

**THE PRODUCTION OF GASOLINE AND AROMATICS
FROM ETHANOL**

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หัวข้อวิทยานิพนธ์	การผลิตน้ำมันเชื้อเพลิงและสารอะโรมาติกส์จากเอทานอล
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บทคัดย่อ

วิทยานิพนธ์นี้เป็นการศึกษาการผลิตน้ำมันเชื้อเพลิงและสารอะโรมาติกส์จากเอทานอล โดยใช้ตัวเร่งปฏิกิริยาซีโอไลต์ชนิด ZSM5 ที่ได้รับการปรับปรุงโดยการเติมแต่ง แพลทินัม แกลเลียม และเงิน การเร่งปฏิกิริยาคำนึงการที่ความดันบรรยากาศในถังปฏิกรณ์แบบเบดคงที่ อิทธิพลของสภาวะที่ใช้ในการทำปฏิกิริยา เช่น ความเร็วสเปส (1.73-5.76 ต่อชั่วโมง) อุณหภูมิ (350-525 องศาเซลเซียส) และองค์ประกอบของสารป้อน (น้ำ เอทานอล และเอททิลีน) ทดสอบได้ในระยะเวลา 6 ชั่วโมง ผลึกภัณฑ์ที่เกิดขึ้นสามารถเก็บเป็นช่วงและนำไปวิเคราะห์ด้วยเทคนิคก๊าซโครมาโทกราฟี

จากการทดลองพบว่าเมื่อเวลาที่สัมผัสตัวเร่งปฏิกิริยาเพิ่มขึ้นจะเกิดผลิตภัณฑ์ที่มีน้ำหนักโมเลกุลสูงขึ้น แต่เมื่อเวลาที่สัมผัสตัวเร่งปฏิกิริยาลดลงจะได้ผลิตภัณฑ์ส่วนใหญ่เป็นก๊าซ ที่อุณหภูมิ 350-375 องศาเซลเซียส ไฮโดรคาร์บอนสามารถเกิดปฏิกิริยาโอลิโกเมโรเซชันและไอโซเมโรเซชันให้ผลิตภัณฑ์ที่เหมาะสมสำหรับใช้เป็นน้ำมัน ในขณะที่อุณหภูมิ 400-450 องศาเซลเซียส จะได้สารอะโรมาติกส์เป็นผลิตภัณฑ์หลัก ในกรณีที่ใช้อเอทานอลเป็นสารป้อนที่อุณหภูมิ 425 องศาเซลเซียสตัวเร่งปฏิกิริยาชนิด HZSM5 AgHZSM5 และ [Ga]HZSM5 จะให้อะโรมาติกส์ 7.55 9.83 และ 6.59 เปอร์เซ็นต์โมลตามลำดับ เมื่อเติมน้ำเป็นสารป้อนร่วมในปฏิกิริยาที่ใช้ 95 เปอร์เซ็นต์ของเอทานอลเป็นสารป้อนจะทำให้ปริมาณอะโรมาติกส์ลดลงโดย HZSM5 และ AgHZSM5 จะให้สารอะโรมาติกส์ 4.30 และ 7.31 เปอร์เซ็นต์โมลตามลำดับ ขณะที่ [Ga]HZSM5 ให้ปริมาณอะโรมาติกส์เพิ่มขึ้นเป็น 8.16 เปอร์เซ็นต์โมล สันนิษฐานว่าตำแหน่งกรดจะเพิ่มขึ้นจากอันตรกิริยาของแกลเลียมกับน้ำ ในกรณีที่ใช้อเอทานอลเป็นสารป้อนเมื่อใช้ตัวเร่งปฏิกิริยาดังกล่าว อะโรมาติกส์จะถูกผลิตขึ้นโดยปฏิกิริยาฟอรัมมิงของผลิตภัณฑ์ซึ่งเกิดจากปฏิกิริยาโอลิโกเมโรเซชัน อย่างไรก็ตามมีความแตกต่างกันในประสิทธิภาพการเร่งปฏิกิริยาของ [Ga]HZSM5 เมื่อใช้อเอททิลีนเป็นสารป้อนโดยอะโรมาติกส์จะถูกผลิตขึ้นจากปฏิกิริยาอะโรมาไทเซชันของโอเลฟินส์ขนาดเล็ก นอกจากนั้นพบว่าซีโอไลต์ [Pt]HZSM5 จะขัดขวางปฏิกิริยาโอลิโกเมโรเซชันของเอททิลีน ในขณะที่ซีโอไลต์ที่ได้รับการเติมแต่งด้วยวิธีการฝังตัวของเงิน ([Ag]HZSM5) มีความสามารถในการผลิตอะโรมาติกส์ต่ำกว่า

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ABSTRACT

In this thesis the production of gasoline and aromatics from ethanol over modified zeolites was studied. Catalysts were prepared by incorporation of platinum, gallium, and silver into ZSM5 zeolite. Catalytic reactions were carried out at atmospheric pressure in a fixed bed flow reactor. The influence of reaction conditions, such as weight hourly space velocity (1.73-5.76 hr⁻¹), temperature (350-525 °C), and feed composition (water, ethanol, and ethylene) were investigated. The reaction was tested for 6 hours on stream and the gas products were periodically collected and analyzed by Gas Chromatography (GC).

The experiments show that higher contact time results in a higher selectivity for high molecular weight hydrocarbons, whereas at lower contact time the gas products become predominant. At temperature 350-375 °C, hydrocarbons can undergo oligomerization and isomerization to give high quality gasoline, while at higher reaction temperature 400-450 °C, higher hydrocarbons shift toward the aromatic fraction. In the reaction using ethanol as feed, aromatic yields of 7.55, 9.83, and 6.59 % mole were obtained at 425 °C over HZSM5, AgHZSM5, and [Ga]HZSM5, respectively. Addition of water as co-feed in the reaction using 95 wt% ethanol, decreases aromatic yields to 4.30, and 7.31 % mole over HZSM5 and AgHZSM5, respectively. However, the enhanced activity of [Ga]HZSM5 can be obtained, yielding 8.16 % mole of aromatic, due to the additional acid sites which are largely produced by an interaction of gallium extra-framework with water. In ethanol conversion over these catalyst, aromatic is namely produced by reforming of the oligomerized hydrocarbons. However, in the reaction using ethylene, aromatic can be produced from small olefin aromatization over [Ga]HZSM5. On the other hand, [Pt]HZSM5 is found to inhibit the rate of ethylene oligomerization, while silver impregnated HZSM5 ([Ag]HZSM5) shows relatively low activity for the aromatic production.

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Finally, the author dedicates this thesis to His Majesty the King for Royal Opinion to make him think about the good of the community.

Artit Ausavasukhi

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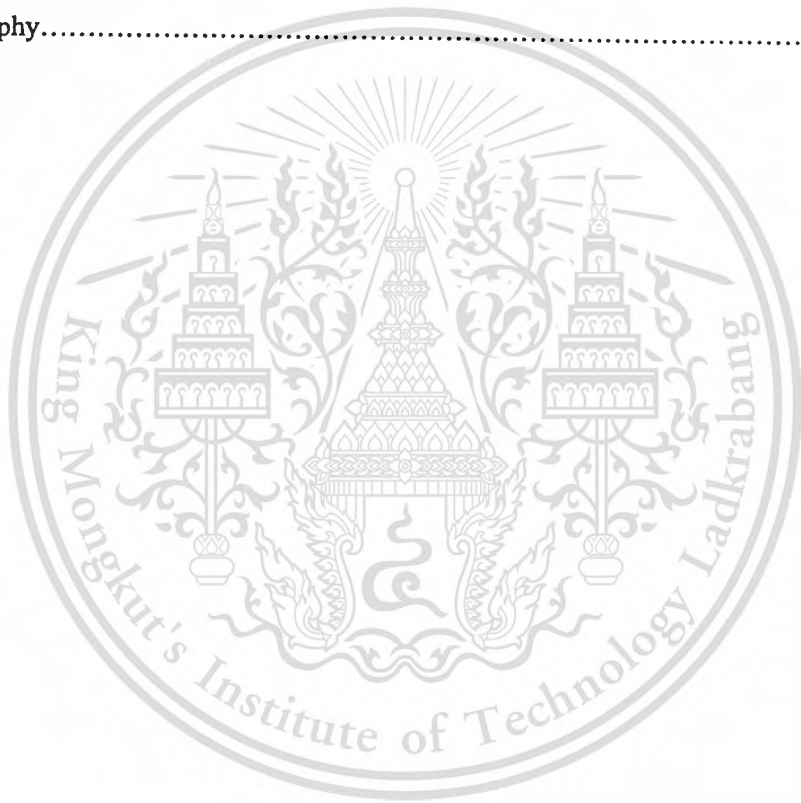
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Chapter 1

Introduction

"I have often said to such audience as this one that to be a tiger is not important. The importance for us is to have a self-supporting economy. A self-supporting economy means to have enough to survive [1]." (His Majesty King Bhumibol Adulyadej)

This royal speech made me think about the rectification of Thailand development. Our country is rich in natural resources and we have been designated to become an economic power. Development of renewable sources of energy from biomass has the advantage of promoting agro-industrial linkage. The production of fuel and petrochemicals from agro-products is one of the alternative ways of fostering the development of liquid energy and petrochemical for the agricultural countries. Therefore, the research on "The Production of Gasoline and Aromatics from Ethanol " is recommended for self-supporting development.

1.1 Statement and significance of the problems

Effective utilization of the material resources and available energy is one of the vital goals of modern catalytic research. At present most of our energy needs and petrochemicals are met by fossil fuels. It is better if all the requirements of chemical industry and portions of other needs can be shared by agricultural products. One of the alternatives is the conversion of ethanol, produced by fermentation of agricultural products, to gasoline and aromatics over zeolite catalyst. This is considerable for an agricultural country, like Thailand. Moreover, it can increase the value of agricultural products and help reducing petroleum import.

1.2 Goal and objectives

The specific objectives of the study are as follows:

- 1.2.1 To obtain the appropriate reaction condition which allows high gasoline and aromatic yields.
- 1.2.2 To investigate the modified zeolite which allows high selectivity of aromatics.

- 1.2.3 To understand the effect of water content in ethanol and obtain the optimum water concentration for low value of raw materials.
- 1.2.4 To apply the cleaner technology for converting agro-products into liquid energy and petrochemical feedstocks.

1.3 Scope of the study

- 1.3.1 Synthesis and modification of ZSM5 zeolite.
- 1.3.2 Characterization of the zeolites.
- 1.3.3 Investigation of appropriate reaction conditions for high aromatic yields.
- 1.3.4 Investigation of the effect of water content in ethanol.
- 1.3.5 Analysis of the amounts of gasoline and aromatics.

1.4 Expected results

- 1.4.1 This research would provide the appropriate catalyst for producing high aromatic yields for ethanol and aqueous ethanol conversion.
- 1.4.2 This research would lead to understanding in the activity of metal species, namely platinum, gallium, and silver incorporated with ZSM5 for ethylene and ethanol conversion.
- 1.4.3 This research would provide not only a potential to develop a technology for producing gasoline and aromatics from ethanol, but also a guide for converting agricultural product to high value product.
- 1.4.4 This research would provide appropriate policies on conservation of petroleum resources through a greater economy and efficiency in its utilization and distribution.

Chapter 2

Literature review

In recent years, development of renewable sources of energy and petrochemicals have been given to the conversion of biomass. Biomass offers the potential to replace the reducing reserves of non-renewable fossil fuels with fuels derived from agricultural products [2]. Moreover, biomass offers significant promise as an alternative power source to increase energy efficiency, reduce pollution, and minimize our dependence on imported oil [3].

2.1 Ethanol

2.1.1 Ethanol production

Ethanol is produced from the fermentation of organic matter in anoxic environments expected to rapidly biodegrade in essentially all environments with conditions that support microbial activity. In most of the fermentation, ethanol is made from corn, however, it can be made from a variety of agricultural products such as other grains, sugar cane and beets, fruit, and whey. Moreover, studies are under way to ferment garbage to ethanol [4]. Many sorts of raw materials used in the ethanol production are conveniently classified under three types of agricultural raw materials; sugar, starches, and cellulose materials. Sugars (from sugar cane, sugar beets, molasses, or fruit) can be converted to ethanol directly. However, starches (from grains, potatoes, or root crops) must first be hydrolyzed to fermentable sugars by the action of enzymes from malt or molds. While, cellulose (from wood, agricultural residues, or waste sulfite liquor from pulp and paper mills) must likewise be converted to sugars, generally by the action of mineral acids. Once simple sugars are formed, enzymes from yeast can readily convert them to ethanol [2-5]. Usually the fermentation proceed until the ethanol concentration reaches about 10 %, when the activity of the yeast becomes inhibited by the alcohol.

2.1.2 Distillation and separation

The traditional method for concentrating the ethanol from the fermentation stage (~10 % ethanol in water) is distillation having two disadvantages of this. The first problem is that the ethanol-water system forms a low boiling point azeotrope of ethanol content 96% v/v or 95%

w/w. and the second problem is that the distillation process involves the provision of substantial amounts of heat [2,6].

However, the addition of a third component, termed an entrainer, can be broken the binary ethanol-water azeotrope by the formation of a lower boiling ternary azeotrope with a higher water content. Several chemicals may be used as the entrainer in this system, the most common is benzene, but also trichloroethylene, cyclohexane or gasoline itself. Alternatively, the separation processes include extractive distillation, pervaporation, and adsorption (molecular sieve) can be used to separate ethanol-water mixtures [6].

2.1.3 Alcohol fuels

Since the energy crises of the seventies, utilization of biomass based ethanol gained considerable interest as fuel, viz as a fuel extender in engines, straight ethanol use in engines, fuel for rural areas and industrial fuel [3-4]. On ethanol as the fuel extender, there are two different kinds of blends, i.e. blending with gasoline and with diesel. It is a common practice to use anhydrous ethanol for blending gasoline, hydrated ethanol (95 % purity) is also used widely. The former is more expensive and needs more care in handling and storage while the latter is more corrosive to the fuel system. The alcohol-gasoline blending (10-20 % by volume of anhydrous ethanol, 99.5 % purity) shows a lower heating value due to the lower calorific value of ethanol compared to gasoline. In this case, it may give a lower power output when the engines is operated at full-load, full throttle conditions. Moreover, hard starting and engine stalling can be occurred by emulsification of alcohol and by clogging fuel line.

Application of ethanol as fuel extender to the diesel engine is rather more difficult than to the gasoline engine mainly due to poorer fuel economy and phase separation problem. Since in diesel engines fuel is ignited by compression and the cooling effect of ethanol tends to delay ignition. Generally, ethanol in the blends may attack incompatible parts of fuel system such as fuel filter elements, which causes the combustion characteristics of the fuel to change considerably. In order to avoid this problem, it would require large investments to overcome the technical problems particularly engine modification.

In the case of ethanol as straight fuel, there have been a number of studies and experiments both with spark-ignition and diesel engines. The modification in gasoline engines coupled with proper ignition timing arrangement, has resulted in considerable improvement in fuel economy and ethanol cars consume about 20 % by volume more ethanol than the same

models powered by gasoline. In this regard, starting becomes more difficult when used in cold weather, therefore, starting-assisting system is needed. When use of ethanol as blending with diesel fuel or as straight fuel diesel engines, it should be expected that only the heat value of ethanol will be realized as fuel value. Therefore, the ethanol effectiveness is less than the cases of spark-ignition engines. For example, a diesel engine running on ethanol will to consume 1.5 times of the weight of diesel under the same loading condition.

In use of ethanol as fuel in rural areas, ethanol even of lower purity grade, can be produced from locally available biomass, by simple technology and with locally fabricated equipment. It can be used as fuel for prime-movers in many activities such as field irrigation, crop cultivation and harvest, crop handling and processing, and can also readily be used as fuel for local transportation such as motorcycles, utility trucks, boats and, etc.

There have been some studies on utilizing ethanol as industrial fuel, but so far no advantages of ethanol are found in industrial use other than as chemical feedstock. As a boiler fuel, the calorific value of ethanol is about 66% of fuel oil by weight, or 57% by volume. This application, while technically the easiest, is unlikely to prove economic for general practice in the near future. Another application that is being studied is as fuel for gas turbine engines [3-4, 7-8].

The summarizable benefits of ethanol as a renewable fuel source are :

1. Utilization of ethanol can conserve energy, particularly liquid fuels and reduce reliance on imported fossil fuel energy.
2. Biomass, waste, and agricultural feedstocks, which are the raw materials for fermentation of alcohol are worthily utilized.
3. The government can reduce financial supports to agriculture for stabilization of farm income.
4. Utilization of ethanol can support the net economic benefit of a domestic ethanol industry and create the investments in, and spin-offs from, ethanol benefit Thailand's economy directly.
5. A high-protein livestock feed ingredient can be obtained during the ethanol production from grain.
6. Ethanol possesses less toxic than methanol and gasoline and does not pose as severe a threat to the environment in the event of a spill.

However, ethanol emerged as the dominant transportation fuel has many disadvantages. The summarizable retrofits of ethanol as a renewable fuel source are :

1. Vehicles designed for conventional fuel have to be modified, because ethanol has slightly different combustion characteristics and engine parameters such as ignition timing.

2. The parts of engine which contact with ethanol have to be adjusted, because ethanol is more corrosive to metals than gasoline.
3. The problem associated with the storage and transportation of ethanol are received, because substantial quantities of water contaminated in vessels, storage tanks, ship and barges will enter into solution with the ethanol.

Therefore, the conversion of ethanol to fuel over zeolite catalyst is the new way, which not only corrects the ethanol as fuel problem, but also provides the benefits of ethanol produced by agricultural products. Moreover, catalytic conversion of ethanol produces single ring aromatics which are important petrochemical intermediates as well as valuable gasoline components. In the view of aromatic production, separation of BTX aromatics from crude oil distillates is not feasible because they are present in low concentrations. Enriching naphtha fraction with these aromatics is possible mainly through a catalytic reforming process. In addition, liquefied petroleum gas (LPG), a mixture of propane and butanes, is catalytically converted to produce aromatic-rich products. Nevertheless, these processes can raise environmental problem during raw material production [9-11]. Utilization of ethanol produced by agro-product fermentation as feedstock can be an appropriate alternative for avoiding environmental issues.

2.2 Chemical reaction of ethanol to hydrocarbons

Many problems rise when ethanol is used as fuel. An alternative process for the production of gasoline and aromatics based solely on biomass-derived ethanol feedstock is proposed. The first step in this process is ethanol dehydration to produce ethylene. Hydrous ethanol is a particularly attractive feedstock for this step since the production of anhydrous ethanol is expensive. In the next step, the light olefins react to form higher hydrocarbons and aromatics by oligomerization and aromatization, respectively [12]. From the thermochemistry of ethanol reactions, the initial step, dehydration of ethanol, is highly endothermic, and is followed by the highly exothermic oligomerization of ethylene [13]. Consecutively, hydrocarbons formed undergo a variety of acid catalyzed reactions, including double bond isomerization, skeletal isomerization, disproportionation, cracking, hydrogen transfer, and cyclization. These hydrocarbons conversion involving gaseous carbocations is well known from the field of mass spectrometry.

The conversion of either alkanes or alcohols to aromatics over HZSM5 involves, firstly the formation of alkenes, which are then subsequently converted to aromatics. Strong acid sites promote both alkane formation and higher hydrocarbon aromatization. Alkenes react much faster than alkanes and this is in keeping with the deduction that the initial alkane dehydrogenation is a slow step in the overall process [12]. The addition of metals provides additional routes for dehydrogenation of alkanes, alkenes and naphthenes, thus increasing both the overall reaction rate and also the selectivity to aromatics. In fact, dehydrogenation can also be activated by acid sites. This reaction involves hydrogen transfer, together with the formation of low molecular weight alkanes such as methane and ethane, which results in a loss of carbon feedstock. Dehydrogenation activated by metal species, however, produces hydrogen gas (which is a valuable byproduct in refineries) and hence results in a better carbon feedstock utilization.

2.3 Zeolite catalysis

Zeolite has been proved to be an efficient catalyst for the conversion of ethanol to various hydrocarbons [2, 14-15]. In zeolites, catalysis takes place preferentially within the intracrystalline voids affected by aperture size and type of pore system, through which reactants and products must diffuse. Modification techniques including ion exchange, introduction of acidic groups such as bridging $\text{Si}(\text{OH})\text{Al}$ (which impart Brønsted acidity), hydrothermal dealumination or stabilization (which produces Lewis acidity) and introduction of dispersed metal phases such as noble metals species, can markedly increase catalytic activity. The preferred zeolite of ethanol conversion are selected from a class of zeolites which is generally highly effective in alkylation, isomerization, disproportionation and other reactions involving aromatic hydrocarbons. Moreover, the selected catalyst should be able to readily induce profound transformations of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields.

2.3.1 ZSM5 zeolite[14-20]

Zeolite ZSM5 is a member of shape selective catalysts with unique channel structures. The framework of ZSM5 contains a novel configuration of linked tetrahedra shown in Figure 2.1a, consisting of eight five-membered rings. These secondary building units join through the edge to form chains as shown in Figure 2.1b.

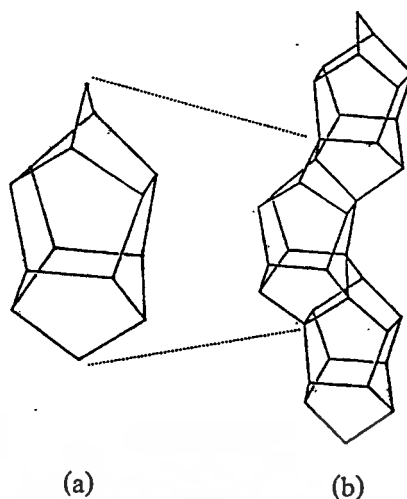


Figure 2.1 Characteristic configuration (a) and its linkage within chains (b) in ZSM5. These chains run parallel to $[001]$. Only T-atoms (Si, Al) are shown.

The chains can be connected to form sheets and the linking of the sheets lead to a three dimensional framework structure. The chains extend along the z-axis. The sheets parallel to (010) and (100) are shown in Figure 2.2 and 2.3, respectively. The ZSM5 framework can be generated by linking the sheets of Figure 2.2 across mirror planes forming five and six-membered rings.

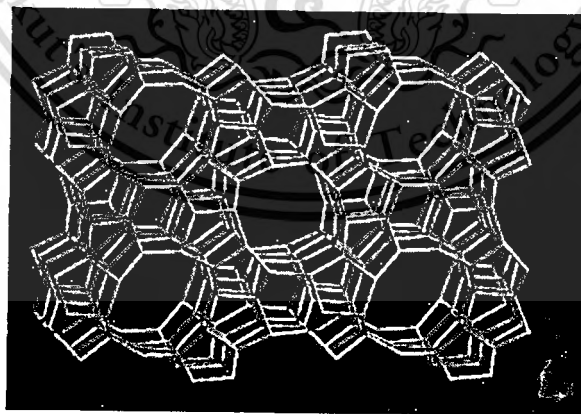


Figure 2.2 Skeletal diagram of the (010) -face of the ZSM5 unit cell. The x-axis is horizontal and the z-axis vertical. Oxygen atoms are not shown. The 10-membered ring apertures shown are the entrances to the straight channels which run parallel to $[010]$.

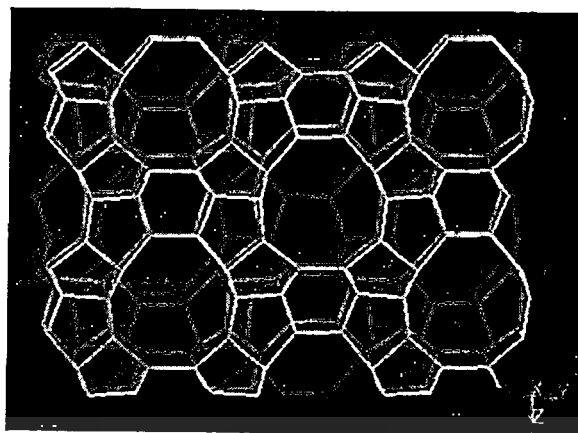


Figure 2.3 Skeletal diagram of the (100)-face of the ZSM5 unit cell. The y-axis is horizontal and the z-axis vertical. Oxygen atoms are not shown. The nearly circular 10-membered ring apertures shown are the entrances to the sinusoidal channels which run parallel to [100].

ZSM5 crystallizes in an idealized orthorhombic system with space group $Pnma$ and lattice constants $a = 20.1$, $b = 19.9$, and $c = 13.4$ angstroms; monoclinic symmetry has also been observed. The unit cell composition of the sodium form are $Na_n Al_n Si_{96-n} O_{192} \cdot \sim 16 H_2O$, where n is less than 27 and typically about 3.

According to Figure 2.2 and 2.3, the ZSM5 framework contains two types of intersecting channels: one type is straight, has elliptical (0.51 to 0.58 nm) openings and runs parallel to the b -axis of the orthorhombic unit cell, while the other has near circular (0.54 to 0.56 nm) opening, is sinusoidal (zig-zag), and directs along the a -axis as illustrated in Figure 2.4.

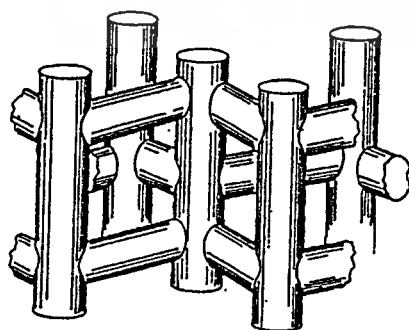


Figure 2.4 Illustration of the channel structure in ZSM5

ZSM5 are used in many catalytic reactions of industrial interest such as xylene isomerization, toluene disproportionation, benzene and toluene ethylation, and methanol-to-gasoline conversion. Their individual catalytic properties are mainly due to their regular framework with a pore size which is intermediate to the large pore sized zeolites (for instance, zeolites X and Y) and the small pore sized zeolites (for instance the A zeolites). The shape selectivity of the pentasil zeolites is catalytically expressed by many features, such as;

1. The sieving effect, i.e. the capability of the zeolite to admit into its pores or to reject reactive molecules having a critical diameter falling within a well defined range;
2. The (reverse) sieving effect, i.e. the capability of the zeolite to allow product molecules having a certain critical diameter to diffuse out of its pores. Thus, in the case of a product molecule having a diameter exceeding the pore size of the zeolite, this molecule will have to undergo additional cracking or rearrangement into a smaller molecule before diffusing out of the zeolite;
3. The effect on the reaction intermediates, i.e. the capability of certain active sites to determine the length and geometry of reaction intermediate species.

The unique catalytic properties of zeolite ZSM5 are attributed to both the three-dimensional system of intersecting channels and its strong acid sites. ZSM5 zeolite has pore system which is believed to be significant for their unusually low coke formation. These factor make it sterically difficult for the formation of large polynuclear hydrocarbons.

The acid sites in ZSM5 zeolites are mainly located at the zeolite channel intersections and originates in the Brønsted centers created by the tetrahedral aluminium sites. Moreover, Lewis acid sites are also formed by dehydroxylation of the zeolite surface by activating the zeolite at high temperature. Although HZSM5 possesses excellent dehydration and oligomerization properties, it is a poor dehydrogenation catalyst for aromatics selectivity and hence the catalyst requires modification by the addition of various promoters.

While most industrial applications of zeolite catalysts make use of these in acid form, zeolite are also excellent support for metals species. Zeolite supported metal species, a bifunctional zeolite catalyst is an acid zeolite on which a metal species phase is deposited. The function of the metal is to catalyze dehydrogenation and hydrogenation reactions. The word “metal species” is used in the non-restrictive sense to describe species in its, not yet fully understood their valency. The advantage of bifunctional catalysis over the monofunctional acid

catalysis is that the metal dehydrogenates the alkanes into alkenes which can further undergo a variety of acid catalyzed reactions to form desirable products.

2.3.2 Gallium incorporated with zeolite [21-25]

The preferred catalyst for alkane aromatization is gallium incorporated HZSM5. The incorporation of gallium can be achieved either by ion exchange or impregnation. Moreover, it can be incorporated into the zeolite structure during the zeolite synthesis. The weight of gallium incorporated is typically between 1 and 5%. In light alkane aromatization, activity is attributed to the presence of bifunctional sites, namely the non-framework gallium species and the zeolitic protons, located close to each other in the zeolite channels. A new effective aromatization process called the Cyclar process employs this catalyst to transform liquefied petroleum gas (LPG) to aromatics.

2.3.3 Silver incorporated with zeolite [22, 26-27]

Although the incorporation of zinc to HZSM5 has also been found to be very effective for light alkane aromatization, it is not a preferred catalyst for high operating temperatures since zinc oxide is slowly lost through volatilization. Silver incorporated HZSM5 catalyst is also an active catalyst for light alkane aromatization and it sharply enhances the C-H bond cleavage of starting alkane, thus, silver incorporated HZSM5 catalyst produce less methane and ethane than [Ga] or [Zn]HZSM5 which enhanced both C-H and C-C cleavage.

2.3.4 Platinum incorporated with zeolite

Platinum itself or on a variety of neutral supports can be selectively converted *n*-hexane to benzene. Considerable attention for converting higher hydrocarbons such as gasoline range to aromatics has been studied over acidic zeolite. With high metal loads, hydrogenolysis is found to be catalyzed preferentially, whereas a high concentration of acid sites enhances cracking.

2.4 Literature review

HZSM5 zeolite has been proved to be an efficient catalyst for the conversion of methanol and ethanol to various hydrocarbons [2, 14-15, 29-32]. Although more extensive works have been carried out on methanol conversion over HZSM5, works on ethanol conversion reactions are rather limited.

The conversion of ethanol to aliphatics and aromatics on HZSM5 is studied in a broad reaction conditions and catalyst acidity. The product distribution and the extent of aromatization have been found to be strongly dependent on the reaction conditions and the acidity of the samples [33]. For any particular zeolites, the amount of aromatics (benzene, toluene, xylene and mesitylene) in the product initially increases with rise in temperature and then decrease sharply. Low space velocity results in a higher selectivity for aromatics, whereas at high space velocity the hydrocarbon gases become predominant [33-34].

The activity as well as the total aromatic yields decrease with the decrease of strong acid sites and no aromatics are found at all below a limiting value of acid sites. Moreover, the conversion of ethanol is studied on the effect of crystallite size on deactivation rates. It was found that [35] the reaction using large ZSM5 crystals deactivates rather quickly, mostly within 24 hours. This is because coke deposition take places on the outer crystal surface.

A number of attempts are made to selectively produce light olefins, gasoline, and aromatics from ethanol. Among those the use of co-feeding is considered. Generally water co-feeding has been found to improve the ethylene selectivity and shown to improve the lifetime of the catalyst [36-37]. At very high water concentrations, however, there is a serious inhibitory effect on the yield of the olefins. Moreover, addition of benzene co-feeding up to 9 wt% in ethanol increases the yield of aromatics from 28 wt% to 53 wt%, while the gaseous products was decreased [34].

2.5 Overview of the thesis

This thesis has concerned with catalyst design for the conversion of ethanol with regard to high aromatic yields. HZSM5 catalyst which possesses silicon/aluminium ratio ~ 15 has been proved to be an efficient catalyst for ethanol to various hydrocarbon [33]. However, the effort to enhance aromatic selectivity have focused on improving the dehydrogenation activity of this catalyst since HZSM5 is a poor dehydrogenation catalyst. Therefore, it is suggested that the modification by the addition of metal species namely platinum, gallium, and silver which place a dehydrogenation function can enhance the aromatic yields. The metal species incorporated with ZSM5 are prepared and characterized using conventional techniques, such as scanning electron microscopy, X-ray diffraction, and etc. which are shown in section 3.5. The general catalytic procedures and parameters, which are used in the catalytic study for the rest of this work, are mentioned in section 3.6. The effect of metal species is focused on the role of metal species in

the reaction pathway (section 4.3-4.4) and the altering of metal species during the reaction and also preparation (section 4.3-4.4). However, the effect of water is also mentioned since the cost of the absolute ethanol production is expensive [2-6]. However, the presence of water in the feed is expected to be lessen the activity of catalyst [36-37]. Accordingly, the effect of water is investigated using variation of feed composition (water, ethanol, and ethylene). In addition, regeneration behavior of the modified catalyst has suggested the predominant influence of temperature and water content.



Chapter 3

Experimental details

3.1 Reagents

Chemicals	Grade of purity	Manufacturers
3.1.1 Air	Air Zero	TIG
3.1.2 1-Amino-2-naphthol-4-sulphonic acid	95 %	CARLO ERBA REAGENTI
3.1.3 Ammonium chloride	99.5 %	MERCK
3.1.4 Ammonium hydroxide solution	30.0 %	BAKER ANALYZED
3.1.5 Ammonium molybdate	≥ 99 %	Fluka Chemika
3.1.6 Ammonium nitrate	99 %	Fluka Chemika
3.1.7 Ammonium tetrachloroplatinate (II)	52 % Pt	Fluka Chemika
3.1.8 Benzene	99.8 %	CARLO ERBA REAGENTI
3.1.9 Buffer pH 4 and 7	-	-
3.1.10 Colloidal silica Ludox ® AS-40	40 % SiO ₂	ALDRICH
3.1.11 Distilled water	-	-
3.1.12 Ethyl alcohol (absolute)	99.8 %	CARLO ERBA REAGENTI
3.1.13 Ethylbenzene	≥ 98 %	Fluka Chemika
3.1.14 Ethylene gas	CP	BOC GASES
3.1.15 Gallium nitrate	99.9 %	ALDRICH
3.1.16 Helium gas	High purity	TIG
3.1.17 <i>n</i> -Heptane	99 %	CARLO ERBA REAGENTI
3.1.18 <i>n</i> -Hexane	99.9 %	Mallinckrodt
3.1.19 Hydrochloric acid	37 %	MERCK
3.1.20 Hydrofluoric acid	48 %	MERCK
3.1.21 Hydrogen gas	High purity	TIG
3.1.22 8-Hydroxyquinoline	99 %	MERCK
3.1.23 Liquid nitrogen	-	TIG
3.1.24 Liquefied petroleum gas	Commercial	SIAM GAS

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3.1.25	Nitric acid	65 %	BAKER ANALYZED
3.1.26	Nitrogen gas	High purity	TIG
3.1.27	<i>n</i> -Nonane	> 99 %	MERCK
3.1.28	<i>n</i> -Pentane	99 %	LAB-SCAN
3.1.29	Silver nitrate	98.5 %	CARLO ERBA REAGENTI
3.1.30	Sodium aluminate	99 %	Rideal-de Haen
3.1.31	Sodium hydrogen sulphite	39%	MERCK
3.1.32	Sodium hydroxide	> 98 %	CARLO ERBA REAGENTI
3.1.33	Sodium tetraborate	99 %	MERCK
3.1.34	Tartaric acid	99.5 %	MERCK
3.1.35	Tetrapropylammonium bromide	> 98 %	Fluka Chemika
3.1.36	Toluene	99.8 %	MERCK
3.1.37	Xylene	≥ 99 %	Fluka Chemika

3.2 Apparatus

- 3.2.1 Autoclave
- 3.2.2 Beaker
- 3.2.3 Buchner flask
- 3.2.4 Buchner funnel
- 3.2.5 Bunsen burner
- 3.2.6 Catalytic testing rig
- 3.2.7 Clamp
- 3.2.8 Condenser
- 3.2.9 Erlenmeyer flask
- 3.2.10 Gas adsorption analyzer
- 3.2.11 Gas chromatography (GC)
- 3.2.12 Graduated cylinder
- 3.2.13 Graduated pipet
- 3.2.14 Heating bath
- 3.2.15 Heating mantle
- 3.2.16 Metal rings

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- 3.2.17 Nickel crucible
- 3.2.18 Pasteur pipet
- 3.2.19 pH meter
- 3.2.20 Round-bottomed flasks
- 3.2.21 Scanning electron microscope (SEM)
- 3.2.22 Separatory funnel
- 3.2.23 Support stand
- 3.2.24 Vial
- 3.2.25 Wash bottle
- 3.2.26 Water circulator
- 3.2.27 X-ray diffractometer (XRD)

3.3 Process of study

A process of the study of the ethanol conversion to gasoline and aromatics over zeolite catalyst comprises the following stages:

3.3.1 Synthesis of zeolites

- 3.3.1.1 Prepare zeolite ZSM5 using hydrothermal crystallization.
- 3.3.1.2 Calcine the materials obtained in 3.3.1.1.
- 3.3.1.3 Modify ZSM5 obtained in 3.3.1.2 by impregnation and/or ion exchange with gallium, platinum, silver, and ammonium ion species.
- 3.3.1.4 Activate the materials obtained in 3.3.1.3.

3.3.2 Characterization of zeolites

- 3.3.2.1 Determine the silicon/aluminium ratio by UV-Vis Spectrophotometry.
- 3.3.2.2 Determine the crystal morphology by Scanning Electron Microscopy.
- 3.3.2.3 Investigate the zeolite structure by X-Ray Diffractometer.
- 3.3.2.4 Determine the metal content in zeolites by Atomic Absorption Spectrometry.
- 3.3.2.5 Determine the surface area by gas adsorption analysis.
- 3.3.2.6 Determine the acidity of HZSM5 by potentiometric titration.

3.3.3 Catalytic testing

- 3.3.3.1 Investigate the effect of contact time.
- 3.3.3.2 Investigate the effect of temperature.
- 3.3.3.3 Investigate the water content in ethanol feed.
- 3.3.3.4 Investigate the effect of metal loading and method of incorporation.

3.3.4 Analysis of products

- 3.3.4.1 Determine the amount of gasoline and aromatics by Gas Chromatography.

3.4 Modification of zeolites

3.4.1 Synthesis of ZSM5 zeolite

ZSM5 was synthesized hydrothermally from aluminosilicate gel by the procedure described in U.S. patent [20], with a nominal gel composition of $28 \text{ SiO}_2 : 1 \text{ Al}_2\text{O}_3 : 10 \text{ Na}_2\text{O} : 17 \text{ TPABr} : 1,820 \text{ H}_2\text{O}$, where TPABr stands for tetrapropylammonium bromide. The gel was prepared by first dissolving the tetrapropyl ammonium bromide (10.33 grams) and sodium hydroxide 1.64 grams in water. To this was added the sodium aluminate 0.39 gram (37.57 wt% Na_2O , 59.54 wt% Al_2O_3) which was previously dissolved in small amount of the water. Finally, 9.60 grams of commercial colloidal silica (Ludox ® AS-40), 40% silica was added to the mixture. This mixture was then charged to an autoclave and held at 150°C under autogeneous pressure without stirring for 6 days. At the end of the crystallization period, the autoclave was quenched in water and the zeolite ZSM5 was filtered and dried overnight at 90°C . The X-ray diffraction patterns of the synthesized zeolite was confirmed that indeed the expected zeolite was obtained. Before the X-ray analysis, zeolite was heated at 550°C for 8 hours in air: under these calcination conditions, the burning of the occluded template was surely achieved.

3.4.2 Preparation of acid form ZSM5 zeolite [30]

Small amount (2 g) of ZSM5 zeolite was cation-exchanged with 1 M ammonium nitrate at 80°C for 4 hours, 3 times. Ammonium cation was employed in a great excess in order to minimize the amount of remaining sodium cation. This was followed by their transformation to their acidic forms by calcination at 550°C for 4 hours in air. This catalyst will be referred to as HZSM5.

3.4.3 Preparation of platinum impregnated with ZSM5 zeolite[38]

The platinum loading onto the ZSM5 zeolite was done according to the following procedure: 0.1154 gram of ammonium tetrachloroplatinate (II) was dissolved in a small amount of water. This solution was added to 2.0000 grams of HZSM5 zeolite, and the resulting mixture was stirred for few minutes. Then the water was gently evaporated to dryness on a hotplate. The resulting solid was further dried at 120 °C for 3 hours and activated in air at 290 °C for 2 hours. The sample was then cooled down to 100 °C under nitrogen atmosphere for 30 minutes. This catalyst was further activated by hydrogen at 300 °C for 4 hours. This catalyst will be referred to as [Pt]HZSM5. The content of platinum in the resulting catalyst are 3.00 wt%.

