AMMOXIMATION OF CYCLOHEXANONE USING Ti-CONTAINING ZEOLITES AS CATALYST IN CONTIUOUS PROCESS

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หัวข้อวิทยานิพนธ์	ปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนโดยใช้ซีโอไลต์ที่มีไททาเนียมเป็นองค์ประกอบเป็นตัวเร่งปฏิกิริยาในกระบวนการแบบต่อเนื่อง
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บทคัดย่อ

วิทยานิพนธ์เล่มนี้เป็นการศึกษากระบวนการต่อเนื่องของปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนเพื่อสังเคราะห์ไซโคลเฮกซาโนนออกซีมโดยมี ไททาเนียม ซิลิกาไลต์ (TS-1) เป็นตัวเร่งปฏิกิริยา โดยใช้แอมโมเนียกับไฮโดรเจนเปอร์ออกไซด์เป็นรีเอเจนต์ในสภาวะของเหลว โดยทำการศึกษาถึงผลของตัวทำละลาย ชนิดของไททาเนียมต่อการเร่งปฏิกิริยา ชนิดของปฏิกรณ์ ความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ เวลาสัมผัส(contact time) ของตัวเร่งปฏิกิริยากับสารตั้งต้น การสูญเสียตำแหน่งที่ว่องไวระหว่างทำปฏิกิริยา และ อายุการใช้งานของตัวเร่งปฏิกิริยา จากงานวิจัยพบว่าการ ใช้กรดแอซิติกเป็นตัวทำละลายทำให้เกิดกรดเปอร์แอซิติกซึ่งเป็นตัวออกซิไดส์ที่ว่องไวได้ผลิตภัณฑ์เป็นไซโคลเฮกซาโนนออกซีมในปริมาณที่มากกว่าการใช้ตัวทำละลายที่มีขั้วสูงอื่นๆ เช่น น้ำ เอทานอล ไอโซบิวทานอล และ อะซิโตไนไตรล์ ในการศึกษาผลของชนิดของไททาเนียมต่อการเร่งปฏิกิริยานั้นพบว่า ไททาเนียมเตตระฮีดรอลในโครงสร้างของซีโอไลต์ที่ว่องไวต่อปฏิกิริยาแอมมอกซิเมชัน ส่วนปฏิกรณ์ที่เหมาะสมในการทำปฏิกิริยาแบบต่อเนื่องคือปฏิกรณ์แบบปั่นกวน เนื่องจากปฏิกิริยาเป็นระบบที่มีสามวัฏภาค คือ สารประกอบอินทรีย์(ไซโคลเฮกซาโนน) สารละลาย(แอมโมเนีย ไฮโดรเจนเปอร์ออกไซด์ และ กรดแอซิติก) และ ของแข็ง(TS-1) โดยความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ที่เหมาะสมในการทำปฏิกิริยามีอัตราส่วน 1:0.6 โมลของไซโคลเฮกซาโนนต่อไฮโดรเจนเปอร์ออกไซด์ และจากการศึกษาเวลาสัมผัส(contact time) ของตัวเร่งปฏิกิริยากับสารตั้งต้น พบว่าเมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยา ผลิตภัณฑ์ไซโคลเฮกซาโนนออกซีมที่ได้มีปริมาณเพิ่มขึ้น ในทำนองเดียวกันเมื่อลดอัตราการไหลของสารตั้งต้นไซโคลเฮกซาโนนออกซีมที่ได้มีปริมาณเพิ่มขึ้นเช่นกัน สำหรับการศึกษาการสูญเสียตำแหน่งที่ว่องไวระหว่างทำปฏิกิริยาพบว่า สามารถลดการสูญเสียตำแหน่งที่ว่องไวได้โดยการเพิ่มอุณหภูมิในการกำจัดสารอินทรีย์ของตัวเร่งปฏิกิริยาตั้งแต่ 550-600 องศาเซลเซียส ส่วนอายุการใช้งานของตัวเร่งปฏิกิริยาสามารถเร่งปฏิกิริยาได้อย่างต่อเนื่องมากกว่า 40 ชั่วโมง

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ABSTRACT

In this thesis liquid phase ammoximation of cyclohexanone to cyclohexanone oxime with hydrogen peroxide and ammonia using TS-1 as catalyst in continuous process was studied. The effect of solvent, Ti-species, reactor type, H_2O_2 concentration, contact time, leaching of Ti framework and catalyst life time were investigated. It was found that the reaction using acetic acid as solvent shows higher activity than that using other hydrophilic solvents such as water, ethanol iso-butanol and acetonitrile due to the formation of the better oxidizing agent, per acetic acid. The investigation of Ti-species showed that titanium tetrahedral framework is an active species for ammoximation reaction. The suitable reactor type for ammoximation reaction is continuous stirred tank reactor (CSTR). This is because the reaction is a tri-phase system. The optimum molar ratio of cyclohexanone/hydrogen peroxide is 1:0.6. The study of contact time shows that increasing amounts of catalyst and decreasing feeding rate leads to an increase yield of cyclohexanone oxime. The study on leaching of titanium framework shows that leaching of titanium active site can be reduced when the calcining temperature is raised (550-600 °C). The investigation of catalyst life time showed that over 40 hours of catalytic testing, a steady yield of cyclohexanone oxime can be promoted.

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Finally, the author dedicated his work to his above perents for the constant love and encouragement.

Pirulh Seehabua

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Chapter 1

Introduction

1.1 Motivation

Cyclohexanone oxime is a precursor of caprolactam, which is a monomer for nylon-6 production. It is currently produced by reaction of cyclohexanone and hydroxylamine, which is an non environmental-friendly reagent. Recently, Titanium containing zeolites have been used as catalyst for cyclohexanone oxime synthesis using ammonia and hydrogen peroxide as oxidising agent [1-9]. The reaction at relatively low temperature gives high conversion and selectivity in a batch process. This is attractive to industrial application, and attempts to develop such process into an industrial scale have been made [10]. This is because the continuous process gives relatively more consistent product specification and less labour intensive, as compared to the batch process. However, solvent is largely consumed in continuous process. Consequently, an effective and reusable solvent is preferred for this application. In this thesis, the effect of solvent will be primarily studied in batch process. Then catalytic testing rig will be designed and constructed for cyclohexanone oxime synthesis in continuous process. The necessary factors for the continuation of production such as Ti-species, reactor volume, feeding rate, catalyst content, reaction temperature and catalytic life time will be investigated.

1.2 Objectives

The overall objective of this thesis is to investigated the ammoximation of cyclohexanone to cyclohexanone oxime using TS-1 as catalyst in continuous process.

The specific objectives of the study are as follow:

1.2.1 To accomplish the cyclohexanone oxime synthesis using TS-1 as catalyst in continuous process.

1.2.2 To obtain suitable conditions for continuous process such as solvent, Ti-species, reactor volume, feeding rate, catalyst content and reaction temperature for the optimum yield and selectivity of cyclohexanone oxime.

1.2.3 To obtain the long life catalyst.

1.3 Scope of Study

1.3.1 Design and construct a catalytic testing reactor for continuous process.

1.3.2 Synthesis and characterize of Titanium Silicalite 1 (TS-1).

1.3.3 Testing of catalytic activity in batch and continuous process.

1.3.4 Study on effect of solvent used in ammoximation reaction.

1.3.5 Study on effect of Ti-species.

1.3.6 Study on effect type of reactor and reactor volume.

1.3.7 Study on effect of feeding rate.

1.3.8 Study on effect of catalyst content.

1.3.9 Study on effect of reaction temperature.

1.3.10 Study on leaching and stability of titanium framework.

1.4 Expected results

1.4.1 The results from this thesis can be used as guidance for development of industrial scaled ammoximation process.

1.4.2 A suitable condition for the optimum productivity and selectivity can be obtained.

1.4.3 The results can also provide a long life catalyst for continuous process.

Chapter 2

Literature Reviews 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 [11]. 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 [12]. 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 [13].

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 as shown in the Figure 2.1 below.

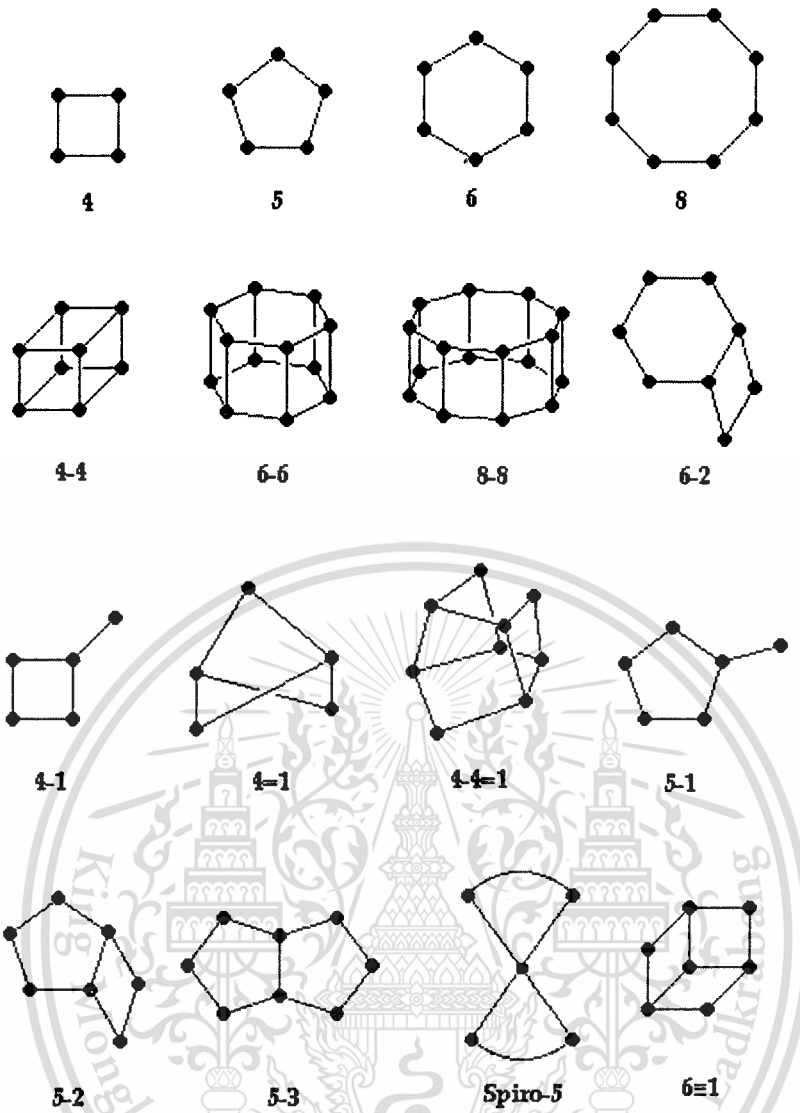


Figure 2.1 Secondary Building Units (SBU's) in zeolites.

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 sodalite "cage" (Figure 2.2).

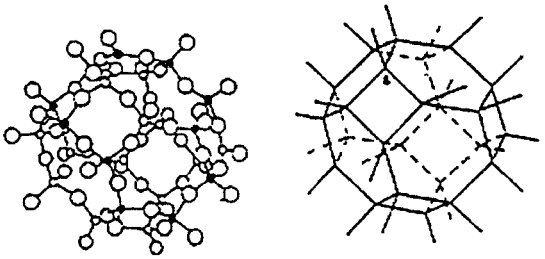


Figure 2.2 A "ball and strick" representation of the structure of the sodalite unit (β-cage, left) with a framework diagram for comparison.

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 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 catalyst, 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.

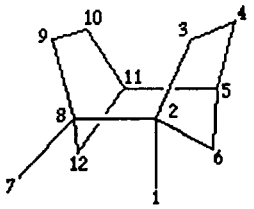


Figure (a)

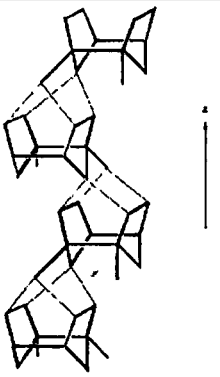


Figure (b)

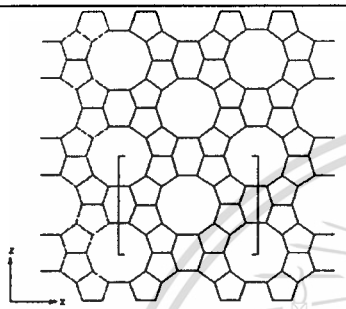


Figure (c)

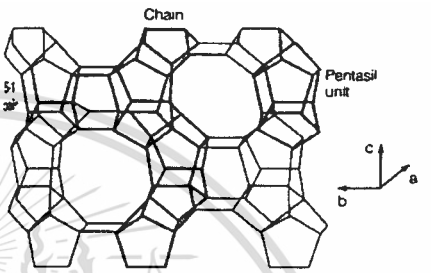


Figure (d)

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).

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 [14].

2.1.2.2 Gas Separation

Another 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 varies 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 [15]. 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 phosphate 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 MAS NMR). 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 twenty 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.[10,16-21]

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.[22-36] 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. The dedication of Ti-active site from FT-IR spectra of the range of 955-970 cm^{-1} is shown in Figure 2.6. The X-ray diffraction pattern of TS-1 shows characteristic peaks of MFI structure type at 2θ 7.89, 8.84, 23.11, 23.81 and 24.4 represented in Figure 2.7. The UV-VIS spectra in Figure 2.8 it is to see the presence of two bands at 215 nm and at about 250

nm. These data seem to suggest the absence of titanium octahedral in the form of anatase and rutile. The spectra of ^{29}Si MAS NMR of TS-1 is shown in Figure 2.9. There is the chemical shift at -114.9 ppm in all these spectra. If only the peak appears, the zeolite exhibits monoclinic symmetry. But with the increase of titanium content, a shoulder at chemical shift at -116.9 ppm appears and becomes stronger, which results the whole peak to be broader. This indicates that the presence of the orthorhombic symmetry of zeolite.

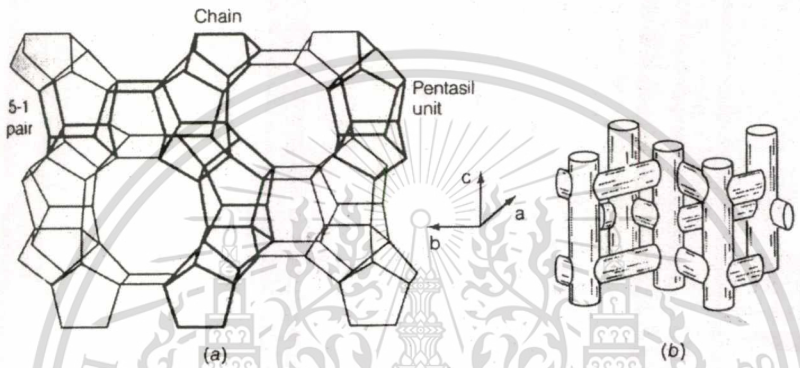


Figure 2.4 Representation of three-dimensional structure of TS-1 (MFI). (a) Structure formed by stacking of sequences. (b) Schematic representation of the intracrystalline pore structure.

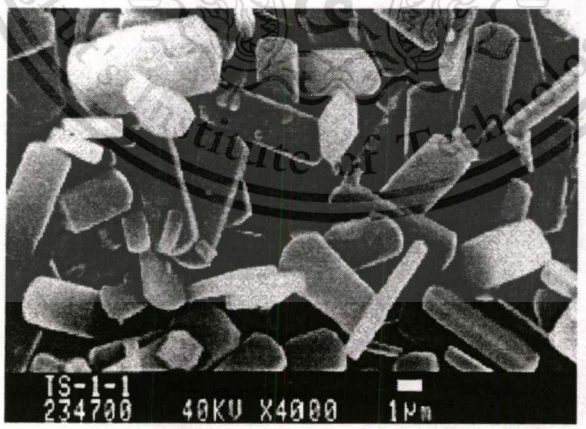


Figure 2.5 Crystals of the zeolite TS-1 (MFI) viewed with a scanning electron microscope. [25]

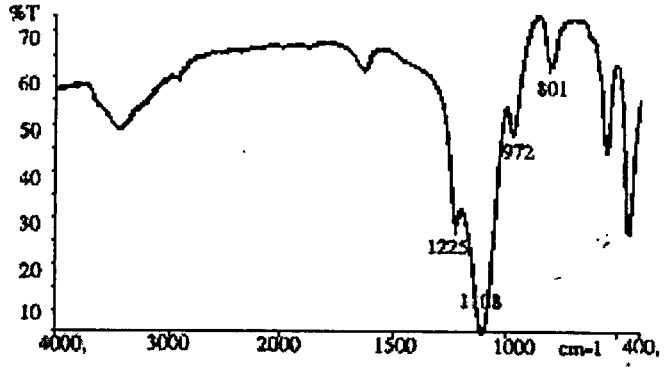


Figure 2.6 Fourier Transformed IR spectra of TS-1. [3]

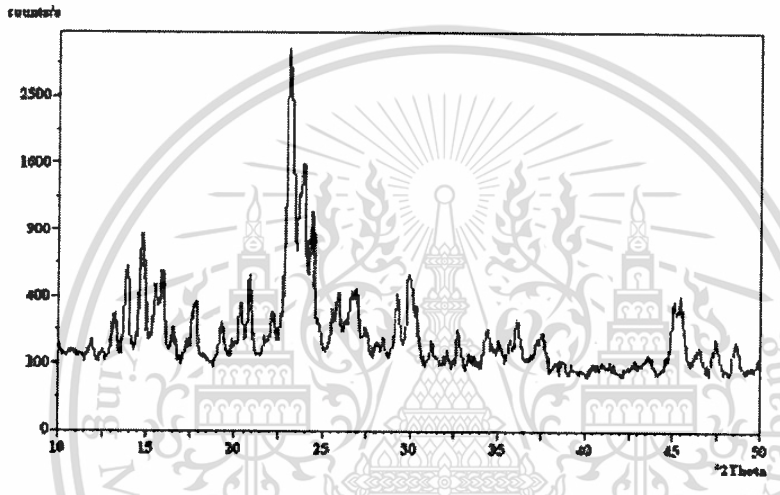


Figure 2.7 X-ray diffraction pattern of TS-1.[3]

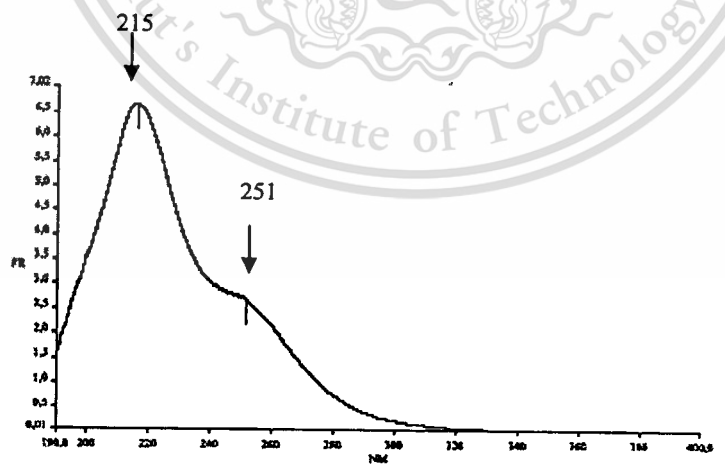


Figure 2.8 UV-Vis spectrum of the TS-1.[22]

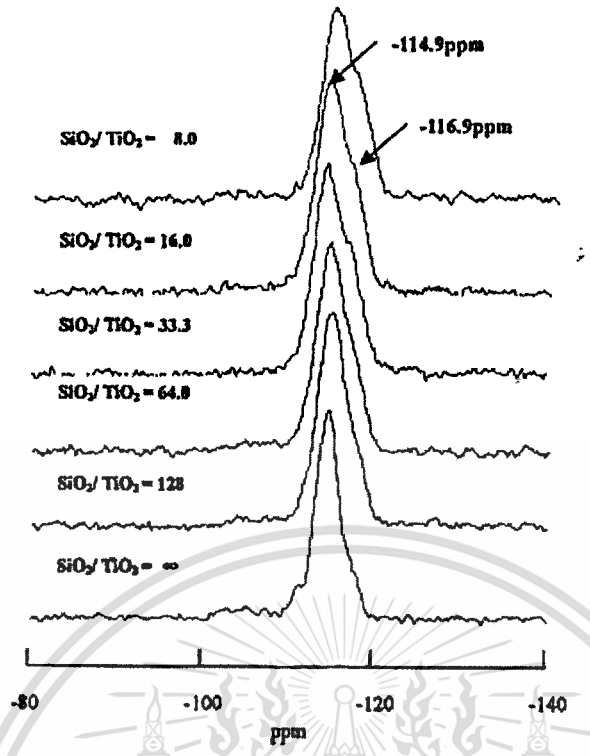


Figure 2.9 ^{29}Si MAS NMR of TS-1 with different titanium content.[22]

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 [3-6,8,16,18,19,37,38-40], using H_2O_2 as oxidant under mild reaction conditions (as shown in Figure 2.10). Unlike the Group IV-VI metal oxide based catalysts, Ti-containing zeolites are active in the presence of diluted aqueous solutions of hydrogen peroxide.

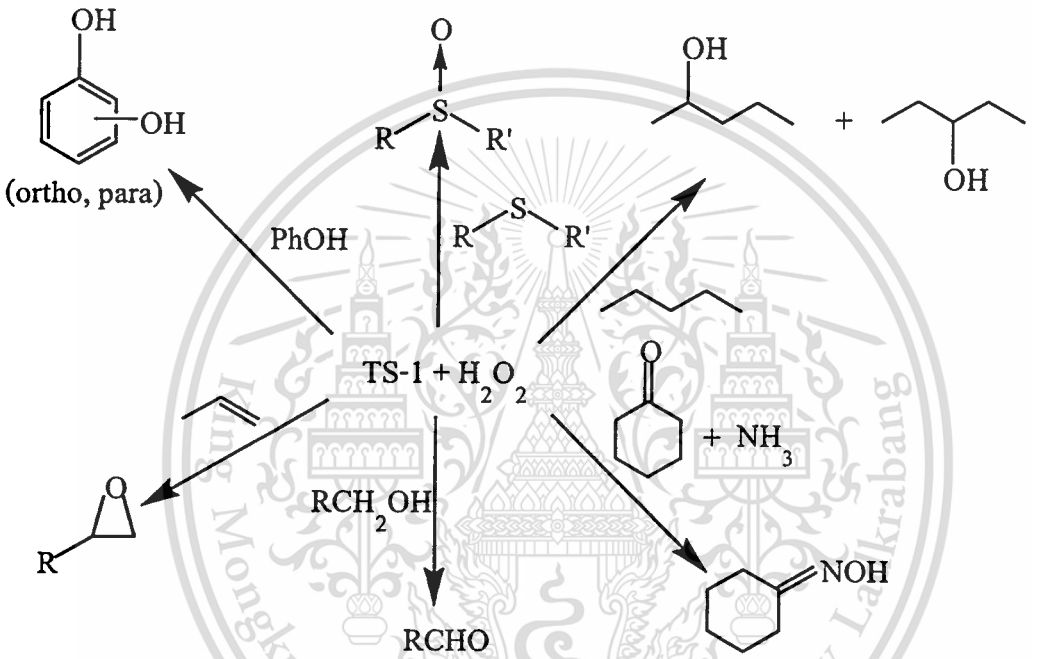


Figure 2.10 Catalytic oxidations by titanium-containing zeolites and aqueous hydrogen peroxide as oxidizing agent.

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 2.11). 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 2.11).

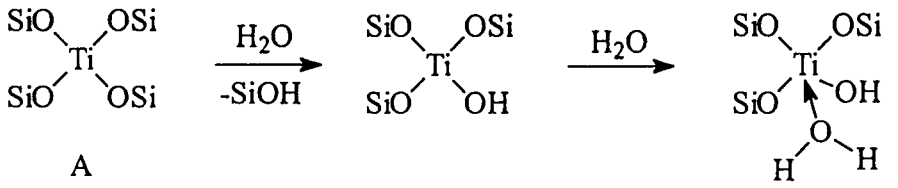


Figure 2.11 Postulated titanium species of the calcined from tetrahedral titanium species (A) and its hydrolysis and hydration

The oxidation mechanism is summarized schematically in Figure 2.12, 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 [41-42]. 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 then released from the Ti site and reacts with (b) again to formed ketone and other products.

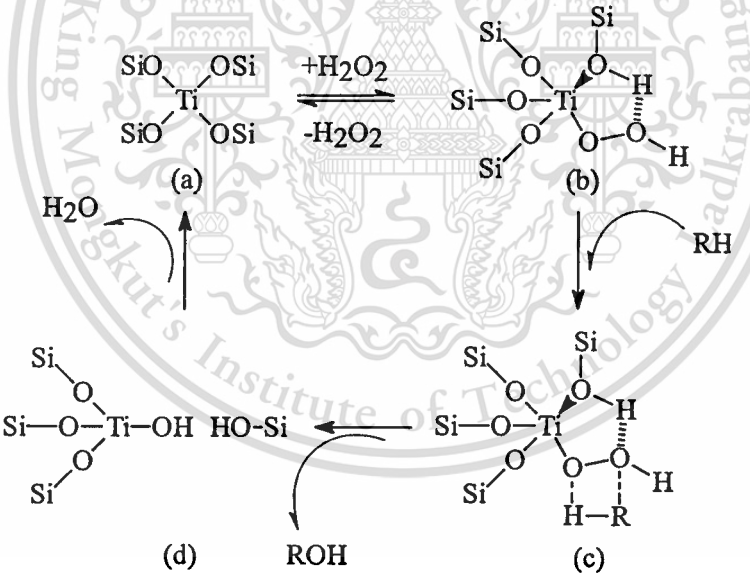


Figure 2.12 Postulated oxidation mechanism [9]

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[43-44].This mechanism is similar to that reported for the gas-phase ammoximation of cyclohexanone in the presence of NH_3 and O_2 as show in Figure 2.13 [45], 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[46]. The groups from Italy[3,6,29,31], 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 shown in Figure 2.14. A clear clarification of the liquid-phase ammoximation mechanism was observed and confirmed the reaction proceeds through imine path way [48].

