RSA4580042 ผศ.ดร.ตะวัน สุขน้อย

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รายงานการวิจัยฉบับสมบูรณ์

โครงการ

การศึกษาความสามารถในการเร่งปฏิกิริยาของซีโอไลต์ที่มีไททาเนียมเป็นองค์ประกอบ

Study on Catalytic Activity of Titanium Containing Zeolites

ผศ. ดร. ตะวัน สุขน้อย
ภาควิชาเคมี คณะวิทยาศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

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ชื่อผู้วิจัย ผศ.ดร. ตะวัน สุขน้อย
ภาควิชาเคมี คณะวิทยาศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

E-mail Address kstawan@kmitl.ac.th

ระยะเวลาดำเนินงาน 3 ปี

บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาการเร่งปฏิกิริยาของซีโอไลต์ที่มีไททาเนียมเป็นองค์ประกอบ โดยศึกษา ปฏิกิริยาการจัดเรียงตัวใหม่แบบเบคมานของไซโคลเฮกซาโนนออกซีม และปฏิกิริยาแอมมอกซิเมชันของไซโคลเฮกซาโนนเพื่อสังเคราะห์ไซโคลเฮกซาโนนออกซีมในกระบวนการแบบกะและแบบต่อเนื่อง

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

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

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Project Title Study on Catalytic Activity of Titanium Containing Zeolites

Investigator Assist. Prof. Dr. Tawan Sooknoi
Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang

E-mail Address kstawan@kmitl.ac.th

Project Period 3 year

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.

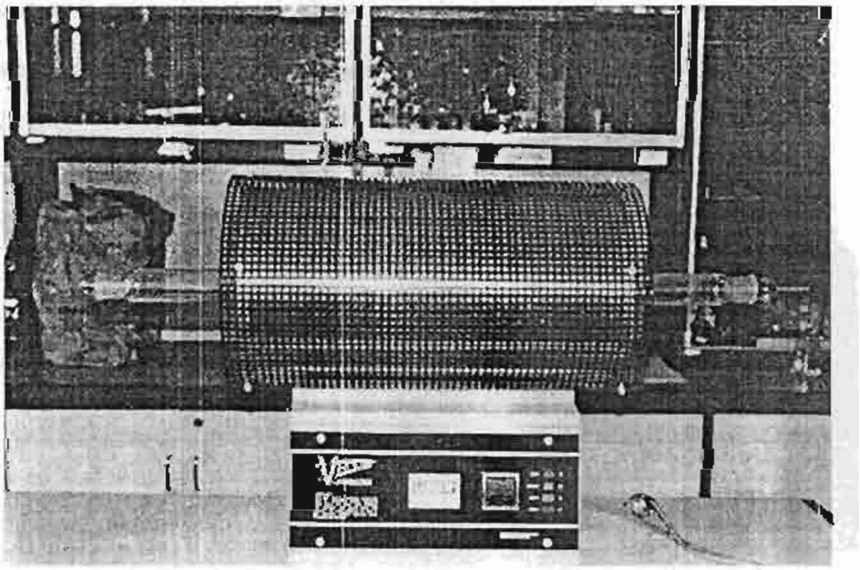


Figure 1.1 Calcination of zeolite in a furnace

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.

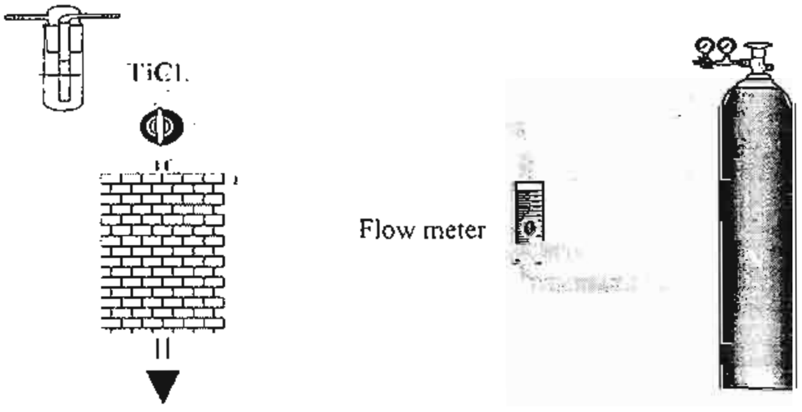


Figure 1.2 Packed-bed chemical vapor deposition (CVD)

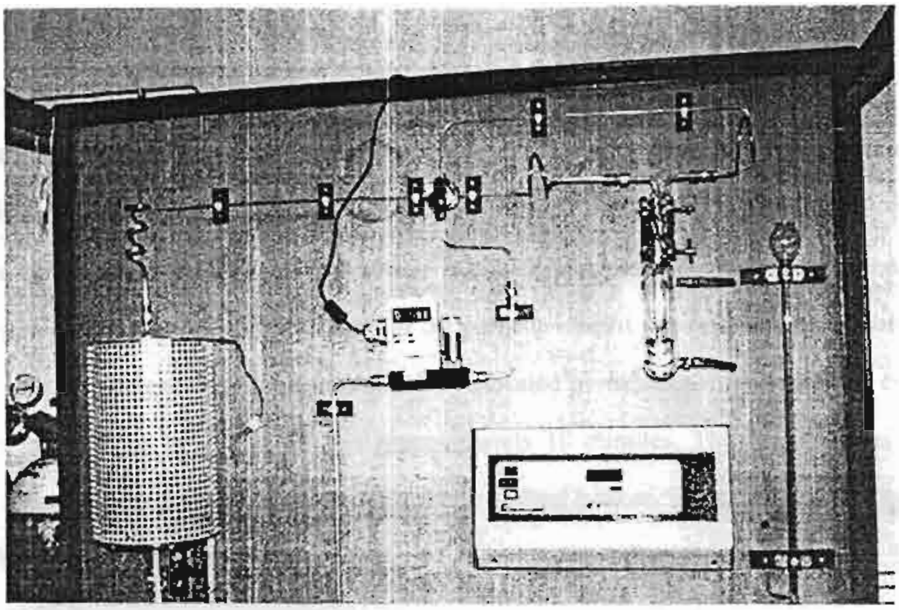


Figure1.3 Diagram of packed-bed chemical vapor deposition (CVD)

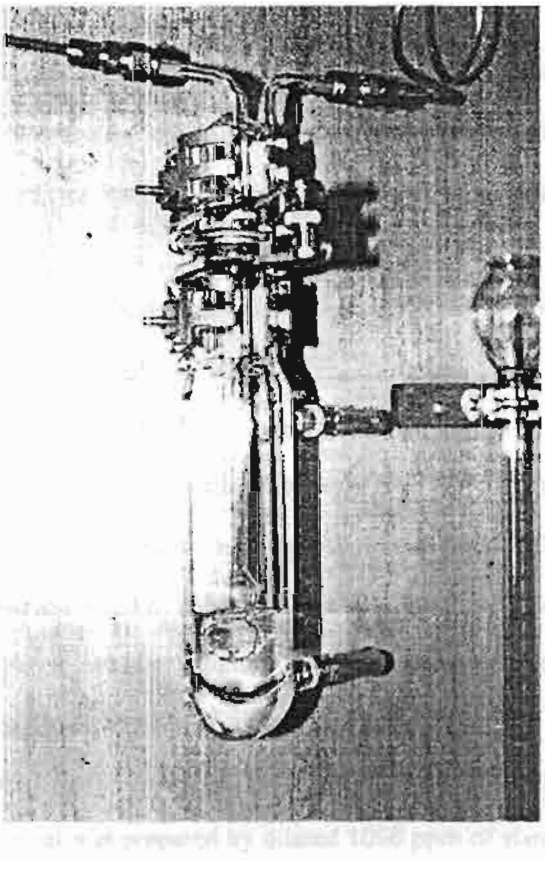


Figure 1.4 Bubbler for saturated vapor of titanium tetrachloride.

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

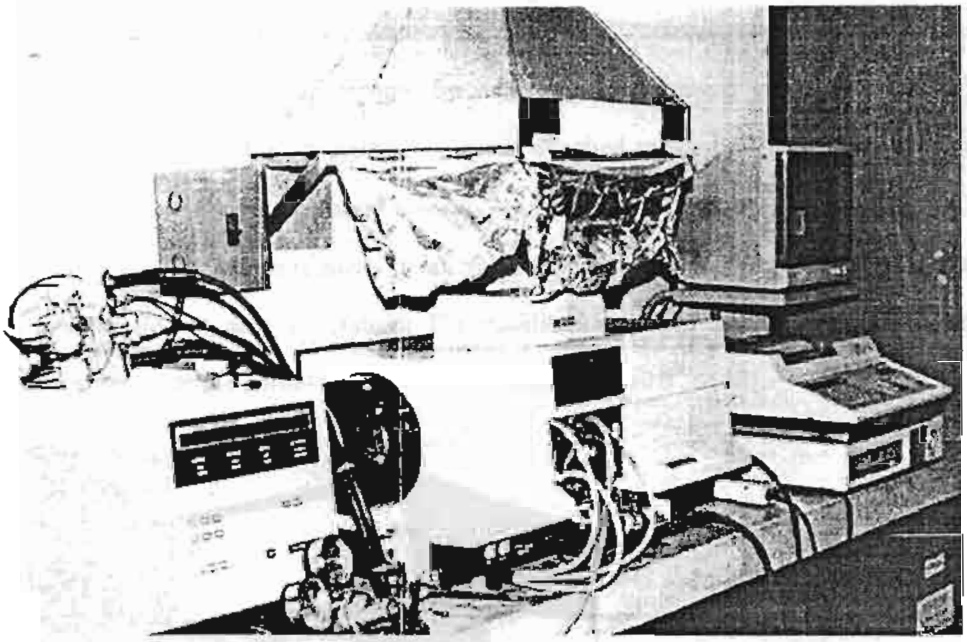


Figure 1.5 Atomic absorption spectrophotometer (AAS), AA-680 Shimadsu

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 $^{\circ}$C. The sample was out-gassed for 24 hours. The sample cell was then removed from the out gassing station after the nitrogen was filled and was attached to the analysis station. The equilibration time is set to 3 minutes and the adsorption was tested at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0.

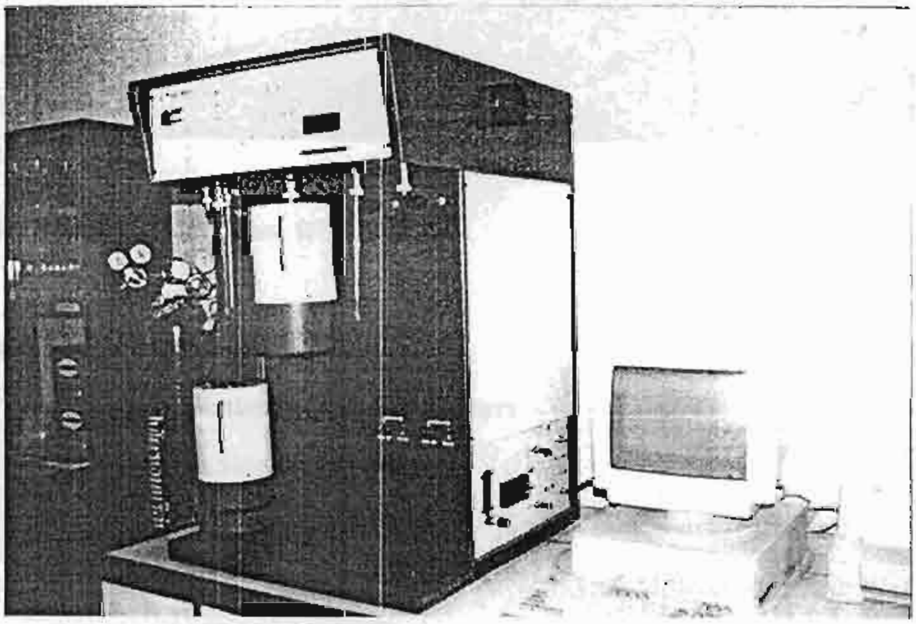


Figure 1.6 Gas Adsorption Analyzer (Autosorb-1, Quantachrome)

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}.

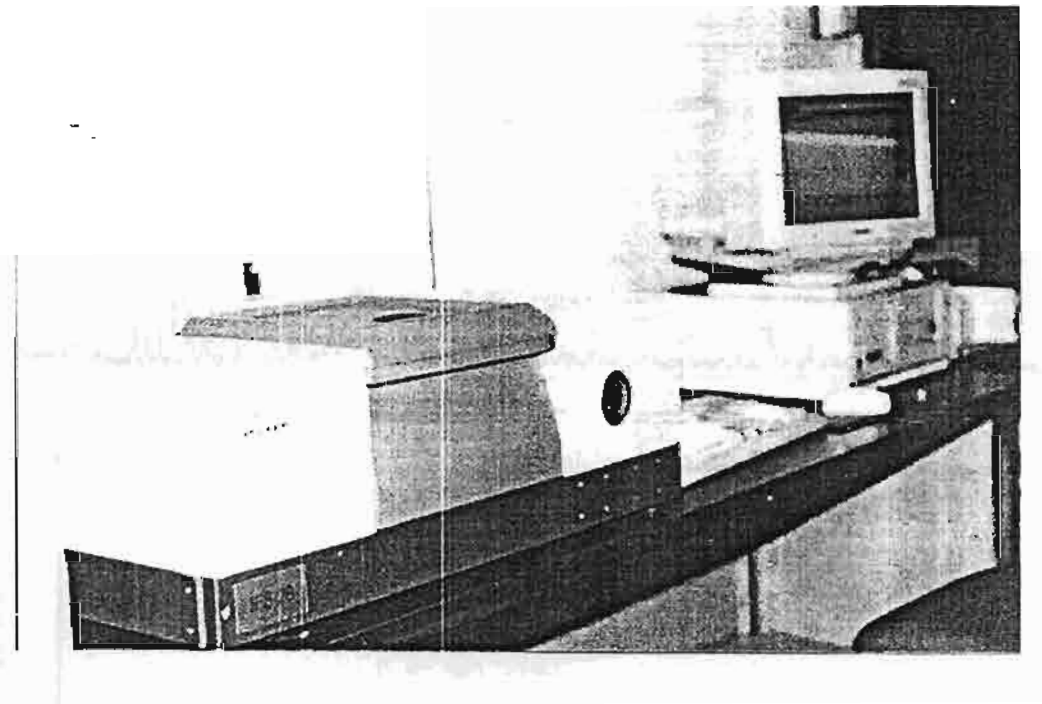


Figure 1.7 Infrared Spectrometer, IFS 28, Bruker.

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.

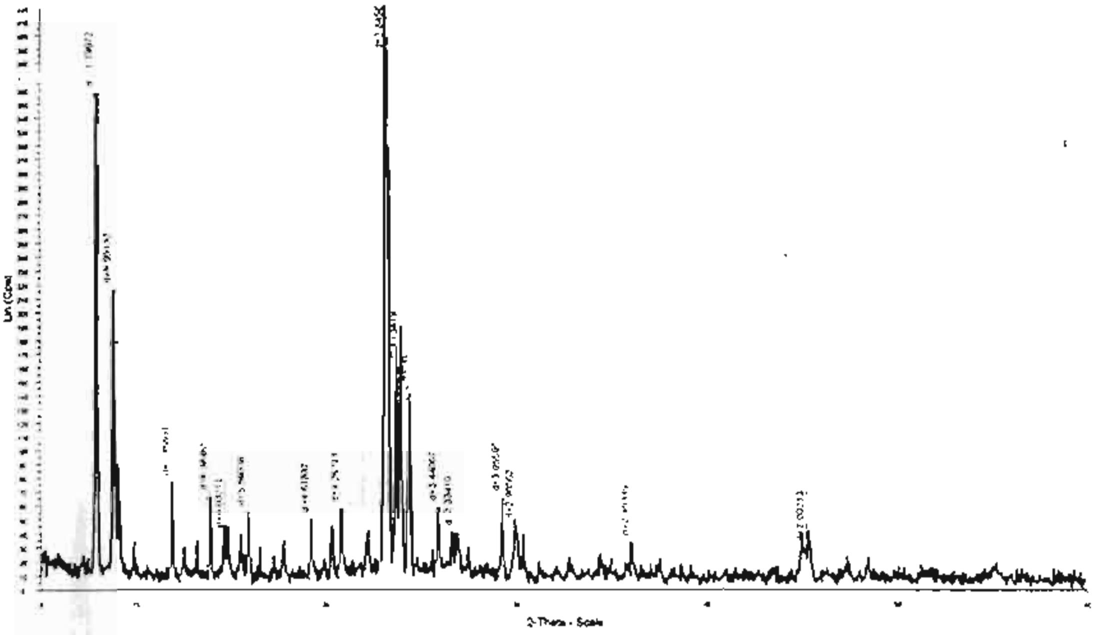


Figure 1.8 X-ray diffraction pattern of TS-1 before calcination.