3.4.4 Preparation of gallium impregnated with ZSM5 zeolite[38]

The gallium loading onto the ZSM5 zeolite was done according to the following procedure: 0.2201 gram of gallium nitrate was dissolved in small amount of water. This solution was added to 2.0000 grams of HZSM5 zeolite, and the resulting mixture was stirred for a few minutes. Then the water was gently evaporated to dryness on a hotplate. The resulting solid was further dried at 120 °C for 3 hours and activated in air at 550 °C for 4 hours. This catalyst will be referred to as [Ga]HZSM5. The content of gallium oxide in the resulting catalyst are 3.00 wt% .

3.4.5 Preparation of silver impregnated with ZSM5 zeolite[38]

The silver loading onto the ZSM5 zeolite was done according to the following procedure: 0.4353 gram of silver nitrate was dissolved in small amount of water. This solution was added to 2.0000 grams of HZSM5 zeolite, and the resulting mixture was stirred for a few minutes. Then the water was gently evaporated to dryness on a hotplate. The resulting solid was further dried at 120 °C for 3 hours and activated in air at 550 °C for 4 hours. This catalyst will be referred to as [Ag]HZSM5. The content of silver species in the resulting catalyst are 7.53 wt% .

3.4.6 Preparation of silver ion-exchanged with $\text{NH}_4\text{ZSM5}$ zeolite

Silver incorporated with ZSM5 has been carried out by ion exchange of ammonium cation by silver cation. The approximately 2 grams of $\text{NH}_4\text{ZSM5}$ zeolite were ion-exchanged in 125 mL of 1 M silver nitrate solution. A cation-exchange at 80 °C for 4 hours was filtered and washed 1 time using 50 mL of distilled water at room temperature. Finally the zeolite was dried

at 120 °C for 3 hours and activated in air at 550 °C for 4 hours. This catalyst will be referred to as AgHZSM5. The silver content was determined by Atomic Absorption Spectrometry. In the case of reduction, this catalyst was further activated by hydrogen at 350 °C for 2 hours. This catalyst will be referred to as red-AgHZSM5.

3.4.7 Preparation of silver ion-exchanged with NaZSM5 zeolite

Silver incorporated with ZSM5 has been carried out by exchange of sodium cation by silver cation. The approximately 2 grams of NaZSM5 zeolite were ion-exchanged in 125 mL of 1 M silver nitrate solution. A cation-exchange at 80 °C for 4 hours was filtered and washed 1 time using 50 mL of distilled water at room temperature. Finally the zeolite was dried at 120 °C for 3 hours and activated in air at 550 °C for 4 hours. This catalyst will be referred to as AgNaZSM5. The silver content was determined by Atomic Absorption Spectrometry. In the case of reduction, this catalyst was further activated by hydrogen at 350 °C for 2 hours. This catalyst will be referred to as red-AgNaZSM5.

3.5 Characterization of catalysts

3.5.1 Determination of silicon content [39]

Before the analysis, NaZSM5 sample were weighed and fused by sodium hydroxide. The silicon in zeolite sample was complexed with ammonium molybdate and determined by UV-Vis Spectrophotometry.

3.5.1.1 Preparation of reagents

1) Preparation of ammonium molybdate

The reagent was prepared by dissolving 8.0 grams ammonium molybdate crystals in water, followed by adding of 9 mL concentrated sulfuric acid. This solution was diluted to 100 mL with distilled water.

2) Preparation of reducing agent.

A solution (A) was prepared by dissolving 10.0 grams sodium hydrogensulphite in 70 mL water. Then, another solution (B) was prepared by dissolving 0.8 gram anhydrous sodium hydrogensulphite in 20 mL water, and added 0.2 gram 1-amino-2-naphthol-4-sulphonic acid. Finally, solution A and solution B were

mixed and diluted to 100 mL with distilled water. This solution must be prepared freshly in use.

3.5.1.2 Preparation of standard solution of silica and sample solution

Accurate 70 mg of NaZSM5 zeolite and 50 mg of standard silica (100% silicon) were weighed. Each portion was transferred to a clean nickel crucible containing 5 mL of 30% sodium hydroxide solution. The covered crucibles were heated to dull redness for about 15 minutes, the zeolite sample (or standard silica) should then have melted. The sample was carefully cooled down and the boiling water was added to dissolve the fused mass. The dissolved solution was transferred to 1 L beaker and about 150 mL of water was added. This solution was stirred by a plastic rod and 5 mL of 1+1 hydrochloric acid was added. The sample solution was diluted to 200 times (250 mL). While, standard solution which have been treated similarly with the sample solution, was diluted to approximately 10 ppm before further dilution. A calibration curve was constructed by using 2.5, 5.0, 7.5, and 10.0 mL of the standard silica solution. After transferring of standard sample (or 5.0 mL of zeolite sample), pH of the solution (containing 0.02-0.10 mg of silicon) was adjusted to 4.5-5.0. Then, 1 mL of ammonium molybdate solution and 5 mL of 10% tartaric acid solution were added. The resulting mixed solution was further added 1 mL of the reducing agent and diluted to 100 mL. After 20 minutes, the absorbance at 815 nm of the sample solution was measured against the blank. Finally, the silicon content of zeolite sample was calculated using the calibration curve.

3.5.2 Determination of aluminium content [40]

3.5.2.1 Preparation of reagent

Reagent solution was prepared by dissolving 2 grams 8-hydroxyquinoline in chloroform to make 100 mL solution. Then, acetate buffer solution was prepared by dissolving 25 grams ammonium acetate in about 70 mL of water and 5 mL acetic acid was added. This solution was diluted to 100 mL with water.

3.5.2.2 Preparation of standard solution of aluminium and sample solution

The accurate 44 mg of zeolite sample was weighed and digested with hydrofluoric acid. This solution was diluted to 100 mL in plastic volumetric flask with further 10 times dilution. Then, 25 mL of the diluted sample solution and 3 mL

of acetate buffer solution were mixed in a beaker. The mixture should exhibit a pH 6 and it was then transferred to a separatory funnel. After mixing, the 20 mL of 8-hydroxyquinoline solution was added and this mixture was shaken vigorously for 3 minutes. The organic phase was separated, filtered, and measured at 410 nm against a blank. The standard aluminium solution was diluted to 50 ppm and a calibration curve was constructed by using 1, 2, 3, and 4 mL of this standard solution. Finally, the aluminium content of zeolite sample was calculated using a calibration curve.

3.5.3 Determination of acid site concentration

3.5.3.1 Preparation of reagents

1) Preparation of primary standard sodium tetraborate 0.1 M

Accurate 9.53 grams of sodium tetraborate was dissolved in a beaker and transferred into a 100 mL volumetric flask. Finally, this solution was diluted to 250 mL with distilled water.

2) Preparation of standard hydrochloric acid

Approximately 100 mL of water was added into a 250 mL volumetric flask and consecutive 2.20 mL of concentrated hydrochloric acid was pipetted. Then, this solution was diluted to 250 mL with distilled water.

3) Preparation of standard ammonium hydroxide

Approximately 0.8 mL of 28 % ammonium hydroxide solution was pipetted into a 250 mL volumetric flask and this solution was diluted to 250 mL with distilled water.

3.5.3.2 Determination of hydrochloric acid concentration

25 mL of hydrochloric acid was pipetted into a 50 mL beaker. Then, a combination glass electrode was immersed into the beaker with stirrer. The potential of this solution was read. Hydrochloric acid was titrated with 0.1 M sodium tetraborate standard solution by adding a portion of 0.5 mL titrant. When the potential of this solution was constant, the potential was read. The portion of titrant was reduced to 0.2 mL toward the end point of titration. The difference in potential, ΔE and the change in volume, ΔV was calculated and the $\Delta E/\Delta V$ was plotted versus the volume of added sodium tetraborate solution.

Finally, the volume for the equivalent point, V_e , was obtained from the volume which markedly change the potential [41].

3.5.3.3 Determination of ammonium hydroxide concentration

In the case of ammonium hydroxide determination, the potentiometric titration was carried out using ammonium hydroxide as titrand and hydrochloric acid as titrant. V_e have been determined similarly to the case of hydrochloric acid determination.

3.5.3.4 Determination of acid site concentration of zeolite using back titration techniques

Accurate 0.22 gram of zeolite sample was weighed and transferred into a 50 mL beaker. Then, cooled 25 mL of ammonium hydroxide solution and 0.1 gram of ammonium chloride were added. The beaker was placed onto an electronic hotplate and the temperature was increased up to 70 °C for 5 minutes. After the heating, the beaker was cooled to room temperature and the residual ammonium hydroxide was determined as in the case of ammonium hydroxide using hydrochloric acid as titrant. The acid concentration of zeolite is then calculated (as shown in Appendix A).

3.5.4 Determination of silver content

Before the analysis, AgHZSM5 and AgNaZSM5 sample were weighed, and extracted by nitric acid, and filtrated. The residual was filtrated while the silver sample was dissolved in nitric acid solution. The concentration of silver in the solution was determined by flame atomic absorption method and silver content of the zeolite was calculated.

3.5.4.1 Preparation of reagents

1) Preparation of sample

The AgHZSM5 and AgNaZSM5 were accurately weighed to 55 mg and each was transferred to a 50 mL beaker. The 15 mL of distilled water and consecutive 3 mL of concentrated nitric acid were added. The beaker was placed onto an electronic hotplate. The temperature was increased up to 80 °C and the sample was stirred for 30 minutes. After extraction, the sample was filtered and the filtrated was collected in a 100 mL volumetric flask. The sample solution was diluted to 100 mL and further 4 times dilution was applied.

2) Preparation of standard solution

A calibration curve of the standard silver solution was constructed by using 4, 8, 12, 16, and 20 mL of the 100 ppm standard silver solution. The standard solution was transferred to 100 mL of volumetric flask and diluted to 100 mL with water.

3.5.4.2 Determination of silver content

The atomic absorption spectrometer was performed according to the operation manual and parameter set for silver determination [42]. The concentrations of calibration solution were loaded into the computer. Then, the standard solutions 4, 8, 12, 16, and 20 ppm were aspirated. The calibration curve was then calculated. After the calculation, the sample solutions were measured 2 times. The silver content of the sample solution was calculated by using the calibration curve.

3.5.5 Scanning electron microscopy

Scanning electron microscopy (SEM) is the most versatile technique to study the morphology and particle size distribution of zeolites. This technique is done according to the following procedure: the sample was finely divided onto a sample holder. The sample surface was then coated with gold thin film. After that the sample holder was left in sample chamber, and evacuated from ambient pressure to 10^{-4} torr or less. Then, the holding sample adjusted and moved in the X, Y and Z directions. As a consequence, the surface of the most samples can be viewed from almost any perspective.

3.5.6 X-ray diffraction

The best way to check the zeolite structure is by X-ray diffraction (XRD). This method is done according to the following procedure: the sample was finely grinded to a permit packing of the sample into an XRD sample holder. The XRD pattern was obtained by scanning over the angle range from $2\theta = 5$ to 60, step angle 0.040 degree, and detection time 1.50 seconds. The X-ray source is Cu-K α generated from a voltage of 45.0 kV, 30 mA.

3.5.7 Gas adsorption analysis

Gas adsorption analysis is the technique using for determination of the surface area of porous catalyst. This technique was done according to the following procedure: the zeolite sample was weighed accurately about 1 mg and transferred to a clean, dry empty sample cell. This sample cell was attached to the outgassing station. Then, a heating mantle was installed with the sample cell and the temperature was raised to 350 °C for 18 hours. After the residual adsorbate was removed by temperature and reduced pressure. The nitrogen adsorbate was filled by open the gas inlet valve. The sample cell was attached to the sample station. In the initiate adsorption, a dewar flask of liquid nitrogen was placed around the sample cell and the measurement of nitrogen adsorption was set with 2 minutes equilibration time, with 4 scaled tolerance. When adsorption was complete, the sample cell was removed from the sample station. dried thoroughly and reweighed.

3.6 Catalytic testing

Catalytic reaction were performed by feeding 0.4320 gram/hour ethanol or 0.4547 gram/hour (which equal the amount of ethanol plus water added), 95 wt% of ethanol using liquid pump. In the case of pure ethylene feed, this gas was regulated by mass flow controller. 3.88 mL/minute of ethylene gas which is equal to the mole of ethanol feeding was feed to the catalytic testing (see the calculation method in Appendix A). The vaporized ethanol feed (or ethylene) was then carried by the nitrogen gas (or hydrogen gas) through a catalyst bed set in a catalytic reactor, which located inside a temperature-regulated furnace. The gaseous mixture flowing out of the reactor passed a gas sampling.

The preferred reaction conditions used in the experiments were as follows: temperature, 350-525 °C; total pressure, 1 atm; carrier gas, nitrogen; weight hourly space velocity (WHSV), 1.73-5.76 hr⁻¹; time on stream, 6 hours.

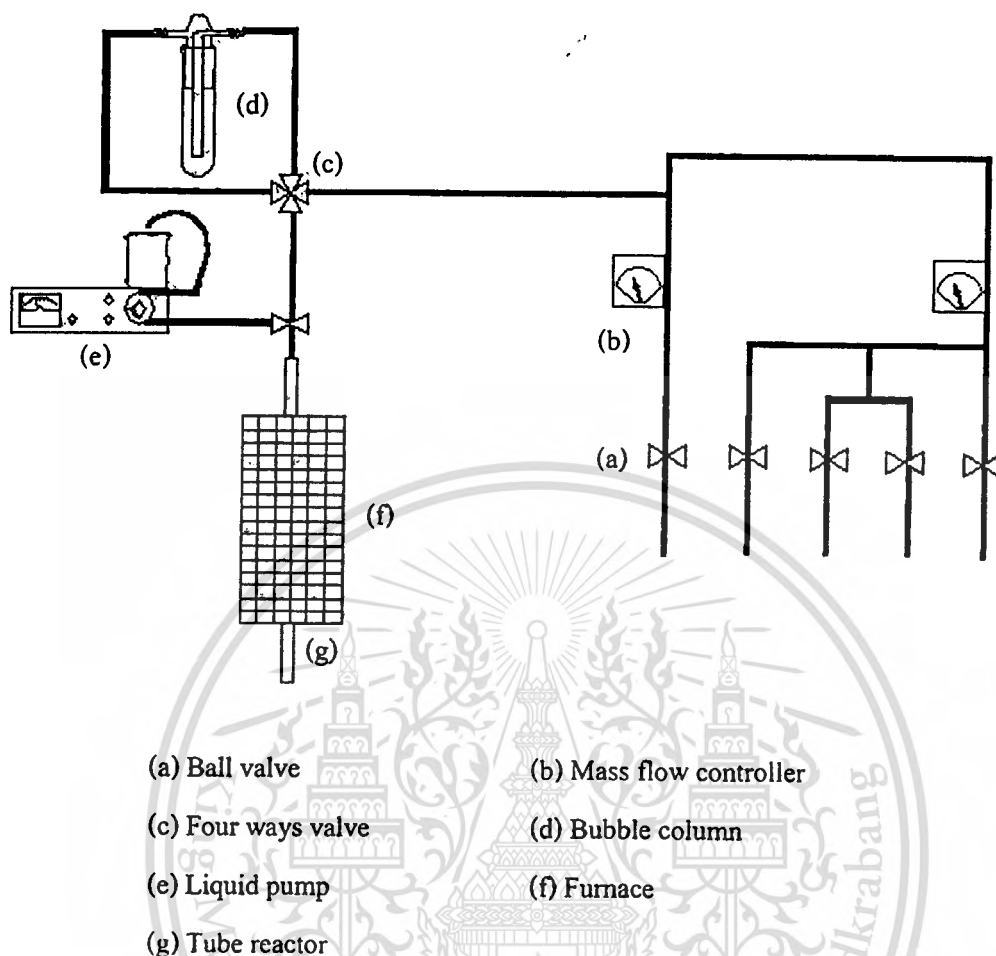


Figure 3.1 Schematic of catalytic testing rig.

3.7 Analysis product

The product were periodically collected by a gas tighted syringe and then analyzed by Gas Chromatography (GC). The sample 250 microliters were injected into a capillary column connected to thermal conductivity and, subsequently flame ionized detectors. The components were separated as they pass through the column with an inert carrier gas and their presence in the effluent is detected and recorded as a chromatogram. The analyzed condition is shown in Appendix B.

The peak area from the chromatogram were measured and calculated as the peak area percentage. Then the unknown peak can be identified by using ethylene, LPG, *n*-pentane, *n*-hexane, *n*-heptane, benzene, toluene, and xylene as standard. The composition of the unknown product was computed by the normalization method (as shown in Appendix A).

Chapter 4

Results and discussion

4.1 Zeolite synthesis and characteristic

4.1.1 X-ray diffraction

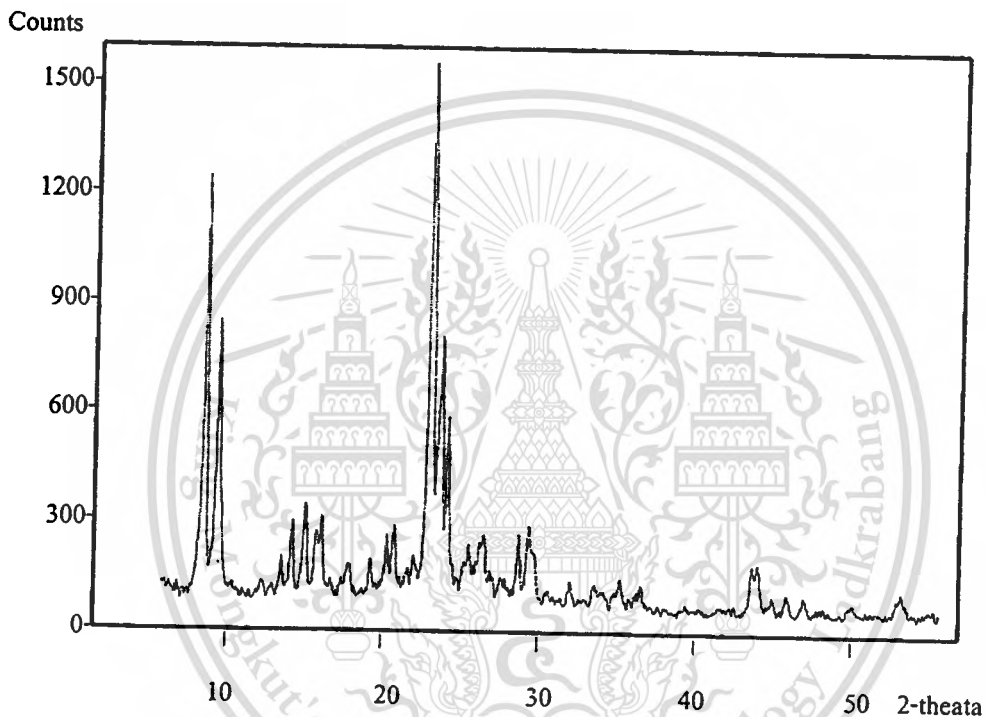


Figure 4.1 XRD pattern of calcined NaZSM5.

X-ray diffraction pattern of the calcined NaZSM5 is shown in Figure 4.1. This indicates that this catalyst has the pentasil pore opening structure, the same crystalline structure as ZSM5. The peak intensities for this catalyst are high indicating the crystallinity, which can be regarded as a well-defined crystalline microporous materials.

4.1.2 Morphology

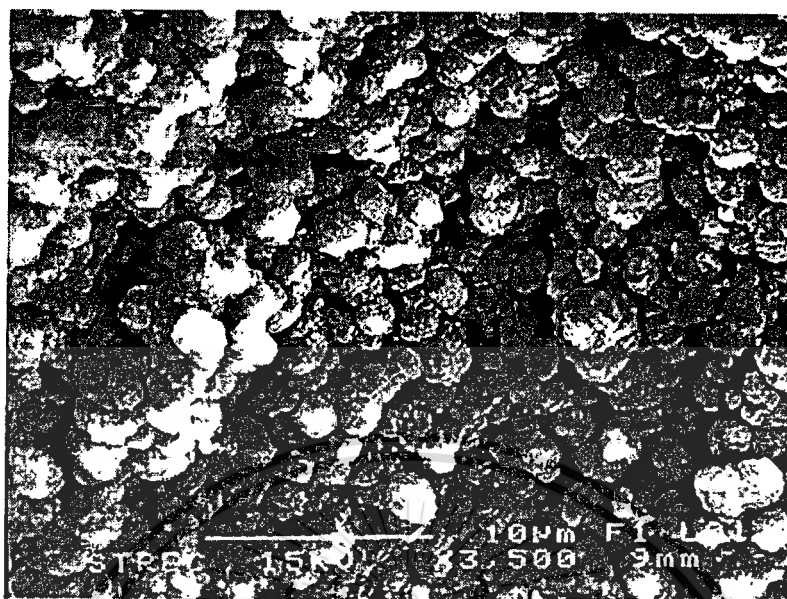


Figure 4.2 Morphology of calcined NaZSM5.

Figure 4.2 shows the scanning electron micrograph of calcined NaZSM5. The crystal is approximately 1 micrometers diameter and has a good particle size distribution. This is consistent with the high crystallinity detected by XRD.

4.1.3 Specific surface area

The BET surface area of calcined NaZSM5 is found to be $416 \text{ m}^2/\text{g}$. This indicates that the calcined NaZSM5 would be an effective catalyst due to its high surface area.

4.1.4 Acidity

The acidity of the modified catalyst (HZSM5) is measured by using the potentiometric titration and the acid concentration of the sample is measured to be 1 mmol/g of zeolite. The result (as shown in Appendix A) indicates that ammonium cation can readily ion exchanges with sodium cation and the exchangeable ammonium cation can be decomposed to give proton by losing ammonia gas.

4.1.5 Chemical analysis

ZSM5 zeolite is prepared by hydrothermally crystallization. According to the results of chemical analysis of UV-Vis Spectrophotometry, the observed silicon to aluminium ratio is 15. This indicates that it possesses the high acidity which is favored for ethanol conversion [33].

The results of chemical analysis from Atomic absorption spectrometry show that the silver content of AgHZSM5 and AgNaZSM5 zeolite were 7.35 and 6.59 wt%, respectively. This is estimated to be 70.50 % and 63.17 % of silver into the exchangeable site of the framework, respectively (as shown in Appendix A).

4.2 The conversion of ethanol over HZSM5

From the Figure 4.3, the product distribution of ethanol conversion obtained over HZSM5 catalyst is plotted.

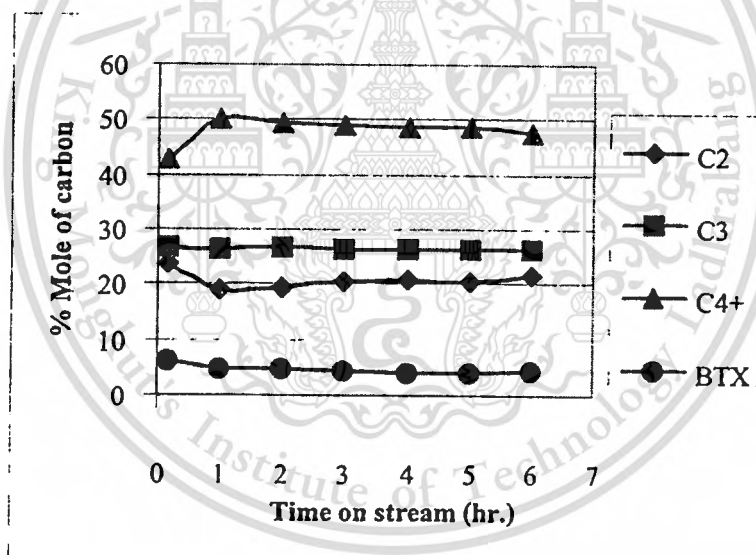
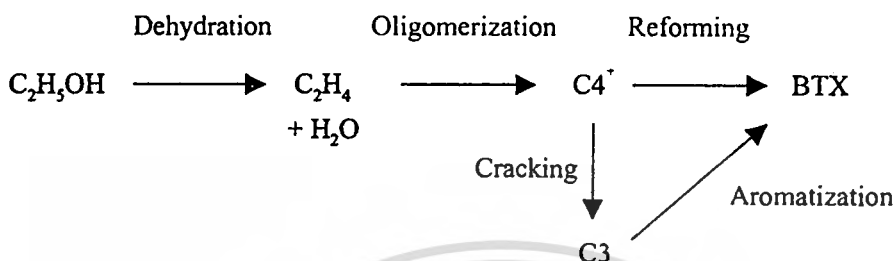


Figure 4.3 Product distribution for ethanol conversion over HZSM5 zeolite.

(Reaction temperature; 375 °C, WHSV: 4.32 hr⁻¹, Carrier gas: nitrogen, 100 % conversion of ethanol)

It can be noticed that ethylene is formed rapidly from the dehydration of ethanol. The subsequent conversion of ethylene to paraffins, aromatics, naphthenes and higher olefins, which proceed via classical carbocation mechanisms with concurrent hydrogen transfer, is well known

from hydrocarbon chemistry over acid catalysts [12, 14-18]. As the low catalyst deactivation is observed, near steady state data can be collected at 2-4 hours on stream, and used for further discussion. The reaction pathway for the formation of higher hydrocarbon and aromatic can be postulated as follows:



4.2.1 The effect of contact time over HZSM5

The conversion of ethanol over HZSM5 has been investigated using variation of contact time and temperature. Under the condition investigated, ethanol is completely converted to ethylene over HZSM5 zeolite and it can be oligomerized to form higher hydrocarbons. The ethanol conversion over HZSM5 at 375 °C as a function of contact time are shown in Figure 4.4.

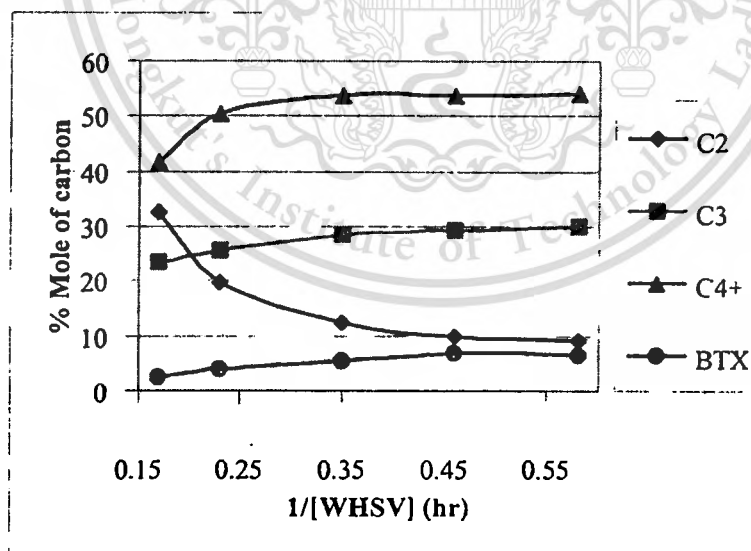


Figure. 4.4 Contact time-dependence of hydrocarbon distribution over HZSM5 catalyst.

(Catalyst; HZSM5, Reaction temperature; 375 °C, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Similar to other works [33-34], it is found that, at low contact time (high space velocity), ethylene can be slightly converted to higher hydrocarbons due to the low rate of ethylene oligomerization. This is because this reaction proceeds initially via a primary carbocation [12]. As the contact time is risen, ethylene can react further to form higher olefins, which undergo double bond isomerization, skeletal isomerization, cracking, and reforming over HZSM5. Products formed by these reactions, namely propylene (C3 hydrocarbon), higher non-aromatic hydrocarbons (C4⁺ hydrocarbons), and aromatics (BTX), are hence increased with the increased contact time. Regarding to the selectivity of aromatics, it is found that when C4⁺ hydrocarbons increase, the aromatics yield is also increased. It is suggested that, the higher hydrocarbons could undergo dehydrocyclization and shift toward aromatics. While the low rate of C3 aromatization is obtained over HZSM5 catalyst. This is because HZSM5 is a poor dehydrogenation catalyst for small olefins, although it possesses excellent dehydration, oligomerization, and reforming activities. Therefore, it requires modification by the addition of metal species which place a dehydrogenation function for enhancement of the aromatic yield (as further discussion in section 4.3 and 4.4). From the result, it can be concluded that the rate of oligomerization plays an important role for the formation of aromatics.

However, at relatively high contact time ($1/\text{WHSV} > 0.45$ hour), there is no significant change of catalytic activity. It is suggested that, at the lower contact time, the reaction rate is proportional to the concentration of catalyst; but at increasingly high contact time, the rate approaches a limit called a saturation value [16]. The reaction is governed by saturation kinetics which is observed frequently in catalysis at high contact time [16]. From the earlier results, this $1/[\text{WHSV}] = 0.35$ hour (2.88 hr^{-1} space velocity) is chosen to study effect of temperature.

4.2.2 The effect of temperature over HZSM5

It is shown in Figure 4.5 that the oligomerization of ethylene and the yield of C4⁺ hydrocarbons decrease with rise in temperature while the yield of C3 hydrocarbon increase when temperature is risen.

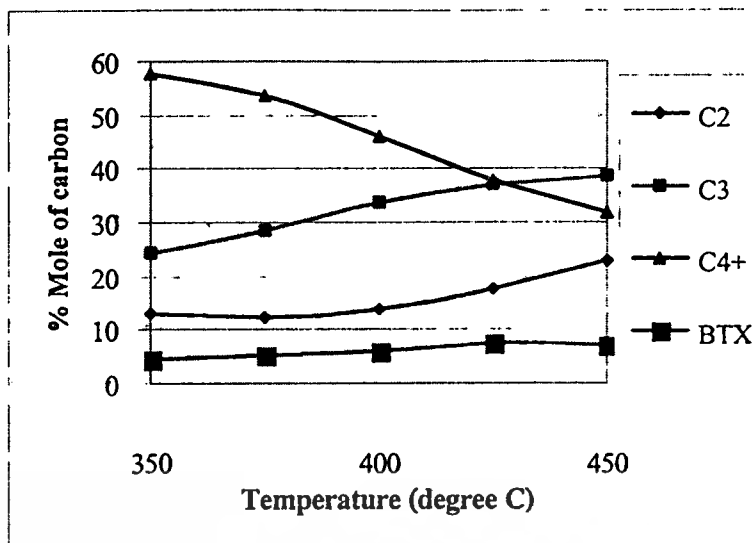


Figure 4.5 Temperature-dependence of hydrocarbon distribution over HZSM5 catalyst.

(Catalyst; HZSM5, WHSV; 2.88 hr^{-1} , Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

According to the principle of thermodynamics [13], olefin oligomerization is highly exothermic. Therefore, at high temperature, the rate of ethylene oligomerization is thermodynamically unfavored. While, the rate of cracking which produce C3 hydrocarbon, is highly endothermic. At high temperature, higher hydrocarbon can be readily cracked to lower hydrocarbons. From the above results, it can be concluded that, at low reaction temperature ($< 400^\circ\text{C}$) cracking can be suppressed, while olefins are readily converted to higher molecular weight hydrocarbons which undergo isomerization to high quality gasoline over HZSM5. This is because shape selectivity of zeolite plays a major role in controlling the length and branching of the products [14-17]. However, effort to convert gasoline to more valuable petrochemical products have focused on improving the conversion of gasoline to aromatic hydrocarbons.

It is found that aromatic yield first increase with rise in temperature ($350\text{-}425^\circ\text{C}$). This is because the higher temperature is favored for hydrogen transfer and the reaction of higher hydrocarbon products shift toward the aromatic fraction. At 450°C , the aromatic product is decreased due to inhibition of higher hydrocarbon formation (Figure 4.5). This supports the earlier discussion that ethylene oligomerization is an important step for the production of aromatic. From the above results, a balance between oligomerization and hydrogen transfer is essential for obtaining high yield of aromatics and in this study, the optimum temperature which

allows high aromatic selectivity is found to be 425 °C. While, at 450 °C, the aromatic selectivity is declined.

4.2.3 The effect of catalyst regeneration

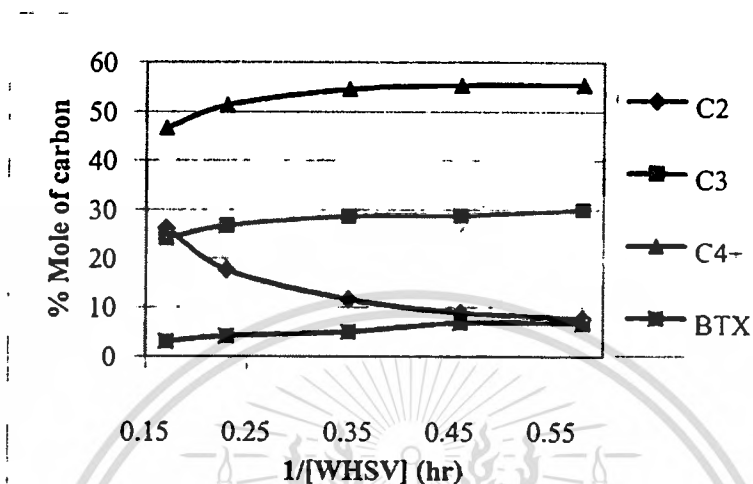


Figure 4.6 Contact time-dependence of hydrocarbon distribution over reg-HZSM5 catalyst.

(Catalyst; reg-HZSM5, Reaction temperature; 375 °C, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

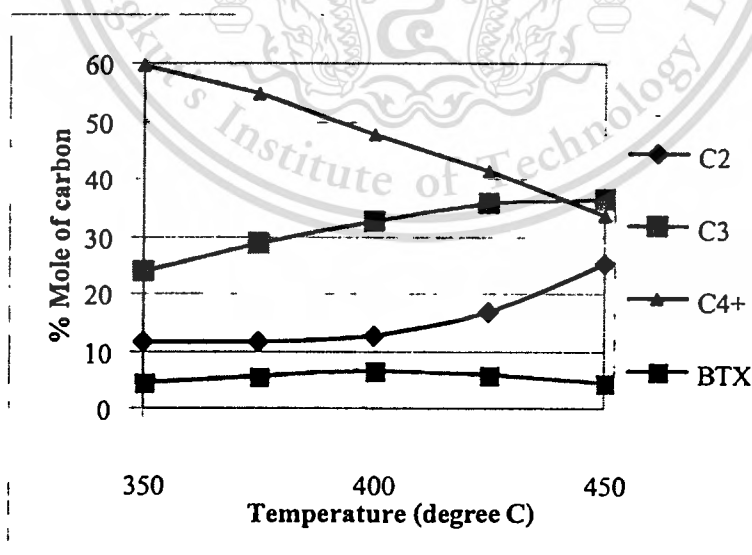


Figure 4.7 Temperature-dependence of hydrocarbon distribution over reg-HZSM5 catalyst.

(Catalyst; reg-HZSM5, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Effect of contact time and temperature on the reaction using regenerated HZSM5 (reg-HZSM5) are shown in Figure 4.6 and 4.7. It is shown that a similar trend can be observed, as compared to the parent HZSM5.

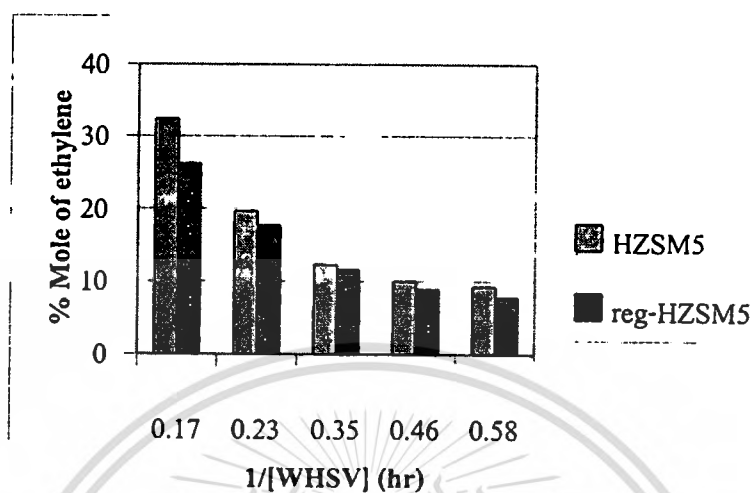
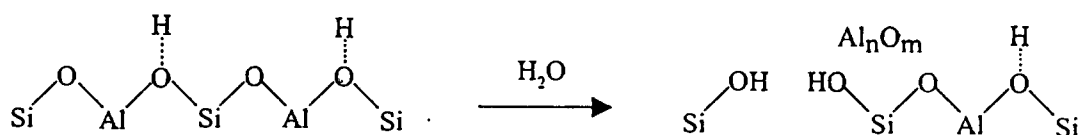


Figure 4.8 Effect of regeneration catalyst at different contact time.

(Catalyst; HZSM5 and reg-HZSM5, Reaction temperature: 375 °C. Carrier gas; nitrogen. Feed: ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

However, the oligomerization of ethylene is increased after the catalyst is regenerated (Figure 4.8). This indicates that the active sites of zeolite could be altered by regeneration. It is suggested that water produced from the dehydration can drive off the aluminium frameworks and coordinatively unsaturated Al^{3+} species can be formed during the reaction, at high temperature [16]. This produces strong Lewis acid site, which enhances the rate of ethylene oligomerization, as depicted schematically below:



It is well recognized that an enhancement of catalytic activity can be observed for zeolites dealuminated under mild conditions, due to a synergistic interaction between Brønsted acid sites in the zeolite and any type of Lewis acid sites from the non-framework aluminium species [16, 43-45]. This results in an increase in acid strength of the bridged hydroxyls [43-44] and thus enhancing the rate of ethylene oligomerization. The dealumination of the zeolite framework also contributes the increase in the number of nearly homopolar (hydrophobic) Si-O-Si bonds and concomitant decrease in the number of partially ionic hydrophilic centers, associated with the tetrahedrally coordinated aluminium [16, 46]. This hydrophobic character is essential to selective sorption of hydrocarbon, against the water, produced by dehydration during the reaction. Therefore, competitive adsorption of water is reduced while ethylene oligomerization is increased (as further discussion in the effect of water).

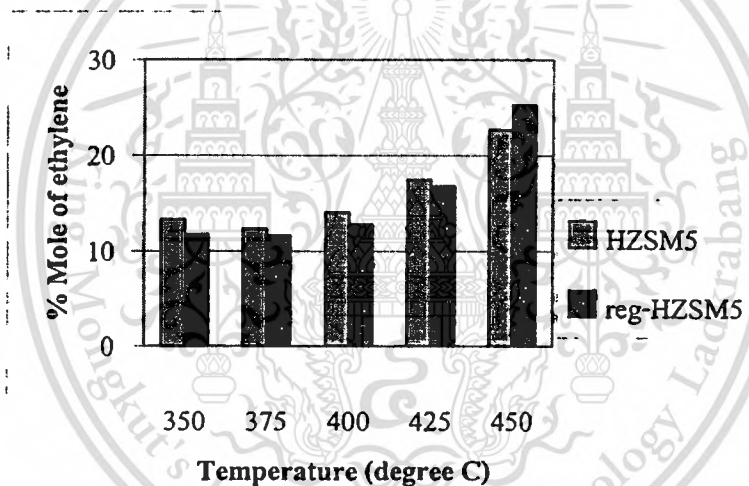


Figure 4.9 Effect of regeneration catalyst at different reaction temperature.

