Chapter 5

Beckmann Rearrangement Of Cyclohexanone Oxime

Most popular industrial route for the synthesis of ε-caprolactam, the starting material for the manufacture of nylon fibers, is through Beckmann rearrangement of cyclohexanone oxime. The environmental regulations and process safety continue to drive the industry to develop solid acids to replace liquid acid processes. The vapour phase Beckmann rearrangement of cyclohexanone oxime over the prepared nano sulfated titania catalysts is described in this chapter. The influence of the main process variables like reaction temperature, oxime feed rate, oxime to solvent molar ratio, reaction time, etc on the conversion and selectivity is investigated in detail. The catalytic performance of various systems for the reaction is correlated with acidity of the prepared systems. The acid sites of medium strength on the catalyst surface play an important role in the selective formation of lactam.

5.1 INTRODUCTION

Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam (Figure 5.1), which is the precursor to nylon-6, is now being carried out using fuming sulfuric acid as the catalyst[1]. However, this process yields the undesirable ammonium sulfate to a greater extent than the desired lactam. Moreover, the use of corrosive sulfuric acid should be avoided for environmental and economical reasons.
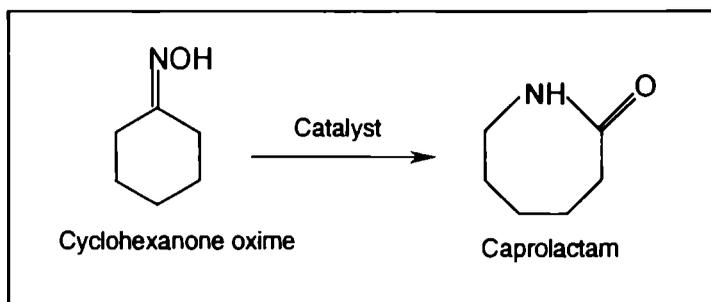
Figure 5.1 General scheme for preparation of caprolactam

There are numerous studies on the rearrangement of cyclohexanone oxime to ε-caprolactam over solid acid catalysts[1-11]. Since vapour-phase Beckmann rearrangement on solid catalyst would eliminate environmental problems, a wide variety of solid acid catalysts have been studied in search for an alternative clean process. Compared with the conventional method of preparation of ε-caprolactam, this is an energetically and economically favorable as well as environmentally friendly alternative route, since there is no inevitable salt formation of ammonium sulfate. The oxide supports used as catalysts are single metal oxides, such as alumina[2], silica[3,4], thoria[5], titania[6], zirconia[7,8] etc.

Corma and co workers[9,10] reported that on H-Na-Y Zeolite cyclohexanone oxime is converted to 5 cyanopent-1-ene. Sato *et al.*[11] found that the use of high siliceous ZSM-5, a catalyst with low acidity, leads to high selectivity of ε-caprolactam due to the smooth desorption of the same. Among the various solid acid catalysts, boron oxide supported on alumina was one of the successful catalysts, showing high lactam selectivity[4,12]. Various factors including catalyst preparation, reaction temperature and surface acidity were shown to have strong influence on oxime conversion, lactam selectivity and the decay rate of the catalysts[12,13]. In table 5.1, we cite some examples from the patents regarding vapour phase Beckmann rearrangement[14]. Till date, no report has been found in literature regarding the Beckmann rearrangement

catalyzed by sulfated titania systems. Nano sulfated titania and its modified forms are shown to be a new catalyst advantageous for the vapour phase Beckmann rearrangement of cyclohexanone oxime, as revealed by this study, which is explained in detail in the following sections.

Table 5.1 Some catalysts for the vapour phase Beckmann rearrangement

Patent assignee	Patent number	Year	Catalyst	Solvent	Conversion (%)
UPO	US4873325	1986	SAPO-11	Acetonitrile	98
Sumitomo	US4709024	1986	High silica MFI	Benzene	74
Sumitomo	US4968793	1989	High silica MFI	Methanol	99
Mobil	US4927924	1989	ZSM-5	Benzene	99
Mitsubishi	EP509493	1991	Ta_2O_5/SiO_2	Benzene	98
Degussa	DE19608660	1995	B-MFI	Methanol	99
Sumitomo	JP-291074	1996	ALPO-5	Ethanol	27
Enichem	EP819675	1996	Amorphous SiO_2/Al_2O_3	Methanol	99
Ube	JP10-87612	1996	Zeolite L	n-Hexanol	99

5.2 PROCESS OPTIMIZATION

The vapour-phase Beckmann rearrangement of cyclohexanone oxime was conducted under atmospheric pressure in a conventional continuous flow fixed bed type reactor. Exactly 0.5 g of the catalyst was placed using quartz wool in a pyrex glass reactor (inner diameter = 14 mm, length = 32 cm). It was heated by an electrical tubular furnace, and the temperature was controlled with a temperature controller with a sensor placed in the center of the catalyst bed. A mixture of oxime and benzene in the liquid phase supplied from a syringe pump at a constant flow rate was fed into the reactor. The effluents were collected in a trap and the liquid products were identified by gas chromatography using SE-30 column and FID detector. Among the various

products formed, only ε-caprolactam and cyclohexanone were estimated separately while all the remaining minor products such as 5-cyanopentane, 5-cyano-pent-1-ene and 2-cyclohexene-1-one were set aside under the banner 'others' during the calculation of selectivity.