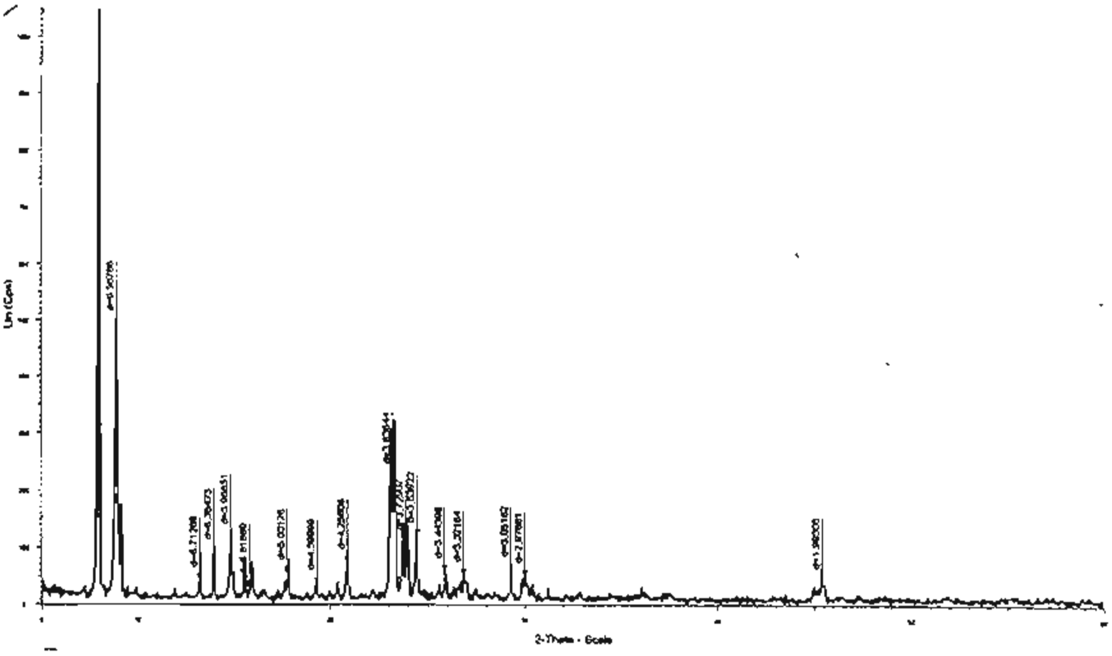


Figure 1.9 X-ray diffraction pattern of TS-1 after calcination.

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

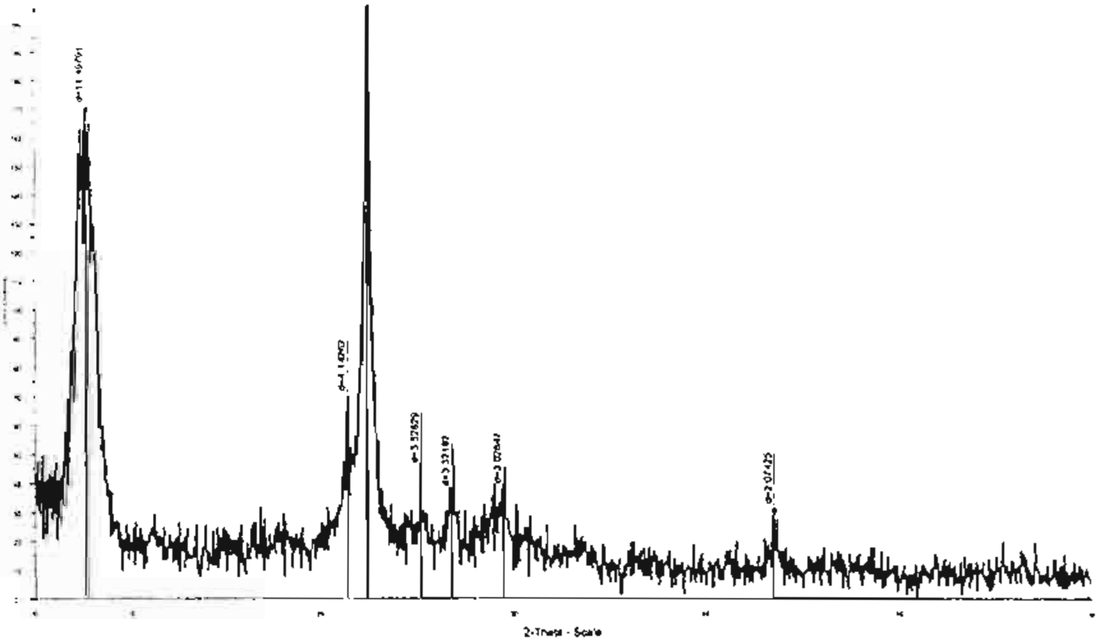


Figure 1.10 X-ray diffraction pattern of zeolite NH_4^+-Beta.

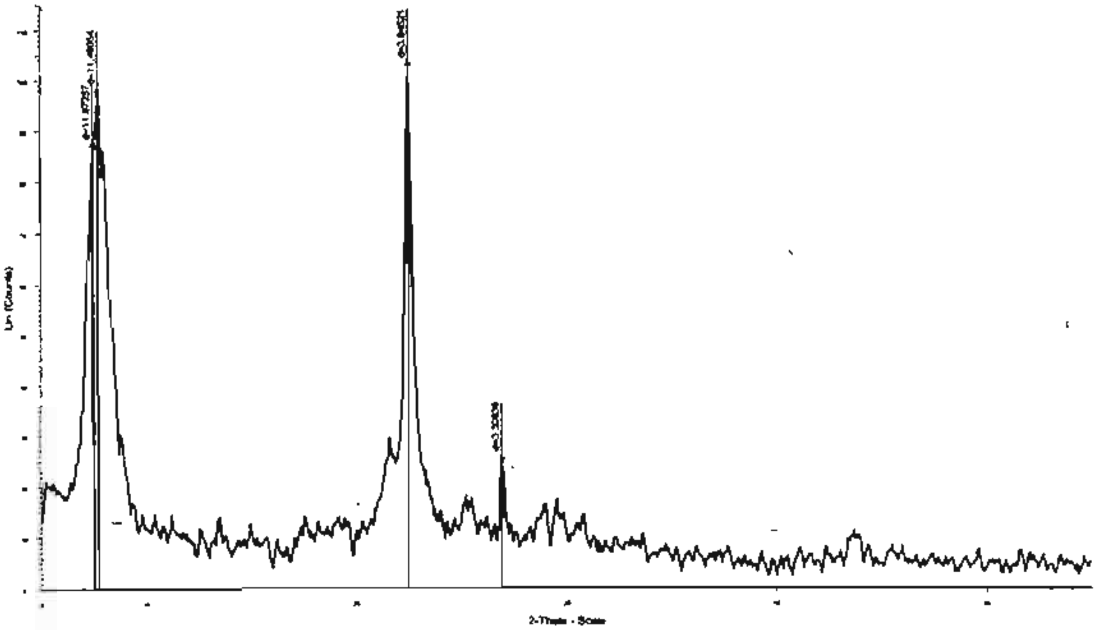


Figure 1.11 X-ray diffraction pattern of dealuminated zeolite Beta before calcination.

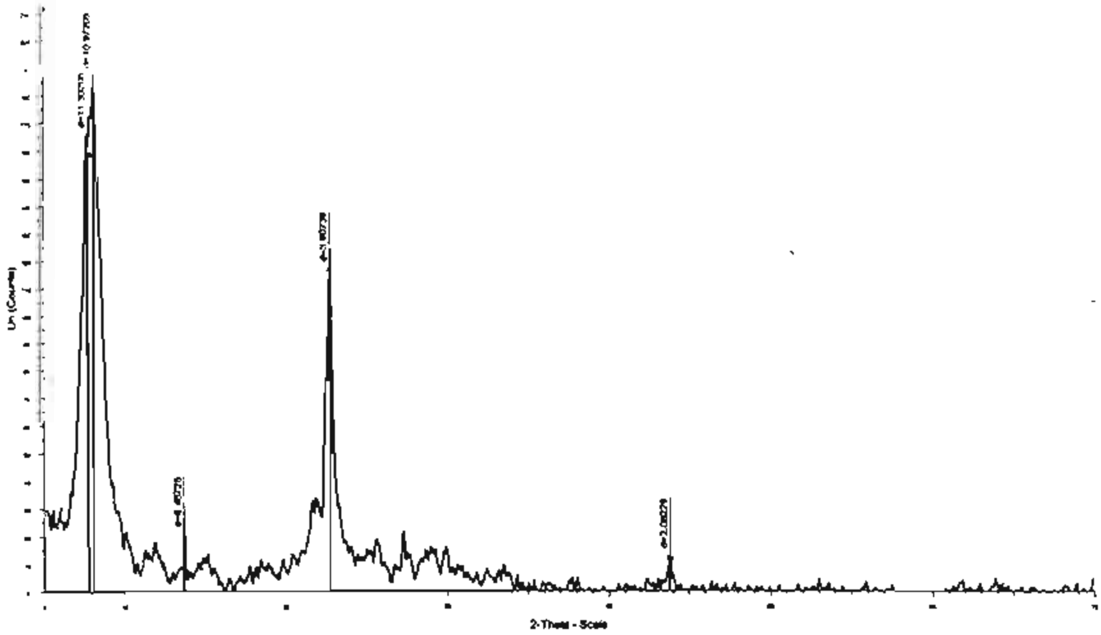


Figure 1.12 X-ray diffraction pattern of dealuminated zeolite Beta after calcination.

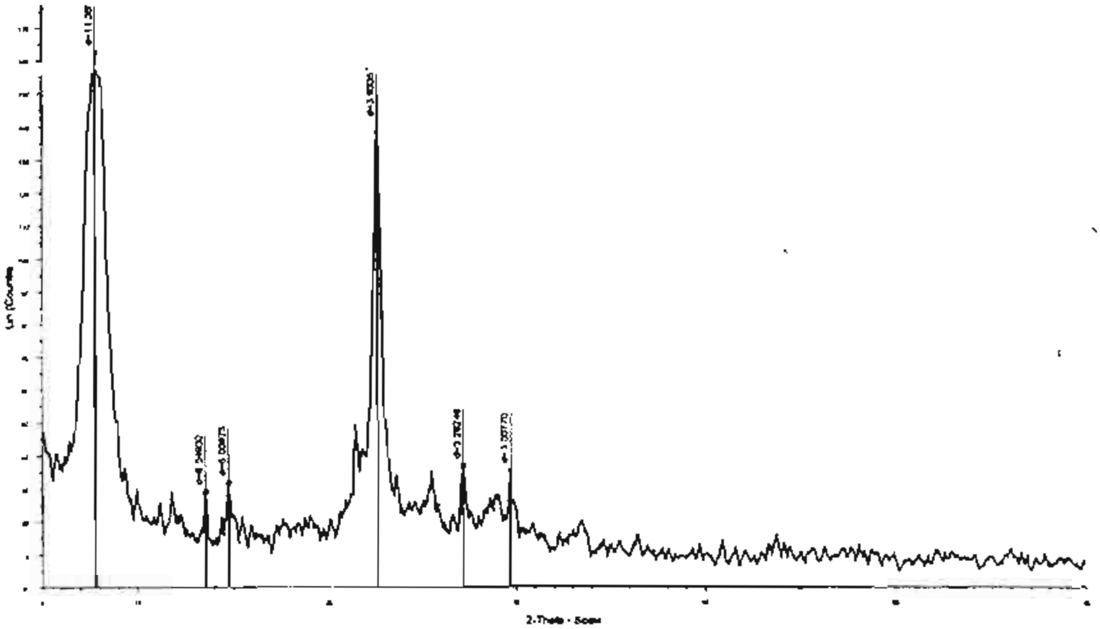


Figure 1.13 X-ray diffraction pattern of zeolite Ti-Beta before washing with sulfuric acid.

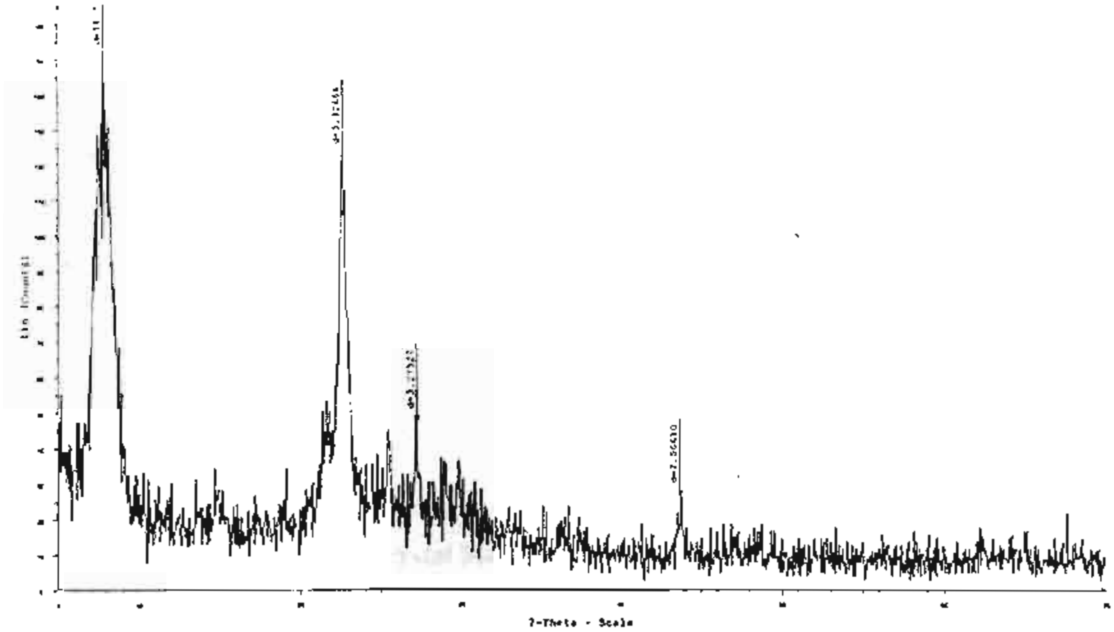


Figure 1.14 X-ray diffraction pattern of zeolite Ti-Beta after washing with sulfuric acid and calcination.

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.

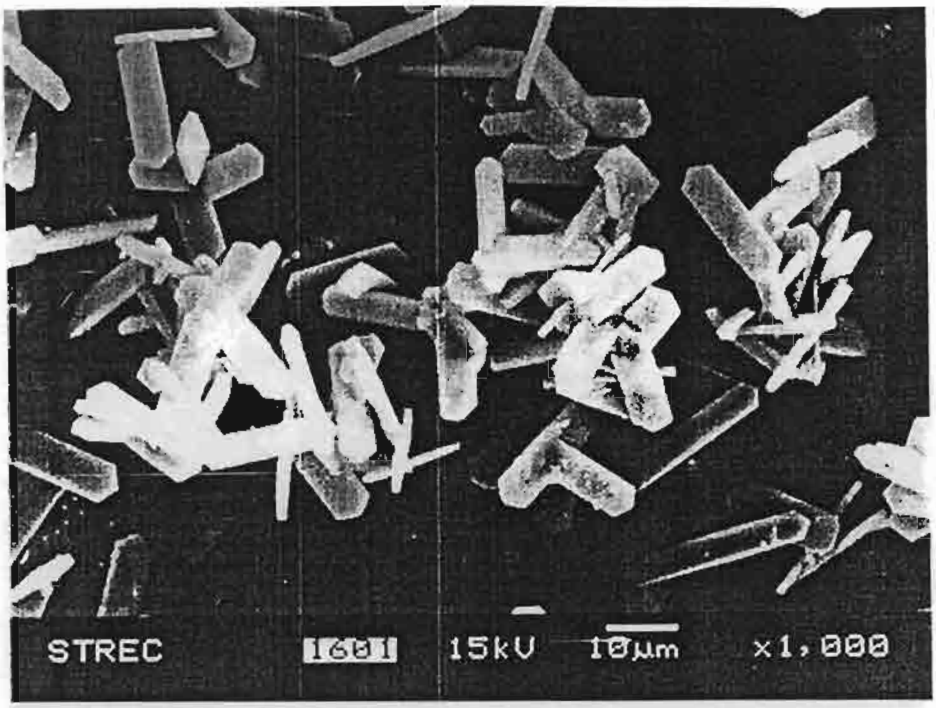


Figure 1.15 Scanning electron micrograph of TS-1 before calcination.

