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รายงานการวิจัยฉบับสมบูรณ์

โครงการ

การศึกษาความสามารถในการเร่งปฏิกิริยาของซีโอไลต์ที่มีไททาเนียมเป็นองค์ประกอบ

Study on Catalytic Activity of Titanium Containing Zeolites

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาการเร่งปฏิกิริยาของซีโอไลต์ที่มีไททาเนียมเป็นองค์ประกอบ โดยศึกษา ปฏิกิริยาการจัดเรียงตัวใหม่แบบเบคมานของไซโคลเฮกซาโนนออกซีม และปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนเพื่อสังเคราะห์ไซโคลเฮกซาโนนออกซีมในกระบวนการแบบกะและแบบต่อเนื่อง

จากการวิจัยพบว่า นั้น ซีโอไลต์บีต้าที่เป็นกรดมีความสามารถในการเร่งปฏิกิริยา(activity) การจัดเรียงตัวใหม่แบบเบคมานของไซโคลเฮกซาโนนออกซีมสูงกว่าซีโอไลต์บีต้าที่กำจัดอะลูมิเนียมและซีโอไลต์ไททาเนียมบีต้า ในขณะที่ซีโอไลต์บีต้าที่กำจัดอะลูมิเนียมมีการเลือกสรร (selectivity) คาโปรแลคตัมสูงที่สุด เมื่ออุณหภูมิและเวลาที่สัมผัสตัวเร่งปฏิกิริยาเพิ่มขึ้นจะทำให้ความสามารถในการเร่งปฏิกิริยาและการเลือกสรรเพิ่มขึ้น นอกจากนั้นเมื่อเติมน้ำลงในตัวทำละลายนอมอร์บิวทานอลจะทำให้ความสามารถในการเร่งปฏิกิริยาและการเลือกสรรเพิ่มขึ้นด้วย ส่วนการศึกษาปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนเพื่อสังเคราะห์ในกระบวนการแบบกะ พบว่าการใช้กรดแอซิติกเป็นตัวทำละลายจะทำให้ได้ผลิตภัณฑ์เป็นไซโคลเฮกซาโนนออกซีมในปริมาณที่มากกว่าการใช้น้ำเป็นตัวทำละลาย นอกจากนั้นพบว่า เกลือแอมโมเนียของกรดอ่อน เช่น เกลือแอมโมเนียมแอซิเตต แอมโมเนียมคาร์บอเนต แอมโมเนียมซิเตรท และ แอมโมเนียมออกซาเลต สามารถใช้ในการทำปฏิกิริยาได้ การเร่งปฏิกิริยาโดยใช้ซีโอไลต์ไทเทเนียมบีต้าได้ผลดีกว่าการใช้ไทเทเนียมซิลิกาไลต์ แต่ทำให้เกิดการจัดเรียงตัวใหม่ของผลิตภัณฑ์คาโปรเลคเทมขึ้นด้วย จากการศึกษาพบว่ากลไกการเกิดปฏิกิริยาแอมมอกซิเมชันสามารถเกิดขึ้นได้ 2 ทาง กล่าวคือ เมื่อใช้กรดแอซิติกเป็นสารละลาย แอมโมเนียเข้าทำปฏิกิริยากับไซโคลเฮกซาโนนก่อนแล้วจึงถูกออกซิไดส์ได้เป็นไซโคลเฮกซาโนนออกซีม ส่วนการใช้น้ำเป็นตัวทำละลาย แอมโมเนียถูกออกซิไดซ์เป็นไฮดรอกซีลามีนก่อนแล้วจึงเข้าทำปฏิกิริยากับไซโคลเฮกซาโนนเป็นไซโคลเฮกซาโนนออกซีม สำหรับปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนในกระบวนการแบบต่อเนื่อง จะใช้

TS-1 เป็นตัวเร่งปฏิกิริยา โดยเครื่องปฏิกรณ์แบบปั่นกวนขนาด 50 มิลลิลิตรให้เปอร์เซนต์การเปลี่ยนแปลง (Conversion) ของไซโคลเฮกซาโนน (40%โมล) และให้การเลือกสรร (Selectivity) ในการเกิดไซโคลเฮกซาโนนออกซึม (90%โมล) สูงกว่าใช้เครื่องปฏิกรณ์แบบท่อไหลและในกระบวนการแบบกะ (20% Conversion, 70% Selectivity) การเพิ่มเวลาสัมผัส (contact time) ทำให้เปอร์เซนต์การเปลี่ยนแปลง (Conversion) เพิ่มขึ้น โดยการลดอัตราการไหลของสารตั้งต้นและเพิ่มปริมาณของตัวเร่งปฏิกิริยา เมื่อทำการลดความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์จะได้การเลือกสรร (Selectivity) ในการเกิดไซโคลเฮกซาโนนออกซึมสูงขึ้น ตัวเร่งปฏิกิริยาสามารถทำการปฏิกิริยาได้มากกว่า 40 ชั่วโมงโดยปริมาณผลิตภัณฑ์ไซโคลเฮกซาโนนออกซึมคงที่ นอกจากนั้นการเพิ่มอุณหภูมิในการกำจัดสารอินทรีย์ของตัวเร่งปฏิกิริยายังช่วยลดการสูญเสียตำแหน่งที่ว่องไวของปฏิกิริยาอีกด้วย

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ABSTRACT

In this research, reactions using titanium-containing zeolite catalysts namely Beckmann rearrangement of cyclohexanone oxime and ammoximation of cyclohexanone to cyclohexanone oxime in bath and continuous process were studied.

It was found that in Beckmann rearrangement of cyclohexanone oxime, H-Beta possessed higher activity, as compared to Dealuminated Beta and Ti-Beta while the Dealuminated Beta possessed the highest selectivity for caprolactam formation. The conversion of cyclohexanone oxime and caprolactam selectivity was increased with an increase in temperature and contact time. Moreover, the use of water/*n*-butanol as solvent shows improved conversion and selectivity. In the ammoximation of cyclohexanone, reaction using acetic acid as a solvent shows higher activity than that using water as a solvent, due to the formation of a better oxidizing agent, peracetic acid. The investigation on alternative sources of ammonia showed that ammonium salts of weak acid, such as ammonium acetate, ammonium carbonate, ammonium citrate and ammonium oxalate can be used for synthesis cyclohexanone oxime. Ammoximation reaction catalyzed by Ti-Beta zeolite produces higher yields of products than that using TS-1. However, further rearrangement of cyclohexanone oxime to caprolactam was observed. The study of the reaction mechanism shows that there are two possible partway for the formation of cyclohexanone oxime. The condensation of ammonia with cyclohexanone to produce primarily cyclohexanone imine followed by oxidation of cyclohexanone is favored in the presence of acetic acid. In contrast, ammonia is primarily oxidized to hydroxylamine, then the hydroxylamine reacts with cyclohexanone to form cyclohexanone oxime in reaction using water as a solvent. For the ammoximation of cyclohexanone in continuous process, the reaction using TS-1 as catalyst in continuous stirred tank reactor (50 ml)gives a better activity (up to 40% mol) and selectivity of the oxidised products (up to 90%mol), as compared with the plug flow reactor and the batch process (20% conversion, 70%selectivity). The increase in contact time (W/F 42-148 g.hr/mol), either by increasing amounts of TS-1 (0.5-2.0 g) or decreasing reactants feeding rate (7-25 ml/min), leads to an increase in cyclohexanone oxime formation. It is also shown that when the molar ratio of cyclohexanone and hydrogen peroxide is increased (0.8-2.5 mol/mol), the selectivity of cyclohexanone oxime is raised (50-90%). Over 40 hours of testing, the catalyst gives a steady yield of cyclohexanone oxime. Leaching of titanium active sites were also found (2-10%), however, this can be reduced when the calcining temperature is raised (500-600°C).

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CONTENTS

Executive Summary

From the study of titanium containing zeolite and zeolite catalysts namely TS-1, Ti-Beta, H-Beta, Dealuminated Beta and titanation of Dealuminated Beta for ammoximation of cyclohexanone, beckman rearrangement of cyclohexanone oxime and ammoximation of cyclohexanone in continuous process, it can be conclude that:

1. **Beckman rearrangement of cyclohexanone oxime**

The H-Beta, Dealuminated Beta and Ti-Beta were prepared by calcination the commercial NH_4^+-Beta zeolite, dealumination of H-Beta and titanation of Dealuminated Beta, respectively. They appear to be appropriate catalysts, due to these small crystallite size (0.2 micrometers) with high surface area (507, 528, and 627, respectively). The silicon/titanium ratio of Ti-Beta is found to be 43. The titanium in zeolites are present in two species: non-framework titanium and framework titanium. The latter can be evident by the characteristic vibration of Ti-O-Si at 960 cm^{-1}.

In the reaction using H-Beta, the conversion of cyclohexanone oxime is higher, as compared to Dealuminated Beta and Ti-Beta, respectively. It is believed that the conversion of cyclohexanone oxime depends largely on the type of active sites. The appropriate active sites should be favor for the adsorption of reactant, but unfavorable for products. It is confirmed by this study that, the reactant can adsorb and rearrangement to products and the products must be desorbed to give free active sites, which allows the adsorption of a forthcoming reactant.

The selectivity of caprolactam in the reaction using Dealuminated Beta is higher than that H-Beta and Ti-Beta, respectively. The selectivity depends largely on the acid strength of active sites; the higher the acid strength, the lower the selectivity of caprolactam. In the case of Ti-Beta, the catalyst possesses framework/non-framework titanium sites and silanol sites. The titanium sites seem to be non-selective for this reaction, due to the strong interaction with the reactant to presumably form a peroxy complex. Only silanol sites can facilitate the reaction of cyclohexanone oxime to desired products. Accordingly the conversion and selectivity of cyclohexanone oxime using Ti-Beta as catalyst is found to be less than others.

The conversion of cyclohexanone oxime and the selectivity of caprolactam are increased with the increase in temperature. The increased temperature, allows faster diffusion rate of the cyclohexanone oxime inside the pore of zeolite catalyst. The product desorption from the active sites would also be enhanced, resulting in increased vacant active sites for the adsorption of cyclohexanone oxime. This decreases the side reactions over the active sites. In addition, the deactivation rate is decreased with increased in temperature.

When the contact time was increased, the conversion of cyclohexanone oxime and the selectivity of caprolactam over any type of zeolites were increased. While the deactivation rate was decreased, due to the facile interaction of solvent with the active sites.

When the water was added in *n*-butanol, the polarity of solvent was increased. Product can be easily desorbed from the active sites, resulting in a rise in the conversion of cyclohexanone oxime. Moreover, the side reaction of adsorbed product to form coke precursor was decreased. Hence, the selectivity of caprolactam was improved. In the case of using ethanol as solvent, the conversion of cyclohexanone oxime and the selectivity of caprolactam over Ti-Beta were higher than those using *n*-butanol as solvent. Therefore, it can be concluded that the polarity of solvent and water added in solvent plays important role in the conversion of cyclohexanone oxime and selectivity of caprolactam.

The framework titanium species and non-framework titanium species gives low selectivity of caprolactam, as compared to Brϕnsted acid sites and silanol sites, respectively. On the other hand, titanium species facilitated the formation of by-products, namely 5-cyanopentane and cyclohexanone.

2. Ammoximation of cyclohexanone

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

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

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

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

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

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

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

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

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

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

3. Ammoximation of cyclohexanone in continuous process

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.

Influence of reactor types study, shows that lower yield of cyclohexanone oxime is produced in continuous plug 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 H_2O_2 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 amounts 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 titanium framework site for catalytic activity, are retained as observed 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. However, calcining temperature should not be exceed to 600 °C because Ti framework can be collapsed into unactive octahedral titaium species.

CHAPTER 1

CATALYST SYNTHESIS AND CHARACTERIZATION

1.1 Catalyst Synthesis

1.1.1 Catalyst Preparations

1.1.1.1 Titanium Silicalite (TS-1)

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

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

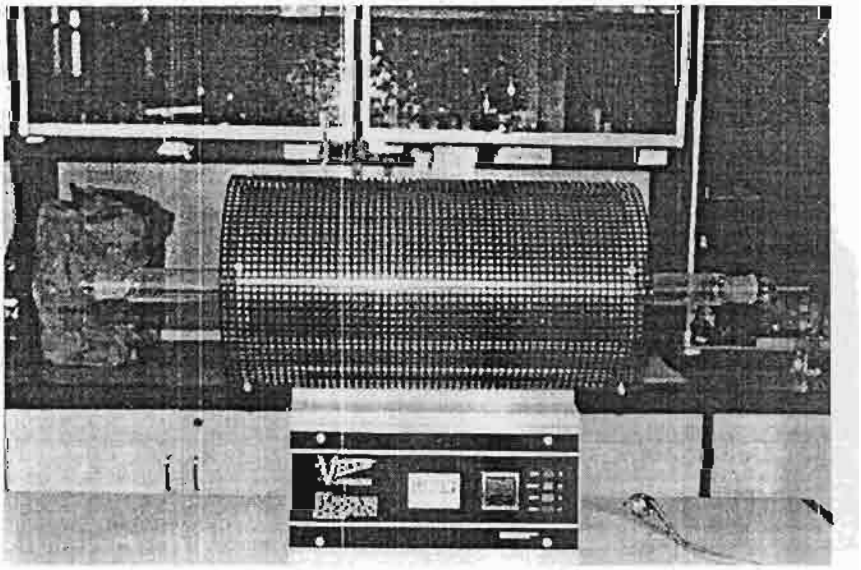


Figure 1.1 Calcination of zeolite in a furnace

1.1.1.2 Titanium Beta

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

Dealumination of Zeolite Beta

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

Titanation

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

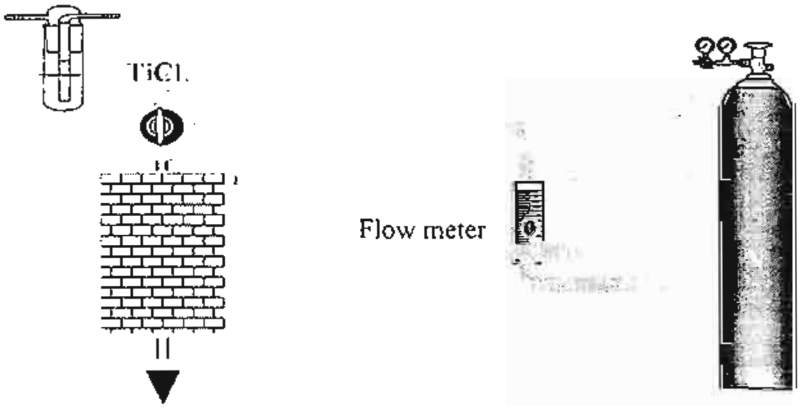


Figure 1.2 Packed-bed chemical vapor deposition (CVD)

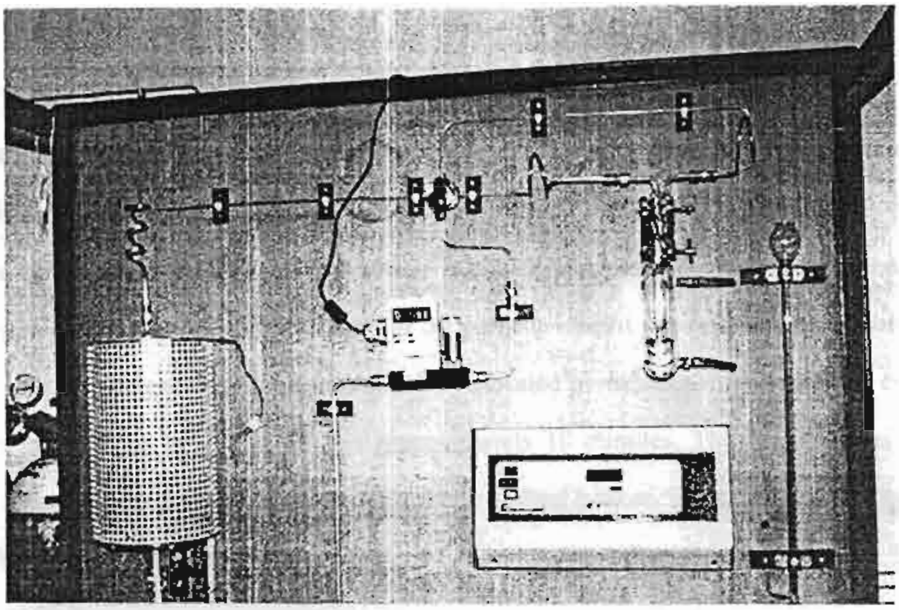


Figure1.3 Diagram of packed-bed chemical vapor deposition (CVD)

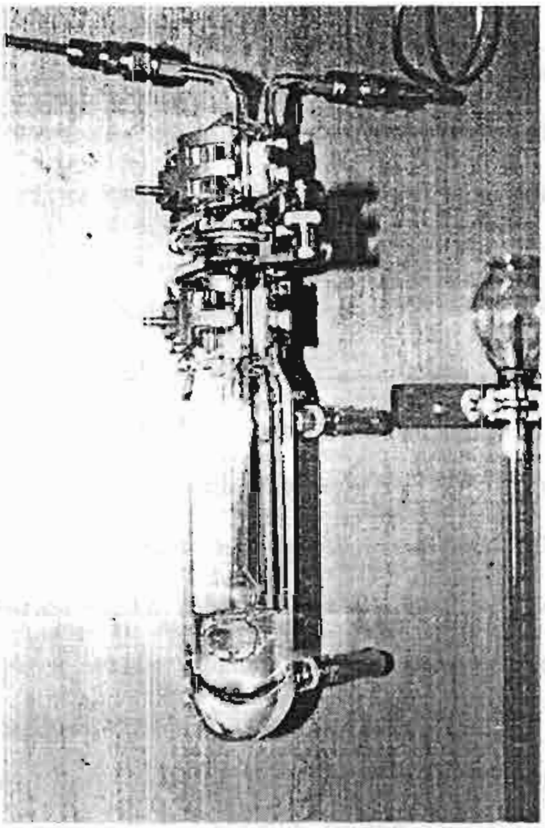


Figure 1.4 Bubbler for saturated vapor of titanium tetrachloride.

1.1.2 Characterization of Catalysts

1.1.2.1 Elemental Analysis

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

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

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

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

Table 1.1 The temperature program for determination of silicon, aluminium and titanium.

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

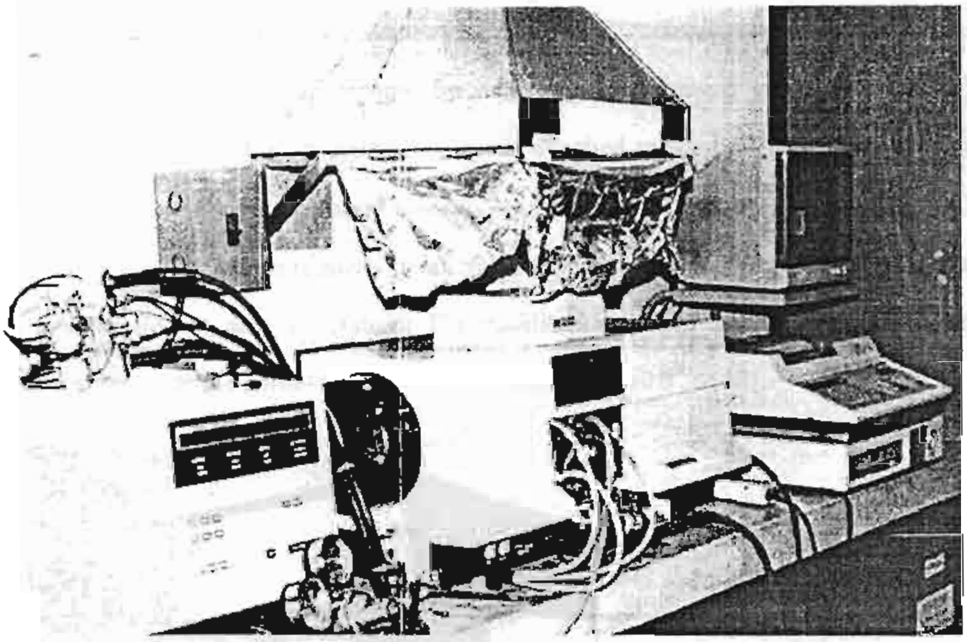


Figure 1.5 Atomic absorption spectrophotometer (AAS), AA-680 Shimadsu

1.1.2.2 Determination of Crystal Morphology of Zeolite

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

1.1.2.3 Determination of Zeolite Structure

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

1.1.2.4 Determination of Surface Area

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

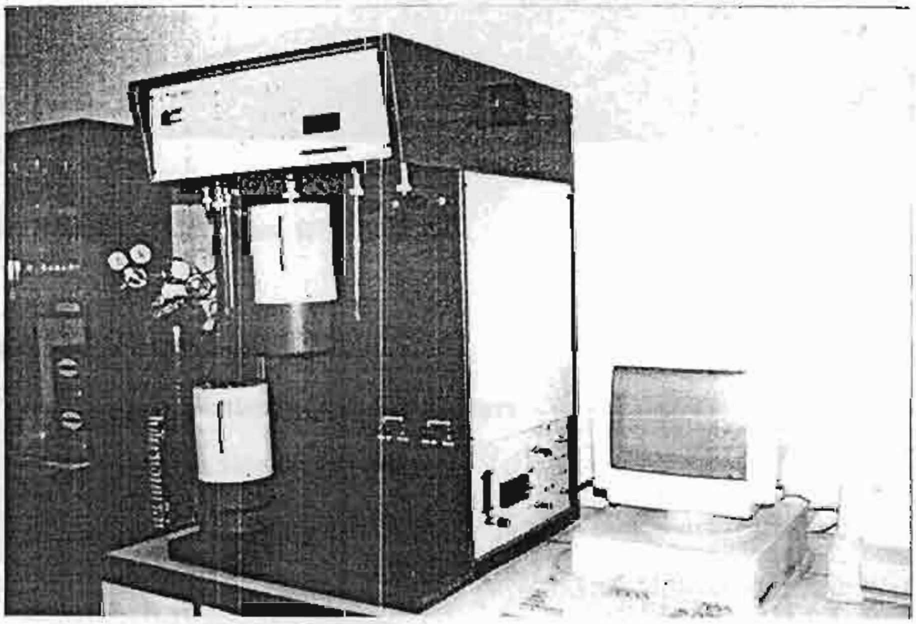


Figure 1.6 Gas Adsorption Analyzer (Autosorb-1, Quantachrome)

1.1.2.5 Determination of the Framework Titanium Species

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

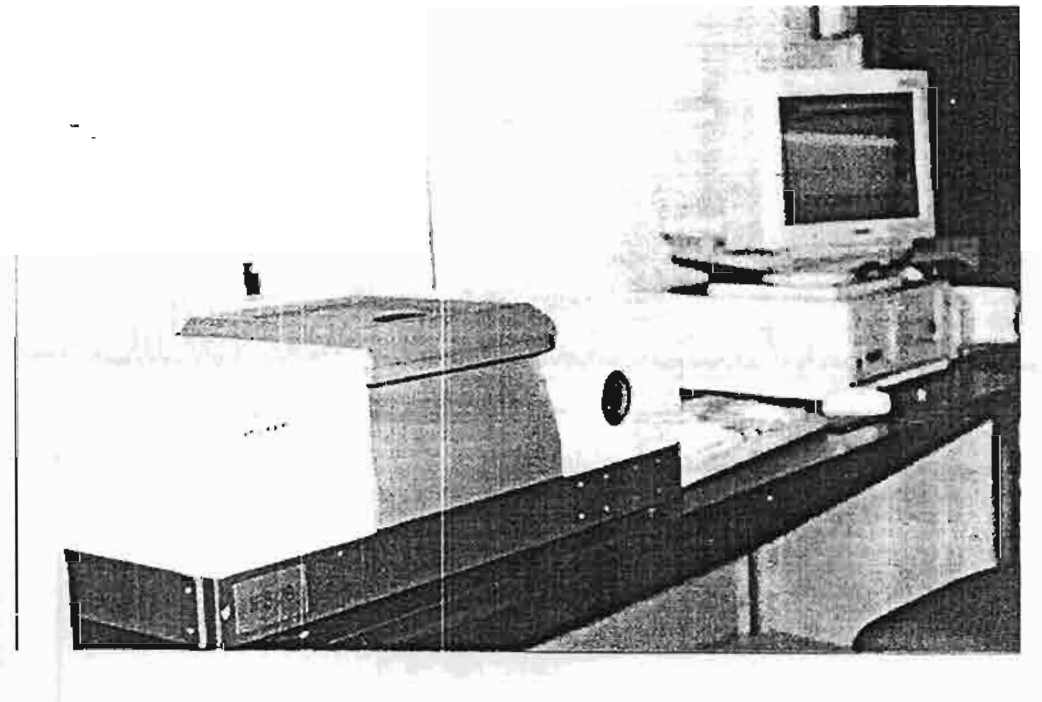


Figure 1.7 Infrared Spectrometer, IFS 28, Bruker.

1.2 Result and Discussion

1.2.1 Determination of Zeolite Structure

1.2.1.1 Titanium Silicalite I (TS-1)

The zeolite structure was determined by X-ray diffractometer. The X-ray diffraction patterns of all catalysts are shown in Appendix A. The X-ray diffraction pattern of TS-1 was compared with the standard X-ray diffraction pattern. It was shown that the synthesized TS-1 (Figure 1.8) 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 1.9) was shown that the structure remains unchanged. However, peak intensity at 2θ 7.88 and 8.84 was increased indicating decomposition of organic template from the pore of TS-1.

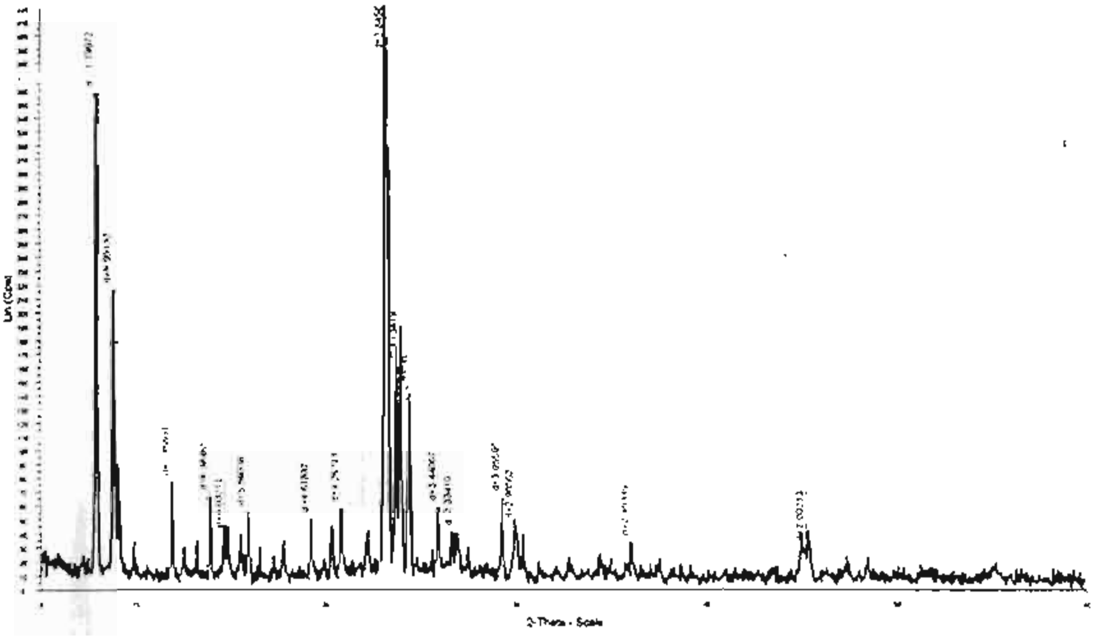


Figure 1.8 X-ray diffraction pattern of TS-1 before calcination.

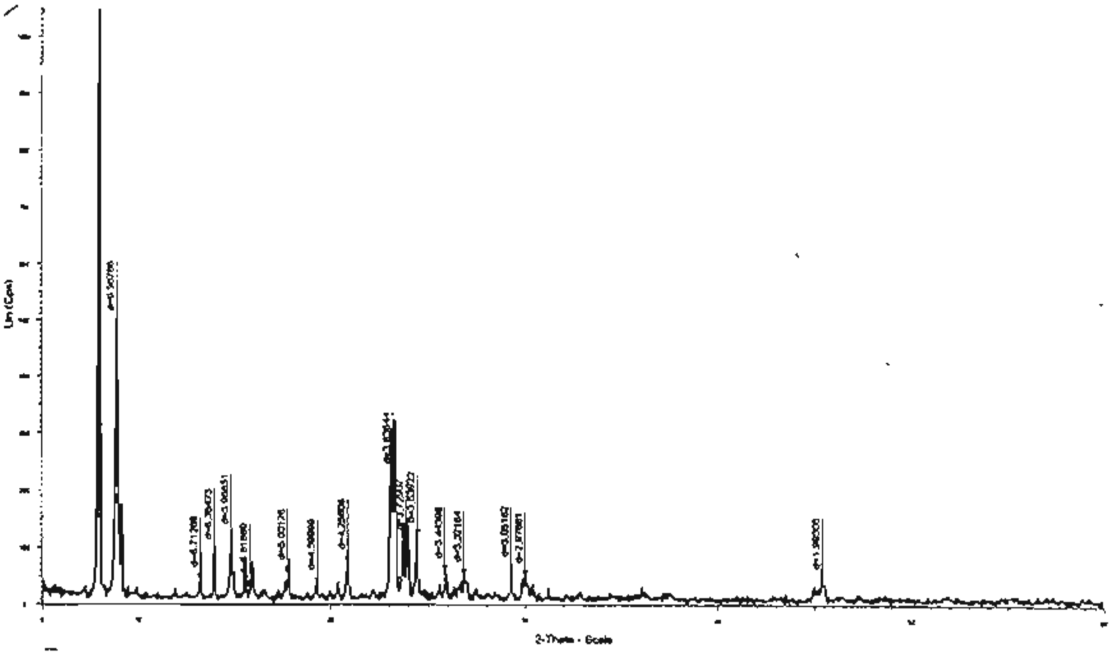


Figure 1.9 X-ray diffraction pattern of TS-1 after calcination.

1.2.1.2 Titanium Beta Zeolite

The X-ray diffraction pattern of parent zeolite Beta (Figure 1.10) was compared with the standard X-ray diffraction pattern. It was confirmed that the zeolite NH_4^+-Beta shows BEA type structure, showing characteristic peaks at 2θ 7.68, 22.45, 25.22, 26.82 and 29.47. After dealumination, X-ray diffraction pattern shows that the structure and crystallinity remain the same. However, when the dealuminated Beta was calcined, the characteristic peaks 2θ of zeolite was shifted from 2θ 7.68 to 7.93 indicating shrinkage of the pore size due to loss of the aluminium tetrahedra from the framework.

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

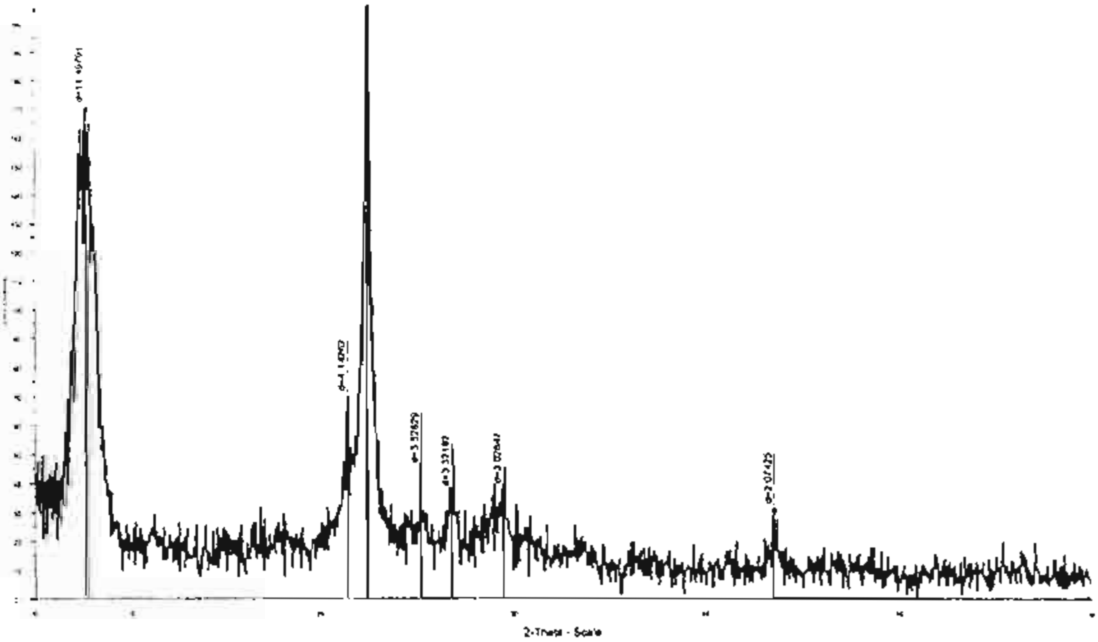


Figure 1.10 X-ray diffraction pattern of zeolite NH_4^+-Beta.

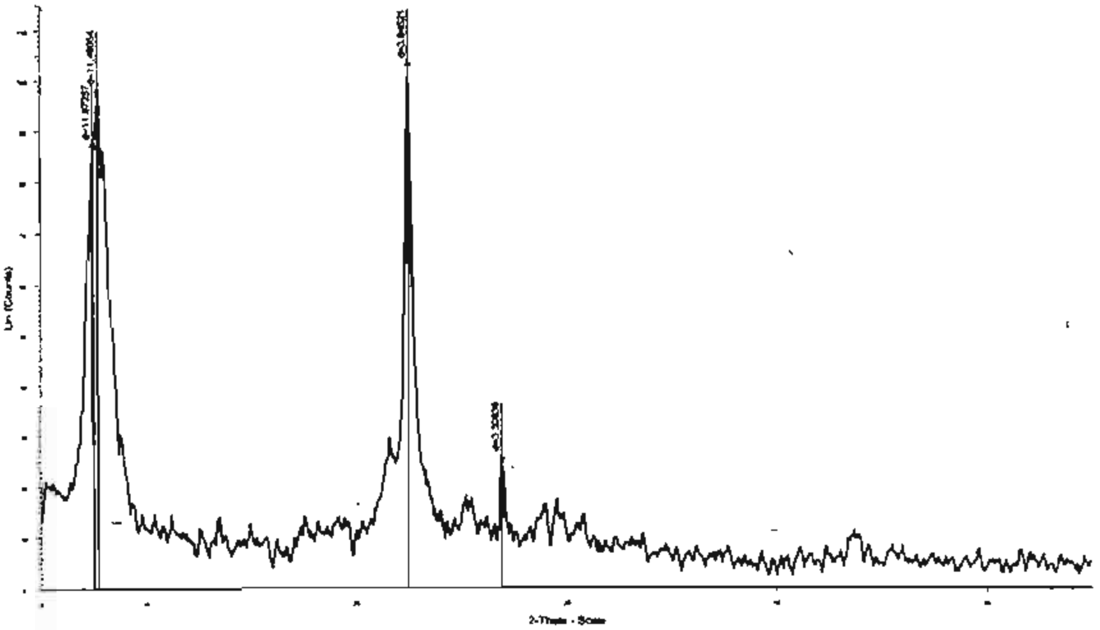


Figure 1.11 X-ray diffraction pattern of dealuminated zeolite Beta before calcination.

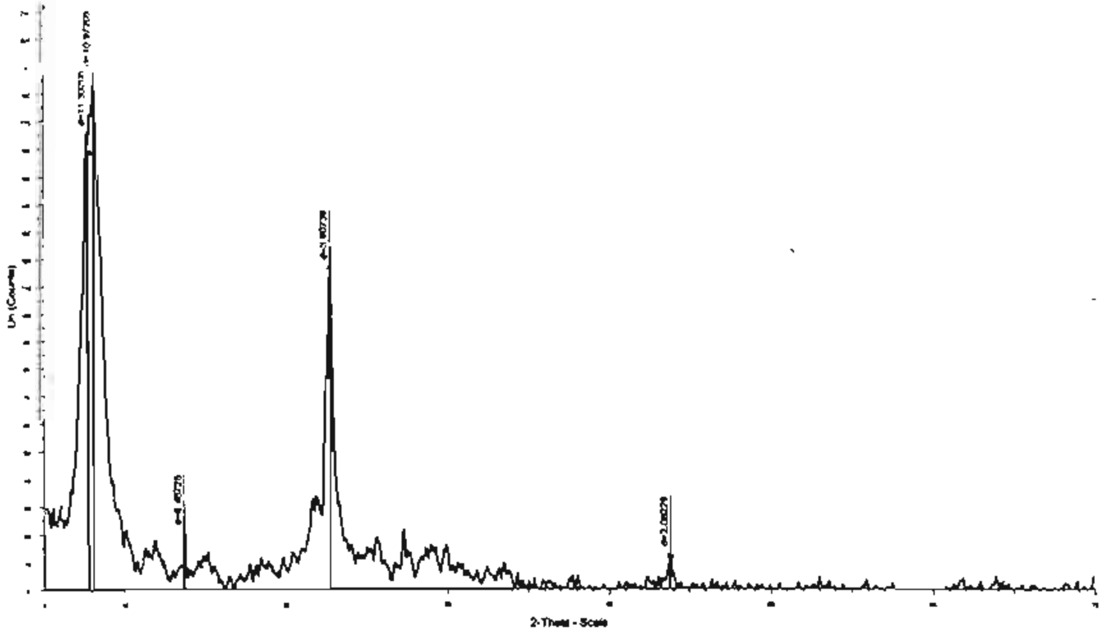


Figure 1.12 X-ray diffraction pattern of dealuminated zeolite Beta after calcination.

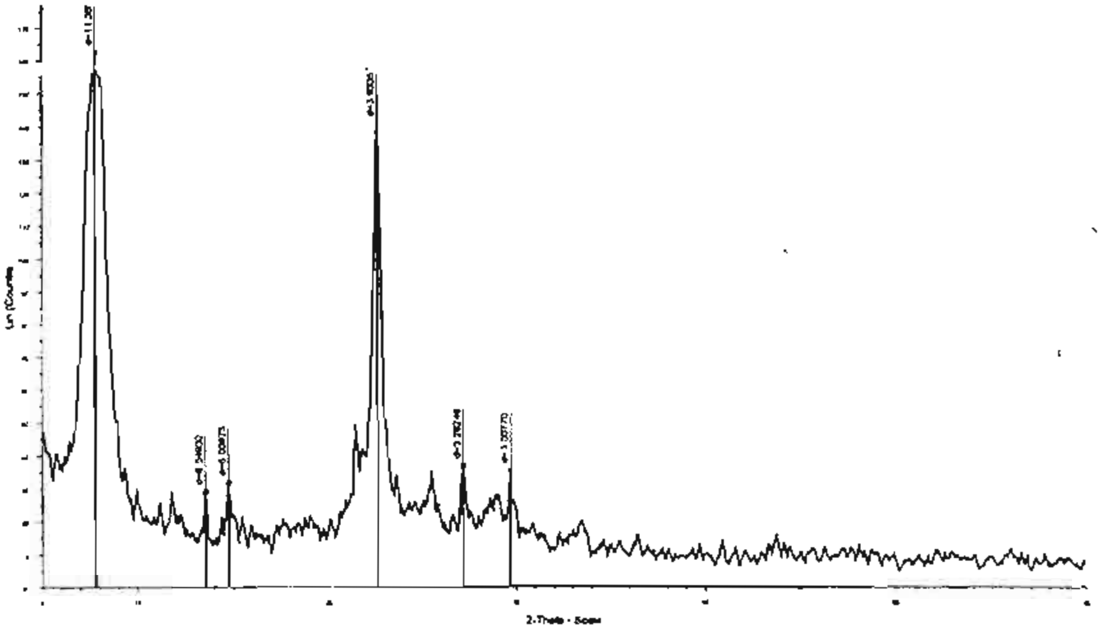


Figure 1.13 X-ray diffraction pattern of zeolite Ti-Beta before washing with sulfuric acid.

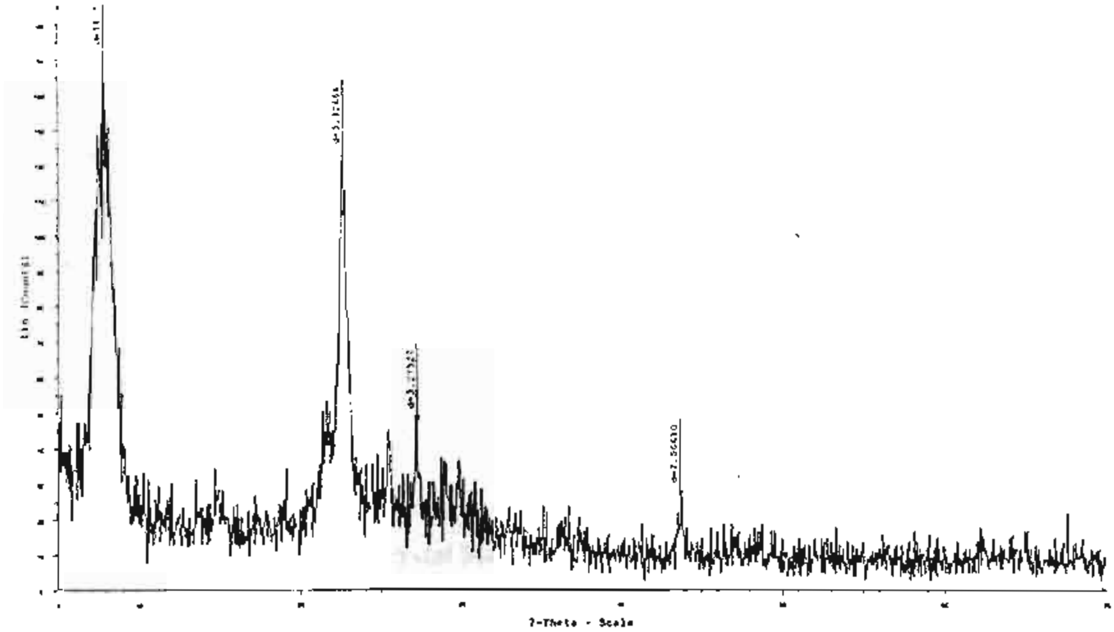


Figure 1.14 X-ray diffraction pattern of zeolite Ti-Beta after washing with sulfuric acid and calcination.

