การเปิดวงอิพอกไซด์โดยใช้ตัวเร่งปฏิกิริยา ZSM-5

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EPOXIDE RING OPENING BY ZSM-5 CATALYSTS

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A Thesis Submitted in Partial Fulfillment of the Requirements

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

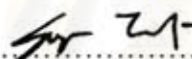Faculty of Science

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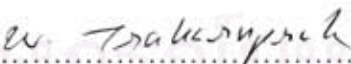
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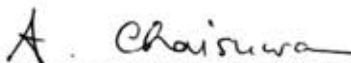
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ได้ทดสอบตัวเร่งปฏิกิริยาซีโอไลต์ ZSM-5 ที่มีอัตราส่วนซิลิกา/อลูมินา 10-50 ในการเปิดวงอิพอกไซด์ ตัวเร่งปฏิกิริยาซีโอไลต์ทั้งหมดเตรียมได้โดยวิธีไฮโดรเทอร์มอล และพิสูจน์เอกลักษณ์ด้วย XRD, SEM/EDX, ^{27}Al MAS NMR และ nitrogen adsorption (BET) ผลจากการพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยา นำมาวิเคราะห์ความสามารถในการเร่งปฏิกิริยาการเปิดวงอิพอกไซด์ ปฏิกิริยาการเปิดวงอิพอกไซด์เกิดขึ้นในระบบตัวเร่งปฏิกิริยาแบบเนื้อผสม การศึกษาปฏิกิริยาการเปิดวงสไตรีนออกไซด์พบว่าตัวเร่ง H-ZSM-5 ที่อัตราส่วน Si/Al = 36 มีประสิทธิภาพในการเร่งปฏิกิริยา และให้ผลิตภัณฑ์ 2-methoxy-2-phenylethanol ในปริมาณที่สูงถึง 80%และมีความเลือกจำเพาะที่ดีต่อการเกิดปฏิกิริยา ภายใต้สภาวะที่เหมาะสม คือที่อุณหภูมิ 70 °C เวลาในการทำปฏิกิริยา 3 ชั่วโมง ได้นำสภาวะที่เหมาะสมประยุกต์ใช้กับอิพอกไซด์ชนิดอื่น ได้แก่ 1-dodecene oxide และ cyclohexanone oxide พบว่าสามารถเปิดวงอิพอกไซด์เหล่านี้เป็นผลิตภัณฑ์ของอนุพันธ์แอลกอฮอล์ในปริมาณปานกลางถึงสูง

นอกจากนี้ได้ทำการศึกษาการนำตัวเร่งปฏิกิริยาที่ใช้แล้วกลับมาใช้ใหม่ในปฏิกิริยาการเปิดวงอิพอกไซด์ โดยทำการปรับสภาพผิวตัวเร่งปฏิกิริยาด้วยการเผาที่อุณหภูมิสูง 540 °C เป็นเวลา 5 ชั่วโมง แล้วนำมาใช้เป็นตัวเร่งปฏิกิริยา หลังจากทำการทดลองทำปฏิกิริยาโดยใช้ตัวเร่งปฏิกิริยาที่ใช้แล้วจำนวน 4 รอบ พบว่าให้ค่าประสิทธิภาพในการเกิดปฏิกิริยาที่สูง รวมไปถึงค่าปริมาณผลิตภัณฑ์และค่าความสามารถในการเลือกเกิดผลิตภัณฑ์ของ 2-methoxy-2-phenylethanol ค่อนข้างสูง

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต....................
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KEY WORD : ZSM-5 CATALYST, EPOXIDE RING OPENING CATALYSIS

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A series of *H*-ZSM-5 zeolites with Si/Al ratios in a range of 10-50 were tested in the epoxide ring opening catalysis. All ZSM-5 catalysts were synthesized by hydrothermal method and characterized by XRD, SEM/EDX, ^{27}Al MAS NMR and nitrogen adsorption (BET), to link catalyst properties to catalytic behavior. The catalysis of epoxide ring opening was carried out in the heterogeneous system. *H*-ZSM-5 with high Si/Al of 36 was an effective catalyst for styrene oxide ring opening, which gave the high yield of 2-methoxy-2-phenylethanol of higher 80% with a good selectivity at the reaction temperature of 70 $^{\circ}$C for 3 h. This optimum condition was further applied for other epoxides: 1-dodecene oxide and cyclohexene oxide. The catalytic reaction of epoxide ring opening over ZSM-5 catalyst could be proceeded and gave the relatively high quantity in product yield of alcohol derivatives. In addition, the reused catalyst with regeneration by calcined at 540 $^{\circ}$C for 5 h was studied for the reaction of epoxide ring opening. The result shows a high efficiency with the high yield of desired product and selectivity to 2-methoxy-2-phenylethanol, after testing for four cycles.

Field of study: Petrochemistry and Polymer Science   Student's signature.Supaporn V.

Academic year: 2006   Advisor's signature. W. Chavasiri

Co-advisor's signature. D. Nuntasri

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LIST OF ABBREVIATIONS

Å	=	aungstrom
J	=	coupling constant (NMR)
s	=	singlet (NMR)
t	=	triplet (NMR)
dd	=	double doublet (NMR)
TLC	=	thin layer chromatography
Σ	=	mass balance
^{o}C	=	degree celsius
mmol	=	millimole(s)
$CDCl_3$	=	deuterated chloroform
MeOH	=	methanol
S.O	=	styrene oxide
1-d.o	=	1-dodecene oxide
SEM	=	scanning electron microscopy
EDX	=	energy dispersive X-ray
GC	=	gas chromatography
XRD	=	X-ray diffraction
$LiNTf_2$	=	lithium bistrifluoro-methane sulfonimide
$Fe(TCA)_3.1.5H_2O$	=	iron (III) trichloroacetate
TMSCl	=	trimethylsilylchloride

CHAPTER I

INTRODUCTION

Epoxides are important and versatile synthetic intermediates in organic synthesis [1]. The products from epoxide ring opening are also important in pharmaceutical industries, and other chemical fields. For instance the higher alcohols can be separated into plasticizers (C_6-C_{11}) and fatty acid alcohols (C_{12}-C_{18}) for detergent. Moreover, aliphatic alcohols are used as solvents and diluents for paints, as intermediates in the manufacturing of ester and in the preparation of a wide range of organic compounds [2]. Many studies of epoxide ring opening catalysis have been reported, although most of them have dealt with homogeneous catalysts such as acid, Lewis acid, Lewis base and Lewis acidic metal complexes [2 - 5]. Acid-catalyzed epoxide rearrangement leads to ketones and aldehydes, whereas the main products of base-catalyzed reaction are allylic alcohols. The use of homogeneous catalysis presents numerous drawbacks: loss of catalyst after reaction, corrosivity, toxicity and in most cases, generation of contaminated streams [6]. Accordingly, many efforts have been attempted to find out the heterogeneous catalysts to cope with these problems. With this reason, heterogeneous catalysts such as amorphous catalysts (SiO_2 and Al_2O_3), zeolitic catalysts (TS-1, ZSM-5, Al-beta, Mordenite and Al-MCM-41) and metal-containing zeolites have been extensively studied for epoxide rearrangement reaction [2, 7 - 8]. From these previous works motivated us to study the catalytic epoxide ring opening by ZSM-5 catalysts which were synthesized by hydrothermal method.

In this research, attempts have been investigated on the catalysis of epoxide ring opening using ZSM-5 catalyst and the effect of acidity and structural feature of ZSM-5 catalysts were discussed. The desired product from this reaction, 2-methoxy-2-phenylethanol has been applying to the pharmaceutical and petrochemical industries such as using this product for the ingredient of relief pain medicine, additive of polyethylene glycol for improve the solubility and stability.

Objectives

1. To study the catalysis of epoxide ring opening in methanol using ZSM-5 catalyst and to investigate other factors influenced on styrene oxide conversion to 2-methoxy-2-phenylethanol.

2. To apply the optimum condition for other epoxide ring opening.

Scope of work

1. To prepare ZSM-5 zeolite by hydrothermal synthesis method including the study on range of molar ratio of Si/Al 10-50.

2. To characterize the synthesized ZSM-5 catalysts by X-ray diffraction (XRD), Scanning Electron Microscope/Electron Dispersive X-ray, ^{27}Al-MAS NMR as well as nitrogen adsorption.

3. To apply the optimum conditions for other epoxides such as 1-dodecene oxide and cyclohexene oxide.

CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

2.1 Zeolites

2.1.1 Introduction of zeolites [9]

Zeolites are microporous crystalline aluminosilicates, composed of TO_4 tetrahedral (T = Si, Al) with O atoms connecting neighboring tetrahedral. The structure based on an extensive three–dimensional framework formed by connection of tetrahedral $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ linkage. The AlO_4 tetrahedral or empirically AlO_2 in the structure determines the framework charge and it was balancing cations occupied on non-framework positions. The zeolite composition can be described as having three components:

$$Mx/n \quad . \quad [(AlO_2)_x \, (SiO_2)_y] \quad .w.H_2O$$

extraframework cation   *framework*   *sorbed phase*
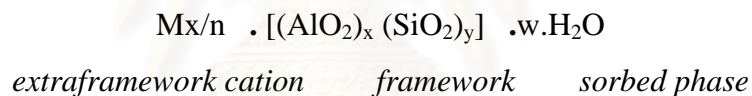
Where M is the exchangeable cations of valence, generally elements of group I or II in the periodical table and n is the number of cation oxidation state. The ratio of y/x is Si/Al molar ratio and it is equal to or greater than one because Al^{3+} was not occupied the adjacent tetrahedral sites, otherwise the negatively charged units next to each other will be obtained, w is the number of water molecules located inside the channels and cavities of zeolites. The framework of zeolite is shown in Figure 2.1.
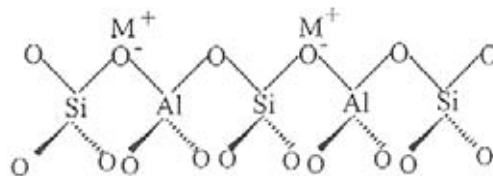
Figure 2.1 Framework of zeolite.

The extraframework cations are ion exchangeable and give rise to the rich ion exchange chemistry of these materials. The novelty of zeolites stems from their microporosity and is a result of the topology of the framework. The amount of Al within the framework can be varied over a wide range, with Si/Al = 1 to α, the completely siliceous form being polymorphs of SiO_2. The lower limit of Si/Al =1 of zeolite framework arises because placement of adjacent AlO^{4-} tetrahedral is not favored because of electrostatic repulsions between the negative charges. The framework composition depends on the synthesis conditions. Post-synthesis modifications that insert Si or Al into the framework have also been developed. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases.

Typically, in as-synthesized zeolites, water present during synthesis occupies the internal voids of the zeolite. The second phase and organic non-framework cations can be removed by thermal treatment/oxidation, making the intracrystalline space available. The fact that zeolites retain their structural integrity upon loss of water makes them different from other porous hydrates, such as $CaSO_4$.

2.1.2 Zeolite structure

The structure commission of the International Zeolite Association (IZA) periodically reviews publications containing new tetrahedral frameworks and assigns a three-letter code to each distinct new framework. For example, GIS is the three letter code for the mineral gismondine. These distinct tetrahedral frameworks are formally known as framework types.

The structure of zeolite is consisted of three dimensional framework of the tetrahedral primary building units which the tetrahedral atoms are silicon or aluminum as shown in Figure 2.2(a). These tetrahedral of silicon and aluminum are coordinated with each other through shared oxygen atoms which its forming a secondary building unit (SBU). SBU of ZSM-5 is 5-1 type as shown in Figure 2.2(b).

(a) primary building unit   (b) secondary building unit
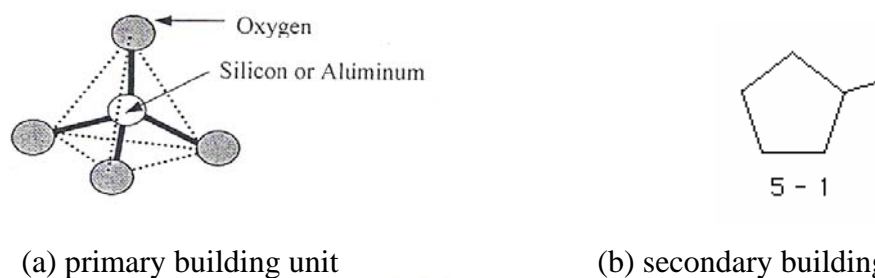
Figure 2.2 Structure of zeolite, (a) primary building unit, (b) secondary building unit.

ZSM-5 is in the family of 10-membered oxygen ring zeolite and it has the MFI structure. ZSM-5 structure is described as the SBU with 5-1 type because there are five oxygen atoms in one ring. ZSM-5 has two types of channel system, a straight and zigzag channel as shown in Figure 2.3. The straight channel has cavity 5.4 x 5.6 Å free diameter and sinusoidal channel has a cavity 5.1 x 5.4Å free diameter. These intersecting channels are generating a three dimensional framework as shown in Figure 2.4.
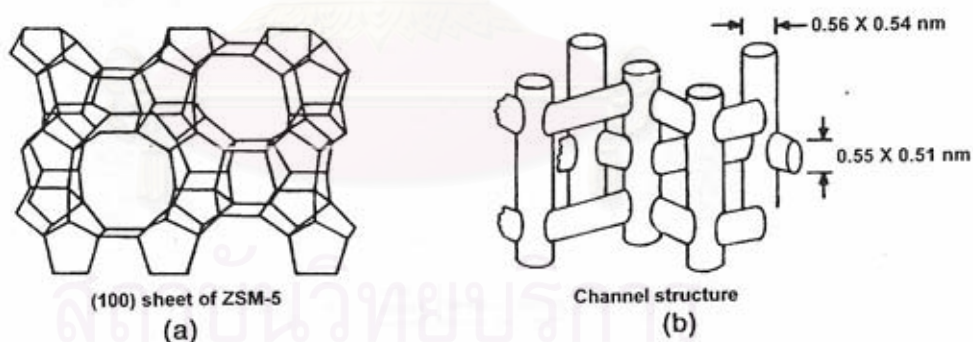
Figure 2.3 Structure of zeolite, (a) skeletal diagram of the (100) face of ZSM-5
(b) channel structure of ZSM-5.
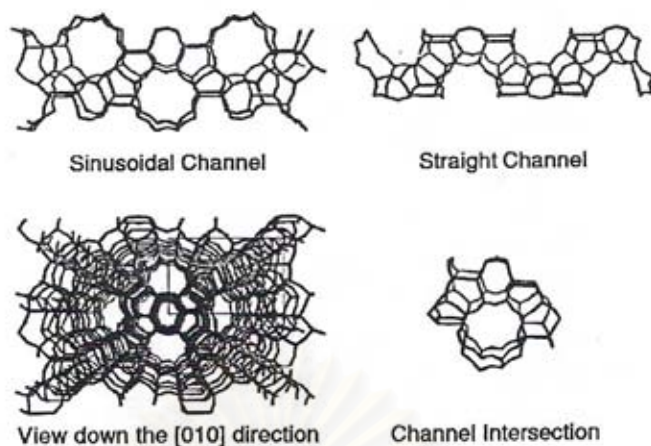
Figure 2.4 Framework structure of zeolite ZSM-5 (MFI) illustration the straight and sinusoidal pores and the pore intersections. A view of the complete structure down the straight pores is depicted in the left lower corner.

Cavities, channels and larger SBUs

　　　　Cavities are polyhedral units that differ from cages by the fact that they contain windows that allow the passage of molecules in and out of the cavity. Cavities should not be infinitely extended and should be distinguished from other units such as pores and channels. The cavities that describe the intersections of 10-ring channels in both framework types are depicted in Figure 2.5.
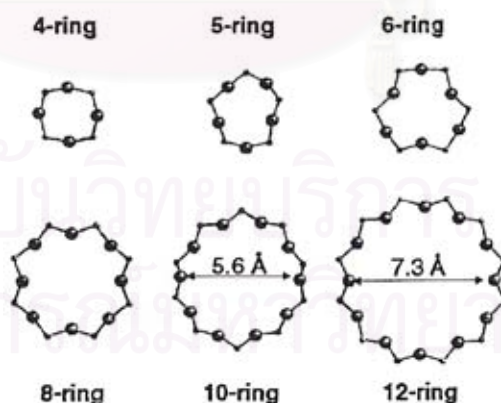
Figure 2.5 Relative sizes of n-rings frequently found in zeolites and related molecular sieves. The scale of pore aperture is given for the 10-ring to give sense of scale.

Channel is a pore that is infinitely extended in at least one dimension with a minimum aperture size (*n* ring) that allows guest molecules to diffuse along the pore. In various zeolites the channels intersect forming two- and three-dimension channel systems. The dimensions of the pore are one of the critical properties of zeolite materials since this dimension determines the maximum size of the molecules that can enter from the exterior of the zeolite crystal into its micropores. The pore descriptors are added. The connection of the cavities is illustrated in Figure 2.5.

