BAEYER-VILLIGER OXIDATION OF CYCLOHEXANONE USING Ti-CONTAINING ZEOLITE CATALYSTS

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บทคัดย่อ

วิทยานิพนธ์เล่มนี้เป็นการศึกษาปฏิกิริยาเบเยอร์-วีลิเกอร์ออกซิเดชันของไซโคลเฮกซาโนนเพื่อสังเคราะห์คาร์โปรแลคโทนโดยใช้สารละลายไฮโดรเจนเปอร์ออกไซด์ที่มีความเข้มข้นต่ำเป็นตัวออกซิไดส์แทนสารที่เป็นพิษต่อสิ่งแวดล้อมประเภทกรดเปอร์คาร์บอกซิลิก ไททาเนียมซีโอไลต์ถูกนำมาใช้เป็นตัวเร่งปฏิกิริยาในสภาวะที่ไม่รุนแรง โดยทำการทดสอบปฏิกิริยาในชุดทดสอบปฏิกิริยาขนาดเล็กที่อุณหภูมิ 40-70 องศาเซลเซียส อัตราส่วนโดยโมลของสารตั้งต้นที่ใช้ในการศึกษาเป็นดังนี้ ตัวทำละลาย: ไฮโดรเจนเปอร์ออกไซด์: คีโตน = 8.36: 1.2: 1 อัตราส่วนโดยน้ำหนักของคีโตน: ตัวเร่งปฏิกิริยาเท่ากับ 9.5: 1 จากการศึกษาพบว่า ความสามารถในการเกิดปฏิกิริยาดีขึ้นเมื่อใช้ตัวเร่งปฏิกิริยาไททาเนียมบีต้าซีโอไลต์ ตัวทำละลายเป็นปัจจัยสำคัญต่อความสามารถในการเกิดปฏิกิริยาโดย กรดแอซิติก > อะซิโตไนไตร์ล > น้ำ ทั้งนี้ตัวออกซิไดส์ที่ว่องไวที่เกิดขึ้นในตัวทำละลายข้างต้นคือ กรดเปอร์แอซิติก กรดเปอร์ออกซีคาร์บอกซิอิมิดิก และไฮโดรเจนเปอร์ออกไซด์ ตามลำดับ ความเฉพาะเจาะจงของการเกิดคาร์โปรแลคโทนลดลงเมื่อเกิดปฏิกิริยาต่อเนื่องของคาร์โปรแลคโทนในตัวทำละลายที่สามารถแตกตัวให้โปรตอนได้ และการใช้อะซิโตไนไตร์ลเป็นตัวทำละลายให้ความเฉพาะเจาะจงของการเกิดคาร์โปรแลคโทนเหมาะสมที่สุด ไททาเนียมที่มีโครงสร้างแบบทรงเหลี่ยมสี่หน้าเท่านั้นที่ช่วยให้เกิดตัวออกซิไดส์ที่ว่องไวต่อปฏิกิริยาและปฏิกิริยานี้เกิดขึ้นภายในรูพรุนของตัวเร่งปฏิกิริยา เมื่อมีน้ำในปฏิกิริยามากขึ้น ความสามารถในการเกิดปฏิกิริยาจะลดลงเนื่องด้วยเกิดการแข่งขันของดูดซับของน้ำภายในรูพรุนของตัวเร่งปฏิกิริยาเพิ่มมากขึ้น

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ABSTRACT

In this thesis, Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone was studied using diluted aqueous hydrogen peroxide as oxidant, instead of non-environmental friendly peroxycarboxylic acid. Ti-containing zeolites were tested as catalysts under mild condition. The reaction was studied in micro-batch reactors at 40-70 $^{\circ}$C. Typically, the molar ratio of reactant was used as follows; solvent: H_2O_2: ketone = 8.36: 1.2: 1. The weight ratio of ketone: catalyst was 9.5: 1. It was found that the reaction activity was promoted mainly by Ti-beta zeolite catalyst. The solvents play important role in reactivity in the order of acetic acid > acetonitrile > water. The active oxidizing species generated in solvents: peracetic acid, peroxycarboximidic acid and hydrogen peroxide, respectively. Selectivity of ε-caprolactone was relatively low due to the series reaction of ε-caprolactone in the presence of protic solvent. An optimum selectivity can be obtained from the reaction using acetonitrile as a solvent. Only the tetrahedral coordinated of titanium site could be promoted the active oxidizing species and the reaction might takes place within the catalyst pore. When the reaction system was modified into hydrophilic character, the reaction activity was slightly low due to the highly competitive adsorption of water in the catalyst pores.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

The century-old Baeyer-Villiger reaction, in which ketones are oxidized to esters or lactones [1], is used to produce various compounds needed in everything from plastics manufacture to pharmaceutical syntheses. In particular, ε-caprolactone is an intermediate for producing poly ε-caprolactone which is a biodegradable polymer. Traditionally, Baeyer-Villiger reaction is carried out using peracid as oxidants, such as peracetic acid, perbenzoic acid, *m*-chloroperbenzoic acid (*m*-CPBA), etc. However, the preparation of these reagents requires highly concentrated hydrogen peroxide, which has been removed from commercial recently because of it danger involved in transportation and handling.

Over the past decades, many hetrogeneous catalysts such as, zeolite [2-6], hydrotalcite [7] and Pt supported polymer [8] were reported to be active for Beayer-Villiger oxidation of cyclic ketone with "aqueous hydrogen peroxide". It is an ideal oxidant for organic substrates, because it is cheap, mild and environmentally benign reagent with high contents of active oxygen. Additionally, it produces only water as a by-product. However, the selectivity of lactone is too low in the presence of acid catalytic system.

Ti-containing zeolites are highly efficient catalysts for the selective oxidation of large number of organic substrates, such as alkanes, alkenes, alcohols, aromatics and phenol [9-17]. The reaction carried out under mild reaction conditions using H_2O_2 as oxidant. TS-1 is found to be the best catalyst for the oxidation of small molecules [9-10], but Ti-Beta is more active for the oxidation of bulkier substrates [11-12], such as cyclic and branched molecules.

Solvents also play important roles for liquid phase oxidation. They do not only modify the homogenity of the system [3], but also largely influence on side reactions which produce by-products [11, 13]. Protic solvents give more activity, but the stability of product was reduced by the hydrolysis reaction. In addition, solvent may even become promoter in some catalytic cycles. A recent report showed that the oxidation of cyclohexane to cyclohexanone was enhanced when acetic acid was used as a solvent [18]. It was suggested that peracetic acid, which was locally generated by the active sites within the pore of Ti-containing zeolite catalysts, facilitated stability and activity of the active oxidising species. Since $\mathcal{E}$-caprolactone can be produced by peracetic acid, it is worth investigating the Baeyer-Villiger oxidation of cyclohexanone over Ti-containing zeolite catalysts, in which carboxylic peroxy acids is replaced by aqueous hydrogen peroxide. In addition, acetonitrile is reported to promote oxidation by H_2O_2 [7, 19]. Accordingly in this thesis, the effect of Ti-containing zeolite catalysts and the reaction conditions on the activity and selectivity in the production of $\mathcal{E}$-caprolactone using aqueous hydrogen peroxide will be highlighted.

1.2 Objectives

1.2.1 To understand the effect of Ti-containing zeolite catalysts, solvent system, feed composition and resident time on the activity and selectivity for the production of $\mathcal{E}$-caprolactone

1.2.2 To understand the pathway of Baeyer-Villiger oxidation using aqueous hydrogen peroxide with Ti-containing zeolites as catalysts.

1.3 Scope of Study

1.3.1 Preparation and characterization of Ti-containing zeolite catalysts (TS-1 and Ti-Beta).

1.3.2 Study on the effect of solvents in Baeyer-Villiger oxidation of cyclohexanone using aqueous hydrogen peroxide with Ti-containing zeolite catalysts.

1.3.3 Study on the effect of catalyst topology and functionality.

1.3.4 Study on the effect of temperature in a range of 40-70 °C.

1.3.5 Study on the feed composition by varying the solvents ratio of H_2O_2: cyclohexanone.

1.4 Expected Results

This research can provide a novel choice of a catalytic system for the optimum productivity of $\mathcal{E}$-caprolactone from Baeyer-Villiger oxidation of cyclohexanone.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Zeolites

The word "zeolite" is Greek in origin, derived from the words "zein" and "lithos" meaning to boil and rock. It was first used by a Swedish chemist who found that upon heating the zeolite sample evolved steam [20].

Zeolites are hydrated aluminosilicates that are built from an infinite extending three dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen atoms [21]. Each AlO_4 tetrahedral in the framework bears a net negative charge which is balanced by a cation, normally from the group IA or IIA. According to Lowenstein's rule, Al-O-Al linkages in zeolitic frameworks are forbidden. As a result, all aluminate tetrahedra must be linked to four silicate tetrahedra.

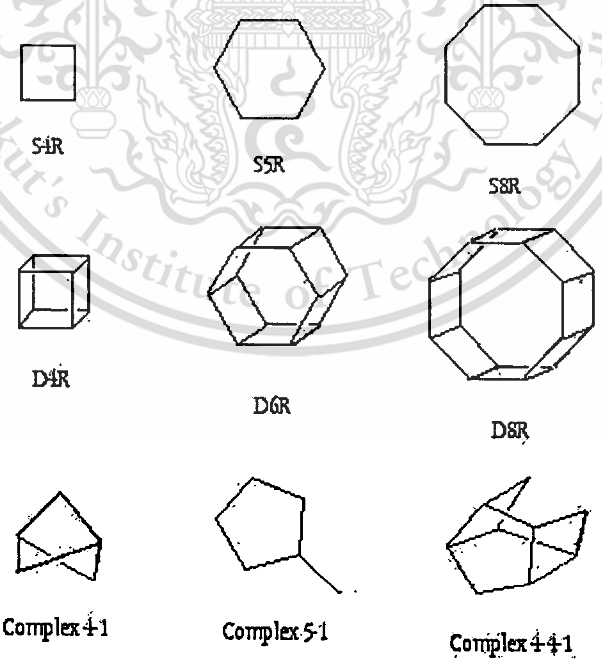


Figure 2.1 Secondary Building Units (SBU) in zeolites.

Zeolite structures can be thought to exist of finite or infinite (chains, layers, etc.) component units. The finite unit is so called secondary building units (SBU). In the Figure 2.1, the T atom of tetrahedral primary unit is located at each of corners, and the oxygens are located towards the midpoints of the lines joining each T atom. The oxygens are not shown to aid clarity. Some materials can have different combinations of SBU within the zeolite framework. For example, ZSM-5 and silicalite-1 shown in Figure 2.2 are materials with MFI topology built up by 5-1 SBU.

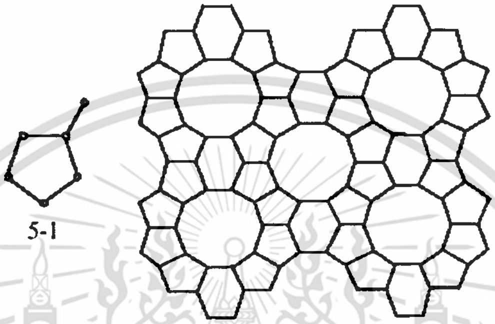


Figure 2.2 A 5-1 secondary building unit and the MFI structure.

The conventional zeolite synthesis involves the hydrothermal crystallization of reactive aluminosilicate gels or solutions in basic environment. These gels are formed upon mixing a silica and an aluminate solution in the presence of alkali hydroxides or/and organic based. The temperature, alkalinity (pH), the composition of the reaction mixture, nature of reactants and pretreatments can all affect crystallization kinetics and the type of zeolite formed. The addition of quaternary ammonium ions to the zeolite synthesis gels can facilitate the formation of novel structures. In the presence of organic amines, new structures can be formed and that in some cases the organic ions are trapped inside the pores. These additives behave as structure-directing agents or templates around which the zeolite pores are formed [22]. The organic templates are held tightly at these sites and can be removed only by calcination.

The Si/Al ratio is another important characteristic of zeolites. The charge is not balance due to the presence of aluminum in zeolite framework determines the ion exchange properties of zeolites and induces potential acidic sites. As the Si/Al ratio increases, the cation content decreases, the thermal stability increases and the surface selectivity changes from hydrophilic to hydrophobic nature.

One interesting in zeolite synthesis is zeotype materials which are the zeolite containing elements other than Si or Al in tetrahedral framework sites. Since 1982, more than 50 new prospective zeotypes have been described. Some of which have been well characterized. Direct synthesis has expanded considerably in the past decade and has been shown to provide a route to many more structures. Before these are synthesized, other elements can often be explained by the presence of species encapsulated in the cavities of zeolite frameworks rather than in the tetrahedral sites.

2.1.1 Applications of Zeolites

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

2.1.1.1 Ion Exchange

Hydrated cations within the zeolite pores are bonded 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 [23].

2.1.1.2 Gas Separation

The porous structure of zeolites can be used to "sieve" molecules having certain dimensions and allow them to enter the pores, such as *n*-paraffins from branched paraffins and *p*-xylene from its isomer. This property can be fine-tuned by variating the structure by changing the size and number of cation around the pores.

2.1.1.3 Catalyst

Zeolites are extremely useful as catalysts for several important reactions involving organic molecules; such as 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 allow a greater degree of product control.

2.1.2 Titanium-containing Zeolite

Titanium-containing zeolites are the isomorphous substitution of Si by Ti into the zeolite framework provide useful catalysts for the oxidation of organic compounds under mild conditions [24-25].

2.1.2.1 Titanium Silicalite (TS-1)

Titanium silicalite-1 or TS-1 is the framework substitution of T atom by Ti into the MFI structure of silicalite [24-26]. The three-dimensional pore system consists of 10-ring channels (5.1 x 5.5 Å) and intersecting straight 10-ring channels (5.3 x 5.6 Å). The structure of TS-1 is presented in Figure 2.3 (a). The 10-membered rings provide access to a network of intersecting pores within the crystal. The pore structure is depicted schematically in Figure 2.3 (b). There is a set of straight, parallel pores intersected by a set of perpendicular zigzag pores. The size of molecules are small enough to penetrate into this intracrystalline pore structure where they may be catalytically converted.

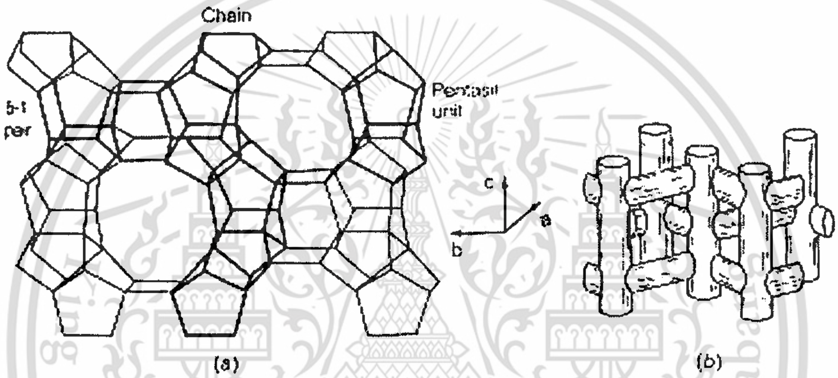


Figure 2.3 (a) Structure formed by stacking of sequences. (b) Schematic representation of the intracrystalline pore structure. [26]

2.1.2.2 Zeolite Titanium Beta (Ti-Beta)

Zeolite Ti-Beta is the framework substitution of T atom by Ti into the BEA structure [13, 27]. Zeolite Beta was the first molecular sieve to be synthesized as a high-silica variety. Its most interesting property is its highly disordered framework. The structure consists of layers formed by five and six-rings that may be stacked in different sequences forming 12-ring pores. The structures of Ti-Beta are shown in Figure 2.4. The presence of significant amounts of aluminium has been found to severely affect the performance of Ti-Beta as an epoxidation catalyst, unless the protons associated with aluminum are substituted with ammonium, alkali or alkali earth cations.

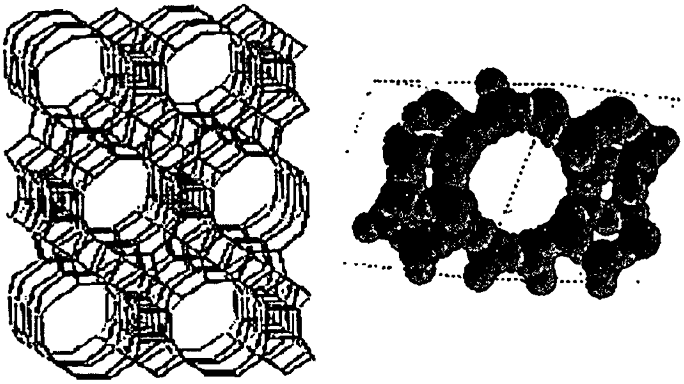


Figure 2.4 Skeletal diagram of the (100)-face of the Beta unit cell [28]

2.2 Oxidation by Titanium-containing Zeolites

Titanium-containing zeolites are highly efficient catalysts for the selective oxidation of the large number of organic substrates, such as alkanes, alkenes, alcohols, aromatics and phenol as shown in Figure 2.5. Unlike the Group IV-VI metal oxide based catalysts, the reaction can be carried out under mild reaction conditions using H_2O_2 as oxidant.

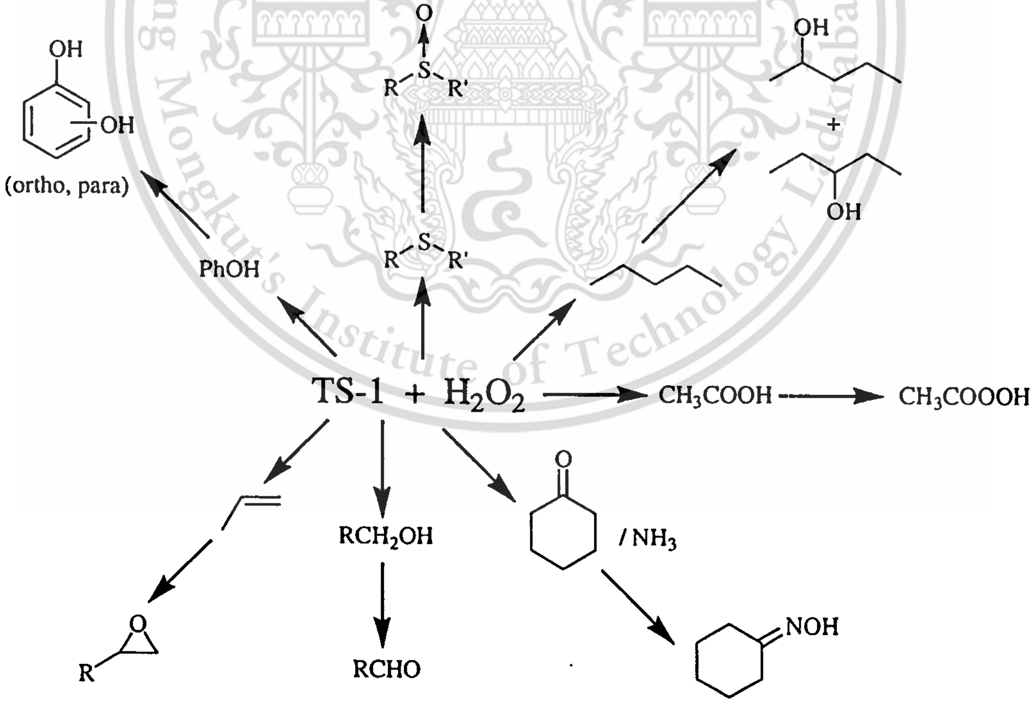


Figure 2.5 Catalytic oxidations by titanium-containing zeolites and aqueous hydrogen peroxide as oxidizing agent.