1.2.2 Elemental Analysis

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

Table 1.2 The determination of silicon, aluminium and titanium of zeolites

Zeolite	Silicon/Titanium	Silicon/Aluminium
TS-1	26	-
NH$_4^+$-Beta	-	27
Dealuminated Beta	-	> 200
Ti-Beta (before wash with sulfuric acid)	36	-
Ti-Beta (after wash with sulfuric acid)	47	-

It was shown that TS-1 has silicon/titanium ratio of 26. Parent zeolite NH$_4^+$-Beta possesses silicon/aluminium ratio of 27 (as certified by supplier). After dealumination of zeolite NH$_4^+$-Beta with 7 molar of nitric acid, aluminium in framework of zeolite was virtually removed. Silicon/titanium ratio of the zeolite after the titanation was found to be 36. However, after washing with sulfuric acid, the silicon/titanium ratio of the sample was increased to 47. This is suggested that there are 2 species of titanium in the zeolite; the framework and the non-framework titanium. The later can be washed out by sulfuric acid. It is believed that the titanium remained in the Ti-Beta after washing with acid are only the framework titanium species.

1.2.3 Determination of Crystal Morphology of Zeolite

The morphology of zeolite crystal and crystallite size was determined by scanning electron microscope. The electron micrograph of TS-1 both before and after calcination shows that crystallite size is about 18×5 micron (Figure 1.15 and 1.16). The sample appears to be a well-defined crystalline material. However, the crystallite size is relatively large for catalytic applications. The electron micrograph of NH$_4^+$-Beta (Figure 1.17), dealuminated Beta (Figure 1.18-a), calcined dealuminated Beta (Figure 1.18-b), Ti-Beta before washing with sulfuric acid (Figure 1.19-a) and Ti-Beta after washing with sulfuric acid (Figure 1.19-b) are shown that all of Beta samples have spherical shape with crystallite size of 0.5 micron in diameter. The small crystallite size of the sample is suitable for catalytic purposes.

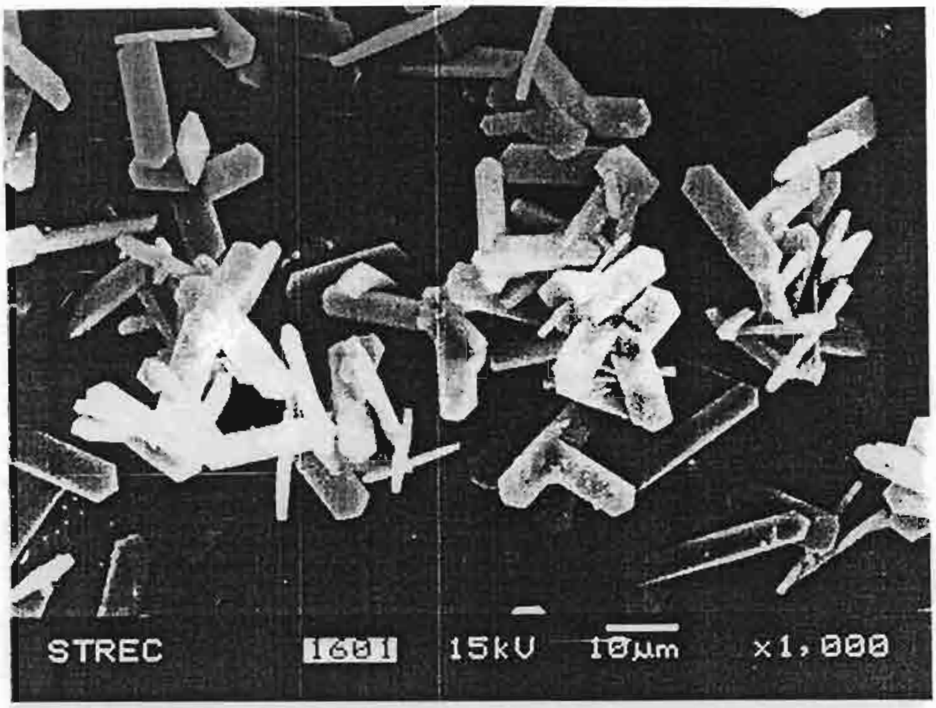


Figure 1.15 Scanning electron micrograph of TS-1 before calcination.

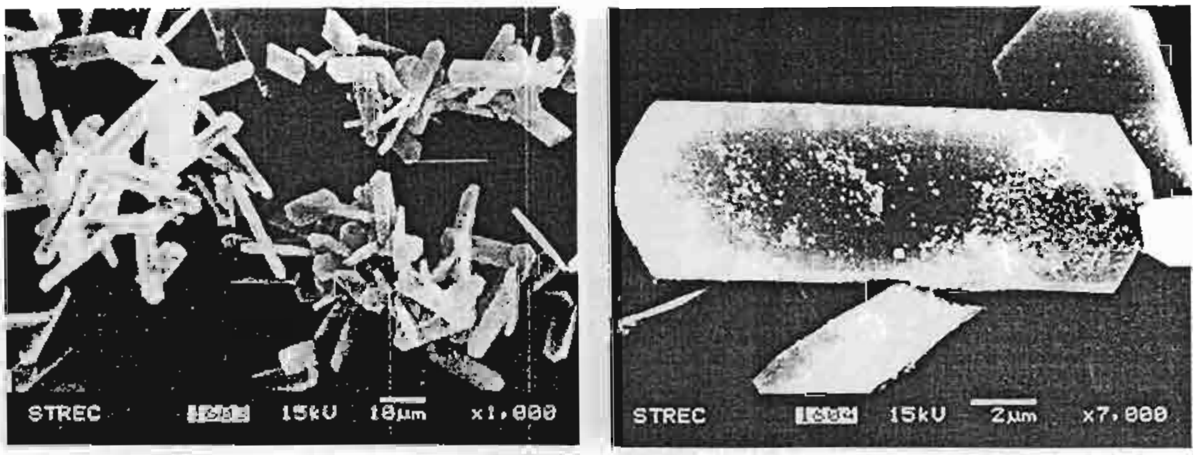


Figure 1.16 Scanning electron micrograph of TS-1 after calcination.

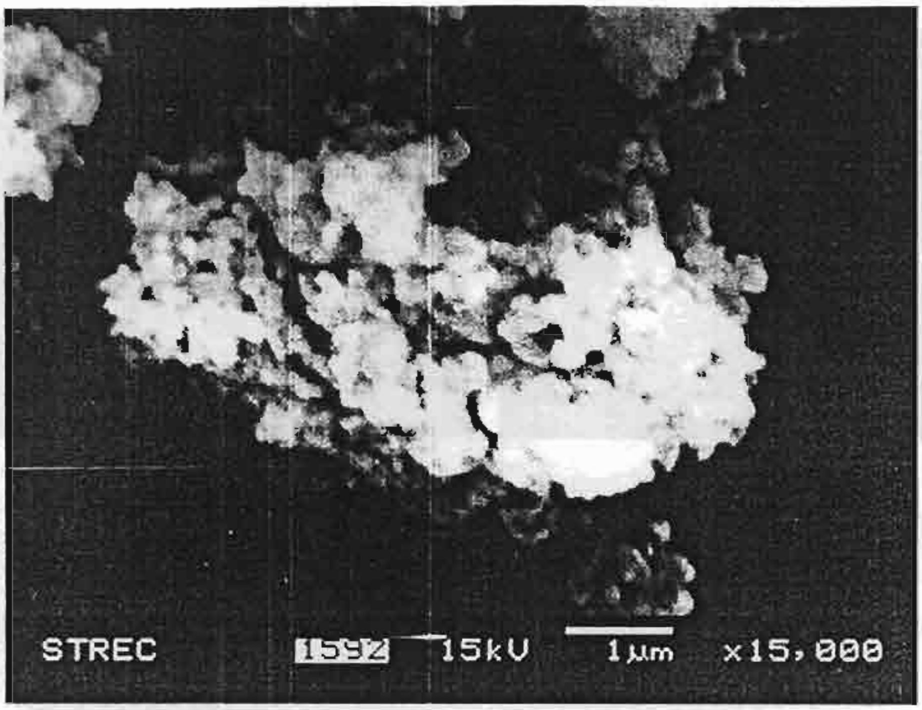
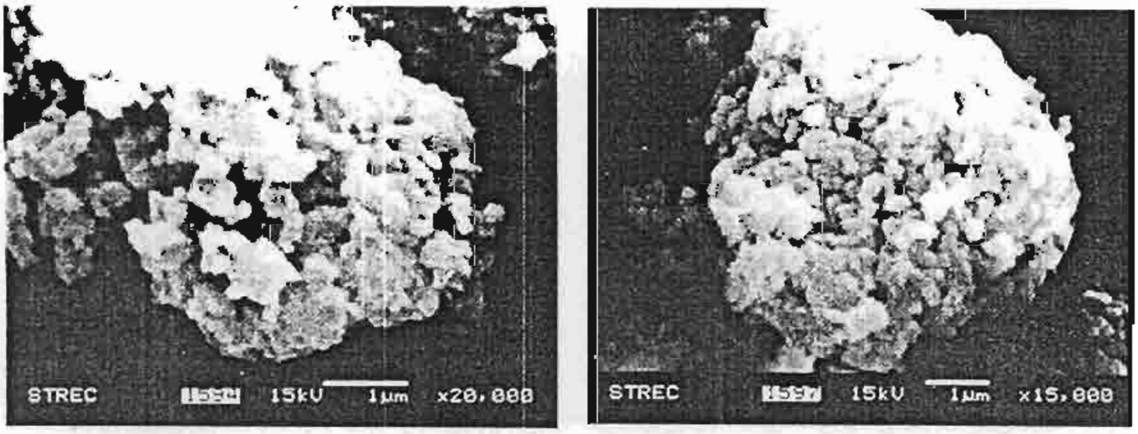
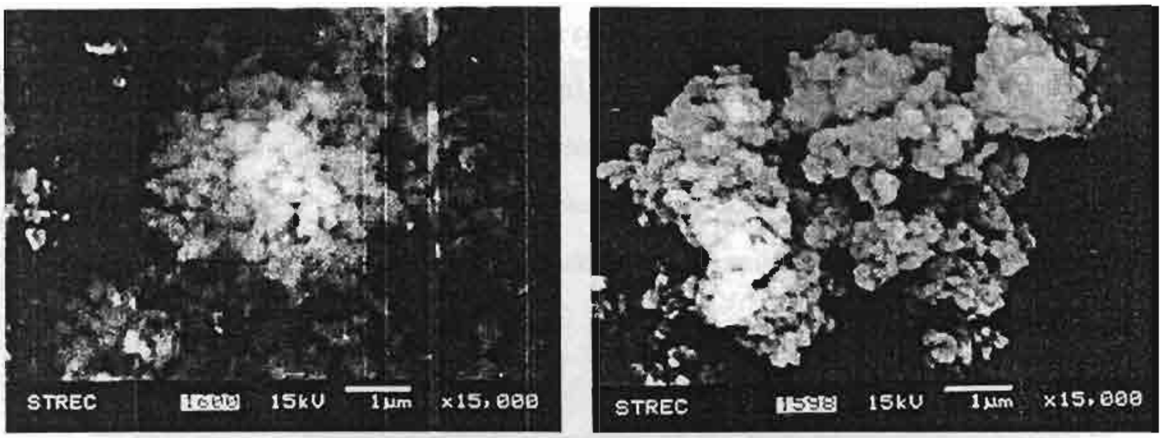


Figure 1.17 Scanning electron micrograph of zeolite NH_4^+-Beta.



(a) (b)

Figure 1.18 Scanning electron micrograph of zeolite dealuminated Beta before (a) and after (b) calcination.



(a)

(b)

Figure 1.19 Scanning electron micrograph of zeolite Ti-Beta before (a) and after (b) washing with sulfuric acid and calcination.

1.2.4 Determination of Titanium in Framework

Titanium in framework (tetrahedral form) can be determined by infrared spectroscopy (FT-IR). Titanium in the framework shows the characteristic signal of Ti-O-Si vibration at 960 cm^{-1}. Both Ti-Beta and TS-1 samples show this characteristic band, which suggests that titanium species are present in both samples as framework cations. Fourier Transformed IR spectra of zeolites are shown in Figure 1.20 and 1.21.

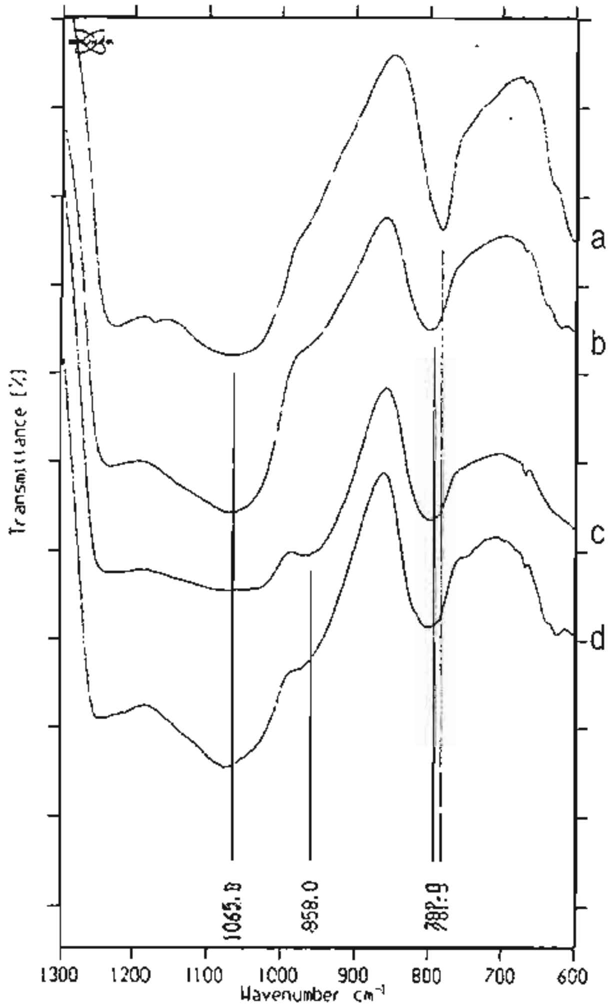


Figure 1.20 Fourier Transformed IR spectra of zeolite NH_4^+-Beta (a), Dealuminated Beta (b), Ti-Beta before (c) and after (d) washing by sulfuric acid

From the Figure 1.20, it was shown that before titanation of zeolite Beta (NH_4^+-Beta, Dealuminated Beta), there is definitely no characteristic peak of Ti-O-Si vibration (a, b) because no titanium is present in the zeolite framework. After titanation, the characteristic peak of Ti-O-Si vibration appeared (c). It is believed that lost aluminium is replaced by titanium species.

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

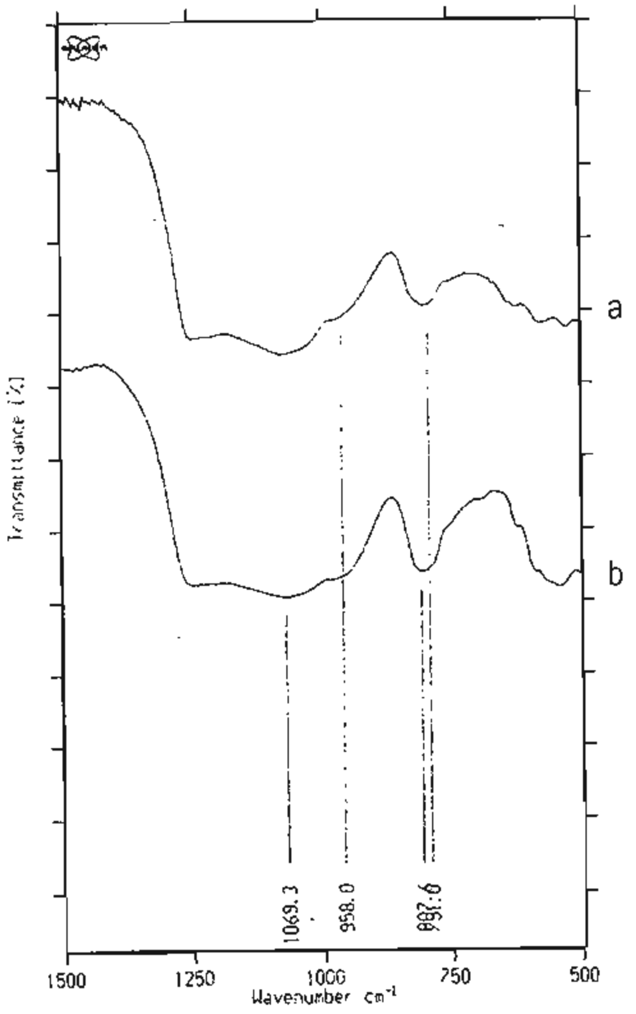


Figure 1.21 Fourier Transformed IR spectra of zeolite Ti-Beta after washing by sulfuric acid (a) and TS-1 (b)

The result from elemental analysis shows that the titanium content of TS-1 is higher than that of zeolite Ti-Beta. Figure 1.21, however, it is shown that the characteristic peak of zeolite Ti-Beta can be clearly distinguished, as compared to the TS-1. It may well be described that the titanium tetrahedral located mostly in the zeolite crystal. Accordingly, the relative higher number of external silanol of the large crystallite TS-1 would interfere the vibration signal of the Ti-O-Si, causing characteristic peak (960 cm^{-1}) of TS-1 to appear as a shoulder peak of the large Si-O vibration bands (1000-1200 cm^{-1}).

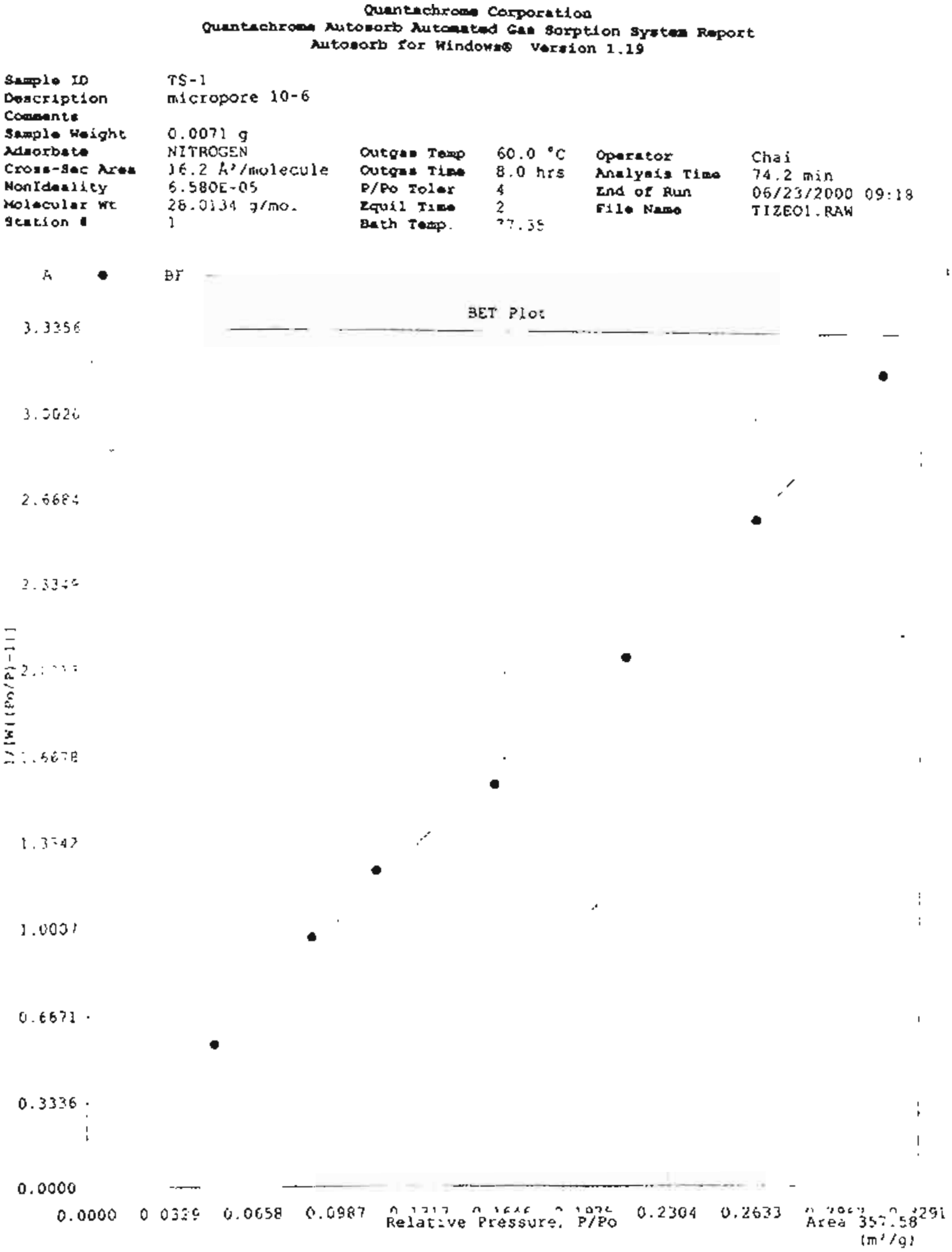
1.2.5 Determination of Surface Area

The surface area of zeolites are shown in Table 1.3

Table 1.3 The surface area of zeolite

Zeolite	Surface Area (m^2/g)
TS-1 after calcination	358
NH$_4^+$-Beta	665
Ti-Beta before washing by sulfuric acid	536
Ti-Beta after washing by sulfuric acid and calcined	625

From the result, it was shown that zeolite Beta have higher surface area than TS-1. This may be accounted partly from the fact that the crystal of TS-1 is larger than Beta. After titanation of the zeolite Beta, the surface area was reduced. This can be attributed to the pore blockage by the incorporated titanium species. Since there could be two species of titanium in the zeolites; the framework and the non-framework titanium, the later can readily block the pore of zeolite. This can result in a relative lower surface area of the titanated sample, as compared to the parent dealuminated Beta. Washing by sulfuric acid can remove the non-framework titanium from the pore of zeolite leading to an increased surface area. This is also in consistent with the results from the elemental analysis and FT-IR indicating the reduced titanium content with the retaining tetrahedral titanium (section 2.4). The BET plots of zeolites were shown in Figure 1.22-1.25.



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

Sample ID        TS-1
Description      micropore 10-6
Comments
Sample Weight    0.0071 g
Adsorbate        NITROGEN             Outgas Temp   60.0 °C    Operator        Chai
Cross-Sec Area   16.2 Å²/molecule     Outgas Time   8.0 hrs    Analysis Time   74.2 min
NonIdeality      6.580E-05            P/Po Toler    4          End of Run      06/23/2000 09:18
Molecular Wt     28.0134 g/mo.        Equil Time    2          File Name       TIZE01.RAW
Station #        1                    Bath Temp.    77.35
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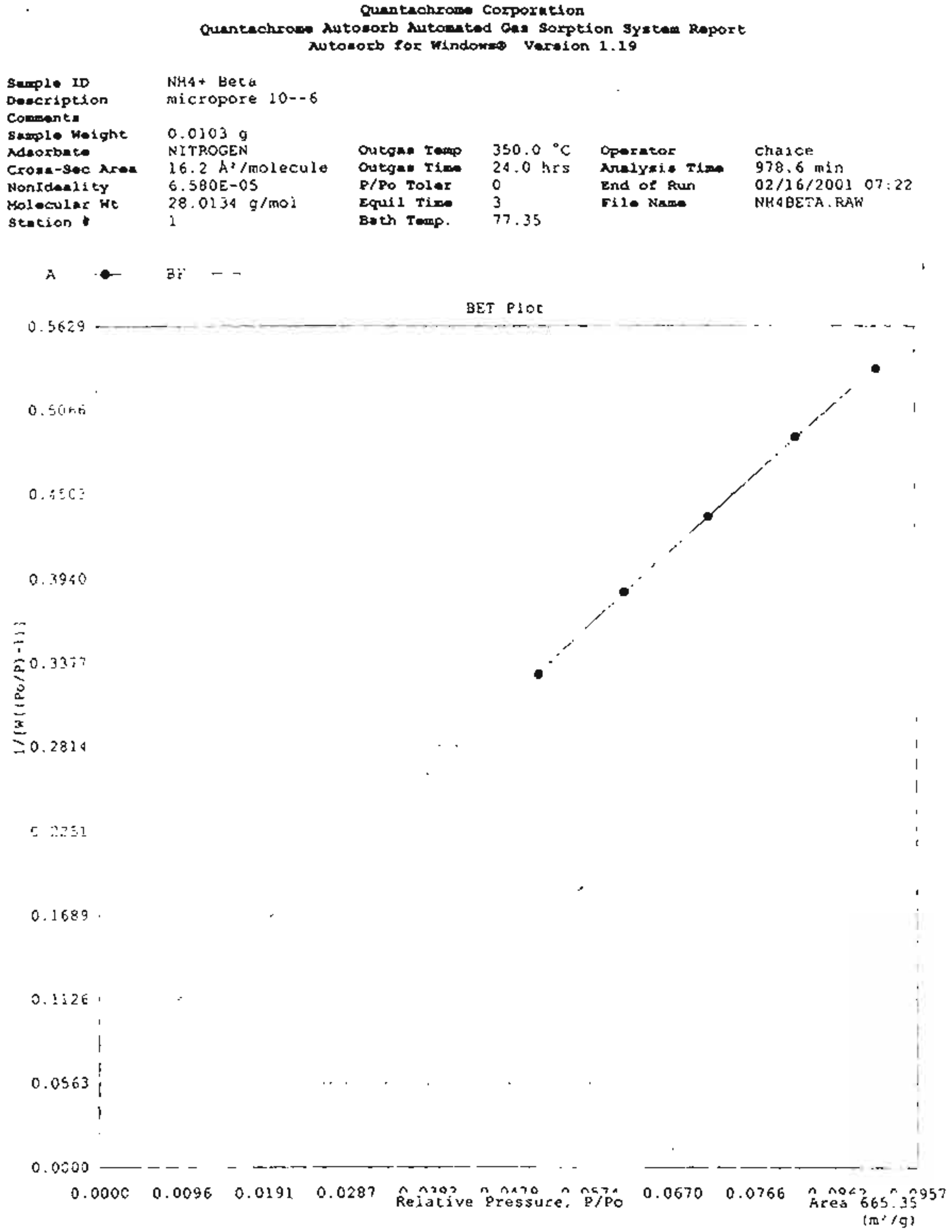
Figure 1.22 BET plot of TS-1 after calcination.



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

Sample ID         NH4+ Beta
Description       micropore 10--6
Comments
Sample Weight     0.0103 g
Adsorbate         NITROGEN            Outgas Temp   350.0 °C   Operator        chaice
Cross-Sec Area    16.2 Å²/molecule    Outgas Time   24.0 hrs   Analysis Time   978.6 min
NonIdeality       6.580E-05           P/Po Toler    0          End of Run      02/16/2001 07:22
Molecular Wt      28.0134 g/mol       Equil Time    3          File Name       NH4BETA.RAW
Station #         1                   Bath Temp.    77.35
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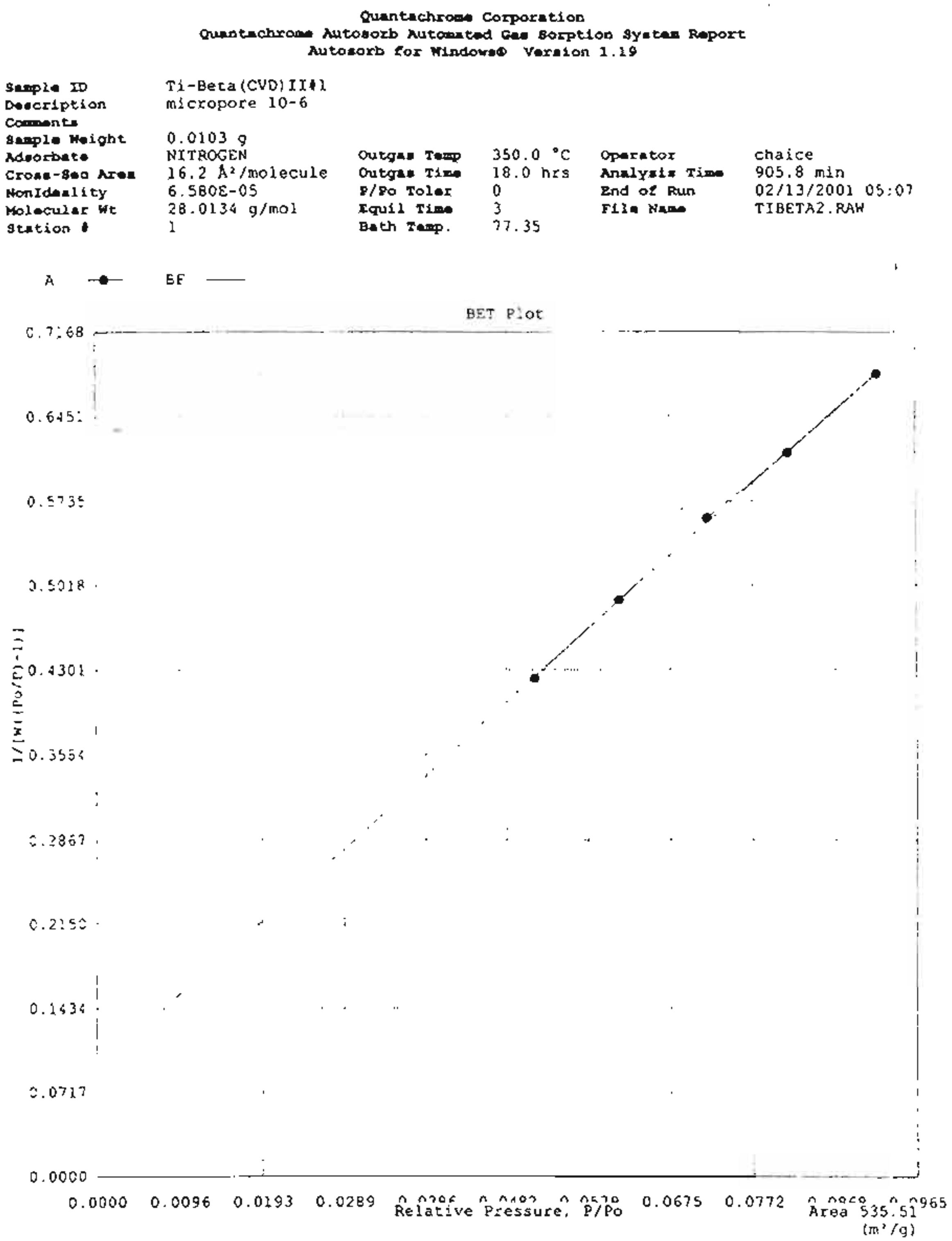
Figure 1.23 BET plot of zeolite NH_4^+-Beta.



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

Sample ID          Ti-Beta(CVD)II#1
Description        micropore 10-6
Comments
Sample Weight      0.0103 g
Adsorbate          NITROGEN            Outgas Temp    350.0 °C    Operator         chaice
Cross-Sec Area     16.2 Å²/molecule    Outgas Time    18.0 hrs    Analysis Time    905.8 min
NonIdeality        6.580E-05           P/Po Toler     0           End of Run       02/13/2001 05:07
Molecular Wt       28.0134 g/mol       Equil Time     3           File Name        TIBETA2.RAW
Station #          1                   Bath Temp.     77.35
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Figure 1.24 BET plot of zeolite Ti-Beta before washing with sulfuric acid.

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

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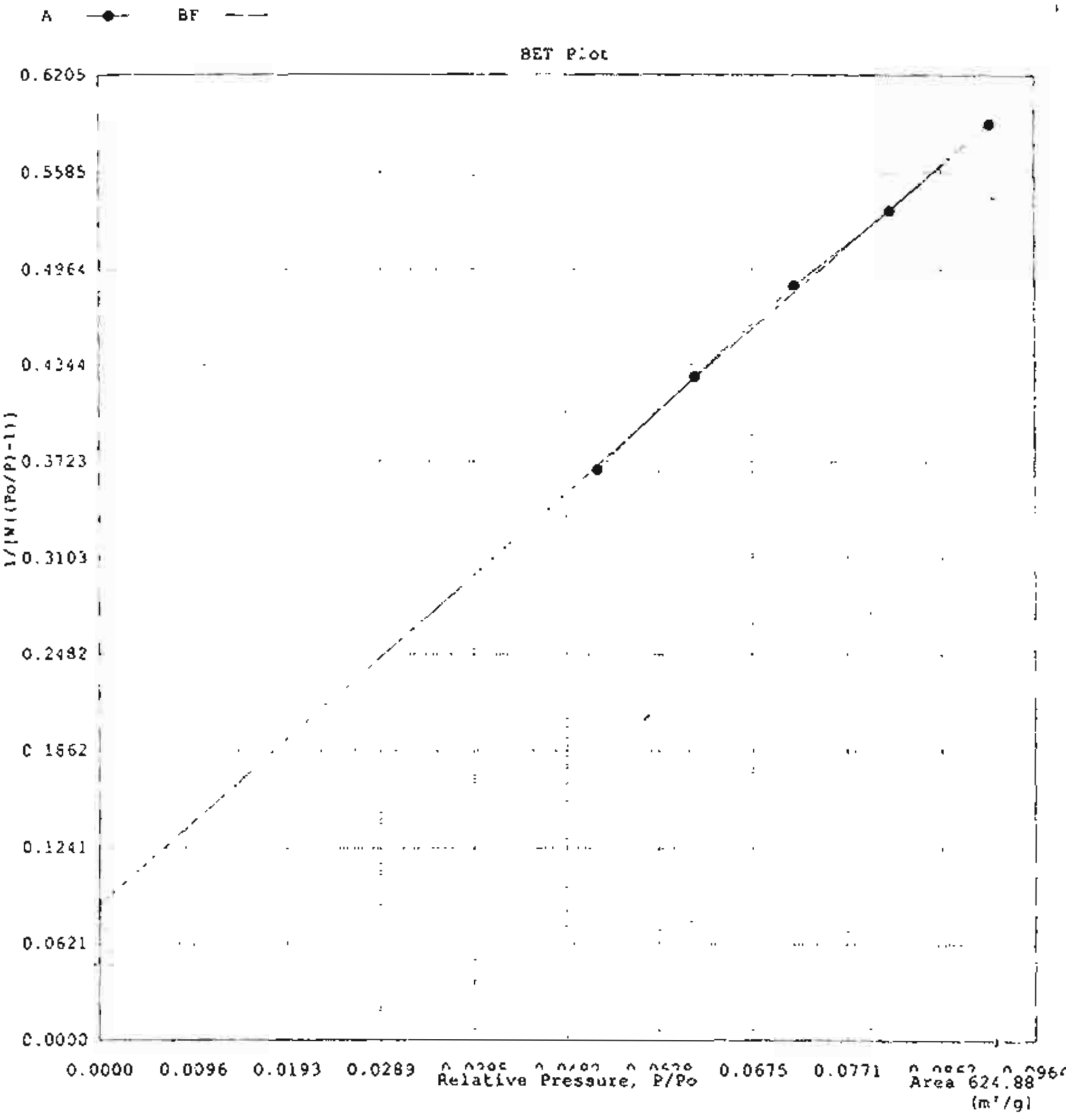


Figure 1.25 BET plot of zeolite Ti-Beta after washing with sulfuric acid and calcination.

CHAPTER 2

BECKMAN REARRANGEMENT OF CYCLOHEXANONE OXIME

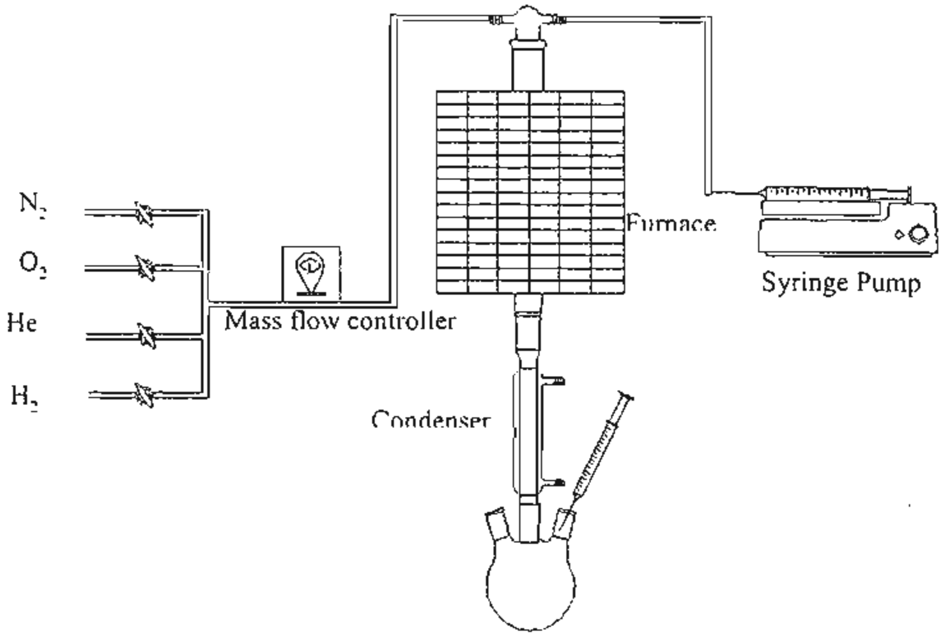
2.1 Objectives

To study mechanism of Beckman rearrangement of cyclohexanone oxime. To obtain appropriate reaction condition which allow high selectivity of caprolactam . To obtain a certain type of zeolite which gives high selectivity of caprolactam. To understand the influence of solvent on conversion and selectivity of caprolactam and understand the pathway of reaction using titanium containning zeoltes as catalyst.

2.2 Catalytic testing

The vapor phase Beckmann rearrangement reaction of cyclohexanone oxime was conducted under atmospheric pressure using a continuous flow reactor. The cyclohexanone oxime was dissolved in *n*-butanol and fed by a syringe pump. In the presence of nitrogen as a carrier gas, the fluid mixture was passed over the packed bed of zeolite catalyst at various reaction temperature and contact time for 90 minutes on stream. The products was passed over the condenser and condensed at 5°C. The product mixture was analyzed by Gas Chromatography and Gas Chromatography-Mass Spectrometer. Figure 2.1 shows diagram of the catalytic flow reactor.

Figure 2.1 Schematic of catalytic reactor



From previous study [4] the feed ratio used in the experiments are as follows: cyclohexanone oxime: diluent: nitrogen gas, 1 : 9 : 10 (molar) was used for the investigation.

2.3 Result and discussion

2.3.1 The Beckmann rearengement in H-Beta

The Beckmann rearrangement of cyclohexanone oxime over H-Beta catalyst was investigated using *n*-butanol as solvent. It was found that cyclohexanone oxime converted to caprolactam as major product The by-products of this reaction were found to be cyclohexanone, cyclohexenone, 5-cyanopentane and 5-cyano-1-pentene. The conversion of cyclohexanone oxime is shown in Figure 2.2.

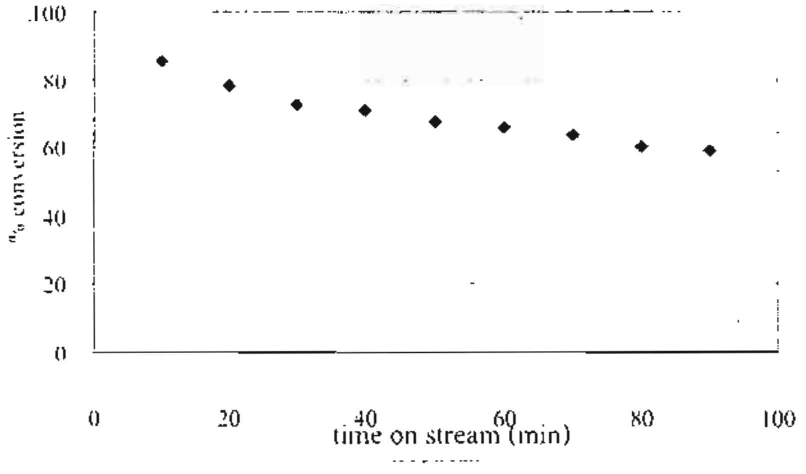


Figure 2.2 Conversion of cyclohexanone oxime over H-Beta catalyst. *Reaction condition : temperature: 350* $^{\circ}C$, *pressure: 1 atm, W/F: 13.6* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *diluent: n-butanol, carrier gas:* N_2, *time on stream: 90 min*

It is shown in Figure 2.2 that, conversion of cyclohexanone oxime was decreased with the increase in time on stream. It is suggested that, the decrease in the conversion of cyclohexanone oxime due to the coke formation, presumably from polymerization of caprolactam and by-products [5]. The undesirable-product can be formed by hydrolysis of cyclohexanone oxime and ring opening of caprolactam intermediates. Polymerized products can deposit on the active sites, inhibiting adsorption of cyclohexanone oxime. This would result in a decreased conversion as time on stream was increased. The coke formation in H-Beta can be confirmed by thermogravimetric analysis (Figure 2.3). It was found that after reaction the H-Beta possesses 16.8 percent weight loss, which decomposition at 450°C and 650°C. It should be expected that the weight loss at 450 °C is contributed to the decomposition of high molecular weight species, while the fixed carbon is decomposed at 650°C.