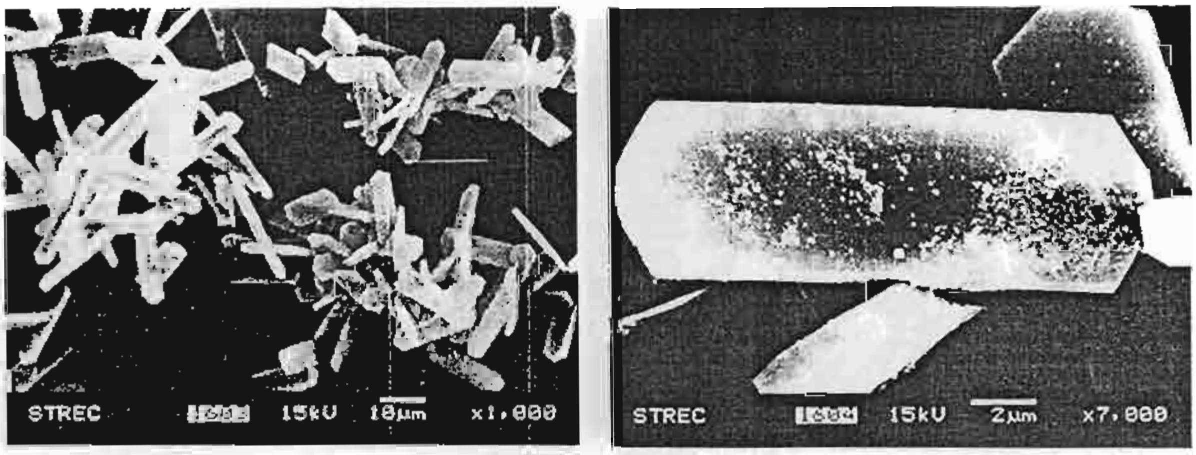


Figure 1.16 Scanning electron micrograph of TS-1 after calcination.

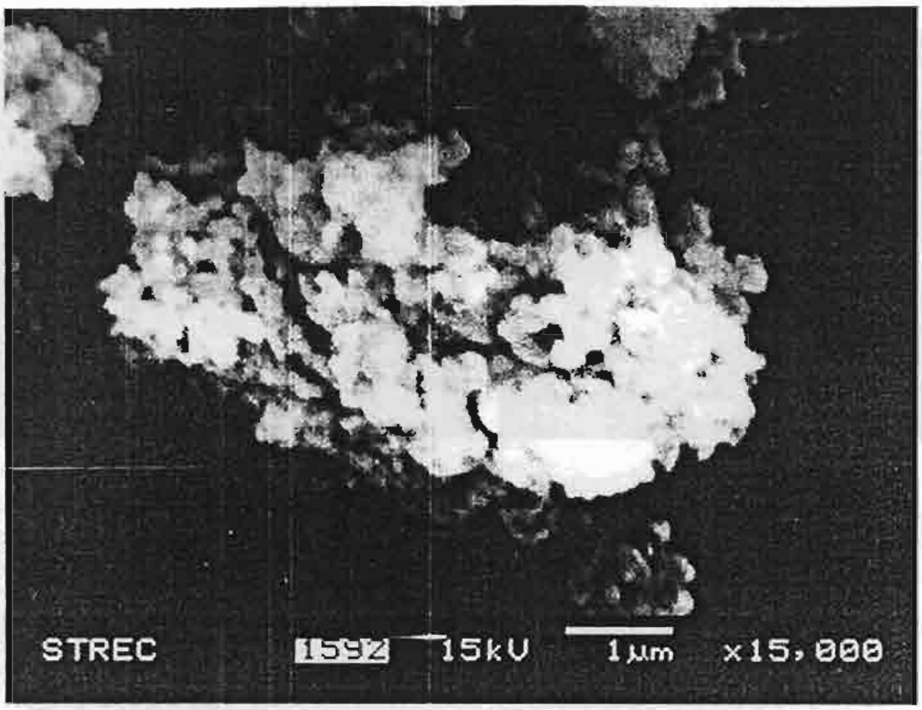
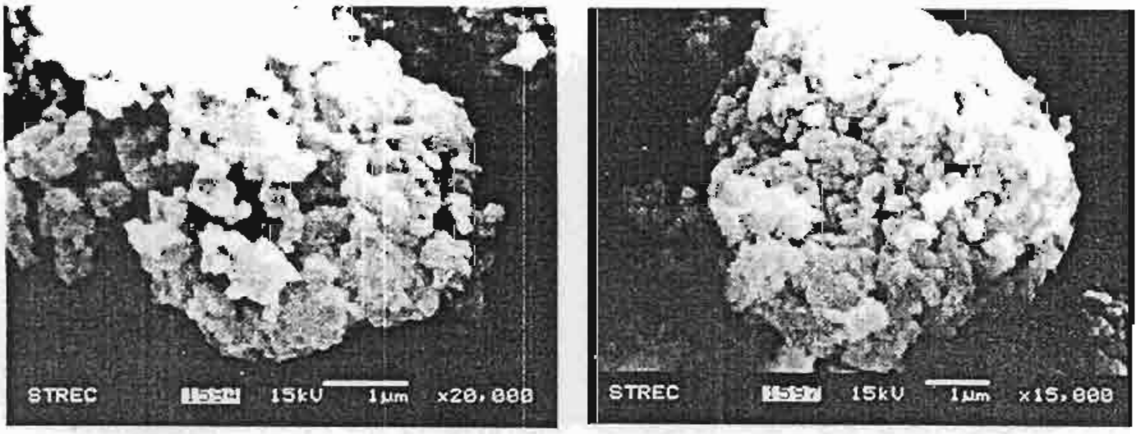
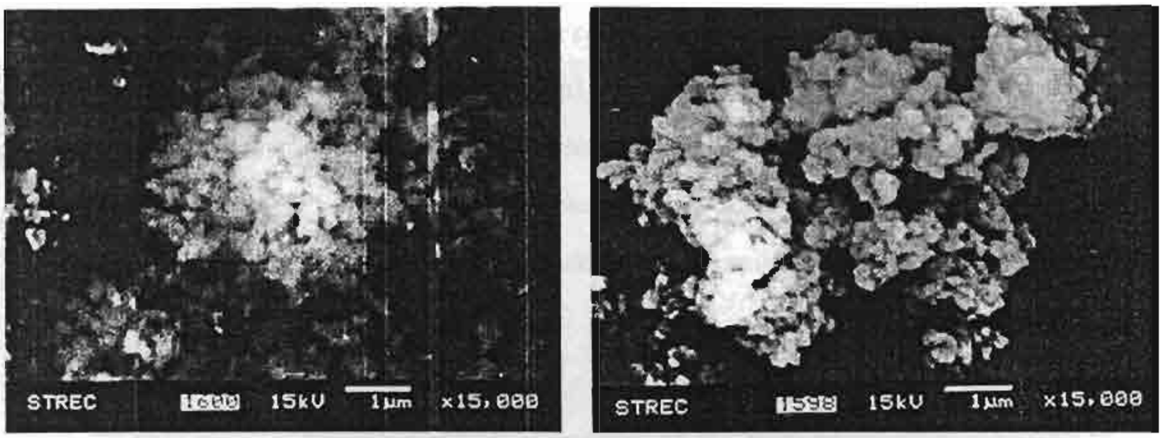


Figure 1.17 Scanning electron micrograph of zeolite NH_4^+-Beta.



(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.

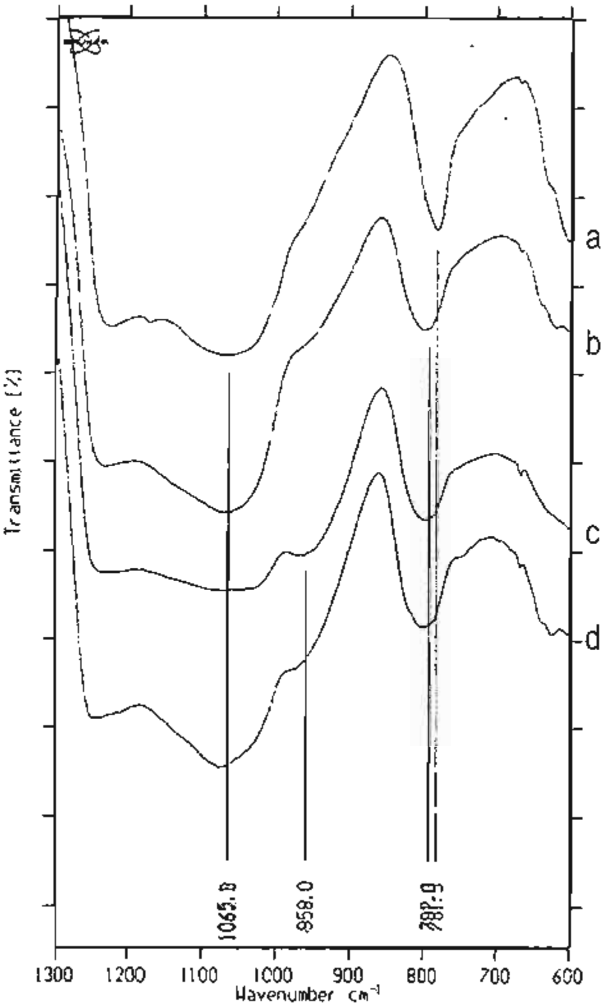


Figure 1.20 Fourier Transformed IR spectra of zeolite NH_4^+-Beta (a), Dealuminated Beta (b), Ti-Beta before (c) and after (d) washing by sulfuric acid

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.

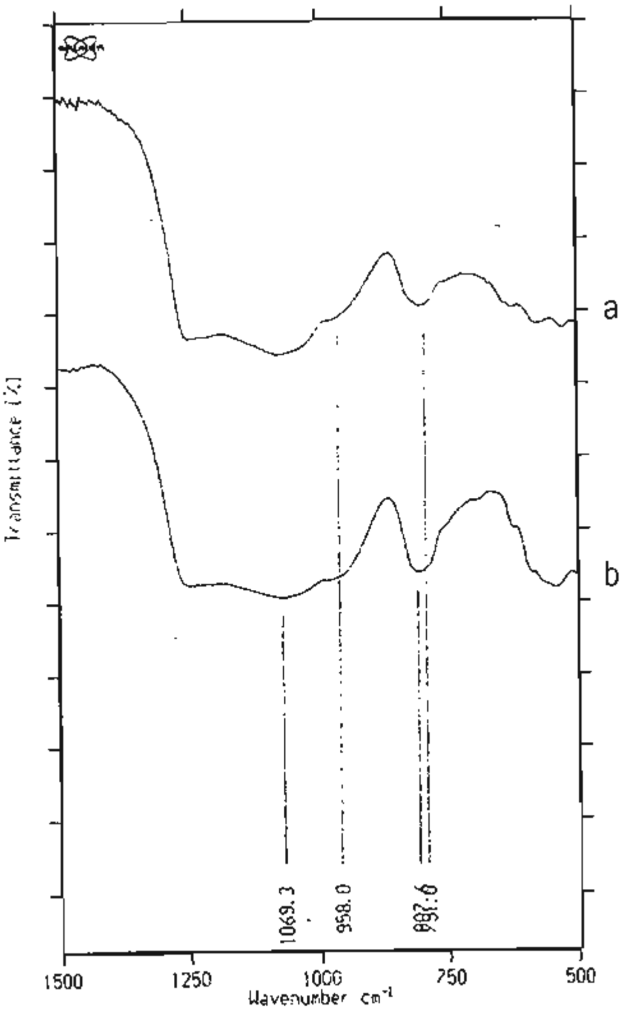


Figure 1.21 Fourier Transformed IR spectra of zeolite Ti-Beta after washing by sulfuric acid (a) and TS-1 (b)

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.

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

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

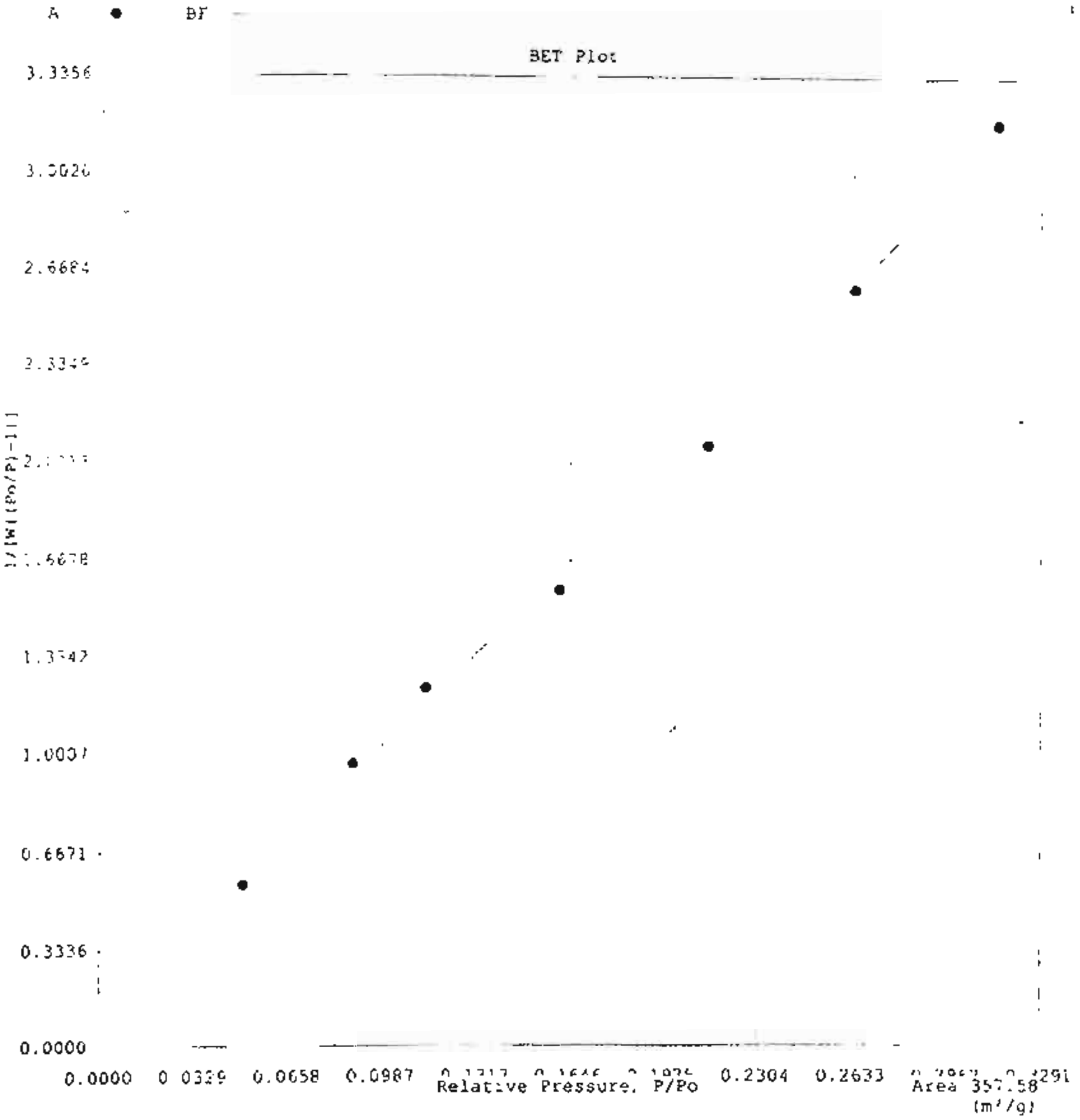
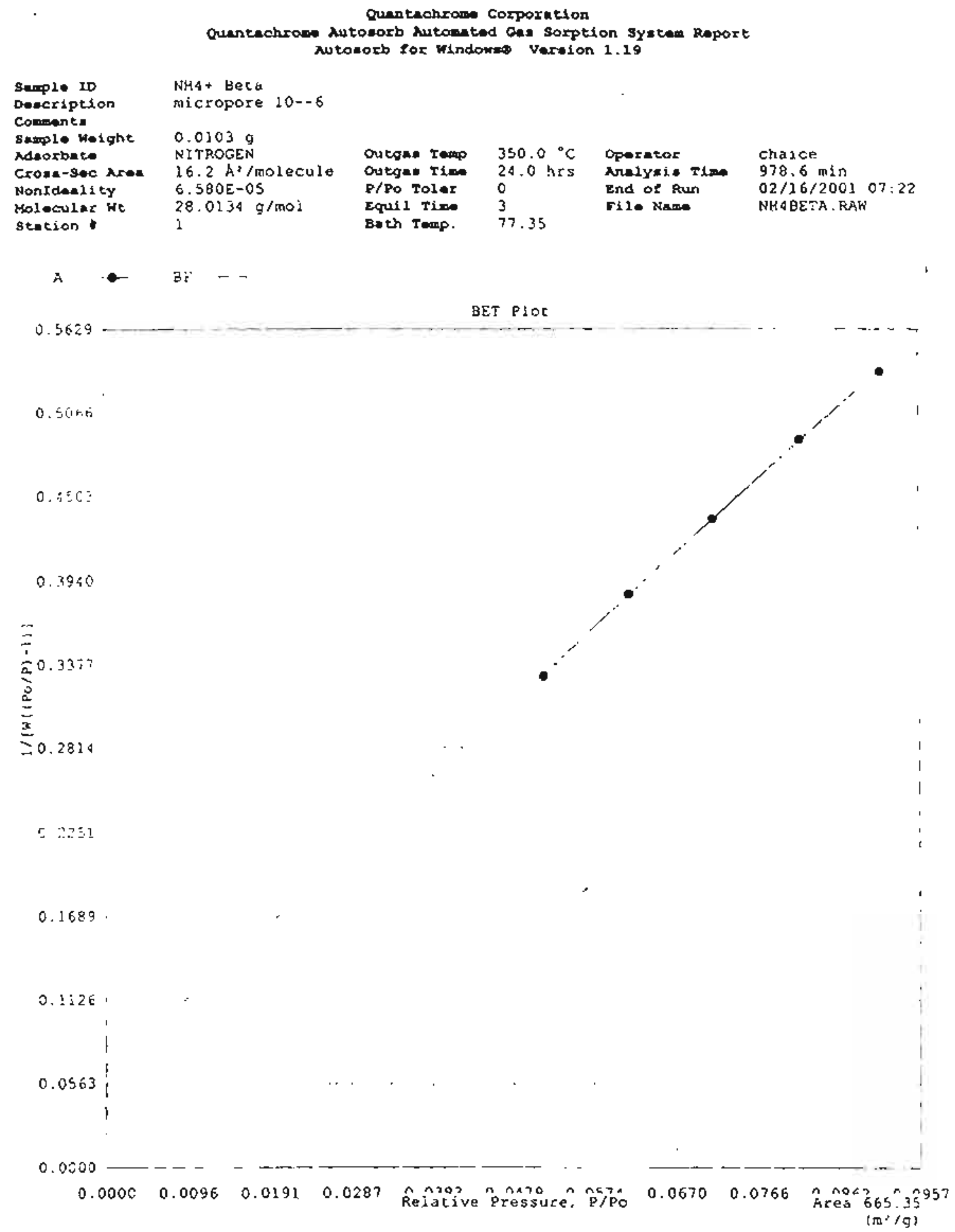