(Catalyst; HZSM5 and reg-HZSM5, WHSV: 2.88 hr^{-1} . Carrier gas; nitrogen. Feed: ethanol. average time on stream 2-4 hours, 100 % conversion of ethanol)

In Figure 4.9, a similar effect of temperature can be observed in the reaction using reg-HZSM5 catalyst. The slightly activity enhancement for reg-HZSM5 is consistent with the above conclusion. However, the enhancement in activity for HZSM5 only occurs at low temperature (mild steaming). When the reg-HZSM5 is used at higher reaction temperature (450 °C), a decrease in ethylene oligomerization is observed (Figure 4.9). This is suggested that under severe steaming (at 450 °C) the active acid sites can be effectively decreased, even though the increased

hydrophobic character of zeolite can reduce the water adsorption. Thus, it can be concluded that a balance between acidity and hydrophobic character is essential for enhancement of ethylene oligomerization.

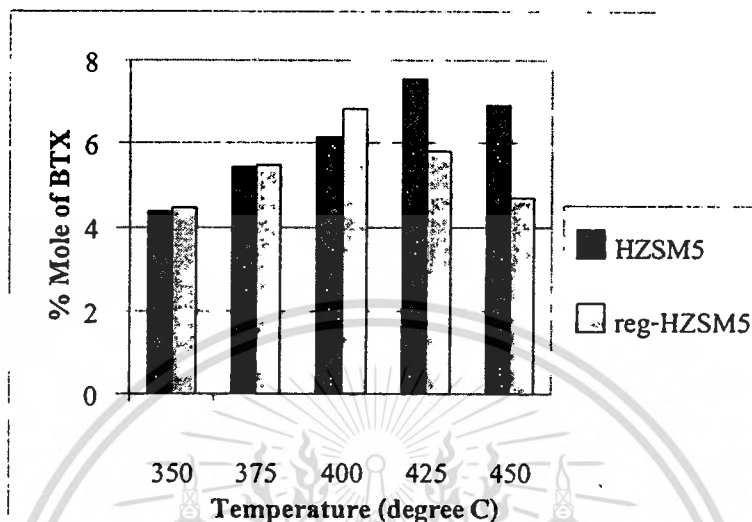


Figure 4.10 Effect of regeneration catalyst for aromatic selectivity at different reaction temperature.

(Catalyst; HZSM5 and reg-HZSM5, WHSV; 2.88 hr^{-1} , Carrier gas; nitrogen. Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

In Figure 4.10 a similar trend of temperature effect can be observed for aromatic yield in the reaction using reg-HZSM5, however, the optimum aromatic selectivity shift toward lower temperature. This is because the increased hydrophobic character and acid strength after catalyst regeneration. Consequently, the new catalytic sites are relatively more active than the fresh ones. Thus, the optimum aromatic yield is observed at the lower reaction temperature (400°C). However, a balance between oligomerization and hydrogen transfer is still essential for the formation of aromatic. Therefore, the aromatic selectivity is reduced when the temperature is risen (as discussed in section 4.2.2).

4.2.4 The effect of water over HZSM5

The effect of water content in the reaction over HZSM5 has been investigated using different feed (pure ethylene, ethanol, and 95 wt% ethanol).

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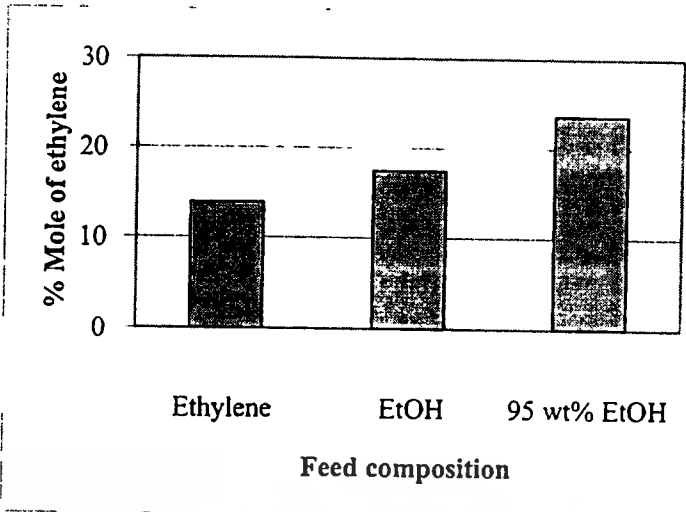


Figure 4.11 Effect of water content over HZSM5 catalyst at different feed composition.
(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

From the Figure 4.11, the conversion of ethylene decreases with rise in water content of the feed.

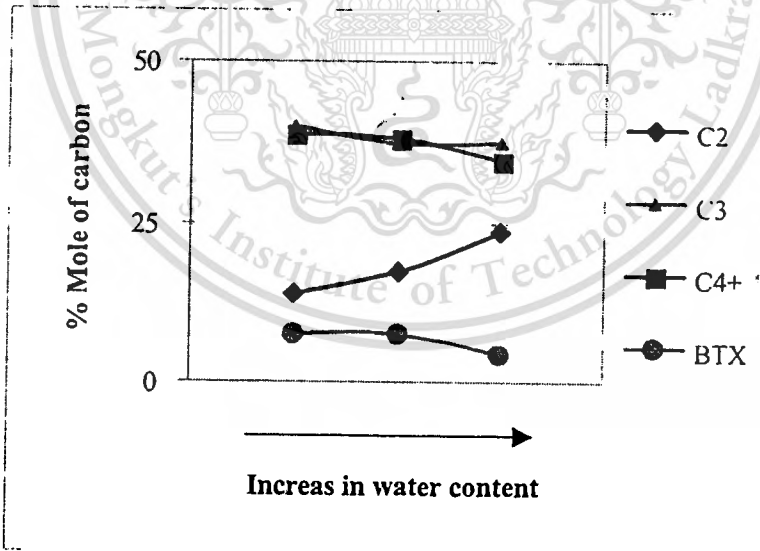


Figure 4.12 Product distribution over HZSM5 catalyst at different feed composition.
(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

It indicates that water either produced by ethanol dehydration or present as co-feed can inhibit oligomerization of ethylene. This may well derived from the competitive adsorption of water over the active acid sites. Consequently, yields of higher hydrocarbons including C₄ and aromatic are also decreased (Figure 4.12). This result supports the earlier suggestion that, over a relatively high aluminium framework of ZSM5 (Si/Al ~ 15), water can be adsorbed on the active sites, particularly when large amount of water is present in the feed.

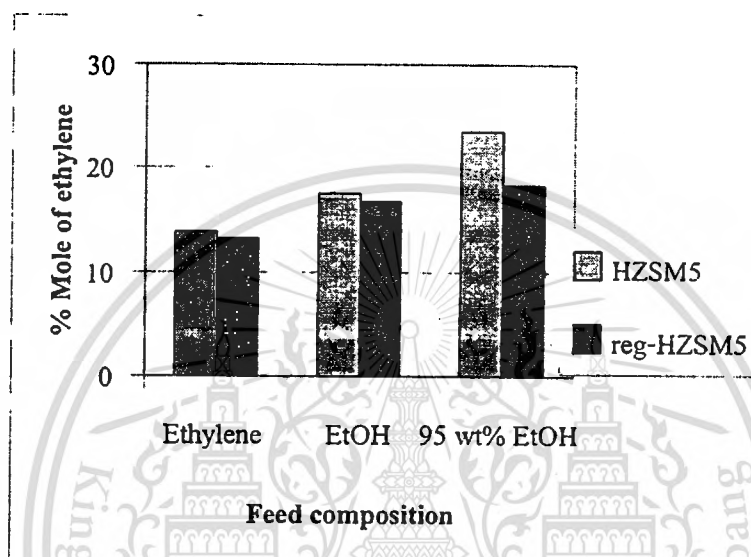


Figure 4.13 Effect of water content for oligomerization activity over reg-HZSM5.

(Catalyst; HZSM5 and reg-HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹. Carrier gas: nitrogen, Feed; ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

In Figure 4.13, as compared to HZSM5, the oligomerization of ethylene is slightly increased when catalyst was regenerated, except for the reaction using 95 wt% ethanol as feed. the ethylene oligomerization was markedly enhanced. This is due to the increase in acid strength and hydrophobic character after catalyst regeneration, as discussed previously in section 4.2.3. It can be claimed that this regenerated catalyst possesses a better resistivity to the presence of water.

4.3 The conversion of ethanol over [Pt]HZSM5, [Ga]HZSM5, and [PtGa]HZSM5

4.3.1 The effect of temperature over [Pt]HZSM5

The results of the ethanol conversion over platinum impregnated on HZSM5 ([Pt]HZSM5) at different reaction temperature are shown in Table 4.1.

Table 4.1 Comparison data for conversion of ethanol over [Pt]HZSM5.

Temperature Catalyst	350 °C		425 °C	
	[Pt]HZSM5	HZSM5	[Pt]HZSM5	HZSM5
% Mole				
C2	34.56	13.24	68.24	17.44
C3	20.29	24.46	15.78	36.96
C4 ⁺	43.54	57.93	14.55	38.05
BTX	1.61	4.37	1.43	7.55

(Catalyst; [Pt]HZSM5, and HZSM5, WHSV: 2.88 hr⁻¹. Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Conversion of ethanol at 350 °C and at 425 °C are carried out over [Pt]HZSM5 for comparison. From Figure 4.14, it is seen that ethylene oligomerization decrease with rise in temperature. This is consistent with the earlier observation over HZSM5 (section 4.2.2) that the rate of ethylene oligomerization is thermodynamically retarded at high temperature.

However, it is found that over the range of reaction temperature, the selectivity of higher hydrocarbons over [Pt]HZSM5 is much lower than that HZSM5. Although [Pt]HZSM5 has been proved to be an active catalyst for naphtha reforming [9, 12, 14-16] and light alkane aromatization [47-48], it cannot produce a high yield of aromatics in ethanol conversion. It is suggested that [Pt]HZSM5 inhibits ethylene oligomerization and platinum is a selective catalyst for light olefin production. This can be clearly seen from the result that a small amount of ethylene is converted to higher hydrocarbons. The fact that incorporated metal, particular the late transition metal, can stabilize the lower olefins, has been previously reported [47] in the methanol conversion using nickel incorporated with HZSM5 as catalyst. This is consistent with the observed high yield of ethylene in ethanol conversion using [Pt]HZSM5.

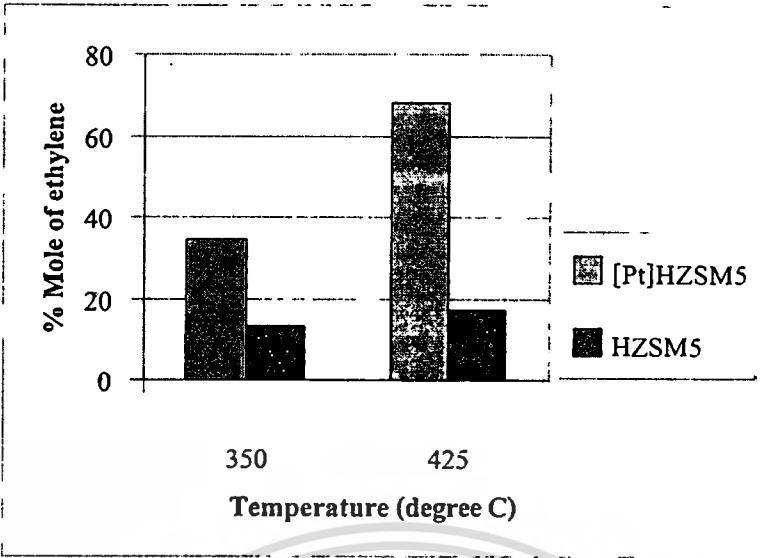


Figure 4.14 Effect of temperature over [Pt]HZSM5 in ethanol conversion.
(Catalyst; HZSM5 and [Pt]HZSM5, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

4.3.2 The effect of regeneration over [Pt]HZSM5

In the case of regenerated platinum loaded on zeolite (regen-[Pt]HZSM5), the trend of hydrocarbon selectivity is similar to the fresh one. However, ethylene oligomerization over regenerated platinum is higher than that parent catalyst (Figure 4.15).

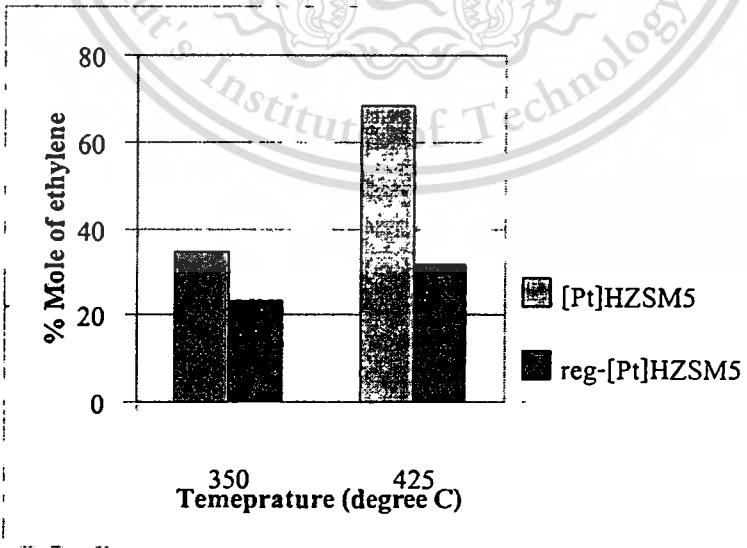


Figure 4.15 Effect of regeneration catalyst at different reaction temperature.
(Catalyst; [Pt]HZSM5 and reg-[Pt]HZSM5, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

This is presumably because the regeneration is frequently responsible for clustering of platinum, in addition to the increased acid strength as discussed earlier (section 4.2.3). This suggestion is supported by previously report [15] that observed clustering generally take place at high temperature and are generally accelerated by the presence of water vapor (from the ethanol dehydration in this case). Thus, ethylene oligomerization can be promoted to higher hydrocarbon due to the decrease in platinum active sites (Table 4.2).

Table 4.2 Comparison data for conversion of ethanol over reg-[Pt]HZSM5.

Temperature Catalyst	350 °C		425 °C	
	[Pt]HZSM5	reg-[Pt]HZSM5	[Pt]HZSM5	reg-[Pt]HZSM5
% Mole				
C2	34.56	23.38	68.24	32.01
C3	20.29	23.91	15.78	31.89
C4 ⁺	43.54	50.56	14.55	32.52
BTX	1.61	2.15	1.43	3.58

(Catalyst; [Pt]HZSM5, and reg-[Pt]HZSM5. WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen. Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

4.3.3 The effect of water over [Pt]HZSM5

The effect of water over [Pt]HZSM5 has been accordingly investigated using different feed composition. It is found that oligomerization of ethylene in the reaction using 95 wt% ethanol as feed is higher than that using ethanol, but it is lower than that using pure ethylene (Figure 4.16).

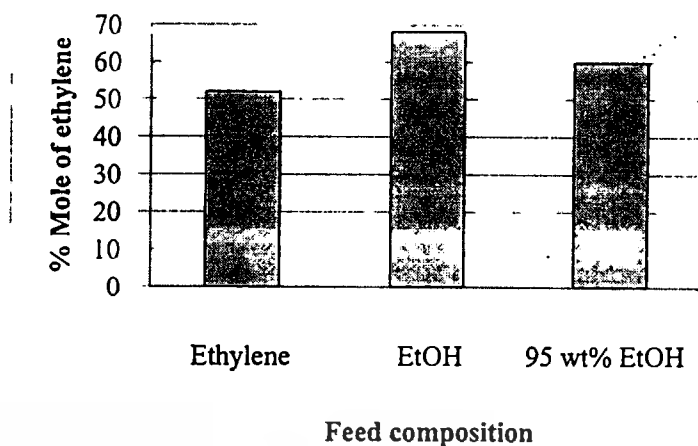
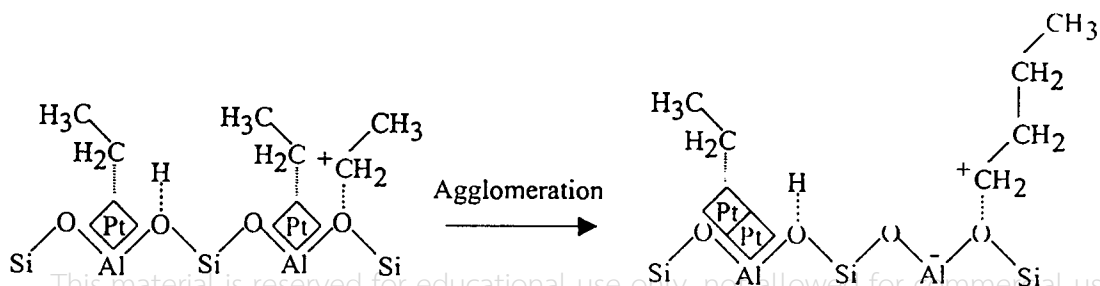


Figure 4.16 Effect of water content over [Pt]HZSM5 catalyst.

(Catalyst; [Pt]HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Using pure ethylene as feed would increase the ethylene oligomerization to a certain extent, although relatively higher platinum active site may well be present in the catalyst. This is because there is no the competitive adsorption of water over hydrocarbon which decreases in ethylene oligomerization.

However, it can be suggested from the reaction using 95 wt% ethanol that the presence of water can accelerate the platinum clustering, as compared to the reaction using absolute ethanol. Consequently, the active surface of platinum which inhibits ethylene oligomerization is decreased and the acidity is pronounced upon the agglomeration of platinum metal. This allows an increase in the rate of ethylene oligomerization as observed above. Therefore, high conversion of ethylene can be observed in 95 wt% ethanol, as compared to ethanol. The enhanced ethylene oligomerization which decrease the active surface of platinum can be depicted schematically as follows:



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In contrast to the fresh [Pt]HZSM5, the ethylene oligomerization can be increased when this catalyst is regenerated (Figure 4.17). This is because a clustering of platinum is expected in a higher extent over reg-[Pt]HZSM5, retaining the active activity for ethylene oligomerization. Moreover, the hydrophobicity of the framework could also be attained in reg-[Pt]HZSM5, in a similar manner as observed in reg-HZSM5 catalyst. In the reaction using ethylene as feed, the low activity for ethylene oligomerization is observed over reg-[Pt]HZSM5, as compared to the reaction using ethanol, and 95 wt% ethanol as feed. This is probably because there is no significant change of clustering in the reaction without water, while the presence of water can dramatically accelerate severe clustering of reg-[Pt]HZSM5.

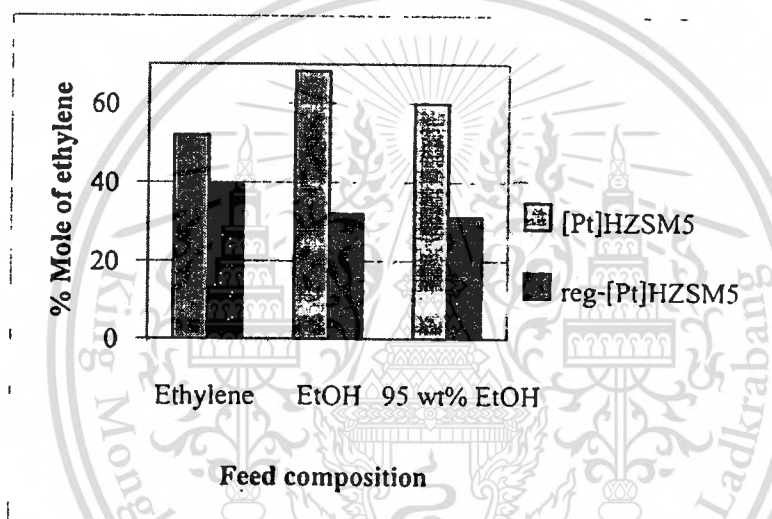
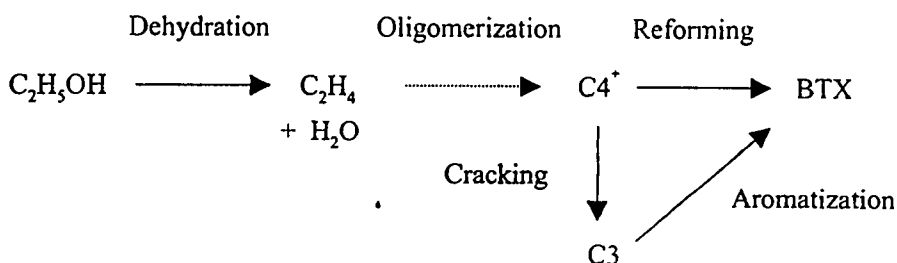


Figure 4.17 Effect of catalyst regeneration at different feed composition.

(Catalyst; [Pt]HZSM5 and reg-[Pt]HZSM5. Reaction temperature; 425 °C. WHSV; 2.88 hr⁻¹. Carrier gas; nitrogen, Feed; ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

From the above results, it can be concluded that although platinum incorporated ZSM5 has been proved to be an active catalyst for aromatic enhancement in the reaction of light alkane and naphthas, it is not an appropriate catalyst for ethanol conversion. This is because this catalyst inhibits ethylene oligomerization.



However, the presence of water in feed could readily promote clustering over [Pt] HZSM5, and retain acidity of the framework. Consequently, the ethylene oligomerization can be improved in the reaction using ethanol and 95 wt% ethanol as feed. The incorporated platinum metal does no function for enhancing yield of higher hydrocarbons.

4.3.4 The effect of temperature over [Ga]HZSM5

In the case of ethanol conversion over gallium incorporated HZSM5 by impregnation ([Ga]HZSM5), it is found that oligomerization of ethylene decreases with rise in temperature and concomitant decrease in C_4^+ hydrocarbons can be observed (Figure 4.18).

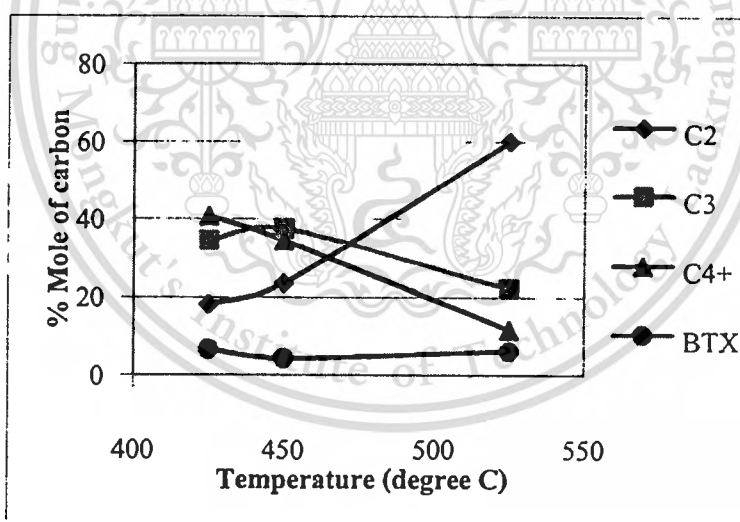
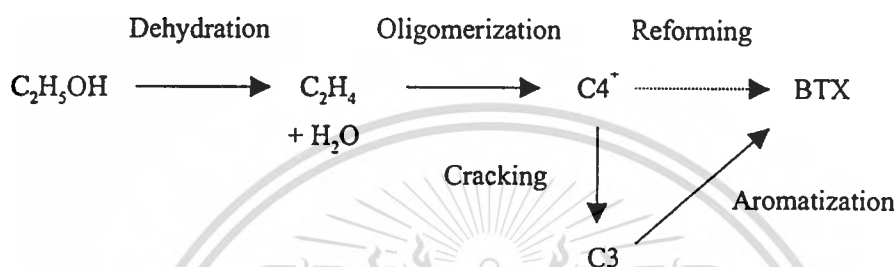


Figure 4.18 Temperature-dependence of hydrocarbon distribution over [Ga]HZSM5 catalyst.

(Catalyst; [Ga]HZSM5, WHSV; 2.88 hr⁻¹. Carrier gas; nitrogen. Feed; ethanol. average time on stream 2-4 hours, 100 % conversion of ethanol)

This result is consistent with the above suggestion that oligomerization reaction is thermodynamically retarded at higher temperature. While, rate of cracking which produce C3 hydrocarbon increase when temperature is risen. However, yield of C3 hydrocarbon at 525 °C is

exceedingly decreased. This may well be ascribed that the presence of gallium species could possibly converted C3 hydrocarbon to aromatic which is consistent with the observed higher yield of aromatic, although reforming reaction is inhibited by decrease in ethylene oligomerization. The assumption is well agreed with the previously report that gallium impregnated with HZSM5 is an active catalyst for light alkane aromatization at high temperature [21-25]. Consequently, the observed decrease in C3 hydrocarbon and increase in aromatic yield at 525 °C could only be account for aromatization activity of [Ga]HZSM5.



4.3.5 The effect of [Ga]HZSM5 regeneration

In Figure 4.19, after regeneration, the activity of regenerated [Ga]HZSM5 (reg-[Ga] HZSM5) appear to be in the same manner as observed in the fresh catalyst at 425 and 450 °C. On the other hand, there is significant effect of regeneration over this catalyst at high temperature (525 °C). It is found that a decrease in higher extent of ethylene oligomerization is observed.

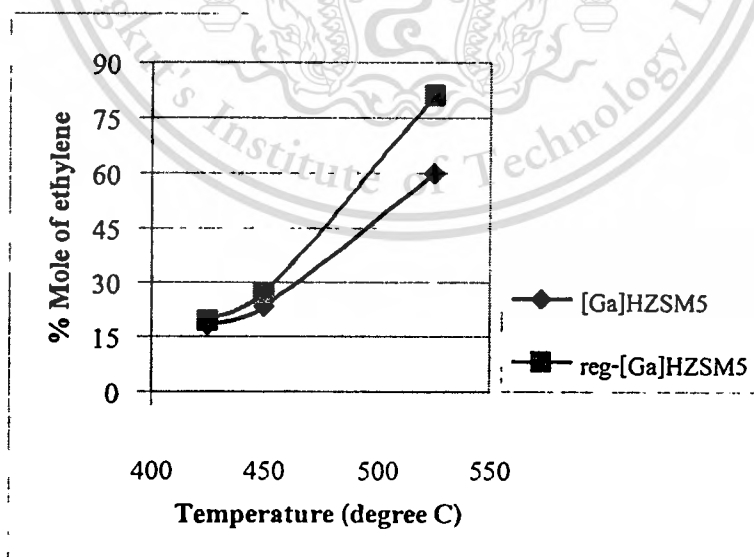


Figure 4.19 Effect of catalyst regeneration in ethanol conversion.

(Catalyst; [Ga]HZSM5 and reg-[Ga]HZSM5, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

This becomes clear that deep steaming during the ethanol conversion can damage framework of zeolite [15, 45]. This is confirmed by XRD pattern as shown in Figure 4.20.

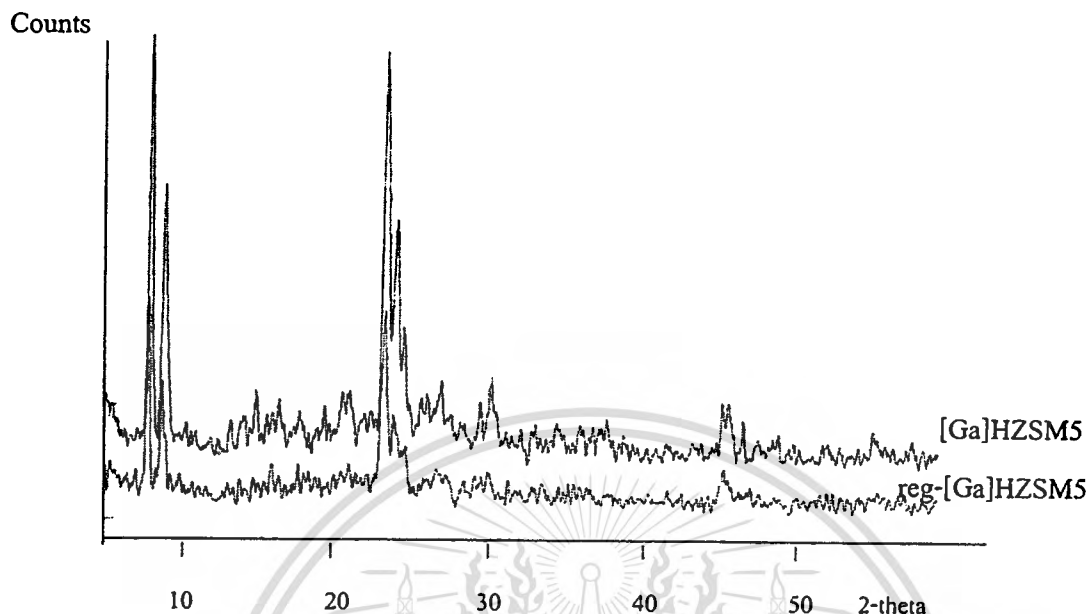


Figure 4.20 XRD pattern of [Ga] and reg-[Ga]HZSM5 after ethanol conversion at 525 °C.

It can be clearly seen that the peak intensity of [Ga]HZSM5 after the reaction at high temperature (525 °C) is lower than that the fresh catalyst which indicates the loss in crystallinity of the zeolite.

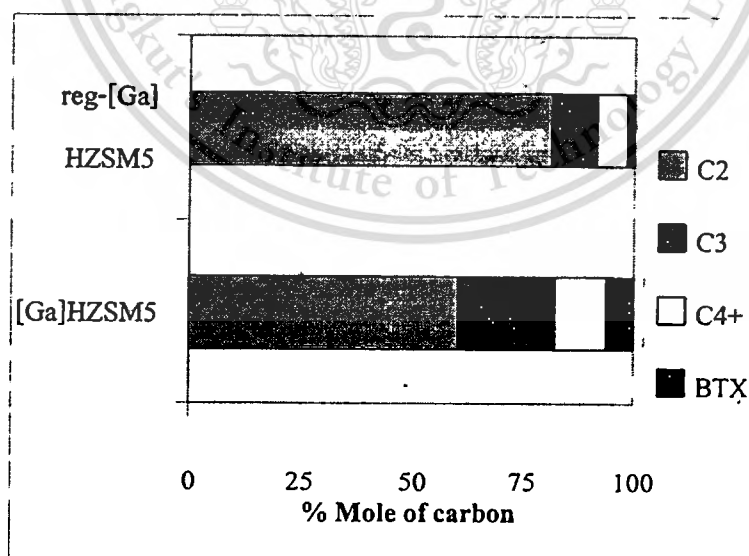


Figure 4.21 Effect of catalyst regeneration on product selectivity at 525 °C reaction temperature.

(Catalyst; [Ga]HZSM5 and reg-[Ga]HZSM5, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

In Figure 4.21, the significant difference in catalytic activity of bifunctional catalyst after framework damaging (525 °C) indicates the important role of acid function for aromatization activity. It is seem clear that, the extra-framework species alone are not active. Their combination with zeolitic acid sites is essential for high aromatization activity. Therefore, the limit of reaction temperature is found to be less than 450 °C for [Ga]HZSM5.

4.3.6 The effect of water over [Ga]HZSM5

In the case of the reaction using pure ethylene, ethanol, and 95 wt % ethanol as feed, it is surprised that ethylene oligomerization and yield of C₄⁺ hydrocarbon increase with rise in water content (Figure 4.22). It is worth noting that the presence of water either produced by ethanol dehydration or co-feed can change the behavior of [Ga]HZSM5. This is probably because in the presence of water, coordinatively unsaturated gallium oxide can be formed by the interaction of extra-framework gallium species with water. There would be additional strong acid sites which increase the rate of ethylene oligomerization. However, this shall not be the case for HZSM5 since the coordinatively unsaturated aluminium cations formed in the presence of water would also decrease the number of Brønsted acid sites. Thus, the decrease in ethylene oligomerization can be observed over HZSM5 when water is present. In contrast, the enhanced activity of [Ga] HZSM5 can promote reforming of higher hydrocarbon to aromatic, particularly in the presence of high water content (Table 4.3).

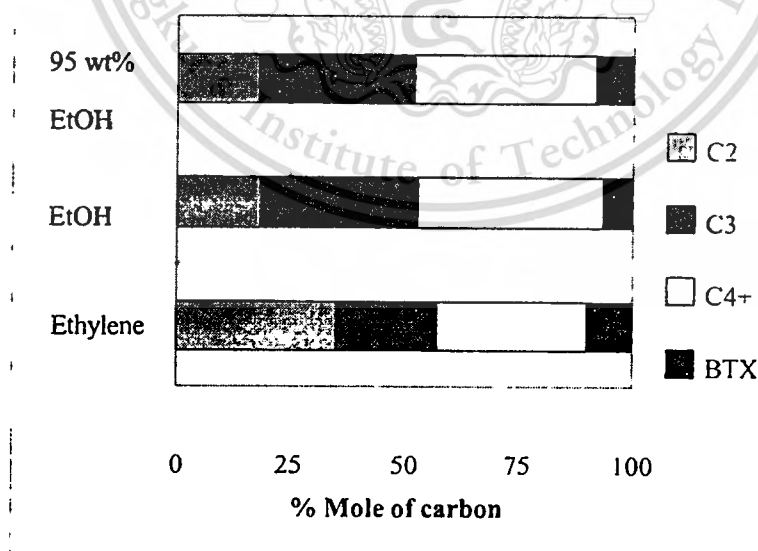


Figure 4.22 Hydrocarbon distribution over [Ga]HZSM5 at different feed composition.

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas: nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

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Table 4.3 Conversion of ethanol and 95 wt% ethanol over HZSM5 and [Ga]HZSM5 catalyst.

Feed Catalyst	Ethanol		95 wt% Ethanol	
	[Ga]HZSM5	HZSM5	[Ga]HZSM5	HZSM5
% Mole				
C2	18.16	17.44	17.83	23.61
C3	34.52	36.96	34.22	37.47
C4 ⁺	40.72	38.05	39.79	34.61
BTX	6.60	7.55	8.16	4.31

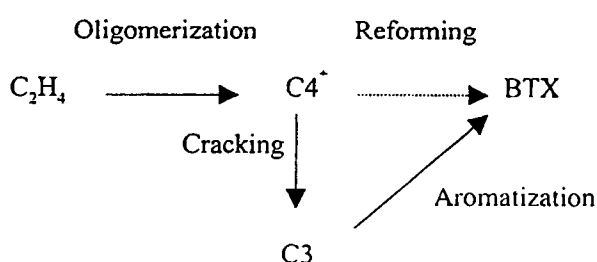
(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Table 4.4 Conversion of ethylene over HZSM5 and [Ga]HZSM5 catalyst.

% Mole of hydrocarbon	Type of catalyst	
	HZSM5	[Ga]HZSM5
C2	13.86	34.86
C3	39.93	22.14
C4 ⁺	38.68	32.81
BTX	7.53	10.19

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethylene, average time on stream 2-4 hours)

In the reaction using pure ethylene as feed over [Ga]HZSM5, although ethylene oligomerization is exceedingly lower than that HZSM5, yield of aromatic is still relatively high (Table 4.4). It is suggested that the increase yield of aromatic observed in the reaction using [Ga] HZSM5 would be predominantly derive from C3 aromatization. The reaction pathway for aromatic production in [Ga]HZSM5 could be illustrated as below:



After regeneration of [Ga]HZSM5, a similar trend of activity can be observed as in the reaction using fresh catalyst (Figure 4.23). It seems clear that, [Ga]HZSM5 catalyst can be regenerated to recover its activity. Moreover, the loss of activity would not be observed during the reaction (425 °C) and regeneration condition (550 °C). This is probably because the gallium species possess a strong interaction with the zeolite framework which arise from a high electrostatic field of the cationic species (presumably $(\text{GaO})^+$ [25, 49] in the reaction using ethylene as feed, and $\text{Ga}(\text{OH})$ [50-51] in the presence of water in the reaction). In contrast, platinum in the incorporated platinum metal catalyst can undergo agglomeration during the reaction because it is lacked of coulombic forces to bound in the zeolite framework. As the surface of the metal species is reduced, the activity of the catalyst would therefore be altered, as compared to the fresh catalyst.

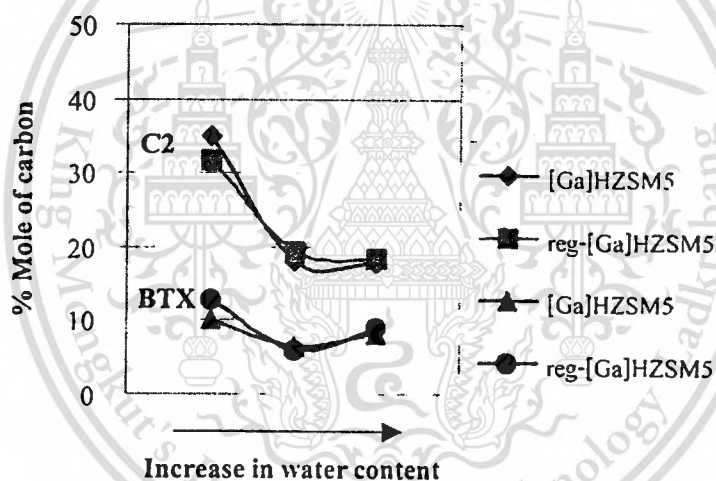


Figure 4.23 Effect of regeneration catalyst at different feed composition.

(Catalyst: [Ga]HZSM5, and reg-[Ga]HZSM5. Reaction temperature: 425 °C, WHSV: 2.88 hr⁻¹, Carrier gas; nitrogen, Feed: ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Regarding to the activity of [Ga]HZSM5 and reg-[Ga]HZSM5 using 95 wt % ethanol as feed, it is found that this catalyst is an appropriate catalyst for conversion of azeotropic ethanol (95 wt%) since it can enhance the aromatic selectivity and the low cost feed can be used.

4.3.7 The effect of polyfunctional catalyst [PtGa]HZSM5

From the above results, light olefin is namely produced in the reaction using [Pt]HZSM5 while [Ga]HZSM5 enhance aromatization of light olefin. Accordingly, it is suggested that the mixture of these metals ([PtGa]HZSM5) would probably increase yield of aromatic in the ethanol conversion. This is derived from the concept of polyfunctional catalyst, in which the metal presented can function separately. Thus, [PtGa]HZSM5, a so called polyfunctional catalyst is investigated using ethylene and ethanol as feed.

Table 4.5 Conversion of ethylene over [Ga]HZSM5, [Pt]HZSM5, [PtGa]HZSM5 and cal-[PtGa]HZSM5 catalyst.

% Mole of hydrocarbon	Type of catalyst			
	[Pt]HZSM5	[Ga]HZSM5	[PtGa]HZSM5	cal-[PtGa]HZSM5 ^a
C2	52.06	34.86	43.98	43.47
C3	22.98	22.14	23.00	22.56
C4 ⁺	22.20	32.81	26.20	27.50
BTX	2.76	10.19	6.82	6.47

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethylene, average time on stream 2-4 hours)

^aAverage % mole of products, calculated from each individual catalyst [Yield of products over [Pt]HZSM5 + Yield of the same product over [Ga]HZSM5]/2

The study of this mixed catalyst shows that the activity of the catalyst [PtGa]HZSM5 is in between the activity of [Ga]HZSM5 and [Pt]HZSM5. It is evident that the catalytic activity of the mixed catalyst using ethylene as feed is similar to the average activity of [Pt]HZSM5 and [Ga]HZSM5 (cal-[PtGa]HZSM5, Table 4.5). This is clearly shown that the metal presented in the mixed catalyst independently promote its own catalytic activity. Since, there is 50 % of [Ga]HZSM5 and [Pt]HZSM5 in the mixture, each catalyst contributes only half of activity, as compared to the parent catalysts ([Pt]HZSM5 and [Ga]HZSM5). As a results, total product obtained from the mixed catalyst is an average of the parents ones.

Table 4.6 Conversion of ethanol over [Ga]HZSM5, [Pt]HZSM5, [PtGa]HZSM5 and cal-[PtGa]HZSM5 catalyst.