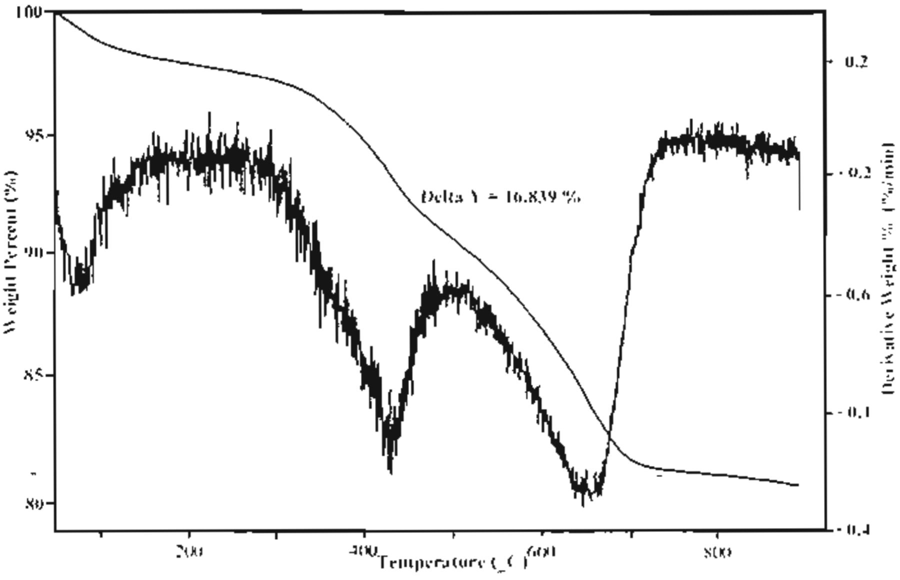


Figure 2.3 Thermogravimetric analysis of H-Beta

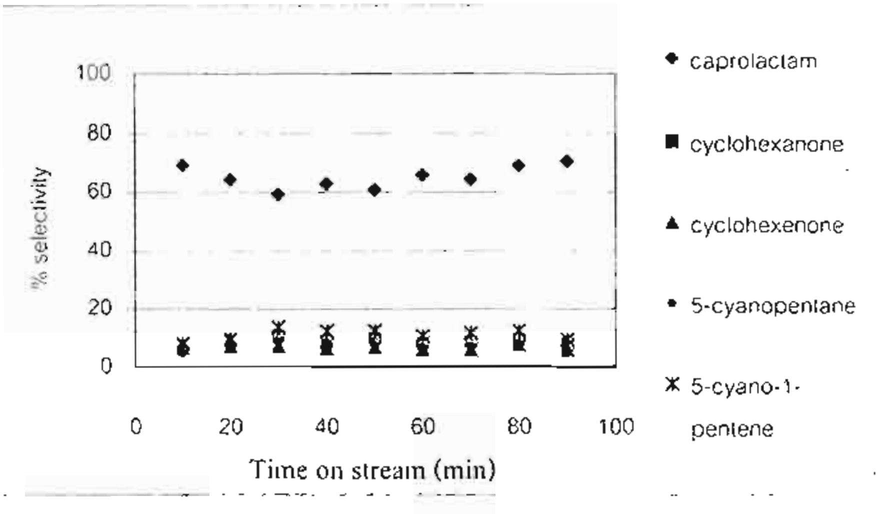


Figure 2.4 Selectivity of caprolactam, cyclohexanone, cyclohexenone, 5-cyanopentane and 5-cyano-1-pentene over H-Beta catalyst. *Reaction condition: temperature: 350 °C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}$ *h* mol^{-1}_{oxime}, *diluent : n-butanol, carrier gas:* N_2, *time on stream: 90 min*

The products from the reaction were analyzed using GC and GC-MS. It was found that, selectivity of caprolactam is higher than the other product (Figure 2.4). It was suggested that the formation of caprolactam can be promoted by the acid sites of the catalysts [6]. T.Komatsu et al.

proposed that a reaction pathway is ascribed by the Langmuir-Hinshelwood mechanism, as follows;

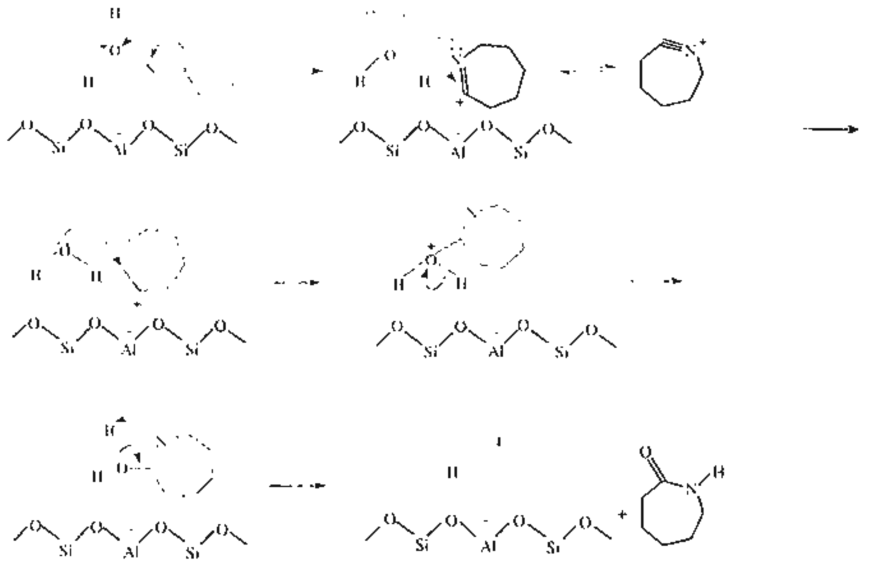
$\mathrm{Ox} + \mathrm{A} \longleftrightarrow \mathrm{Ox(a)}$ ....(1)

$\mathrm{Ox(a)} \longleftrightarrow \mathrm{Cp(a)}$ ....(2)

$\mathrm{Cp(a)} + \mathrm{Sv} \longleftrightarrow \mathrm{Cp} + \mathrm{Sv(a)}$ ....(3)

$\mathrm{Sv} + \mathrm{A} \longleftrightarrow \mathrm{Sv(a)}$ ....(4)

First the reactant, cyclohexanone oxime (Ox), is adsorbed on an active site (A) of the catalyst to form adsorbed cyclohexanone oxime (Ox(a)). This adsorbed species can be converted into caprolactam, adsorbing on the active site (Cp(a)). The product would then desorb by a solvent molecule (Sv) which subsequently adsorb on the active site (Sv(a)). This adsorbed solvent (Sv(a)) must be desorbed from the active leaving vacant site (A) for further sorption of reactants. Therefore, an appropriated solvent would possesses a weaker interaction with the active sites, as compared to the reactant, but stronger as compared to the products. The possible pathway for Beckmann rearrangement reaction of cyclohexanone oxime to caprolactam on the active sites of zeolite is depicted as follow;



However, not only caprolactam was formed over the active sites, but other by-products can also be produced. The results from GC-MS reveal that the by-products included cyclohexanone, cyclohexenone, 5-cyanopentane and 5-cyano-1-pentene. The selectivity of the by-products in this reaction is shown in Figure 2.5.

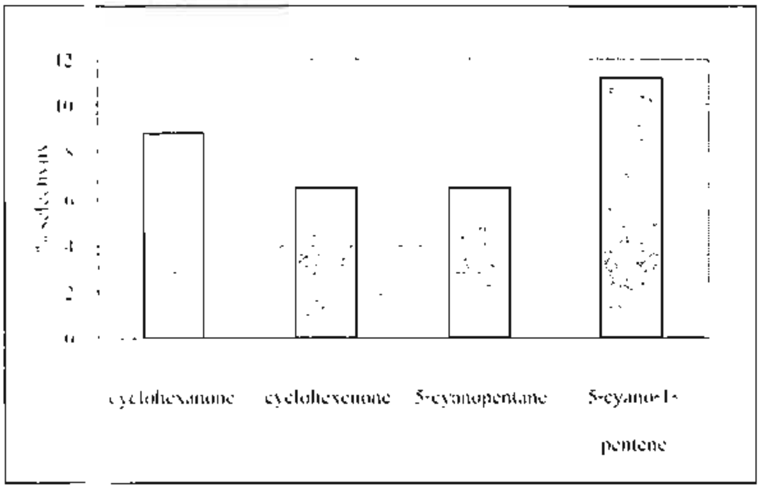
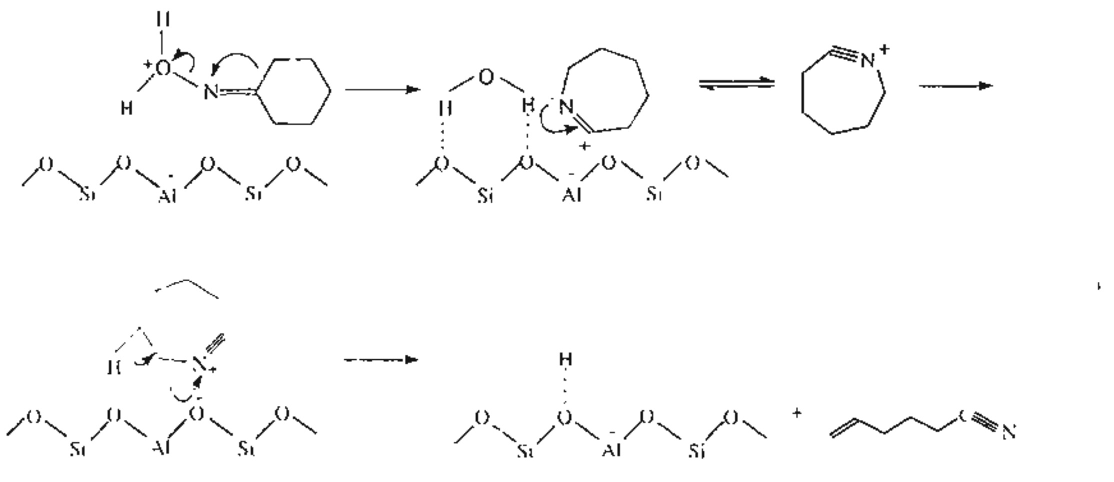


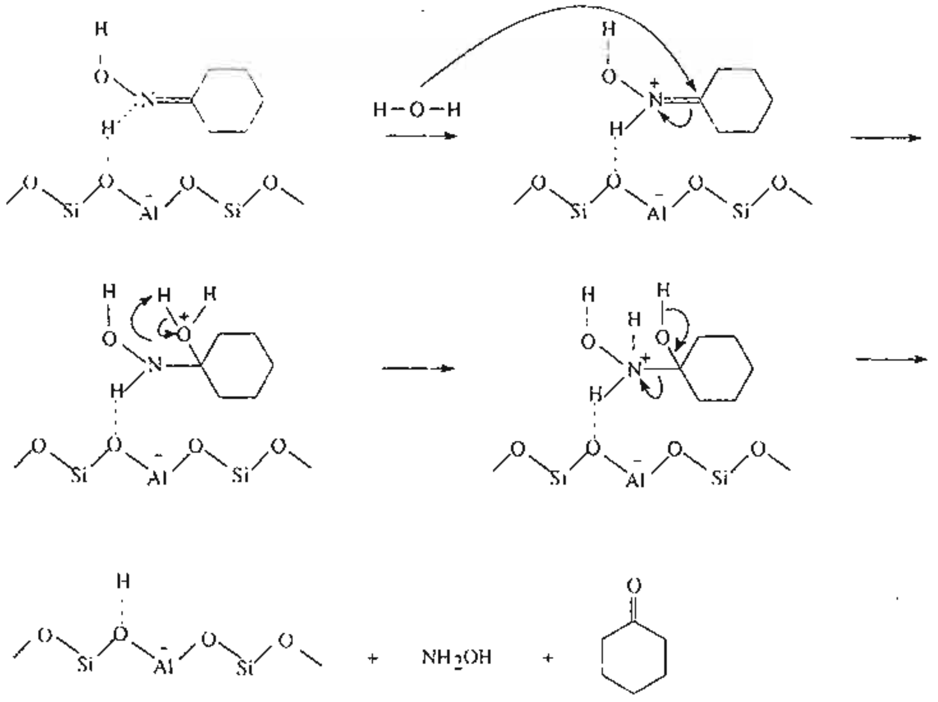
Figure 2.5 Selectivity of by-products: cyclohexanone, cyclohexenone, 5-cyanopentane and 5-cyano-1-pentene over H-Beta catalyst. *Reaction condition: temperature: 350 °C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *diluent: butanol, carrier gas:* N_2, *average time on stream 10-90 min*

From Figure 2.5, it was found that yield of 5-cyano-1-pentene is higher than that of cyclohexanone, cyclohexenone and 5-cyanopentane. The by-product, 5-cyano-1-pentene is suggested to from via the decomposition of cyclohexanone oxime when water sorption is inhibited (A). The Beckmann rearrangement is commonly assumed to proceed via formation of *O*-protonated cyclohexanone oxime, followed by migration of α-carbon to the imine nitrogen, with subsequent lost of water. The lost water would then react with the rearrange species to form oxonium ion and caprolactam respectively. However at high temperature, adsorption of the lost water can be limited, thus the decomposition of the iminium intermediate can take place, produce 5-cyano-1-pentene as by-product. The possible pathway for the formation of 5-cyano-1-pentene is shown as follows.

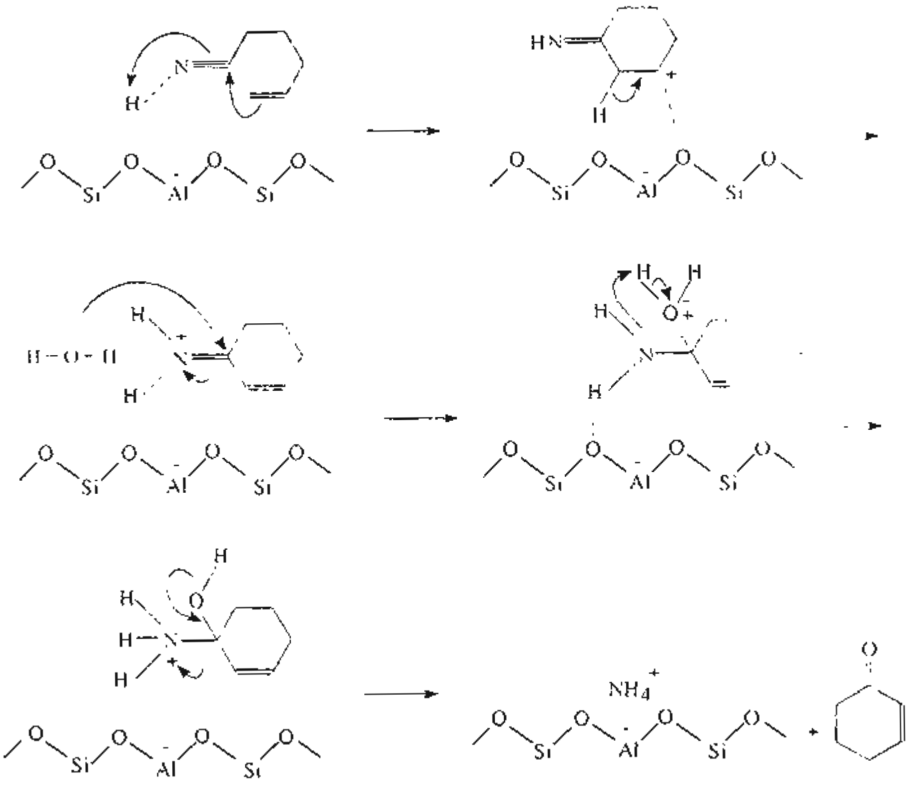


(A)

Another by-product, 5-cyanopentane, cannot formed by decomposition of cyclohexanone oxime as its unsaturated countered part, but it was suggested to form by reduction of cyclohexanone oxime which will be discussed further in the selectivity of caprolactam section. The other two by-product, cyclohexanone and cyclohexenone are presumably produced by hydrolysis of cyclohexanone oxime and 5-cyano-1-pentene, respectively. The possible pathway for hydrolysis of cyclohexanone oxime to cyclohexanone is shown as follows:



A more complicated hydrolysis is suggested for the formation of cyclohexenone. It is possible that the major by-product (5-cyano-1-pentene) can undergo cyclization over the acid sites. Subsequently, the cyclized product can be hydrolyzed to form cyclohexenone as postulated.



It seems that the water sorption in this reaction is responsible for selectivity of caprolactam and by-product. For example, when water sorption is inhibited 5- cyano-1-pentene can be formed. In contrast, cyclohexanone can be readily produced in the presence of large amount of water. Accordingly, effect of water was investigated by addition of water into the solvent. This will be further discussed in effect of solvent section .

Not only the low selectivity of caprolactam is observed, but the deactivation rate over H-Beta is also high. This may well be derived from the stronger acid sites of H-Beta. Over the stronger acid sites, desorption of products is somewhat retarded. This leads to further undesirable reaction to form by-product and high molecular weight products. The latter can undergo polymerization to form coke in the pores of zeolite, which consequently reduce the active center for the reaction. Therefore, the reaction over weaker acid sites and titanium active sites were investigated in the next section.

2.3.2 Effect of type of zeolite catalysts

2.3.2.1 Activity of catalyst

Beckmann rearrangement of cyclohexanone oxime was investigated over various types of zeolite catalysts, namely H-Beta, Dealuminated Beta and Ti-Beta (washed Ti-Beta by sulfuric acid). Figure 2.6 shows the conversion of cyclohexanone oxime over those catalysts.

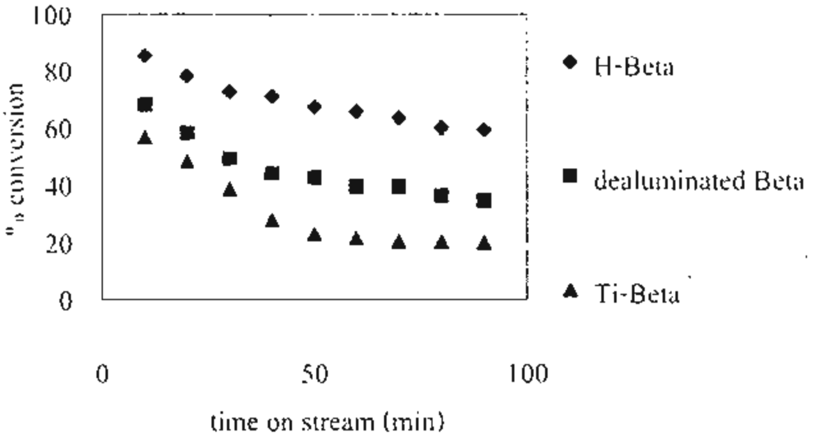
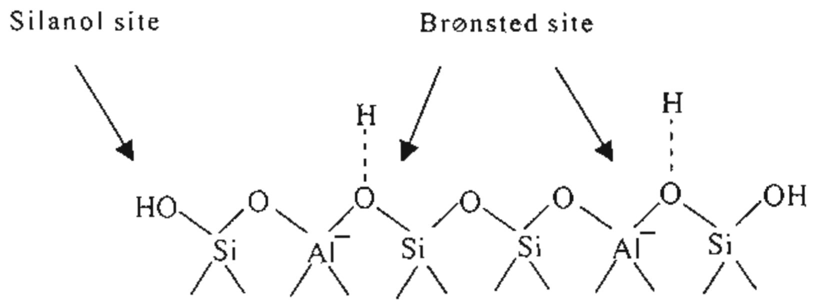


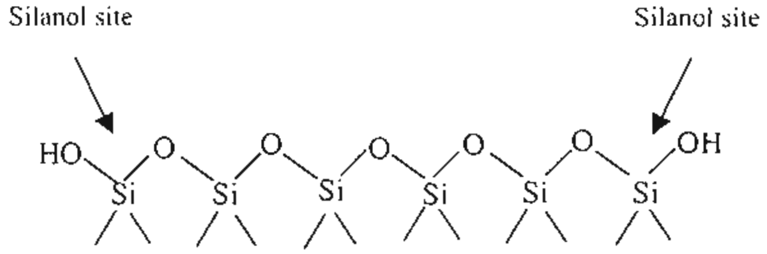
Figure 2.6 Conversion of cyclohexanone oxime over H-Beta, dealuminated Beta and Ti-Beta catalysts. *Reaction condition: temperature; 350°C, pressure; 1 atm, W/F; 13.6* $g_{catalyst}\,h\,mol^{-1}_{reactant}$ *diluent; butanol, carrier gas;* N_2, *time on stream; 90 min*

Form Figure 2.6, it was found that the conversion of cyclohexanone oxime over H-Beta was higher than that over Dealuminated Beta and Ti-Beta. It is suggested that the activity of H-Beta is higher than the other two catalysts. This is because H-Beta, contains a large number of active sites, as compared to the Dealuminated Beta and Ti-Beta. In H-Beta there are both Brønsted acid sites and silanol sites, which were suggested to be able to promote these reactions within the pores of zeolite and on the external surface, respectively [32]. The active sites in H-Beta can be depicted as follow.

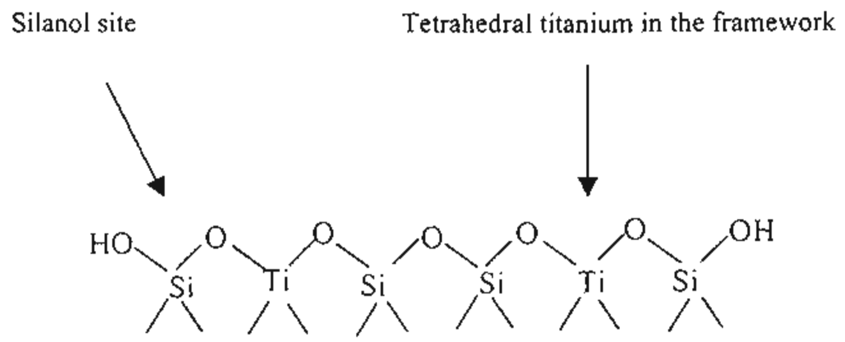


The conversion of cyclohexanone oxime depends largely on number of active sites. As discussed earlier that the sorption and desorption of reactant play important role in the catalytic activity. The conversion of cyclohexanone oxime would be increased when there is a large number of active sites available for adsorption of the reactant.

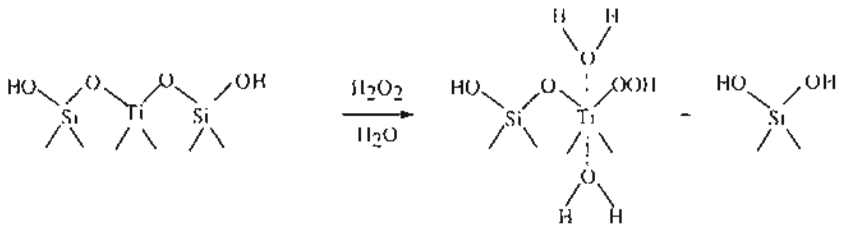
In the case of Dealuminated Beta, it possesses only silanol active sites. These species could be present within the pore and on the external surface of the zeolite crystals. It is believed that there is negligible amount of BrØnsted acid sites present in this catalyst. This can be confirmed by the elemental analysis of Dealuminated Beta that there is only trace of aluminium retained in the framework after dealumination. In accordance, only silanol active sites are responsible for the adsorption of the cyclohexanone oxime. Therefore, the dealuminated Beta would contribute a relatively lower activity, as compared to the H-Beta, which possess both silanol and BrØnsted acid sites. The active sites in the dealuminated Beta is shown as follows.



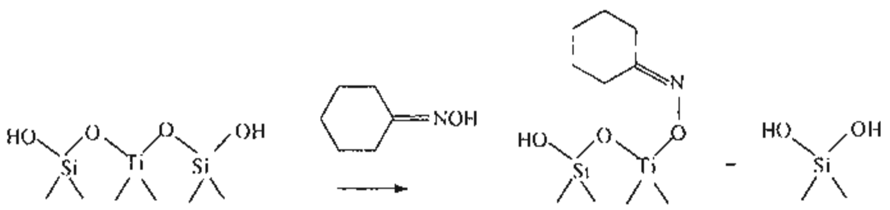
Ti-Beta also contains silanol active sites and additional weakly Lewis acid sites arising from the tetrahedral titanium species in the framework, as shown.



It could be expected that this catalyst would possess a higher activity, as compared to the dealuminated Beta. However from the Figure 2.6 it was found that conversion of cyclohexanone oxime over Ti-Beta is lower than that H-Beta and Dealuminated Beta. This is implied that only the silanol sites in Ti-Beta is responsible for Beckmann rearrangement of cyclohexanone oxime. The tetrahedral titanium sites may not only be inactive, but also leads to the formation of by-product. This suggestion can be described from the fact that cyclohexanone oxime can be strongly adsorbed on the tetrahedral titanium active sites, and probably forming a peroxy complex, which can undergo reductive elimination to give by-products (section 2.3.2.2). In fact, the formation of peroxy complex by hydrogen peroxide with tetrahedral titanium framework has been previously reported in solution [39]. Accordingly, it is possible that the peroxy complex can be formed by the reaction of cyclohexanone oxime with the tetrahedral titanium framework as illustrated below;



(1)



(2)

This adsorbed species can be speculated by the Thermogravimatric analysis (Figure 2.7) that the Ti-Beta shows a unique weight loss at temperature about 180 °C which is closed to the decomposition temperature of cyclohexanone oxime (about 160°C). The decomposition of adsorbed species would take place at relatively higher temperature, as compared to that of free cyclohexanone oxime. This suggests that cyclohexanone oxime could be strongly adsorbed over the tetrahedral titanium sites of zeolite and possibly form a peroxy complex. It should be noted that this decomposition (180°C) takes place via oxidation under oxygen flow. In contrasts, Thermogravimetric analysis of H-Beta and Dealuminated Beta do not show the decomposition at temperature 180 °C. Since in fact there is no tetrahedral titanium sites present in these catalysts for the formation of cyclohexanone oxime peroxidic species. However, H-Beta, Dealuminated Beta and Ti-Beta possess common decomposition temperature of coke at about 425 °C and 650 °C (Figure 2.7).

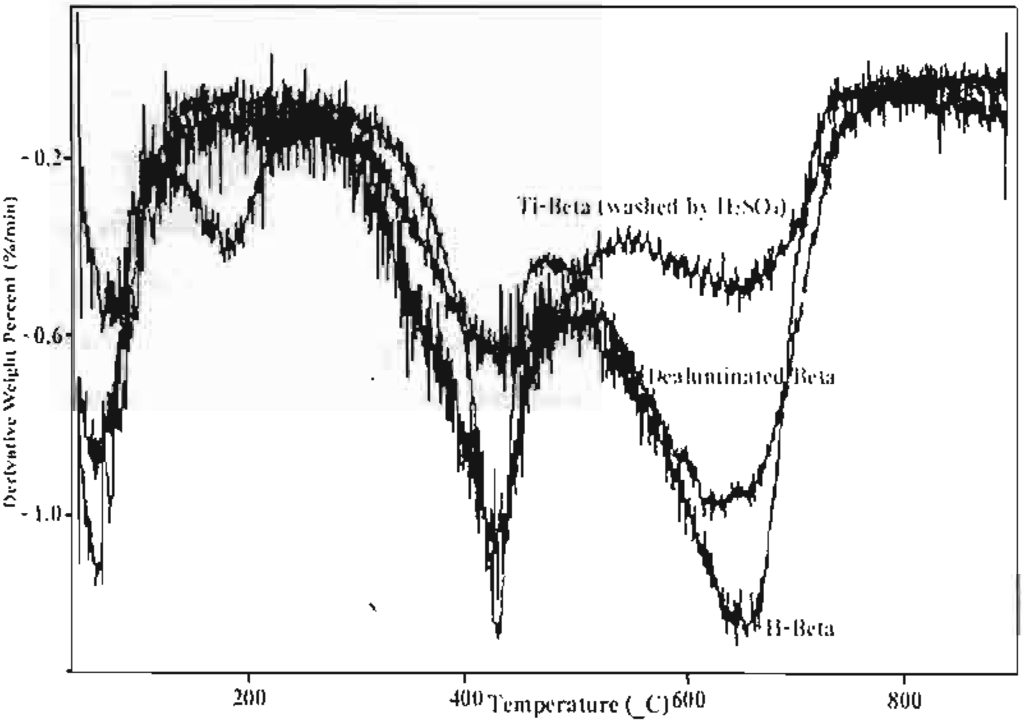
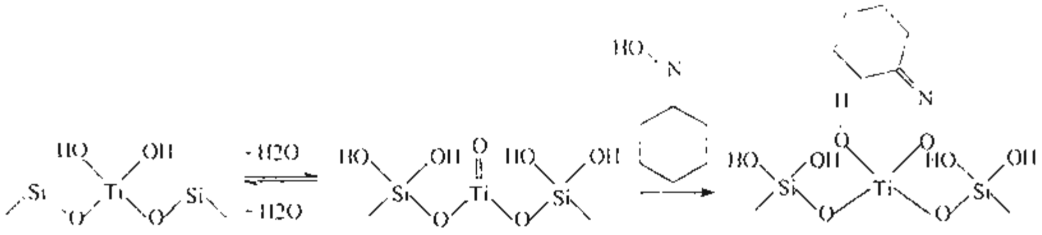


Figure 2.7 Thermogravimetric analysis of H-Beta, Dealuminated Beta and Ti-Beta

From the Thermogravimetric analysis (Figure. 2.7), it is found that H-Beta possesses a higher percent weight loss, as compared to Dealuminated Beta and Ti-Beta, respectively. It is suggested that over the stronger acid strength of Brønsted acid sites in H-Beta, the desorption of product is somewhat retarded as discussed earlier (section 2.3.1). Therefore, the stronger acid strength of Brønsted acid sites in H-Beta leads to a higher coke formation, as compared to the weaker acid strength of silanol active sites in Dealuminated Beta. The coke formation in the case of Ti-Beta is lower than that of Dealuminated Beta, which suggests that Ti-Beta possesses weaker acid strength than the Dealuminated Beta and H-Beta, respectively. Moreover, coke formation largely depends on the amounts of active sites in the pore of zeolite catalyst. H-Beta possesses both BrØnsted acid sites and silanol sites, so there are higher coke formation, as compared to Dealuminated Beta, which has only silanol active sites. Ti-Beta possesses relatively small amounts of silanol active sites thus, it shows lower coke formation.

Furthermore, it was found from the previous report [28], that the titanium species in the framework of the zeolite can be present as both internal and external surface species. The external surface species was also suggested to be able to sorb cyclohexanone oxime as illustrated:



These adsorbed species are somewhat so stable that the adsorbed cyclohexanone oxime species would be relatively less active for Beckmann rearrangement. However, the surface of titanium active sites can also reduce cyclohexanone oxime to a by-product due to the oxidizing ability of the peroxidic complex (as further discussion in the section 3.2.2). Therefore, in the case of Ti-Beta, only the silanol sites would be responsible for the conversion of the cyclohexanone oxime to caprolactam. This causes a lower conversion of cyclohexanone oxime over the Ti-Beta , as compared to H-Beta and Dealuminated Beta.

From the above results, it can be concluded that the conversion of cyclohexanone oxime depends largely on the type of active sites. The reactant must adsorb on the active sites and also rearrange to products. In addition, the product must be desorbed to give free active sites, which allows the adsorption of a forthcoming reactant. Accordingly, appropriate active sites should be favor for the adsorption of reactants, but unfavorable for the products. Moreover, the conversion of cyclohexanone oxime depends on the amounts of active sites. In the case of Ti-Beta, the catalyst possesses internal/external titanium sites and silanol sites. The titanium sites is inactive for this reaction, due to the strongly interaction with reactant to form peroxidic complex. However, titanium sites can convert cyclohexanone oxime to by-product, which will be discussed in section 2.3.2.2 Only silanol active sites can facilitate the adsorption of cyclohexanone oxime to form desired products. Therefore, Ti-Beta shows lower conversion of cyclohexanone oxime than those using Dealuminated Beta and H-Beta. However, the interaction of solvent can also affect the competitive adsorption of reactant, which will be discussed in section 2.3.5

2.3.2.2 Selectivity of caprolactam

It was observed that the selectivity of caprolactam in the reaction using Dealuminated Beta is higher than that the case of H-Beta and Ti-Beta, as catalysts (Figure 2.8).

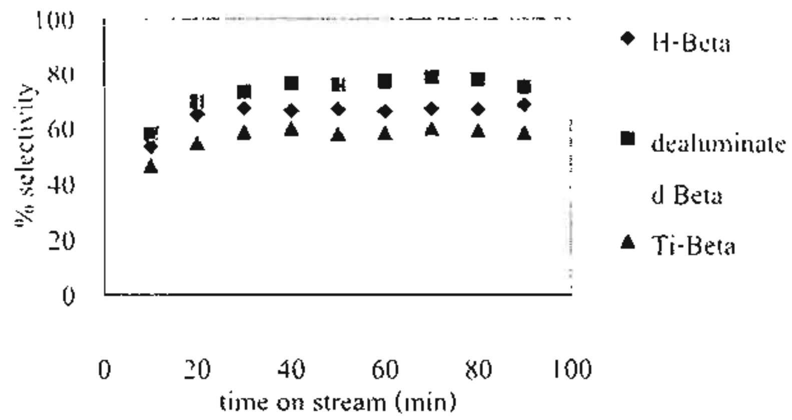


Figure 2.8 Selectivity of caprolactam over H-Beta, dealuminated Beta and Ti-beta as catalysts. *Reaction condition: temperature: 350°C, pressure; 1 atm, W/F; 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent; butanol, carrier gas;* N_2*, average time on stream 10-90 min*

Form the previous report [30,32], it was found that the high acid strength can enhance the selectivity of by-product. Regarding to the acid strength of H-Beta and Dealuminated Beta, it was found that the active sites of Dealuminated Beta is only silanol site, a weakly acid site while the active sites of H-Beta are both silanol sites and BrØnsted acid sites, a stronger acid site. This is consistent with the observed high by-product selectivity over H-Beta, while the by-product selectivity over Dealuminated Beta is relatively low (Figure 2.9). Therefore, the reaction using H-Beta gives relatively low selectivity of caprolactam, as compared to the Dealuminated Beta.

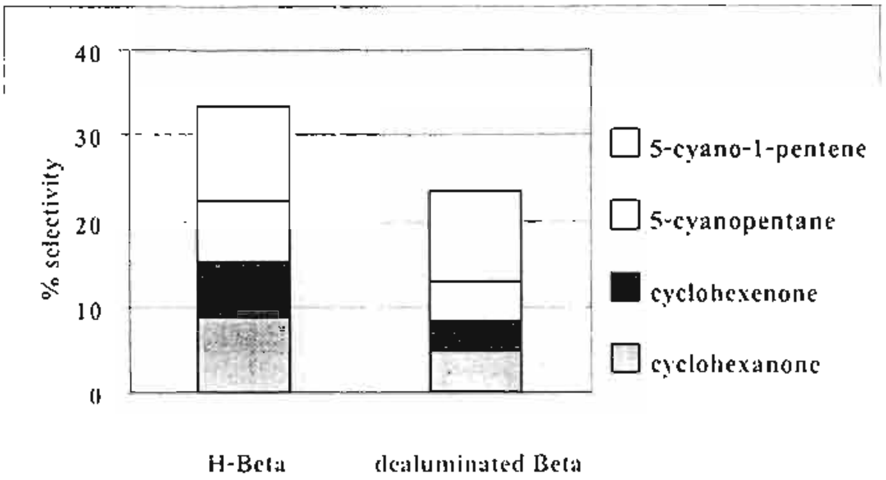


Figure 2.9 Selectivity of by product over H-Beta and Dealuminated Beta as catalysts.

Reaction condition: temperature: 350°C, pressure: 1 atm, W/F: 13.6 $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, average time on stream 10- 90 min*

In the case of the Ti-Beta, the observed selectivity of by product is higher than that of Dealuminated Beta, particularly for cyclohexanone and 5-cyanopentane while no significant change in cyclohexenone and 5-cyano-1-pentene is observed as shown in Figure 2.10.

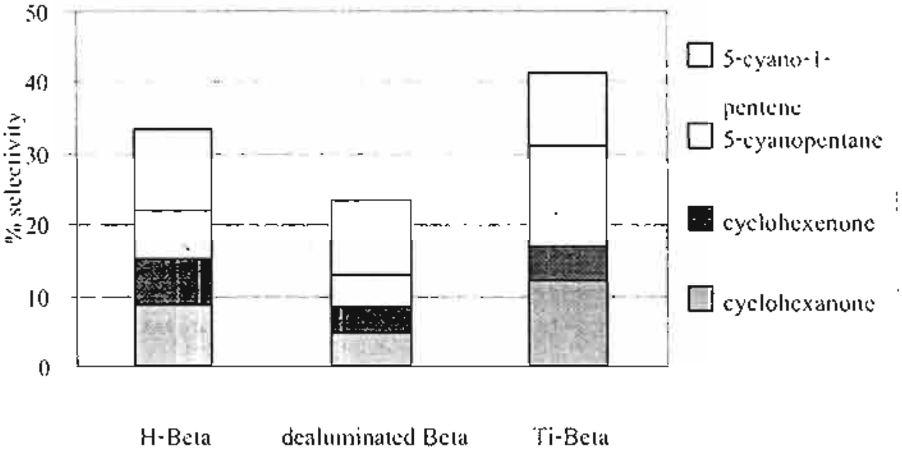


Figure 2.10 Selectivity of by-products over H-Beta and Dealuminated Beta and Ti-Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, W/F: 13.6 $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, average time on stream 10- 90 min*

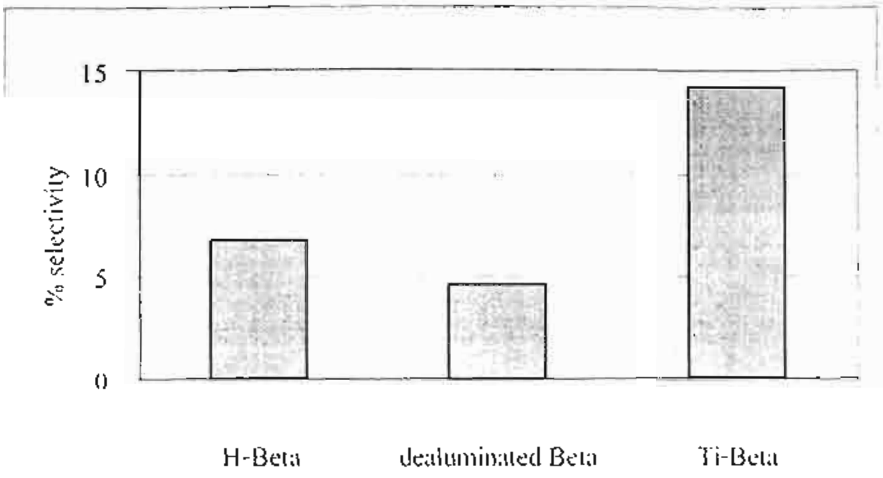
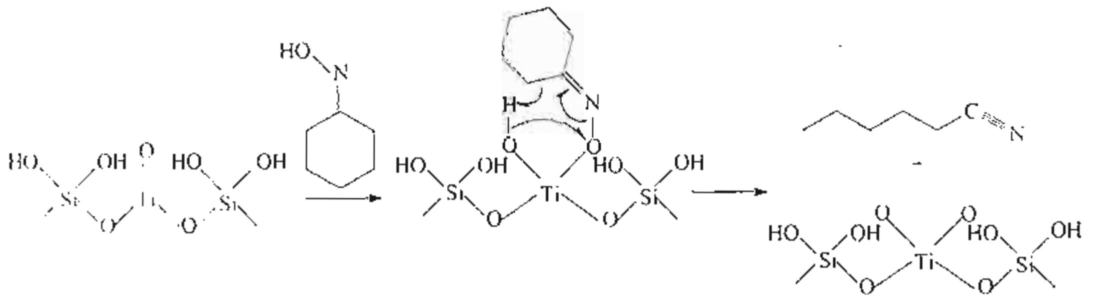


Figure 2.11 Selectivity of 5-cyanopentane over H-Beta. Dealuminated Beta, Ti-Beta as catalysts. *Reaction condition: temperature, 350°C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}$ *h* mol^{-1}_{oxime}, *diluent: butanol, carrier gas:* N_2, *average time on stream 10- 90 min*

It may well be described from the assumption that, the cyclohexanone and 1-cyanopentane can be promoted by the tetrahedral titanium framework. As shown in Figure 2.11, the high selectivity of 5-cyanopentane is observed over the Ti-Beta, as compared to that over the Dealuminated Beta and H-Beta. It is suggested that the framework titanium species could possibly promote 5-cyanopentane. It is likely that the peroxy titanium complex, which is formed by the adsorption of cyclohexanone oxime on the framework titanium species, can undergo decomposition, to form peroxo titanium on the framework [38]. The associated peroxy ligand would be subsequently reduced to form 5-cyanopentane. The possible pathway for the reduction of cyclohexanone oxime to 5-cyanopentane over titanium species on the surface is postulated below.



Regarding to the the cyclohexanone selectivity, it is found that the selectivity of cyclohexanone over Ti-Beta is also higher than that over H-Beta and Dealuminated Beta (Figure 2.12).

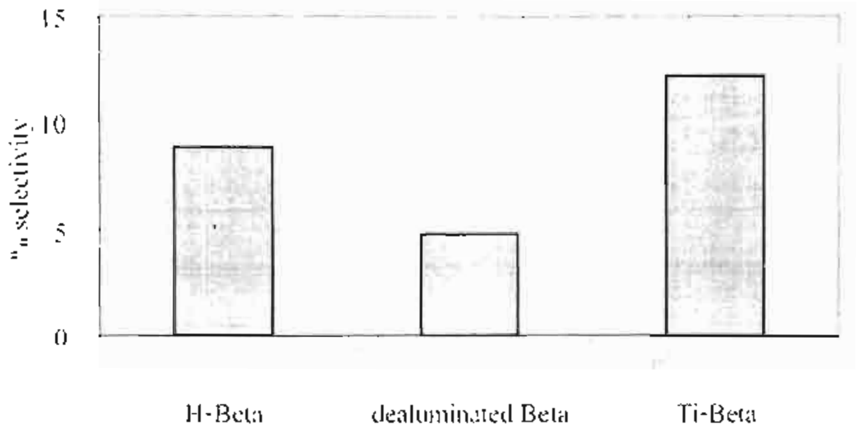
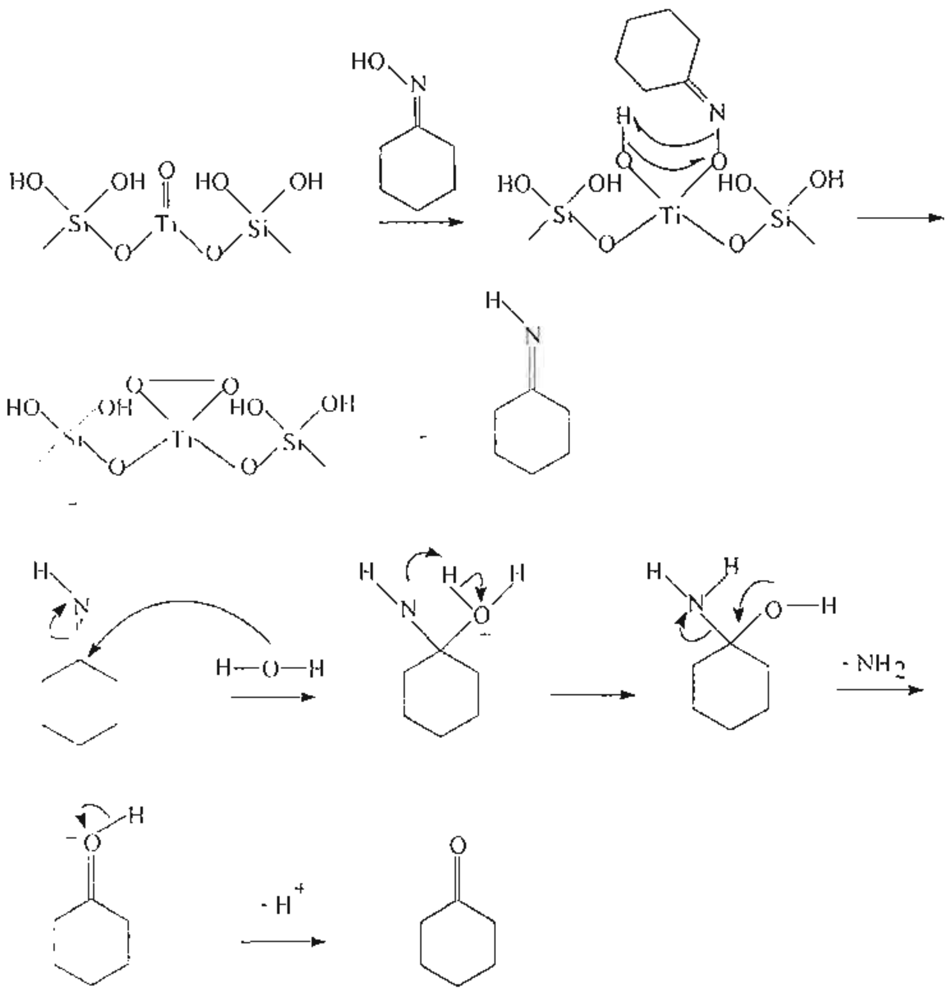


Figure 2.12 Selectivity of cyclohexanone over H-Beta, Dealuminated Beta, Ti-Beta as catalysts. *Reaction condition: temperature, 350°C, pressure: 1 atm W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$, *diluent: butanol, carrier gas:* N_2, *average time on stream 10- 90 min*

It is again suggestion that, the titanium species could possibly promote the formation of cyclohexanone. In similar manner to the formation of 5-cyanopentane, the peroxy titanium complex, which is formed by the adsorption of cyclohexanone oxime on the titanium species, can undergo decomposition and consecutive hydrolysis to form cyclohexanone, as illustrated;



Therefore, in the case of Ti-Beta, the selectivity of caprolactam is lower than H-Beta and Dealuminated Beta because the titanium species can facilitate the formation of by-product. It is concluded that the product selectivity depends largely on type of active sites. It seems that the caprolactam selectivity for the active sites is in the order of silanol sites, BrØnsted acid sites, framework titanium active sites.

