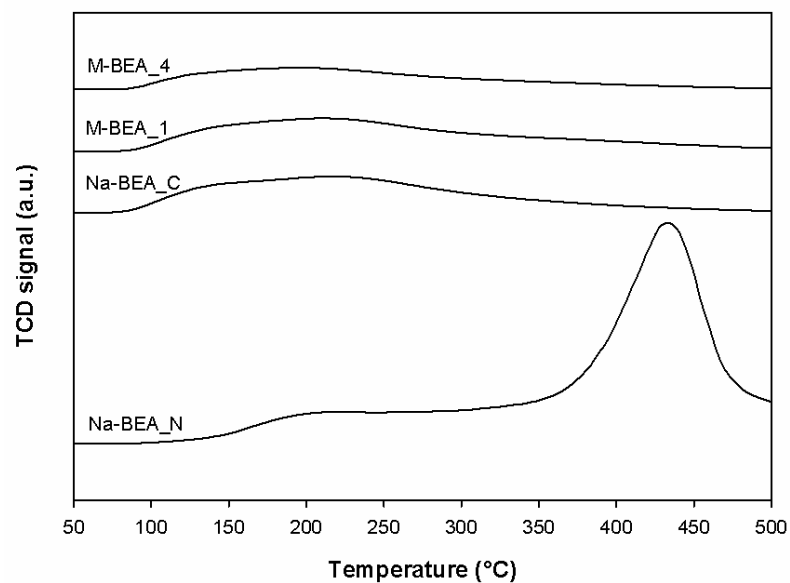
Figure 14 NH$_3$ TPD profiles of different form in beta zeolite catalysts.

Table 11 Acidity analysis by NH$_3$ TPD of different form in beta zeolite catalysts.

Catalysts	Acidity			
	(μmol NH$_3$/g cat.)			
	Weak	Moderate	Strong	Total acidity
Na-BEA_N	485.9	70.4	4,191.5	4,747.7
Na-BEA_C	226.8	1,193.8	516.9	1,937.6
M-BEA_1	135.7	1,232.6	519.7	1,888.0
M-BEA_4	519.6	405.7	536.9	1,462.2

4.1.2 ACTIVITY TEST OF DIFFERENT FORM IN BETA ZEOLITE CATALYSTS

The catalyst with different form in beta zeolite structure was investigated for the catalytic activity by dehydration reaction under condition at atmospheric pressure, the temperature program (150-400 °C) and WHSV=11.4 h^{-1}. The ethanol conversion of different form is shown in Figure 15. All catalyst exhibited increased ethanol conversion with increasing the temperature due to an increase in the reaction temperature give a rise the equilibrium constant (K) resulting in a shift of reactant to the product [38]. It can be seen that the mixed Na-H form (M-BEA_1) has the highest the ethanol conversion.

Furthermore, the selectivity of products in dehydration is presented in Figures 16 and 17 indicating that the main products are DEE and ethylene. It is shown that The selectivity of DEE decreased with increasing the temperature, but the ethylene selectivity is increased. It can be seen that M-BEA_1 has the complete DEE selectivity at 150 °C. The DEE yields of different form are shown in Figure 17. The DEE yield increased when the reaction temperature reached 250 °C and quickly dropped with increased reaction temperature. The results showed the maximum of DEE yield on M-BEA_1 that was slightly higher than Na-BEA_C and M-BEA_4 because this catalyst has the highest surface area and the amount of moderate acid site corresponding to Tables 9 and 11, respectively. From all product yields in Table 12, it can be concluded that the mixed Na-H form catalyst with one cycle in ion-exchange method (M-BEA_1) exhibited the highest DEE yield of 27.3% at 250 °C.

Finally, from the results in Table 12, it was observed that at the low temperature (< 250 °C) the main product selectivity is DEE. Therefore, studying the optimum condition by various factor to increase the conversion value and to shift the maximum value of DEE yield at a low temperature in Part 4.2.
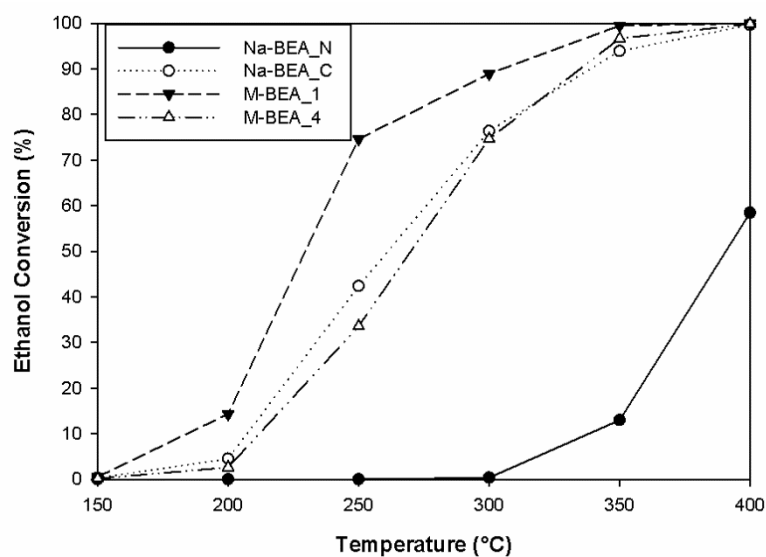
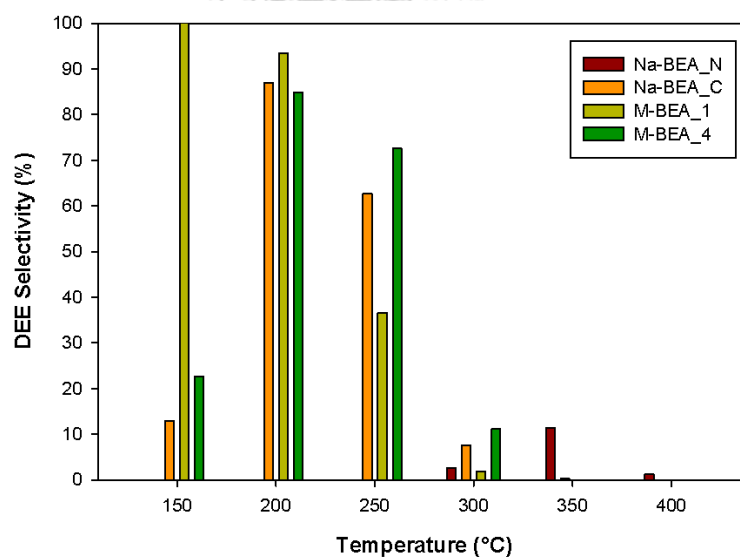**Figure 15** Ethanol conversion of different form in beta zeolite catalysts at WHSV of 11.4 h^{-1}.

Figure 16 DEE selectivity of different form in beta zeolite catalysts at WHSV of 11.4 h^{-1}.
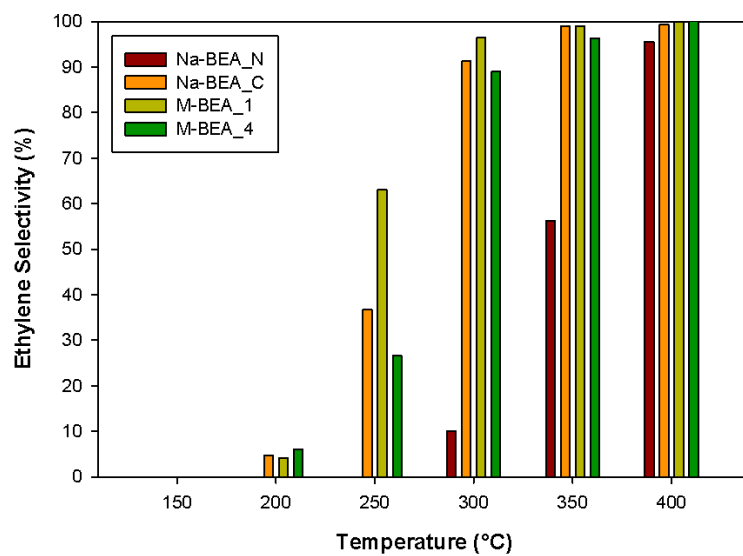
Figure 17 Ethylene selectivity of different form in beta zeolite catalysts
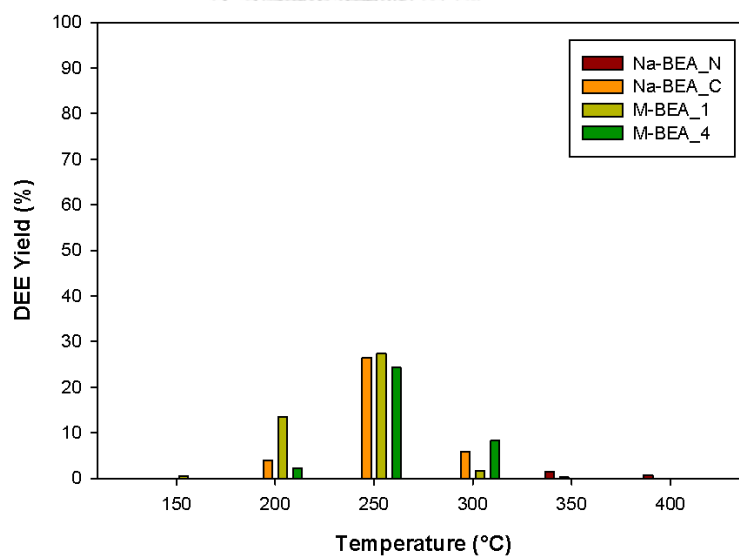at WHSV of 11.4 h^{-1}.

Figure 18 DEE yield of different form in beta zeolite catalysts
at WHSV of 11.4 h^{-1}.

Table 12 All product yields of different form in beta zeolite catalysts
at WHSV of 11.4 h^{-1}.

Catalysts	Temperature (°C)	Product yield (%)		
		DEE	Ethylene	Acetaldehyde
Na-BEA_N	150	0.0	0.0	0.0
	200	0.0	0.0	0.0
	250	0.0	0.0	0.0
	300	0.0	0.0	0.3
	350	1.5	7.3	4.2
	400	0.7	55.8	1.9
Na-BEA_C	150	0.0	0.0	0.2
	200	3.9	0.2	0.4
	250	26.5	15.6	0.3
	300	5.8	69.6	0.9
	350	0.2	92.9	0.8
	400	0.0	98.9	0.7
M-BEA_1	150	0.5	0.0	0.0
	200	13.4	0.6	0.4
	250	27.3	47.0	0.3
	300	1.7	85.7	1.5
	350	0.0	98.3	1.1
	400	0.0	99.7	0.2
M-BEA_4	150	0.0	0.0	0.1
	200	2.2	0.2	0.2
	250	24.3	8.9	0.3
	300	8.3	66.3	0.0
	350	0.1	93.1	3.5
	400	0.0	99.8	0.0

PART 2: INVESTIGATION THE SUITABLE CONDITION BY
VARIOUS FACTORS IN ETHANOL DEHYDRATION

4.2 STUDY OF THE APPROPRIATE CONDITIONS IN DEHYDRATION REACTION BY VARIOUS FACTOR

From the results in Part 4.1, the mixed Na-H form catalyst with one cycle in ion-exchange method (M-BEA_1) exhibited the highest catalytic activity in dehydration reaction of ethanol to DEE. In this part, the M-BEA_1 was chosen to study the appropriate conditions to produce the DEE yield better by various factor including the weight hourly space velocity (WHSV), the factor of carrier gas (N_2) flow rate by controlled a constant ethanol flow rate and the factor of ethanol concentration by controlled a constant N_2 flow rate.