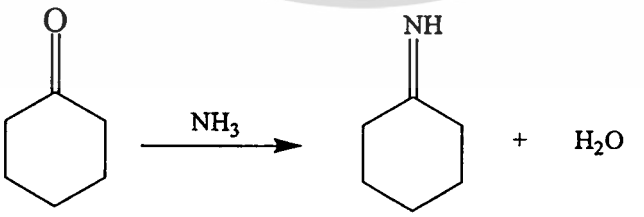


Figure 2.13 A possible pathway for ammoximation of cyclohexanone by titanium-containing zeolites

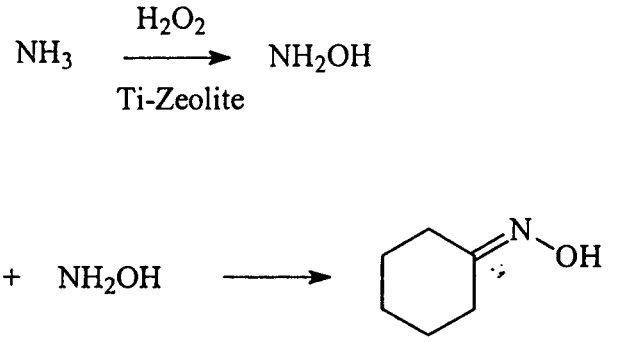


Figure 2.14 A possible pathway for ammoximation of cyclohexanone by titanium-containing zeolites

2.5 Literature Reviews

2.5.1 Effect of Titanium Content

The effect of titanium content in zeolite framework was studied [9,16,31] 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 [3,9,31].

2.5.2 Study on Temperature Effect

The study on temperature effect was investigated by varying the reaction temperature [3,9,47]. The results showed that the temperature that suitable for ammoximation reaction was 60 ^{o}C. The reaction activity increased when the temperature was increased, until 60 ^{o}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 [47]. 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 [9,16].

2.5.5 Effect of Leaching of Titanium Framewoek

The leaching of titanium framework of Ti-containing zeolites were studied in epoxidation reaction. The result showed less titanium leaching of TS-1, as compared to other catalysts such as Ti-Beta ,Ti-MCM-41 and Ti-xerogel. This due to more perfectly coordinated to four -O-Si groups of TS-1 as compared to other catalysts[37].

2.5.6 Effect of Ammonium Salt

The study on effect of ammonium salt was inveatigated by using various ammonium salts namely ammonia solution, ammonium acetate, ammonium citrate, ammonium carbonate, ammonium oxalate, ammonium chloride and ammonium sulphate. The result showed that when weakly acid salts, such as acetate, citrate and carbonate were used as reagent in the presence of acetic acid, The higher yield of cyclohexanone oxime can be produced than when strong acid salts were used [48].

Chapter 3

Experimental Details

3.1 Reagent

1. Acetic acid glacial
2. Ammonia solution (25% w/w)
3. Caprolactam (Fluka)
4. Cyclohexanone (Carlo Erba Reagenti)
5. Cyclohexanone oxime (Fluka)
6. Deionized water
7. Hydrogen peroxide (30% w/w, Merck)
8. Ludox (colloid silica, 40% SiO_2) (Aldrich)
9. Sodium hydroxide (Merck)
10. Sulfuric acid (Merck)
11. Tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$) (Fluka)
12. Tetrapropylammonium bromide (TPABr) (Fluka)
13. Hydrochloric acid (Merck)

3.2 Apparatus

1. Autoclave
2. Condenser
3. Cooling
4. Vial
5. Furnace (Vecstar Furnaces)
6. Gas Adsorption Analyzer (Autosorb-1, Quantachrome)
7. Gas Chromatograph (3800 Gas Chromatograph, Varian)
8. Hot plate & Stirrer
9. Infrared Spectrometer (FT-IR)
10. Magnetic Sterrer
11. Oven (50-200 °C)
12. Scanning Electron Microscope
13. Universal Indicator

14. X-ray Diffractometer
15. X-ray Fluorescence
16. Microkid reactor
17. Buchner flask
18. Buchner funnel
19. Clamp
20. Graduated cylinder
21. Graduated pipet
22. Heating bath
23. Three neck round-bottomed flasks
24. Support stand

3.3 Experiment

3.3.1 Catalyst Preparations

3.3.1.1 Titanium Silicalite-1 (TS-1)

Tetrabutyl orthotitanate was used as titanium source to prepare TS-1. 2.01 grams of Tetrabutyl orthotitanate were mixed with 4.72 grams of deionized water at 5 $^{\circ}$C, followed by adding 8.58 grams of hydrogen peroxide solution (30%) under stirring for 30 minutes. Then, 16.68 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 45 minutes. ammonia solution (25%) 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 18.72 grams of deionized water, 6.16 grams of tetrapropylammonium bromine (TPABr) and 21.62 grams of Ludox. The mixture was stirred at 100 rpm for 8 hours. 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 $^{\circ}$C. After 7 days, the synthetic zeolite was filtrated, washed and dried at 80 $^{\circ}$C. The catalyst was calcined at 550 $^{\circ}$C by a heating rate of 2 $^{\circ}$C/min. and hold at that temperature for 4 hours in air zero. Then, the catalyst was washed by 5 molar of sulphuric acid until pale-yellow of effluent by hydrogen peroxide dropping was disappeared and the complete TS-1 was calcined by same previous condition.

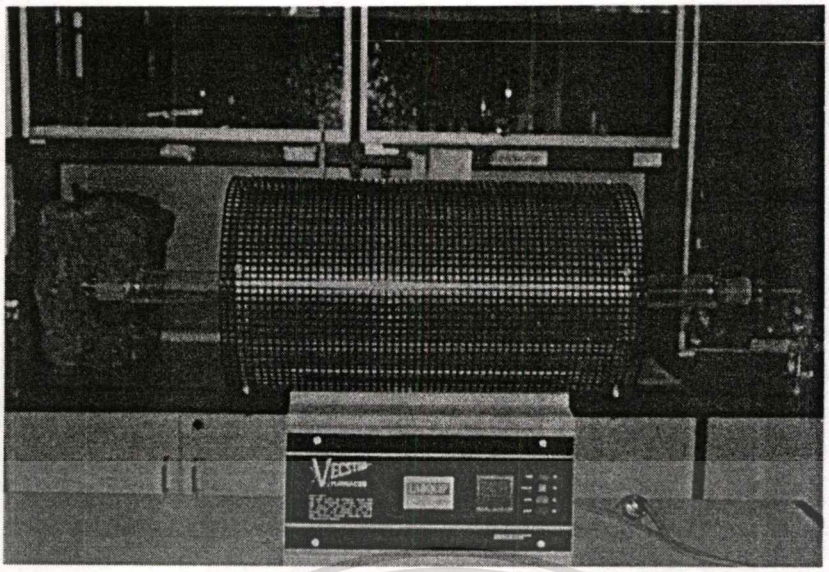


Figure 3.1 Calcination of zeolite in a furnace

3.3.2 Characterization of Catalysts

3.3.2.1 Determination of crystal morphology of zeolite

The crystal morphology and crystal size were determined by scanning electron microscope. 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^{-1} mbar. The scanning electron micrographs were taken at the magnification of 1,000, 7,000, 15,000 and 20,000 times.

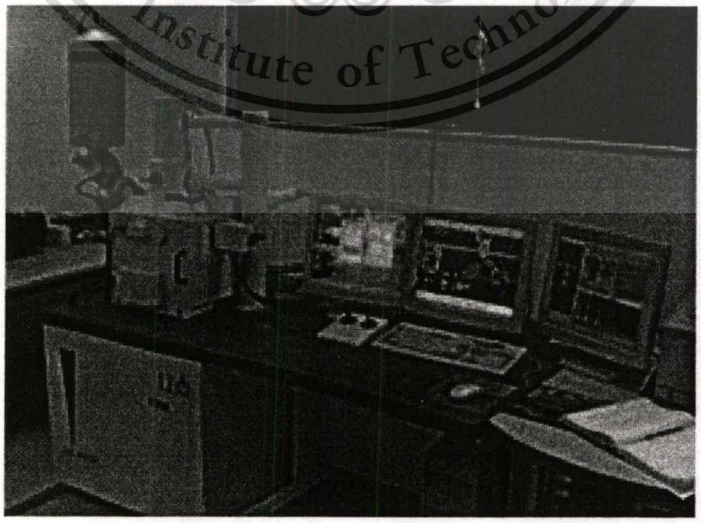


Figure 3.2 Scanning electron microscope

3.3.2.2 Determination of zeolite structure

The zeolite structure was determined by X-ray diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre, KMITL). The sample was prepared by packing the zeolite in the sample holder. CuKα X-ray beam was used for analysis at 30 kV, 30 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.

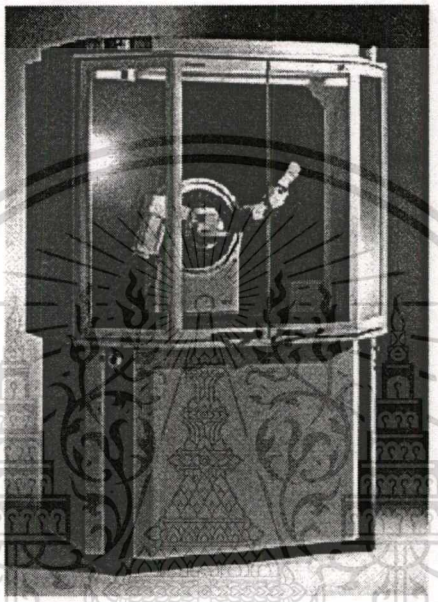


Figure 3.3 X-ray diffractometer (D8 Advance, Bruker)

3.3.2.3 Determination of silicon/titanium ratio

The ratio of silicon/titanium was determined by X-ray fluorescence spectrometer (SRS 3400, Bruker, Scientific Instruments Service Centre, KMITL). The sample was prepared by mixing 0.5 grams of zeolite and 4.5 grams of boric acid as a binder and grind into powder by tungsten carbine (Rock Lab grinder). The mixture was packed onto aluminium cup and then compressed at 150 kN. The sample was placed in the sample chamber. Lithium fluoride, pentaerythrite and W/Si multilayer were used as diffracting crystal and Rhodium as source for measure at 50 kV, 60 mA.

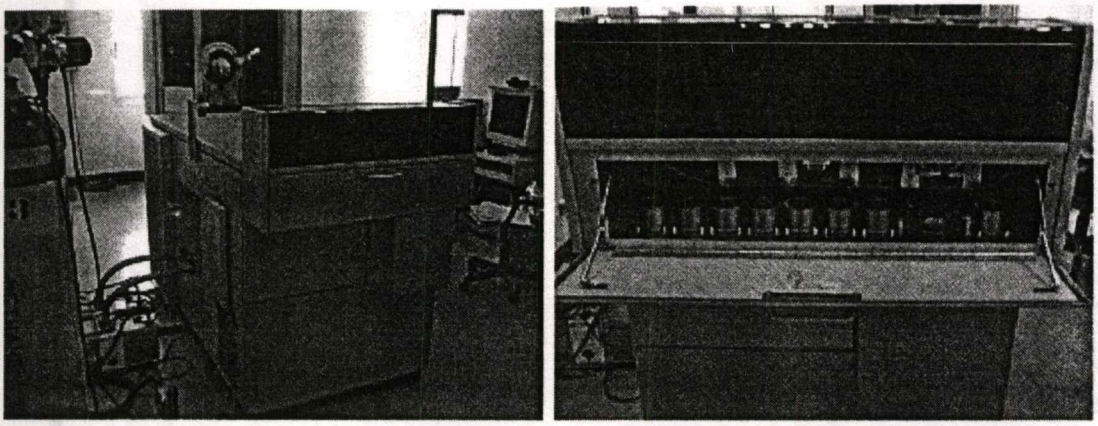


Figure 3.4 X-ray fluorescence spectrometer (SRS 3400, Bruker)

3.3.2.4 Determination of titanium active species

Titanium species in the framework of zeolite can be determined by Infrared Spectrometer (Perkin Elmer FT-IR system). The characteristic vibration frequency at 960 cm^{-1} represents the stretching vibration of Ti-O-Si bond in the tetrahedral coordination. The sample determination was carried out using attenuated total reflection (ATR) technique. 16 measurement scans was applied in reflecttance mode and the resolution was set to be 5. The sample was scanned over the frequency 4000-650cm^{-1}.

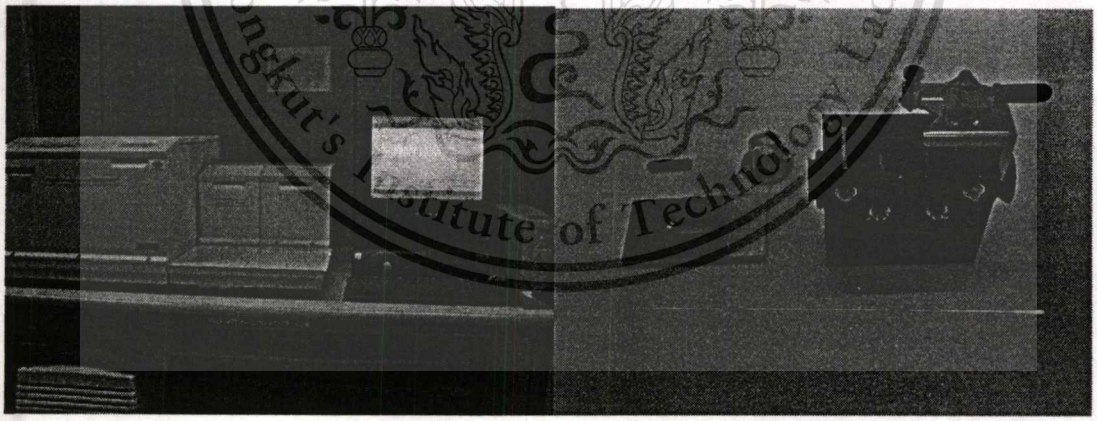


Figure 3.5 Infrared Spectrometer (Perkin Elmer FT-IR system)

3.3.2.5 Determination of surface area

Surface area of zeolite was determined by Gas Adsorption Analyzer (Autosorb-1, Quantachrome). The sample was prepared by weighting 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 $^{\circ}$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 was set to 3 minutes and the adsorption was tested at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0.

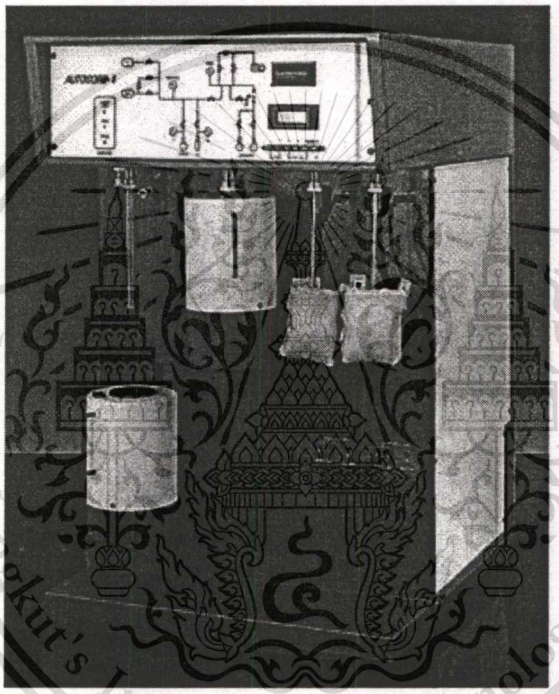


Figure 3.6 Gas Adsorption Analyzer (Autosorb-1, Quantachrome)

3.3.3 Catalytic testing

3.3.3.1 Batch process

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 solvents 2.4 grams. The molar ratio of feed used in the ammoximation reaction was as follows: cyclohexanone: NH_3: H_2O_2 = 1:1.5:1.2. After a period of time, the reaction was stopped by removing heat.

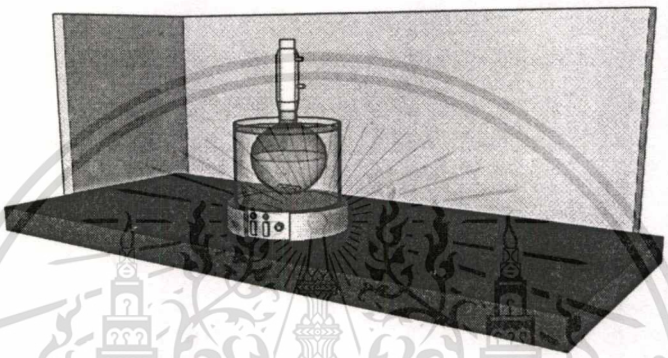


Figure 3.7 Schematic of catalytic testing in batch reactor

3.3.3.2 Continuous process

Packed bed flow reactor (PBFR) and continuous stirred tank reactor (CSTR) are choosen for studying ammoximation of cyclohexanone in continuous process [49]. In PBFR process reaction was carried out at 60 °C in a 20 ml and 1 cm diameter continuous packed bed flow reactor (PBFR) using 1.00 grams of TS-1. The catalyst was packed into the bottom of reactor. Glass beads were then packed into two sites of reactor.

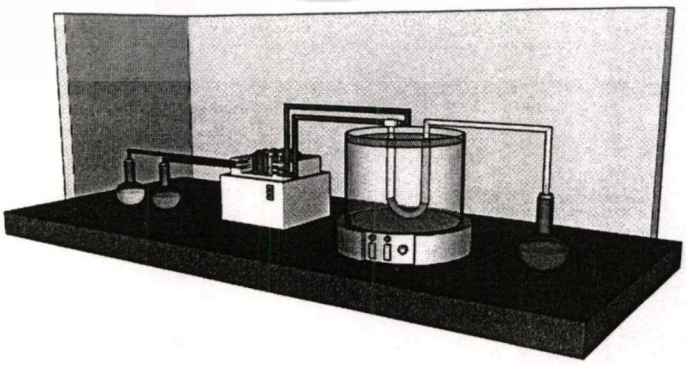


Figure 3.8 Schematic of catalytic testing of continuous process in plug flow reactor

The schematic diagram of continuous process in a 20 ml continuous packed bed flow reactor is shown in Figure 3.8. The contact time is estimated from batch reactor. H_2O_2 and a portion of acetic acid were primarily mixed in the first reservior. Whilst cyclohexanone, NH_3 and another portion of acetic acid were prepared in the second reservior. Both reservior were kept under 5 °C for preventing any reaction and H_2O_2 decomposition. Then the two mixtures were fed at the same flow rate (2x12.5 g./hr.) into CSTR by peristatic pump (GILSON miniplus3). The feeding ratio for continuous process was as follows: cyclohexanone: NH_3: H_2O_2 = 1:1.5:1.2 [2].

In case of continuous stirred tank process, the 50 ml continuous stirred tank reactor (CSTR) was tested using the same conditions as in a 20 ml continuous packed bed flow reactor (PBFR). Typically, 4.250 grams of cyclohexanone was added to 9.125 grams of ammonia solution (28%w/w) and 6.625 grams of hydrogen peroxide solution (30%w/w) in acetic acid 30 grams. The CSTR primarily contain all reactant and catalyst and kept at reaction temperature for 4 hours before feeding. The schematic diagram of continuous process in a 50 ml continuous stirred tank reactor (CSTR) is shown in Figure 3.9.

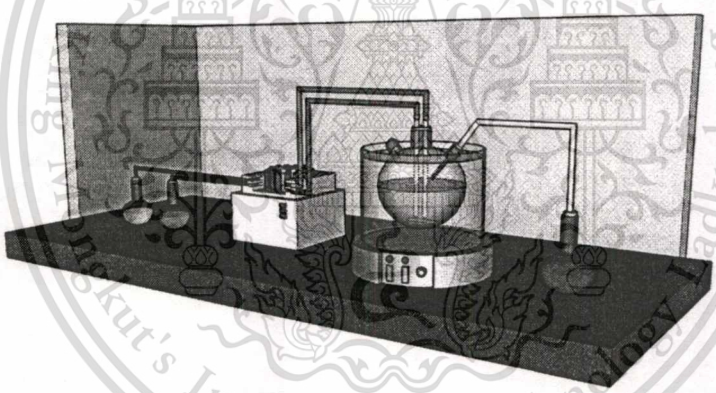


Figure 3.9 Schematic of catalytic testing of continuous process in stirred tank reactor

The effluent of the CSTR and the packed be flow reactor were collected and analized every an hour. The solution was analyzed by gas chromatography using 3800 Gas Chromatography, Varian, with capillary DB-5.625 column (30m x 0.25μm). Liquid sample 0.2 μl was injected to the injection port (200 °C) using split ratio of 200. The seperation temperature was started at 100 °C for 4 minutes. Then, the temperature was raised to 200 °C with a heating rate of 20 °C/min. and hold at that temperature for 11 minutes. N_2 was used as carried gas at a flow rate of 28.1 cm/sec.

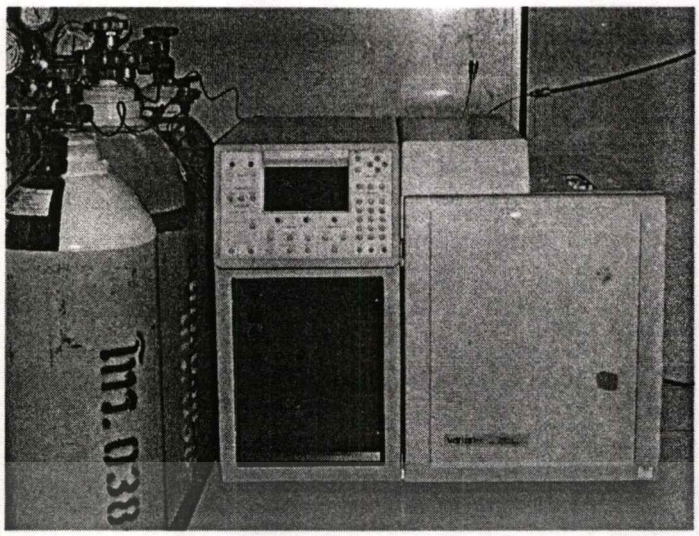


Figure 3.10 3800 Gas Chromatography, Varian

The structure of products generated in the reaction using acetic acid as solvent was also confirmed by gas chromatography-mass spectrometer(Scientific Instruments Service Centre, KMITL) using the same column and conditions.

The reaction condition for study of ammoximatoin of cyclohexanone is summarized in Table 3.2.

Table 3.1 The study of ammoximation reaction

Reaction Number	Time (hr.)	Solvent	Process	Reactor Type	Temp. (°C)	Contat Time g.hr/mol^{-1}	Catalyst	Cyclohexanone : H_2O_2
1	6	Acetic acid	Batch		60		TS-1	1 : 1.2
2	6	Water	Batch		60		TS-1	1 : 1.2
3	6	Iso-butanol	Batch		60		TS-1	1 : 1.2
4	6	Ethanol	Batch		60		TS-1	1 : 1.2
5	6	Acetonitrile	Batch		60		TS-1	1 : 1.2
6	2	Acetic acid	Batch		60		TS-1	1 : 1.2
7	4	Acetic acid	Batch		60		TS-1	1 : 1.2
8	8	Acetic acid	Batch		60		TS-1	1 : 1.2
9	12	Acetic acid	Batch		60		TS-1	1 : 1.2
10	6	Acetic acid	Batch		60		$Ti(Obu)_4$ catalyst	1 : 1.2
11	6	Acetic acid	Batch		60		Reused TS-1	1 : 1.2
12	6	Acetic acid	Batch		60		Without catalyst	1 : 1.2
13	6	Acetic acid	Batch		50		TS-1	1 : 1.2
14	6	Acetic acid	Batch		70		TS-1	1 : 1.2
15	12	Acetic acid	Continuous	Plug flow	60	41.26	TS-1(1g.)	1 : 1.2
16	12	Acetic acid	Continuous	Plug flow	60	82.52	TS-1(1g.)	1 : 1.2
17	12	Acetic acid	Continuous	Plug flow	60	123.78	TS-1(1g.)	1 : 1.2
18	12	Acetic acid	Continuous	Stirred tank	60	41.26	TS-1(1g.)	1 : 1.2
19	12	Acetic acid	Continuous	Stirred tank	60	20.63	TS-1(0.5 g.)	1 : 1.2

Table 3.1 (Continued)

Reaction Number	Time (hr.)	Solvent	Process	Reactor Type	Temp. (°C)	Contat Time g.hr/mol^{-1}	Catalyst	Cyclohexanone : H_2O_2
20	12	Acetic acid	Continuous	Stirred tank	60	82.52	TS-1(2 g.)	1 : 1.2
21(100ml)	12	Acetic acid	Continuous	Stirred tank	60	41.26	TS-1(1 g.)	1 : 1.2
22	12	Acetic acid	Continuous	Stirred tank	60	41.26	TS-1(1g.)	1 : 0.6
23	12	Acetic acid	Continuous	Stirred tank	50	41.26	TS-1(1g.)	1 : 0.6
24	12	Acetic acid	Continuous	Stirred tank	70	41.26	TS-1(1g.)	1 : 0.6
25	12	Acetic acid	Continuous	Stirred tank	60	-	Without catalyst	1 : 0.6
26	12	Acetic acid	Continuous	Stirred tank	60	148.76	TS-1(1g.)	1 : 0.6
27	12	Acetic acid	Continuous	Stirred tank	60	64.94	TS-1(1g.)	1 : 0.6
28	12	Acetic acid	Continuous	Stirred tank	60	41.26.	TS-1(1g.)	1 : 0.4
29	40	Acetic acid	Continuous	Stirred tank	60	64.94	TS-1(1g.)	1 : 0.6
30	12	Acetic acid	Continuous	Stirred tank	60	64.94	575 °C calcined	1 : 0.6
31	12	Acetic acid	Continuous	Stirred tank	60	64.94	600 °C calcined	1 : 0.6

3.3.3.3 Effect of Solvent

The effect of solvent was determined by the reaction using acetic acid, water, iso-butanol, ethanol and acetonitrile as solvent with 6 hours resident time. The procedures of the study were followed by reaction number 1-5 in Table 3.1.

3.3.3.4 Effect of Resident time

The reaction on effect of resident time (2, 4, 6,8 and 12 hours) was tested in batch process with different residential time (2-12). The procedures of the study were followed by reaction number 1, 6-9 in Table 3.1.

3.3.3.5 Effect of Ti-species

In this reaction using acetic acid as solvent, Ti-species was determined by using TS-1, tetrabutyl orthotitanate, reused TS-1 and without catalyst. The condition for this study is shown in Table 3.1, reaction number 1, 10-12.

3.3.3.6 Effect of Reactor types and reactor volume

The effect of reactor types for continuous process was tested by two types of reactor namely packed bed flow reactor (PBFR) and continuous stirred tank reactor (CSTR). The condition for PFR and CSTR studies are shown in Table 3.1, reaction number 15-17 and 18-31 respectively. The effect of reactor volume was tested in CSTR by reactor size 50 ml and 100 ml followed by reaction number 18 and 21.

3.3.3.7 Influence of Catalyst content

The effect of catalyst content was studied by continuous stirred tank reactor (CSTR) with different amount of catalyst (0.5, 1.0 and 2.0 grams of TS-1). The result were obtained from the reaction number 18-20.

3.3.3.8 Effect of reagent concentration

For the reaction using continuous stirred tank reactor (CSTR), reagent concentration was studied with different the molar ratio of cycloheanone and hydrogen peroxide (1/1.2, 1/0.6, 1/0.4). The result were obtained from the reaction number 18, 22 and 28.