2.3.3 Effect of temperature

2.3.3.1 Activity of catalyst

The effect of temperature on the Beckmann rearrangement of cyclohexanone oxime over H-Beta catalyst was investigated at 350-400 °C. It was found that, conversion of cyclohexanone oxime was increased with rise in temperature (Figure 2.13).

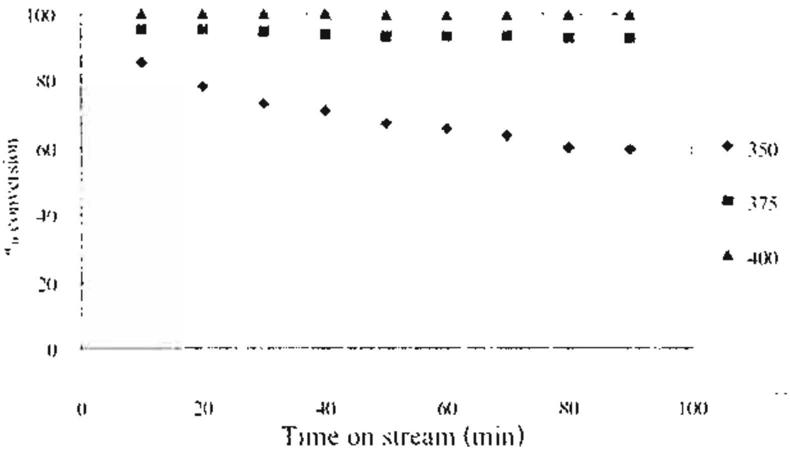


Figure 2.13 Effect of reaction temperature on the conversion of cyclohexanone oxime over H-Beta. *Reaction condition : pressure: 1 atm, W/F: 13.6* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *diluent: butanol, carrier gas:* N_2, *time on stream 90 min, temperature: 350, 375, 400 °C*

The conversion of cyclohexanone oxime at high temperature is higher than those at low temperature because the increase in temperature allows faster diffusion rate of the cyclohexanone oxime inside the pore of H-Beta zeolite. Moreover, the product desorption from the active sites would also be increased resulting in the increased vacant active sites for the adsorption of cyclohexanone oxime. This is consistent with the report by J. Weikamp et al. that [27], the conversion of cyclohexanone oxime over ZSM-5 increase drastically with rise in temperature due to the faster diffusion rate of cyclohexanone oxime inside the pore of catalyst. Therefore, at the higher reaction temperature the more cyclohexanone oxime would readily penetrate into the pore of Beta. This leads to an increase in the overall conversions of cyclohexanone oxime. The conversion of cyclohexanone oxime over Dealuminated Beta and Ti-Beta (washed Ti-Beta by sulfuric acid) is shown in Figure 2.14.

It was found that, the conversion of cyclohexanone oxime over all catalysts were increased with rise in temperature. It is clear that the effect of temperature for the dealuminated Beta is in a similar manner as that for H-Beta. However, it is worth noted that when the temperature is risen, the increased conversion of cyclohexanone oxime over Ti-Beta is increased in a higher extent, as compared to Dealuminated Beta and H-Beta, respectively (Figure 2.14).

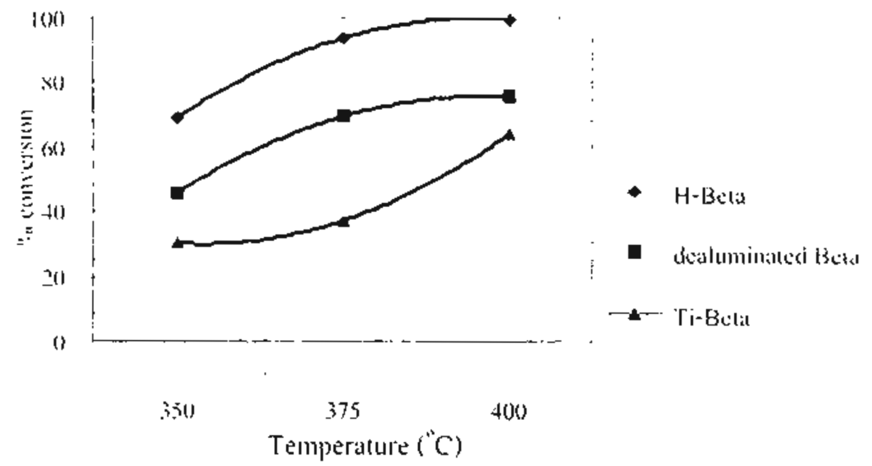


Figure 2.14 Effect of reaction temperature on the conversion of cyclohexanone oxime over H-Beta. Dealuminated Beta and Ti-Beta.

Reaction condition: pressure: 1 atm, W/F: 13.6 $g_{catalyst}$ *h* $mol^{-1}_{reaction}$, *diluent; butanol, carrier gas;* N_2, *average time on stream 10-90 min, temperature; 350, 375, 400 °C*

It is suggested that, when the temperature is increased, the desorption of product which strongly adsorbed over titanium active sites, is facilitated and consequently this provides free active sites for further adsorption of cyclohexanone oxime. As temperature increased, the active surface was just revealed and the conversion of cyclohexanone oxime was drastically increased in the case of Ti-Beta. This implies that the activity of Ti-Beta is not so different from Dealuminated Beta, but the active surface was occupied by strong adsorb species. As seen from the effect of temperature, it is likely that only the silanol sites in Ti-Beta is responsible for Beckmann rearrangement. Again this is consistent with previous discussion (section 2.3.2.1) that the framework titanium sites would be inactive in this reaction.

2.3.3.2 Deactivation rate of catalyst

In the case of H-Beta, the deactivation rate is drastically reduced when the temperature is risen (Figure 2.13). This may well be ascribed that high temperature can facilitate the desorption of product from the pore size of zeolite. This leads to a decrease in agglomerated species on the active sites. Consequently, coke formation and deactivation rate of catalyst was decreased with the increase in temperature. This is consistent with the previous suggested mechanism that if the solvent could desorb the product molecule, which reduces the polymerization of adsorbed product to form coke precursor, the deactivation rate would be retarded. It is evident by the thermogravimetric analysis of H-Beta that percent weight loss decrease with an increase in reaction temperature (Table 2.1). Moreover, it can be confirmed by the gas adsorption analysis that the surface area of the spent catalyst used in the reaction at the higher temperature is higher than that at low temperature (Table 2.1).

Table 2.1 Percent weight loss and surface area of the H-Beta catalyst

Reaction Temperature	H-Beta	
	Percent weight lost (%)	Surface area (m^2/g)
350°C	16.84	409
400°C	14.56	436

In the case of Dealuminated Beta the deactivation rate was also decreased with increase in temperature (Figure 2.15), however at high temperature the deactivation rate of Dealuminated Beta is still higher than the deactivation rate of H-Beta. This is because butanol, which is the high polar molecule, can easily desorb the product from the high acid strength Brϕnsted acid sites within H-Beta, but over weakly acid strength of silanol sites within Dealuminated Beta butanol is relatively less effective for desorption of product. Therefore, only small amounts of coke formed on the active sites of Dealuminated Beta, can result in marked decrease in catalytic activity. This is consistent with the thermogavimetric analysis results that smaller amounts of coke is formed in Dealuminated Beta, as compared to H-Beta. Although the temperature was increased, only slightly decrease in percent weight loss was observed in dealuminated Beta. (Table 2.2).

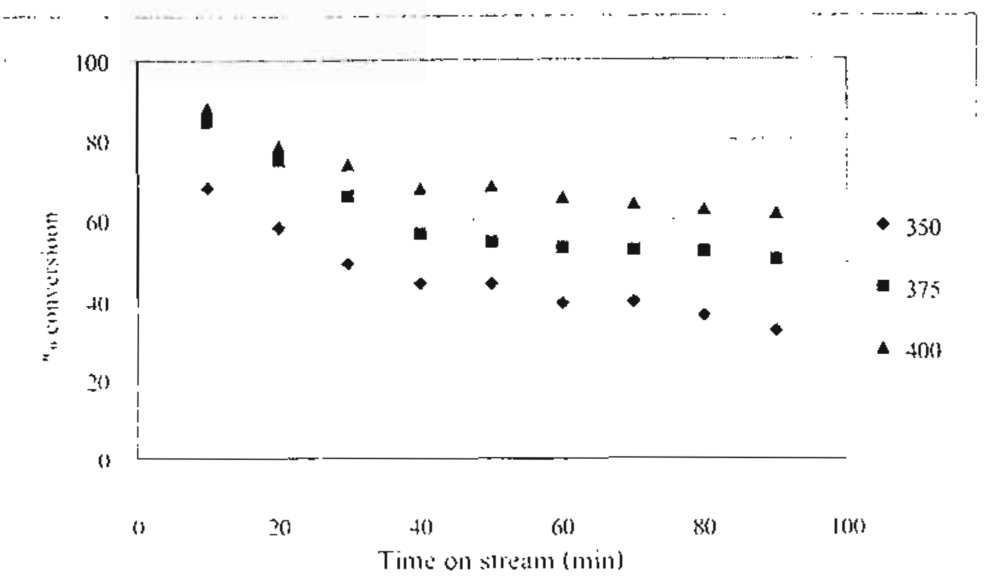


Figure 2.15 Effect of reaction temperature on the conversion of cyclohexanone oxime over Dealuminated Beta

Reaction condition: pressure: 1 atm, W/F: 13.6 $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, time on stream: 90 min, temperature: 350, 375, 400 °C*

Table 2.2 Percent weight loss of the H-Beta, dealuminated Beta and Ti-Beta

Temperature	H-Beta	Dealuminated Beta	Ti-Beta
350°C	16.84	14.13	12.03
400°C	14.56	13.50	10.45

In the case of Ti-Beta (Figure 2.15) the deactivation rate was also decreased with an increase in temperature, but in relatively lower extent, as compared to dealuminated Beta and H-Beta. It is suggested that small amounts of coke formation on Ti-Beta, can result in a marked decrease in catalytic activity. This is consistent with the thermogavimetric analysis results that smaller amounts of coke are formed in Ti-Beta, as compared to dealuminated Beta and H-Beta. This leads to the concluded that the active sites on Ti-Beta is less active, as compared to dealuminated Beta and H-Beta, which is consistent with the previous discussion (section 2.3.2.1).

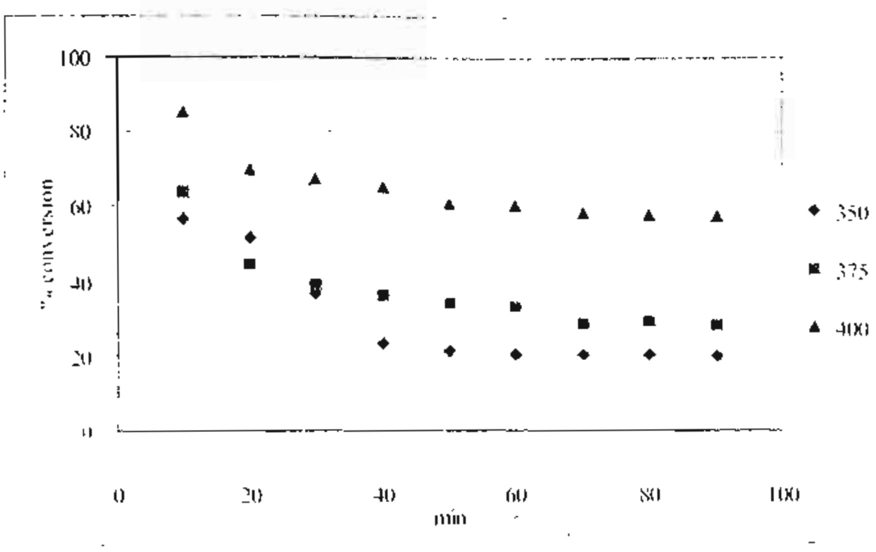


Figure 2.16 Effect of reaction temperature on the conversion of cyclohexanone oxime over Ti-Beta

Reaction condition: pressure: 1 atm, W/F: 13.6 $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, time on stream: 90 min, temperature: 350, 375, 400 °C*

2.3.3.3 Selectivity of caprolactam

It was observed that the selectivity of caprolactam in H-Beta was increased with rise in temperature (Figure 2.17).

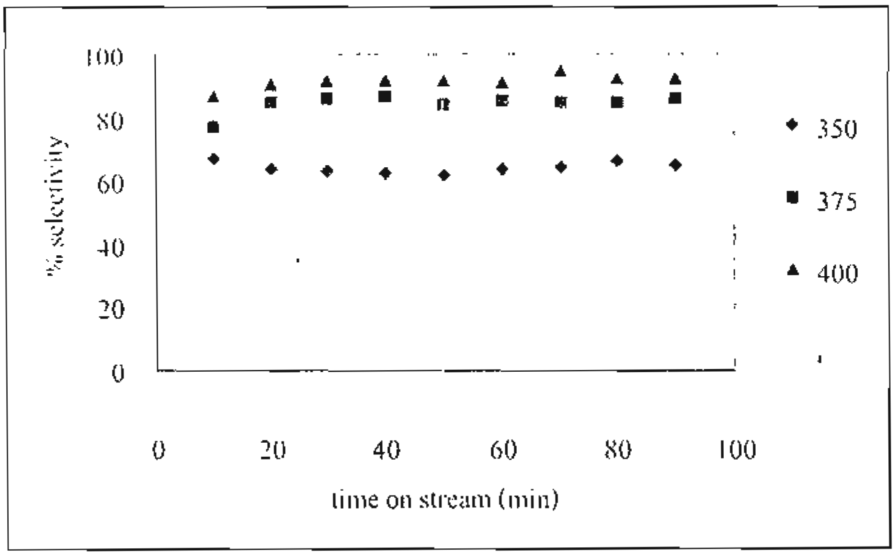


Figure 2.17 Effect of reaction temperature on the selectivity of caprolactam over H-Beta

Reaction condition: pressure: 1 atm, W/F: 13.6 $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, time on stream: 90 min, temperature: 350, 375, 400 °C*

This is different from the previous report [27], which is found in ZSM-5 that when the temperature is increased the selectivity of caprolactam is decreased. Due to the fact that caprolactam is seven membered rings, its molecular size would be larger than the pore window of ZSM-5 zeolite. Therefore the formation of caprolactam within the pore of ZSM-5 zeolite would be suppressed, while the formation of by-product with the smaller molecular size can be facilitated (Figure 2.18). On the other hand, the selectivity of caprolactam is increased with increase in temperature in the case of Beta catalyst, because of its unique structure with a three-dimensional pore system containing 12-membered ring, which possesses a certain free capacity for the transformation of the six-membered ring cyclohexanone oxime into the seven-membered ring caprolactam (Figure 2.19).

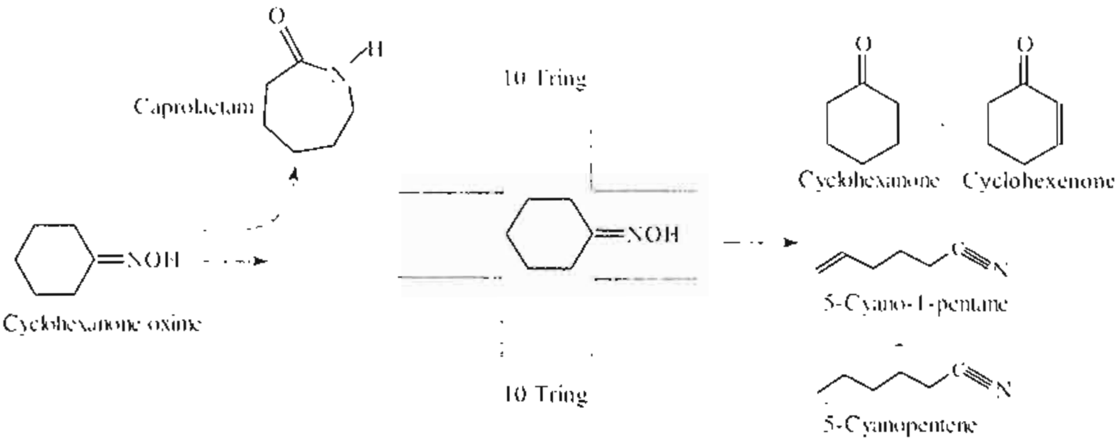


Figure 2.18 Show the reaction in the pore size of ZSM-5 zeolite catalyst

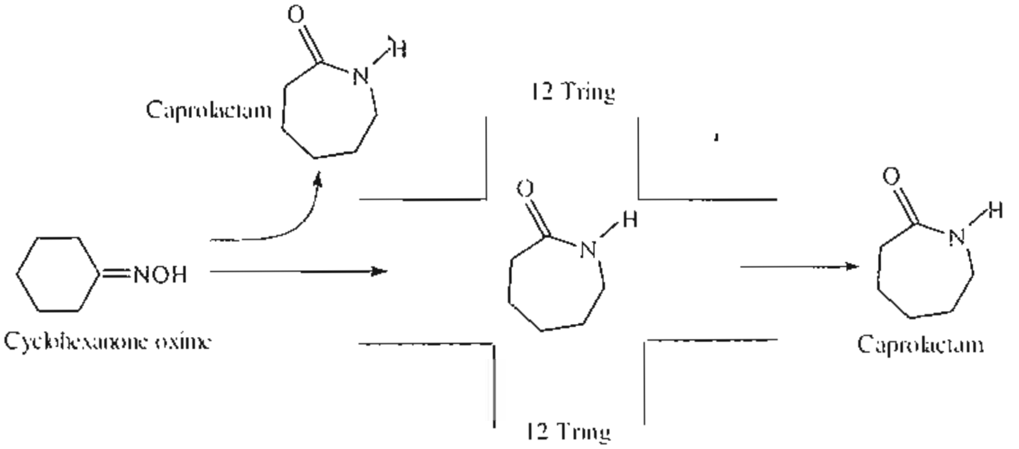


Figure 2.19 Show the reaction in the pore size of Beta zeolite catalyst

It is suggested that, as the temperature increases, the diffusion rate of both reactant (cyclohexanone oxime) and solvent (butanol) would also be increased. Therefore, relatively more reactant can be present in the framework at a certain period of time at high temperature. Additionally the product can be readily desorbed from the active sites due to the increased solvent interaction. This decreases the side reactions over the active sites. Consequently, the high temperature contributes a relatively lower activity for by-product formation. High selectivity of caprolactam is thus obtained.

In the case of dealuminated Beta and Ti-Beta, it was found that the selectivity of caprolactam was also increased with rise in temperature. It is suggested that the effect of temperature for selectivity of caprolactam over dealuminated Beta and Ti-Beta are in a similar manner as H-Beta. However, over the temperature range, the selectivity of caprolactam for dealuminated Beta is higher than H-Beta and Ti-Beta, respectively (Figure 2.20). This is influenced by the type of active sites and interaction of the active sites with the reactant, the product and the solvent as discussed earlier in section 2.3.2.2.

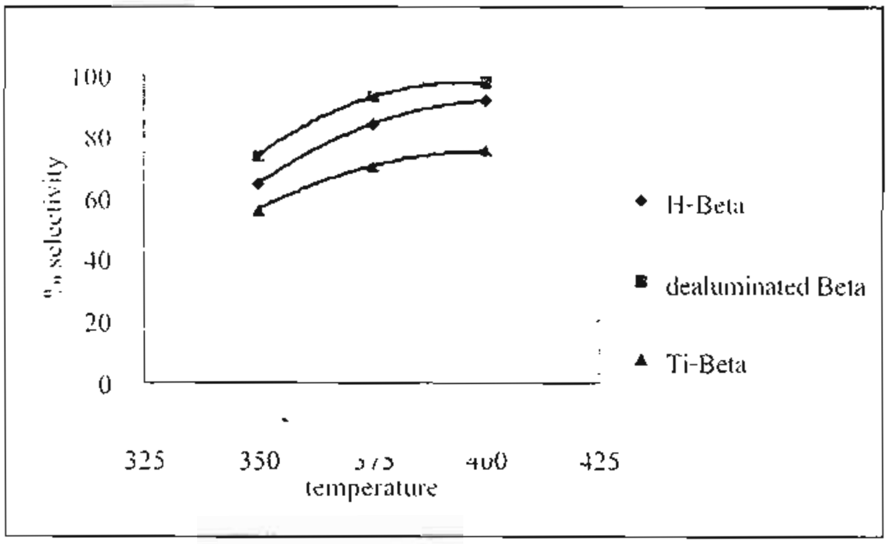


Figure 2.20 Effect of reaction temperature on the selectivity of caprolactam over H-Beta. Dealuminated Beta and Ti-Beta *Reaction condition: pressure: 1 atm, W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, average time on stream: 10-90 min, temperature: 350, 375, 400 °C*

2.3.4 Effect of contact time

2.3.4.1 Activity of catalyst

The effect of contact time on the Beckmann rearrangement of cyclohexanone oxime over H-Beta catalyst was investigated from 13.6 and 27.2 $g_{catalyst}$ h $mol^{-1}_{reactant}$. It was found that conversion of cyclohexanone oxime was drastically improved with rise in contact time.

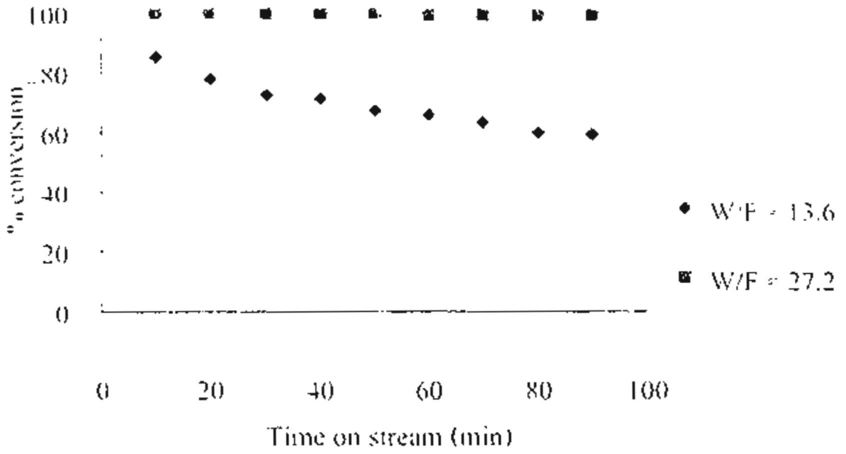


Figure 2.21 Effect of contact time on the conversion of cyclohexanone oxime over H-Beta *Reaction condition : temperature; 350 °C, pressure; 1 atm, diluent; butanol, carrier gas;* N_2, *time on stream; 90 min, contact time; 13.6 and 27.2* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$

It was suggested that, when contact time is increased there are more available the active sites for cyclohexanone oxime adsorption. This leads to an increased in overall conversion of cyclohexanone oxime. Moreover, at higher contact time, butanol can facilitate the desorption of product from the active sites therefore, the vacant sites for the further adsorption of reactant was increased. Consequently, conversion of cyclohexanone oxime was also increased.

The conversion of cyclohexanone oxime in Dealuminated Beta is shown in Figure 2.22 It was found that, the conversion of cyclohexanone oxime in Dealuminated Beta was increased with rise in contact time. It is suggested that the effect of contact time for Dealuminated Beta is a similar manner as H-Beta.

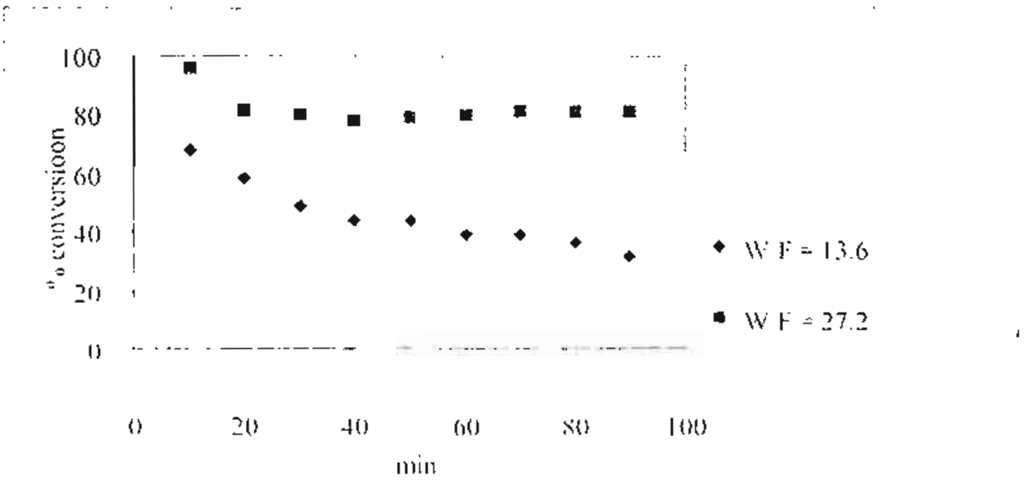


Figure 2.22 Effect of contact time on the conversion of cyclohexanone oxime over Dealuminated Beta

Reaction condition : temperature; 350 °C, pressure; 1 atm, diluent; butanol, carrier gas; N_2*, time on stream; 90 min, contact time: 13.6 and 27.2* $g_{catalyst}\ h\ mol^{-1}_{reactant}$

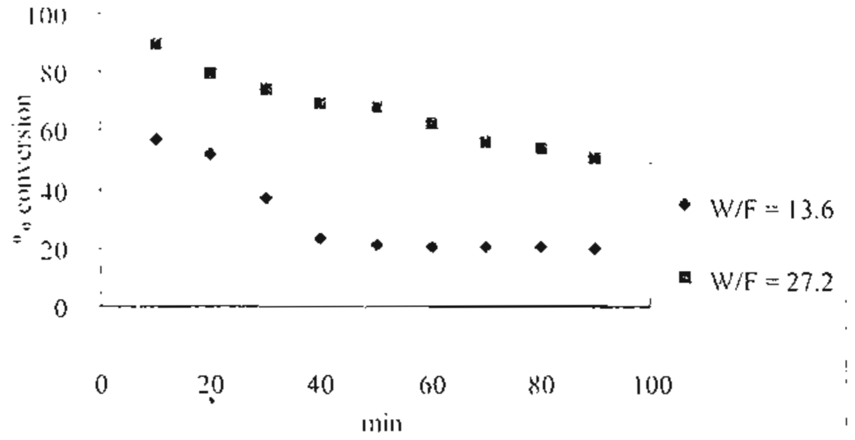


Figure 2.23 Effect of contact time on the conversion of cyclohexanone oxime over Ti-Beta

Reaction condition : temperature; 350 °C, pressure; 1 atm, diluent; butanol, carrier gas; N_2*, time on stream; 90 min, contact time: 13.6 and 27.2* $g_{catalyst}\ h\ mol^{-1}_{reactant}$

In the case of Ti-Beta Figure 2.23, it was found that, the conversion of cyclohexanone oxime was also increased with an increase in contact time. However, this is in smaller extent, as compared to dealuminated Beta and H-Beta. Since at 350 °C the activity of Ti-Beta is less than dealuminated Beta and H-Beta, respectively.

2.3.4.1 Deactivation rate of catalyst

In the case of H-Beta, the deactivation rate is drastically reduced when the contact time is risen (Figure 2.21). This may well be ascribed that when the contact time was increased, butanol can facilitated the desorption of product. This leads to a decreased in polymerization of the adsorbed product to form coke precursor. This suggestion is also confirmed by the thermogravimetric analysis of H-Beta, which shows the decrease in percent weight loss with an increase in contact time (Figure 2.24). Moreover, it is evident by the surface area analysis that the surface area of the H-Beta used at higher contact time is relatively high, as compared to that used at the lower contact time (Table 2.3).

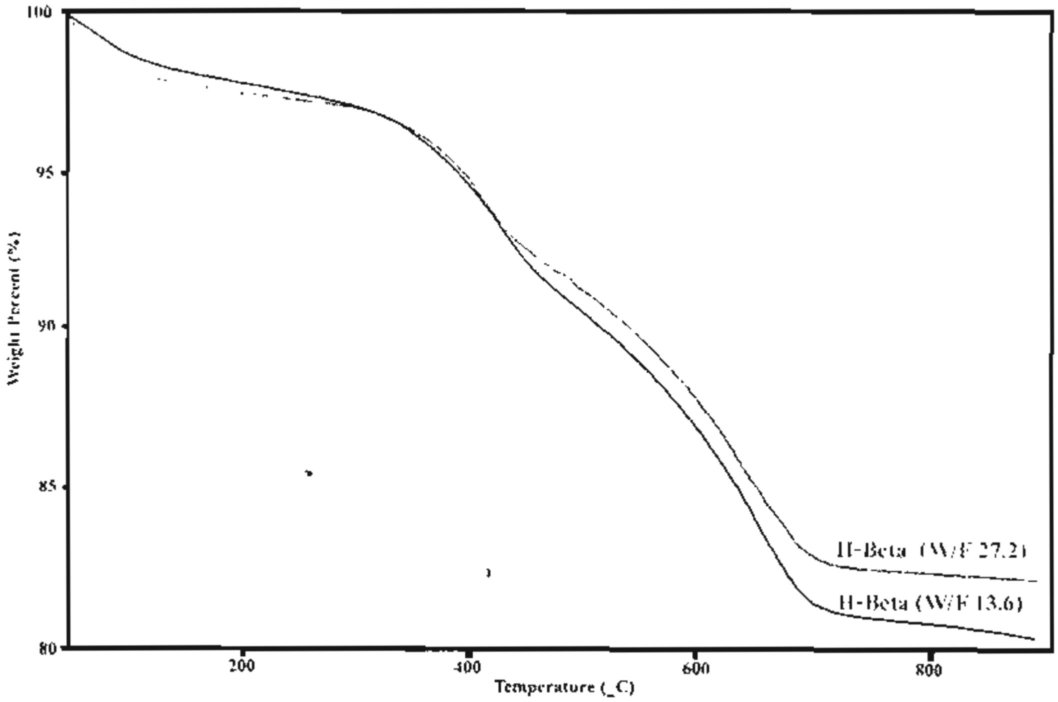


Figure 2.24 Thermogravimetric analysis of H-Beta used at different contact time

Table 2.3 Show surface area of H-Beta with an increase in contact time

Contact time	Surface area (m^2/g)
13.6	409
27.2	452

In the case of Dealuminated Beta the deactivation rate was also decreased which increased in contact time (Figure 2.22). The effect of contact time for deactivation rate of Dealuminated Beta is in a similar manner as H-Beta. It can be evidenced by thermogavimetric analysis that the coke formation of polymerization product which decomposed at temperature 450 °C and 650 °C was decreased (Figure 2.25). However, the decomposition at temperature 300 C was observed in the catalyst at high contact time. It may well be ascribed that as the contact time is risen, the desorption of high molecular weight can be facilitated by solvent. However, since the interaction of butanol with silanol active sites is poor, as discussed earlier, some small molecular species can still deposit on the active sites. This species is likely to decomposition at relatively low temperature (i.e. 300 °C) as observed by thermogavimetric analysis. Therefore, this is no significant different in the overall percent weight loss of Dealuminated Beta when the contact time is increased. Despite, higher contact time leads to high activity.

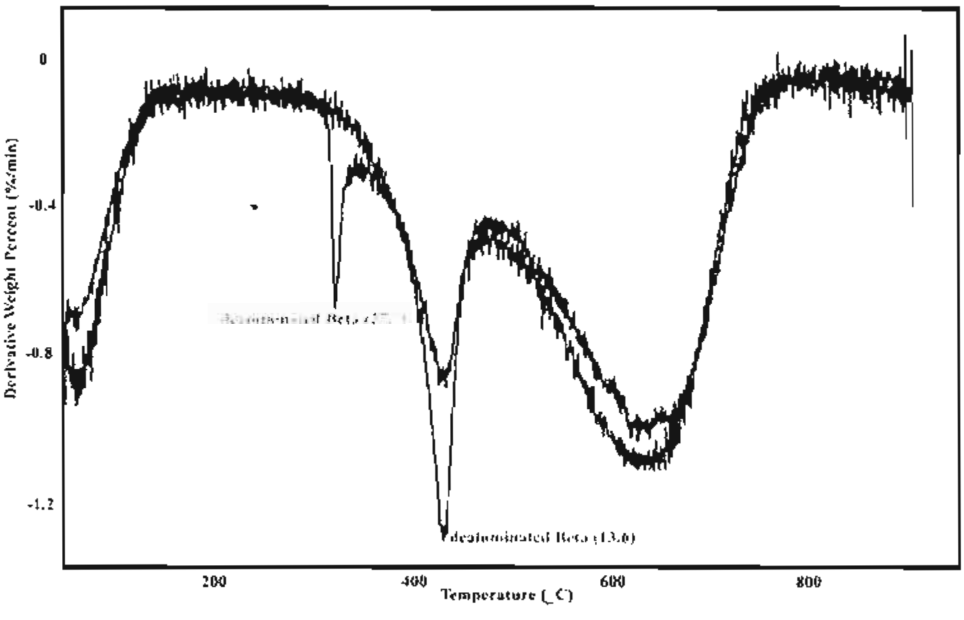


Figure 2.25 Thermogravimetric analysis of Dealuminated Beta with an increase in contact time

However, in Ti-Beta it was found that, the coke formation was increased with an increased in contact time (Figure 2.26). It was suggested that butanol cannot facilitate desorption of reactant and product from the active sites at this temperature, despite of rise in contact time. Moreover, this leads to the polymerization of the adsorbed species over the active sites. Therefore, the coke formation was increased. This suggestion was consistent with observed the high percent weight loss when contact time is increased (Figure 2.26). Therefore, no improvement in deactivation rate of Ti-Beta is observed with the rise in contact time. However the improve activity is expected, since proportion of active sites/reactants is increased when contact time is increased. In addition, it was found that decomposition at temperature 180°C, presumably decomposition of adsorb reactant over the framework of titanium sites disappears. This is because the pore size of this catalyst can be blocked by the increased coke formation. Consequently, the adsorbed reactant over titanium sites was not observed.

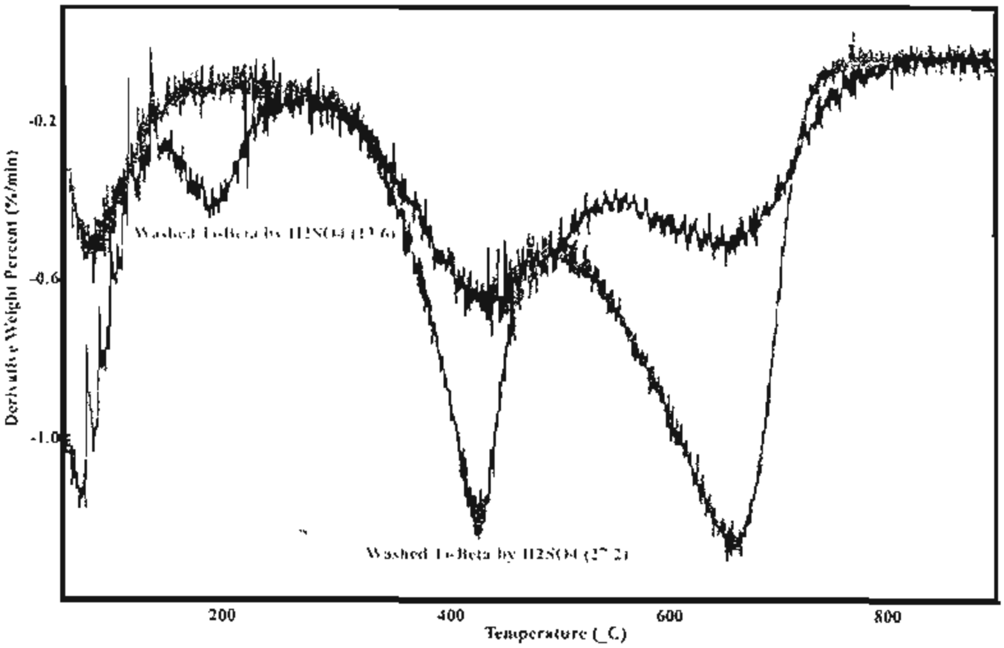


Figure 2.26 Thermogravimetric analysis of Ti-Beta with an increase in contact time

2.3.4.3 Selectivity of caprolactam

It was observed that the selectivity of caprolactam was increased with risen in contact time (Figure 2.27).

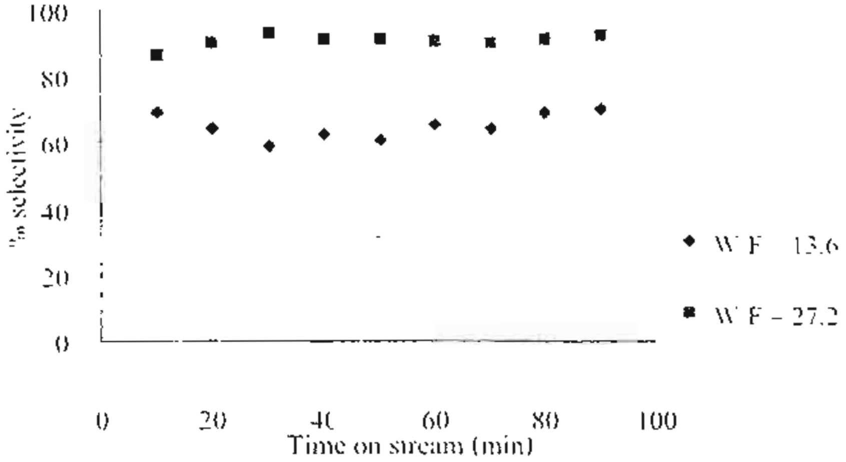


Figure 2.27 Effect of contact time on the selectivity of caprolactam over H-Beta

Reaction condition : temperature; 350 °C, pressure; 1 atm, diluent; butanol, carrier gas; N_2, time on stream; 90 min, contact time; 13.6 and 27.2 $g_{catalyst}\ h\ mol^{-1}_{reactant}$

From earlier discussion it was found that, butanol can facilitate desorption of product from the active sites, particular at high contact time. Therefore, the side reaction was decreased, especially the polymerization of product over the active sites. Consequently, the selectivity of by-product was relatively low (Figure 2.28). High selectivity of caprolactam can be obtained at high contact time.

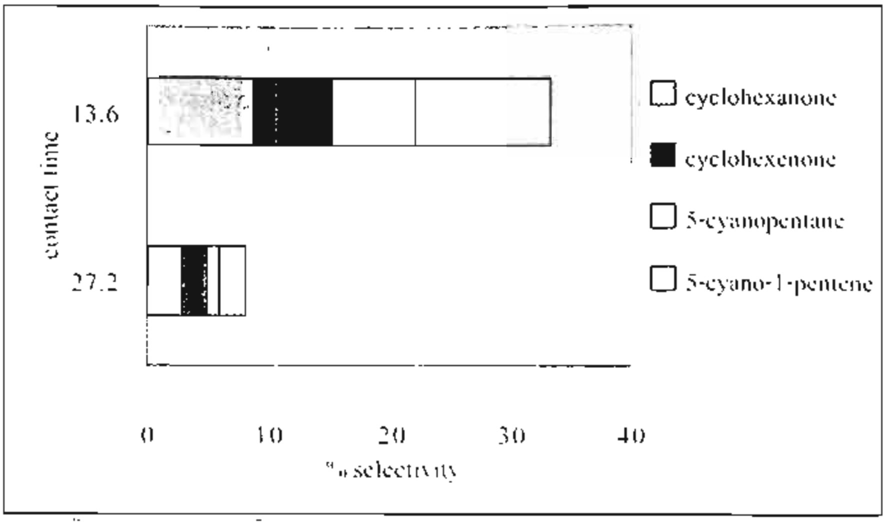


Figure 2.28 Effect of contact time on the selectivity of by-product over H-Beta

Reaction condition : temperature: 350 °C, pressure: 1 atm, diluent: butanol, carrier gas: N_2, *average time on stream: 10-90 min, contact time: 13.6 and 27.2* $g_{catalyst}\ h\ mol^{-1}_{reactant}$

In Dealuminated Beta, the selectivity of caprolactam was also increased with rise in contact time (Figure 2.29). In the same way, the effect of contact time on the selectivity of caprolactam over Ti-Beta is in a similar manner as H-Beta. However, Dealuminated Beta shows the highest selectivity of caprolactam, as previously discussed in section 3.2.2.