The aperture dimensions of a channel are qualitatively determined by the number of T atoms (or oxygen atoms) of the n-ring that defines the channel. Structures with 8, 10, or 12-ring channel apertures are the most common and these are usually known as small, medium and large pore zeolite, respectively. The topological description of the channel aperture is free-diameter or metrical description of the pore size is also used. Thus 8-ring channels have a free diameter of ~ 4.0 Å; 10- ring channels have a free-diameter of ~ 5.6 Å and 12-ring channels have a free-diameter of ~7.6 Å. Moreover, the framework of zeolite is very flexible, with plenty of internal void space, and adsorbed molecules perturb the position of the framework atoms and change the exact dimensions of the free-diameter.

2.1.3 Shape selectivity of zeolites

There are three types of shape selectivity: reactant, product and transition-state shape selectivity.

Reactant shape selectivity results from the limited diffusivity of the reactant that entries and diffuses into the catalyst cavity, *e.g.* linear and branch chain of reactant. Product shape selectivity can be explained for the diffusing rate of product molecules from cavity, for example *o*- and *m*-xylene, cannot rapidly escape from the catalyst cavity except *p*-xylene. Restricted transition-state shape selectivity can be explained by the decrease of the rate constant for a certain reaction mechanism when the required transition state is too bulky to form readily as shown in Figure 2.6.

REACTANT SELECTIVITY

PRODUCT SELECTIVITY

CH₃OH +

RESTRICTED TRANSITION–STATE SELECTIVITY
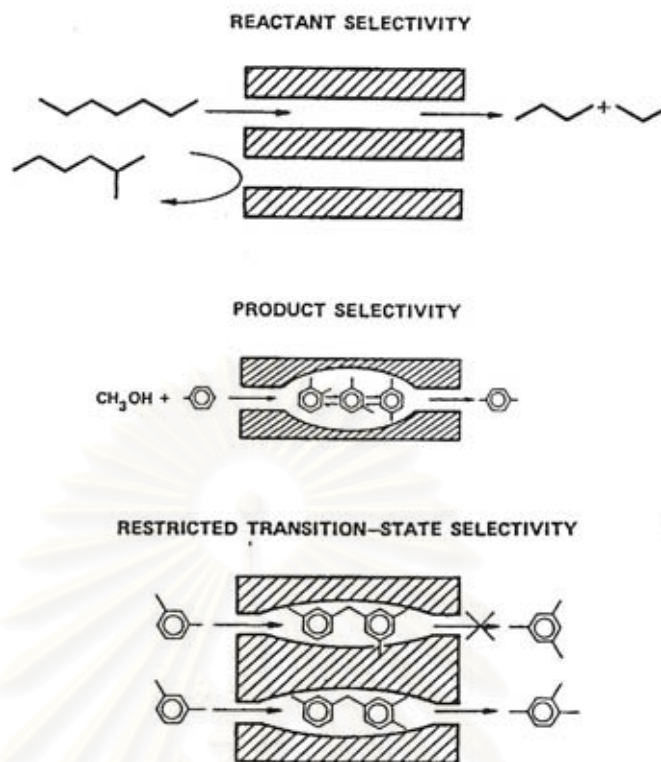
Figure 2.6 Different types of reaction selectivity imposed by the rigid pore structure of the zeolite.

Zeolite ZSM-5 is one type of shape-selective catalysts which have pore opening of *ca* 5.5 Å and exhibits as acid activity as well. ZSM-5 is nowadays the catalyst used to convert methanol to gasoline and to affect xylene isomerization (so as to maximize production of *p*-xylene) and a number of other key industrial processes.

2.1.4 Acid sites in zeolites

Classical Brönsted and Lewis acid models of acidity can be used to classify the acid sites of zeolites. Brönsted acidity is the proton donor site and electron deficient atom that can accept an electron pair behaves as Lewis acid site. Both types of acid sites occur in zeolites as shown in Figure 2.7.
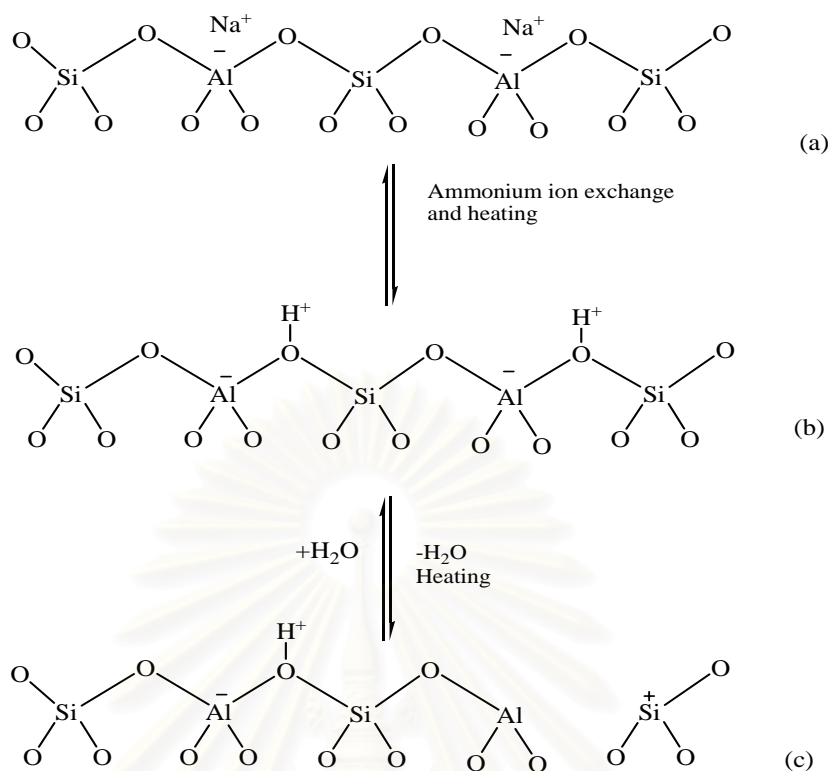
Figure 2.7 Acidity forms in zeolite: (a) calcined zeolite, (b) Brönsted acid site and (c) Lewis acid.

To produce the zeolite acid catalyst, a first step is to remove large organic quaternary amine cations occluded during synthesis by combustion in air or calcination. The obtained material contains alkali cations (*e.g.* Na^+) and some protons as shown in Figure 2.7(a). Ammonium exchange of the alkali cations, followed by subsequent denomination, such as thermal treatment releasing ammonia gas and leaving proton, results in the structure shown in Figure 2.7(b). Direct exchange with acid is also possible, but has to be done very carefully otherwise Al atoms will be extracted from the zeolite lattice. Simultaneously, Brönsted acid sites are in equilibrium with Lewis acid if –OH groups are considered to bond totally to Si, leaving tri-coordinated Al atoms. Upon heating at high temperature, acid sites are transformed to Lewis acid sites by dehydration as shown in Figure 7(c). This process is reversible. Other cations such as rare earths can be introduced into zeolites by ion exchange method as well.

2.2 Zeolite synthesis

ZSM-5 synthesis was first reported in the patent by Arguer and Landolt in 1972 [10]. The ratios of various reaction components claimed for successful synthesis is shown in Table 2.1. Reaction mixture was heat at 100-150 $^{\circ}$C for 6 h to 60 days. ZSM-5 was claimed to be able to catalyze the following reactions: cracking and hydrocracking of oils, isomerization of *n*-paraffins and naphthenes, polymerization of compounds containing an olefinic or acetylenic carbon, reforming, alkylation, isomerization of polyalkyl substituted aromatics and disproportionation of aromatics.

Table 2.1 Reactant molar ratios claimed for zeolite synthesis [10]

Reactant molar ratio	Broad	Preferred	Particularly preferred
OH^-/SiO_2	0.07-10.0	0.1-0.8	0.2-0.75
$(n\text{-}C_3H_7)_4N^+/$ $[n\text{-}C_3H_7)_4N^+ + Na^+]$	0.2-0.95	0.3-0.9	0.4-0.9
H_2O/OH^-	10 - 300	10-300	10-300
SiO_2/Al_2O_3	5-100	10-60	10-40

2.3 Literature review on epoxide ring opening

Epoxides and β-alkoxy alcohol are important intermediates in organic synthesis [11]. Thus, epoxides ring opening reaction to give β- substituted alcohols with nucleophiles are useful tools in organic synthesis and most of epoxides ring opening reactions generally proceed under acidic or basic conditions. Several reagents have been reported in the literature that can promote ring opening of epoxides, although most of them dealt with homogeneous catalysts (acid, Lewis acid, Lewis base, metal complexes such as metal Schiff's base and metal carboxylate). Regarding to the use of homogeneous catalysis has the disadvantage: corrosivity, toxicity and contamination to the stream of products. Therefore, the heterogeneous catalysts have been investigated to overcome these problems.

2.3.1 Epoxide ring opening by homogeneous catalyst

Many reagents have been reported in the literature to promote ring opening of epoxides in the homogeneous catalytic system.

2.3.1.1 Epoxide ring opening by acid

The common acid catalyst has been reported in a few literatures such as H_2SO_4, HCl and HBr. In 2001, Girdhar *et al.* reported that epoxide ring could be opened under mild conditions using acid as a catalyst. The steroidal skeletal rearrangements of 16α,17α-epoxy-20-one (**1**) has proven to quite resistant to nucleophilic/Lewis acid catalyzed ring opening. The only reported ring opening of the latter epoxide ring is the conversion by HBr-AcOH, of (**1**) to bromohydrin (**2**) [11].
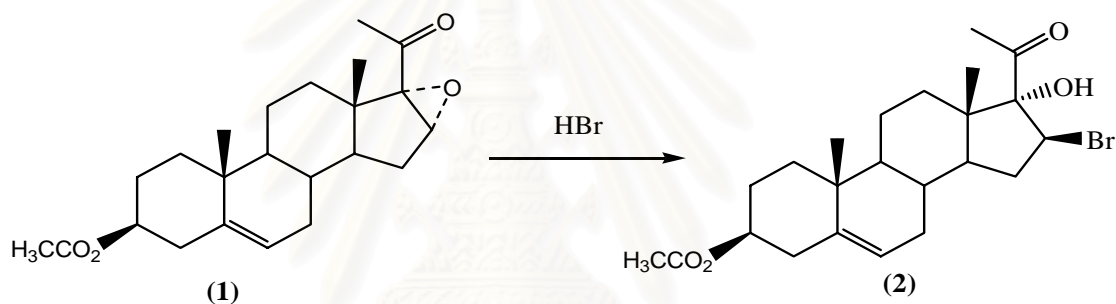
2.3.1.2 Epoxide ring opening by Lewis acid

Several Lewis acid reagents that use for epoxide ring opening have been reported in the literature such as $FeCl_3$ [5], $LiNTf_2$ [12], $BiCl_3$ [17], $ZnCl_4$ [28], $CeCl_3.7H_2O$ [29].

In 2000, Cossy *et al.* reported that lithiumbistrifluoro-methanesulfonimide ($LiNTf_2$), can be efficiently used in the ring opening of epoxides with nucleophiles such as amines, hydrazines and thiophenol, at room temperature, in CH_2Cl_2 or even without any solvent in excellent yield. Furthermore, when $LiNTf_2$ is used instead of Lewis acids, the work-up is easier as no emulsion was formed. Ring opening of styrene oxide (**3**) with 2-phenylethylamine in the presence of $LiNTf_2$ (0.1 equiv) led to **4** and **5** with a yield of 77% and in a ratio of 80/20. Cyclohexene oxide (**6**) was transformed to amino alcohol **7** when treated with 2-phenylethylamine 77% yield and to **8** when reacted with aromatic amine such as aniline 89% yield [12].

(3)

(4)

(5)

(6)

(7) 77%

(6)

(8) 89%
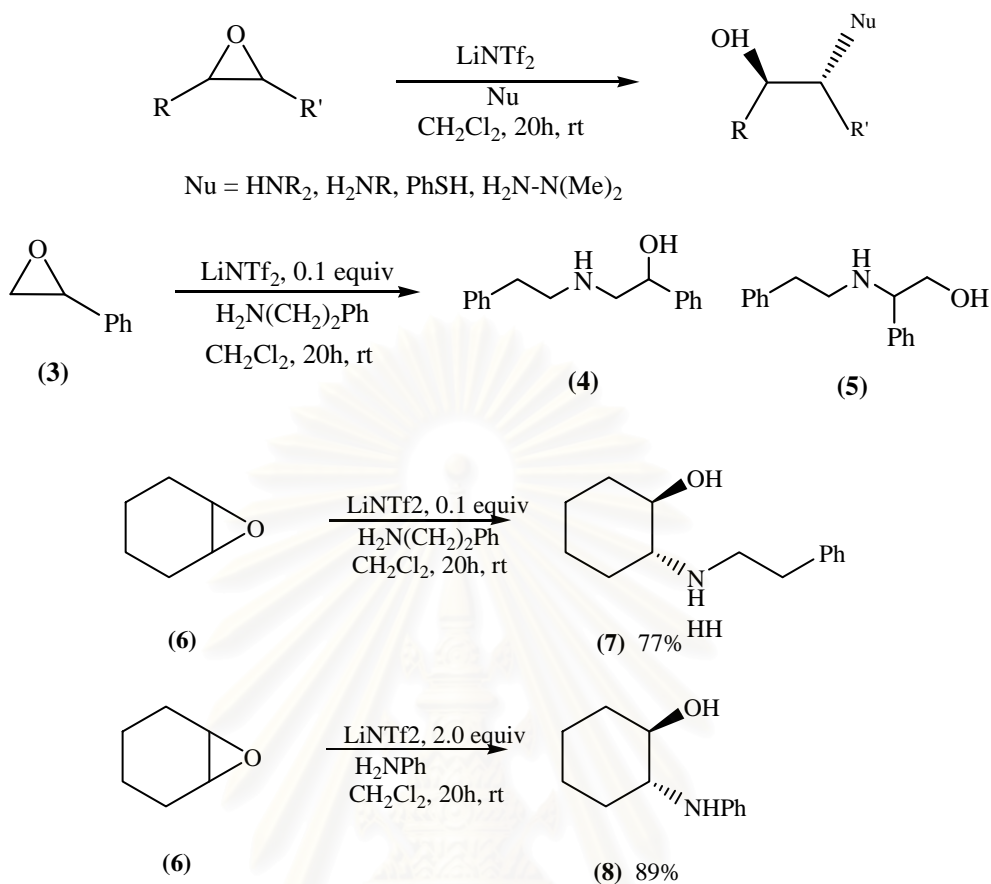
In 2005, Mc Cluskey *et al.* reported that the opening of epoxides could be taken place by using Lewis acid catalyst, $BiCl_3$. This catalyst is a relatively new catalyst, which has considerable green chemistry advantages, of low toxicity and mild reaction conditions. Reaction of styrene oxide and cyclohexene oxide with 10% $BiCl_3$ and various anilines were tested. Good conversion to amino alcohols (**9** and **11**) could be obtained (% yield >70) [17].
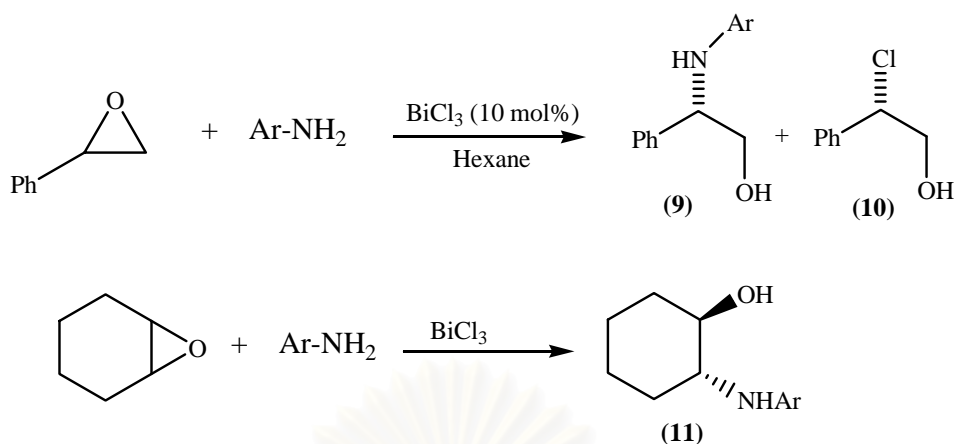
2.3.1.3 Epoxide ring opening by Lewis base

In 2002, Lowden and Mendoza reported that chiral styrene oxide could be opened with secondary amines to yield amino alcohol regioisomers. The alcohol products were then mesylated to form a relatively stable aziridinium intermediate which was opened regiospecifically with primary amines at the benzylic carbon to form 1,2-phenethyldiamine products [18].
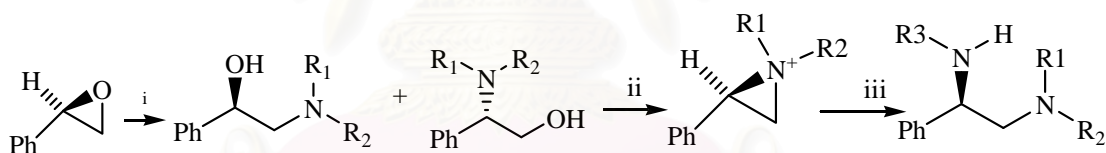
2.3.1.4 Epoxide ring opening by Lewis acidic metal complexes

Many metal complexes have been reported in the literature to use for epoxide ring opening, for instance Jacobsen's (salen) metal complex, [13], Fe(TCA)$_3$.1.5H$_2$O [4] and metalloporphyrin [15].