4.2.1 The factor of weight hourly space velocity (WHSV)

Normally, the contact time is an important factor that affects the value of the conversion. The M-BEA_1 catalyst was performed in dehydration reaction to study the factor of WHSV including 11.4, 6.3 and 3.1 h^{-1}. The ethanol conversion is shown in Figure 19. It indicated that the ethanol conversion increased when decreasing the WHSV. Due to the lower space velocity, the catalyst has a longer time to contact the ethanol substrate than the higher space velocity that resulting in greater ethanol conversion.

In addition, the DEE and ethylene selectivity by various WHSV are shown in Figures 20 and 21, respectively. At lower WHSV, lower DEE selectivity is clearly observed at 250 °C because the catalyst has long time contact with the substrate, causing DEE to break down into ethylene. The DEE yield is shown in Figure 22. The lower WHSV causes of DEE yield shift down to a lower temperature. At the temperature of 200 °C, WHSV of 3.1 gives the highest DEE (66.4%) as seen in Figure 23. All product yields in Table 13, it was found that the lower WHSV produced more acetaldehyde product.
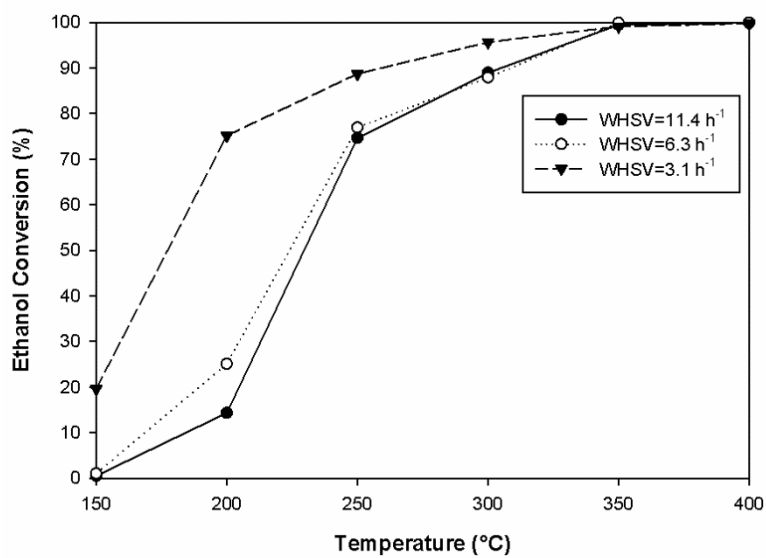
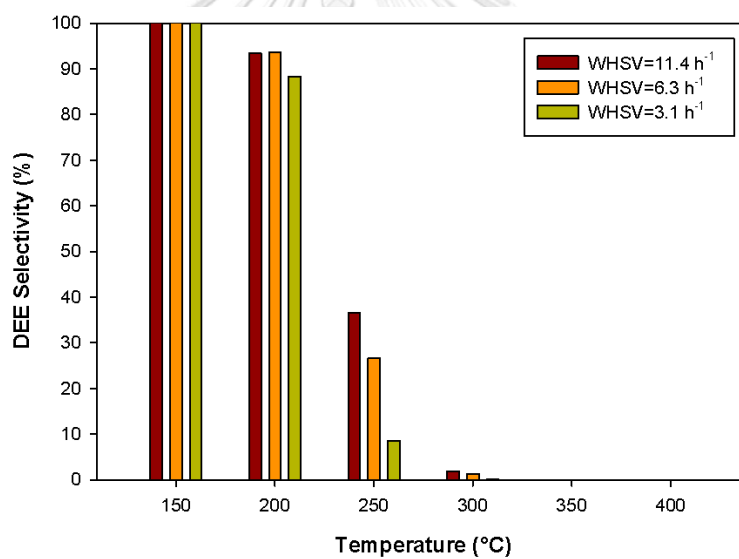**Figure 19** Ethanol conversion of M-BEA_1 catalyst by various WHSV.

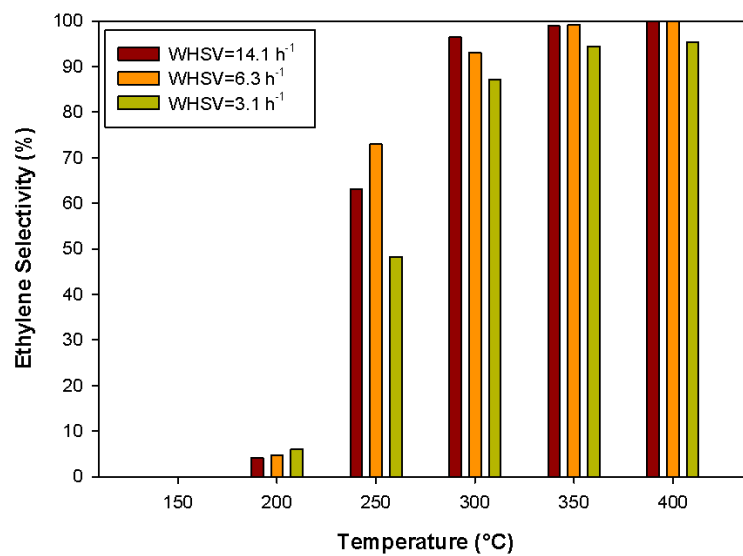
Figure 20 DEE selectivity of M-BEA_1 catalyst by various WHSV.

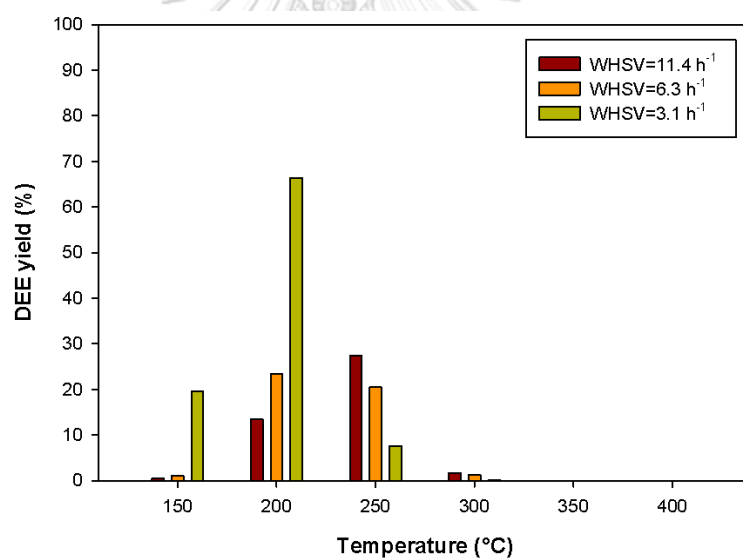**Figure 21** Ethylene selectivity of M-BEA_1 catalyst by various WHSV.

Figure 22 DEE yield of M-BEA_1 catalyst by various WHSV.
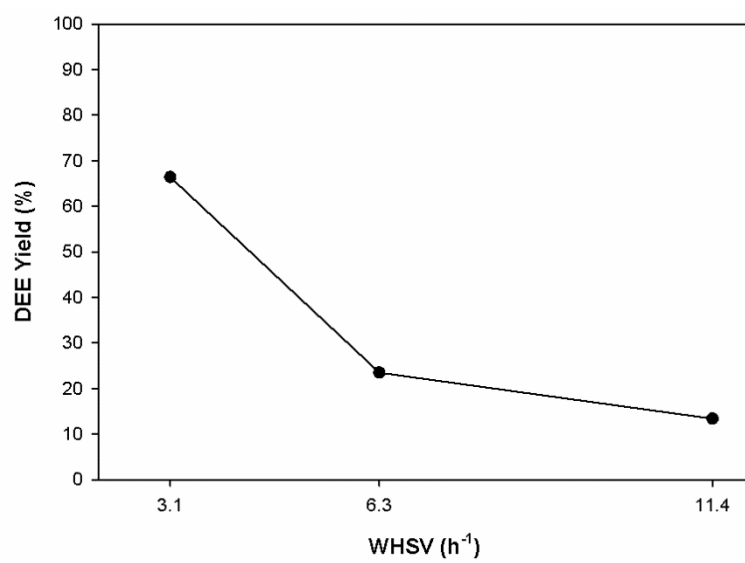
Figure 23 DEE yield of M-BEA_1 catalyst by various WHSV at 200 °C.

Table 13 All product yields of M-BEA_1 catalyst by various WHSV.

WHSV (h⁻¹)	Temperature (°C)	Product yield (%)		
		DEE	Ethylene	Acetaldehyde
11.4	150	0.5	0.0	0.0
	200	13.4	0.6	0.4
	250	27.3	47.0	0.3
	300	1.7	85.7	1.5
	350	0.0	98.3	1.1
	400	0.0	99.7	0.2
6.3	150	1.0	0.0	0.0
	200	23.4	1.1	0.5
	250	20.5	56.0	0.4
	300	1.2	81.7	5.0
	350	0.0	98.9	0.9
	400	0.0	99.7	0.2
3.1	150	19.6	0.0	0.0
	200	66.4	4.4	4.3
	250	7.6	42.8	38.3
	300	0.2	83.4	12.1
	350	0.1	93.5	5.4
	400	0.1	95.1	4.6

4.2.2 The factor of carrier gas (N_2) flow rate

The carrier (N_2) gas was used to transfer the substrate into a fixed-bed continuous flow microreactor for the catalytic dehydration reaction. The carrier gas is one factor that affects the cost of production. In this factor, the N_2 gas was examined in dehydration by various N_2 flow rate including 3,600, 1800 and 900 ml/h with controlled a constant ethanol flow rate at 0.397 ml/h. The ethanol conversion by various N_2 flow rate is shown in Figure 24. The conversion increased with decreasing the N_2 flow rate and at 900 ml/h the conversion is slightly greater than 1,800 ml/h.