The catalytic activity of these zeolites is derived from the titanium tetrahedral in the framework. Ti-O-Si bond can be hydrolyzed, but the tetrahedral coordination is kept intact. Subsequent addition of another water molecular generates a pentacoordinated titanium species (Figure 2.6).

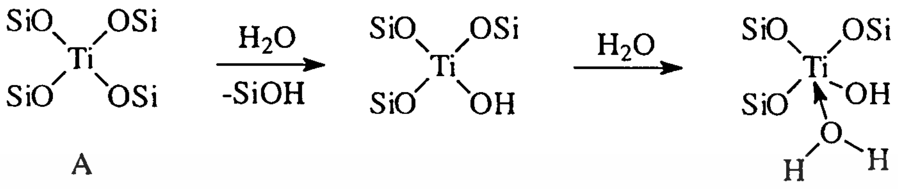


Figure 2.6 Postulated titanium species of the calcined from tetrahedral titanium species (A) and its hydrolysis and hydration

The oxidation mechanism is summarized schematically in Figure 2.7, H_2O_2 first interacts with the tetrahedrally coordinated titanium sites to form Ti-OOH species, which is probably present in a five-membered cyclic structure [10, 12-13, 29-30]. The alkane penetrates into the pore to attack this active site to form a precursor for the formation of alcohols. The peroxyl group from the Ti-OOH is transferred to the adsorbed molecule to form alcohols. The alcohol is then released from the titanium site leaving vacant site for further reaction with H_2O_2. In similar manner, other substrate can react with Ti-OOH species to form ketone, ester, epoxide, etc.

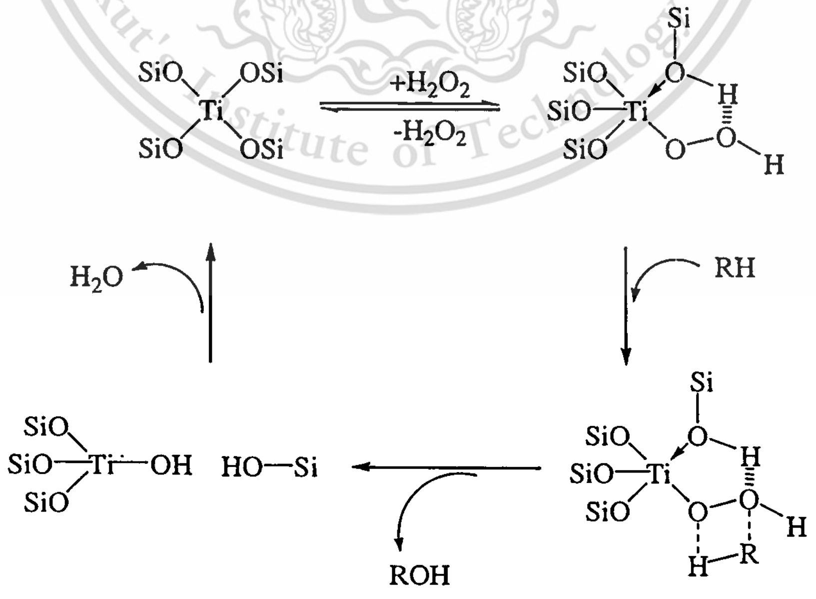


Figure 2.7 Postulated oxidation mechanism [31]

2.3 Baeyer-Villiger Oxidation

The oxidative transformation of cyclic carbonyl compounds into lactones was first reported by Baeyer and Villiger in 1899 when they converted menthone, camphor and carvone into the corresponding lactones with Caro's acid as an oxidant [1]. Traditional oxidising agents include peracids such as *m*-chloroperbenzoic acid [32], trifluoroperacetic acid [33] and perbenzoic acid [34]. This classic transformation has been widely used to manufacture many compounds needed for processes ranging from plastic manufacture to pharmaceutical syntheses.

The mechanism shown in Figure 2.8 involves a nucleophilic attack on the carbonyl group by the oxidant followed by a concerted rearrangement with retention of the configuration at the migrating carbon atom.

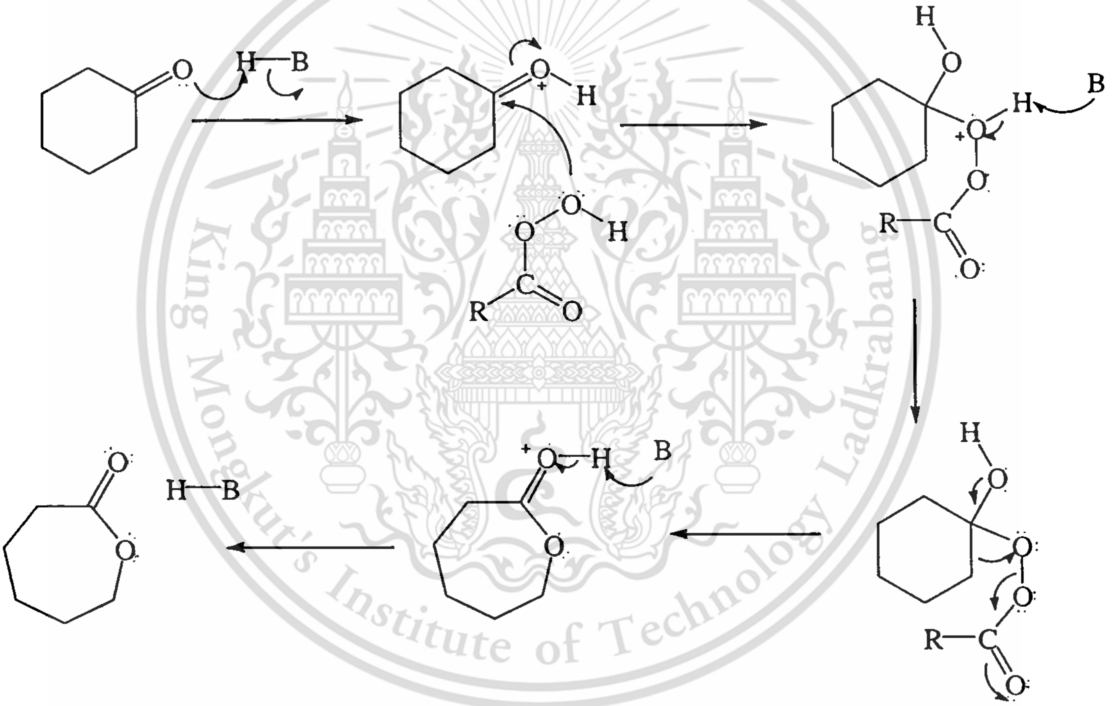


Figure 2.8 Proposed mechanism for the Baeyer-Villiger oxidation

However, the classical reaction produces large amounts of acid waste product [32-34]. Thus, a development of the reaction into heterogeneous processes, has been initiated using polymer-supported peracids as oxidants. The catalyst can be prepared from commercially available polymer resins and hydrogen peroxide [35]. Over the last ten years, many heterogeneous catalysts have been developed namely, zeolites [2-6], hydrotalcites [7] and platinum supported polymers [8].

2.4 ε-Caprolactone

ε-Caprolactone [36] is an intermediate for producing poly ε–caprolactone which is a biodegradable polymer. It is particularly valuable as a flexibilising monomer in formulating thermosetting acrylic resins and unsaturated polyester gel coats. It can also be used as a reactive diluent in expoxy resins.

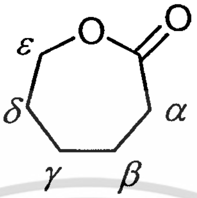


Figure 2.9 Structure of ε–caprolactone

Caprolactone monomer is a colourless, hygroscopic liquid. It is miscible with water in all proportions and soluble in most organic solvents. The lactone ring is relatively easily open by compounds containing active hydrogen atoms such as alcohol.

2.5 Literature Review

The application of acid zeolite as catalyst on Baeyer-Villiger oxidation was developed by Mobil Oil Corporation in 1989 [37]. Nevertheless, the reaction for tranforming cyclic ketone to lactone requires organic solvent and a reaction partner. For example, benzaldehyde is used as oxidising medium which was later converted to benzoic acid as co-products (Figure 2.10). The results show that the higher Si/Al ratio of acid zeolite catalyst give more activity for the bulkier substrates. Lactone and Ω-hydroxycarboxylic acids are two main products.

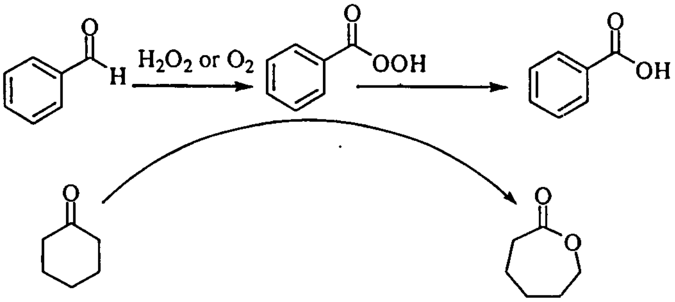


Figure 2.10 The reaction scheme for Baeyer-Villiger oxidation with a reaction partner

Baeyer-Villiger oxidation with aqueous hydrogen peroxide using acid zeolite catalyst was reported by Fischer's group in 1999 [2]. Zeolite H-Beta shows good results in Baeyer-Villiger oxidation of cyclopentanone. The reaction activity reaches an optimum at 60-70 °C with limitation of H_2O_2 decomposition. Acid zeolite was found to give the best result among the acid catalysts used in the reaction. Undesired products would be reduced by zeolite shape selectivity. Nevertheless, lactone ring is easily opened in the presence of acid. For example, the Baeyer-Villiger oxidation of cyclohexanone is shown in Figure 2.11. The formed lactone can be further hydrolyzed to give the 6-hydroxyhexanoic acid (B). Furthermore, cyclohexanone can react with two hydrogen peroxide molecules to give dicyclohexylidene diperoxide (C) in the presence of strong acidic condition.

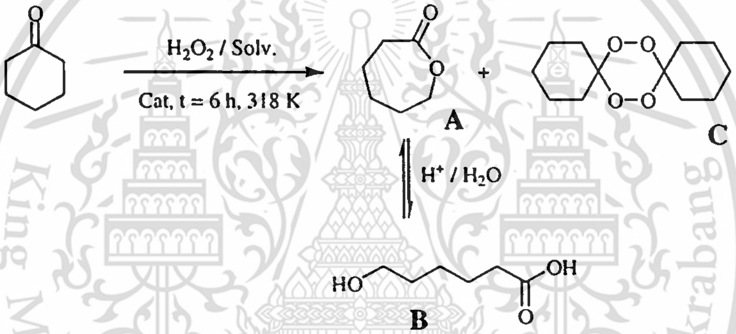


Figure 2.11 The formation of the ε-caprolactone and important byproducts from cyclohexanone oxidation [4]

Ti-containing zeolites are highly efficient catalysts for the selective oxidation under mild reaction conditions using H_2O_2 as oxidant. TS-1 is the best catalyst for the oxidation of small molecules [9-10], but Ti-Beta is shown to be more active for the oxidation of bulkier substrates [11-12], such as cyclic and branched molecules.

In 2001, Corma's group [6] are performed the Baeyer-Villiger oxidation in non-acid catalytic system using aqueous hydrogen peroxide as the oxidizing agent and zeolite infused with tin as catalysts. For unsaturated carbonyl compounds, Ti-containing zeolite was inactive for Baeyer-Villiger oxidation, only epoxide product was obtained. Tin zeolite catalysts give higher selectivity to carbonyl group than C=C bond. The catalyst activates to carbonyl group of ketone, instead of H_2O_2.

Solvent also plays an important role for liquid phase oxidation. It does not only modify the homogenity of the system, but also largely influence on the side reaction which produces by-products. In addition, solvent may even become promoter in some catalytic system. For example, the protic solvent; such as H_2O and methanol, gives more epoxidation activity than aprotic solvent such as acetonitrile. However, a higher selectivity was obtained in aprotic solvent because the ring opening of epoxide is a major side reaction for epoxidation. This side reaction can be largely promoted by the protic solvent forming the glycols or glycol ether [11, 13]. Since Baeyer-Villiger oxidation was carried out in triphase system (solid catalyst, H_2O and organic substrate) over TS-1 [3], modification of homogenity by solvent plays a marked role in TS-1 catalysis. The report has shown that a higher activity was obtained when acetonitrile solvent was used instead of water. This is because the reaction becomes more homogeneous as it turned into a biphase system.

Acetonitrile is also used as a solvent in non-acid system for Baeyer-Villiger oxidation over tin exchanged hydrotalcite with aqueous hydrogen peroxide [7]. The report has shown that initial step of the reaction is the generation of peroxycarboximidic acid [19, 38-40]. This intermediate was suggested to be a good oxygen transfer agent for Baeyer-Villiger oxidation. Furthermore, by-products were not found in non-acid system.

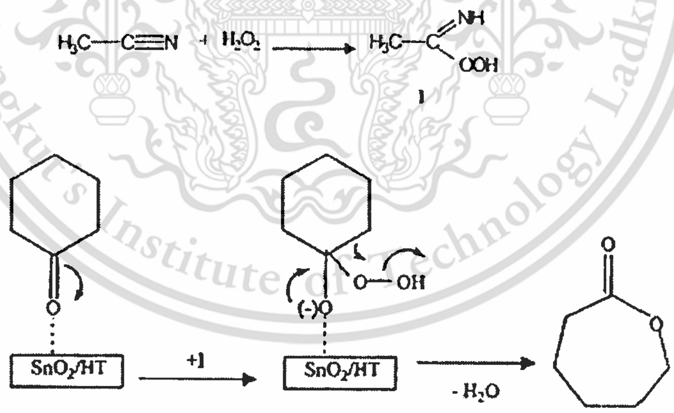


Figure 2.12 Postulated mechanism of Baeyer-Villiger oxidation in acetonitrile medium [7]

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

1. Acetic acid (Carlo Erba Reagenti)
2. Acetone (Carlo Erba Reagenti)
3. Acetonitrile (Lab Scan)
4. Ammonia solution (30% w/w) (Carlo Erba Reagenti)
5. Caprolactone (Fluka Chemika)
6. Chloroform (Fluka Chemika)
7. Cyclohexanone (Carlo Erba Reagenti)
8. Deionized water
9. Hydrogen peroxide (40% w/v) (Carlo Erba Reagenti)
10. Hydrogen peroxide (30% w/w) (Carlo Erba Reagenti)
11. Hydroquinone (Merck)
12. Isopropanol (Lab Scan)
13. Potassium chloride (Merck)
14. Ludox (suspension silica, 40%w/w SiO_2) (Aldrich)
15. Sodium hydroxide (Merck)
16. Sulfuric acid (Mallinackrodt)
17. Tetrahydrofuran (Lab Scan)
18. Tetrabutyl orthotitanate (Fluka Chemika)
19. Tetrapropylammonium bromide (Fluka Chemika)
20. Zeolite Beta (SiO_2/Al_2O_3, 27) (Tosoh Corporation)

3.2 Apparatus

1. Autoclave reactor
2. CHNS/O analyzer (CHNS/O 2400, Perkin Elmer, Mahidol University)
3. Cooling bath
4. Fourier transform infrared spectroscopy (FTIR Spectrum GX, Perkin Elmer)
5. Furnace (Vecstar Furnaces)
6. Gas adsorption analyzer (Autosorb-1, Quantachrome)
7. Gas chromatography (3800 Gas Chromatograph, Varian)
8. Gas chromatography/Mass spectrometer (6890N/5973N, Agilent, Scientific Instruments Service Centre, KMITL)
9. Gas chromatography/Mass spectrometer (Trace GC/Polaris Q, Thermo Finnigan, Mahidol University)
10. Hot plate & stirrer
11. Magnetic stirrer
12. Laboratory glassware
13. Laboratory plasticware
14. Mass spectrometer (VG Autospec 7070E, Fison Instruments, the Petroleum and Petrochemical College, Chulalongkorn University)
15. Nuclear Magnetic Resonance Spectrometer (Advanced DPX300, Bruker AG)
16. Oven (50-200 °C)
17. Scanning electron microscopy (LEO 1455VP, LEO Electron Microscopy, Scientific Instruments Service Centre, KMITL)
18. Water aspirator and vacuum filtration
19. X-ray diffractometer (D8 Advance, Bruker AG, Scientific Instruments Service Centre, KMITL)
20. X-ray fluoresence spectroscopy (SRS 3400, Bruker AG, Scientific Instruments Service Centre, KMITL)

3.3 Experiments

3.3.1 Catalyst Preparations

3.3.1.1 Titanium Silicalite (TS-1)

The procedure for TS-1 synthesis was modified from that reported in literature [41]. Briefly, 2.49 grams of tetrabutyl orthotitanate, used as titanium source, were mixed with 5.67 grams of deionized water (5 °C), followed by adding 10.33 grams of hydrogen peroxide solution (30 %w/w) under stirring for 30 minutes. Then, 20.18 grams of Ammonia solution (25 %w/w, 5 °C) was added and stirred. The solution was kept overnight at room temperature. The solution was then heated at 80-90 °C for 30 minutes. Cold ammonia solution was added to the solution until the last solution has just as much weight as the solution before heating. After that this solution was mixed with the mixture of 22.43 grams of deionized water, 26.19 grams of Ludox and 7.44 grams of tetrapropylammonium bromide (TPABr). The mixture was stirred for a day. Finally, the yellow gel with a molar composition of 15 TPABr : 3.8 TiO_2 : 94 SiO_2 : 2168 H_2O : 212 NH_3 : 12.3 H_2O_2 was loaded in an autoclave reactor and heated to 185 °C in an oven. After 7 days, the synthetic zeolite was filtrated, washed and dried at 80 °C.

The synthetic zeolite was then calcined under Air-zero at 500 °C with a heating rate of 2 °C/minute for 5 hours and cooled under stream of nitrogen. The calcined zeolite was washed by 1 M sulfuric acid until the non-framework titanium cannot be detected by color change upon adding of hydrogen peroxide.

3.3.1.2 H-Beta

H-Beta was prepared by calcinating the parent NH_4^+-Beta, which was commercially obtained from Tosoh Corporation, under Air-zero at 550 °C with a heating rate of 2 °C/minute for 5 hours and cooled under stream of nitrogen.

3.3.1.3 Dealuminated Beta

Dealuminated Beta was prepared by refluxing 1 gram of the parent NH_4^+-Beta with 100 ml of the 7 molar nitric acid solution for 5 hours. Then, the sample was filtered, washed with deionized water until no acidity was detected and dried at 80 °C. The sample was subsequently calcined under Air-zero at 550 °C with a heating rate of 2 °C/minute for 5 hours and cooled under stream of nitrogen.