In 2000, Bruns and Haufe reported that epoxide could be opened with hydrofluorinating agents mediated by chiral non-racemic Lewis acids. The reaction of cyclohexene oxide with KHF$_2$/18-crown-6 was *trans*-diastereoselective and proceeded with 55% *ee* to form (*R,R*)-(-)-2-fluorocyclohexanol **(12)** in the presence of Jacobsen's (*S,S*)-(+)-(salen)chromium chloride (complex A). From racemic epoxides such as styrene oxide or phenyl glycidylether **(15),** mainly or exclusively the products with

fluorine in primary position are formed with 90 or 62%*ee*, respectively. In all cases minor amounts of the corresponding chlorohydrins are formed [13].

(Complex A)

12 (90%*ee*) **13** **14**

15 **16** (62% *ee*) **17**
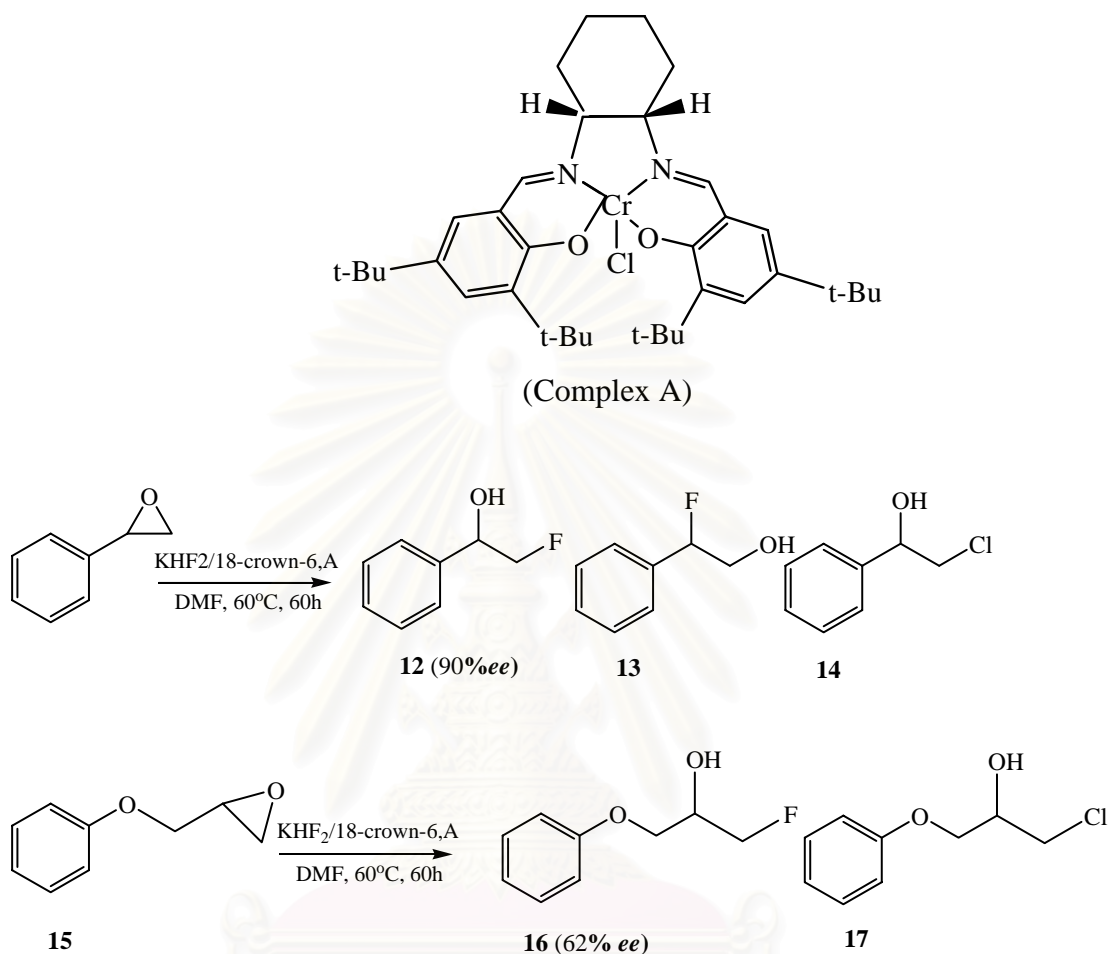
In 2003, Jetipattaranat studied the epoxide ring opening catalyzed by three groups of catalyst: transition metal salt, metal Schiff's base and metal carboxylate complexes. Fe(TCA)$_3$.1.5H$_2$O exhibited the most effective catalyst for styrene oxide ring opening reaction. The obtained product was 2-methoxy-2-phenylethanol **(18)** in almost 100% yield at ambient condition for 10 min [4].

(18) **(19)**
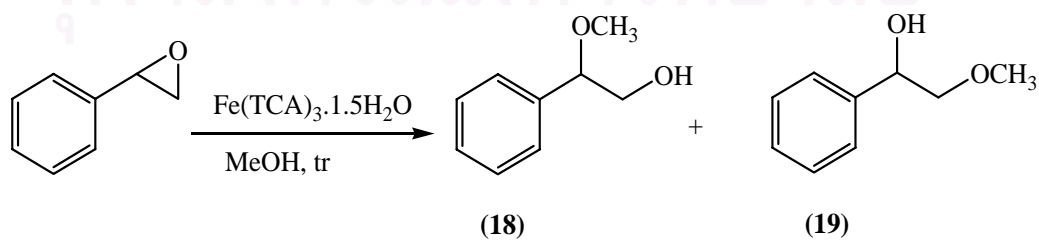
In 2004, Moghadam *et al.* reported that the newly synthesized $Sn^{IV}(tpp)(OTf)_2$ could act as an efficient catalyst for the alcoholysis, hydrolysis, acetolysis of epoxides which gave a high yield and good selectivity to product. For the conversion of epoxides to thiranes with ammonium thiocyanate and thiourea, and also the preparation of acetonides from epoxides and acetone [15].
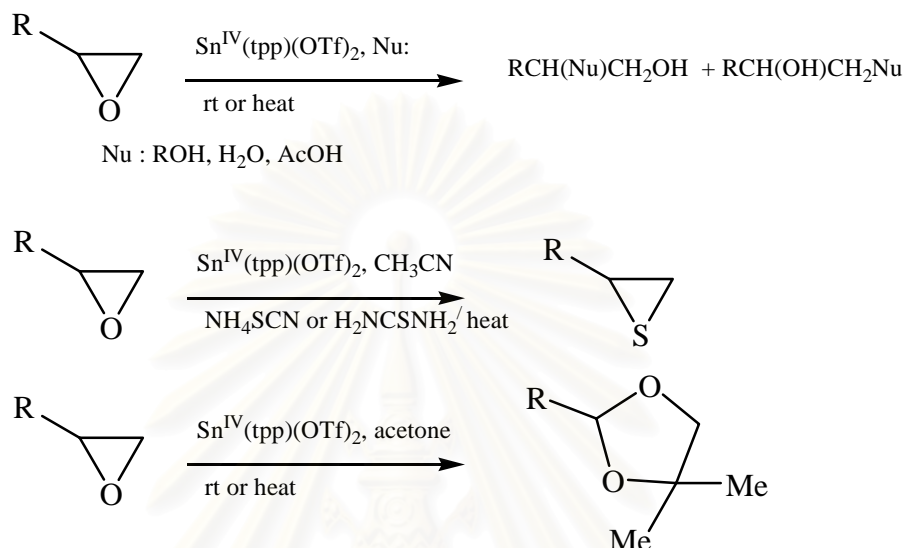
In 2004, Xu *et al.* reported that the synthesis of chlorohydrins could be proceeded by the cleavage of epoxides using TMSCl in recyclable ionic liquid, $bmimPF_6$. The reaction was underwent at mild condition. The synthesis of chlorohydrin using styrene oxide as a substrate was performed in ionic liquids for 1 h at room temperature, high phenylchlorohydrin product 98% was obtained [16].
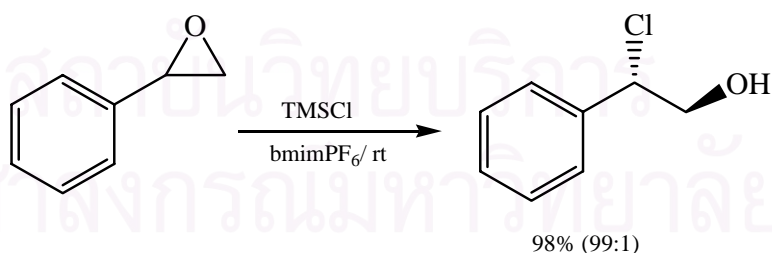
2.3.2 Epoxide ring opening by heterogeneous catalysts

Several substances have been reported in the literature to use for epoxide ring opening in the heterogeneous catalytic system such as Raney nickel, Pd-C [19], zeolite [2, 7], amorphous aluminosilicate and montmorillonite K10 [20], $(NH_4)_8[CeW_{10}O_{36}].20H_2O$ [14].

In 1996, Dimitrova *et al.* studied the styrene oxide ring opening in MeOH by using various zeolite catalysts such as beta zeolite, *H*-ZSM-5, *H*-ZSM-35 and ZSM-35 modified with Ag^+. Catalysis of styrene oxide ring opening has been achieved over acidic forms of zeolites possessing two dimentional intersecting channels of different sizes (*H*-ZSM-5 and *H*-ZSM-35), as well as over two silver modifications of the latter. Beta zeolite type has been tested for determining the influence of the channel structure to the selectivity of reactions. Selective formation of 2-phynylethanol on *H*-ZSM-35 has been observed. On the Ag modified with ZSM-35 significant quantities of phenylacetic acid have been determined together with the expected product 2-phenylethanol. When the reaction was carried out at $80\,^{o}C$, styrene oxide ring opening catalysis over *H*-ZSM-5 and *H*-ZSM-35 gave a high conversion of 80% but beta zeolite and ZSM-35 with Ag^+ modification gave a moderate conversion of 60% and 40%, respectively. *H*-ZSM-5 and beta zeolite have the selectivity to 1-phenylethanol product while *H*-ZSM-35 has the selectivity to 2-phenylethanol [7].

In 1999, Ravichandran and Divakar studied the styrene oxide ring opening catalysis by different reagents like Raney nickel, Pd-C and $NaBH_4$ with β-cyclodextrin. The obtained products are ethylbenzene, 1-phenylethanol and 2-phenylethanol. The use of Raney nickel catalyst in the hydrogenation of styrene oxide yielded ethylbenzene 69.0% and the use of Pd-C provided 2-phenylethanol 89.9%. Moreover, the use of $NaBH_4$ as a reducing agent with β–cyclodextrin gave a product selectivity to 1-phenylethanol in almost 100%. Observed selectivities have been correlated to arise directly from the disposition adopted by styrene oxide inside the β–cyclodextrin cavity [19].

In 2003, Rios *et al.* studied the nucleophilic addition of alcohols to epoxidized oils by using the crystalline and amorphous aluminosilicates, Y zeolite and clays of montmorillonite type as catalysts. Zeolites with higher mesopores content, were more active because the active Brönsted sites are more accessible to the bulky substrate. Aluminosilicates in lamellar form like clays of the type montmorillonite were the most active aluminosilicates for the epoxide alcoholysis [20].

In addition, Mirkhani *et al.* reported that epoxides could be opened by $(NH_4)_8[CeW_{10}O_{36}].20H_2O$ catalyst under mild condition and gave β–alkoxy and β–acetoxy alcohols in high yields [14].

A recent literature has been revealed that main catalysis of epoxide ring opening is dealt with the use of Lewis acid and Lewis acidic metal complex as catalysts but few of acid-catalyzed zeolite ZSM-5 was reported in the literature. Thus, this research was focused on the use of ZSM-5 catalyst for epoxide ring opening reaction.

CHAPTER III

EXPERIMENTAL

3.1 Equipment and apparatus

X-ray Diffractrometer (XRD)

All synthesized ZSM-5 catalysts were analyzed by means of Rigaku D/Max-2200X-ray powder diffractrometer, with nickel filtered CuK_{α} radiation (30kV, 30mA) at an angle of 2θ ranged from $5-50^{o}$. The scan speed was 5°/min, scan step was 0.02^{o}. Scattering, divergent and receiving slits were fixed at 0.5^{o}, 0.5^{o} and 0.3 mm, respectively.

Scanning Electron Microscope & Energy Dispersive X-ray (SEM/EDX)

ZSM-5 catalysts were performed the surface and quantitative analysis by SEM/EDX model SEM Hitachi S-4200 at Hitachi Global Storage Technologies (Thailand), Ltd. SEM condition for surface analysis of ZSM-5 were performed by Secondary Electron mode (SE), Accelerating voltage (Vacc) 15 kV, Working Distance (WD) = 10 mm and scanning image in a high magnification and EDX analysis for studied the composition of synthesized ZSM-5 were performed at Accelerating voltage (Vacc) = 15 kV, Working Distance (WD) = 20 mm.

Nuclear Magnetic Resonance Spectrometer (NMR)

^{27}Al MAS NMR

Solid state ^{27}Al MAS NMR, model Bruker Advance DPX 300 MHz NMR at MTEC was used for analyzed the Al form in ZSM-5 framework.

^{1}H-NMR

^{1}H-NMR spectra were obtained in $CDCl_3$ with TMS as an internal reference on the Varian nuclear magnetic resonance spectrometer, model Mercury plus 400

NMR spectrometer which was performed at 399.84 MHz. The chemical shifts (δ) are assigned by comparison with residue solvent protons.

Surface Area Analyzer

The specific surface area were analyzed by surface area analyzer, model BELSORP mini II. Use nitrogen as a purge gas, heating temperature in a range from room temperature to 430°C for pretreatment condition.

Gas Chromatograph (GC)

Mixture of products were analyzed by Shimadzu gas chromatograph GC-14A with HP-5 column (30-m long and 0.32-mm OD, 0.25 μm film thickness) and FID (Flame Ionization Detector).

3.2 Chemical and materials

Sodium aluminate (alumina source) was a product of Riedel-de Haën. Silica source was a sodium silicate solution (water glass), (10.13 wt% Na_2O, 29.71 wt% SiO_2, 59.80 wt% H_2O) which provided by Thai Silicate, Ludox HS-40 colloidal silica, 40 wt% suspension in water was a product of Aldrich. NaOH analytical reagent (A.R) was a product of LAB-SCN. TPABr (Tetrapropylammonium bromide), styrene oxide, 1-dodecene oxide and cyclohexene oxide were purchased from Fluka Chemical Company.

3.3 Synthesis of ZSM-5

3.3.1 Preparation of aluminosilicate gel

ZSM-5 catalyst was synthesized by hydrothermal method. [10,21]. Aluminosilicate gel with Si/Al molar ratio = 20 (or $SiO_2/Al_2O_3 = 40$) was prepared by mixing of TPABr solution and $NaAlO_2$ solution. TPABr solution was obtained by 5.11 g TPABr dissolved in 52.63 g of water and $NaAlO_2$ solution was obtained by 0.79 g $NaAlO_2$ dissolved in 52.63 g of water. These solutions were stirred separately for an hour and then dropwise of TPABr solution into $NaAlO_2$ solution by addition funnel. The mixture of these solutions were stirred for an hour and then dropwise into a four-neck round bottom flask containing 38.79 g of water glass solution. The mixture was stirred for 2 h with rotation speed 500 rpm. Molar

composition of obtained gel solution is $1SiO_2 : 0.36Na_2O : 0.025Al_2O_3 : 0.10TPABr : 37.2H_2O$. After that the pH of aluminosilicate gel was adjusted to be 10.5 by adding conc H_2SO_4. In the next step, pH adjusted gel was kept in the stainless-steel autoclave vessel with teflon sidewall 150 mL and aluminosilicate gel was crystallized under 170 ^{o}C for 7 days. After that the solid product was separated from solution by centrifugal 6000 rpm and washed with deionized water until the pH is equal to DI water. The ZSM-5 synthesis procedure is shown in Figure 3.1.
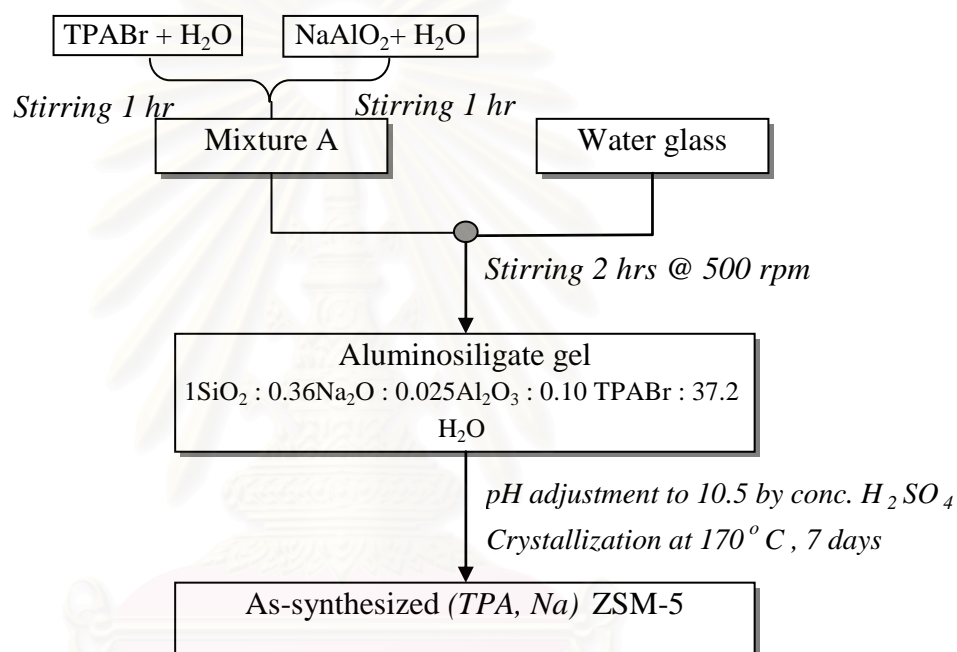
Figure 3.1 ZSM-5 synthesis procedure.

