AMMOXIMATION BY TITANIUM-CONTAINING ZEOLITES

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หัวข้อวิทยานิพนธ์	การใช้ซีโอไลต์ที่มีไทเทเนียมเป็นองค์ประกอบเป็นตัวเร่งในปฏิกิริยาแอมมอกซิเมชัน
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บทคัดย่อ

วิทยานิพนธ์เล่มนี้เป็นการศึกษาปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนเพื่อสังเคราะห์ไซโคลเฮกซาโนนออกซีมโดยใช้ไทเทเนียม ซิลิกาไลต์ (TS-1) และไทเทเนียมบีต้าซีโอไลต์ (Ti-Beta) เป็นตัวเร่งปฏิกิริยาในสภาวะของเหลว โดยทำการศึกษาถึงผลของตัวทำละลาย แหล่งของแอมโมเนียจากเกลือแอมโมเนีย ขนาดรูพรุนจุลภาคของซีโอไลต์ ผลของการเติมซีโอไลต์เอ และ ผลของระยะเวลาที่ตัวเร่งปฏิกิริยาสัมผัสกับสารตั้งต้น จากงานวิจัยพบว่าการใช้กรดแอซิติกเป็นตัวทำละลายจะทำให้ได้ผลิตภัณฑ์เป็นไซโคลเฮกซาโนนออกซีมในปริมาณที่มากกว่าเมื่อใช้น้ำเป็นตัวทำละลาย ทั้งนี้เป็นผลเนื่องมาจากการเกิดกรดเปอร์แอซิติกซึ่งเป็นตัวออกซิไดส์ที่ว่องไว แต่จะทำให้ความเฉพาะเจาะจง (Selectivity) ในการเกิดไซโคลเฮกซาโนนออกซีมมีค่าต่ำ และเมื่อทำการเติมซีโอไลต์เอ ลงไปในปฏิกิริยาพบว่า ซีโอไลต์เอ จะช่วยทำให้ผลิตภัณฑ์ข้างเคียงเกิดน้อยลง ในการศึกษาความเป็นไปได้ที่จะใช้เกลือแอมโมเนียเป็นสารตั้งต้นพบว่า เกลือแอมโมเนียที่เกิดจากกรดอ่อนเช่น เกลือแอมโมเนียมแอซิ-เตด แอมโมเนียมคาร์บอเนต แอมโมเนียมซิเตรท และแอมโมเนียมออกซาเลต สามารถทำให้เกิดปฏิกิริยาได้ และจากการศึกษาถึงผลของรูพรุนจุลภาคที่มีต่อการเกิดปฏิกิริยาพบว่า การเร่งปฏิกิริยาโดยใช้ซีโอไลต์ไทเทเนียมบีต้าได้ผลดีกว่าการใช้ไทเทเนียมซิลิกาไลต์ แต่สามารถทำให้เกิดการจัดเรียงตัวใหม่ของผลิตภัณฑ์ที่เกิดขึ้นทำให้ได้ผลิตภัณฑ์เป็นคาโปรเลกเทมอีกด้วย นอกจากนี้ยังพบว่ากลไกการเกิดปฏิกิริยาแอมมอกซิเมชันสามารถเกิดขึ้นได้ 2 ทาง แต่ไซโคลเฮกซาโนนออกซีมที่เกิดขึ้นในปฏิกิริยาที่ใช้กรดแอซิติกเป็นสารละลายส่วนใหญ่จะเกิดผ่านกลไกการเกิดปฏิกิริยาซึ่งแอมโมเนียเข้าทำปฏิกิริยากับไซโคลเฮกซาโนนก่อนแล้วจึงถูกออกซิไดส์ได้เป็นไซโคลเฮกซาโนนออกซีม

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ABSTRACT

In this thesis the ammoximation of cyclohexanone to cyclohexanone oxime with hydrogen peroxide and ammonia, in liquid phase, over TS-1 and Ti-Beta zeolites, was studied. The effects of solvent, source of ammonia, pore size of zeolites, addition of zeolite A and contact time were investigated. It was found that the reaction using acetic acid as solvent shows higher activity than that using water as solvent due to the formation of a better oxidizing agent, per acetic acid. Selectivity of cyclohexanone oxime, on the other hand, was relatively low in the case of that using acetic acid. Addition of zeolite A can reduce the formation of by-product and consequently give a higher selectivity. The investigation on alternative sources of ammonia showed that ammonium salts of weak acid, such as ammonium acetate, ammonium carbonate, ammonium citrate and ammonium oxalate can be used for synthesis cyclohexanone oxime. Ammoximation reaction catalyzed by Ti-Beta zeolite produces higher yields of products than that using TS-1. However, further rearrangement of cyclohexanone oxime to caprolactam was observed. The study of the reaction mechanism shows that there are two possible partway for the formation of cyclohexanone oxime. The condensation of ammonia with cyclohexanone to produce primarily cyclohexanone imine followed by oxidation of cyclohexanone is favored in the presence of acetic acid.

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Veerachai Chitranuwatkul

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Chapter 1

Introduction

1.1 Motivation

Cyclohexanone oxime is the key intermediate in the manufacture of caprolactam. In industrial process, cyclohexanone oxime is produced from cyclohexanone and hydroxylamine (or hydroxylamine salts). The reaction used to produce hydroxylamine employed number of hazardous chemicals. Titanium containing zeolite can be used for synthesis of cyclohexanone oxime at a relatively mild condition. This reaction gives high conversion and selectivity. However, there is limited report on process development to industrial scale. In this thesis, the necessary factors for large-scale production such as solvent system and contact time will also be investigated.

1.2 Objectives

The overall objective of this study is to study the ammoximation of cyclohexanone to cyclohexanone oxime.

The specific objectives of the study are as follow:

1.2.1 To understand the necessary factors for large-scale production.

1.2.2 To obtain a suitable condition for the maximum yield of product such as temperature, titanium species, and effect of solvent.

1.2.3 To obtain the alternative choice of ammonia resource for easier operating process.

1.3 Scope of study

1.3.1 Synthesis of Ti-Beta and titanium silicalite (TS-1).

1.3.2 Testing on catalytic activity of Ti-Beta and titanium silicalite (TS-1) in ammoximation of cyclohexanone.

1.3.3 Study on effect of temperature.

1.3.4 Study on effect of titanium content in framework of zeolite.

1.3.5 Study on effect of solvent used in ammoximation reaction.

1.3.6 Study on effect of contact time.

1.3.7 Seeking for the alternative choice of ammonia resource.

1.4 Expected results

1.4.1 The result of this thesis can be used for as guidance development of industrial scale process.

1.4.2 A suitable condition for a maximum productivity can be obtained.

1.4.3 This thesis can provide appropriate choice of ammonia resource.

Chapter 2

Literature review and Theory

2.1 Zeolite

The word "zeolite" is Greek in origin, derived from the words "zein" and "lithos" meaning to boil and rock. It was first used by the Swedish chemist who found that upon heating, the zeolite sample evolved steam [1]. There was little interest in zeolites until the late 1930's when the modern founder of zeolite chemistry, Barrer began the characterization of zeolite structure and chemistry. His initial work studying zeolites confirmed the molecular sieving properties of the microporous solids and was reported in a paper titled "The sorption of polar gases by zeolites" and published in the Proceedings of the Royal Society [2]. These discoveries sparked huge interest in the synthesis of shape selective zeolite catalysts in companies such as Union Carbide and Mobil in the late 1950's. Today, one of the most industrially important uses of zeolites is chemical catalysis, most notably in the petrochemical industry where zeolites are used in oil refining as cracking catalysts and in the Methanol to Gasoline (MTG) catalytic conversion process [3].

2.1.1 Structure

Like most silicates, the zeolites are based on TO_4 tetrahedra, where T is an aluminium or silicon atom. The vast 3-dimensional networks are a result of all four corners from the tetrahedra being shared, producing low-density microporous materials. Zeolite structures can be thought to exist of finite or infinite (chains, layers etc) component units. The finite units so called secondary building units (SBU's) which have been found to occur are shown in the Figure 2.1 below.

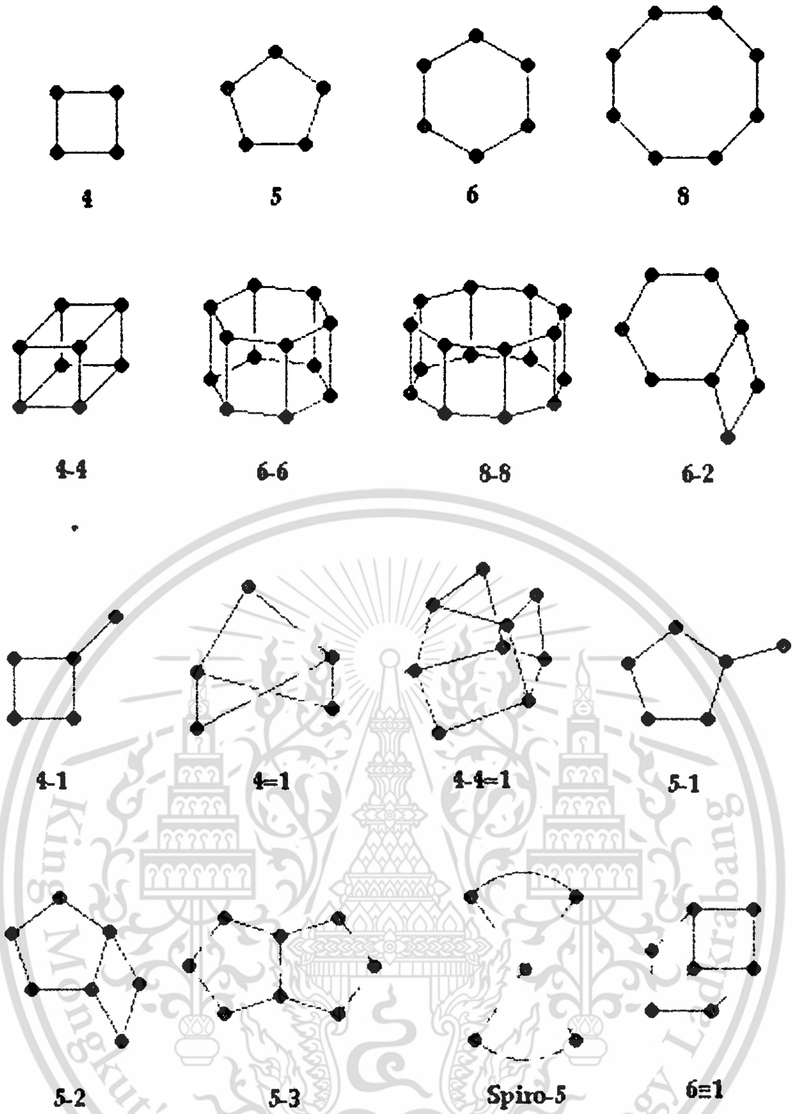


Figure 2.1 Secondary Building Units (SBU's) in zeolites.

In the Figure 2.1, the T atom of the TO$_4$ tetrahedral primary building unit is located at each of the corners, and the oxygens are located towards the midpoints of the lines joining each T atom (the oxygens are not shown to aid clarity). These secondary building units (SBU's), can contain up to 16 T atoms. It can be noted that SBU's are non-chiral (neither left or right "handed"). A unit cell always contains the same number of SBU's, and although rare, some materials can have different combinations of SBU's within the zeolite framework. The framework may be considered in terms of large polyhedral building blocks forming characteristic cages. For example, sodalite, zeolite A and zeolite X and Y (Faujasite) can all be generated by the truncated octahedron known as the "cage" (Figure 2.2).

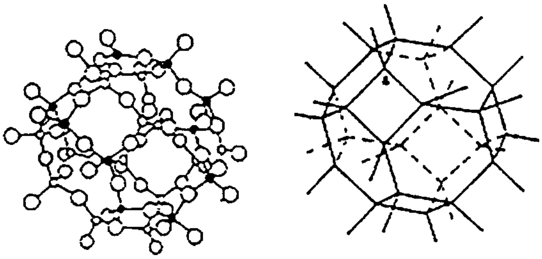


Figure 2.2 A "ball and strick" representation of the structure of the sodalite unit (β-cage, left) with a framework diagram for comparison.

As shown in Figure 2.2, the β-cage has both four-membered and six-membered rings in its structure. The cage formed has an internal diameter of approx. 6Å - sufficient to encapsulate small molecules. By fusing together the four-membered rings, sodalite is formed - and is a naturally occuring material. By bridging (not fusing) the four-membered rings, zeolite A is formed. This does not occur in nature, but is industrially produced on a massive scale for its use in ion exchange, gas separation and drying. If the six-membered rings are bridged, then possibly the most important zeolite structure, zeolite X and Y is formed. The zeolite Y possess higher the silicon/aluminum ratio than zeolite X, despite they exist in the same structure. This structure has very large microporous spaces, allowing organic molecules to diffuse in and out. Zeolite Y is one of the most important catalytic systems, and is used in the cracking of long chain hydrocarbons into shorter chain length fuels.

Another important class of materials are the pentasil zeolites (channel). It is named so because they are constructed of five-membered rings. The most important example is that of ZSM-5, which is shown in Figure 2.3.

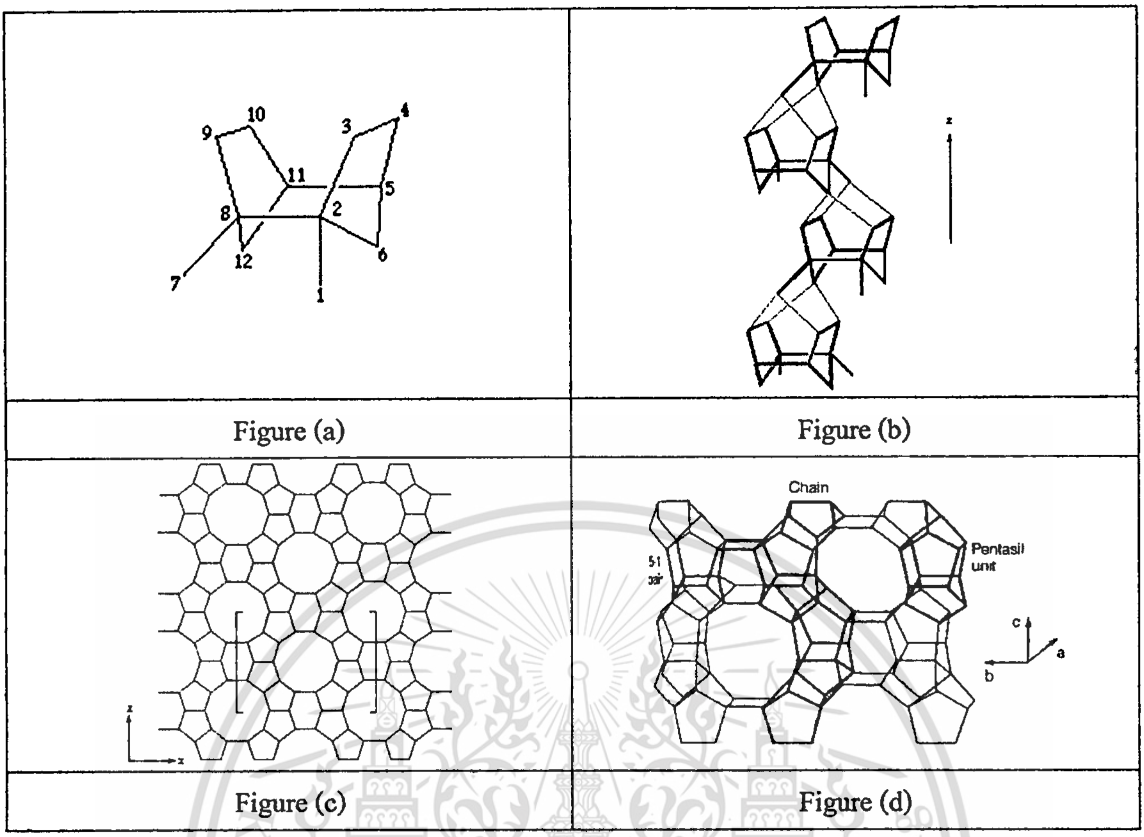


Figure (a)

Figure (b)

Figure (c)

Figure (d)

Figure 2.3 (a) SBU in pentasil zeolites, (b) SBU linked chains, (c) Layer formed from linked chains in ZSM-5 structure, and (d) Chimed model of ZSM-5.

ZSM-5 is used in a variety of catalytic applications, including the catalysis of methanol into fuel hydrocarbons. The individual pentasil units are shown in Figure 2.3 (a). These combine to form long chains, Figure 2.3 (b), which then join together to form layers, Figure 2.3. (c).

One interesting problem in zeolite chemistry is the distribution of silicon and aluminium atoms among the T sites. According to Lowenstein's rule, Al-O-Al linkages in zeolitic frameworks are forbidden. As a result, all aluminate tetrahedra must be linked to four silicate tetrahedra, and in general this is proved to be the case, but recent investigations into zeolites synthsised at high temperatures have shown non-Lowenstein distributions in sodalite materials.

The range of Si/Al ratios varies between zeolites. ZSM-5 is a high silicate zeolite, whereas zeolite X/Y can be prepared in low silicate forms, but is usually produced with a Si/Al ratio close to unity with a fully ordered Si-Al distribution over the tetrahedral sites, in accordance with Lowenstein's rule.

2.1.2 Applications of Zeolites

There are three main uses for zeolites in industry, the most important is ion exchange, but others include gas separation and catalysis:

2.1.2.1 Ion Exchange

Hydrated cations within the zeolite pores are bound loosely to the zeolite framework, and can be readily exchanged with other cations in aqueous media. Applications of this can be seen in water softening devices, and the use of zeolites in detergents and soaps. It is even possible to remove radioactive ions from contaminated water, as demonstrated at nuclear accidents at Chernobyl and at Three-Mile Island [4].

2.1.2.2 Gas Separation

A widely used property of zeolites is that of gas separation. The porous structure of zeolites can be used to "sieve" molecules having certain dimensions and allow them to enter the pores. This property can be fine-tuned by variating the structure by changing the size and number of cations around the pores.

2.1.2.3 Catalysis

Zeolites are extremely useful as catalysts for several important reactions involving organic molecules. The most important are cracking, isomerisation and alkylation. Zeolites can promote a diverse range of catalytic reactions including acid-base and metal induced reactions. The reactions can take place within the pores of the zeolite, which allows a greater degree of product control.

2.1.3 Zeolite-like materials (zeotypes) containing elements other than Si or Al in tetrahedral framework sites

The best known examples of such minerals are viseite and keoheite, both claimed to have phosphorus-containing analcime-type frameworks [5]. The existence of these materials, coupled with the wide knowledge of ions able to occupy tetrahedral sites in oxide structures, offers the prospect of synthesizing a wide range of heteroatom framework structures—hopefully with open structures appropriate to novel catalytic, ion exchange and molecular sieving properties.

Likely candidate elements for such isomorphous replacement are gallium (close to aluminium in Group 3 of the periodic table) and germanium (close to silicon in Group 4). In addition many compounds based upon linkages of (PO_4^{3-}) coordination polyhedra are well known (but not of open character except the layer phosphates such as zirconium phosphate).

Two general approaches have been made to place elements other than Si and Al into zeolitic structures namely by (i) direct synthesis and (ii) modification of existing zeolites. Modification have been accomplished using various treatments to improve zeolite catalyst performance. These treatments have resulted in, for instance, boron being substituted into framework sites (confirmed by MASNMR). In all these modifications the number of framework sites substituted is small—although in the case of high-silica ZSM-5 the replacement of aluminium by boron can be high, as a proportion of the original aluminium being replaced.

Direct synthesis has expanded considerably in the last five years and has been shown to provide a route to many more structures. This can be seen from the literature which, since 1982, has described more than 50 new prospective zeotypes, some of which have been well characterized. Before these are synthesized, they can often be explained by the presence of species encapsulated in the cavities of zeolite frameworks rather than in the tetrahedral sites.

2.2 Titanium Containing Zeolites

Titanium containing zeolites are the isomorphous substitution of Si by Ti into the zeolite framework provides useful catalysts for the oxidation of organic compounds under mild conditions.[5-8]

2.2.1 Zeolite titanium silicalite-1 (TS-1)

Zeolite titanium silicalite-1 or TS-1 is the framework substitution of T atom by Ti into the zeolite ZSM-5 framework.[5-7,9-15,29] It has the MFI structure. The three-dimensional structure of TS-1 is represented in Figure 2.4 (a). The 10-membered rings provide access to a network of intersecting pores within the crystal. The pore structure is depicted schematically in Figure 2.4 (b); there is a set of straight, parallel pores intersected by a set of perpendicular zigzag pores. Numbers of molecules are small enough to penetrate into this intracrystalline pore structure, where they may be catalytically converted.

The crystalline nature of MFI is evident in the electron micrograph of Figure 2.5. With a high-resolution electron microscope, it is even possible to see evidence of the regularity in the pore structure of this material.

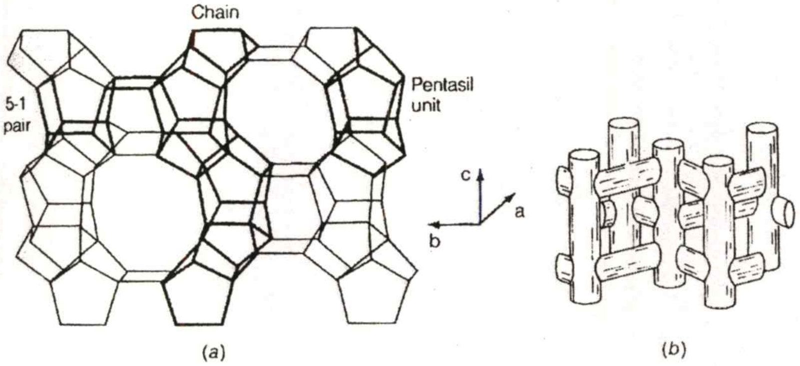


Figure.2.4 Representation of three-dimensional structure of TS-1 (MFI). (a) Structure formed by stacking of sequences. (b) Schematic representation of the intracrystalline pore structure.

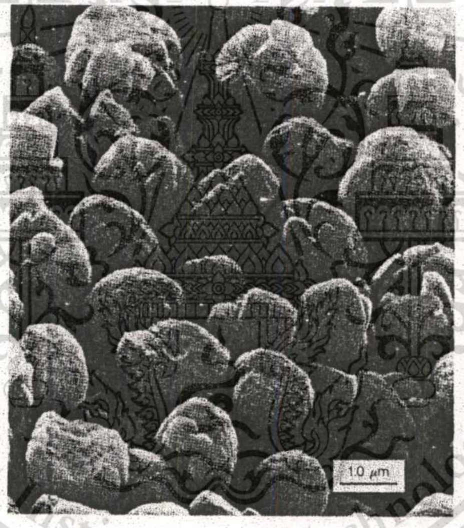
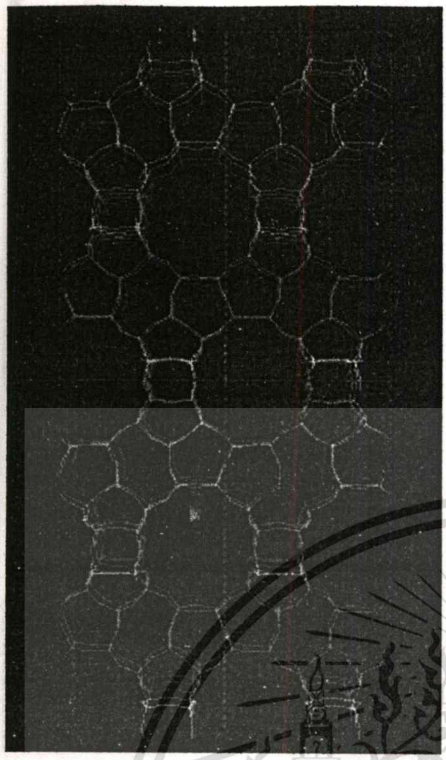


Figure.2.5 Crystals of the zeolite TS-1 (MFI) viewed with a scanning electron microscope.[14]

2.2.2 Zeolite Titanium Beta (Ti-Beta)

Zeolite Ti-Beta is the framework substitution of T atom by Ti into the zeolite Beta framework.[8,10-12,16-17,30-32] It has the BEA structure. Zeolite Beta was the first molecular sieve to be synthesized as a high-silica variety. Its most interesting property is its highly disordered framework. The structure consists of layers formed by five- and six-rings that may be stacked in different sequences forming 12-ring pores. The structure of Ti-Beta and The X-ray diffraction pattern of Ti-Beta are represented in Figure 2.6 and 2.7 respectively.



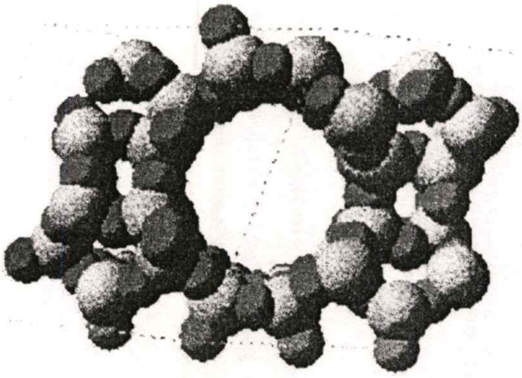


Figure.2.6 Structure of zeolite Ti-Beta

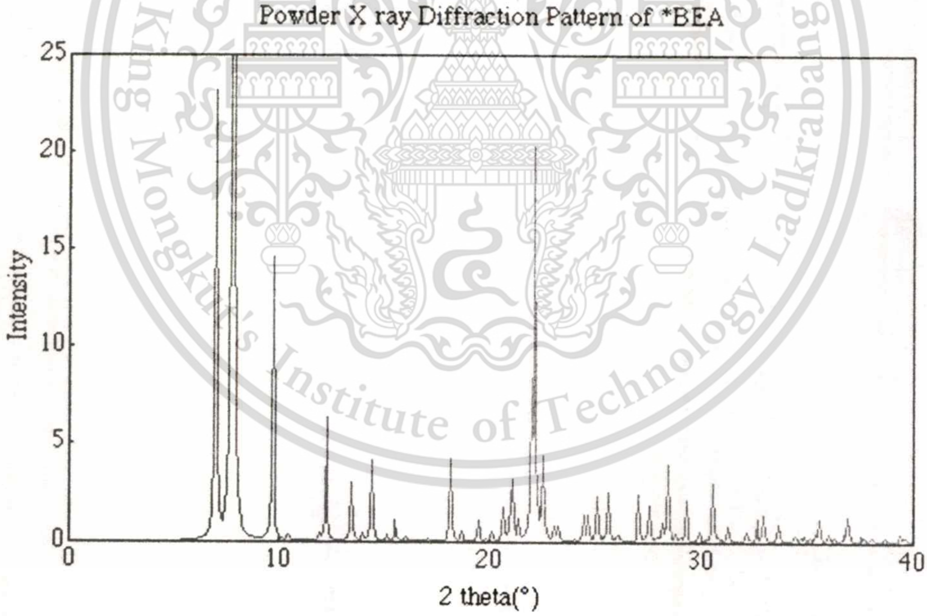


Figure.2.7 X-ray diffraction pattern of BEA

2.3 Oxidation Reaction by Ti-Containing Zeolites

Ti-containing zeolites are highly efficient catalysts for the selective oxidation of a large number of organic substrates, such as alkenes, alcohols, aromatics and phenol, and alkanes[18-22], using H_2O_2 as oxidant under mild reaction conditions (as shown in Figure 2.8). Unlike the Group IV-VI metal oxide based catalysts, Ti-containing zeolites are active in the presence of diluted aqueous solutions of hydrogen peroxide.

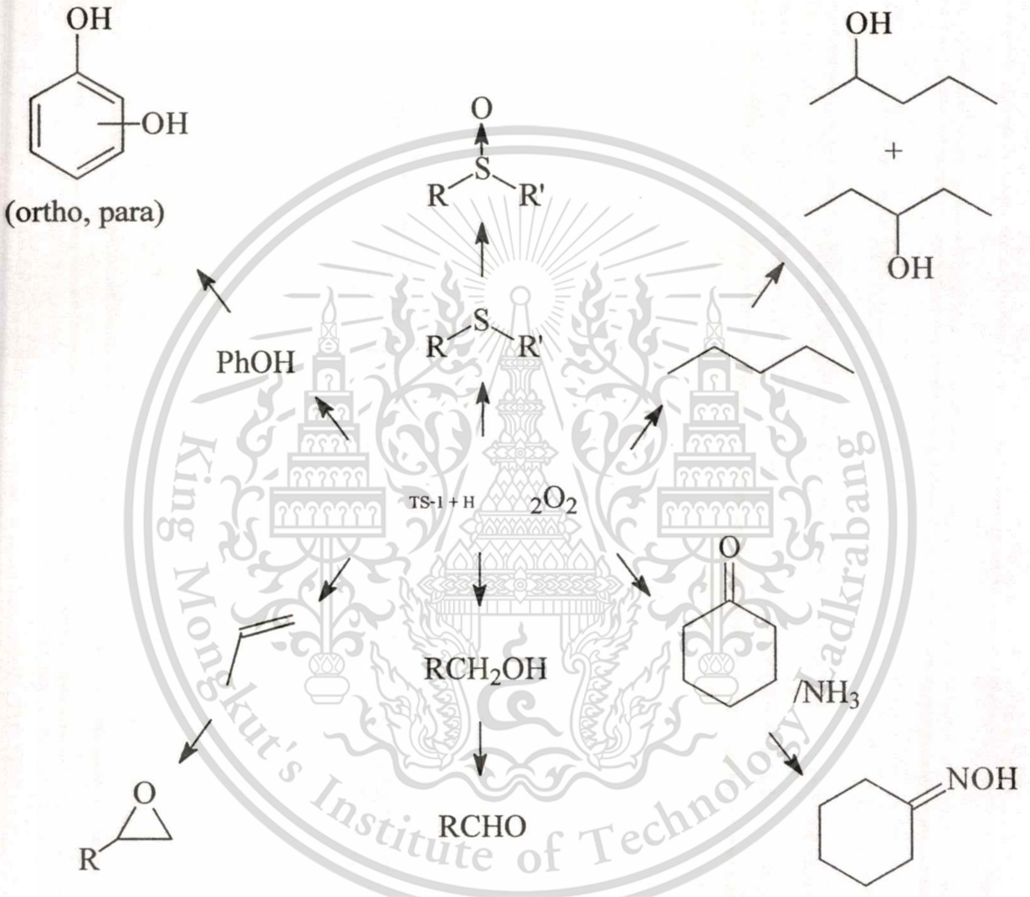


Figure.2.8 Catalytic oxidations by titanium-containing zeolites and aqueous hydrogen peroxide as oxidizing agent.

The catalytic activity of these zeolites is derived from the titanium atoms that substitutes isomorphously silicon atoms in the lattice. From the EXAFS analysis of non-calcined and of calcined TS-1 and Ti-Beta samples, valuable structural information on the titanium environment in the zeolite lattice has become available. It was shown that calcination decreases the coordination number from 5 or 6 to 4 (structure A in Figure.2.9). On addition of water, one Ti-O-Si bond can be hydrolyzed, but the tetracoordination is kept intact. Subsequent addition of another water molecular generates a pentacoordinated titanium species (Figure.2.9).

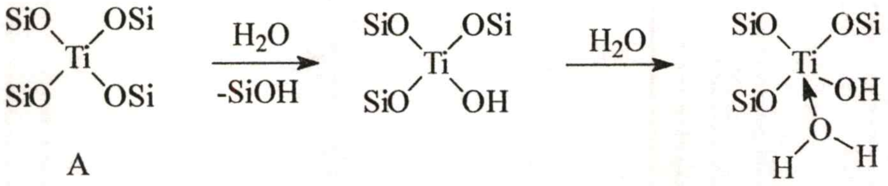


Figure.2.9 Postulated titanium species of the calcined from tetrahedral titanium species (A) and its hydrolysis and hydration

The oxidation mechanism is summarized schematically in Figure 2.10, H_2O_2 first interacts with the tetrahedrally coordinated Ti sites in a regular form (a) or in hydrated form (d) to form Ti-OOH species (b), which is probably present in a five-membered cyclic structure through the interaction with a protic species[23-24]. The alkane or another molecule, which is used as reducing agent, then penetrates into the pores to attack this active site to form a precursor for the formation of alcohol (c). The peroxyl group from the Ti-hydroperoxo complex is transferred to the adsorbed alkane to form alcohol. The alcohol is there released from the Ti site and reacts with (b) again to formed ketone and other products.