3.3.1.4 Titanium Beta (Ti-Beta)

Titanium Beta was prepared by heating non-calcined dealuminated Beta with tetrabutyl orthotitanate and hydrogen peroxide solution. The weight composition of 0.7254 $Ti(OBu_4)$: 13 H_2O_2 (30%w/w) : 2 H_2O : 1 zeolite was heated at 70°C for 4 hours. Then, the sample was filtered and washed with deionized water. The sample was calcined under Air-zero at 550 °C with a heating rate of 2 °C/minute for 5 hours and cooled under stream of nitrogen. Finally, the sample was washed by 1 molar sulfuric acid until the non-framework titanium cannot be detected by color change upon dropping hydrogen-peroxide.

3.3.1.5 Potassium-Titanium Beta (K-Ti-Beta)

The procedure for K-Ti-Beta preparation was prepared by cation exchange Ti-Beta with potassium chloride solution as reported in literature [42]. Briefly, 1 gram of Ti-Beta was stirred in 75 ml of 0.5 molar potassium chloride solution at 60 °C for 3 hours. After centrifuging the solid was recovered and the process was repeated for 3 times. Then, the sample was filtered and washed with deionized water. The sample was calcined under Air-zero at 450 °C with a heating rate of 2 °C/minute for 12 hours and then cooled under stream of nitrogen.

3.3.2 Characterization of Catalysts

3.3.2.1 Elementals Analysis

The silicon/aluminium and silicon/titanium ratio of the catalysts were determined by X-ray fluoresence spectroscopy (SRS 3400, Bruker AG, Scientific Instruments Service Centre, KMITL). The sample was prepared by mixing with boric acid.

3.3.2.2 Crystal Morphology

The crystal morphology of the catalysts were determined by scanning electron microscope (LEO 1455VP, LEO Electron Microscopy, Scientific Instruments Service Centre, KMITL). The sample was prepared by coating with gold ion sputtering.

3.3.2.3 Catalyst Structure

The structure of the catalysts was determined by powder X-ray diffraction (D8 Advance, Bruker AG, Scientific Instruments Service Centre, KMITL). CuKα X-ray beam was used for analysis. X-ray diffraction pattern of the sample was compared with those of the standard materials for structure elucidation.

3.3.2.4 Specfic Surface Area

The specific surface area of catalysts was determined by gas adsorption analysis (Autosorb-1, Quantachrome). Approximately 0.02-0.04 grams of sample was loaded into a cleaned and dried sample cell. The sample was degassed at out-gas station at 350 °C for 24 hours. Then, nitrogen was filled and the sample cell was moved to the analysis station. The adsorption isotherm was measured in a pressure range of 0.05-0.30 P/P_0.

3.3.2.5 Titanium Species

Titanium species in the catalysts was determined by Fourier transform infrared spectroscope (FTIR Spectrum GX, Perkin Elmer). The sample was analyzed using attenuated total reflectance (ATR) technique. The characteristic vibration frequency at 960 cm^{-1} represents the vibration of Ti-O-Si bond in tetrahedral coordination [43-45].

3.3.3 Catalytic Testing

The Baeyer-Villiger reaction of cyclohexanone was carried out at 40-70 °C in 10 ml stirred reactor. Typically, the molar ratio of reactant was as follows : solvent : H_2O_2 : ketone = 8.36 : 1.2 : 1. The weight ratio of ketone : catalyst was 9.5 : 1. After a period of time, the reaction was stopped by adding hydroquinone as free radical inhibitor and removing heat.

The solution was then filtered. The filtrate was separated and the solid residual was dissolving with acetone to remove products from the catalysts. The acetone was evaporated and the solid product was recrystallined in isopropanol/water mixtures.

The structure of solid products was identified by mass spectrometer (VG Autospec 7070E, Fison Instruments, the Petroleum and Petrochemical College, Chulalongkorn University), nuclear magnetic resonance spectrometer (Advanced DPX300, Bruker AG), elemental analysis (CHNS/O 2400, Perkin Elmer, Mahidol University) and fourier transform infrared spectrometer (FTIR Spectrum GX, Perkin Elmer).

The products in the filtrate were analyzed by gas chromatography using Varian 3800 Gas Chromatograph with DB-FFAP capillary column (0.25mm x 30 m). 0.2 μl of liquid sample was injected to an injection port (220 °C) of gas chromatography using a split ratio of 150. The seperation temperature was started at 110 °C and held for 6 minutes. Then, the temperature was raised to 200

°C with a heating rate of 20°C/minute and held at that temperature for 20 minutes. Helium was used as carrier gas at a flow rate of 28.5 cm/sec.

The structure of soluble products was confirmed by gas chromatography/mass spectrometer (6890N/5973N, Agilent, Scientific Instruments Service Centre, KMITL) using the same condition.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst Preparation and Characterization

4.1.1 Elementals Analysis

The silicon/aluminium and silicon/titanium ratio of the zeolites were determined by X-ray fluoresence spectroscopy. The results are shown in Table 4.1

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

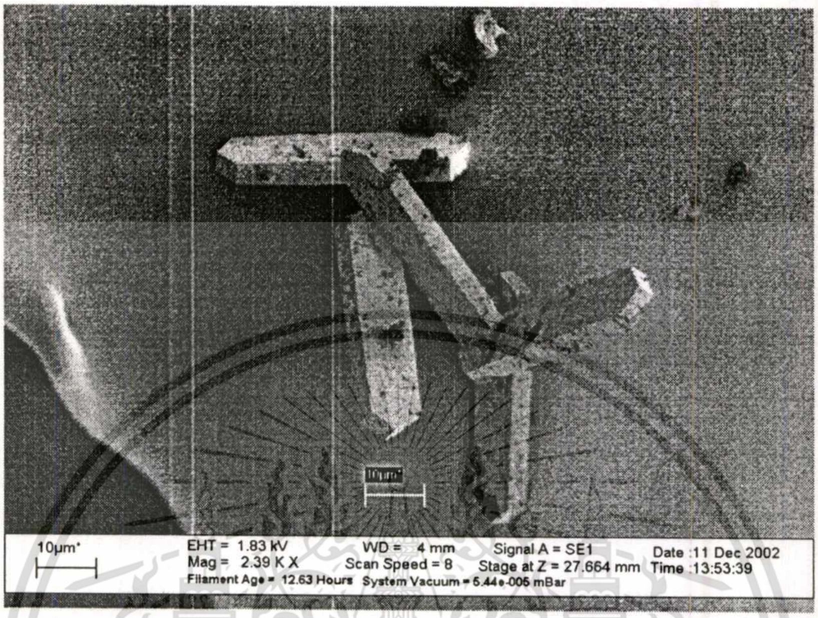
Zeolite	Silicon/Aluminium	Silicon/Titanium
TS-1	-	18.54
H-Beta	12.64	-
Dealuminated Beta	55.64	-
Ti-Beta	67.23	10.74

From Table 4.1, Beta type zeolite that used in this work was modified from commercial NH_4^+-Beta (Tosoh Corporation). Some of aluminium was left in zeolite framework after refluxing the commercial NH_4^+-Beta with 7 molar of nitric acid. Most of aluminium in zeolite framework was leached into the acid solution.

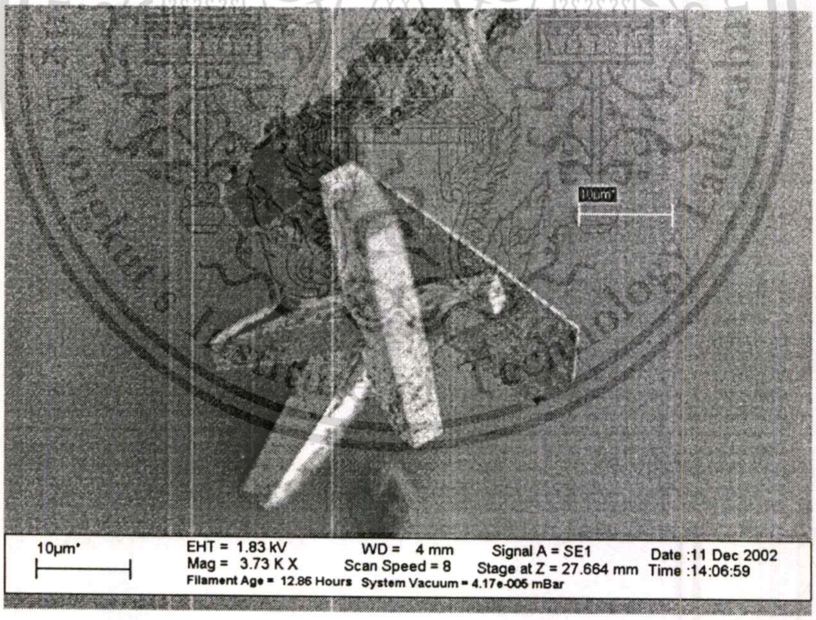
Ti-Beta was modified from the non-calcined dealuminated beta. The titanation process was applied from the TS-1 synthesis method [41]. The void of aluminium site was replaced by titanium. There appears to be two species of titanium occurred after titanation; (i) titanium in tetrahedral framework of zeolite and (ii) non-framework of titanium dioxide. The non-framwork titanium can be removed when washing by sulfuric acid, but the framework titanium was suggested to be retained.

4.1.2 Crystals Morphology

Figure 4.1 shows scanning electron micrograph of TS-1. The crystal size is approximately 2 x 10 x 60 micrometers with good size distribution.



(A)



(B)

Figure 4.1 Morphology of TS-1 as-synthesized (A) and calcined (B).

The particle size of commercial NH_4^+-Beta and Ti-Beta are approximately 2-5 micrometers. The small crystallite size of the sample is suitable for catalytic propose. The electron micrographs were shown in Figure 4.2 and 4.3.

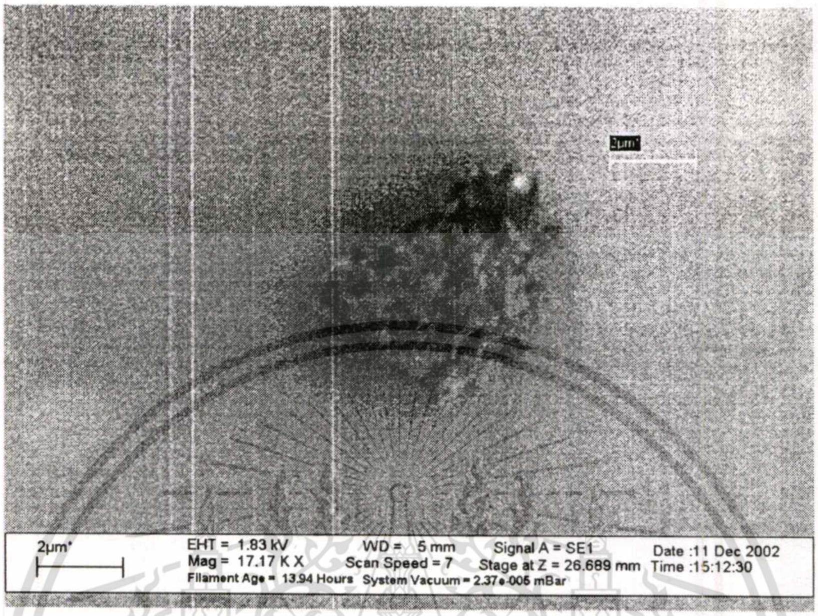


Figure 4.2 Morphology of commercial NH_4^+-Beta .

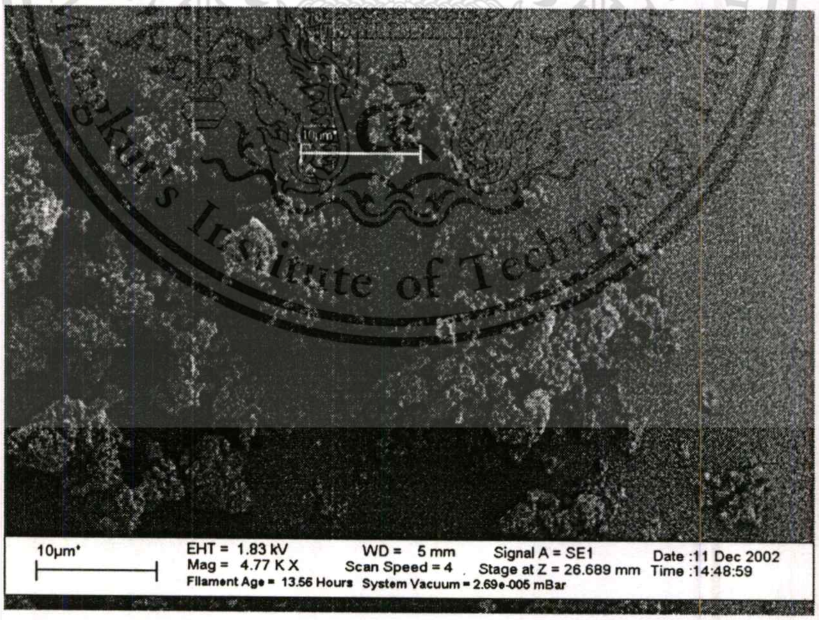


Figure 4.3 Morphology of Ti-Beta .

4.1.3 Catalyst Structure

X-ray diffraction pattern of catalysts are obtained from Bruker X-ray powder diffractometer using $CuK\alpha$ radiation. X-ray diffraction pattern of TS-1 was shown in Figure 4.4. After calcination, the peak intensity at low angle was increased indicating decomposition of organic template from the pore of TS-1.

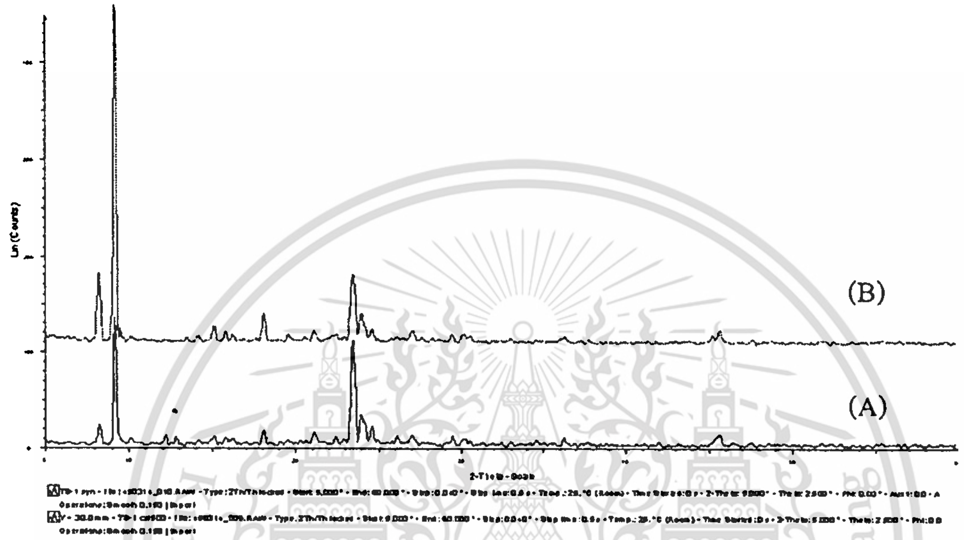


Figure 4.4 X-ray diffraction pattern of TS-1 as-synthesized (A) and calcined (B).

X-ray diffraction pattern of Beta type catalysts are shown in Figure 4.5 and 4.6. The structure of dealuminated beta remained the same as the commercial NH_4^+-Beta, but the crystallinity was reduced after dealumination. For the Ti-Beta, which is prepared by titanation of the dealuminated beta, the X-ray diffraction pattern shows that the beta type zeolites appear to be well-defined crystalline microporous materials with crystallite size 7.1 *n*m (calculated by Scherrer equation).

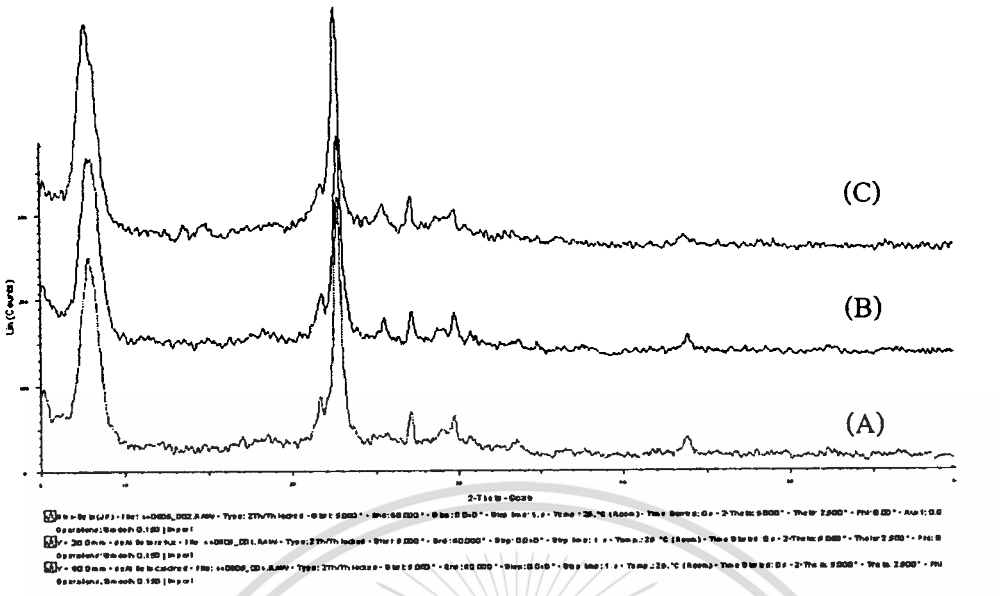


Figure 4.5 X-ray diffraction pattern of commercial NH_4^+-Beta (A), non-calcined dealuminated beta (B) and calcined dealuminated beta (C).

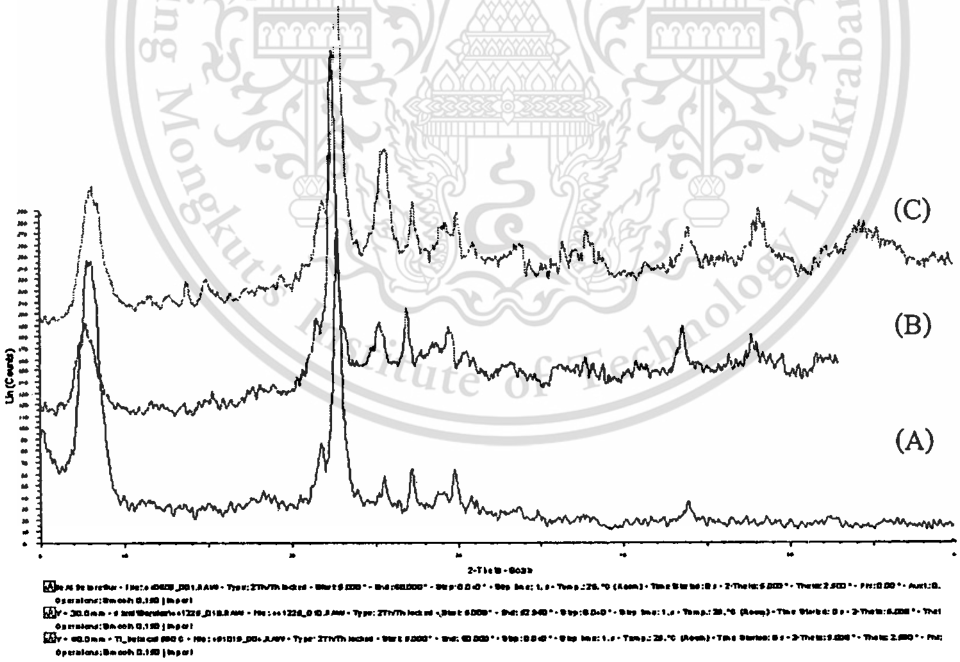


Figure 4.6 X-ray diffraction pattern of dealuminated beta (non-calcined) (A), Ti-Beta (non-calcined) (B) and Ti-Beta (calcined) (C).