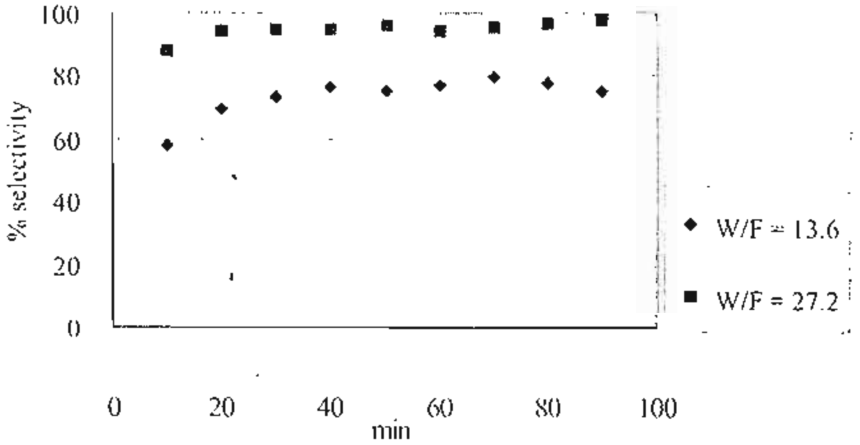


Figure 2.29 Effect of contact time on the selectivity of caprolactam over Dealuminated Beta

Reaction condition : temperature: 350 °C, pressure: 1 atm, diluent: butanol, carrier gas: N_2, *time on stream: 90 min, contact time: 13.6 and 27.2* $g_{catalyst}\ h\ mol^{-1}_{reactant}$

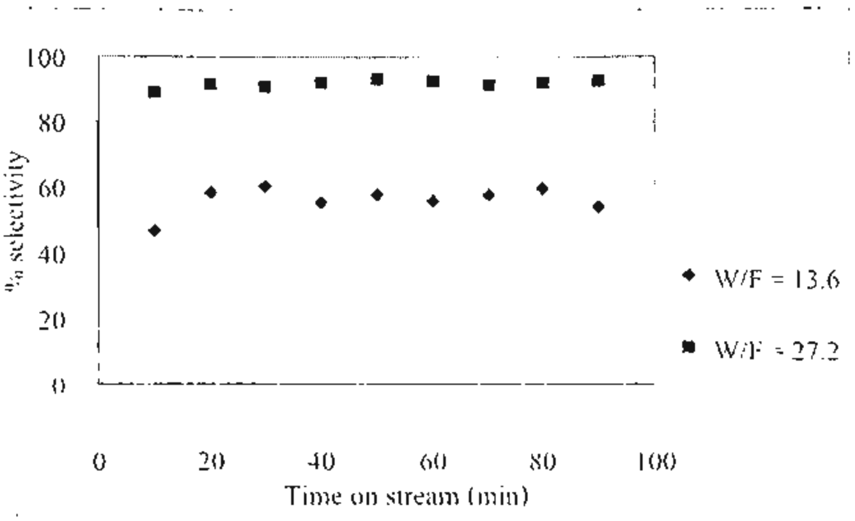


Figure 2.30 Effect of contact time on the selectivity of caprolactam over Ti-Beta

Reaction condition : temperature: 350 °C, pressure: 1 atm, diluent: butanol, carrier gas: N_2, time on stream: 90 min, contact time: 13.6 and 27.2 $g_{catalyst}$ *h* $mol^{-1}_{reactant}$

In the case of Ti-Beta (Figure 2.30), it was found that the selectivity of caprolactam was also increased with increased in contact time. Since butanol cannot facilitate desorption of products from the active sites which is confirmed by increased coke formation, the free titanium active sites which convert reactant to by-product is prohibited. (as discussed in section 2.3.2.2). This leads to an increase in the selectivity of caprolactam when contact time is increased.

It can be concluded that, when the contact time is increased, the conversion of cyclohexanone oxime and the selectivity of caprolactam over any type of zeolites are increased, while the deactivation rate was decreased. When the contact time is 27.2 $g_{catalyst}$ h $mol^{-1}_{reactant}$, the conversion of cyclohexanone oxime in H-Beta is ~100% and no significant deactivation rate can be observed. The selectivity of caprolactam over all samples of zeolites are higher than 90%, and dealuminated Beta gives the highest selectivity of caprolactam. However, the interaction between solvent and active sites would be considerably important. Therefore, in the further sections, the effect of solvent in this reaction was studied.

2.3.5 Effect of solvent

2.3.5.1 Activity of catalyst

In previous report, [30-31, 33] it was found that the effect of solvent was important for the conversion of the cyclohexanone oxime. This is because solvent must desorb product to give free active sites for further adsorption of reactant. Solvent must possesses stronger interaction with active sites than the product, but weaker interaction with active sites, as compared to the reactant. Moreover, an appropriate solvent can increase the selectivity of caprolactam, which will be discussed in section 2.3.5.3.

In this study, water was added in the solvent (butanol) at 1/53 molar ratio. It was found that, the conversion of cyclohexanone oxime was increased, when the water was added (Figure 2.31).

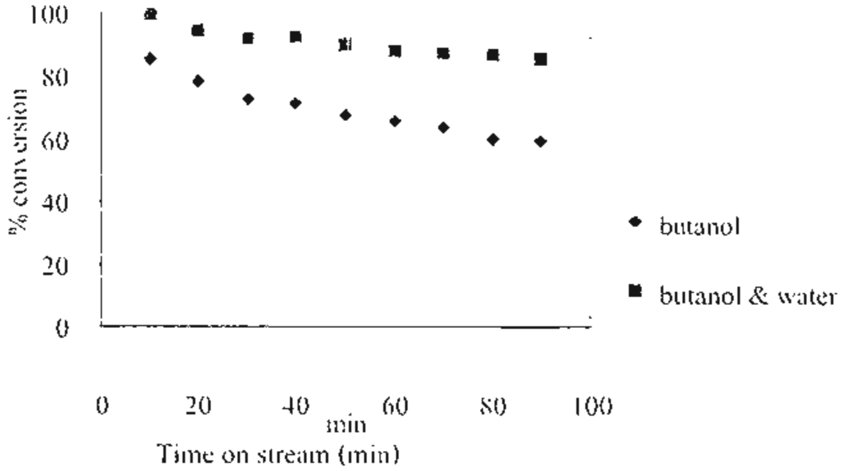


Figure 2.31 Effect of water added in solvent on the conversion of cyclohexanone oxime over H-Beta

Reaction condition; temperature; 350°C, pressure, 1 atm, diluent; butanol, butanol : water; 1:53 molar ratio, carrier gas; N_2, time on stream; 90 min, contact time; 13.6 $g_{catalyst}\ h\ mol^{-1}_{reactant}$

It is suggested that, water added in butanol can increase the polarity of solvent so, product can be easily desorbed from the active site. As a consequence, more available vacant active site are expected and more cyclohexanone oxime can adsorb on these sites. The rate of reaction is then increased resultind in a rise in the conversion of cyclohexanone oxime. Moreover the polymerization of the adsorbed product to the coke precursor is decreased. This can be confirmed by the thermogravimetric analysis that the percent weight loss of coke over H-Beta was decreased when water was added in the solvent (Figure 2.32).

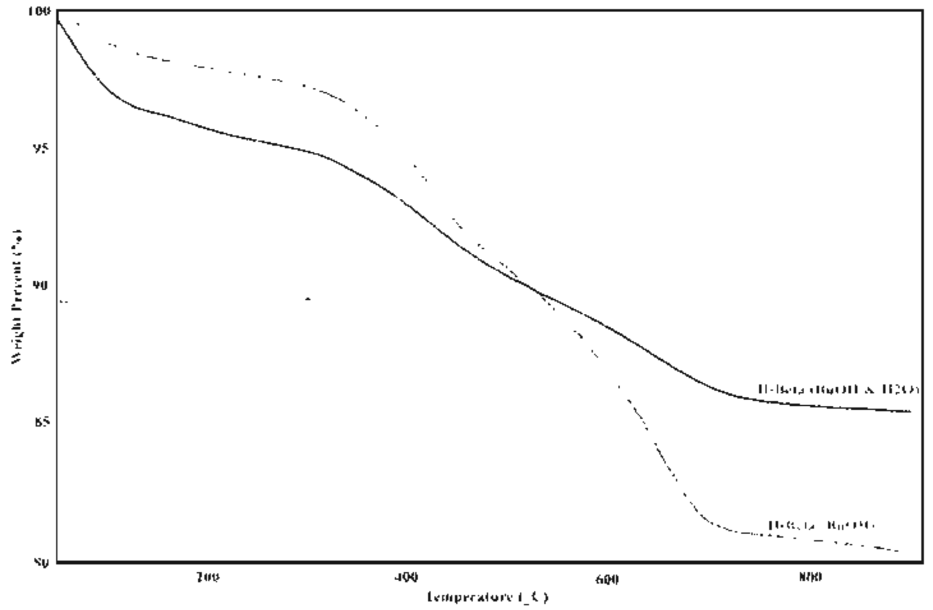


Figure 2.32 Thermogravimetric analysis of H-Beta in the reaction using butanol and water added in butanol as solvent

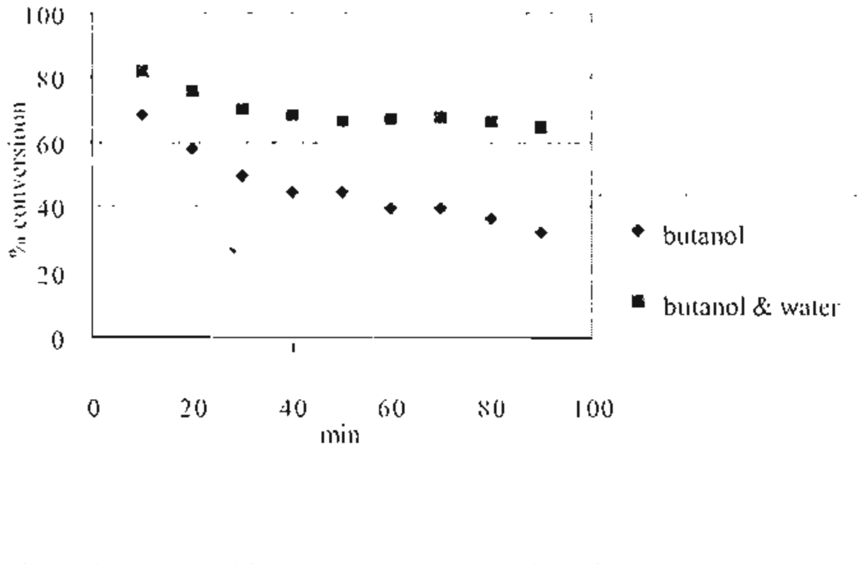


Figure 2.33 Effect of water added in solvent on the conversion of cyclohexanone oxime over Dealuminated Beta

Reaction condition; temperature: 350°C, pressure: 1 atm, diluent: butanol, butanol : water; 1:53 molar ratio, carrier gas: N_2, time on stream; 90 min, contact time: 13.6 $g_{catalyst}\ h\ mol^{-1}_{reactant}$

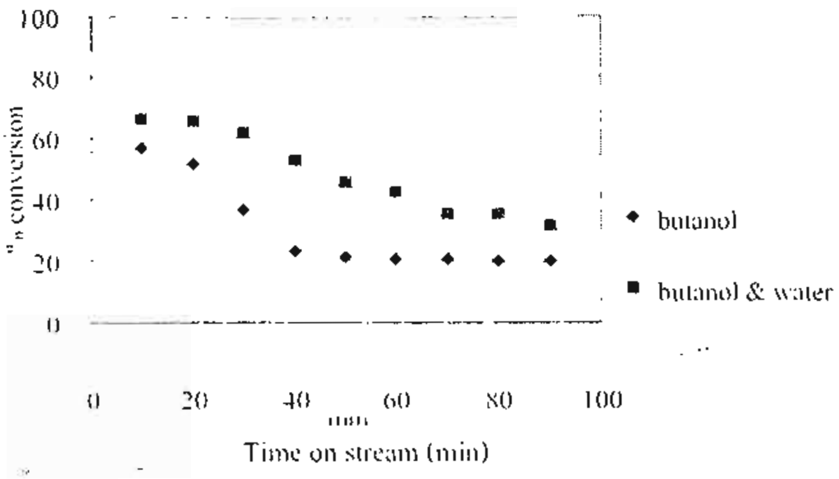


Figure 2.34 Effect of water added in solvent on the conversion of cyclohexanone oxime over Ti-Beta

Reaction condition; temperature, 350°C, pressure; 1 atm, diluent: butanol, butanol : water; 1.53 molar ratio, carrier gas, N_2, time on stream; 90 min, contact time: 13.6 $g_{catalyst}\ h\ mol^{-1}_{reactant}$

In the case of dealuminated Beta and Ti-Beta it was found that the conversion of cyclohexanone oxime was also increased with water added in butanol (Figure 2.33 and Figure 2.34). It seems that the effect of water co-feeding for dealuminated Beta and Ti-Beta are in a similar manner as H-Beta. The increased polarity of the solvent can facilitate the desorption of product from the active sites for all zeolite catalysts. However, the conversion of cyclohexanone oxime is in the order of H-Beta, Dealuminated Beta and Ti-Beta, respectively.

2.3.5.2 Deactivation rate of catalyst

In the case of H-Beta, the deactivation rate was decreased with water added in the butanol (Figure 2.31). This is because the higher polarity solvent can facilitate the desorption of product from the active sites. Consequently, polymerized product over the active sites is decreased leading to a decrease coke formation. In the case of Dealuminated Beta and Ti-Beta, it was found that the deactivation rate was also decreased with water addition (Figure 2.32 and Figure 2.33). It was suggested that the effect of water added in butanol on Dealuminated Beta and Ti-Beta are in a similar manner as H-Beta. This is consistent with the thermogravimetric analysis of those catalyst that percent weight loss decreases with butanol/water as solvent in the reaction (Table 2.4).

Table 2.4 Percent weight loss of the butanol and butanol/water as solvent

	H-Beta	Dealuminated Beta	Ti-Beta
Butanol	16.84	14.13	12.03
Butanol/Water	10.53	13.60	10.65

However when water is added in butanol as solvent the deactivation rate is in the order of Ti-Beta, Dealuminated Beta and H-Beta. This is because water, which possesses nucleophilicity can be strongly adsorbed on the Brønsted acid sites within H-Beta which possess electrophilicity. This facilitates the desorption of the adsorbed products, as compared to in the case of dealuminated Beta, which possesses silanol as active sites. In the case of Ti-Beta the cyclohexanone oxime can be strongly adsorbed on titanium sites in framework. Therefore, water added in butanol on H-Beta, can result in marked increase in catalyst activity, as compared to Dealuminated Beta and Ti-Beta.

2.3.5.3 Selectivity of caprolactam

In H-Beta, it was found that the selectivity of caprolactam was increased when the reaction using water as a co-feeding (Figure 2.35).

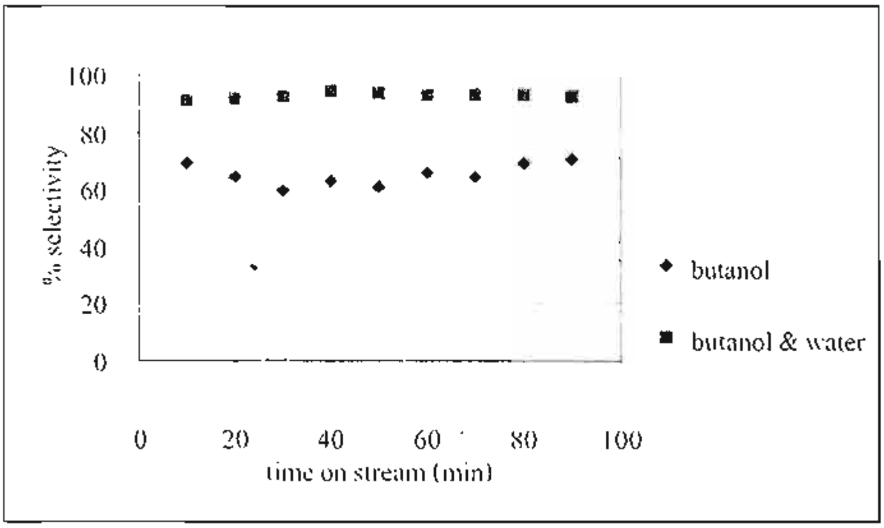
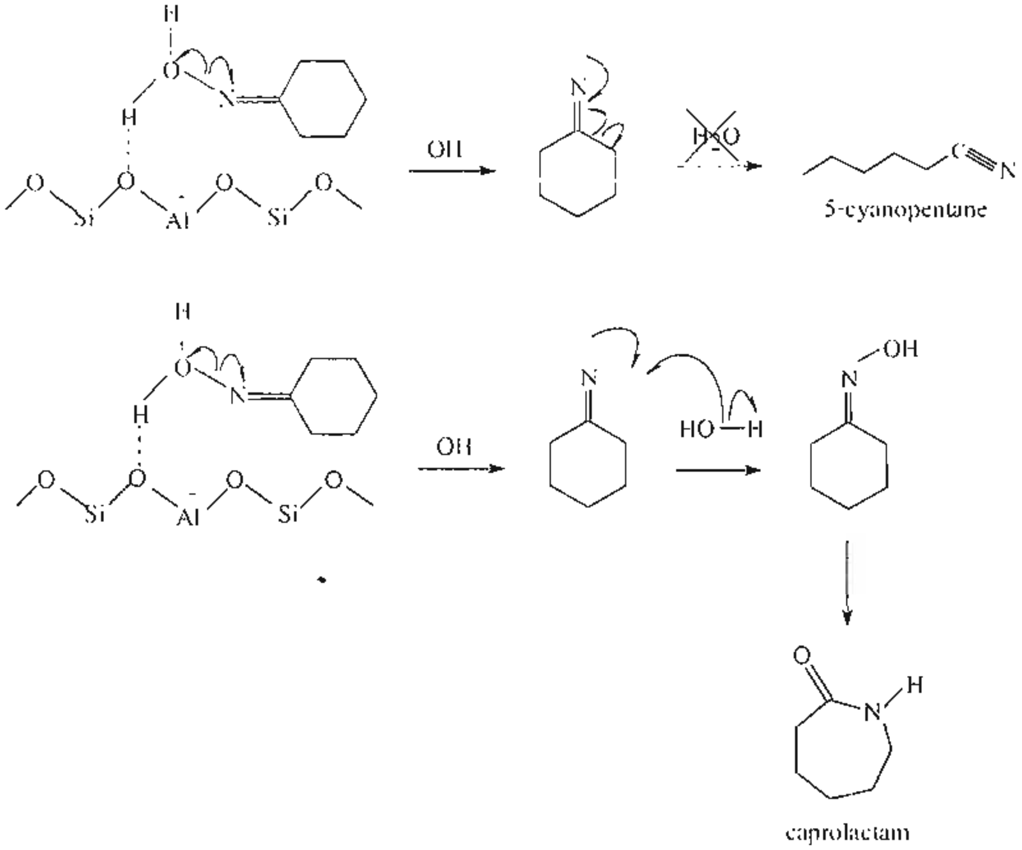


Figure 2.35 Effect of water added in solvent on the selectivity of caprolactam over H-Beta

Reaction condition; temperature: 350°C, pressure: 1 atm, diluent: butanol, butanol : water: 1:53 molar ratio, carrier gas: N_2, time on stream: 90 min, contact time: 13.6 $g_{catalyst}\ h\ mol^{-1}_{oxime}$

This is because the polarity of solvent was rised, desorption of product from active sites was increased. This leads to a decrease in the rate of side-reaction, namely polymerization of the adsorbed product on the active sites. Moreover it was found that the selectivity of 5-cyano-1-pentene was drastically decreased when the water was added in solvent (Figure 2.36).

In the presence of water as co-feeding, 5-cyanopentane, which is formed by the cyclohexanone oxime oxidation, was not observed. This is because water can reduce the intermediate, which is formed during the oxidation process. The reaction pathway for the inhibition of 5-cyanopentane formation, is proposed follows:



However, small amount of 5-cyano-1-pentene can be formed and it can undergo cyclization and the cyclised product can be readily hydrolyzed to form cyclohexenone in the presence of water as co-feeding (as earlier discussion in section 2.3.3.3). Moreover, the hydrolyzed products, namely cyclohexanone and cyclohexenone formed by hydrolysis of cyclohexanone oxime and 5-cyano-1-pentene can still be observed in the reaction using water as co-feeding.

In the case of Dealuminated Beta and Ti-Beta the selectivity of caprolactam was increased when water was added in butanol (Figure 2.37 and Figure 2.38). The effect of water added for Dealuminated Beta and Ti-Beta are in a similar manner as H-Beta.

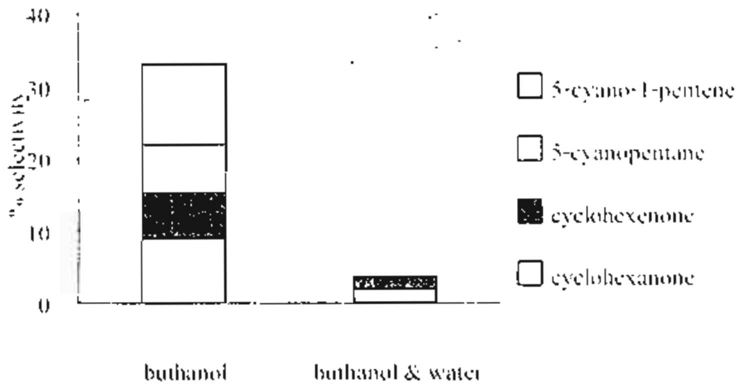


Figure 2.36 Effect of water added in solvent on the selectivity of by-product over H-Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, diluent: butanol, butanol : water: 1:53 molar ratio, carrier gas: N_2, average time on stream: 10-90 min. contact time: 13.6 $g_{catalyst}\ h\ mol^{-1}_{reactant}$

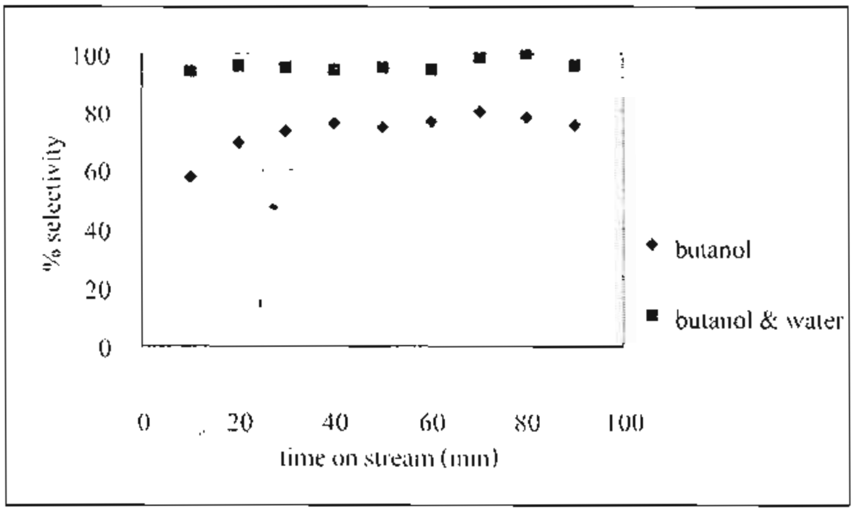


Figure 2.37 Effect of water added in solvent on the selectivity of caprolactam over Dealuminated Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, diluent: butanol, butanol : water: 1:53 molar ratio, carrier gas: N_2, time on stream: 90 min, contact time: 13.6 $g_{catalyst}$ h $mol^{-1}_{reactant}$

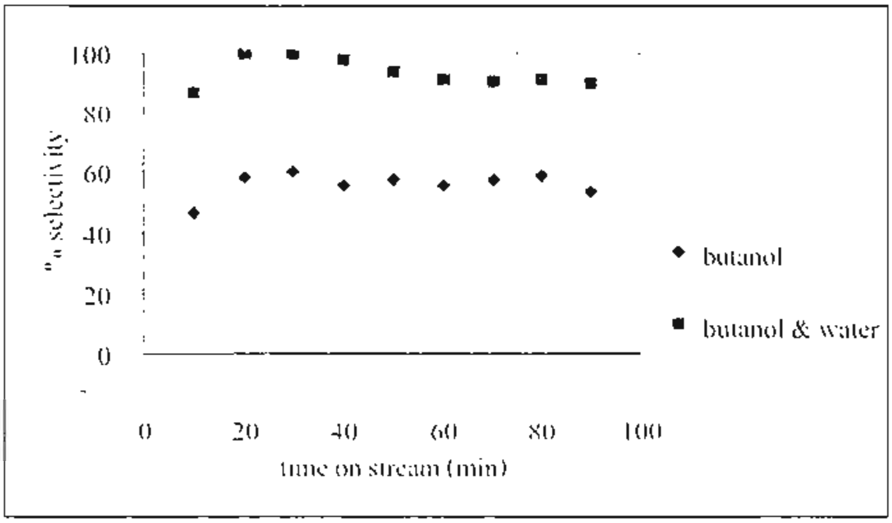


Figure 2.38 Effect of water added in solvent on the selectivity of caprolactam over Ti-Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, diluent: butanol, butanol : water: 1:53 molar ratio, carrier gas: N_2, time on stream: 90 min, contact time: 13.6 $g_{catalyst}$ h $mol^{-1}_{reactant}$

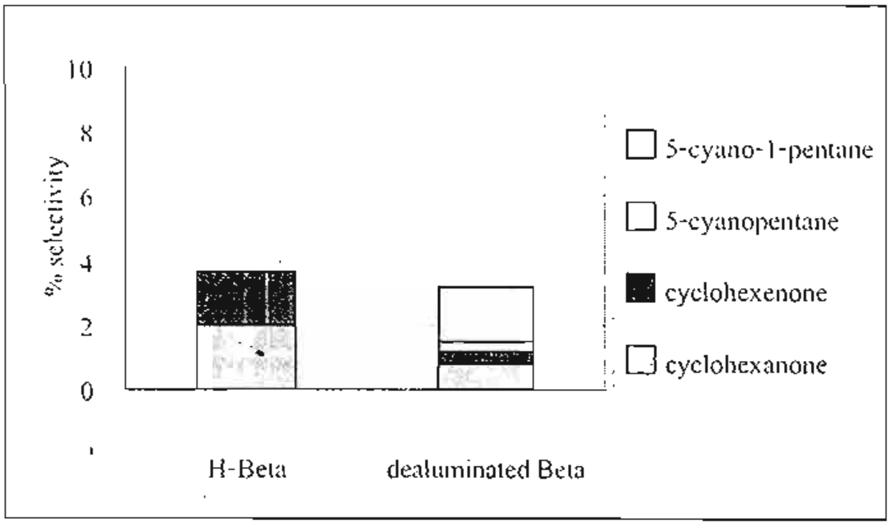
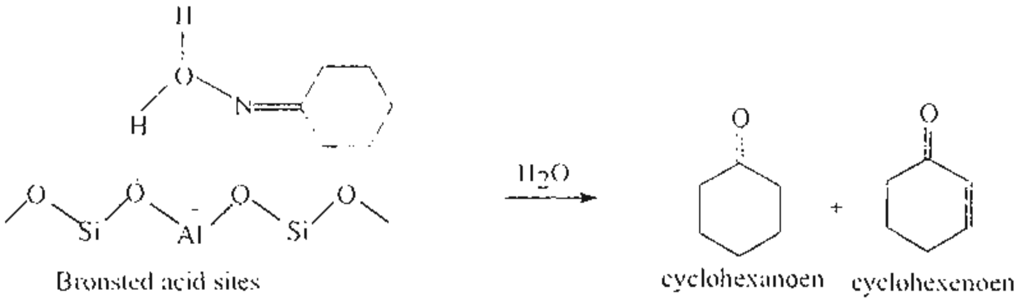


Figure 2.39 Effect of water added in solvent on the selectivity of by-product over H-Beta and Dealuminated Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, diluent: butanol, butanol : water: 1:53 molar ratio, carrier gas, N_2, average time on stream: 10-90 min, contact time: 13.6 $g_{catalyst}$ h $mol^{-1}_{reactant}$

Although, In the case of H-Beta, the formation of 5-cyano-1-pentene formed by decomposition of cyclohexanone oxime in the system lacking of water, cannot be formed in the system containing water. This is not the case for the dealuminated Beta, since the water adsorption ability of dealuminated Beta is relatively low. Therefore, the formation of 5-cyano-1-pentene is still observed.

Moreover, it was clearly shown that the selectivity of cyclohexanone and cyclohexenone, which are formed by hydrolysis of cyclohexanone oxime in dealuminated Beta was lower than H-Beta (Figure 2.39). Since the adsorption of water on Brönsted acid sites within H-Beta is higher than that silanol sites of dealuminated Beta. Hence, hydrolysis of cyclohexanone oxime to cyclohexanone and cyclohexenone in H-Beta is relatively high, as compared to the dealuminated Beta.



The selectivity of by-product in Ti-Beta was also decreased when water was presence as co-feeding in the solvent (Figure 2.40). Regarding to the selectivity of 5-cyanopentane in Ti-Beta, which was predominant formed over Ti-Beta, it was drastically decreased when water was added.

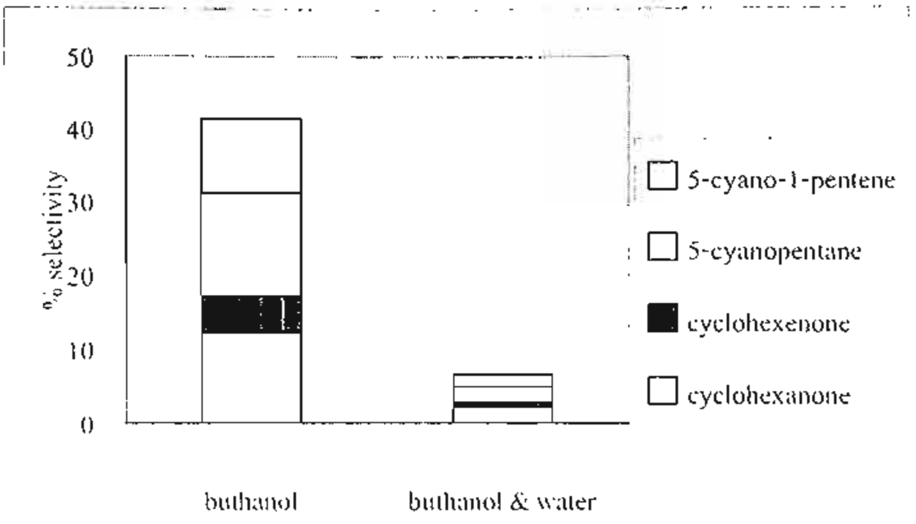
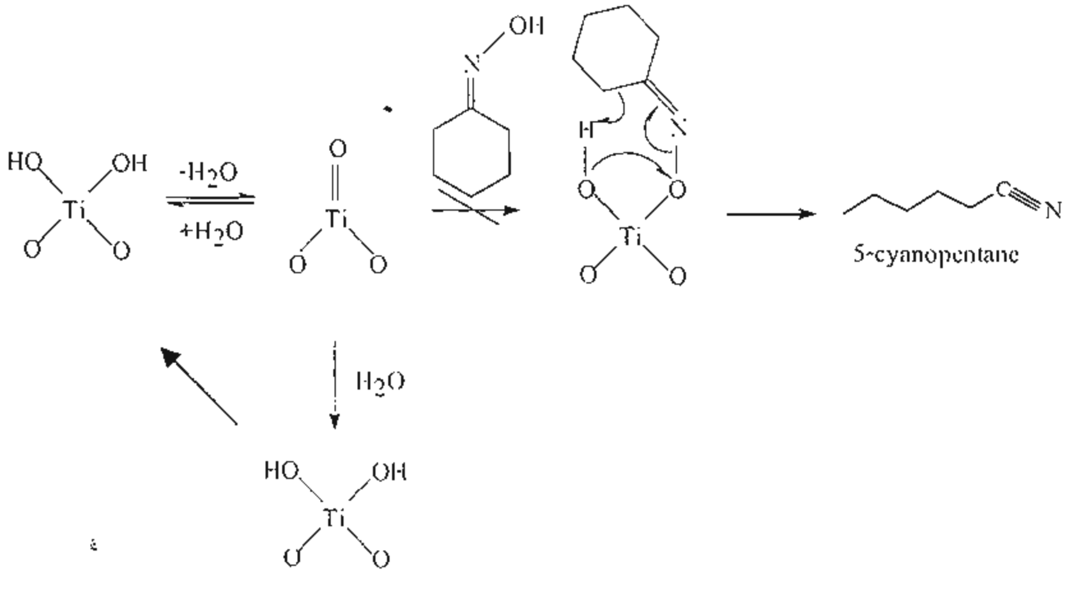


Figure 2.40 Effect of water added in solvent on the selectivity of by-product over Ti-Beta

Reaction condition: temperature: 350 C, pressure: 1 atm, diluent: butanol, butanol : water: 1:53 molar ratio, carrier gas: N_2 *, average time on stream: 10-90 min, contact time, 13.6* $g_{[illegible]}$ *h* $mol^{-1}_{[illegible]}$

This is because the decomposition of cyclohexanone oxime to form 5-cyanopentane was decreased. When the water is present, it can be decreased the active sites which convert cyclohexanone oxime to 5-cyanopentane with depicted as below, in addition to the inhibition as discussed in page 68. Therefore, the selectivity of 5-cyanopentane is exceedingly decreased, in the reaction with addition of water.



It was concluded that, when the water was fed in the reaction, the conversion of cyclohexanone oxime was rised for all zeolite catalysts. Moreover the selectivity of caprolactam was improved. This is because water added decreases the side-reaction, namely decomposition of cyclohexanone oxime and coke. In addition the decomposition of cyclohexanone oxime was also reduced in presence of water, particularly over Ti-Beta catalyst.

2.3.5.4 Effect of solvent in Ti-Beta

From the earlier discussion, the polarity of solvent and water as co-feeding can influence the desorption of product from the active sites. This leads to the increased conversion of cyclohexanone oxime and selectivity of caprolactam. So, a various type of solvent including butanol, ethanol; water added in butanol and water added in ethanol was studied in reaction using Ti-Beta as catalyst. It was found that the conversion of cyclohexanone oxime using ethanol as solvent was higher than that using butanol as solvent (Figure 2.41).

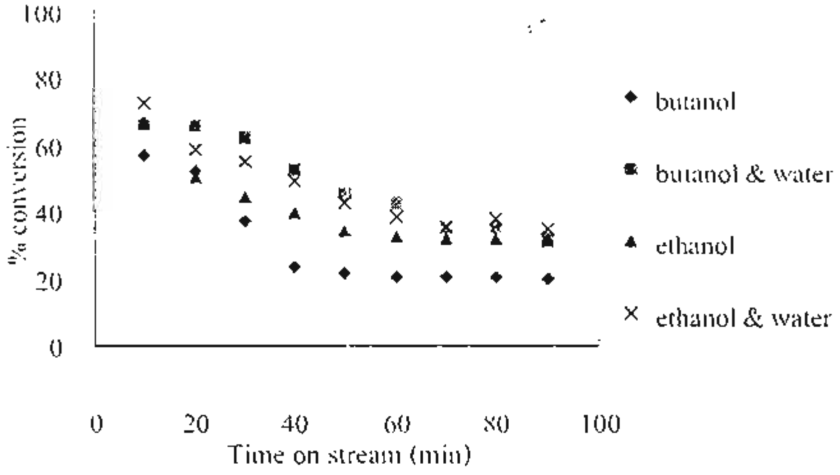


Figure 2.41 Effect of various type of solvent on the conversion of cyclohexanone oxime over Ti-Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, carrier gas: N_2, time on stream, 90 min, contact time: 13.6 $g_{catalyst}$ h $mol^{-1}_{reactant}$, diluent : butanol, ethanol, water added in butanol and ethanol, water : diluent: 1 :53 molar ratio

This is because ethanol which possesses the relatively high polarity, as compared to butanol, can facilitate the desorption of products from the active sites of Ti-Beta. This leads to a high number of free active sites for adsorbing cyclohexanone oxime. Consequently, the conversion of cyclohexanone oxime with ethanol as solvent was higher than that using butanol as solvent. In addition, when the water is present as co-feeding in the ethanol, it is found that the conversion of cyclohexanone oxime is higher than that using pure ethanol as solvent. However, the activity is similar to that using the water as co-feeding in the butanol. This may will be ascribed that the presence of water in ethanol can increased the polarity of this mixed solvent. Although, polarity of solvent play an important role in catalytic activity, it is worth noting that high polar solvent, such as ethanol water mixture, cannot only desorb products, but can also inhibit sorption of the reactant. Therefore, the observed activity is only in a similar manner as that using butanol water system. Accordingly, a balance between adsorption of reactant and desorption of product is required for optimal catalytic activity.

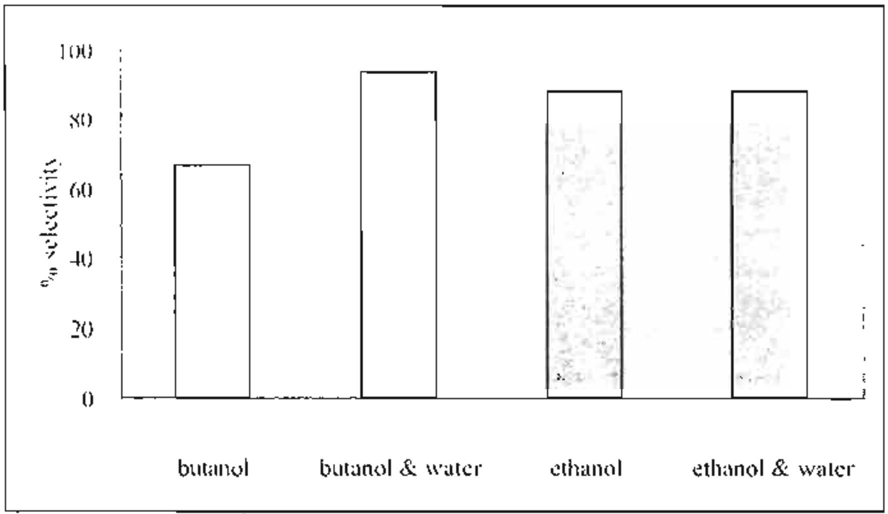


Figure 2.42 Effect of various type of solvent on the selectivity of caprolactam over Ti-Beta

Reaction condition: temperature: 350°C, pressure: 1 atm, carrier gas: N_2, average time on stream: 10-90 min, contact time: 13.6 $g_{catalyst}$ h $mol^{-1}_{reactant}$, diluent : butanol, ethanol, water added in butanol and ethanol, water : diluent: 1 :53 molar ratio

It seems that the selectivity of caprolactam for various type of solvent is in the order of butanol/water, ethanol/water, ethanol and butanol respectively (Figure 2.42). It was suggested that the water as co-feeding decrease side-reactions, such as decomposition of cyclohexanone oxime to form 5-cyano-1-pentane. Water as co-feeding can also decrease the reduction of cyclohexanone oxime to formed 5-cyanopentane. Furthermore, the high polarity of solvent can facilitate the desorption of product from the active sites, leading to a decrease in polymerized product over the active sites. Therefore, the selectivity of caprolactam was increased with rise in polarity of solvent and the presence of water. However, in the reaction using ethanol/water, the selectivity of caprolactam is less than the case of butanol/water. This may well be ascribed that the presence of water in high polar solvent (water added ethanol) can facilitate hydrolyzed products namely cyclohexanone as shown in Figure 2.43. This leads to a slightly lower selectivity of caprolactam, as compared to that using butanol/water. Therefore, it can be concluded that the polarity of solvent and water added in solvent plays important role in the selectivity of caprolactam

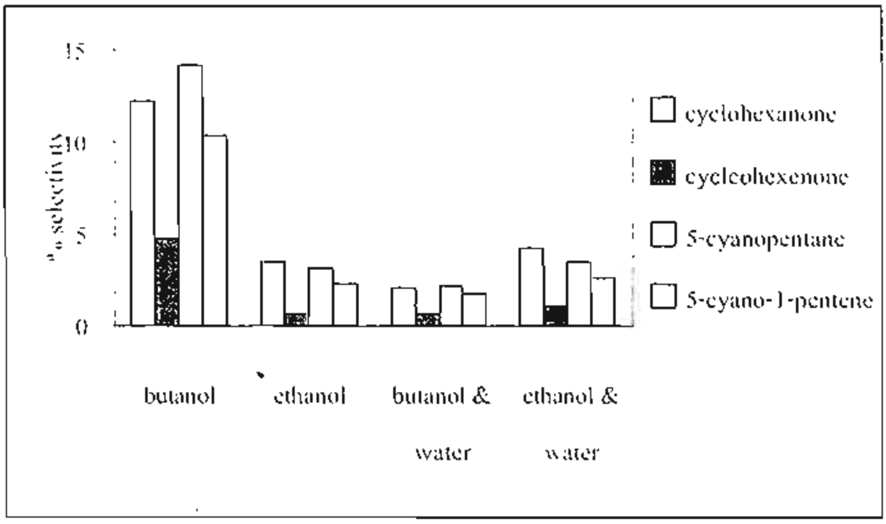


Figure 2.43 Selectivity of by-product over butanol, ethanol, butanol/water and ethanol/water as solvent.

Reaction condition; temperature: 350°C, pressure: 1 atm, carrier gas; N_2 , average time on stream: 10-90 min, contact time; 13.6 $g_{catalyst}$ h $mol^{-1}_{reactant}$, diluent : butanol, ethanol, water added in butanol and ethanol, water : diluent: 1 :53 molar ratio

2.3.6 The effect of titanium content in Ti-Beta zeolite

2.3.6.1 Activity of catalyst

The effect of titanium content in Ti-Beta was investigated over unwashed Ti-Beta and washed Ti-Beta by sulfuric acid. Figure. 2.44 shows the conversion of cyclohexanone oxime over those catalysts.

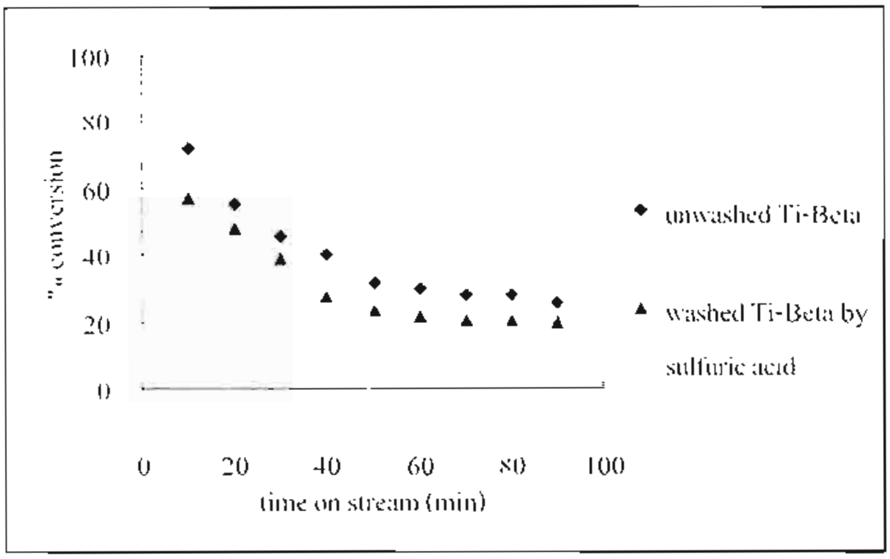


Figure 2.44 Conversion of cyclohexanone oxime over unwashed Ti-Beta and washed Ti-Beta by sulfuric acid as catalyst.

Reaction condition, temperature: 350°C, pressure: 1 atm, W/F: 13.6 $g_{catalyst}\ h\ mol^{-1}_{oxime}$, *diluent, butanol, carrier gas:* N_2, *time on stream: 90 min*

When the non-framework titanium species in the zeolite was leached by washing with sulfuric acid (as shown by elemental analysis in Table 2.5), it was found that the conversion of cyclohexanone oxime is lower than that in the reaction using unwashed Ti-Beta as shown in Figure 2.44. It was suggested that the non-framework titanium species, presumably titanium dioxide is also active for converting cyclohexanone oxime.