The DEE selectivity in Figure 25 shows that lower carrier gas (1,800 and 900 ml/h) is more selective to produce DEE. On the other hands, the ethylene selectivity is generated at the highest N_2 flow rate (3,600 ml/h) as illustrated in Figure 26. The DEE yield, at 200 °C and all product yields are shown in Figures 27, 28 and Table 14, respectively. It can be summarized that at the temperature of 200 °C and N_2 flow rate of 900 ml/h has the highest DEE yield.
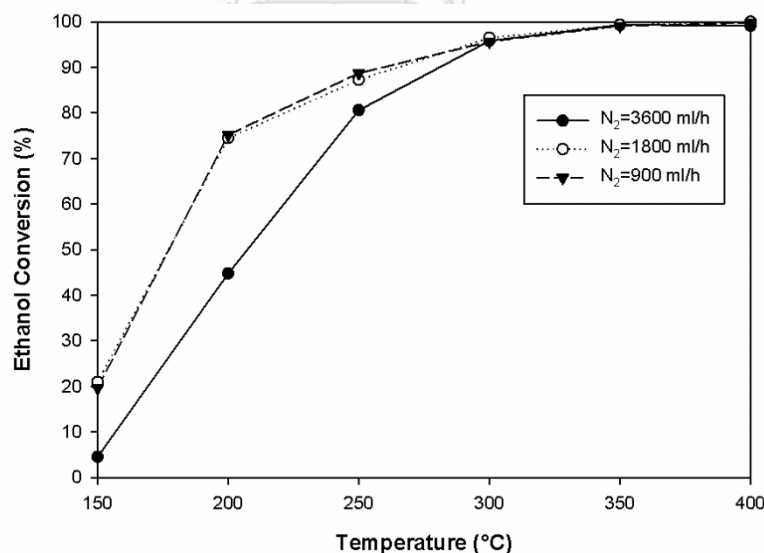

Figure 24 Ethanol conversion of M-BEA_1 catalyst by various N_2 flow rate and controlled a constant ethanol flow rate at 0.397 ml/h.
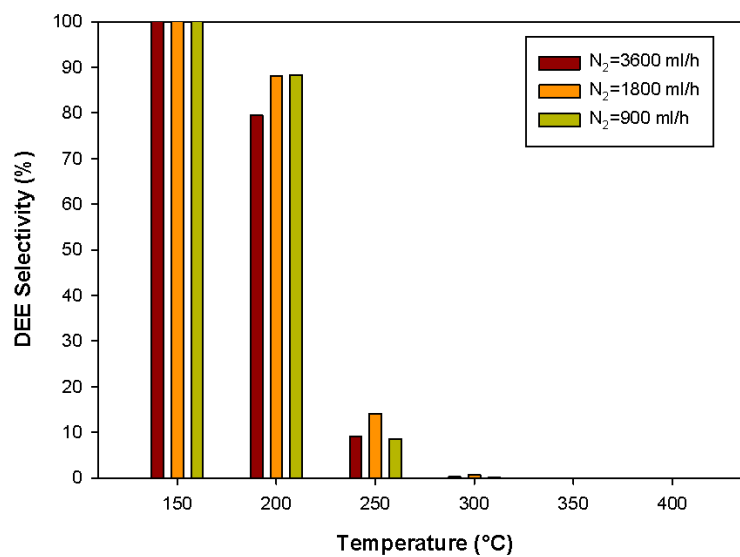
Figure 25 DEE selectivity of M-BEA_1 catalyst by various N_2 flow rate and controlled a constant ethanol flow rate at 0.397 ml/h.
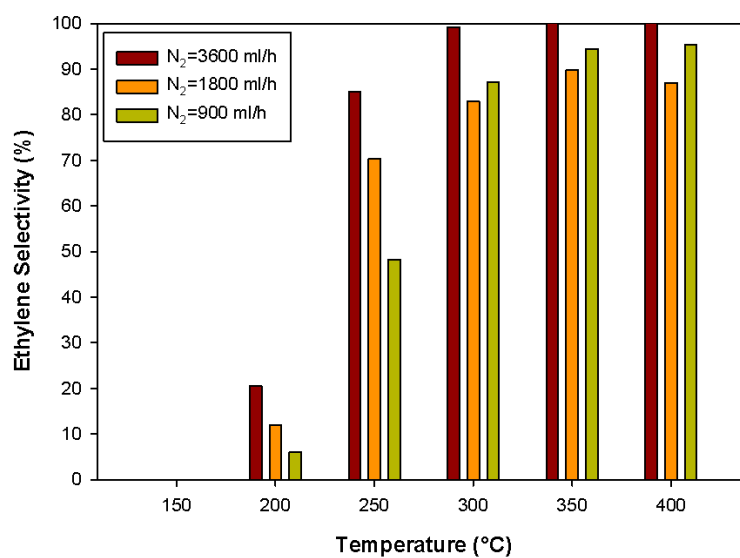

Figure 26 Ethylene selectivity of M-BEA_1 catalyst by various N_2 flow rate and controlled a constant ethanol flow rate at 0.397 ml/h.
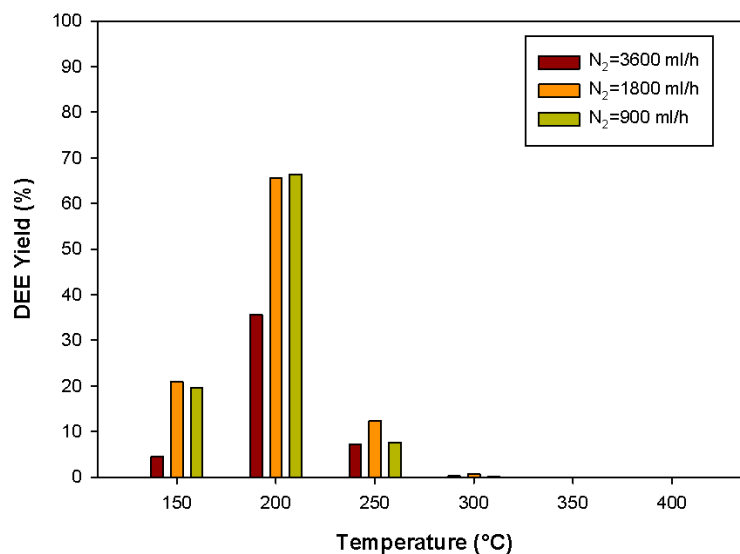
Figure 27 DEE yield of M-BEA_1 catalyst by various N_2 flow rate and controlled a constant ethanol flow rate at 0.397 ml/h.
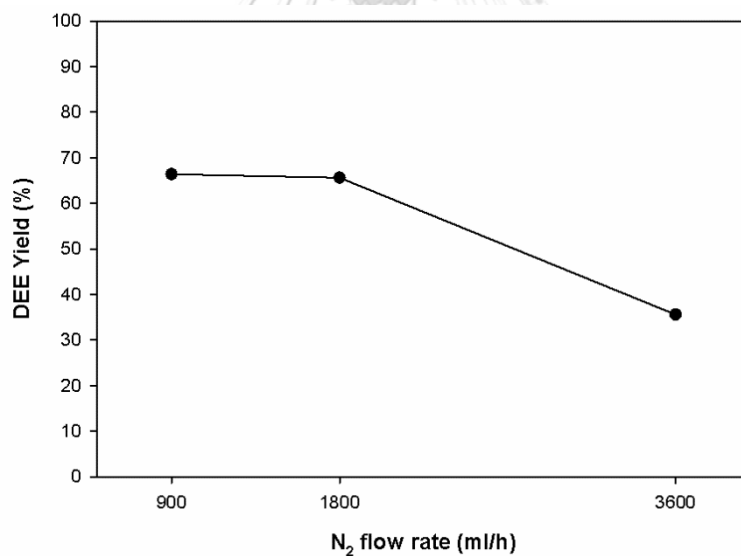

Figure 28 DEE yield of M-BEA_1 catalyst by various N_2 flow rate and controlled a constant ethanol flow rate of 0.397 ml/h at 200 °C.

Table 14 All product yields of M-BEA_1 catalyst by various N_2 flow rate and controlled a constant ethanol flow rate at 0.397 ml/h.

N_2 flow rate (ml/h)	Temperature (°C)	Product yield (%)		
		DEE	Ethylene	Acetaldehyde
3600	150	4.5	0.0	0.0
	200	35.6	9.2	0.0
	250	7.2	68.5	4.8
	300	0.2	95.0	0.6
	350	0.0	99.3	0.0
	400	0.0	99.0	0.0
1800	150	20.9	0.0	0.0
	200	65.6	8.8	0.0
	250	12.3	61.3	13.6
	300	0.6	79.9	16.0
	350	0.0	89.1	10.2
	400	0.0	86.9	13.1
900	150	19.6	0.0	0.0
	200	66.4	4.4	4.3
	250	7.6	42.8	38.3
	300	0.2	83.4	12.1
	350	0.1	93.5	5.4
	400	0.1	95.1	4.6

4.2.3 The factor of ethanol concentration

Due to the limited amount of active site in catalyst. Therefore, the exceed of ethanol concentration causes waste of production costs. Reducing the ethanol concentration from 3.5 x 10^{-4} to 1.7 x 10^{-4} g_{EtOH}/ml by controlled N_2 flow rate at 1800 ml/h was performed to find the appropriate ethanol concentration in the dehydration reaction. Figure 29 shows the ethanol conversion. It can be seen that decreasing the concentration of ethanol leads to increased conversion. The DEE selectivity and ethylene selectivity are shown in Figures 30 and 31, respectively. The ethanol can be converted to DEE and ethylene at the high ethanol concentration (3.5 x 10^{-4} g_{EtOH}/ml) since the production of DEE requires bimolecules of ethanol, where one molecule is an adsorbent on the active site of the catalyst and one molecule was used by ethoxy group intermediate. The mechanism is shown in Figure 2. However, the DEE yield and all product yields are shown in Figures 32, 33 and Table 15, respectively. It can be summarized that the ethanol concentration of 1.7 x 10^{-4} g_{EtOH}/ml has the highest DEE yield of 65.6% at 200 °C.
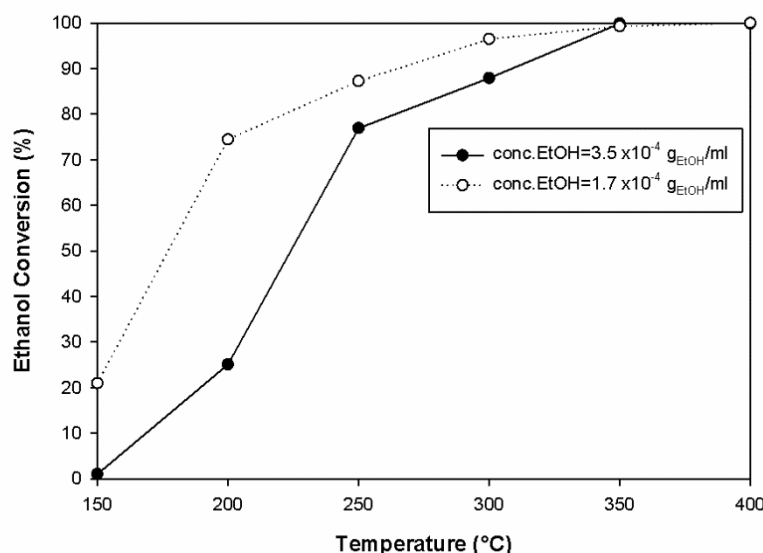

Figure 29 Ethanol conversion of M-BEA_1 catalyst by various ethanol concentration and controlled N_2 flow rate at 1800 ml/h.
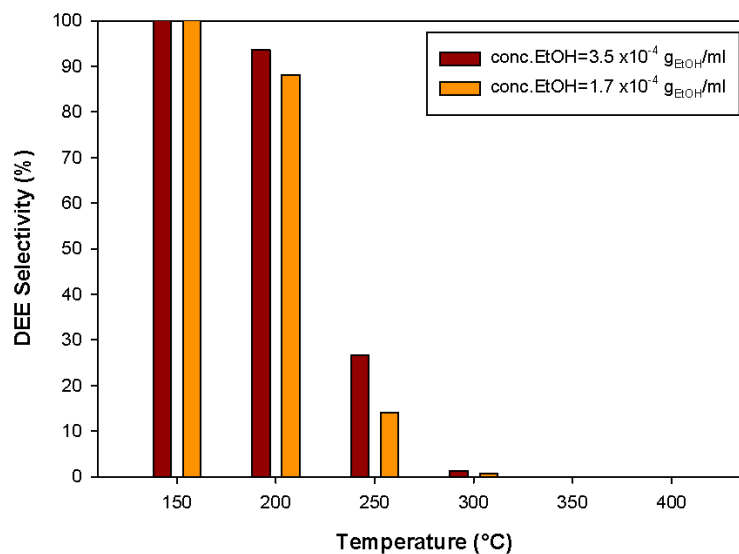
Figure 30 DEE selectivity of M-BEA_1 catalyst by various ethanol concentration and controlled N_2 flow rate at 1800 ml/h.