3.3.2 Organic template removal

TPABr is used as the template of catalyst in the preparation step. After the (*TPA, Na*) ZSM-5 was obtained from the crystallization process, TPABr was removed from the catalyst pores by calcining in a muffle furnace under temperature program from room temperature to 600 ^{o}C and aging at 600 ^{o}C for 12 h. The calcined zeolite was derived as (*Na,H*)ZSM-5. Temperature program for the template removal is shown in Figure 3.2.

3.3.3 Ammonium Ion Exchange

Ammonium ion exchange step is used for converting the (*Na,H*)ZSM-5 to *H*-ZSM-5 which is active form for acid catalysis. NH_4Cl was used for ammonium ion exchange with (*Na, H*)ZSM-5. The amount of NH_4Cl that used for ion exchange was calculated as following equation.

$$\text{amount of } NH_4Cl \quad = \quad n \text{ x MW. } NH_4Cl \text{ x mole ratio of } NH_4^+/Na^+$$

Where, *n* - mole of Na^+ in ZSM-5 [mole of Na^+ = (mole of Na^+ in ZSM-5 empirical formular x amount of ZSM-5)/FW of ZSM-5], the empirical formular of ZSM-5 is $Na_nAl_nSi_{96-n}O_{192}.16H_2O$), mole ratio of NH_4^+/Na^+ = 50. Where *n* of Si/Al ratio 10, 20 and 50 has a value as 9.2, 4.9 and 1.9, respectively. The volume ratio of zeolite: water was kept at 1:75 constantly. The obtained solution was refluxed at boiling temperature for 2 h. After that the zeolite part was separated from the solution by centrifugation and stirred with DI water until the solution was free from chloride ion testing by sliver nitrate. The obtained zeolite was dried overnight and calcined at 540 ^{o}C for 5 h by temperature program in air. The catalyst was performed the ammonium ion exchange and calcination twice in order to obtain the proton form of ZSM-5 completely. The temperature programs of template and ammonia removal are shown in Figure 3.2(b).
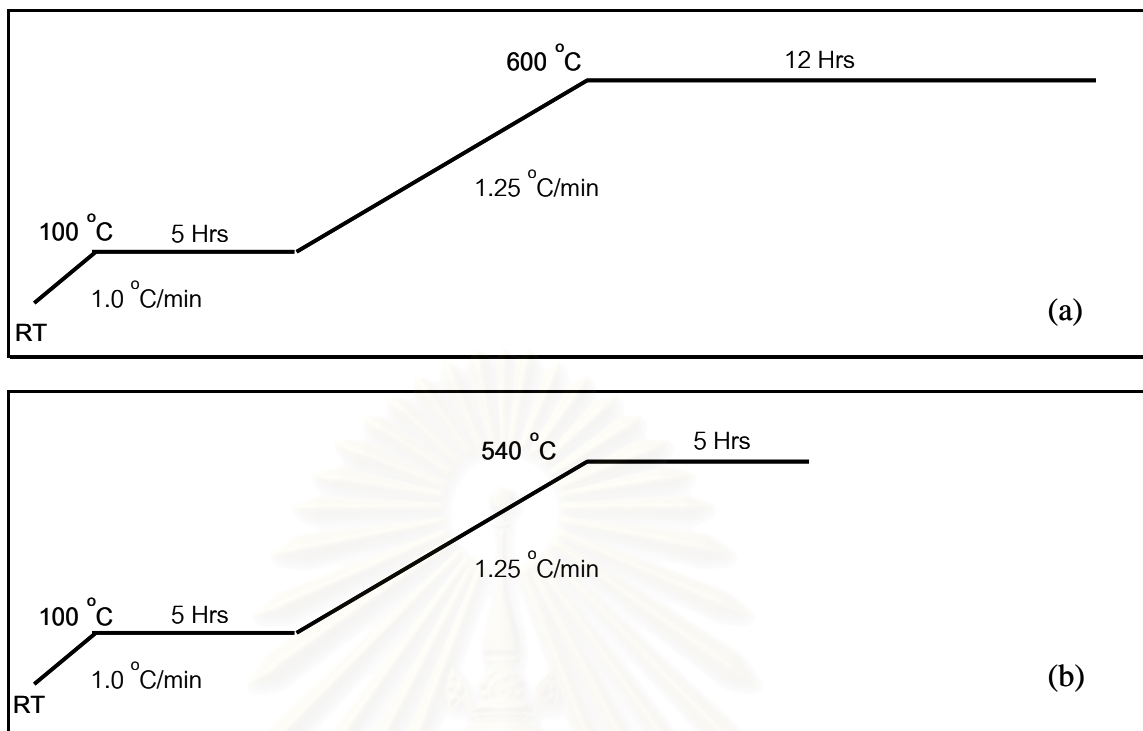
Figure 3.2 Temperature programs for (a) organic template removal and (b) ammonia
removal and catalyst regeneration.

3.4 Characterization of ZSM-5 catalysts

The synthesized ZSM-5 catalysts with various Si/Al molar ratios of 10, 20,
50 were characterized by different techniques shown as followings:

3.4.1 X-ray diffraction (XRD)

Crystallinity of zeolitic sample and mesoscopic ordering of mesostructured
materials were checked though XRD pattern.

3.4.2 Scanning Electron Microscopy (SEM)

Morphology and particle size of catalysts were analyzed by SEM Hitachi-
4200.

3.4.3 Energy Dispersive X-ray (EDX)

Chemical composition of catalysts was determined by Hitachi EDAX.

3.4.4 Surface Area Analyzer

The physical surface area of catalysts were determined by BET equation and micropore volume and micropore surface area of catalysts were determined by *t*-plot.

3.4.5 ^{27}Al MAS NMR

The coordination of the aluminium atoms and alumina form in ZSM-5 framework was determined by ^{27}Al MAS NMR spectra which derived from solid state ^{27}Al MAS NMR, model Bruker Advance DPX 300 MHz NMR.

3.5 Catalysis of epoxide ring opening by ZSM-5

All synthesized ZSM-5 catalysts were studied in the catalysis of epoxide ring opening. Generally, the catalytic system of epoxide ring opening consists of epoxide substrate, solvent and catalyst. In this research, styrene oxide was chosen as a model substrate and MeOH as nucleophile in the preliminary study. Other substrates such as 1-dodecene oxide and cyclohexene oxide were selected to study the epoxide ring opening catalysis in a part of extending the scope of this research.

General procedure of styrene oxide ring opening was started with mixing the styrene oxide 1 mmol (0.12 g) and 3 mL of MeOH in a round bottom flask 50 mL and loading the ZSM-5 catalyst by 100%wt of starting reagent. The solution mixture with catalyst was refluxed at 70°C for 3 h. At the end of reaction, the mixture of products was separated from the ZSM-5 catalyst by filtration and rinsed with Et$_2$O. The amount of products was quantitatively analyzed by GC with the addition of an exact amount of internal standard (cyclohexanone).

3.6 Study on the optimum conditions for styrene oxide ring opening
3.6.1 Effect of catalyst loading

The effect of ZSM-5 catalyst loading was studied in the reaction of styrene oxide ring opening and the catalysis condition was carried out according to the mentioned general procedure by varying the amount of ZSM-5 as 50, 75, 100, 150%wt of starting reagent.

3.6.2   Effect of reaction time

The styrene oxide ring opening was carried out according to the mentioned general procedure by using ZSM-5 with Si/Al ratio of 20, but the reaction time was varied as 30 min, 1, 3, 5 and 12 h.

3.6.3   Effect of reaction temperature

The styrene oxide ring opening was carried out according to the mentioned general procedure but the temperature of reaction was studied at 30 $^{\circ}$C and 70 $^{\circ}$C.

3.7   Effect of Si/Al ratio of ZSM-5 on styrene oxide ring opening

The styrene oxide ring opening was carried out according to the mentioned general procedure earlier but using different Si/Al mole ratio 10, 20 and 50.

3.8   Ring opening of other epoxides catalyzed by ZSM-5

The optimum condition of styrene oxide ring opening by using ZSM-5 catalyst was applied to other epoxides such as 1-dodecene oxide and cyclohexene oxide.

3.9   Study of ZSM-5 reused catalyst on epoxide ring opening

The studied ZSM-5 with the optimum Si/Al ratio was chosen to investigate the efficiency of recycling catalyst for styrene oxide ring opening. The reused catalyst was treated before the next run by washed with acetone and the dried catalyst powder was calcined in the maffle furnace under temperature program from room temperature to 540 $^{\circ}$C and aging for 5 h (Figure 3.2 (b)) in order to remove organic substance and other contaminants from catalyst. Styrene oxide ring opening by reused catalyst was studied for four cycles.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of synthesized ZSM-5

All the synthesized ZSM-5 catalysts with various molar ratios of Si/Al =10, 20 and 50 were characterized by different techniques. Crystallinity of zeolitic samples and mesoscopic ordering of mesostructured materials were checked through XRD patterns. Morphology and particle size of catalysts were obtained by SEM Hitachi-4200. Chemical composition was performed by EDX. The surface area of catalysts was determined by BET. Micropore volume and external surface area were determined by t-plot. The coordination of the aluminium atoms in the catalysts was checked by ^{27}Al MAS NMR spectra of the calcined H-ZSM-5.

4.1.1 X-ray diffraction of ZSM-5

All synthesized ZSM-5 catalysts were characterized the crystallinity and also determined the mesostructure of zeolite by means of XRD. The XRD patterns reveal specific diffraction of MFI type zeolite structure which is mainly reflected in the peaks located at around $2\theta = 7$-10 degree with two reflections, in around 22-25 degree range with three reflections, and at around 29-30 degree with two reflections (the summation integral of peak from the three regions is assigned to the MFI phase) [30,31]. The XRD pattern of both the template–free of ZSM-5 and after performed ammonium ion exchange to be the proton form catalyst are shown the MFI structure without any phase of other material is shown in Table 4.1 and Figure 4.1. In addition, all synthesized ZSM-5 with molar ratio of Si/Al as 10, 20 and 50 are also given the MFI structure. Crystallinity of synthesized ZSM-5 from different ratios of Si/Al were determined by the summation of peak intensity of 2θ at 7-10 degree are shown in Figure 4.2. The crystallinity of H-ZSM-5 with Si/Al ratio of 50, 20 and 10 was given as 100, 46 and 39%, respectively. This result indicated that the crystallinity increased with the Al content in aluminosilicate gel decreased.

Table 4.1 The values of selected 2θ of calcined ZSM-5 before and after ammonium ion exchange in each Si/Al ratio

Si/Al ratio	Before and after ion exchange	2theta/degree						
		2θ = 7-10 deg		2θ = 23-25 deg			2θ = 29-30 deg	
10	(*Na, H*)ZSM-5	7.84	8.76	23.00	23.78	24.26	29.08	29.90
	H-ZSM-5	7.90	8.78	22.92	23.78	24.24	29.08	29.84
20	(*Na, H*)ZSM-5	7.90	8.78	23.02	23.80	24.26	29.10	29.90
	H-ZSM-5	7.90	8.80	23.02	23.84	24.30	29.26	30.00
50	(*Na, H*)ZSM-5	7.90	8.82	23.10	23.92	24.38	29.28	29.90
	H-ZSM-5	7.92	8.78	23.12	23.94	24.38	29.32	30.02
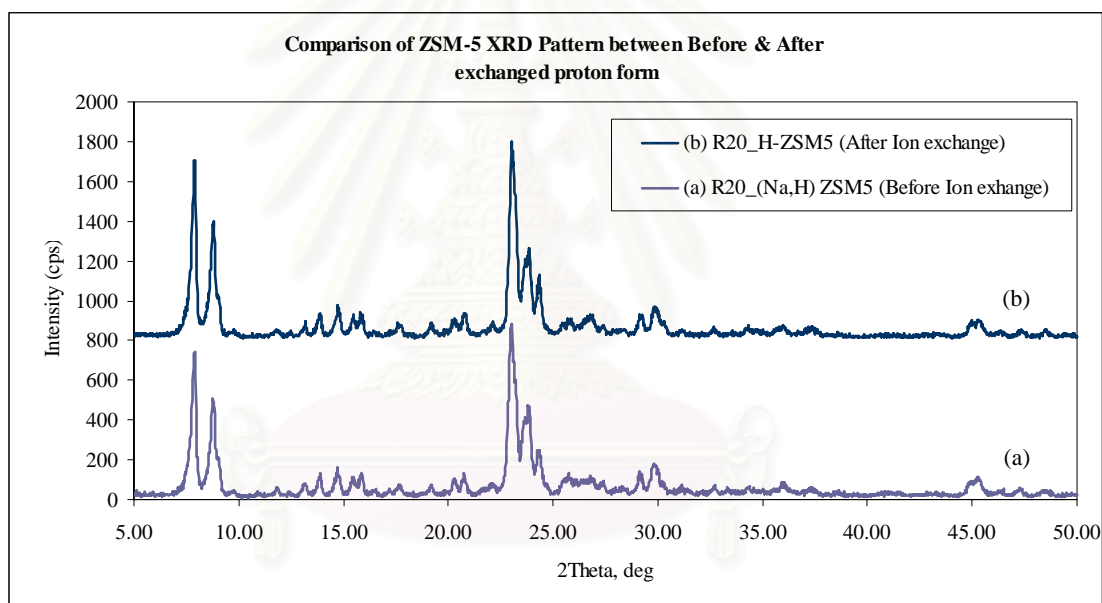
Figure 4.1 XRD patterns of (a) Calcined ZSM-5, Si/Al ratio = 20 or (*Na, H*) ZSM-5 and (b) After ion exchange (*H*-ZSM-5).
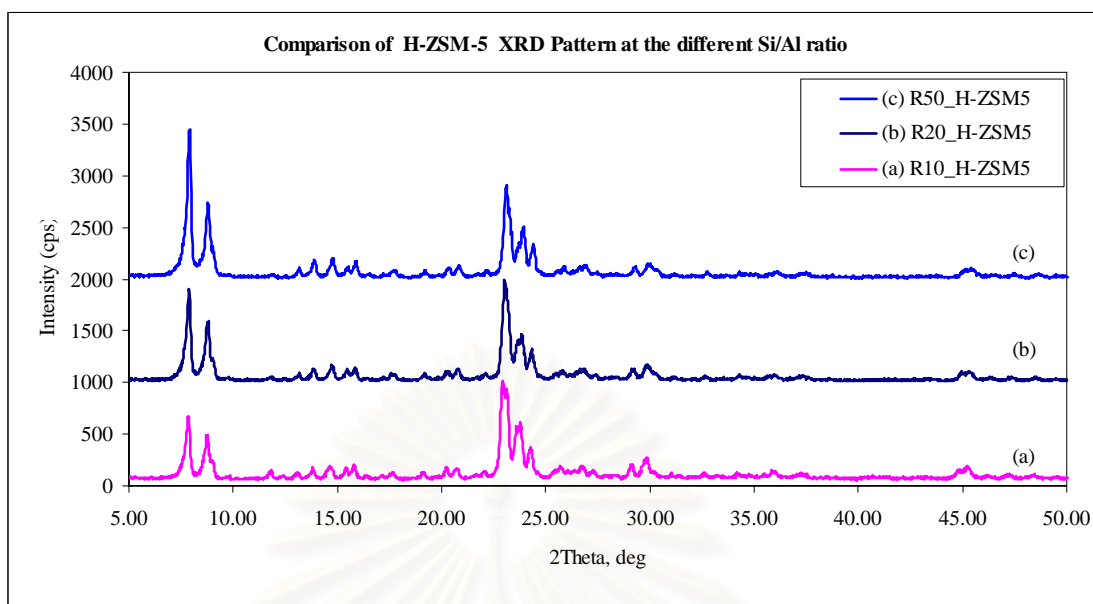
Figure 4.2 XRD pattern of (a) *H*-ZSM-5, Si/Al ratio = 10, (b) *H*-ZSM-5, Si/Al ratio = 20 and (c) *H*-ZSM-5, Si/Al ratio = 50.