Table 2.5 Si/Al ratio and surface area of the unwashed Ti-Beta and the washed Ti-Beta by sulfuric acid

Type of zeolite	Si/Ti	Surface area (m^2/g)
Unwashed Ti-Beta	26	307
Washed Ti-Beta with sulfuric acid	43	627

It appears that the activity of Ti-Beta was not described only from the silanol active sites and the framework titanium active sites but it can also be attributed to the non-framework titanium. This can be confirmed by the thermogravimetric analysis of the unwashed Ti-Beta and washed Ti-Beta by sulfuric acid that coking is reduced in wash sample (Figure 2.45).

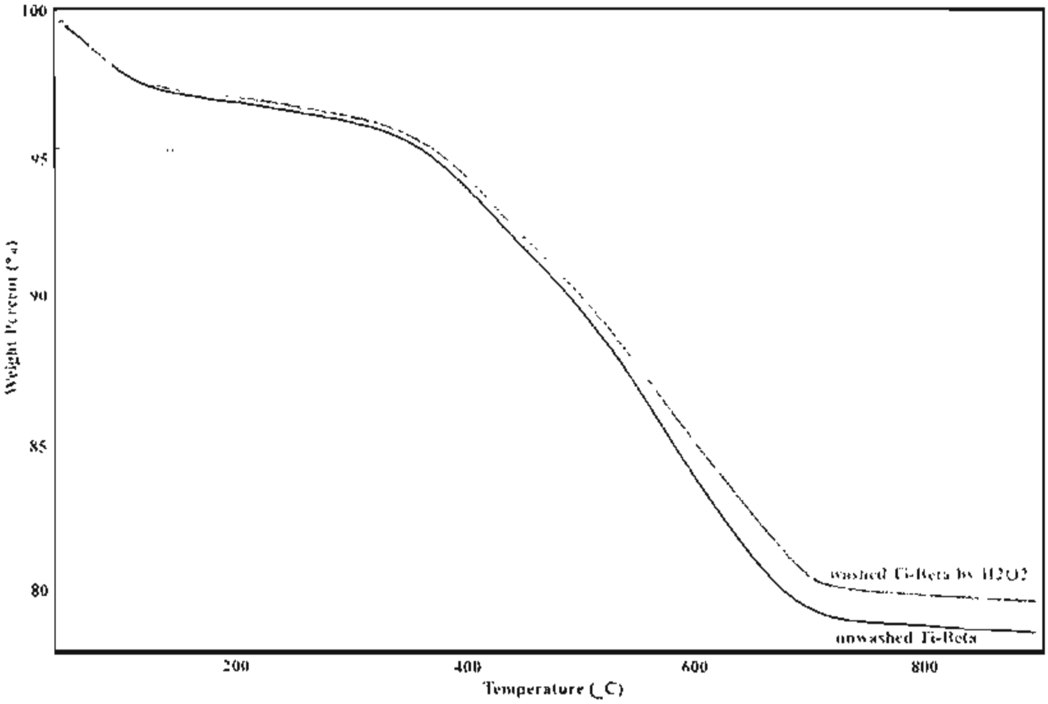


Figure 2.45. Thermogravimetric analysis of the unwashed Ti-Beta and washed Ti-Beta by sulfuric acid with using in the reaction.

It was found that the unwashed Ti-Beta gave higher percent weight loss, as compared to washed Ti-Beta by sulfuric acid. This is evidenced that non-framework titanium should possess higher activity, as compared to washed non-framework titanium. It can be described form the fact that the non-framework titanium within the pore of unwashed Ti-Beta can probably activate cyclohexanone oxime to form products, which desorption are somewhat retarded. This leads to further undesirable reactions to produce high molecular weight products and coke deposited in the pore of zeolite. When the non-framework titanium was leached by washing with sulfuric acid, the coke deposited in the pore of zeolite was decreased. Therefore, the percent weight loss from thermogravimetric analysis of the washed Ti-Beta by sulfuric acid is lower than that unwashed Ti-Beta.

2.3.6.2 Selectivity of caprolactam

The effect of non-framework titanium in Ti-Beta on the product can be investigated by washing with hydrogen peroxide and sulfuric acid. It is evident by the elemental analysis that the Si/Ti ratio and surface area of the Ti-Beta washed by sulfuric acid is higher than that the Ti-Beta washed by hydrogen peroxide and unwashed Ti-Beta, respectively (Table 2.6).

Table 2.6 Si/Al ratio and surface area of the unwashed Ti-Beta, the washed Ti-Beta by hydrogen peroxide and the washed Ti-Beta by sulfuric acid

Type of zeolite	Si/Ti	Surface area
Unwashed Ti-Beta	26	307
Washed Ti-Beta by hydrogen peroxide	32	467
Washed Ti-Beta by sulfuric acid	43	627

It was found that the washed Ti-Beta by sulfuric acid gave higher selectivity of caprolactam, as compared to washed Ti-Beta by hydrogen peroxide and unwashed Ti-Beta, respectively (Figure 2.46). The selectivity of by-product in those catalyst are shown in Figure 2.47.

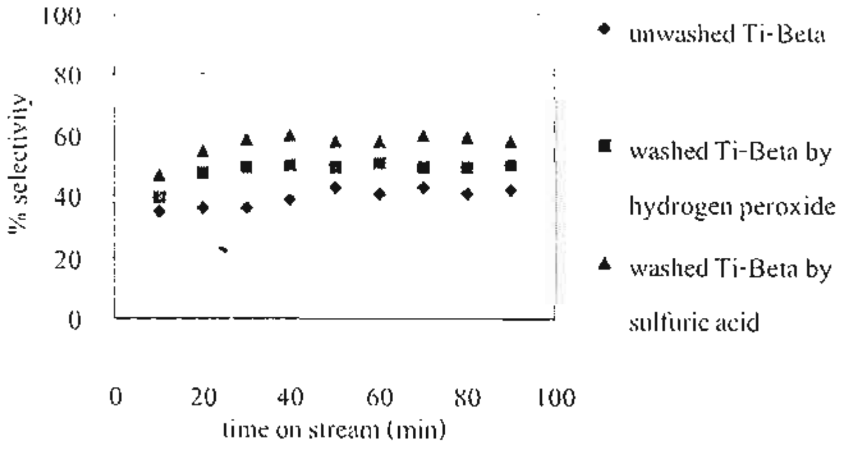


Figure 2.46 Selectivity of caprolactam over unwashed Ti-Beta, washed Ti-Beta by hydrogen peroxide and washed Ti-Beta by sulfuric acid as catalyst.

Reaction condition: temperature: 350°C, pressure: 1 atm, W/F: 13.6 $g_{catalyst}\ h\ mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, time on stream: 90 min*

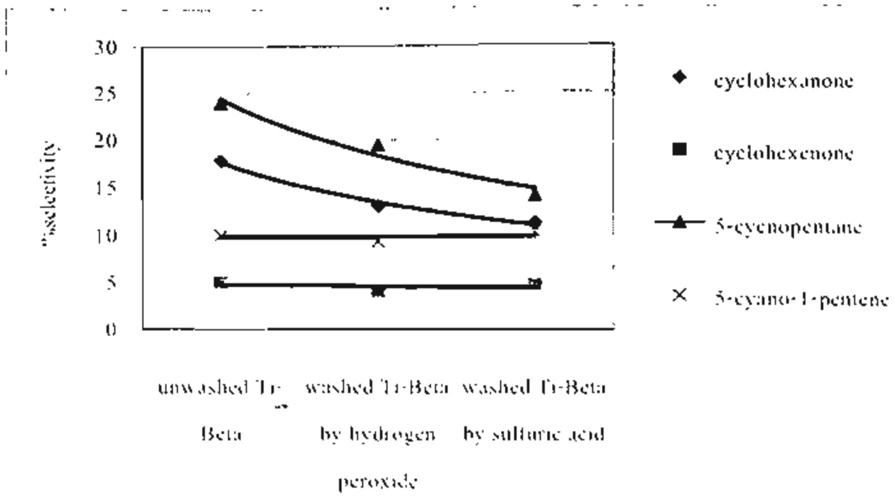
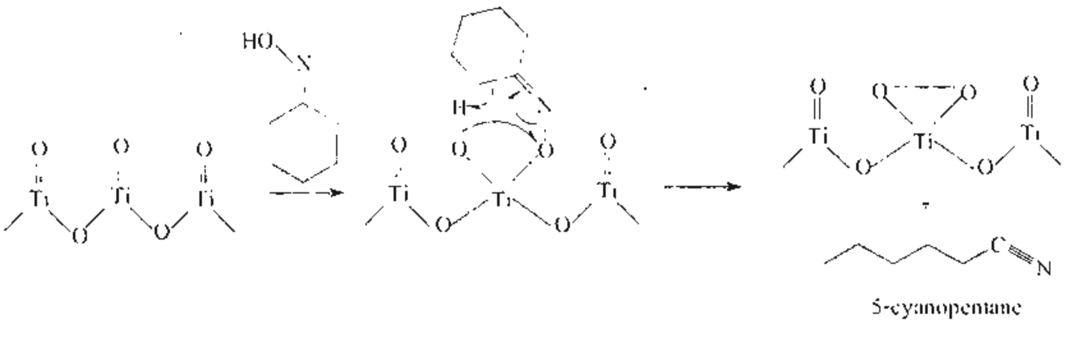
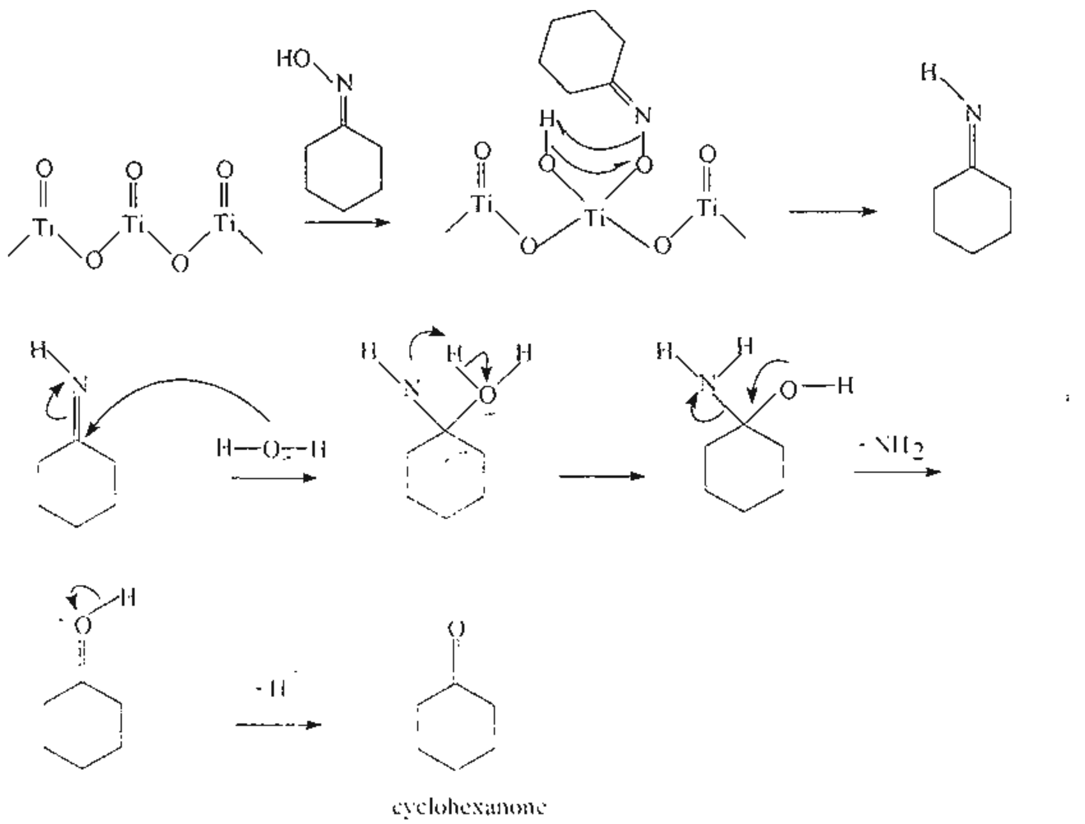


Figure 2.47 Selectivity of by-product over unwashed Ti-Beta and washed Ti-Beta by hydrogen peroxide and washed Ti-Beta by sulfuric acid as catalyst.

Reaction condition; temperature; 350°C, pressure; 1 atm, W/F; 13.6 $g_{catalyst}$ h $mol^{-1}_{[illegible]}$, diluent; butanol, carrier gas; N_2, time on stream; 90 min

It was also found from Figure 2.47 that the selectivity of cyclohexanone and 1-cyanopentane were particularly decreased after washing Ti-Beta with hydrogen peroxide and sulfuric acid while no significant change in cyclohexenone and 5-cyano-1-pentene yield was observed. This was implied that cyclohexanone and 5-cyanopentane were probably promoted by non-framework titanium species, while the non-framework titanium species has no effect on cyclohexenone and 5-cyano-1-pentene yield. It can be concluded that not only framework titanium species could possibly promote 5-cyanopentane and cyclohexanone as discussed earlier in section 2.3.2.2 but the non-framework titanium species can largely promote those products as postulated below:





Therefore, the selectivity of caprolactam over washed Ti-Beta by sulfuric acid is higher than that washed Ti-Beta by hydrogen peroxide and unwashed Ti-Beta, respectively. The framework titanium species and non-framework titanium species gives low selectivity of caprolactam, as compared to Brφnsted acid sites and silanol sites. It is concluded that the product selectivity depends largely on type of active sites.

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CHAPTER 3

AMMOXIMATION OF CYCLOHEXANONE BY TITANIUM-CONTAINING ZEOLITE

3.1 Objectives

To understand the necessary factors for large-scale production. To obtain a suitable condition for the maximum yield of product such as temperature, titanium species, and effect of solvent. To obtain the alternative choice of ammonia resource for easier operating process.

3.2 Catalytic testing

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

Figure 3.1 Ammoximation Reactor (Batch)

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

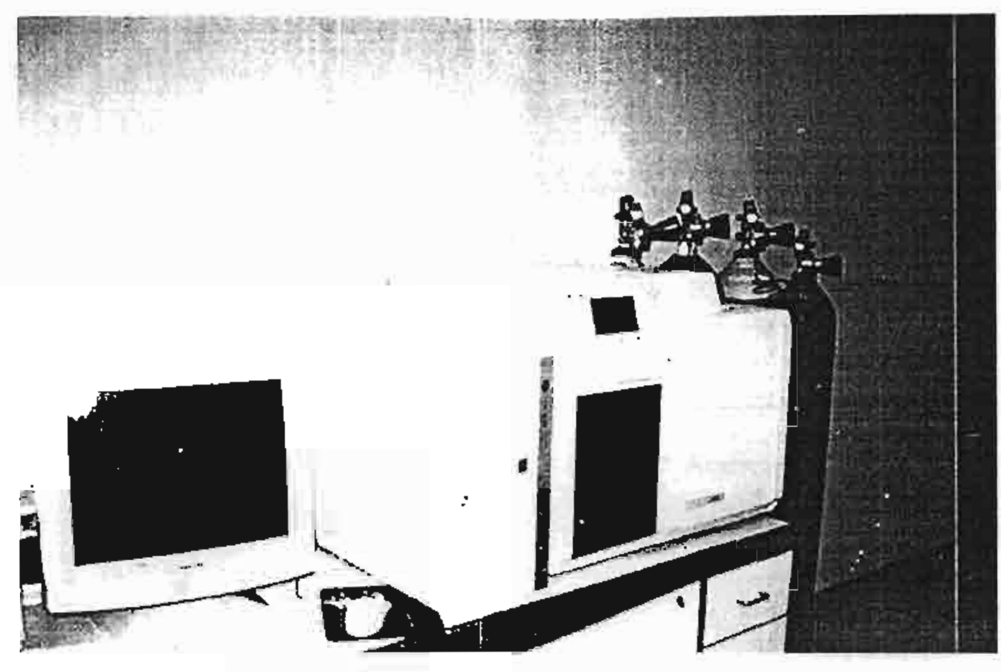


Figure 3.2 3800 Gas Chromatograph, Varian

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

3.3 Result and discussion

3.3.1 Effect of Solvent

The conversion and selectivity from the reaction using water and acetic acid as solvent are shown in Figure 3.3 and 3.4 respectively.

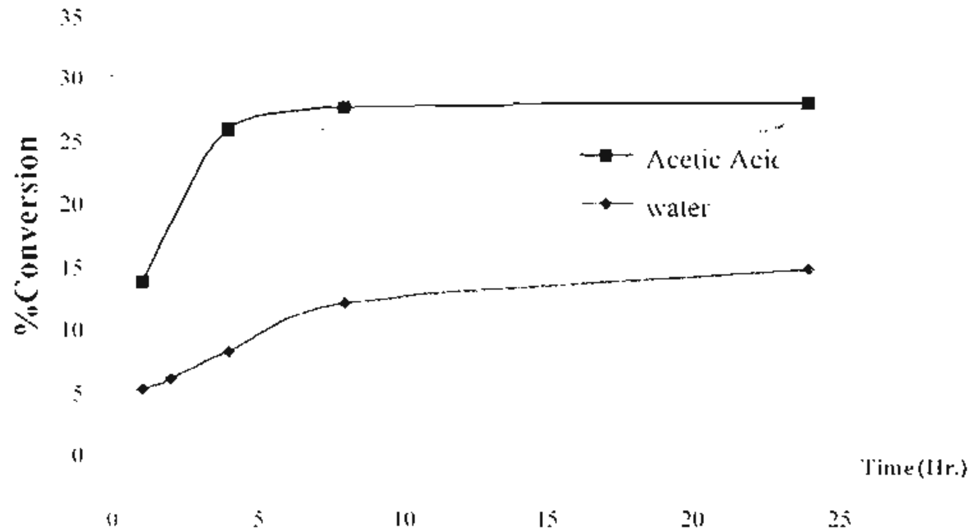
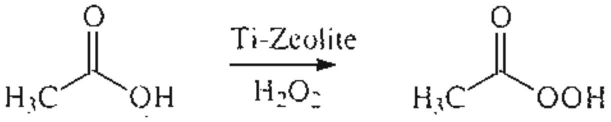


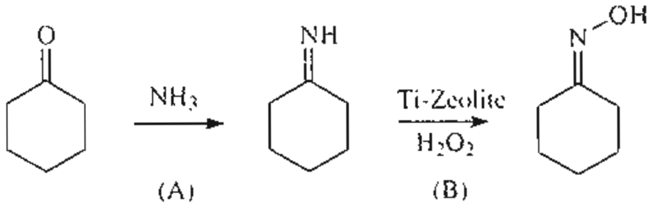
Figure 3.3 The conversion of reaction using water and acetic acid as solvent. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours*

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



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

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



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

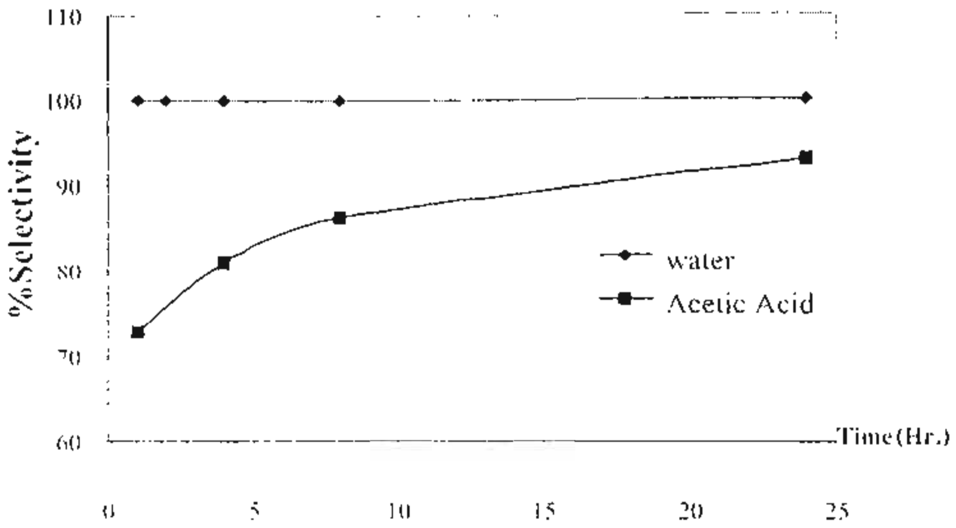
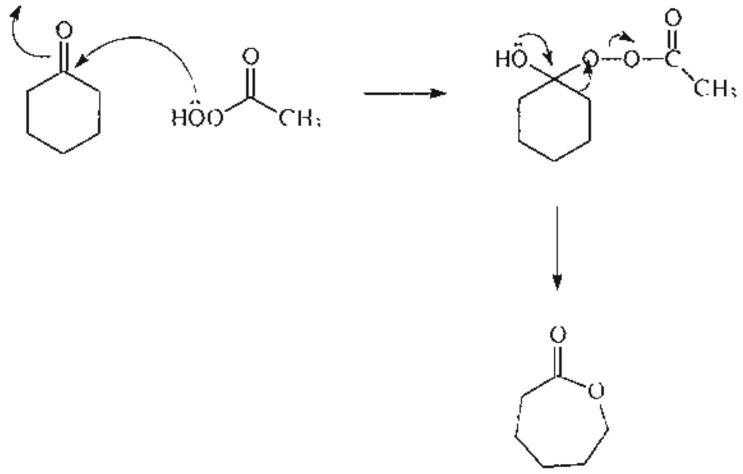


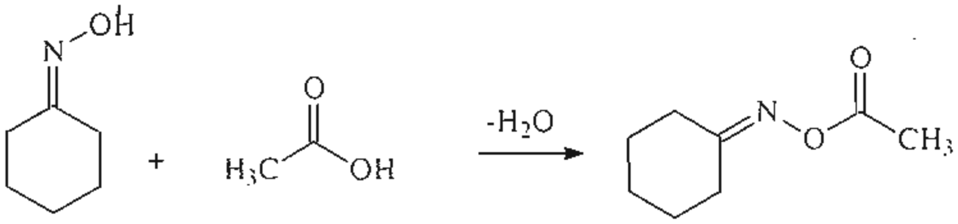
Figure 3.4 The selectivity of cyclohexanone oxime in the reactions using water and acetic acid as solvent. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml,TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours.*

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



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

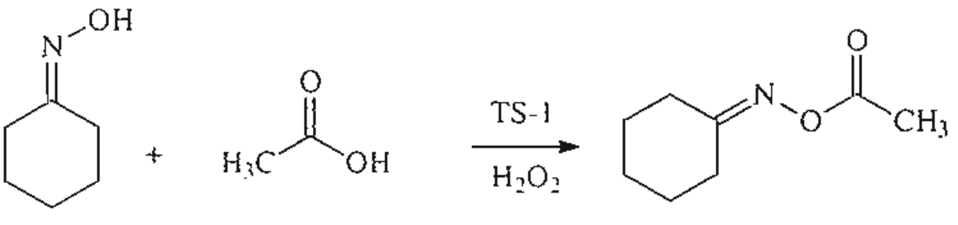
The second by-product appears to be acetyl cyclohexanone oxime. The results from the Gas Chromatography-Mass Spectrometer (Figure G.3) shows that the seconded by-product contains acetyl group and have a molecular fragmentation in a manner similar to the cyclohexanone oxime. The acetyl cyclohexanone oxime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



(A)

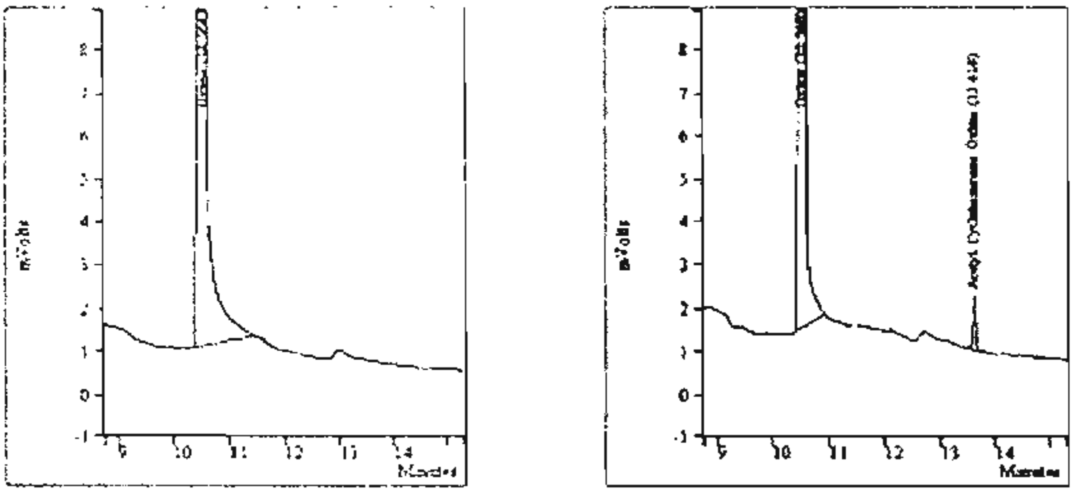
Path A: Condensation of cyclohexanone oxime and acetic acid

(B)



Path B: Oxidative coupling of cyclohexanone oxime with acetic acid

In order to verify the above possibilities, the reaction of cyclohexanone oxime with acetic acid was then tested to prepare acetyl cyclohexanone oxime. The path A was tested by heating and stirring cyclohexanone oxime with acetic acid without hydrogen peroxide and TS-1 for 4 hours. While path B was tested in the presence of hydrogen peroxide and TS-1. It was found that acetyl cyclohexanone oxime cannot be generated in the reaction for path A. However, the reaction for path B produce notably amounts of acetyl cyclohexanone oxime [Figure 3.5].



(A)

(B)

Figure 3.5 Gas chromatograms of acetyl cyclohexanone oxime synthesis from path A and B

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

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

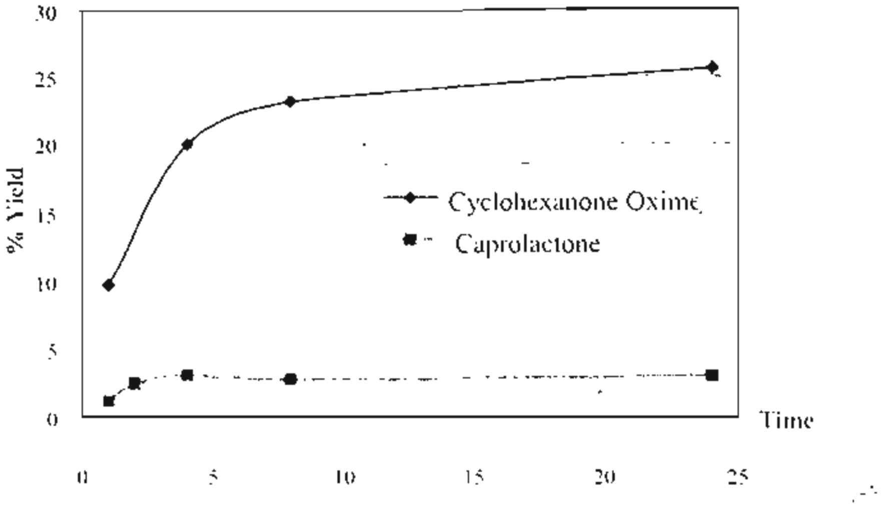
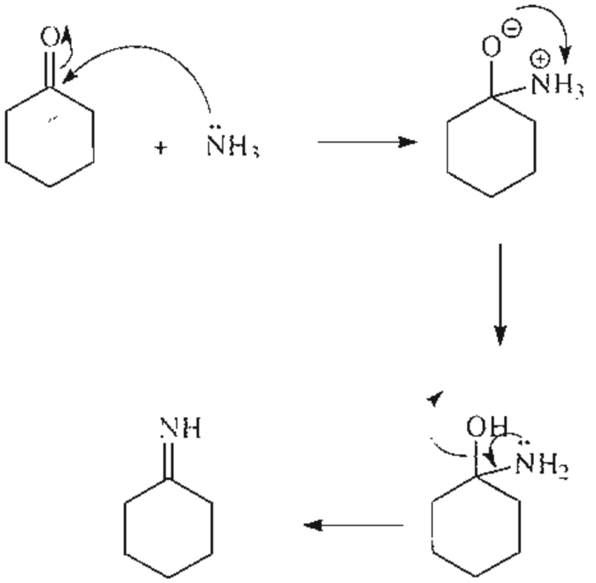


Figure 3.6 The yield of cyclohexanone oxime and caprolactone from the reaction using acetic acid as solvent. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Solvent 2.4 ml, TS-1 0.04 grams, Reaction Time 1, 2, 4, 8, 24 hours.*

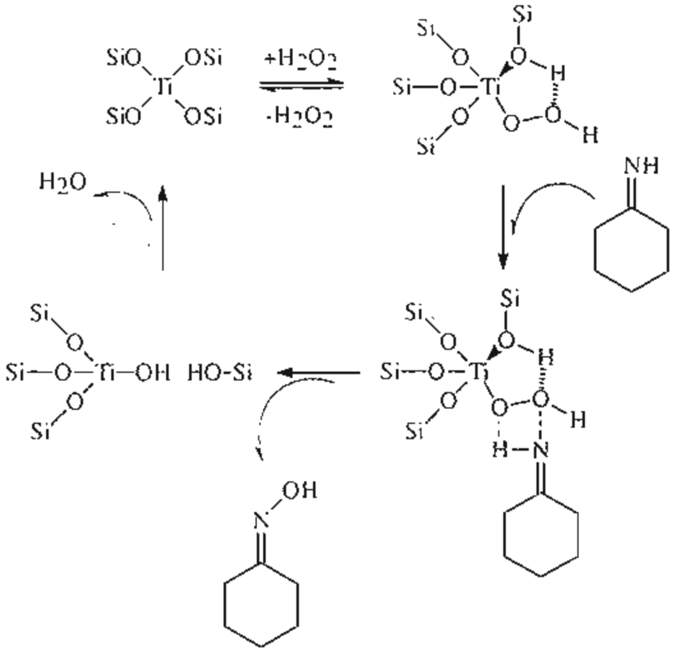
From the Figure 3.4, it was shown that the selectivity of cyclohexanone oxime in the reaction using acetic acid as solvent was increased with time. It can be explained that at the beginning of the reaction, rate of ammoximation was limited by competitive formation of caprolactone via Baeyer-Villiger Rearrangement. This is because the ammoximation reaction is a multi-step reaction. Caprolactone formation, on the other hand, is a single step reaction. The direct reaction of cyclohexanone and peracetic acid could readily compete with the condensation of cyclohexanone and ammonia. Therefore, the initial selectivity of cyclohexanone oxime is low. After a period of time, (Figure 3.6), the cyclohexanone oxime was increased while the formation of caprolactone was slightly changed. This can be attributed to the fact that cyclohexanone was converted to cyclohexanone imine and subsequently cyclohexanone oxime resulting in reduced concentration of cyclohexanone in the system. In consequence, the rate of caprolactone formation would be decreased with time and the selectivity of cyclohexanone oxime was increased.

3.3.2 Mechanistic Study

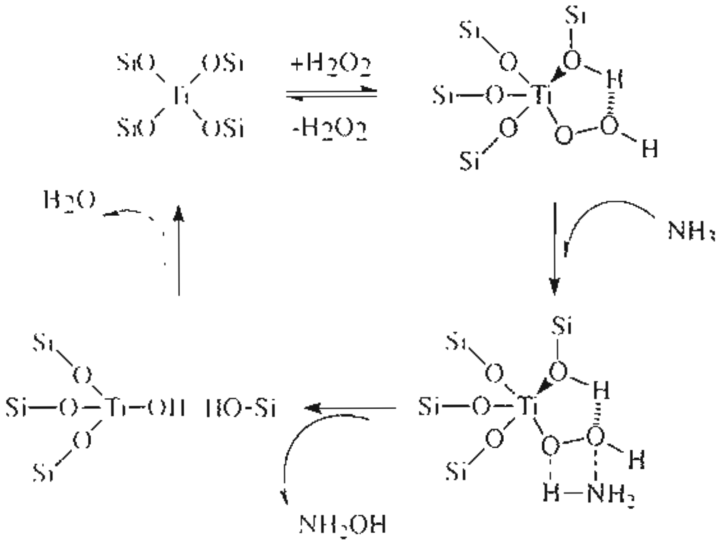
In the mechanistic point of view, it was suggested that [15] ammoximation produce via condensation of cyclohexanone with ammonia to produce cyclohexanone imine in the presence of acid as shown.



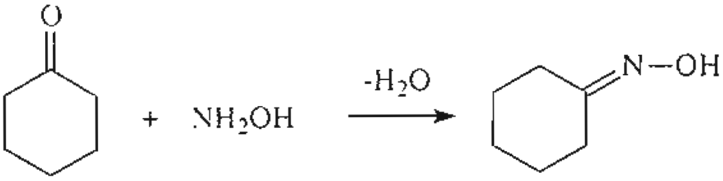
Then cyclohexanone imine will react with the active site, generated from the reaction of framework titanium in the zeolite and hydrogen peroxide or peracetic acid, to produce cyclohexanone oxime as shown.



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



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



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

On the other hand, the hypothesis that ammoximation proceeds via the oxidation of ammonia to produced hydroxylamine (test II) was tested by the reaction of only ammonia with catalyst and hydrogen peroxide. After 2 hours, the catalyst was filtrated and cyclohexanone was added. The mixture was allowed to react for about 4 hours. The results are shown in Table 3.1 and 3.2.

Table 3.1 The yield of cyclohexanone oxime generated from hypothesis of cyclohexanone condensation and typical reaction

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

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

Table 3.2 The yield of cyclohexanone oxime generated from hypothesis of ammonia oxidation and typical reaction

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

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

From the result in Table 3.1 and 3.2, it is shown that when ammonia is allowed to react with catalyst in the presence of acetic (test II), cyclohexanone oxime cannot be observed. While, cyclohexanone oxime can be only formed via the condensation of cyclohexanone with ammonia (test I). This is can be explained that, when acetic acid is used as solvent, ammonia was protonated i.e. as ammonium acetate and cannot be readily oxidized to hydroxylamine. On the other hand, the condensation of cyclohexanone with ammonia to form cyclohexanone imine is facilitated in the presence of acetic acid (test I). Synergistically, a better interaction of cyclohexanone imine with the hydrophobic acid site, formed by complexation of peracetic acid with the framework titanium, would enhance the cyclohexanone imine oxidation and subsequently the formation of cyclohexanone oxime. Whist the interaction of ammonia with the active site is then inhibited in test II and no hydroxylamine can be produced. Conclusively, in the reaction using acetic acid as solvent, only the pathway proceeded via the condensation of cyclohexanone with ammonia is responsible for the formation of cyclohexanone oxime.

In the reaction using water as solvent, on the other hand, cyclohexanone oxime can be formed by both mechanisms but mainly via condensation of cyclohexanone and ammonia as show in Table 3.3 and 3.4. Ammonia was not readily protonated in reaction using water as solvent. Hence, it can directly react with the active sites to produce hydroxylamine (test II). Additionally, cyclohexanone can react with ammonia to produce cyclohexanone imine which was subsequently oxidized to produce cyclohexanone oxime. Since the yield of cyclohexanone oxime produce in test I is similar to the typical reaction, but the considerably less is observed in test II, the condensation of cyclohexanone and ammonia appears to be a major pathway. This may be accounted for the fact that TS-1 is a hydrophobic framework (non polar framework) and the interaction between cyclohexanone imine with framework is relatively better than the interaction with ammonia (a higher polar reactant). In consequence, the rate of hydroxylamine production would be lower than the rate of imine oxidation.

3.3.3 Effect of Water

According to the above discussion, it is clear that the condensation of cyclohexanone with ammonia is essential for the ammoximation. This step could be interfered by the presence of water and pH of the solution. The effect of water can be investigated by adding zeolite A (a water adsorbent) into the system. From Figure 3.7 and 3.8, it was clearly shown that the yield and selectivity of cyclohexanone oxime was increased with the amount of zeolite A added.

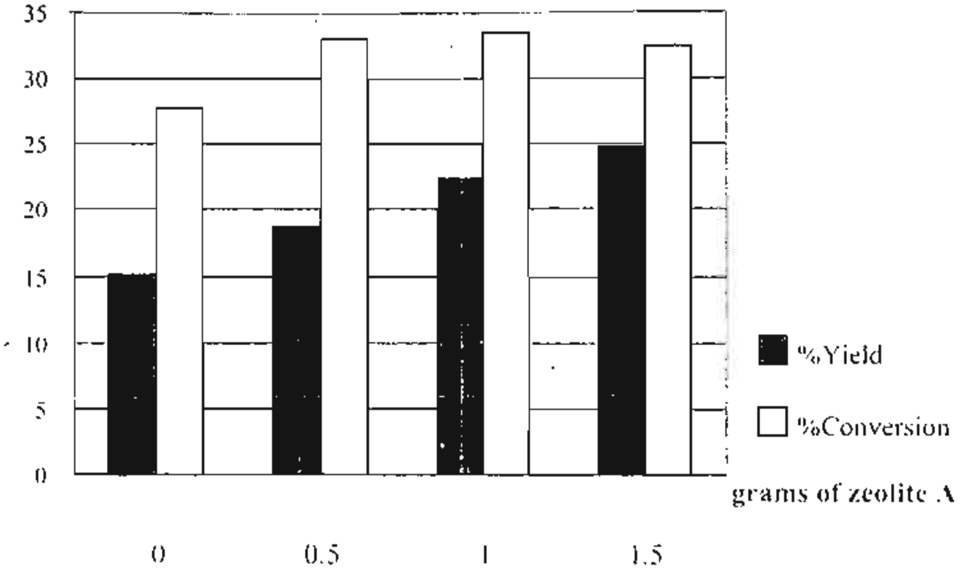
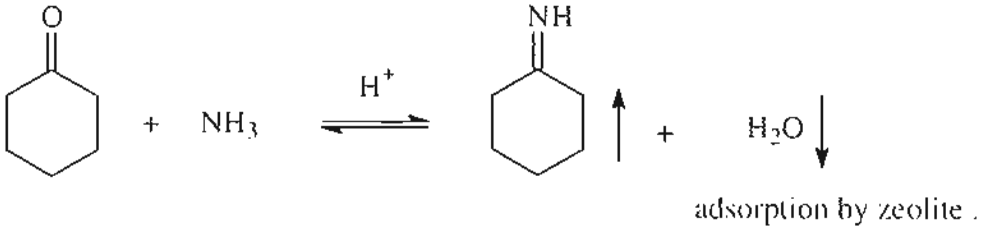


Figure 3.7 The yield and conversion of ammoximation reaction with addition of zeolite A. *Reaction condition: Temperature 60°C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml,TS-1 0.04 grams, Reaction Time 4 hours, Added 0.5, 1.0 and 1.5 g of zeolite A*

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



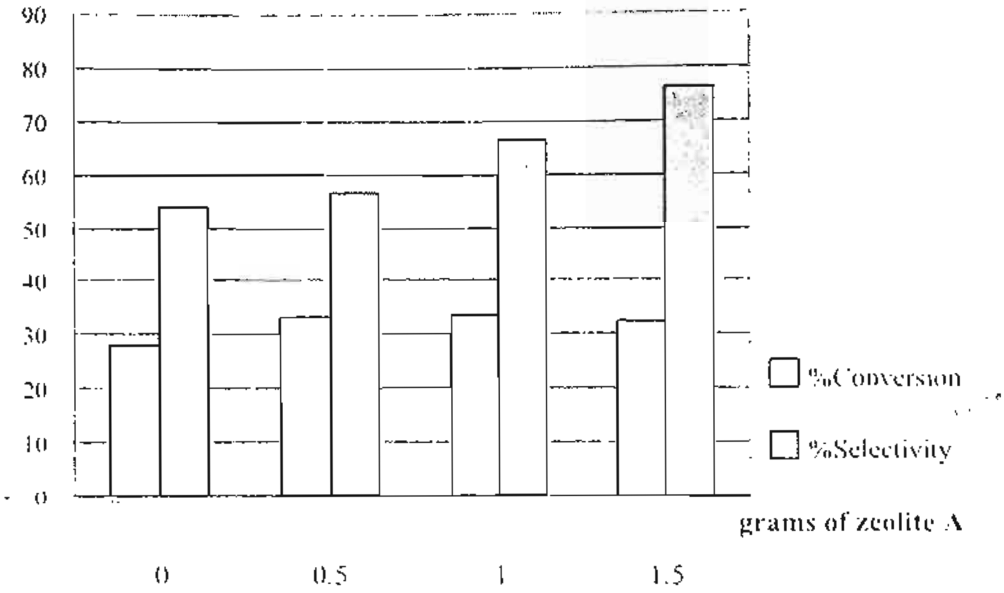
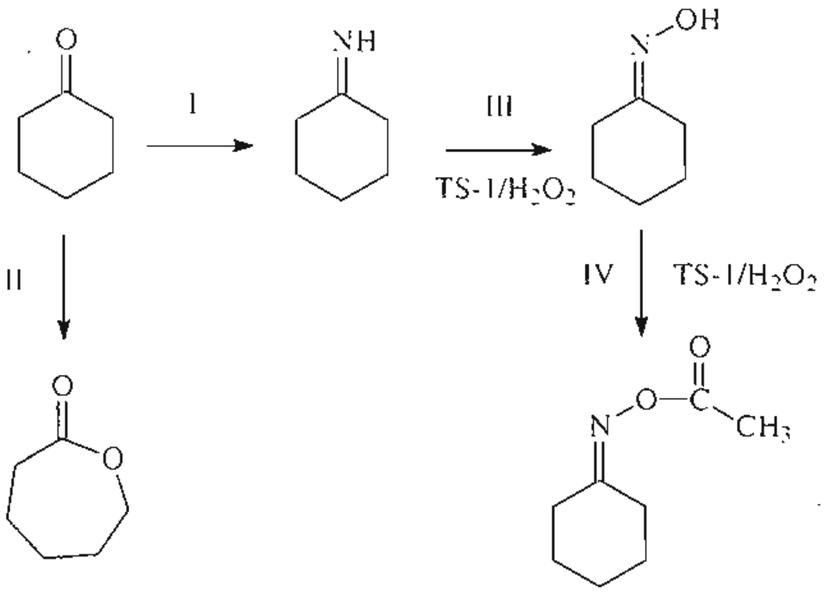


Figure 3.8 The conversion and selectivity for ammoximation reaction with addition of zeolite A. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, TS-1 0.04 gram, Reaction Time 4 hours, Added 0.5, 1.0 and 1.5 g of zeolite A*

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

As more cyclohexanone oxime was generated when zeolite A was added, a higher yield of acetyl cyclohexanone oxime could be expected. Surprisingly, the yield of acetyl cyclohexanone oxime (by-product) was also decreased when added zeolite A. It can be explained that the formation of acetyl cyclohexanone oxime was inhibited by competitive formation of cyclohexanone oxime. This is because when zeolite A was added, a higher amount of cyclohexanone imine was promoted. The rate of cyclohexanone imine oxidation to cyclohexanone oxime was then increased when the higher concentration of cyclohexanone imine was tained. The reaction of active sites with cyclohexanone imine is favored over that with cyclohexanone oxime because the interaction between the hydrophobic titanium framework (suggested in section 3.3.1) with cyclohexanone imine would be stronger than the interaction with cyclohexanone oxime. The oxidative coupling of cyclohexanone oxime with acetic acid is then limited. Therefore, the formation of acetyl cyclohexanone oxime is low. The reaction pathway was shown as follows:



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

3.3.4 Effect of Pore Size

Influence of pore size is studied by the reaction using large pore zeolite, Ti-Beta, as catalyst, compared to that using TS-1. The conversion from the reaction using zeolite Ti-Beta and TS-1 as catalysts in acetic acid are shown in Figure 3.9.