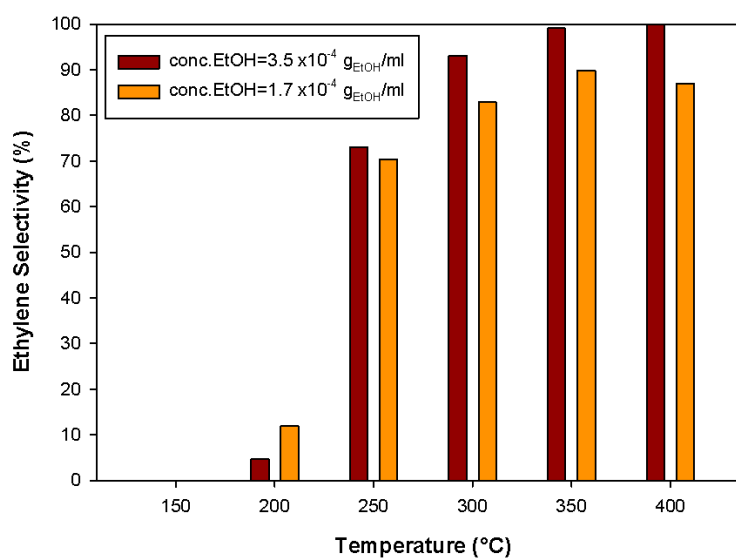**Figure 31** Ethylene selectivity of M-BEA_1 catalyst by various ethanol concentration and controlled N_2 flow rate at 1800 ml/h.
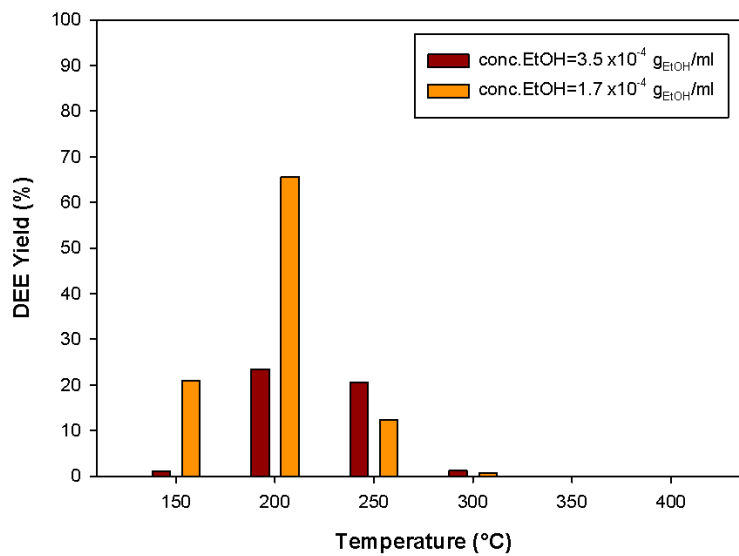
Figure 32 DEE yield of M-BEA_1 catalyst by various ethanol concentration and controlled N_2 flow rate at 1800 ml/h.
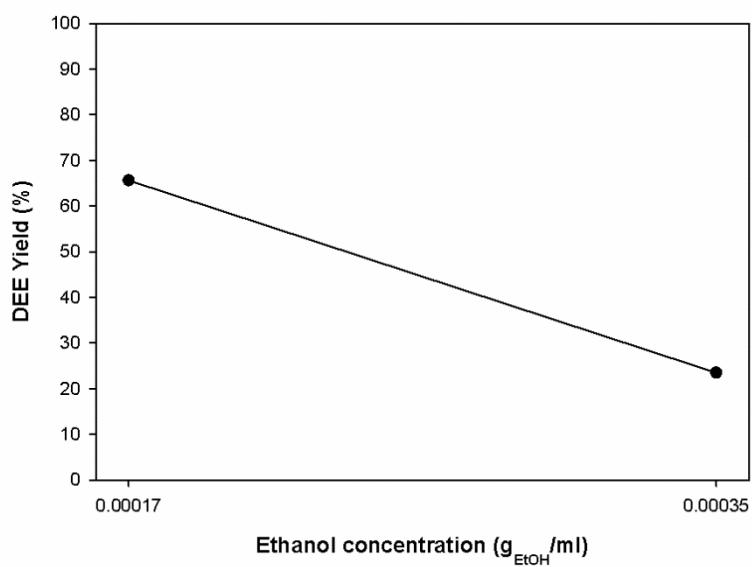
Figure 33 DEE yield of M-BEA_1 catalyst by various ethanol concentration and controlled N_2 flow rate of 1800 ml/h at 200 °C.

Table 15 All product yields of M-BEA_1 catalyst by various ethanol concentration and controlled N_2 flow rate at 1800 ml/h.

Ethanol concentration (g_{EtOH}/ml)	Temperature (°C)	Product yield (%)		
		DEE	Ethylene	Acetaldehyde
3.5×10^{-4}	150	1.0	0.0	0.0
	200	23.4	1.1	0.5
	250	20.5	56.0	0.4
	300	1.2	81.7	5.0
	350	0.0	98.9	0.9
	400	0.0	99.7	0.2
1.7×10^{-4}	150	20.9	0.0	0.0
	200	65.6	8.8	0.0
	250	12.3	61.3	13.6
	300	0.6	79.9	16.0
	350	0.0	89.1	10.2
	400	0.0	86.9	13.1

PART 3: INVESTIGATION THE INFLUENCE OF MODIFICATION CATALYST WITH YTTRIUM OR PHOSPHORUS

4.3 THE MODIFICATION BETA ZEOLITE CATALYST WITH YTTRIUM OR PHOSPHORUS

The acidity of the catalyst is an important key in catalyzing the dehydration reaction to produce DEE. In this part, the M-BEA_1 catalyst was modified the amount of acid site and strength acid site by adding the metallic to increase the acidity. In this part, yttrium and phosphorus were chosen to study the physical and chemical properties.

4.3.1 Comparative characterization of beta zeolite catalyst with non-modified and Yttrium or Phosphorus modified.

The mixed Na-H form in beta zeolite catalyst with one cycle in ion-exchange method which is called non-modified or M-BEA_1 catalyst was used to modify with 0.5% of Y and 5% of P by incipient wetness impregnation method. All catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption (BET and BJH), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (SEM-EDX) and temperature programmed desorption (NH_3-TPD).

4.3.1.1 X-ray diffraction (XRD)

Figure 34 is a comparison of XRD patterns for non-modified and Y or P modified with Y or P in beta zeolite catalyst. It was observed that the addition of Y and P on beta zeolite exhibited the similar characteristic peaks of zeolite phase at $2\theta = 13.4°$, 21.5°, 22.6°, 25.4°, 27.0° and 29.7°.
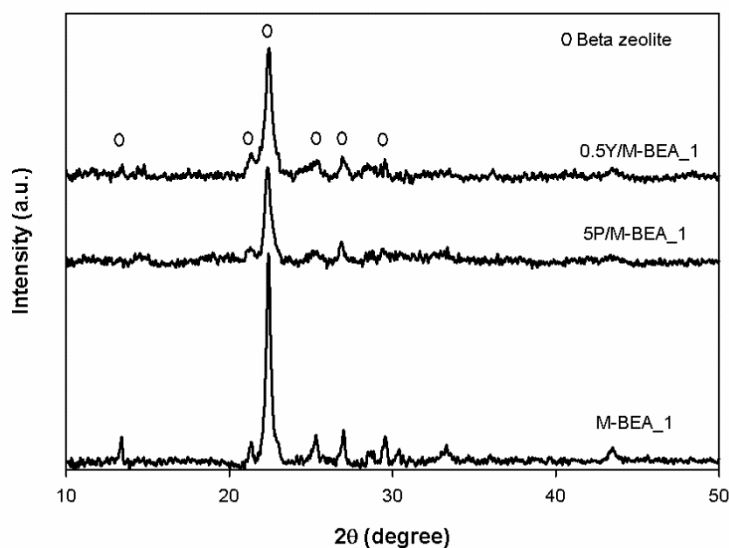
Figure 34 XRD patterns of non-modified and modified Y or P on beta zeolite catalyst.

4.3.1.2 N$_2$ physisorption (BET and BJH)

The BET surface area, pore size diameter and pore volume of mixed Na-H form (M-BEA_1) and modified Y (0.5Y/M-BEA_1) or P (5P/M-BEA_1) catalysts are shown in Table 16. It can be seen that the modification with Y or P decreased the BET surface area. It may be caused by blockage of the zeolite channel by Y or P clusters and/or pore structure [39]. The 0.5Y/M-BEA_1 has higher surface area than 5P/M-BEA_1 due to the percent loading of Y exhibits lower than P loading.

In addition, Figure 35 is presented the isotherm graph of non-modified and modified Y or P on beta zeolite catalyst. It can be demonstrated that an isotherm type of all catalyst is displayed the isotherm characteristic between type 1 as a micropores and 4 as a mesopores with the hysteresis loop. It concluded that the non-modified and modified catalysts with Y or P are not change regarding with the porous type materials.

Table 16 BET surface area, pore size diameter and crystallite size of non-modified and modified Y or P on beta zeolite catalyst.

Catalysts	BET surface area^a, S_{BET} (m²/g)	Pore size diameter^b (nm)	Pore volume^c (cm³/g)
M-BEA_1	392.4	4.4	0.05
5P/M-BEA_1	241.3	5.1	0.03
0.5Y/M-BEA_1	333.4	4.1	0.05

^{a} calculated from BET method

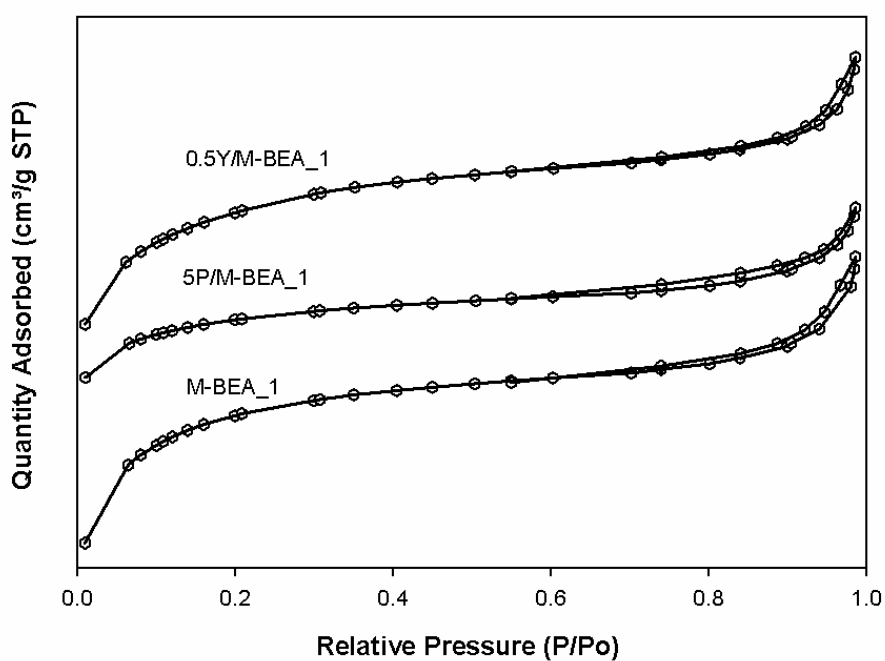^{b,c} calculated from BJH adsorption and desorption method

Figure 35 Isotherm graph of non-modified and modified Y or P on beta zeolite catalyst.