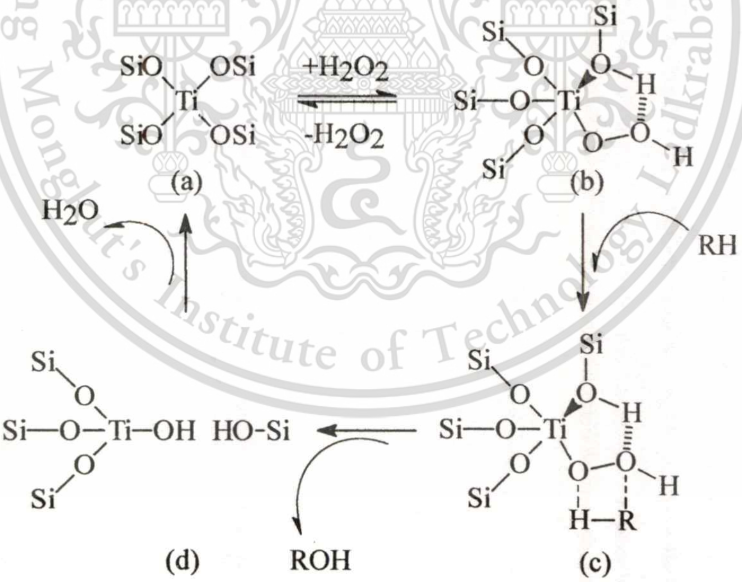
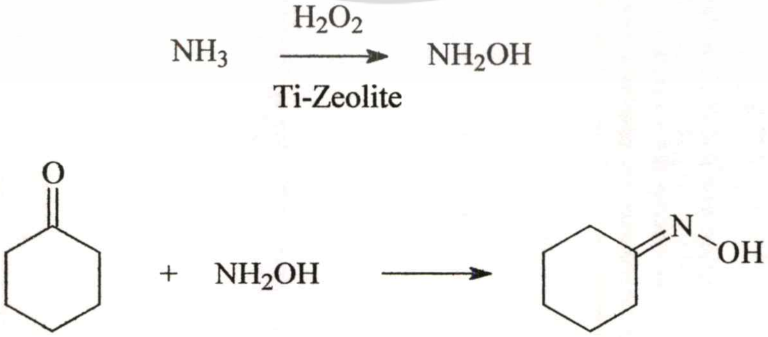


Figure 2.10 Postulated oxidation mechanism [29]

2.4 Ammoximation Reaction by Ti-Containing Zeolites

The liquid-phase ammoximation of cyclohexanone over titanium zeolite in the presence of NH_3 and H_2O_2 to synthesize oxime is another important process attracting the industrial interests as cyclohexanone oxime is the key intermediate in the manufacture of caprolactam through Beckmann rearrangement. Compared with the current commercial process, liquid-phase ammoximation of cyclohexanone over titanium zeolite shows various advantages, such that only one step is involved, without use of environmentally undesirable chemicals like oleum, halides, and oxide of nitrogen, and only a small amount of by-product are formed. Despite of the excellent catalytic performances reported by several groups using TS-1 and TS-2 zeolites, the reaction mechanism for the liquid-phase ammoximation, however, is still debated. In order to explain the formation of oxime and a by-product of peroxydicyclohexylimine, Ratnasamy *et al.*have proposed a possible mechanism that the ammoximation proceeds through an intermediate of unstable imine[25-26].This mechanism is similar to that reported for the gas-phase ammoximation of cyclohexanone in the presence of NH_3 and O_2[27], and has been supported by IR spectroscopy which proves the formation of adsorbed imine species formed from cyclohexanone and NH_3 on the surface of TS-1[28]. The groups from Italy, on the other hand, postulated a different pathway for the ammoximation, that is, through an intermediate of hydroxylamine, NH_2OH since TS-1 still showed high activity for those ketones hardly diffusing into the pores and NH_2OH was really produced from the oxidation of NH_3 with H_2O_2 in the absence of ketone as show in Figure 2.11. Therefore, a clear clarification of the liquid-phase ammoximation mechanism is not only scientifically valuable, but also industrially important.



$$NH_3 \xrightarrow[\text{Ti-Zeolite}]{H_2O_2} NH_2OH$$

Figure 2.11 A possible pathway for ammoximation of cyclohexanone by titanium-containing zeolites

2.5 Literature Review

2.5.1 Effect of Titanium Content

The effect of titanium content in zeolite framework was studied [15,29] in ammoximation of cyclohexanone to cyclohexanone oxime. The result showed that when the titanium content of zeolite was increased, cyclohexanone oxime, product, was also increased. Additionally, it was shown that the active titanium species for ammoximation catalysis is the tetrahedral titanium in the framework of zeolite. Titanium in octahedral or other species has no activity for this reaction [13,29].

2.5.2 Study on Temperature Effect

The study on temperature effect was investigated by varying the reaction temperature [29-30]. The results show that the temperature that suitable for ammoximation reaction is 60 °C. The reaction activity increase when the temperature was increased, until 60 °C, the activity started to decrease. This is resulted from the decomposition of hydrogen peroxide used as oxidizing agent. Additionally, evaporation of ammonia can inhibit the reaction at higher temperature.

2.5.3 Effect of Catalyst support

The ammoximation reaction of cyclohexanone was studied by using titanium silicates supported on alumina as catalyst [30]. The result showed that when the ratio of γ-alumina in TiO_2: SiO_2 was increased, higher co-product (caprolactam) were generated. This is because cyclohexanone oxime, major product, can be rearranged to caprolactam over acidic (alumina) support.

2.5.4 Effect of Solvent

Study of solvent effect on ammoximation reaction was carried out in the reactor using water, ethanol, methanol, 2-propanol, t-butanol as solvent and that with solvent free. The result showed that there is no direct conclusion of solvent effect from the investigation [15,29].

2.6 Overview of the Thesis

In this thesis the ammoximation of cyclohexanone to cyclohexanone oxime with hydrogen peroxide and ammonia, in liquid phase, over titanium containing-zeolites, is studied. The titanium containing zeolites using in this thesis are titanium silicalite (TS-1) and Ti-Beta. The catalysts are characterized using conventional techniques, such as scanning electron microscope, X-ray diffraction, FT-IR, etc. In this thesis, TS-1 and Ti-Beta are used as catalysts because TS-1 is the first titanium containing-zeolite that used as oxidation catalyst. For the study on the effect of pore size, Ti-Beta was used as catalyst. Ti-Beta is the large pore zeolite as compared with TS-1. In addition, Ti-Beta is favored for oxidation reaction in previous studies [8,10,12,14,16-17,32,34-36].

It was suggested [29-30] that the suitable temperature for ammoximation is 60 ^{o}C. So, the reaction temperature for ammoximation used in this thesis is 60 ^{o}C. The previous study [29] shows that the molar ratio of feed that used in ammoximation reaction was as follows: ketone: NH_3: H_2O_2 = 1:1.5:1.2.

In this thesis, the effect of solvents was studied in section 4.2.1 using acetic acid and water as solvents. It was suggested [32] that acetic acid enhances the cyclohexane oxidation activity by the generation of peracetic acid. In ammoximation, using acetic acid as solvent could enhance activity of reaction. Additionally, the amount of water content in reaction using acetic acid as solvent could affect the ammoximation activity, so the effect of water content was studied in section 4.2.3 by the addition of zeolite A (water adsorbent).

It was suggested in previous reports [15,29] that ammoximation of cyclohexanone to cyclohexanone oxime can be produced via two pathways, condensation of cyclohexanone and oxidation of ammonia. Thus the mechanism was tested in section 4.2.2.

In section 4.2.4, the effect of pore size was studied using TS-1, a medium pore zeolite, and Ti-Beta, a large pore zeolite, as catalyst. However, the titanium species in the zeolite could affect the ammoximation activity. Therefore, the effect of titanium species was investigated in section 4.2.5 by using Ti-Beta, before and after washing out of non-framework titanium species, as catalyst.

In the reaction using acetic acid as solvent, it was shown that ammonium acetate can serve as ammonia sources. Therefore, other ammonium salts could be used as ammonia sources, so the effect of ammonium salts was studied in section 4.2.8 and the effect of ammonium acetate concentration was also studied in section 4.2.9.

For the development in industrial scale, the effect of contact time (section 4.2.6), the effect of pressure (section 4.2.7), and the effect of zeolite deactivation (section 4.2.10) were determined. The effect of contact time was investigated by varying amount of the catalyst. The effect of pressure was studied under pressure of nitrogen and the effect of zeolite deactivation was determined by reusing the zeolite catalyst.

Chapter 3

Experimental details

3.1 Reagent

1. Acetic acid glacial (Mallinckrodt)
2. Ammonia solution (25% w/w, Univar)
3. Ammonium acetate (Merck)
4. Ammonium carbonate (Merck)
5. Ammonium chloride (Merck)
6. Ammonium citrate (Merck)
7. Ammonium oxalate (Merck)
8. Ammonium sulfate (Merck)
9. Caprolactam (Fluka)
10. Cyclohexanone (Carlo Erba Reagenti)
11. Cyclohexanone oxime (Fluka)
12. Deionized water
13. Hydrogen peroxide (30% w/w, Merck)
14. Ludox (colloid silica, 40% SiO_2) (Aldrich)
15. Sodium hydroxide (Merck)
16. Sulfuric acid (Merck)
17. Tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$) (Fluka)
18. Tetrapropylammonium bromide (TPABr) (Fluka)
19. Zeolite Beta (Si/Al, 27) (Tosoh Corporation)

3.2 Apparatus

1. Atomic Absorption Spectrophotometer (AA-680, Shimadzu)- Graphite Furnace Atomizer (GFA-4B, Shimadzu)
2. Autoclav
3. Condenser
4. Cooling
5. Flask

6. Furnace (Vecstar Furnaces)
7. Gas Adsorption Analyzer (Autosorb-1, Quantachrome)
8. Gas Chromatograph (3800 Gas Chromatograph, Varian)
9. Graphite Furnace Atomizer (GFA-4B, Shimadzu)
10. Heating Mental
11. Hot plate & Stirrer
12. Infrared Spectrometer (FT-IR) (IFS 28, Bruker)
13. Magnetic Stirrer
14. Oven (50-200 °C)
15. pH Meter
16. Scanning Electron Microscope (Scanning Microscope 6400, Joel)
17. Universal Indicator
18. Water Aspirator and Vacuum Filtration
19. X-ray Diffractometer (D8 Advance, Bruker)

3.3 Experiment

3.3.1 Catalyst Preparations

3.3.1.1 Titanium Silicalite (TS-1)

Tetrabutyl orthotitanate was used as titanium source to prepare TS-1. 2.36 grams of Tetrabutyl orthotitanate were mixed with deionized water at 5 °C, followed by adding 4.29 grams of hydrogen peroxide solution (30%) under stirring for 30 minutes. Then, 8.34 grams of ammonia solution (25%, 5 °C) was added and stirred. The solution was left overnight at room temperature. The solution was then heated at 80-90 °C for 30 minutes. Deionized water was added to the last solution until the last solution has just as much weight as solution before heating. After that this solution was mixed with the mixture of 9.36 grams of deionized water, 3.08 grams of tetrapropylammonium bromine (TPABr) and 10.81 grams of Ludox. The mixture was stirred at 100 rpm for a day. Finally, the yellow gel with a molar composition of 15 TPABr : 3.8 TiO_2 : 94 SiO_2 : 2168 H_2O : 212 NH_3 : 12.3 H_2O_2 was loaded in the autoclave and crystallized at 185 °C. After 5 days, the synthetic zeolite was filtrated, washed and dried at 80 °C.

The synthetic zeolite was then calcined by packing 2 grams of the synthetic zeolite in a column. Then, the column containing synthetic zeolite was loaded in a furnace. Temperature was set at 500°C with a heating rate of 2 °C/min. Calcination was carried out in air for 5 hours and the column was cooled under stream of nitrogen gas after calcination.

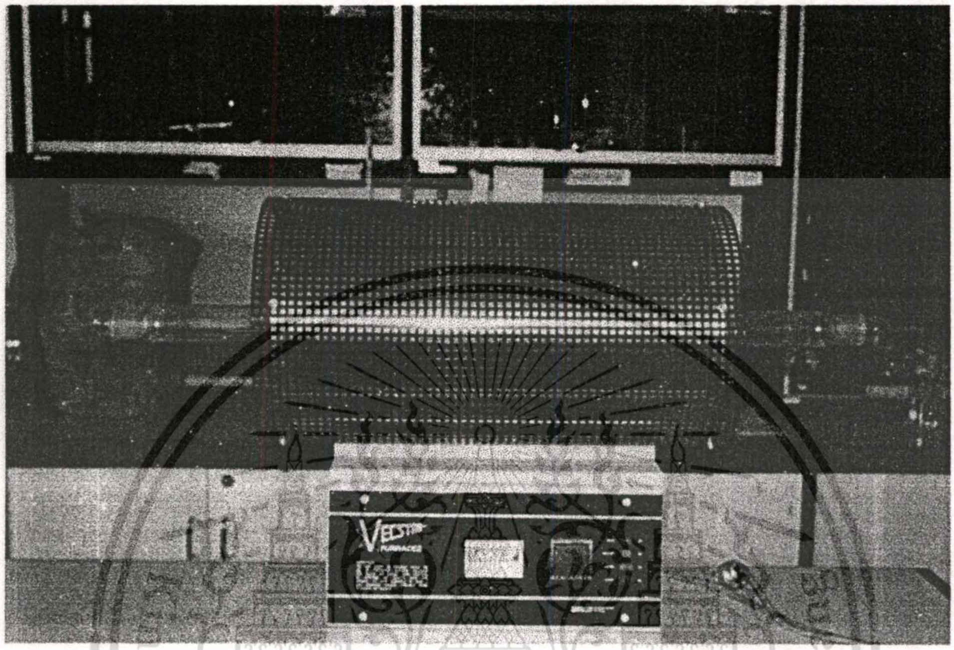


Figure 3.1 Calcination of zeolite in a furnace

3.3.1.2 Titanium Beta

Zeolite Ti-Beta was prepared by dealuminating the parent NH_4^+-Beta. Then the position of aluminium in tetrahedral units was replaced by titanium using chemical vapor deposition technique.

Dealumination of Zeolite Beta

All dealuminations were performed in a 500 ml of round bottom flask. Zeolite Beta (40 grams) was refluxed in 7 molar nitric acid (400 ml) for 5 hours under vigorous stirring. Then, the sample was filtered, washed thoroughly and dried at 80 °C. The sample was subsequently calcined in air at 550°C for 5 hours under stream of dried air.

Titanation

Titanation of the dealuminated Beta was carried out by packed-bed chemical vapor deposition (CVD). 2 grams of dried dealuminated Beta zeolite sample was packed in a quartz column. The sample was dried in a nitrogen stream of typically 60 ml/min at 120 °C for an hour. After which the temperature was raised to 500 °C and a titanium tetrachloride vapor ($TiCl_4$) was introduced. Saturated vapor of titanium tetrachloride ($TiCl_4$) was prepared by bubbling nitrogen as a carrier gas into pure titanium tetrachloride at 20 °C as shown in Figure 3.4. After 30 minutes reaction, the sample was purged with nitrogen for 90 minutes at 500 °C to free the zeolite sample of all unreacted titanium chloride species. Then the sample was calcined in air at 550 °C for 4 hours. After that, the calcinated sample was washed by 5 molar of sulfuric acid until the non-framework titanium cannot be detected by a drop of hydrogen peroxide. Finally, the sample was then calcined in air at 550 °C for 4 hours.

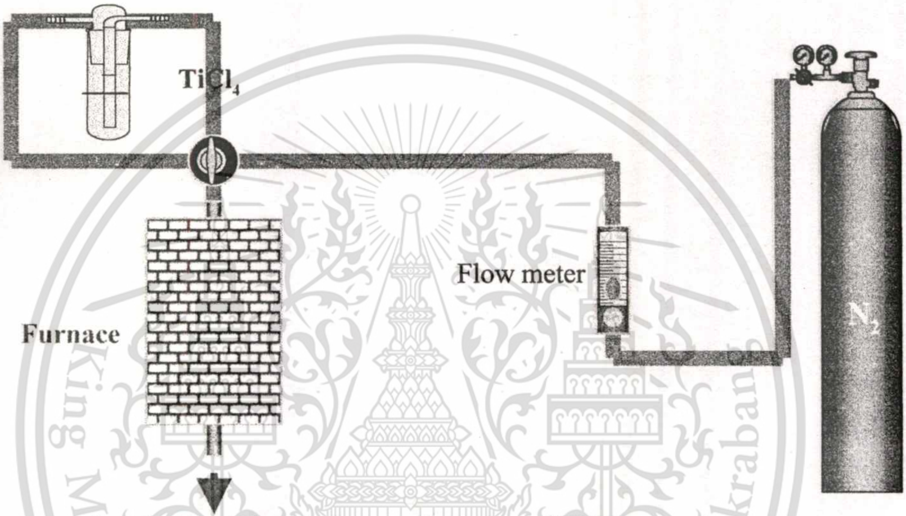


Figure3.2 Diagram of packed-bed chemical vapor deposition (CVD)

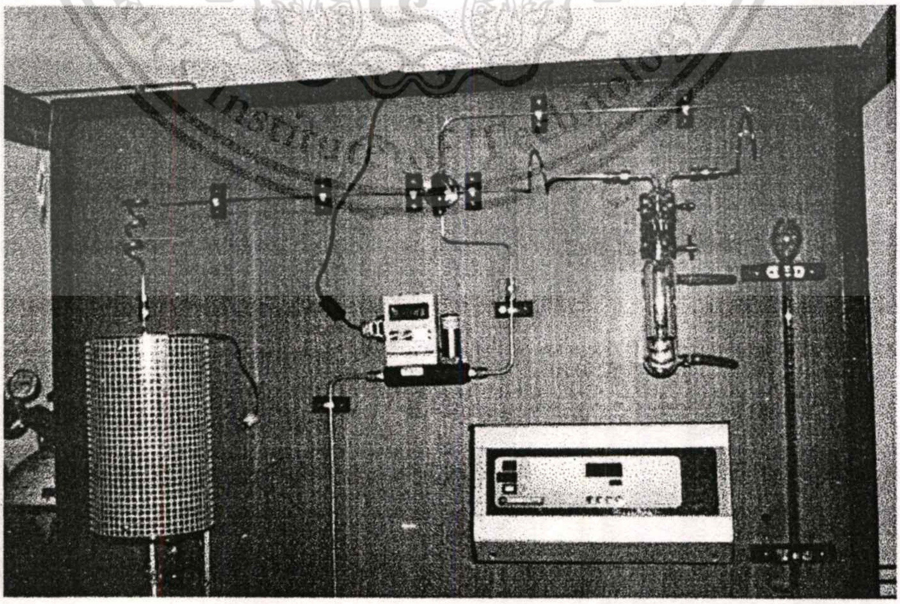


Figure 3.3 Packed-bed chemical vapor deposition (CVD)

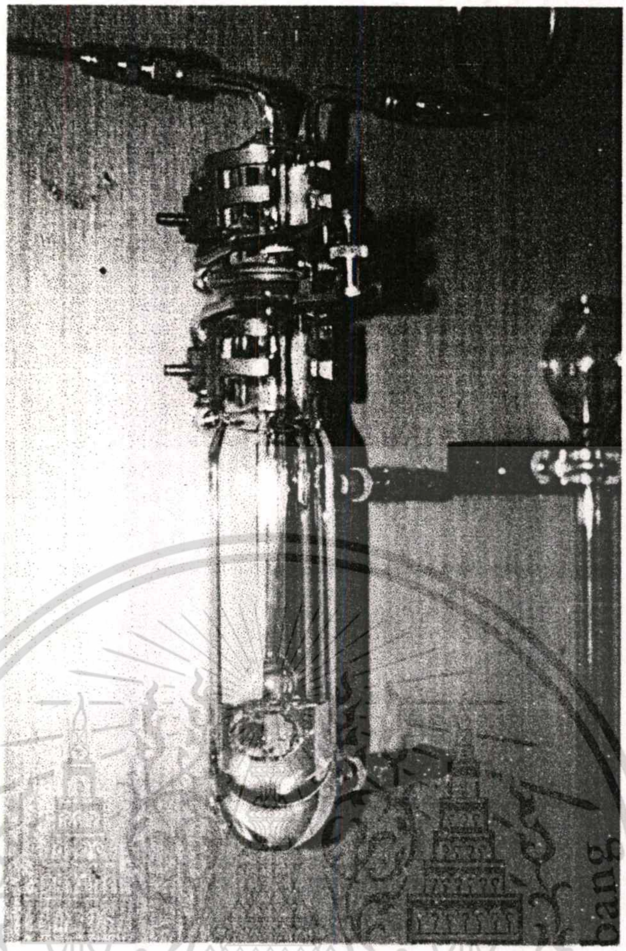


Figure 3.4 Bubbler for saturated vapor of titanium tetrachloride.

3.3.2 Characterization of Catalysts

3.3.2.1 Elemental Analysis

The silicon/titanium and silicon/aluminium ratio were determined by graphite furnace atomic absorption spectrophotometer (AAS), AA-680 Shimadsu. For this purpose the sample was prepared by heating the zeolite sample at 650 °C for 3 hours and 50 milligrams of treated zeolite was weighed in Ni-crucible. Then, 5 ml of 30 percent weight sodium hydroxide solution (30% NaOH) was transferred into the crucible and evaporated by heating. After that, the crucible was heated with swirling by gas burner for approximately 10 minutes. The crucible was washed by boiling water and the solution was transferred to a 100 ml beaker. Then, 5 ml of 1+1 hydrochloric acid solution was added to beaker and stirred. Finally, the solution was diluted to 250 ml in a graduated flask.

For the determination of silicon, 0.5 ml of solution was diluted to 50 ml in a volumetric flask. Absorption wavelength is set to 251.6 nm. 10 μl of sample was injected to the graphite furnace atomic absorption spectrometry by micropipette. The sample in graphite furnace was dried at 150 °C for 30 seconds. Then the temperature was raised to 900 °C for 20 seconds for ashing. Finally, the ash was atomized at 2700 °C for 5 seconds. Argon was used as carrier gas at a flow rate at 1.5 l/min.

For the determination of titanium and aluminium, 10 ml of solution was diluted to 50 ml in a volumetric flask. Absorption wavelength is set to 364.3 nm and 309.3 nm for determining titanium and aluminium, respectively. 10 μl of sample was injected to the graphite furnace atomic absorption spectrometry by micropipette. The sample of aluminium in graphite furnace was dried at 150 °C for 30 seconds. Then the temperature was raised to 800 °C for 20 seconds for ashing. Finally, the ash was atomized at 2600 °C for 3 seconds. Argon was used as carrier gas at a flow rate at 1.5 l/min. The temperature program for determination of titanium is the same as that used for silicon determination as shown in Table 3.1.

The concentration of each metal was calculated by using calibration curve of standard sample. The standard of the metal was prepared by diluted 1000 ppm of standard silicon, titanium and aluminium solution to 1, 2, 4, 6, 8 and 10 ppm in 50 ml graduated flask. The standard concentration was determined by graphite furnace atomic absorption spectrometry at the same condition for determining the sample. The calibration curve was plotted and the concentration of sample can be calculated by comparing with the standard calibration curve [Appendix H].

Table 3.1 The temperature program for determination of silicon, aluminium and titanium.

Element	Wavelength (nm.)	Dried	Ashing	Atomized
Silicon	251.6	150 °C, 30 sec	900 °C, 20 sec	2700 °C, 5 sec
Aluminium	309.3	150 °C, 30 sec	800 °C, 20 sec	2600 °C, 3 sec
Titanium	364.3	150 °C, 30 sec	800 °C, 20 sec	2600 °C, 3 sec

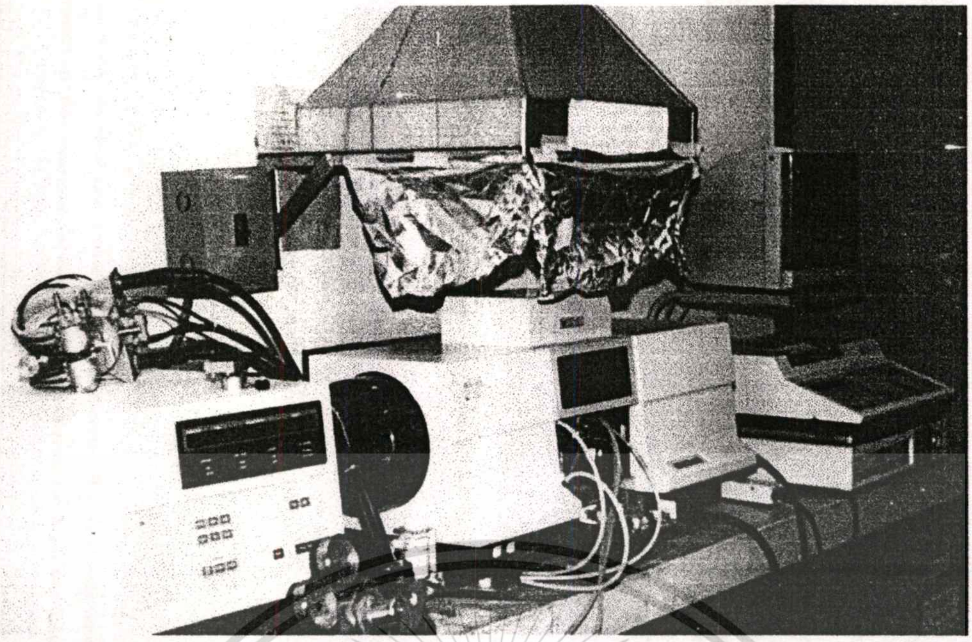


Figure 3.5 Atomic absorption spectrophotometer (AAS), AA-680 Shimadsu

3.3.2.2 Determination of Crystal Morphology of Zeolite

The crystal morphology and crystal size were determined by scanning electron microscope (Jeol 6400 Scanning Microscope, Chulalongkorn University Instruments Service Center). The sample was prepared by thoroughly placing zeolite onto the sample holder. It was then coated with gold by ion sputtering. The sample was placed in the sample chamber of scanning electron microscope and evacuated from ambient pressure to 10^{-4} torr. The scanning electron micrographs were taken at the magnification of 1,000, 7,000, 15,000 and 20,000 times.

3.3.2.3 Determination of Zeolite Structure

The zeolite structure was determined by X-ray diffractometer (D8 Advance, Bruker, Scientific Instruments Service Center, KMITL). The sample was prepared by packing the zeolite in the sample holder. $CuK\alpha$ X-ray beam was used for analysis at 40 kV, 40 mA. The sample were scanned from 2θ angle 5° to 60° with 1 second/step time and 0.04 2θ/step increment. X-ray diffraction pattern of the sample was compared with the X-ray diffraction pattern of standard zeolite for determining the structure.

3.3.2.4 Determination of Surface Area

Surface area of zeolite was determined by Gas Adsorption Analyzer (Autosorb-1, Quantachrome). The sample was prepared by weighing 1 milligrams of zeolite sample into a cleaned and dried sample cell. The sample cell was attached to the out gassing station. Heating mantle was installed and the temperature was raised to 350 °C. The sample was out-gassed for 24 hours. The sample cell was then removed from the out gassing station after the nitrogen was filled and was attached to the analysis station. The equilibration time is set to 3 minutes and the adsorption was tested at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0.

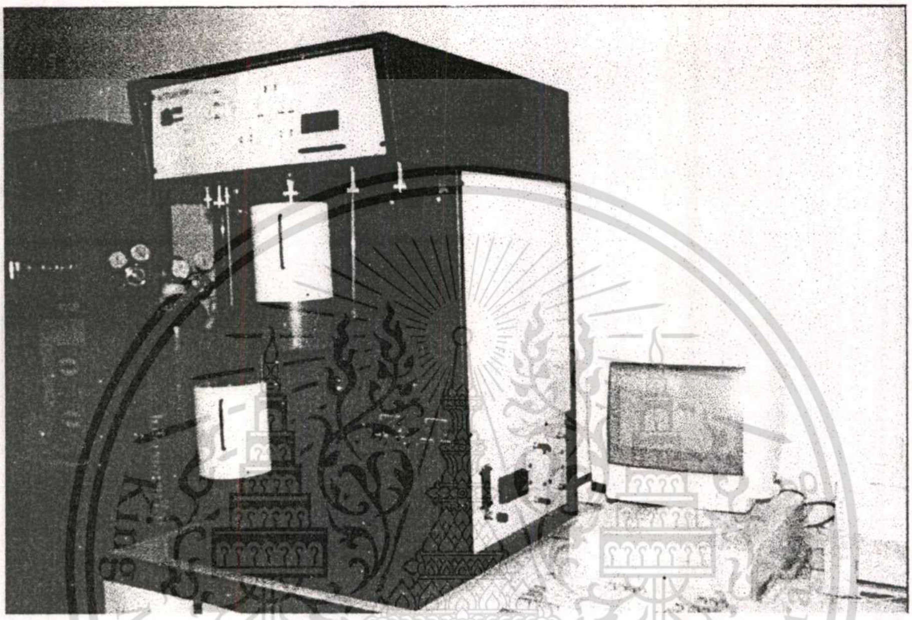


Figure 3.6 Gas Adsorption Analyzer (Autosorb-1, Quantachrome)

3.3.2.5 Determination of the Framework Titanium Species

Titanium species in the framework of zeolite can be determined by Infrared Spectrometer (IFS 28, Bruker). The characteristic vibration frequency at 960 cm^{-1} represents the stretching vibration of Ti-O-Si bond in the tetrahedral coordination. The thin pallet of zeolite was prepared by compressing 0.01 grams of zeolite sample with 6 tons pressure loading. 16 measurement scans was applied in transmittance mode and the resolution was set to be 4. The sample was scanned over the frequency 4000-400cm^{-1}.

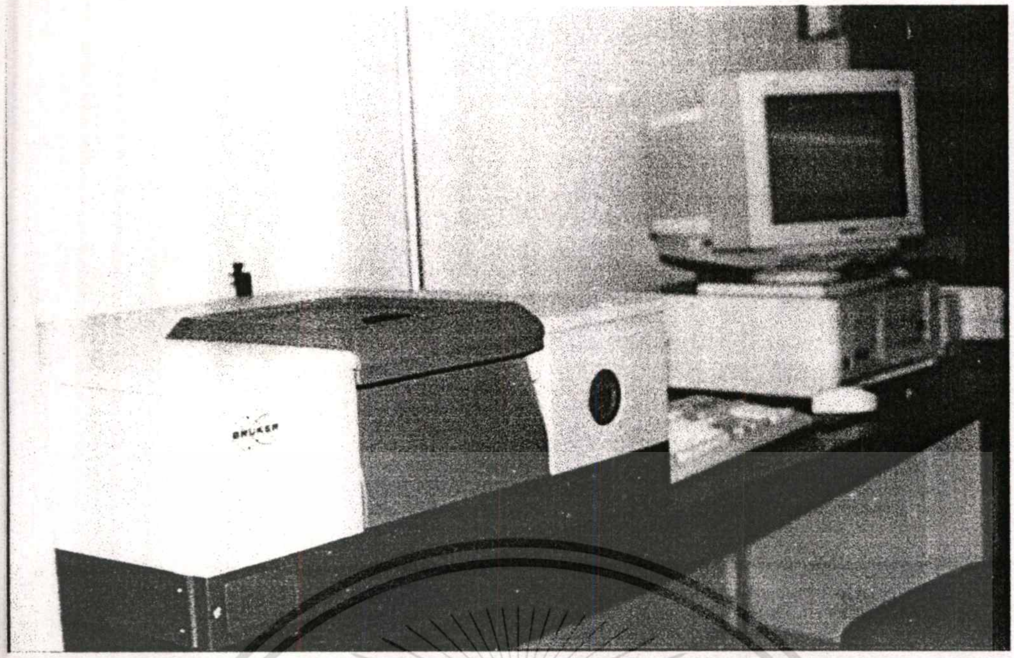


Figure 3.7 Infrared Spectrometer, IFS 28, Bruker.

3.3.3 Catalytic testing

Ammoximation reaction was carried out at 60 °C in a 10 ml stirred reactor using 0.04 grams titanium zeolite. Typically, 0.38 grams of cyclohexanone was added to 0.73 grams of ammonia solution (28%w/w) and 0.53 grams of hydrogen peroxide solution (30%w/w) in water or acetic acid 2.4 ml. The molar ratio of feed used in the ammoximation reaction was as follows: ketone: NH_3: H_2O_2 = 1:1.5:1.2. After a period of time, the reaction was stopped by removing heat and 4 ml of 2-propanol was added to the reaction mixture to make a single-phase solution.