3.3.3.9 Effect of Reaction temperature

The effect of reaction temperature (50, 60 and 70 $^{\circ}$C) was determined by using acetic acid as solvent in batch and continuous stirred tank reactor (CSTR). The condition for these studies are shown in reaction number 1, 13-14 for batch process and 18, 23-24 for continuous process.

3.3.3.10 Influence of Feeding rate

The effect of feeding rate was determined by using 1/0.6 molar ratio of cycloheanone and hydrogen peroxide with different total rate of feed (7, 15 and 25 g./hr.). The result were obtained from the reaction number 22, 26 and 27.

3.3.3.11 Effect of Leaching of Titanium framework and catalytic life time

The effect of leaching of titanium framework was studied with different temperature of calcination (550 °C, 575 °C and 600 °C). The result were obtained from the reaction number 27, 30 and 31. The catalytic life time was studied in 40 hours of testing in reaction number 29.

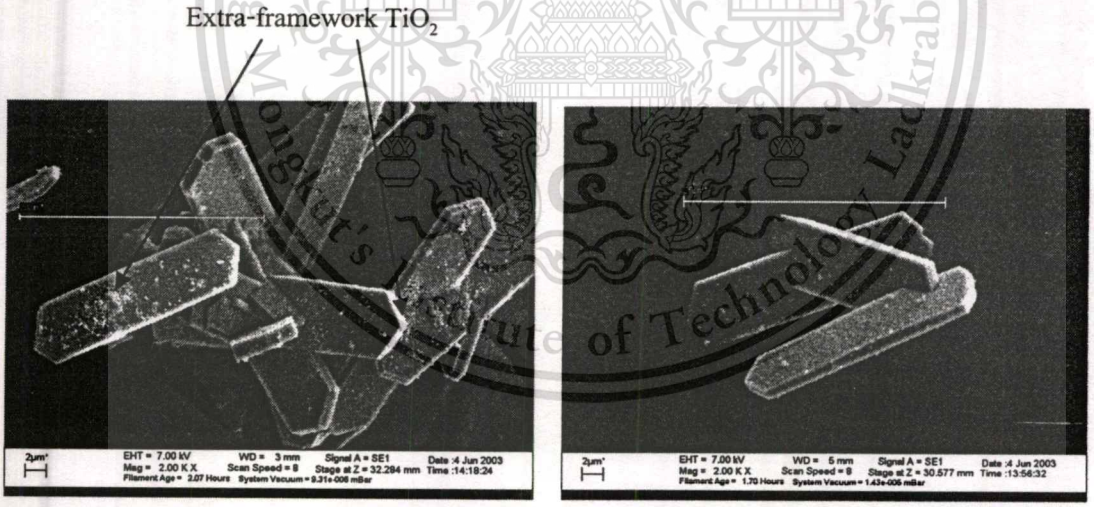
Chapter 4

Results and Discussion

4.1 Characterization of Catalyst

4.1.1 Crystal Morphology of Titanium Silicalite 1 (TS-1)

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 30×5 micron (Figure 4.1 (a) and (b)). The sample appears to be a well-defined crystalline material. Nevertheless, extra-framework titanium oxide is present in the sample before washing by sulfuric acid. This species can be washed away by sulfuric acid. This is because titanuim extra-framework is soluble in strong acid solutions. Therefore, crystals of TS-1 sample after washing by sulfuric acid appears to be cleaner, as compared with that before washing by sulfuric acid. Electron micrographs of all TS-1 sample are shown in Appendix A .



(a) (b)

Figure 4.1 Scanning electron micrograph of TS-1 (a) before and (b) after washing by sulfuric acid

4.1.2 Structure of 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 B. 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 B.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 B.2) shows that the structure remains unchanged. However, peak intensity at 2θ 7.88 and 8.84 is increased indicating decomposition of organic template from the pore of TS-1.

4.1.3 Silicon/titanium ratio of Titanium Silicalite 1 (TS-1)

The silicon and titanium content of TS-1 was determined by X-ray fluorescence spectrometer. The results are shown in Table 4.1 and Appendix C.

Table 4.1 The determination of silicon and titanium content of TS-1

Zeolite	Si/Ti
TS-1 (before washing with sulfuric acid)	25
TS-1 (after washing with sulfuric acid)	31

It was shown that before washing by sulfuric acid TS-1 possessed silicon/titanium ratio of 25. However, after washing with 5 molar of sulfuric acid, the silicon/titanium ratio of the sample was increased to 31. This is suggested that after hydrothermal crystallization there are 2 species of titanium present in the zeolite structure; the framework and the non-framework titanium. The later can be washed away by sulfuric acid. This is confirmed by dropping of hydrogen peroxide to the rinsed water after washing by sulfuric acid, which shall reveal no colour change into pale-yellow. After washing with sulfuric acid, it is believed that the titanium remained in the TS-1 are only the framework titanium species.

4.1.4 Surface Area of Titanium Silicalite 1 (TS-1)

The surface area of zeolites are shown in Table 4.2.

Table 4.2 The surface area of TS-1

Zeolite	Surface Area (m^2/g)
TS-1 before washing by sulfuric acid	444
TS-1 after washing by sulfuric acid and calcination	498

From the result, it was shown that TS-1 before washing by sulfuric acid and calcination have lower surface area than that after washing by sulfuric acid. This can be attributed to the pore blockage by incorporated titanium species. Since there could be two species of titanium in the zeolites; the framework and the non-framework titanium, the later and can readily block the pore of TS-1. This can result in a relative lower surface area of the sample before calcination and washing by sulfuric acid. Washing by sulfuric acid can remove the non-framework titanium from the pore of TS-1 leading to an increased surface area. This is also in consistent with the results from the elemental analysis and FT-IR which show the reduced titanium content with the retaining tetrahedral titanium (section 4.1.5). The BET plots of all TS-1 sample are shown in Appendix D.

4.1.5 Tetrahedral Titanium Species in Titanium Silicalite 1 (TS-1) Framework

Titanium in the 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 955 cm^{-1}. The TS-1 sample shows this characteristic band, which suggests that titanium species are present in samples as framework cations. Fourier Transformed IR spectra of zeolites are shown in Figure 4.2 and Appendix G.

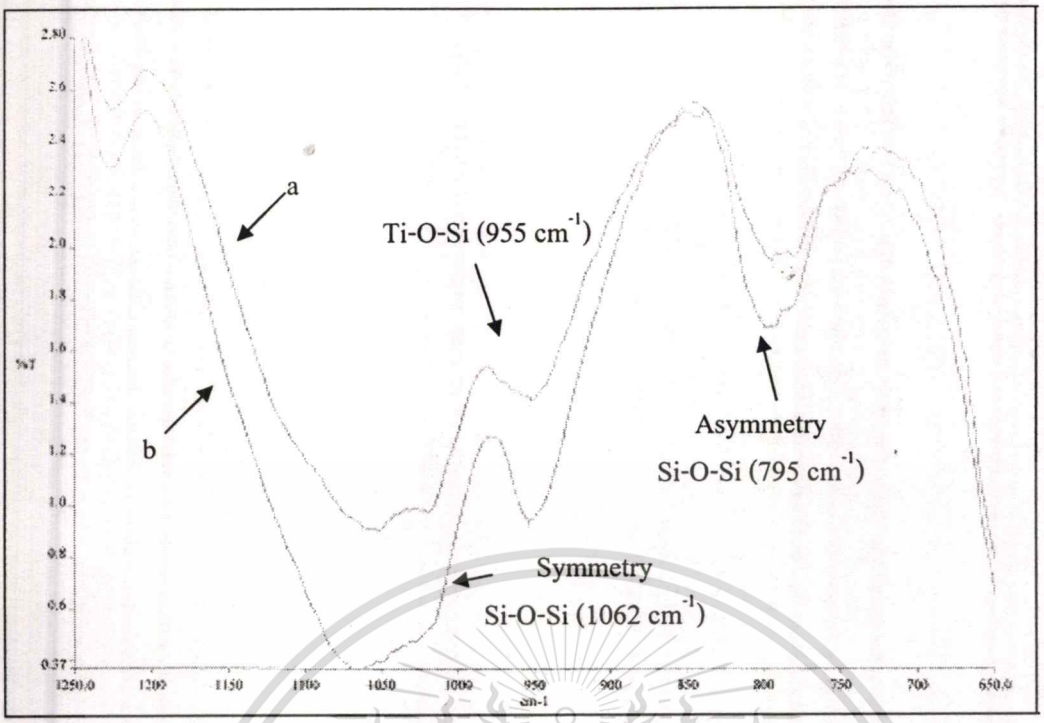


Figure 4.2 Fourier Transformed IR spectra of TS-1 (a) before and (b) after washing by sulfuric acid

From the Figure 4.2, it was shown that after washing by sulfuric acid of TS-1, the characteristic peak of Ti-O-Si (955 cm^{-1}) vibration is remained. However, the intensity of characteristic peak of Ti-O-Si (955 cm^{-1}) after washing by sulfuric acid is slightly higher than before washing by sulfuric acid. Although, titanium content is reduced (increase in Si/Ti, this shows in section 4.1.3) washing of TS-1 by sulfuric acid not only removes titanium octahedral extra-framework but also provides tetrahedral a better coordination of titanium-framework after recalcination. Therefore, this again suggests that only the tetrahedral titanium is mainly present in the framework after washing with sulfuric acid.

4.2 Catalytic Testing Batch Process

4.2.1 Effect of Solvent

The conversion, yield and selectivity from the reaction using acetic acid, water, iso-butanol, ethanol and acetonitrile as solvents are shown in Figure 4.3

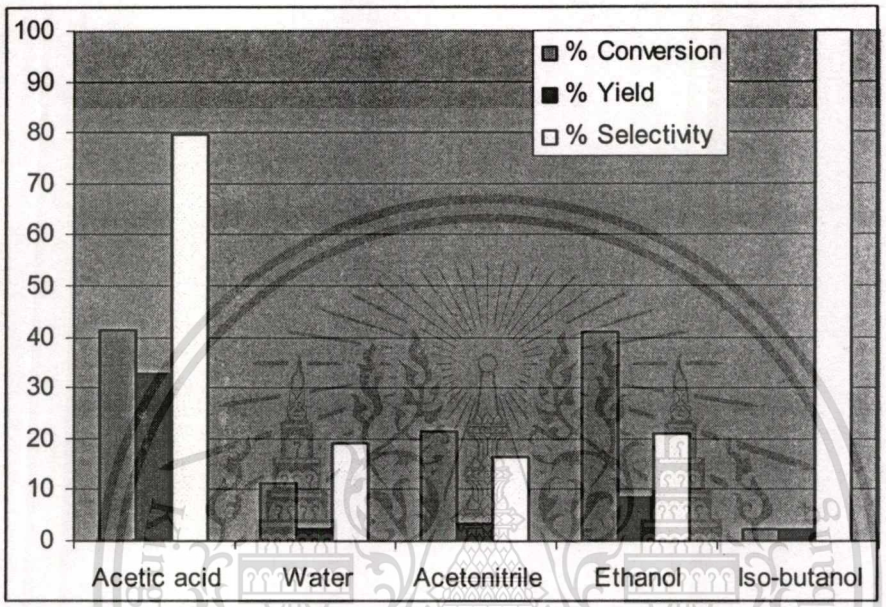
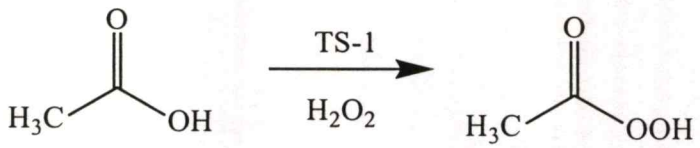


Figure 4.3 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst from the study on effect of solvent. *Reaction condition : temperature; 60 °C, W/F; 41.26* $g_{catalyst}\ h\ mol^{-1}_{reactant}$ *, ;reaction time 4 hours in batch process*

It was shown that the reaction using acetic acid as solvent produce higher yield of cyclohexanone oxime than other solvent. This can be attributed to the fact that, in the reaction using acetic acid, peracetic acid can be generated by reaction of acetic acid and hydrogen peroxide. This has been reported in the previous study [48], that peracetic acid seems to be a better oxidizing agent leading to higher activity as discussed earlier.



In the case of using water, lower yield of cyclohexanone oxime were produced as compared to that using acetic acid as a solvent. It was found that, in the reaction using water as solvent, ammonia is primarily oxidised to form hydroxylamine followed by condensation with cyclohexanone to form cyclohexanone oxime [48]. However, water can strongly adsorb on the active site and sorption of ammonia is inhibited by such competitive adsorption. In addition to that, condensation of hydroxylamine with cyclohexanone will not be readily facilitated in water and products in the reaction using water can also be produced by homogeneuos reaction, such as ring opening and oligomerisation. In particularly, solid product is formed in the reaction. This by-product was suggested earlier to be dicyclohexylidene diperoxide and 6-hydroxyhexanoic acid [50]. This leads to a low selectivity of cyclohexanone oxime in the reaction using water as a solvent.

In the reaction using acetonitrile as a solvent, higher conversion of cyclohexanone was also observed, as compared to that using water as a solvent. This suggests that in the reaction using acetonitrile with hydrogen peroxide, peroxyimidic acid can be produced. This is known to be an active oxidising agent toward various organic substrates[39]. However, low selectivity of cyclohexanone oxime was obtained. This is because formation of by-products namely acetamide, caprolactone, 1,4-cyclohexanedione and aldol condensation product.

In case of ethanol as a solvent, higher conversion than that using water as a solvent was also obtained. This is because ethanol is less polar than water and ammonia, and its sorption on active site is reduced. Therefore, conversion of cyclohexanone is relatively high as compared to that using water as a solvent. However, low selectivity of cyclohexanone oxime in this solvent is still observed because products can undergo ring opening and oligomerisation in a manner similar to that take place in reaction using water as a solvent.

By-product is not found in the reaction using iso-butanol as a solvent. This is because iso-butanol is a free radical scavenger and inhibitor for free radical reaction such as oxidative coupling. Therefore, the reaction using iso-butanol as a solvent produce higher selectivity of cyclohexanone oxime than those using other solvents. However, reaction using iso-butanol as a solvent produces very low cyclohexanone conversion, as compared to that using acetic acid as a solvent. Accordingly, acetic acid which produces a reasonable selectivity and conversion is choosen for further study on ammoximation of cyclohexanone to synthesis cyclohexanone oxime.

4.2.2 Effect of Titanium species

The conversion, yield and selectivity from the reaction using TS-1, non-catalyst, Tetrabutyl Orthotitanate, and reused catalyst as catalysts are shown in Figure 4.4

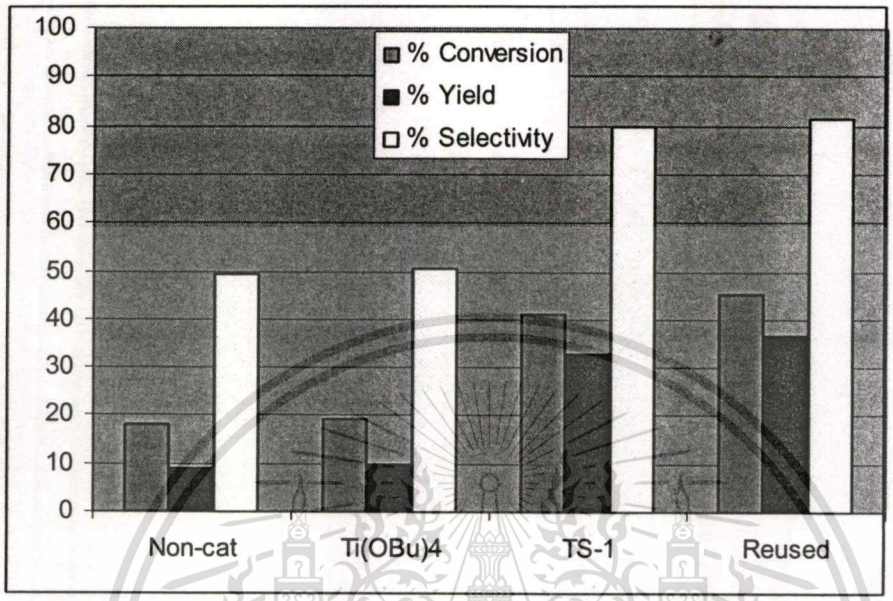
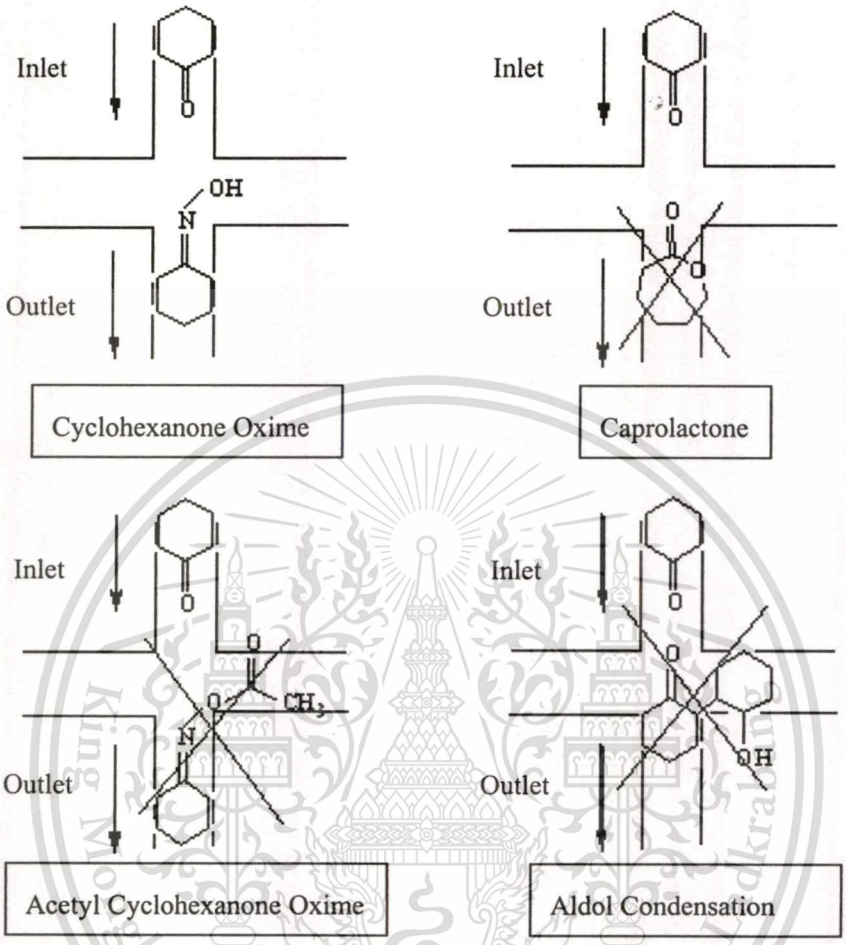


Figure 4.4 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst from the study on effect of Ti-species. *Reaction condition : temperature; 60 ^{o}C, W/F; 41.26 $g_{catalyst}$ h $mol^{-1}_{reactant}$, solvent; acetic acid, reaction time 4 hours in batch process*

From Figure 4.4 a poor selectivity of cyclohexanone oxime was obtained in the reaction without catalyst. In contradiction the presence of TS-1 catalyst leads to a better activity and selectivity of the oxidised products. This is not only because TS-1 can promote the formation of peracetic acid [10] but also due to the presence of active oxidising species formed by the peracetic acid and titanium framework. Hence, the activity towards oxidation is enhanced, as compared to that without catalyst. When an equivalent mole of tetrabutyl orthotitanate was used instead of TS-1 , a similar result to the non-catalysed reaction was also observed. Therefore, it is clear that the enhanced ammoximation activities are not mainly derived from neither the homogeneous reaction nor the leached titanium species, if applicable. It is believed that, only cyclohexanone oxime can be produced in the pore. This is because the fact that TS-1 possesses the medium pore size (5.5 A^{o}). Therefore, other products namely caprolactone, acetyl

cyclohexanone oxime and aldol condensation having molecular size larger than its pore size cannot be generated within the pore of TS-1 as illustrated below.



After TS-1 was used as a catalyst in a reaction, the catatyst was removed by filtration and then washed by distillation water and dried at 100 °C. The catalyst was reused in a reaction under the same condition. It was found that similar yield of cyclohexanone oxime is produced, as compared to the fresh catalyst. This is indicated that active species is retained in the catalyst framework. It can be concluded that TS-1 is relatively stable within the reaction condition and may well be used for continuous catalytic process without significant loss of activity.

4.2.3 Effect of Resident Time

The conversion, yield and selectivity from the reaction using TS-1 as catalysts are shown in Figure 4.5

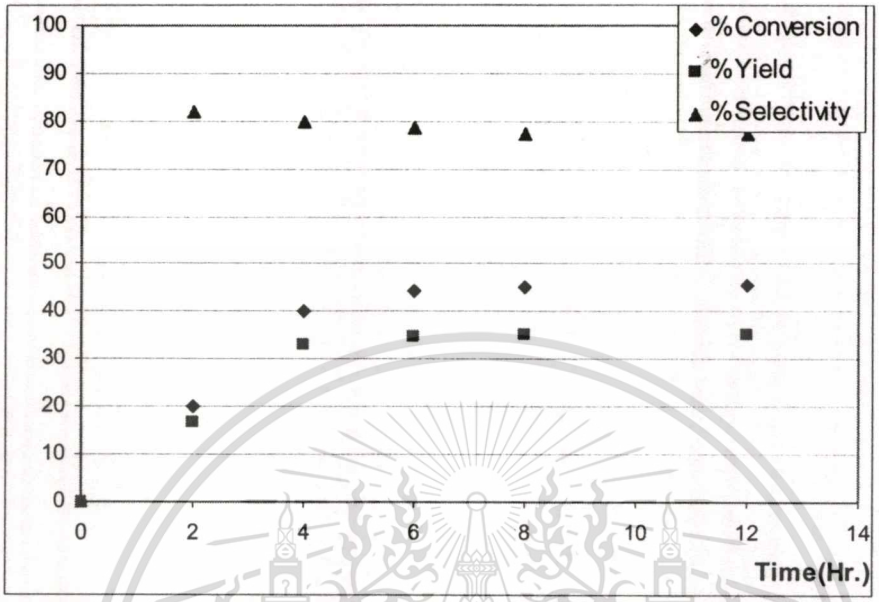


Figure 4.5 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst from the study on effect of resident time . *Reaction condition : temperature; 60 ^{o}C, W/F; 41.26 $g_{catalyst}$ h $mol^{-1}_{reactant}$, solvent; acetic acid, reaction time 2,4,6,8 and 12 hours in batch process*

The result from Figure 4.5 shown that increase in resident time of ammoximation reaction raise the conversion of cyclohexanone. However, when resident time of reaction over 6 hours conversion of cyclohexanone and yield of cyclohexanone oxime become unchanged. This is because the reaction have exhausted hydrogen peroxide to generate products indicating that the consumption of hydrogen peroxide in reaction are limited for 6 hours reaction time by hydrogen peroxide decomposition. Accordingly, selectivity of cyclohexanone oxime seem to be unchanged after 6 hours of reaction time. This is because, without hydrogen peroxide no product can be produced including by-products from oxidative coupling and aldol condensation. Therefore, it is pointless to exceed the resident time over 6 hours.

4.2.4 Effect of Temperature

The conversion, yield and selectivity from the reaction using TS-1 as catalysts at various reaction temperature in batch process are shown in Figure 4.6

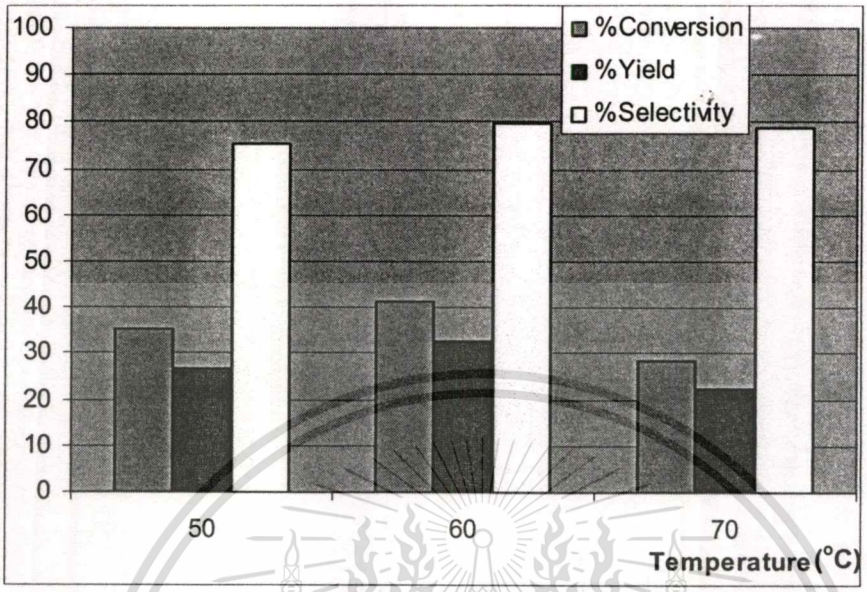


Figure 4.6 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst from the study on effect of temperature. *Reaction condition : temperature; 50, 60 and 70 °C, W/F; 41.26* $g_{catalyst}\ h\ mol^{-1}_{reactant}$ *, solvent ; acetic acid, reaction time 4 hours in batch process*

From the Figure 4.6, it was shown that the conversion of cyclohexanone increased with increasing the reaction temperature from 50 °C up to 60 °C, the selectivity to cyclohexanone oxime also increased slightly. Both the conversion and selectivity reached maximum at 60 °C. The further increase in temperature up to 70 °C result in the slightly decrease in both conversion and selectivity. From the result, it can be explained that below 60 °C the conversion of cyclohexanone is reduced because low catalytic activity for ammoximation of cyclohexanone. However, the reaction from the non-catalyzed to generate by product such as acetylcyclohexanone oxime, caprolactone and aldol condensation are facilitated. The decrease in the conversion of cyclohexanone at temperature higher than that 60 °C is reasonably attributed to easier vaporisation of ammonia and decomposition of hydrogen peroxide. Thus, when the ammoximation is carried out at higher temperature (over 60 °C), the reduce of cyclohexanone conversion is obtained due to lower reagent concentration as compared to that at 60 °C. Conclusively, the optimum temperature for the synthesis of cyclohexanone oxime is 60 °C.

4.3 Continuous Process

4.3.1 Influence of Reactor types

The conversion, yield and selectivity from the reaction in packed bed flow reactor and continuous stirred tank are shown in Figure 4.7 and Figure 4.8 respectively.