4.1.4 Specific Surface Area

The BET surface area of the TS-1 and beta type zeolite catalysts are shown in Table 4.2.

Table 4.2 The specific surface area of zeolites

Zeolite	Specific Surface Area (m^2/g)
TS-1 as-synthesized	368
TS-1 calcined	396
NH_4^+-Beta (commercial)	630
Dealuminated Beta	495
Ti-Beta	550
K-Ti-Beta	420

It was found that the zeolite samples were effective catalysts due to their high surface area. The surface area of beta type zeolite catalyst was markedly reduced after modified. This suggests that some of the zeolite pore structure may be collaped or blocked by non-framework species which results in a relative lower surface area of dealuminated beta as compared to the commercial NH_4^+-Beta. However, the surface area of Ti-Beta was higher than dealuminated beta.. This was because titanium was replaced into the void of dislodged aluminium site. With the thermal treatment and intensive washing with acid, non-framework aluminium and titanium can be removed, while the tetrahedral titanium species retain in the beta pore structure.

4.1.5 Titanium Species

Titanium in the zeolite framework can be identified by Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra of these zeolites are shown in Figure 4.7.

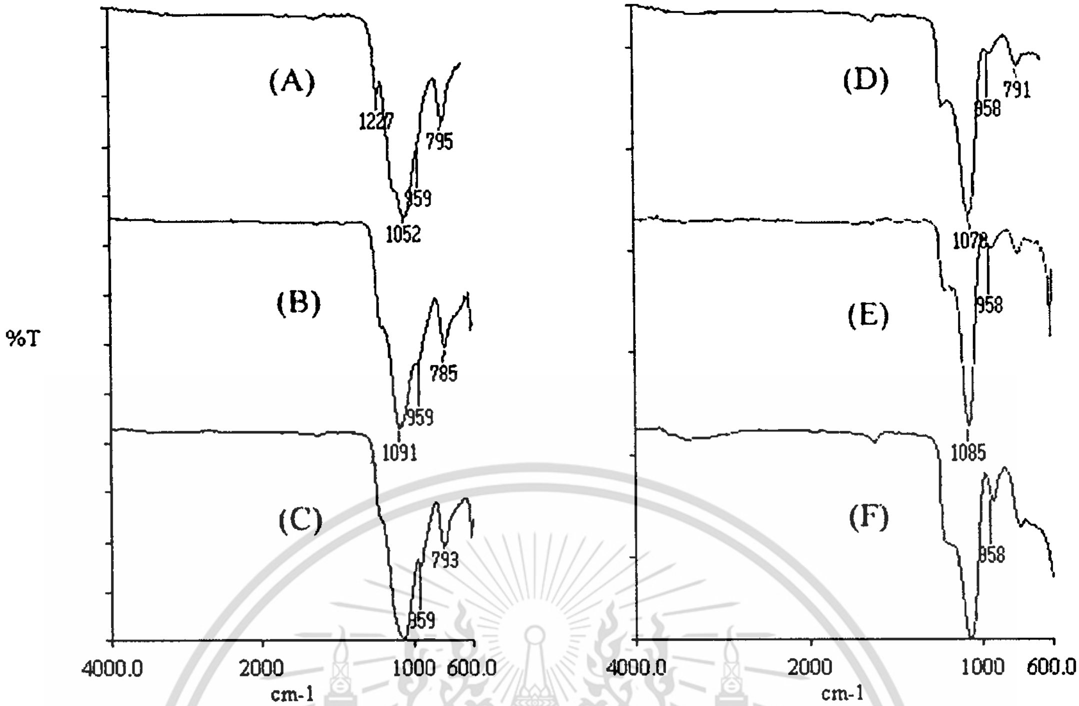


Figure 4.7 Fourier Transformed Infrared Spectra of silicatite (A), TS-1 (as-synthesized) (B), TS-1 (calcined) (C), dealuminated beta (D), Ti-Beta (non-calcined) (E) and Ti-Beta (calcined) (F).

The characteristic peak of Si-O-Si vibration at 1050 cm^{-1} was shown in all of zeolite sample with highest intensity. The characteristic peak of Al-O-Si was presence in all of beta type zeolite at 1250 cm^{-1}. Silicalite has show only the characteristic peak of Si-O-Si vibration. TS-1 showd the characteristic peak of Ti-O-Si vibration at 960 cm^{-1}, which suggested that titanium was present in these zeolite as framework species [27, 29, 43-45]. After calcination, the Ti-O-Si vibration of TS-1 was higher than that of the as-synthesized. The dealuminated beta had definitely no characteristic peak of Ti-O-Si vibration (Figure 4.7 (D)) because no titanium was present in the zeolite framework. The characteristic peak of Ti-O-Si vibration was present after titanation (Figure 4.7 (E, F)).

4.2 Catalytic Testing

4.2.1 Effect of Solvent

The conversion and ε-caprolactone selectivity from the reaction using water, acetic acid and acetonitrile as solvent are shown in Figure 4.8

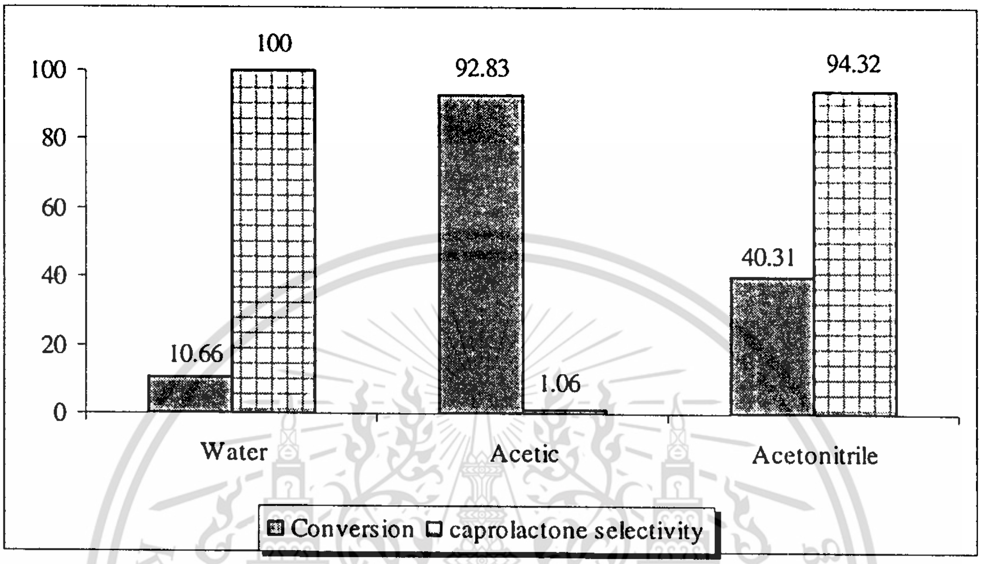
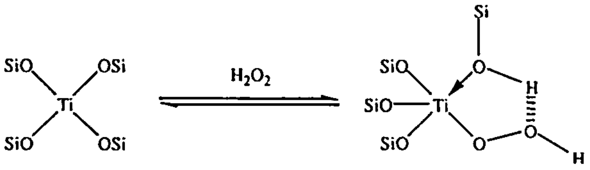


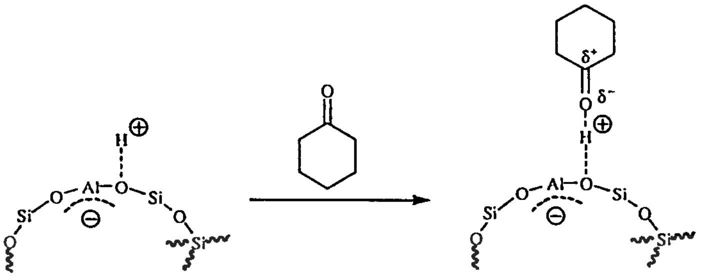
Figure 4.8 The conversion and ε-caprolactone selectivity of reaction using Ti-Beta catalyst.

Reaction condition: Temperature 60 ^{o}C. Reaction time 6 hr. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 solvent, Weight ratio of ketone: catalyst = 9.5: 1

The study on the effect of solvent showed that the reaction using water as a solvent produced high selectivity of ε-caprolactone. However the reaction activity was quite low. This is because the reaction mechanism is initiated by reaction of active oxidizing species and ketone, which readily adsorb on the catalyst surface. The active oxidizing species can be formed by interaction of hydrogen peroxide and titanium active site (A), whilst it is believed that cyclohexanone would adsorb on trace of acid site in catalyst (B). In a more polar system, competitive adsorption of water against the ketone can be expected. This reduced the ketone adsorption, and hence the conversion of reaction was limited.



(A)



(B)

In the reaction using acetic acid as solvent, the reaction activity was enhanced. This was because peracetic acid was *in-situ* generated by hydrogen peroxide and acetic acid [18, 38, 46-47]. The peracetic acid facilitated a stable complexation with titanium active sites in the framework of zeolite. This species can be served as a better oxidizing agent due to the higher electron density of the active site. Therefore, an improved activity of the reaction was obtained.

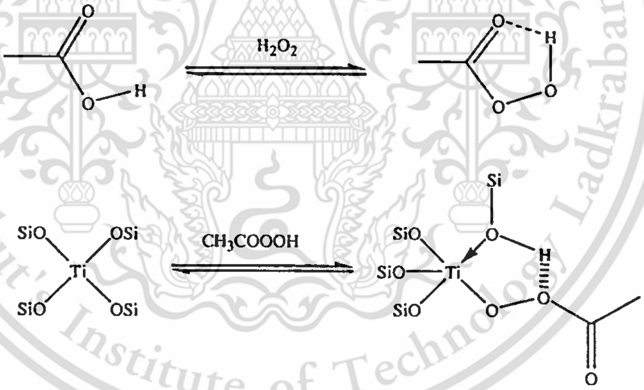


Figure 4.9 showed that peracetic acid alone is also active for oxidation, furthermore the activity of the reaction is improved with the presence of Ti-Beta catalyst. It confirmed that the active oxidizing species formed by peracetic acid and titanium framework is more active than the peracetic acid alone.

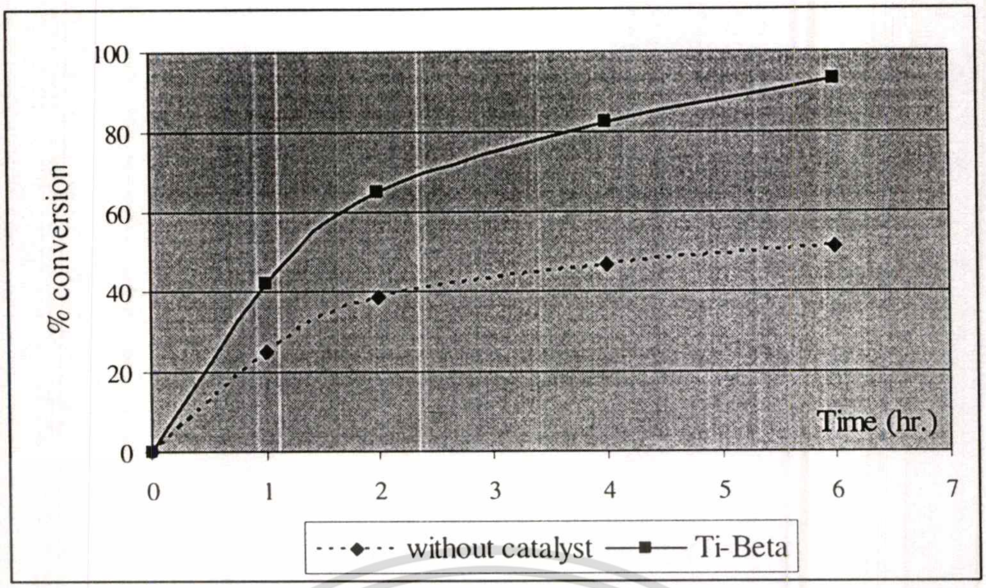
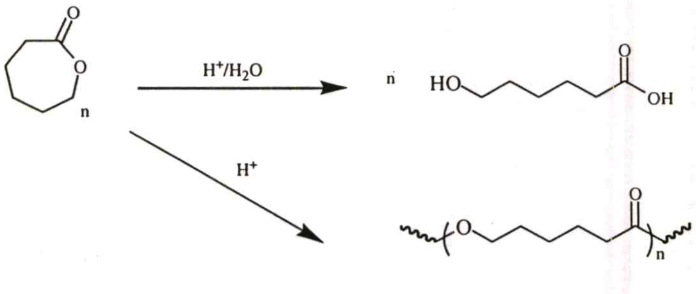
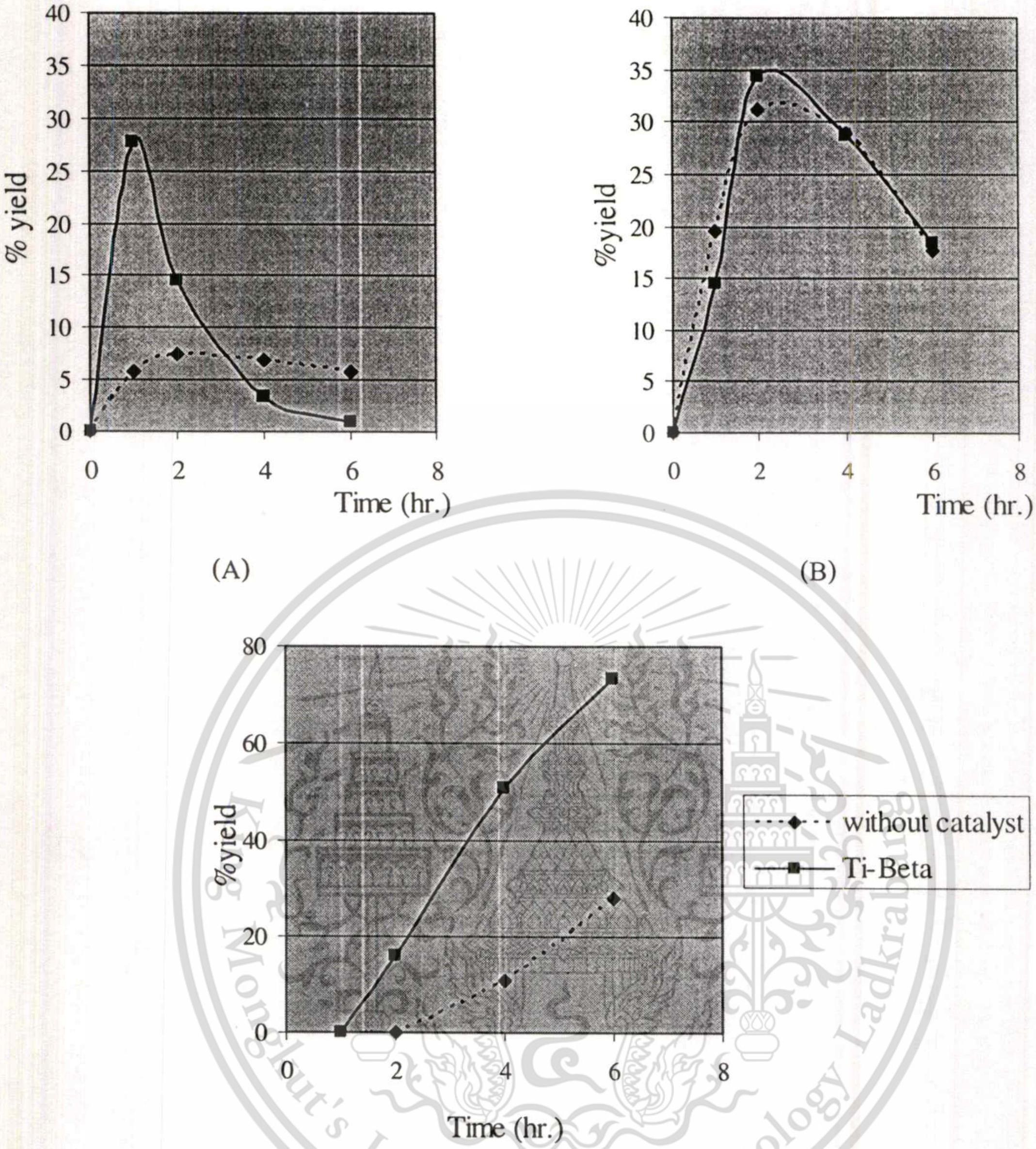


Figure 4.9 The conversion of reaction using acetic acid as a solvent. *Reaction condition: Temperature 60 °C, Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetic acid, Weight ratio of ketone: catalyst = 9.5: 1*

However, $\mathcal{E}$-caprolactone selectivity was too low in the reaction using acetic acid as a solvent. This is because $\mathcal{E}$-caprolactone can be easily hydrolyzed in acid to 6-hydroxyhexanoic acid as described in section 2.4. Moreover, $\mathcal{E}$-caprolactone can polymerize to form poly ($\mathcal{E}$-caprolactone). The results in Figure 4.10 showed product yields of the reaction with acetic acid as a solvent. It can be seen that yields of 6-hydroxyhexanoic acid in the reaction without catalyst is similar to that using Ti-Beta catalyst (Figure 4.10: B). Therefore, it can be concluded that the 6-hydroxyhexanoic acid and poly ($\mathcal{E}$-caprolactone) are formed by homogeneous acid catalyzed systems. Other oxygenated species such as: pentanoic acid, δ-valerolactone, 4-hexenoic acid, 3-hydroxycyclohexanone, 4-hydroxycyclohexanone, 1,4-cyclohexanedione, methyl hexanoate, etc. might be obtained from acid catalyzed reactions.