Figure 1.22 BET plot of TS-1 after calcination.



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		

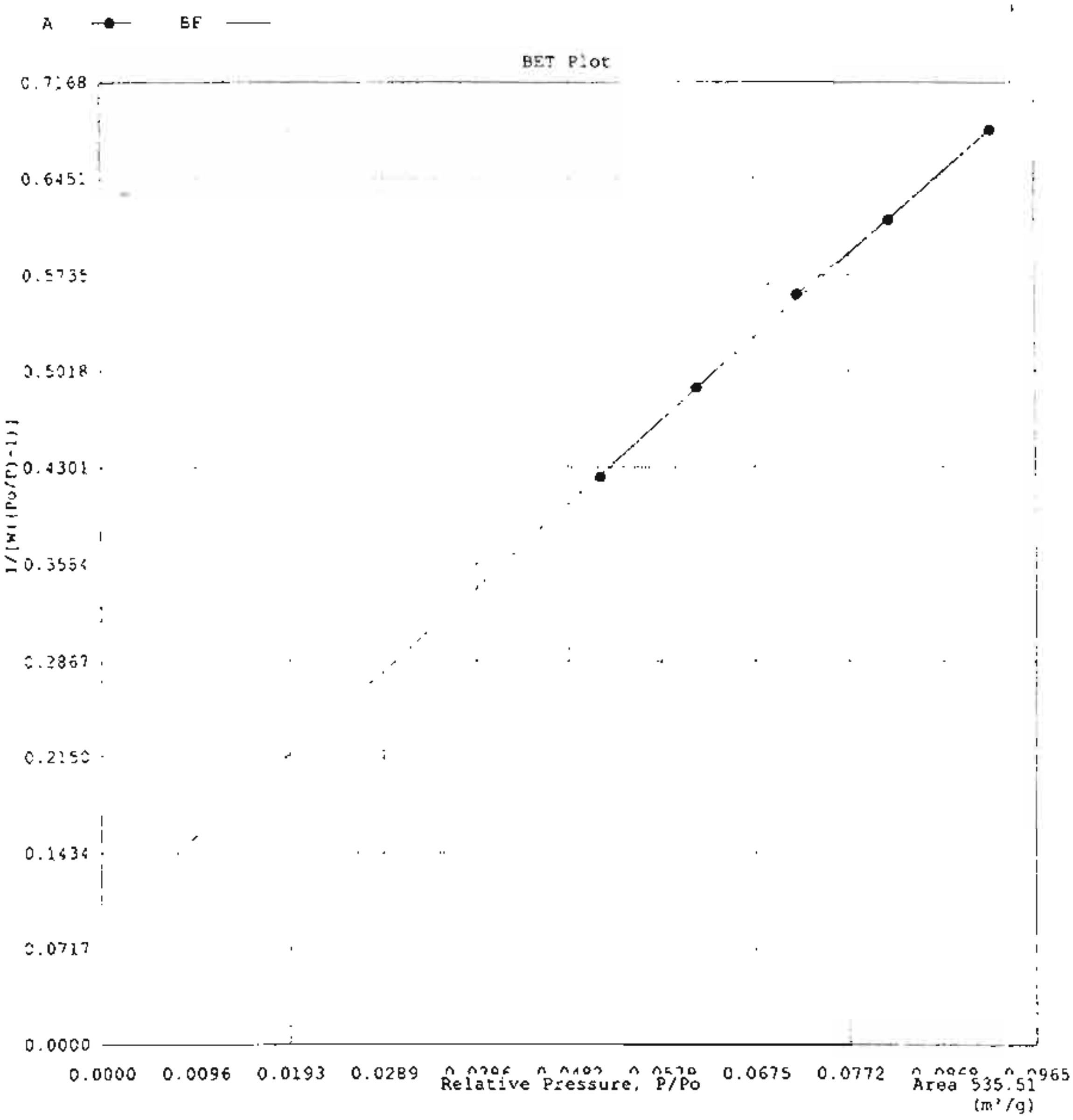


Figure 1.24 BET plot of zeolite Ti-Beta before washing with sulfuric acid.

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		

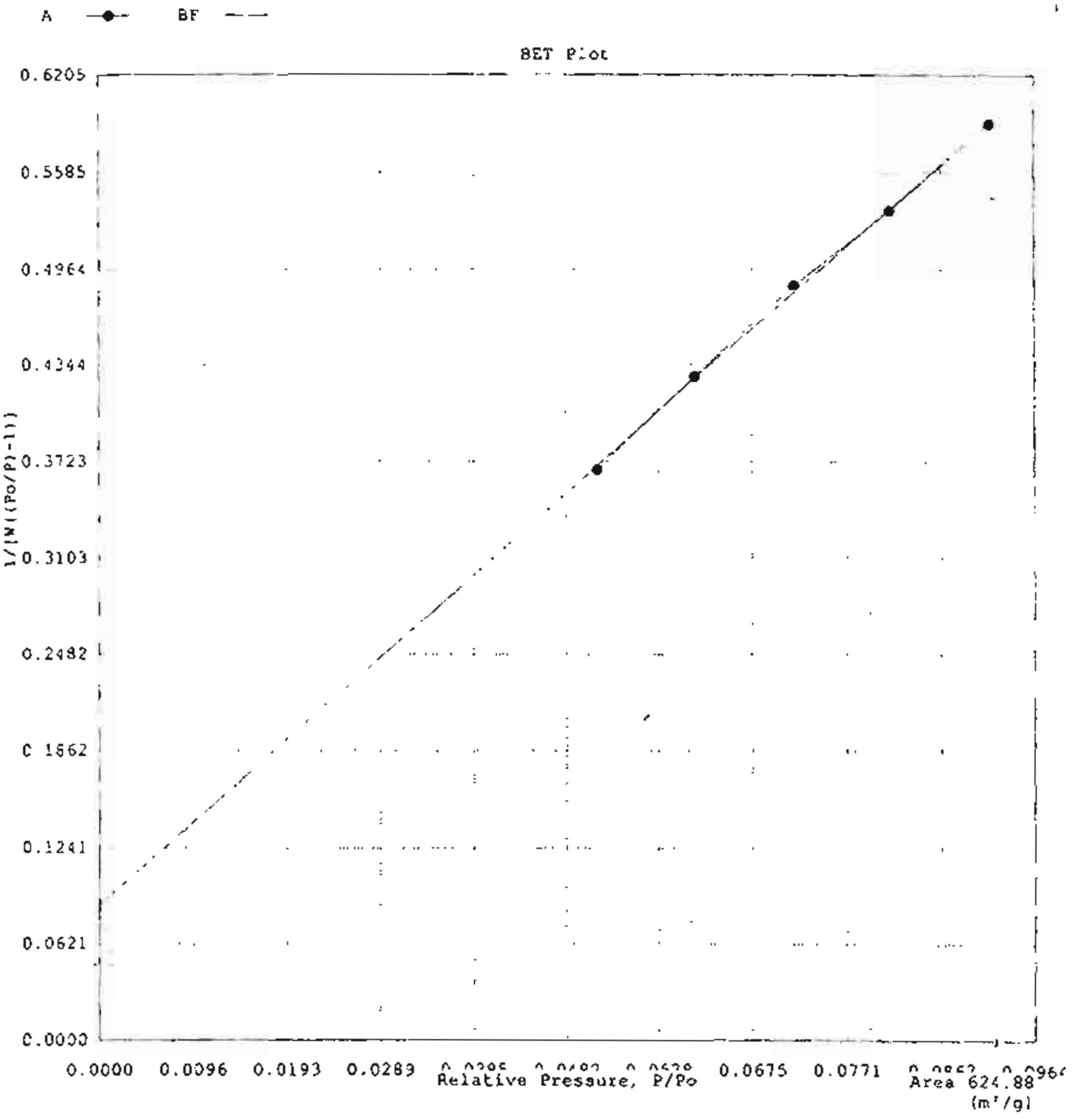


Figure 1.25 BET plot of zeolite Ti-Beta after washing with sulfuric acid and calcination.

CHAPTER 2

BECKMAN REARRANGEMENT OF CYCLOHEXANONE OXIME

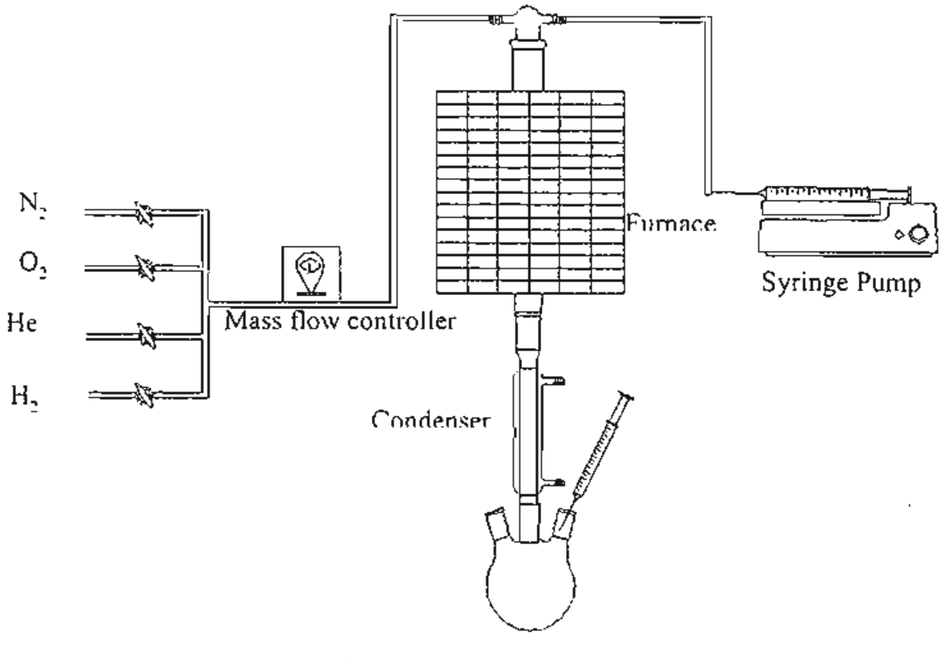
2.1 Objectives

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.

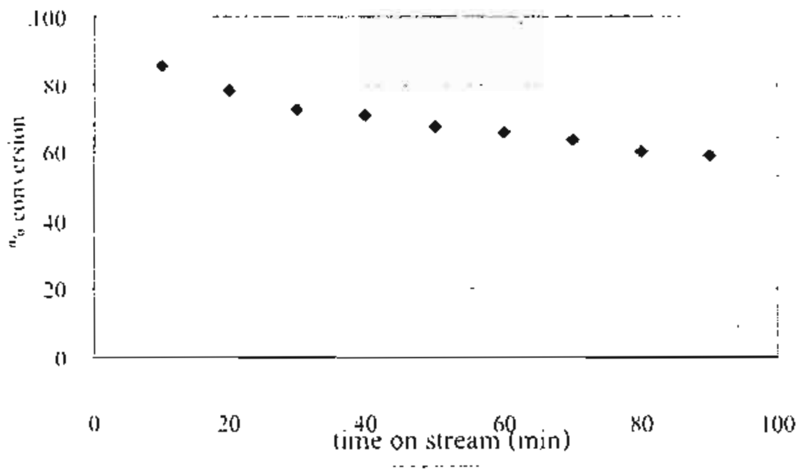


Figure 2.2 Conversion of cyclohexanone oxime over H-Beta catalyst. *Reaction condition : temperature: 350 °C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$, *diluent: n-butanol, carrier gas:* N_2, *time on stream: 90 min*

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.