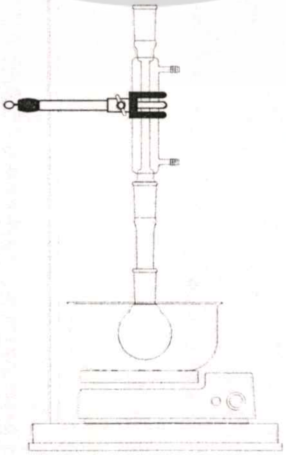


Figure 3.8 Ammoximation Reactor (Batch)

The solution was filtered and analyzed by gas chromatography using 3800 Gas Chromatograph, Varian, with capillary DB-FFAP column (30 m). 1.5 μl of liquid sample was injected to the injection port (200 °C) of gas chromatography using split ratio of 200. The separation temperature was started at 110 °C for 6 minutes. Then, the temperature was raised to 170 °C with rate of 20 °C/min and hold at that temperature for 12 minutes Helium was used as carried gas at a flow rate at 28.1 cm/sec.

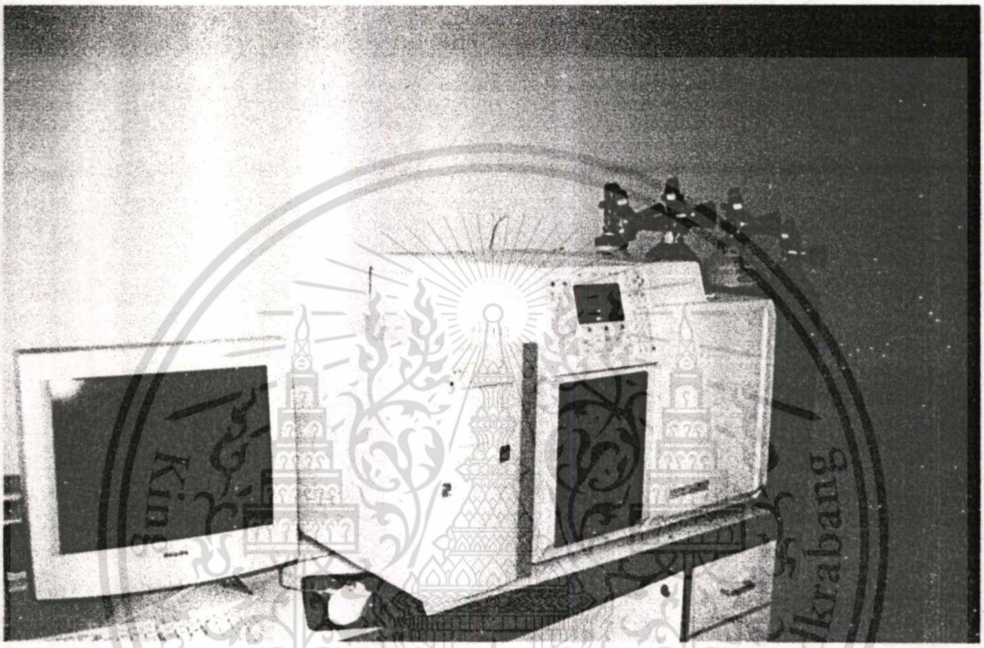


Figure 3.9 3800 Gas Chromatograph, Varian

The structure of products generated in the reaction using acetic acid as solvent was also analyzed by gas chromatography-mass spectrometer (PTT Research and Technology Institute Petroleum Authority of Thailand) using the same column and condition.

The reaction condition for study of ammoximation of cyclohexanone were summarized in Table 3.2.

Table 3.2 The study of Ammoximation Reaction at 60 °C

Reaction Number	Catalyst	Time (hr.)	Solvent	Ammonium Source	Note
1	TS-1	1	Water	NH_4OH (30% w/w)	-
2	TS-1	2	Water	NH_4OH (30% w/w)	-
3	TS-1	4	Water	NH_4OH (30% w/w)	-
4	TS-1	8	Water	NH_4OH (30% w/w)	-
5	TS-1	24	Water	NH_4OH (30% w/w)	-
6	TS-1	1	Acetic acid	NH_4OH (30% w/w)	-
7	TS-1	2	Acetic acid	NH_4OH (30% w/w)	-
8	TS-1	4	Acetic acid	NH_4OH (30% w/w)	-
9	TS-1	8	Acetic acid	NH_4OH (30% w/w)	-
10	TS-1	24	Acetic acid	NH_4OH (30% w/w)	-
11	TS-1	4	Acetic acid	$NH_4(OCOCH_3)$	Added 0.5 g of zeolite A
12	TS-1	4	Acetic acid	$NH_4(OCOCH_3)$	Added 1.0 g of zeolite A
13	TS-1	4	Acetic acid	$NH_4(OCOCH_3)$	Added 1.5 g of zeolite A
14	TS-1	4	Water	$NH_4(OCOCH_3)$	-
15	TS-1	4	Water	$(NH_4)_2CO_3$	-
16	TS-1	4	Water	$(NH_4)_2HC_6H_5O_7$	-
17	TS-1	4	Water	NH_4Cl	-
18	TS-1	4	Water	$(NH_4)_2(COO)_2$	-
19	TS-1	4	Water	$(NH_4)_2SO_4$	-
20	TS-1	4	Acetic acid	$NH_4(OCOCH_3)$	-
21	TS-1	4	Acetic acid	$(NH_4)_2CO_3$	-
22	TS-1	4	Acetic acid	$(NH_4)_2HC_6H_5O_7$	-
23	TS-1	4	Acetic acid	NH_4Cl	-
24	TS-1	4	Acetic acid	$(NH_4)_2(COO)_2$	-
25	TS-1	4	Acetic acid	$(NH_4)_2SO_4$	-
26	Ti-Beta	1	Water	NH_4OH (30% w/w)	-
27	Ti-Beta	2	Water	NH_4OH (30% w/w)	-
28	Ti-Beta	4	Water	NH_4OH (30% w/w)	-
29	Ti-Beta	8	Water	NH_4OH (30% w/w)	-
30	Ti-Beta	24	Water	NH_4OH (30% w/w)	-
31	Ti-Beta	1	Acetic acid	NH_4OH (30% w/w)	-
32	Ti-Beta	2	Acetic acid	NH_4OH (30% w/w)	-

Table 3.2 (continued)

Reaction Number	Catalyst	Time (hr.)	Solvent	Ammonium Source	Note
33	Ti-Beta	4	Acetic acid	NH_4OH (30% w/w)	-
34	Ti-Beta	8	Acetic acid	NH_4OH (30% w/w)	-
35	Ti-Beta	24	Acetic acid	NH_4OH (30% w/w)	-
36	Unwash Ti-Beta	4	Acetic Acid	NH_4OH (30% w/w)	-
37	TS-1	4	Acetic Acid	-	-
38	Ti-Beta	4	Acetic Acid	-	-
39	TS-1	4	Acetic Acid	NH_4OH (30% w/w)	0.02 g of TS-1
40	TS-1	4	Acetic Acid	NH_4OH (30% w/w)	0.08 g of TS-1
41	TS-1	4	Acetic Acid	$NH_4(OCOCH_3)$	Excess ammonium acetate
42	Ti-Beta	4	Acetic Acid	$NH_4(OOOCH_3)$	Excess ammonium acetate
43	Used TS-1	4	Acetic Acid	NH_4OH (30% w/w)	-
44	Used Ti-Beta	4	Acetic Acid	NH_4OH (30% w/w)	-
45	TS-1	4	Water	NH_4OH (30% w/w)	N_2 10 bar

3.3.3.1 Effect of Solvent

The effect of solvent was determined by the reaction using water and acetic acid as solvent with different residential time (1-24 hours). The procedures of the study were followed by reaction number 1-10 in Table 3.1.

3.3.3.2 Mechanistic Study

The reaction pathway for ammoximation reaction can be tested for two hypothesis. The first pathway involves the condensation of cyclohexanone with ammonia to form cyclohexanone imine followed by its oxidation to cyclohexanone oxime. The other proceeds via oxidation of ammonia to produce hydroxylamine, followed by reaction with cyclohexanone to form cyclohexanone oxime. The first hypothesis was tested by reacting ammonia with cyclohexanone in solvent for 2 hours for production of cyclohexanone imine. Then the catalyst (TS-1) and hydrogen peroxide were added to produce cyclohexanone oxime. After 4 hours, the catalyst was filtrated and the products were analyzed by gas chromatography. The second was evaluated by reacting ammonia with hydrogen peroxide without cyclohexanone to produce hydroxylamine. Then the catalyst (TS-1) was filtrated from the reaction after 2 hours. The mixture was then allowed to react with cyclohexanone for 4 hours (60 ^{o}C) to produce cyclohexanone oxime. In the reaction using acetic acid as solvent, ammonium acetate was used as source of ammonia but in the reaction using water, ammonium hydroxide solution was used.

3.3.3.3 Effect of Water

Zeolite A was added to decrease the water content in the system. This allows the study on effect of water on the condensation of cyclohexanone with ammonia. Zeolite A 0.5, 1 and 1.5 was added in the system The condition for this study is shown in Table 3.1, reaction number 20, 11-13.

3.3.3.4 Effect of Ammonium Salts

In the reaction using acetic acid as solvent, ammonia would react with acetic acid to produce ammonium acetate as reactant. Accordingly, other ammonium salts could be used as the reagent in the reactions using water and acetic acid as solvent. The effect of ammonium salts was determined by using various ammonium salts as reactant. The condition for this study is shown in Table 3.1, reaction number 14-25.

3.3.3.5 Effect of Pore Size

The effect of pore size was studied by using zeolite Ti-Beta, which possess a relatively large pore size as compared to TS-1 (medium pore size), as catalyst. The results were obtained from the reaction number 1-10 and 26-35.

3.3.3.6 Effect of the Titanium Species

The method for preparing titanium beta zeolite can produce two titanium species, the framework and the non-framework titanium. The non-framework titanium can be washed out by sulfuric acid. The ability of titanium species were studied by reaction number 33 and 36.

3.3.3.7 The Formation of By-Product (Caprolactone)

In the reaction using acetic acid as solvent, by-product was generated. The generation of by-product (caprolactone) was studied by reacting cyclohexanone directly without ammonia in the system using TS-1 and Ti-Beta as catalyst. The formation of by-product (caprolactone) was studied by the reaction number 37 and 38.

3.3.3.8 Influence of Contact Time

The effect of contact time was studied by using acetic acid as solvent with different amounts of catalyst (0.02, 0.04 and 0.08 grams of TS-1). The results were obtained from the reaction number 8 and 39-40.

3.3.3.9 Effect of Pressure

For the ammoximation using water as solvent, ammonia can be evaporated causing a low yield of cyclohexanone oxime. Pressure reactor was used to overcome this problem. The reaction was studied using total mixture of 200 ml at 10 bar of nitrogen atmospheric. The results were obtained from the reaction number 3 and 45.

3.3.3.10 Effect of Ammonium Acetate Concentration

It is suggested that the condensation of cyclohexanone with ammonia is a rate-determining step for the ammoximation of cyclohexanone. The effect of ammonium acetate concentration was studied. The reaction was tested using 0.45 and 1 grams of ammonium acetate as reactants in the ammoximation reaction. This effect was investigated in reaction number 41 and 42.

3.3.3.11 Effect of Zeolite Deactivation

The deactivation of zeolite was studied by using reused zeolite as catalyst. The catalyst was prepared by washing the previously used zeolite with deionized water and dried at 100 °C. The study was carried out by reaction number 8, 33, 43-44.

Chapter 4

Results and Discussion

4.1 Characterization of Zeolites

4.1.1 Determination of Zeolite Structure

- **Titanium Silicalite 1 (TS-1)**

The zeolite structure was determined by X-ray diffractometer. The X-ray diffraction patterns of all catalysts are shown in Appendix A. The X-ray diffraction pattern of TS-1 was compared with the standard X-ray diffraction pattern. It was shown that the synthesized TS-1 (Figure A.1) having MFI type structure shows characteristic peaks at 2θ 7.89, 8.84, 23.11, 23.81 and 24.4.

After calcination, the X-ray diffraction pattern of the calcined TS-1 (Figure A.2) was shown that the structure remains unchanged. However, peak intensity at 2θ 7.88 and 8.84 was increased indicating decomposition of organic template from the pore of TS-1.

- **Titanium Beta Zeolite**

The X-ray diffraction pattern of parent zeolite Beta (Figure A.3) was compared with the standard X-ray diffraction pattern. It was confirmed that the zeolite NH_4^+-Beta shows BEA type structure, showing characteristic peaks at 2θ 7.68, 22.45, 25.22, 26.82 and 29.47. After dealumination, X-ray diffraction pattern shows that the structure and crystallinity remain the same. However, when the dealuminated Beta was calcined, the characteristic peaks 2θ of zeolite was shifted from 2θ 7.68 to 7.93 indicating shrinkage of the pore size due to loss of the aluminium tetrahedra from the framework.

X-ray diffraction pattern of titanated zeolite Beta shows that the crystallinity and structure are unchanged. After the titanium zeolite was washed with sulfuric acid, there was also no significant change in crystallinity. All the zeolites appear to be well-defined crystalline microporous materials.

4.1.2 Elemental Analysis

The silicon, aluminium and titanium content of zeolites were determined by graphite furnace atomic absorption spectrophotometer. The results are shown in Table 4.1

Table 4.1 The determination of silicon, aluminium and titanium of zeolites

Zeolite	Silicon/Titanium	Silicon/Aluminium
TS-1	26	-
NH_4^+-Beta	-	27
Dealuminated Beta	-	> 200
Ti-Beta (before wash with sulfuric acid)	36	-
Ti-Beta (after wash with sulfuric acid)	47	-

It was shown that TS-1 has silicon/titanium ratio of 26. Parent zeolite NH_4^+-Beta possesses silicon/aluminium ratio of 27 (as certified by supplier). After dealumination of zeolite NH_4^+-Beta with 7 molar of nitric acid, aluminium in framework of zeolite was virtually removed. Silicon/titanium ratio of the zeolite after the titanation was found to be 36. However, after washing with sulfuric acid, the silicon/titanium ratio of the sample was increased to 47. This is suggested that there are 2 species of titanium in the zeolite; the framework and the non-framework titanium. The later can be washed out by sulfuric acid. It is believed that the titanium remained in the Ti-Beta after washing with acid are only the framework titanium species.

4.1.3 Determination of Crystal Morphology of Zeolite

The morphology of zeolite crystal and crystallite size was determined by scanning electron microscope. The electron micrograph of TS-1 both before and after calcination shows that crystallite size is about 18×5 micron (Figure B.1 and B.2). The sample appears to be a well-defined crystalline material. However, the crystallite size is relatively large for catalytic applications. The electron micrograph of NH_4^+-Beta (Figure B.3), dealuminated Beta (Figure B.4-a), calcined dealuminated Beta (Figure B.4-b), Ti-Beta before washing with sulfuric acid (Figure B.5-a) and Ti-Beta after washing with sulfuric acid (Figure B.5-b) are shown that all of Beta samples have spherical shape with crystallite size of 0.5 micron in diameter. The small crystallite size of the sample is suitable for catalytic purposes. All electron micrograph are shown in Appendix B.

4.1.4 Determination of Titanium in Framework

Titanium in framework (tetrahedral form) can be determined by infrared spectroscopy (FT-IR). Titanium in the framework shows the characteristic signal of Ti-O-Si vibration at 960 cm^{-1}. Both Ti-Beta and TS-1 samples show this characteristic band, which suggests that titanium species are present in both samples as framework cations. Fourier Transformed IR spectra of zeolites are shown in Figure 4.1, 4.2 and Appendix D.

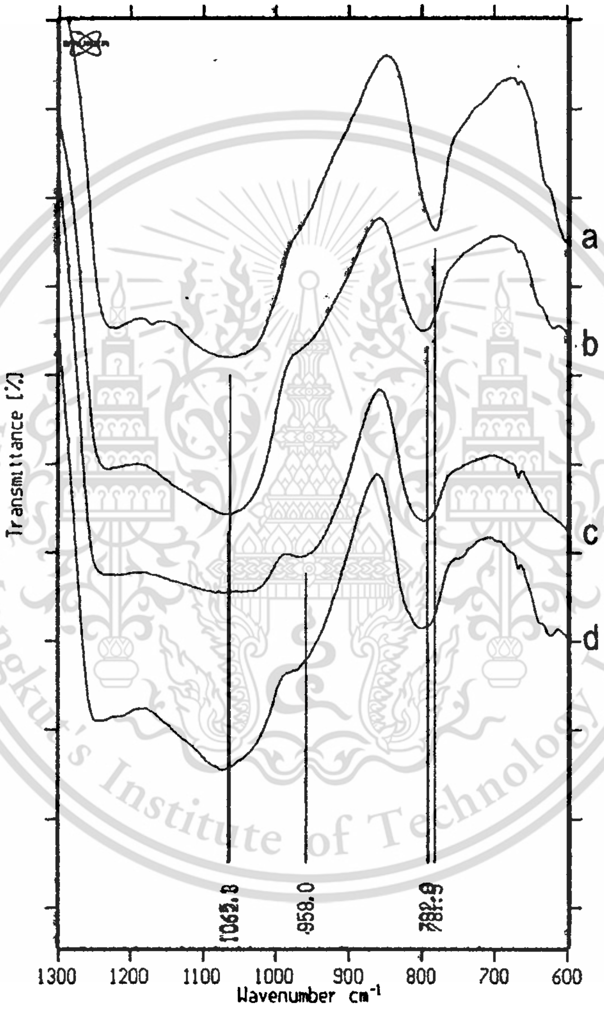


Figure 4.1 Fourier Transformed IR spectra of zeolite NH_4^+-Beta (a), Dealuminated Beta (b), Ti-Beta before (c) and after (d) washing by sulfuric acid

From the Figure 4.1, it was shown that before titanation of zeolite Beta (NH_4^+-Beta, Dealuminated Beta), there is definitely no characteristic peak of Ti-O-Si vibration (a, b) because no titanium is present in the zeolite framework. After titanation, the characteristic peak of Ti-O-Si vibration appeared (c). It is believed that lost aluminium is replaced by titanium species.

Although, the titanium content is reduced by washing with sulfuric acid (increase in Si/Ti), the washing only removes the non-framework titanium. Therefore the intensity of the characteristic peak (960 cm^{-1}) remains the same (d), which indicated that only the tetrahedral titanium is present in the framework after washing with sulfuric acid.

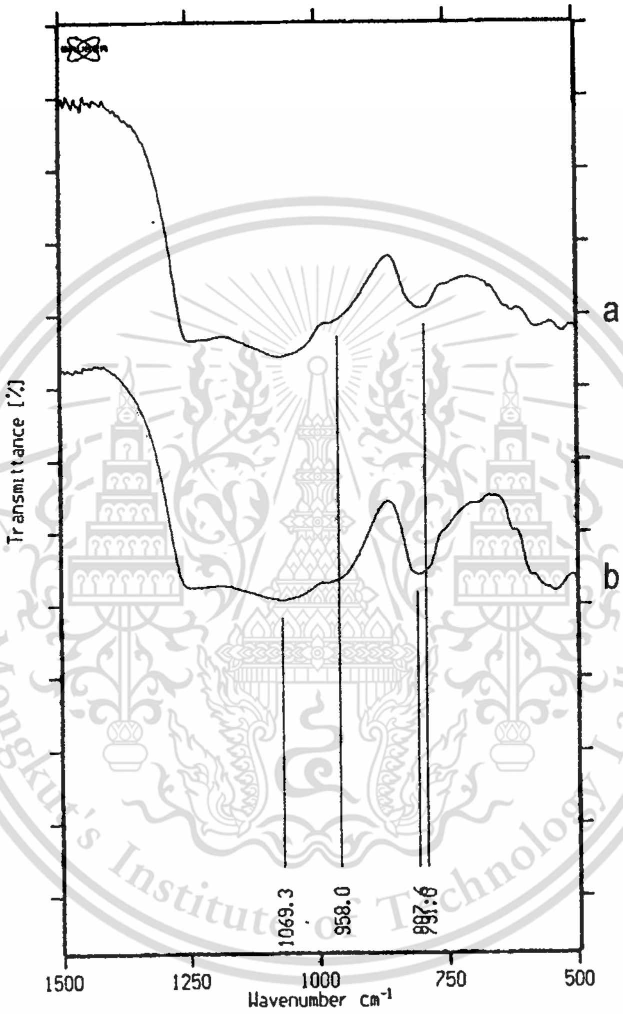


Figure 4.2 Fourier Transformed IR spectra of zeolite Ti-Beta after washing by sulfuric acid (a) and TS-1 (b)

The result from elemental analysis shows that the titanium content of TS-1 is higher than that of zeolite Ti-Beta. Figure 4.2, however, it is shown that the characteristic peak of zeolite Ti-Beta can be clearly distinguished, as compared to the TS-1. It may well be described that the titanium tetrahedral located mostly in the zeolite crystal. Accordingly, the relative higher number of external silanol of the large crystallite TS-1 would interfere the vibration signal of the Ti-O-Si, causing characteristic peak (960 cm^{-1}) of TS-1 to appear as a shoulder peak of the large Si-O vibration bands (1000-1200 cm^{-1}).

4.1.5 Determination of Surface Area

The surface area of zeolites are shown in Table 4.2

Table 4.2 The surface area of zeolite

Zeolite	Surface Area (m^2/g)
TS-1 after calcination	358
NH_4^+-Beta	665
Ti-Beta before washing by sulfuric acid	536
Ti-Beta after washing by sulfuric acid and calcined	625

From the result, it was shown that zeolite Beta have higher surface area than TS-1. This may be accounted partly from the fact that the crystal of TS-1 is larger than Beta. After titanation of the zeolite Beta, the surface area was reduced. This can be attributed to the pore blockage by the incorporated titanium species. Since there could be two species of titanium in the zeolites; the framework and the non-framework titanium, the later can readily block the pore of zeolite. This can result in a relative lower surface area of the titanated sample, as compared to the parent dealuminated Beta. Washing by sulfuric acid can remove the non-framework titanium from the pore of zeolite leading to an increased surface area. This is also in consistent with the results from the elemental analysis and FT-IR indicating the reduced titanium content with the retaining tetrahedral titanium (section 4.1.4). The BET plots of zeolites were shown in Appendix C.

4.2 Catalytic Testing

4.2.1 Effect of Solvent

The conversion and selectivity from the reaction using water and acetic acid as solvent are shown in Figure 4.3 and 4.4 respectively.

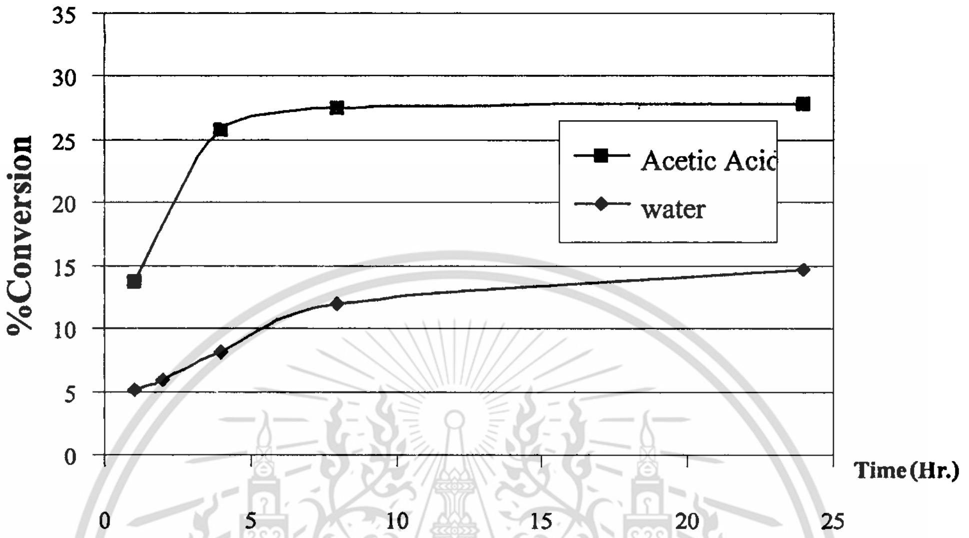
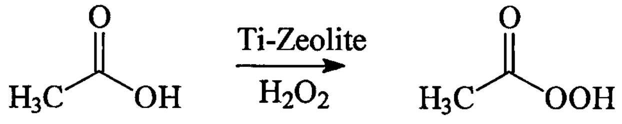


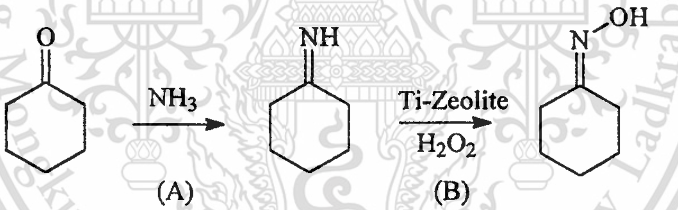
Figure 4.3 The conversion of reaction using water and acetic acid as solvent, *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours.*

The study on effect of solvent shows that the reaction using acetic acid as solvent produce higher yield of cyclohexanone oxime than that using water. This can be attributed to the fact that, in the reaction using acetic acid, peracetic acid can be generated. Acetic acid can readily react with hydrogen peroxide to form peracetic acid. This has been previously reported in the oxidation of cyclohexane using Ti-Zeolite as catalyst [31].



Peracetic acid can further react with titanium active sites in the framework of zeolite producing relatively more stable active sites than those generated from hydrogen peroxide. The peracetic acid can facilitate a stable complexation with the framework titanium active sites, as compared with the hydrogen peroxide. This is because the peracetic acid is more hydrophobic than the hydrogen peroxide, and can be regarded as a soft ligand. Consequently, the complexation with a soft ligand is relatively more stable causing a higher amount of active sites available for the reaction. Additionally, the complexation with soft ligand possesses a better oxidizing activity due to the higher electron density of the active sites. This leads to an improved activity to produce cyclohexanone oxime.

Moreover, the enhanced activity in the reaction using acetic acid can be resulted from the enhanced formation of cyclohexanone imine. Since the ammoximation reaction proceeds via the condensation of cyclohexanone (A) with ammonia to produce cyclohexanone imine, followed by the oxidation (B) of cyclohexanone imine to cyclohexanone oxime [15], the condensation (A) of cyclohexanone with ammonia in acetic acid would be favored, as compared to the reaction using water. This is because rate of cyclohexanone imine formation is facilitated at pH approximately 4.5 or in the presence of acid as catalyst [32]. Therefore, the yield of cyclohexanone imine in the reaction using acetic acid as solvent is higher than that using water. As cyclohexanone imine is increased, the oxidation of cyclohexanone imine is also accelerated, resulting in a higher yield of cyclohexanone oxime in the reaction using acetic acid, as compared to that using water. The reaction pathway can be illustrated as follows;



The vaporization of ammonia during the reaction could also be another factor influencing a reduced activity for the reaction using water, as compared to that using acetic acid. In the reaction using acetic acid as solvent, ammonia was trapped in the liquid phase as ammonium acetate. However, the reaction using water as solvent, ammonia can be vaporized leading to a lower concentration of ammonia in the liquid phase. Consequently, a lower yield of cyclohexanone oxime was generally observed. It can be then concluded at this stage that, the formation of peracetic acid and the enhanced production of cyclohexanone imine are responsible for the higher activity in the reaction using acetic acid, as compared to the reaction using water as solvent which is limited by the vaporization of ammonia.

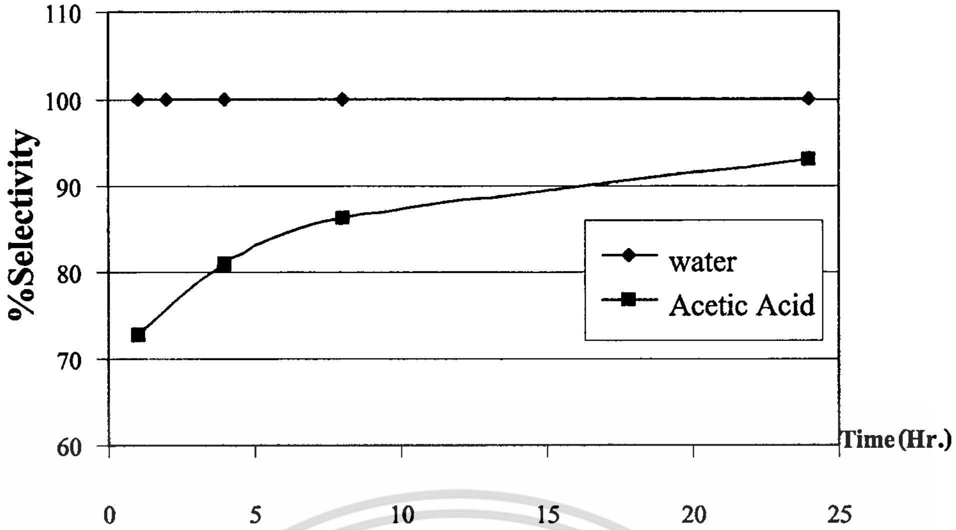
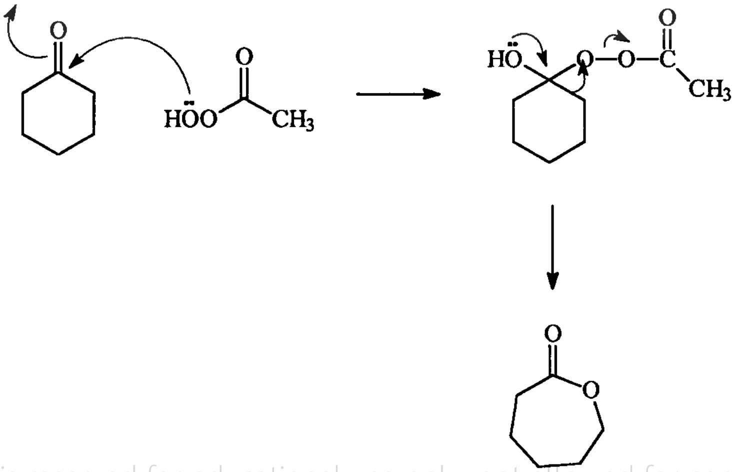


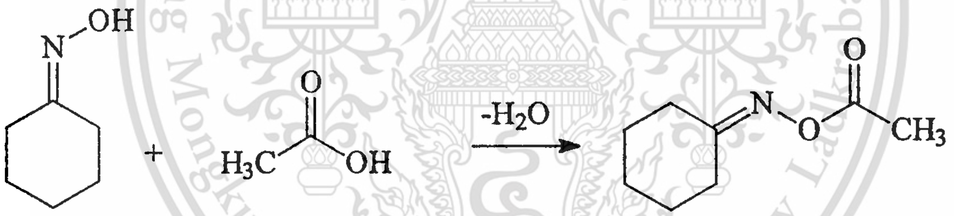
Figure 4.4 The selectivity of cyclohexanone oxime in the reactions using water and acetic acid as solvent, *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours.*

Although, the reaction using acetic acid as solvent produces higher amounts of products than that using water, selectivity of cyclohexanone oxime in the reaction using acetic acid as solvent was lower than that using water. This is due to the fact that the reaction using acetic acid as solvent produces by-products. Gas Chromatography-Mass Spectrometer results (Figure G.2 and G.3) show that one of the by-product is caprolactone and the other is acetyl cyclohexanone oxime. The first is formed by "Baeyer-Villiger Rearrangement" where cyclohexanone react directly with peracetic acid in the presence of acid as catalyst [33]. The mechanism for the formation of caprolactone is illustrated. as below;



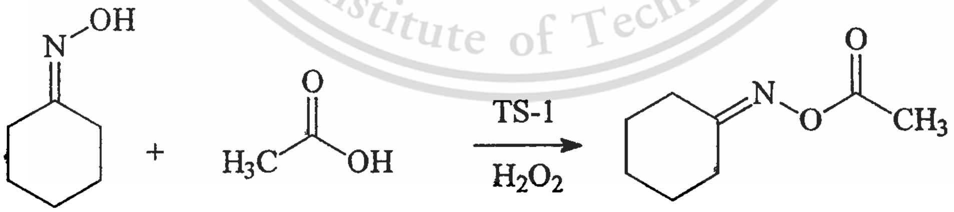
As TS-1 possesses the medium pore size (5.5 Å), a product with molecular size larger than its pore size cannot be generated internally. Therefore it is unlikely that caprolactone is generated in the pore of TS-1 because caprolactone, a seven membered ring, is relatively larger than the pore size of TS-1. It may be concluded that caprolactone was generated homogeneously in the liquid phase without aid of TS-1. In contrast, the Baeyer-Villiger rearrangement was not observed in the reaction using water as solvent because no peracetic acid was present and hydrogen peroxide alone cannot promote this reaction. Thus, no caprolactone was generated in the reaction using water as solvent.