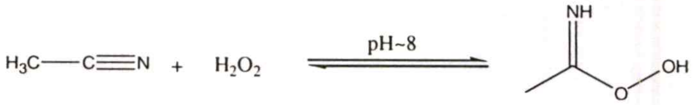
(A)

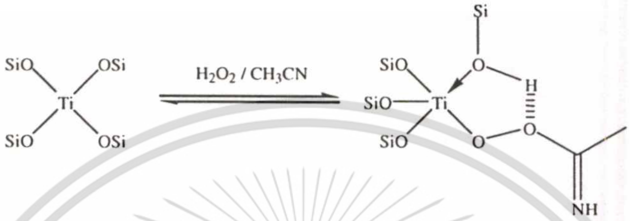
(B)

(C)

Figure 4.10 The product yields of reaction using acetic acid as a solvent. (A: $\mathcal{E}$-caprolactone, B: 6-hydroxyhexanoic acid, C: Other oxygenated product) *Reaction condition: Temperature 60 ^{O}C, Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetic acid, Weight ratio of ketone: catalyst = 9.5: 1*

When acetonitrile was used as a solvent, the reaction activity was lower than that using acetic acid. This is because the active oxidizing species which is presumably formed by peroxycarboximidic acid and the titanium framework is less stable than that formed by peracetic acid. The peroxycarboximidic acid is suggested as an intermediate in the reaction of hydrogen peroxide and acetonitrile in basic solution [7, 19, 38, 48]. Therefore, it is possible that peroxycarboximidic acid could be readily formed on the catalyst surface. Although, lower conversion was obtained, $\mathcal{E}$-Caprolactone selectivity was increased as compared to that using acetic acid as a solvent. This was because of no hydrolysis and the ring opening polymerization of $\mathcal{E}$-caprolactone as observed in the reaction with acetic acid as a solvent.





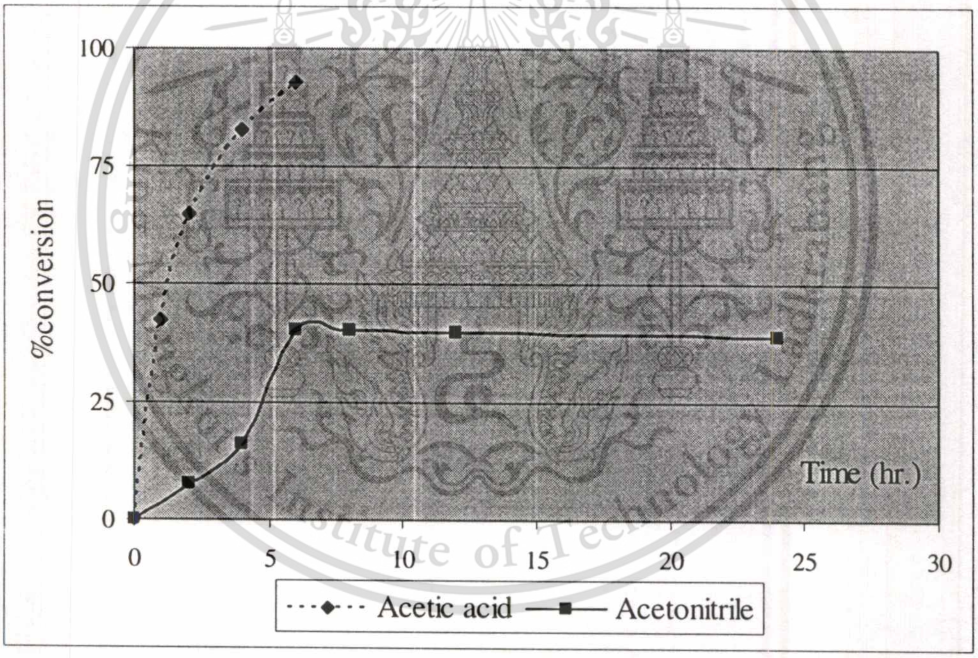


Figure 4.11 The conversion of reaction with Ti-Beta catalyst. *Reaction condition: Temperature 60* ^{o}C *Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 solvent* *Weight ratio of ketone: catalyst = 9.5: 1*

The results of reaction using acetonitrile solvent with Ti-Beta catalyst are shown in Figure 4.11. The conversions of cyclohexanone were limited with the decomposition of hydrogen peroxide within 6 hours.

$$2\,H_2O_2 \xrightarrow{\Delta} 2\,H_2O + O_2$$

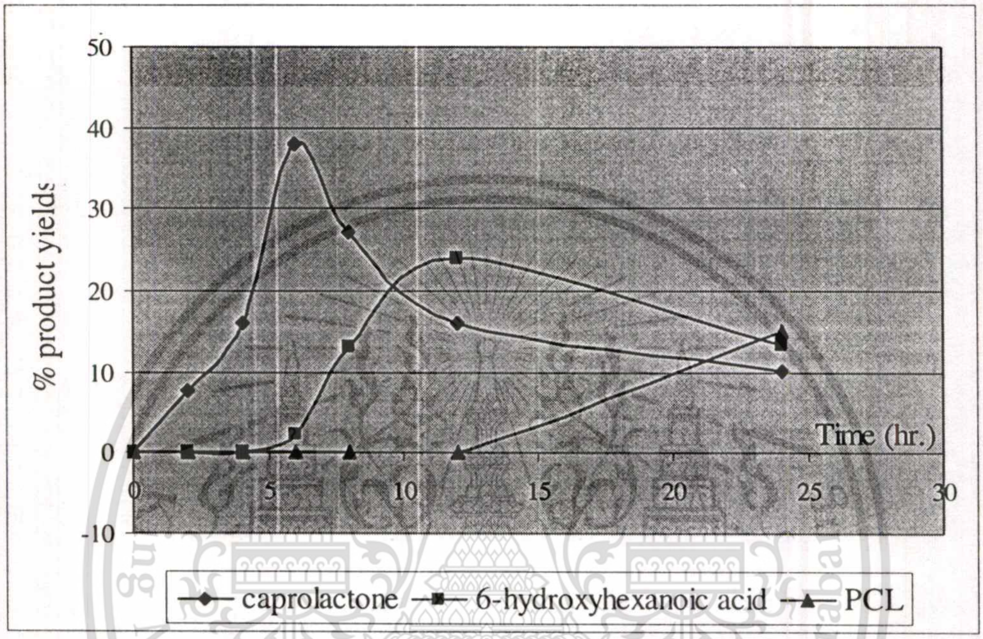


Figure 4.12 The product yields of reaction using acetonitrile as a solvent with Ti-Beta catalyst.
Reaction condition: Temperature 60 °C, Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1

However, 6-hydroxyhexanoic acid were formed after 6 hours and poly (ε-caprolactone) was produced on this system after 12 hours (Figure 4.12). The formation of by-products at high resident time could be derived from trace of acid site present in Ti-Beta catalyst. Such acid sites may well be formed by incompleted dealmination of NH_4^+-Beta

The previous results [7] show that acetonitrile does not only modify the homogeneity of the system, but it also become a promoter in the catalytic cycle. Therefore, the concentration of acetonitrile should largely influences to the reaction activity. This is confirmed by the reaction using various acetonitrile/water ratio and the results are shown in Figure 4.13.

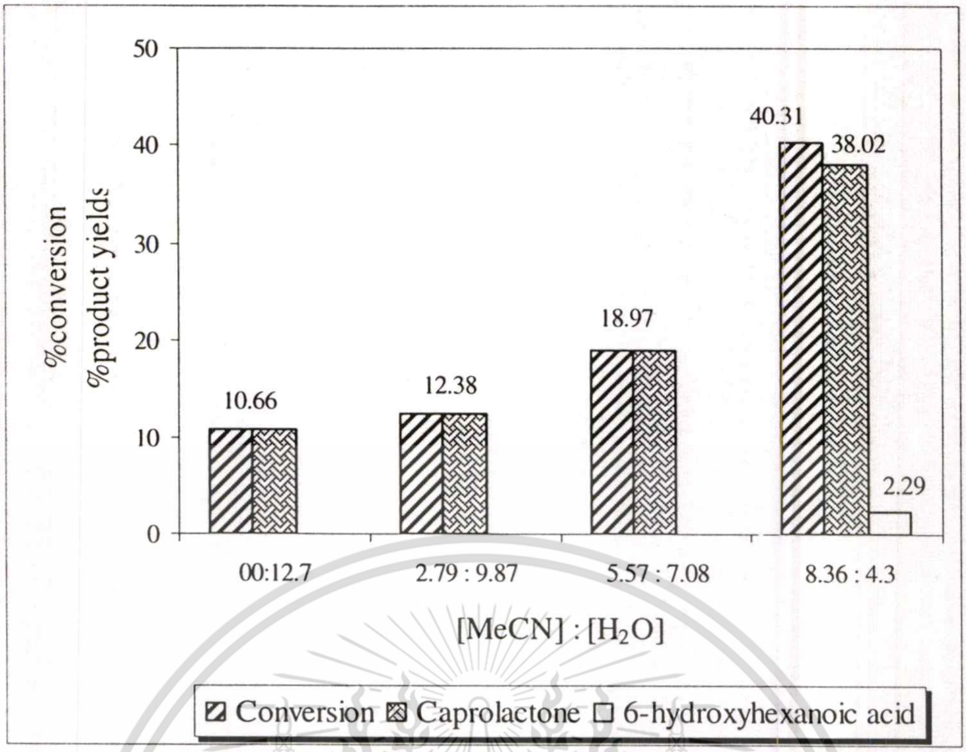
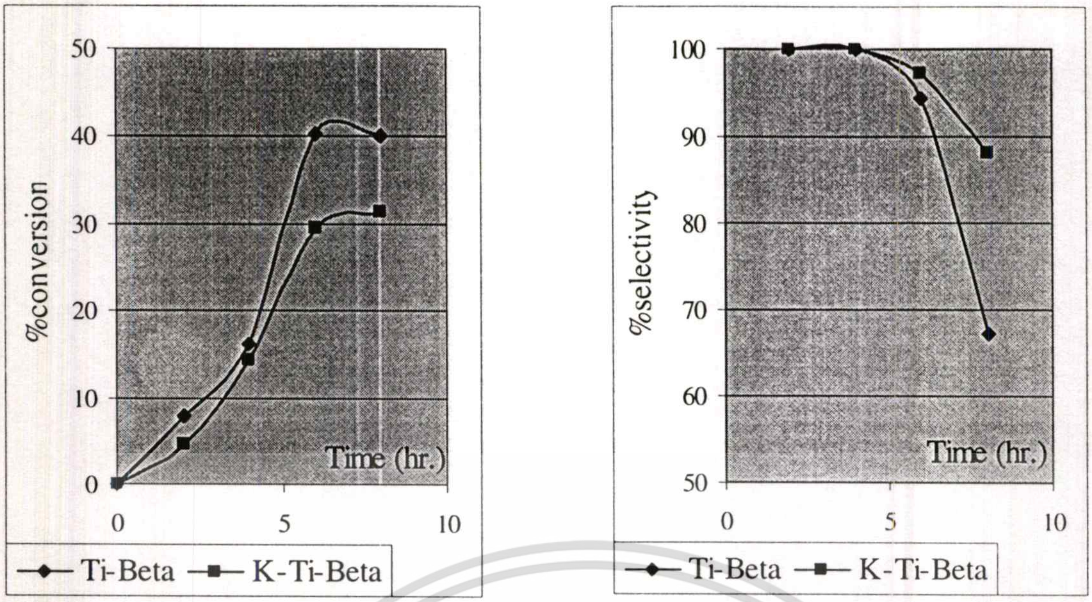


Figure 4.13 The conversion and product yields of reaction using Ti-Beta catalyst. *Reaction condition: Temperature 60 °C. Reaction time 6 hr, Molar ratio of reactant = 1 cyclohexanone: 12.7 solvent: 1.2 hydrogen peroxide, Weight ratio of ketone: catalyst = 9.5: 1*

The results show that the conversion is increased with high acetonitrile ratio. This is because the homogeneity of system is improved with higher acetonitrile ratio medium and leads to a relatively less hydrophilic system. Accordingly, ketone adsorption on the catalyst surface is increased since competitive adsorption of water is reduced. In addition, the concentration of acetonitrile is relative to the amount of generated peroxycarboximidic acid. Therefore, more active oxidizing species can be readily generated in the reaction with high acetonitrile/water ratio.



(A) (B)

Figure 4.14 The conversion of reaction (A) and ε-caprolactone selectivity (B) using acetonitrile as a solvent. *Reaction condition: Temperature 60 °C, Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

As discussed earlier, trace of acid in Beta zeolite leads to low selectivity of ε-caprolactone. Therefore, ε-caprolactone selectivity may well be increased when acid site in the catalysts is reduced. This can be tested by using cation substituted Ti-Beta as a catalyst. From the results in Figures 4.14, it was shown that ε-caprolactone selectivity was improved when using K-Ti-Beta catalyst. This is because catalyst acidity was reduced. ε-Caprolactone was more stable in low acid system. However, the lower surface area of K-Ti-Beta catalyst [Table4.2] leads the slightly lower reaction activity.

The improved ε-caprolactone selectivity can also be observed even for the reaction using acetic acid as a solvent (Figure 4.15). This is clear that acid sites in Beta zeolite lead to low selectivity of ε-caprolactone.

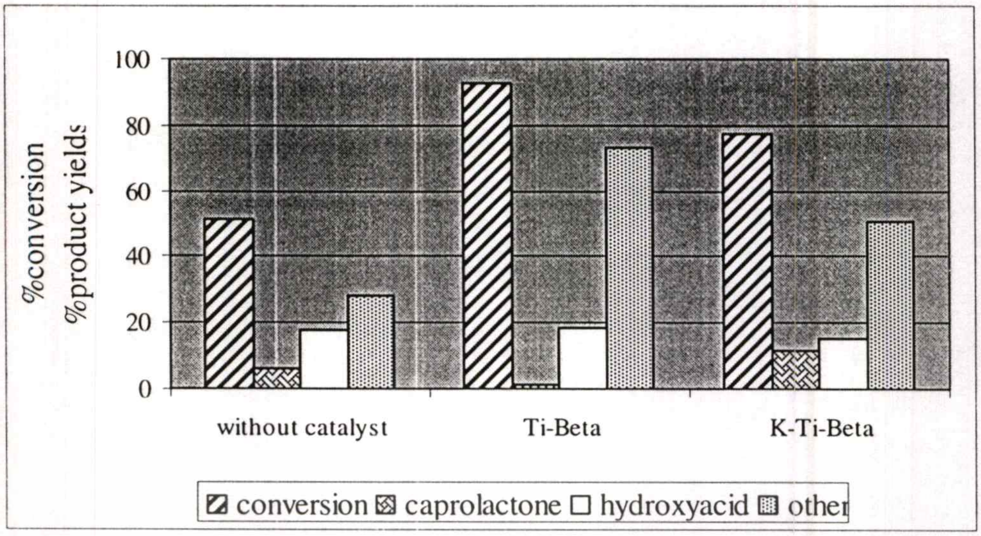


Figure 4.15 The conversion and product yields of reaction using acetic acid as a solvent. *Reaction condition: Temperature 60 °C. Reaction time 6 hr. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetic acid, Weight ratio of ketone: catalyst = 9.5: 1*

4.2.2 Effect of Temperature

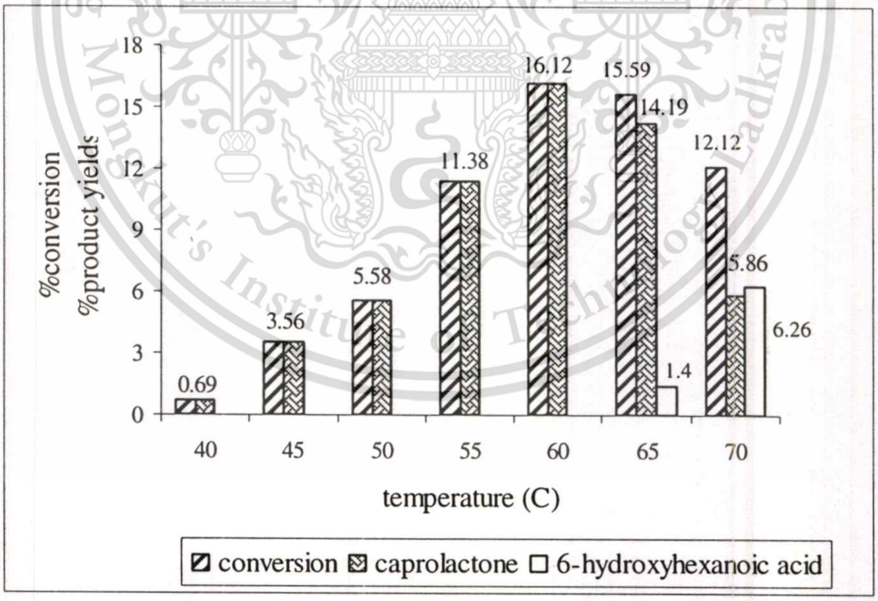


Figure 4.16 The conversion and product yields of reaction using acetonitrile as a solvent with Ti-Beta catalyst. *Reaction condition: Reaction time 4 hr. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

From Figure 4.16, it was shown that the reaction activity reached an optimum at 60 °C with a limitation of hydrogen peroxide decomposition. Hydrogen peroxide was decomposed to water and oxygen. Water contents increased and effected on the homogeneity of the system. The ketone adsorption and diffusion on the catalyst was then reduced.

$$2\,H_2O_2 \xrightarrow{\Delta} 2\,H_2O + O_2$$

Morever, when the reaction temperature was above 60 °C, ε-caprolactone selectivity was decreased by ring opening of ε-caprolactone forming 6-hydroxyhexanoic acid, and high molecular weight polymeric compounds. In Figure 4.12, the ring opening of ε-caprolactone were normally generated after 6 hours, but it was found within 4 hours at the temperature above 65 °C.

4.2.3 Effect of Hydrogen Peroxide

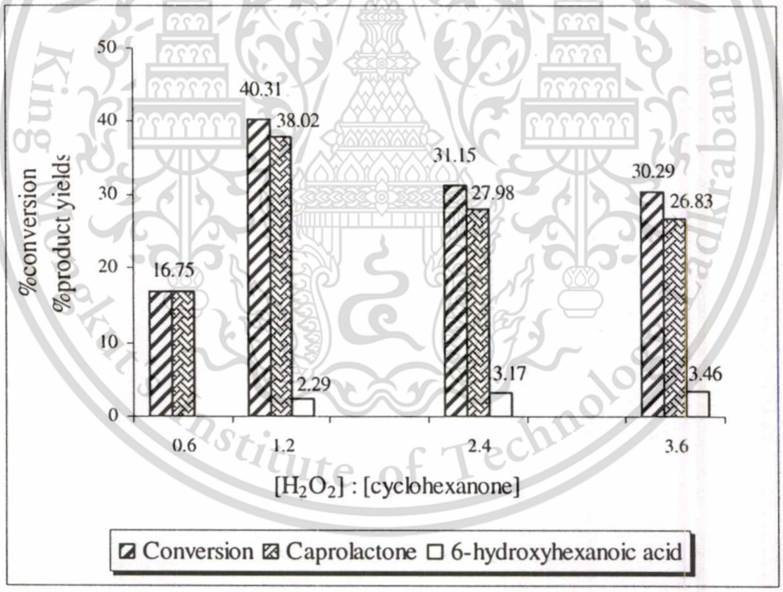


Figure 4.17 The conversion and product yields of reaction using Ti-Beta catalyst. *Reaction condition: Temperature 60 °C. Reaction time 6 hr, Molar ratio of reactant = 1 cyclohexanone: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1, hydrogen peroxide:* H_2O *= 1.2: 4.3 (*H_2O_2*40%w/v)*

The result in Figure 4.17 showed that the conversion of cyclohexanone was optimized at the molar ratio of hydrogen peroxide: cyclohexanone was 1.2: 1. When the mole ratio of hydrogen peroxide: cyclohexanone less than 1.2, the generated active oxidizing species was limited by the quantity of hydrogen peroxide. On the other hand, when the molar ratio of hydrogen peroxide: cyclohexanone was greater than 1.2, the reaction activity was slightly decreased. This was because water in the reaction was increased as more aqueous hydrogen peroxide was used. The reaction became more polar and cyclohexanone was also diluted. Consequently, cyclohexanone adsorption and diffusion was decreased by the competitive adsorption of water on the catalyst.