4.3.1.3 scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (SEM-EDX)

SEM micrographs of non-modified and modified Y or P on beta zeolite catalyst are shown in Figure 36. It indicated the particle shape of catalyst, which did not change after it through the loading of Y or P by incipient wetness impregnation method. All catalysts are mostly spherical and partially irregular.

However, Figure 37 and 38 are shown the elemental mapping of oxygen, silicon, aluminium, sodium and phosphorus (O, Si, Al, Na and P) and elemental mapping of oxygen, silicon, aluminium, sodium and yttrium (O, Si, Al, Na and Y) on surface catalyst, respectively. It indicated that all elements are well dispersed on the surface catalyst.

Furthermore, the quantity of elemental distribution in weight and atom percent is shown in Tables 17 and 18, respectively. The weight and atom percent of Y or P does not match with the actual loading in the experiment because this technique can only analyze the surface of the catalyst, not the bulk.
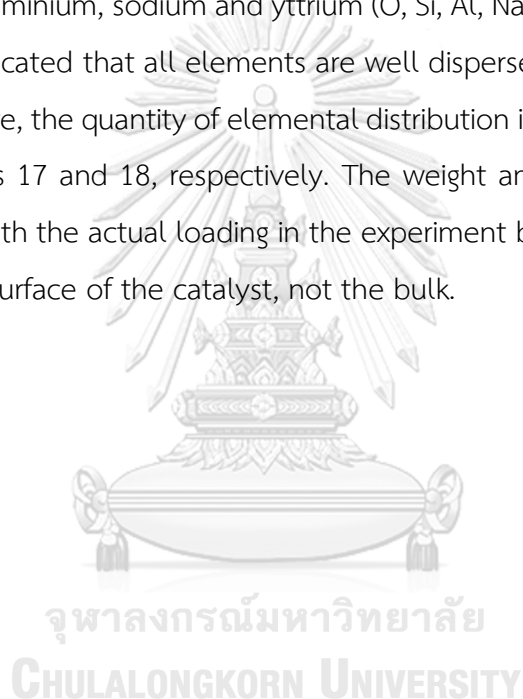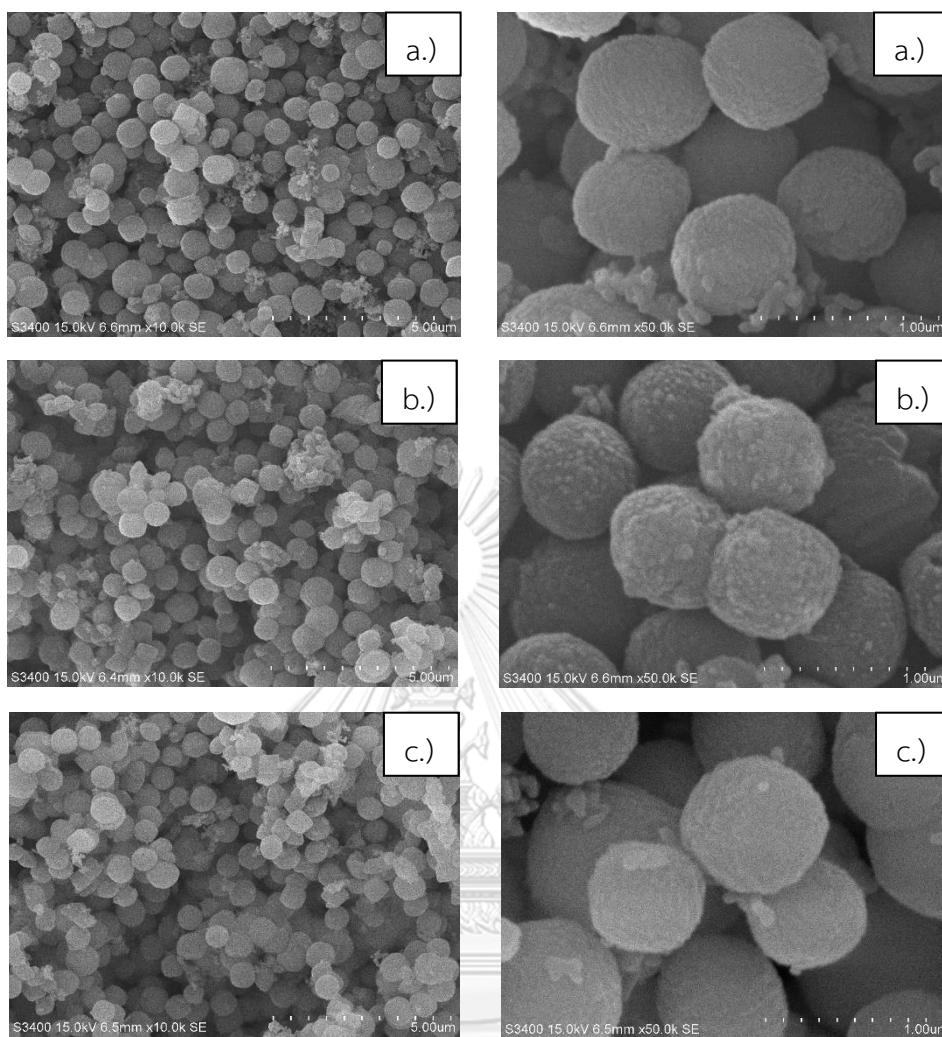
Figure 36 SEM micrographs of non-modified and modified Y or P on beta zeolite
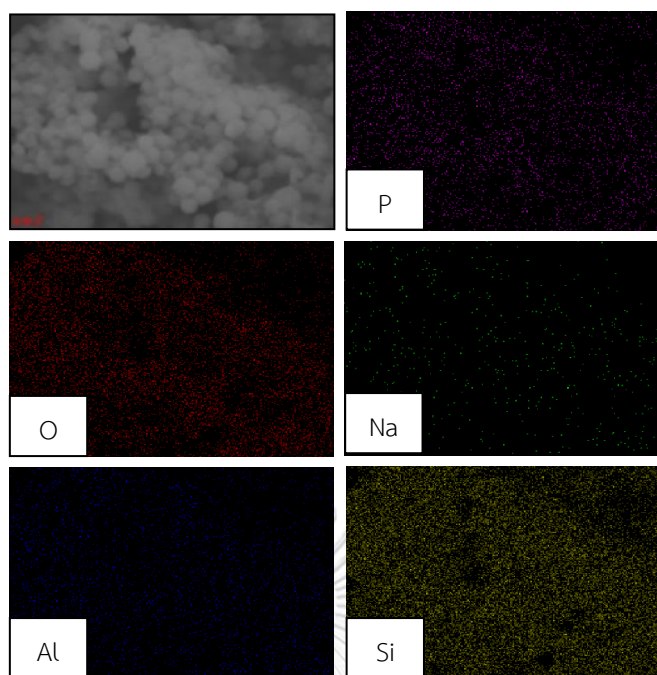catalyst a.) M-BEA_1, b.) 5P/M-BEA_1 and c.) 0.5Y/M-BEA_1.

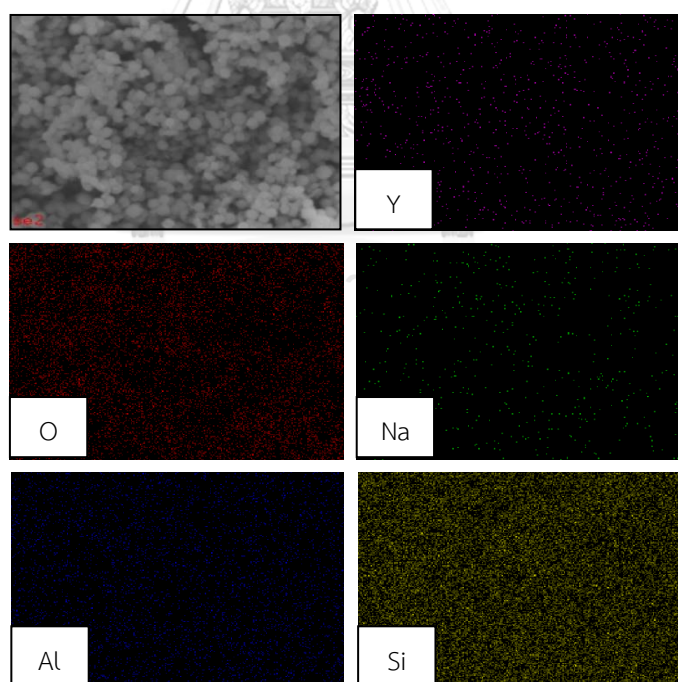**Figure 37** SEM-EDX mapping of 5P/M-BEA_1 catalyst.

Figure 38 SEM-EDX mapping of 0.5Y/M-BEA_1 catalyst.

Table 17 Element distribution in weight percent of non-modified and modified Y or P on beta zeolite catalyst.

Catalysts	Element distribution						
	% weight						
	Al	Si	O	Na	P	Y	Si/Al
M-BEA_1	6.7	52.0	40.8	0.5	-	-	7.8
5P/M-BEA_1	5.3	46.1	38.9	0.4	9.3	-	8.7
0.5Y/M-BEA_1	7.4	54.3	37.2	0.4	-	0.7	7.3

Table 18 Element distribution in atom percent of non-modified and modified Y or P on beta zeolite catalyst.