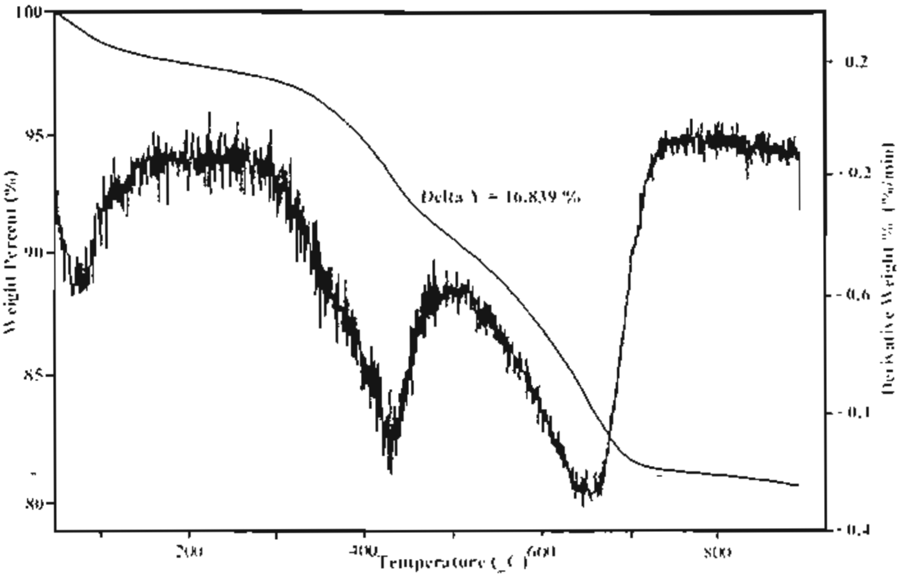


Figure 2.3 Thermogravimetric analysis of H-Beta

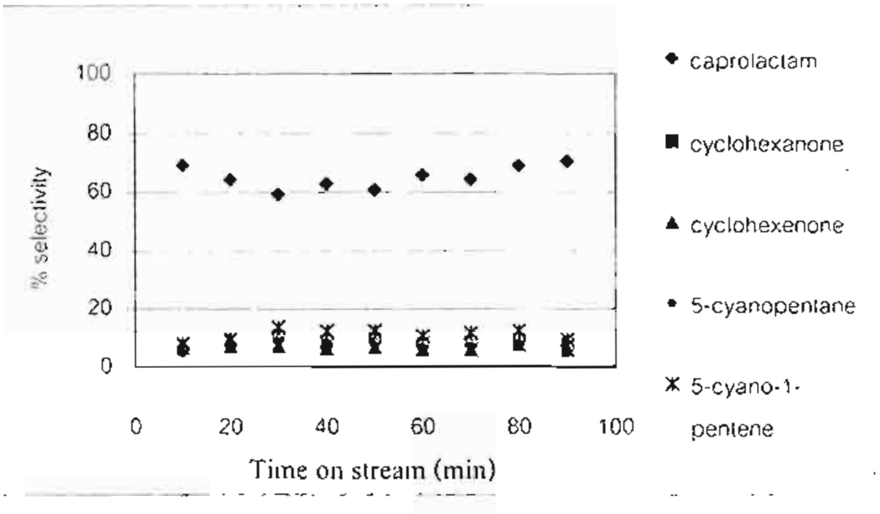


Figure 2.4 Selectivity of caprolactam, cyclohexanone, cyclohexenone, 5-cyanopentane and 5-cyano-1-pentene over H-Beta catalyst. *Reaction condition: temperature: 350 °C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$, *diluent : n-butanol, carrier gas:* N_2, *time on stream: 90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

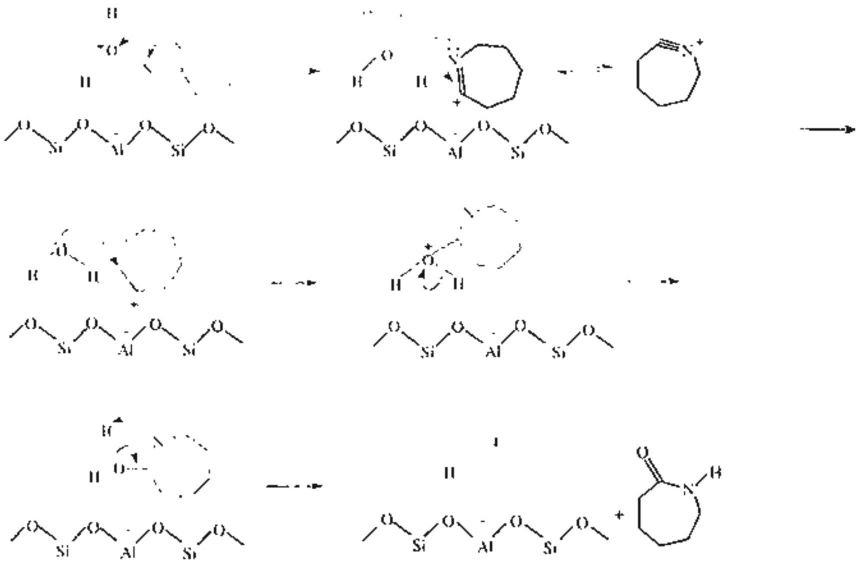
$$\mathrm{Ox} + \mathrm{A} \longleftrightarrow \mathrm{Ox(a)} \qquad \ldots\ldots\ldots(1)$$

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

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

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

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.

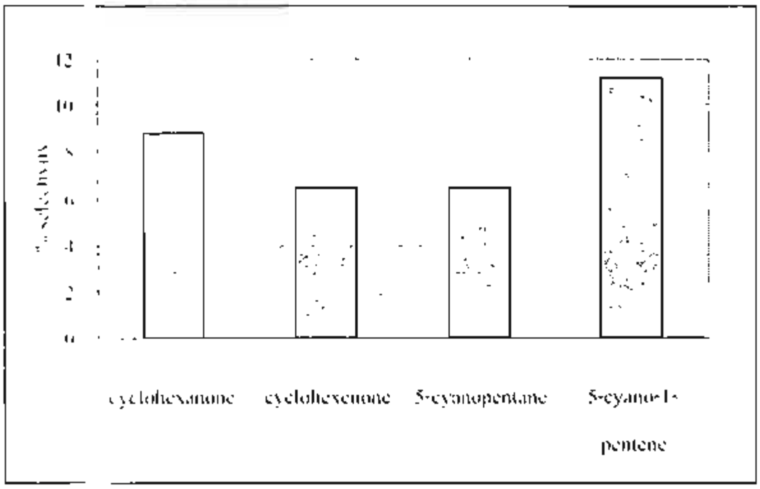
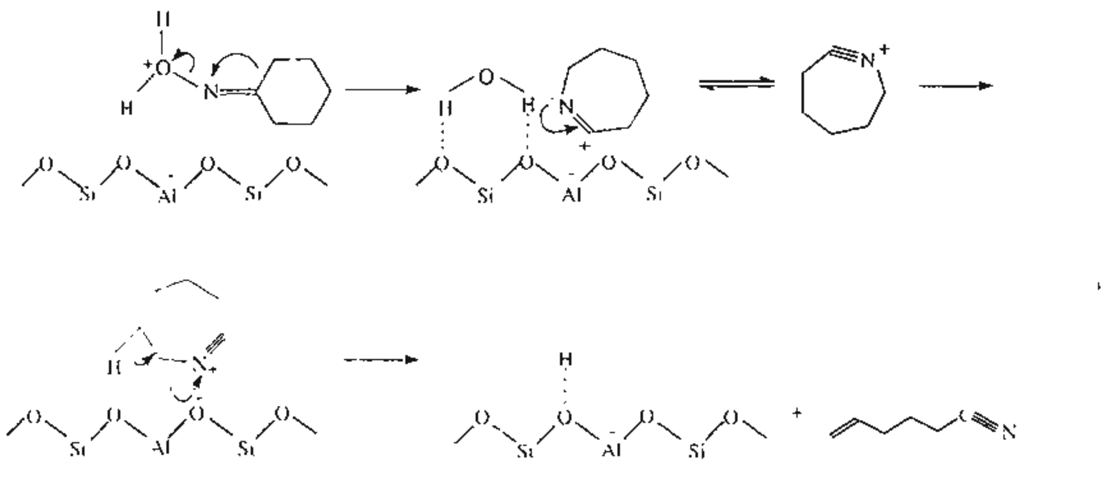


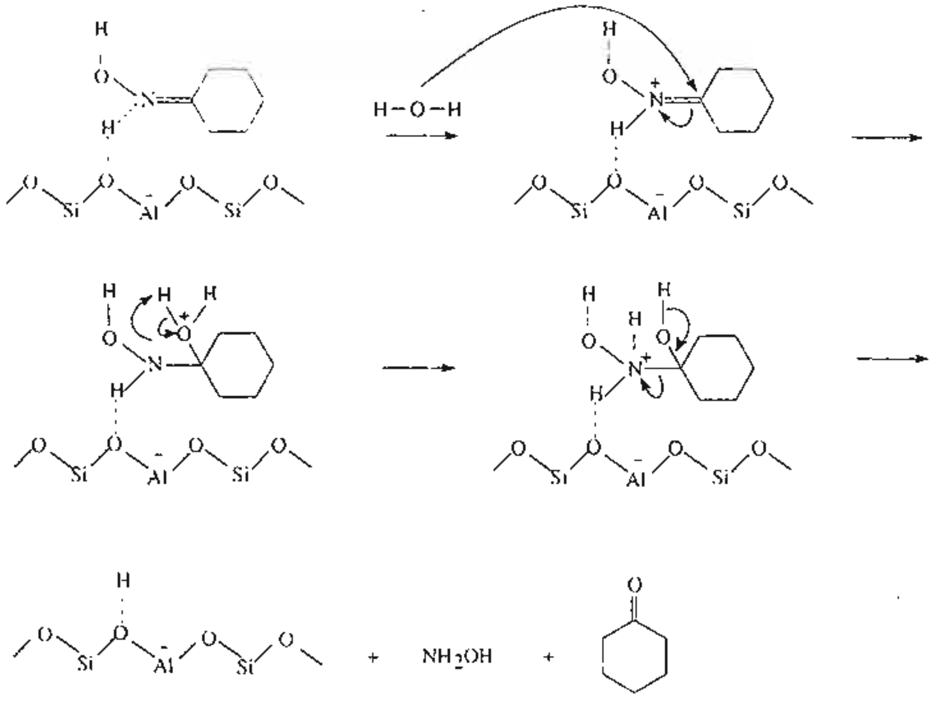
Figure 2.5 Selectivity of by-products: cyclohexanone, cyclohexenone, 5-cyanopentane and 5-cyano-1-pentene over H-Beta catalyst. *Reaction condition: temperature: 350 °C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *diluent: butanol, carrier gas:* N_2, *average time on stream 10-90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

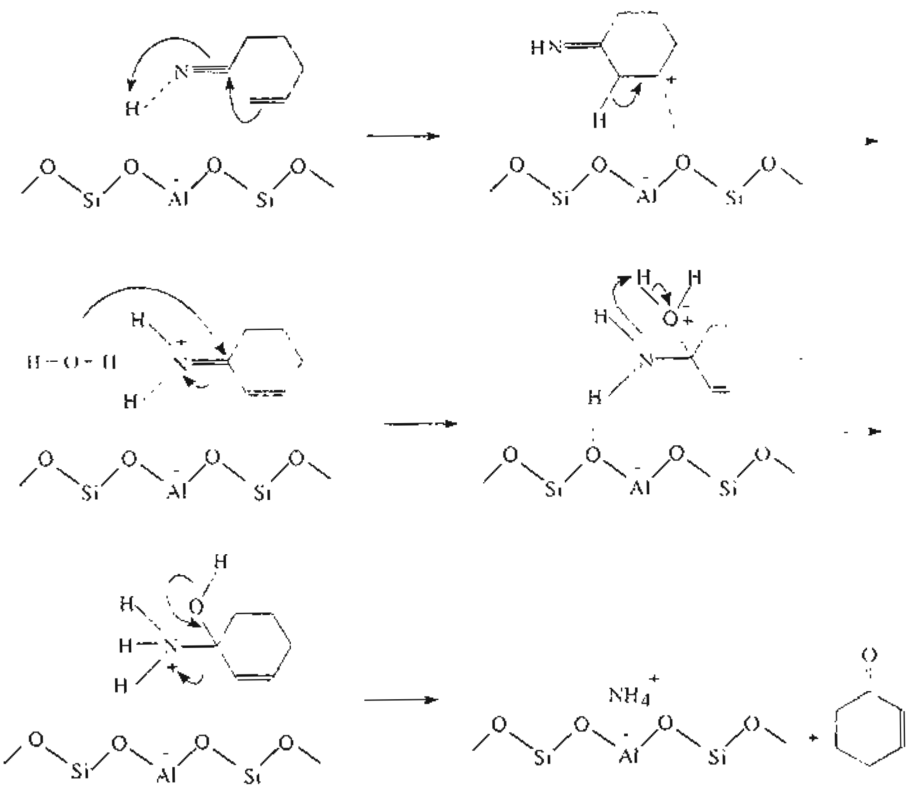


(A)

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.

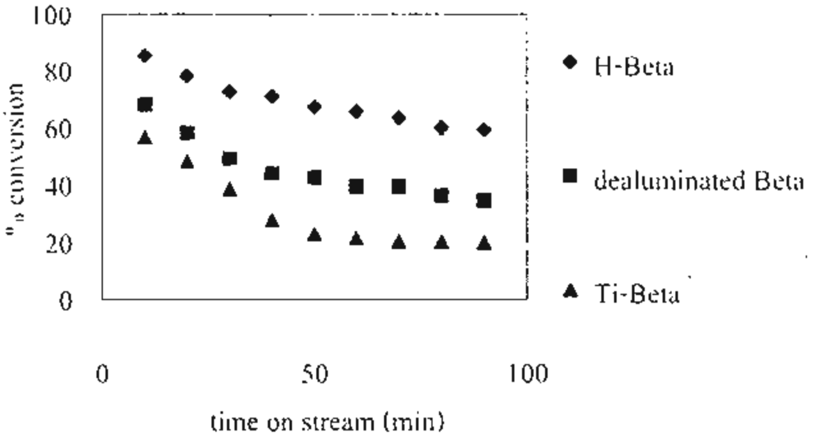
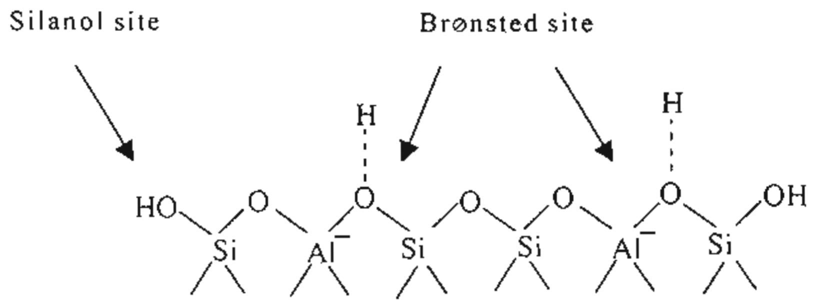


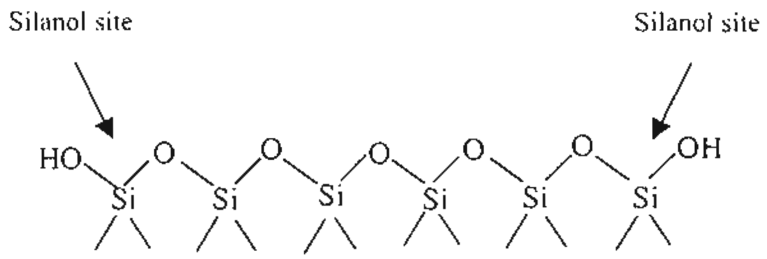
Figure 2.6 Conversion of cyclohexanone oxime over H-Beta. dealuminated Beta and Ti-Beta catalysts. *Reaction condition: temperature; 350°C, pressure; 1 atm, W/F: 13.6* $g_{catalyst}$ *h* mol^{-1}_{oxime} *diluent; butanol, carrier gas;* N_2*, time on stream; 90 min*

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.