% Mole of hydrocarbon	Type of catalyst			
	[Pt]HZSM5	[Ga]HZSM5	[PtGa]HZSM5	cal-[PtGa]HZSM5 ^a
C2	68.24	18.16	29.58	43.20
C3	15.78	34.52	30.96	25.15
C4 ⁺	14.55	40.72	34.12	27.64
BTX	1.43	6.60	5.34	4.01

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹. Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

^aAverage % mole of products, calculated from each individual catalyst [Yield of products over [Pt]HZSM5 + Yield of the same product over [Ga]HZSM5]/2

On the other hand, there is significant change in the activity of the mixed catalyst in the reaction using ethanol as feed (Table 4.6). It is suggested that the presence of water can increase the products owing to the increase in oligomerization activity of gallium loaded catalyst when water is presented (as discussed in section 4.3.6). As higher yields of high molecular weight hydrocarbon are obtained, [Pt]HZSM5 can consequently reform the oligomerized products to aromatics. This result is an additional evidence supporting the change in behavior of [Ga]HZSM5 when water is presented. However, there is no synergetic effect on catalytic activity for the mixed catalyst. Accordingly, [PtGa]HZSM5 can be regarded as a polyfunctional catalyst, even though it is a poor catalyst for ethanol conversion.

4.4 The conversion of ethanol over silver incorporated ZSM5

4.4.1 The effect of silver species

Regarding to the initial conversion (Figure 4.24), it is found that the ethylene oligomerization over both AgHZSM5 and AgNaZSM5 is exceedingly low, as compared to HZSM5.

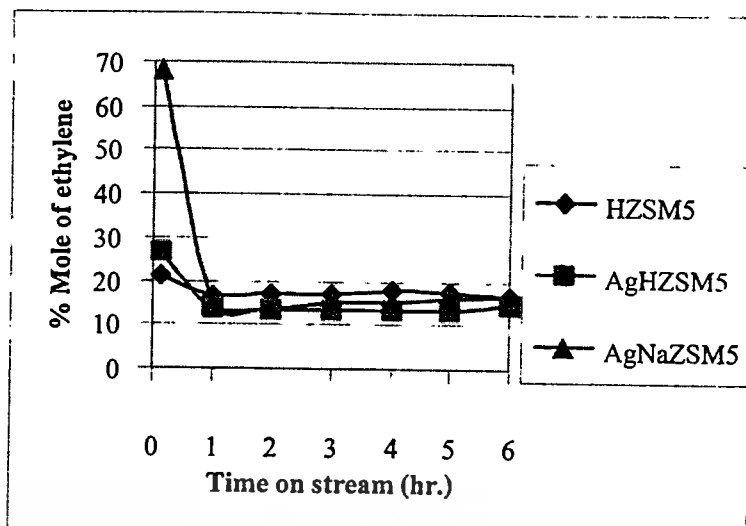
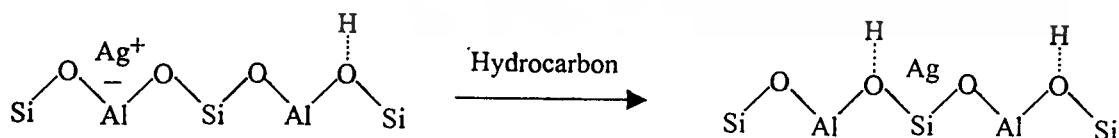


Figure 4.24 Change in oligomerization activity with time on stream over HZSM5, AgHZSM5, and AgNaZSM5 catalyst.

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, 100 % conversion of ethanol)

It becomes clear that the concentration of acid site is initially responsible for the oligomerization activity. As the order of acidity is in the rank of HZSM5 > AgHZSM5 > AgNaZSM5, the oligomerization activity was reduced accordingly. Surprisingly, after an hour on stream, the increase in an extensive oligomerization over both of silver incorporated ZSM5s was observed (Figure 4.24). It indicates that silver cation could possibly be reduced during the reaction, to form silver metal, bearing consecutive acid sites within the framework. Formation of the silver metal and the acid site are depicted schematically as follows:



This conclusion is supported by the observed XRD pattern of AgHZSM5 with high intensity after the reaction (Figure 4.25). It can be clearly seen that there is an additional phase of silver metal (100) formed after the reaction.

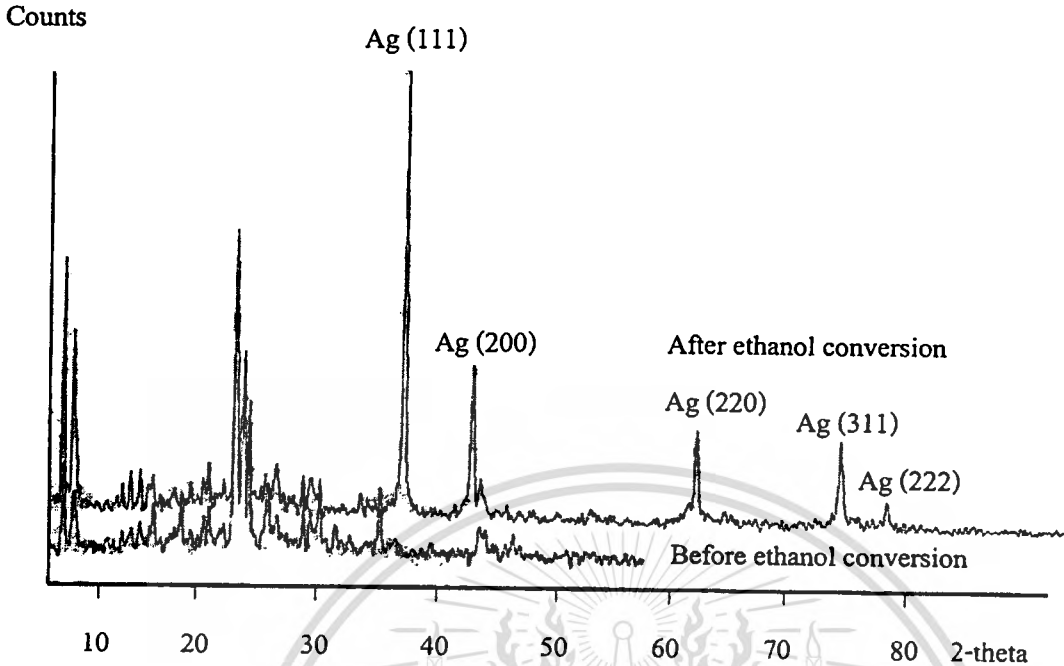


Figure 4.25 XRD pattern of AgHZSM5 after ethanol conversion at 425 °C.

As the acidity is recovered upon the reduction of silver cation, the oligomerization is therefore enhanced. This is also observed over AgNaZSM5. However, a slightly lower activity of this catalyst can be attributed to a relatively smaller number of active sites since 36.83 % of sodium is also presented as exchangeable cations (see elemental analysis, Appendix A).

Further evidence supporting the improved activity was observed, when the silver incorporated zeolite was regenerated. It is shown in Figure 4.26 that a higher extent of ethylene oligomerization at initial conversion was registered.

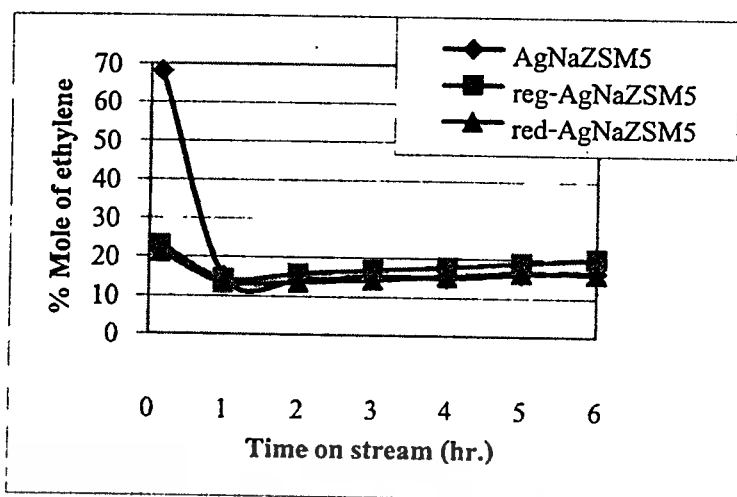


Figure 4.26 Change in oligomerization activity with time on stream over AgNaZSM5, regenerated of AgNaZSM5 (reg-AgNaZSM5)^a; and pretreatment with hydrogen of AgNaZSM5 (red-AgNaZSM5)^b catalyst.

^aCalcination by air at 550 °C for 5 hours.. ^bReduction by hydrogen at 350 °C for 2 hours.

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Moreover, the activity of the catalyst, previously pretreated with hydrogen at 350 °C for 2 hours, is similar to the regenerated catalyst (Figure 4.26). This is also consistent with the above suggestion that the reduction of silver cation plays a key role for creating an acid site of the silver incorporated zeolites.

Not only the increased oligomerization activity is obtained from the silver loaded catalysts, but also a significant increase in the aromatic selectivity is revealed at steady state (Figure 4.27).

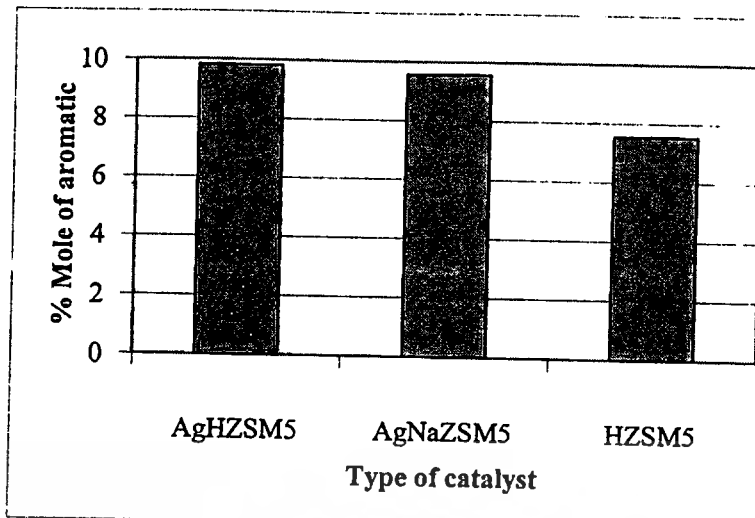


Figure 4.27 Effect of incorporated silver by ion exchange on aromatic selectivity.

(Catalyst; AgHZSM5, AgNaZSM5, and HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Using zeolites containing silver by ion exchange and impregnation as catalysts were previously reported for the observed high aromatic yield in light alkane [27] and methanol conversion [27]. Nevertheless, the role of silver species in the catalyst was not studied. In ethanol conversion, the improved aromatic selectivity is presumably accounted for the enhanced oligomerization activity. This is suggested from the observed increase in aromatic yield, together with oligomerization of ethylene activity (Figure 4.28).

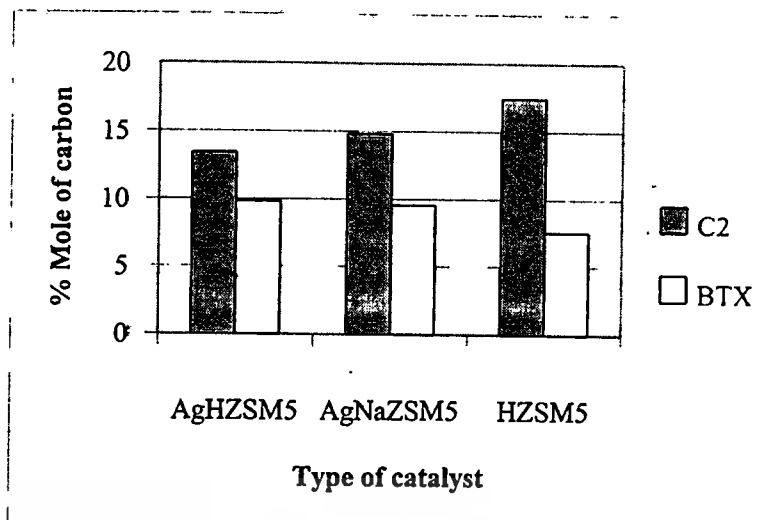
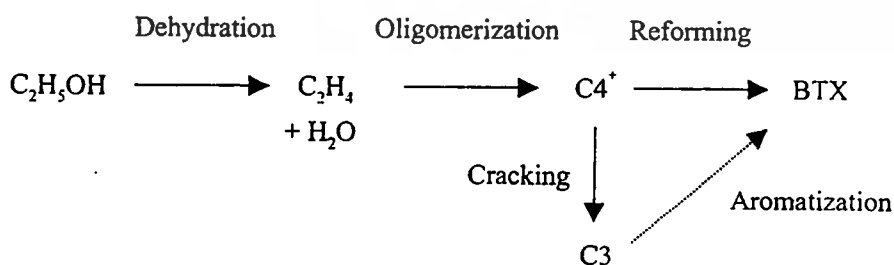


Figure 4.28 Effect of incorporated silver by ion exchange on oligomerization activity and aromatic formation.

(Catalyst; AgHZSM5, AgNaZSM5, and HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹. Carrier gas; nitrogen. Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

This is probably because ethylene can readily adsorb on silver species which would facilitate the oligomerization over acid catalyst. The fact that ethylene can adsorb on silver metal, has been previously reported [16]. In addition, silver loaded catalyst can enhance C-H bond cleavage [27] which would promote dehydrocyclization of higher molecular weight hydrocarbon to aromatics. This supports the improved aromatic selectivity when the enhanced oligomerization activity is observed.



The fact that dehydrocyclization is essential for aromatic selectivity can be justified by the reaction using hydrogen as carrier gas. It is found that the yield of aromatic was decreased in the presence of hydrogen (Figure 4.29).

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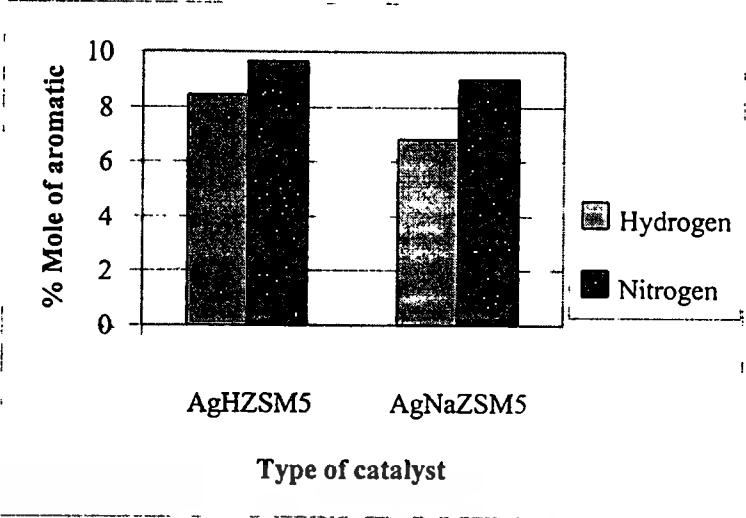


Figure 4.29 Effect of carrier gas for aromatic formation.

(Catalyst; AgHZSM5, and AgNaZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, and hydrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

This is because hydrogen can thermodynamically reduce the dehydrogenation activity of high molecular weight hydrocarbon. Therefore, the increase in C4⁺ hydrocarbon was observed in the reaction using hydrogen as carrier gas, while oligomerization activity is slightly the same (Figure 4.30).

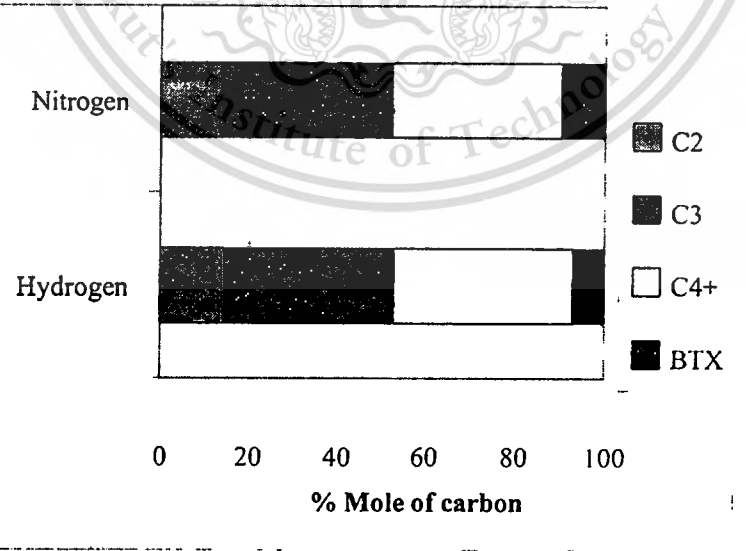


Figure 4.30 Effect of carrier gas on product distribution.

(Catalyst; AgHZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, and hydrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

In the case of silver incorporated HZSM5 by impregnation ([Ag]HZSM5), it is found that the activity of this catalyst is much lower than those incorporated by ion exchange and HZSM5 (Figure 4.31).

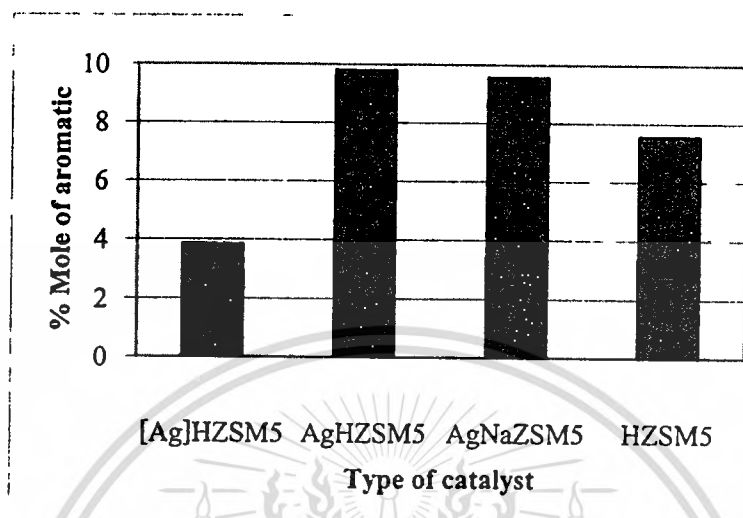


Figure 4.31 Effect of incorporated silver by impregnation on aromatic selectivity.

(Catalyst; [Ag]HZSM5, AgHZSM5, AgNaZSM5, and HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

It is suggested that the incorporated silver species by impregnation may well be present in large proportion on the external surface of a zeolite crystal [15]. After calcination, this silver species is likely to be an agglomeration of silver oxide. The pore window of the zeolite can also be blocked by the silver oxide which is evidenced by the reduced surface area (82 m²/g), as compared to AgHZSM5 (263 m²/g) and AgNaZSM5 (196 m²/g). This would result in the decrease in both aromatic yield and oligomerization of ethylene, as observed in Figure 4.32.

It may be concluded that silver oxide is not an active species for the ethylene oligomerization. Moreover, this species is hardly reduced to silver metal, the active species, as claimed. This assumption is confirmed by the observed low-intensity XRD pattern of silver metal in [Ag]HZSM5 after the reaction (Figure 4.33).

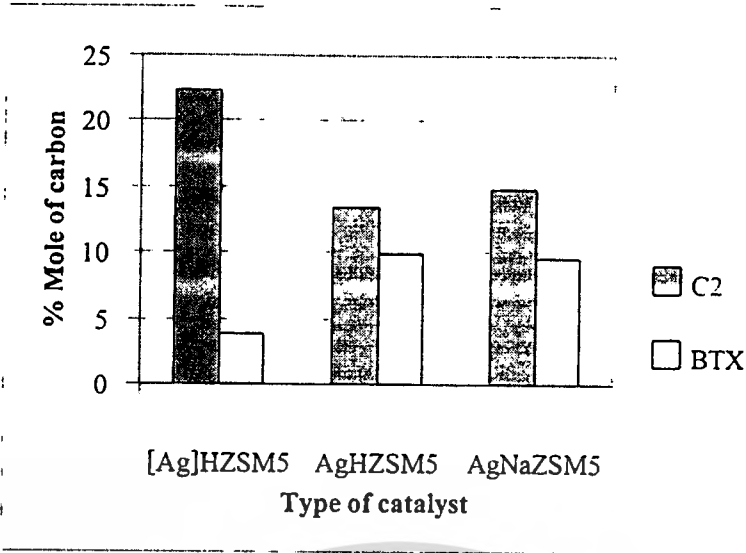


Figure 4.32 Effect of incorporated silver by impregnation on oligomerization activity and aromatic formation.

(Catalyst; [Ag]HZSM5, AgHZSM5, and AgNaZSM5. Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

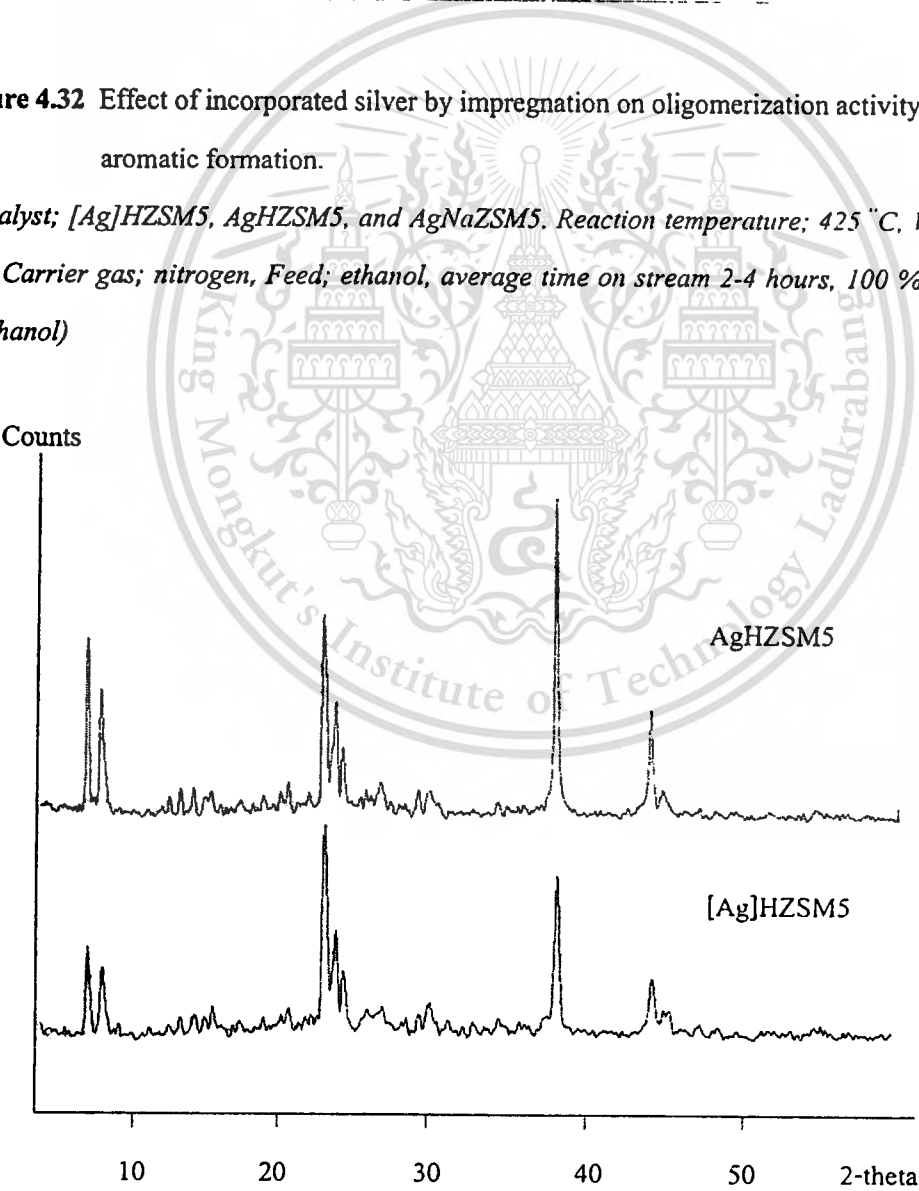


Figure 4.33 XRD pattern of AgHZSM5 and [Ag]HZSM5 after ethanol conversion at 425 °C.

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4.4.2 The effect of temperature over silver incorporated ZSM5

The study on effect of temperature shows that a similar trend of activity can be obtained, as compared to HZSM5 (Figure 4.34). Yield of ethylene, and C3 hydrocarbon increase with rise in temperature while C4⁺ hydrocarbons decrease when the temperature is risen. However, the selectivity of aromatic increase with rise in temperature but then decrease at 450 °C.

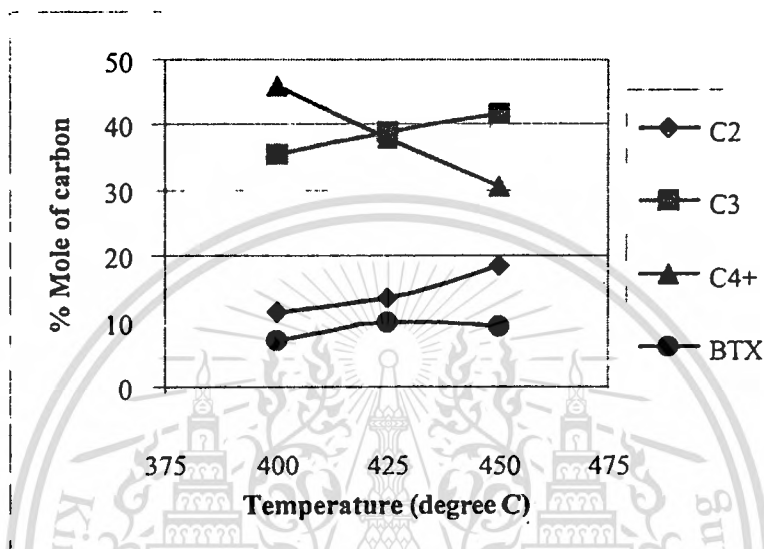


Figure 4.34 Temperature-dependence of hydrocarbon distribution over AgHZSM5 catalyst.

(WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

This can be explained by the thermodynamic point of view that the rate of ethylene oligomerization is promoted at low temperature, while, at higher temperature, hydrogen transfer to form aromatic is favored. Thus, a balance between oligomerization and hydrogen transfer is essential for obtaining the high aromatic yield which is already discussed in section 4.2.2.

As compared to AgHZSM5, there is no significant change in the activity of regenerated catalyst (reg-AgHZSM5) at 400-425 °C. However, at 450 °C the selectivity of aromatic over reg-AgHZSM5 is exceedingly lower than the fresh catalyst (Figure 4.35). While, a higher yield of C4⁺ hydrocarbons, the intermediate reactant of reforming reaction is observed, as compared to the fresh catalyst. From the Figure 4.35, it indicated that at high temperature the dehydrocyclization or reforming activity is retarded in the regenerated catalyst which imply to loss of silver metal during the reaction presumably by clustering.

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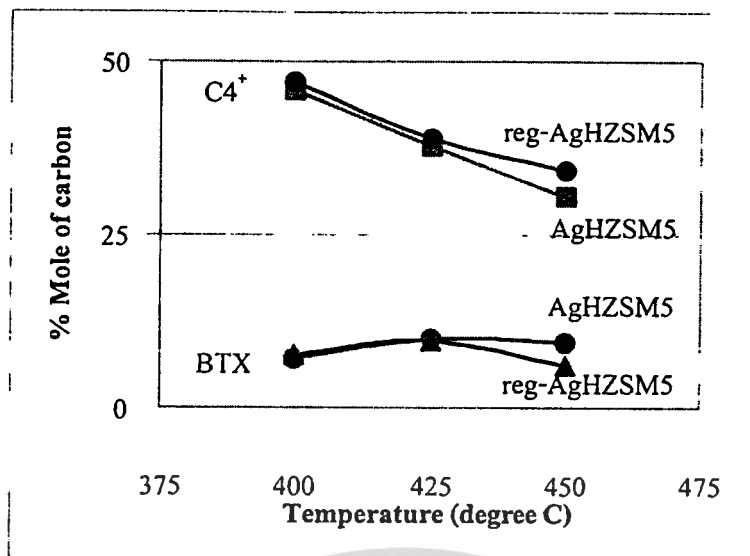


Figure 4.35 Temperature-dependence of C4⁺ and aromatic hydrocarbon over reg-AgHZSM5 catalyst.

(Catalyst; AgHZSM5 and reg-AgHZSM5; WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

The thermally induced deactivation of catalyst by loss of the catalytic surface area has been previously reported [15] to result from the crystal growth in the metal phase. This is expected in the regeneration catalyst at high temperature because a clustering of silver metal can take place in the temperature range of 340-480 °C [15]. Moreover, clustering process is generally accelerated by the presence of water vapor, which is consistent with the results obtained from regenerated [Pt]HZSM5 catalyst (as discussed in section 4.3.2). As the surface area of the active species is reduced by regeneration, the activity of the catalyst would therefore be decreased at high temperature.

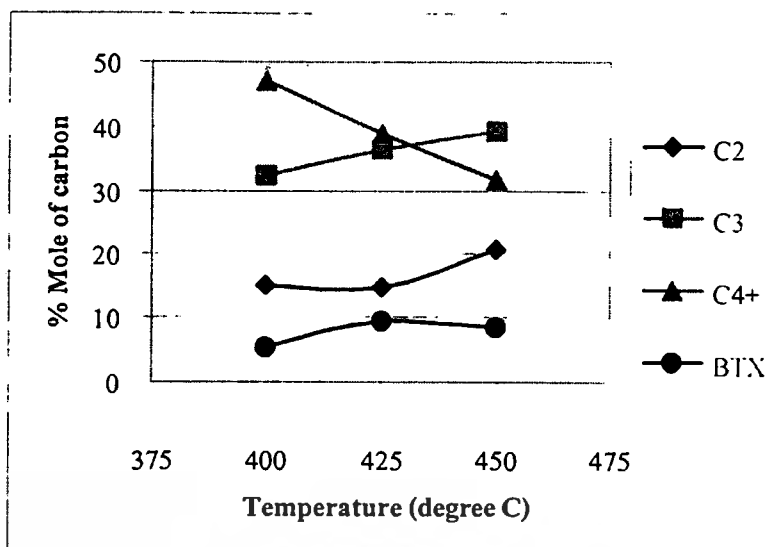


Figure 4.36 Temperature-dependence of hydrocarbon distribution on ethanol conversion over AgNaZSM5 catalyst.

(WHSV; 2.88 hr^{-1} , Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

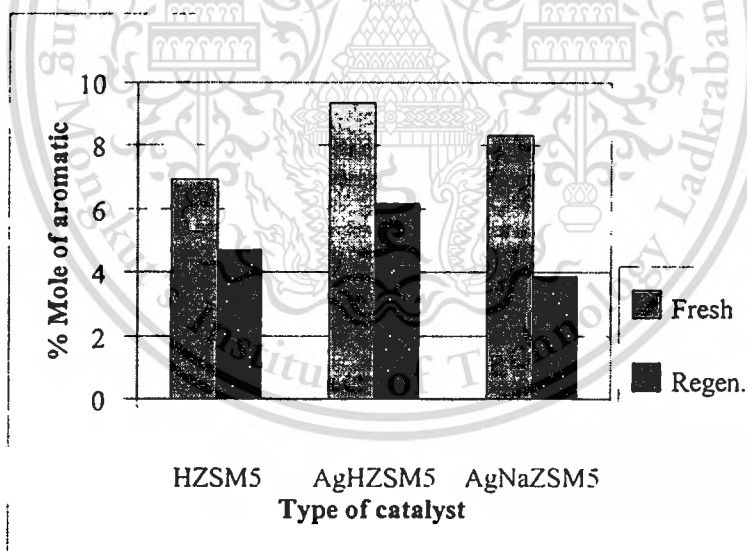


Figure 4.37 Effect of catalyst regeneration on aromatic formation.

(Catalyst; HZSM5, AgHZSM5, and AgNaZSM5, Reaction temperature: 450°C , WHSV: 2.88 hr^{-1} , Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

The effect of temperature on product selectivity over AgNaZSM5 is similar to that over AgHZSM5 (Figure 4.36). Except for the regenerated AgNaZSM5, a decrease in higher extent of

aromatic selectivity is obtained in the reaction, as compared to reg-AgHZSM5 (Figure 4.37). This may well arise from the decrease in effective pore diameter of the catalyst after severe clustering. Since there is a number of exchangeable sodium cation in the framework. The metal cluster formed at high temperature may inhibit diffusion of high molecular weight hydrocarbon and consequently the formation of aromatic. The decrease in effective pore diameter can be evidenced by a shift in XRD pattern of AgNaZSM5, as compared to AgHZSM5 (Figure 4.38).

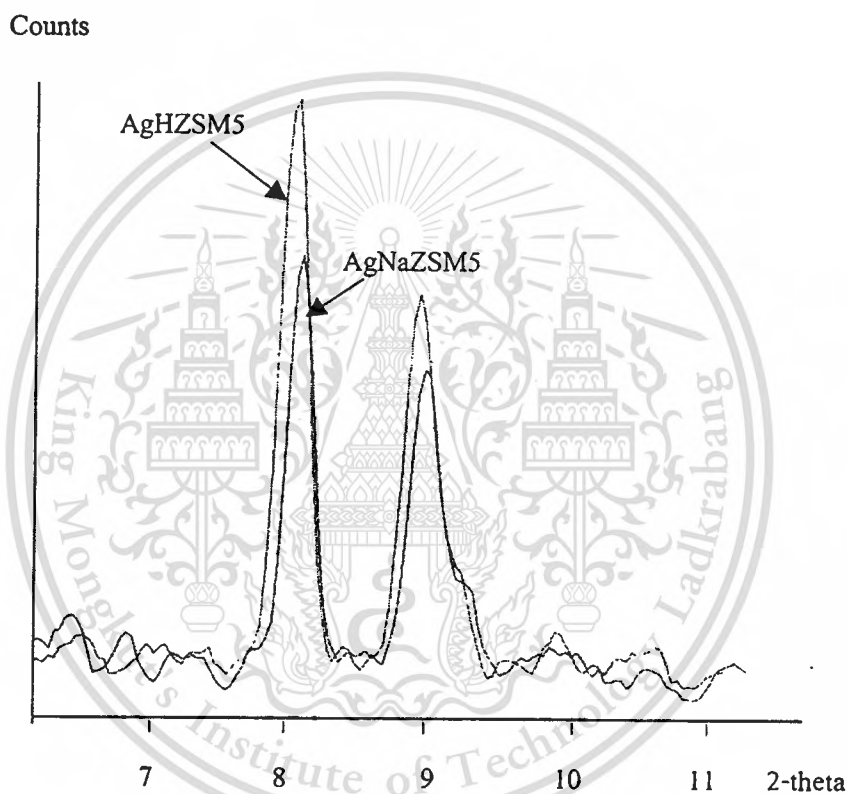


Figure 4.38 XRD pattern of AgHZSM5 and AgNaZSM5 after ethanol conversion at 450 °C.

Further evidence supporting the decreased pore diameter after severe clustering were observed by the reduced measured-pore width which obtained by gas adsorption analysis of red-AgNaZSM5 (3.90 angstroms) and red-AgHZSM5 (4.79 angstroms), as compared to fresh AgNaZSM5 (5.20 angstroms) and fresh AgHZSM5 (5.28 angstroms), respectively. The HK plot for pore width analysis of these catalyst are shown in Appendix E.

Accordingly, as a severe clustering take places over reg-AgNaZSM5 at high temperature, a marked decrease in aromatic yield is just revealed.

4.4.3 The effect of water over silver incorporated ZSM5

In the case of AgHZSM5 and AgNaZSM5, it can be clearly seen that oligomerization activity of silver incorporated catalyst is slightly reduced when water is present in the feed (Figure 4.39). Accordingly, these catalysts appear to be more resistant to water, as compared to HZSM5.

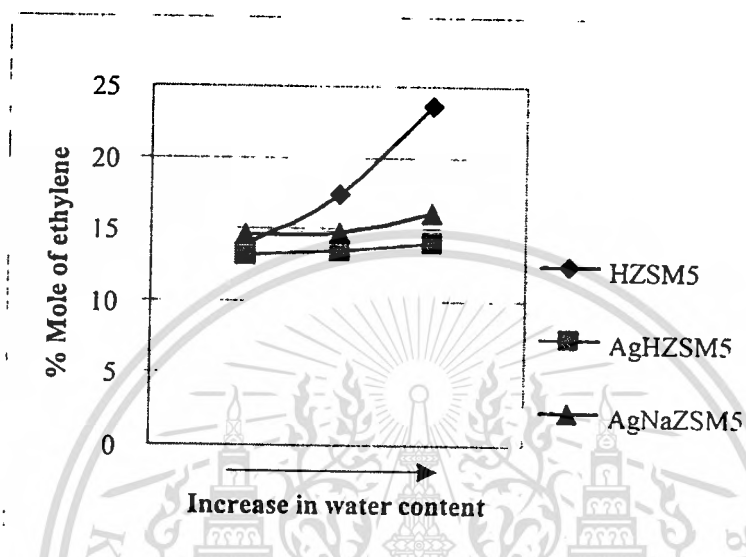


Figure 4.39 Effect of water content over silver incorporated ZSM5 by ion exchange.

(Catalyst; HZSM5, AgHZSM5, and AgNaZSM5. Reaction temperature; 425 °C. WHSV; 2.88 hr⁻¹. Carrier gas; nitrogen, Feed; ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

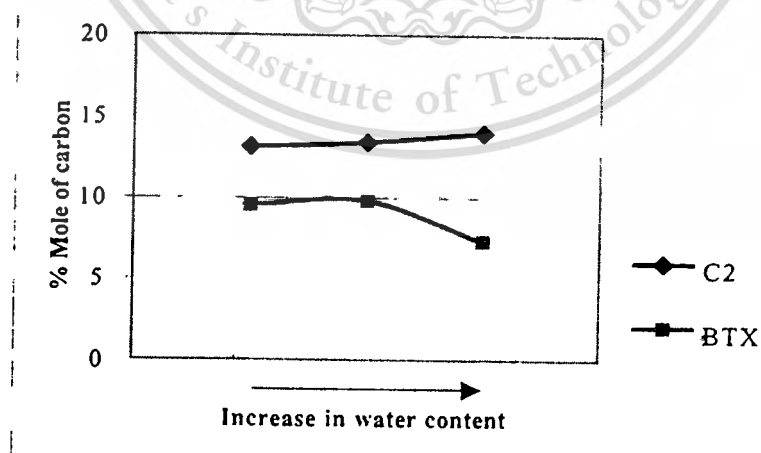


Figure 4.40 Effect of water content for aromatic formation over AgHZSM5 catalyst.

(Catalyst; AgHZSM5, Reaction temperature; 425 °C. WHSV; 2.88 hr⁻¹. Carrier gas; nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

However, the yield of aromatic is extensively decreased when a large amount of water is present in the feed (Figure 4.40). Despite, oligomerization of ethylene is slightly change since the silver species facilitate the adsorption of ethylene. This is probably because the water can reduce rate of hydrogen transfer for aromatic formation. This assumption is well agree with the previous report, on the methanol conversion over HZSM5 using water as co-feed [36-37]. The presence of water was also shown to inhibit the formation of the polynuclear aromatics which results in the coke formation. Accordingly, the lower yield of aromatics (the coke precursors) can imply the inhibition of hydrogen transfer. This is consistent with the decrease in aromatic yield, despite ethylene oligomerization is slightly changed in the reaction using water as co-feed.

In contrast to other silver incorporated HZSM5, [Ag]HZSM5, shows an extensive decrease in oligomerization, when the water is increased (Figure 4.41). This is similar to the results obtained in the case of HZSM5 which indicates that this silver species, presumably silver oxide is not responsible for ethylene oligomerization and only the active acid sites take part in the catalytic activity. Accordingly, the competitive adsorption of water over acid site would readily reduce rate of the reaction, as observed in the reaction with high water content.