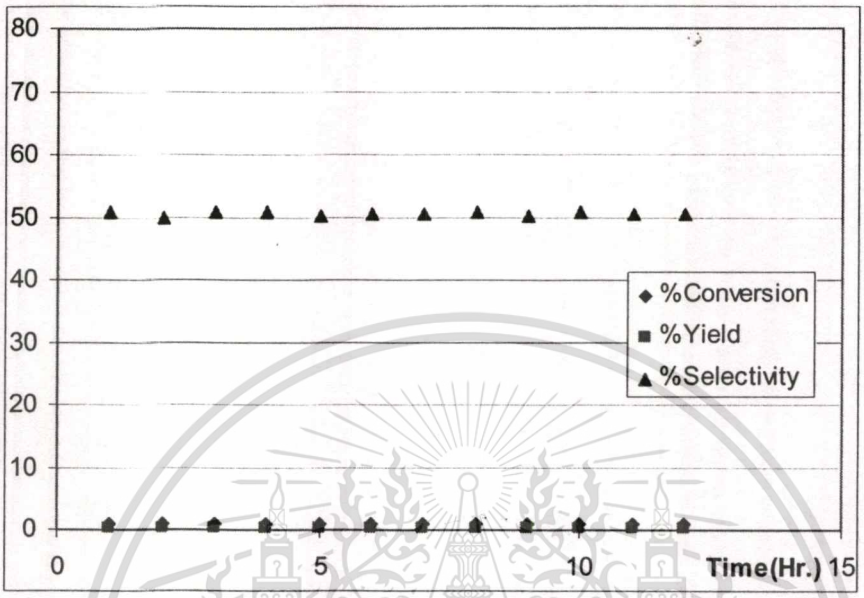


Figure 4.7 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, W/F; 41.26* $g_{catalyst}$ *h mol* $^{-1}_{reactant}$, *solvent; acetic acid, time o f process ; 12 hours , in packed bed flow reactor*

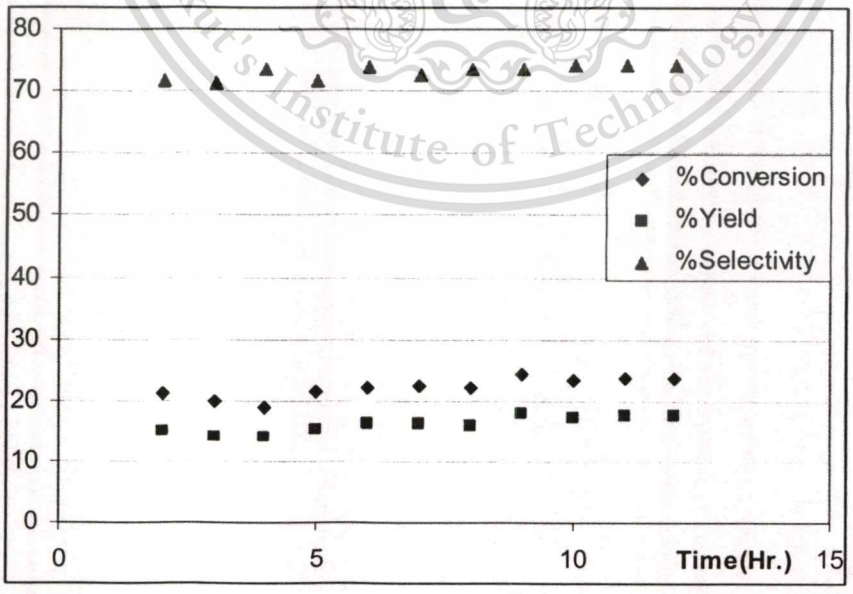


Figure 4.8 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, W/F; 41.26* $g_{catalyst}$ *h mol* $^{-1}_{reactant}$, *solvent;acetic acid, time o f process ; 12 hours , in stirred tank reactor*

From the result, it was shown that both system can produce a steady conversion of cyclohexanone. However, a lower yield of cyclohexanone oxime is produced in continuous packed bed flow reactor (Figure 4.7), as compared to that from continuous stirred tank reactor (Figure 4.8). This is because the ammoximation of cyclohexanone using acetic acid as solvent is a tri-phase system [20]. As the heterogeneous mixture flow through the catalyst bed, the sites contacted with hydrophilic phase (H_2O, H_2O_2, ammonia) cannot be easily accessed by hydrophobic phase (cyclohexanone) and vice versa. This can inhibit the reaction rate since both hydrogen peroxide and cyclohexanone are required to interact with the same active site. Accordingly, the ammoximation of cyclohexanone is hardly promoted in continuous packed bed flow reactor. On the other hand, well-mixing can be achieved in continuous stirred tank reactor and there is a higher opportunity of cyclohexanone to react with active sites, previously interacted with hydrogen peroxide. Therefore, continuous stirred tank reactor appears to be appropriated for ammoximation of cyclohexanone using acetic acid as a solvent in continuous process.

4.3.2 Effect of Retention volume

In continuous process, retention volume determined both activity and productivity. Influence of retention volume is studied by reducing the volume of reactor from 100 ml to 50 ml reactor volume. The conversion, yield and selectivity from 100 ml and 50 ml reactor volume are shown in Figure 4.9.

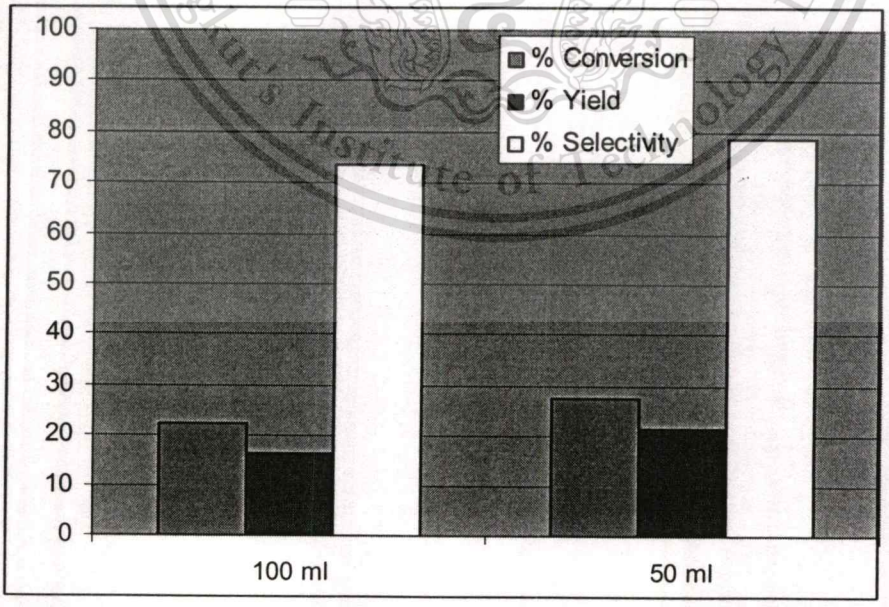


Figure 4.9 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, W/F; 41.26 $g_{catalyst}$ h mol $^{-1}_{reactant}$, solvent; acetic acid, time of process ; 12 hours, 100 ml and 50 ml reactor volume*

The result from Figure 4.9 shows that the reaction in larger reactor size (100 ml) gives lower conversion of cyclohexanone, as compared to the reaction in smaller reactor size (50 ml). This can be explained that, the reaction in a smaller reactor, there is higher opportunity for hydrogen peroxide to react with the catalyst. Hence higher hydrogen peroxide consumption rate can be expected, as compared to the hydrogen peroxide decomposition rate. In addition, when reactor size is decreased, catalytic system does not only lead to an increase in cyclohexanone oxime formation, but also provides less chance for noncatalyzed reaction to generate by-products such as acetylcyclohexanone oxime, caprolactone and aldol condensation. This leads to a high selectivity of cyclohexanone oxime for the reaction in smaller reactor size. Accordingly, reaction in smaller reactor (50 ml) can produce high yield and high selectivity of cyclohexanone oxime and will be used activity testing in continuous process. However, lower yield of cyclohexanone oxime is obtained in continuous process, as compared to batch process. This is due to the increased scale of operation which may well lead to an increase in hydrogen peroxide decomposition.

4.3.3 Effect of Amount of Catalyst

As seen from the above result (section 4.3.2) that when the reactor size is reduced, higher yield of cyclohexanone oxime was obtained. This is because of high opportunity of catalyst to contact with reactant. Therefore, increase of catalyst content is expected to increase yield of cyclohexanone oxime. The conversion, yield and selectivity from the reaction using TS-1 0.5 grams, 1.0 gram and 2.0 grams in continuous process are shown in Figure 4.10.

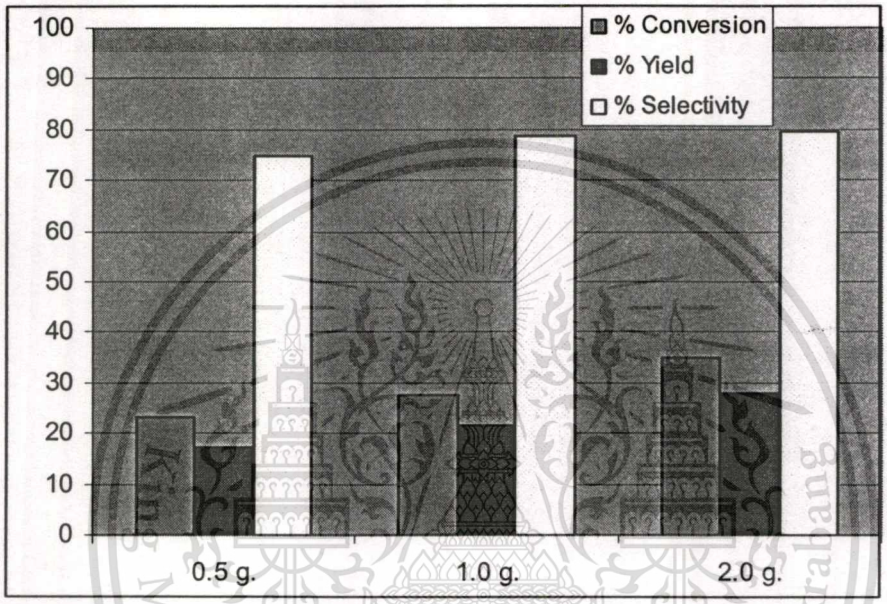


Figure 4.10 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C , solvent; acetic acid, 0.5, 1.0 and 2.0 grams of Catalyst , time o f process ; 12 hours, 50 ml reactor volume*

From the result it is shown that when amounts of TS-1 was increased in the reaction upto 2.0 grams, an increase in cyclohexanone oxime formation was obtained. In a manner similar to the effect of reactor volume, (section 4.3.2), the catalyst/reactant ratio was linearly increased with increasing amount of catalysts. The reactants (cyclohexanone and hydrogen peroxide) have a higher possibility to react with the active sites and hence higher yield of cyclohexanone oxime was obtained. However, the selectivity is only slightly increased and seems to be limited at about 80%. This suggests that an increase in the amount of catalyst does not affect non-catalyzed reaction taking place in solution. This indicates that feeding rate used in this system is probably too high that part of reactant stream may flow through the reactor without contacting the catalyst.

4.3.4 Effect of H_2O_2 concentration

From previous result (section 4.3.3) when the amounts of catalyst is increased the conversion of cyclohexanone is raised. However, the selectivity of cyclohexanone oxime seems to be limited. The reduction of hydrogen peroxide concentration is expected to increase cyclohexanone selectivity and decrease non-catalyzed reactions. The conversion, yield and selectivity from the reaction using various H_2O_2 concentration in continuous process are shown in Figure 4.11.

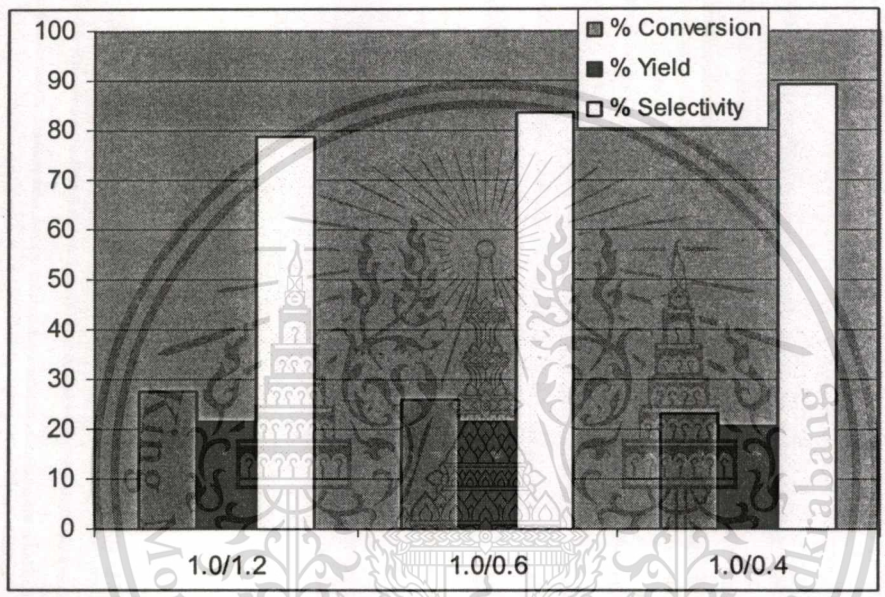


Figure 4.11 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 ^{o}C, W/F; 41.26 $g_{catalyst}$ h $mol^{-1}_{reactant}$, solvent; acetic acid, time o f process ; 12 hours , molar ratio of cyclohexanone/H_2O_2: 1.0/1.2, 1.0/0.6 and 1.0/0.4*

The result from Figure 4.11 shows that when the molar rartio of cyclohexanone and hydrogen peroxide is increased, the selectivity of cyclohexanone oxime is raised. This is because increasing molar rartio of cyclohexanone and hydrogen peroxide can reduce rate of homogeneous reaction. Accordingly, by-products from non-catalyzed reaction such as acetyl cyclohexanone oxime, caprolactone and aldol condensation [47] are decreased. However, when the ratio of cyclohexanone and hydrogen peroxide increased, low conversion of cyclohexanone and yield of cyclohexanone oxime was obtained. This is because small concentration of hydrogen peroxide would leads to a small number of active oxidising species. Althought, this can inhibit non-

catalyzed reaction, high yield of cyclohexanone oxime cannot be produced. However, efficiency of hydrogen peroxide consumption can be improved by increasing the ratio of cyclohexanone and hydrogen peroxid as shows in Figure 4.12..

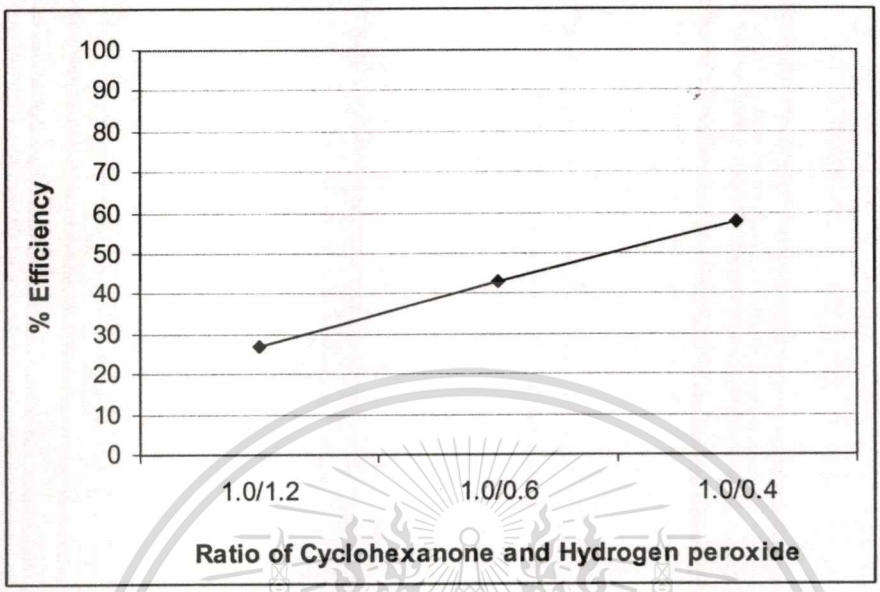


Figure 4.12 Efficiency of hydrogen peroxide consumption. *Reaction condition : temperature; 60 °C, W/F; 41.26* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$, *solvent; acetic acid, time o f process ; 12 hours , molar ratio of cyclohexanone/*H_2O_2*,: 1.0/1.2, 1.0/0.6 and 1.0/0.4*

The result from Figure 4.12 shows that when the molar ratio of cyclohexanone and hydrogen peroxide increased, high efficiency of hydrogen peroxide consumption was obtained. However, lower yield of cyclohexanone oxime based on cyclohexanone was observed. This is because hydrogen peroxide concentration for catalytic activity is reduced. Accordingly, the molar ratio of cyclohexanone and hydrogen peroxide (1/0.6) provide satisfied yield and selectivity of cyclohexanone oxime. Thus, this ratio is choosen for further study on the ammoximation of cyclohexanone oxime in continuous stirred tank reactor.

4.3.5 Effect of Temperature

Influence of temperature is studied by the reaction carried out at 50 °C , 70 °C, as compared to that 60 °C. The conversion, yield and selectivity from the reaction using TS-1 as catalysts 50 °C, 60 °C and 70 °C reaction temperature in continuous process are shown in Figure 4.13.

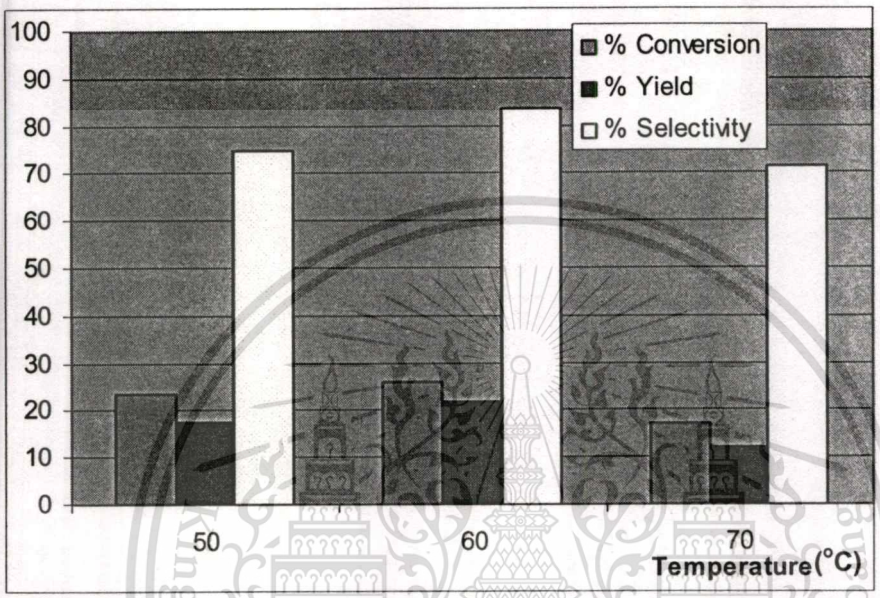


Figure 4.13 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature;50, 60 and 70 °C, W/F; 41.26* $g_{catalyst}\ h\ mol^{-1}{}_{reactant}$ *, solvent; actic acid, in continuous process*

The result from Figure 4.13. shows that the conversion of cyclohexanone increased with increasing the reaction temperature from 50 °C upto 60 °C, the selectivity to cyclohexanone oxime also increased slightly. Both the conversion and selectivity reached maximum at 60 °C. The further increase in temperature upto 70 °C results in a slight decrease in both conversion and selectivity. When these results were compared to the result from batch process, conversion, yield and selectivity seem to be in the same trend, as already discussed in section 4.2.3..

4.3.6 Influence of Feed rate

From previous section, it can be seen that hydrogen peroxide decomposition plays important role in limiting activity and efficiency of the reaction. Accordingly, reduction of hydrogen peroxide decomposition in continuous process can be rectified by reducing the flow rate. The conversion, yield and selectivity from the reaction using various feed rate in continuous process are shown in Figure 4.14.

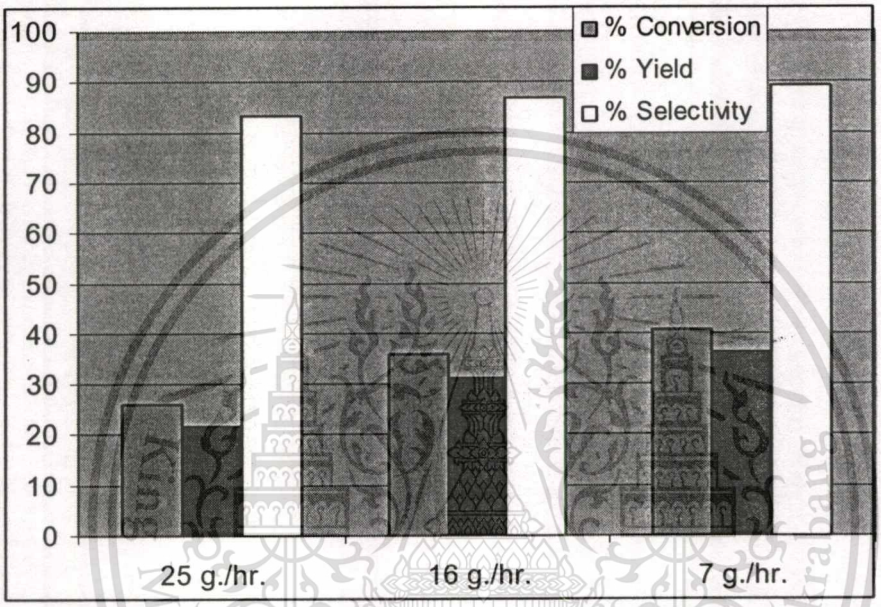


Figure 4.14 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, solvent; acetic acid, time of process ; 12 hours , feed rate 25, 16 and 7 grams/hour*

Although increase in molar ratio of cyclohexanone and hydrogen peroxide can suppress hydrogen peroxide decomposition and increase selectivity of cylohexanone oxime, this reduces the conversion of cyclohexanone. Accordingly, reducing feeding rate would increase contact time, and hence the conversion. The result from Figure 4.14 shows that when feeding rate is decreased not only higher cyclohexanone conversion was obtained but also higher selectivity of cyclohexanone oxime can be seen, as compared to high feeding rate. This can be explained that reduction of feeding rate can also increase an opportunity for reactant to contact with catalyst. Therefore, hydrogen peroxide is mainly consumed in catalytic process, and hence homogeneous reactions are diminished. This subsequently inhibit formation of by-product and higher yield of product can be obtained. However, using feeding rate at 7 grams/hour low productivity was

obtained. Accordingly, feeding rate of 16 grams/hour is choosen for further study on ammoximation of cyclohexanone oxime in continuous stirred tank reactor.

4.3.7 Influence of Catalytic life time

The long catalyst life time is an important target for cyclohexanone oxime synthesis in continuous process. Catalyst life time determined time on stream for continuation of production. The conversion, yield and selectivity of long run over 40 hrs. is shown in Figure 4.15

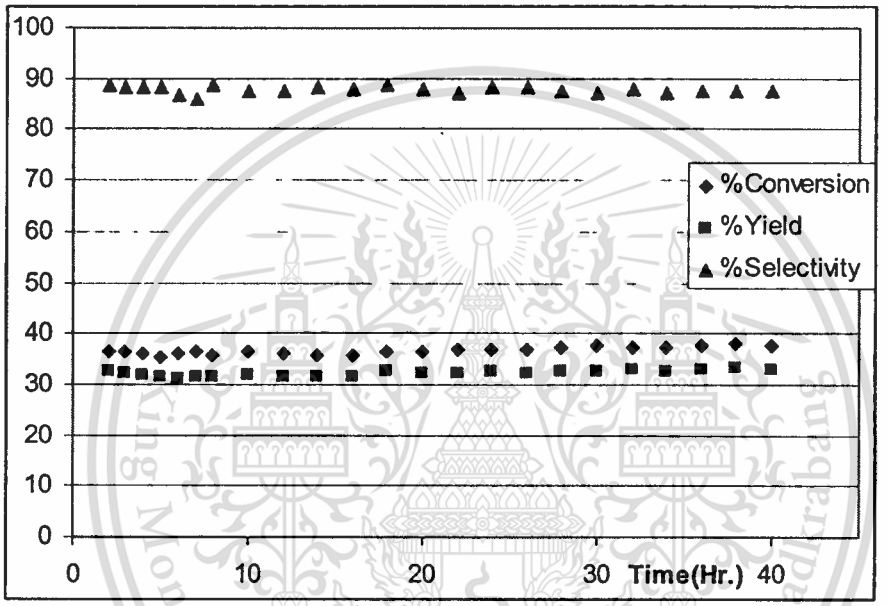


Figure 4.15 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 ^{o}C, W/F; 64.93 $g_{catalyst}$ h $mol^{-1}_{reactant}$, solvent; acetic acid, time o f process ;40 hours, molar ratio of cyclohexanone/H_2O_2: 1/0.6*

The result from Figure 4.15 shows a long life catalytic activity of TS-1 for ammoximation of cyclohexanone. Over 40 hours of testing, the catalyst can promote a steady conversion, selectivity of cyclohexanone and of cyclohexanone oxime, respectively. This indicates that the Ti-active site is retained as observed by FT-IR in Figure 4.16. However, X-ray fluorescence shows that Ti content of catalyst after used for (Si/Ti of 34) is slightly lower than that fresh catalyst (Si/Ti of 30). The result is indicated that small amount Ti-framework are leached from the catalyst. Although, some Ti are leached to solution, the catalyst is still active. Previous report [1] suggest that Si/Ti ratio of catalyst more than 120 can provide high activity for

oxidation reaction. The result shows that TS-1 is an high performance catalyst for this reaction and a development of the system into industrail process, appears to be attractive.

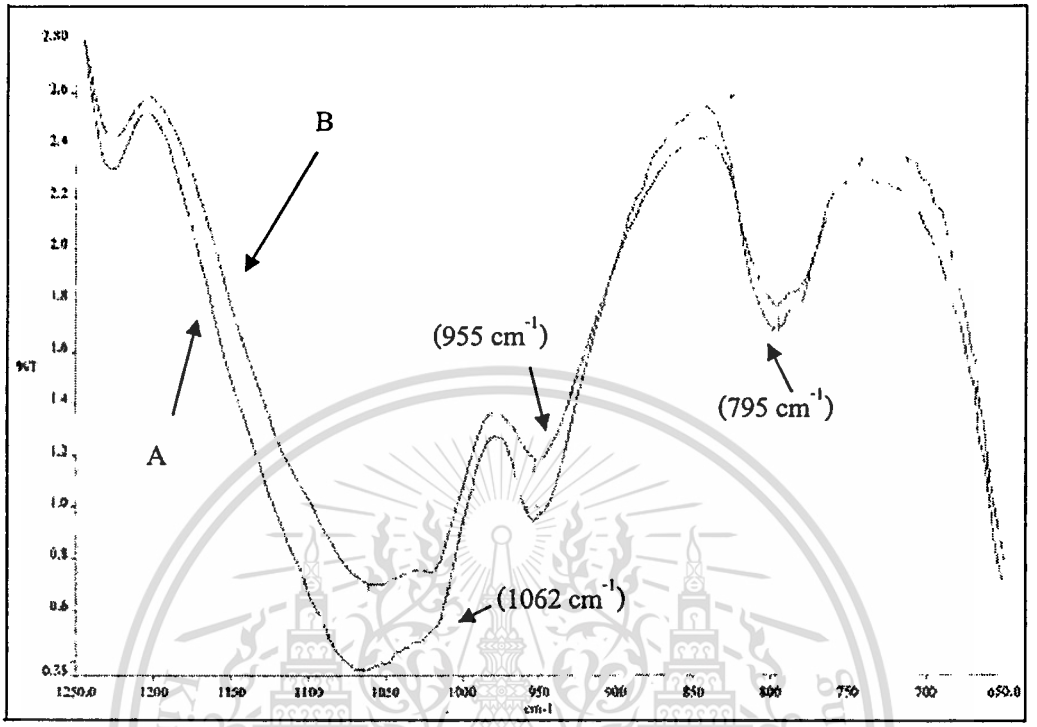


Figure 4.16 Fourier Tranformed IR spectra of TS-1 before(A) and after(B) using

It can be seen that after 40 hours testing, TS-1 catatyst exhibit characteristic adsorption of Ti-O-Si at 955 cm^{-1} [3,34-35].