4.2.4 Effect of Catalyst

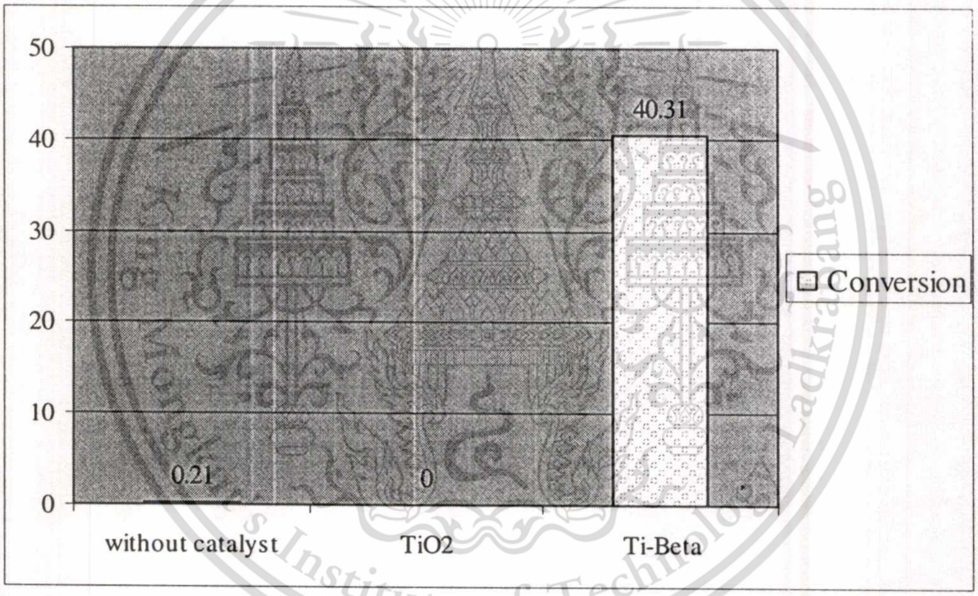
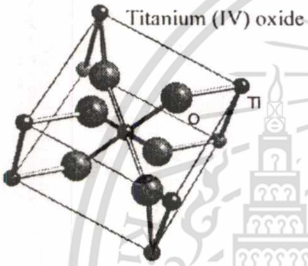
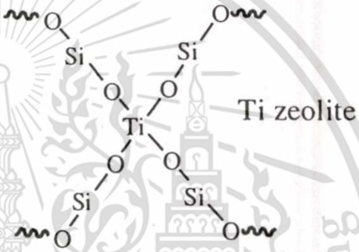


Figure 4.18 The conversion of reaction using acetonitrile as a solvent with various titanium site catalysts. *Reaction condition: Temperature 60 °C, Reaction time 6 hr. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

The results from Figure 4.18 showed that the reaction cannot be promoted without catalysts and with titanium oxide. This is due to the fact that acetonitrile cannot readily react with hydrogen peroxide to form peroxycarboximidic acid in liquid medium. Additionally, hydrogen peroxide alone cannot promote Baeyer-Villiger rearrangement. Thus, ε-caprolactone was not generated in the reaction without catalysts. Furthermore, octahedrally coordinated titanium in titanium oxide is inactive for promoting this reaction. This was because the octahedrally coordinated titanium did not react with hydrogen peroxide to form active oxidizing species. This can be concluded that the peroxycarboximidic acid, the five-membered active oxidizing species, is only generated on the titanium with tetrahedrally coordination.





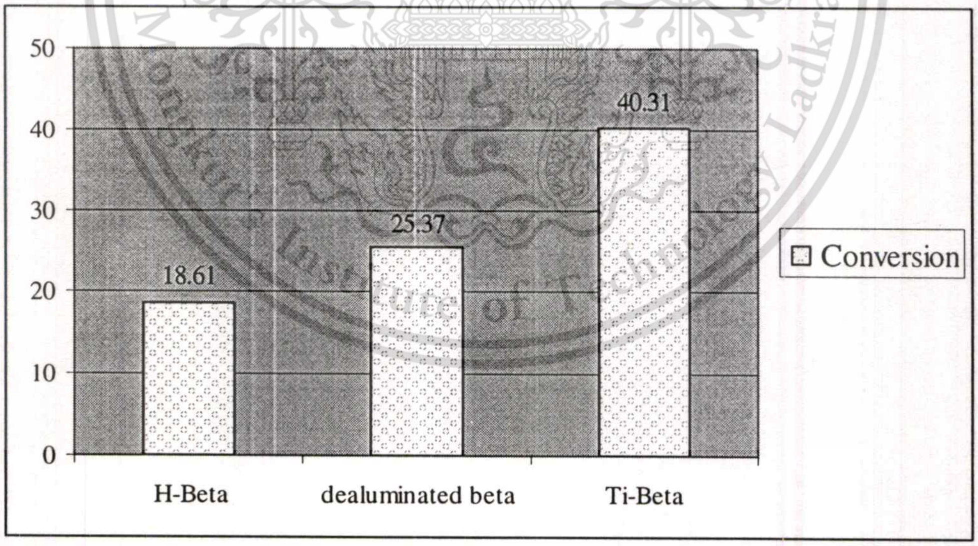
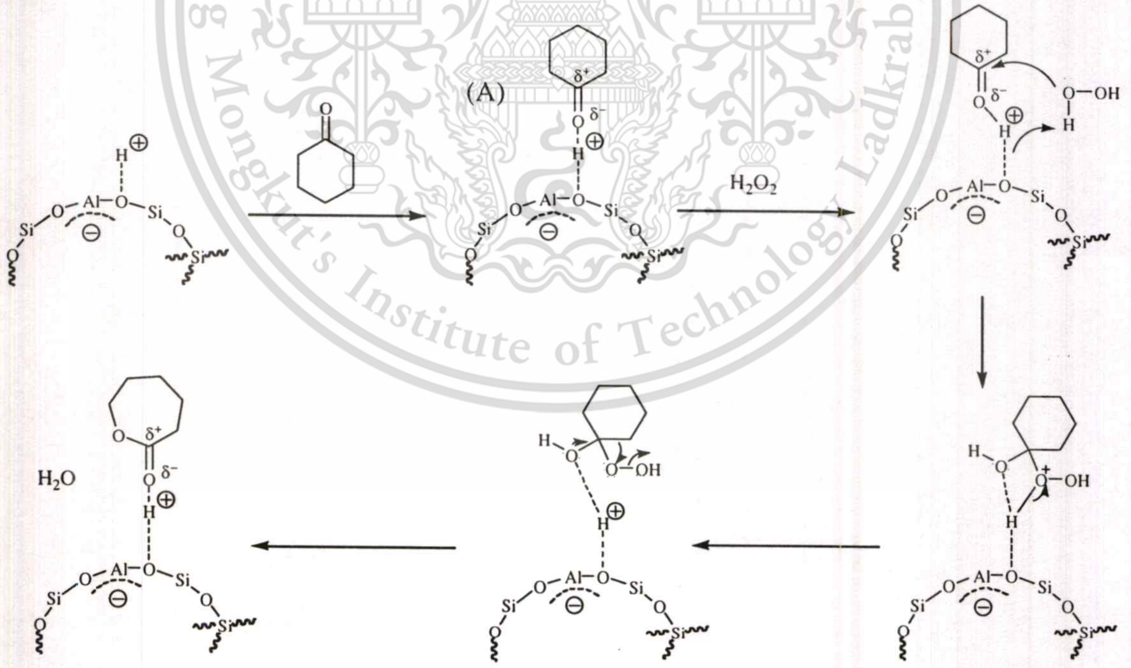
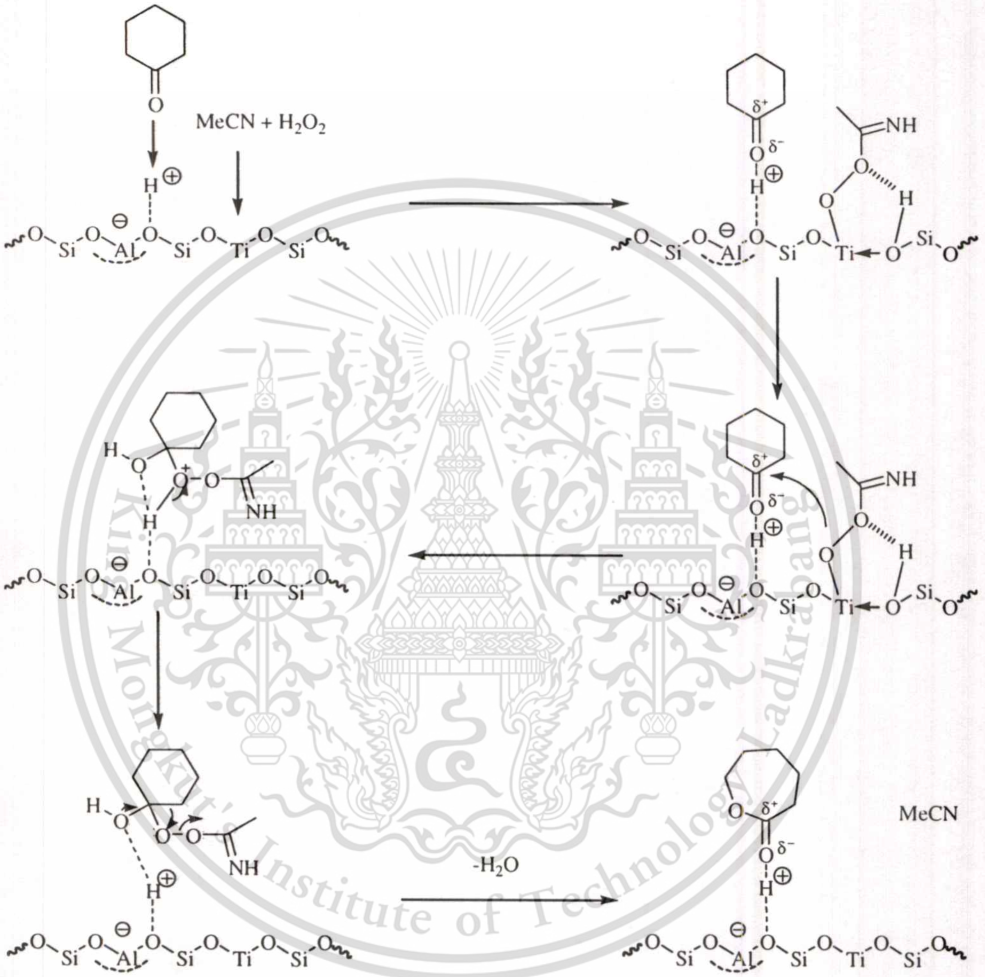


Figure 4.19 The conversion of reaction using acetonitrile as a solvent with various beta type zeolites. *Reaction condition: Temperature 60 ^{o}C, Reaction time 6 hr. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

Not only Ti-containing zeolite is active for this reaction, the acid zeolite catalysts can also promote Baeyer-Villiger oxidation of cyclohexanone as shown in Figure 4.19. H-Beta and dealuminated beta are zeolites without titanium active site. Therefore, it is likely that the reaction mechanism should not involve the generation of active oxidizing species, but may well be activated by the protonation of cyclohexanone as proposed below (A). The reaction starts with the adsorption of cyclohexanone on acid sites of zeolite catalysts. Hydrogen peroxide reacts with the adsorbed cyclohexanone directly. However, H-Beta gives the lower activity than dealuminated beta. This is because the H-Beta framework is more hydrophilic. Cyclohexanone adsorption could be reduced by the competitive adsorption of water on the active sites. On the other hand, the framework of dealuminated beta is relatively hydrophobic, as compared to H-Beta. Ketone adsorption can be improved and the reaction activity is also accelerated, resulting in the higher conversion of cyclohexanone in the reaction using dealuminated beta, as compared to that using H-Beta.



In Ti-Beta, cyclohexanone adsorbs on trace of acid sites whist hydrogenperoxide and acetonitrile forms the 5-membered complex of peroxycarboximidic acid on Ti site. However, if the resident time of the reaction is too long, trace of acid site can promote the $\mathcal{E}$-caprolactone into the series reaction.



In addition to the active sites, catalyst pore size plays an important role on Baeyer-Villiger oxidation of cyclohexanone. The results of the reaction that using medium pore of TS-1 and the large pore of Ti-Beta are in Figure 4.20.

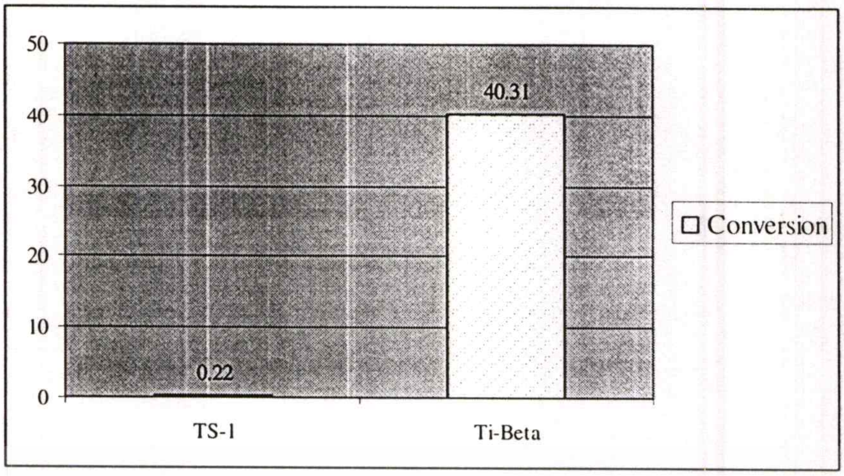
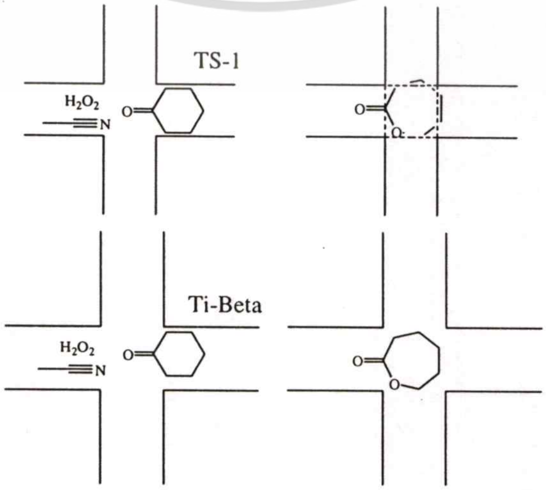


Figure 4.20 The conversion of reaction using acetonitrile as a solvent with various Ti-containing zeolites. *Reaction condition: Temperature 60 °C, Reaction time 6 hr. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

Only Ti-Beta promoted this reaction. It is clear that the reaction mechanism take place on the internal catalyst pore. Peroxycarboximidic acid was generated on the internal surface and must be stabilized on the titanium active site. This oxidizing species reacted with the ketone and rearrange into 7-membered lactone in the pore of zeolite Beta. ε-Caprolactone was not generated in the reaction using TS-1. This is due to the fact that TS-1 possesses the medium pore size (5.5Å), but ε-caprolactone possesses the molecular size larger than the pore size diameter of TS-1. Thus, ε-caprolactone was not generated inside the TS-1 catalyst. On the other hand, Ti-Beta which large pore sizes (7.6Å) can readily promote this reaction.



CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

The study on the effect of solvent shows that the reaction activity is in the order of acetic acid > acetonitrile > water. This is because a better active oxidizing species of peracetic acid is *in-situ* generated and the complex of peracetic acid with titanium tetrahedral produces better oxidizing species than that of hydrogen peroxide. Peroxycarboximidic acid can also be generated from a acetonitrile on the catalyst surface in a similar manner as the complex of peracetic acid with the titanium active site.

The selectivity of ε-caprolactone was relatively low in the presence of protic solvent, which lead to the ring opening of the ε-caprolactone to 6-hydroxyhexanoic acid and its polymeric counterparts. Therefore, the selectivity of ε-caprolactone in the reaction that using acetic acid as a solvent is lower than that using acetonitrile and water. In addition, the trace of acid site in the catalyst can promote the ring opening of the ε-caprolactone at high resident time.

The competitive adsorption of water against cyclohexanone can inhibit the reaction activity. Such obstacle is enhanced in the reaction system with more hydrophilic character.

The role of the solvent in this reaction can be concluded as:

- Modify the homogeneity of the system
- Control the series reaction, namely ring opening and polymerisation
- Promote the catalytic cycle

The study on the effect of temperature shows that the reaction activity reaches an optimum at 60 °C with a limitation of hydrogen peroxide decomposition. The selectivity of ε-caprolactone is decreased when the reaction temperature is above 60 °C due to an increase in the rate of series reactions.

In our mechanistic study shows that the reaction pathway is initiated by reaction of active oxidizing species and ketone. The titanium active site for this reaction is tetrahedrally coordinate species in the zeolite framework. The active oxidizing species can be formed by interaction with titanium active site. The peroxycarboximidic acid is generated on the internal surface and must be stabilize on titanium active site. The cyclohexanone can be activated by protonation on trace of acid site in the catalyst and the reaction mechanism take place on the catalyst pore.

The reaction condition for the liquid phase Baeyer-Villiger oxidation of cyclohexanone as follows:

Catalyst: Ti-Beta.

Reaction temperature 60 °C

Resident time within 6 hr.

Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile.

Weight ratio of ketone: catalyst = 9.5: 1

5.2 Suggestion for Future Studies

5.2.1 Trace of acid site in the catalyst leads to low ε-caprolactone selectivity. The catalyst preparation should be modified for preparation of the aluminium free Ti-Beta.

5.2.2 The reaction activity are limited by hydrogen peroxide decomposition. Then, hydrogen peroxide should be slowly added in to the reaction system.

5.2.3 The Ti-Beta catalyst is quite stable and small deactivation is observed. Accordingly, the liquid phase Baeyer-Villiger oxidation of cyclohexanone should be tested in continuous process for large scaled development.