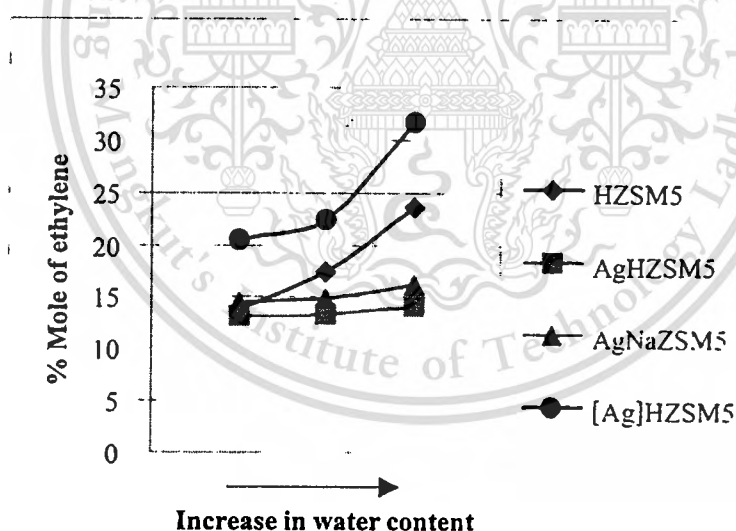


Figure 4.41 Effect of water content over silver incorporated ZSM5 by impregnation.

(Catalyst; HZSM5, AgHZSM5, AgNaZSM5, and [Ag]HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

In conclusion, it is shown that both AgHZSM5 and [Ga]HZSM5 can enhance the aromatic selectivity, as compared with HZSM5. However, the difference in catalytic activity of

AgHZSM5 and [Ga]HZSM5 can be revealed in the reaction using ethylene (Figure 4.42). [Ga]HZSM5 can produce aromatic from C3 aromatization, while in the case of AgHZSM5, aromatic is namely produced by C4⁺ hydrocarbons reforming (as discussed in the section 4.3.6 and 4.4.3).

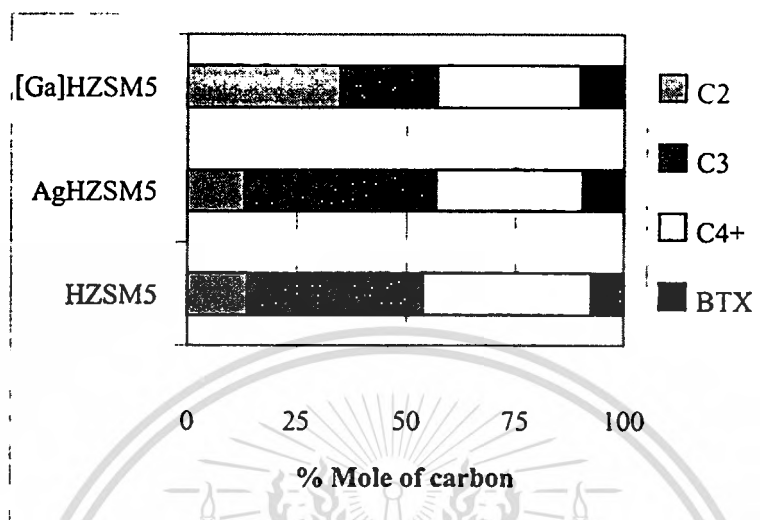


Figure 4.42 Hydrocarbon yield on ethylene conversion over HZSM5, AgHZSM5, and [Ga]HZSM5 catalyst.

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, average time on stream 2-4 hours)

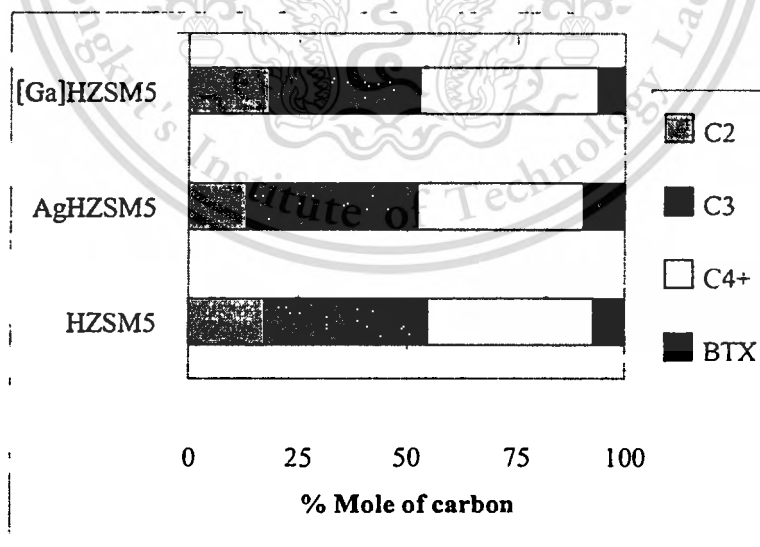


Figure 4.43 Hydrocarbon yield on ethanol conversion over HZSM5, AgHZSM5, and [Ga]HZSM5 catalyst.

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹; Carrier gas; nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

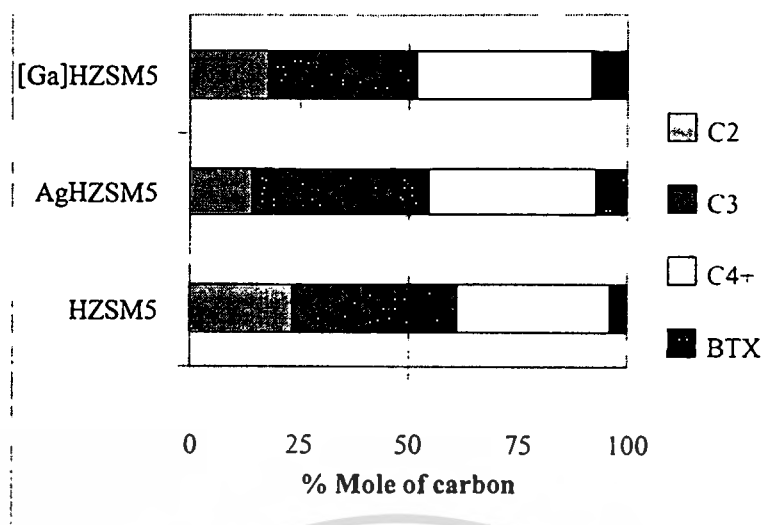


Figure 4.44 Hydrocarbon yield on 95 wt% ethanol conversion over HZSM5, AgHZSM5.

and [Ga]HZSM5 catalyst.

(Reaction temperature; 425 °C, WHSV: 2.88 hr⁻¹. Carrier gas: nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

The presence of water in the reaction using HZSM5 play a significant role in determination of ethylene oligomerization and product yields by its competitive adsorption against the hydrocarbon precursors. However, in the silver incorporated catalyst, AgHZSM5 is resistant to water, as compared with HZSM5 and this catalyst is appropriate for the reaction using absolute ethanol as feed (Figure 4.43). This shall not be the case of [Ga]HZSM5 since coordinatively unsaturated gallium species can be formed by interaction of gallium extra-framework with water. There is no longer active sites for lower olefin aromatization, in [Ga]HZSM5 for the reaction containing water in feed. The enhanced activity of [Ga]HZSM5 can only be obtained in the reaction using 95 wt% ethanol as feed, where additional acid sites are largely produced (Figure 4.44). This increases the oligomerization of ethylene and aromatics produced by reforming, in a similar manner to those using HZSM5 and AgHZSM5 as catalysts.

4.5 The BTX selectivity over HZSM5, AgHZSM5, and [Ga]HZSM5 catalyst

The BTX selectivity (benzene, toluene, and C8 aromatics including *o*-xylene, *m*-xylene, *p*-xylene, and ethyl benzene) for ethanol conversion obtained over HZSM5 catalyst as a function of contact time are shown in Figure 4.45.

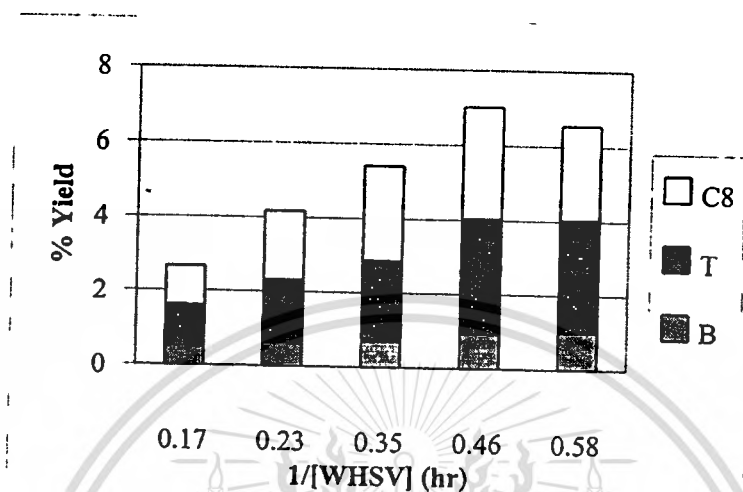
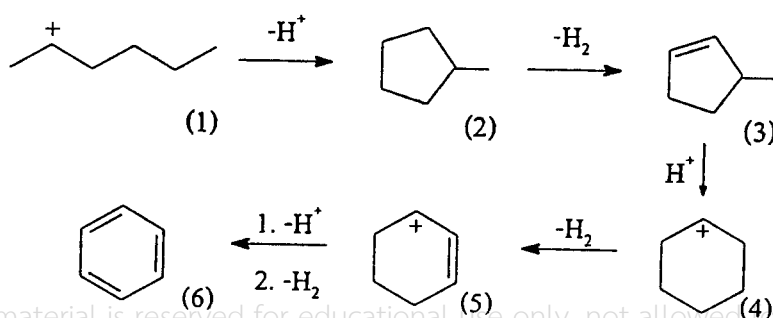


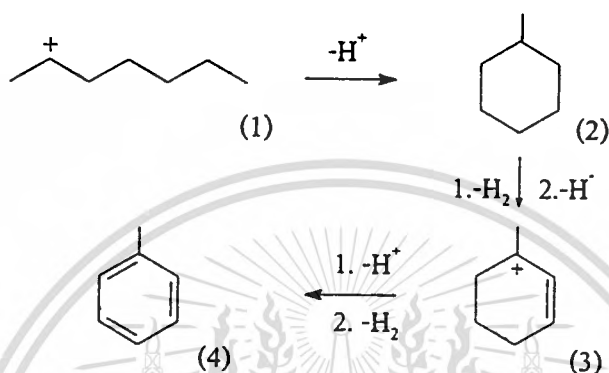
Figure 4.45 Contact time-dependence of aromatic distribution over HZSM5.

(Catalyst; HZSM5, Reaction temperature; 375 °C, Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

It is found that over the range of contact time, the benzene selectivity is lower than the toluene and C8 aromatics selectivity. It is suggested that the reforming of C6 hydrocarbons to benzene is slow. This is because the sequence of reactions involves a protonated C6 hydrocarbons (1) which can be converted primarily into methylcyclopentane (2). This species can be dehydrogenated to give methylcyclopentene (3), which undergoes isomerization to give protonated cyclohexane (4), and subsequent reforming to benzene (6) [12, 22]. The reaction pathway for the formation of benzene via C6 hydrocarbons reforming can be postulated as follows:



In the case of toluene and C8 aromatics, cyclization can be readily directed to the formation of a six-membered ring (i.e. 1, 6 carbon-carbon closure) [12]. The dehydrogenation step would be relatively fast, since the formation of an allylic carbocation (3) would be readily facilitated leading to the formation of benzene derivatives (alkyl benzene). For example, the formation of toluene can occur by the following successive step:



However, not only the aromatic formation involves cyclization to form five and six-membered ring, but aromatic could also undergo consecutive alkylation, disproportionation, and isomerization [14-17]. This can be clearly seen from the results that the benzene selectivity is slightly increased, when the contact time is risen (Figure 4.45). In addition, toluene and C8 aromatics selectivity predominantly increase with rise in contact time. This indicates a feasibility for the formation of higher aromatics (> C7) against benzene, which is common in hydrocarbon conversion over acid catalysts [14-17].

Further evidence supporting the low rate of benzene formation was observed, when the reactions were investigated using variation of temperature. It is shown in Figure 4.46 that a lower yield of benzene is obtained, as compared to higher aromatics.

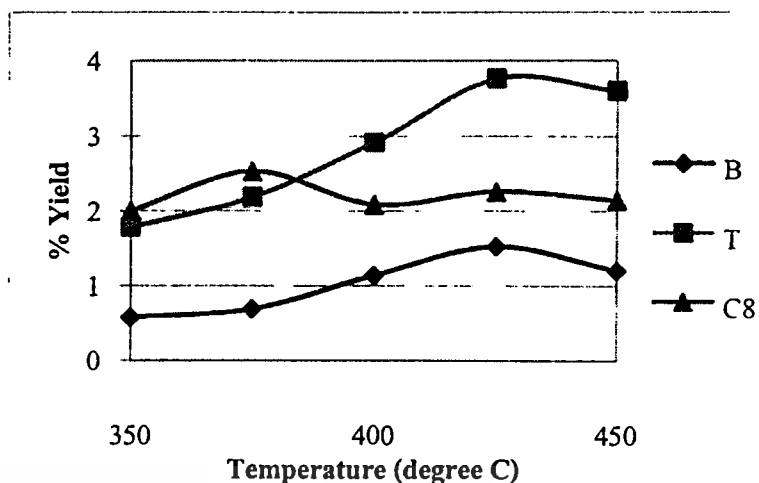


Figure 4.46 Temperature-dependence of aromatic distribution over HZSM5.

(Catalyst; HZSM5, WHSV; 2.88 hr^{-1} , Carrier gas; nitrogen, Feed; ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

Moreover, it is found that the observed benzene and toluene selectivity are increased with the rise in temperature (350-425 °C). This is because the higher temperature is favored for hydrogen transfer (as discussed in section 4.2.2). However, at higher reaction temperature (400-425 °C), the C8 aromatics selectivity is low, as compared to the 375 °C reaction temperature. This is probably because the inhibition of ethylene oligomerization particularly to form C8 hydrocarbons (precursors of C8 aromatics) at higher temperature which is already discussed in section 4.2.2.

In addition, the aromatic yield in the reaction using different feed composition over HZSM5 is shown in Figure 4.47.

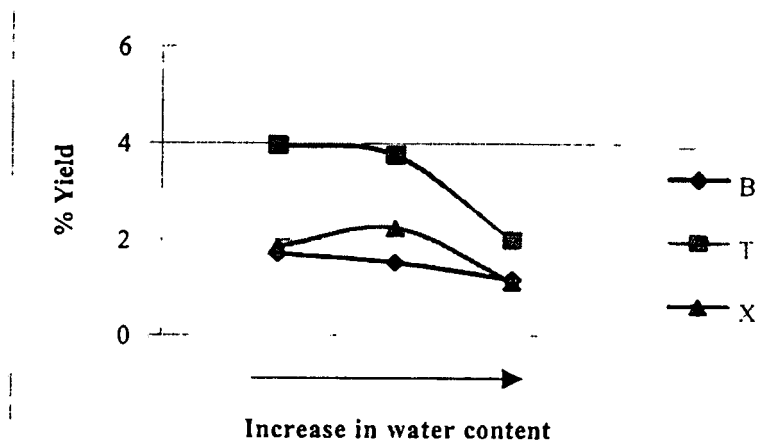


Figure 4.47 Effect of water for aromatic yield over HZSM5.

(Catalyst; HZSM5, Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas: nitrogen. Feed: ethylene, ethanol, and 95 wt% ethanol, average time on stream 2-4 hours, 100 % conversion of ethanol)

It is found that the major product in aromatic fraction happens to be toluene. This indicates that there is no significant change of BTX yield in the presence of water either produced by ethanol dehydration or present as co-feed. Since the 100 % ethanol conversion is obtained, the observed decrease in selectivity is due to decrease in total yield of aromatics fraction. It seems that only temperature takes part in controlling the aromatic selectivity.

The effort to enhance aromatic yield have focused on improving the dehydrogenation activity obtained by metal species. In the case of incorporated metal species, AgHZSM5 and [Ga]HZSM5, it is found that the toluene selectivity is still the major product in aromatic fraction (Table 4.7 and 4.8).

Table 4.7 Aromatic yield on ethanol conversion over HZSM5, AgHZSM5, and [Ga]HZSM5 catalyst.

% Mole of aromatics	Catalyst		
	HZSM5	AgHZSM5	[Ga]HZSM5
Benzene	1.53	2.09	1.32
Toluene	3.76	4.97	3.18
C8 aromatics	2.26	2.77	2.09
Total	7.55	9.83	6.59

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas: nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

Table 4.8 Aromatic yield on 95 wt% ethanol conversion over HZSM5, AgHZSM5, and [Ga]HZSM5 catalyst.

% Mole of aromatics	Catalyst		
	HZSM5	AgHZSM5	[Ga]HZSM5
Benzene	1.18	1.35	1.46
Toluene	2.00	3.20	4.27
C8 aromatics	1.12	2.76	2.43
Total	4.30	7.31	8.16

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, average time on stream 2-4 hours, 100 % conversion of ethanol)

This indicates that the incorporated metal species does not contribute any improvement in BTX selectivity. While, the type of oligomerized hydrocarbons precursors which is promoted by the acid sites of HZSM5, play a significant role for the BTX selectivity.

Table 4.9 Aromatic yield on ethylene conversion over HZSM5, AgHZSM5, and [Ga]HZSM5 catalyst.

% Mole of aromatics	Catalyst		
	HZSM5	AgHZSM5	[Ga]HZSM5
Benzene	1.72	2.22	2.37
Toluene	3.96	4.67	5.58
C8 aromatics	1.85	2.68	2.25
Total	7.53	9.57	10.20

(Reaction temperature; 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen, average time on stream 2-4 hours)

In the reaction using ethylene as feed, although the different in catalytic activity of AgHZSM5 and [Ga]HZSM5 can be revealed (section 4.4.6), toluene is still a major aromatic component over [Ga]HZSM5 (Table 4.9). This is expected because over [Ga]HZSM5, aromatics can be formed not only by C3 hydrocarbons but also the consecutive reaction with C4 hydrocarbons. Ultimately toluene were observed in high yield.

It has to be pointed out that although the conclusion for the formation of the main aromatic products have been established under reaction conditions in this study, the influence of diffusion [15], crystallite size [35], pore size [52], concentration of feed [22], and a balance between acidity and dehydrogenation function [22] can also cause the differences in aromatic yield and selectivity.



Chapter 5

Conclusion and suggestion

5.1 Conclusions

1. The ZSM5 catalyst can be prepared by hydrothermal crystallization and further modified by ion exchange, and impregnation. It appears to be an appropriate catalyst due to its small crystallite size (1 micrometer), with high surface area ($416 \text{ m}^2/\text{g}$) and high crystallinity. The acid concentration of HZSM5 is measured to be 1 mmol/g of catalyst. The silver content of AgHZSM5 and AgNaZSM5 prepared by silver ion exchange is 7.35 and 6.59 wt%, respectively.
2. The oligomerization of ethylene increases with rise in contact time but, decreases with rise in temperature. In the reaction using HZSM5, rate of ethylene oligomerization is important for aromatic enhancement. At 350°C reaction temperature, high quality gasoline can be achieved, while at 425°C , high yield of aromatic is obtained.
3. The presence of water can inhibit oligomerization of ethylene over HZSM5 by its competitive adsorption against hydrocarbon species. After catalyst regeneration, the presence of Lewis acid site and hydrophobic character can reduce the water adsorption and consequently enhance the ethylene oligomerization. However, the presence of water at high reaction temperature (450°C) using regenerated-HZSM5 can reduce aromatic yield with higher extent.
4. Platinum species in [Pt]HZSM5 can inhibit the ethylene oligomerization. The presence of water in the reaction can increase clustering of platinum which improve the ethylene oligomerization. [Ga]HZSM5 is an active catalyst for C3 aromatization in the reaction using pure ethylene as feed. The presence of higher water content can alter the activity of [Ga]HZSM5, and the enhanced catalytic activity of [Ga]HZSM5 can be promoted.
5. In the reaction using pure ethylene over [PtGa]HZSM5, each metal contributes only half of its activity, as compared to the parent. While, the presence of water can increase higher molecular weight product owing to enhanced activity of [Ga]HZSM5 and hence, [Pt]HZSM5 can reform oligomerized product to aromatic. However, there is no synergistic effect of mixed catalyst [PtGa]HZSM5 for aromatic selectivity improvement.

6. The silver metal is claimed to be an active species for ethylene oligomerization and aromatic selectivity improvement. AgHZSM5 and AgNaZSM5 can improve aromatic yield in both conversion of ethylene and ethanol. However, the presence of water under severe reaction conditions can increase clustering of silver which reduces the ethylene oligomerization. The presence of sodium cations and cluster of silver metal can slightly decrease pore diameter of zeolite, affecting the aromatic formation. The silver species prepared by impregnation of ZSM5 can block the pore of [Ag]HZSM5 zeolite and this species is not active for the ethylene oligomerization. While, incorporation of silver into zeolite by ion exchange can dramatically enhance the rate of reforming.

5.2 Suggestions

1. Acidity and hydrophobicity of HZSM5 zeolite affect rate of oligomerization and competitive adsorption of water. Thus, the effect of water over zeolite with various silicon/aluminium ratio should be investigated. Additionally, after catalyst regeneration, the activity of HZSM5 is different from the parent. The enhancement in activity for reg-HZSM5 only occurs at low temperature while reduce in activity is obtained at high reaction temperature. Thus, zeolite with higher silicon/aluminium ratio, which hydrothermal resistant should be studied on catalyst regeneration.
2. Rate of ethylene oligomerization is low due to the fact that it initially proceed via primary carbocation. Thus, the effect of co-feeding which allow active intermediate (for example propylene, and *iso*-propanol) should be studied for enhancing the oligomerization rate.
3. The presence of water in the reaction can reduce activity of HZSM5 and modified HZSM5 catalyst, except the case of [Ga]HZSM5. Thus, incorporated lanthanum species (La) having similar activity as gallium, should be investigated for enhancing the oligomerization and the reforming in the reaction using high water content feed.
4. AgHZSM5 catalyst can enhance C-H bond cleavage and increase ethylene oligomerization. In addition, [Ga]HZSM5 can promote C3 aromatization. Thus, the mixture of these metal Ag [Ga]HZSM5 should be studied for gasoline and aromatic production in the reaction using ethane, which is a component of natural gas as feed.

REFERENCES

- [1] Adulyadej B., King. "Royal Speech." [Online]. Available :
<http://www.kanchanapisek.or.th/speeches/1997/1204.en.html>. 1999.
- [2] Ian M. Campbell. **Biomass, Catalysis and Liquid Fuels**. 1st Ed. Pennsylvania :
 Technomic. 1983.
- [3] Shigeaki Koide. **Regional Study on Production of Fuel Ethanol from Agro-Products**.
 Economic and Social Commission for Asia and the Pacific. 1982.
- [4] Jacqueline I. Kroschwitz, Executive Editor. **Encyclopedia of Chemical Technology**
 vol. 9. 4th Ed. New York : John Wiley & Sons. 1994.
- [5] Lonnie O. Ingram., Maria D. F. and Barbosa Alleyne. "Ethanol Production in Gram-
 Positive Microbes." U.S patent no. 5916768, June 1999.
- [6] Seader J. D., Ernest J. Henley. **Separation Process Principles**. 1st Ed. New York :
 John Wiley & Sons. 1998.
- [7] Jacqueline I. Kroschwitz, Executive Editor. **Encyclopedia of Chemical Technology**
 vol. 1. 4th Ed. New York : John Wiley & Sons. 1991.
- [8] Nicholas P. Cheremisinoff. **Gasohol for Energy Production**. Michigan : Ann Arbor
 Science. 1979.
- [9] Sami Matar., Lewis F. Hatch. **Chemistry of Petrochemical Processes**. 1st Ed.
 Houston : Gulf. 1994.
- [10] Nelson W. L. **Petroleum Refinery Engineering**. 4th Ed. Auckland : McGraw-Hill.
 1985.
- [11] Robert A. Meyers, Editor. **Handbook of Petroleum Refining Processes**. 2nd Ed.
 New York : McGraw-Hill. 1997.
- [12] George A. Olah., Arpad Molnar. **Hydrocarbon Chemistry**. New York : John Wiley &
 Sons. 1995.
- [13] Smith J. M., Van Ness H. C. **Introduction to Chemical Engineering**
 Thermodynamics. 4th Ed. New York : McGraw-Hill. 1987.
- [14] Chen N. Y., William E. Garwood. and Francis G. Dwyer. **Shape Selective Catalysis**
 in Industrial Applications. 2nd Ed. New York : Marcel Dekker. 1996.

- [15] Subhash Bhatia. *Zeolite Catalysis: Principles and Applications*. Florida : CRC Press. 1990.
- [16] Bruce C. Gates. *Catalytic Chemistry*. New York : John Wiley & Sons. 1992.
- [17] Hegedus L. Louis, Editor. *Catalyst Design Progress and Perspectives*. New York : John Wiley & Sons. 1987.
- [18] Bekkum H. Van, Editors. *Introduction to Zeolite Science and Practice*. Amsterdam : Elsevier Science. 1991.
- [19] Kokotailo G. T., Lawton S. L. and Olson D. H. "Structure of Synthetic Zeolite ZSM-5." *Nature*, vol. 272, March 1978. pp. 437-438.
- [20] Robert J. Arganer., Kansington M., George R. Landolt. and Audbon N. J. "Crystalline Zeolite ZMS-5 and Method of Preparing the Same." U.S patent no. 3702886, November 1972.
- [21] Cynthia T-W. Chu. "Aromatization of Aliphatics over a Zeolite Containing Framework Gallium." U.S patent no. 4891463, January 1990.
- [22] Jacobs P. A, Editor. *Zeolite Chemistry and Catalysis*. Amsterdam : Elsevier Science. 1991.
- [23] Laurent Petit., Jean P. Bournonville., Jean L. Guth., Francis Raatz. and Alain Seive. "Catalyst of the Gallosilicate Type and Its Utilization for the Aromatization of Light C₂-C₄ Gases." U.S patent no. 5073672, December 1991.
- [24] Choudhary V. R., Devadas P. "Regenerability of Coked H-GaMFI Propane Aromatization Catalyst, Activity/Selectivity and Deactivation." *Applied Catalysis A : General*, vol. 168, 1998. pp. 187-200.
- [25] Vasant R. Choudhary., Kshudiram Mantri. and Chinta Sivadinarayana. "Influence of Zeolite Factors Affecting Zeolitic Acidity on the Propane Aromatization Activity and Selectivity of Ga/H-ZSM-5." *Microporous and Mesoporous Materials*, vol. 37, 2000. pp. 1-8.
- [26] Wei Q. Lin., Lin Zhao., Gui D. Sun. and En Z. Min. "Saturation of Aromatics and Aromatization of C₃ and C₄ Hydrocarbons over Metal Loaded Pillared Clay Catalysts." *Catalysis Today*, vol. 51, 1999. pp. 135-140.
- [27] Weitkamp J, Editor. *Zeolites and Related Microporous Materials : State of the Art 1994*. Amsterdam : Elsevier Science. 1994.

- [28] Miguel A. Banares. "Supported Metal Oxide and Other Catalysts for Ethane Conversion: a Review." *Catalysis Today*, vol. 51, 1999. pp. 319-348.
- [29] Eric J. Munson., Ali A. Kheir., Noel D. Lazo. and James F. Haw. "*In Situ* Solid-State NMR Study of Methanol-to-Gasoline Chemistry in Zeolite HZSM-5." *J. Phys. Chem.*, vol. 96, 1992. pp. 7740-7746.
- [30] Pedro L. Benito., Ana G. Gayubo., Andres T. Aguayo. and Martin Olazar. "Effect of Si/Al Ratio and of Acidity of H-ZSM5 Zeolites on the Primary Products of Methanol to Gasoline Conversion." *J. Chem. Tech. Biotechnol.*, vol. 66, 1996. pp. 183-191.
- [31] Michael Stocker. "Methanol-to-Hydrocarbons: Catalytic Materials and Their Behavior." *Microporous and Mesoporous Materials*, vol. 29, 1999. pp. 3-48.
- [32] Moller K. P., Bohringer W., Schnitzler A. E., Steen E. Van. and O'Connor C. T. "The Use of a Jet Loop Reactor to Study the Effect of Crystal Size and the Co-feeding of Olefins and Water on the Conversion of Methanol over HZSM-5." *Microporous and Mesoporous Materials*, vol. 29, 1999. pp. 127-144.
- [33] Viswanathan B, Editor. **Recent Developments in Catalysis**. New Delhi : Narosa. 1992.
- [34] Mikhail S. et. al. "Conversion of Ethanol to Hydrocarbons on H-mordenite Zeolite Catalyst." *Bulletin De La Societe Chimique De France*, vol. 1, 1991. pp. 5-9.
- [35] Voogd P. "Shape Effects in the Conversion of Ethanol to Hydrocarbons over Alkaline-Free Synthesized ZSM-5 and aluminated Silicalite-1 Crystals." *Recueil Des Pays-Bas-Journal of the Royal Netherlands Chemical Society*, vol. 110, 1991. pp. 78-84.
- [36] Raymond L. Mao., Le H. Dao. "Ethylene Light Olefins from Ethanol." U.S patent no. 4698452, October 1987.
- [37] Raymond L. Mao. "Catalytic Conversion of Aqueous Ethanol to Ethylene." U.S patent no. 4873392, October 1989.
- [38] Raymond L. Mao. "Hybrid Catalyst Containing a Microporous Zeolite and a Mesoporous Cocatalyst Forming a Pore Continuum for a Better Desorption of Reaction Products." *Microporous and Mesoporous Materials*. vol. 28, 1999. pp. 9-17.
- [39] Kongsakpibal A. **Instrumental Analysis**. Bangkok : n.p. 1994.

- [40] Fries J., Getrost H. **Organic Reagents for Trace Analysis**. E. Merk. Darmstadt. 1977.
- [41] Douglas A. Skoog., James J. Leary. **Principles of Instrumental Analysis**. 4th Ed. Philadelphia : Harcourt Brace College. 1992.
- [42] Pinta M. **Modern Methods for Trace Element Analysis**. 3rd Ed. San Francisco : Ann Arbor Science. 1982.
- [43] Luk'yanov D. B. "On the Role of Enhanced Activity Sites in the Different Steps of Methanol Transformation into Olefins over HZSM5." *Zeolites*, vol. 13, 1993. pp. 64-66.
- [44] Sano T., Uno Y., Wang Z. B., Ahn C. H. and Soga K. "Realumination of Dealuminated HZSM-5 Zeolites by Acid Treatment and Their Catalytic Properties." *Microporous and Mesoporous Materials*, vol. 31, 1999. pp. 89-95.
- [45] Guenter H. Kuehl., Hye K. C. Timken. "Acid Sites in Zeolite Beta: Effects of Ammonium Exchange and Steaming." *Microporous and Mesoporous Materials*, vol. 35-36, 2000. pp. 521-532.
- [46] Olson D. H., Haag W. O. and Borghard W. S. "Use of Water as a Probe of Zeolitic Properties; Interaction of Water with HZSM-5." *Microporous and Mesoporous Materials*, vol. 35-36, 2000. pp. 435-446.
- [47] Tomoyuki I. "Highly Selective Synthesis of Light Olefins from Methanol on Nickel-Incorporated SAPO catalyst." *Proceeding of the International Conference on Recent Developments in Petrochemical and Polymer Technologies*. December 1989. pp. 52-56.
- [48] Akihiko Matsuoka., Jin B. Kim. and Tomoyuki Inui. "Selectivity Improvement in the Aromatization of C₂-C₅ Alkanes Using Polyfunctional Metallosilicate Catalysts." *Microporous and Mesoporous Materials*, vol. 35-36, 2000. pp. 89-98.
- [49] Vladislav Kanazirev., Geoffrey L. Price. and Kerry M. Dooley. "Enhancement in Propane Aromatization with Ga₂O₃/HZSM-5 Catalysts." *J. Chem. Soc., Chem. Commun.*, 1999. pp. 712-713.
- [50] Arean C. Otero., Bellan A. Lopez. and Mentrut M. Penarroya. "Preparation and Characterization of Mesoporous γ -Ga₂O₃" *Microporous and Mesoporous Materials*, vol. 40, 2000. pp. 35-42.

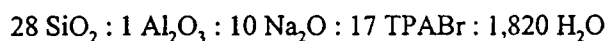
- [51] Bruce R. King, Editor. *Encyclopedia of Inorganic Chemistry*. Chichester : John Wiley. 1994.
- [52] Panagiotis G. smirniotis., Eli Ruckenstein. "Alkylation of Benzene or Toluene with MeOH or C₂H₄ over ZSM-5 or β Zeolite: Effect of the Zeolite Pore Openings and of the Hydrocarbons Involved on the Mechanism of Alkylation." *Ind. Eng. Chem. Res.*, vol. 34, 1995. pp. 1517-1528.



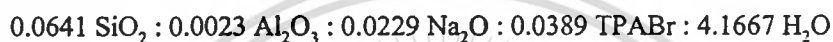
Appendix A

A1 Synthesis of zeolite

ZSM5 is synthesized hydrothermally from aluminosilicate gel with a nominal composition of



From the gel composition, the 75 g of water (approximate volume of autoclave) is basis of calculation. Under this basis, the gel composition is adjusted to



Thus, it requires 3.8460 g of SiO_2 , 0.2346 g of Al_2O_3 , 1.4198 g of Na_2O , 10.3318 g of TPABr, and 75 g of water. The calculation of gel composition is

Material Sources	SiO_2	Al_2O_3	Na_2O	TPABr	Water
0.3940 g of Sodium aluminate (37.57 %wt Na_2O , 59.54 %wt Al_2O_3)	-	0.2346 g	0.1480 g	-	-
1.6410 g of Sodium hydroxide*	-	-	1.2718 g	-	0.3692 g
9.6150 g of Ludox 40 (40 % SiO_2)	3.8460 g	-	-	-	5.7690 g
10.3318 g of Tetrapropyl ammonium bromide	-	-	-	10.3318 g	-
68.8618 g of Water	-	-	-	-	68.8618 g
Total	3.8460 g	0.2346 g	1.4198 g	10.3318 g	75 g



A2 Determination of silicon and aluminium

A2.1 Determination of silicon

The silicon concentration of ZSM5 zeolite is determined by UV-Vis Spectrophotometry. From the Table A1, the curve is plotted in absorbance versus concentration as linear function required for the Beer rule.

Table A1 Concentration and absorbance data obtained from the UV-Vis Spectrophotometry for silicon determination

Sample	Concentration (ppm)	Absorbance
Standard Si	0.231	0.073
	0.462	0.238
	0.693	0.400
	0.924	0.552
NaZSM5	-	0.336

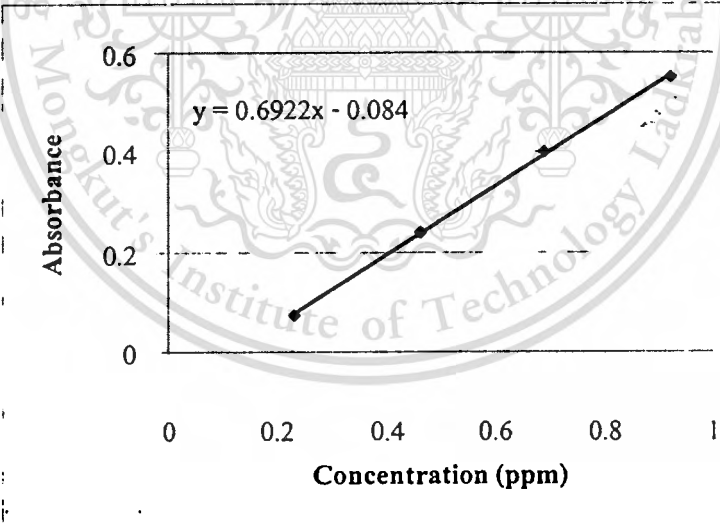


Figure A1 Relation of concentration and absorbance data for silicon determination.

The equation of this curve is convenient for determining silicon of ZSM5. This calculation requires an absorbance of sample by substitution it to the equation. For example, if absorbance of sample is 0.336 then;

Absorbance

$= 0.6922 [\text{Si}]_{\text{NaZSM5}} - 0.084$

$[\text{Si}]_{\text{NaZSM5}}$

$= 0.6068 \text{ ppm}$

The accurate concentration of silicon sample (prior 200 times dilution) is 121.36 ppm (or 30.34 mg/250 mL). Thus, the silicon content of 70.93 mg NaZSM5 is 30.34 mg (or 42.77 wt%).

A2.2 Determination of aluminium

The aluminium concentration of NaZSM5 zeolite is determined by UV-Vis Spectrophotometry. From the Table A2, the curve is plotted in absorbance versus concentration as similar to the case of determination of silicon.

Table A2 Concentration and absorbance data derived by the UV-Vis Spectrophotometry in aluminium determination

Sample	Concentration (ppm)	Absorbance
Standard Al	0.502	0.087
	1.004	0.209
	1.506	0.332
	2.008	0.456
NaZSM5	-	0.261

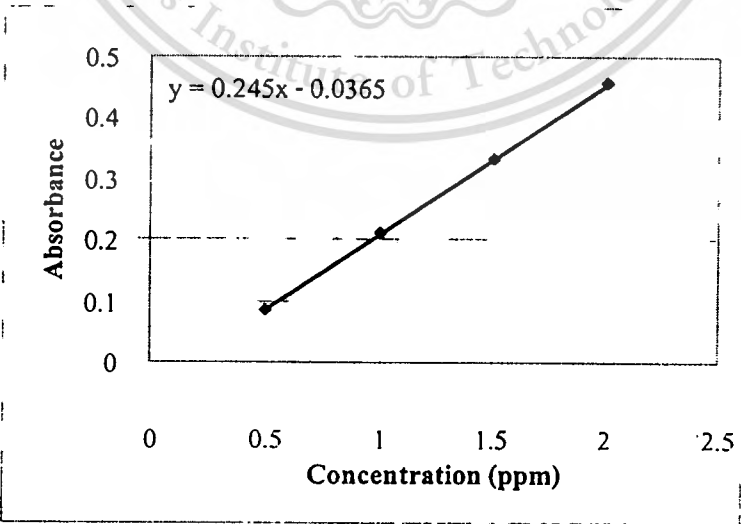


Figure A2 Relation of concentration and absorbance data in aluminium determination.

The equation of this curve is convenient for determining aluminium of ZSM5. This calculation requires an absorbance of sample by substitution it to the equation. For example, if absorbance of sample is 0.261 then;

$$\begin{aligned}\text{Absorbance} &= 0.245 [\text{Al}]_{\text{NaZSM5}} - 0.0365 \\ [\text{Al}]_{\text{NaZSM5}} &= 1.2143 \text{ ppm}\end{aligned}$$

The accurate concentration of aluminium sample (prior 10 times dilution) is 12.143 ppm (or 1.2143 mg/100 mL). Thus, the aluminium content of 44.08 mg NaZSM5 is 1.2143 mg (2.75 wt%).

From the above results, the silicon/aluminium ratio is calculated as follows:

NaZSM5 100 mg possesses silicon 42.77 mg and aluminium 2.75 mg.

$$\begin{aligned}\text{Thus;} \quad \text{Si/Al} &= \frac{[42.77 / 28]}{[2.75 / 27]} \\ &= 15\end{aligned}$$

The unit cell of NaZSM5 zeolite is calculated as follows:

The general unit cell of NaZSM5 is $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}$

$$\text{Thus;} \quad \text{Si} + \text{Al} = 96 \quad [\text{Eq.1}]$$

$$\text{Si/Al} = 15 \quad [\text{Eq.2}]$$

From the Eq.1 and Eq.2

$$\text{Si} = 90$$

$$\text{Al} = 6$$

Thus, the unit cell of NaZSM5 is $\text{Na}_6\text{Al}_6\text{Si}_{90}\text{O}_{192}$ and silicon/aluminium ratio is 15.