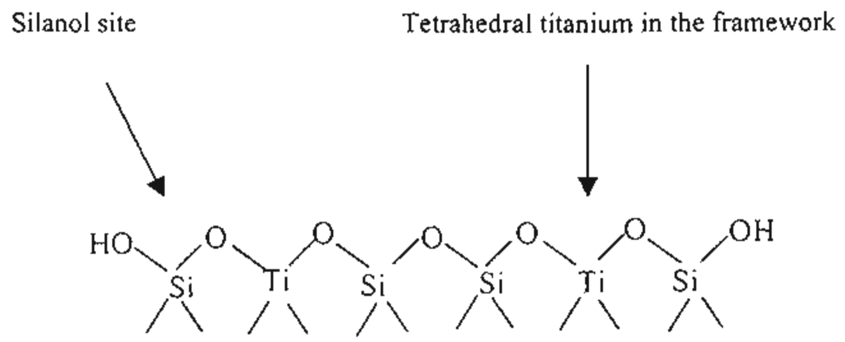


The conversion of cyclohexanone oxime depends largely on number of active sites. As discussed earlier that the sorption and desorption of reactant play important role in the catalytic activity. The conversion of cyclohexanone oxime would be increased when there is a large number of active sites available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

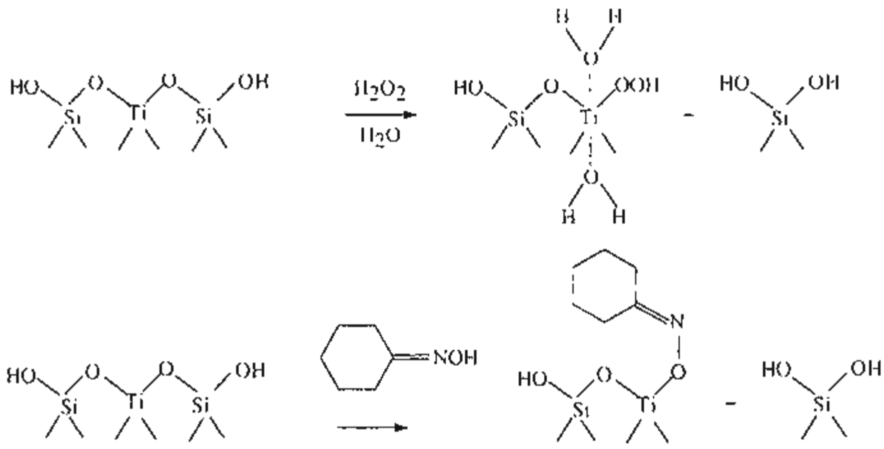
In the case of Dealuminated Beta, it possesses only silanol active sites. These species could be present within the pore and on the external surface of the zeolite crystals. It is believed that there is negligible amount of BrØnsted acid sites present in this catalyst. This can be confirmed by the elemental 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).

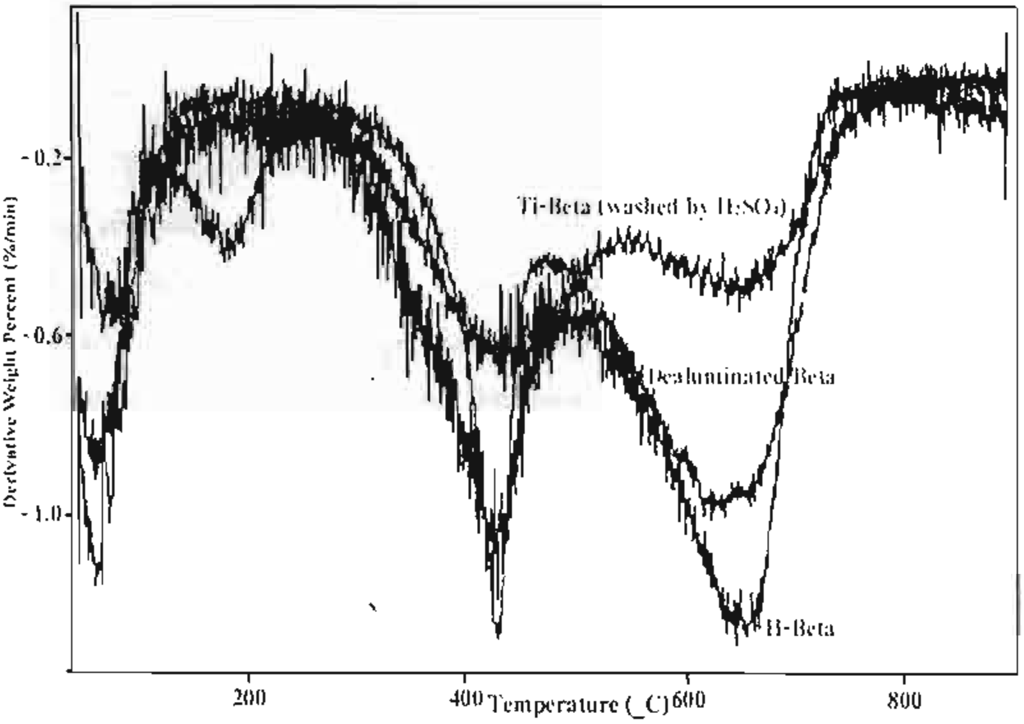
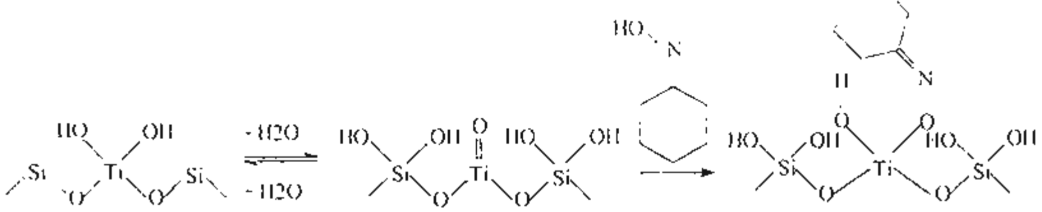


Figure 2.7 Thermogravimetric analysis of H-Beta, Dealuminated Beta and Ti-Beta

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).

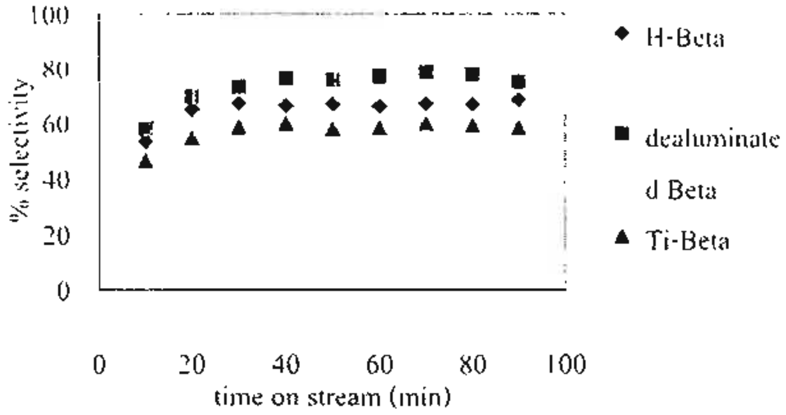


Figure 2.8 Selectivity of caprolactam over H-Beta, dealuminated Beta and Ti-beta as catalysts. *Reaction condition: temperature: 350°C, pressure: 1 atm. W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$*, diluent: butanol, carrier gas;* N_2*, average time on stream 10-90 min*

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.

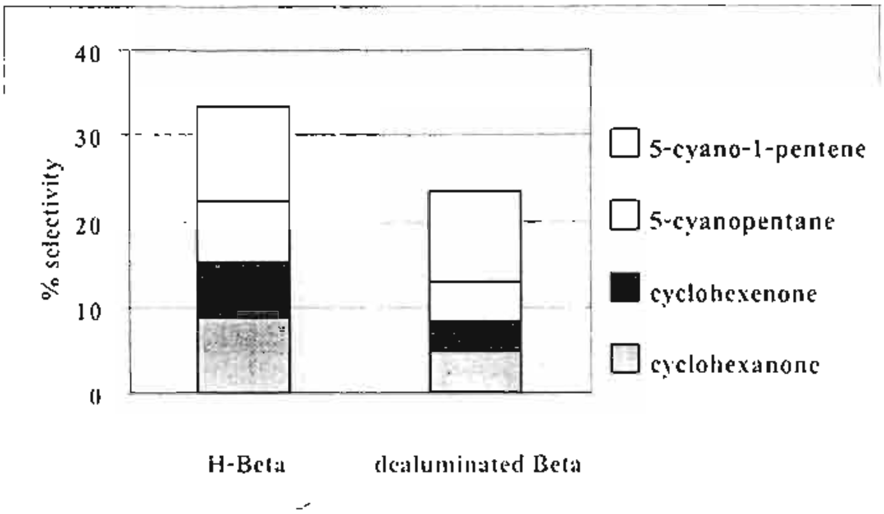


Figure 2.9 Selectivity of by product over H-Beta and Dealuminated Beta as catalysts.

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.

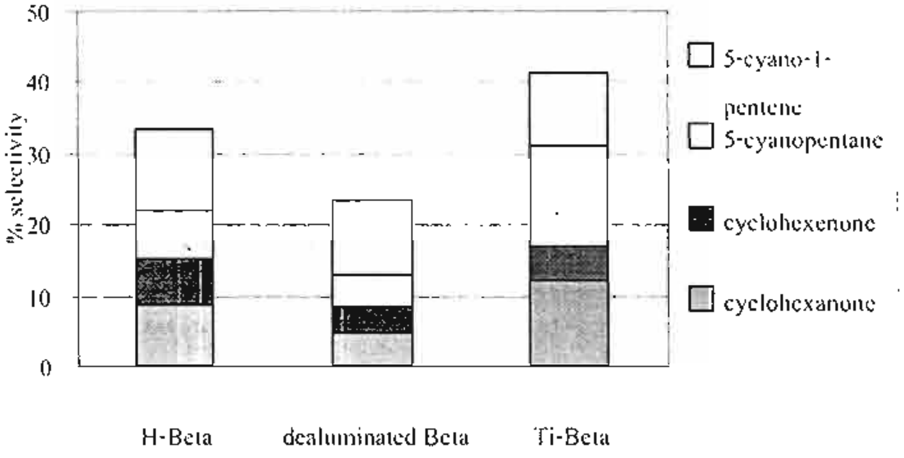


Figure 2.10 Selectivity of by-products over H-Beta and Dealuminated Beta and Ti-Beta

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*

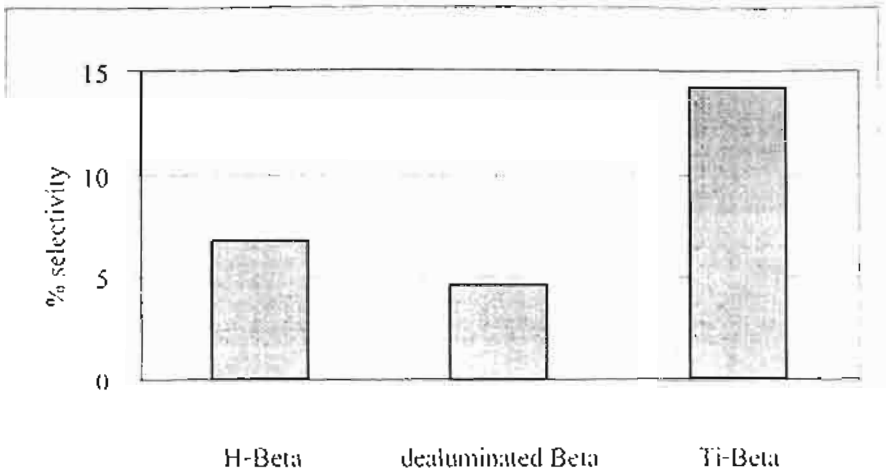
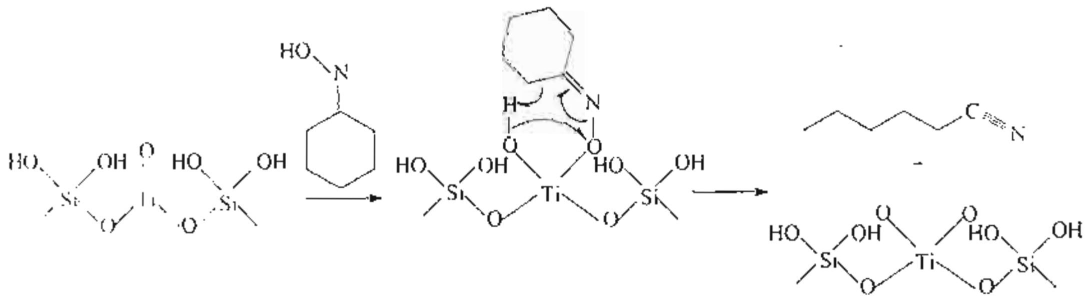


Figure 2.11 Selectivity of 5-cyanopentane over H-Beta. Dealuminated Beta, Ti-Beta as catalysts. *Reaction condition: temperature, 350°C, pressure: 1 atm, W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$ *, diluent: butanol, carrier gas:* N_2*, average time on stream 10- 90 min*

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).

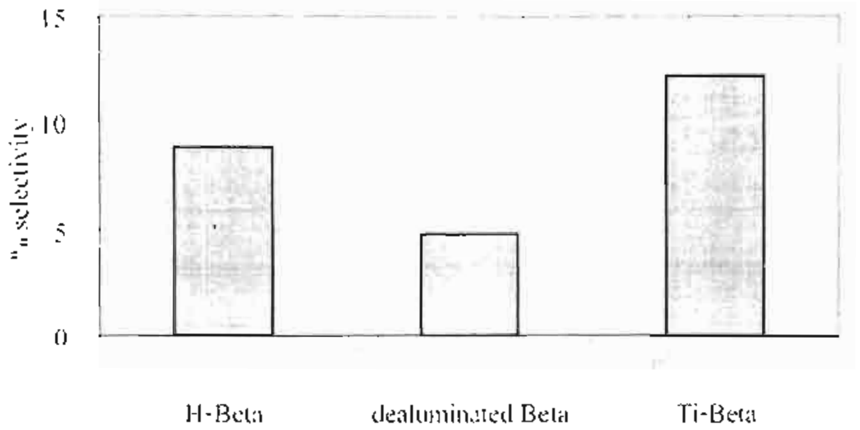
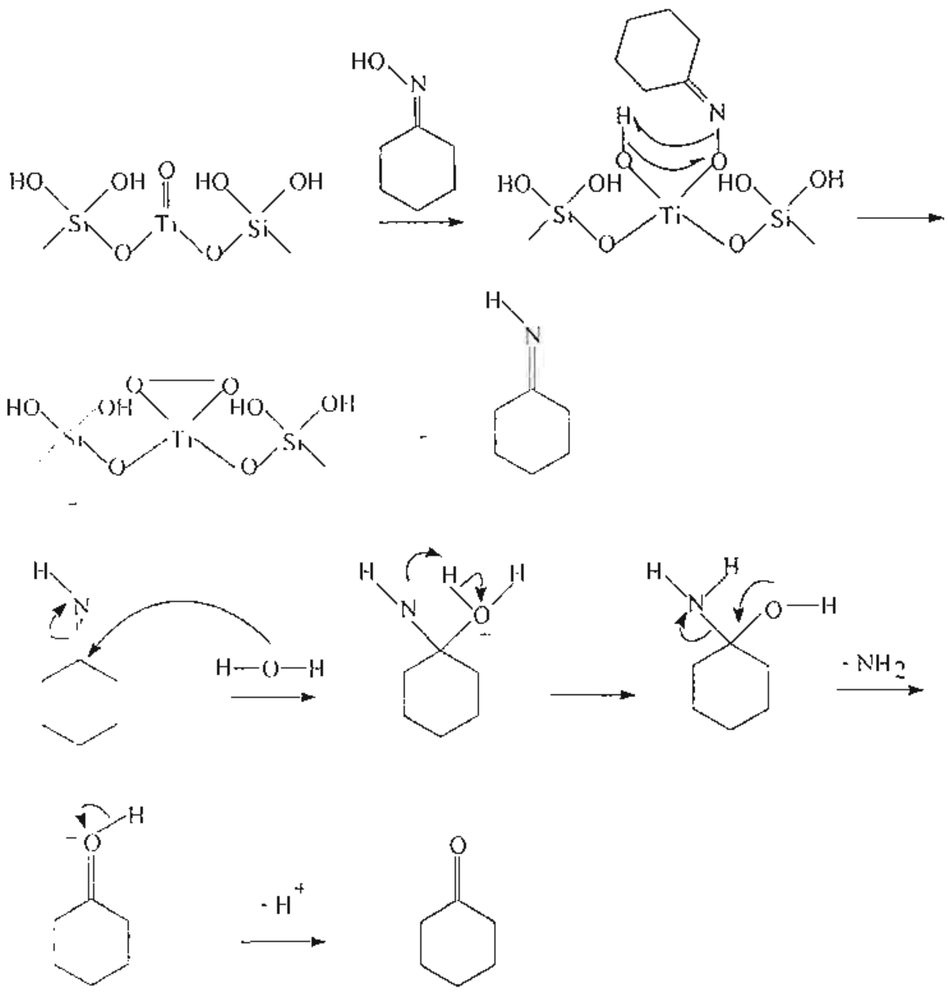


Figure 2.12 Selectivity of cyclohexanone over H-Beta, Dealuminated Beta, Ti-Beta as catalysts. *Reaction condition: temperature, 350°C, pressure: 1 atm W/F: 13.6* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$, *diluent: butanol, carrier gas:* N_2, *average time on stream 10- 90 min*

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).