4.3.8 Effect of Titanium framework leaching

Although, the observed long life activity, it can be seen that small amount of Ti was leaching from the catalyst. This depends on stability of Ti active site which can be improved by increasing of calcining temperature. The fresh TS-1 (Si/Ti of 30.10) calcined at different temperature (500-600 °C, 4 hours of hold time) were used as catalyst and silicon and titanium content of before and after used TS-1 were demtermined by X-ray Fluorescence (XRF). The result are shown in Table 4.3

Table 4.3 The determination of silicon and titanium of TS-1 after used for 12 hours testing.

Calcining temperature	Silicon/Titanium	%Conversion	%Yield	%Selectivity
550 °C	33.68	28.92	24.94	86.23
575 °C	32.26	29.63	25.66	86.60
600 °C	30.69	29.72	25.75	86.64

The result from Table 4.3 shows that increase of calcining temperature does not effect the activity for cyclohexanone oxime production. As expected, leaching of titanium active site is reduced when the temperature for calcination is raised. In other words, the Ti active site is more stable when high temperature treatment is applied. However, calcining temperature should not be exceed to 600 °C because Ti-framework can be collapsed into inactive octahedral titaium species.

Chapter 5

Conclusion and Suggestion

5.1 Conclusion

The study on effect of solvent shows that acetic acid is the best solvent to produce cyclohexanone oxime. This is because the reaction of acetic acid and hydrogen peroxide generated *in situ* active oxidising species namely peracetic acid. In the reaction using hydrophilic solvents namely water, ethanol and acetonitrile, lower yield of cyclohexanone oxime were produced as compared to that using acetic acid as a solvent. This is because these hydrophilc solvents strongly adsorb on the active sites. Sorption of the reactant, cyclohexanone is inhibited by competitive adsorption of such hydrophilic solvent. The catalytic testing in iso-butanol as solvent also give low yield of cyclohexanone oxime. Nevertheless, by-product is not found in the reaction using iso-butanol as solvent. This is because iso-butanol is a free radical scavenger and an inhibitor for free radical reaction.

From the study on effect of titanium species, reaction using TS-1 as catalyst leads to a better activity and selectivity of the oxidised products. This is not only because TS-1 can promote the formation of peracetic acid but also due to the presence of active oxidising species formed by the peracetic acid and titanium framework. Hence, the activity towards oxidation is enhanced, as compared to that without catalyst. When an equivalent mole of tetrabutyl orthotitanate was used instead of TS-1 , a similar result to the non-catalysed reaction was also observed. This indicates that soluble Ti in solution does not active for ammoximation reaction.

For continuous process, the influence of reactor types study, shows that lower yield of cyclohexanone oxime is produced in continuous packed bed flow reactor as compare to that from continuous stirred tank reactor. This is because the ammoximation of cyclohexanone using acetic acid as solvent is a tri-phase system. As the heterogeneuos mixture flow through catalyst bed. The sites contact with hydrophlic phase cannot be easily accessed. In contrast, well-mixing can be achieved in continuous stirred tank reactor resulting in higher opportunity of cyclohexanone to react with the active sites.

Decreasing reactor size leads to a slighly increase in cyclohexanone oxime formation. This is because the reaction in smaller reactor reduces decomposition of H_2O_2. Consequently, H_2O_2 is selectively consumed by oxidation process.

The study on effect of hydrogen peroxide concentration shows that when the molar rartio of cyclohexanone and hydrogen peroxide is increased, the selectivity of cyclohexanone oxime is raised. This is because hydrogen peroxide is consumed in catalytic process, and hence homogeneous is diminished.

An increase in contact time could be achieved either by reducing flow rate of the feeds or increasing amounts of the catalyst. When feeding rate is decreased the conversion of cyclohexanone is raised. Additionally, 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.

Over 40 hours of testing, the catalyst can promote a steady yield of cyclohexanone oxime. This indicate that of tetrahedral titanium active site for, are retained during the long time on stream of reaction as confirmed by FT-IR.

The study on leaching of titanium framework shows that leaching of titanium active site is reduced when the temperature for calcination is raised. High stability of Ti active site can be obtained by increase of treatment temperature.

5.2 Suggestion for Future Studies

5.2.1 For reducing by-product namely aldol condensation, decreasing of ammonia concentration should be investigated.

5.2.2 In the study on effect of feed rate, when feed rate is decreased high cyclohexanone conversion was obtained. This lead to an improved activity of reaction. For future study, the higher activity could be obtained if the lower feed rate can be applied.

5.2.3 For improving catalytic activity, the effect of particle size of catalyst should be studied.

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Appendix A

Scanning Electron Micrograph

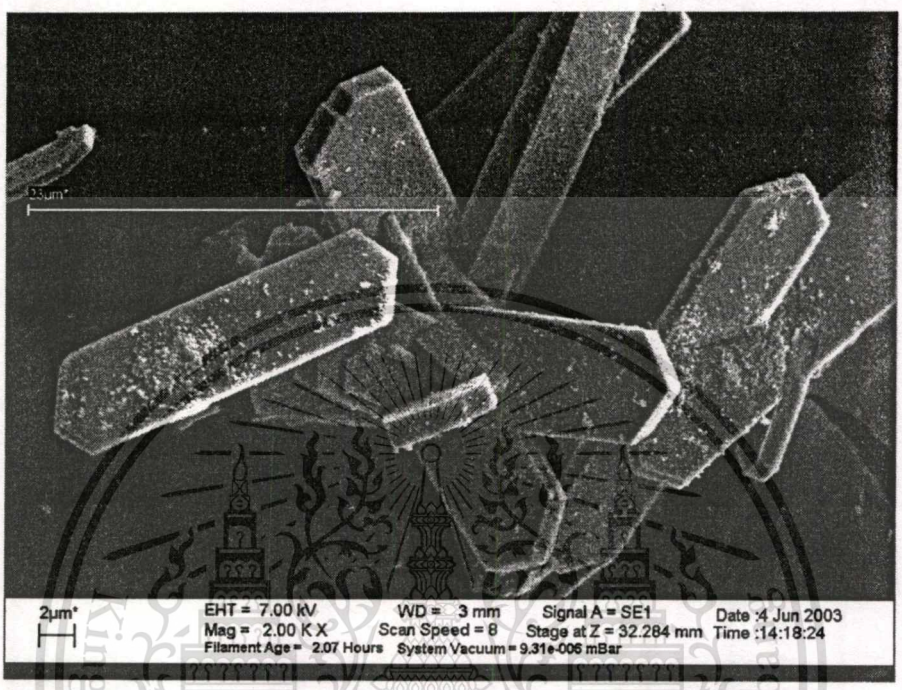

Figure A.1 Scanning electron micrograph of TS-1 before calcination and washig by sulfuric acid.

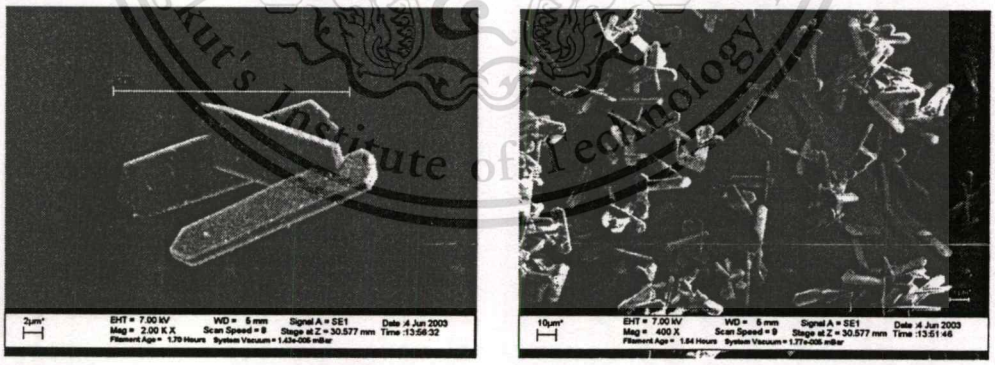

Figure A.2 Scanning electron micrograph of TS-1 after washig by sulfuric acid and calcination.

Appendix B

X-Ray Diffraction Patterns of TS-1

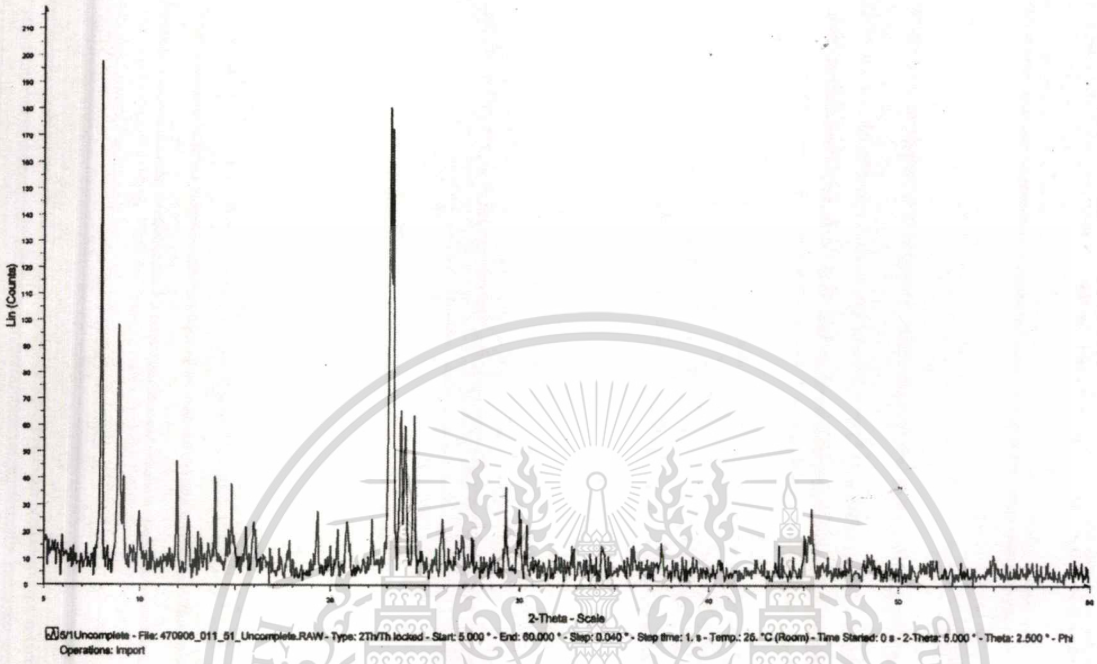

Figure B.1 X-ray diffraction pattern of TS-1 before calcination.

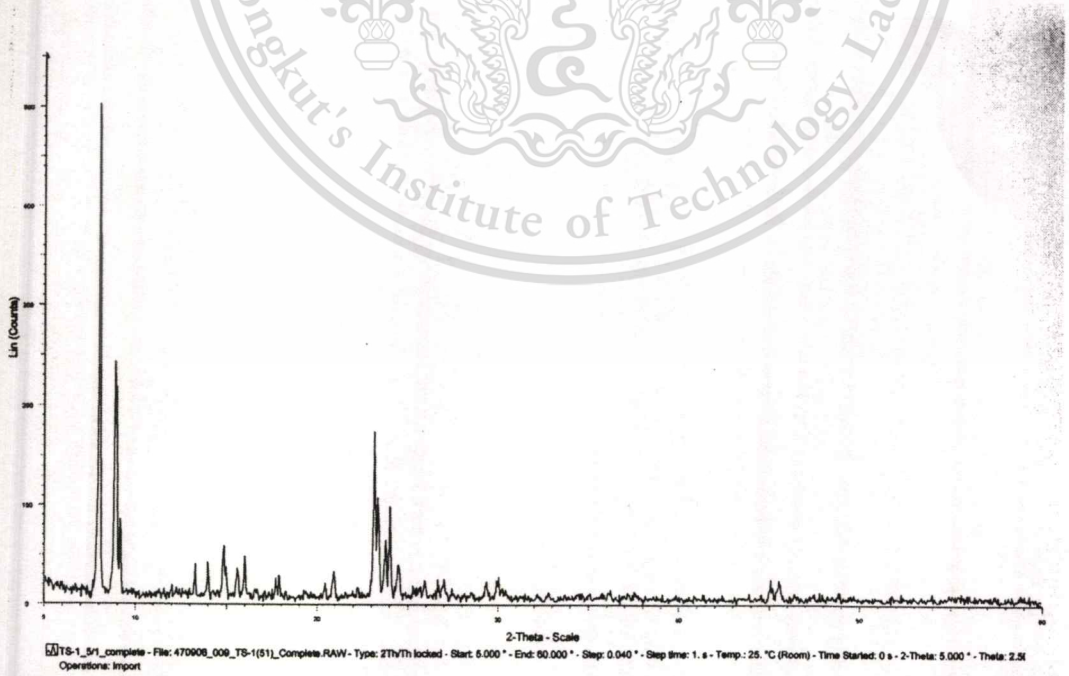

Figure B.2 X-ray diffraction pattern of TS-1 after calcination.

Appendix C

X-Ray Fluorescence of TS-1

SiO2	TiO2	Compton	Rayleigh	Sum
71.9 KCps	25.8 KCps			
94.6 %	5.04 %	0.90	0.99	100.00 %

Figure C.1 Percentage of SiO_2 and TiO_2 of TS-1 before washing by sulfuric acid.

SiO2	TiO2	Compton	Rayleigh	Sum
80.5 KCps	23.9 KCps			
95.5 %	4.23 %	0.91	1.00	100.00 %

Figure C.2 Percentage of SiO_2 and TiO_2 of TS-1 after washing by sulfuric acid and 550, 575 and 600 $^{\circ}C$ calcination.

SiO2	TiO2	Compton	Rayleigh	Sum
91.2 KCps	24.2 KCps			
96.0 %	3.80 %	0.88	0.99	100.00 %

Figure C.3 Percentage of SiO_2 and TiO_2 of TS-1 550 $^{\circ}C$ calcination after using in reaction.

SiO2	TiO2	Compton	Rayleigh	Sum
88.8 KCps	24.7 KCps			
95.8 %	3.96 %	0.90	0.99	100.00 %

Figure C.4 Percentage of SiO_2 and TiO_2 of TS-1 575 $^{\circ}C$ calcination after using in reaction.

SiO2	TiO2	Compton	Rayleigh	Sum
54.5 KCps	27.1 KCps			
95.3 %	4.14 %	0.90	1.00	100.00 %

Figure C.5 Percentage of SiO_2 and TiO_2 of TS-1 600 °C calcination after using in reaction.

Appendix D

Surface Area and BET Plot from Gas Adsorption Analyzer

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

Sample ID	TS-1 No2 Complete				
Description	BET 11 point				
Comments					
Sample Weight	0.0359 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	jeab
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	25.0 hrs	Analysis Time	152.9 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	01/10/2006 15:16
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	490110_1.RAW
Station #	1	Bath Temp.	77.40		

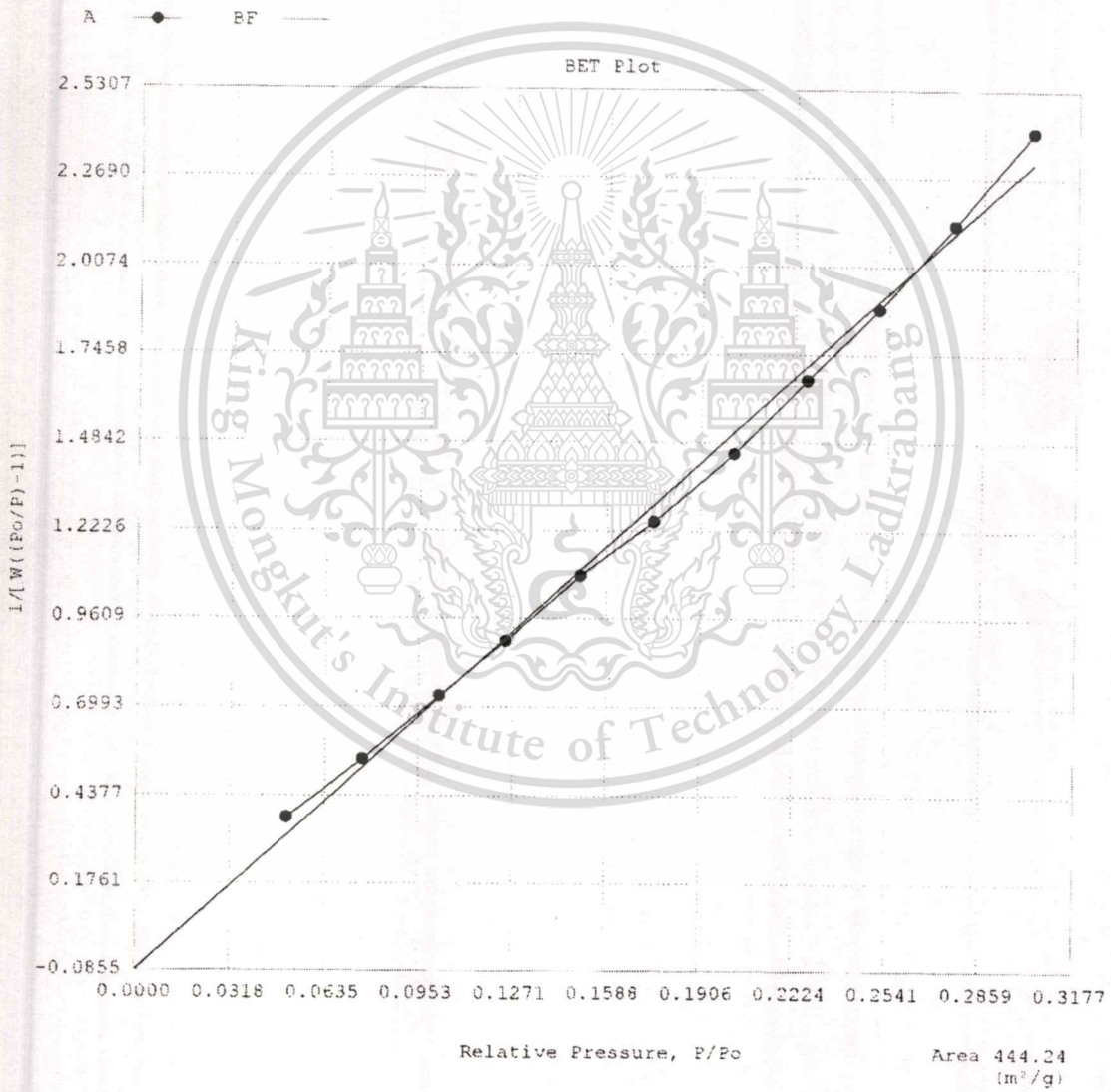

Figure D.1 BET plot of TS-1 before washing by sulfuric acid.

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

Sample ID	TS-1 No3 Complete				
Description	BET 11 point				
Comments					
Sample Weight	0.0200 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	jeab
Cross-Sec Area	16.2 A²/molecule	Outgas Time	25.0 hrs	Analysis Time	154.6 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	01/09/2006 16:49
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	490109_1.RAW
Station #	1	Bath Temp.	77.40		

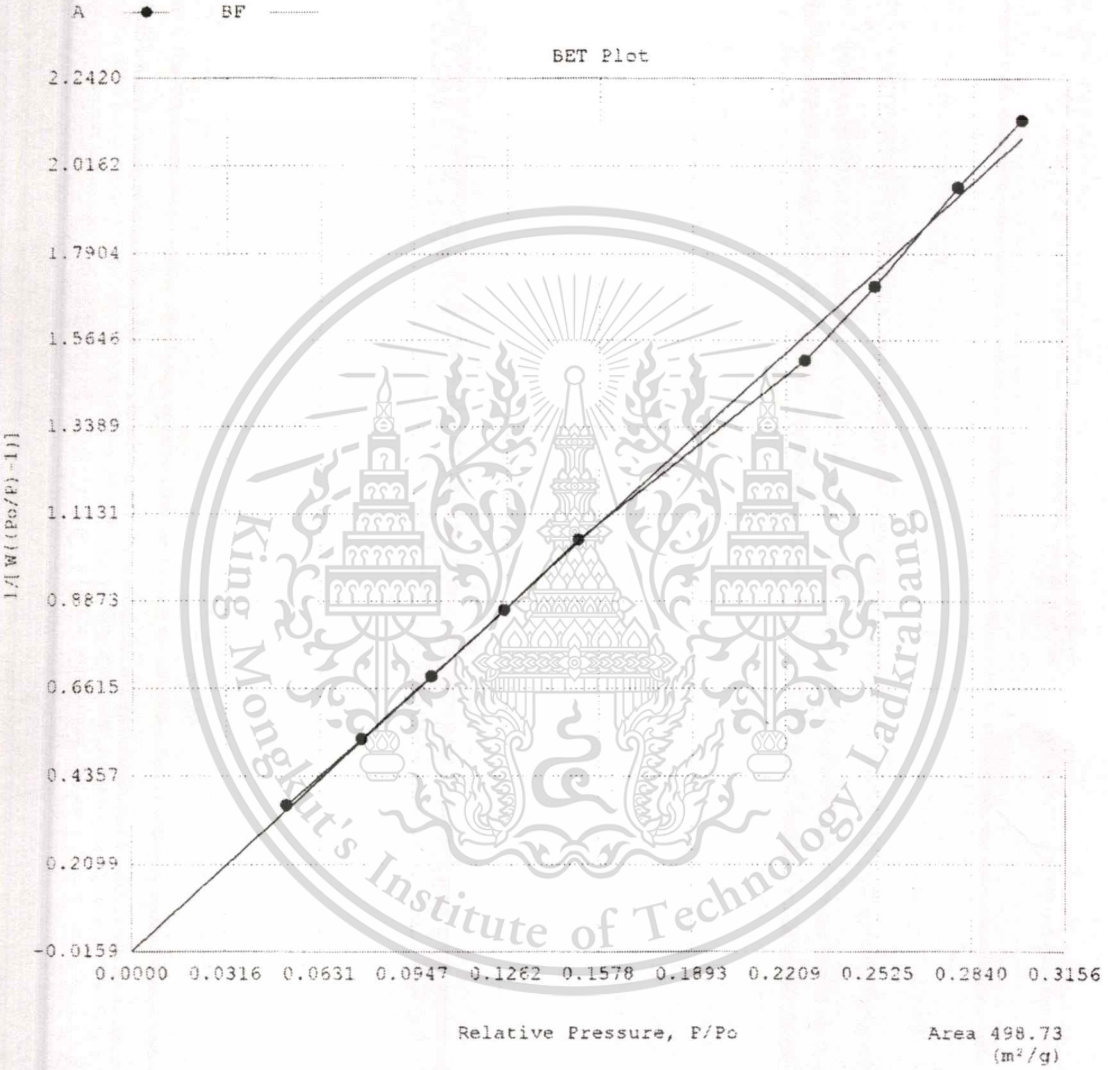

Figure D.2 BET plot of TS-1 after washing by sulfuric acid.

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

Sample ID	TS-1 No8 calcine				
Description	BET 11 point				
Comments					
Sample Weight	0.0176 g				
Adsorbate	NITROGEN	Outgas Temp	350.0 °C	Operator	nam
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	14.0 hrs	Analysis Time	155.8 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	01/06/2006 15:40
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	490106_1.RAW
Station #	1	Bath Temp.	77.40		

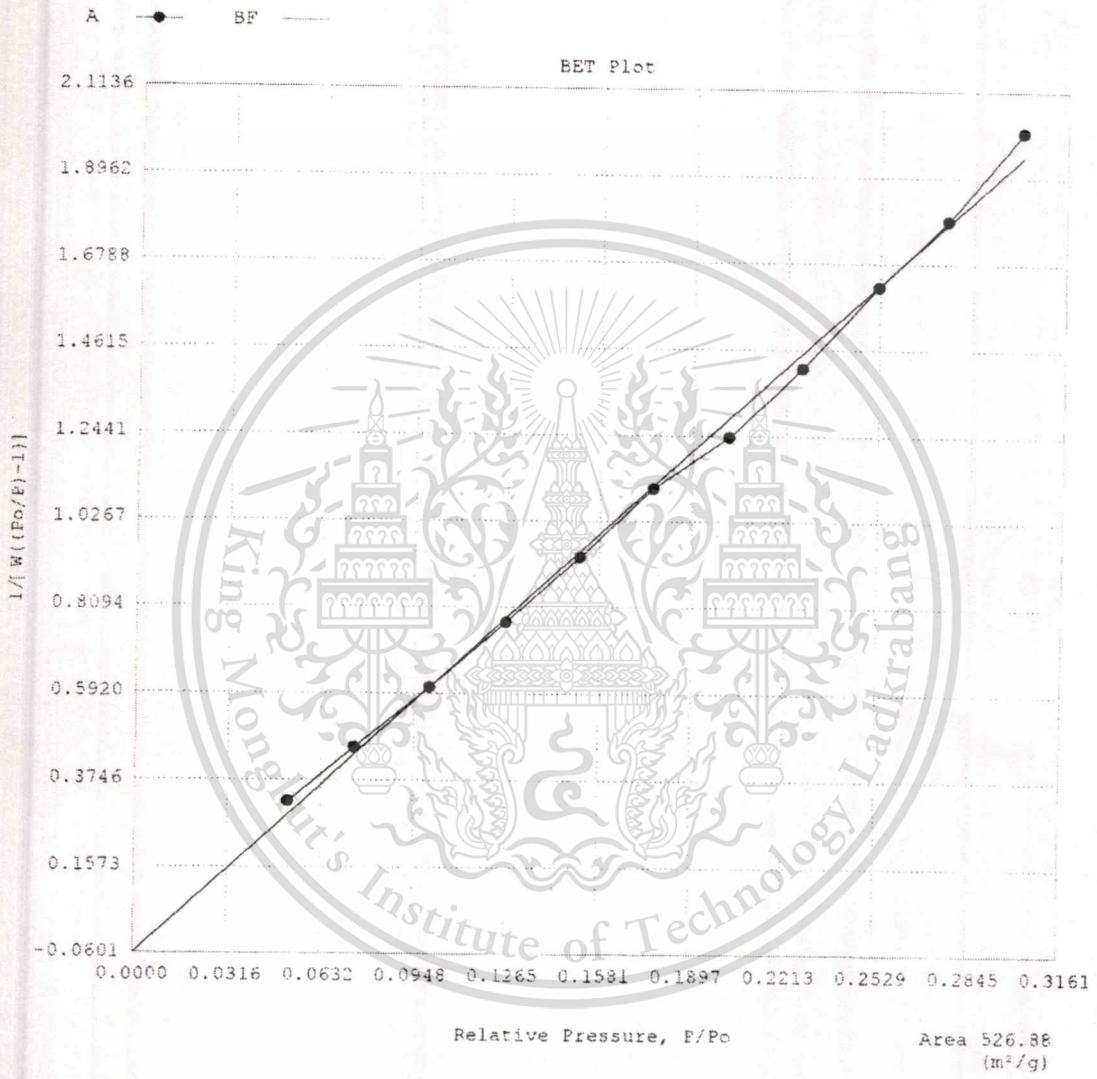

Figure D.3 BET plot of TS-1 after using in ammoximation reaction.