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APPENDIXES

APPENDIX A

Calculation of Product Concentration

Conversion

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

$$\text{\% conversion of cyclohexanone} = \frac{\text{Mole of cyclohexanone consumed}}{\text{Initial moles of the cyclohexanone}} * 100$$

Mole of cyclohexanone consumed = Initial moles of cyclohexanone - Mole of cyclohexanone remained

Selectivity

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

$$\text{\% selectivity of a product} = \frac{\text{\% Yield of the product}}{\text{\% Conversion of cyclohexanone}} * 100$$

APPENDIX B

Catalytic Testing Results

Table B.1 Catalytic testing condition

Batch	Catalyst	Solvent	Time (hr)	Mole ratio Solvent : H_2O_2 : H_2O : $C_6H_{10}O$	Temperature (^{o}C)
1	Ti-Beta	H_2O	6	0 : 1.2 : 12.66 : 1	60
2	-	Acetic acid	1	8.36 : 1.2 : 4.3 : 1	60
3	-	Acetic acid	2	8.36 : 1.2 : 4.3 : 1	60
4	-	Acetic acid	4	8.36 : 1.2 : 4.3 : 1	60
5	-	Acetic acid	6	8.36 : 1.2 : 4.3 : 1	60
6	Ti-Beta	Acetic acid	1	8.36 : 1.2 : 4.3 : 1	60
7	Ti-Beta	Acetic acid	2	8.36 : 1.2 : 4.3 : 1	60
8	Ti-Beta	Acetic acid	4	8.36 : 1.2 : 4.3 : 1	60
9	Ti-Beta	Acetic acid	6	8.36 : 1.2 : 4.3 : 1	60
10	-	Acetonitrile	0.5	8.36 : 1.2 : 4.3 : 1	60
11	-	Acetonitrile	1	8.36 : 1.2 : 4.3 : 1	60
12	-	Acetonitrile	1.5	8.36 : 1.2 : 4.3 : 1	60
13	-	Acetonitrile	2	8.36 : 1.2 : 4.3 : 1	60
14	-	Acetonitrile	2.5	8.36 : 1.2 : 4.3 : 1	60
15	-	Acetonitrile	3	8.36 : 1.2 : 4.3 : 1	60
16	-	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60
17	-	Acetonitrile	12	8.36 : 1.2 : 4.3 : 1	60
18	Ti-Beta	Acetonitrile	2	8.36 : 1.2 : 4.3 : 1	60
19	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	60
20	Ti-Beta	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60

* Weight ratio of ketone: catalyst = 9.5: 1

Table B.1 (continued) Catalytic Testing condition

Batch	Catalyst	Solvent	Time (hr)	Mole ratio	Temperature (^{o}C)
				Solvent : H_2O_2 : H_2O : $C_6H_{10}O$	
21	Ti-Beta	Acetonitrile	8	8.36 : 1.2 : 4.3 : 1	60
22	Ti-Beta	Acetonitrile	12	8.36 : 1.2 : 4.3 : 1	60
23	Ti-Beta	Acetonitrile	24	8.36 : 1.2 : 4.3 : 1	60
24	Ti-Beta	Acetonitrile	6	2.79 : 1.2 : 9.87 : 1	60
25	Ti-Beta	Acetonitrile	6	5.57 : 1.2 : 7.08 : 1	60
26	K-Ti-Beta	Acetonitrile	2	8.36 : 1.2 : 4.3 : 1	60
27	K-Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	60
28	K-Ti-Beta	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60
29	K-Ti-Beta	Acetonitrile	8	8.36 : 1.2 : 4.3 : 1	60
30	K-Ti-Beta	Acetic acid	6	8.36 : 1.2 : 4.3 : 1	60
31	TiO_2	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60
32	H-Beta	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60
33	Dealuminated Beta	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60
34	TS-1	Acetonitrile	6	8.36 : 1.2 : 4.3 : 1	60
35	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	40
36	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	45
37	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	50
38	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	55
39	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	65
40	Ti-Beta	Acetonitrile	4	8.36 : 1.2 : 4.3 : 1	70
41	Ti-Beta	Acetonitrile	6	8.36 : 0.6 : 2.15 : 1	60
42	Ti-Beta	Acetonitrile	6	8.36 : 2.4 : 8.6 : 1	60
43	Ti-Beta	Acetonitrile	6	8.36 : 3.6 : 12.9 : 1	60

* Weight ratio of ketone: catalyst = 9.5: 1

Table B.2 Baeyer-Villiger oxidation of cyclohexanone using acetic acid as a solvent. (without catalyst)

Reaction time (hr)	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
1	25.36	5.76	19.6	-	22.71	2
2	38.62	7.42	31.2	-	19.21	3
4	46.78	6.94	28.94	10.90	14.84	4
6	51.37	5.80	17.62	27.95	11.29	5

Reaction condition: Temperature 60 °C. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetic acid

Table B.3 Baeyer-Villiger oxidation of cyclohexanone using acetic acid as a solvent. (Ti-Beta catalyst)

Reaction time (hr)	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
1	42.25	27.75	14.5	-	65.68	6
2	64.98	14.56	34.43	15.99	22.41	7
4	82.61	3.31	28.65	50.65	4.01	8
6	92.83	0.98	18.46	73.39	1.06	9

Reaction condition: Temperature 60 °C. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetic acid, Weight ratio of ketone: catalyst = 9.5:1

Table B.4 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent. (without catalyst)

Reaction time (hr)	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly (ε-caprolactone)	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
0.5	-	-	-	-	-	-	10
1	-	-	-	-	-	-	11
1.5	-	-	-	-	-	-	12
2	-	-	-	-	-	-	13
2.5	Trace	Trace	-	-	-	-	14
3	Trace	Trace	-	-	-	-	15
6	Trace	Trace	-	-	-	-	16
12	Trace	Trace	-	-	-	-	17

Reaction condition: Temperature 60 °C. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile

Table B.5 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent. (Ti-Beta catalyst)

Reaction time (hr)	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly (ε-caprolactone)	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
2	7.73	7.73	-	-	-	100	18
4	16.12	16.12	-	-	-	100	19
6	40.31	38.02	2.29	-	-	94.32	20
8	40.175	27.01	13.16	-	-	67.23	21
12	40.04	16	24.03	-	-	39.97	22
24	38.85	10.26	13.43	15.15	-	26.42	23

Reaction condition: Temperature 60 ^{o}C. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1

Table B.6 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent. (Ti-Beta catalyst)

Solvent ratio H_2O : Acetonitrile	%Conversion of cyclohexanone	%Yields of $\mathcal{E}$-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly ($\mathcal{E}$-caprolactone)	%Yields of other oxygenated compound	%Selectivity of $\mathcal{E}$-caprolactone	Batch
0 : 12.66	10.66	10.66	-	-	-	100	1
2.79 : 9.87	12.38	12.38	-	-	-	100	24
5.57 : 7.08	18.97	18.97	-	-	-	100	25
8.36 : 4.3	40.31	38.02	2.29	-	-	94.32	20

Reaction condition: Temperature 60 ^{o}*C. Reaction time 6 hr, Molar ratio of reactant = 1 cyclohexanone: 12.7 solvent: 1.2 Hydrogen peroxide, Weight ratio of ketone: catalyst = 9.5: 1*

Table B.7 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent. (K-Ti-Beta catalyst)

Reaction time (hr)	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly (ε-caprolactone)	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
2	4.61	4.61	-	-	-	100	26
4	14.21	14.21	-	-	-	100	27
6	29.47	28.65	0.82	-	-	97.22	28
8	31.24	27.53	3.71	-	-	88.12	29

Reaction condition: Temperature 60 ^{o}*C. Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

Table B.8 Baeyer-Villiger oxidation of cyclohexanone using acetic acid as a solvent.

Catalyst	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
-	51.37	5.80	17.62	27.95	11.29	5
Ti-Beta	92.83	0.98	18.46	73.39	1.06	9
K-Ti-Beta	77.38	11.85	14.98	50.55	15.31	30

Reaction condition: Temperature 60 ^{o}*C. Reaction time 6 hr, Molar ratio of reactant =1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetic acid, Weight ratio of ketone: catalyst = 9.5: 1*

Table B.9 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent.

Catalyst	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly (ε-caprolactone)	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
Without catalyst	Trace	Trace	-	-	-	-	16
TiO_2	0	-	-	-	-	-	31
H-Beta	18.61	18.61	-	-	-	100	32
Dealuminated Beta	25.37	25.37	-	-	-	100	33
TS-1	0.22	0.22	-	-	-	100	34
Ti-Beta	40.31	38.02	2.29	-	-	94.32	20

Reaction condition: Temperature 60 ^{o}*C, Reaction time 6 hr., Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1*

Table B.10 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent. (Ti-Beta catalyst)

Temerature (°C)	%Conversion of cyclohexanone	%Yields of ℰ-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly (ℰ-caprolactone)	%Yields of other oxygenated compound	%Selectivity of ℰ-caprolactone	Batch
40	0.69	0.69	-	-	-	100	35
45	3.56	3.56	-	-	-	100	36
50	5.58	5.58	-	-	-	100	37
55	11.38	11.38	-	-	-	100	38
60	16.12	16.12	-	-	-	100	20
65	15.59	14.19	1.4	-	-	91.02	39
70	12.12	5.86	6.26	-	-	48.35	40

Reaction condition: Reaction time 4 hr., Molar ratio of reactant = 1 cyclohexanone: 1.2 hydrogen peroxide: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1

Table B.11 Baeyer-Villiger oxidation of cyclohexanone using acetonitrile as a solvent. (Ti-Beta catalyst)

H_2O_2 : Cyclohexanone	%Conversion of cyclohexanone	%Yields of ε-caprolactone	%Yields of 6-hydroxyhexanoic acid	%Yields of poly (ε-caprolactone)	%Yields of other oxygenated compound	%Selectivity of ε-caprolactone	Batch
0.6	16.75	16.75	-	-	-	100	41
1.2	40.31	38.02	2.29	-	-	94.32	20
2.4	31.15	27.98	26.83	-	-	89.82	42
3.6	30.29	3.17	3.46	-	-	88.58	43

Reaction condition: Temperature 60 ^{o}C. Reaction time 6 hr, Molar ratio of reactant = 1 cyclohexanone: 8.36 acetonitrile, Weight ratio of ketone: catalyst = 9.5: 1, Hydrogen peroxide: H_2O = 1.2: 4.3 ($H_2O_2$40%w/v)

APPENDIX C

Results from Gas Chromatography/Mass Spectrometer

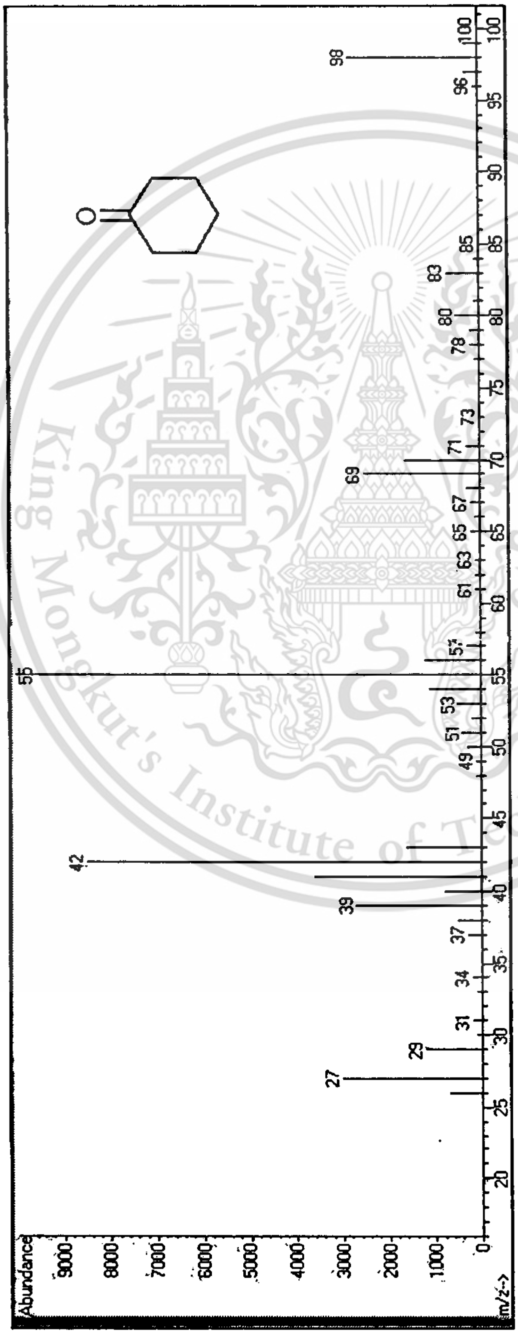

Figure C.1 Mass spectrum of cyclohexanone.

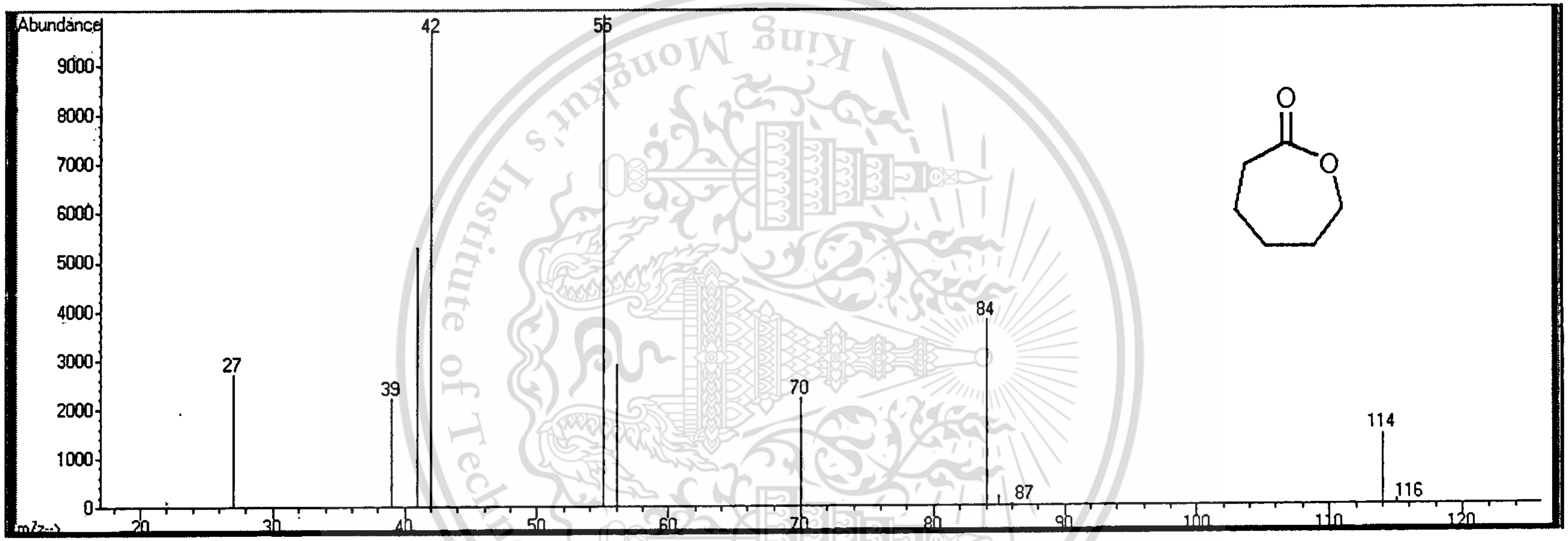

Figure C.2 Mass spectrum of ε-caprolactone from Baeyer-Villiger oxidation.

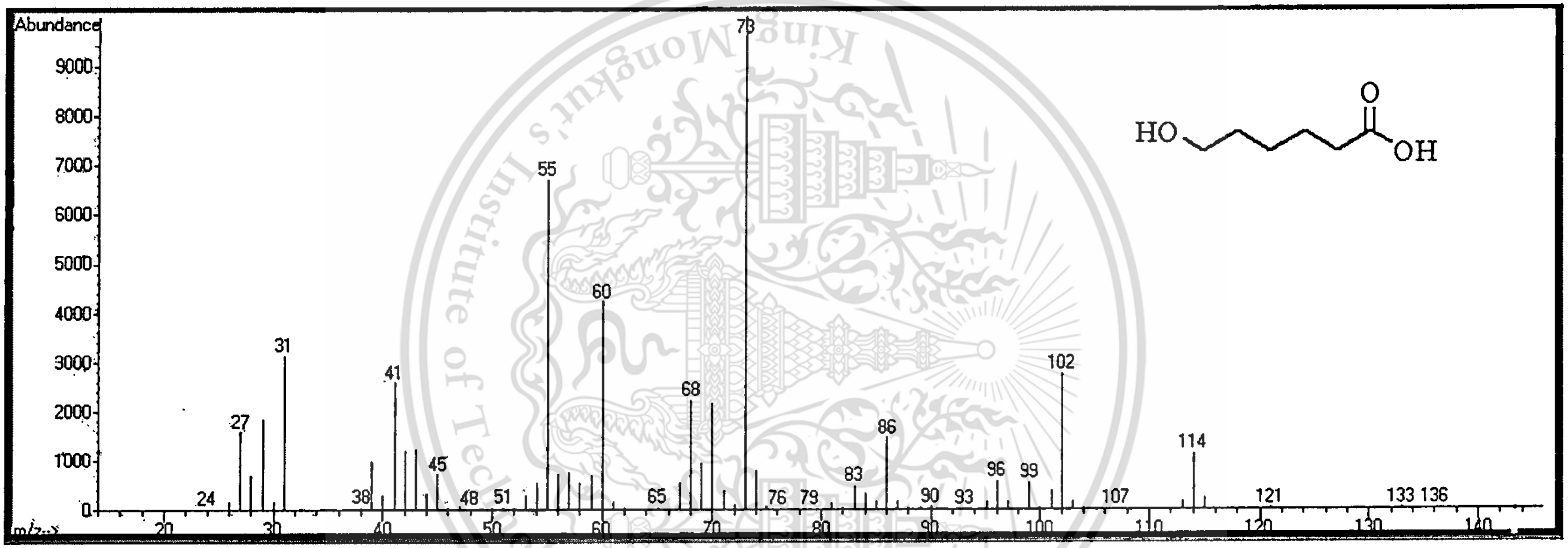

Figure C.3 Mass spectrum of 6-hydroxyhexanoic acid from ε-caprolactone hydrolysis.