Catalysts	Element distribution						
	% Atom						
	Al	Si	O	Na	P	Y	Si/Al
M-BEA_1	5.3	39.6	54.6	0.5	-	-	7.5
5P/M-BEA_1	4.3	35.8	53.0	0.4	6.5	-	8.4
0.5Y/M-BEA_1	6.0	42.4	51.1	0.4	-	0.2	7.0

4.3.1.4 temperature programmed desorption (NH_3-TPD)

The NH_3 TPD profiles of non-modified and modified Y or P on beta zeolite catalyst are shown in Figure 39. It was observed that when loading of Y or P, the peak profile is changed to a lower temperature that means the addition of Y or P shifts the strength of acid site from moderate to weak and strong. The acidity analysis by NH_3 TPD of non-modified and modified Y or P on beta zeolite catalyst is presented in Table 19. It can be seen that the addition of Y or P increased the total acid site, 5P/M-BEA_1 has the highest total acidity. It can be summarized that the loading of Y or P apparently decreased the moderate acid site in M-BEA_1 catalyst.
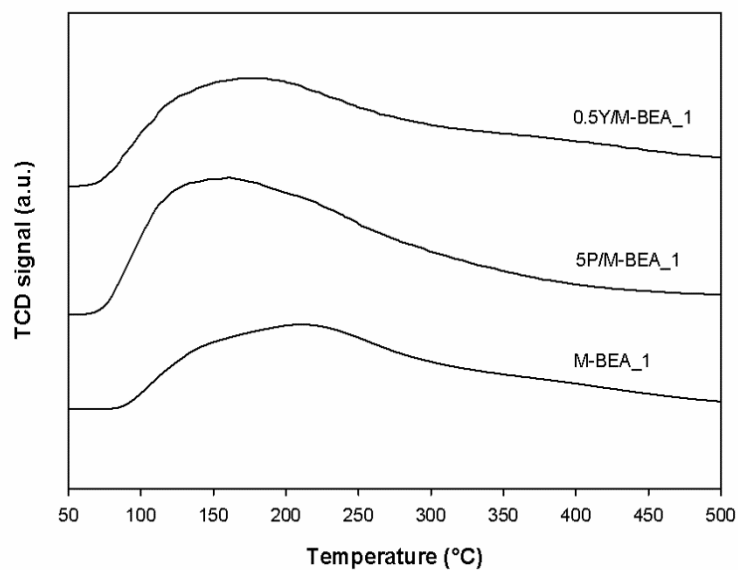
Figure 39 NH$_3$ TPD profiles of non-modified and modified Y or P on beta zeolite catalyst.

Table 19 Acidity analysis by NH$_3$ TPD of non-modified and modified Y or P on beta zeolite catalyst.

Catalysts	Acidity			
	(μmol NH$_3$/g cat.)			
	Weak	Moderate	Strong	Total acidity
M-BEA_1	135.7	1,232.6	519.7	1,888.0
5P/M-BEA_1	1,331.6	651.6	852.5	2,835.7
0.5Y/M-BEA_1	500.5	1,150.0	629.4	2,280.0

4.3.2 COMPARATIVE ACTIVITY TEST OF NON-MODIFIED AND MODIFIED Y OR P ON BETA ZEOLITE CATALYST

The non-modified (M-BEA_1) and modified with Y or P catalysts were investigated in dehydration under the condition at atmospheric pressure, the temperature program (150-400 °C) and WHSV=3.1 h^{-1} to compare the activity of the catalyst. The ethanol conversion of non-modified and modified Y or P on beta zeolite catalyst is shown in Figure 40. The conversion tends to be in order 0.5Y/M-BEA_1 > M-BEA_1 > 5P/M-BEA_1. This conversion trend is consistent with the BET surface area in Table 16. So, the surface area is an important parameter in the adsorption of the substrate. The selectivity of DEE and ethylene is shown in Figures 41 and 42, respectively. The 5P/M-BEA_1 presented the highest DEE selectivity at each temperature.

In addition, DEE yield of catalysts are illustrated in Figure 43. It can be represented that M-BEA_1 has higher DEE yield at low temperature (≤ 250 °C) than 5P/M-BEA and 0.5Y/M-BEA_1 catalysts. The M-BEA_1 has the highest ethylene yield at each temperature as shown in Figure 44. Table 20 shows all product yields of catalysts. It can be seen that byproduct such as acetaldehyde is remarkably generated at temperature of 250 °C in M-BEA_1 and 0.5Y/M-BEA_1.

However, the ethanol conversion of non-modified and modified Y or P on beta zeolite catalyst was tested to measure the stability under the condition at atmospheric pressure, the temperature of 200 °C and WHSV=3.1 h^{-1} as seen in Figure 45, it can be concluded that the catalyst can be used in dehydration reaction at 200 °C for 10 h.

The comparison of the efficiency of catalysts between this work and other research for ethanol dehydration to DEE are shown in Table 21. It can be seen that M-BEA_1 catalyst has three advantages including active at the low temperature (200 °C), high yield of DEE and high stability for 10 h.
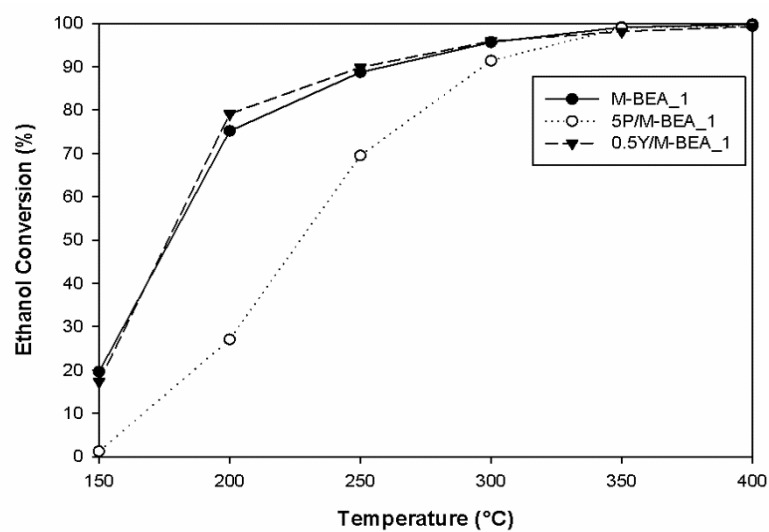
Figure 40 Ethanol conversion of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h^{-1}.

Figure 41 DEE selectivity of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h^{-1}.
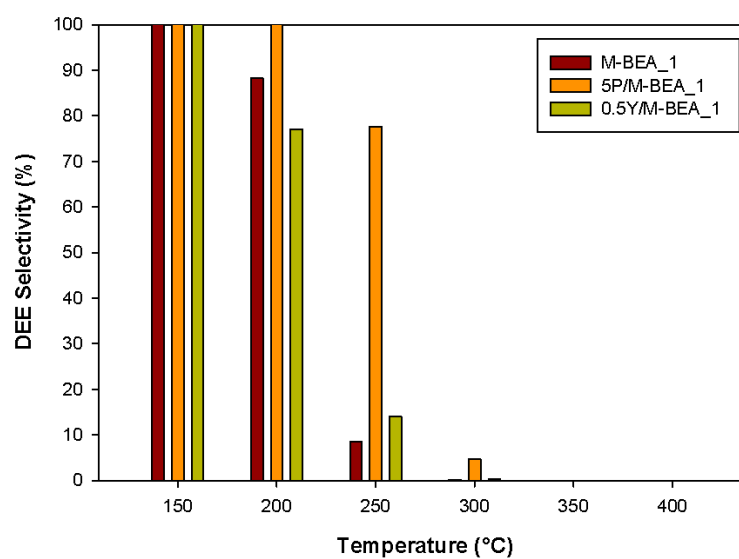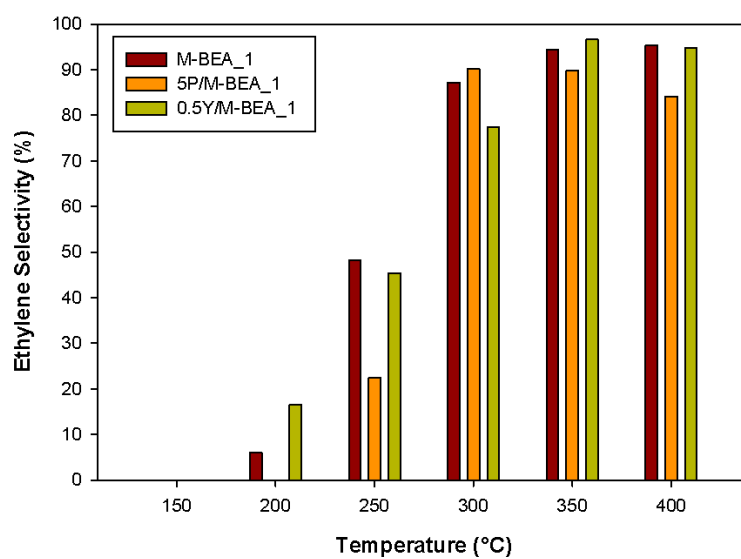
Figure 42 Ethylene selectivity of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h^{-1}.
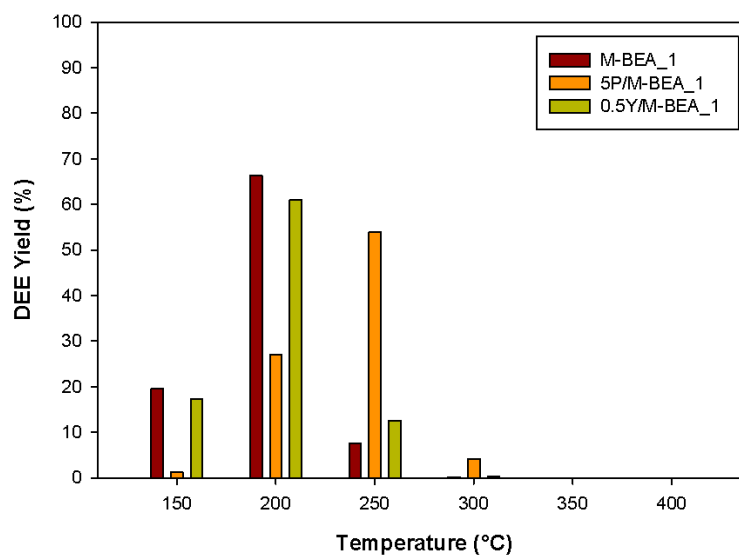

Figure 43 DEE yield of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h^{-1}.
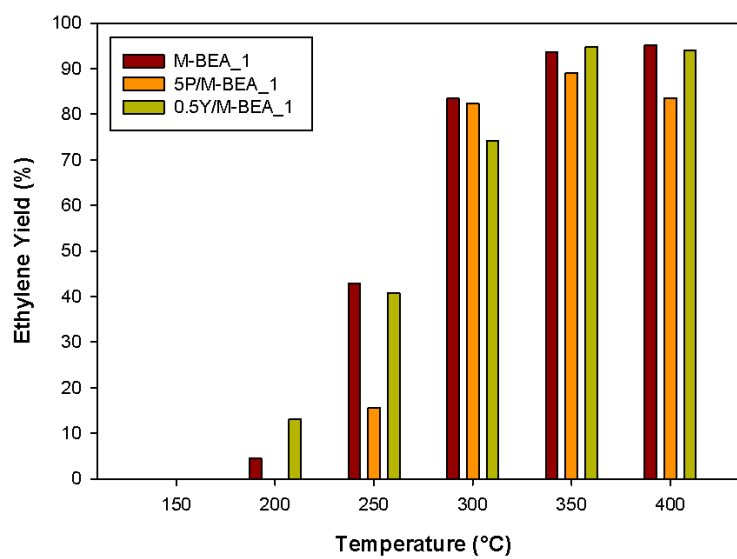
Figure 44 Ethylene yield of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h^{-1}.
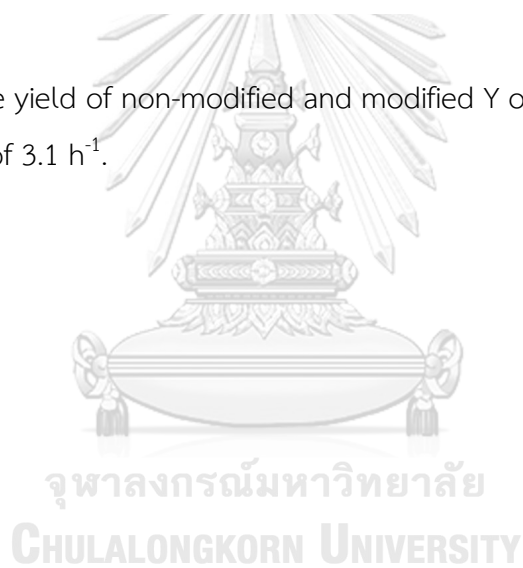
Table 20 All product yields of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h⁻¹.