Generally, crystallinity should be determined from the summation of peak intensity in range of 23-25 deg of 2theta in case of as-synthesized ZSM-5 (before calcining) because peak around 7-10 deg will be interfered from organic template.

4.1.2 Surface analysis by ZSM-5

All synthesized ZSM-5 catalysts were performed the surface analysis by SEM in order to study the morphology and particle size of catalysts. The SEM photos of template-free form and proton form of ZSM-5 sample are shown in Figure 4.3 and the particle sizes are shown in Table 4.2. The different features and particle sizes of synthesized ZSM-5 were clearly observed. The ZSM-5 at Si/Al mole ratio of 10 has a spherical shape with the particle size of approximately 5-6 μm, while ZSM-5 at Si/Al mole ratio of 20 has a sphere-like shape with particle size of about 4-5 μm. ZSM-5 at Si/Al mole ratio of 50 has a square-like shape and the particle size is around 2-3 μm, which is smaller than other Si/Al ratio. From this result, the feature of ZSM-5 at Si/Al mole ratio of 50 is different from other ratios. The possible causes might due to the use of different silica sources; ZSM-5 catalysts at Si/Al mole ratios of 10 and 20 were derived from sodium silicate solution (water glass), while ZSM-5 at Si/Al mole ratio 50 was derived from Ludox HS-40 colloidal silica with 40%wt. suspension in water.
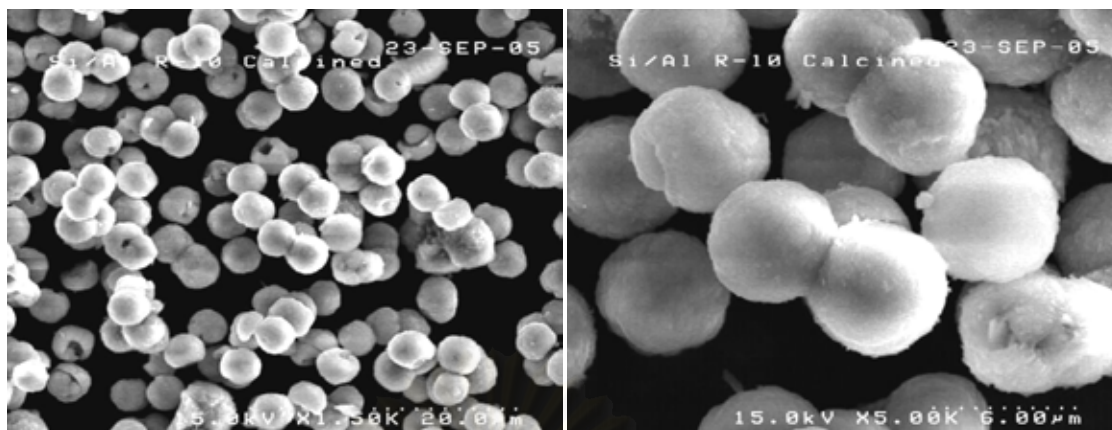
(a) SEM photos of *(H, Na)* ZSM-5 with Si/Al ratio of 10 (template-free ZSM-5)
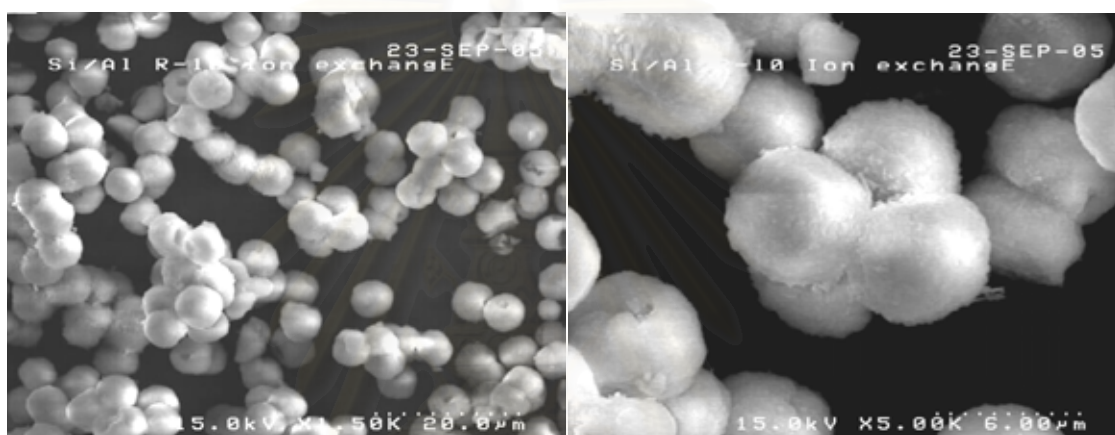
(b) SEM photos of *H-* ZSM-5 with Si/Al ratio of 10 (after ammonium ion exchange).
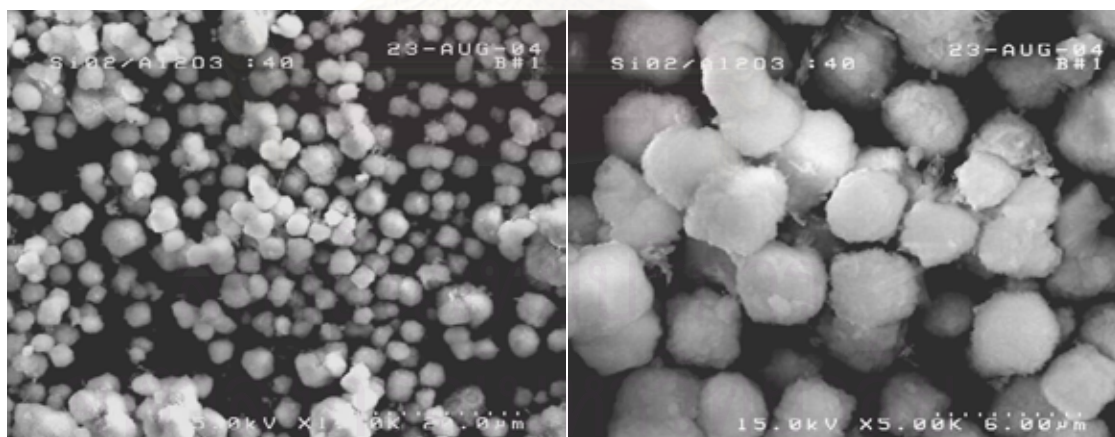
(c) SEM photos of *(H, Na)* ZSM-5 with Si/Al ratio of 20 (template-free ZSM-5).
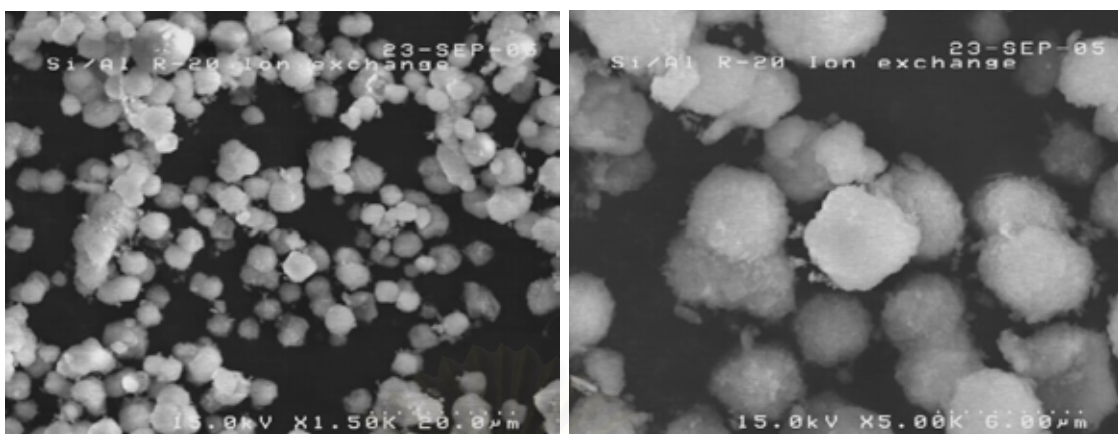
(d) SEM photos of *H*- ZSM-5 with Si/Al ratio of 20 (after ammonium ion exchange).
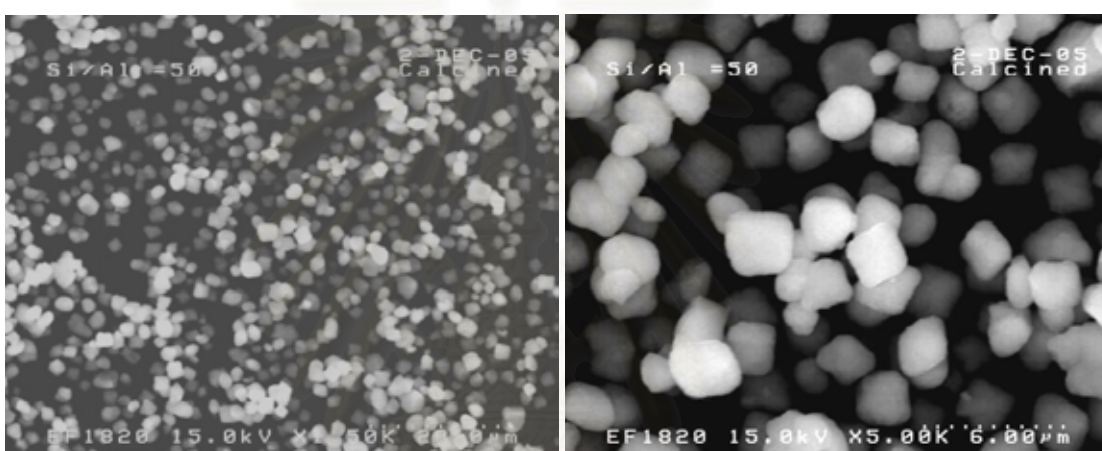
(e) SEM photos of *(H, Na)* ZSM-5 with Si/Al ratio of 50 (template-free ZSM-5).
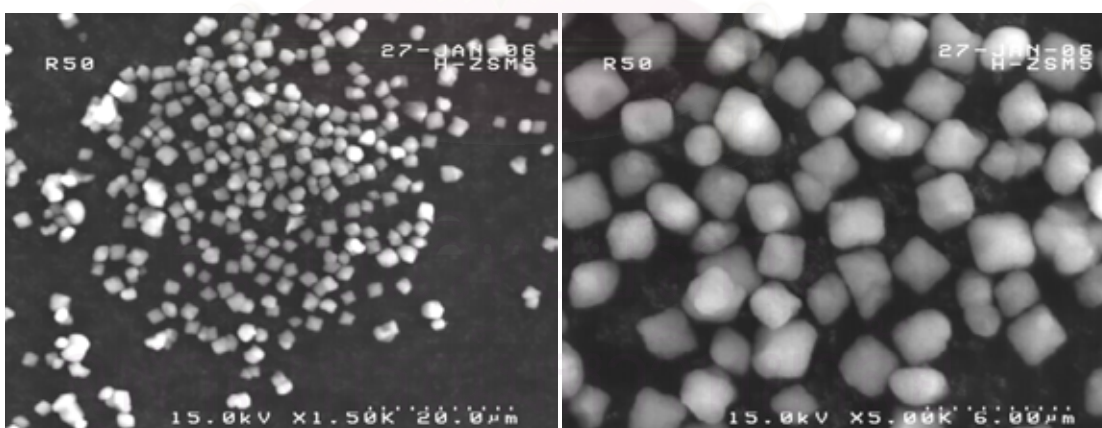
 (f) SEM photos of *H*- ZSM-5 with Si/Al ratio of 50 (after ammonium ion exchange).

Figure 4.3 SEM photos of *(Na,H)* ZSM-5 (a,c,e) and *H*-ZSM-5 (b,d,f) at the different
ratios of Si/Al.

4.1.3 Composition analysis of ZSM-5

Chemical compositions of ZSM-5 catalysts were analyzed by means of EDX analysis. Both of (*Na, H*) ZSM-5 and *H*-ZSM-5 catalysts were analyzed the Si/Al and Na/Al ratio as summarized in Table 4.2.

Table 4.2 Chemical composition of ZSM-5 at different Si/Al ratios

ZSM-5 (Si/Al ratio)	ZSM-5 type	Particle size (um)	Si/Al ratio	Na/Al ratio
10	(*Na, H*) ZSM-5	5-6 um	9.47	0.43
	H-ZSM-5	5-6 um	8.87	0.00
20	(*Na, H*) ZSM-5	4-5 um	18.56	0.22
	H-ZSM-5	4-5 um	21.99	0.00
50	(*Na, H*) ZSM-5	2-3 um	39.90	0.19
	H-ZSM-5	2-3 um	36.45	0.00

Based on EDX results in Table 4.2, the catalysts after treated with ammonium ion exchange have the value of Na/Al as zero. It indicates that the catalysts are completely ion exchanged to be the proton form. In addition to the result of Si/Al ratio, the Si/Al values of obtained catalysts are approximately close to the chemical composition of aluminosilicate gel.

4.1.4 Surface area analysis

All synthesized *H*-ZSM-5 catalysts were determined the surface area by N_2 adsorption experiment. The total specific surface area was determined by BET equation, micropore area and pore volume were determined by *t*-plot. The surface analysis results are shown in Table 4.3. From BET equation analysis, the result shows that the total specific surface area increased with increasing the molar ratio of Si/Al. Additionally, the *t*-plot analysis result illustrates that the micro-pore area, external surface area and micropore volume of ZSM-5 with Si/Al ratio of 50 are higher than other ratios.

Table 4.3 Surface area analysis result

ZSM-5 (Si/Al ratio)	Total specific surface area[a] $[m^2.g^{-1}]$	Total specific surface area[b] $[m^2.g^{-1}]$	Internal surface area[b] $[m^2.g^{-1}]$	External surface area[b] $[m^2.g^{-1}]$	Micropore volume [b] $(cm^3.g^{-1})$	Total pore volume[c] $(cm^3.g^{-1})$
R 10	349.68	507.40	428.10	79.30	0.12	0.20
R 20	382.53	537.44	402.05	135.39	0.11	0.27
R 50	414.89	590.84	444.19	146.65	0.12	0.24

(a) multi-point BET specific surface area

(b) *t*-plot method

(c) measure at $P/P_0 = 0.99$

Figure 4.4 shows the N_2 adsorption-desorption isotherms at 77 K corresponding to *H*-ZSM-5 samples. The isotherms are clearly identified to type I isoterm, which is typically microporous zeolite [33]. At the same relative pressure, N_2 adsorption-desorption over *H*-ZSM-5 with three different Si/Al ratios increased in the following order: 50> 20> 10.
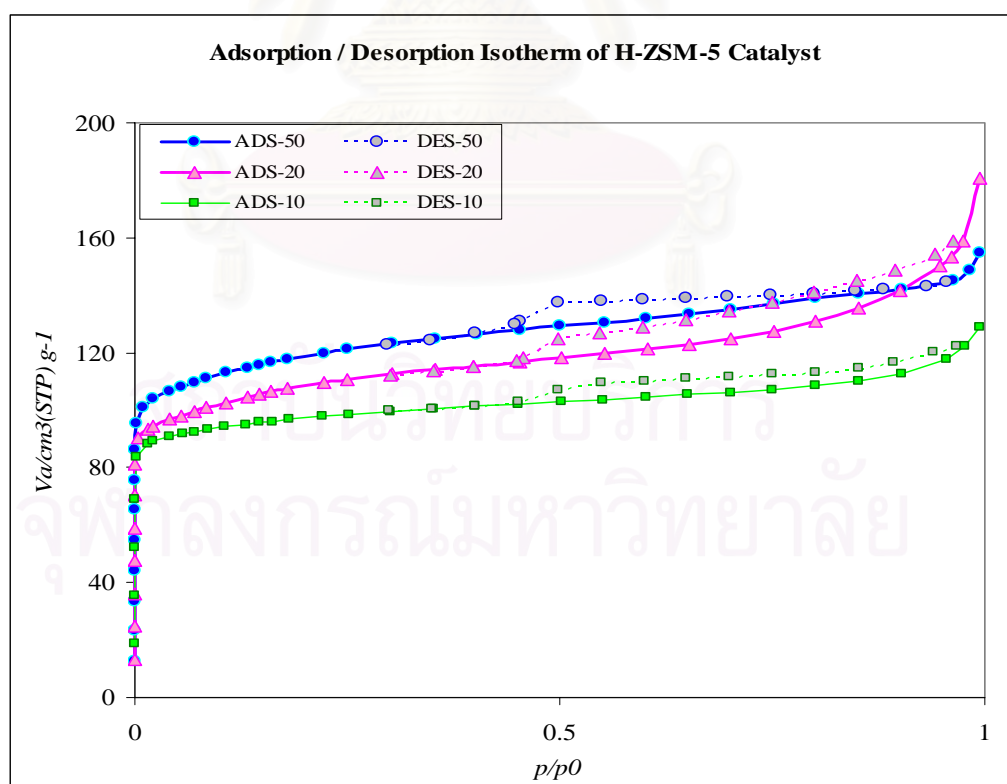
Figure 4.4 Nitrogen adsorption–desorption isotherms at 77 K corresponding to *H*-ZSM-5 with Si/Al mole ratios of 10, 20 and 50, respectively.