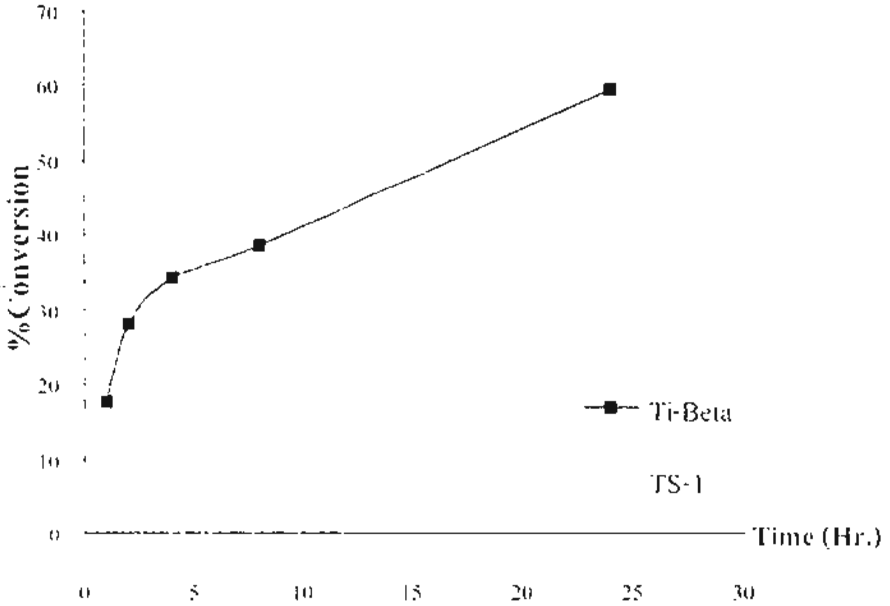
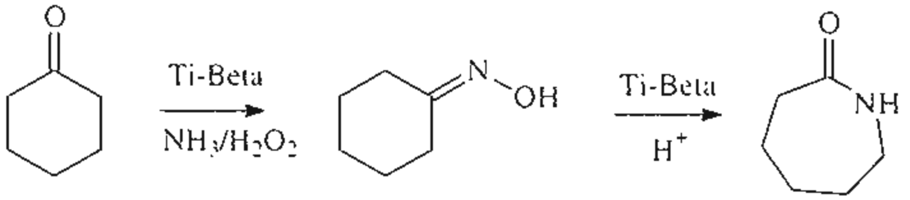


Figure 3.9 The conversion of cyclohexanone, reaction in acetic acid. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time1, 2, 4, 8 and 24 hours, Ti-Beta and TS-1 0.04 grams as catalyst.*

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

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



The subsequent formation of caprolactam promote the formation of cyclohexanone oxime leading to the high conversion of cyclohexanone. Moreover, at the high residential time, the yield of caprolactam was particularly increased resulting in the low concentration of cyclohexanone oxime in the system. This is because, as the concentration of cyclohexanone oxime was increased with time, the rate of caprolactam formation was also increased. However, the formation of cyclohexanone oxime, at high residential time, was limited by the lack of oxidizing agent. So, only the rearrangement of cyclohexanone oxime takes place at high residential time, leading to the reduction of cyclohexanone oxime. Consequently, the selectivity of cyclohexanone oxime was reduced as shown in Figure 3.10.

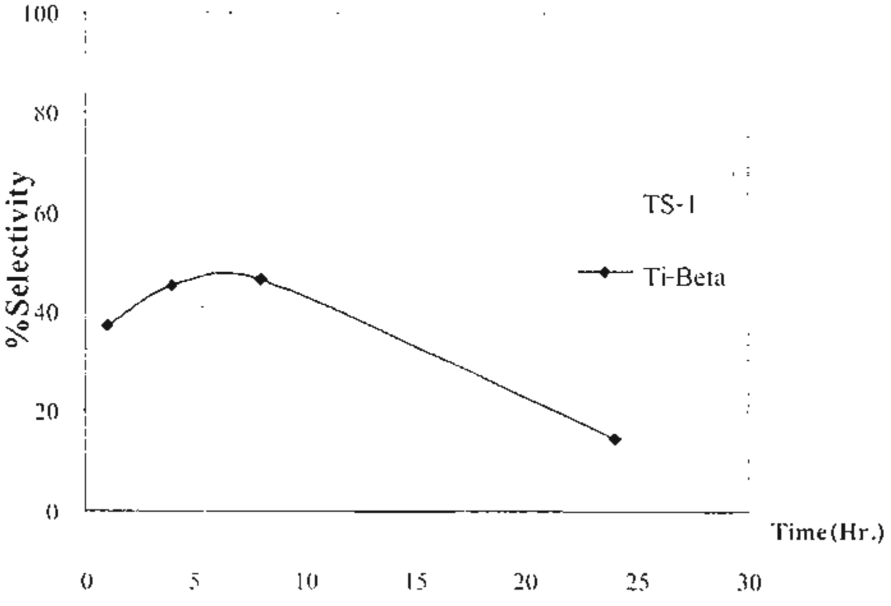


Figure 3.10 The selectivity of cyclohexanone oxime, reaction in acetic acid. *Reaction condition: Temperature 60 °C. Cyclohexanone 0.3796 grams, ammonia solution (28%w/w) 0.7253 grams and hydrogen peroxide solution (30%w/w) 0.5261 grams, Acetic*

Acid 2.4 ml, Reaction Time1, 2, 4, 8 and 24 hours, Ti-Beta and TS-1 0.04 grams as catalyst.

This is not the case for the reaction using TS-1 as catalyst, because TS-1 has no acid site and TS-1 has a medium pore (5.5 A°) which is smaller than the molecular diameter of caprolactam. Therefore, the caprolactam cannot be generated in the pore of TS-1 leading to the high selectivity of cyclohexanone oxime throughout the residential time.

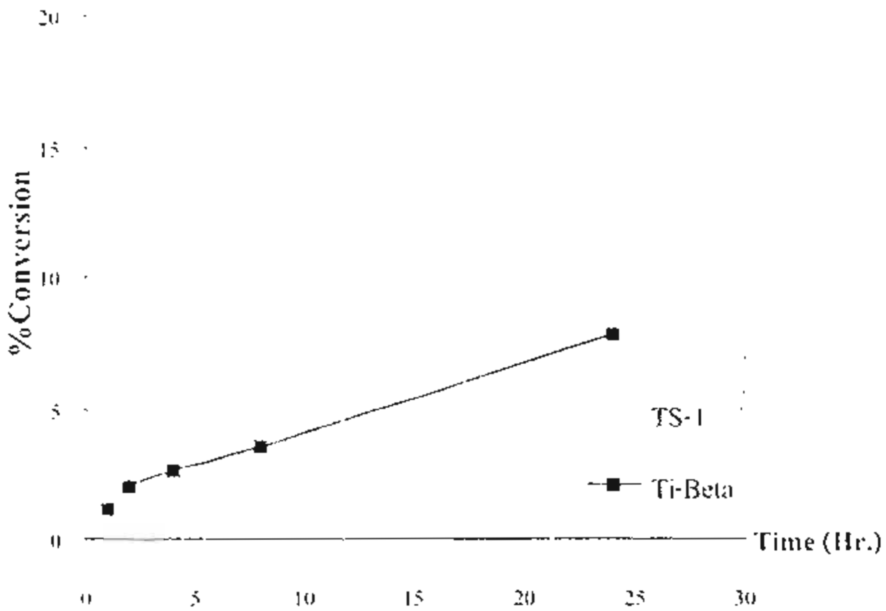


Figure 3.11 The conversion of cyclohexanone, reaction in water. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Water 2.4 ml, Reaction Time1, 2, 4, 8 and 24 hours, Ti-Beta and TS-1 0.04 grams as catalyst.*

The affect of pore size is also investigated in the reaction using water as solvent. The result is shown in Figure 3.11. It is shown that products from the reaction using zeolite Ti-Beta, as catalyst in water, is lower than that using TS-1 as catalyst which is resulted from the lower titanium content in zeolite Ti-Beta, as compared to TS-1. Additionally, the formation of caprolactam (via rearrangement) which promoted the formation of cyclohexanone oxime was not observed in water. This is because in the reaction using water as solvent, water would readily reduce the acidity of the zeolite by strong adsorption on the trace acid sites. Conclusively, the effect of pore size cannot be virtually evaluated in the reaction using water as solvent, as it appears that the effect of titanium content play an important role in this system.

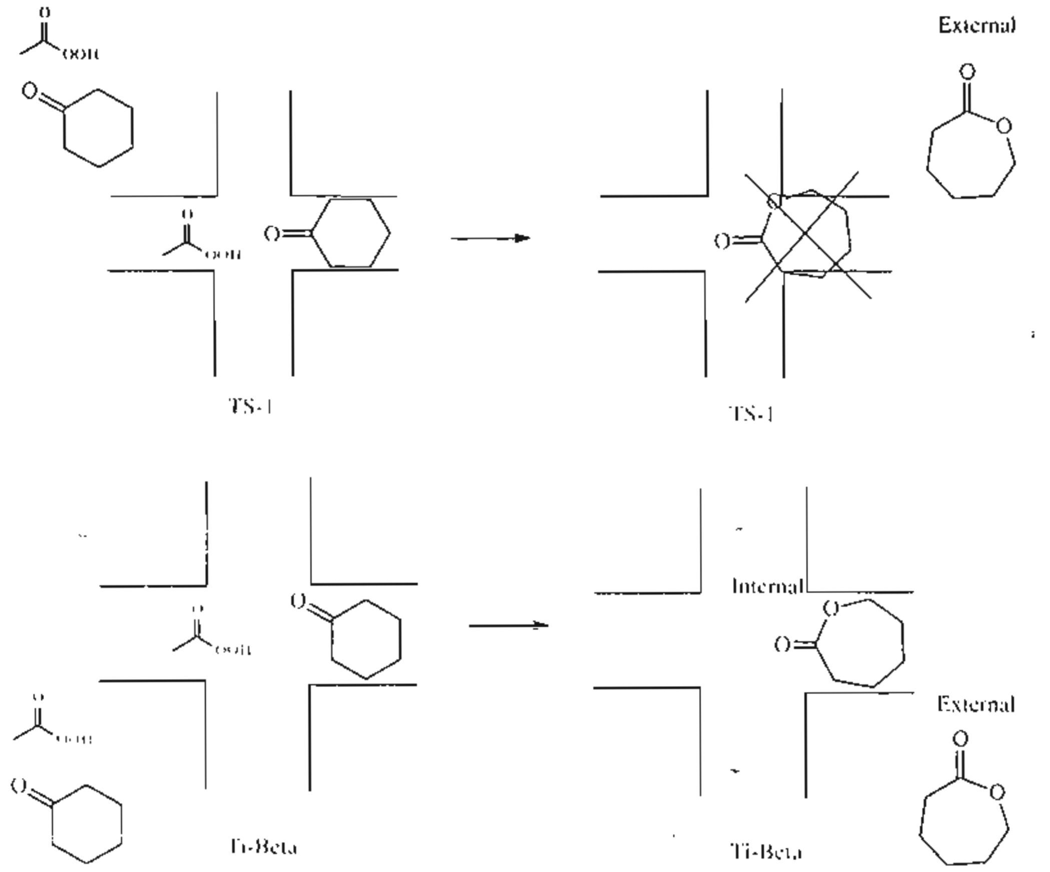
The effect of pore size can also be seen from the increased formation of caprolactone in the reaction using zeolite Ti-Beta as catalyst, as shown in Table 3.3.

Table 3.3 The yield of caprolactone in ammoximation reaction using TS-1 and zeolite Ti-Beta as catalyst

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

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

From the above discussion (section 3.3.1). It was concluded that caprolactone was generated homogeneously in liquid phase without aid of TS-1. This is because of the fact that TS-1 possesses the medium pore size (5.5 A°). caprolactone with molecular size larger than its pore size cannot be generated internally. Therefore caprolactone was produced only external pore of zeolite. However, the result from the reaction using zeolite Ti-Beta (Table 3.3) shows that the large pore zeolite can promote higher yield of caprolactone with high selectivity. This is suggested from the fact that zeolite Ti-Beta possesses a large pore size (7.6 A°). Caprolactone can be both generated on the external surface and in the pore of the zeolite as illustrated below;



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

Since caprolactone which is a by-product in the ammoximation, is a valuable industrial chemicals. The study on synthesis of caprolactone was further investigated. Reaction for synthesis of caprolactone was tested by reacting cyclohexanone with hydrogen peroxide in acetic acid using TS-1 and Ti-Beta as catalyst for 4 hours. The results are shown in table 3.4.

Table 3.4 The yield and conversion for the synthesis caprolactone using TS-1 and zeolite Ti-Beta as catalyst

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

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

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

3.3.5 Effect of the Titanium Species

As it can be seen from the above results [page 52] that titanium content of zeolites play a significant role in oxidation activity, the effect of titanium species was further investigated in Ti-Beta. After the titanation of dealuminated zeolite Beta, titanium is expected to replace the position of aluminium in the tetrahedral units. Nevertheless, titanium tetrachloride can diffuse into the pore of zeolite, and deposit to form a non-framework titanium, which results in an increased titanium content of the zeolite [Table Table 2.1 in part 1]. Therefore, titanium can be present in zeolite as two species, the framework titanium (tetrahedral form) and the non-framework titanium. The catalytic property of these two species was evaluated by the reaction using zeolite Ti-Beta before and after washing out of the non-framework as catalyst. Yield and conversion of reaction using zeolite Ti-Beta before and after washing with sulfuric acid show in Table 3.5.

Table 3.5 The yield and conversion for the reaction using Ti-Beta before and after washing by sulfuric acid

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

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

From the result, it was shown that the reaction using zeolite Ti-Beta before washing with sulfuric acid produces much lower yield of cyclohexanone oxime than the washed zeolite Ti-Beta. It can be suggested that the reduced activity of zeolite Ti-Beta before washing with sulfuric acid may well derive from the blockage of pore by the non-framework titanium. This is evident by a reduced surface area of zeolite Ti-Beta before washing with sulfuric acid (Table Table 2.2 in part I). Blockage by titanium in the pore of zeolite results in a difficulty for cyclohexanone to diffuse and react with the active sites in pore of zeolite, leading to the observed low activity of the zeolite Ti-Beta before washing with acid, as compared to the zeolite Ti-Beta after washing. Therefore, the zeolite with high titanium content would not be an effective catalyst, if the titanium species are present as the non-framework titanium. It seems clear that, the non-framework titanium has no activity to catalyze the reaction, but inhibit the diffusion of the reaction. The reaction was catalyzed only by the framework titanium (tetrahedral form).

3.3.6 Influence of Contact Time

In the large-scale production, the higher yield of cyclohexanone oxime is required. Contact time, in the other words, the amounts of catalyst concentration, would affect the activity, selectivity and operation cost. In order to verify the influence of contact time, the reactions using various amount of catalyst were tested in the reaction using acetic acid as solvent. The results are shown in Figure 3.12 and 3.13.

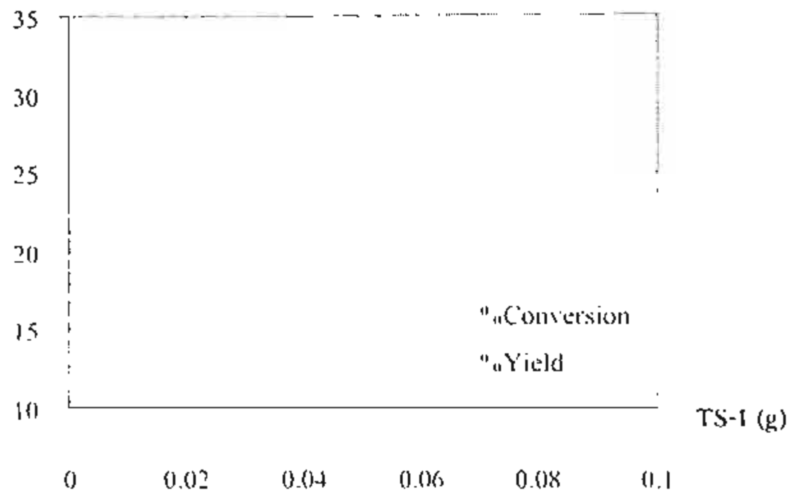


Figure 3.12 Effect of contact time on the conversion of cyclohexanone and yield of cyclohexanone oxime. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, TS-10.02, 0.04 and 0.08 grams as catalyst.*

The result from Figures 3.12 shows that the increased amount of TS-1 in the reaction leads to an increase in cyclohexanone oxime formation. This is because cyclohexanone have a higher possibility to react with active sites and higher yield of product can be obtained.

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

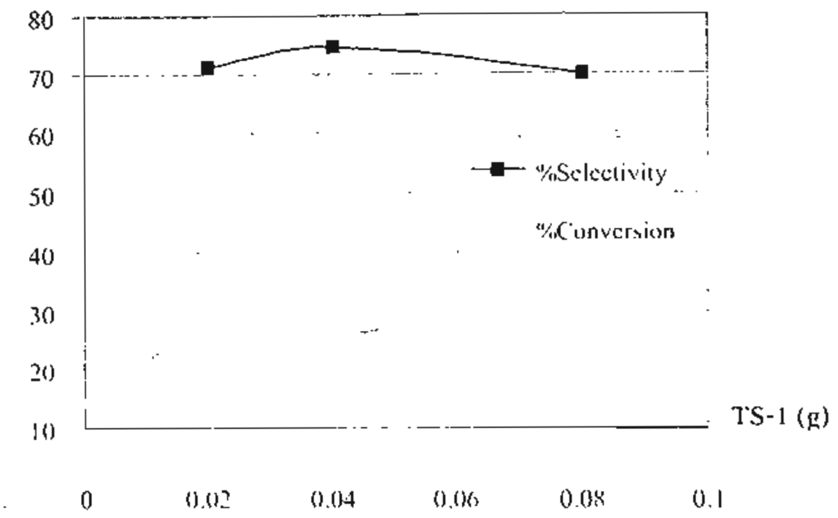
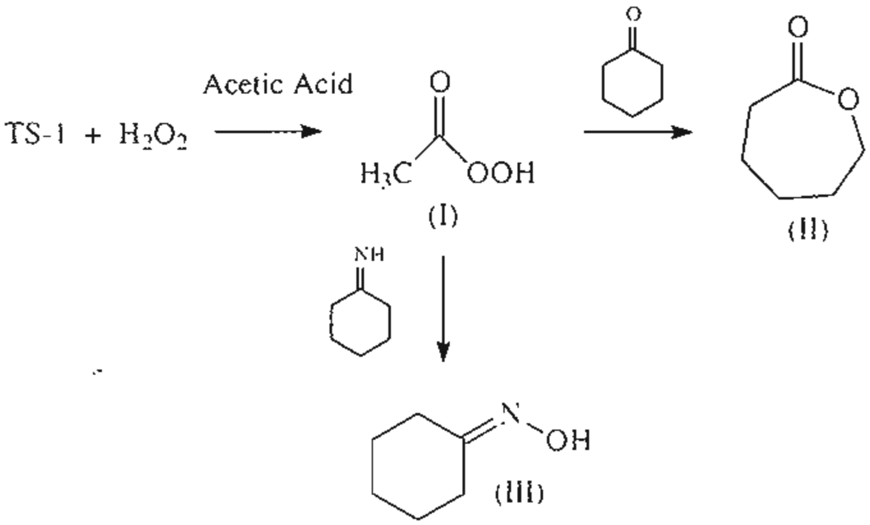


Figure 3.13 Effect of contact time on the conversion of cyclohexanone and selectivity of cyclohexanone oxime. *Reaction condition: Temperature 60 °C, Cyclohexanone 0.38 grams, ammonia solution (28%w/w) 0.73 grams and hydrogen peroxide solution (30%w/w) 0.53 grams, Acetic Acid 2.4 ml, Reaction Time 4 hours, TS-1 0.02, 0.04 and 0.08 grams as catalyst.*

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



3.3.7 Effect of Pressure

The reaction using water as solvent confronts with the loss of ammonia by vaporization. Reaction under pressure could be an alternative choice for this problem. The results of reaction under pressure are shown in Table 3.6.

Table 3.6 The yield of cyclohexanone oxime and conversion of cyclohexanone for the reaction at atmospheric pressure and under pressure

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

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

* *up scale to total mixture 200 ml*

From Table 3.6, it was shown that the reaction under pressure gives a slightly improved activity, as compared to the reaction at atmospheric pressure. This can be attributed to the fact that, under pressure, ammonia can be dissolved in the liquid phase slightly batter than the reaction at atmospheric pressure. However, the vapor pressure of ammonia is so high (26.35 bar) that the pressure used for testing the effect of pressure (10 bar) shows fairly improvement in the solubility of ammonia. Therefore, a small change in activity can be observed. Accordingly to the limitation of the experiment, the higher activity could be obtained if the higher pressure (30 bar) can be applied.

3.3.8 Effect of Ammonium Salts

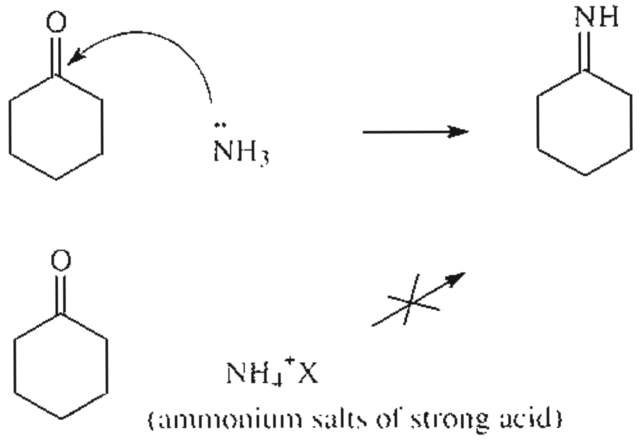
From the fact that ammonia in reaction using water as solvent can vaporize to the gas phase leading to a low concentration of ammonia in liquid phase, an alternative for solving this problem is the use of the ammonium salts as reagent. In the reaction using acetic acid as solvent, ammonia was trapped in the liquid phase as ammonium acetate. This indicates an ability of ammonium acetate to serve as reagent. Accordingly, other ammonium salts could be used as the reagent in the reactions using water and acetic acid as solvent. The results are shown in Table 3.7.

Table 3.7 The yield of cyclohexanone oxime from the reaction using ammonium salts as reactant

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

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

From the Table 3.7, it was revealed that ammonium salts of strong acid such as, ammonium oxalate, ammonium chloride and ammonium sulfate, cannot be used as reagent in both reaction using acetic acid and water as solvent. This is because the K_a of the conjugated acid of ammonium salts is high. Consequently the ammonia was strongly protonated by the conjugated acid, leading to deactivation of the lone pair electrons. The protonated ammonia is not efficient for both condensation with cyclohexanone to produce cyclohexanone imine and oxidation to hydroxylamine.



In the case of using ammonium acetate as a reagent, the reaction using ammonium acetate shows relatively high activity than ammonia solution in the system that using acetic acid as solvent. This can be derived from the low concentration of water in system when ammonium acetate was used. The condensation of cyclohexanone with ammonia can be facilitated in the reaction with low water content, as discussed in section 3.3.3. However, in the reaction using water as solvent, the use of ammonium acetate shows lower activity than ammonia solution. This can be resulted from the fact that ammonium acetate could be highly dissociated in the water than in acetic acid. Accordingly, ammonia was mostly present in a protonated form. The lone pair electrons of ammonia could be deactivated and the reaction with cyclohexanone to form cyclohexanone imine was inhibited. Consequently, no cyclohexanone oxime can be formed in the reaction using water as solvent, when ammonium acetate was employed.

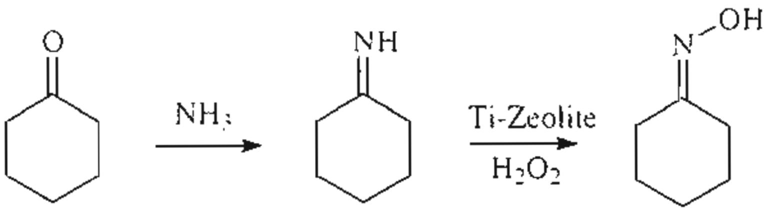
In the case of using ammonium citrate as reagent, the above explanation can be applied for an observed low activity in the reaction using water as solvent. However, in the reaction using acetic acid, ammonium citrate shows a lower activity, as compared with ammonium acetate. It can be explained that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

In the case of using ammonium carbonate as reagent, a relatively higher yield of cyclohexanone oxime can be obtained in both reaction using acetic acid and water as solvent.

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

3.3.9 Effect of Ammonium Acetate Concentration

From the mechanism,



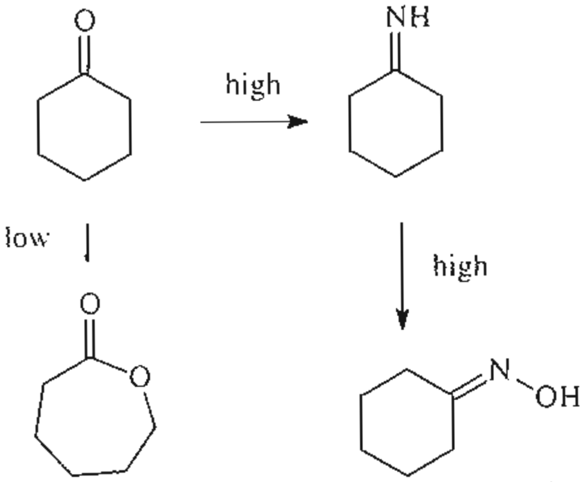
It was suggested earlier [section 3.3.2] that, cyclohexanone imine could be a key intermediate of the reaction. Accordingly the concentration of ammonium acetate would play an important role in the determination of reaction rate. Influence of excess ammonium acetate was studied in the reaction using acetic acid as solvent and the result is shown in Table 3.8.

Table 3.8 The yield, selectivity and conversion for the reaction using excess ammonium acetate over TS-1 and zeolite Ti-Beta

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

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

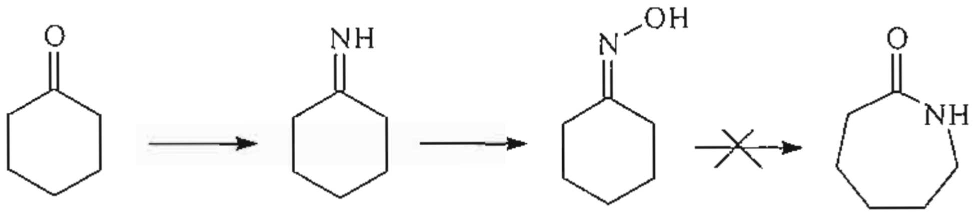
Shows that the reaction using excess ammonium acetate produces higher cyclohexanone oxime than the typical reaction. This is a further evidence confirming that the ammoximation proceeds via condensation of ammonia and cyclohexanone. Additionally, a higher selectivity of cyclohexanone oxime was obtained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



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

Additionally, the results from Table 3.8 show that in the reaction using zeolite Ti-Beta as catalyst, caprolactam was not produced as co-product when excess ammonium acetate was used. This can be attributed to the fact that high concentration of ammonium acetate would readily reduce trace of acid site in the framework (as discussed in section 3.4), which inhibits the rearrangement of cyclohexanone oxime to produce caprolactam.

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



3.3.9 Effect of Zeolite Deactivation

In industrial processes, catalyst used in the process could be deactivated. The catalyst regeneration contributes higher cost to the product. From the economic point of view, a catalyst with long catalytic lifetime or a catalyst that can be reused without regeneration was expected. In the ammoximation, the catalyst could be deactivated by various factors. They include loss of titanium active site from the framework and the blocking of zeolite pore. In this thesis the reuse of catalyst was investigated and the results are shown in Table 3.9.

Table 3.9 The yield of cyclohexanone oxime and caprolactam generated from the reaction using reused Ti-Zeolite as catalyst

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

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

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

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CHAPTER 4

AMMOXIMATION OF CYCLOHEXANONE USING TITANIUM-CONTAINING ZEOLITE CATALYST IN CONTINUOUS PROCESS

4.1 Objectives

To accomplish the cyclohexanone synthesis in continuous process. To obtain suitable conditions for continuous process such as solvent, feed rate, Amount of catalyst and reaction temperature for the optimum yield and selectivity of products. To obtain the long catalytic life time.

4.2 Catalytic testing in continuous process

Continuous stirred tank reactor (CSTR) and plug flow reactor (PFR) are choosen for studying ammoximation of cyclohexanone in continuous process [1]. In CSTR process reaction was carried out at 60 °C in a 50 ml continuous stirred tank reactor (CSTR) using 1.00 grams of TS-1. Typically, 4.25 grams of cyclohexanone was added to 9.125 grams of ammoniasolution (28%w/w) and 6.625 grams of hydrogen peroxide solution (30%w/w) in acetic acid 30 grams. The feed rate(molar/hr.) ratio for continuous process was as follows: substance : NH_3 : H_2O_2 = 1:1.5:1.2 control by peristatic pump(GILSON miniplus3).

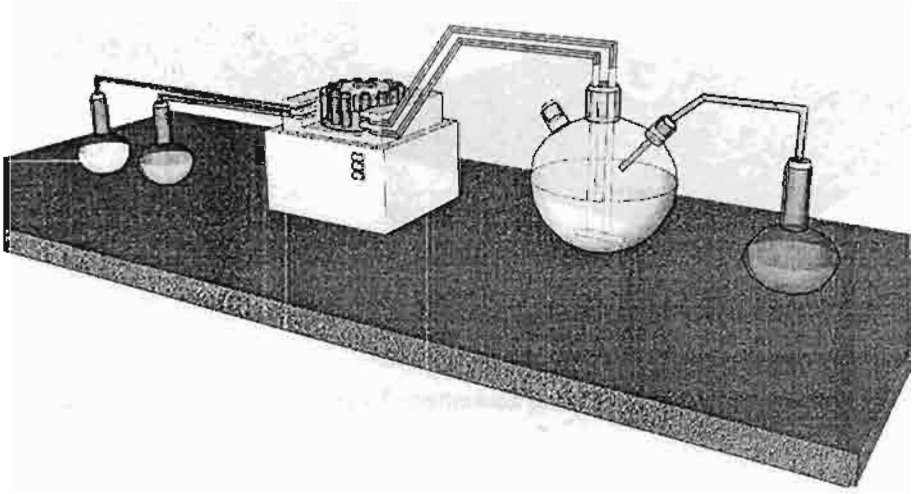


Figure 4.1 Schematic of catalytic testing of continuous process in stirred tank reactor

The schematic diagram of continuous process in a 50 ml continuous stirred tank reactor (CSTR) is shown in Figure 4.1. The contact time is estimate from batch reactor. It is shown in batch process that conversion was reached optimum after 4 hours residence time. Accordingly, retention volume, amount of catalyst and feeding rate were calculated to meet the condition for continuous process. H_2O_2 and a portion of acetic acid were primarily mixed in the first resrevior.

Whilst cyclohexanone, NH_3 and another portion of acetic acid were prepared in the second resrevior. Both reservior were kept at 5 ^{o}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]. The CSTR primarily contain all reactant and catalyst and kept at reaction temperature for 4 hours before feeding.

In case of plug flow process, a 20 ml continuous plug flow reactor (PFR) were tested using the same conditions as in the 50 ml continuous stirred tank reactor (CSTR).The schematic diagram of continuous process in a 20 ml continuous plug flow reactor (PFR) is shown in Figure 4.2.

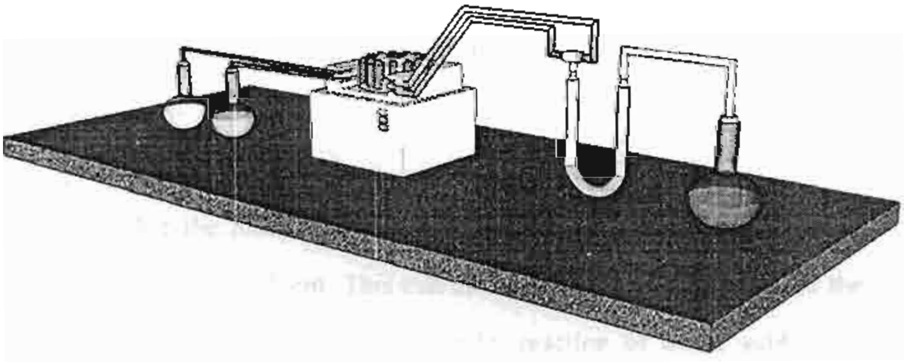


Figure 4.2 Schematic of catalytic testing of continuous process in plug flow reactor

The effluent of the CSTR and the CPFR were collected and analized every an hour. The solution was analyzed by gas chromatography using 3800 Gas Chrolmatography, Varian, with capillary DB-5.625 column (30m x 0.25μm). Liquid sample 0.2 μl was injected to the injection port (200 ^{o}C) using split ratio of 200. The seperation temperature was started at 100 ^{o}C for 4 minutes. Then, the temperature was raised to 200 ^{o}C with a heating rate of 20 ^{o}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.

The structure of products generated in the reaction using acetic acid as solvent was also confirmed by gas chromatography-mass spectrometer using the same column and conditions.

4.3 Result and discussion

4.3.1 Effect of Solvent

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

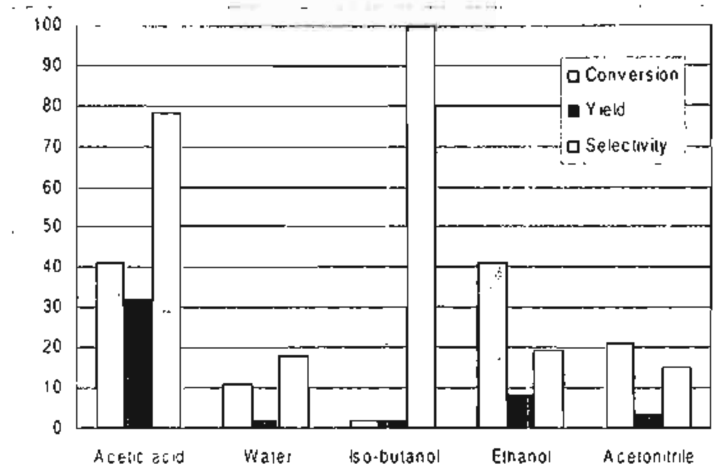


Figure 4.3 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, W/F; 41.26* $g_{catalyst}\ h\ mol^{-1}_{reactant}$ *;reactionrtime 6 hours in batch process*

It was shown that the reaction using acetic acid as solvent produce higher yield of cyclohexanone oxime than other solvent. This can be attribuled 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 first year study, peracetic acid seem as better oxidizing agent leading to higher activity as choosen earlier [2]. In case of hydrophilc 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 site. Sorption of 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 routed using iso-butanol as solvent. This is because iso-butanol is a free radical scavenger and inhibitor for free radical reaction. Therefore, the reaction using iso-butanol as solvent produce higher selectivity of cyclohexanone oxime than other solvent. Accordingly, acetic acid is choosen for ammoximation of cyclohexanone oxime in continuous process.

4.3.2 Effect of Titanium species

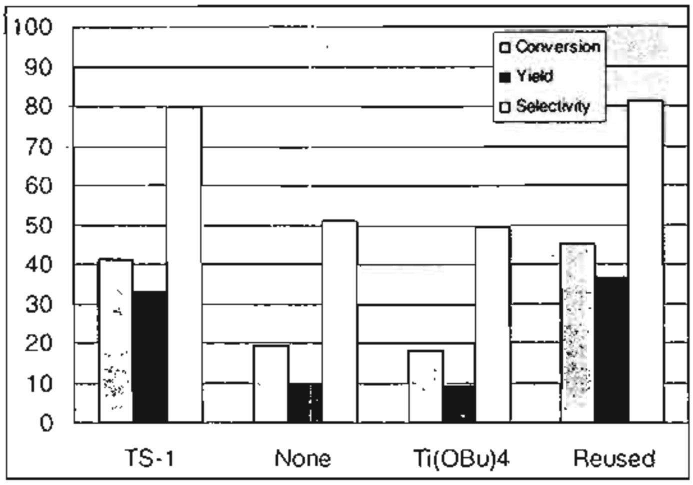
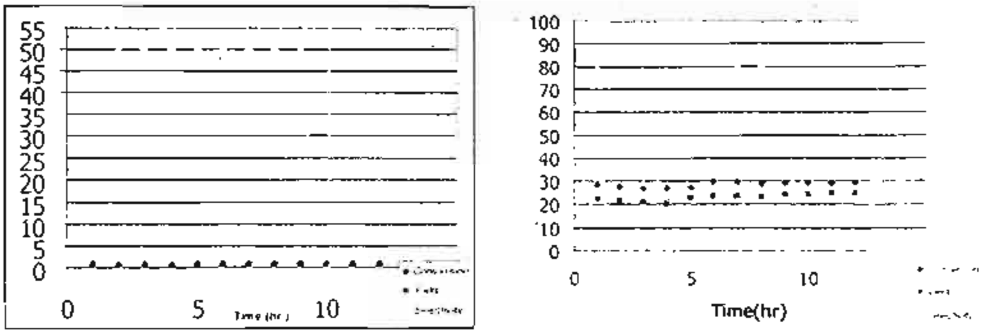


Figure 4.4 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, W/F; 41.26* $g_{catalyst}$ *h* $mol^{1}_{reactant}$. *;reactionrtime 6 hours in batch process*

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 [3] 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 with out 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 mainly derived from neither the homogeneous reaction nor the leached titanium species, if applicable.

4.3.3 Influence of Reactor types

The conversion, yield and selectivity from the reaction in (PFR) and (CSTR) are shown in Figure 4.5

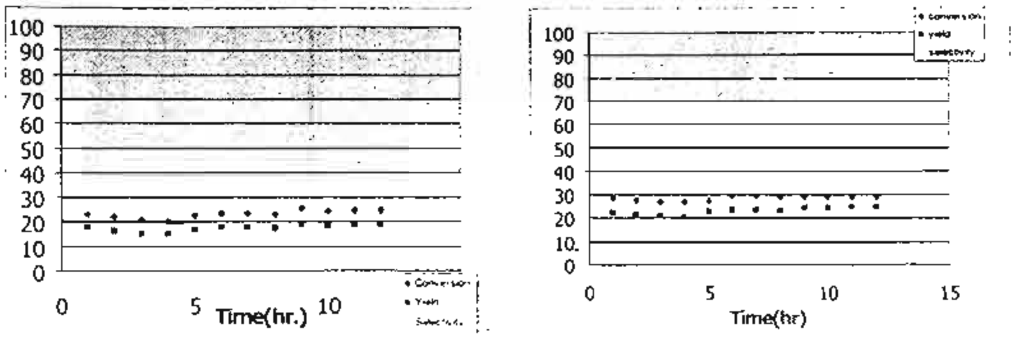


(A) (B)

Figure 4.5 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}_{ketone} , time of process : 12 hours . (A) = plug flow reactor and (B) = stirred tank reactor*

From Figure 4.5 it is shown that lower yield of cyclohexanone oxime is produced in continuous plug flow reactor (A) as compare to that from continuous stirred tank reactor (B). This is because the ammoximation of cyclohexanone using acetic acid as solvent is a tri-phase system[4]. As the heterogeneous mixture flow through catalyst bed. The sites contact with hydrophlic phase (H_2O – H_2O_2) can not be easily. Accessed by hydrophilic phase (cyclohexanone) and vise versa. Accordingly, the ammoximation of cyclohexanone is hardly promoted in continuous plug flow reactor. On the other hand, well-mixing can be achieved in continuous stirred tank reactor. higher opportunity of cyclohexanone to react with active site. Accordingly, continuous stirred tank reactor appear to be best suited for ammoximation of cyclohexanone using acetic acid as solvent.

4.3.4 Influence of Retention volume



(A) (B)

Figure 4.6 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 $mol^{-1}_{reactant}$, time of process : 12 hours . (A) = 100 ml and (B) = 50 ml*

The result from Figures 4.6 shows that the decreased reactor size for catalytic testing leads to a slighly increase in cyclohexanone oxime formation. This is because the reaction in smaller reactor is higher H_2O_2 consumption rate than H_2O_2 decomposition rate. Therefore, the small retention volume can reduced the decomposition rate of H_2O_2 and produce higher yield of product.