Catalysts	Temperature (°C)	Product yield (%)		
		DEE	Ethylene	Acetaldehyde
M-BEA_1	150	19.6	0.0	0.0
	200	66.4	4.4	4.3
	250	7.6	42.8	38.3
	300	0.2	83.4	12.1
	350	0.1	93.5	5.4
	400	0.1	95.1	4.6
5P/M-BEA_1	150	1.2	0.0	0.0
	200	27.0	0.0	0.0
	250	53.9	15.5	0.0
	300	4.2	82.4	4.8
	350	0.0	88.9	10.0
	400	0.0	83.5	15.8
0.5Y/M-BEA_1	150	17.3	0.0	0.0
	200	60.9	13.1	5.1
	250	12.6	40.7	36.5
	300	0.2	74.1	21.5
	350	0.1	94.7	3.2
	400	0.1	94.0	5.2
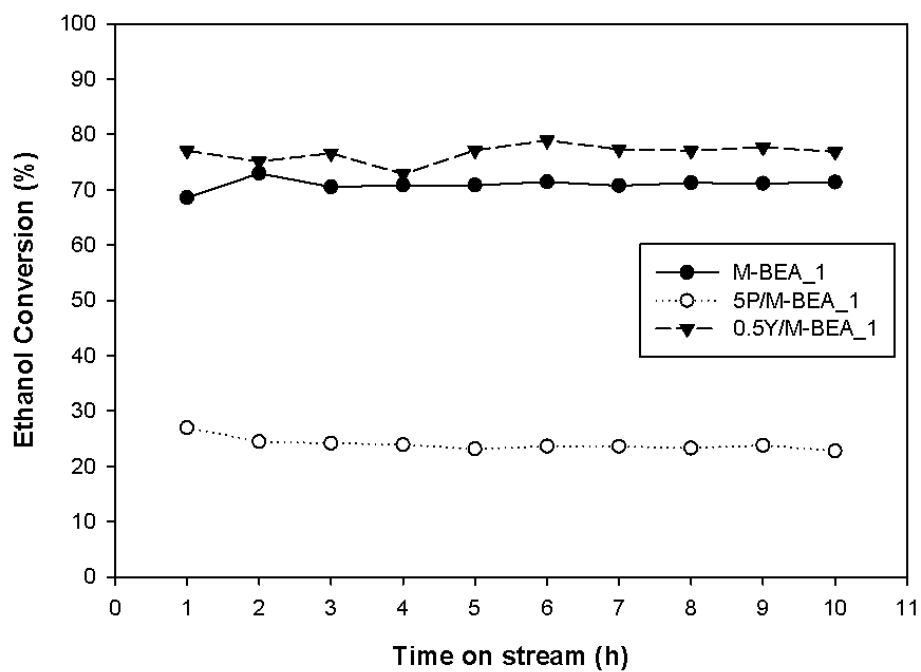
Figure 45 Stability of non-modified and modified Y or P on beta zeolite catalyst at WHSV of 3.1 h^{-1}.

Table 21 Comparison of catalysts for ethanol dehydration to DEE.

Catalysts	Reaction temperature (^{0}C)	Ethanol conversion (%)	DEE selectivity (%)	DEE yield (%)	Ref.
M-BEA_1	200	75	88	66	This work
H-MFI (280) Zeolite	200	43	100	43	[5]
Alumina	250	79	80	63	[31]
WO$_3$/ZrO$_2$	200	8	94	8	[40]
tungstophosphoricacid (TPA)	200	40	74	30	[26]
W-silicate-based nanocomposite	200	20	65	13	[28]
γ-Χ Alumina (70:30)	200	43	54	23	[4]
H-BEA	250	66	53	35	[34]
0.5%LaHZSM5	200	86	34	29	[41]
PWA/γ-Al$_2$O$_3$	190	75	99	74	[6]
Fe5/ZSM5	200	79	70	55	[32]

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Chapter 5 is the conclusion of the experiment data about the effect of catalytic preparation with different forms in Part 4.1, the optimal condition for DEE production by various the space velocity (WHSV), N_2 flow rate and ethanol concentration in Part 4.2 and the influence of modification catalyst with yttrium and phosphorus in Part 4.3. Furthermore, the recommendation for thesis research development is shown in this chapter.

5.1 CONCLUSIONS

5.1.1   The synthesized catalyst is "beta zeolite" which can be confirmed by XRD and N_2 physisorption techniques.

5.1.2   For comparison, the activity of catalyst with different form, it summarized that the mixed Na-H form in catalyst with one cycle in ion-exchange method (M-BEA_1) is the suitable catalyst to convert ethanol to DEE. It exhibited the highest DEE yield of 27.3% at 250 °C because this catalyst has highest surface area resulting in increased accessibility for the number of adsorbed ethanol reactant and the amount of moderate acid site that selective to DEE.

5.1.3   The study of optimal condition by various factor is summarized as follows:

- The factor of WHSV is important key to increase the conversion value and to shift the maximum value of DEE yield at a lower temperature. It was observed that decreased WHSV, resulted in increased conversion because for lower space velocity, the catalyst has a longer time to contact with the ethanol substrate

- The factor of carrier (N_2) gas shows the increased conversion with decreasing the N_2 flow rate. The optimal N_2 flow rate is 900 ml/h. The conversion and DEE yield are slightly greater than 1,800 ml/h.

- The factor of ethanol concentration indicated that the conversion increased with decreasing the ethanol concentration. Moreover, ethanol

concentration of 1.7 x 10^{-4} g_{EtOH}/ml has the highest DEE yield of 65.6% at 200 °C

5.1.4 The modification of beta zeolite catalyst with Y or P does not result in higher value of DEE yield due to the addition of Y or P to reduce the surface area and moderate acid site in beta zeolite catalyst

5.2 RECOMMENDATIONS

5.2.1 It is important to differentiate the acidity type (Bronsted and Lewis) by IR technique with pyridine-adsorbed

5.2.2 XRF technique should be characterized to investigate the percent of Si, Al, Y and P in bulk catalyst

5.2.3 It is interesting to study the percent loading of Y or P that would affect the catalytic activity in dehydration reaction
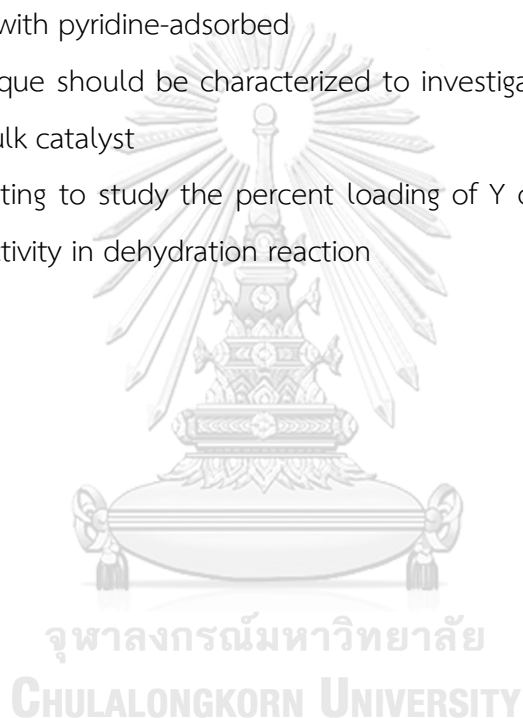
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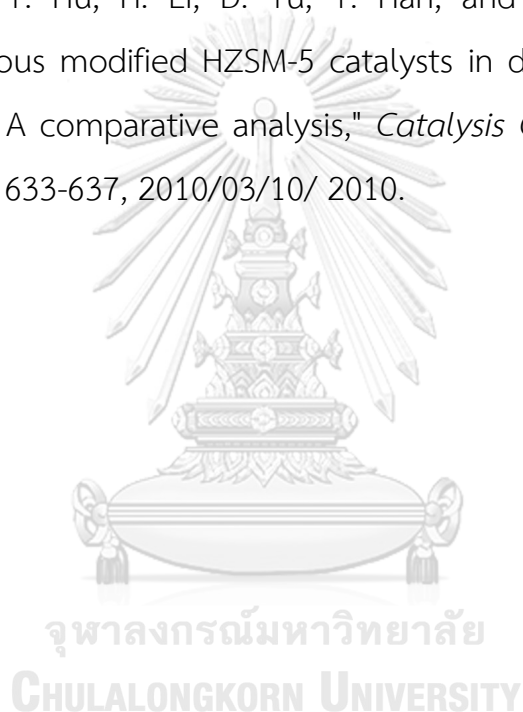
จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX

APPENDIX A

MODIFICATION BETA ZEOLITE BY ION-EXCHANGE METHOD

The Na form of beta zeolite catalyst (Na-BEA_C) was modified using 1 M ammonium nitrate by ion-exchange method with the v/w ratio of 20 ml ammonium nitrate per 1 g of catalyst.

Precursor

- Ammonium nitrate (NH_4NO_3)   M.W. = 80 g / mol

Based on 1 M of Ammonium nitrate

For solution 1,000 ml consists of NH_4NO_3 1 mol

consists of NH_4NO_3 80 g

80 g of NH_4NO_3 was added into distilled water for preparing 1 M of NH_4NO_3

Na-BEA_C catalyst was mixed with NH_4NO_3 solution for 2 h/cycle, washed with distilled and dried at 110 °C for overnight. Finally, the sample was calcined with air at 550 °C for 6 h.

APPENDIX B

CALCULATION OF SYNTHETIC CATALYSTS BY INCIPIENT WETNESS IMPREGNATION

Calculation of 5% loading of P on beta zeolite

The 5% loading on M-BEA_1 catalyst was prepared by incipient wetness impregnation method. Then, dried in an oven at 110 °C and calcined under air flow at 550 °C for 4.5 h to obtain the 5P/M-BEA_1.