Appendix E

Gas

Chromatogram

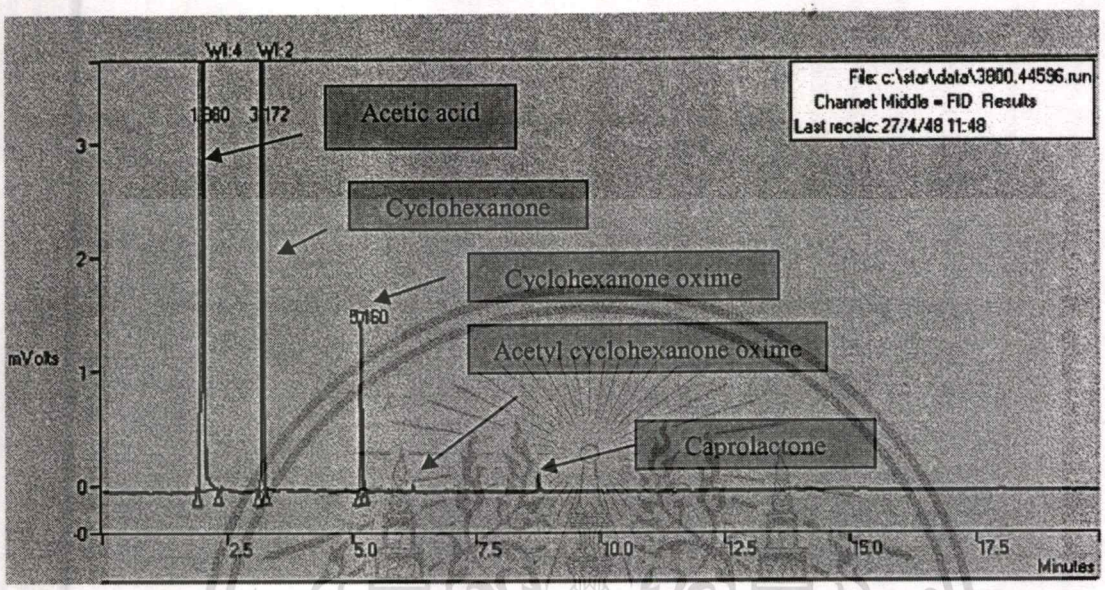

Figure E.1 Gas chromatogram from ammoximation of cyclohexanone at 60 °C in acetic acid by using TS-1 as catalyst.

Appendix F

Result from Gas Chromatography-Mass Spectrometer

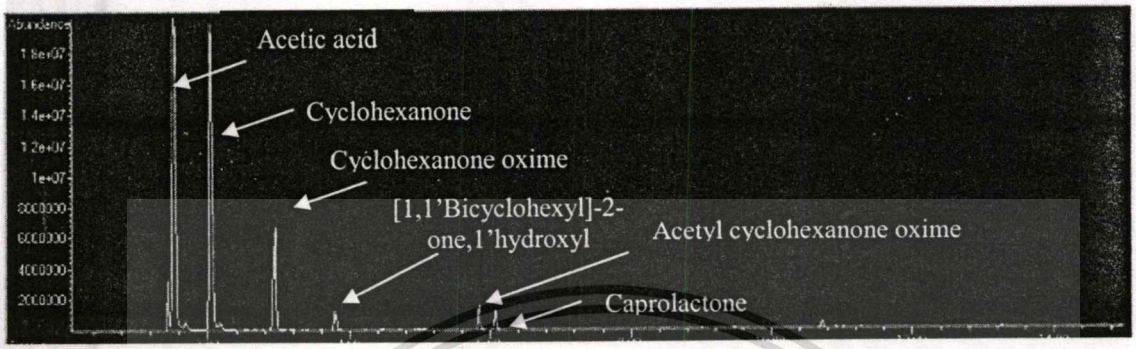

Figure F.1 Chromatogram from ammoximation reaction in acetic acid.

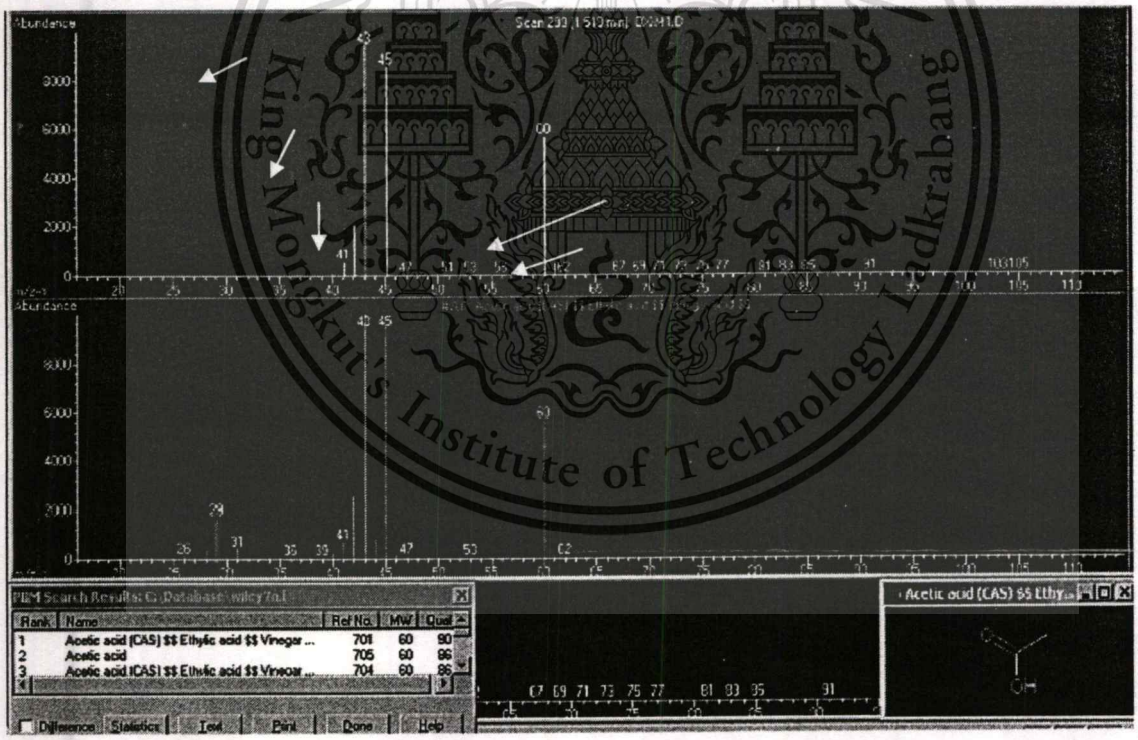

Figure F.2 Mass spectrum of acetic acid from ammoximation reaction in acetic acid.

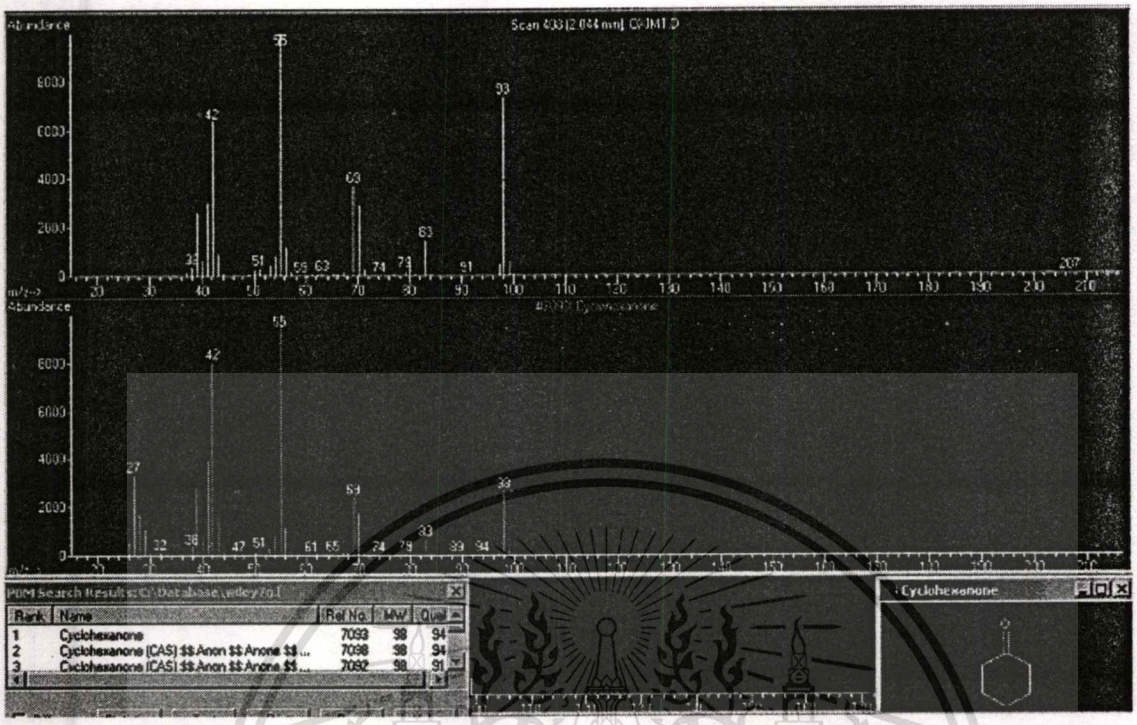

Figure F.3 Mass spectrum of cyclohexanone from ammoximation reaction in acetic acid.

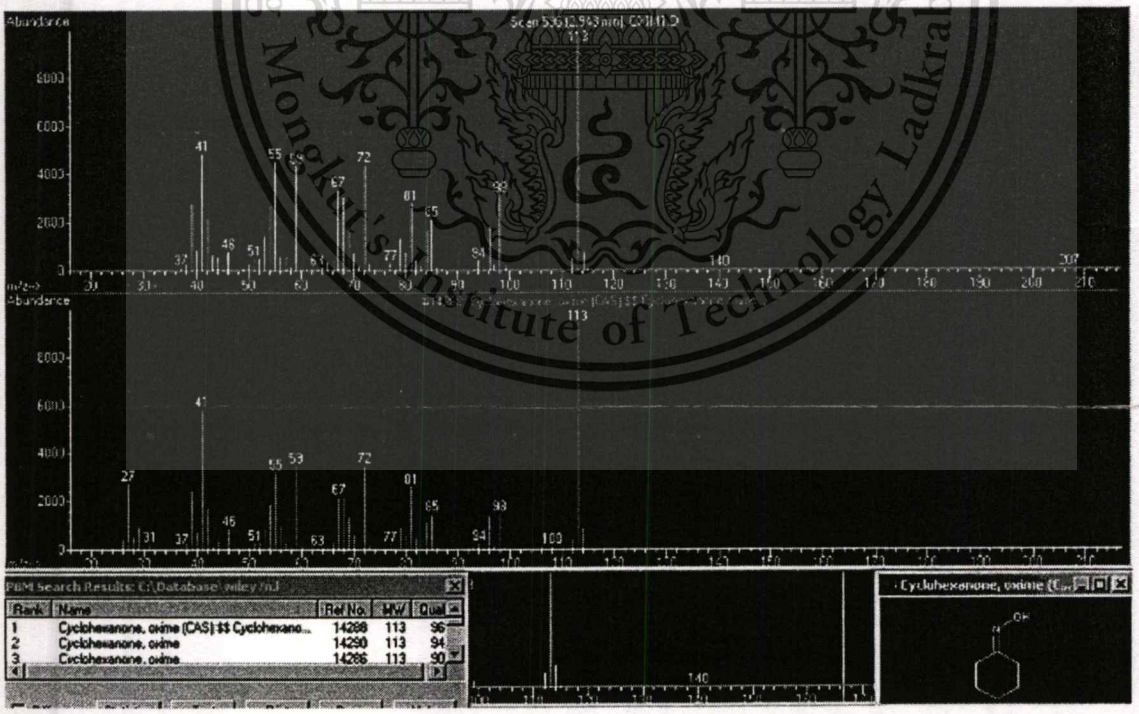

Figure F.4 Mass spectrum of cyclohexanone oxime from ammoximation reaction in acetic acid.

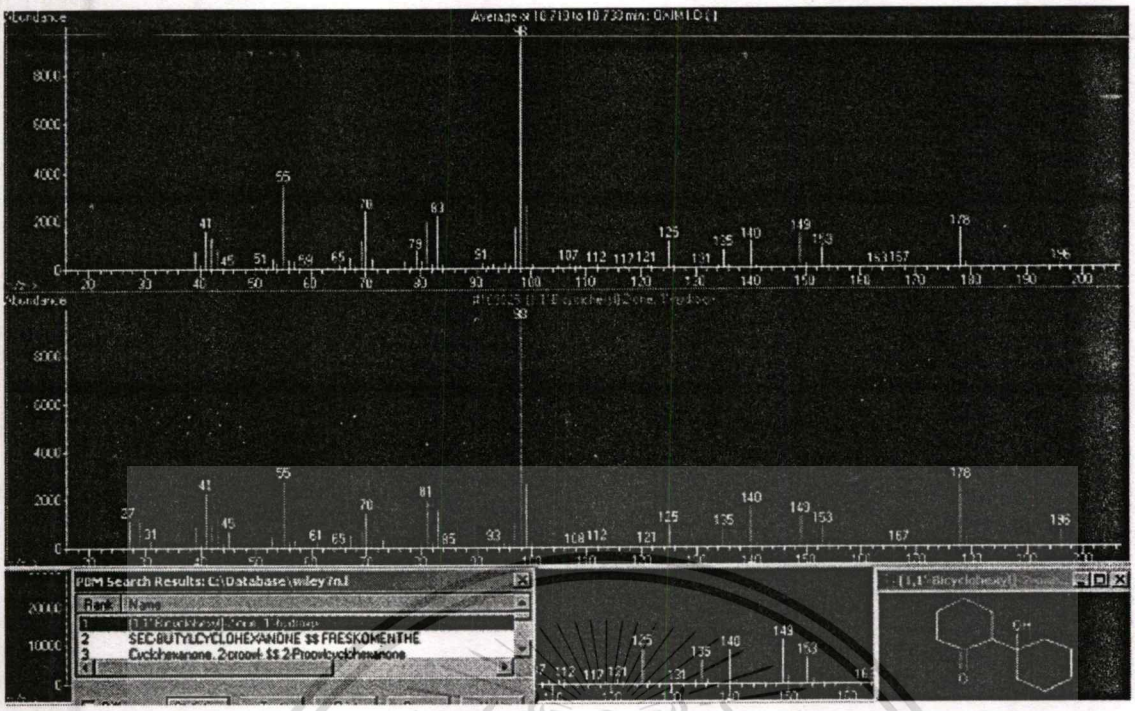

Figure F.5 Mass spectrum of aldol condensation from ammoximation reaction in acetic acid.

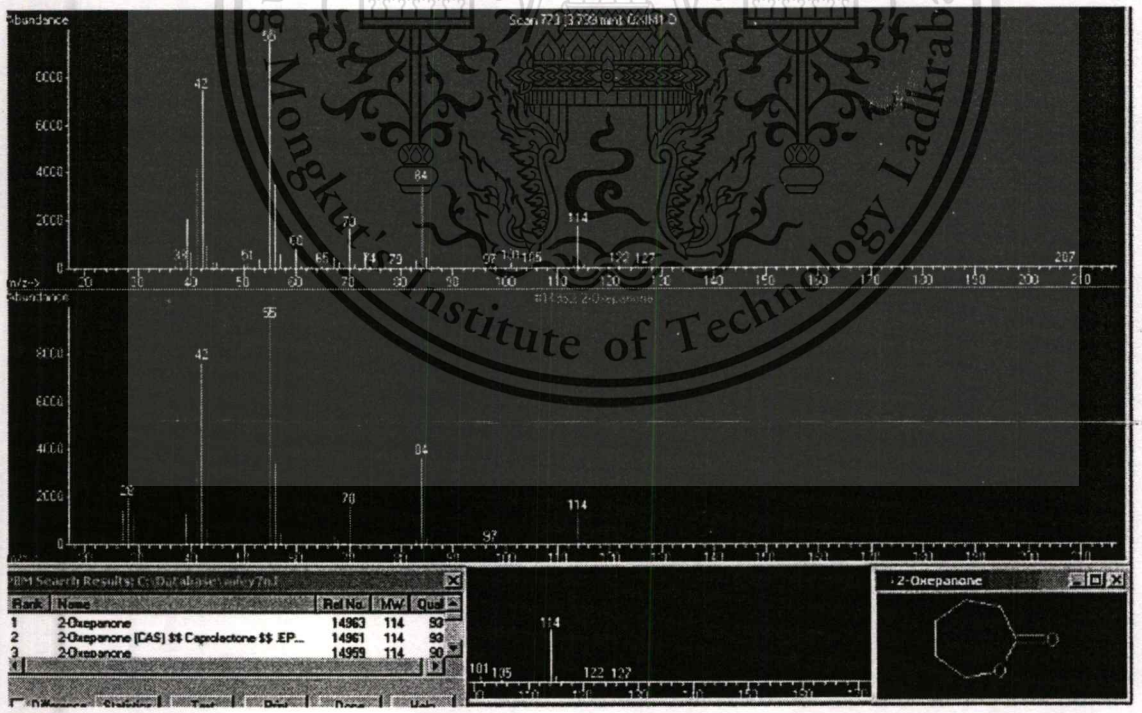

Figure F.6 Mass spectrum of caprolactone from ammoximation reaction in acetic acid.

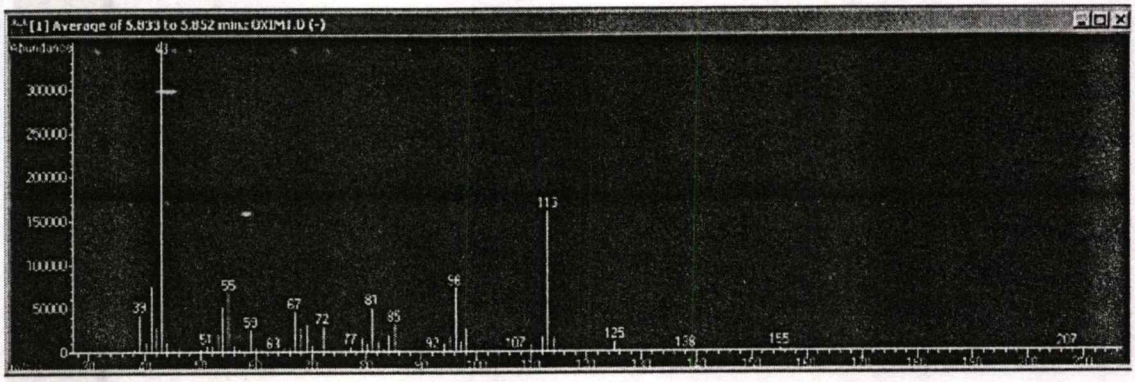

Figure F.7 Mass spectrum of acetyl cyclohexanone oxime from ammoximation reaction in acetic acid.

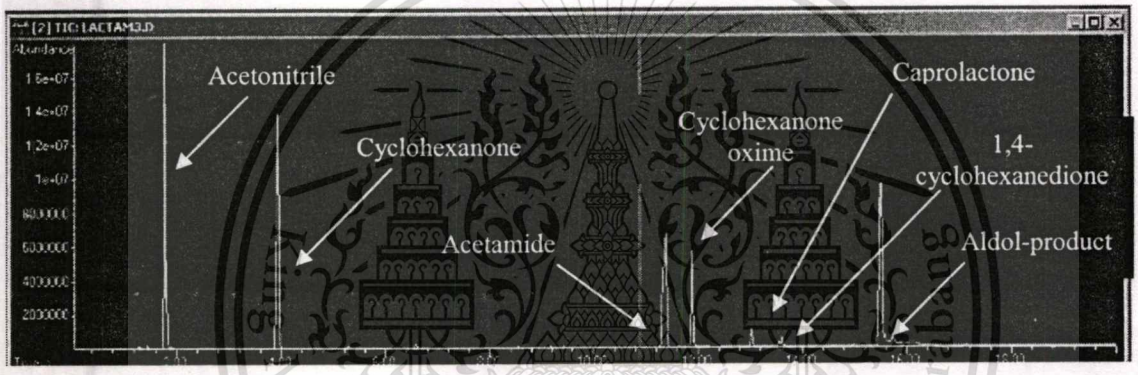

Figure F.8 Chromatogram from ammoximation reaction in acetonitrile.

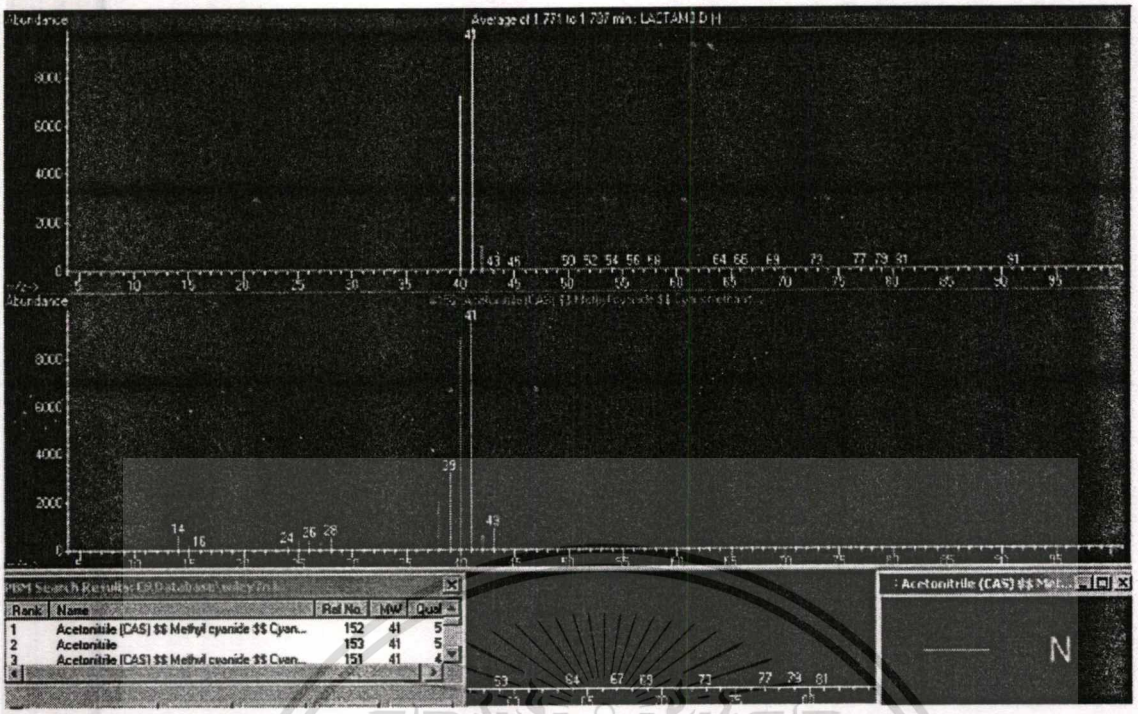

Figure F.9 Mass spectrum of acetonitrile from ammoximation reaction in acetonitrile.

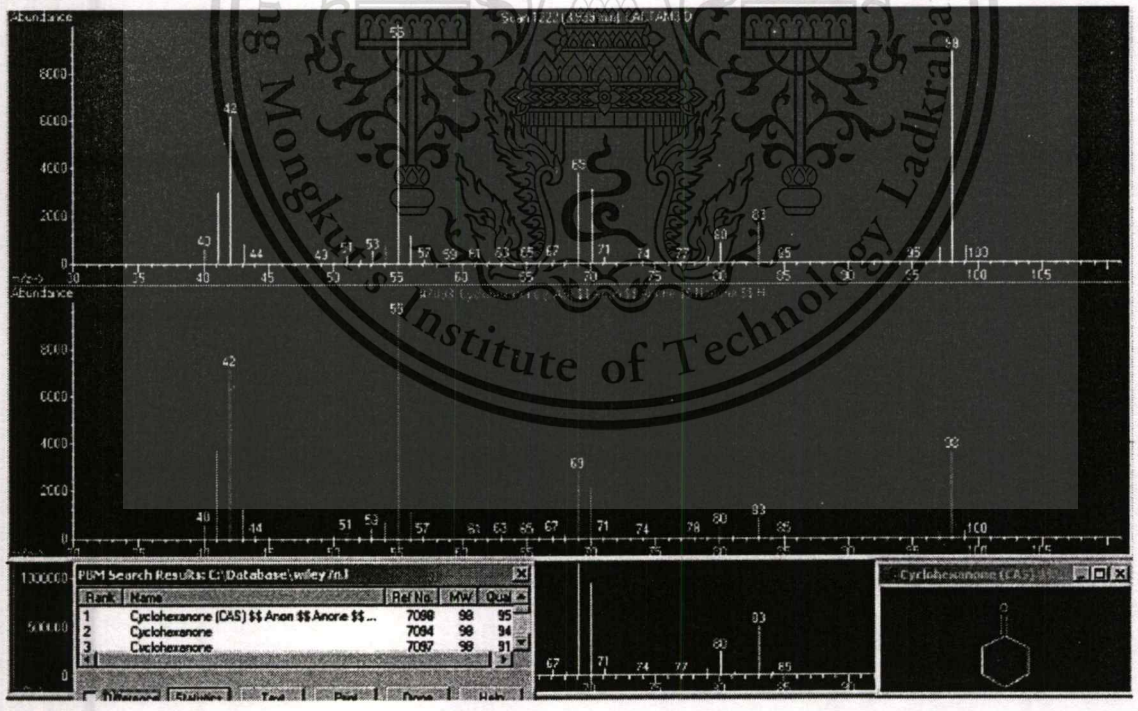

Figure F.10 Mass spectrum of cyclohexanone from ammoximation reaction in acetonitrile.