A3 Determination of acidity

The acidity of HZSM5 is determined by potentiometric titration. The accurate concentration of primary standard 9.5353 grams sodium tetraborate diluted to 250 mL is

$$\begin{aligned} [g/MW] &= [CV/1000] \\ C_{Na_2B_4O_7} &= [9.5353 \times 1000]/[381.24 \times 250] \\ &= 0.10 \text{ mol/L} \end{aligned}$$

The accurate concentration of hydrochloric is determined by potentiometric titration using sodium tetraborate as titrant. The curve is plotted in $\Delta E/\Delta V$ versus the volume of solution.

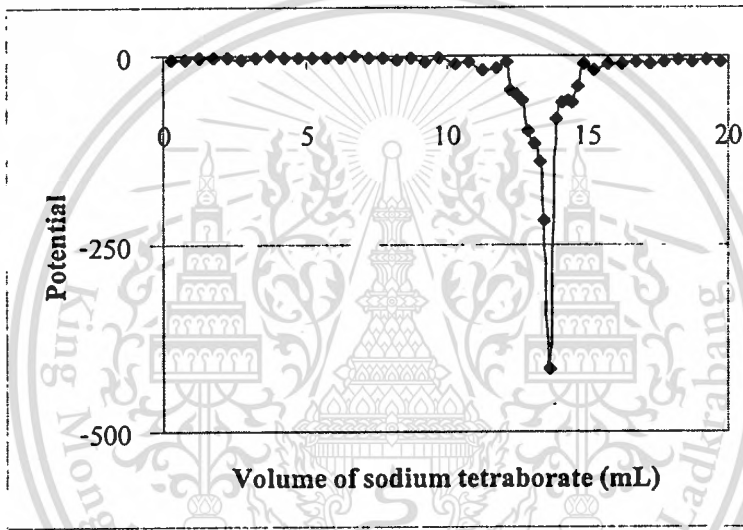


Figure A3 The titration curve of sodium tetraborate and hydrochloric (the first titration).

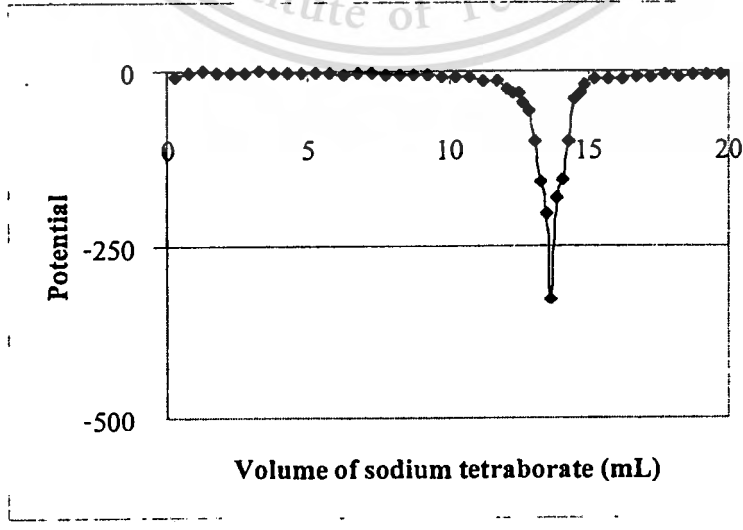


Figure A4 The titration curve of sodium tetraborate and hydrochloric (the second titration).

From the curve, the average volume belonging to the equivalent point, average V_e is 13.7. Thus, the accurate concentration of hydrochloric acid, C_{HCl} titrated with 25 mL of hydrochloric acid is

$$\begin{aligned} [n_{\text{Na}_2\text{B}_4\text{O}_7}/n_{\text{HCl}}] &= 1/2 \\ C_{\text{HCl}} &= [2 \times 0.1 \times 13.7]/25 \\ &= 0.1096 \text{ mol/L} \end{aligned}$$

Similar determination is used in the case of ammonium hydroxide concentration.

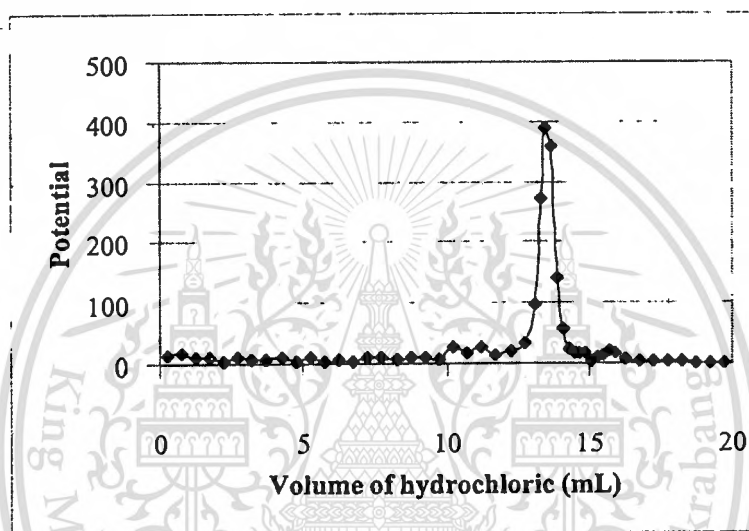


Figure A5 The titration curve of hydrochloric and ammonium hydroxide (the first titration).

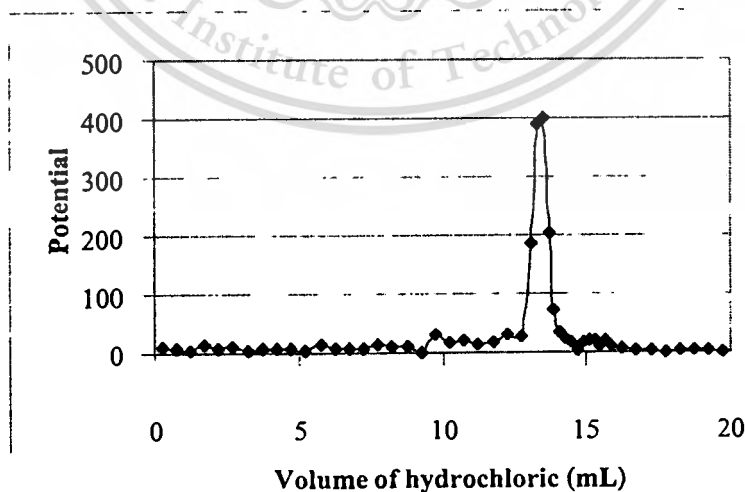


Figure A6 The titration curve of hydrochloric and ammonium hydroxide (the second titration).

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From the curve of ammonium hydroxide-hydrochloric titration, average V_e is 13.5. The accurate concentration of ammonium hydroxide, $C_{\text{NH}_4\text{OH}}$ titrated with 25 mL of ammonium hydroxide is

$$\begin{aligned}
 [n_{\text{HCl}}/n_{\text{NH}_4\text{OH}}] &= 1/1 \\
 C_{\text{NH}_4\text{OH}} &= [0.1096 \times 13.5]/25 \\
 &= 0.0592 \text{ mol/L}
 \end{aligned}$$

From the above results, acid amount of HZSM5 zeolite is determined by using back titration techniques.

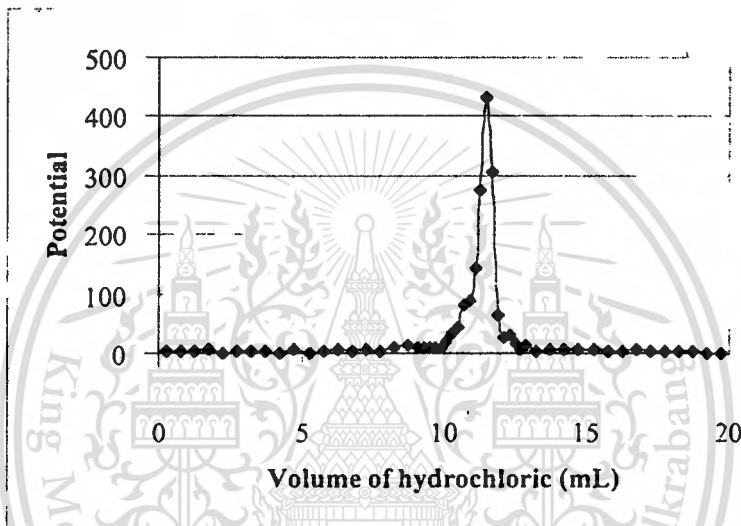


Figure A7 The titration curve of hydrochloric and residual ammonium hydroxide (the first titration).

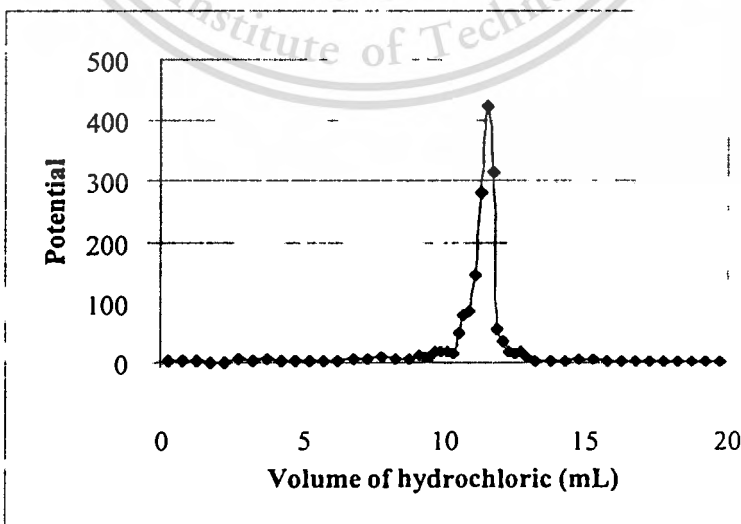


Figure A8 The titration curve of hydrochloric and residual ammonium hydroxide (the second titration).

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It is found that the curve of residual ammonium hydroxide-hydrochloric titration obtains average $V_e = 11.5$ by using initially 25 mL of ammonium hydroxide solution and 0.2179 gram of HZSM5 sample. Thus, the concentration of residual ammonium hydroxide is

$$\begin{aligned} [n_{HCl}/n_{NH_4OH}] &= 1/1 \\ C_{NH_4OH} &= [0.1096 \times 11.5]/25 \\ &= 0.0504 \text{ mol/L} \end{aligned}$$

The concentration of acid site of 0.2179 g HZSM5 is calculated by using the initially added mole of ammonium hydroxide minus the residual mole of ammonium hydroxide.

$$\begin{aligned} n(NH_4OH)_i - n(NH_4OH)_f &= [(0.0592 - 0.0504) \times 25]/1000 \\ &= 0.22 \text{ mmol} \end{aligned}$$

Thus; the acidity of HZSM5 is 1.0 mmol/g of zeolite (0.22 mmol/0.2179 grams of zeolite) .

A4 Determination of silver

Silver concentration of AgHZSM5 and AgNaZSM5 are determined by Atomic Absorption Spectroscopy. From the Table A3, the curve is plotted in absorbance versus concentration.

Table A3 Concentration and absorbance data derived by the Atomic Absorption Spectroscopy in silver determination

Sample	Concentration (ppm)	Absorbance
Standard Ag	4	0.450
	8	0.823
	12	1.095
	16	1.327
	20	1.522
AgHZSM5	-	0.914
AgNaZSM5	-	0.850

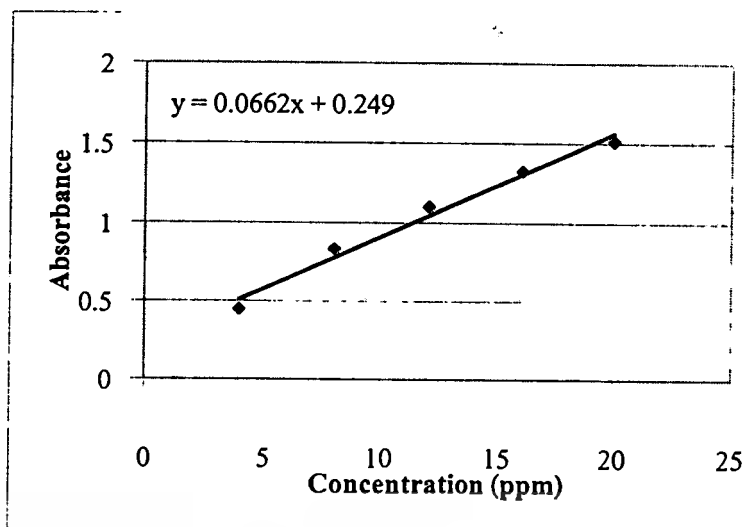


Figure A9 Relation of concentration and absorbance data in silver determination

The equation of this curve is computed for determining silver sample. This calculation requires an absorbance of sample by substitution it to the equation. For example, if absorbance of sample are 0.914 and 0.850, respectively then;

$$\text{Absorbance} = 0.0662 [\text{Ag}] + 0.249$$

$$[\text{Ag}]_{\text{AgHZSM5}} = 10.0453 \text{ ppm}$$

$$[\text{Ag}]_{\text{AgNaZSM5}} = 9.0785 \text{ ppm}$$

The accurate silver concentration of AgHZSM5 and AgNaZSM5 (prior 4 times dilution) are 40.1812 (or 4.01812 mg/100 mL) and 36.3140 ppm (or 3.6314 mg/100 mL), respectively. Thus, the silver content of 54.70 mg AgHZSM5 and 55.10 mg AgNaZSM5 are 4.02 and 3.63 mg (7.35 and 6.59 wt%), respectively.

The calculation of silver loaded in unit cell is

AgHZSM5;

The weight of unit cell, U of AgHZSM5 ($\text{Ag}_n\text{H}_{6-n}\text{Al}_6\text{Si}_{90}\text{O}_{192}$)

$$\begin{aligned} U &= n[\text{Ag}] + (6-n)[\text{H}] + 6[\text{Al}] + 90[\text{Si}] + 192[\text{O}] \\ &= 107.87n + (6-n) + 162 + 2520 + 3072 \quad [\text{Eq.1}] \end{aligned}$$

The silver content loaded zeolite sample is

$$[107.87n/U] = [7.35/100] \quad [\text{Eq.2}]$$

From the Eq.1 and Eq.2,

$n = 4.23$ and hence the unit cell of AgHZSM5 is $\text{Ag}_{4.23}\text{H}_{1.77}\text{Al}_6\text{Si}_{90}\text{O}_{192}$. The ion exchange of silver into the exchangeable site of the framework is estimated to be 70.50 %.

Similar calculation is used in the case of AgNaZSM5

AgNaZSM5;

The weight of unit cell, U of AgNaZSM5 ($\text{Ag}_n\text{Na}_{6-n}\text{Al}_6\text{Si}_{90}\text{O}_{192}$)

$$\begin{aligned} U &= n[\text{Ag}] + (6-n)[\text{Na}] + 6[\text{Al}] + 90[\text{Si}] + 192[\text{O}] \\ &= 107.87n + 23(6-n) + 162 + 2520 + 3072 \quad [\text{Eq.3}] \end{aligned}$$

The silver content loaded zeolite sample is

$$[107.87n/U] = [6.59/100] \quad [\text{Eq.4}]$$

From the Eq.3 and Eq.4,

$n = 3.79$ and hence the unit cell of AgNaZSM5 is $\text{Ag}_{3.79}\text{Na}_{2.21}\text{Al}_6\text{Si}_{90}\text{O}_{192}$. The ion exchange of silver into the exchangeable site of the framework is estimated to be 63.17 %.

A5 Catalytic parameter

$$\text{WHSV} = [\text{Weight of liquid reactant feed (g/hr)}/\text{Weight of catalyst (g)}]$$

In the reaction using 0.432 gram/hour of ethanol as feed and using 0.075 gram of catalyst. the WHSV is calculated as follows:

$$\begin{aligned} \text{WHSV} &= [0.432 \text{ (g/hr)}/0.075 \text{ (g)}] \\ &= 5.76 \text{ hr}^{-1} \end{aligned}$$

In a similar manner; WHSV of catalyst 0.10, 0.15, 0.20, and 0.25 g at constant feed are 4.32, 2.88, 2.16, and 1.73 hr^{-1} , respectively.

In the case of pure ethylene feed at 303 K, the flow rate of ethylene gas which equaled the mole of ethanol feeding (0.432 gram/hour) or mole of ethylene formation is calculated as follows:

Volumetric flow rate of ethylene;

$$\begin{aligned} PV &= nRT \\ 1 \text{ atm} \times V &= [0.432/(46 \times 60)] \text{ mol/min} [82.06] \text{ atm.mL/mol.K} [303] \text{ K} \\ V &= 3.88 \text{ mL/min.} \end{aligned}$$

Thus, the volumetric flow rate of ethylene gas is regulated at 3.88 mL/minute.

A6 Calculation of % mole of carbon from gas chromatography

From the chromatogram, the peak of hydrocarbon sample were identified using of reference standard for comparison. The peak area of hydrocarbon which possesses the equal number of carbon was summerized. The summarized peak area data which obtained from chromatogram of a mixture hydrocarbon product is shown in Table A4.

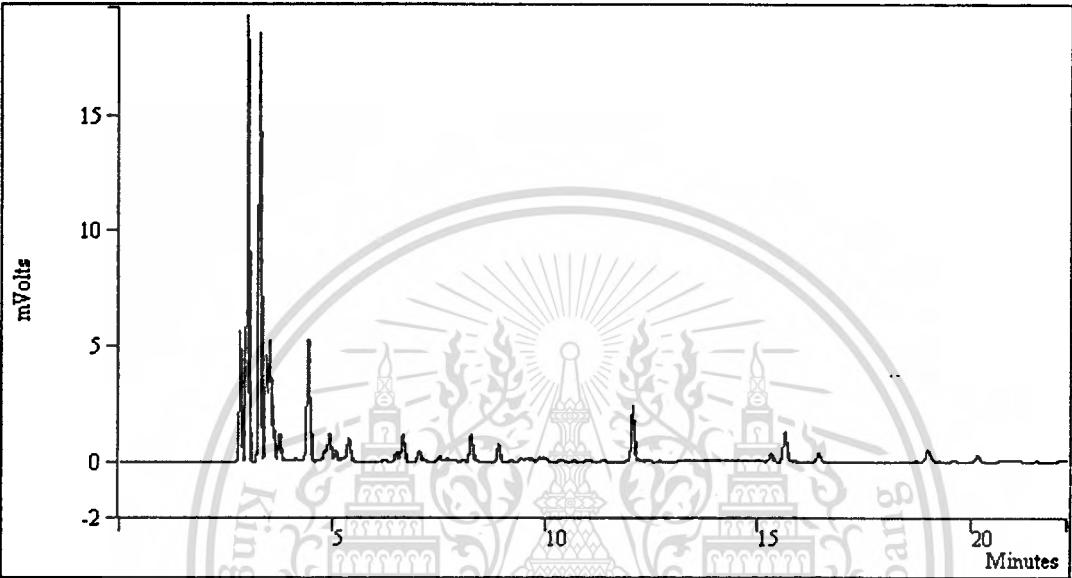


Figure A10 Chromatogram of hydrocarbon product and standard.

Table A4 The summarized peak area of a mixture hydrocarbon product.

Number of carbon	% summarized area
C2	7.6526
C3	32.9690
C4	32.0851
C5	10.3235
C6	0.7131
B	3.0167
T	7.8808
X	4.6998
C9	0.6595
	100

In the normalization method, the areas of all eluted peak were computed; after correcting these areas for differences in the detector response to different compounds. In this study, the flame ionization detector (FID) was used because for hydrocarbon it responded proportionally to the number of carbon atoms in the molecule entering the detector per unit time [41]. After correcting % areas, the mole fraction of the analyte was obtained from the ratio of its area to the total area of all peaks.

Calculate the corrected area for normalization of the equaled carbon as follows:

$$\text{Corrected area of } C_n = [\text{area of } C_n / n]$$

Where n is the response factor of the analyte C_n hydrocarbons which is equaled to number of carbon atom in the hydrocarbon molecule [41].

For example;

$$\text{Corrected area for } C_2 = [7.6526/2]$$

$$= 3.8263$$

$$\text{Corrected area for } C_3 = [32.9690/3]$$

$$= 10.9897$$

Calculate the mole percent of each component in the sample as follows:

$$\text{Mole \% of } C_n = [\text{corrected area of } C_n / \text{Total corrected area}] \times 100$$

For example;

$$\text{Mole \% of } C_2 = [3.8263 / 27.3102] \times 100$$

$$= 14.0105$$

$$\text{Mole \% of } C_3 = [10.9897 / 27.3102] \times 100$$

$$= 40.2402$$

The % mole of each product which is obtained from above calculation is shown in Table A5.

Table A5 % Mole of carbon derived by normalization method.

Number of Carbon	% Area	Corrected area	%Mole
C2	7.6526	3.8263	14.0105
C3	32.9690	10.9897	40.2402
C4	32.0851	8.0213	29.3710
C5	10.3235	2.0647	7.5602
C6	0.7131	0.1189	0.4352
B	3.0167	0.5028	1.8410
T	7.8808	1.1258	4.1224
X	4.6998	0.5875	2.1511
C9	0.6595	0.0733	0.2683
Total	100	27.3102	100

(Catalyst; AgHZSM5. Reaction temperature: 425 °C, WHSV; 2.88 hr⁻¹, Carrier gas; nitrogen.

Feed; ethanol, 1 hours on stream, 100 % conversion of ethanol)

Appendix B

B1 Gas Chromatography Condition

Valve Table

Valve 1 : Gas sampling valve
Initial : Fill

Front Injector

Oven Power : On
Temperature : 250 °C

Time (min)	Split State	Split Ratio
Initial	Off	Off
0.01	On	100
0.20	Off	Off

Column Oven

Coolant : Off
Enable Coolant : 50 °C
Coolant Timeout : 20.0 min.
Stabilization Time : 0.50 min.

Temp. (°C)	Rate (°C/min)	Hold (min)	Total (min)
30	0	5.0	5.0
160	5.0	1.0	32.0
200	20.0	11.0	45.0

FID Detector

Oven Power : On
Temperature : 250 °C
Electronics : Off

B2 Column parameter

Type	:	VA-1
Length (meters)	:	15
I.D. (mm.)	:	0.53
Film (μm)	:	1.5
Theoretical Plates/Meter	:	Pentadecane 1488



Appendix C

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	NaZSM5				
Description	BET surface area				
Comments	Nitrogen adsorption				
Sample Weight	0.0010 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	Artit
Cross-Sec Area	16.2 Å ² /molecule	Outgas Time	18.0 hrs	Analysis Time	529.3 min
NonIdeality	6.580E-05	P/Po Toler	4	End of Run	07/06/2000 06:46
Molecular Wt	28.0134 g/mol	Equil Time	2	File Name	ETGAN1.RAW
Station #	1	Bath Temp.	77.35		

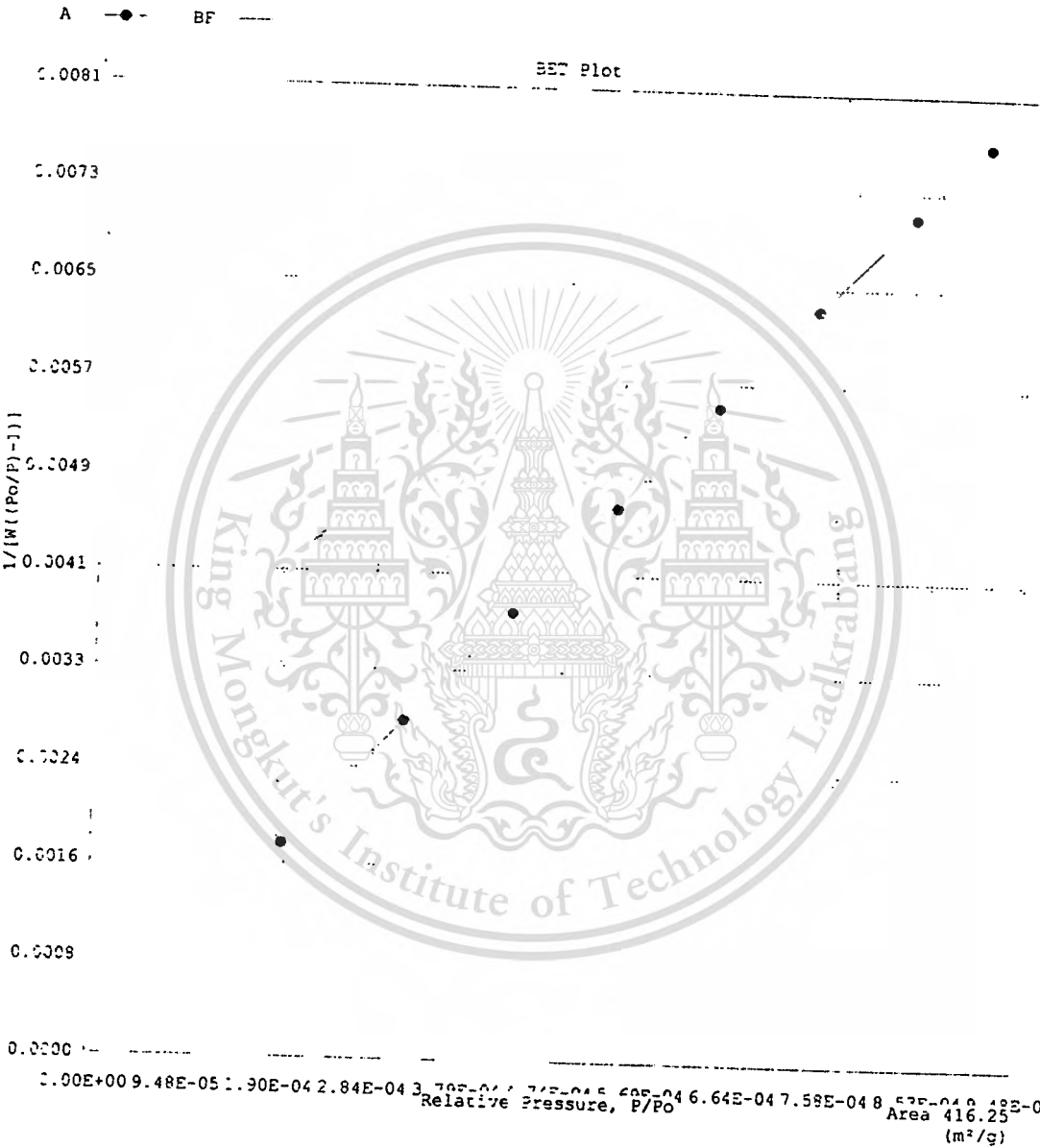


Figure C1 BET surface area of NaZSM5

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	AgHZSM5				
Description	BET surface area				
Comments	Nitrogen adsorption				
Sample Weight	0.0011 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	ARTIT
Cross-Sec Area	16.2 Å ² /molecule	Outgas Time	18.0 hrs	Analysis Time	483.0 min
NonIdeality	6.580E-05	P/Po Toler	4	End of Run	07/12/2000 08:30
Molecular Wt	28.0134 g/mol	Equil Time	2	File Name	ETGAN3.RAW
Station #	1	Bath Temp.	77.35		

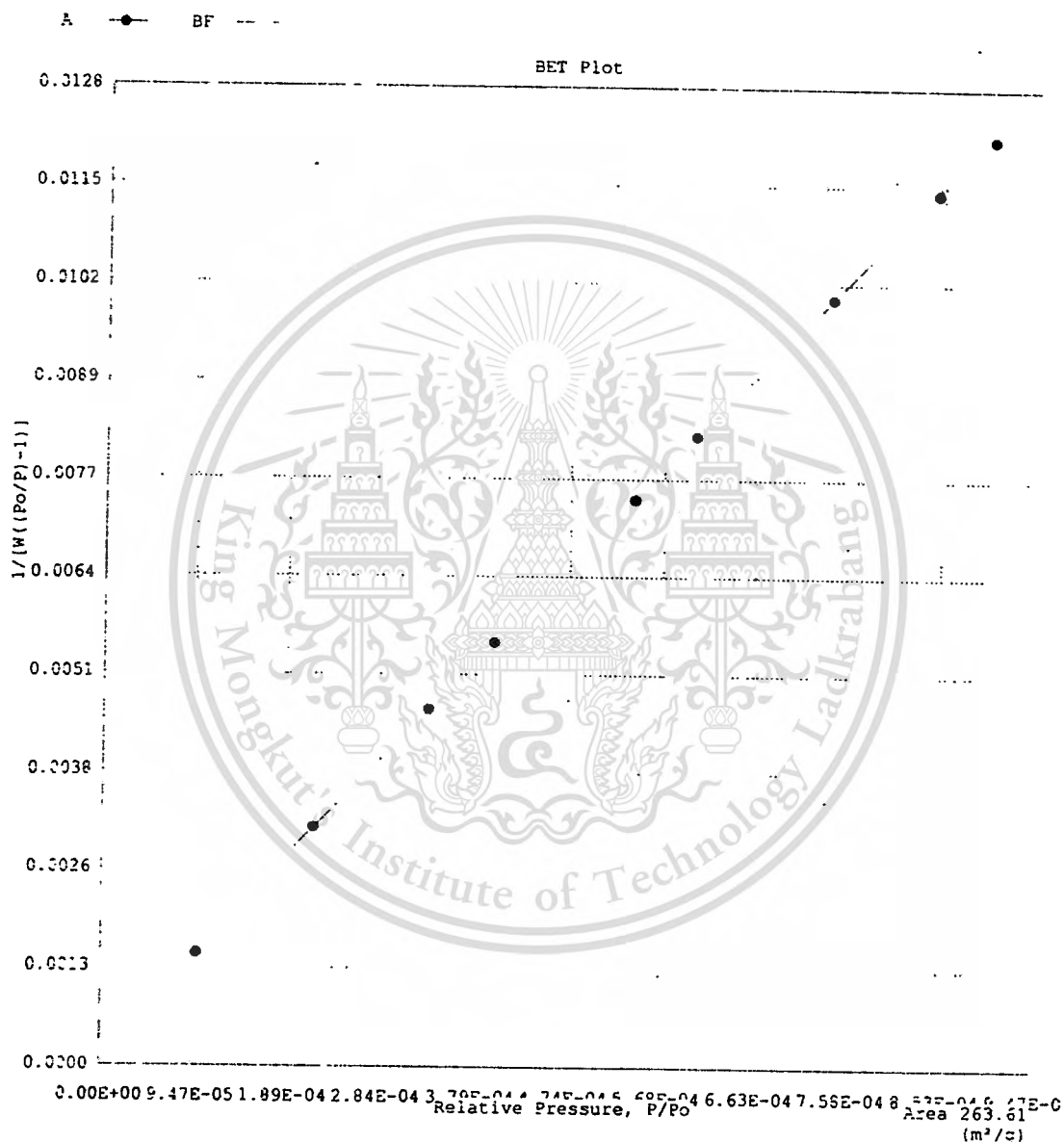


Figure C2 BET surface area of AgHZSM5

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	AgNaZSM5			Operator	ARTIF
Description	BET surface area			Analysis Time	471.1 min
Comments	Nitrogen adsorption			End of Run	07/21/2000 18:57
Sample Weight	0.0010 g	Outgas Temp	350.0 °C	File Name	ETGA04.RAW
Adsorbate	NITROGEN	Outgas Time	18.0 hrs		
Cross-Sec Area	16.2 Å ² /molecule	P/Po Toler	4		
NonIdeality	6.580E-05	Equil Time	2		
Molecular Wt	28.0134 g/mol	Bath Temp.	77.35		
Station #	i				

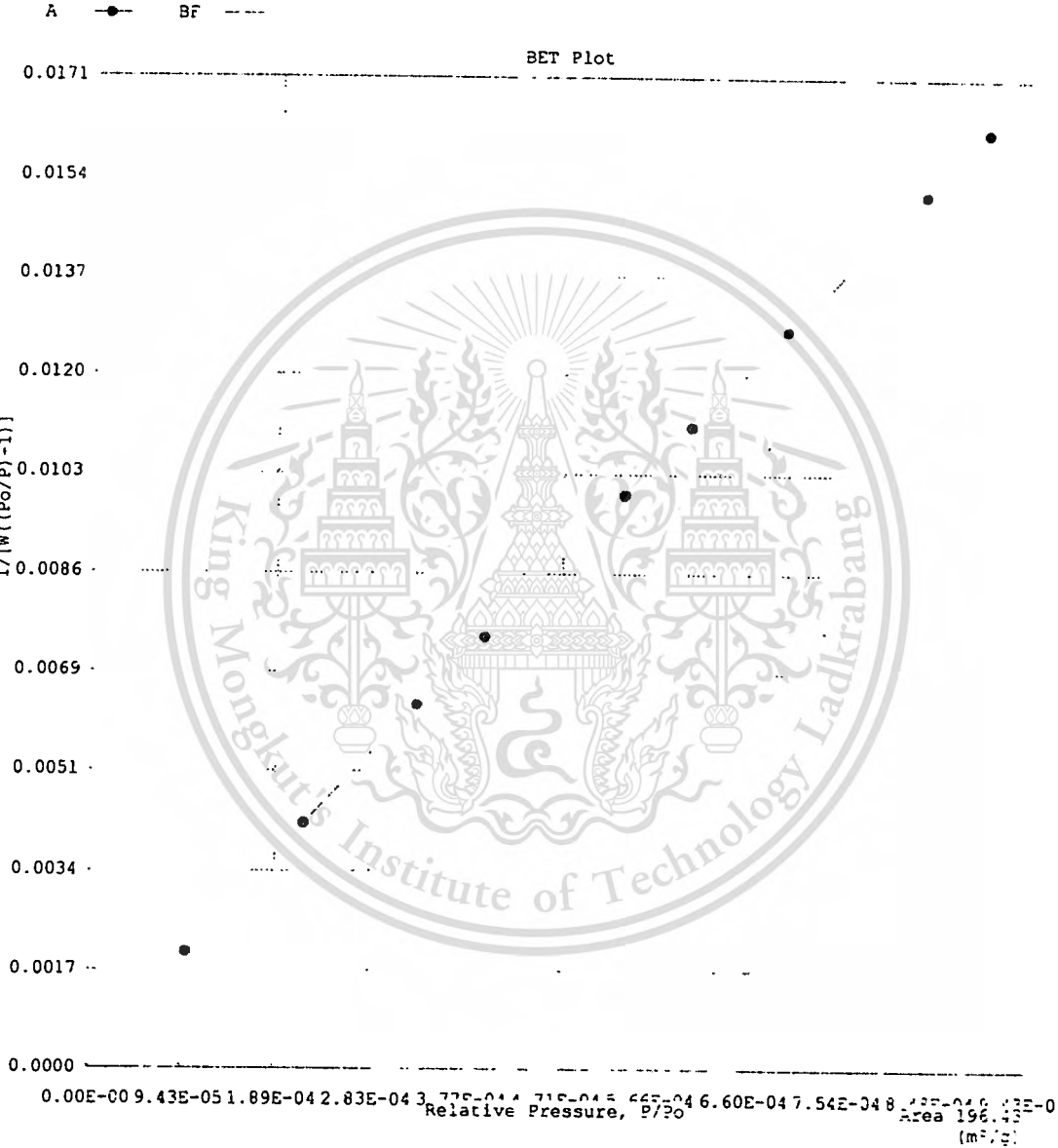


Figure C3 BET surface area of AgNaZSM5

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	[Ag]HZSM5				
Description	BET surface area				
Comments	Nitrogen adsorption				
Sample Weight	0.0013 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	ARTIT
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	18.0 hrs	Analysis Time	443.0 min
NonIdeality	6.580E-05	P/Po Toler	4	End of Run	06/03/2000 08:20
Molecular Wt	28.0134 g/mol	Equil Time	2	File Name	ETGAN6.RAW
Station #	1	Bath Temp.	77.35		