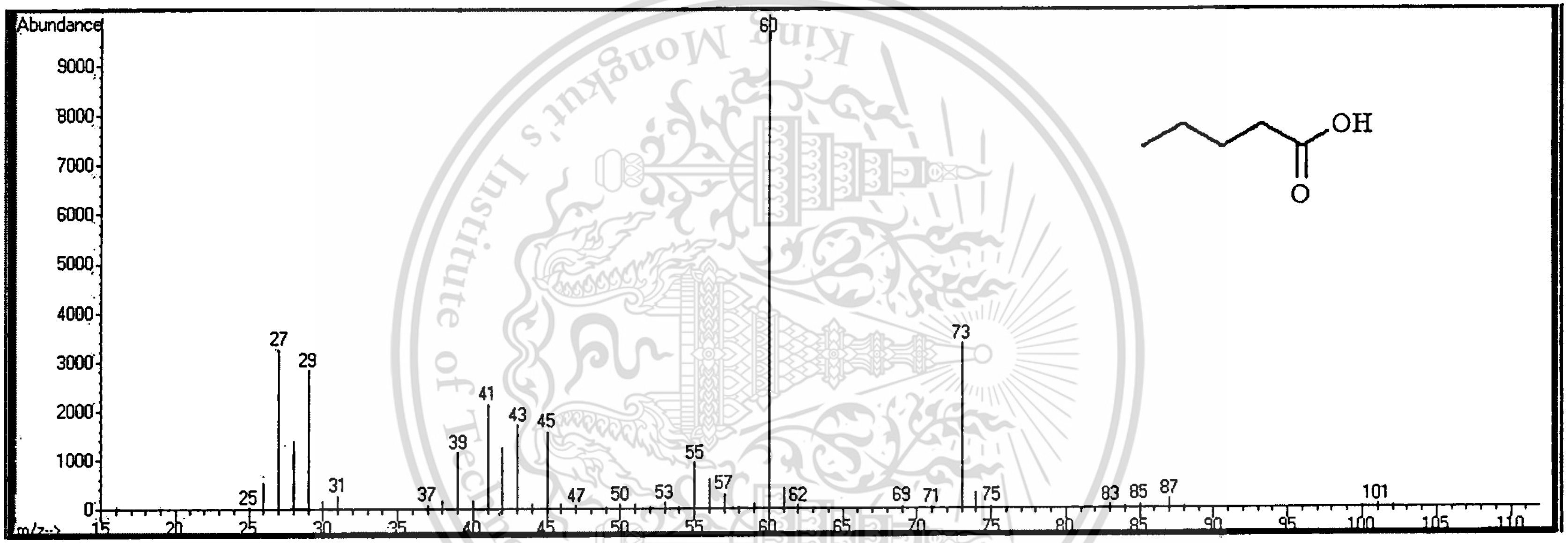

Figure C.4 Mass spectrum of pentanoic acid. (Other oxygenated product from oxidation in acetic acid)

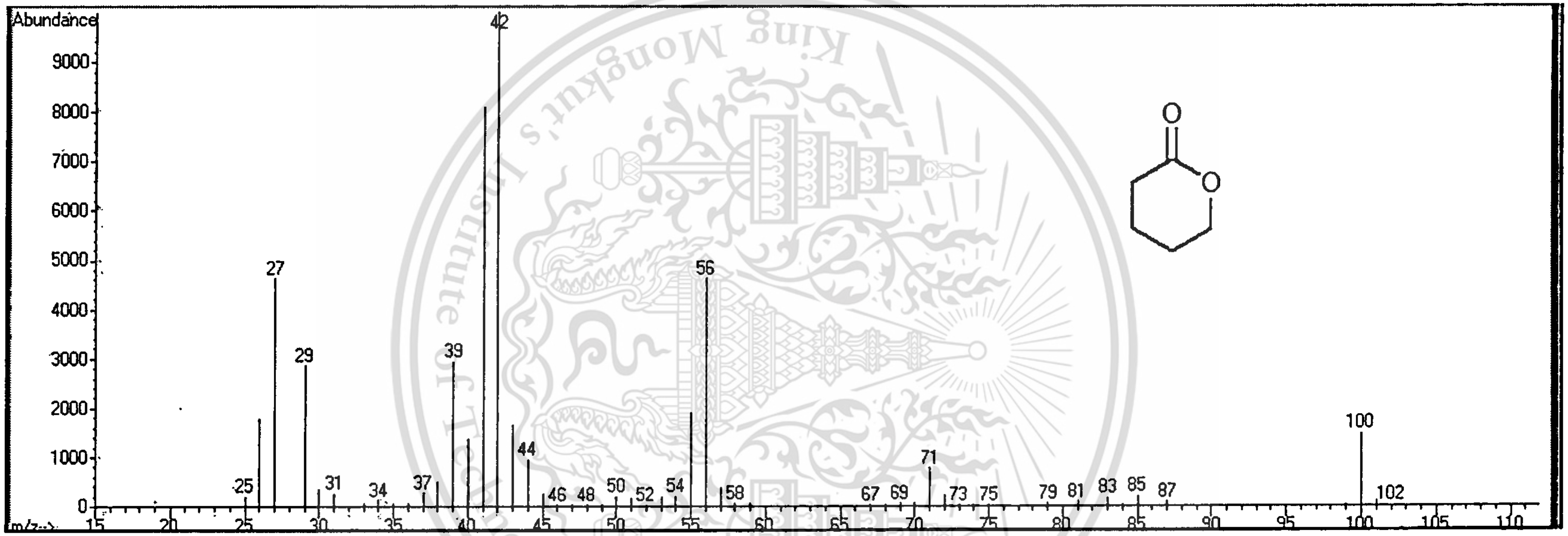

Figure C.5 Mass spectrum of δ-valerolactone. (Other oxygenated product from oxidation in acetic acid)

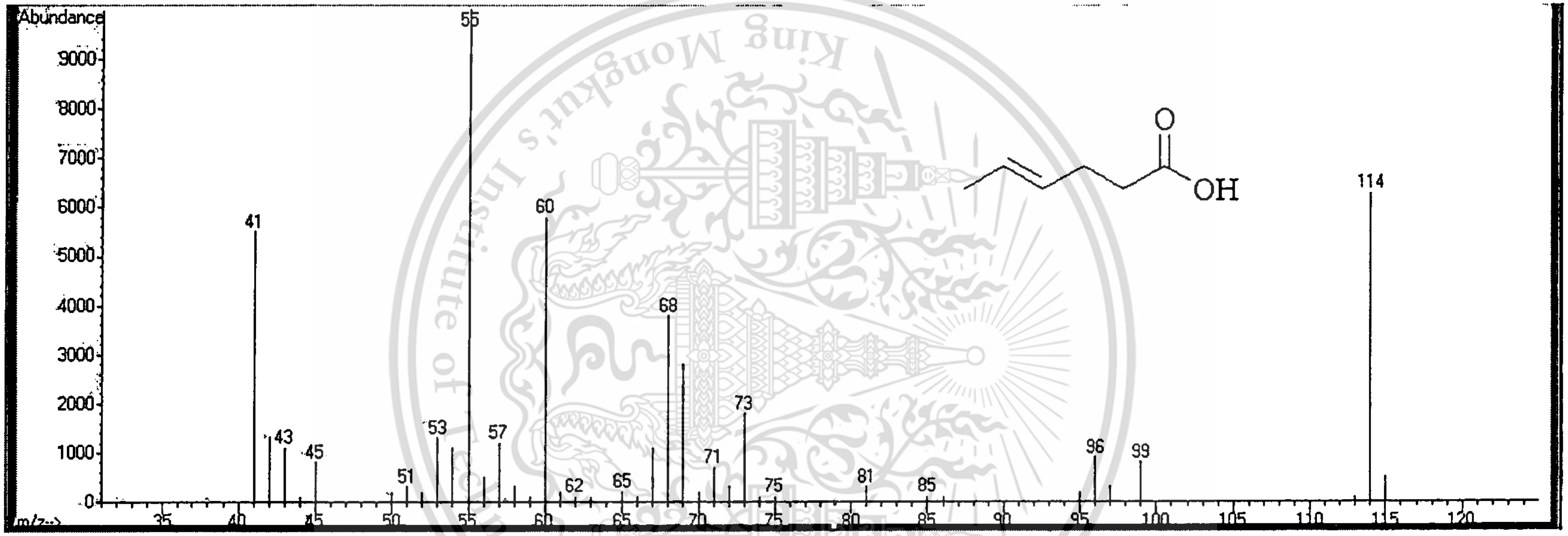

Figure C.6 Mass spectrum of 4-hexenoic acid. (Other oxygenated product from oxidation in acetic acid)

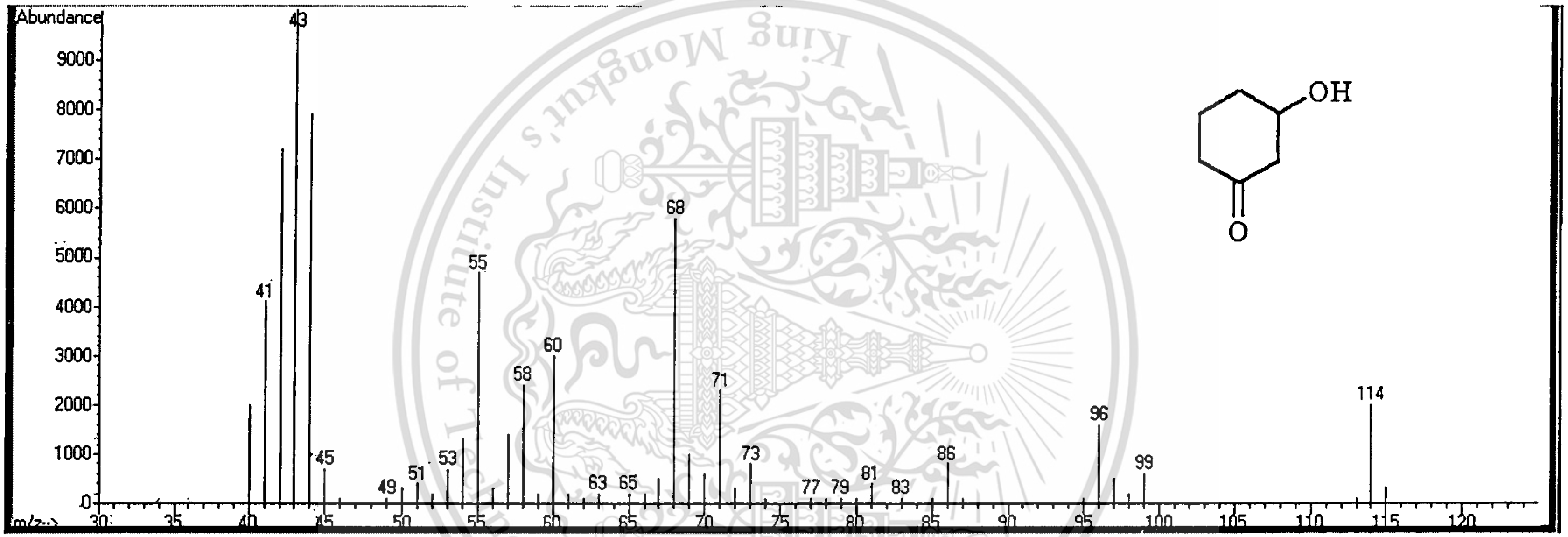

Figure C.7 Mass spectrum of 3-hydroxycyclohexanoe. (Other oxygenated product from oxidation in acetic acid)

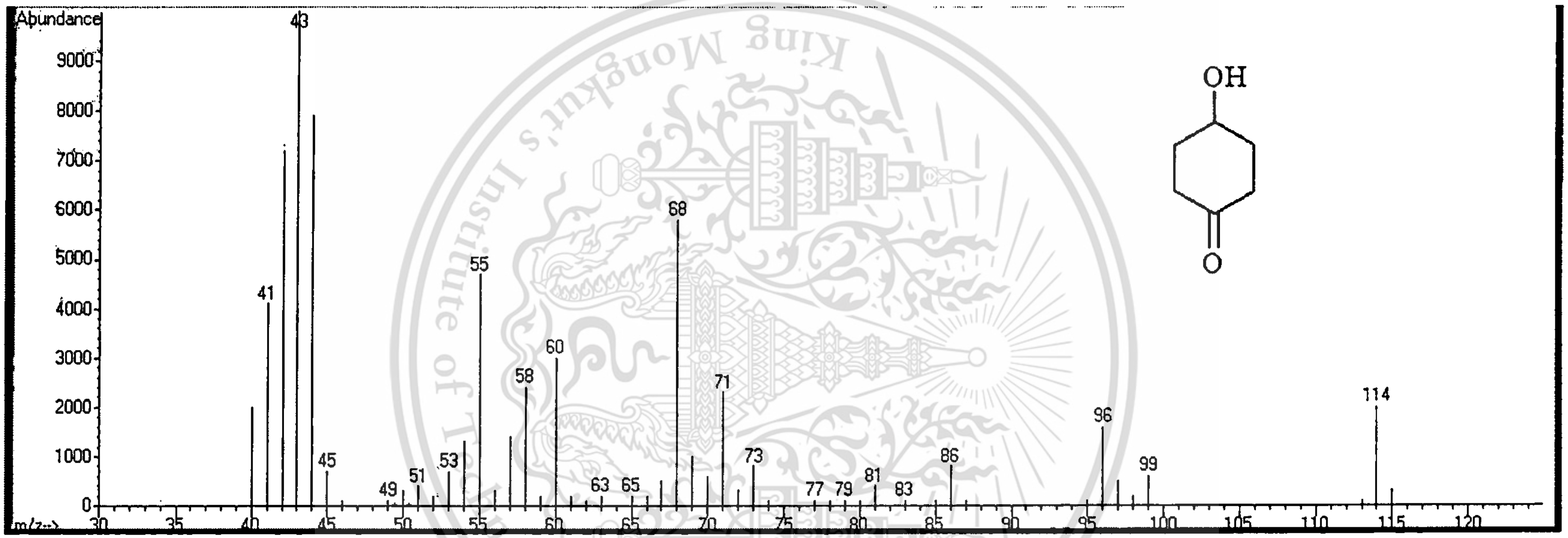

Figure C.8 Mass spectrum of 4-hydroxycyclohexanoe. (Other oxygenated product from oxidation in acetic acid)

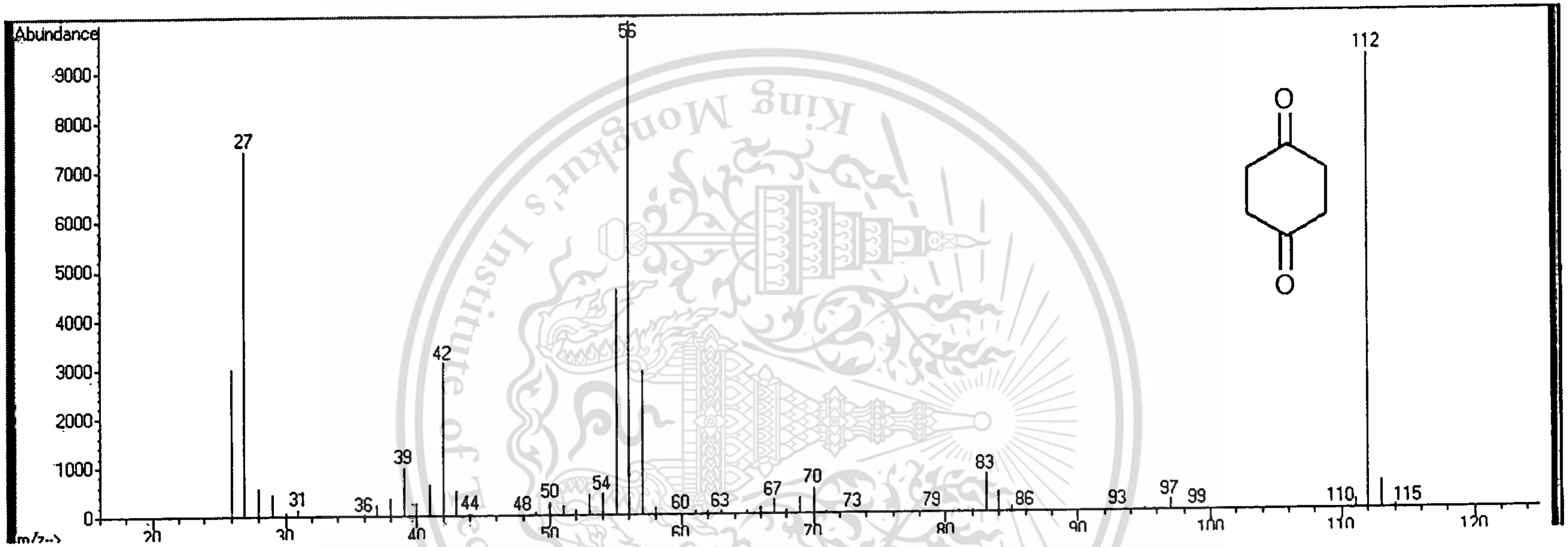

Figure C.9 Mass spectrum of 1,4-cyclohexanedione. (Other oxygenated product from oxidation in acetic acid)

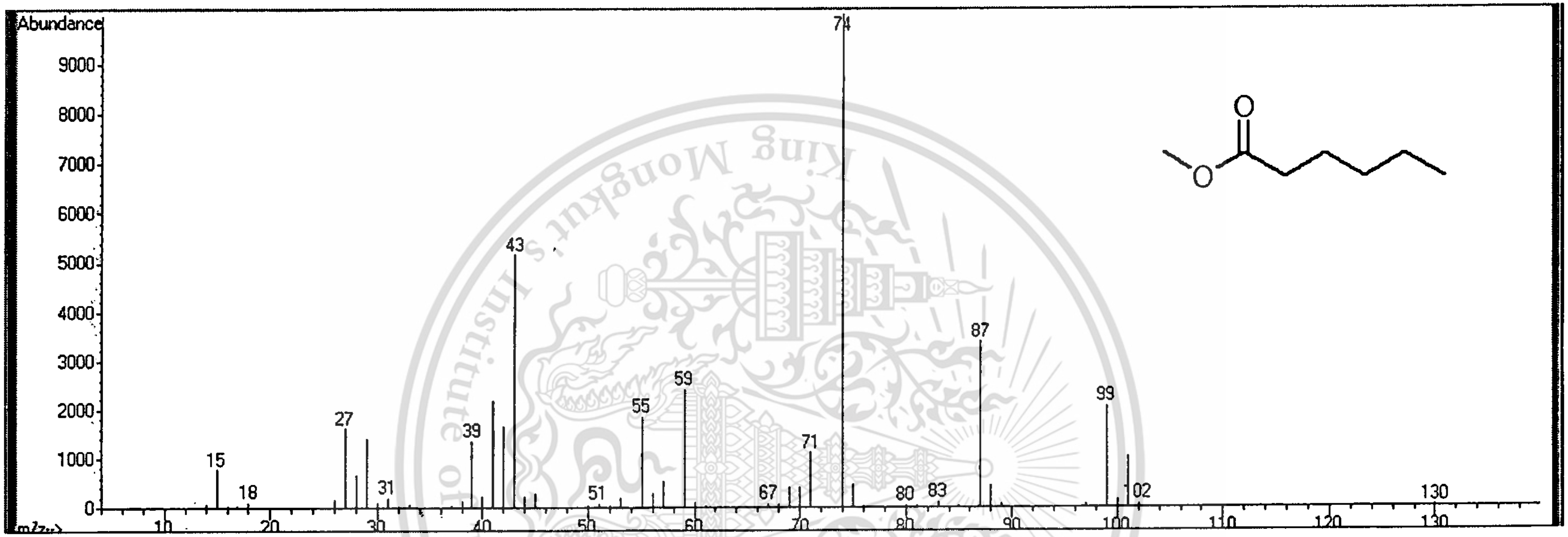

Figure C.10 Mass spectrum of methyl hexanoate. (Other oxygenated product from oxidation in acetic acid)

AUTHOR BIOGRAPHY

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