The second by-product appears to be acetyl cyclohexanone oxime. The results from the Gas Chromatography-Mass Spectrometer (Figure G.3) shows that the seconded by-product contains acetyl group and have a molecular fragmentation in a manner similar to the cyclohexanone oxime. The acetyl cyclohexanone oxime could be possibly generated from a simple condensation of cyclohexanone oxime and acetic acid (A) or oxidative coupling of cyclohexanone oxime with acetic acid (B) in the presence of titanium zeolite as catalyst, as follows.



(A)

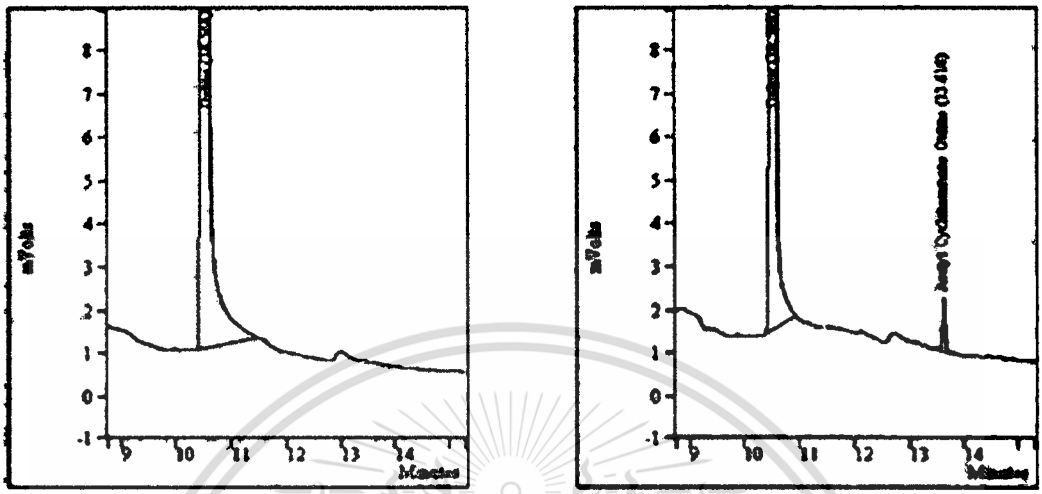
Path A: Condensation of cyclohexanone oxime and acetic acid



(B)

Path B: Oxidative coupling of cyclohexanone oxime with acetic acid

In order to verify the above possibilities, the reaction of cyclohexanone oxime with acetic acid was then tested to prepare acetyl cyclohexanone oxime. The path A was tested by heating and stirring cyclohexanone oxime with acetic acid without hydrogen peroxide and TS-1 for 4 hours. While path B was tested in the presence of hydrogen peroxide and TS-1. It was found that acetyl cyclohexanone oxime cannot be generated in the reaction for path A. However, the reaction for path B produce notably amounts of acetyl cyclohexanone oxime [Figure 4.5].



(A) (B)

Figure 4.5 Gas chromatograms of acetyl cyclohexanone oxime synthesis from path A and B

Consequently, it is likely that acetyl cyclohexanone oxime was generated by the oxidative coupling of cyclohexanone oxime with acetic acid in the presence of titanium-containing zeolite and hydrogen peroxide.

On the other hand, no peracetic acid was present in the reaction using water as solvent. Therefore no caprolactone and acetyl cyclohexanone oxime was generated. Conclusively, selectivity of cyclohexanone oxime in the reaction using water as solvent is considerably high.

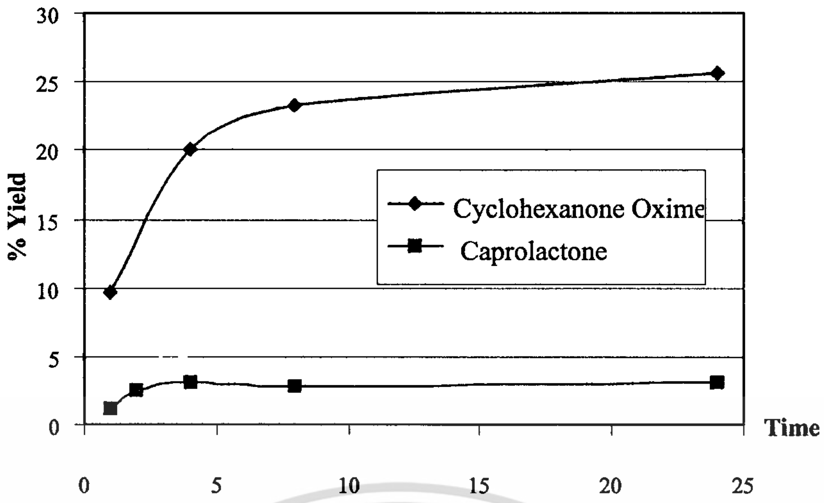
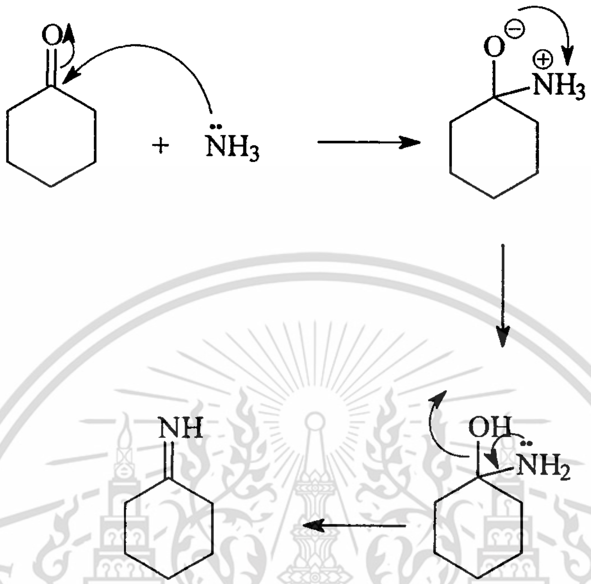


Figure 4.6 The yield of cyclohexanone oxime and caprolactone from the reaction using acetic acid as solvent, *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours.*

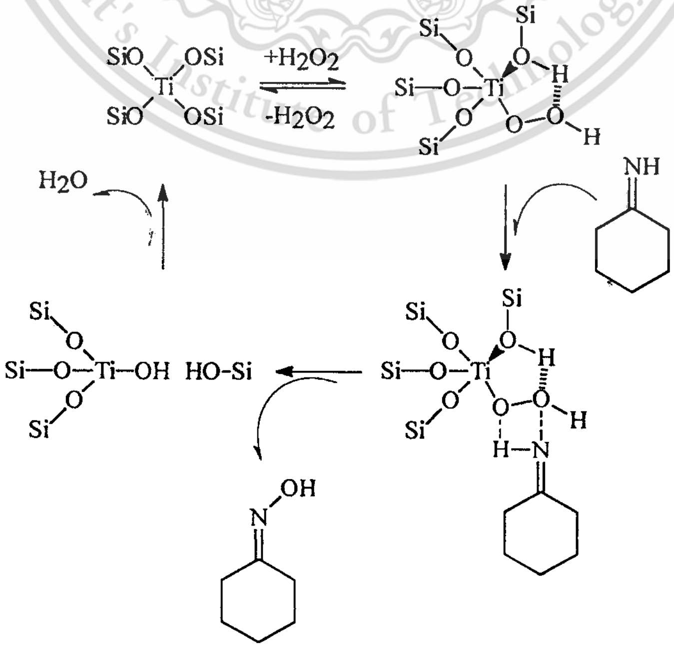
From the Figure 4.4, it was shown that the selectivity of cyclohexanone oxime in the reaction using acetic acid as solvent was increased with time. It can be explained that at the beginning of the reaction, rate of ammoximation was limited by competitive formation of caprolactone via Baeyer-Villiger Rearrangement. This is because the ammoximation reaction is a multi-step reaction. Caprolactone formation, on the other hand, is a single step reaction. The direct reaction of cyclohexanone and peracetic acid could readily compete with the condensation of cyclohexanone and ammonia. Therefore, the initial selectivity of cyclohexanone oxime is low. After a period of time, (Figure 4.6), the cyclohexanone oxime was increased while the formation of caprolactone was slightly changed. This can be attributed to the fact that cyclohexanone was converted to cyclohexanone imine and subsequently cyclohexanone oxime resulting in reduced concentration of cyclohexanone in the system. In consequence, the rate of caprolactone formation would be decreased with time and the selectivity of cyclohexanone oxime was increased.

4.2.2 Mechanistic Study

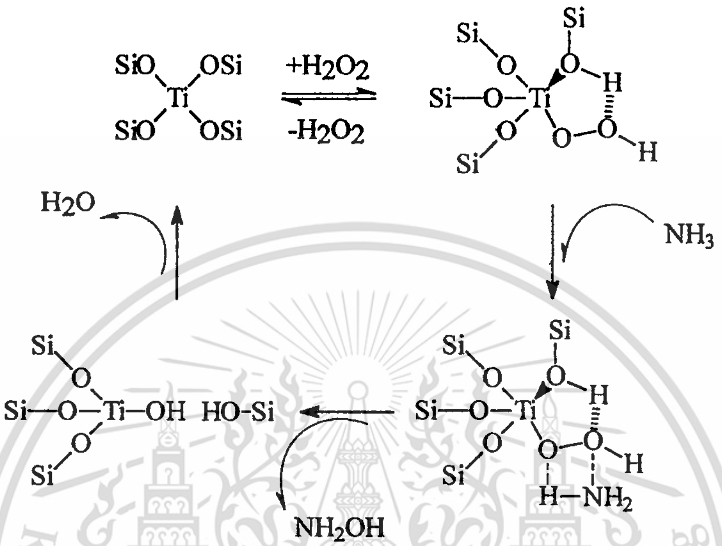
In the mechanistic point of view, it was suggested that [15] ammoximation produce via condensation of cyclohexanone with ammonia to produce cyclohexanone imine in the presence of acid as shown.



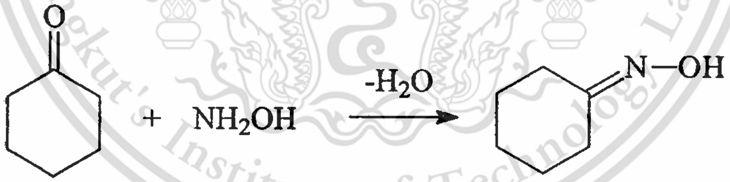
Then cyclohexanone imine will react with the active site, generated from the reaction of framework titanium in the zeolite and hydrogen peroxide or peracetic acid, to produce cyclohexanone oxime as shown.



Although, the results from the reaction using acetic acid, suggests that the reaction proceeds via condensation of cyclohexanone with ammonia as discussed above, other report [29] suggested that the reaction may well proceed via the oxidation of ammonia over titanium zeolite to form primarily hydroxylamine as shown;



After that, hydroxylamine can readily react with cyclohexanone to produce cyclohexanone oxime as shown.



These two possibilities can be tested by changing the order of reagent addition. The reaction of ammonia with only cyclohexanone (test I) was carried out for 2 hours prior to addition of TS-1 and hydrogen peroxide. This can be employed to test hypothesis that ammoximation was promoted via condensation of cyclohexanone with ammonia.

On the other hand, the hypothesis that ammoximation proceeds via the oxidation of ammonia to produced hydroxylamine (test II) was tested by the reaction of only ammonia with catalyst and hydrogen peroxide. After 2 hours, the catalyst was filtrated and cyclohexanone was added. The mixture was allowed to react for about 4 hours. The results are shown in Table 4.3 and 4.4.

Table 4.3 The yield of cyclohexanone oxime generated from hypothesis of cyclohexanone condensation and typical reaction

	%Yield of Cyclohexanone oxime	
	Water	**Acetic Acid**
Typical Reaction	8.1	20.8
Tested Reaction I	7.4	14.9

Note: *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours.*

Table 4.4 The yield of cyclohexanone oxime generated from hypothesis of ammonia oxidation and typical reaction

	%Yield of Cyclohexanone oxime	
	Water	**Acetic Acid**
Typical Reaction	8.1	20.8
Tested Reaction II	1.7	0.27

Note: *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours.*

From the result in Table 4.3 and 4.4, it is shown that when ammonia is allowed to react with catalyst in the presence of acetic (test II), cyclohexanone oxime cannot be observed. While, cyclohexanone oxime can be only formed via the condensation of cyclohexanone with ammonia (test I). This is can be explained that, when acetic acid is used as solvent, ammonia was protonated i.e. as ammonium acetate and cannot be readily oxidized to hydroxylamine. On the other hand, the condensation of cyclohexanone with ammonia to form cyclohexanone imine is facilitated in the presence of acetic acid (test I). Synergistically, a better interaction of cyclohexanone imine with the hydrophobic acid site, formed by complexation of peracetic acid with the framework titanium, would enhance the cyclohexanone imine oxidation and subsequently the formation of cyclohexanone oxime. Whist the interaction of ammonia with the active site is then inhibited in test II and no hydroxylamine can be produced. Conclusively, in the reaction using acetic acid as solvent, only the pathway proceeded via the condensation of cyclohexanone with ammonia is responsible for the formation of cyclohexanone oxime.

In the reaction using water as solvent, on the other hand, cyclohexanone oxime can be formed by both mechanisms but mainly via condensation of cyclohexanone and ammonia as show in Table 4.3 and 4.4. Ammonia was not readily protonated in reaction using water as solvent. Hence, it can directly react with the active sites to produce hydroxylamine (test II). Additionally, cyclohexanone can react with ammonia to produce cyclohexanone imine which was subsequently oxidized to produce cyclohexanone oxime. Since the yield of cyclohexanone oxime produce in test I is similar to the typical reaction, but the considerably less is observed in test II, the condensation of cyclohexanone and ammonia appears to be a major pathway. This may be accounted for the fact that TS-1 is a hydrophobic framework (non polar framework) and the interaction between cyclohexanone imine with framework is relatively better than the interaction with ammonia (a higher polar reactant). In consequence, the rate of hydroxylamine production would be lower than the rate of imine oxidation.

4.2.3 Effect of Water

According to the above discussion, it is clear that the condensation of cyclohexanone with ammonia is essential for the ammoximation. This step could be interfered by the presence of water and pH of the solution. The effect of water can be investigated by adding zeolite A (a water adsorbent) into the system. From Figure 4.7 and 4.8, it was clearly shown that the yield and selectivity of cyclohexanone oxime was increased with the amount of zeolite A added.

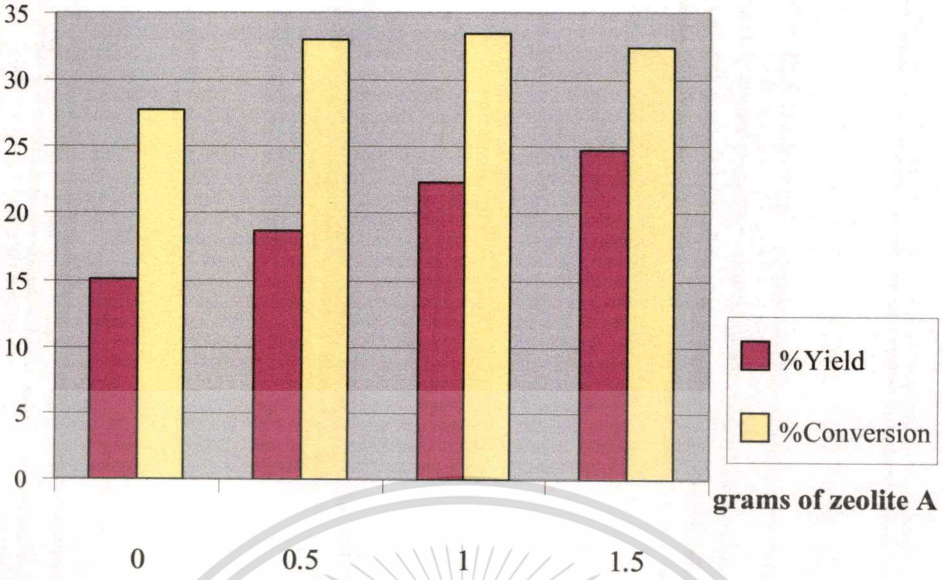
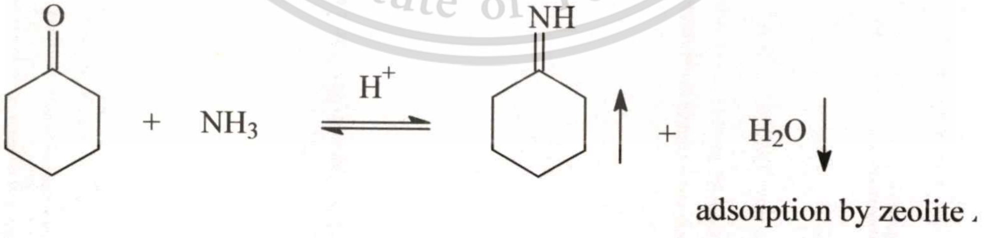


Figure 4.7 The yield and conversion of ammoximation reaction with addition of zeolite A. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours.* Added 0.5, 1.0 and 1.5 g of zeolite A

It can be explained that the increase in cyclohexanone oxime yield was resulted from the decrease in water in the reaction system. The zeolite A can adsorb water and the condensation reaction of ammonia with cyclohexanone can be promoted. More cyclohexanone imine can be obtained when water was removed from the system. Accordingly, higher yield of cyclohexanone oxime can be expected.



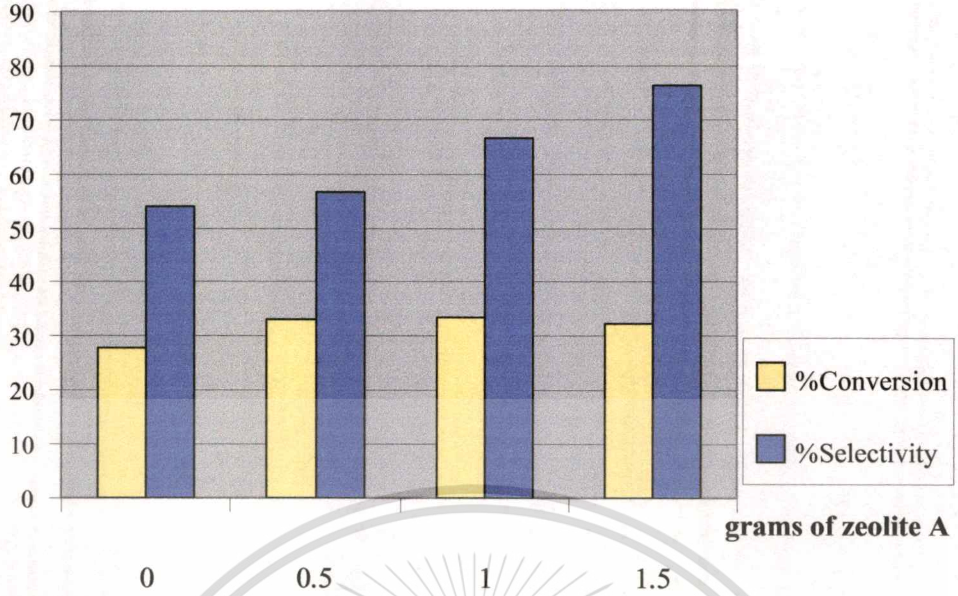
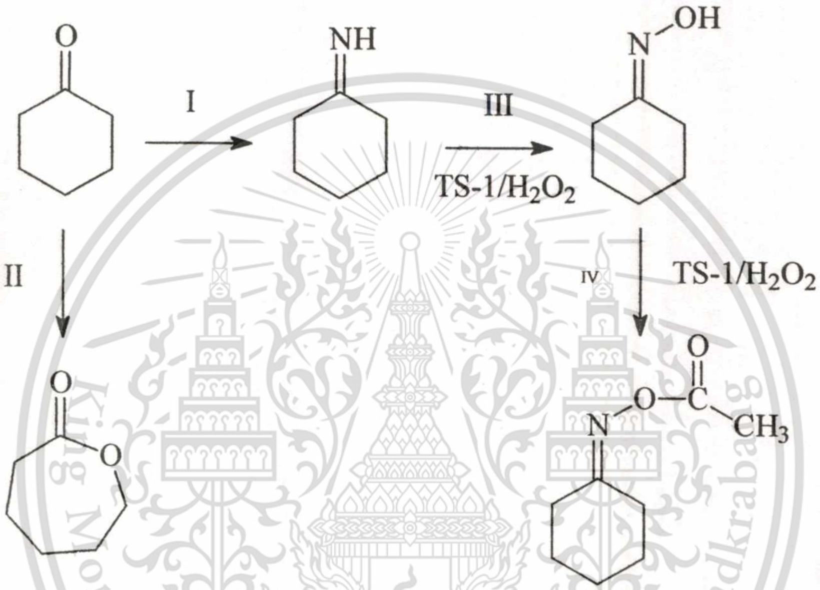


Figure 4.8 The conversion and selectivity for ammoximation reaction with addition of zeolite A. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, TS-1 0.04 gram, Reaction Time 4 hours. Added 0.5, 1.0 and 1.5 g of zeolite A*

Moreover, the yield of caprolactone (by-product) was decreased when zeolite A was added. This is probably because caprolactone was formed from cyclohexanone. The addition of zeolite A promotes the condensation of cyclohexanone (I) with ammonia to produce a higher yield of cyclohexanone imine, which is then oxidized to form cyclohexanone oxime. Accordingly, peracetic acid is largely consumed by oxidation process. The direct reaction of peracetic acid with cyclohexanone (II) was subsequently reduced as the more cyclohexanone imine was generated. Therefore, a higher selectivity of cyclohexanone oxime was obtained when zeolite A was added.

As more cyclohexanone oxime was generated when zeolite A was added, a higher yield of acetyl cyclohexanone oxime could be expected. Surprisingly, the yield of acetyl cyclohexanone oxime (by-product) was also decreased when added zeolite A. It can be explained that the formation of acetyl cyclohexanone oxime was inhibited by competitive formation of cyclohexanone oxime. This is because when zeolite A was added, a higher amount of cyclohexanone imine was promoted. The rate of cyclohexanone imine oxidation to cyclohexanone oxime was then increased when the higher concentration of cyclohexanone imine was tained. The reaction of active sites with cyclohexanone imine is favored over that with cyclohexanone oxime because the interaction between the hydrophobic titanium framework (suggested in section 4.2.1) with cyclohexanone imine would be stronger than the interaction with cyclohexanone oxime. The oxidative coupling of cyclohexanone oxime with acetic acid is then limited. Therefore, the formation of acetyl cyclohexanone oxime is low. The reaction pathway was shown as follows;



Conclusively, the low water concentration (such as in the reaction using acetic acid as solvent) is ideal for the ammoximation reaction. This is because a lower concentration of by-products and a higher yield of cyclohexanone oxime were obtained. Additionally, it can be seen from the result that the condensation of cyclohexanone with ammonia is the essential step. Therefore, the high concentration of ammonia could be promoted the condensation of cyclohexanone and the higher yield of cyclohexanone oxime could be expected.

4.2.4 Effect of Pore Size

Influence of pore size is studied by the reaction using large pore zeolite, Ti-Beta, as catalyst, compared to that using TS-1. The conversion from the reaction using zeolite Ti-Beta and TS-1 as catalysts in acetic acid are shown in Figure 4.9.

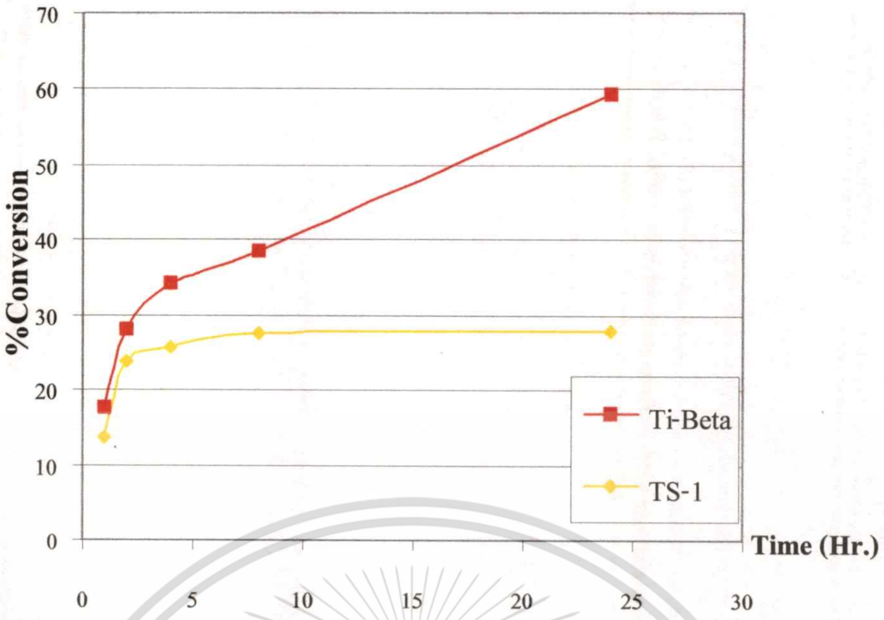
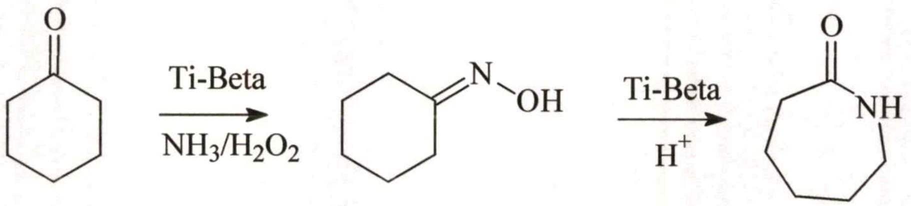


Figure 4.9 The conversion of cyclohexanone, reaction in acetic acid. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time1, 2, 4, 8 and 24 hours, Ti-Beta and TS-1 0.04 grams as catalyst.*

From the result, it was shown that conversion of cyclohexanone in reaction using Ti-Beta is higher than that using TS-1. It can be explained that the diffusion of the reactant into the pore of zeolite Ti-Beta is faster than that of TS-1. This is because Ti-Beta has a larger pore size (6.4-7.6 Å) than TS-1 (5.5 Å). Additionally, The crystallite size of TS-1 is larger than Ti-Beta leading to a difficulty for cyclohexanone and cyclohexanone oxime to enter and leave the pore, respectively. Therefore, in the case of zeolite Ti-Beta, reactant can diffuse faster to react with the active sites leading to the high activity for ammoximation.

However, the "Beckmann Rearrangement" of cyclohexanone oxime to produce caprolactam can be observed from the reaction using zeolite Ti-Beta in the presence of acetic acid. This is concluded from the observed low selectivity of cyclohexanone oxime and significant increase in yield of caprolactam in the reaction using zeolite Ti-Beta, particularly at high residential time. The cyclohexanone oxime produced primarily, can possibly be activated by trace of acid sites within the framework of zeolite Ti-Beta and undergoes rearrangement to form caprolactam.



The subsequent formation of caprolactam promote the formation of cyclohexanone oxime leading to the high conversion of cyclohexanone. Moreover, at the high residential time, the yield of caprolactam was particularly increased resulting in the low concentration of cyclohexanone oxime in the system. This is because, as the concentration of cyclohexanone oxime was increased with time, the rate of caprolactam formation was also increased. However, the formation of cyclohexanone oxime, at high residential time, was limited by the lack of oxidizing agent. So, only the rearrangement of cyclohexanone oxime takes place at high residential time, leading to the reduction of cyclohexanone oxime. Consequently, the selectivity of cyclohexanone oxime was reduced as shown in Figure 4.10.

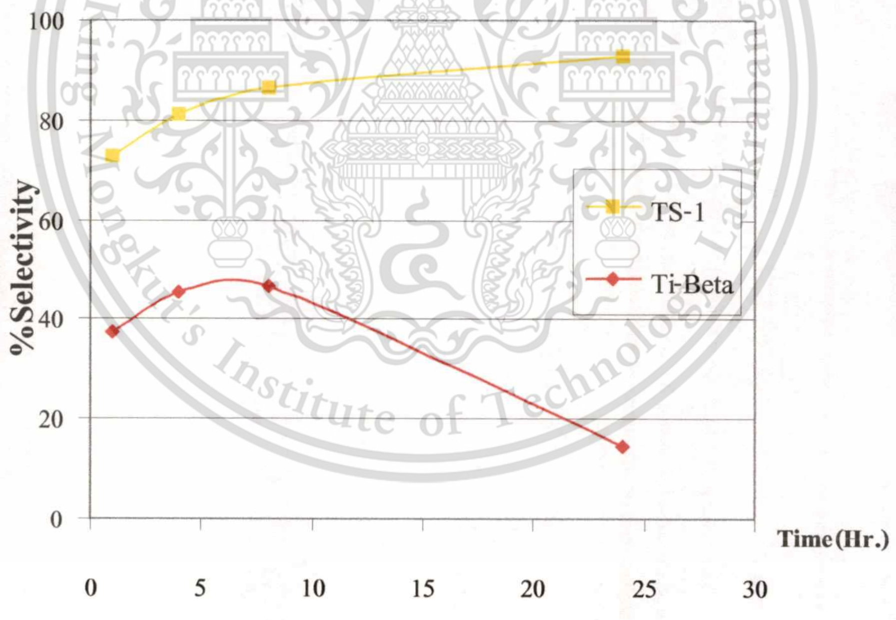


Figure 4.10 The selectivity of cyclohexanone oxime, reaction in acetic acid. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.3796 grams, ammonia solution (28%w/w) 0.7253 grams and hydrogen peroxide solution (30%w/w) 0.5261 grams, Acetic Acid 2.4 ml, Reaction Time1, 2, 4, 8 and 24 hours, Ti-Beta and TS-1 0.04 grams as catalyst.*

This is not the case for the reaction using TS-1 as catalyst, because TS-1 has no acid site and TS-1 has a medium pore (5.5 Å) which is smaller than the molecular diameter of caprolactam.

Therefore, the caprolactam cannot be generated in the pore of TS-1 leading to the high selectivity of cyclohexanone oxime throughout the residential time.

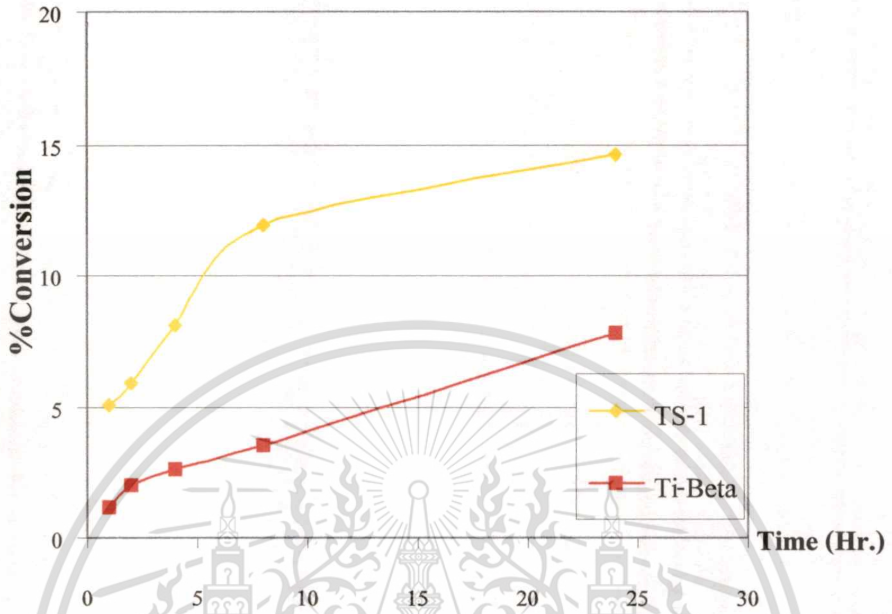


Figure 4.11 The conversion of cyclohexanone, reaction in water. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Water 2.4 ml, Reaction Time1, 2, 4, 8 and 24 hours, Ti-Beta and TS-1 0.04 grams as catalyst.*

The affect of pore size is also investigated in the reaction using water as solvent. The result is shown in Figure 4.11. It is shown that products from the reaction using zeolite Ti-Beta, as catalyst in water, is lower than that using TS-1 as catalyst which is resulted from the lower titanium content in zeolite Ti-Beta, as compared to TS-1 (Table 4.1). Additionally, the formation of caprolactam (via rearrangement) which promoted the formation of cyclohexanone oxime was not observed in water. This is because in the reaction using water as solvent, water would readily reduce the acidity of the zeolite by strong adsorption on the trace acid sites. Conclusively, the effect of pore size cannot be virtually evaluated in the reaction using water as solvent, as it appears that the effect of titanium content play an important role in this system.