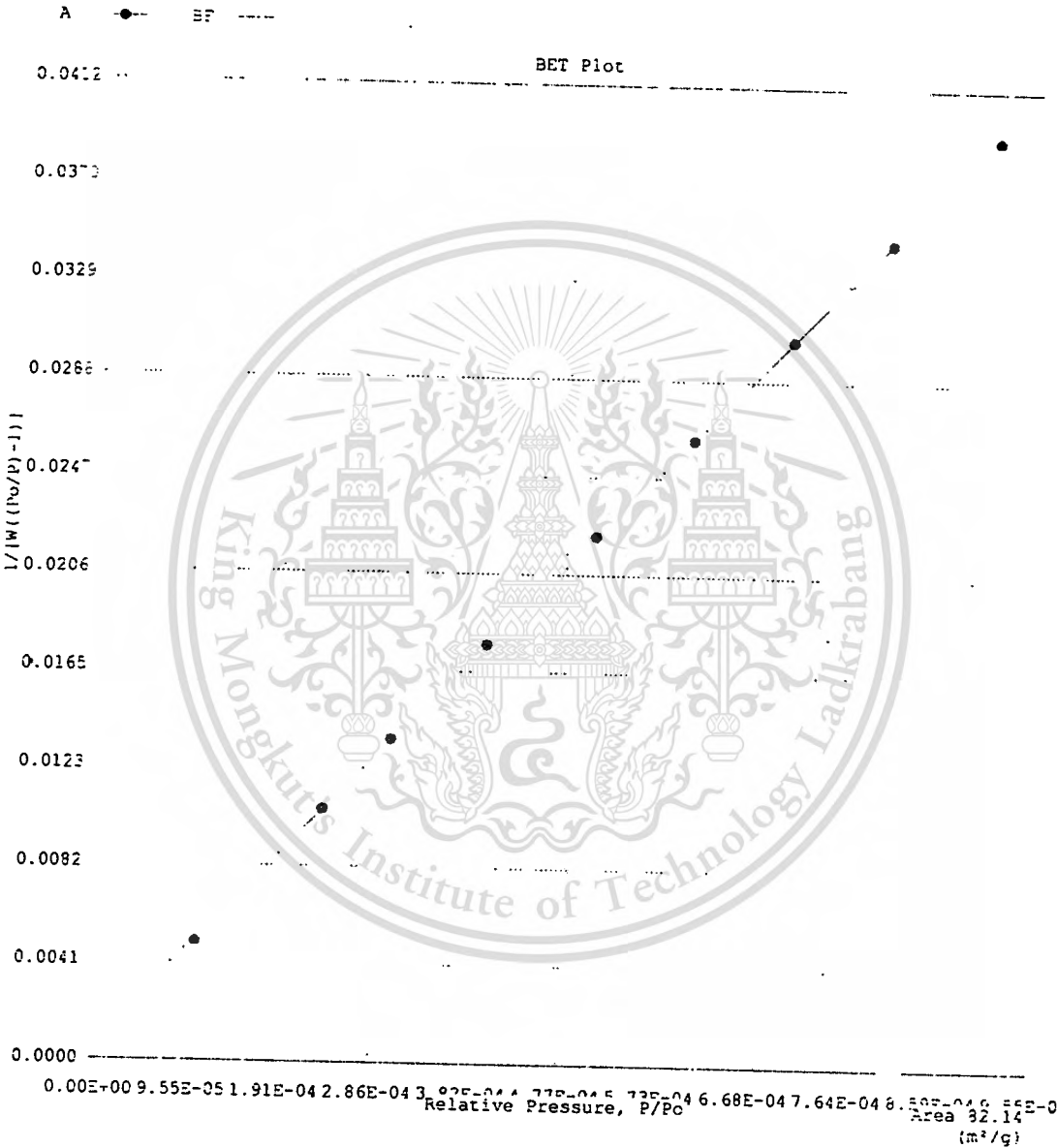


Figure C4 BET surface area of [Ag]ZSM5

Appendix D

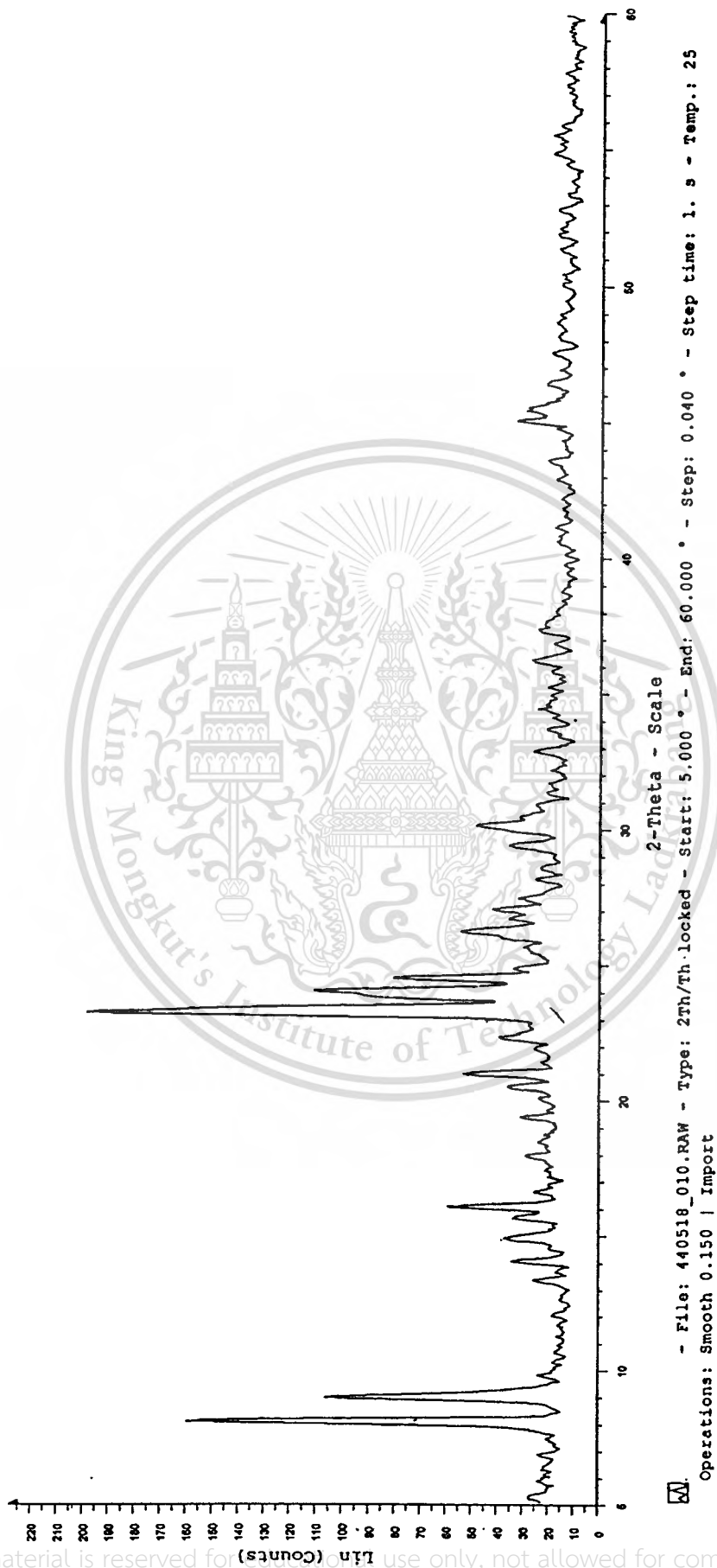


Figure D1 XRD pattern of HZSM5

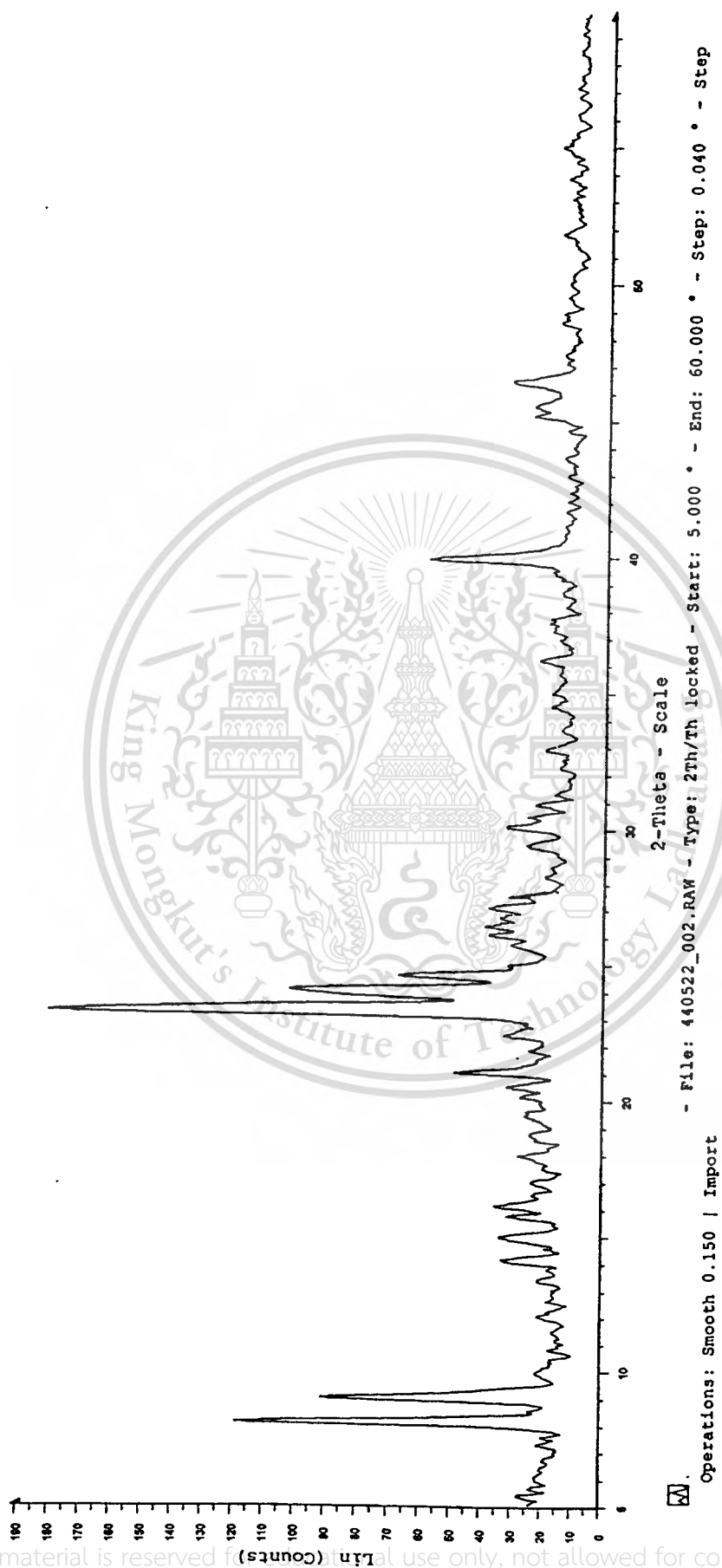


Figure D2 XRD pattern of [Pt]HZSM-5

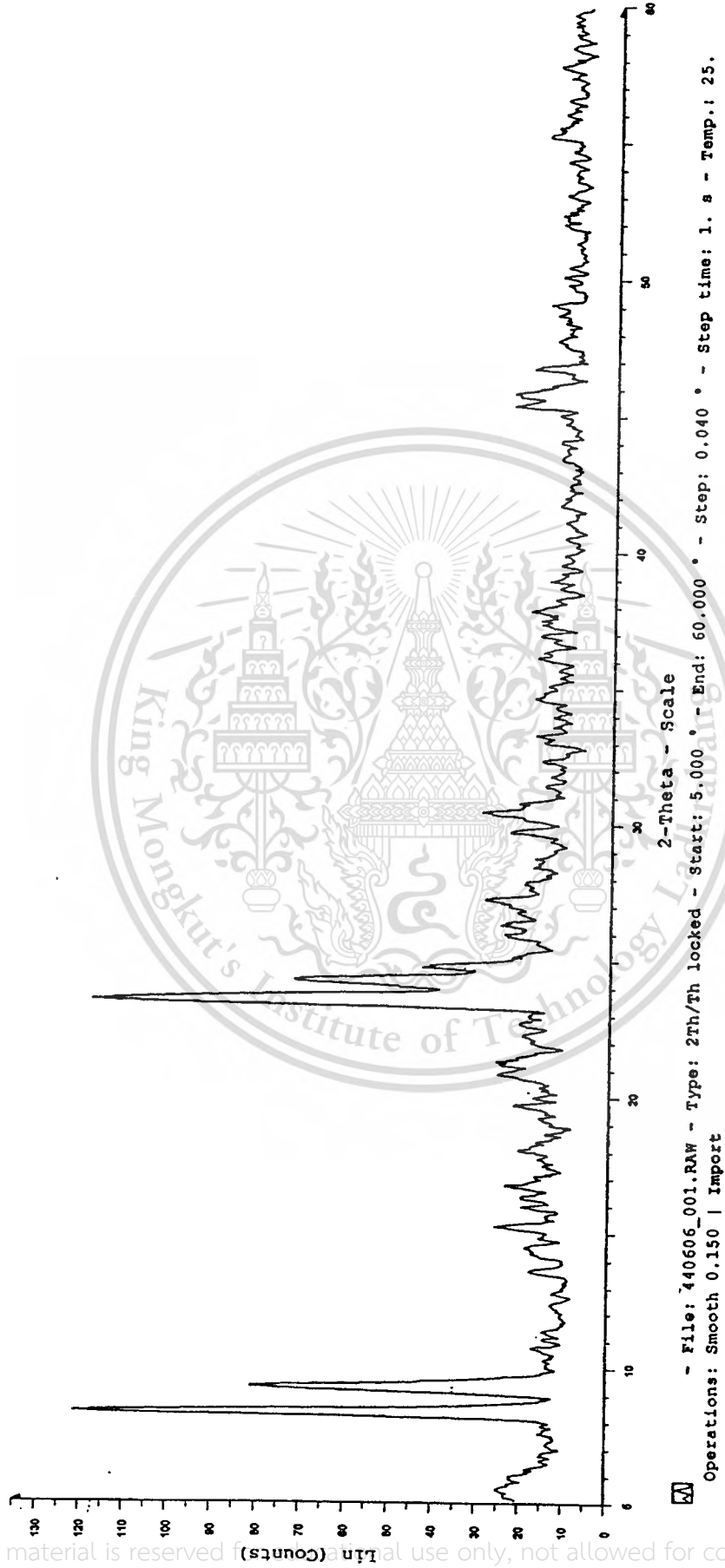


Figure D3 XRD pattern of [Ga]HZSM5

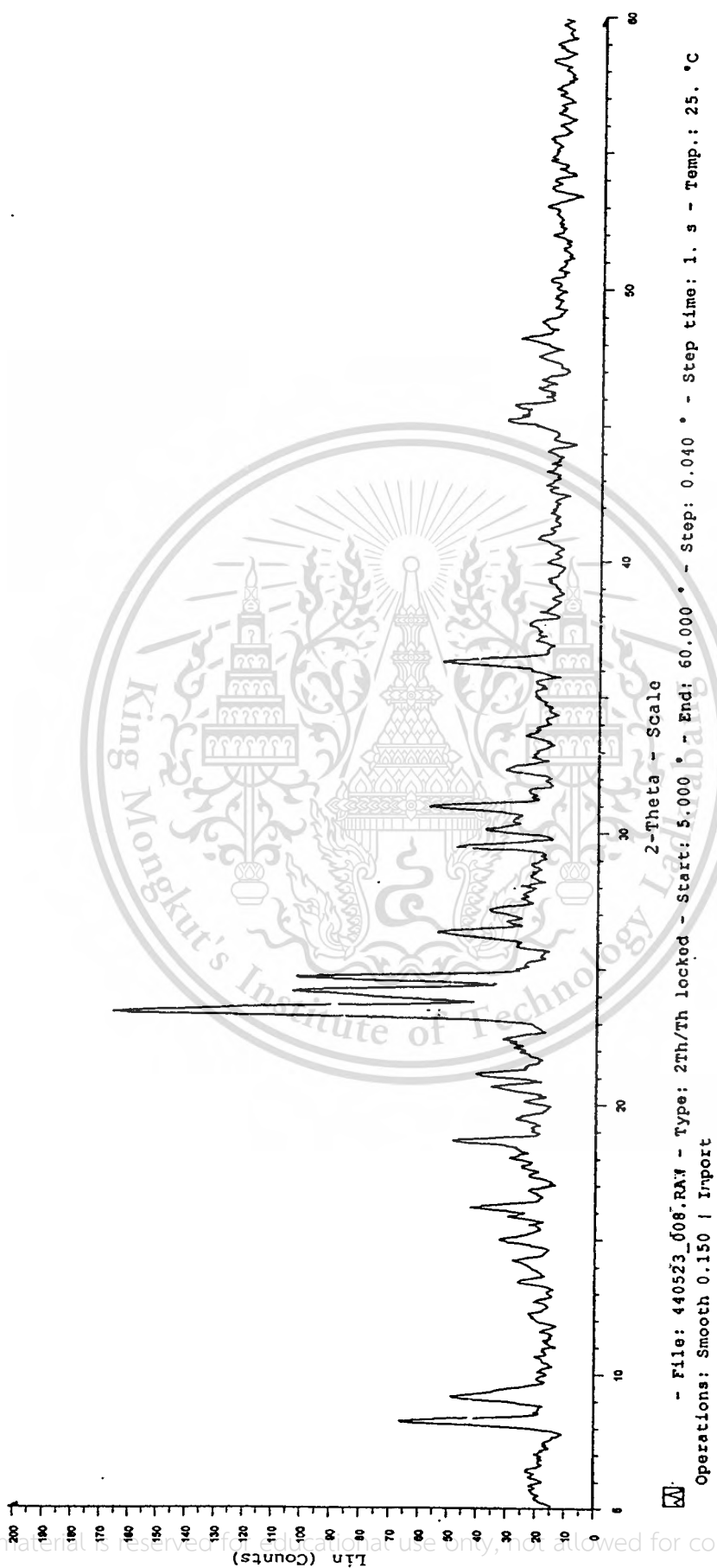


Figure D4 XRD pattern of AgH7SM5

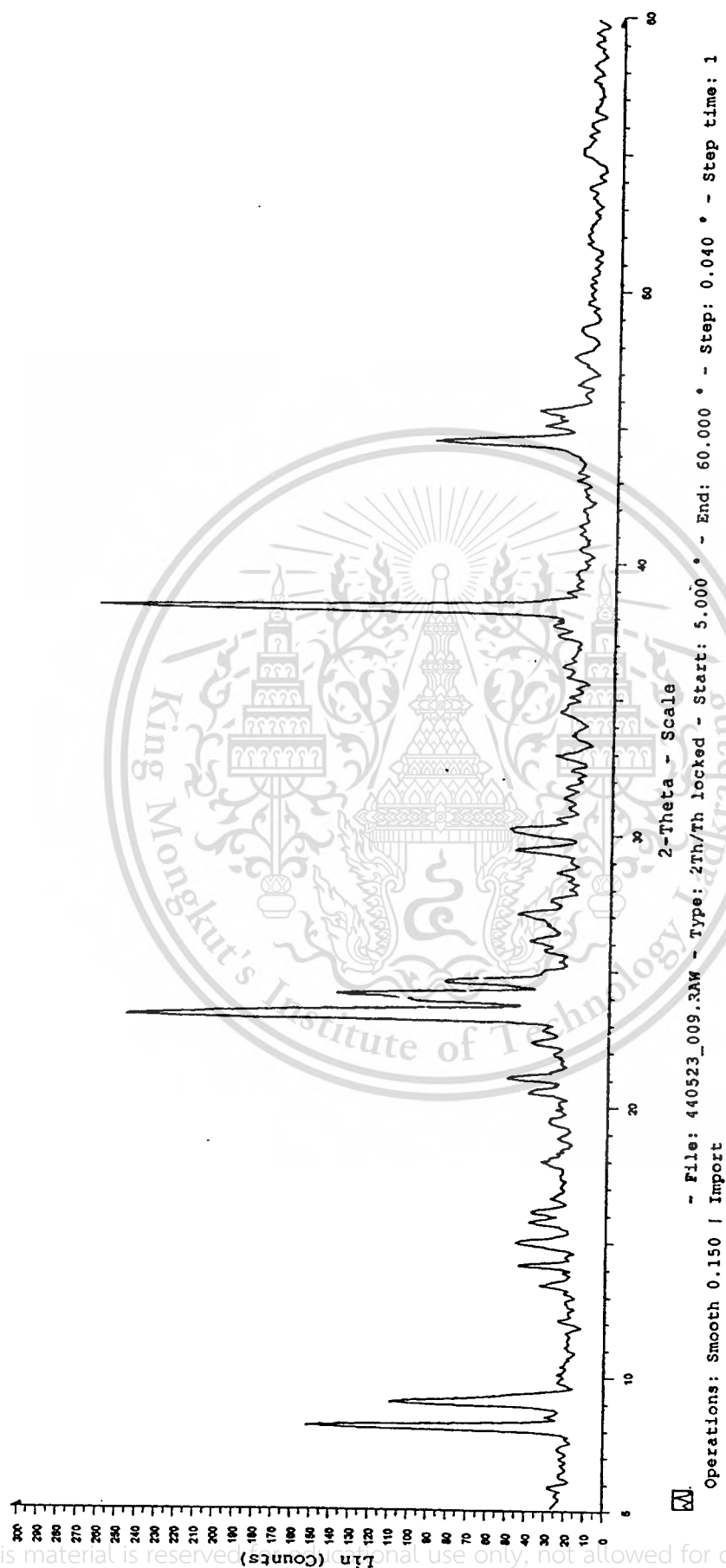


Figure D5 XRD pattern of pretreatment with hydrogen of AgHZSM5

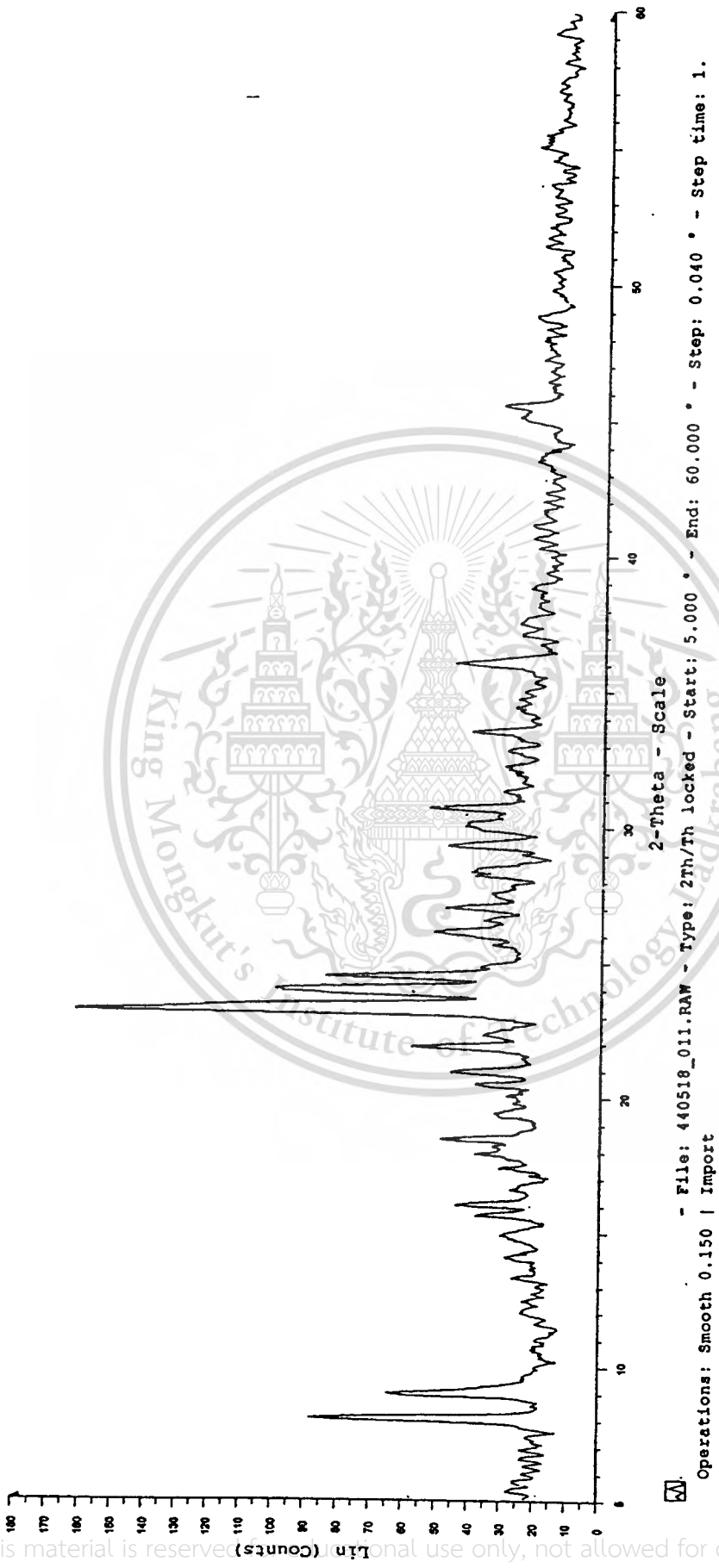


Figure D6 XRD pattern of AgNaZSM5

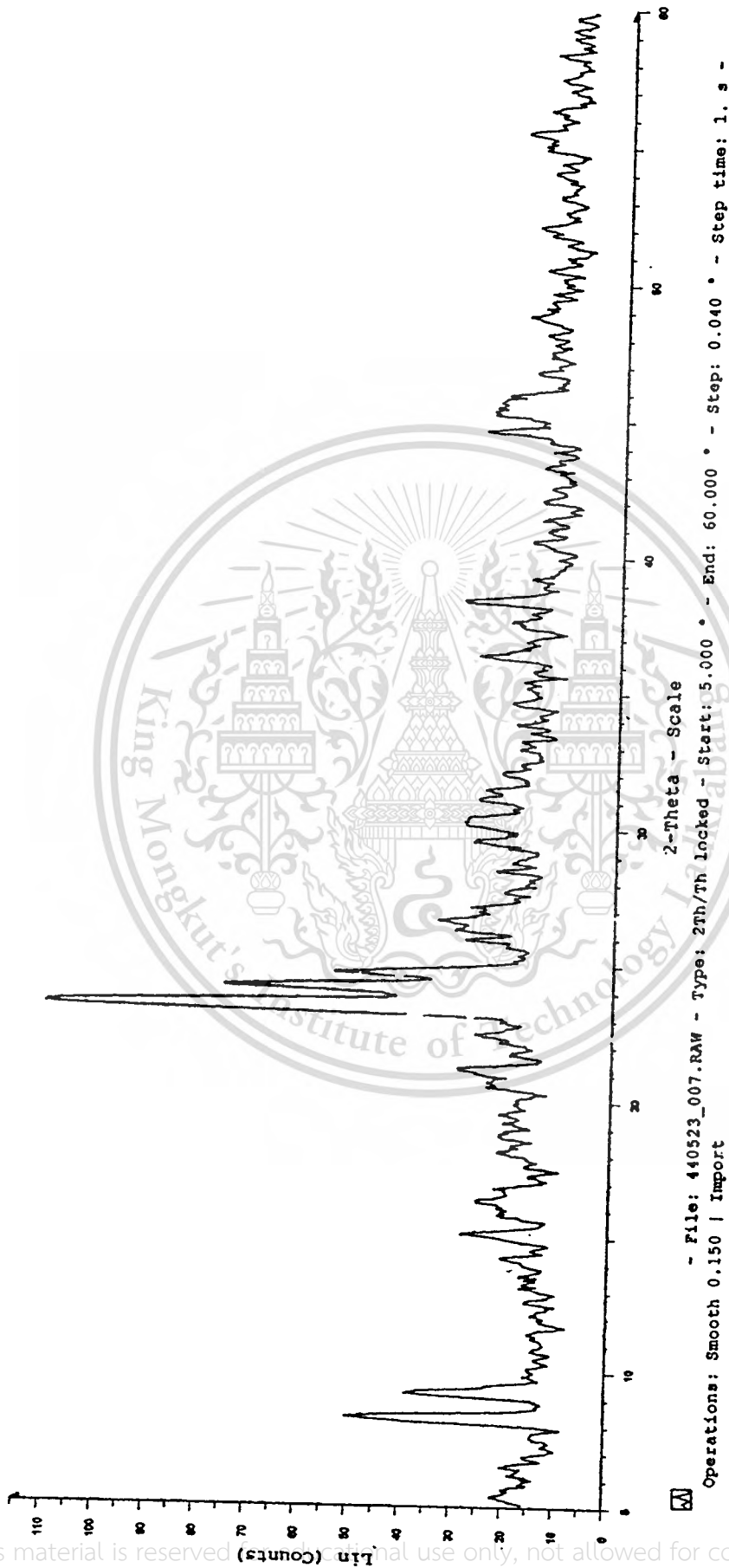


Figure D7 XRD pattern of [Ag]HZSM5

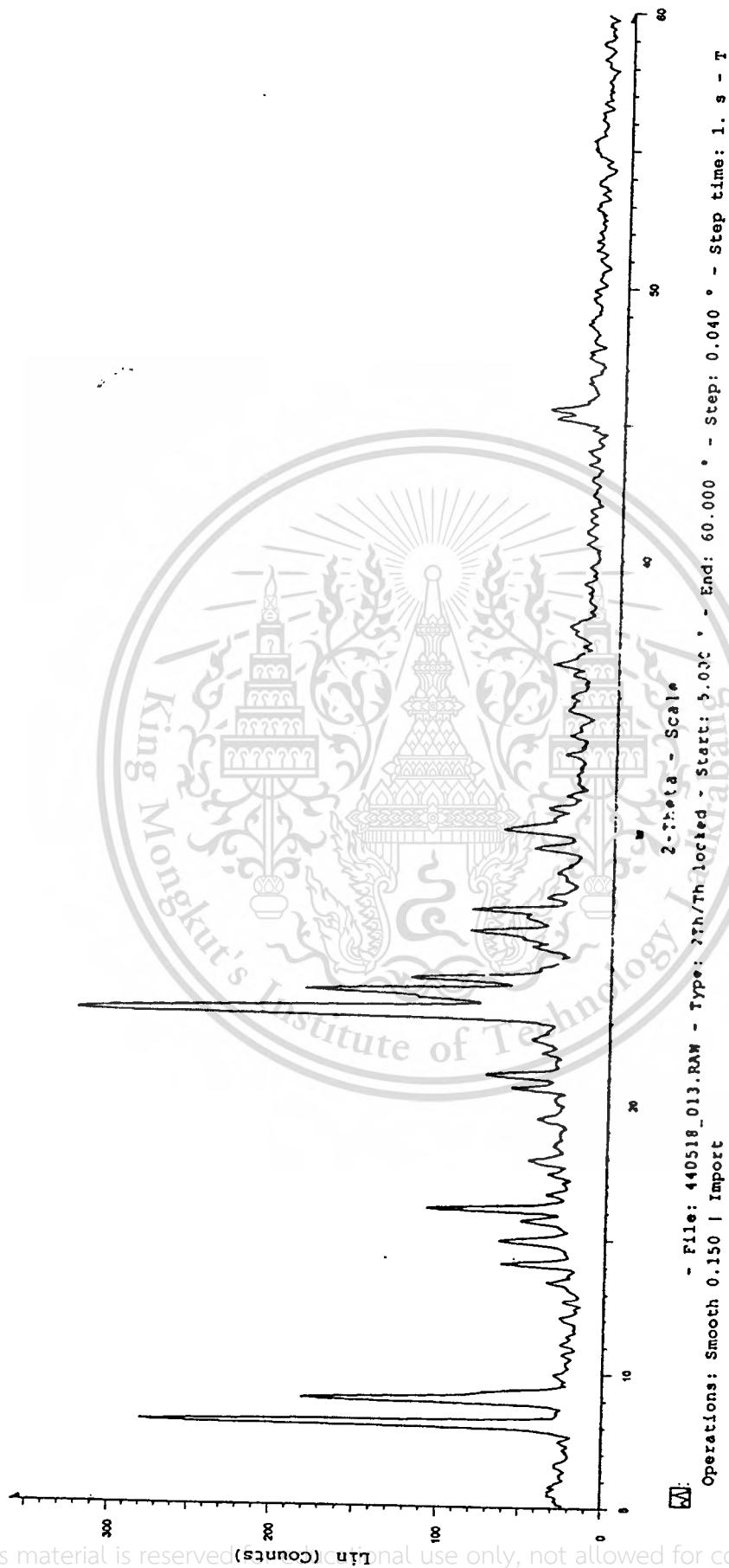


Figure D8 XRD pattern of HZSM5 after ethanol conversion at 425 °C.

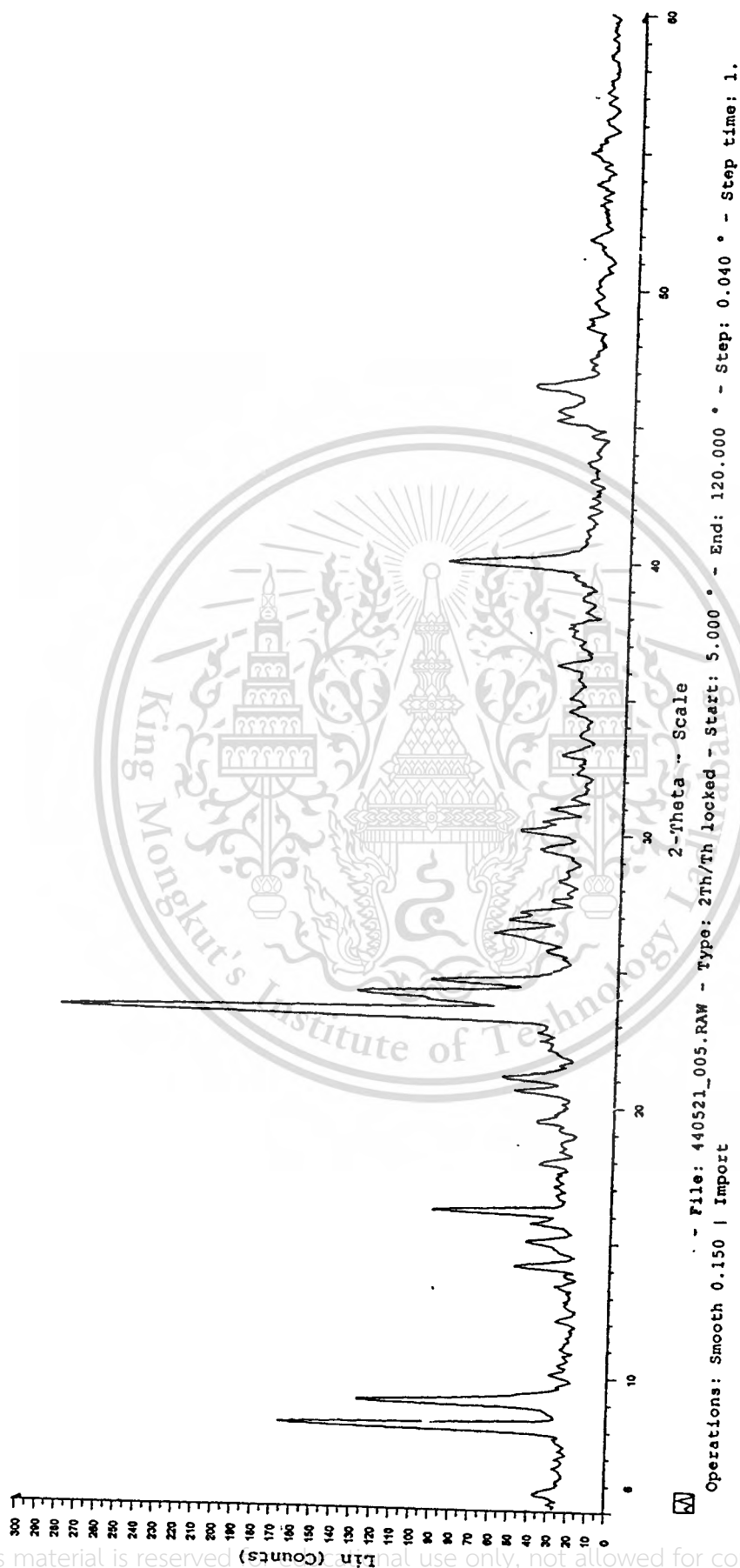


Figure D9 XRD pattern of [Pt]HZSM5 after ethanol conversion at 425 °C

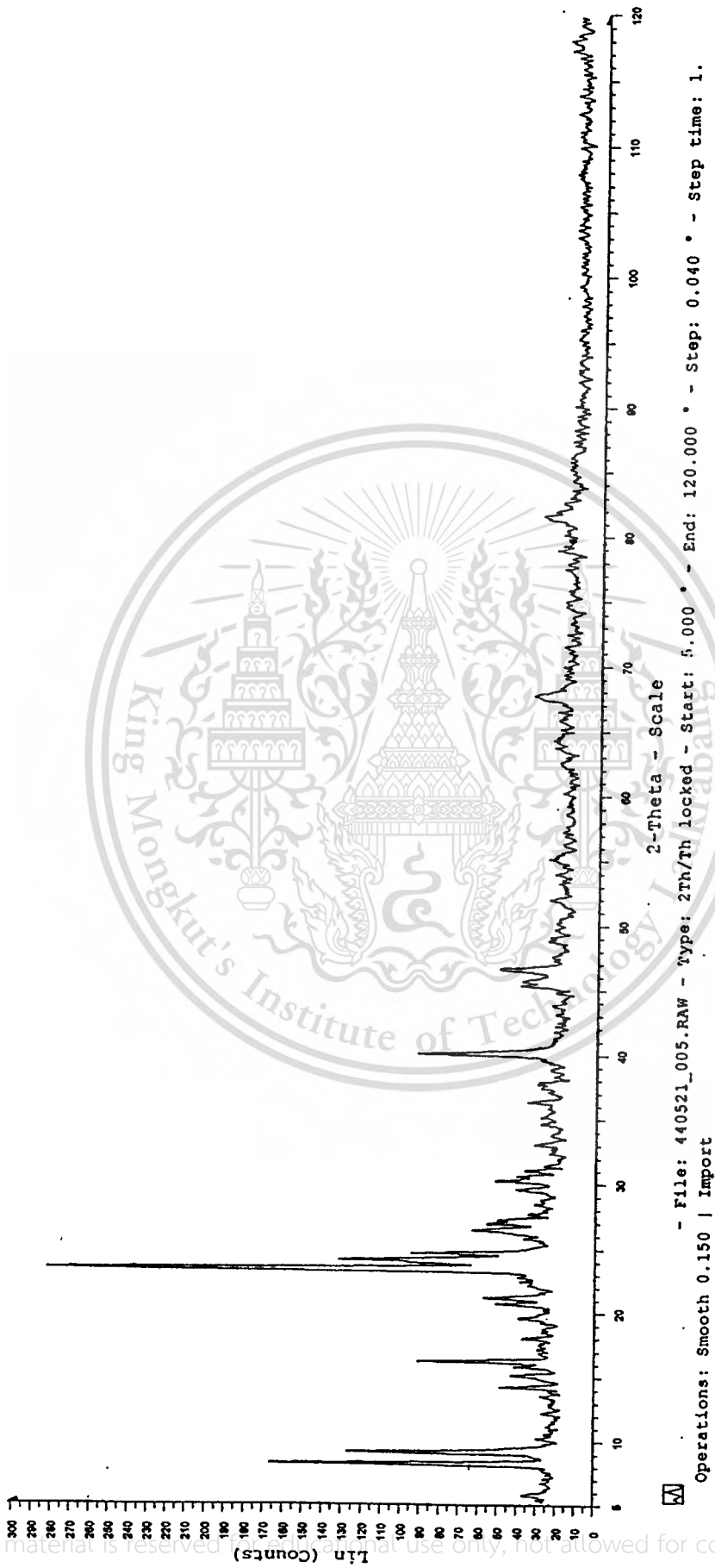


Figure D10 XRD pattern of [Pt]HZSM5 after ethanol conversion at 425 °C (2 theta = 5 to 120)