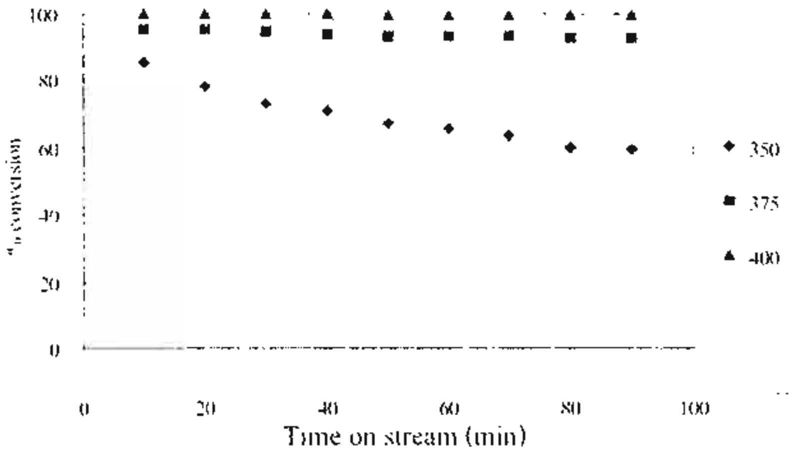


Figure 2.13 Effect of reaction temperature on the conversion of cyclohexanone oxime over H-Beta. *Reaction condition : pressure: 1 atm, W/F: 13.6* $g_{catalyst}\ h\ mol^{-1}_{reactant}$, *diluent: butanol, carrier gas:* N_2, *time on stream 90 min, temperature: 350, 375, 400 °C*

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).

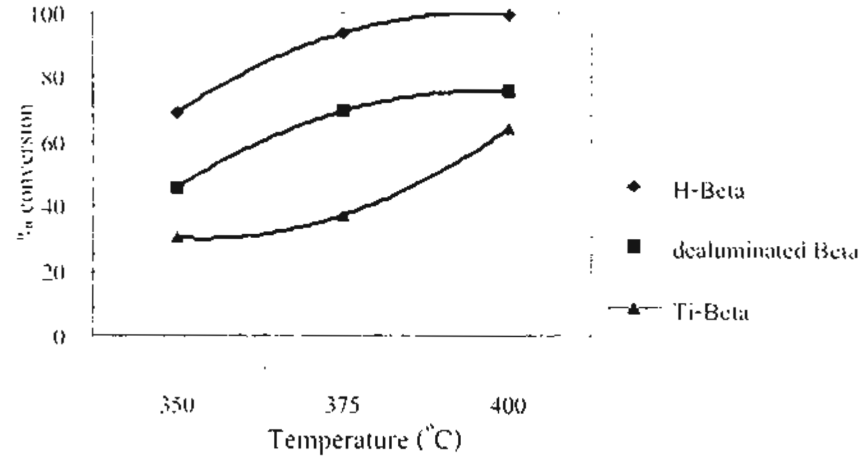


Figure 2.14 Effect of reaction temperature on the conversion of cyclohexanone oxime over H-Beta. Dealuminated Beta and Ti-Beta.

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).

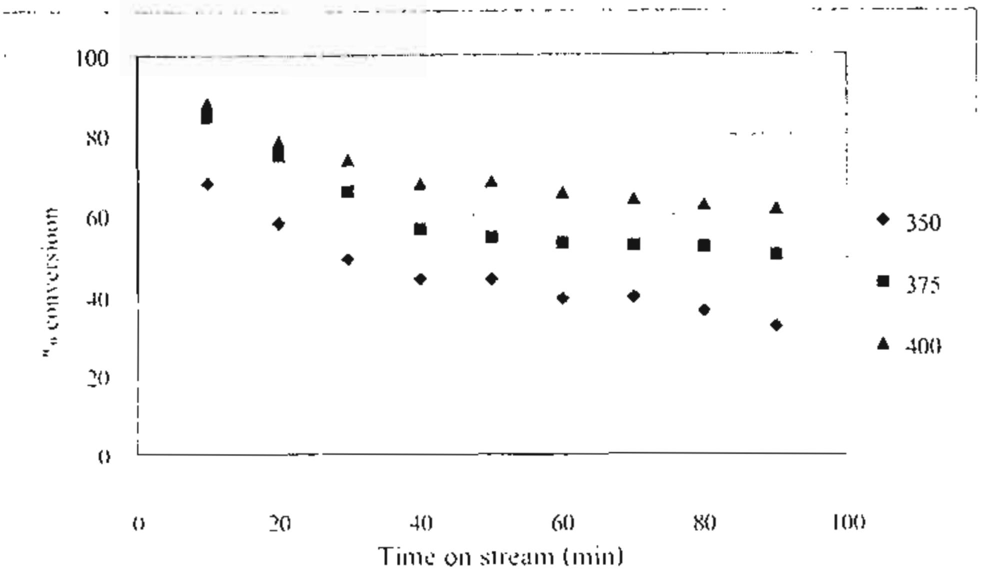


Figure 2.15 Effect of reaction temperature on the conversion of cyclohexanone oxime over Dealuminated Beta

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).

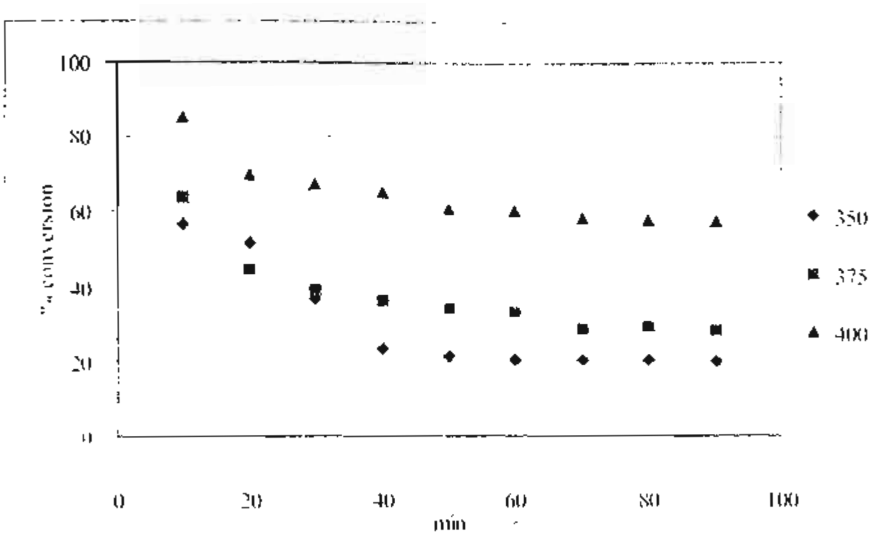


Figure 2.16 Effect of reaction temperature on the conversion of cyclohexanone oxime over Ti-Beta

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).

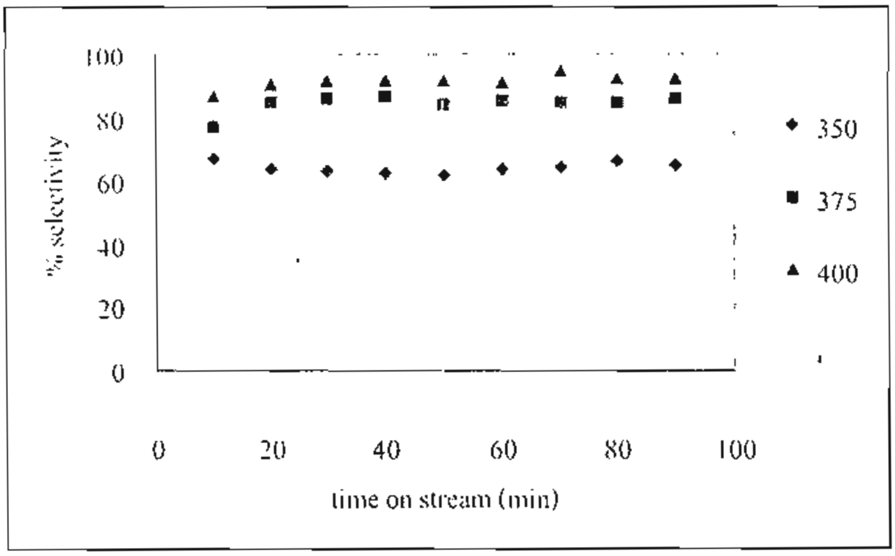


Figure 2.17 Effect of reaction temperature on the selectivity of caprolactam over H-Beta

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).

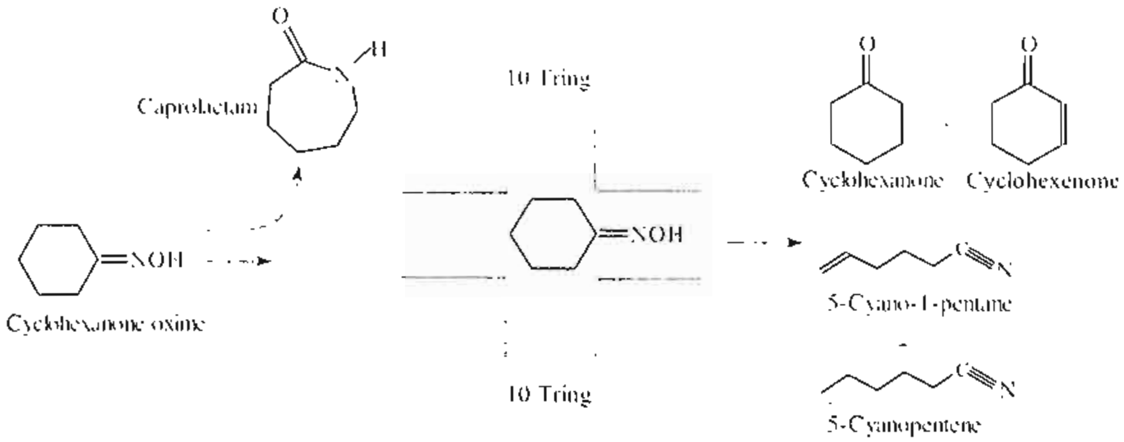


Figure 2.18 Show the reaction in the pore size of ZSM-5 zeolite catalyst

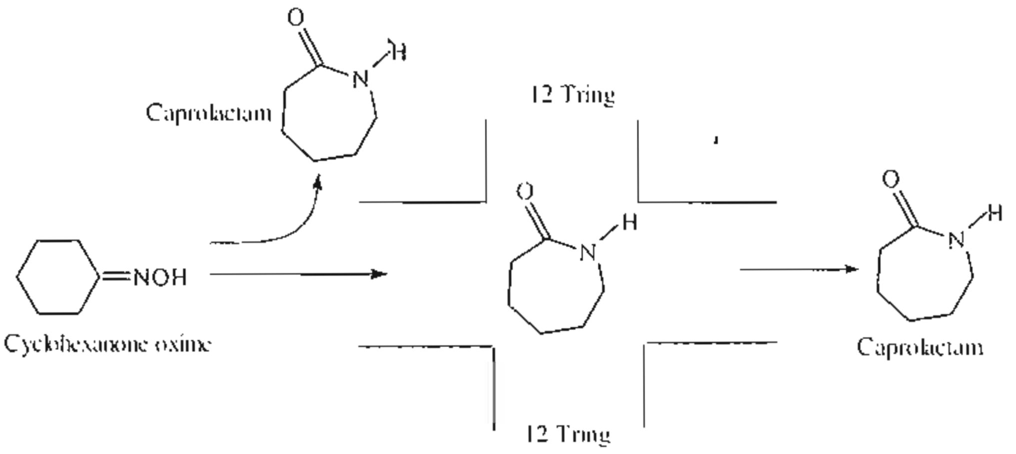


Figure 2.19 Show the reaction in the pore size of Beta zeolite catalyst

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.

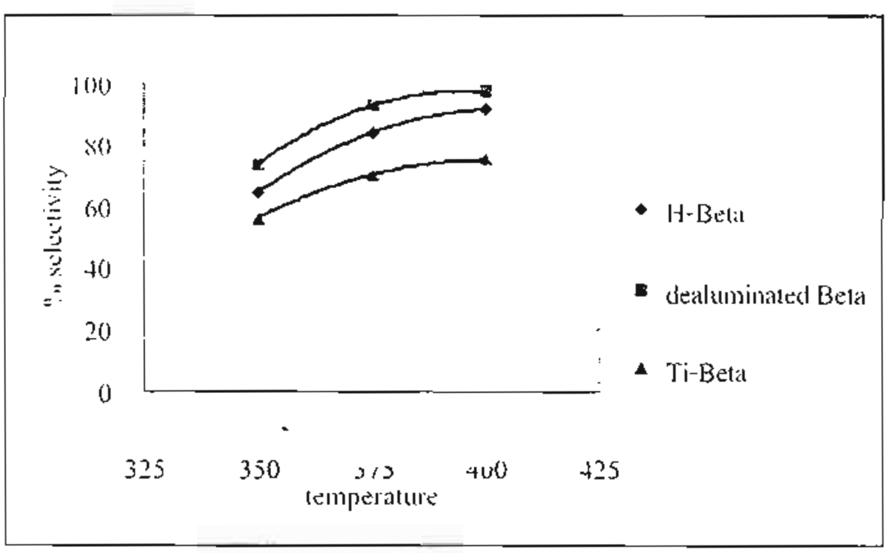


Figure 2.20 Effect of reaction temperature on the selectivity of caprolactam over H-Beta, Dealuminated Beta and Ti-Beta. *Reaction condition: pressure: 1 atm, W/F: 13.6* $g_{catalyst}\ h\ mol^{-1}_{reactant}$*, diluent: butanol, carrier gas:* N_2*, average time on stream: 10-90 min, temperature: 350,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

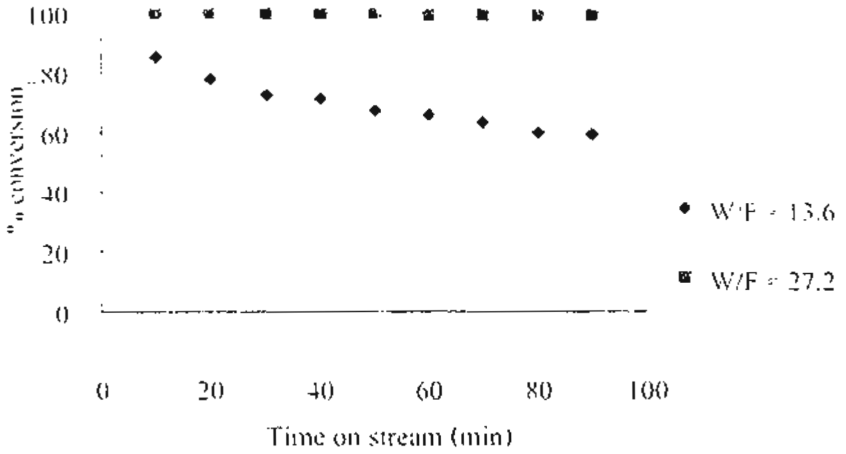


Figure 2.21 Effect of contact time on the conversion of cyclohexanone oxime over H-Beta
Reaction condition : temperature: 350 °C, pressure: 1 atm, diluent: butanol, carrier gas: N_2, *time on stream; 90 min, contact time: 13.6 and 27.2* $g_{catalyst}$ *h* $mol^{-1}_{reactant}$

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.