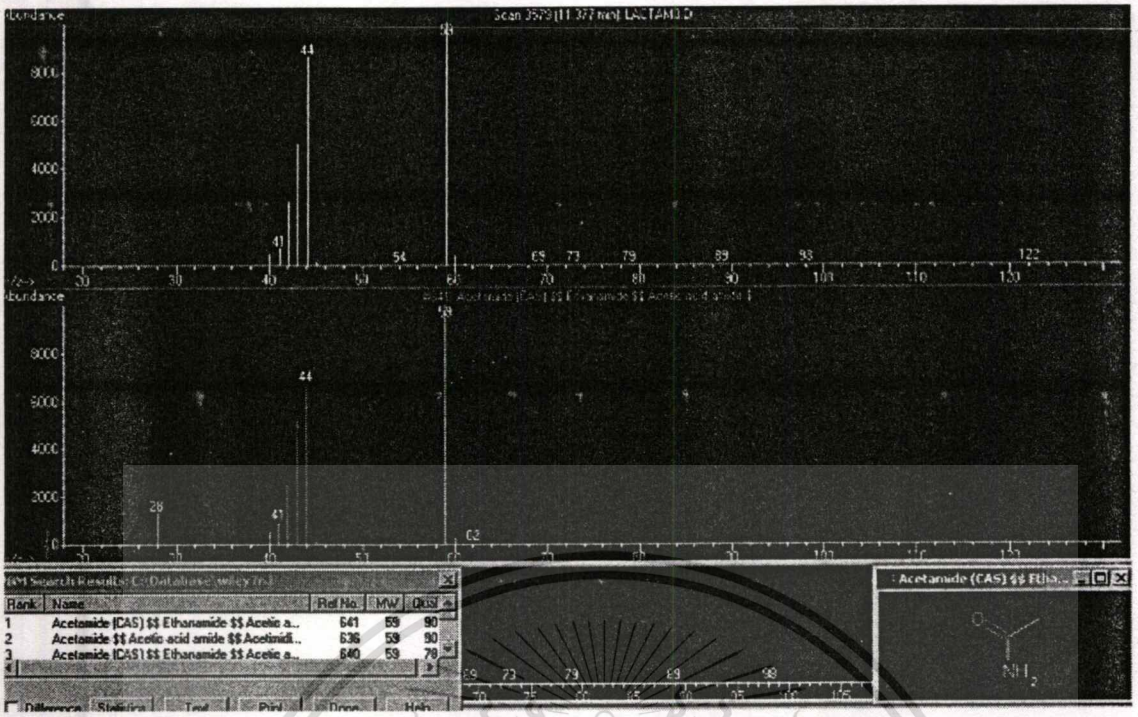

Figure F.11 Mass spectrum of acetamide from ammoximation reaction in acetonitrile.

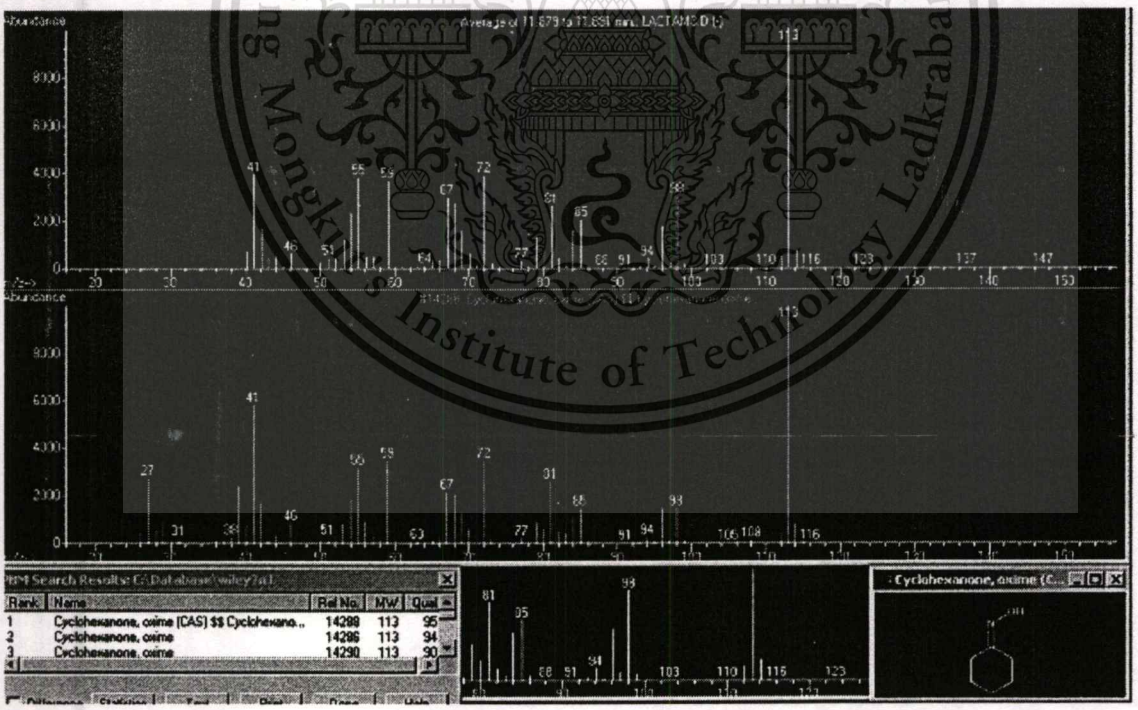

Figure F.12 Mass spectrum of cyclohexanone oxime from ammoximation reaction in acetonitrile.

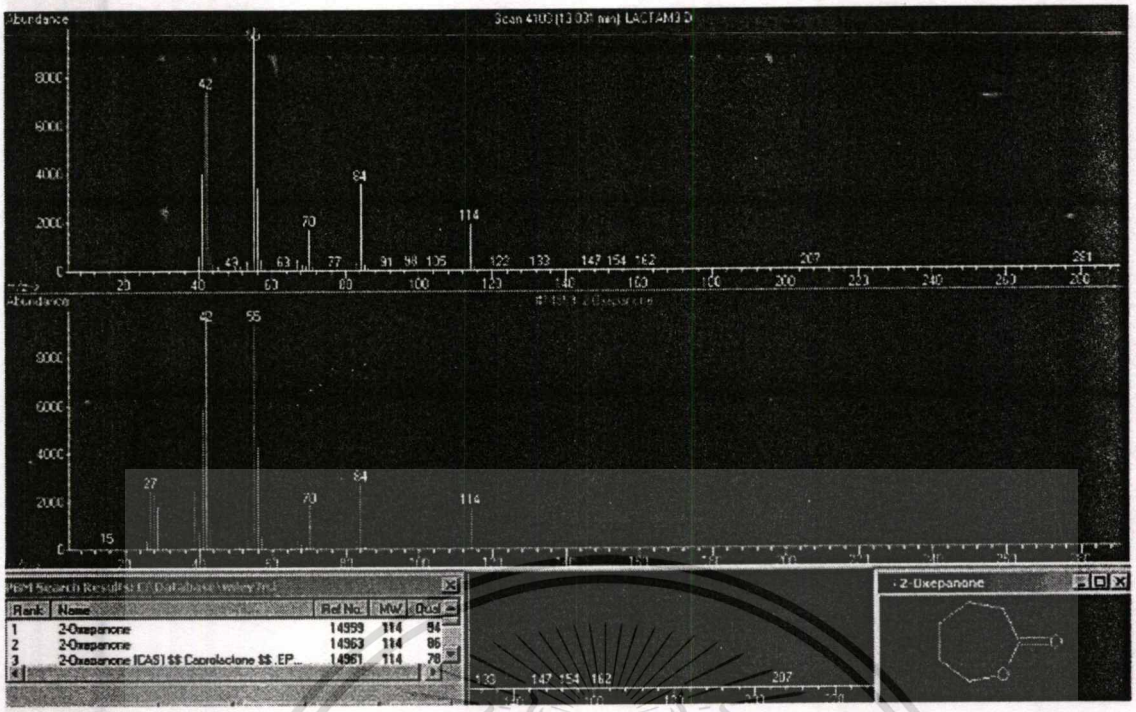

Figure F.13 Mass spectrum of caprolactone from ammoximation reaction in acetonitrile.

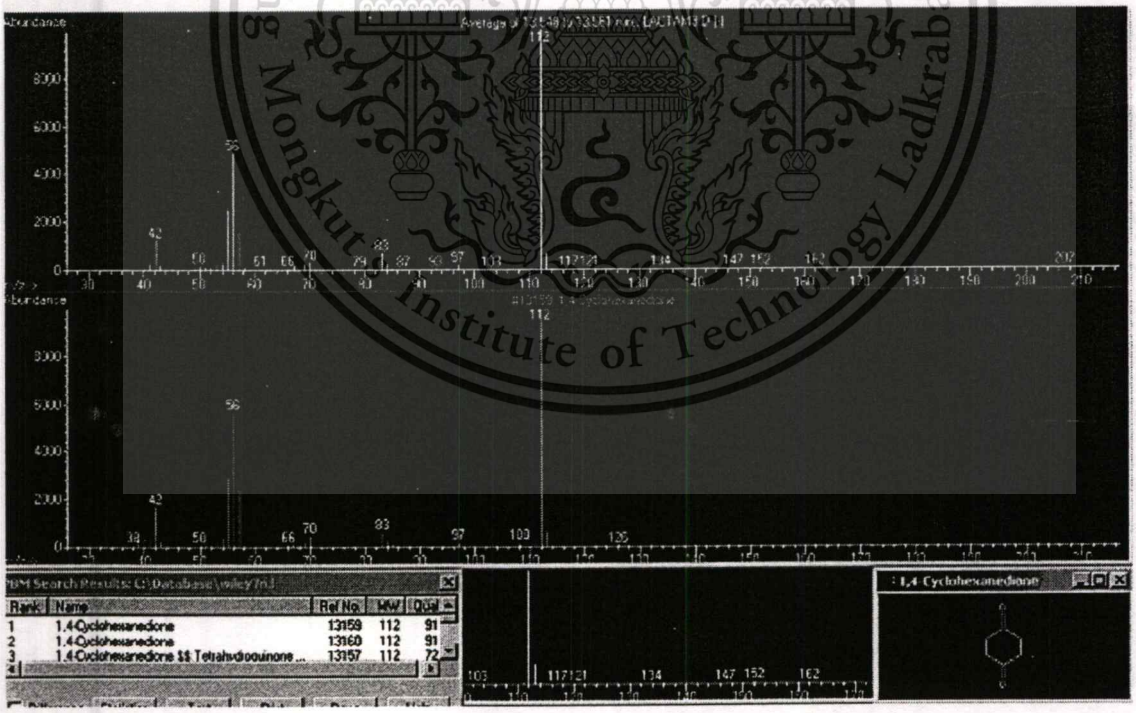

Figure F.14 Mass spectrum of 1,4-cyclohexanedione from ammoximation reaction in acetonitrile.

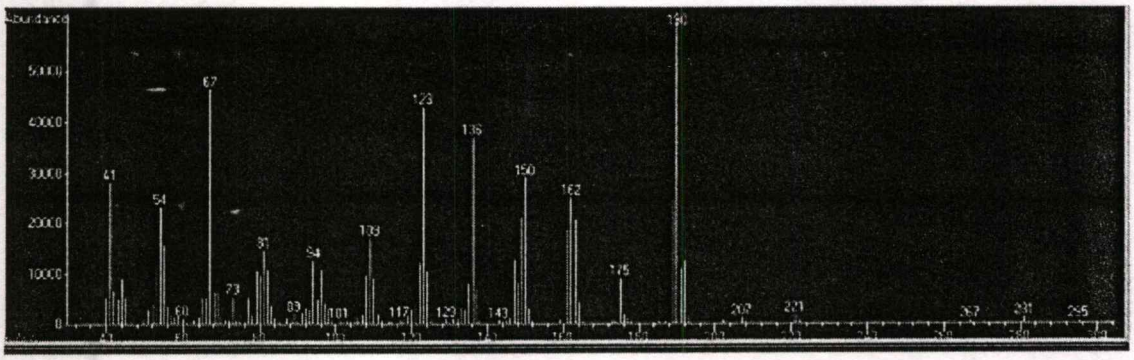

Figure F.15 Mass spectrum of aldol condensation product from ammoximation reaction in acetonitrile.

Appendix G

The Fourier Infrared Spectrum

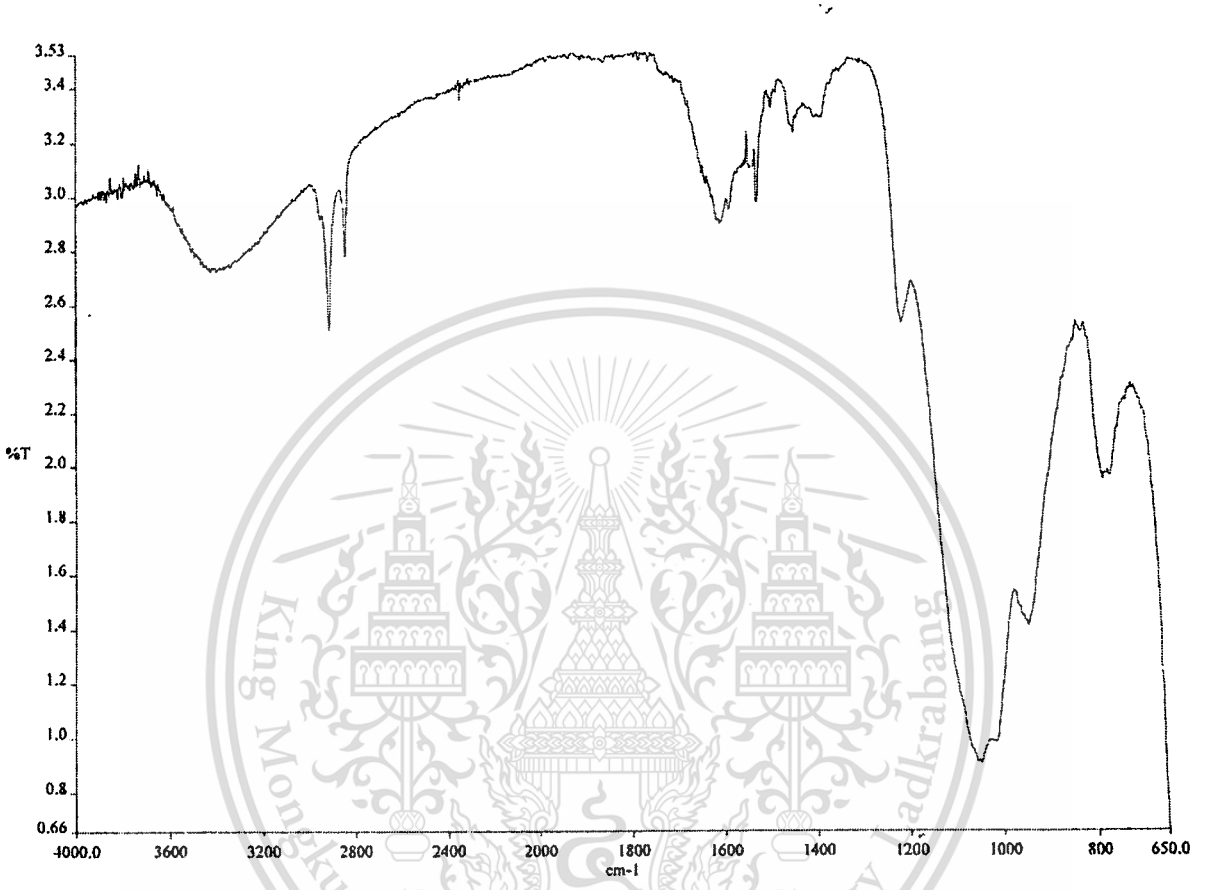

Figure G.1 Fourier IR spectrum of TS-1 before washing by sulfuric acid.

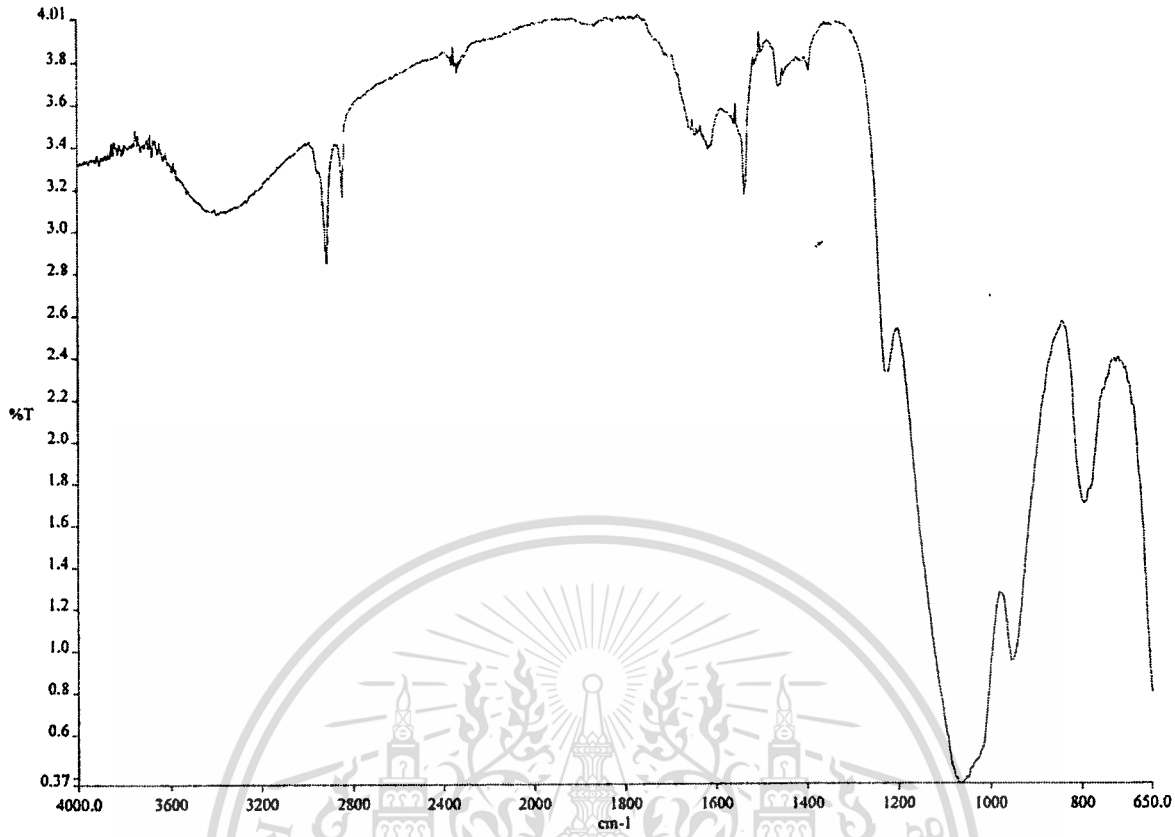

Figure G.2 Fourier IR spectrum of TS-1 after washing by sulfuric acid.

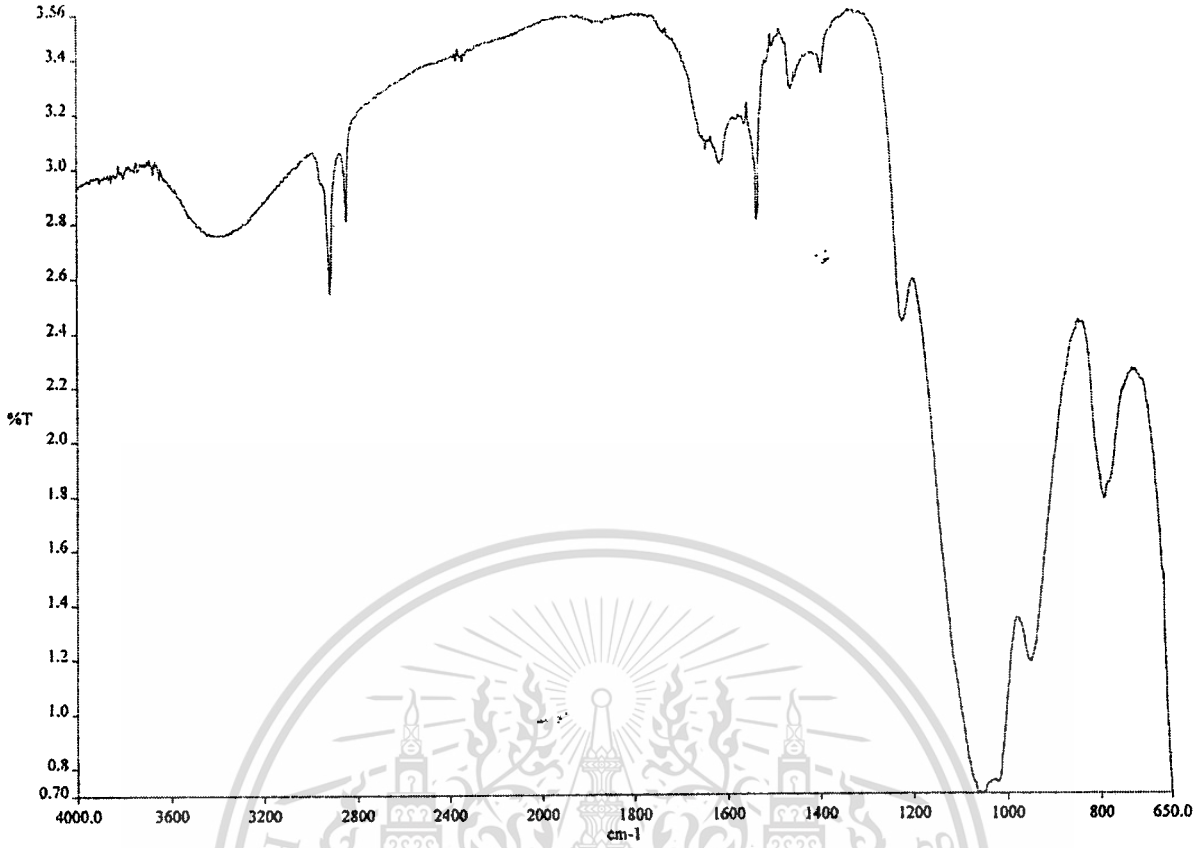

Figure G.3 Fourier IR spectrum of TS-1 after using in ammoximation reaction.

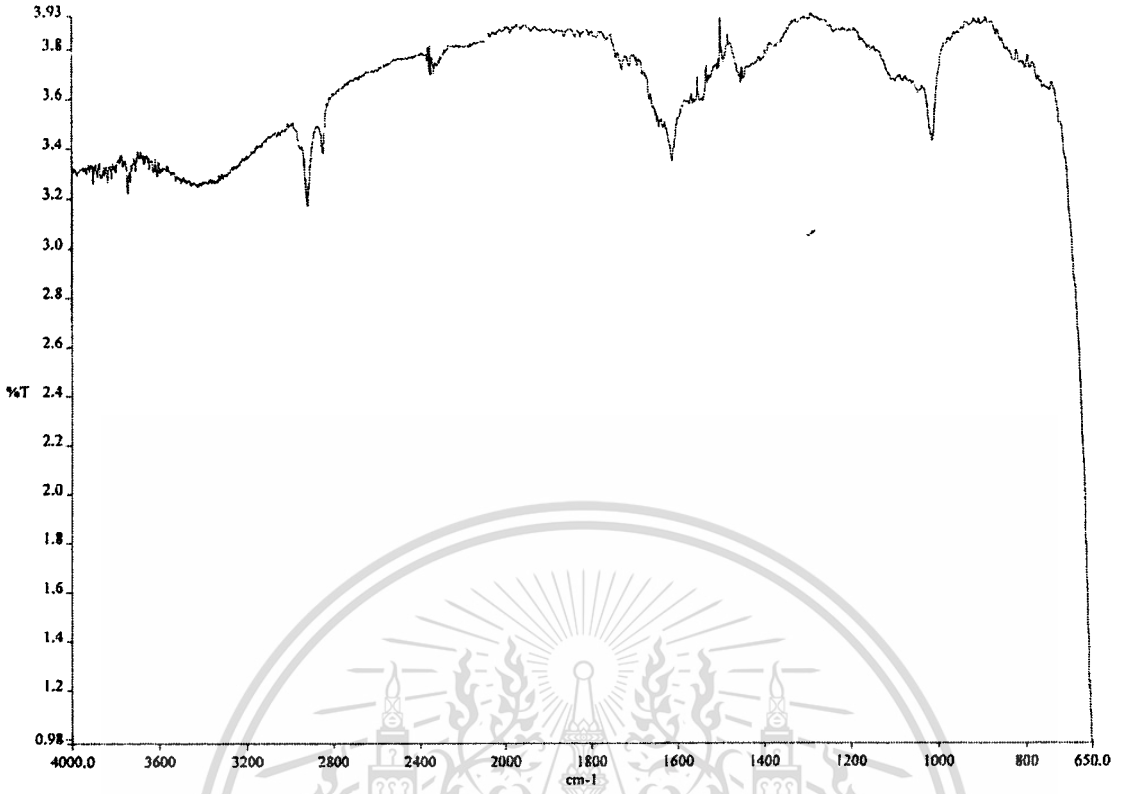

Figure G.4 Fourier IR spectrum of non sample.

Appendix H

Correction Factor Curve for Gas Chromatography Analysis and Product Calculation

Correction Factor Curve Preparation

The 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, cyclohexanone oxime and caprolactam using gas chromatography. Standard molar concentration percentage was plotted with the area percentage of the sample.