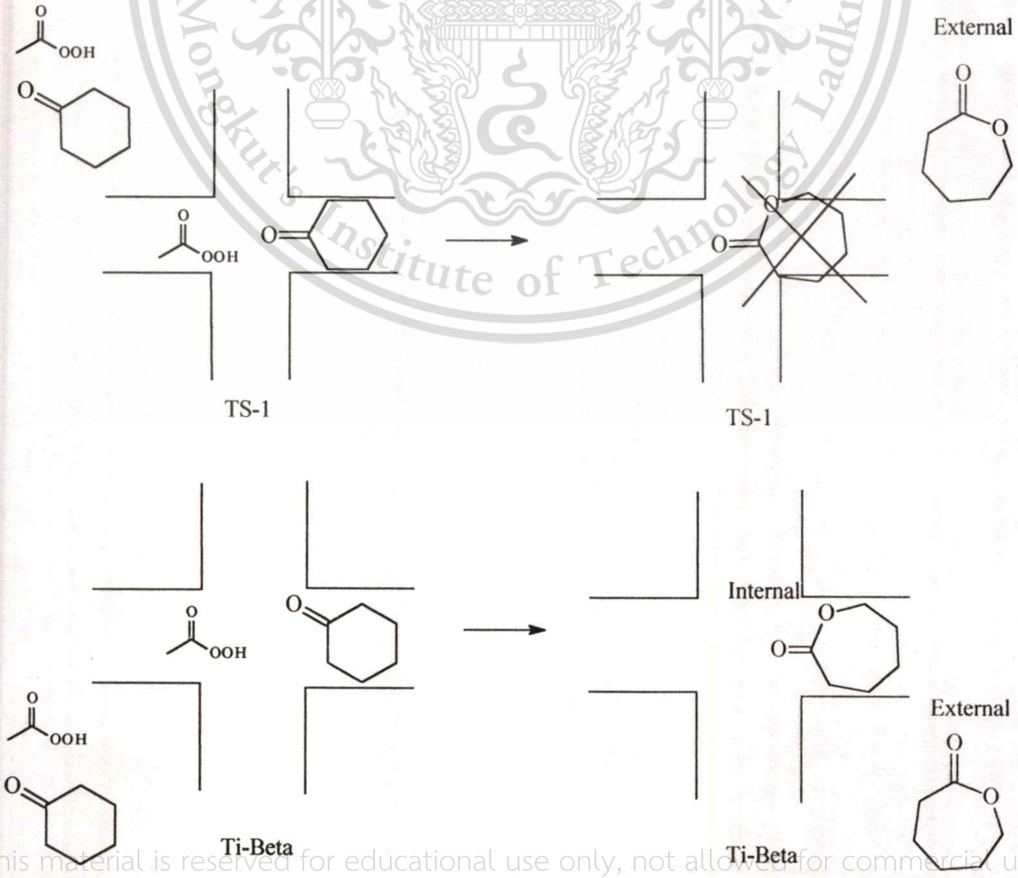
The effect of pore size can also be seen from the increased formation of caprolactone in the reaction using zeolite Ti-Beta as catalyst, as shown in Table 4.5.

Table 4.5 The yield of caprolactone in ammoximation reaction using TS-1 and zeolite Ti-Beta as catalyst

Catalyst	% Yield of Caprolactone
TS-1	3.2
Ti-Beta	4.1

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, Ti-Beta and TS-1 0.04 grams as catalyst.

From the above discussion (section 4.2.1), It was concluded that caprolactone was generated homogeneously in liquid phase without aid of TS-1. This is because of the fact that TS-1 possesses the medium pore size (5.5 Å), caprolactone with molecular size larger than its pore size cannot be generated internally. Therefore caprolactone was produced only external pore of zeolite. However, the result from the reaction using zeolite Ti-Beta (Table 4.5) shows that the large pore zeolite can promote higher yield of caprolactone with high selectivity. This is suggested from the fact that zeolite Ti-Beta possesses a large pore size (7.6 Å). Caprolactone can be both generated on the external surface and in the pore of the zeolite as illustrated below;



Peracetic acid was locally generated by the active sites within the pore. There would readily be a higher concentration of peracetic acid in the pore of zeolite and the formation of caprolactone within the pore can be facilitated, as compared to the external surface of the zeolites. This leads to the observed higher yield of caprolactone in the reaction using zeolite Ti-Beta as catalyst.

Since caprolactone which is a by-product in the ammoximation, is a valuable industrial chemicals. The study on synthesis of caprolactone was further investigated. Reaction for synthesis of caprolactone was tested by reacting cyclohexanone with hydrogen peroxide in acetic acid using TS-1 and Ti-Beta as catalyst for 4 hours. The results are shown in table 4.6.

Table 4.6 The yield and conversion for the synthesis caprolactone using TS-1 and zeolite Ti-Beta as catalyst

Catalyst	**% Yield of Caprolactone**	**% Conversion of Cyclohexanone**
TS-1	5.7	8.8
Ti-Beta	45.9	46.0

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic acid 2.4 ml, Reaction Time 4 hours, Ti-Beta and TS-1 0.04 grams as catalyst.

The results are consistent with the observed higher yield of caprolactone in ammoximation using Ti-Beta as catalyst. This is confirmed that the "Baeyer-Villiger Rearrangement" is not only generated by homogeneous reaction but also by the catalysis over titanium containing zeolites. It is also shown that Ti-Beta is an effective catalyst for the formation of caprolactone.

4.2.5 Effect of the Titanium Species

As it can be seen from the above results [page 52] that titanium content of zeolites play a significant role in oxidation activity, the effect of titanium species was further investigated in Ti-Beta. After the titanation of dealuminated zeolite Beta, titanium is expected to replace the position of aluminium in the tetrahedral units. Nevertheless, titanium tetrachloride can diffuse into the pore of zeolite, and deposit to form a non-framework titanium, which results in an increased titanium content of the zeolite [Table 40.1]. Therefore, titanium can be present in zeolite as two species, the framework titanium (tetrahedral form) and the non-framework titanium. The catalytic property of these two species was evaluated by the reaction using zeolite Ti-Beta before and after washing out of the non-framework as catalyst. Yield and conversion of reaction using zeolite Ti-Beta before and after washing with sulfuric acid show in Table 4.7.

Table 4.7 The yield and conversion for the reaction using Ti-Beta before and after washing by sulfuric acid

Catalyst	Si/Ti Ratio	% Yield of Cyclohexanone Oxime	% Conversion of Cyclohexanone
Ti-Beta (unwashed)	36	4.3	5.2
Ti-Beta (washed)	47	15.5	34.2

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, , ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic acid 2.4 ml, Reaction Time 4 hours, Ti-Beta 0.04 grams as catalyst.

From the result, it was shown that the reaction using zeolite Ti-Beta before washing with sulfuric acid produces much lower yield of cyclohexanone oxime than the washed zeolite Ti-Beta. It can be suggested that the reduced activity of zeolite Ti-Beta before washing with sulfuric acid may well derive from the blockage of pore by the non-framework titanium. This is evident by a reduced surface area of zeolite Ti-Beta before washing with sulfuric acid (Table 4.2). Blockage by titanium in the pore of zeolite results in a difficulty for cyclohexanone to diffuse and react with the active sites in pore of zeolite, leading to the observed low activity of the zeolite Ti-Beta before washing with acid, as compared to the zeolite Ti-Beta after washing. Therefore, the zeolite with high titanium content would not be an effective catalyst, if the titanium species are present as the non-framework titanium. It seems clear that, the non-framework titanium has no activity to catalyze the reaction, but inhibit the diffusion of the reaction. The reaction was catalyzed only by the framework titanium (tetrahedral form).

4.2.6 Influence of Contact Time

In the large-scale production, the higher yield of cyclohexanone oxime is required. Contact time, in the other words, the amounts of catalyst concentration, would affect the activity, selectivity and operation cost. In order to verify the influence of contact time, the reactions using various amount of catalyst were tested in the reaction using acetic acid as solvent. The results are shown in Figure 4.12 and 4.13.

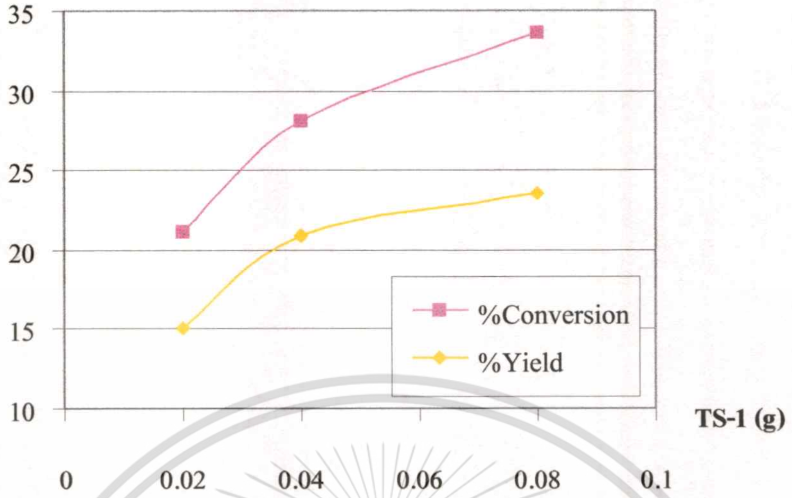


Figure 4.12 Effect of contact time on the conversion of cyclohexanone and yield of cyclohexanone oxime. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, TS-10.02, 0.04 and 0.08 grams as catalyst.*

The result from Figures 4.12 shows that the increased amount of TS-1 in the reaction leads to an increase in cyclohexanone oxime formation. This is because cyclohexanone have a higher possibility to react with active sites and higher yield of product can be obtained.

The conversion, however, seem not to be significantly changed when the catalyst was increased from 0.04 gram to 0.08. It may be resulted from the reaction approaching saturation kinetics. Therefore the higher amount of catalyst does not help to promote higher conversion. On the other hand, it leads to an increase in operation cost.

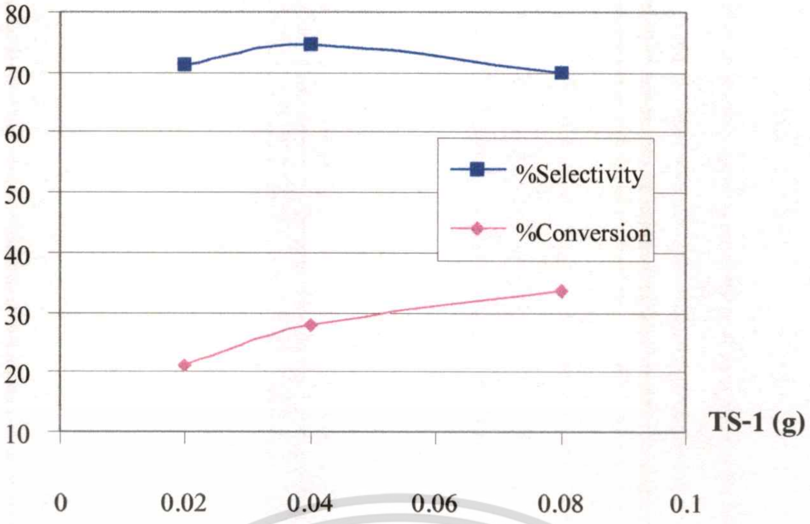
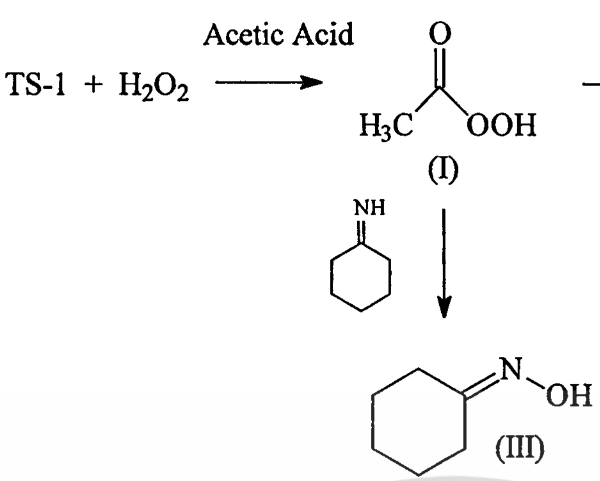


Figure 4.13 Effect of contact time on the conversion of cyclohexanone and selectivity of cyclohexanone oxime. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, TS-10.02, 0.04 and 0.08 grams as catalyst.*

In general, selectivity of a product would be changed when the conversion was increased. This depends on the activity for the formation of each product. If the conversion of the by-product was increased, a low selectivity of the designed product could be observed. However, if the by-product was formed homogeneously or was not generated from catalytic system, the increase in the amounts of catalyst could promote only the catalyzed products and suppress the formation of the by-products. In this case, selectivity would be increased at high contact time. However, above are not the case for ammoximation reaction since the selectivity of cyclohexanone oxime was not significantly changed. This is because major by-product in ammoximation (caprolactone) (II) was generated from reaction of cyclohexanone with the primary product, peracetic acid (I). Additionally, peracetic acid can react with the cyclohexanone imine to form the main product, cyclohexanone oxime (III). As the catalyst was increased, more peracetic acid can be obtained. Consequently, yield of both cyclohexanone oxime and caprolactone can be increased. Therefore, the selectivity was not significantly changed when catalyst was increased.



4.2.7 Effect of Pressure

The reaction using water as solvent confronts with the loss of ammonia by vaporization. Reaction under pressure could be an alternative choice for this problem. The results of reaction under pressure are shown in Table 4.8.

Table 4.8 The yield of cyclohexanone oxime and conversion of cyclohexanone for the reaction at atmospheric pressure and under pressure

Reactor	**% Yield of Cyclohexanone Oxime**
Reaction at atmospheric pressure	8.1
Reaction at 10 Bar of N_2*	8.8

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Water 2.4 ml, Reaction Time 4 hours, TS-1 0.04 grams as catalyst.

** up scale to total mixture 200 ml*

From Table 4.8, it was shown that the reaction under pressure gives a slightly improved activity, as compared to the reaction at atmospheric pressure. This can be attributed to the fact that, under pressure, ammonia can be dissolved in the liquid phase slightly batter than the reaction at atmospheric pressure. However, the vapor pressure of ammonia is so high (26.35 bar) that the pressure used for testing the effect of pressure (10 bar) shows fairly improvement in the solubility of ammonia. Therefore, a small change in activity can be observed. Accordingly to the limitation of the experiment, the higher activity could be obtained if the higher pressure (30 bar) can be applied.

4.2.8 Effect of Ammonium Salts

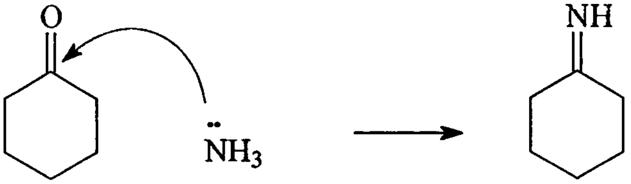
From the fact that ammonia in reaction using water as solvent can vaporize to the gas phase leading to a low concentration of ammonia in liquid phase, an alternative for solving this problem is the use of the ammonium salts as reagent. In the reaction using acetic acid as solvent, ammonia was trapped in the liquid phase as ammonium acetate. This indicates an ability of ammonium acetate to serve as reagent. Accordingly, other ammonium salts could be used as the reagent in the reactions using water and acetic acid as solvent. The results are shown in Table 4.9.

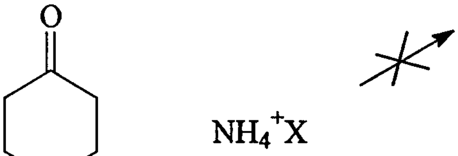
Table 4.9 The yield of cyclohexanone oxime from the reaction using ammonium salts as reactant

Ammonium Salts		**% Yield of Cyclohexanone Oxime**	
		Water	**Acetic Acid**
Ammonia Solution	NH_4OH	8.1	20.8
Ammonium Acetate	$NH_4(OCOCH_3)$	0.68	21.5
Ammonium Carbonate	$(NH_4)_2CO_3$	6.3	8.3
Ammonium Citrate	$(NH_4)_2HC_6H_5O_7$	0.47	6.6
Ammonium Oxalate	$(NH_4)_2(COO)_2$	trace	1.8
Ammonium Chloride	NH_4Cl	trace	trace
Ammonium Sulfate	$(NH_4)_2SO_4$	trace	trace

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, Reaction Time 4 hours, TS-1 0.04 grams as catalyst.

From the Table 4.9, it was revealed that ammonium salts of strong acid such as, ammonium oxalate, ammonium chloride and ammonium sulfate, cannot be used as reagent in both reaction using acetic acid and water as solvent. This is because the K_a of the conjugated acid of ammonium salts is high. Consequently the ammonia was strongly protonated by the conjugated acid, leading to deactivation of the lone pair electrons. The protonated ammonia is not efficient for both condensation with cyclohexanone to produce cyclohexanone imine and oxidation to hydroxylamine.





(ammonium salts of strong acid)

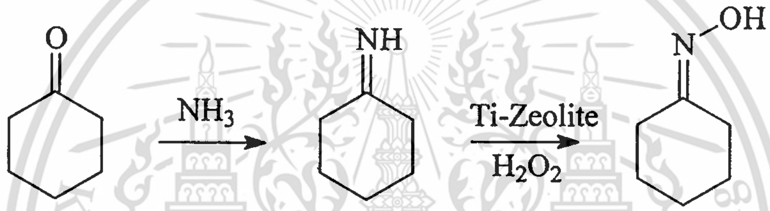
In the case of using ammonium acetate as a reagent, the reaction using ammonium acetate shows relatively high activity than ammonia solution in the system that using acetic acid as solvent. This can be derived from the low concentration of water in system when ammonium acetate was used. The condensation of cyclohexanone with ammonia can be facilitated in the reaction with low water content, as discussed in section 4.2.3. However, in the reaction using water as solvent, the use of ammonium acetate shows lower activity than ammonia solution. This can be resulted from the fact that ammonium acetate could be highly dissociated in the water than in acetic acid. Accordingly, ammonia was mostly present in a protonated form. The lone pair electrons of ammonia could be deactivated and the reaction with cyclohexanone to form cyclohexanone imine was inhibited. Consequently, no cyclohexanone oxime can be formed in the reaction using water as solvent, when ammonium acetate was employed.

In the case of using ammonium citrate as reagent, the above explanation can be applied for an observed low activity in the reaction using water as solvent. However, in the reaction using acetic acid, ammonium citrate shows a lower activity, as compared with ammonium acetate. It can be explained that ammonium citrate is a hydroxy polyacid. Therefore, it can be highly dissociated in acetic acid, as compared to ammonium acetate. In consequence, reactivity for the reaction with cyclohexanone to generate cyclohexanone imine is relatively lower than the reaction using ammonium acetate.

In the case of using ammonium carbonate as reagent, a relatively higher yield of cyclohexanone oxime can be obtained in both reaction using acetic acid and water as solvent. This is because ammonium carbonate is an ammonium salt of a weak acid, carbonic acid. It can be readily decomposed to give ammonia at reaction temperature. However, in the reaction using acetic acid as solvent, yield of cyclohexanone oxime was lower than that expected. This may be resulted from the fact that ammonium carbonate reacts vigorously with acetic acid used as solvent, producing carbon dioxide, ammonia and exhaust heat. Under this circumstance, the vaporization of carbon dioxide may well lead to the loss of ammonia. This could reduce the rate of condensation with cyclohexanone, resulting in a lower production of cyclohexanone oxime. In the case of the reaction using water as solvent, it was shown that the activity of ammonium carbonate is somewhat similar to the reaction using only the ammonia solution. This is because ammonium carbonate can be gradually decomposed to give ammonia and the reaction can proceed in the same manner as that using ammonia solution.

4.2.9 Effect of Ammonium Acetate Concentration

From the mechanism,



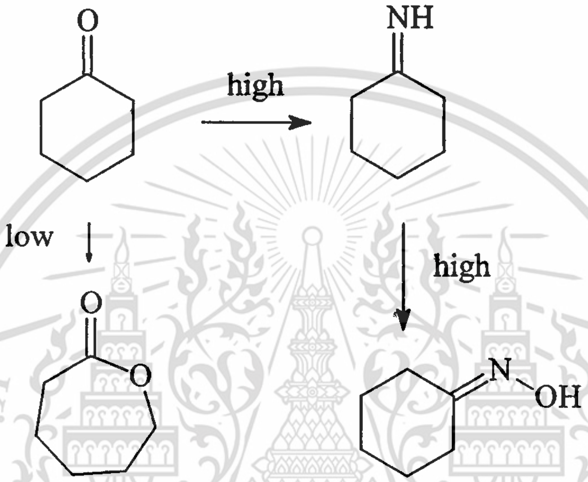
It was suggested earlier [section 4.2.2] that, cyclohexanone imine could be a key intermediate of the reaction. Accordingly the concentration of ammonium acetate would play an important role in the determination of reaction rate. Influence of excess ammonium acetate was studied in the reaction using acetic acid as solvent and the result is shown in Table 4.10.

Table 4.10 The yield, selectivity and conversion for the reaction using excess ammonium acetate over TS-1 and zeolite Ti-Beta

Catalyst	**TS-1**		**Ti-Beta**	
Ammonium Acetate (g)	**0.45**	**1**	**0.45**	**1**
% Conversion of Cyclohexanone	25.7	56.2	34.2	52.8
% Yield of Cyclohexanone Oxime	20.8	43.7	15.5	48.1
% Selectivity of Cyclohexanone Oxime	81.0	77.8	45.3	91.0
% Yield of Caprolactam	-	-	12.3	-

***Reaction condition:** Temperature 60 °C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, Reaction Time 4 hours, TS-1and Ti-Beta 0.04 grams as catalyst.*

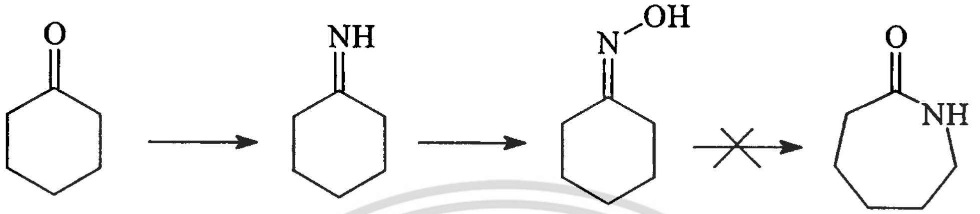
Shows that the reaction using excess ammonium acetate produces higher cyclohexanone oxime than the typical reaction. This is a further evidence confirming that the ammoximation proceeds via condensation of ammonia and cyclohexanone. Additionally, a higher selectivity of cyclohexanone oxime was obtained because the higher amount of ammonium acetate can facilitate the condensation of cyclohexanone with ammonia to produce more cyclohexanone imine, which reduces a probability of cyclohexanone to react directly with peracetic acid to give by-product, caprolactone.



The increase in cyclohexanone oxime could also lead to a higher production of acetyl cyclohexanone oxime. However, acetyl cyclohexanone oxime was found to be low in the reaction using excess ammonium acetate as reagent. This may be resulted from the lower interaction of cyclohexanone oxime with non-polar framework of zeolite, as compared to that of cyclohexanone imine. As more cyclohexanone imine is produced, less probability of cyclohexanone oxime to react with the active site can be limited. Therefore, selectivity of cyclohexanone oxime was improved.

Additionally, the results from Table 4.10 show that in the reaction using zeolite Ti-Beta as catalyst, caprolactam was not produced as co-product when excess ammonium acetate was used. This can be attributed to the fact that high concentration of ammonium acetate would readily reduce trace of acid site in the framework (as discussed in section 4.2.4), which inhibits the rearrangement of cyclohexanone oxime to produce caprolactam.

However, in the reaction using zeolite Ti-Beta as catalyst, yield of cyclohexanone oxime was lower than that expected (the conversion of cyclohexanone should be higher than the reaction using TS-1 as catalyst). This may be resulted from the fact that the reaction using excess ammonium acetate, rearrangement of cyclohexanone oxime to caprolactam was not promoted (as discussed above). In consequence, there is no thermodynamic driving force for the reaction to proceed forward to the formation of caprolactam. Subsequently, the enhanced activity for ammoximation was not observed. Therefore, the yield of cyclohexanone oxime in the reaction using zeolite Ti-Beta as catalyst is not as high as it would have been.



4.2.10 Effect of Zeolite Deactivation

In industrial processes, catalyst used in the process could be deactivated. The catalyst regeneration contributes higher cost to the product. From the economic point of view, a catalyst with long catalytic lifetime or a catalyst that can be reused without regeneration was expected. In the ammoximation, the catalyst could be deactivated by various factors. They include loss of titanium active site from the framework and the blocking of zeolite pore. In this thesis the reuse of catalyst was investigated and the results are shown in Table 4.11.

Table 4.11 The yield of cyclohexanone oxime and caprolactam generated from the reaction using reused Ti-Zeolite as catalyst

Catalyst	**TS-1**		**Ti-Beta**	
	Fresh	**Reused**	**Fresh**	**Reused**
% Conversion of Cyclohexanone	25.7	29.1	34.2	36.2
% Yield of Cyclohexanone Oxime	20.8	19.5	15.5	19.1
% Yield of Caprolactam	-	-	12.3	6.4

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, used Ti-Zeolite 0.04 grams as catalyst.

The results show that the activity of TS-1 remains unchanged after use. This implies that there is no deactivation in TS-1. In the case of zeolite Ti-Beta, selectivity of cyclohexanone oxime was improved and yield of caprolactam is diminished in the reaction of used Ti-Beta. This may be resulted from a slightly blocking of zeolite Ti-Beta pore by the products deposited, which inhibits the rearrangement of cyclohexanone oxime to caprolactam. It can be concluded that titanium-containing zeolite can be reused in ammoximation with the same activity as the fresh one. Moreover, in the case of zeolite Ti-Beta, selectivity of cyclohexanone oxime can be improved without change in catalyst activity.

Chapter 5

Conclusion and Suggestion

5.1 Conclusion

From the results of ammoximation by titanium-containing zeolites using hydrogen peroxide as oxidizing agent, it can be concluded that:

The study on effect of solvent shows that the reaction using acetic acid as solvent produce higher yield of cyclohexanone oxime than that using water. This is because, in the reaction using acetic acid as solvent, peracetic acid, a better oxidizing agent, can be produced and the complexation of peracetic acid with titanium tetrahedral produce relatively more stable active site than that of hydrogen peroxide. This leads to an improved activity of the catalyst. However the reaction using acetic acid as solvent shows lower cyclohexanone oxime selectivity, as compared to the reaction using water because peracetic acid can react with cyclohexanone and cyclohexanone oxime to make two by-products, caprolactone and acetyl cyclohexanone oxime.

In the mechanistic study, the reaction using water as solvent shows that there are two possible pathways for the ammoximation cyclohexanone. However, the condensation of ammonia with cyclohexanone to produce cyclohexanone imine followed by oxidation of cyclohexanone is favored. In the case of using acetic acid as solvent, only the pathway proceeded via the condensation of cyclohexanone with ammonia is responsible for the formation of cyclohexanone oxime.

From the study on effect of water content, when the concentration of water in system was reduced (by addition of water adsorbent, zeolite A) the by-product formation was also reduced, leading to the higher selectivity of cyclohexanone oxime. This is because the condensation of cyclohexanone with ammonia to generate cyclohexanone imine, which can be directly oxidized to cyclohexanone oxime, was largely promoted in low water system. This leads to the lower reaction rate of cyclohexanone with peracetic acid to produce caprolactone.

The study on effect of pore size shows that in the reaction using acetic acid as solvent the conversion of cyclohexanone in reaction using large pore zeolite, Ti-Beta, is higher than that using TS-1. This is because in the large pore zeolite, reactant can diffuse faster to react with the active sites. However, the rearrangement of cyclohexanone oxime to caprolactam can be generated in pore of Ti-Beta. This facilitates the formation of cyclohexanone oxime leading to the high activity for ammoximation, but low selectivity for cyclohexanone oxime.

The study on the effect of titanium species shows that the reaction was catalyzed only by the framework titanium (tetrahedral form) species. The non-framework titanium has no activity to catalyze the reaction.

The study on the influence of contact time shows that the increased amount of catalyst in the reaction leads to an increase in cyclohexanone oxime formation. This is because cyclohexanone have a higher possibility to react with active sites and higher yield of product can be obtained.

The study on the effect of pressure shows that the reaction under pressure gives only a little improved activity, as compared to the reaction at atmospheric pressure. This is because reaction under pressure, ammonia can be dissolved in the liquid phase slightly better than the reaction at atmospheric pressure, leading to a higher reaction rate, as compared to that at atmospheric pressure.

The study on the effect of ammonium salts shows that ammonium salts of strong acid such as, ammonium oxalate, ammonium chloride and ammonium sulfate, cannot be used as reagent but ammonium salts of weak acid such as ammonium acetate, ammonium carbonate and ammonium citrate can be used as reagent. This is because in the case of ammonium salts of strong acid, the ammonia was strongly protonated by the conjugated acid leading to a reduced activity of ammonia condensations with cyclohexanone to produce cyclohexanone imine.

From the study on the effect of ammonium acetate concentration, it is shown that reaction that using excess ammonium acetate gives higher product than the typical reaction. The higher amount of ammonium acetate can facilitate the condensation of cyclohexanone with ammonia to produce more cyclohexanone imine. This confirms that cyclohexanone condensation is a significant step for the cyclohexanone oxime production.

The study on the effect of zeolite deactivation shows that the activity of TS-1 remains unchanged after use. However, in the case of Ti-Beta, selectivity of cyclohexanone oxime can be improved by the slightly blockage of the pores without change in catalyst activity.

5.2 Suggestion for Future Studies

5.2.1 In the ammoximation using acetic acid as solvent, caprolactone, a valuable industrial chemicals, is formed as by-product by "Baeyer-Villiger" rearrangement. The "Baeyer-Villiger" rearrangement should be studied using titanium-containing zeolites as catalyst.

5.2.2 The ammoximation using acetic acid as solvent, peracetic acid is formed and served as active oxidizing agent. However, using other solvent [15,29] showed that there is no direct conclusion of solvent effect from the investigation. Therefore, investigation on effect of other solvent could be studied.

5.2.3 For future study on the effect of ammonium acetate concentration, various concentration of ammonium acetate should be investigated. Additionally, the effect of all ammonium salts concentration could be studied.

5.2.4 A study on the effect of pressure, the vapor pressure of ammonia is so high (26.35 bar) that the pressure used for testing the effect of pressure (10 bar) shows fairly improvement in the solubility of ammonia. This lead to a slightly improved activity of reaction. For future study, the higher activity could be obtained if the higher pressure (30 bar) can be applied.

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Appendix A

X-Ray Diffraction Patterns of Zeolite

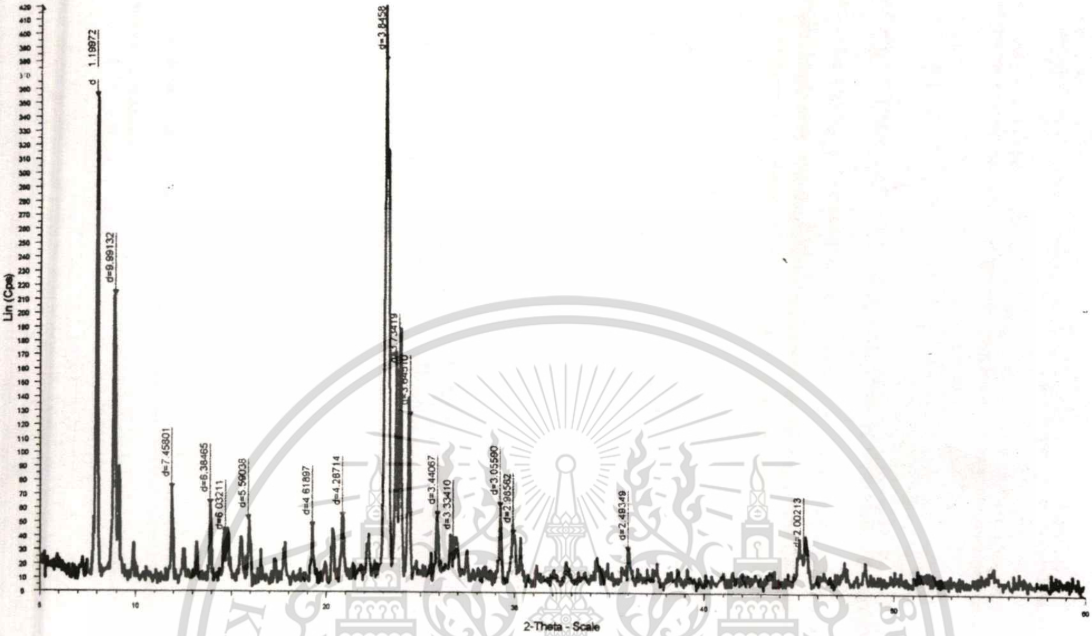


Figure A.1 X-ray diffraction pattern of TS-1 before calcination.