4.3.5 Effect of Amount of Catalyst

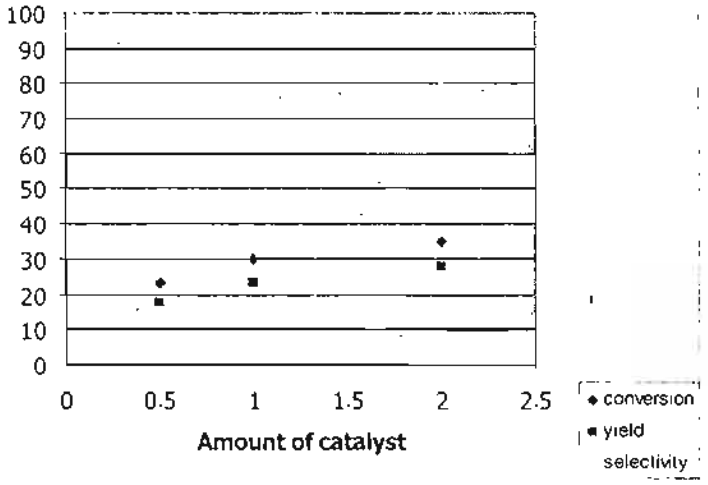
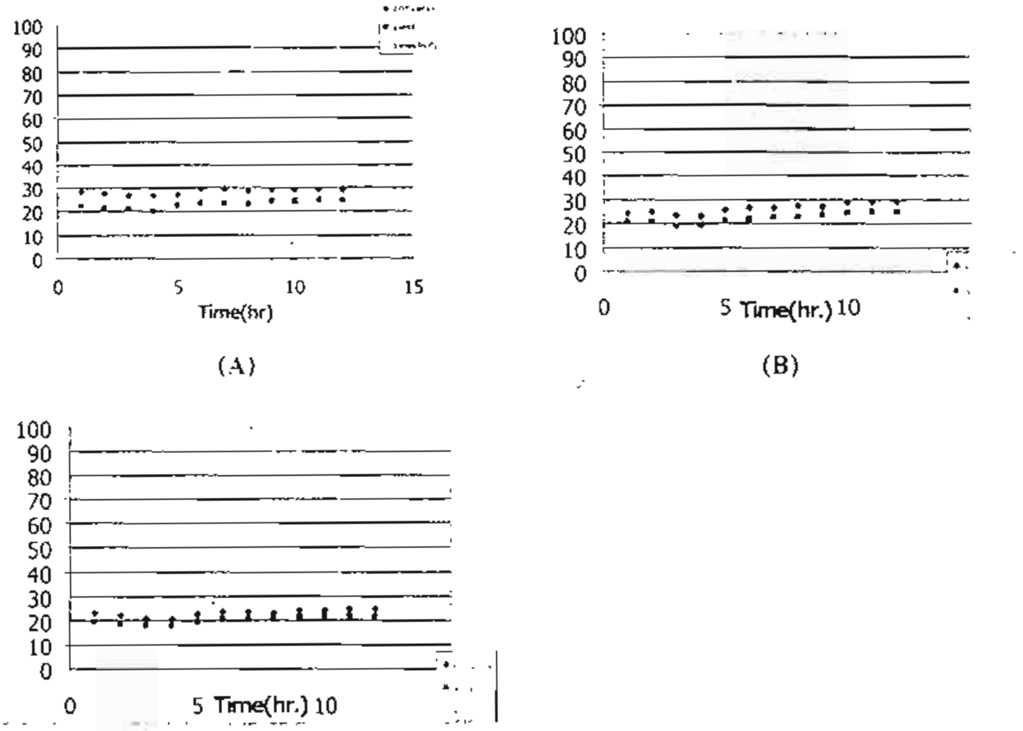


Figure 4.7 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature: 60 °C, time of process : 12 hours*

The result from Figure 4.7 shows that the increased amount of TS-1 in the reaction leads to an increase in cyclohexanone oxime formation. This is because cyclohexanone have a higher possibility to react with active sites and higher yield of product can be obtained. However the conversion seems to be limited by decomposition of H_2O_2. This is because high feeding rate is used in this system.

4.3.6 Effect of H_2O_2 concentration



(A)

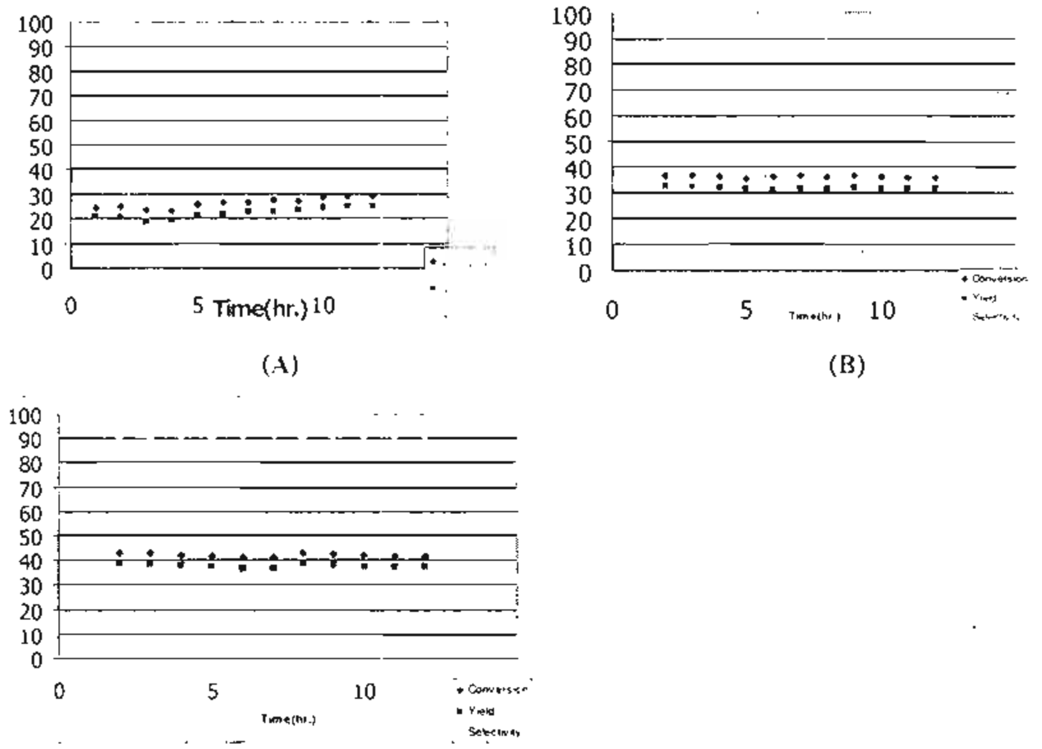
(B)

(C)

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* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *time of process : 12 hours . (A) = molar ratio of cyclohexanone/*H_2O_2 *: 1/1.2 , (B) = molar ratio of cyclohexanone/*H_2O_2 *: 1/0.6 and (C) = molar ratio of cyclohexanone/*H_2O_2 *: 1/0.4*

The result from Figure 4.8 shows that when the molar rartio of cyclohexanone and hydrogen peroxide is increased, the selectivity of cyclohexanone oxime is raised. This is because the increasing of molar rartio of cyclohexanone and hydrogen peroxide is reduce rate of honogeneous reaction. Accordingly, side products such as aldol condensation and acetyl cyclohexanone oxime[2] are decreased and the suitable molar ratio(1/0.6) of cyclohexanone and hydrogen peroxide is choosen for ammoximation of cyclohexanone oxime in continuous stirred tank reactor.

4.3.7 Influence of Contact time



(A) (B)

(C)

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* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *time of process : 12 hours , (A) = 41.26* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *(B) = 64.93* $g_{catalyst}\ h\ mol^{-1}_{reactant}$ *(C) = 148.75* $g_{catalyst}\ h\ mol^{-1}_{reactant}$

Although increase in molar ratio of cyclohexanone oxime and hydrogen peroxide can increased selectivity of cylohexanone oxime this reduces conversion of cyclohexanone. Accordingly, increase contact time would solve the problem. This could be done by reducing flow rate of the feeds. The result from Figure 4.9 shows that when feeding rate is decrease the conversion of cyclohexanone is raised. Additionally, increase molar rartio of cyclohexanone and hydrogen peroxide also slightly increase selectivity. This is because hydrogen peroxide is consumed in catalytic process, and hence homogeneous is diminished.

The suitable contact time(64.93 $g_{catalyst}$ h $mol^{-1}_{reactant}$) is choosen for ammoximation of cyclohexanone oxime in continuous stirred tank reactor.

4.3.8 Influence of Catalytic life time

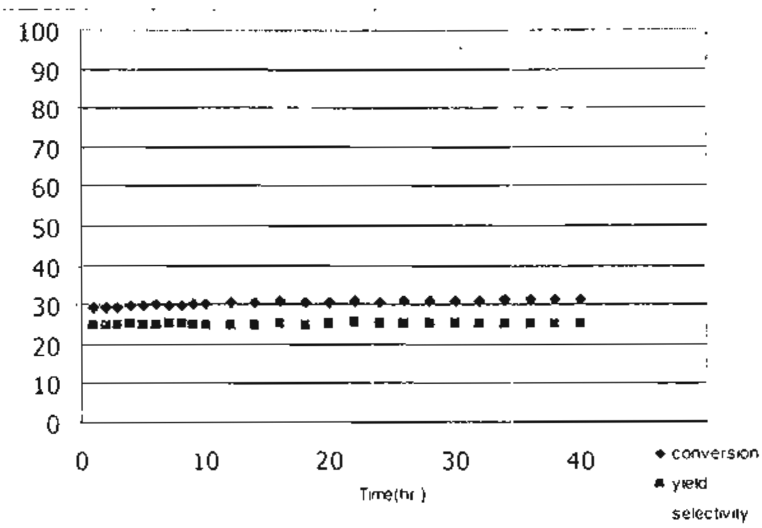


Figure 4.10 Conversion of cyclohexanone with yield and selectivity of cyclohexanone oxime over TS-1 catalyst. *Reaction condition : temperature; 60 °C, W/F; 41.26 $g_{catalyst}$ h $mol^{-1}_{reactant}$, time of process ;40 hours, molar ratio of cyclohexanone/H_2O_2: 1/0.6*

The result from Figure 4.10 shows the long life catalytic activity of TS-1 for ammoximation of cyclohexanone. Over 40 hours of testing, the catalyst can promote a steady yield of cyclohexanone oxime. This indicate that of titanium frame work site for catalytic activity, is retained as observed by FT-IR in Figure 4.11.

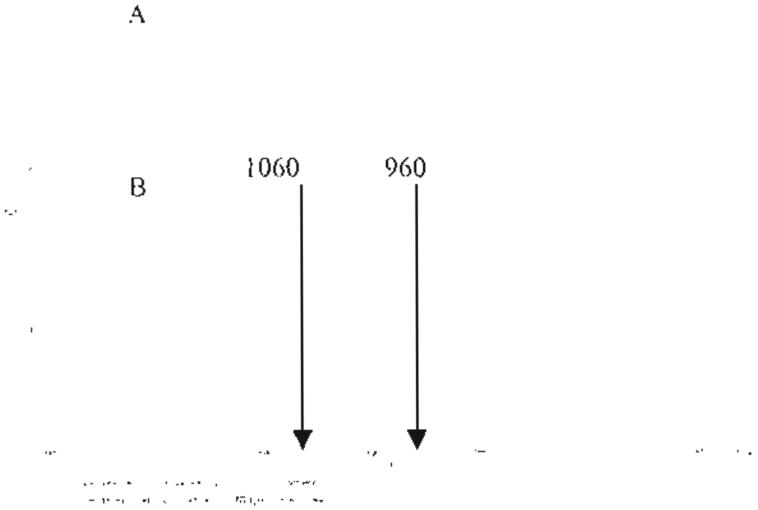


Figure 4.11 Fourier Tranformed IR spectra of TS-1 before and after using

It can be seem that after 40 hours testing, TS-1 catalyst exhibit characteristic adsorption of Ti-O-Si at 960 cm^{-1}[5,6,7].

4.3.9 Effect of Titanium framework leaching

In consistantwith the observed long life activity, it can be seem that small amount of Ti was leaching from the catalyst. The silicon and titanium content of zeolites were demtermined by X-ray Fluorescence (XRF). The result are shown in table 4.1

Table 4.1 The determination of silicon and titanium of TS-1 before and after used for 12 hours testing.

Calcining temperature	Silicon/Titanium
Fresh	30.10
550 °C	33.68
575 °C	32.26
600 °C	30.69

It was shown that fresh TS-1 has silicon /titanium ratio of 30.10. Calcining at 550 °C of TS-1, the silicon /titanium ratio increase to 33.68 after using. This suggest lost of titanium active site form titanium framework. When calcining temperature raise to 575 °C and 600 °C the silicon /titanium ratio are decreased to 32.26 and 30.69 respectively. This indicate that leaching of titanium active site is reduce when the temperature for calcination is raise. In other words, 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.

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Suggestion for Future Studies

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

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

3. Various reactor types for oxidation using titanium containing zeolties such as capillary reactor and chamber of slide reactor should be studied.

4. The interest sulfoxidation using TS-1 as catalyst in oils will be studied.

Output

1. Publication
    1.1 Tawan Sooknoi and Veerachai Chitranuwatkul "Ammoximation of cyclohexanone in acetic acid using titanium silicalite-1." catalyst:Activity and reaction pathway. Journal of Molecular Catalysis A, Chem. 236, 2005. pp. 220-22
2. Manuscript
    2.1 Tawan Sooknoi and Pirulh Seehabua "Continuous liquid phase ammoximation of cyclohexanone using titanium containing zeolites catalyst." Submitted to Applied catalysis A General.
3. M.SC. graduates
    3.1 Miss. Umaporn Yangjan Thesis title : Beckmann rearrangement of cyclohexanone oxime.
    3.2 Mr. Veerachai Chitranuwatkul Thesis title : Amoximation of cyclohexanone by Ti-containing zeolites catalyst.
    3.3 Mr. Pirulh Seehabua Thesis title : Ammoximation of cyclohexanone using Ti-containing zeolites catalyst in cotinuous Process.

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Ammoximation of cyclohexanone in acetic acid using titanium silicalite-1 catalyst: Activity and reaction pathway

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Abstract

The activity of titanium silicalite (TS-1) and the reaction pathway for the ammoximation of cyclohexanone to produce cyclohexanone oxime were studied using acetic acid as a solvent at 60 °C. The effect of solvent, sources of nitrogen, water content and the active site stability were also evaluated. It was found that, in the reaction using acetic acid as a solvent, the ammoximation of cyclohexanone proceeded mainly via the oxidation of imine, which was primarily formed in situ by the condensation of ketone with ammonia. In addition, the ammonium salts of weak acids, such as acetate, citrate and carbonate, can be used as nitrogen sources for the ammoximation in acetic acid. Water was shown to inhibit the formation of imine, and also prevent the side reactions. Moreover, TS-1 possessed an excellent stability, and can be reused without significant loss of activity.

Keywords: Ammoximation; Acetic acid; TS-1; Reaction pathway

1. Introduction

Titanium-containing zeolites are found to be efficient catalysts for the selective oxidation of a large number of organic substrates, such as alkanes, alkenes, alcohols, aromatics and phenol [1–5]. The liquid-phase ammoximation of ketone over titanium zeolites to synthesise oxime is another important process attracting industrial interests. As cyclohexanone oxime is the key intermediate for the manufacture of caprolactam through Beckmann rearrangement, the ammoximation of cyclohexanone using NH_3 and H_2O_2 is widely investigated [6–14]. Compared with the current commercial processes, liquid-phase ammoximation of cyclohexanone over titanium-containing zeolites can be carried out in one step, without use of environmentally undesirable chemicals, and only small amounts of by-products formed by homogeneous reactions are obtained [11]. This is because the oxime can only be produced by the reaction of substrate(s) with titanium active sites, which is previously generated by an interaction of the framework titanium with H_2O_2 [9,13]. A clear clarification of the reaction pathway for this reaction is not only scientifically valuable, but also industrially important.

Since early 1990s, a debate on the reaction pathway for the ammoximation of ketone has widely become interesting. In order to explain the formation of peroxydicyclohexylimine, Thangaraj et al. [6] have proposed a mechanism that the ammoximation proceeds through an unstable intermediate, imine. This mechanism is similar to that reported for the gas-phase ammoximation of cyclohexanone in the presence of NH_3 and O_2 [15], and has been supported by IR spectroscopy which proves the formation of adsorbed imine species on the surface of TS-1 [16]. The imine intermediate is then oxidised by the titanium active sites to an oxime. Despite the restricted diffusion of cyclohexanone and its oxime in the medium pore zeolites, an excellent catalytic performance was observed by several groups using TS-1 [6–8]. This is later drawn into recent conclusion that the reaction proceeds via the oxidation of ammonia to hydroxylamine, which subsequently reacts with the ketone to form a corresponding oxime [12–14].

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In this work, acetic acid that was recently reported to improve the catalytic activity for cyclohexane oxidation [17], was used as a solvent in the ammoximation of cyclohexanone. Comparing with the reaction using water, an enhanced catalytic activity was also observed in the reaction using acetic acid as a solvent. The results from this study also suggest that, in the presence of acetic acid, the reaction pathway was different from the well-accepted pathway that observed in the reaction using water and other nucleophilic solvents. The difference in the reaction mechanism accordingly effects the product selectivity, and the causes of such observation were discussed.

2. Experimental procedure

Na-free TS-1 were synthesised using a procedure modified from that report in literature [18]. Tetrabutyl orthotitanate (2.36 g) was mixed with deionised water at 5 °C, followed by 30% hydrogen peroxide solution (4.29 g) under stirring for 30 min. Then, 25% ammonia solution (8.34 g at 5 °C) was added and stirred. The solution was left overnight at room temperature. The solution was then heated at 80–90 °C for 30 min. Ammonia solution was added until the last solution has just as much weight as before heating. After that this solution was added into the mixture of deionised water (9.36 g), tetrapropylammonium bromine (TPABr, 3.08 g) and Ludox (10.81 g) under vigorous stirring. The mixture was stirred for a day and the final 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 crystallised at 185 °C. After 5 days, the synthetic zeolite was filtered, washed and calcined at 550 °C with a heating rate of 2 °C/min. Calcination was carried out in dry air for 5 h and the sample was left to cool in the furnace under stream of nitrogen. After cooling, the calcined sample was repeatedly washed by 5 M of sulphuric acid until non-framework titanium species cannot be detected by a colour change upon dropping hydrogen peroxide. Finally, the sample was calcined again in air at 550 °C for 4 h. The TS-1 catalyst was then characterised using XRD, XRF, SEM and FTIR. Surface area of the TS-1 catalyst was determined by nitrogen adsorption technique.

Catalytic studies of cyclohexanone ammoximation were carried out in a micro batch reactor (10 ml) using 0.04 g of TS-1. Typically, cyclohexanone (0.38 g) was added to 28% (w/w) ammonia solution (0.73 g) and solvent (2.4 ml). The mixture was then heated to the reaction temperature under vigorous stirring. Finally, 30% (w/w) hydrogen peroxide solution (0.53 g) was added into the mixture. The molar ratio of the feed used in the reaction was as follows: ketone:NH_3:H_2O_2 = 1:1.5:1.2. After a period of time, the reaction was halted by removing heat and quenching in an ice bath. 2-Propanol (4 ml) was then added to homogenise the reaction mixture. The solution was filtered and analysed by GC-FID with DB-FFAP capillary column (0.25 mm × 30 m). The separation temperature was started from 110 to 170 °C with a heating rate of 20 °C/min. Helium was used as a carrier gas at a linear velocity of 28 cm/s.

3. Results and discussion

3.1. *Catalyst characterisation*

X-ray diffraction and scanning electron microscope show that TS-1 sample is a well-defined, crystalline microporous material. The TS-1 sample with large and uniform crystallite size (5 μm × 20 μm) was chosen in this study. Although a reduced activity could be expected from the restricted diffusion of cyclohexanone in TS-1 channels, using catalyst with large primary crystals can ensure that the observed catalytic activity was mainly derived from that in the pore of TS-1. The catalyst also showed a characteristic adsorption of tetrahedrally coordinated Ti–O–Si at ~960 cm^{-1}. Elemental analysis by X-ray fluorescence showed that a constant Si/Ti ~26 was obtained after repeatedly washing with 5 M sulphuric acid. The specific surface area of 358 m^2/g was obtained by nitrogen adsorption at 77 K.

3.2. *Catalytic activity*

The ammoximation of cyclohexanone over TS-1 is shown in Fig. 1. It can be seen that the reaction using acetic acid as a solvent give a higher conversion than that using water. As previously discussed elsewhere [17], this can be attributed to the fact that peracetic acid was generated in the reaction using acetic acid as a solvent. The peracetic acid can further react with titanium tetrahedral producing peroxo-complex in a manner similar to that generated from hydrogen peroxide. The fact that the peracetic acid is more hydrophobic than the hydrogen peroxide, the peroxo-complex formed by peracetic acid (a softer ligand) would be relatively more stable. Therefore, higher amounts of active sites are available for the reaction. Additionally, the active site formed by peracetic acid would possess a better oxidising activity due to its higher electron density. These would lead to an improved activity for cyclohexanone conversion when acetic acid was used as a solvent.

3.3. *Product selectivity*

However, selectivity of cyclohexanone oxime in the reaction using acetic acid as a solvent was lower than that using water. Other products confirmed by GC–MS are 2-oxepanone and acetyl cyclohexanone oxime. The first could be formed by "Baeyer–Villiger Rearrangement" when cyclohexanone react directly with peracetic acid in the presence of acid [19]. As TS-1 possesses the medium pore size (~5.5 Å), it is unlikely that 2-oxepanone, a seven membered ring, is generated in the pore of TS-1. It may be postulated that 2-oxepanone was generated homogeneously in the liquid-phase without aid of TS-1. The second by-product, acetyl cyclohexanone

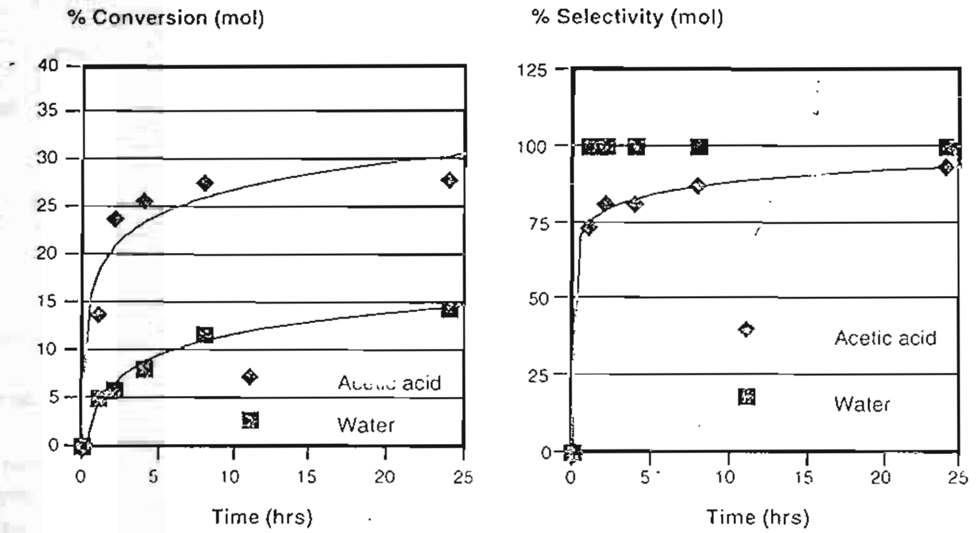

Fig. 1. Conversion of cyclohexanone and selectivity of cyclohexanone oxime from the reaction using acetic acid and water as solvent (reaction condition: at 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g, hydrogen peroxide solution (30%, w/w) 0.53 g, solvent 2.4 ml, TS-1 0.04 g).

oxime, could be possibly generated either from (i) a simple condensation of cyclohexanone oxime formed in the reaction with acetic acid or (ii) an oxidative coupling of cyclohexanone oxime with acetic acid in the presence of hydrogen peroxide and TS-1. In order to verify the above possibilities, the path (i) was tested by heating and stirring cyclohexanone oxime with acetic acid without hydrogen peroxide and TS-1 for 4 h. While the path (ii) was tested in the presence of hydrogen peroxide and TS-1. It was found that acetyl cyclohexanone oxime cannot be generated by path (i) test. However, the reaction tested for path (ii) produce notably amounts of acetyl cyclohexanone oxime. Consequently, it seems that acetyl cyclohexanone oxime was generated by coupling of cyclohexanone oxime with acetyl radical, which is presumably decomposed from the acetyl peroxo-titanium complex. The acetyl peroxo-titanium species were earlier suggested [17] to be formed by an interaction of tetrahedral titanium with peracetic acid and their decomposition would lead to the generation of active oxidising species [20] as proposed in Fig. 2. Typically, the decomposition of peroxo-titanium species (a) may well be driven by the reaction with hydrogen peroxide to give acetic acid (or water). However, thermal decomposition to give acetyl radical (or hydrogen radical) could also take place. Fig. 3 demonstrates the formation of 2-oxepanone and acetyl cyclohexanone oxime. In addition to the oxidised products, adducts from aldol condensation are also observed from the reaction using acetic acid as a solvent. This is probably due to the decreased pH of the media, which

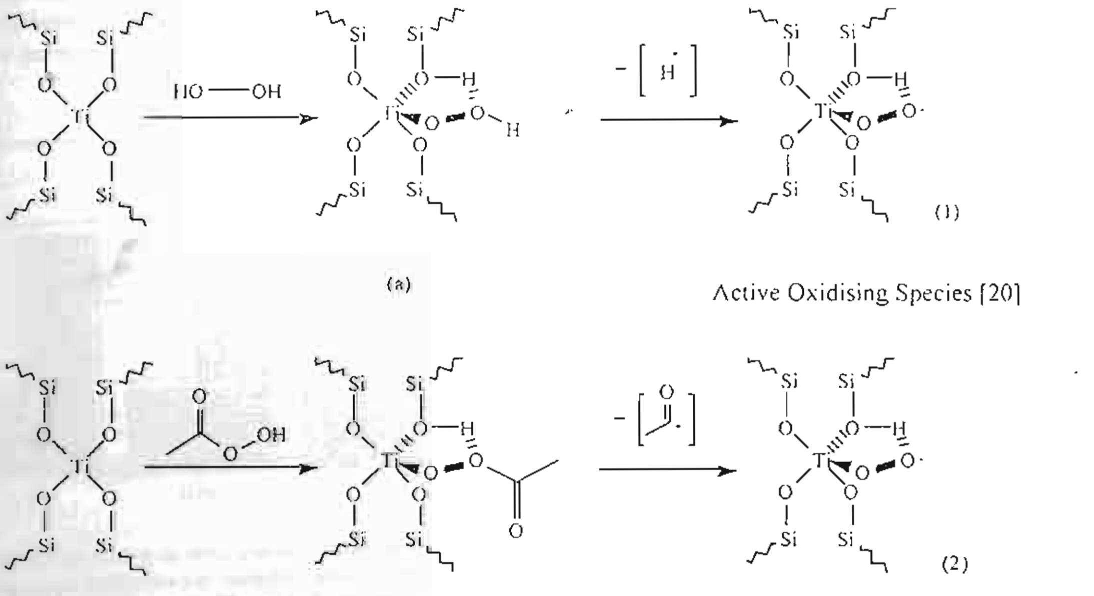

Fig. 2. A proposed reaction pathway for the formation of active oxidising species in the reaction using (1) water and (2) acetic acid as solvent.

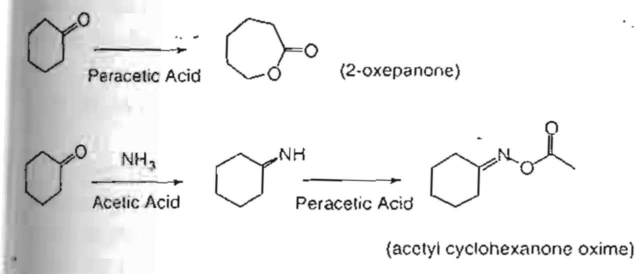

Fig. 3. Formation of 2-oxepanone and acetyl cyclohexanone oxime.

readily promotes acid-catalysed condensation of cyclohexanone.

Despite the conversion was increased by increasing amount of catalysts used, the selectivity of cyclohexanone oxime was not significantly changed (Fig. 4). This is because, in presence of acetic acid, 2-oxepanone (the major by-product) was generated by the homogeneous reaction of cyclohexanone with peracetic acid, as discussed earlier. When the amount of catalyst was increased, more peracetic acid can also be obtained. Therefore, yield of both cyclohexanone oxime and 2-oxepanone would be increased without a marked change in product selectivity.

In the reaction using water as a solvent, peracetic acid was not present and hydrogen peroxide alone is not effective for the Baeyer–Villiger reaction. Therefore, there is no 2-oxepanone and also acetyl cyclohexanone oxime produced. Thus, selectivity of cyclohexanone oxime in the reaction using water as a solvent is considerably high.

3.4. Active sites and its stability

Since peracetic acid, generated in situ from hydrogen peroxide and acetic acid, can be a strong oxidising agent, one may argue that the observed activity may well be derived solely from the homogeneous reaction. Moreover, the strong interaction of peracetic acid with the titanium active sites could result in the dissolution of titanium as peroxo-complex into acetic acid. The leached Ti species may also be responsible for some parts of the observed activity as suggested elsewhere [21]. To verify the above possibility, the ammoximation of cyclohexanone without TS-1 was tested, together with that using tetrabutyl orthotitanate as a catalyst.

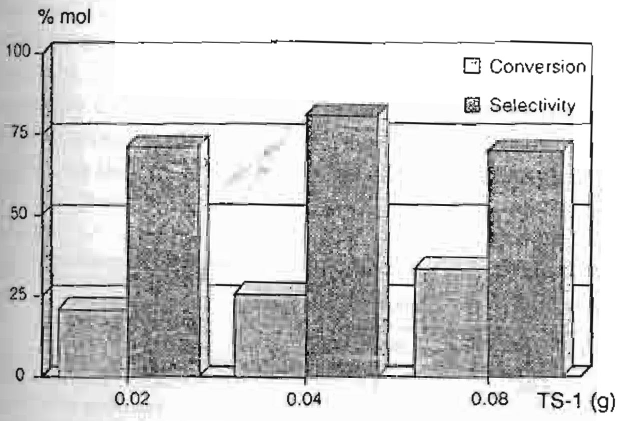

Fig. 4. Effect of catalyst loading on conversion of cyclohexanone and selectivity of cyclohexanone oxime (reaction condition: at 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, acetic acid 2.4 ml, reaction time 4 h, TS-1 0.02, 0.04 and 0.08 g as catalyst).

Table 1
Conversion of cyclohexanone and yield of products (mol%) from the reactions without catalyst, with tetrabutyl orthotitanate and with reused TS-1 as catalysts

Catalyst	TS-1	None	Ti(OBu)$_4$	Reused TS-1
Conversion of cyclohexane	47.8	31.7	31.1	55.3
Yield of cyclohexane oxime	37.8	17.8	22.2	46.1
Yield of 2-oxepanone	3.0	4.8	2.9	4.1
Aldol products	2.0	4.0	–	1.9
Yield of acetyl cyclohexane oxime	2.5	1.1	1.6	0.9
Yield of coupling products	2.5	3.9	3.5	2.0

Reaction condition: Temperature 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, acetic acid 2.4 ml, reaction time 6 h, titanium-containing zeolites 0.04 g as catalyst (or equivalent mol of titanium species).

From Table 1, it was found that part of the observed activity was also contributed from the homogeneous oxidation by peracetic acid. However, in addition to the oxidised products, adducts from aldol condensation were increasingly promoted. Thus, 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 [17], but also due to the presence of active oxidising species formed by the peracetic acid and the 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 mainly derived from neither the homogeneous reaction nor the leached titanium species, if applicable.

Although the tetrahedral titanium framework of TS-1 is relatively stable, the strong interaction of peracetic acid with the titanium framework could lead to the leaching of titanium active sites into the solution. This was indeed observed in the oxidation of cyclohexane using acetic acid as a solvent [17]. According to this study, the homogeneous titanium species has no significant effect on the ammoximation of cyclohexanone in acetic acid. Nevertheless, leaching of titanium active sites during the reaction is not preferable and has become one of the major drawbacks for industrial applications. Actually, such circumstance is not the case for the ammoximation of cyclohexanone. No notable amount of dissolved titanium was detected in the solution (by UV–vis adsorption) and when the catalyst was reused without thermal regeneration, the activity of TS-1 is even enhanced (Table 1). The cause of the slightly improved activity of the reused TS-1 cannot be evaluated at this stage. However, a better stability of TS-1 in acetic acid is probably derived from the presence of nitrogen sources, which would increase pH of the solution and, hence, suppress the dissolution of the framework titanium species.

3.5. Mechanistic study

Unless the reaction pathway proceed via oxidation of ammonia to produce primarily hydroxylamine, the enhanced activity in the reaction using acetic acid may well be resulted from the enhanced formation of cyclohexanone imine. The formation of imine was previously evidenced by an absorption band at ~1653 cm^{-1} when ammonia and cyclohexanone was introduced to Ti-mordenite at 60 °C [12]. As the amount of cyclohexanone imine is increased, the oxidation of cyclohexanone imine would also be accelerated, resulting in a higher yield of cyclohexanone oxime in the reaction using acetic acid, as compared to that using water.

From the mechanistic point of view, the condensation of cyclohexanone with ammonia in acetic acid would be favoured because cyclohexanone imine formation is facilitated at pH approximately 4–5 or in the presence of acid catalyst [22]. However, a recent report [14] demonstrated that in the reaction using water, hydroxylamine was primarily formed. These possibilities can be readily tested either by the reaction of ammonia with only cyclohexanone prior to the addition of TS-1 and hydrogen peroxide (test I), or the reaction of only ammonia with catalyst and hydrogen peroxide, followed by catalyst removal and cyclohexanone addition (test II). The test I can be employed to verify the hypothesis that ammoximation proceeds via condensation of cyclohexanone with ammonia. On the other hand, the hypothesis for hydroxylamine formation can be demonstrated by the test II.

From Table 2, it shows that cyclohexanone oxime can be only formed in test I when acetic acid is used as a solvent. Thus, the condensation of cyclohexanone with ammonia in homogeneous phase is facilitated in the presence of acetic acid (test I). It is also possible that the cyclohexanone imine could interact with a relatively hydrophobic active site, formed by complexation of peracetic acid and the framework titanium. Therefore, the oxidation of the imine to the oxime could be expected. In contrast, when acetic acid is used as a solvent, ammonia was protonated in test II and may not be readily oxidised to hydroxylamine. Conclusively, in the reaction using acetic acid as a solvent, only the pathway proceeded via the condensation of cyclohexanone with ammonia should be responsible for the formation of cyclohexanone oxime. Fig. 5 illustrates the reaction pathway, which is proposed from the results observed in this study.

Table 2
Yield of cyclohexanone oxime (mol%) from reaction pathway testing

Test	Solvent	
	Water	Acetic acid
Typical reaction	8.1	20.8
Test I (imine pathway)	7.4	14.9
Test II (hydroxylamine pathway)	4.7	0.27

Reaction condition: Temperature 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, Solvent 2.4 ml, TS-1 0.04 g, reaction time: 2 h/4 h (step 1/step 2).

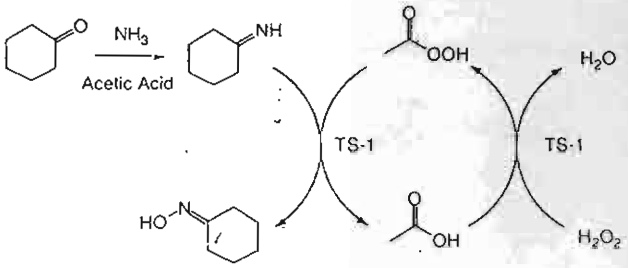

Fig. 5. Proposed reaction pathway for cyclohexanone ammoximation using acetic acid as a solvent.

In the reaction using water as a solvent, on the other hand, cyclohexanone oxime can be formed by both tests. Since ammonia was not readily protonated in the reaction using water as a solvent, it can directly react with the active sites to produce hydroxylamine. The observed smaller yield of cyclohexanone oxime in test II may be derived from (i) an incomplete formation of hydroxylamine when the catalyst was removed, and/or (ii) the oxidation of hydroxylamine to nitrite and nitrate species [14] before cyclohexanone was added.

3.6. Ammonium salts as reagents

The fact that the observed catalytic pathway is inconsistent with the pervious report when acetic acid is used as a solvent can be accounted for a poor activity of protonated ammonia towards the oxidation. However, such species are readily active for condensation with cyclohexanone. This can be further investigated using various types of ammonium salts as sources of nitrogen. It is reasonable to postulate that in the reaction using acetic acid as a solvent, ammonium acetate is formed. This salt must be able to react with cyclohexanone, which is indeed observed together with other weakly acid salts as shown in Table 3.

When weakly acid salts, such as ammonium acetate, citrate and carbonate, were used as reagent in the presence

Table 3
Yield of cyclohexanone oxime (mol%) from reaction using ammonium salts as reagent

Reagent	Solvent	
	Water	Acetic acid
Ammonia solution (NH_4OH)	8.1	20.8
Ammonium acetate (NH_4OAc)	0.68	21.5
Ammonium citrate ($(NH_4)_2HC_6H_5O_7$)	0.47	6.6
Ammonium carbonate ($(NH_4)_2CO_3$)	6.3	8.3
Ammonium oxalate ($(NH_4)_2C_2O_4$)	Trace	1.8
Ammonium chloride (NH_4Cl)	Trace	Trace
Ammonium sulphate ($(NH_4)_2SO_4$)	Trace	Trace

Reaction condition: Temperature 60 °C, cyclohexanone 0.38 g, hydrogen peroxide solution (30%, w/w) 0.53 g, solvent 2.4 ml, TS-1 0.04 g, reaction time 4 h.

of acetic acid, cyclohexanone oxime was indeed generated. Particularly, there is no significant difference between the reaction using ammonia solution and that using ammonium acetate as reagent. This confirms that ammonium salts is quite active for ammoximation. A relatively lower activity was observed when ammonium citrate was used as reagent. This is because ammonium citrate is a salt of hydroxy polyacid, therefore it can be somewhat dissociated in acetic acid. Consequently, reactivity for the reaction with cyclohexanone to generate cyclohexanone imine is relatively lower than the reaction using ammonium acetate. For ammonium carbonate, yield of cyclohexanone oxime in the reaction using acetic acid, was lower than that expected. This may be resulted from the fact that ammonium carbonate reacts vigorously with acetic acid producing carbon dioxide, ammonia and exhaust heat. Under this circumstance, a rapid vaporisation of carbon dioxide may well lead to the loss of ammonia. This could reduce the rate of condensation with cyclohexanone resulting in a lower production of cyclohexanone oxime as observed.

On the other hand, in the reaction using water as a solvent, the use of ammonium acetate and citrate show much lower activity than that of ammonia solution. This can be resulted from the fact that ammonium acetate and citrate could be highly dissociated in the water. Accordingly, ammonia is mostly present in a protonated form. The lone pair electrons of ammonia could be deactivated and either the reaction with cyclohexanone to form cyclohexanone imine or the direct oxidation to hydroxylamine were inhibited in the reaction using water as a solvent. Nevertheless, this is not the case for ammonium carbonate. As being a salt of weak carbonic acid, it can be readily decomposed to give ammonia at reaction temperature. Therefore, the activity of ammonium carbonate in water is somewhat similar to the ammonia solution.

The ammonium salts of strong acid such as, ammonium oxalate, ammonium chloride and ammonium sulphate, cannot be used as reagent in both reactions using acetic acid and water as solvent. This is because the K_a of the conjugated acid of ammonium salts is high. Consequently, the salt is highly dissociated, leading to the deactivation of the lone pair electrons of ammonia. Therefore, the strongly protonated ammonia is not efficient for both condensation with cyclohexanone to produce cyclohexanone imine and oxidation to give hydroxylamine.

3.7. Effect of water content

According to the above discussion, the condensation of cyclohexanone with ammonia becomes an essential step for the ammoximation. This step could be notably interfered by the pH of the solution and also by the presence of water. It is expected that less amount of water present in the reaction shall lead to a better activity. As hydrogen peroxide solution was used as an oxidising agent, the presence of water cannot be avoided. Nevertheless, the effect of water can be investigated by adding dried zeolite A (a water adsorbent) into the system.

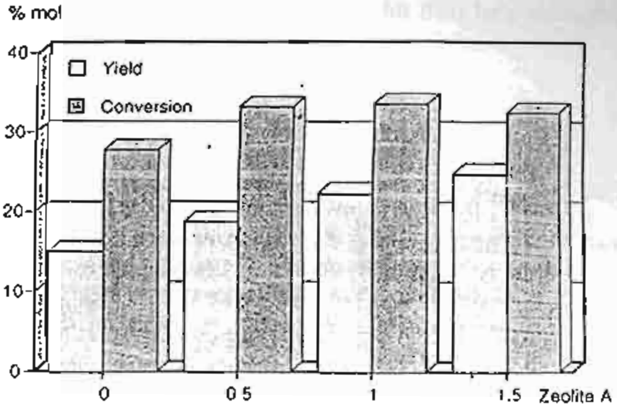

Fig. 6. Effect of water content on the yield of cyclohexanone oxime and conversion of cyclohexanone (reaction condition: at 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, acetic acid 2.4 ml, TS-1 0.04 g, reaction time 4 h, added 0.5, 1.0 and 1.5 g of zeolite)

From Fig. 6, it was clearly shown that the conversion of cyclohexanone and the yield of cyclohexanone oxime was increased with the amount of zeolite A added. The zeolite A, which is highly hydrophilic and possesses small pore size, can readily adsorb water. This would facilitate the condensation of ammonia with cyclohexanone to give the corresponding imine since water was removed from the system. As the formation of the imine is promoted, a higher yield of cyclohexanone oxime can be expected. In addition, the yield of 2-oxepanone and acetyl cyclohexanone oxime (by-products) were decreased when zeolite A was added. This is probably because cyclohexanone and peracetic acid are largely consumed by the ammoximation process. Hence, the direct reaction of peracetic acid with cyclohexanone or the coupling of cyclohexanone oxime with acetyl radical would be limited. Accordingly, a higher selectivity of cyclohexanone oxime was also obtained when zeolite A was added.

4. Conclusion

Ammoximation activity of cyclohexanone is enhanced in the reaction using acetic acid as a solvent. However, selectivity of the corresponding oxime is reduced due to formation of by-products, 2-oxepanone, acetyl cyclohexanone oxime and aldol adducts. Together with the strong oxidising species like peracetic acid, the tetrahedrally coordinated titaniums are active species and they are relatively stable. Leaching of active sites was not observed in this reaction, presumably due to the presence of ammonia in the system. However, further investigation using larger amounts of catalysts or testing in a continuous process should be made to really prove on this. Nevertheless, this study shows that soluble titanium species plays no role in ammoximation of cyclohexanone using acetic acid as a solvent.

The mechanistic study shows that there are two possible pathways for the ammoximation of cyclohexanone. In the reaction using water as a solvent, the oxidation of ammonia to produce hydroxylamine, followed by its condensation of cyclohexanone seems to be favoured. However, only the pathway proceeded via the condensation of cyclohexanone with ammonia is responsible for the formation of cyclohexanone oxime in the reaction using acetic acid as a solvent. This also leads to an improved catalytic activity because the formation of cyclohexanone imine, an oxime precursor, is enhanced in presence of acetic acid. In addition, peracetic acid, which is formed in situ, can be served as a better oxidising agent, as compared to the hydrogen peroxide alone. However, the reaction using acetic acid as a solvent shows a lower cyclohexanone oxime selectivity because peracetic acid can directly react with the reactant and the product to produce two other by-products, 2-oxepanone and acetyl cyclohexanone oxime, respectively. From the economic point of view, this could be a major obstacle to an industrial development even though high conversion is obtained.

In the reaction using acetic acid as a solvent, it is also evident that the source of nitrogen can be obtained from ammonium salts of the weak acid, such as acetate, citrate and carbonate. These species are active for the formation of imine. However, this is not the case for the reaction using water because the reaction pathway involves ammonia oxidation. The protonated ammonia is inactive for the oxidation to hydroxylamine and the reaction in water can be carried out only with ammonia in slightly basic solution. The presence of water in the reaction using acetic acid does not only inhibit the ammoximation activity, but also facilitate the formation of by-products. Hence, selectivity of cyclohexanone oxime is improved when water is removed from the system.

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