4.1.5 ^{27}Al MAS NMR analysis

To investigate the position of incorporated aluminum atom in the structure of aluminum containing support, ^{27}Al–solid NMR spectra can provide this information [36].

As can be seen in Figure 4.5, the aluminium-containing zeolite materials were analyzed by means of ^{27}Al MAS NMR in order to bear out the degree of aluminum incorporated into the zeolite framework. All the samples show a distinct peak at 55 ppm corresponding to tetrahedral aluminium and a fairly small one placed at 0 ppm assigned to the presence of low amounts of extra-framework of aluminum species with octahedral coordination [36]. The relative proportion of tetrahedral to octahedral type is higher in ZSM-5 with Si/Al molar ratios of 36, 22 and 9, respectively.
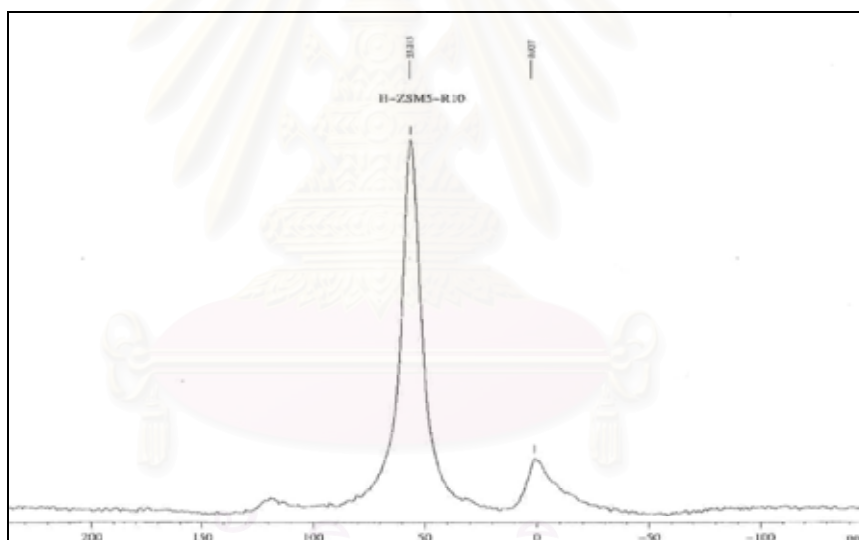
(a) ^{27}Al MAS NMR spectrum of *H*-ZSM-5, Si/Al molar ratio = 9.
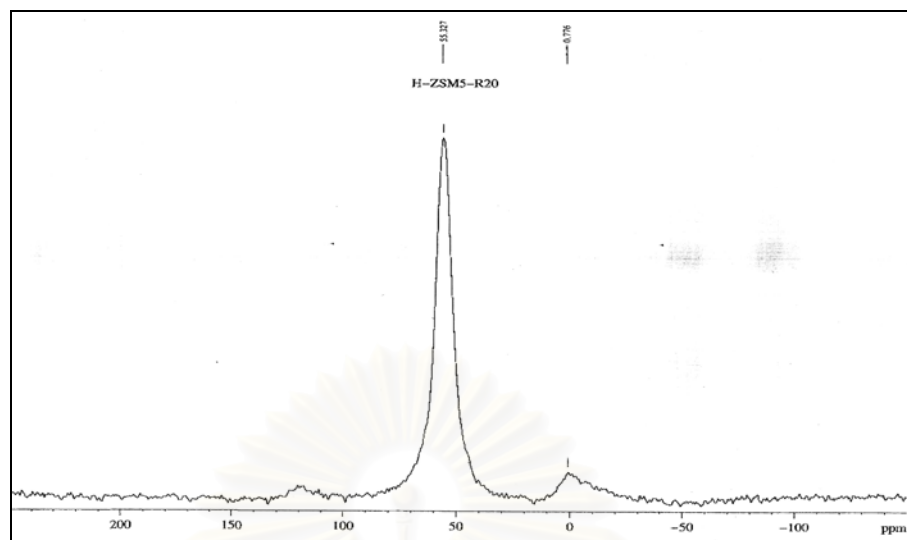
(b) ^{27}Al MAS NMR spectrum of *H*-ZSM-5, Si/Al molar ratio = 22.
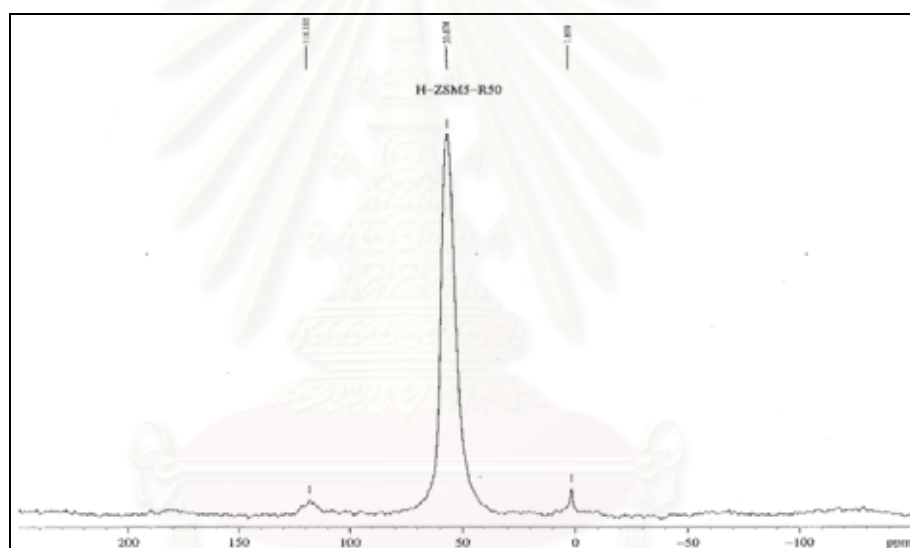
(c) ^{27}Al MAS NMR spectrum of *H*-ZSM-5, Si/Al molar ratio = 36.

Figure 4.5 ^{27}Al MAS NMR spectra of *H*-ZSM-5 with different Si/Al mole ratios**.**

Many research studies have been extensively reported that ZSM-5 is typically an acidic zeolite using NH$_3$-TPD technique to prove its acidic characteristic. Furthermore, the specific structural framework of *H*-ZSM-5 could be observed from the TPD spectrum at 500 and 670 K from ammonia desorption. [2,7,27]. Therefore, with the obtained result of ^{27}Al-NMR characterization, it could reasonably confirm that all synthesized catalysts contain mainly a tetrahedral aluminum within framework, of which is the major part of acid site.

4.2 Catalysis of epoxide ring opening by ZSM-5

All synthesized ZSM-5 catalysts were studied on the catalysis of epoxide ring opening. In general, the catalytic system of epoxide ring opening consists of epoxide substrate, solvent and catalyst. In this work, styrene oxide was chosen as a model substrate and methanol as solvent and nucleophile in the preliminary study. Afterwards, other substrates such as 1-dodecene oxide and cyclohexene oxide were chosen for the study on the epoxide ring opening catalysis in another part of extended scope of this research.

4.2.1 Effect of catalyst loading

The effect of ZSM-5 catalyst loading was studied in the reaction of styrene oxide ring opening. The catalysis condition was carried out according to the general procedure in the preliminary study using *H*-ZSM-5 (Si/Al ratio = 22) by varying the amount of catalyst loading as 50, 75, 100 and 150%wt of styrene oxide. The results are presented in Table 4.4.

From the scope of the preliminary investigation, styrene oxide was reacted with methanol in the presence of ZSM-5. The mixture of products was quantitatively analyzed by GC. The mixture was evaporated in vacuum system, and then the residue of mixture was separated by siliga gel column chromatography eluting with hexane and ethyl acetate (hexane : ethyle acetate = 6:1). All products were characterized by ^{1}H-NMR analysis. Under this general condition, the styrene oxide ring opening provided 2-methoxy-2-phenylethanol (**2**) as a major product, meanwhile 2-methoxy-1-phenylethanol (**3**) being a minor product.

       (1)   **(2)**   **(3)**
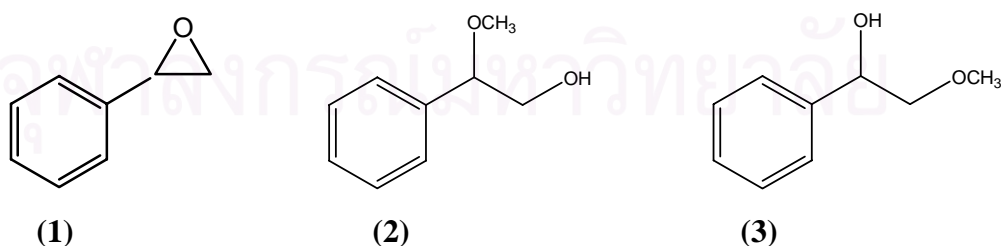
From the outcome of reaction, styrene oxide ring opening could be taken place *via* S_N-1 like and S_N2 mechanisms. First of all, epoxide ring could be protonated by proton supplied from *H*-ZSM-5 to form a coordination bond with the oxygen of

epoxide ring and induced the partial positive charge at carbon atom of epoxide ring on both sites. C-O bond was then broken in the way to form carbocation, and nucleophile could possibly attack the carbocation on either sites. However, the effect of carbocation delocalization in benzene ring may feasibly result in the main resonance stabilization, therefore leading to 2° carbocation being more stable than 1° carbocation. Thus, the reaction pathway is preferable to be S_N-1 like mechanism, which corresponds to catalysis result showing the high selectivities of product **2** to **3**. The proposed mechanism of styrene oxide ring opening is shown in Scheme 4.1.

2-methoxy-2-phenylethanol **(2)**   2-methoxy-1-phenylethanol **(3)**
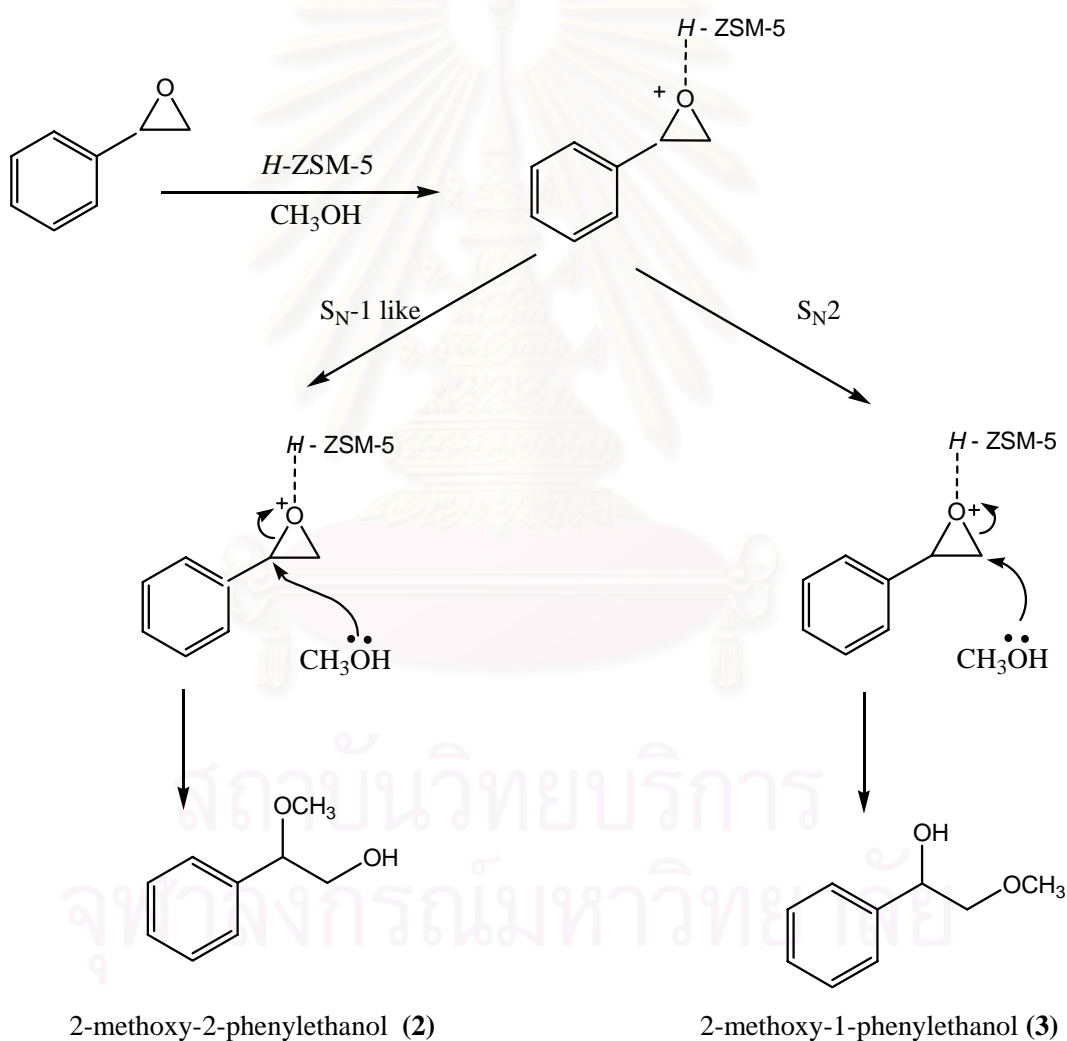
Scheme 4.1 The proposed mechanism of styrene oxide ring opening by *H*-ZSM-5 catalyst.
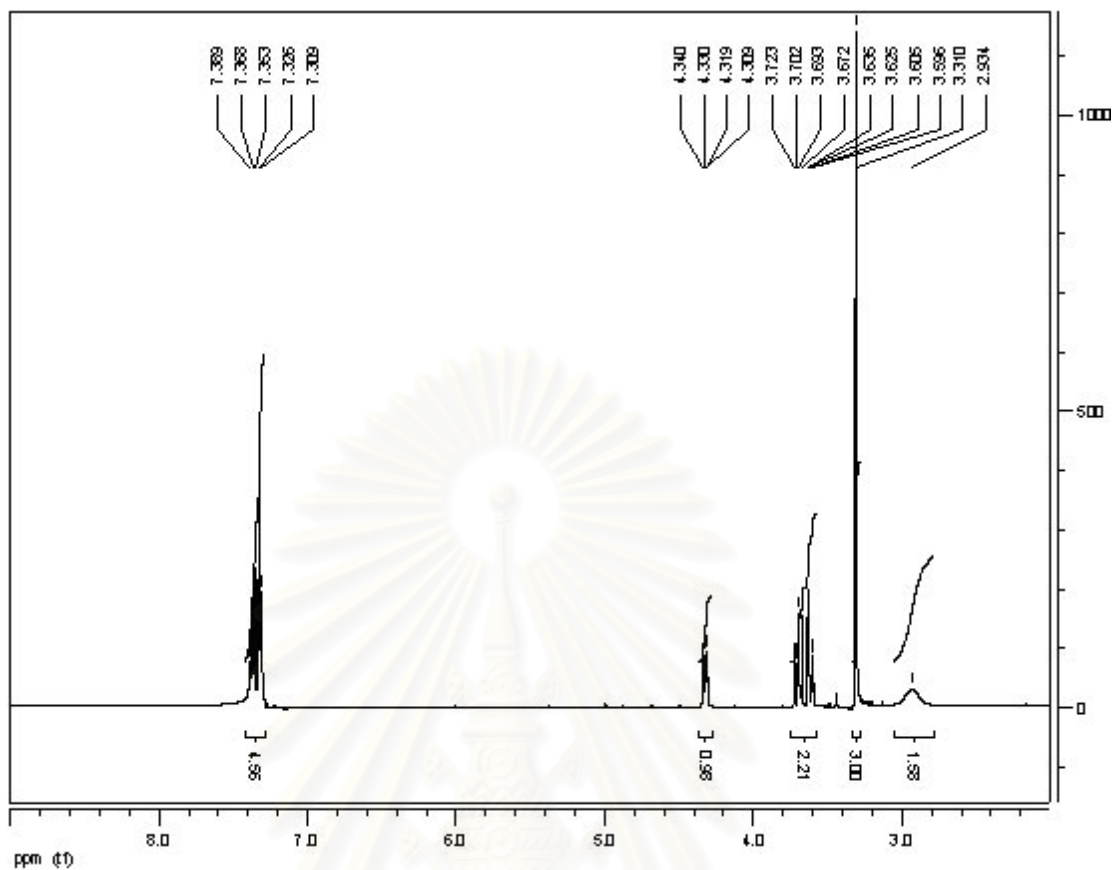
Figure 4.6 ¹H-NMR spectrum of 2-methoxy-2-phenylethanol **(2)**.
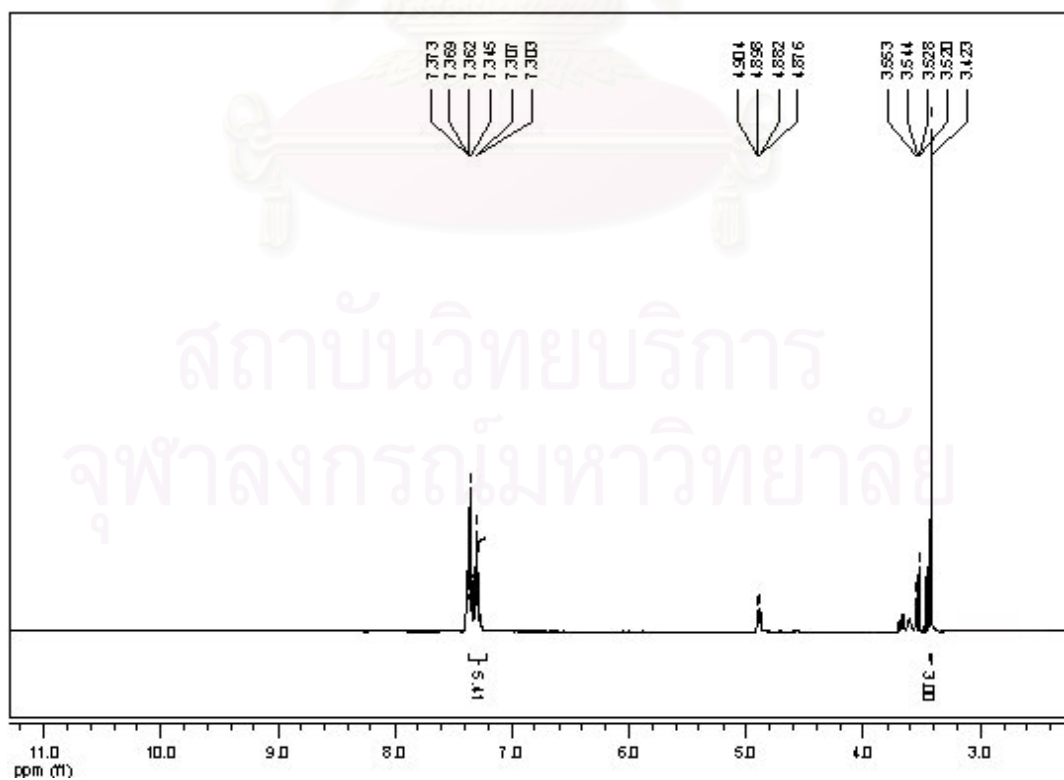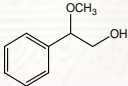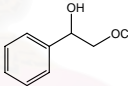
Figure 4.7 ¹H-NMR spectrum of 2-methoxy-1-phenylethanol **(3)**.