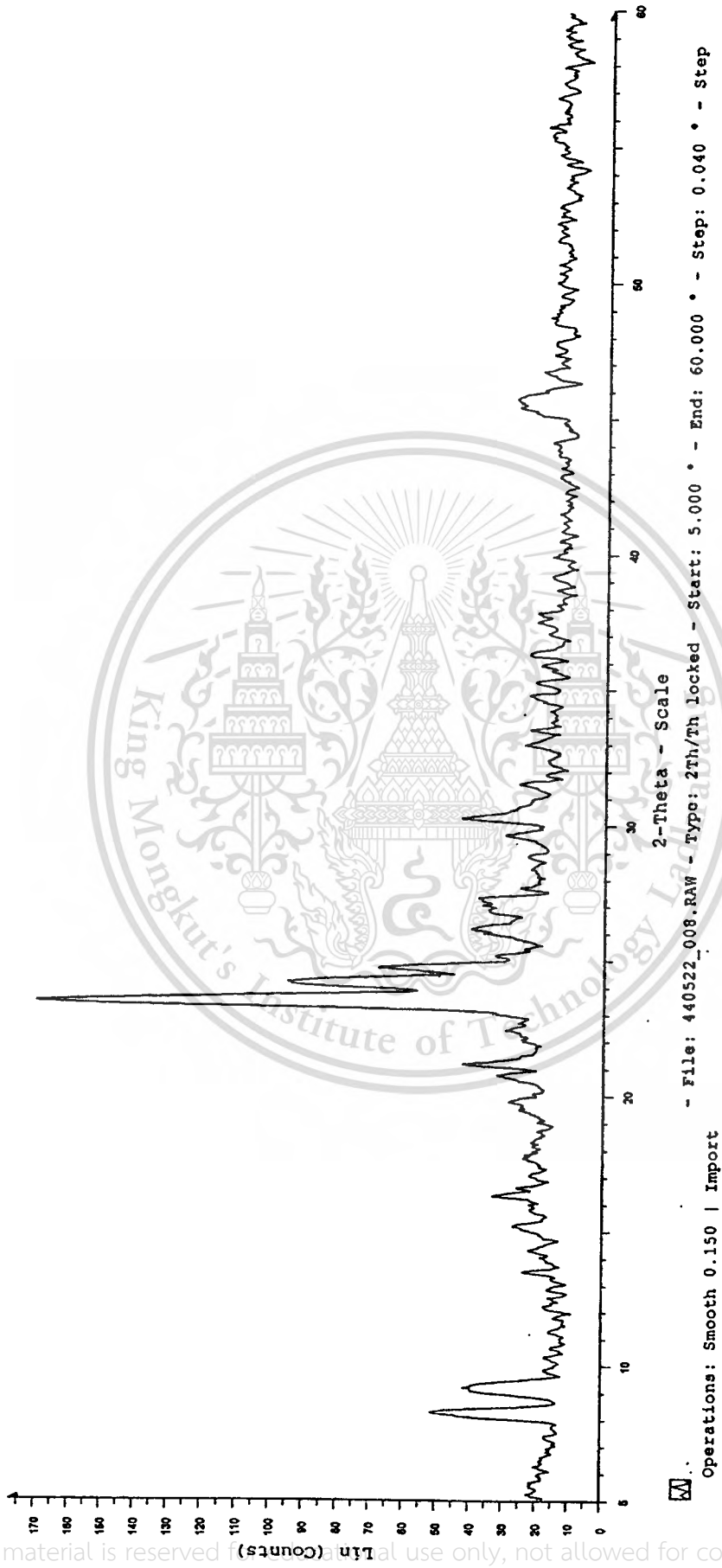


Figure D11 XRD pattern of [Ga]HZSM-5 after ethanol conversion at 425 °C

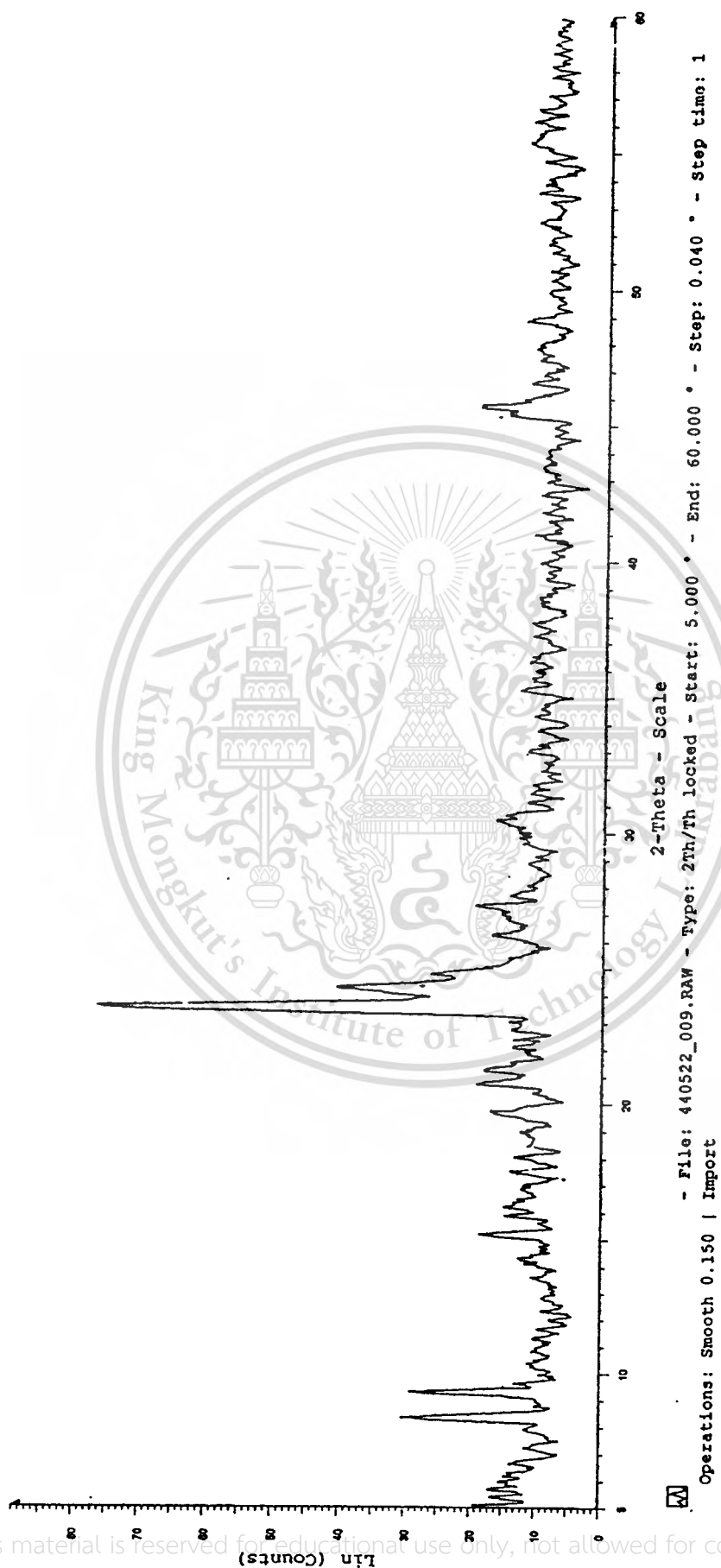


Figure D12 XRD pattern of [Ga]HZSM5 after ethylene conversion at 425 °C

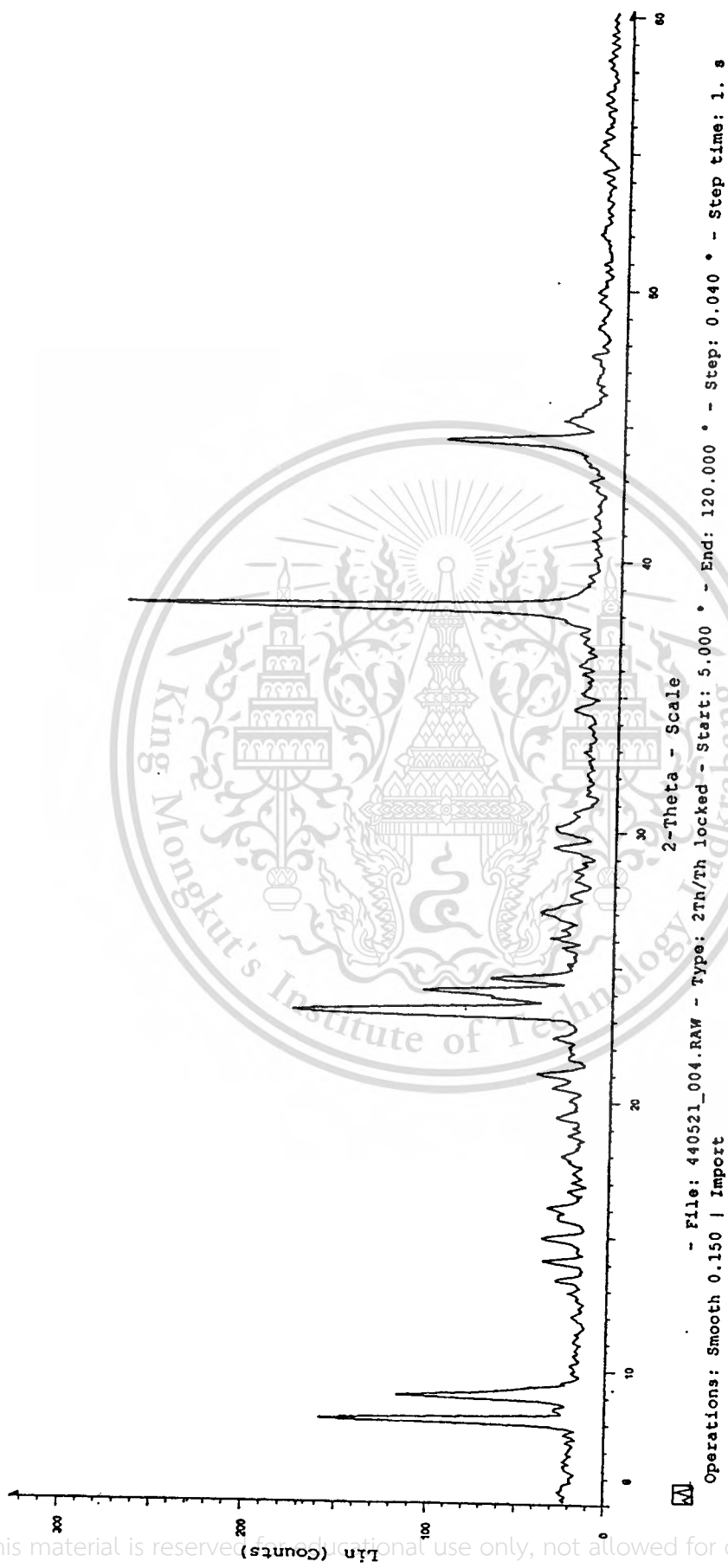


Figure D13 XRD pattern of AgH7SM5 after ethanol conversion at 425 °C

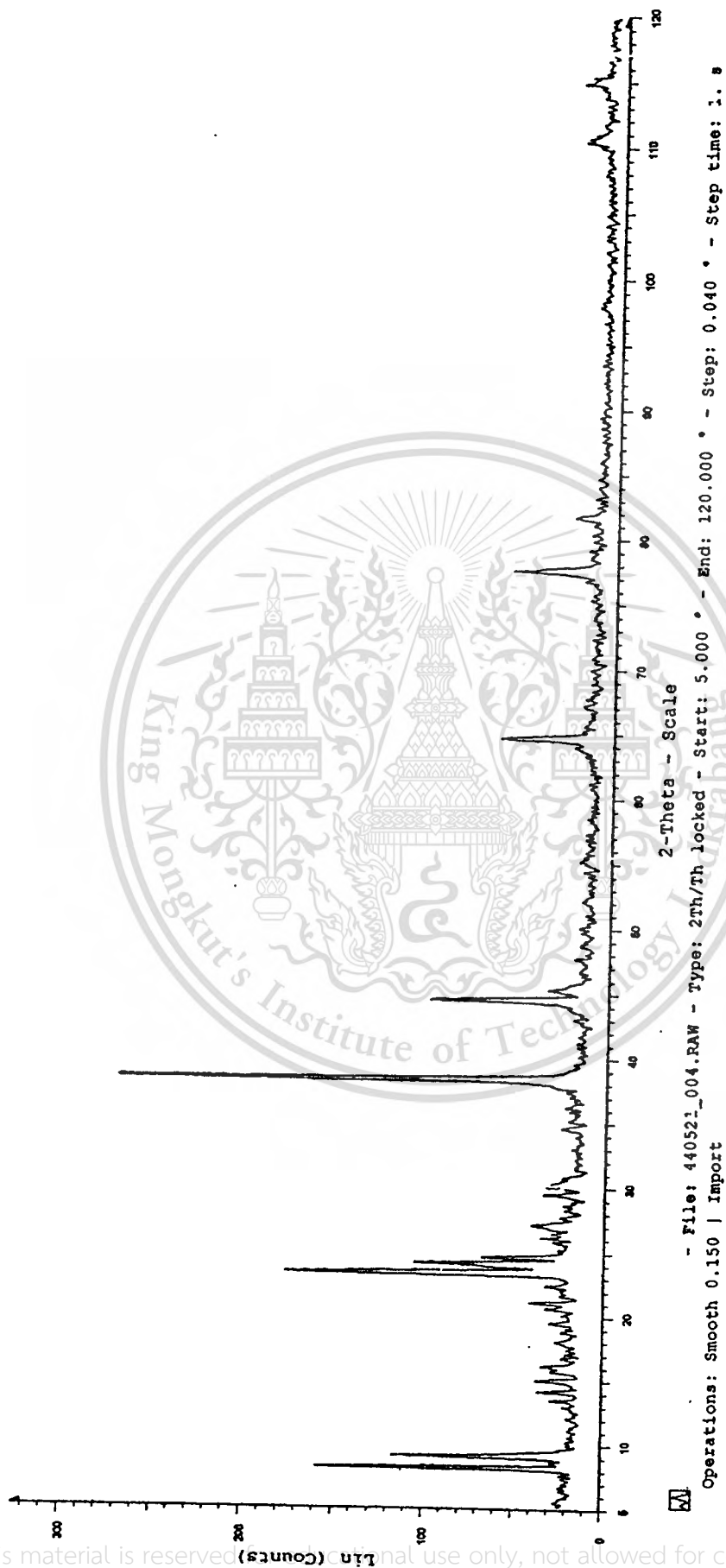


Figure D14 XRD pattern of AgHZSM5 after ethanol conversion at 425 °C (2 theta = 5 to 120)

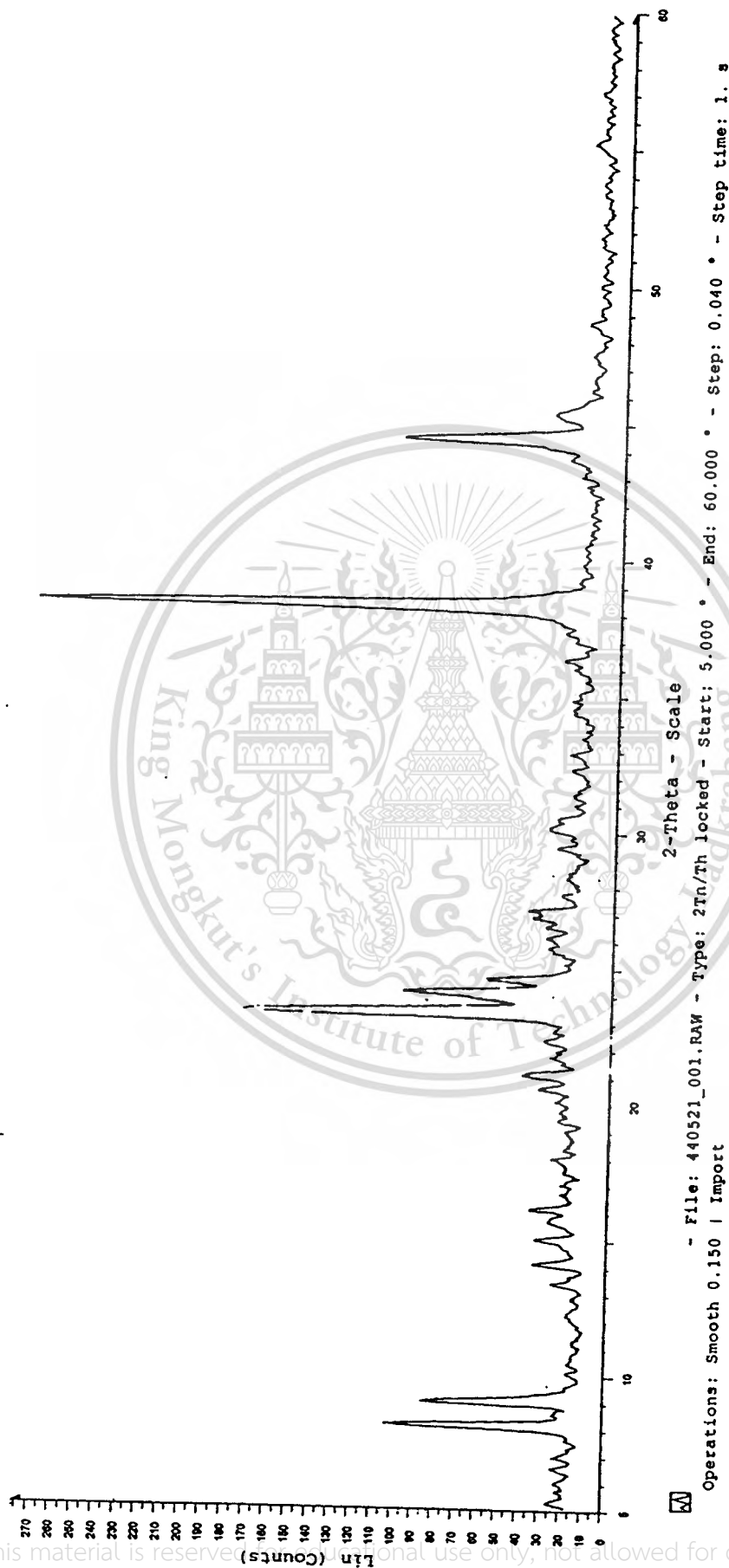


Figure D15 XRD pattern of AgNaZSM5 after ethanol conversion at 425 °C

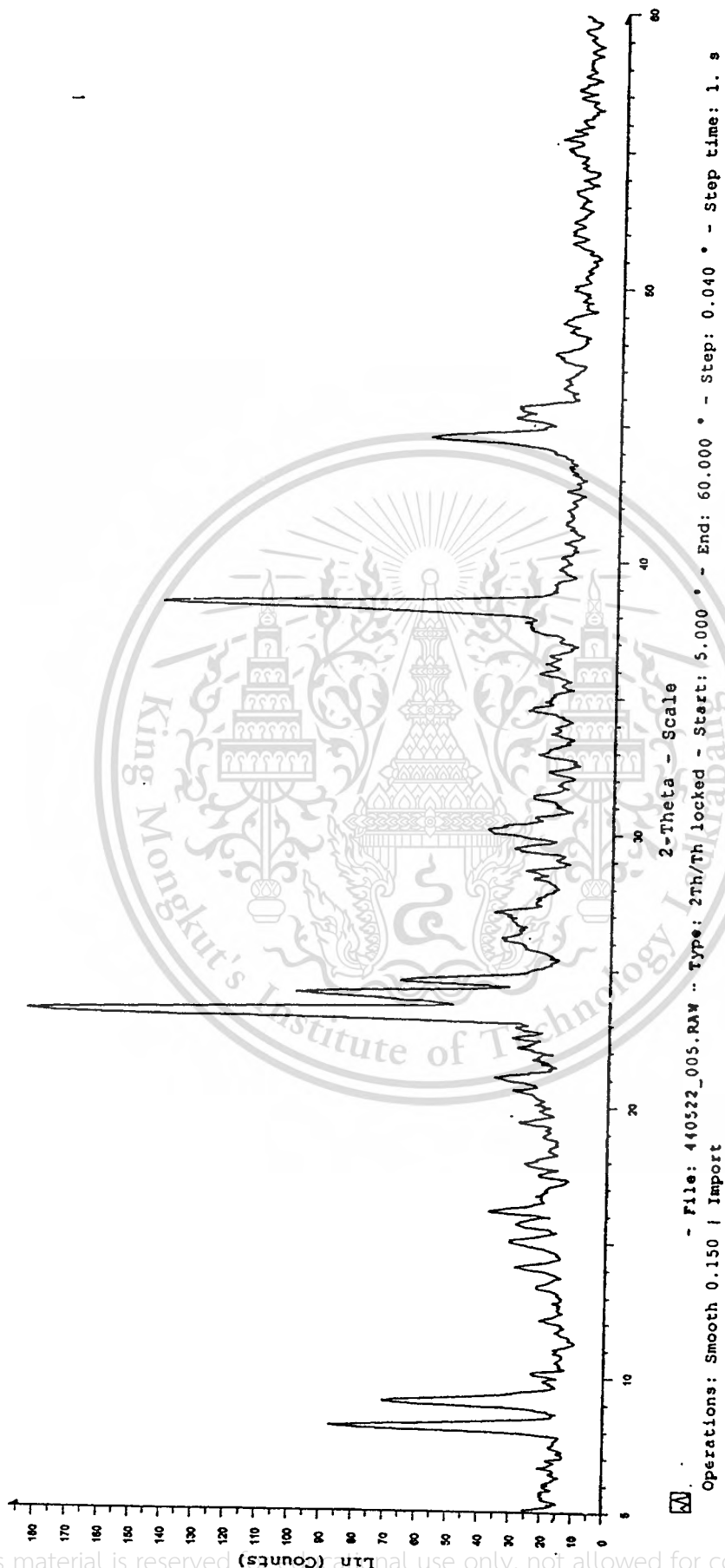


Figure D16 XRD pattern of [Ag]HZSM5 after ethanol conversion at 425 °C

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID HZSM5
Description micropore analysis
Comments HK Method
Sample Weight 0.0010 g
Adsorbate NITROGEN
Cross-Sec Area 16.2 Å²/molecule
NonIdeality 6.530E-05
Molecular Wt 28.0134 g/mol
Station # 1

Outgas Temp 350.0 °C
Outgas Time 18.0 hrs
P/Po Toler 0
Equil Time 3
Bath Temp. 77.35

Operator ARTIT
Analysis Time 2122.6 min
End of Run 08/13/1999 05:54
File Name ETG_6.RAW

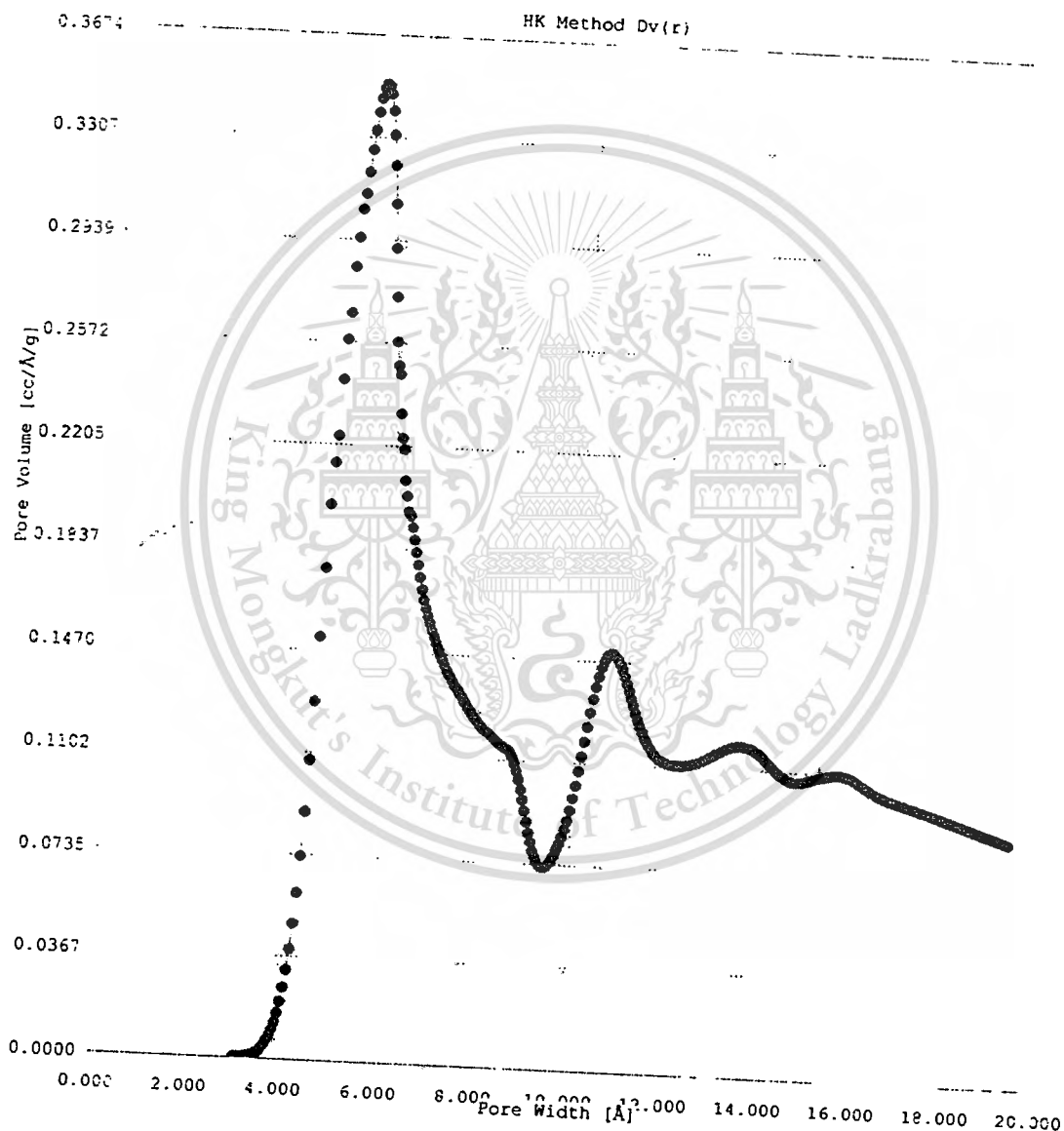


Figure E1 HK plot of HZSM5

Quantachrome Corporation
 Quantachrome Autosorb Automated Gas Sorption System Report
 Autosorb for Windows® Version 1.19

Sample ID	AgHZSM5				
Description	micropore analysis				
Comments	HK method				
Sample Weight	0.0012 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	APRIT
Cross-Sec Area	16.2 Å ² /molecule	Outgas Time	18.0 hrs	Analysis Time	1997.5 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	19 16/1999 10:32
Molecular Wt	28.0134 g/mol	Equil Time	5	File Name	ETS_8.RAW
Station #	1	Bath Temp.	-77.35		

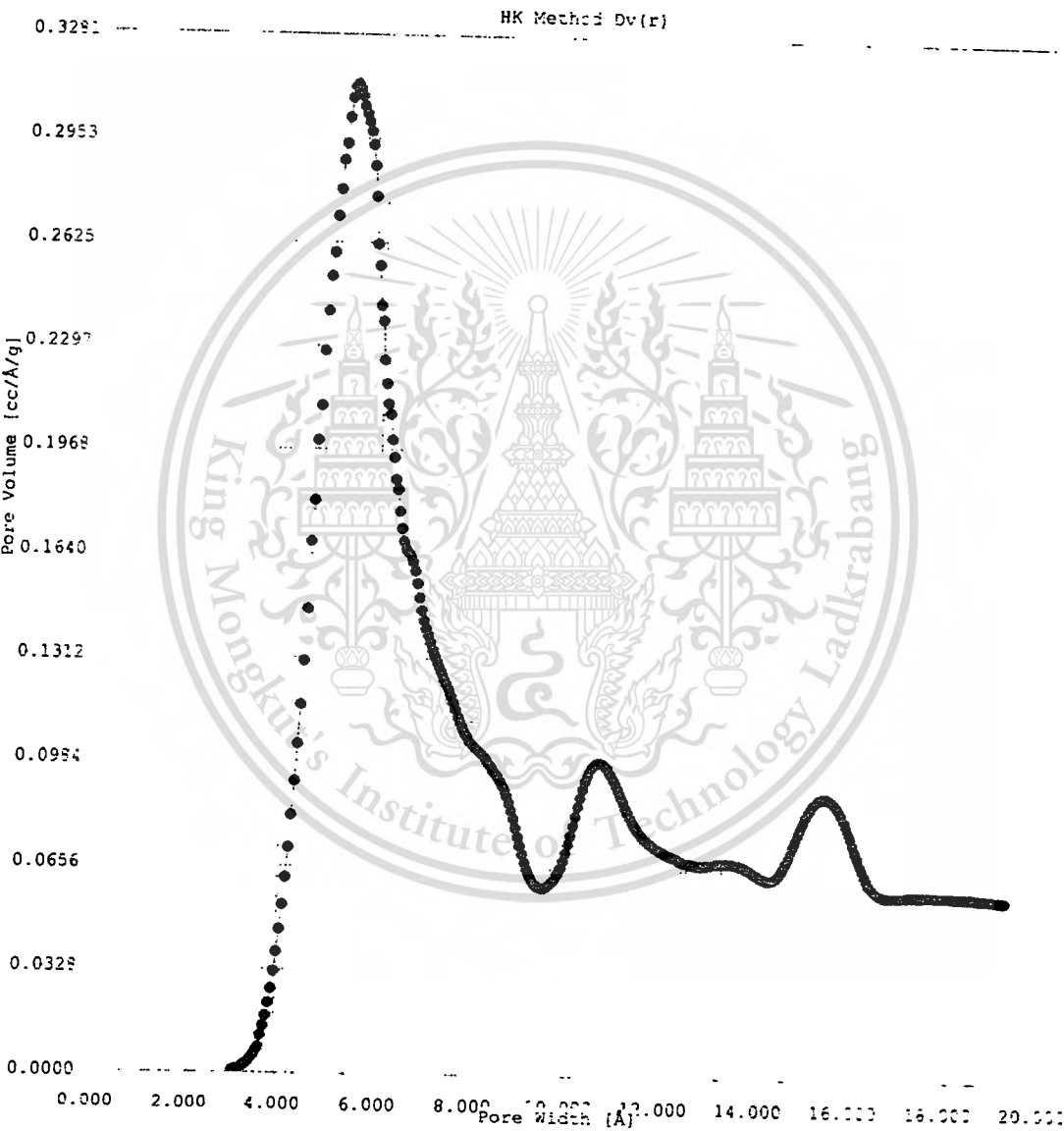


Figure E2 HK plot of AgHZSM5

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	AgNaZSM5				
Description	micropore analysis				
Comments	HK method				
Sample Weight	0.0010 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	ARJIT
Cross-Sec Area	16.2 Å ² /molecule	Outgas Time	18.0 hrs	Analysis Time	16:17 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	07/18/1999 08:39
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	ET05.PAW
Station #	1	Bath Temp.	77.35		

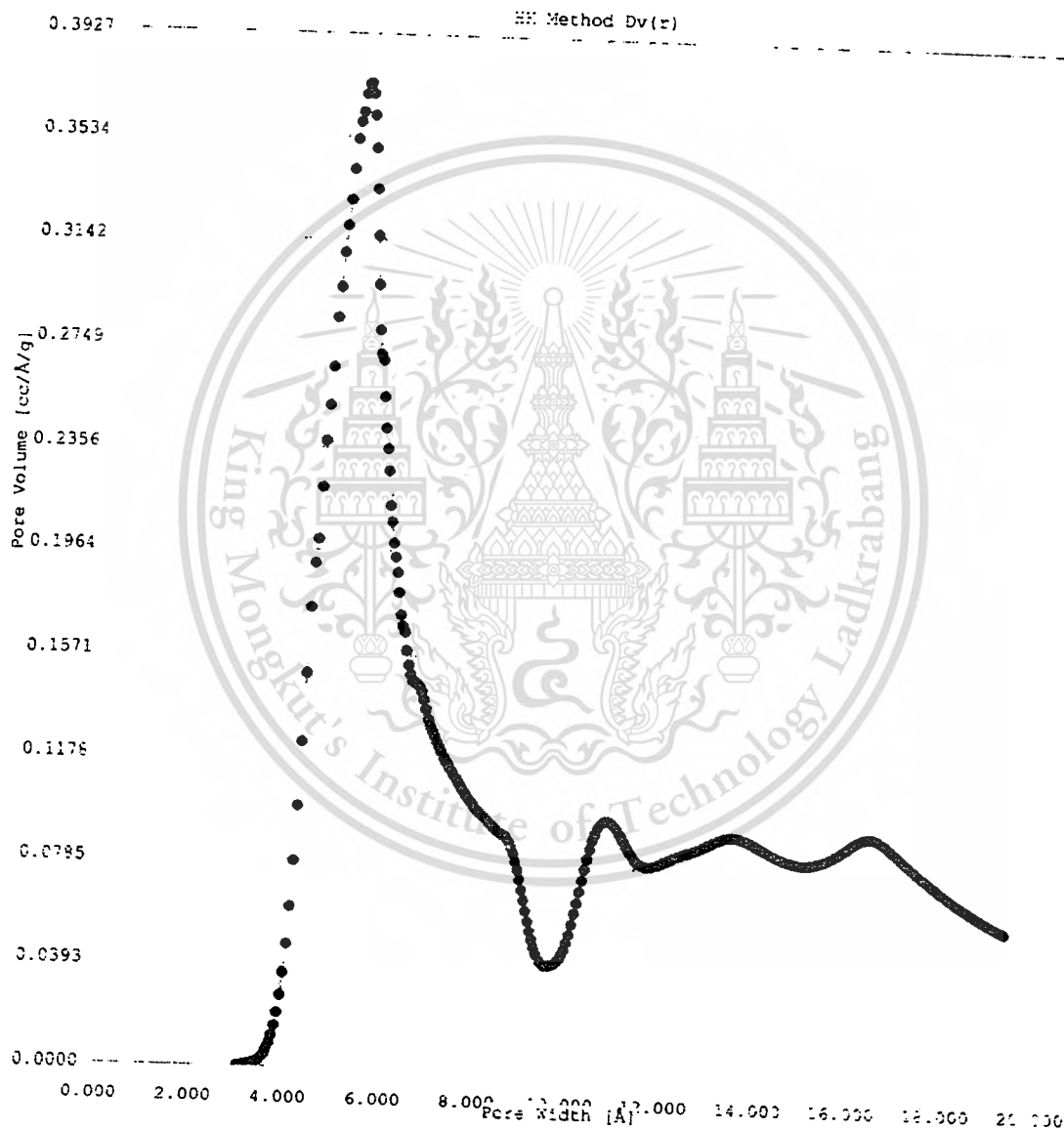


Figure E3 HK plot of AgNaZSM5

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	red-AgHZSM5 at 450 oC				
Description	micropore analysis				
Comments	HK method				
Sample Weight	0.0011 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	Artit
Cross-Sec Area	16.2 Å ² /molecule	Outgas Time	18.0 hrs	Analysis Time	398.0 min
NonIdeality	6.590E-05	P/Po Toler	0	End of Run	12/27/2000 10:26
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	ET3.RAW
Station #	:	Bath Temp.	77.35		

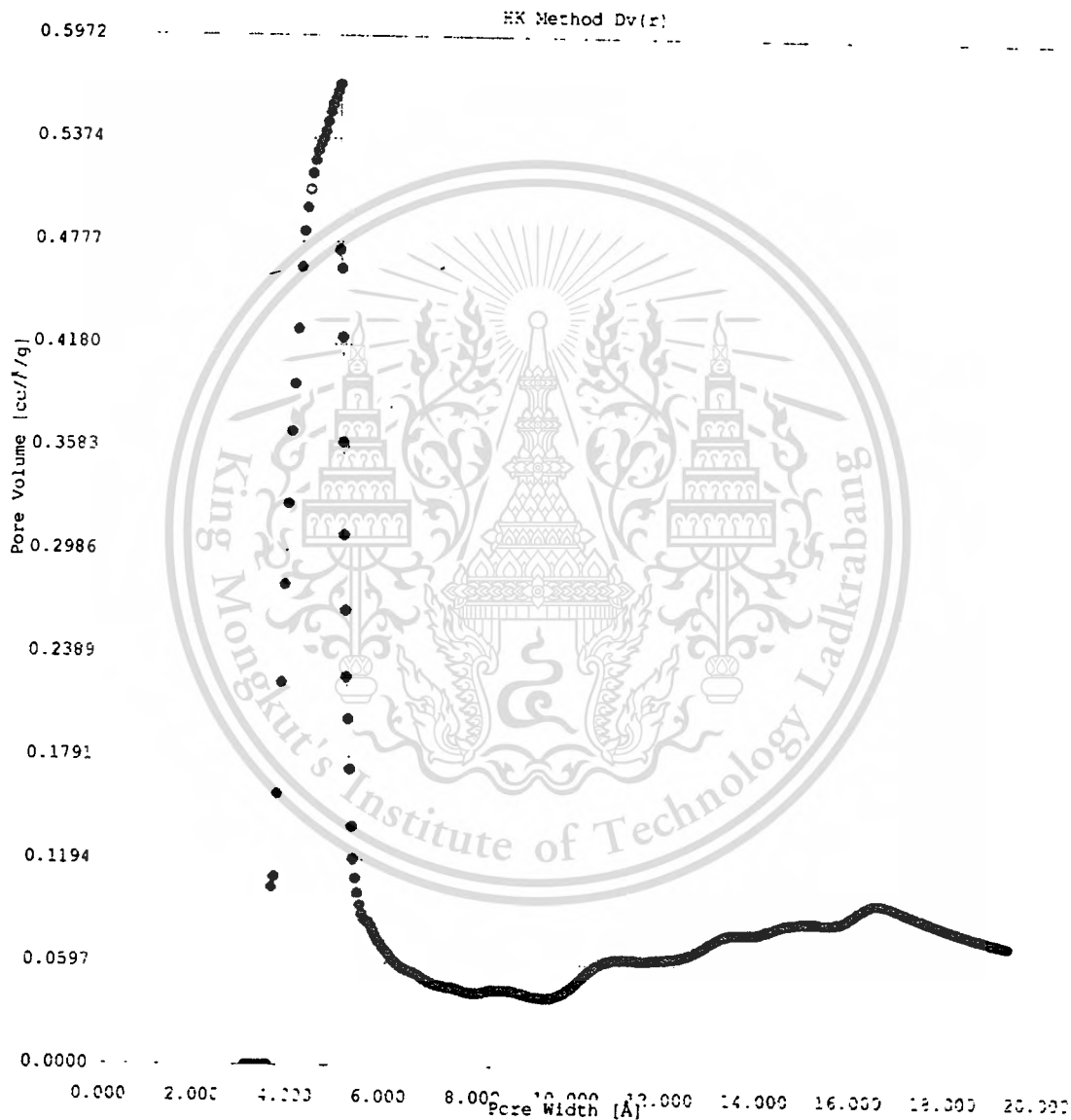


Figure E4 HK plot of red-AgHZSM5 pretreated with hydrogen at 450 °C for 6 hours

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	red-AgNaZSM5 at 450 °C				
Description	micropore analysis				
Comments	HK method				
Sample Weight	0.0013 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	ARJIT
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	18.0 hrs	Analysis Time	111.5 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	11/07/2000 08:51
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	ETGA3.PAW
Station #	1	Bath Temp.	77.40		

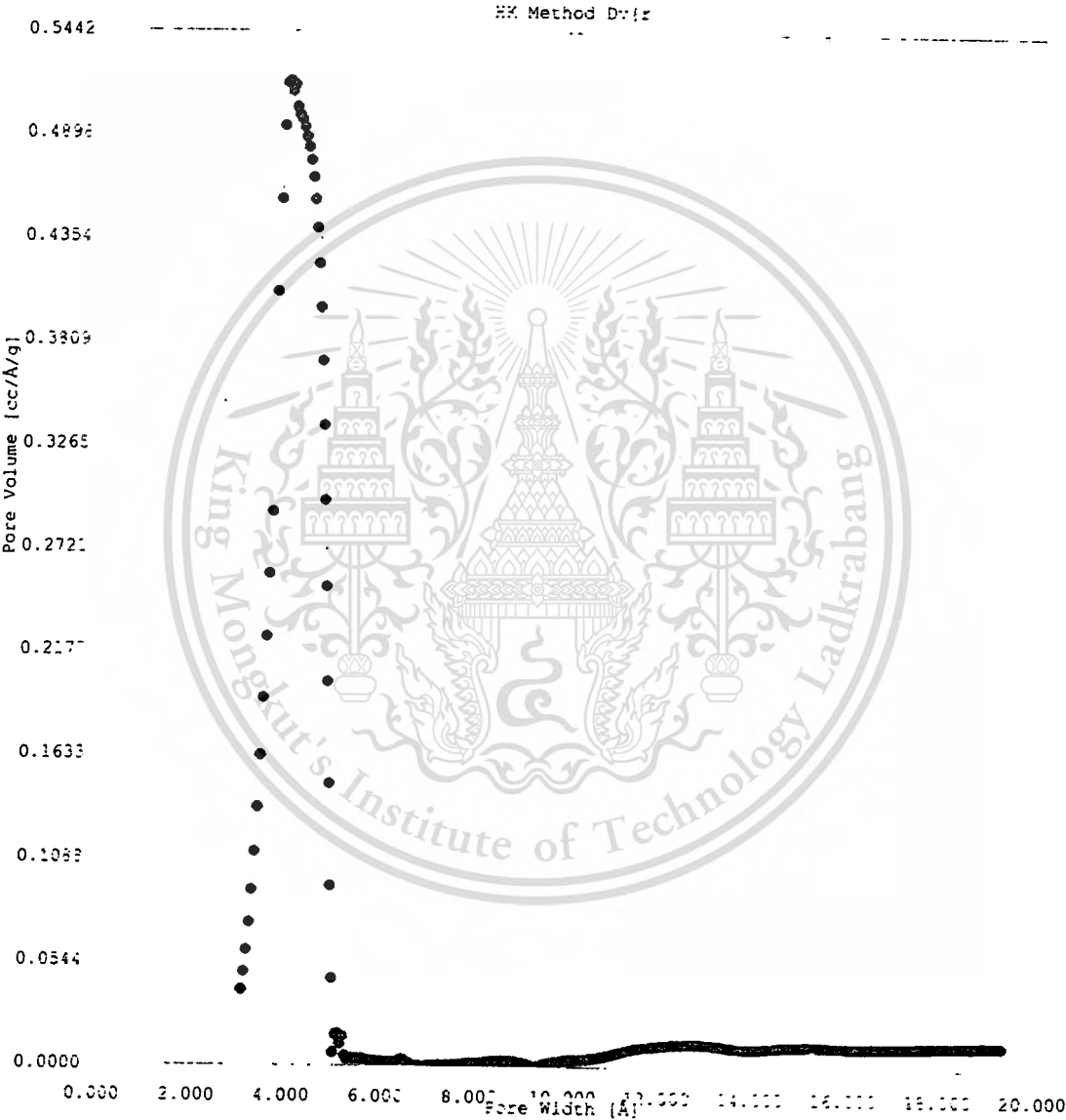


Figure E5 HK plot of red-AgNaZSM5 pretreated with hydrogen at 450 °C for 6 hours

AUTHOR BIOGRAPHY

Mr. Artit Ausavasukhi was born on August 8, 1976 in Bangkok. He received a Bachelor Degree in Industrial Chemistry from the Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang in 1998. He has been a graduate student of the Program of Petrochemicals and Hydrocarbon Chemistry since 1999.