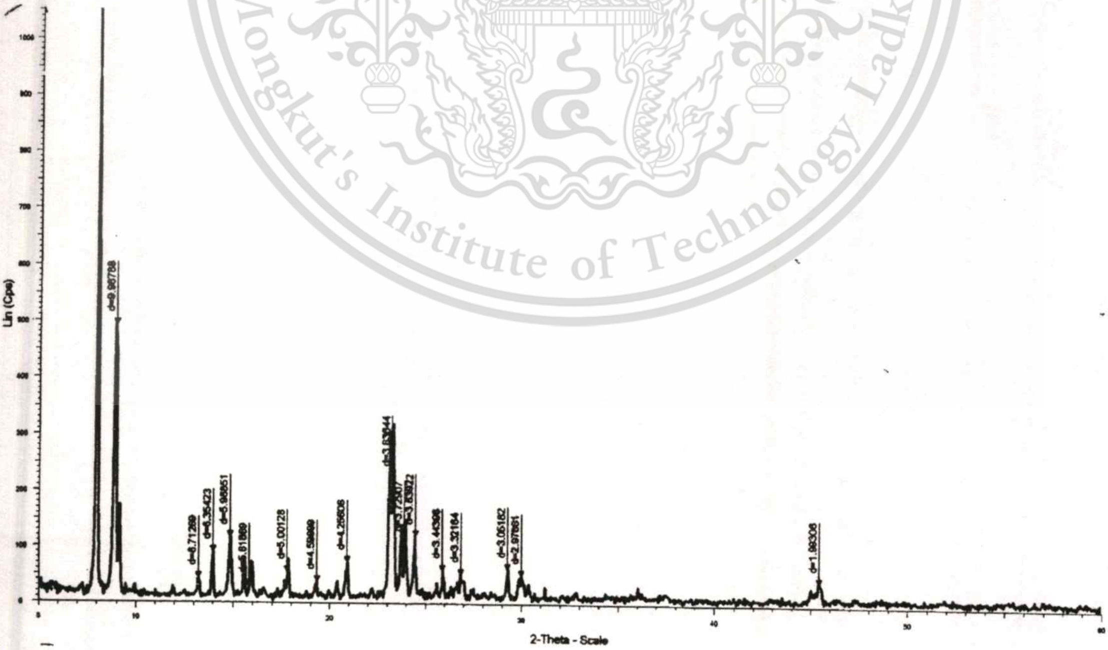


Figure A.2 X-ray diffraction pattern of TS-1 after calcination.

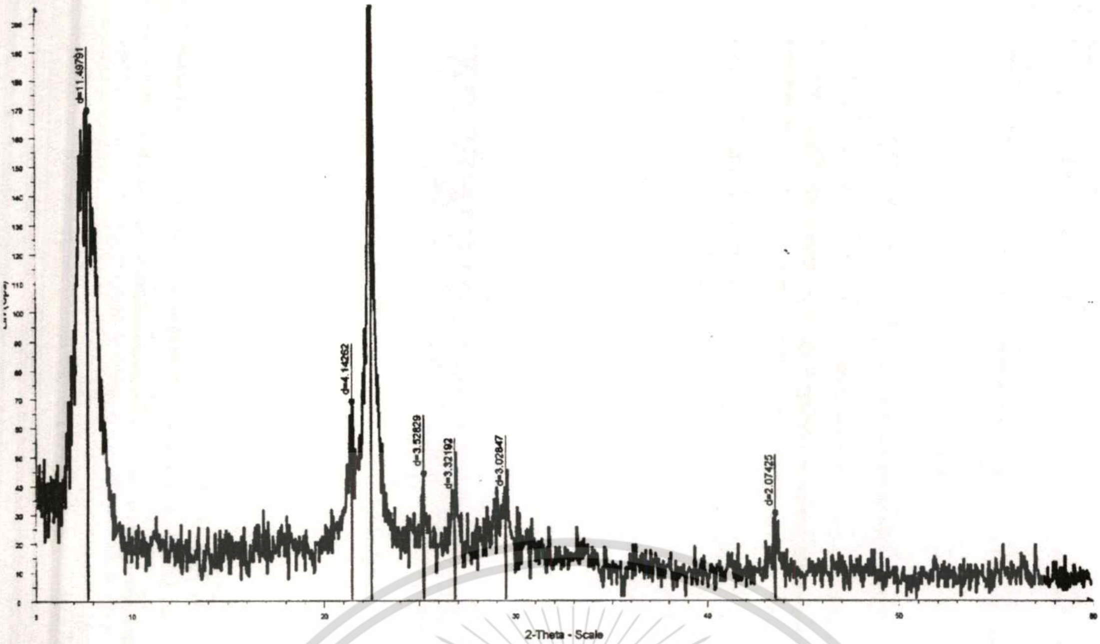


Figure A.3 X-ray diffraction pattern of zeolite NH_4^+-Beta.

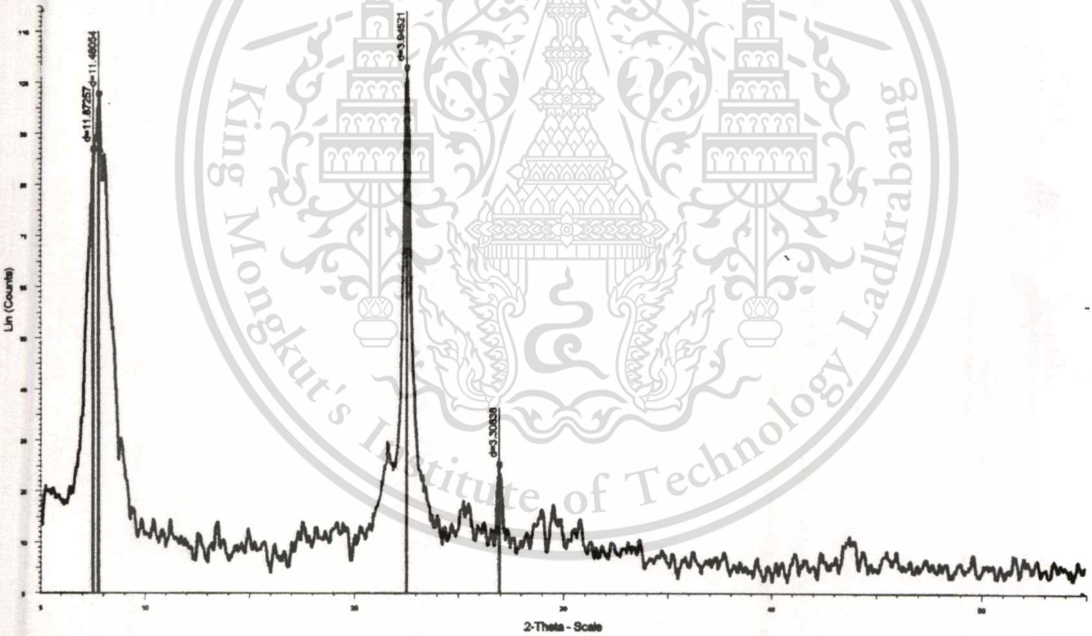


Figure A.4 X-ray diffraction pattern of dealuminated zeolite Beta before calcination.

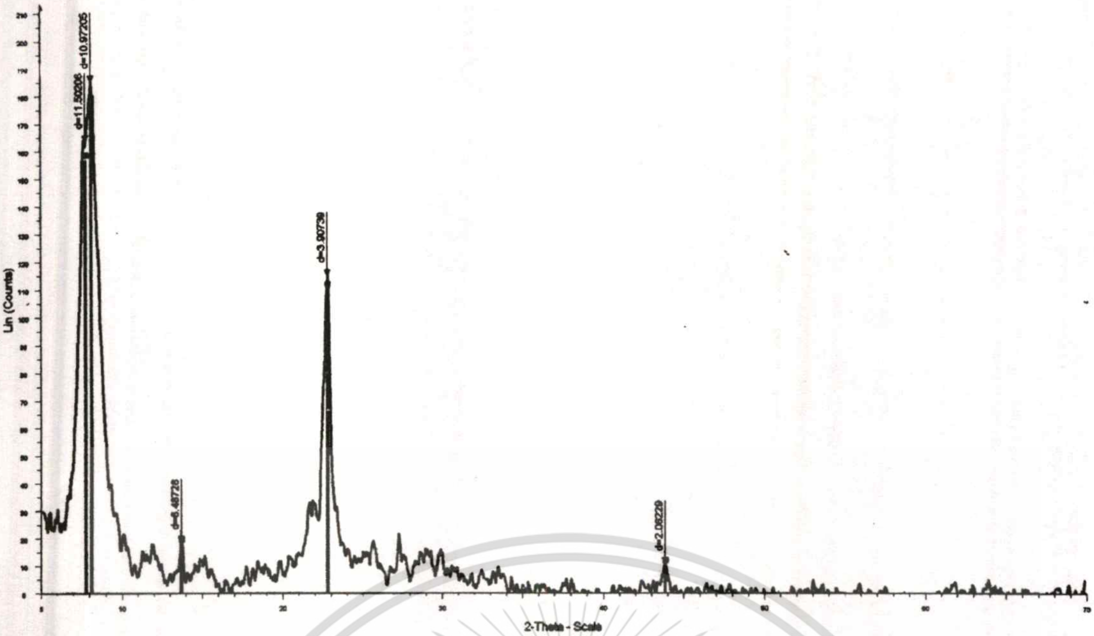


Figure A.5 X-ray diffraction pattern of dealuminated zeolite Beta after calcination.

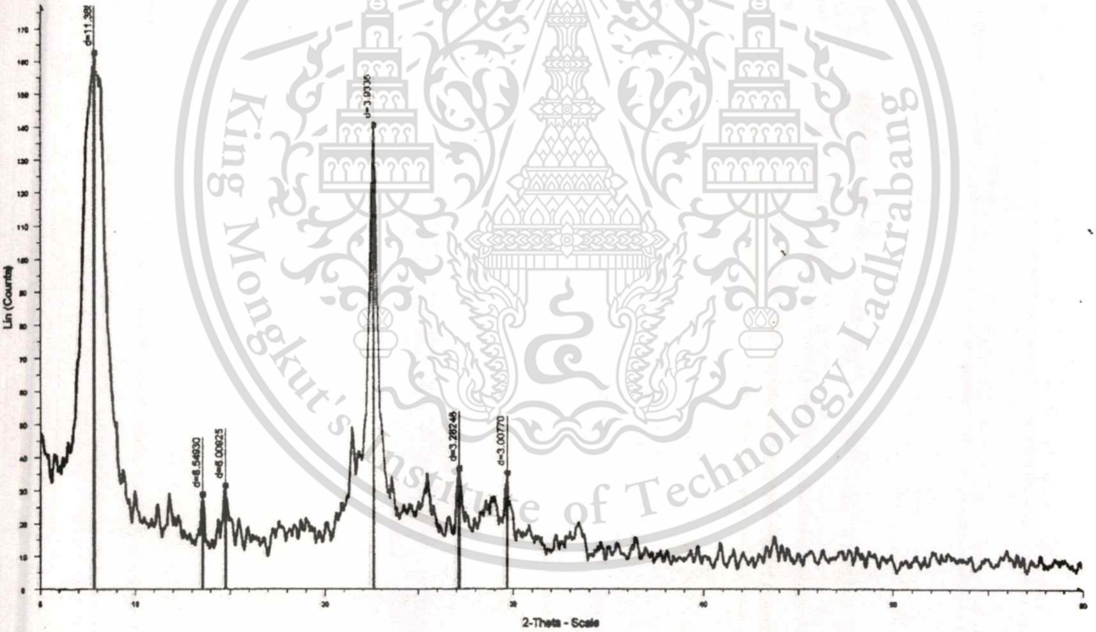


Figure A.6 X-ray diffraction pattern of zeolite Ti-Beta before washing with sulfuric acid.

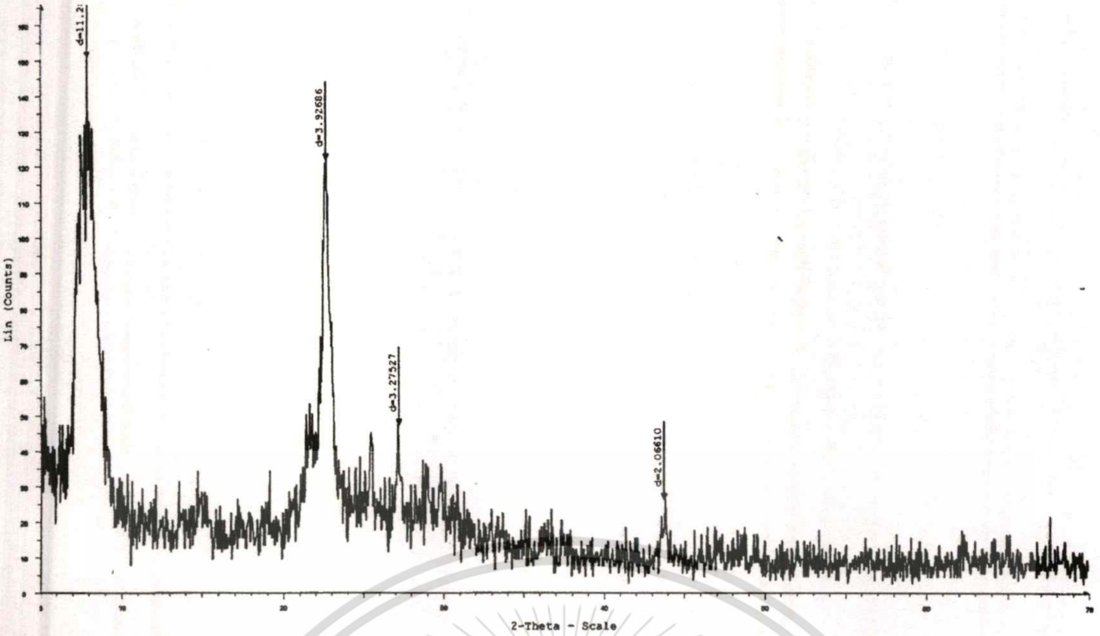


Figure A.7 X-ray diffraction pattern of zeolite Ti-Beta after washing with sulfuric acid and calcination.

Appendix B

Scanning Electron Micrographs

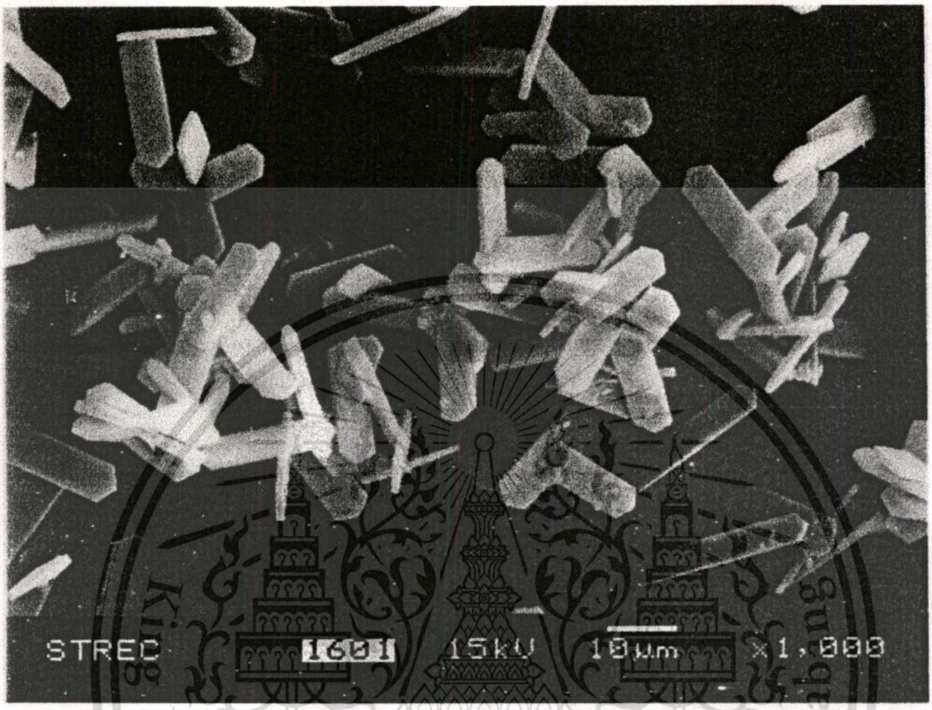


Figure B.1 Scanning electron micrograph of TS-1 before calcination.

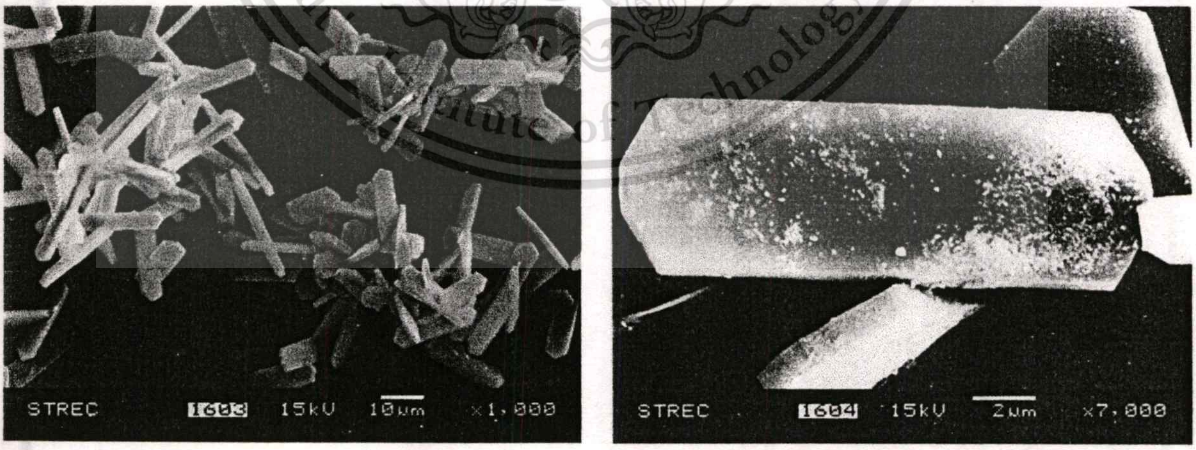


Figure B.2 Scanning electron micrograph of TS-1 after calcination.

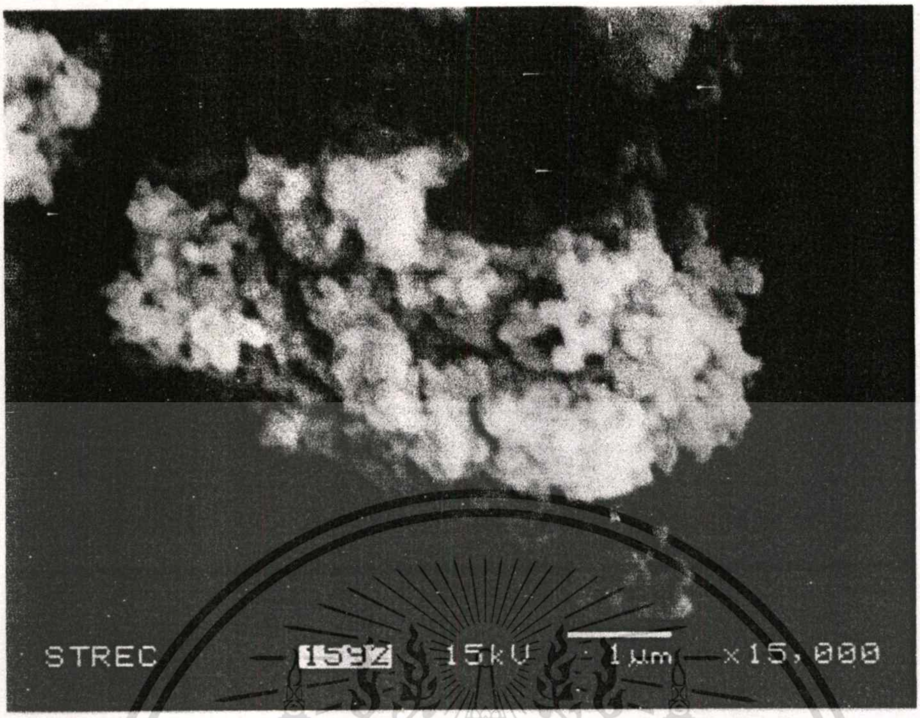
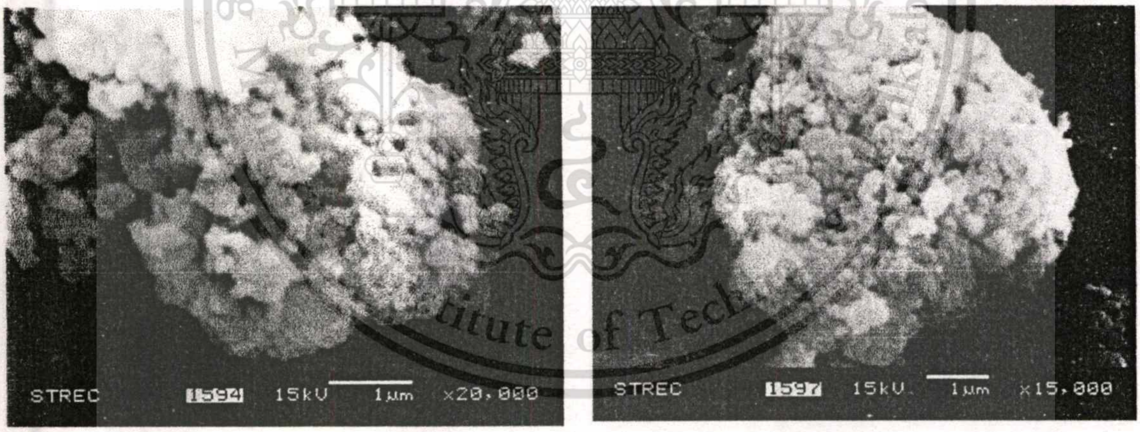


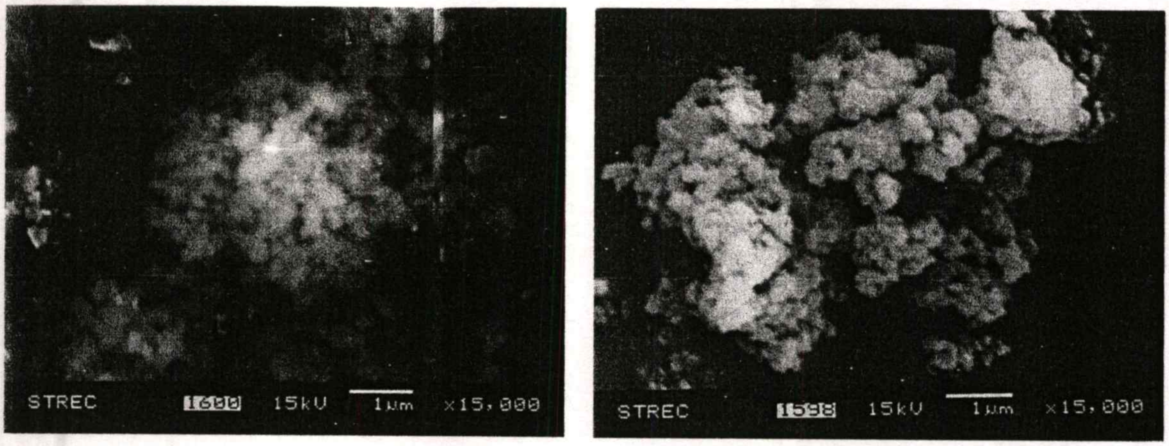
Figure B.3 Scanning electron micrograph of zeolite NH_4^+-Beta.



(a)

(b)

Figure B.4 Scanning electron micrograph of zeolite dealuminated Beta before (a) and after (b) calcination.



(a) (b)

Figure B.5 Scanning electron micrograph of zeolite Ti-Beta before (a) and after (b) washing with sulfuric acid and calcination.

Appendix C

Surface Area and BET Plot from Gas Adsorption Analyzer

Table C.1 Surface area of zeolites analyzed by gas adsorption analyzer.

Zeolite	Surface Area (m^2/g)
TS-1 after calcination	358
Zeolite NH_4^+-Beta	665
Calcined zeolite Ti-Beta before washing with sulfuric acid	536
Calcined zeolite Ti-Beta after washing with sulfuric acid	625

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

Sample ID	TS-1				
Description	micropore 10-6				
Comments					
Sample Weight	0.0071 g				
Adsorbate	NITROGEN	**Outgas Temp**	60.0 °C	**Operator**	Chai
Cross-Sec Area	16.2 Å²/molecule	**Outgas Time**	8.0 hrs	**Analysis Time**	74.2 min
NonIdeality	6.580E-05	**P/Po Toler**	4	**End of Run**	06/23/2000 09:18
Molecular Wt	28.0134 g/mol	**Equil Time**	2	**File Name**	TIZEO1.RAW
Station #	1	**Bath Temp.**	77.35		

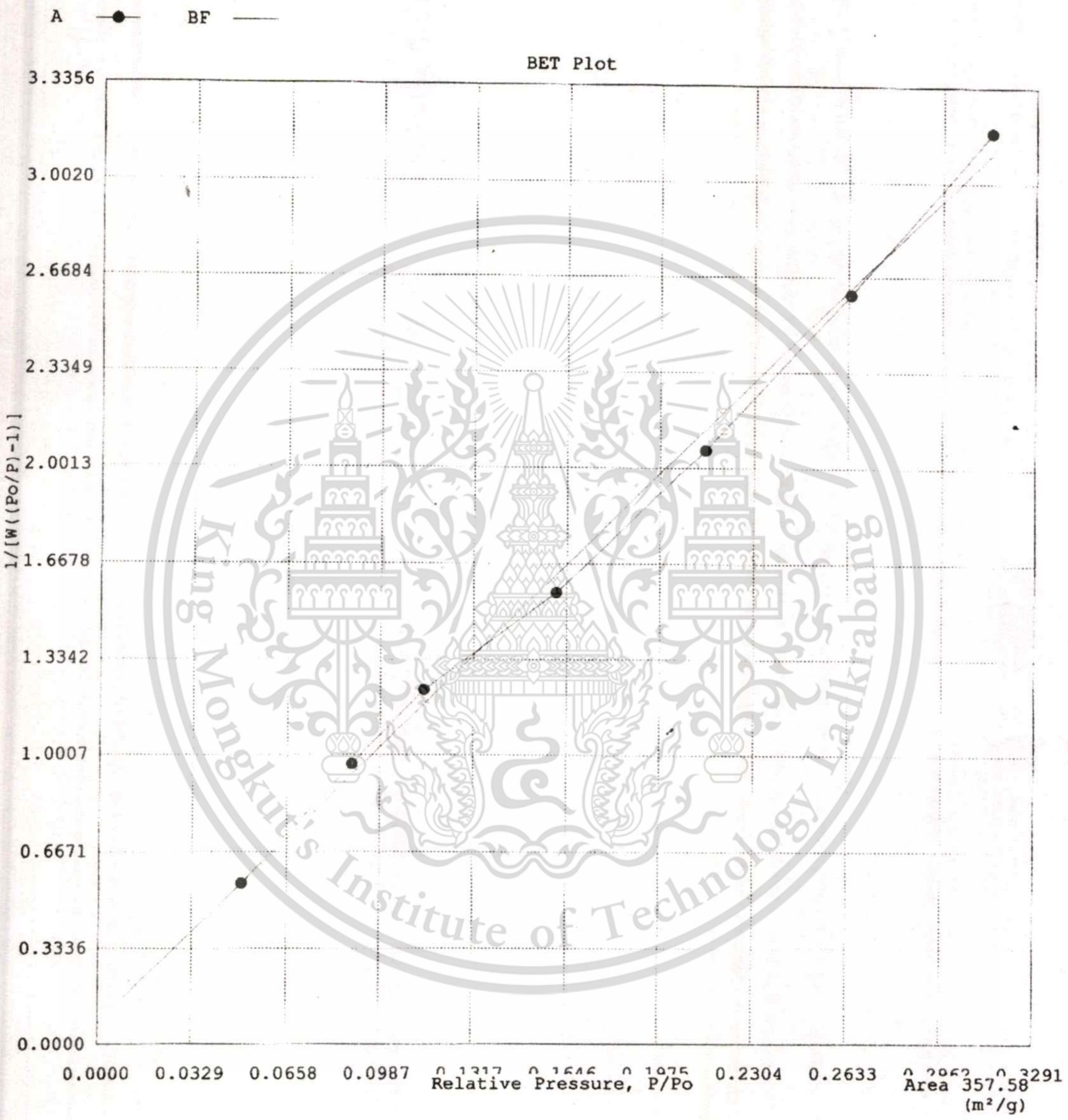


Figure C.1 BET plot of TS-1 after calcination.

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

Sample ID	NH4+ Beta				
Description	micropore 10--6				
Comments					
Sample Weight	0.0103 g				
Adsorbate	NITROGEN	**Outgas Temp**	350.0 °C	**Operator**	chaice
Cross-Sec Area	16.2 Å²/molecule	**Outgas Time**	24.0 hrs	**Analysis Time**	978.6 min
NonIdeality	6.580E-05	**P/Po Toler**	0	**End of Run**	02/16/2001 07:22
Molecular Wt	28.0134 g/mol	**Equil Time**	3	**File Name**	NH4BETA.RAW
Station #	1	**Bath Temp.**	77.35		

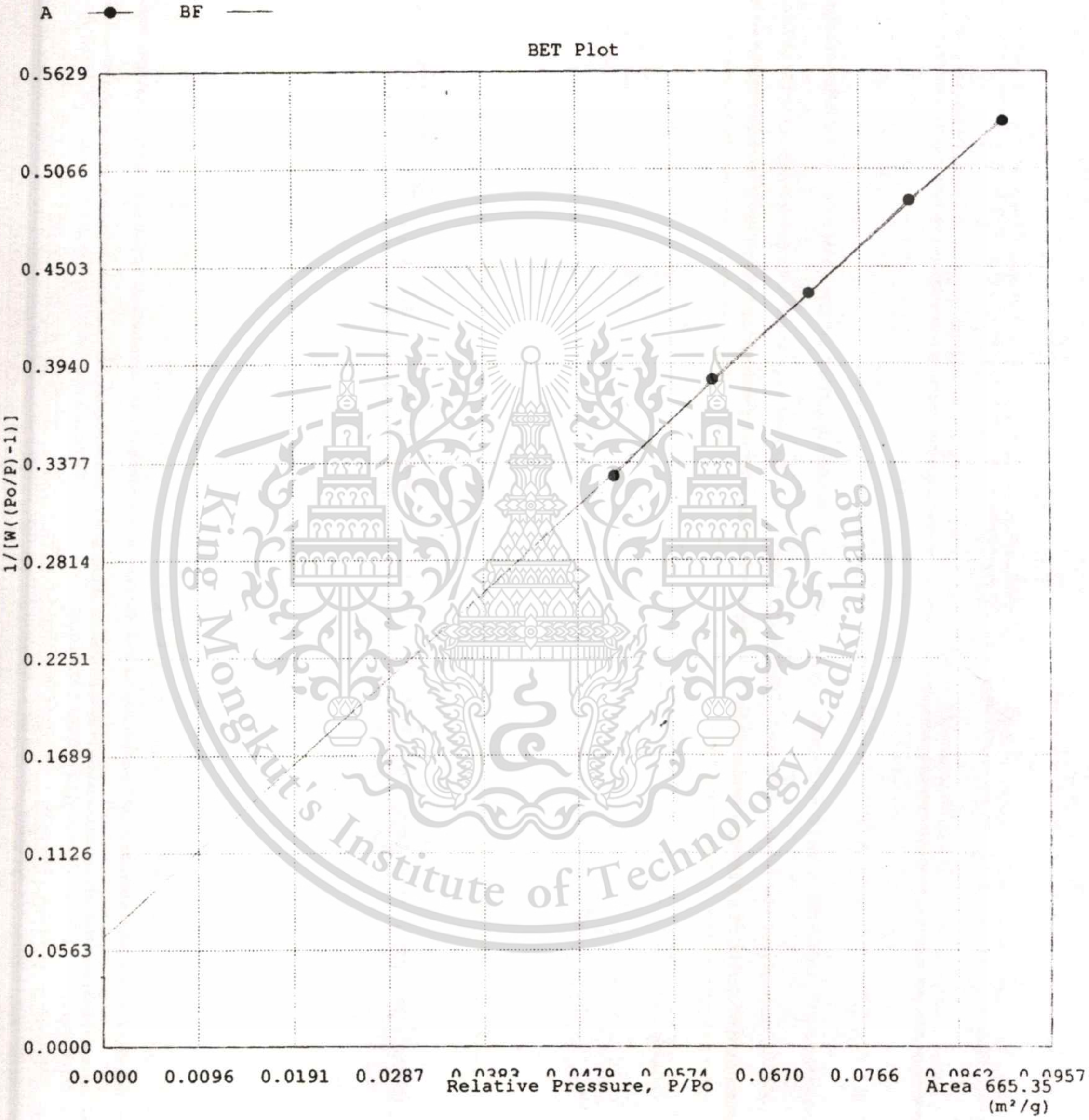


Figure C.2 BET plot of zeolite NH_4^+-Beta.