The mixture of products was evaporated in vacuum system and the residue was separated by siliga gel column chromatography eluting with hexane and ethyl acetate. All products were characterized by ^{1}H-NMR analysis. The ^{1}H-NMR spectrum of **2** as shown in Figure 4.6 reveals the peak of -C**H₂**OH as a double doublet with 1H intensity at 3.70 ppm (J = 8.50; 11.78 Hz) and a double doublet at 3.62 ppm (J = 3.73; 11.75 Hz), aromatic protons as a multiplet (5H) at 7.39-7.31 ppm, -OC**H₃** as a singlet (3H) at 3.31 ppm, -C**H**OCH₃ as a double doublet (1H) at 4.32 ppm (J = 3.68; 8.46 Hz). From the result of the ^{1}H-NMR spectrum of product **3**, as shown in Figure 4.7, it reveals the peak of –C**H**OH as a double doublet with 1H intensity, at 4.90 ppm (J=8.70; 2.46 Hz), -C**H₂**OCH₃ as a double doublet with 2H intensity at 3.55 ppm (J = 9.94; 3.20 Hz), aromatic protons as a multiplet (5H) at 7.37-7.30 ppm, -OCH₃ as a singlet (3H) at 3.42 ppm.

Table 4.4 Effect of catalyst loading on styrene oxide ring opening catalyzed by ZSM-5 at Si/Al molar ratio of 22

| Entry | Catalyst ZSM-5 (%wt of substrate) | S.O (1) (recovered) (%) | %Yield (based on substrate) | | | | Select-ivity (2)/(3) |
			Product (2)	Product (3)	Product (2) + (3)	Mass balance	
1	0	104.20	0	0	0	104.20	-
2	50	13.51	76.52	5.08	81.60	95.11	15
3	75	7.34	80.30	6.21	86.51	93.84	13
4	100	12.84	82.91	7.35	90.26	103.11	11
5	150	8.67	78.32	10.51	88.83	97.50	7

Reaction condition : styrene oxide (S.O) 1 mmole , methanol 3 mL, 70 ^{o}C, 3 h.
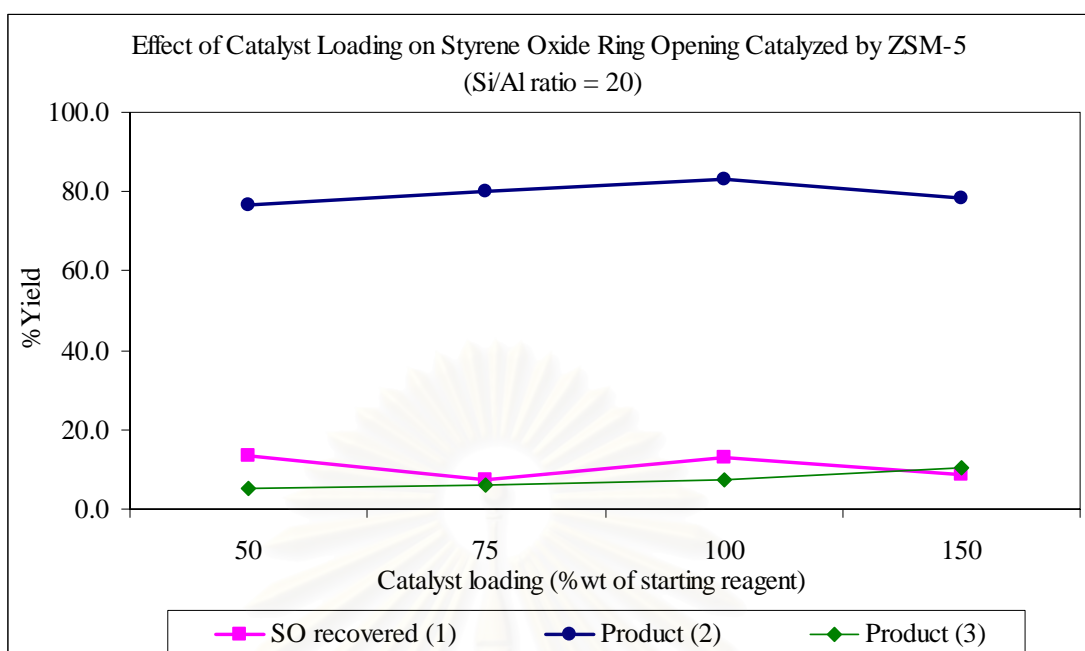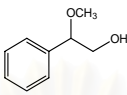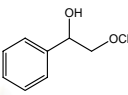
Figure 4.8 Effect of catalyst loading on styrene oxide ring opening catalyzed by
ZSM-5 at Si/Al molar ratio of 22.

From Table 4.4, the blank experiment clearly reveals that the catalysis of styrene oxide ring opening without using ZSM-5 catalyst, did not occur. The effect of ZSM-5 catalyst loading in the range of 50-150%wt of starting reagent was not clearly seen the major difference in terms of the yield of products and the styrene oxide conversion in a range of 80-90%. In terms of product selectivity, product (**3**) was promoted as increasing the amount of catalyst in reaction. This might be due to the increased acid site of catalyst, which corresponds to the catalyst loading.

4.2.2 Effect of time

The styrene oxide ring opening was carried out according to the general procedure as mentioned earlier by using *H*-ZSM-5. In order to investigate the effect of reaction time, the time was varied as 30 min, 1, 3, 5 and 12 h, respectively. The results are presented in Table 4.5.

Table 4.5 Effect of reaction time on styrene oxide ring opening catalyzed by ZSM-5 at Si/Al molar ratio of 22

Entry	Reaction time (h)	S.O. (1) (recovered) (%)	%Yield (based on substrate)				Selecti-vity
			Product (2)	Product (3)	Product (2) + (3)	Mass Balance	
1	0.5	45.73	51.49	1.82	53.31	99.04	28
2	1	31.53	68.53	2.96	71.49	103.02	23
3	3	12.84	82.91	7.35	90.26	103.11	11
4	5	3.30	83.88	10.51	94.39	97.70	8
5	12	2.67	86.81	10.44	97.25	99.93	8

Reaction condition : styrene oxide (S.O.) 1 mmole, methanol 3 mL, *H*-ZSM-5

(Si/Al =20) 100%wt of substrate, temp. 70°C, time 3 h.
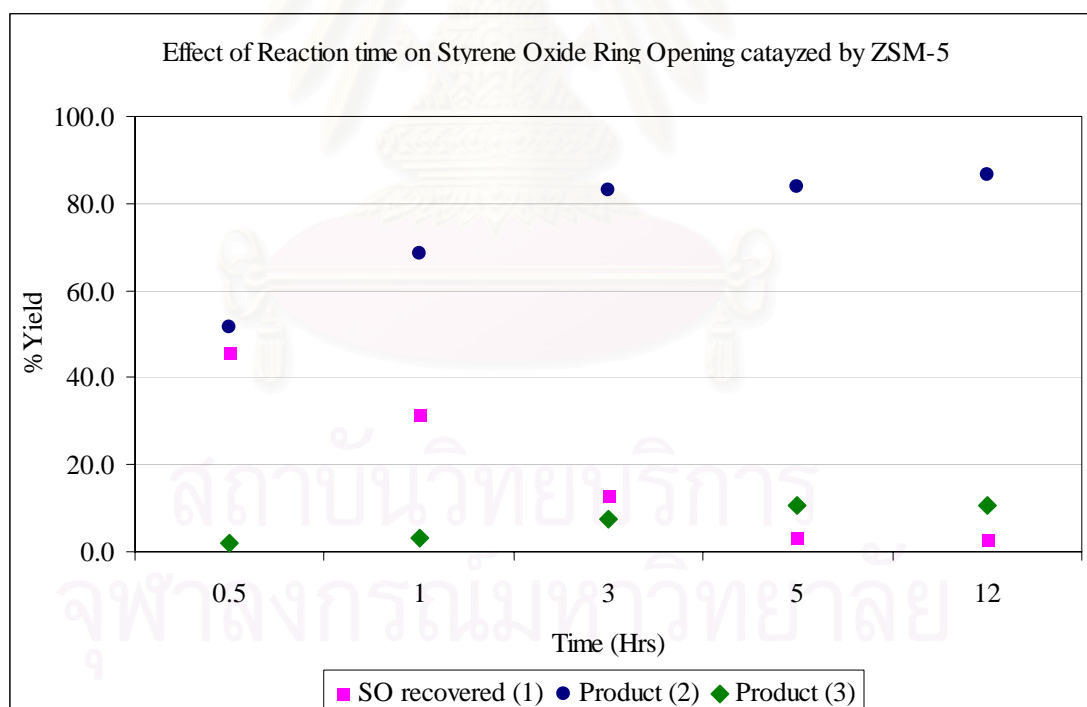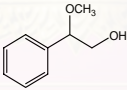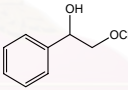
Figure 4.9 Effect of reaction time on styrene oxide ring opening catalyzed by ZSM-5 at Si/Al molar ratio of 22.

As noticed from Table 4.5 and Figure 4.9, it was clearly seen that the reaction time affected the increased yield of the desired product. The optimum reaction time was found to be 3 h at 70 ^{o}C, since no significant change in the yield of products was observed. In term of product selectivity, product (**3**) was promoted as increasing the reaction time. This might be due to the diffusion of product (**3**) from cavity increased with increasing the reaction time.

4.2.3 Effect of Temperature

The styrene oxide ring opening reaction was carried out over *H*-ZSM-5 catalyst according to the general procedure as mentioned earlier and the effect of reaction temperature was studied at 30 ^{o}C and 70 ^{o}C. The results are presented in Table 4.6.

Table 4.6 Effect of temperature on styrene oxide ring opening catalyzed by ZSM-5 at Si/Al ratios of 9, 22 and 36

ZSM-5 Si/Al ratio	Temp (^{o}C)	S.O (1) (recovered) (%)	%Yield (based on substrate)				Selecti-vity (2)/(3)
			Product (2)	Product (3)	Product (2) + (3)	Mass Balance	
9	30	26.78	70.31	-	70.31	97.10	-
	70	15.16	78.01	5.91	83.92	99.08	13
22	30	38.13	61.79	-	61.79	99.92	-
	70	12.84	82.91	7.35	90.26	103.11	11
36	30	41.37	51.67	-	51.67	93.04	-
	70	9.98	84.66	2.11	86.77	96.75	40

Reaction condition: styrene oxide 1 mmole, methanol 3 mL , ZSM-5 catalyst 100% wt of substrate, 3 h.

As shown in Table 4.6, the effect of reaction temperature on styrene oxide ring opening catalyzed by *H*-ZSM-5 (Si/Al ratios of 9, 22 and 36) was clearly seen that the increasing of reaction temperature from room temperature (30°C) to reflux temperature of methanol was affected the increment of desired product yield when compared with the same catalyst. [In the study of styrene oxide ring opening catalysis
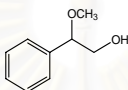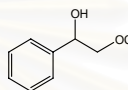
over *H*-ZSM-5 catalyst under room temperature at three different Si/Al ratios of 9, 22 and 36. In this present study, the result show that the product yield increased in the following order: Si/Al ratios of 9 > 22 > 36. This might be due to the fact that, ZSM-5 with high Al content contains the number of acid site as active site higher than ZSM-5 with low Al content; therefore, allowing the higher values of %yield of product. In contrast, at the high reaction temperature of 70°C, the result shows no significant change in product yield. It implies that the amount of acid site may not strongly affect the reaction activity, since there may have some other factors to accelerate the reaction. The additional heat energy should be an important factor to help the reaction occurring easier in case of high reaction temperature. As a result, the reaction under high temperature condition may not require the high number of acid site inside the catalyst. Moreover, the different values of obtained product **2** + **3** yield between the reaction temperature of 30 °C and 70 °C might result from the change of kinetic pore diameter of catalyst. Pore diameter generally increases along with the reaction temperature is increased. This result of changing indicates the shape of reactant molecule that entry to catalyst cavity and the shape of product molecule that diffuses from cavity.

In addition to the previous works, Jetipattaranat and Moghadam [4,15] have reported that styrene oxide ring opening could be catalyzed by Lewis acidic metal complexes such as $Fe(TCA)_3.1.5H_2O$ and $Sn^{IV}(tpp)(OTf)_2$ in homogeneous catalysis. systems under ambient conditions. Product **2** is also attained with the product yield of more than 90%. Moreover, Jetipattaranat [4] has reported that styrene oxide ring opening could be catalyzed by Lewis acid such as Cr(salen)Cl, the reaction proceeded at 70 °C for 2-4 h to yield product **2** more than 80%. Nevertheless, there were some advantages of heterogeneous catalysis of epoxide ring opening which could overcome these homogeneous reactions including: reusable of catalyst, non-toxic and easy to separate from product mixture, as previously mentioned.

4.2.4 Effect of Si/Al mole ratio of *H*-ZSM-5

The styrene oxide ring opening was carried out according to the general procedure as mentioned earlier by using *H*-ZSM-5 with various Si/Al mole ratios of 9, 22 and 36. The results are addressed in Table 4.7.

Table 4.7 Effect of Si/Al mole ratio of *H*-ZSM-5 on styrene oxide ring opening

Entry	ZSM-5 Si/Al ratio	S.O (1) (recovered) (%)	%Yield (based on substrate)				Selecti-vity (2)/(3)
			Product (2)	Product (3)	Product (2) + (3)	Mass Balance	
1	9	15.16	78.01	5.91	83.92	99.08	13
2	22	12.84	82.91	7.35	90.26	103.11	11
3	36	7.65	89.84	1.87	91.71	99.36	48

Reaction condition : styrene oxide 1 mmole, methanol 3 mL, ZSM-5 0.12 g, 70 $^{\circ}$C, 3 h.

The results are shown in Table 4.7, the increasing of Si/Al ratio of *H*-ZSM-5 was affected the increased styrene oxide conversion and the increased yield of the desired products **2** and **3** in the range of 83.92 to 91.71%. In order to more clearly explain about the effect of Si/Al mole ratio at the reaction temperature of 70 $^{\circ}$C, the above table shows the comparative result of various Si/Al ratios. As already mentioned earlier, the result of product yield shows no significant change with increasing the Si/Al ratio. However, the yield of product **2** slightly increased with increasing the Si/Al molar ratio. ZSM-5 at Si/Al = 36 gives the highest yield of product **2** at the value of 89.84%, resulting from the effect of smaller particle and higher surface area of the catalyst at this mole ratio (Tables 4.2 and 4.3).

4.3 Other epoxides ring opening catalyzed by ZSM-5

The optimum condition for styrene oxide ring opening using ZSM-5 catalyst was applied to other epoxide substrates such as 1-dodecene oxide and cyclohexene oxide, in order to extend the scope of utilizing ZSM-5 catalyst in epoxide ring opening.