<u>Precursor</u>

- 85% of Phosphoric acid, H_3PO_4 M.W. = 98 g/mol

- Phosphorus   M.W. = 31 g/mol

Density of H_3PO_4 1.71 g / cm3

Based on solution 100 ml , 85 ml of H_3PO_4

Concentration of Phosphoric acid

$$[\text{Phosphoric acid}] = \frac{85}{100}\% \text{ x } 1.71\frac{g}{cm^3} \text{ x} \frac{1}{98}\frac{mol}{g} \text{x} 1000\frac{cm^3}{L} = 14.83\frac{mol}{L}$$

Based on M-BEA_1 catalyst = 1 g

There is 0.05 g of phosphorus in M-BEA_1 catalysts = 1 - 0.05 g

So, 0.95 g of HZSM-5 catalysts

For Phosphorus 0.05 g = $\frac{0.05}{31}$ = 0.001613 mol

<u>For mole balance equation</u>

$$C_1V_1 = C_2V_2$$

$$14.832 \times V_1 \, (mol/L) = 0.001613 \, mol$$

$$V_1 = 0.00010875 \, L$$

$$V_1 = 108.75 \, \mu L$$

108.75 μL of 85% Phosphoric acid is used to prepare 5% wt P on M-BEA_1 catalyst

Pore volume of 1 g M-BEA_1 catalyst = 510 μL

So, it added distilled water = 510 − 108.75 = 401.25 μL

Calculation of 0.5% loading of Y on beta zeolite

The 0.5% loading on M-BEA_1 catalyst was prepared by incipient wetness impregnation method. Then, dried in an oven at 110 °C and calcined under air flow at 450 °C for 3 h to obtain the 0.5Y/M-BEA_1.

Precursor

- 99.9% of Yttrium (III) nitrate hexahydrate, $Y(NO_3)_3 \cdot 6H_2O$ M.W. =383.01 g/mol
- Yttrium   M.W. =88.81 g/mol

Based on M-BEA_1 catalyst = 1 g consisted of yttrium 0.005 g

precursor 1 mol consisted of Y = 1 x 0.999 = 0.999

precursor 383.01 g   consisted of Y = 88.9 x 0.999 = 88.81 g

Therefore, Y = 88.81 g   from precursor 383.01 g

Y = 0.005 g   from precursor $\dfrac{0.005 \, x \, 383.01}{88.81}$ = 0.022 g

So, the precursor = 0.022 g and M-BEA_1 = 0.995 g

APPENDIX C

CALIBRATION CURVE FOR ETHANOL DEHYDRATION REACTION

The calibration curve was estimated by injection the substance into GC-FID and detected by chromatogram in area of substance versus quantity of injection substance. The calibration curve of substrate and product were shown in Figure AC 1-4.
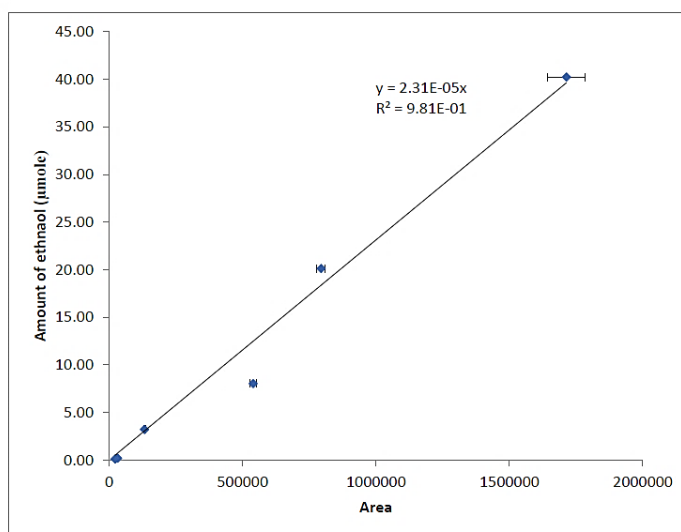

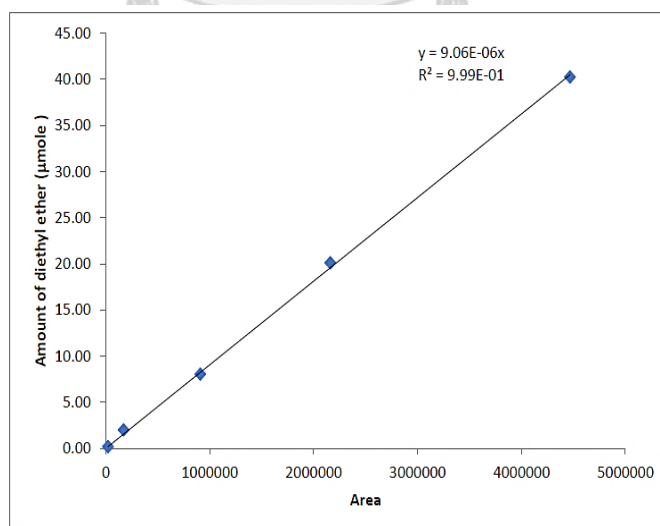**Figure AC 1** The calibration curve of substrate (Ethanol)

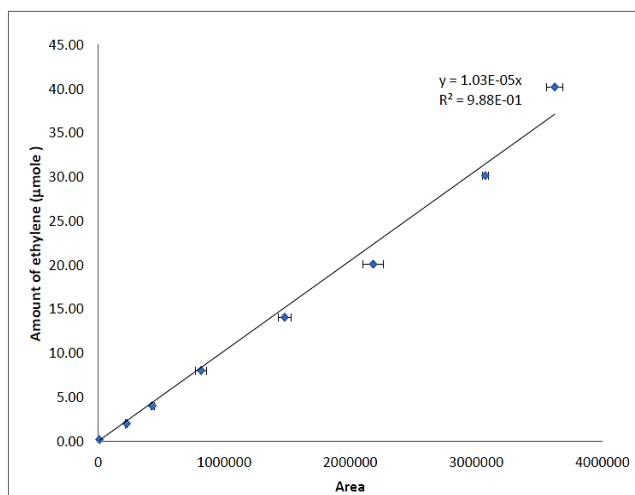**Figure AC 2** The calibration curve of diethyl ether product
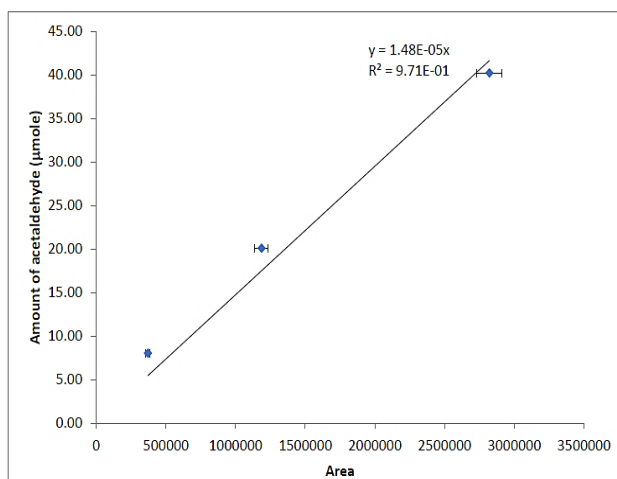
Figure AC 3 The calibration curve of ethylene product

Figure AC 4 The calibration curve of acetaldehyde product

APPENDIX D

CALCULATION OF ACIDITY IN CATALYST WITH NH$_3$-TPD

Acidity of catalyst was detected by ammonia temperature programmed desorption. The calibration curve of ammonia gas is shown in Figure AD 1.
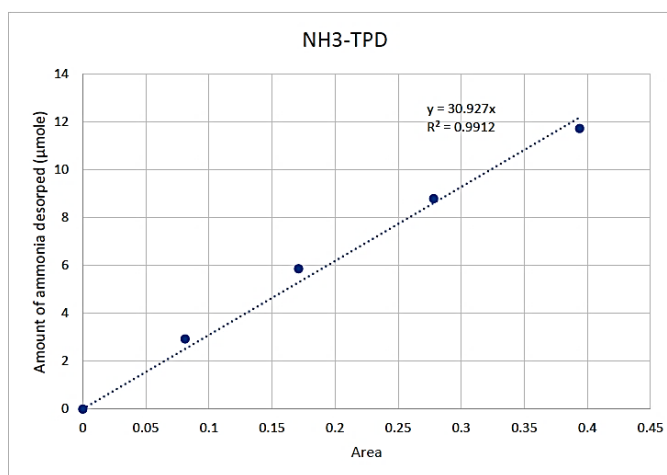

Figure AD 1 Calibration curve of NH$_3$ TPD

$$\text{Total acidity} = \frac{\text{mole of NH}_3 \text{ desorption (μmole NH}_3)}{\text{weight of dry catalyst (g)}}$$

Where, mole of NH$_3$ desorption were estimated from calibration curve of NH$_3$ TPD

Mole of desorbed NH$_3$ (**μ**mole NH$_3$) = Area of TCD signal × 30.93

(slope of calibration curve from desorption of

ammonia gas)

APPENDIX E

CALCULATION OF CONVERSION, SELECTIVITY, YIELD WHSV AND RATE

The catalytic activity in a dehydration reaction was evaluated in term of ethanol conversion, product selectivity and product yield.

Conversion of substrate

$$\text{Ethanol conversion (\%)} = \frac{(\text{mole of ethanol feed} - \text{mole of ethanol in product})}{\text{mole of ethanol feed}} \times 100$$

Selectivity

$$\text{DEE selectivity (\%)} = \frac{\text{mole of DEE in product}}{\text{mole of total products}} \times 100$$

$$\text{Ethylene selectivity (\%)} = \frac{\text{mole of ethylene in product}}{\text{mole of total products}} \times 100$$

$$\text{Acetaldehyde selectivity (\%)} = \frac{\text{mole of acetaldehyde in product}}{\text{mole of total products}} \times 100$$

Where : Total products = DEE+ Ethylene+Acetaldehyde

Yield

$$\text{DEE yield (\%)} = \frac{\text{DEE selectivity x ethanol conversion}}{100}$$

$$\text{Ethylene yield (\%)} = \frac{\text{Ethylene selectivity x ethanol conversion}}{100}$$

$$\text{Acetaldehyde yield (\%)} = \frac{\text{Acetaldehyde selectivity x ethanol conversion}}{100}$$

WHSV

$$WHSV\ (h^{-1}) = \frac{Mass\ flow\ rate\ of\ substrate\ (\frac{g}{h})}{Weight\ of\ catalyst\ (g)}$$

APPENDIX F

RAW DATA

รายงานการทดสอบ

กรมวิทยาศาสตร์บริการ

ชื่อวัตถุตัวอย่าง	เครื่องหมาย / ตรา	หมายเลขปฏิบัติการ
Beta zeolite	-	L62/02098.1

ผลการทดสอบ

		ครั้งที่ 1	ครั้งที่ 2	ครั้งที่ 3	ค่าเฉลี่ย
1. ซิลิคอน (Si)	ร้อยละ	30.6	31.2	32.0	31.3
2. อะลูมิเนียม (Al)	ร้อยละ	4.8	4.6	4.8	4.7

ชื่อผู้ใช้บริการ   โครงการ CAT-REAC Industrial Project

ที่อยู่ผู้ใช้บริการ จุฬาลงกรณ์มหาวิทยาลัย แขวงวังใหม่ เขตปทุมวัน กรุงเทพมหานคร 10330

ลักษณะตัวอย่าง ผงละเอียดสีเทา

วันที่ทดสอบ   25 มีนาคม – 4 เมษายน 2562

วิธีทดสอบ   1. รายการที่ 1 ทดสอบด้วยวิธี gravimetry

2. รายการที่ 2 ทดสอบด้วยเครื่อง inductively couple plasma optical emission spectrometer

ผู้รับรอง

(นางสาววันดี ลือสายวงศ์)

นักวิทยาศาสตร์ชำนาญการพิเศษ

ผู้รายงาน

(นายจิ๊ระ สวนไธสง)

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