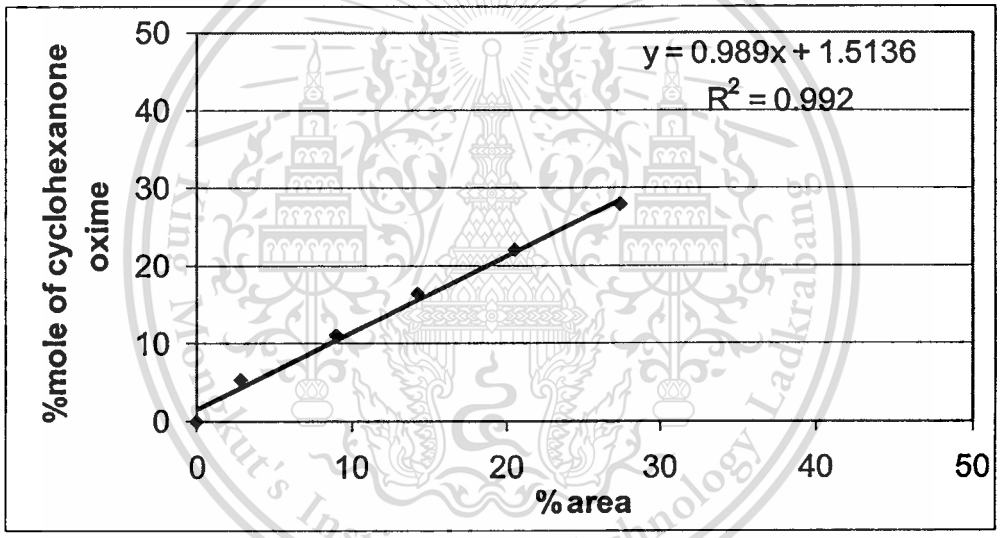

Figure H.1 Correction factor curve of cyclohexanone oxime

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

$$y = 0.989x + 1.5136$$

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

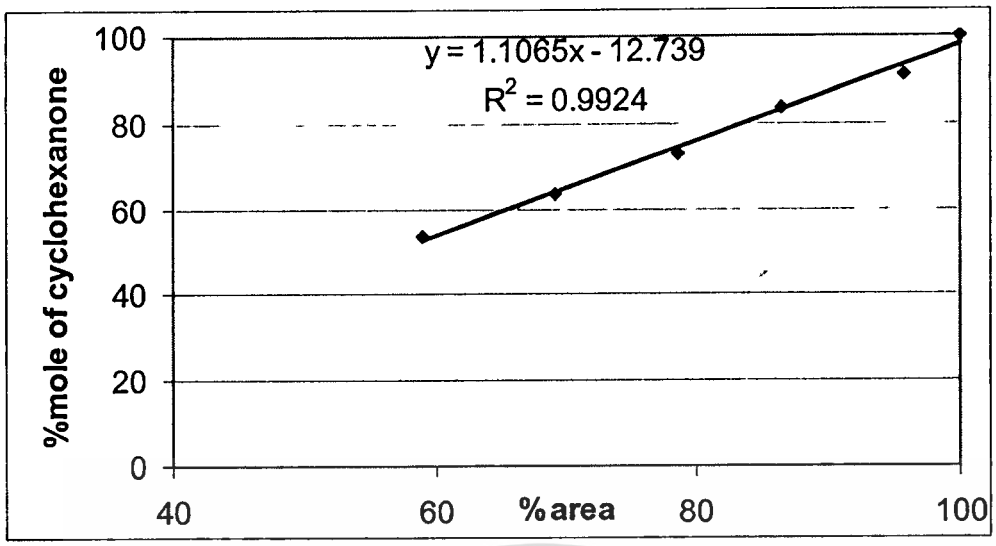

Figure H.2 Correction factor curve of cyclohexanone

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

$$y = 1.1065x - 12.739$$

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

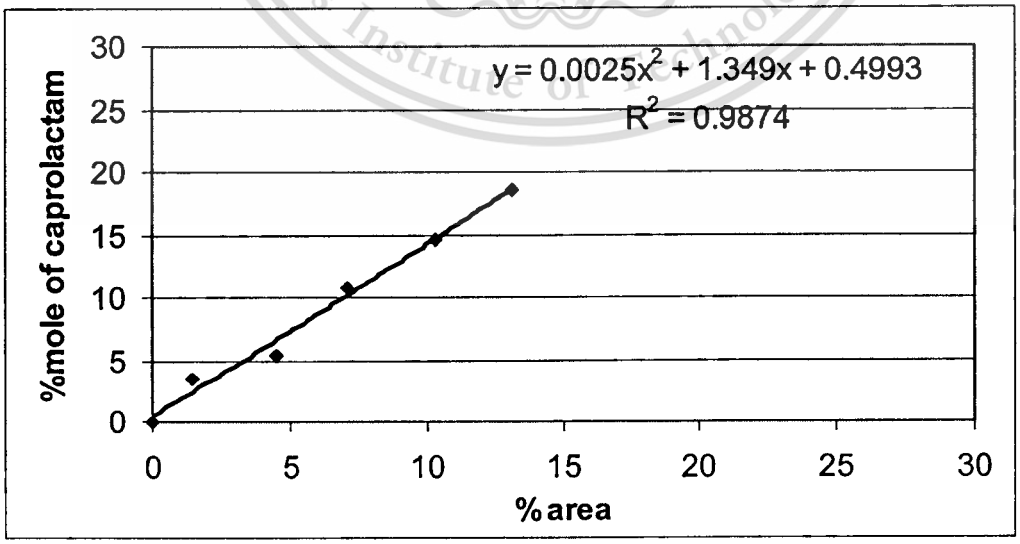

Figure H.3 Correction factor curve of caprolactam

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

$$y = 0.0025x^2 + 1.349x + 0.4993$$

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

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

Calculation of Product Concentration

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

Conversion

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

% Conversion of cyclohexanone = 100 – mole percent of remaining of cyclohexanone

Selectivity

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

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

Example

The product concentration was calculated from GC result. For example, the area percentage from the reaction using zeolite TS-1 as catalyst in acetic acid for 6 hours is shown in figure H.4.

```
Operator   :                        Detector Type: 3800 (10 Volts)
Workstation:                        Bus Address  : 44
Instrument : Varian Star #1         Sample Rate  : 10.00 Hz
Channel    : Middle = FID           Run Time     : 16.485 min

** Star Chromatography Workstation (Demo) Version 5.52 ** 05000-1A60-DAE-1BE9 **

Run Mode        : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

                                  Ret.    Time                          Width
 Peak     Peak        Result      Time    Offset      Area     Sep.     1/2     Status
  No.     Name          ()        (min)   (min)     (counts)  Code     (sec)   Codes
 ---- ------------ ---------- ------- ------- ---------- ---- ------ -------
    1 Cyclohexanon    58.1500   2.760  -0.000     813321   VV    3.0
    2 Cyclohexanon    32.3387   3.791   0.000     452308   VV    6.6
    3 Acetyl cyclo     1.6348   4.278   0.000      22865   VV    1.9
    4 Caprolactone     7.8765   9.602   0.000     110166   VV    3.3
 ---- ------------ ========== ======= ======= ========== ---- ------ -------
      Totals:        100.0000           0.000    1398660

Total Unidentified Counts :        0 counts

Detected Peaks: 221        Rejected Peaks: 217    Identified Peaks: 4

Multiplier: 1         Divisor: 1         Unidentified Peak Factor: 0

Baseline Offset: 0 microVolts

Noise (used): 1 microVolts - monitored before this run

*******************************************************************************
```

Figure H.4 Area percentage of substance remanning reaction from gas chromatography

Product with retention time 3.791 is cyclohexanone oxime, 4.278 is acetyl cyclohexanone oxime and 9.602 is caprolactone.

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

$$y = 1.1065x - 12.739$$

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

The relative molar concentration of cyclohexanone $= 1.1065(58.15) - 12.739$

$= 51.60$

The relative molar concentration of cyclohexanone oxime

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

$$y = 0.989x + 1.5136$$

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

The relative molar concentration of cyclohexanone oxime = $0.989(32.3389) + 1.5136$

= 33.49

The relative molar concentration of all by product

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

$$y = 0.0025x^2 + 1.349x + 0.4993$$

- x is the area percentage of by product in sample
- y is the relative molar concentration of by product

The relative molar concentration of acetyl cyclohexanone oxime

= $0.0025(1.6348)^2 + 1.349(1.6348) + 0.4993$

= 2.71

The relative molar concentration of caprolactone

= $0.0025(7.8765)^2 + 1.349(7.8765) + 0.4993$

= 11.28

Normalization

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

Total relative molar concentration of sample = 51.60 + 33.49 + 2.71 +11.28

= 99.08

Normalized to 100 percent

Mole percentage of cyclohexanone = (51.60 x 100)/99.08

= 52.07

Mole percentage of cyclohexanone oxime = (33.49 x 100)/99.08

= 33.80

Mole percentage of acetyl cyclohexanone oxime = (2.71 x 100)/99.08

= 2.73

Mole percentage of caprolactone = (11.28 x 100)/99.08

= 11.38

Conversion of cyclohexanone

The conversion of cyclohexanone was calculated by equation as foollowing.

% Conversion of cyclohexanone = 100 – mole percent of remaining of cyclohexanone

= 100 – 52.07

= 47. 93

Selectivity of cyclohexanone oxime

The conversion of cyclohexanone was calculated by equation as foollowing.

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

= (33.80/52.07) x 100

= 64.91

Appendix I

Result from Gas Chromatography

Table I.1 Result from ammoximation of cyclohexanone using TS-1 as catalyst in various solvents.

Solvent	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
Acetic acid	41.25	32.89	79.73
Water	11.61	2.24	19.29
Iso-butanol	2.36	2.36	100.00
Ethanol	41.14	8.65	21.02
Acetonitrile	21.45	3.51	16.36

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) 0.73 grams and hydrogen peroxide solution (30% w/w) 0.53 grams, solvent 2.4 grams, TS-1 0.04 grams, reaction time 4 hours. (Reaction Number 1-5)

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

Time (Hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
0	-	-	-
2	20.15	16.55	82.14
4	41.25	32.89	79.73
6	44.45	34.89	78.51
8	45.12	34.99	77.57
12	45.75	35.21	77.46

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) 0.73 grams and hydrogen peroxide solution (30% w/w) 0.53 grams, solvent 2.4 grams, TS-1 0.04 grams, reaction time 2, 4, 6, 8, 12 hours. (Reaction Number 1,6-9)

Table I.3 Result from the study of Ti-species.

Catalyst	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
TS-1	41.25	32.89	79.73
$Ti(Obu)_4$	18.21	9.02	49.53
Without Catalyst	19.36	9.84	50.82
Reused TS-1	45.29	36.65	81.35

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) 0.73 grams and hydrogen peroxide solution (30% w/w) 0.53 grams, solvent (acetic acid) 2.4 grams, reaction time 4 hours. (Reaction Number 1,10-12)

Table F.4 Result from the study of temperature.

Temperature (°C)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
50	35.18	26.58	75.56
60	41.25	32.89	79.73
70	28.26	22.30	78.92

Reaction condition: Temperature 50, 60 and 70 °C Cyclohexanone, ammonia solution (25%w/w) 0.73 grams and hydrogen peroxide solution (30% w/w) 0.53 grams, solvent (acetic acid) 2.4 grams, TS-1 0.04 grams, reaction time 4 hours. (Reaction Number 1,13,14)

Table I.5 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
1	0.83	0.43	50.79
2	0.82	0.41	50.00
3	0.83	0.42	50.66
4	0.83	0.42	50.78
5	0.86	0.43	50.17
6	0.86	0.43	50.46
7	0.86	0.43	50.46
8	0.87	0.44	50.74
9	0.88	0.44	50.06
10	0.87	0.44	50.91
11	0.88	0.45	50.36
12	0.88	0.45	50.36

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 25.00 g./hr. in plug flow reactor (Reaction Number 15)

Table I.6 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
1	2.23	1.39	62.35
2	2.24	1.39	62.05
3	2.22	1.38	62.16
4	2.23	1.39	62.33
5	2.25	1.40	62.22
6	2.26	1.40	61.94
7	2.26	1.41	62.38
8	2.28	1.42	62.28
9	2.27	1.41	62.11
10	2.28	1.42	62.28
11	2.30	1.43	62.17
12	2.30	1.43	62.17

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 12.50 g./hr. in plug flow reactor (Reaction Number 16)

Table I.7 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Selectivity of Cyclohexanone Oxime
1	4.13	2.74	66.48
2	4.14	2.74	66.18
3	4.12	2.73	66.26
4	4.13	2.74	66.34
5	4.15	2.75	66.26
6	4.16	2.75	66.10
7	4.16	2.76	66.34
8	4.18	2.77	66.26
9	4.17	2.76	66.18
10	4.18	2.77	66.26
11	4.19	2.78	66.34
12	4.20	2.79	66.42

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 6.25 g./hr. in plug flow reactor (Reaction Number 17)

Table I.8 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	23.23	17.42	2.94	1.93	0.94	74.98
2	22.25	16.22	3.05	2.13	0.85	72.89
3	20.78	15.10	3.04	1.95	0.69	72.66
4	20.04	15.01	2.74	1.54	0.75	74.90
5	22.50	16.41	3.15	2.08	0.86	72.93
6	23.32	17.47	3.24	1.86	0.75	74.91
7	23.64	17.42	3.41	1.92	0.89	73.68
8	23.01	17.18	3.14	1.76	0.93	74.66
9	25.31	18.86	3.52	2.06	0.87	74.51
10	24.48	18.41	3.32	1.89	0.86	75.20
11	24.74	18.59	3.28	1.98	0.89	75.14
12	24.78	18.62	3.34	1.92	0.90	75.14

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 0.5 grams, reaction time 12 hours, feed rate 25.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 19)

Table I.9 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	26.45	21.12	2.73	1.87	0.73	79.85
2	26.63	20.71	2.92	2.10	0.90	77.77
3	25.30	20.61	2.53	1.69	0.47	81.46
4	25.20	20.83	2.44	1.21	0.72	82.65
5	26.71	21.27	2.76	1.65	1.03	79.63
6	27.67	21.78	3.12	2.05	0.72	78.71
7	27.26	22.54	2.56	1.58	0.58	82.68
8	28.39	22.74	3.24	1.74	0.67	80.09
9	29.06	23.30	3.14	1.85	0.77	80.17
10	28.61	23.02	3.32	1.62	0.65	80.46
11	28.89	23.38	3.20	1.58	0.73	80.29
12	28.92	23.34	3.31	1.76	0.51	80.70

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1.0 grams, reaction time 12 hours, feed rate 25.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 18)

Table I.10 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	35.72	29.52	3.13	2.02	1.05	82.64
2	34.52	28.64	3.16	1.96	0.76	82.96
3	35.15	28.32	3.62	2.17	1.04	80.56
4	35.84	28.84	3.68	2.23	1.09	80.46
5	34.65	28.54	3.15	1.89	1.07	82.36
6	35.22	28.01	3.76	2.32	1.13	79.52
7	35.62	28.64	3.57	2.27	1.14	79.75
8	35.91	28.74	3.82	2.16	1.19	80.03
9	36.04	29.94	3.26	1.94	0.90	83.07
10	36.22	30.12	3.28	1.84	0.98	83.15
11	36.78	30.47	3.27	1.96	1.08	82.82
12	36.99	30.97	3.28	1.82	0.92	83.72

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 2.0 grams, reaction time 12 hours, feed rate 25.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 20)

Table I.11 Result from study of hydrogen peroxide concentration in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	26.45	21.12	2.73	1.87	0.73	79.85
2	26.63	20.71	2.92	2.10	0.90	77.77
3	25.30	20.61	2.53	1.69	0.47	81.46
4	25.20	20.83	2.44	1.21	0.72	82.65
5	26.71	21.27	2.76	1.65	1.03	79.63
6	27.67	21.78	3.12	2.05	0.72	78.71
7	27.26	22.54	2.56	1.58	0.58	82.68
8	28.39	22.74	3.24	1.74	0.67	80.09
9	29.06	23.30	3.14	1.85	0.77	80.17
10	28.61	23.02	3.32	1.62	0.65	80.46
11	28.89	23.38	3.20	1.58	0.73	80.29
12	28.92	23.34	3.31	1.76	0.51	80.70

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, reaction time 12 hours, TS-1 1 gram, feed rate 25.00 g./hr. in 50 ml stirred tank reactor, ratio of Cyclohexanone/Hydrogen peroxide : 1/1.2 (Reaction Number 18)

Table I.12 Result from study of hydrogen peroxide concentration in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	24.45	21.12	2.13	0.84	0.36	86.38
2	24.62	21.17	2.25	0.86	0.34	85.98
3	23.30	19.67	2.08	0.92	0.63	84.42
4	23.20	19.72	2.14	1.03	0.31	85.00
5	25.71	21.86	2.19	1.12	0.54	85.02
6	26.07	21.78	2.46	1.34	0.50	83.54
7	26.62	22.54	2.18	1.28	0.62	84.67
8	26.98	22.74	2.38	1.19	0.67	84.28
9	27.06	23.30	2.07	1.23	0.46	86.10
10	28.61	24.51	2.26	1.28	0.56	85.66
11	28.89	24.78	2.31	1.58	0.53	85.77
12	28.92	24.94	2.29	1.24	0.45	86.23

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, reaction time 12 hours, TS-1 1 gram, feed rate 25.00 g./hr. in 50 ml stirred tank reactor, ratio of Cyclohexanone/Hydrogen peroxide : 1/0.6 (Reaction Number 22)

Table I.13 Result from study of hydrogen peroxide concentration in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	23.23	20.22	1.86	0.92	0.23	87.04
2	22.25	19.62	1.62	0.82	0.19	88.17
3	20.78	18.60	1.42	0.66	0.10	89.50
4	20.44	18.46	1.35	0.52	0.11	90.31
5	22.50	19.91	1.56	0.84	0.19	88.48
6	23.32	20.77	1.46	0.91	0.13	89.06
7	23.64	20.82	1.65	0.95	0.22	88.07
8	23.01	20.38	1.59	0.96	0.08	88.57
9	24.31	21.75	1.64	0.81	0.11	89.46
10	24.48	21.61	1.68	0.94	0.25	88.27
11	24.74	21.89	1.74	0.87	0.24	88.48
12	24.78	21.92	1.78	0.95	0.13	88.45

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, reaction time 12 hours, TS-1 1 gram, feed rate 25.00 g./hr. in 50 ml stirred tank reactor, ratio of Cyclohexanone/Hydrogen peroxide : 1/0.4 (Reaction Number 28)

Table I.14 Result from study of reaction temperature in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	20.00	14.87	2.54	1.92	0.67	74.35
2	20.06	14.82	2.62	1.89	0.73	73.87
3	20.72	15.64	2.42	1.89	0.77	75.48
4	20.71	15.84	2.34	1.62	0.91	76.48
5	20.50	15.37	2.67	1.75	0.71	74.97
6	20.75	15.25	2.78	1.86	0.86	73.49
7	21.47	15.80	2.86	1.88	0.93	73.59
8	21.03	15.55	2.84	1.94	0.70	73.94
9	21.14	15.59	2.86	1.95	0.74	73.74
10	21.01	15.43	2.90	1.72	0.96	73.44
11	21.60	16.01	2.85	1.88	0.86	74.12
12	21.63	15.78	2.95	1.96	0.94	72.95

Reaction condition: Temperature 50 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, reaction time 12 hours, ratio of Cyclohexanone/Hydrogen peroxide : 1/0.6, TS-1 1 gram, feed rate 25.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 23)

Table I.15 Result from study of reaction temperature in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	16.32	11.80	2.21	1.42	0.89	72.30
2	16.54	11.76	2.16	1.92	0.70	71.10
3	16.92	11.89	2.32	1.88	0.83	70.29
4	17.20	12.21	2.32	1.92	0.75	70.98
5	17.09	12.01	2.72	1.67	0.69	70.27
6	17.25	12.34	2.72	1.52	0.67	71.30
7	17.31	12.41	2.68	1.67	0.55	71.69
8	17.36	12.46	2.58	1.49	0.83	71.77
9	17.65	12.79	2.72	1.46	0.68	72.46
10	17.59	12.74	2.71	1.53	0.61	72.42
11	17.82	12.59	2.86	1.86	0.51	70.65
12	17.74	12.68	2.76	1.68	0.62	71.47

Reaction condition: Temperature 70 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, reaction time 12 hours, ratio of Cyclohexanone/Hydrogen peroxide : 1/0.6, TS-1 1 gram, feed rate 25.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 24)

Table I.16 Result from study of retention volume in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	-	-	-	-	-	-
2	21.25	15.22	3.05	2.13	0.85	71.62
3	19.78	14.10	3.04	1.95	0.69	71.28
4	19.04	14.01	2.74	1.54	0.75	73.58
5	21.50	15.41	3.15	2.08	0.86	71.67
6	22.32	16.47	3.24	1.86	0.75	73.79
7	22.64	16.42	3.41	1.92	0.89	72.52
8	22.01	16.18	3.14	1.76	0.93	73.51
9	24.31	17.86	3.52	2.06	0.87	73.46
10	23.48	17.41	3.32	1.89	0.86	74.14
11	23.74	17.59	3.28	1.98	0.89	74.09
12	23.78	17.62	3.34	1.92	0.90	74.09

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, reaction time 12 hours, TS-1 1 gram, feed rate 25.00 g./hr. in 100 ml stirred tank reactor (Reaction Number 21)

Table I.17 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	-	-	-	-	-	-
2	36.66	32.55	2.72	1.10	0.29	88.78
3	36.47	32.28	2.65	1.13	0.41	88.51
4	36.04	31.79	2.78	1.08	0.39	88.20
5	35.56	31.35	2.63	1.16	0.42	88.16
6	36.02	31.27	2.97	1.38	0.40	86.81
7	36.50	31.40	3.02	1.46	0.62	86.02
8	35.71	31.70	2.14	1.35	0.51	88.77
9	36.41	31.93	2.68	1.39	0.41	87.69
10	36.02	31.55	2.59	1.29	0.59	87.59
11	35.79	31.59	2.64	1.16	0.40	88.26
12	35.78	31.46	2.49	1.34	0.49	87.92

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 16.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 27)

Table I.18 Result from ammoximation of cyclohexanone using TS-1 as catalyst in system of acetic acid in continuous process.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	-	-	-	-	-	-
2	42.78	38.60	2.89	1.03	0.26	90.22
3	42.78	38.50	2.96	1.12	0.20	89.99
4	42.05	37.74	3.02	0.98	0.31	89.75
5	41.38	37.25	2.86	1.01	0.26	90.01
6	40.83	36.41	3.13	0.96	0.33	89.17
7	40.98	36.28	3.24	1.14	0.32	88.53
8	42.71	38.67	2.65	1.16	0.23	90.54
9	42.25	37.85	2.81	1.25	0.34	89.58
10	41.89	37.39	2.69	1.39	0.42	89.25
11	41.57	37.45	2.68	1.23	0.21	90.08
12	41.55	37.30	2.68	1.28	0.29	89.77

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 7.00 g./hr. in 50 ml stirred tank reactor (Reaction Number 26)

Table I.19 Result from study of leaching of Ti-framework.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	24.45	21.12	2.13	0.84	0.36	86.38
2	24.62	21.17	2.25	0.86	0.34	85.98
3	23.30	19.67	2.08	0.92	0.63	84.42
4	23.20	19.72	2.14	1.03	0.31	85.00
5	25.71	21.86	2.19	1.12	0.54	85.02
6	26.07	21.78	2.46	1.34	0.50	83.54
7	26.62	22.54	2.18	1.28	0.62	84.67
8	26.98	22.74	2.38	1.19	0.67	84.28
9	27.06	23.30	2.07	1.23	0.46	86.10
10	28.61	24.51	2.26	1.28	0.56	85.66
11	28.89	24.78	2.31	1.58	0.53	85.77
12	28.92	24.94	2.29	1.24	0.45	86.23

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 25 g./hr. in 50 ml stirred tank reactor, calcining temperature 550 °C (Reaction Number 22)

Table I.20 Result from study of leaching of Ti-framework.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	24.67	21.18	2.19	0.91	0.39	85.85
2	24.59	21.08	2.23	0.87	0.41	85.72
3	24.21	20.96	2.02	0.91	0.32	86.57
4	24.72	21.14	2.24	0.94	0.39	85.51
5	25.25	21.36	2.24	1.09	0.56	84.59
6	26.17	22.16	2.38	1.14	0.49	84.67
7	26.38	22.54	2.23	1.17	0.44	85.44
8	26.89	22.69	2.34	1.21	0.65	84.38
9	26.97	23.28	2.11	1.16	0.32	86.31
10	28.48	24.51	2.19	1.17	0.61	86.00
11	28.94	24.85	2.25	1.26	0.57	85.86
12	29.63	25.66	2.29	1.24	0.45	86.60

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 25 g./hr. in 50 ml stirred tank reactor, calcining temperature 575 °C (Reaction Number 30)

Table I.21 Result from study of leaching of Ti-framework.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	24.96	21.52	2.24	0.75	0.45	86.21
2	24.59	21.16	2.15	0.96	0.32	86.05
3	23.30	19.67	2.08	0.92	0.63	84.42
4	24.72	21.14	2.24	0.94	0.39	85.51
5	25.71	21.86	2.19	1.12	0.54	85.02
6	26.07	21.78	2.46	1.34	0.50	83.54
7	26.62	22.54	2.18	1.28	0.62	84.67
8	26.98	22.74	2.38	1.19	0.67	84.28
9	27.06	23.30	2.07	1.23	0.46	86.10
10	28.61	24.51	2.26	1.28	0.56	85.66
11	28.89	24.78	2.31	1.58	0.53	85.77
12	29.72	25.75	2.29	1.24	0.45	86.64

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 12 hours, feed rate 25 g./hr. in 50 ml stirred tank reactor, calcining temperature 600 °C (Reaction Number 31)

Table I.22 Result from study of catalytic lifetime.

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
1	-	-	-	-	-	-
2	36.66	32.55	2.72	1.10	0.29	88.78
3	36.47	32.28	2.65	1.13	0.41	88.51
4	36.04	31.79	2.78	1.08	0.39	88.20
5	35.56	31.35	2.63	1.16	0.42	88.16
6	36.02	31.27	2.97	1.38	0.40	86.81
7	36.50	31.40	3.02	1.46	0.62	86.02
8	35.71	31.70	2.14	1.35	0.51	88.77
10	36.41	31.93	2.68	1.39	0.41	87.69
12	36.02	31.55	2.59	1.29	0.59	87.59
14	35.79	31.59	2.64	1.16	0.40	88.26
16	35.78	31.46	2.49	1.34	0.49	87.92

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 40 hours, feed rate 25 g./hr. in 50 ml stirred tank reactor (Reaction Number 29)

Time (hour)	% Conversion of Cyclohexanone	% Yield of Cyclohexanone Oxime	% Yield of Caprolactone	% Yield of Acetyl Cyclohexanone Oxime	% Yield of Aldol Condensation	% Selectivity of Cyclohexanone Oxime
18	36.64	32.53	2.69	1.06	0.36	88.78
22	36.76	32.36	2.58	1.21	0.61	88.03
22	36.86	32.19	2.96	1.26	0.45	87.33
24	37.03	32.78	2.93	1.04	0.28	88.52
26	36.83	32.47	2.97	1.18	0.21	88.16
28	37.23	32.60	3.12	1.14	0.37	87.56
30	37.62	32.73	3.01	1.32	0.56	87.00
32	37.41	32.92	2.98	1.19	0.32	87.99
34	37.52	32.75	3.15	1.06	0.56	87.28
36	37.79	33.09	3.14	1.14	0.42	87.56
38	38.16	33.46	2.69	1.36	0.38	87.68
40	37.86	33.12	2.76	1.41	0.57	87.48

Reaction condition: Temperature 60 °C, Cyclohexanone, ammonia solution (25%w/w) and hydrogen peroxide solution (30% w/w) , acetic acid as solvent, TS-1 1 gram, reaction time 40 hours, feed rate 25 g./hr. in 50 ml stirred tank reactor (Reaction Number 29)

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