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

Sample ID        Ti-Beta(CVD)II#1
Description      micropore 10-6
Comments
Sample Weight    0.0103 g
Adsorbate        NITROGEN          Outgas Temp   350.0 °C   Operator        chaice
Cross-Sec Area   16.2 Å²/molecule  Outgas Time   18.0 hrs   Analysis Time   905.8 min
NonIdeality      6.580E-05         P/Po Toler    0          End of Run      02/13/2001 05:07
Molecular Wt     28.0134 g/mol     Equil Time    3          File Name       TIBETA2.RAW
Station #        1                 Bath Temp.    77.35
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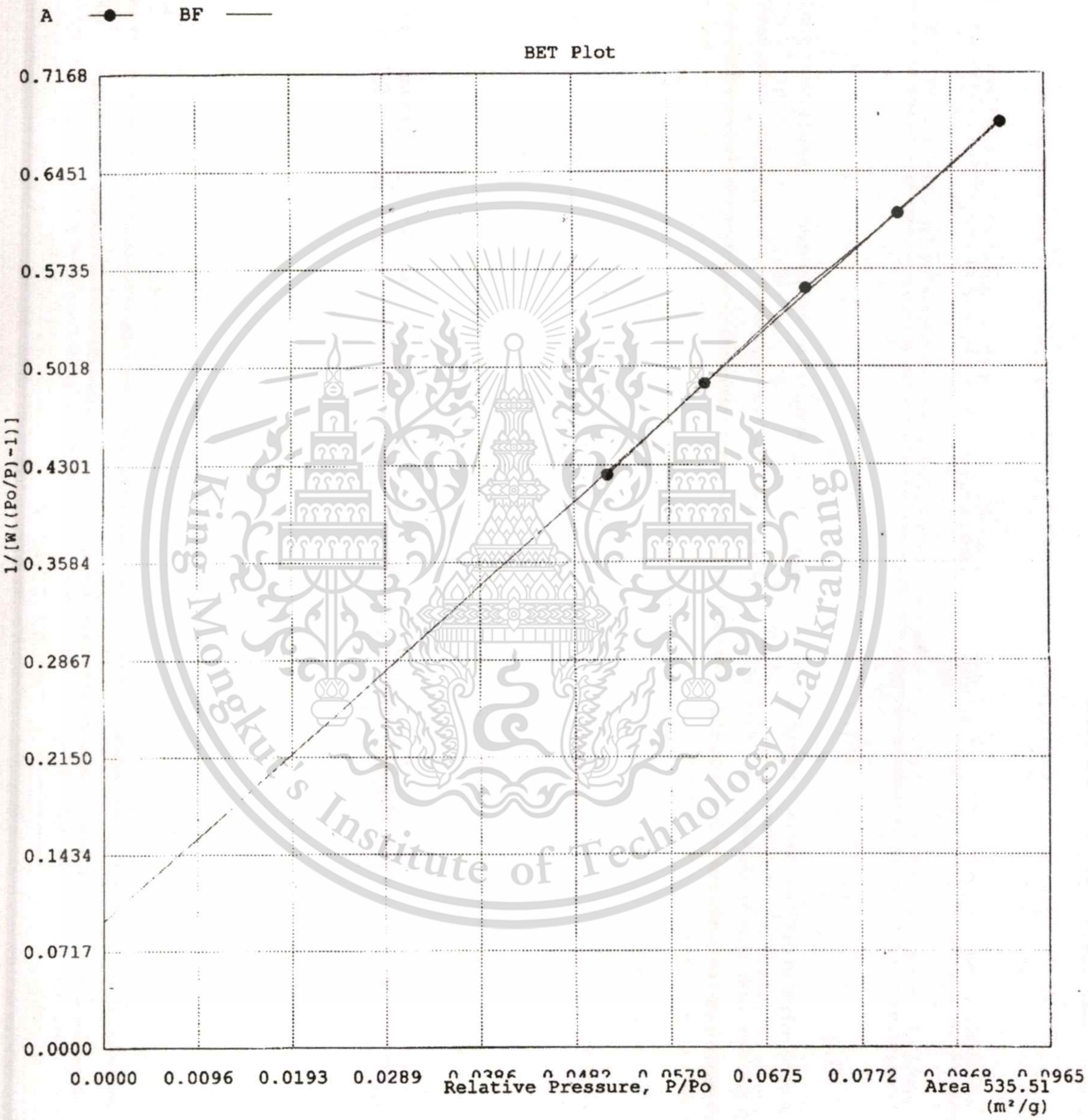
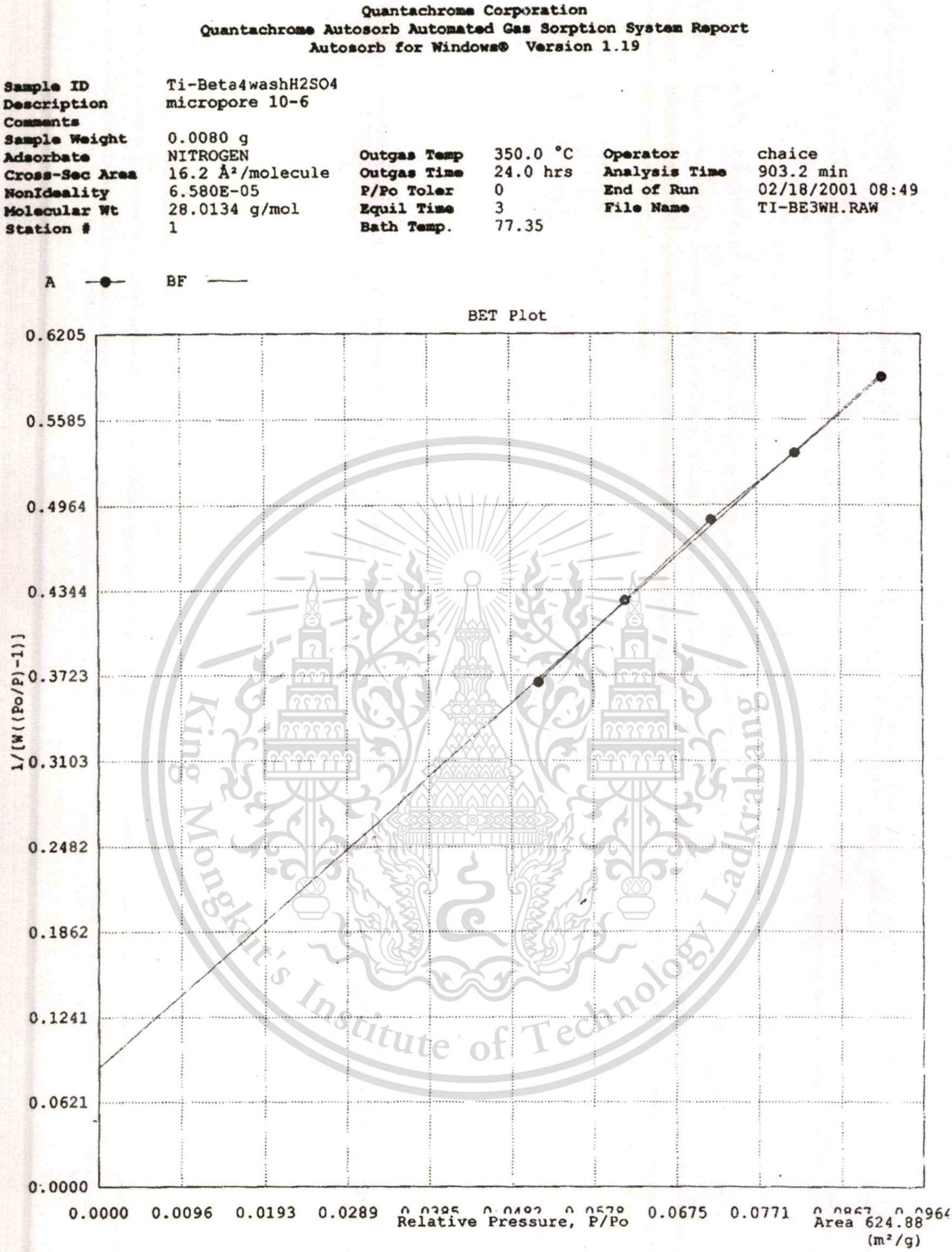


Figure C.3 BET plot of zeolite Ti-Beta before washing with sulfuric acid.



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

Sample ID        Ti-Beta4washH2SO4
Description      micropore 10-6
Comments
Sample Weight    0.0080 g
Adsorbate        NITROGEN            Outgas Temp   350.0 °C   Operator        chaice
Cross-Sec Area   16.2 Å²/molecule    Outgas Time   24.0 hrs   Analysis Time   903.2 min
NonIdeality      6.580E-05           P/Po Toler    0          End of Run      02/18/2001 08:49
Molecular Wt     28.0134 g/mol       Equil Time    3          File Name       TI-BE3WH.RAW
Station #        1                   Bath Temp.    77.35
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Figure C.4 BET plot of zeolite Ti-Beta after washing with sulfuric acid and calcination.

Appendix D

The Fourier Infrared Spectrum

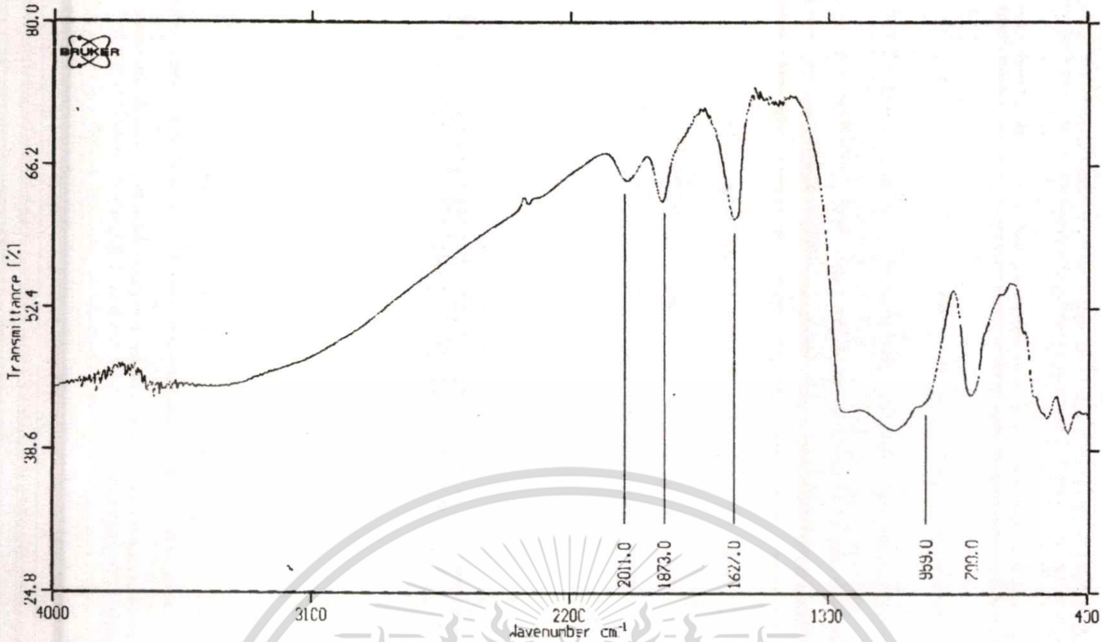

Figure D.1 Fourier IR spectrum of TS-1.

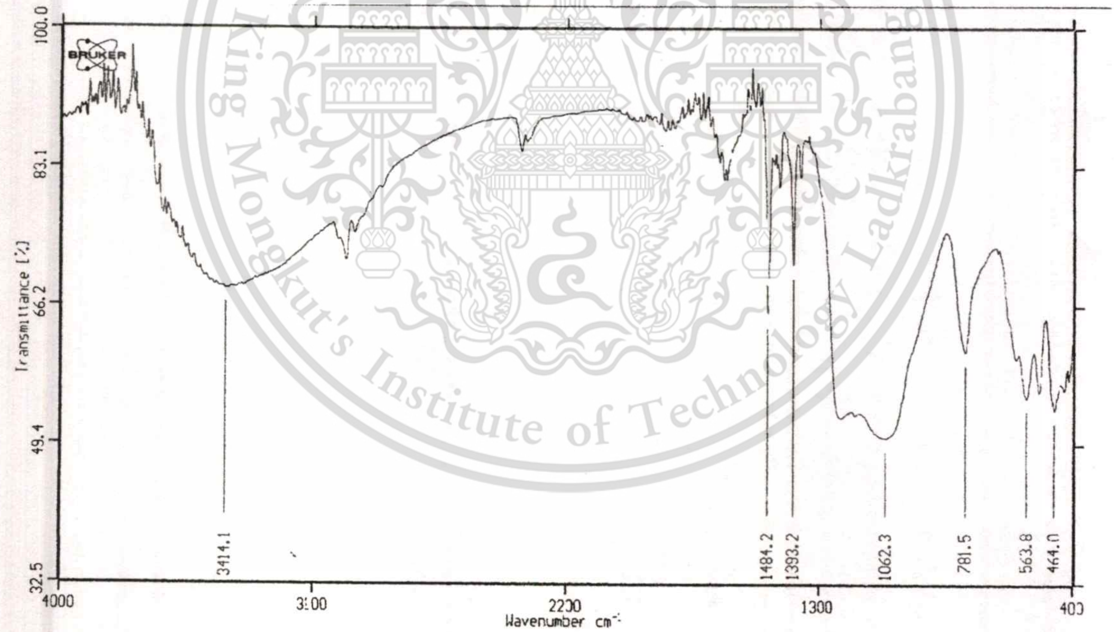

Figure D.2 Fourier IR spectrum of zeolite NH_4^+-Beta.

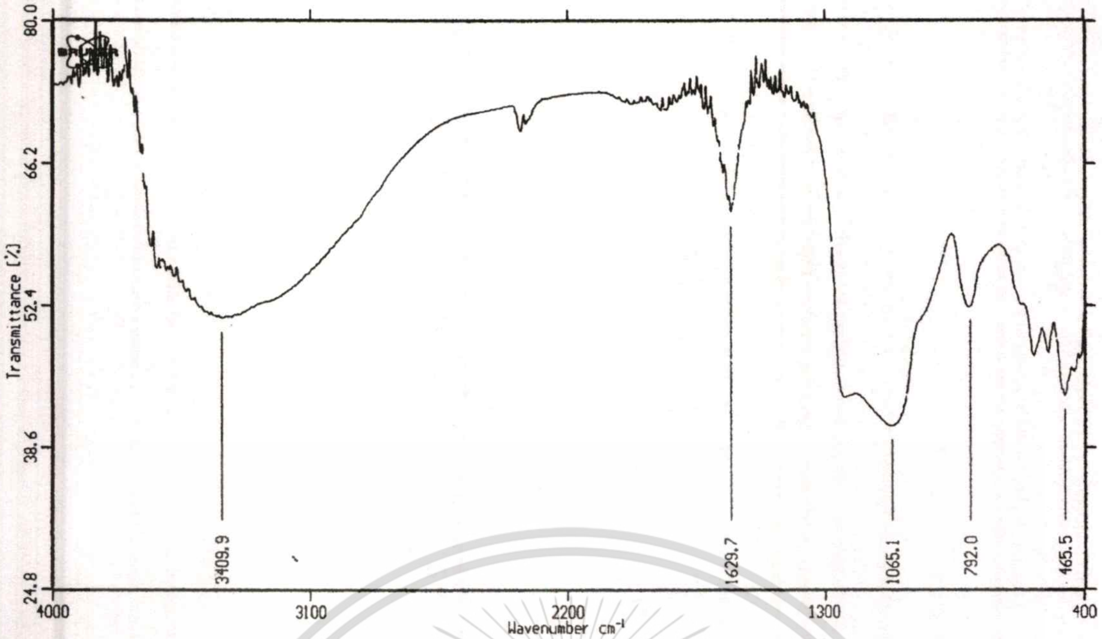

Figure D.3 Fourier IR spectrum of zeolite dealuminated Beta.

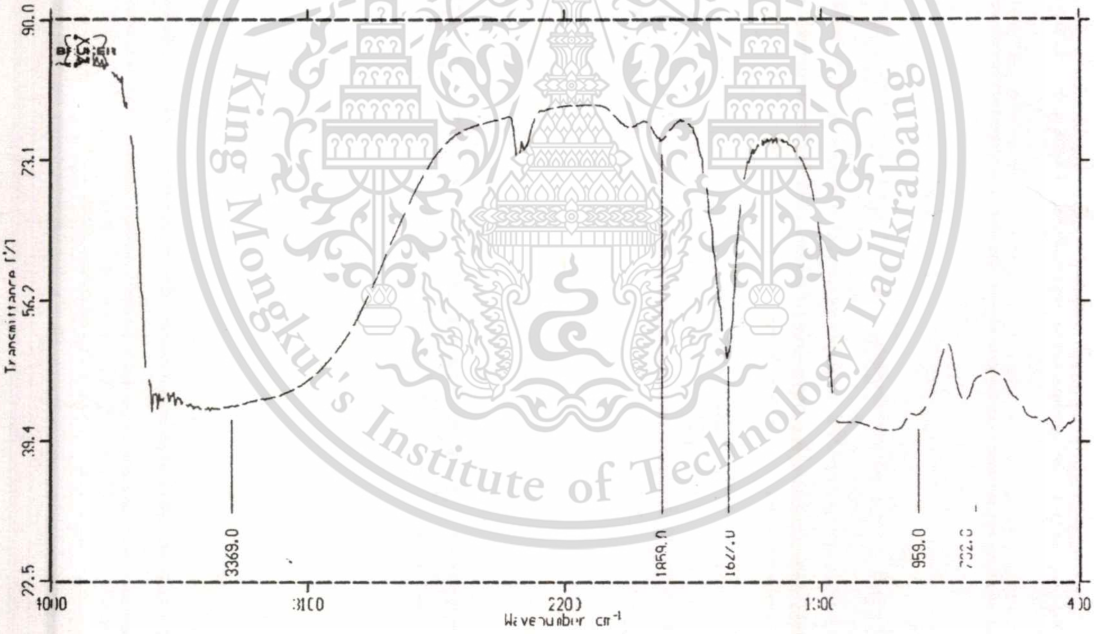

Figure D.4 Fourier IR spectrum of zeolite Ti-Beta before washing with sulfuric acid.

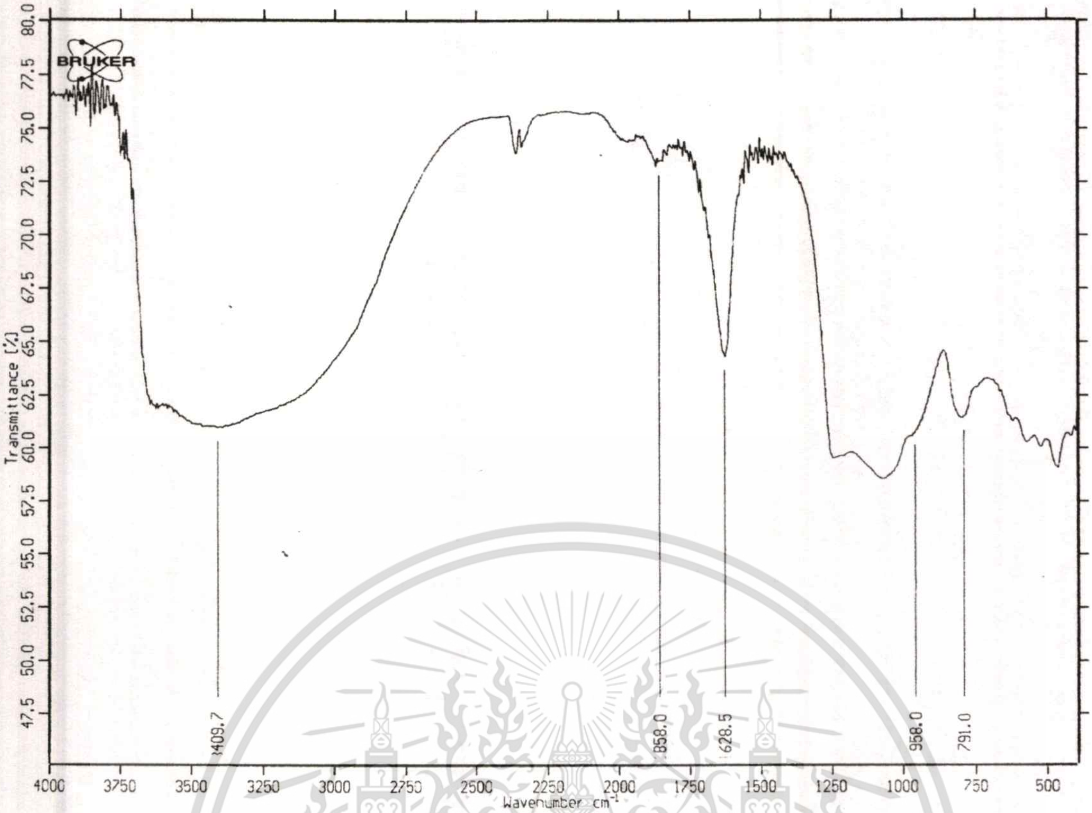

Figure D.5 Fourier IR spectrum of zeolite Ti-Beta after washing with sulfuric acid.

Appendix E

Gas Chromatogram

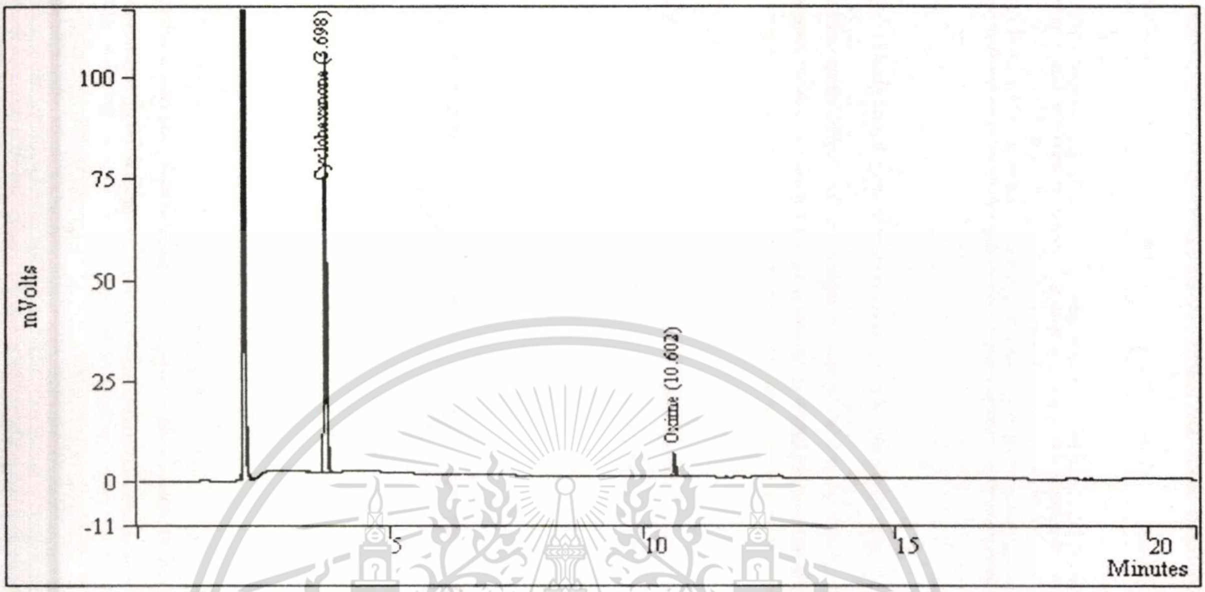

Figure E.1 Gas chromatogram from ammoximation of cyclohexanone at 60 °C in water by using TS-1 as catalyst.

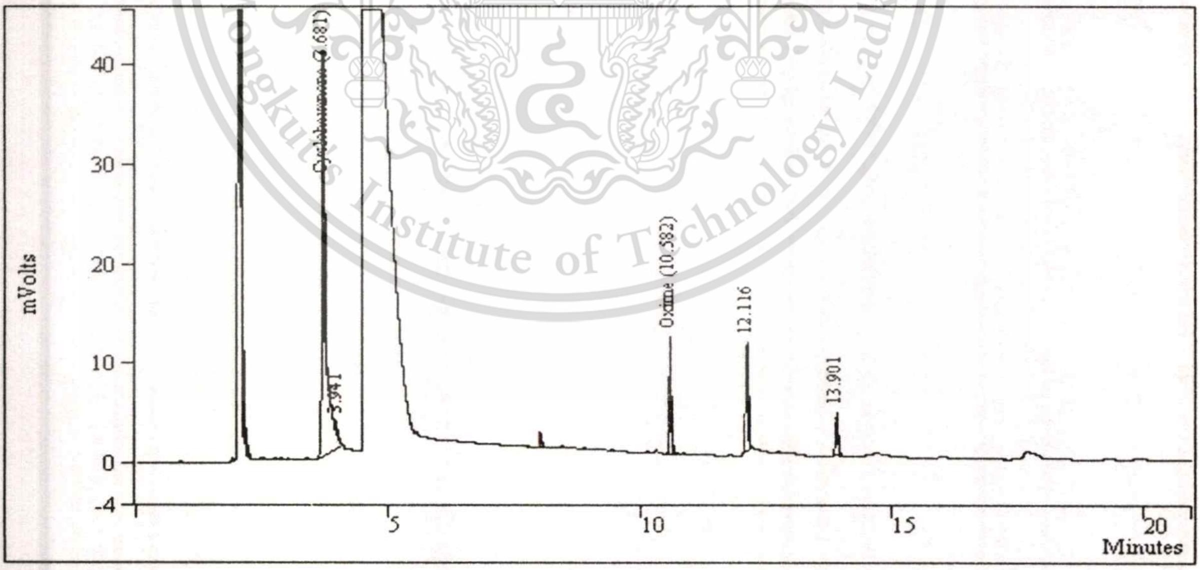

Figure E.2 Gas chromatogram from ammoximation of cyclohexanone at 60 °C in acetic acid by using TS-1 as catalyst.

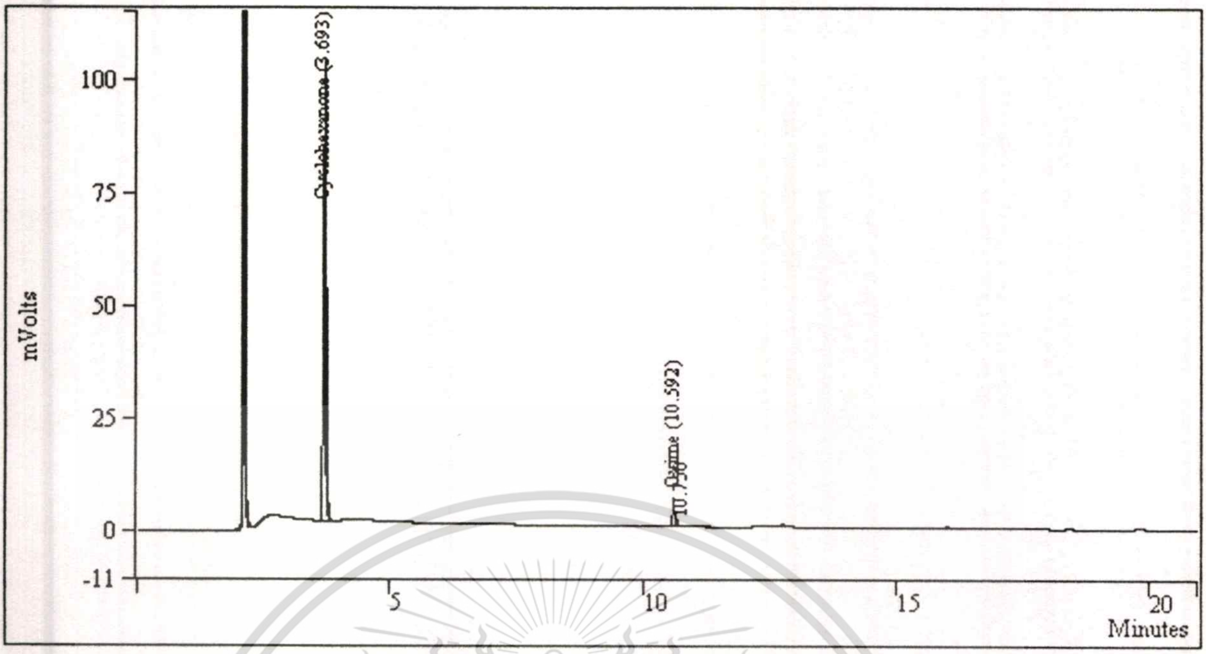

Figure E.3 Gas chromatogram from ammoximation of cyclohexanone at 60 °C in water by using zeolite Ti-Beta as catalyst.

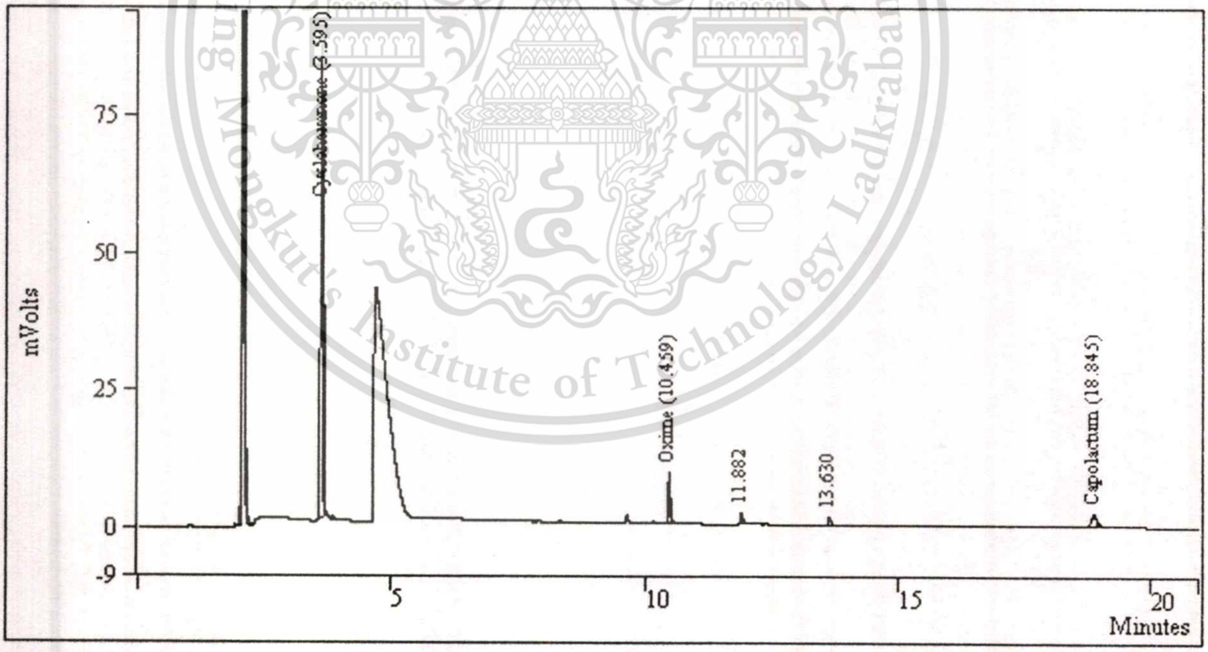

Figure E.4 Gas chromatogram from ammoximation of cyclohexanone at 60 °C in acetic acid by using zeolite Ti-Beta as catalyst.