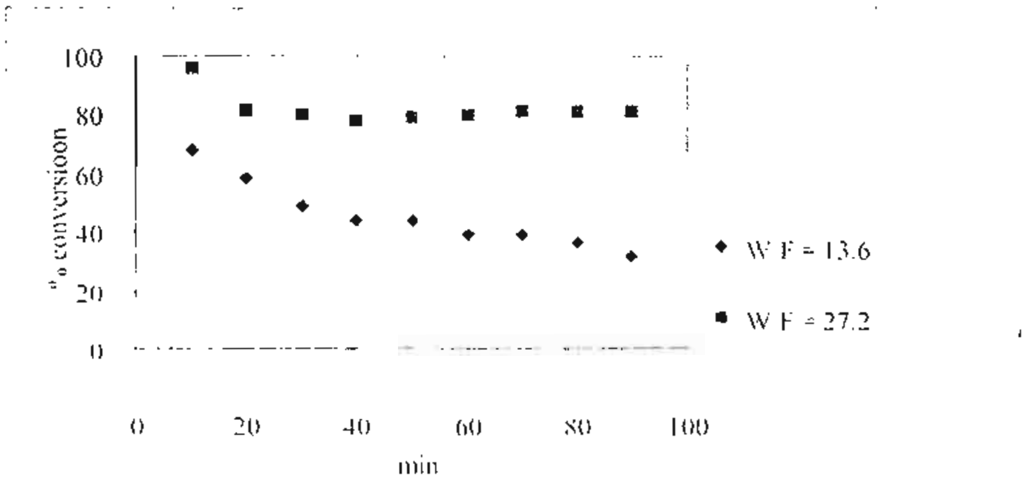


Figure 2.22 Effect of contact time on the conversion of cyclohexanone oxime over Dealuminated Beta

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 $g_{catalyst}\ h\ mol^{-1}_{reactant}$

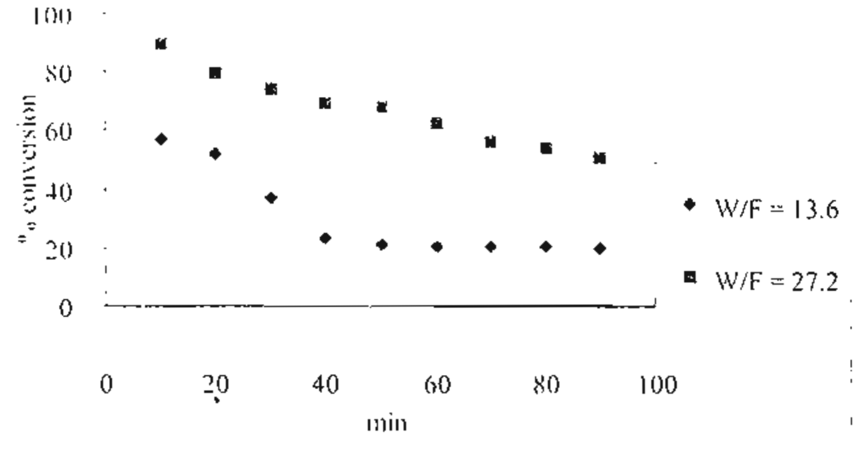


Figure 2.23 Effect of contact time on the conversion of cyclohexanone oxime over Ti-Beta

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).

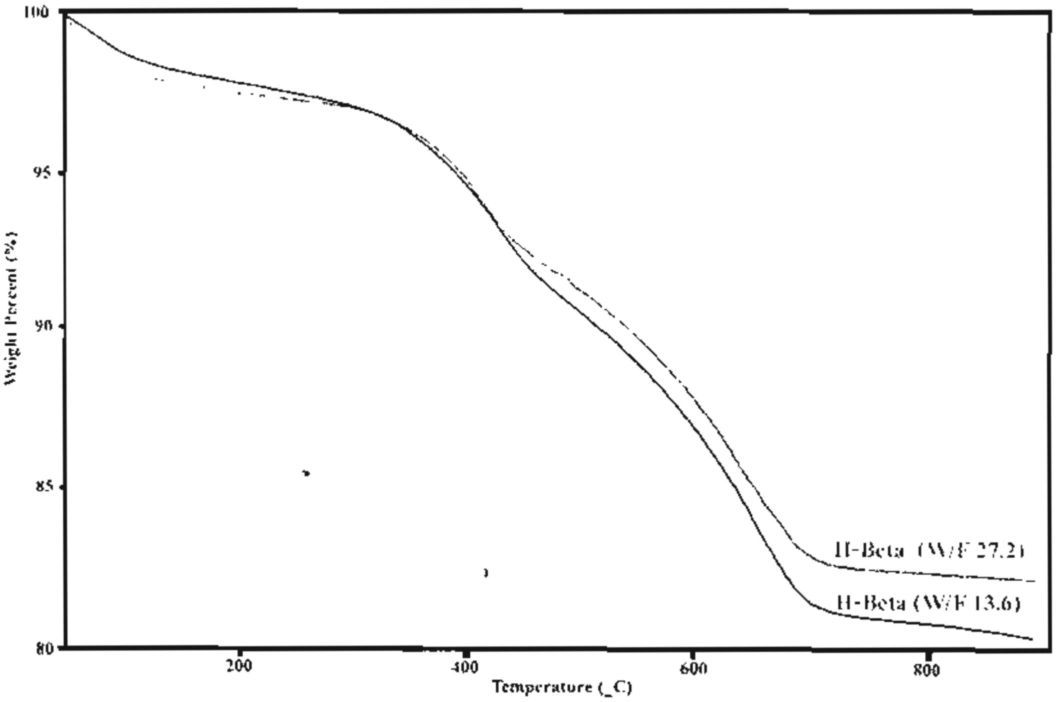


Figure 2.24 Thermogravimetric analysis of H-Beta used at different contact time

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.

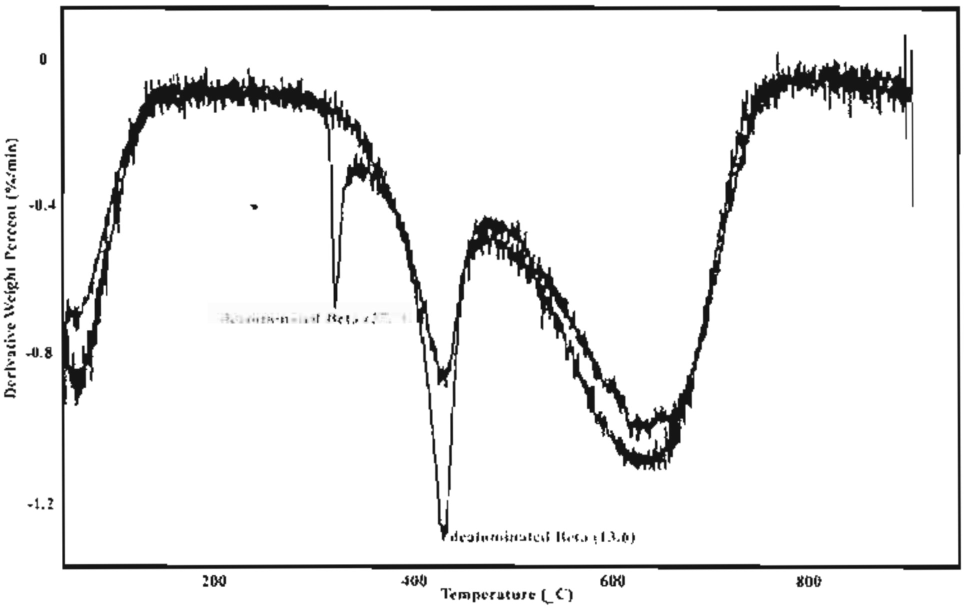


Figure 2.25 Thermogravimetric analysis of Dealuminated Beta with an increase in contact time

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.

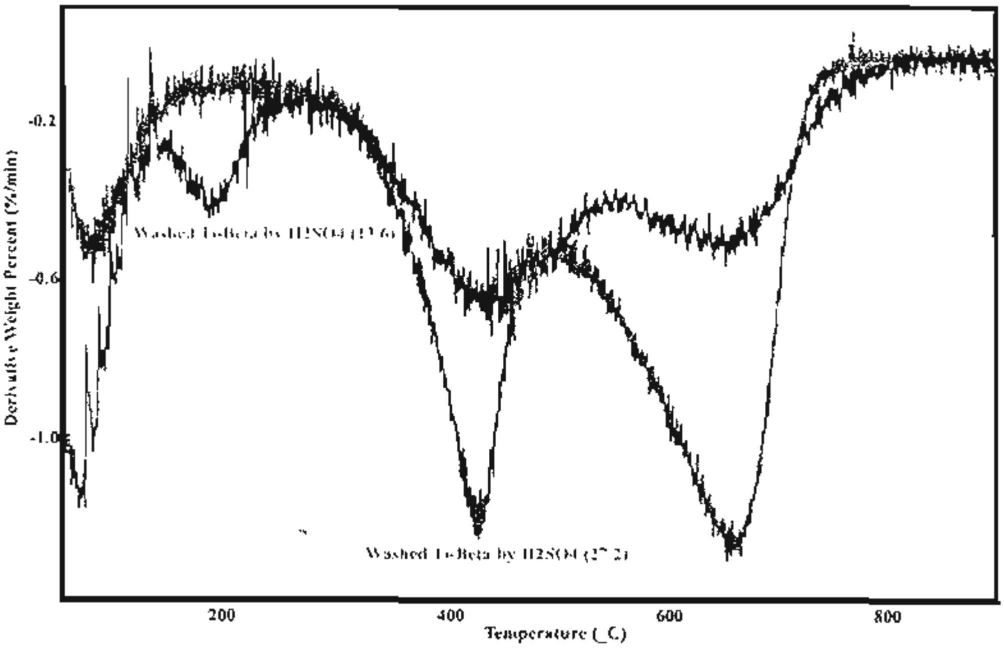


Figure 2.26 Thermogravimetric analysis of Ti-Beta with an increase in contact time

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).

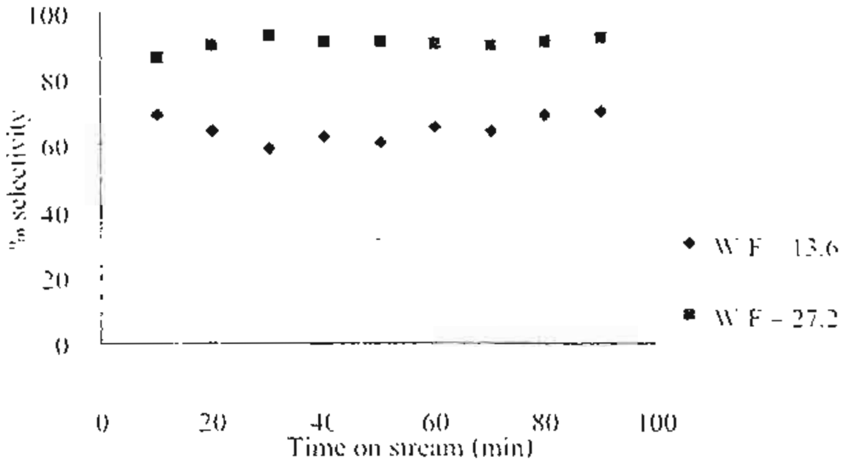


Figure 2.27 Effect of contact time on the selectivity of caprolactam over H-Beta

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.

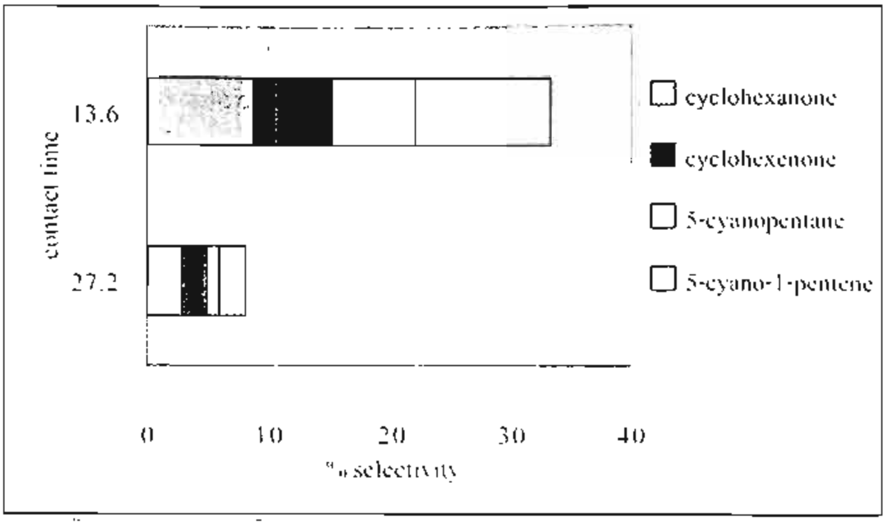


Figure 2.28 Effect of contact time on the selectivity of by-product over H-Beta

Reaction condition : temperature: 350 ^{o}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.

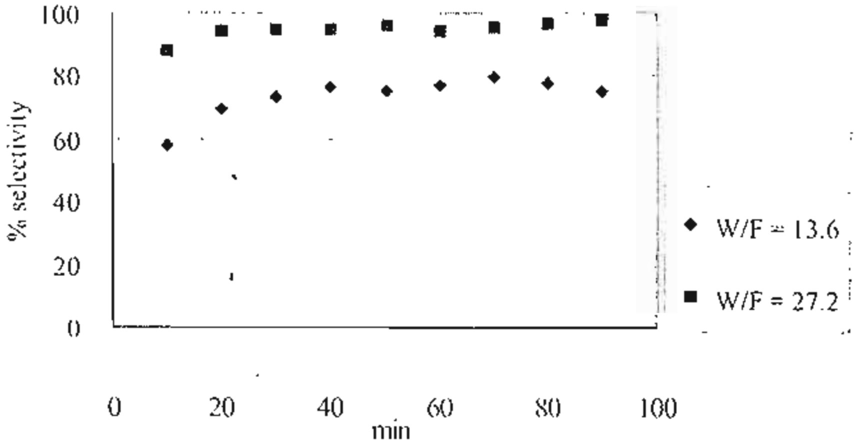


Figure 2.29 Effect of contact time on the selectivity of caprolactam over Dealuminated Beta

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

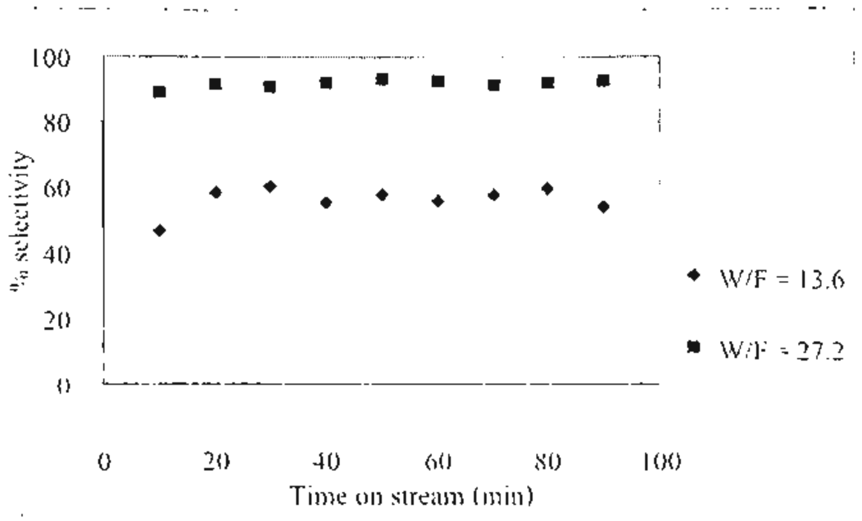


Figure 2.30 Effect of contact time on the selectivity of caprolactam over Ti-Beta

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).

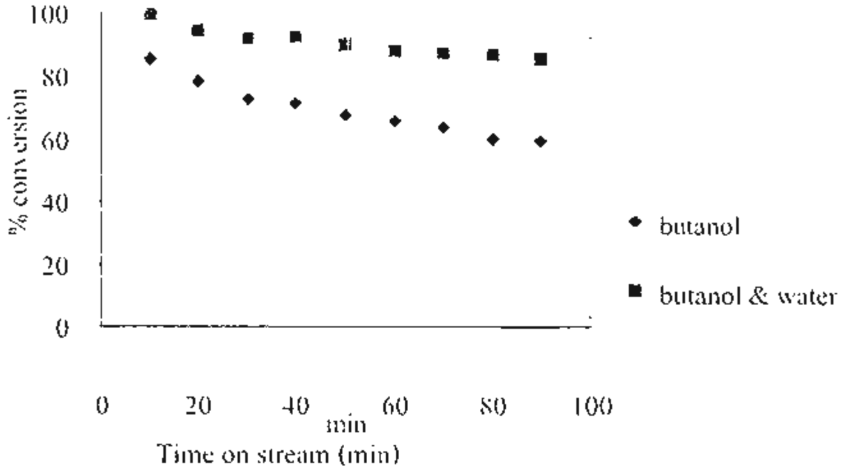


Figure 2.31 Effect of water added in solvent on the conversion of cyclohexanone oxime over H-Beta

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