4.3.1 Ring opening of 1-dodecene oxide

1-Dodecene oxide was selected as a representative of terminal aliphatic epoxide. This type of epoxide was stable and not easy to be opened, as compared to other epoxides. The catalysis of 1-dodecene oxide ring opening was studied at 70 °C for 3 h catalyzed using ZSM-5 with Si/Al = 36 and the results are tabulated in Table 4.8.
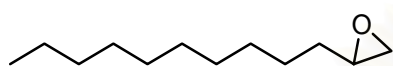
1-dodecene oxide **(4)**
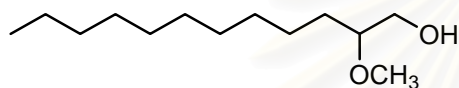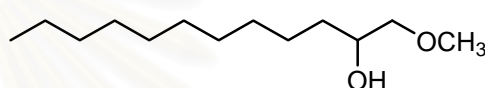
2-methoxy-1-dodecanol **(5)**   1-methoxy-2-dodecanol **(6)**

Table 4.8 1-Dodecene oxide ring opening by *H*-ZSM-5 with Si/Al ratio = 36

Entry	Catalyst	1-D.O **(4)** (recovered)	%Yield (based on substrate)				Selecti-vity **(5)/(6)**
			Product **(5)**	Product **(6)**	Product **(5) + (6)**	Mass Balance	
1	-	98.50	-	-	-	98.50	-
2	*H*-ZSM-5	11.10	58.93	34.38	93.31	104.90	2

Reaction condition: 1-dodecene oxide 1 mmole, methanol 3 mL, *H*-ZSM-5 (Si/Al = 36), 100% wt of substrate, 70 °C, 3 h.

Figure 4.10 ¹H- NMR spectrum of 2-methoxy-1-dodecanol **(5)**.

Figure 4.11 ¹H- NMR spectrum of 1-methoxy-2-dodecanol **(6)**.

From the outcome of reaction, the mechanism of 1-dodecene oxide ring opening could be taken place *via* S_N-1 like and S_N2, as shown in Scheme 4.2.

The mechanism of 1-dodecene oxide ring opening could be taken place by the proton of *H*-ZSM-5 forming a coordination bond with the oxygen of epoxide ring and the induction of the partial positive charge at carbon atom of epoxide ring. After that, C-O bond was broken in the way to form the stable carbocation, as well as nucleophile could be possible to attack the carbocation on either sites. The catalysis result shows that the selectivity of product **5** around 63%. It can be implied that, in case of epoxide ring with straight-chain of hydrocarbon, the stability of 2° carbocation is somewhat more stable than 1° carbocation, so the pathway of reaction is slightly S_N-1 like preferable.
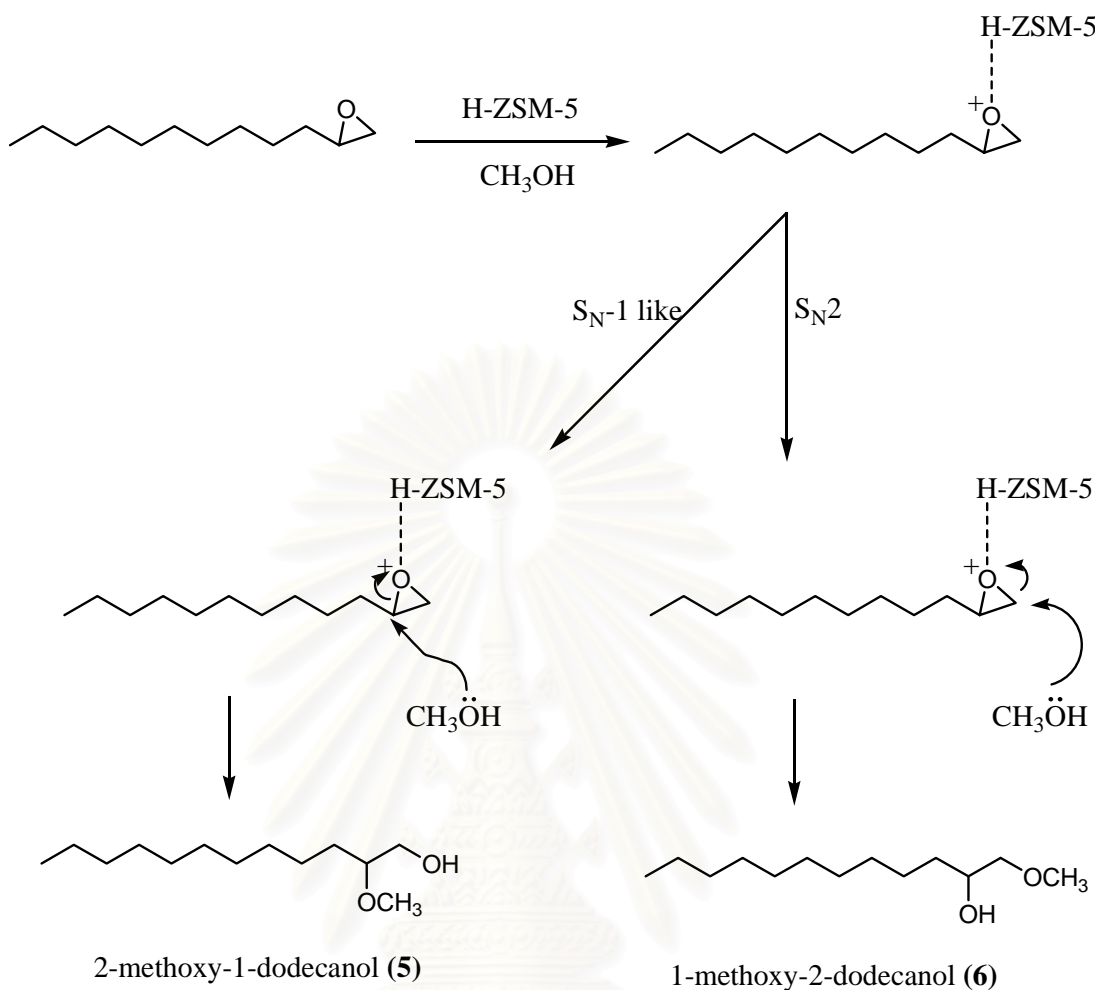
Scheme 4.2 The proposed mechanism of 1-dodecene oxide ring opening by ZSM-5
catalyst.

The mixture of products was evaporated in vacuum system and the residue was separated by siliga gel column chromatography eluting with hexane: ethyl acetate (9:1). All products were characterized by ^{1}H-NMR in CDCl$_3$. The structure of obtained product **5** was characterized by ^{1}H-NMR spectrum as shown in Figure 4.10. The protons were detected at 3.67 (1H, dd, J = 3.28, 11.54 Hz), 3.47 (1H, dd, J = 6.48, 11.47 Hz), 3.40 (3H, s), 3.28-3.23 (1H, m), 1.62 – 1.50 (2H, m), 1.28 (16H, br), 0.87 (3H, t, J = 6.19). The structure of obtained product **6** was characterized by ^{1}H-NMR spectrum as shown in Figure 4.11. The protons were detected at 3.80-3.74 (1H, m), 3.41 (1H, d, J = 2.91), 3.38 (3H, s), 3.23 (1H, t, J = 8.12), 1.43-1.39 (2H, m), 1.25 (16H, br), 0.87 (3H, t, J = 6.57).

4.3.2 Ring opening of cyclohexene oxide

Cyclohexene oxide was selected as a representative of cyclic epoxide. The catalysis of cyclohexene oxide ring opening was studied at 70 $^{\circ}$C for 3 h by using ZSM-5 catalyst with Si/Al = 50.

Table 4.9 Cyclohexene oxide ring opening reaction by *H*-ZSM-5 with Si/Al ratio = 36

Entry	Catalyst	%Yield (based on substrate)		
		C.O (7) (recovered)	Product (8)	Mass balance
1	0	101.53	-	101.53
2	*H*-ZSM-5 (Si/Al=50)	-	99.65	99.65

Reaction condition: cyclohexene oxide 1 mmole, methanol 3 mL, *H*-ZSM-5

(Si/Al = 36), 100% wt of substrate, 70 $^{\circ}$C, 3 h.

Cyclohexene oxide (**7**)   2-methoxy-cyclohexanol (**8**)
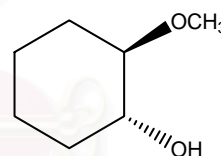
The result shows that the cyclohexene oxide ring opening could be taken place when the reaction was proceeded over ZSM-5 catalysis system with obtained *trans*-2-methoxycyclohexanol almost 100%.

The mechanism of cyclohexene oxide ring opening could be taken place when epoxide ring was protonated by proton supplied from *H*-ZSM-5 and further induced the partial positive charge at the position of carbon atom of epoxide ring. Then, nucleophilic alcohol could attack the carbocation to form the product **8**.

The mixture of products was purified by siliga gel column chromatography eluting with hexane:ethyl acetate (6:4). The product was characterized by ^{1}H-NMR in CDCl$_3$. The structure of obtained product **8** was characterized by ^{1}H-NMR spectrum, as can be seen in Figure 4.12. The protons were detected at 3.37 (3H,s), 2.96-2.90 (2H, m), 2.12-2.09 (2H, m), 2.01-1.96 (2H, m) and 1.73-1.67 (4H, m).
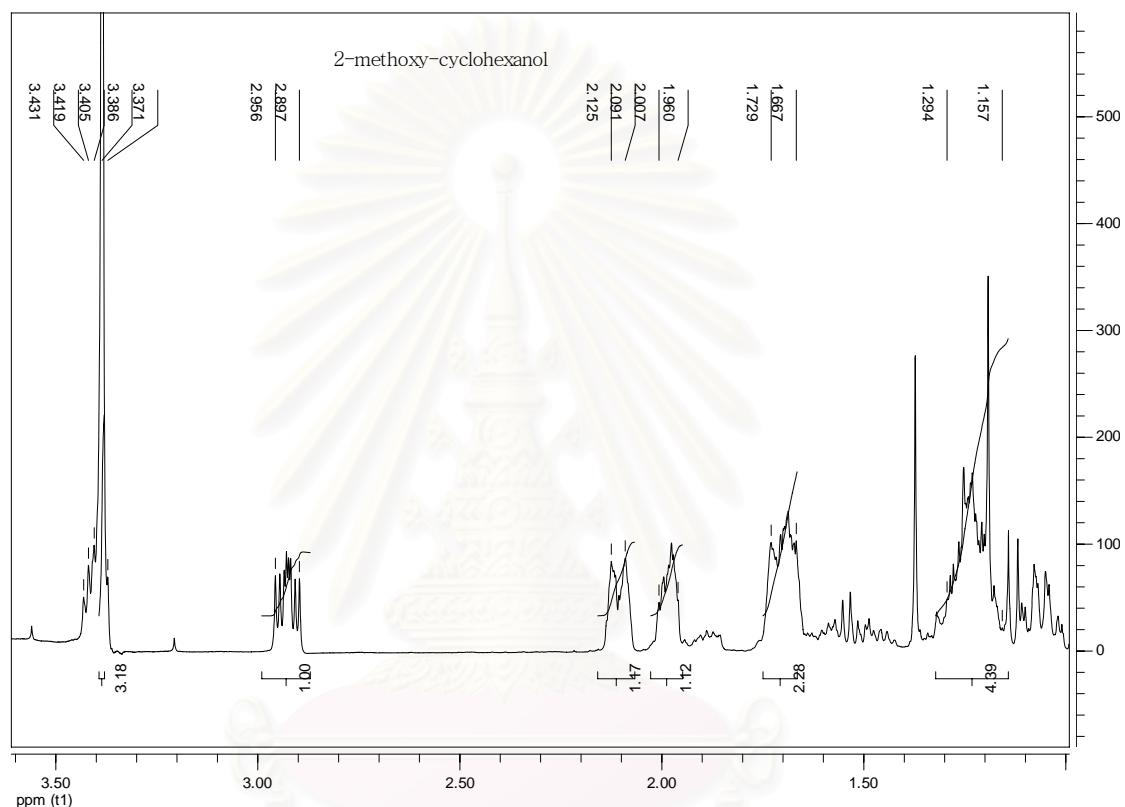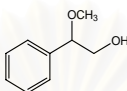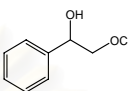
Figure 4.12 ^{1}H- NMR spectrum of 2-methoxycyclohexanol (**8**).

4.4 Study of ZSM-5 reused catalyst on epoxide ring opening

The reused catalyst of ZSM-5 with Si/Al ratio = 36 was chosen to study the catalysis of epoxide ring opening in order to evaluate the efficiency of recycling catalyst. After separated the products from catalyst by filtration through syringe and rinsed with diethyl ether, the separated catalyst was reused for the next experimental run. Firstly, the reused catalyst was washed by acetone. Secondly, the dried catalyst powder was calcined in the maffle furnace under the controllable temperature program from room temperature to 540 $^{\circ}$C for 5 h in order to remove organic

substances and other contaminants from catalyst. The results are accumulated as presented in Table. 4.10.

Table 4.10 Result of epoxide ring opening using reused ZSM-5 catalysts

Entry	ZSM-5 Si/Al ratio	S.O (1) (recovered) (%)	%Yield (based on substrate)				Selecti-vity (2)/(3)
			Product **(2)**	Product **(3)**	Product **(2) + (3)**	Mass Balance	
1	fresh catalyst	7.65	89.84	1.87	91.71	99.36	48
2	reused #1	9.96	90.51	1.31	91.82	101.78	69
3	reused #2	7.76	88.39	0.89	89.29	97.05	99
4	reused #3	15.96	81.13	0.46	81.59	97.55	176

Reaction condition: styrene oxide 1 mmole, MeOH 3 mL, ZSM-5 (Si/Al ratio=36) 0.12 g, 70°C, 3 h.

As shown in Table 4.10, the efficiency of reused catalysts for styrene oxide ring opening after four runs reveals that, the yield of corresponding product **2** was still very high. This result firmly indicates that the reused catalysts exhibit a high efficiency for the reaction of epoxide ring opening. Additionally, the product yield seems slightly decrease after 2 runs of reused catalysts. The selectivity of product **2** decreased when the number of cycle for reused catalyst is increased. From this result, it might be explained that there are some coke and other contaminants occurring on the surface of the active site of catalyst. Additionally, the selectivity of product **2/3** increased when the number of cycle for reused catalyst is increased. The tetrahedral aluminum species in cavity of catalyst might be a possible cause to play the important role as active site more than the one in external surface area. Also, it should be noted that the color change of catalyst was observed from white to orange color, after testing of cycle no.3.

CHAPTER V

CONCLUSION

A series of *H*-ZSM-5 zeolites with Si/Al ratios in a range of 10-50 were tested in the epoxide ring opening catalysis. All ZSM-5 catalysts were synthesized by hydrothermal method and they were characterized by XRD, SEM/EDX, ^{27}Al MAS NMR and nitrogen adsorption (BET), to link catalyst properties to catalytic behavior.

The catalysis of epoxide ring opening was carried out in the heterogeneous system. In this study, styrene oxide is used as a model substrate, methanol as solvent and nucleophile, *H*-ZSM-5 at Si/Al mole ratio = 36 as a catalyst. The optimum condition was found at 70 ^{o}C for 3 h with the high selectivity of 2-methoxy-2-phenylethanol. Moreover, the result shows that the amount of catalyst loading had no significant effect on the reaction activity. With increasing the reaction time and Si/Al ratio, the yield of desired product increased. In addition to the effect of temperature, the desirable product yield gave the high value at the higher temperature, as compared with the same Si/Al ratio. Besides that, at the reaction under room temperature, the amount of acid site is the dominant effect to reaction activity. Meanwhile, at the high temperature of 70 ^{o}C, the amount of acid site may not strongly affect the reaction activity, but the heat energy may be the dominant factor over the number of acid site. Higher value of Si/Al ratio in zeolite catalyst performed higher yield of desired product. The product of 2-methoxy-2-phenylethanol reached for the good yield approximately 80 - 90%, with high selectivity.

The mechanism of epoxide ring opening catalyzed by ZSM-5 was taken place *via* S_N-1 like or S_N2 reaction. The nucleophilic alcohol addition to epoxides occur via a two-step reaction. First of all, the epoxide is activated by acid catalyst. Then, the activated (protonated) epoxide undergoes in classical mechanism of S_N-1 like more than S_N2.

The optimum condition was further applied for other epoxides, 1-dodecene oxide and cyclohexene oxide. The catalysis of epoxide ring opening by ZSM-5 catalyst could be proceed and gave high yield ring opening products.

The reused catalyst has a high efficiency for the reaction of epoxide ring opening, the yield of desired product, 2-methoxy-2-phenylethanol was very high after testing with reused catalyst for four cycles and selective formation of 2-methoxy-2-phenylethanol on ZSM-5 has been observed.

Suggestion for the future work:

To study the catalytic of epoxide ring opening by using the different metal modified ZSM-5 in order to investigate the influence of acidity strength.

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