Appendix F

Result from Gas Chromatograph

Table F.1 Results from ammoximation of cyclohexanone using TS-1 as catalyst in system of water.

Time (Hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0	-	-	-
1	5.1	5.1	100
2	5.9	5.9	100
4	8.1	8.1	100
8	11.9	11.9	100
24	14.6	14.6	100

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours. (Reaction No. 1-5)

Table F.2 Results from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid.

Time (Hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0	-	-	-	-	-
1	13.7	10.0	1.2	2.5	72.7
2	23.8	19.3	2.5	2.0	81.1
4	25.7	20.8	3.2	1.7	81.0
8	27.5	23.8	2.9	0.94	86.2
24	27.8	25.9	1.3	0.66	92.9

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours. (Reaction No. 6-10)

Table F.3 Results from the mechanistic study using water as solvent.

	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Cyclohexanone + NH_4OH (2 hr)/H_2O_2,TS-1(4hr)	7.4	7.4	100
$NH_3 \rightarrow NH_2OH$ (2 hr)/Cyclohexanone 4 hr.	1.7	1.7	100

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours.

Table F.4 Results from the mechanistic study using acetic acid as solvent.

	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Cyclohexanone + CH_3COONH_4 (2 hr)/H_2O_2,TS-1(4hr)	29.1	14.9	11.8	2.9	51.1
$NH_3 \rightarrow NH_2OH$ (2 hr) (acetate)/Cyclohexanone 4 hr.	1.4	0.27	0.51	0.61	19.7

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours.

Table F.5 Results from ammoximation of cyclohexanone by added zeolite A.

Zeolite A (g)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0	27.8	15.0	11.6	1.7	54.1
0.5	33.1	18.7	9.6	7.5	56.5
1	33.5	22.3	9.5	2.7	66.5
1.5	32.4	24.8	6.4	1.9	76.4

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours. Added 0.5, 1.0 and 1.5 g of zeolite A. (Reaction No. 20, 11-13)

Table F.6 Results from the reaction using ammonium salts as reactant in water system.

Ammonium Salts	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Ammonium Hydroxide	8.1	8.1	100
Ammonium Acetate	0.68	0.68	100
Ammonium Carbonate	6.3	6.3	100
Ammonium Citrate	-	0.47	-
Ammonium Oxalate	-	trace	-
Ammonium Chloride	-	trace	-
Ammonium Sulfate	-	trace	-

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, Reaction Time 4 hours, TS-1 0.04 grams as catalyst.. (Reaction No. 14-19)

Table F.7 Results from the reaction using ammonium salts as reactant in acetic acid system.

Ammonium Salts	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Ammonium Hydroxide	25.7	20.8	3.2	1.7	81.0
Ammonium Acetate	46.1	21.5	18.1	8.7	46.7
Ammonium Carbonate	16.4	8.3	6.6	1.7	50.5
Ammonium Citrate	18.5	6.6	-	13.5	35.7
Ammonium Oxalate	15.2	1.8	13.4	-	12.1
Ammonium Chloride	2.2	trace	2.1	-	2.6
Ammonium Sulfate	5.1	trace	5.1	trace	0.73

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, Reaction Time 4 hours, TS-1 0.04 grams as catalyst.. (Reaction No. 20-25)

Table F.8 Results from ammoximation of cyclohexanone using Ti-Beta as catalyst in system of water.

Time (Hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0	-	-	-
1	1.1	1.1	100
2	2.0	2.0	100
4	2.6	2.6	100
8	3.5	3.5	100
24	7.7	7.7	100

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,Ti-Beta 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours. (Reaction No. 26-30)

Table F.9 Results from ammoximation of cyclohexanone using Ti-Beta as catalyst in system of acetic acid.

Time (Hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactam	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0	-	-	-	-	-	-
1	17.7	6.6	5.9	1.9	3.3	37.5
2	28.0	12.5	9.3	3.3	2.9	44.5
4	34.2	15.5	12.3	4.1	2.2	45.3
8	38.4	17.9	14.3	4.6	1.6	46.5
24	59.2	8.7	49.5	0.74	0.31	14.6

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,Ti-Beta 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours. (Reaction No. 31-35)

Table F.10 Results from ammoximation of cyclohexanone using zeolite Ti-Beta before and after washing with sulfuric acid as catalyst.

Catalyst	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactam	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Ti-Beta after washing	34.2	15.5	12.3	4.1	2.2	45.3
Ti-Beta before washing	5.2	4.3	-	0.65	0.19	83.8

Reaction condition: Temperature 60 ^{o}*C, Cyclohexanone 0.38 grams, , ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic acid 2.4 ml, Reaction Time 4 hours, Ti-Beta 0.04 grams as catalyst..* (Reaction No. 33,36)

Table F.11 Results from caprolactone synthesis by using TS-1 and zeolite Ti-Beta as catalyst.

Catalyst	% Conversion of Cyclohexanone	% Yield of Caprolactone	% Selectivity of Caprolactone
TS-1	8.8	5.7	65.0
Ti-Beta	46.0	45.9	99.8

Reaction condition: Temperature 60 ^{o}*C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic acid 2.4 ml, Reaction Time 4 hours, Ti-Beta and TS-1 0.04 grams as catalyst..* (Reaction No. 37,38)

Table F.12 Results from ammoximation of cyclohexanone using 0.02, 0.04 and 0.08 g of TS-1 as catalyst.

TS-1 (g)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0.02	21.1	15.1	3.8	2.3	71.4
0.04	25.7	20.8	3.2	1.7	81.0
0.08	33.6	23.5	6.1	4.0	70.0

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, TS-10.02, 0.04 and 0.08 grams as catalyst.. (Reaction No. 8, 39-40)

Table F.13 Results from ammoximation of cyclohexanone in pressure reactor compared with batch reactor.

Reactor	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Batch Reactor	8.1	8.1	100
Pressure Reactor (10 Bar, N_2)*	8.8	8.8	100

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Water 2.4 ml, Reaction Time 4 hours, TS-1 0.04 grams as catalyst.. (Reaction No. 3,45)

** Up scale to total mixture 200 ml*

Table F.14 Results from ammoximation of cyclohexanone in excess ammonium acetate.

Catalyst	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
TS-1	56.2	43.7	6.5	6.0	77.8
Ti-Beta	52.8	48.1	1.8	2.9	91.0

Reaction condition: Temperature 60 ^{o}C, Cyclohexanone 0.38 grams, hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, Reaction Time 4 hours, TS-1and Ti-Beta 0.04 grams as catalyst.. (Reaction No. 41,42)

Table F.15 Results from ammoximation of cyclohexanone using TS-1 and used TS-1 as catalyst.

Catalyst	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
TS-1	25.7	20.8	3.2	1.7	81.0
Used TS-1	39.0	21.8	4.2	19.0	55.9

Reaction condition: Temperature 60 ^{o}C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, used Ti-Zeolite 0.04 grams as catalyst.. (Reaction No. 8,43)

Table F.16 Results from ammoximation of cyclohexanone using zeolite Ti-Beta and used zeolite Ti-Beta as catalyst.

% Selectivity of Cyclohexanone Oxime	Catalyst	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactam	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime
45.3	Ti-Beta	34.2	15.5	12.3	4.1	2.2
52.9	Used Ti-Beta	36.2	19.1	6.4	6.5	4.0

Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, used Ti-Zeolite 0.04 grams as catalyst.. (Reaction No. 33,44)

Appendix G

Result from Gas Chromatography-Mass Spectrometer

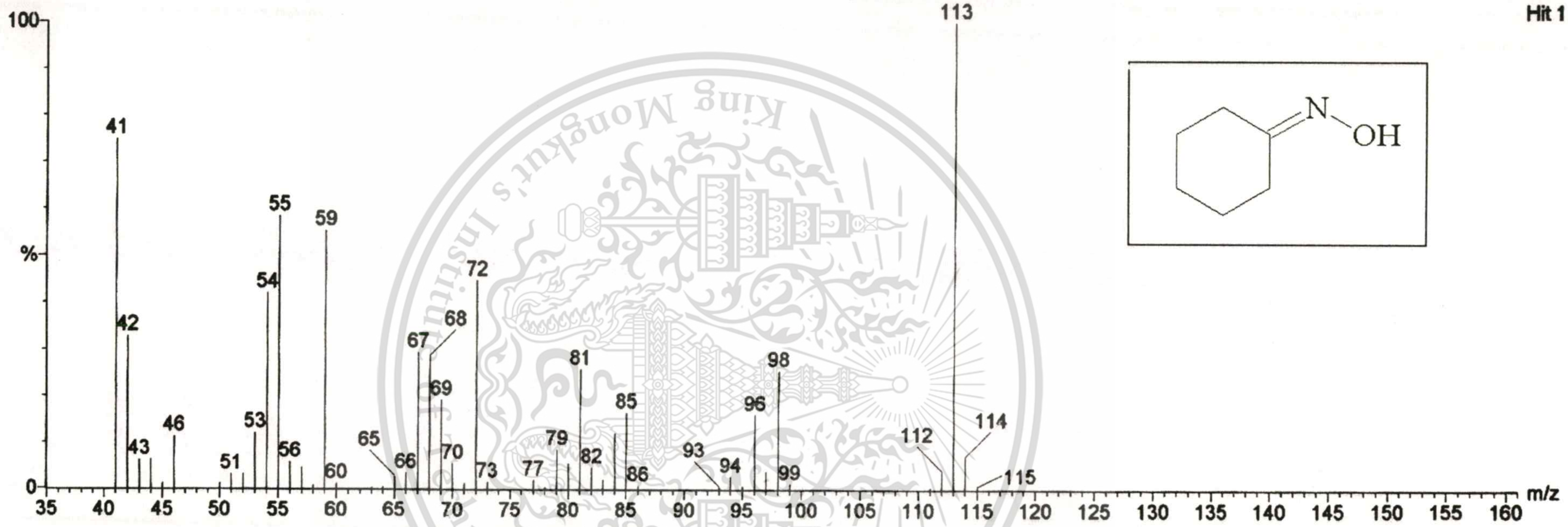

Figure G.1 Mass spectrum of cyclohexanone oxime from ammoximation reaction in acetic acid.

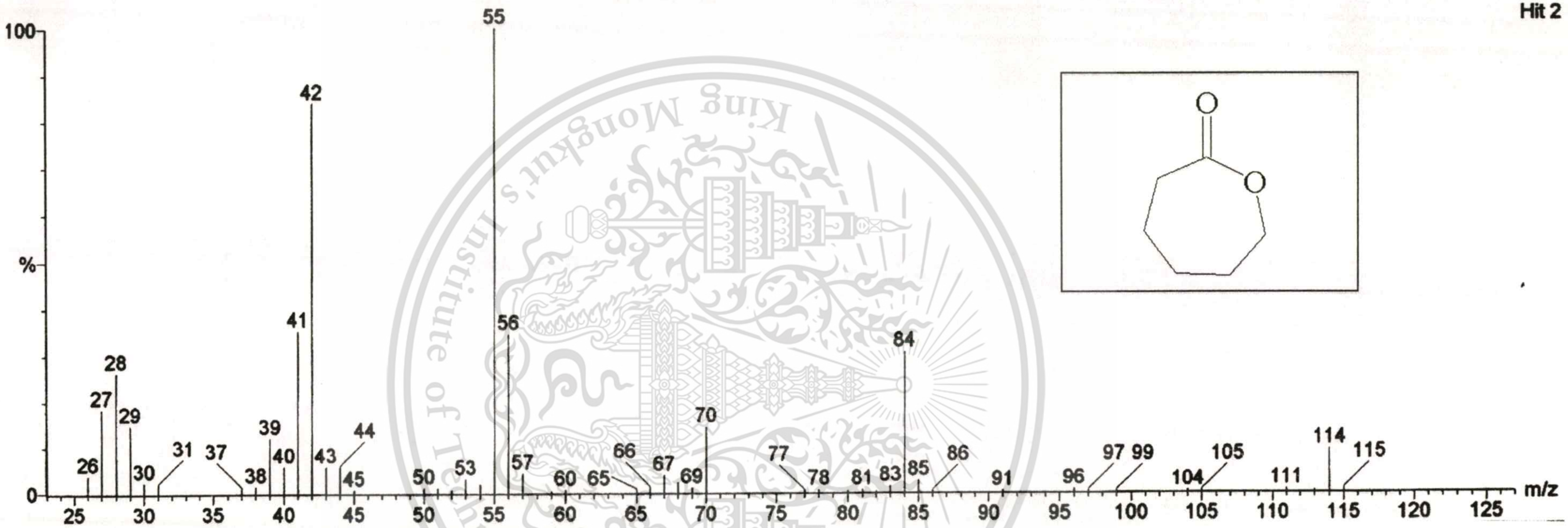

Figure G.2 Mass spectrum of caprolactone from ammoximation reaction in acetic acid.

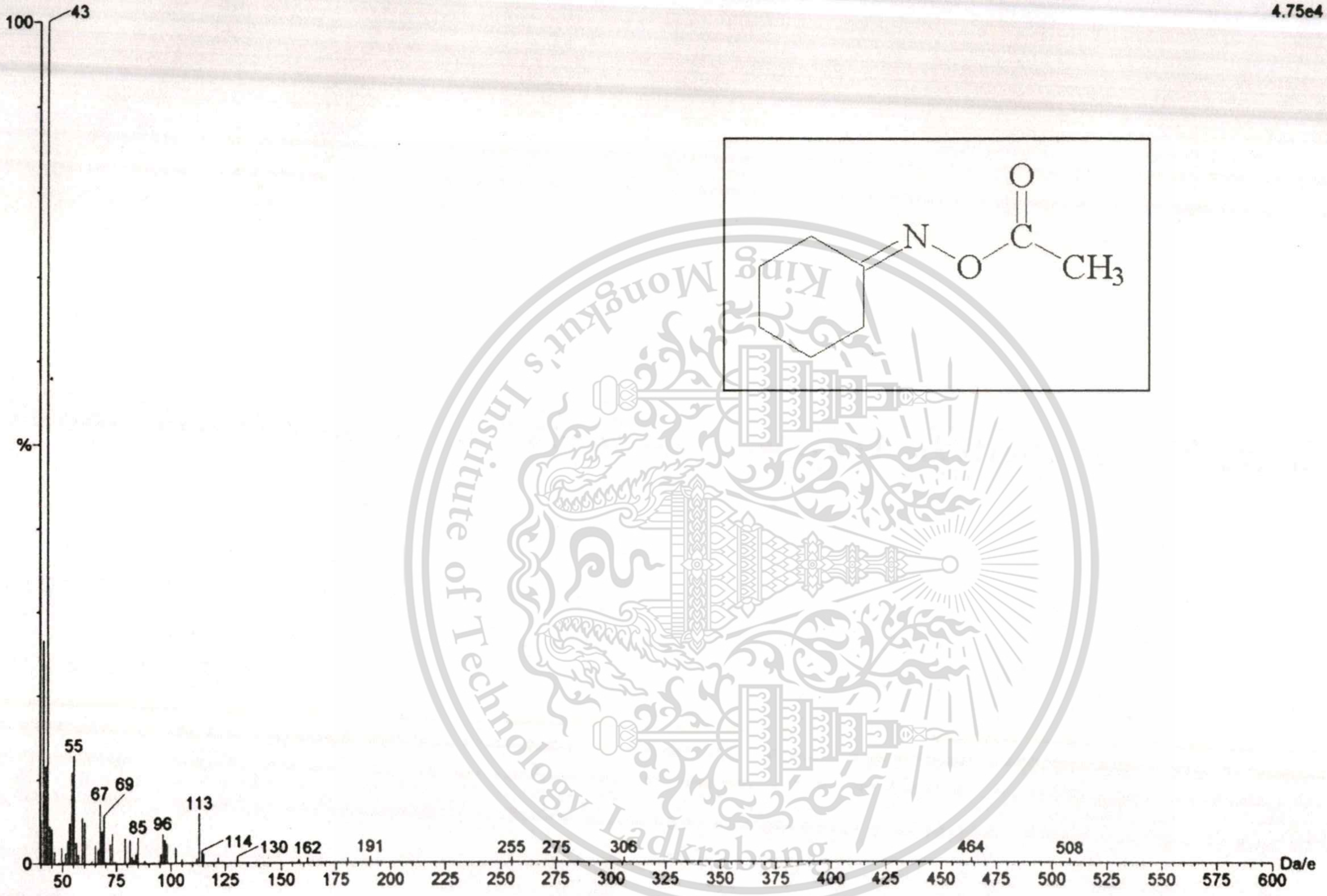

Figure G.3 Mass spectrum of acetyl cyclohexanone oxime from ammoximation reaction in acetic acid.

Appendix H

Elemental Analysis from Graphite Furnace Atomic Absorption Spectrophotometer (AAS)

Table H.1 Silicon/titanium mole ratio of zeolite

Zeolite	Si/Ti
TS-1	26
Titanium beta zeolite before washed with sulfuric acid	36
Titanium beta zeolite after washed with sulfuric acid	47

Elemental Standard Curve Preparation

The calibration curve for silicon, aluminium and titanium was prepared by plotting standard concentration of each element with the absorbance obtained from graphite furnace atomic absorption spectrophotometer.

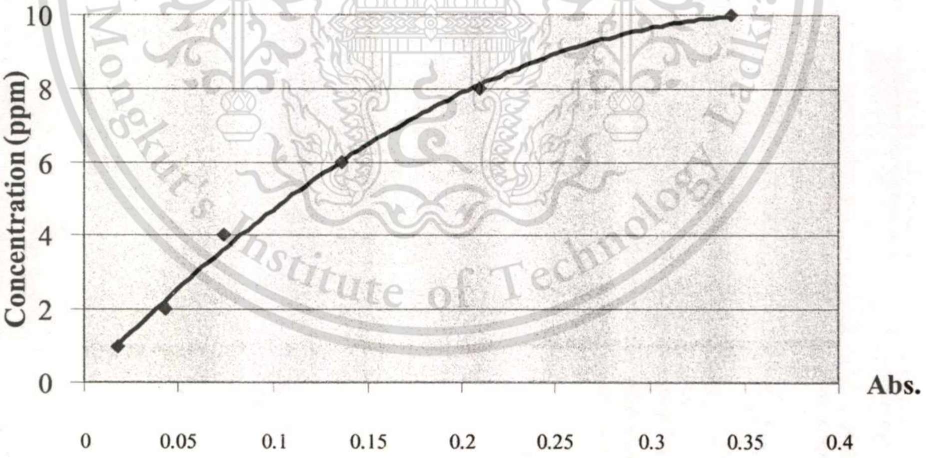

Figure H.1 Calibration curve for silicon.

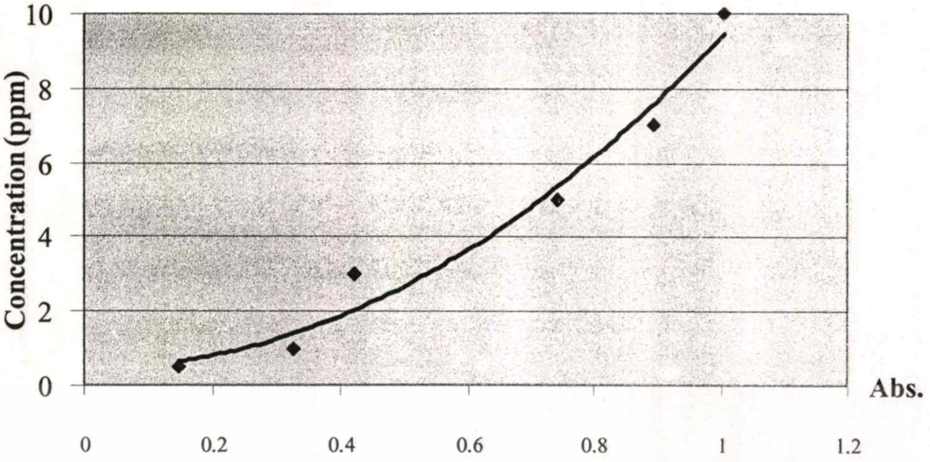

Figure H.2 Calibration curve for aluminium.

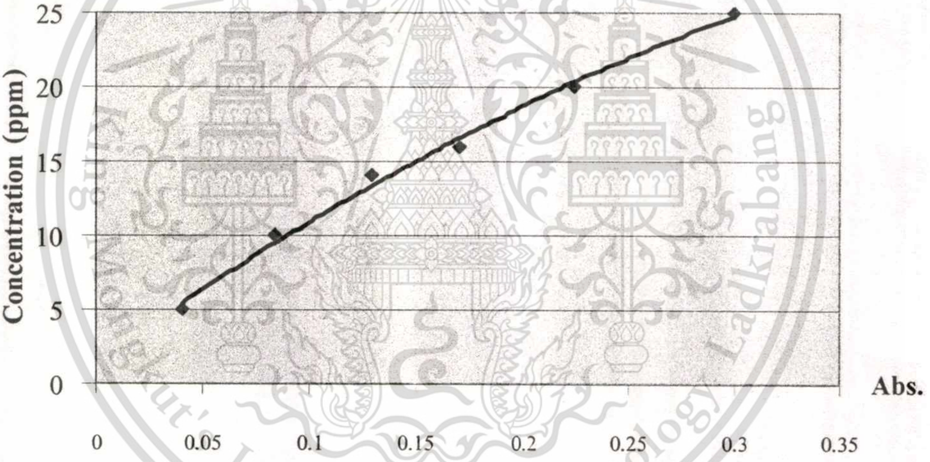

Figure H.3 Calibration curve for titanium.

Elemental Calculation of Zeolite

The elemental analysis of zeolites was followed by comparison the absorbance of sample with the standard calibration curve. Practically, the equation fitted to the calibration curve was employed to calculate the sample concentration.

Equation fitted for the calibration curve of silicon:

$$C = -70.994\, A^2 + 53.157\, A + 0.084$$

- C is the concentration of silicon in sample (ppm)
- A is the absorbance of the sample

Equation fitted for the calibration curve of aluminium:

$$C = 9.0383\, A^2 - 0.1231\, A + 0.4698$$

- C is the concentration of aluminium in sample (ppm)
- A is the absorbance of the sample

Equation fitted for the calibration curve of titanium:

$$C = -85.251\, A^2 + 103.3\, A + 1.4465$$

- C is the concentration of titanium in sample (ppm)
- A is the absorbance of the sample

Appendix I

Correction Factor Curve for Gas Chromatography Analysis and Product Calculation

Correction Factor Curve Preparation

The correction factor curve, a standard curve for correcting the area percentage from gas chromatography analysis to the relative molar concentration of sample, was prepared by analysis of the standard solution containing cyclohexanone and cyclohexanone oxime using gas chromatography. Standard concentration (the percentage that related to percent mole) was plotted with the area percentage of the sample.

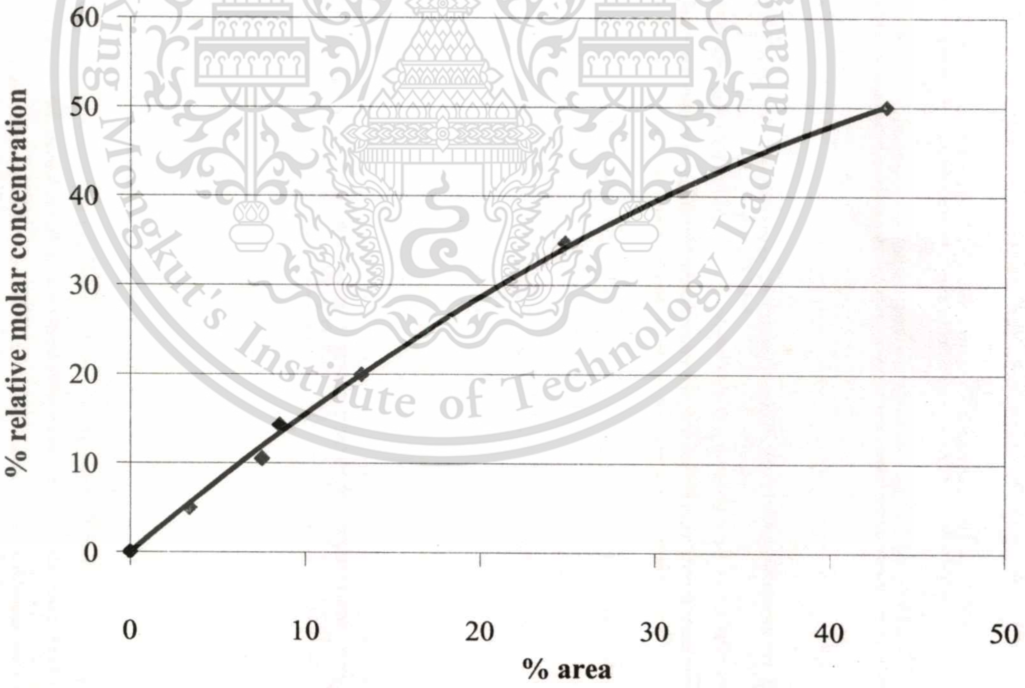

Figure I.1 Correction factor curve of cyclohexanone oxime

Equation fitted the correction factor curve of relative molar concentration of cyclohexanone oxime is shown below;

$$y = -0.0118x^2 + 1.6704x$$

- x is the area percentage of cyclohexanone oxime in sample
- y is the relative molar concentration of cyclohexanone oxime

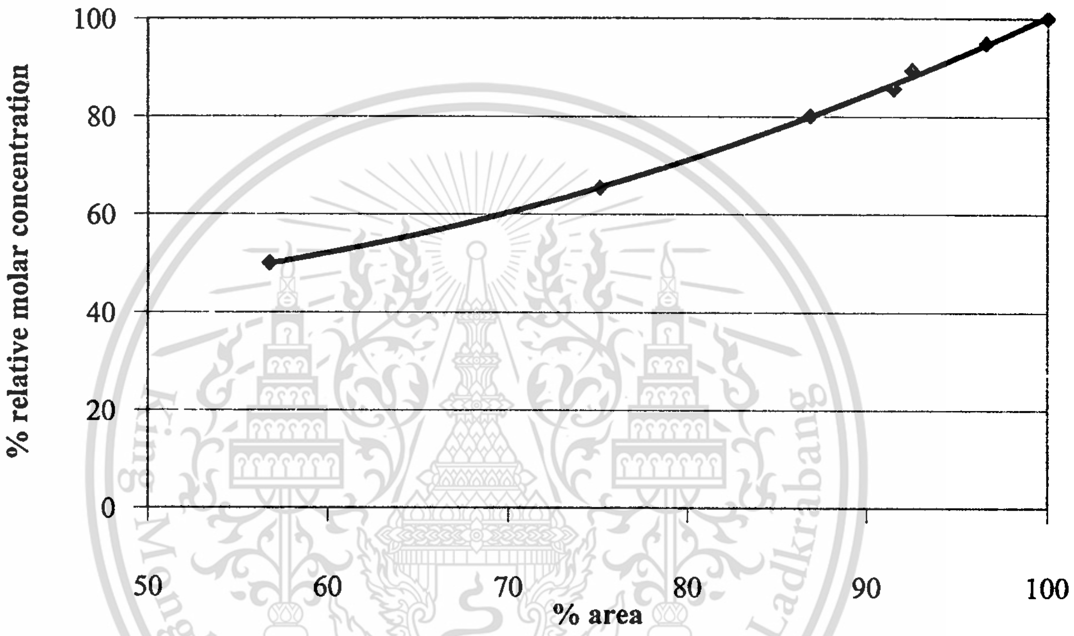

Figure I.2 Correction factor curve of cyclohexanone

Equation fitted the correction factor curve of relative molar concentration of cyclohexanone

$$y = 0.0127x^2 - 0.8239x + 55.756$$

- x is the area percentage of cyclohexanone
- y is the relative molar concentration of cyclohexanone

After correcting the area percentage to relative molar concentration of sample, the mole percentage of sample was calculated by normalization.

Calculation of Product Concentration

Product was calculated using the equation from correction factor curve. Caprolactone, acetyl cyclohexanone oxime and caprolactam were calculated using correction factor curve of cyclohexanone oxime. This is presumably because the chemical composition of the by-products is similar to those of cyclohexanone oxime and they are present in small amount. Therefore, it can be assumed that the correction factor of caprolactone, acetyl cyclohexanone oxime and caprolactam would be similar to that of cyclohexanone oxime.

Conversion

The conversion of cyclohexanone can be calculated from the remaining cyclohexanone in the reaction. It can be expressed as following.

$$\text{\% Conversion of cyclohexanone} = 100 - \text{mole percent of remaining cyclohexanone}$$

Selectivity

The selectivity of cyclohexanone oxime is the ratio of cyclohexanone that converted to cyclohexanone oxime over all cyclohexanone that convert to all products. It can be expressed as following.

$$\text{\% Selectivity of cyclohexanone oxime} = \frac{\text{\% Yield of cyclohexanone oxime}}{\text{\% Conversion of cyclohexanone}} \times 100$$

Example

The product concentration was calculated from GC result. For example, the area percentage from the reaction using zeolite Ti-Beta as catalyst in acetic acid for 4 hours is shown in Figure I.3.

Peak No	Ret. Time (min)	Peak Name	Result ()	Area (counts)
1	3.592	Cyclohexanone	77.484	186722
2	10.463	Oxime	10.382	25019
3	11.888		2.640	6362
4	13.633		1.377	3317
5	18.983	Capolactum	8.117	19561
		Totals	**100.000**	**240981**

Figure I.3 Area percentage of products remaining reaction from gas chromatography

Product with retention time 11.888 is caprolactone and 13.633 is acetyl cyclohexanone oxime.

The relative molar concentration of cyclohexanone

The relative molar concentration of cyclohexanone was calculated from equation fitted the correction factor curve of percent relate with mole of cyclohexanone

$$y = 0.0127x^2 - 0.8239x + 55.756$$

- x is the area percentage of cyclohexanone
- y is the relative molar concentration of cyclohexanone

Relative molar concentration of cyclohexanone $= 0.0127(77.484)^2 - 0.8239(77.484) + 55.756$

$= 68.16$

The relative molar concentration of all products

The relative molar concentration of cyclohexanone oxime, caprolactone, acetyl cyclohexanone oxime and caprolactam can be calculated from the equation fitted the correction factor curve of relative molar concentration of cyclohexanone oxime.

$$y = -0.0118x^2 + 1.6704x$$

- x is the area percentage of cyclohexanone oxime or by-products

- y is the relative molar concentration of cyclohexanone oxime or by-products

The relative molar concentration of cyclohexanone oxime $= -0.0118(10.382)^2 + 1.6704(10.382)$

$= 16.07$

The relative molar concentration of caprolactone $= -0.0118(2.64)^2 + 1.6704(2.64)$

$= 4.33$

The relative molar concentration of acetyl cyclohexanone oxime

$= -0.0118(1.377)^2 + 1.6704(1.377)$

$= 2.28$

The relative molar concentration of caprolactam $= -0.0118(8.117)^2 + 1.6704(8.117)$

$= 12.78$

Normalization

Normalization all of product would lead to yield of product, conversion and selectivity.

Total relative molar concentration of sample $= 68.16 + 16.07 + 4.33 + 2.28 + 12.78$

$= 103.62$

Normalized to 100 percent

Mole percentage of cyclohexanone $= (68.16 \times 100)/103.62$

$= 65.78\ \%$

Mole percentage of cyclohexanone oxime $= (16.07 \times 100)/103.62$

$= 15.51\ \%$

Mole percentage of caprolactone $= (4.33 \times 100)/103.62$

$= 4.18\ \%$

Mole percentage of acetyl cyclohexanone oxime $= (2.28 \times 100)/103.62$

$= 2.20\ \%$

Mole percentage of caprolactam $= (12.78 \times 100)/103.62$

$= 12.33\ \%$

Conversion of cyclohexanone

The conversion of cyclohexanone was calculated by equation as following.

$$
\begin{aligned}
\%\ \text{Conversion of cyclohexanone} &= 100 - \text{mole percent of remaining cyclohexanone} \\
&= 100 - 65.78 \\
&= 34.22\ \%
\end{aligned}
$$

Selectivity of cyclohexanone oxime

The selectivity of cyclohexanone oxime was calculated by equation as following.

$$
\begin{aligned}
\%\ \text{Selectivity of cyclohexanone oxime} &= \frac{\%\ \text{Yield of cyclohexanone oxime}}{\%\ \text{Conversion of cyclohexanone}} \times 100 \\
&= (15.51/34.22) \times 100 \\
&= 45.32\ \%
\end{aligned}
$$

AUTHOR BIOGRAPHY

Mr. Veerachai Chitranuwatkul was born on January 1, 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, Graduate School, King Mongkut's Institute of Technology Ladkrabang, since 1999.