I. Effect of Reaction Temperature

The influence of reaction temperature on the catalytic reaction was investigated in the range of 300 to 500°C. Figure 5.2 shows the dependence of oxime conversion and yield of ε-caprolactam and cyclohexanone with respect to temperature. The conversion is found to increase drastically as the temperature increases from 350 to 400°C. It was assumed that the deactivating compounds desorb more easily at elevated temperatures. At 400°C, the conversion of oxime is 97% with a ε-caprolactam selectivity of 48.54% at 3 h reaction time. On increasing the temperature to 500°C, the conversion reaches 100%, however the ε-caprolactam selectivity declines.

Anand *et al.*[15] has also reported similar results on the same reaction done over different ferrierite zeolites catalysts. The low selectivity of ε-caprolactam may be due to its decomposition at high temperature on the catalyst surface. Another reason suggested is an increased rate of side reaction at higher temperatures. Similar results were obtained over B_2O_3 catalysts supported on Al_2O_3[12,16], SiO_2[4] and ZrO_2[7]. At higher temperatures, the colour of the product solution changes to yellow due to the formation of side products. Murthy *et al.*[17] varied the temperature from 200 to 390°C for the rearrangement reaction over Ti-SAPO-11 catalyst and found that the oxime conversion and lactam selectivity increased with temperature. Above 390°C, selectivity to ε-caprolactam decreased, which was accounted for the decomposition of caprolactam on the catalyst surface.
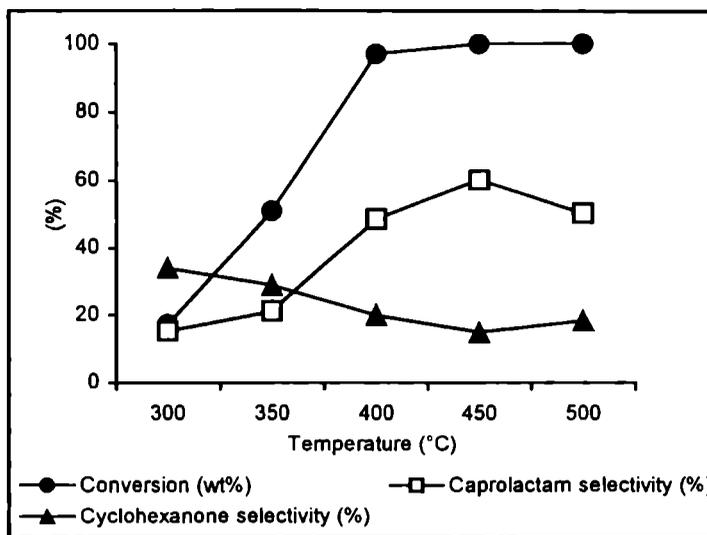
Figure 5.2 Influence of reaction temperature on oxime
conversion and product selectivity.

Amount of catalyst: 0.5 g STMn(3), Flow rate: 4 mL h^{-1}, Reaction time: 3 h,
oxime concentration in feed: 6 % in benzene

Mao *et al.*[18] reported that the conversion of oxime increased with increase in temperature and the selectivity to lactam is high at 300°C over B$_2$O$_3$/TiO$_2$-ZrO$_2$ catalyst. By comparing these results with the observations of the present work, we can conclude that the temperature has a positive effect on Beckmann rearrangement over transition metal loaded sulfated titania in the range of 300-450°C and above 450°C, the selectivity is affected adversely. The increase in cyclohexanone selectivity above 450°C suggests an increased rate of side reactions at higher temperature. The change in the product yield at higher temperature also supplements the formation of side products. The conversion of oxime and selectivity towards ε-caprolactam has a drastic increase at 400°C. Further increase in temperature, though increase the catalytic activity, does not improve the ε-caprolactam selectivity. 400°C is selected as the optimum reaction temperature for further investigations.

II. Effect of Flow Rate

Table 5.2 shows the influence of contact time on the catalytic activity and product selectivity. The flow rate alters the contact time and at high flow rate, the encounter of the reactants and the products with the catalyst surface will be less compared to that at lower feed rates. Progressive decrease in conversion of oxime is noticed with increase in the flow rate. The oxime conversion changes from 100 to 74.17% when we change the flow rate from 3 mL h^{-1} to 6 mL h^{-1}.

Table 5.2 Influence of flow rate on oxime conversion and product selectivity

Flow rate (mL h^{-1})	Conversion of Oxime (wt%)	Selectivity (%)		
		ε-caprolactam	cyclohexanone	others
3	100	40.67	19.58	39.75
4	97.06	48.54	20.08	31.38
5	90.57	51.39	22.62	25.99
6	74.17	49.77	25.74	24.49

Amount of catalyst: 0.5 g STMn(3), Reaction temperature: 400°C, Reaction time: 3 h, oxime concentration in feed: 6 % in benzene

As the contact time is decreased, selectivity increases initially, reaches a maximum and then decreases. The lactam selectivity shows an initial increase and at the flow rate of 5 mL h^{-1} and finally reaches a maximum of 51.39%. Decrease in the lactam selectivity was observed when feed rate is increased from 5 to 6 mL h^{-1}. Thus, the selectivity to caprolactam is maximum at a flow rate of 5 mL h^{-1} suggesting an optimum velocity of the feed for lactam formation. The formation of other products is less at higher feed rate because the reactants are in contact for less time and hence side reaction is suppressed. Thankaraj et al.[19] made similar observations on the effect of feed rate in vapour phase Beckmann rearrangement of cyclohexanone oxime over titanium silicates. For further studies 4 mL h^{-1} is taken as the flow rate, which showed a maximum yield of caprolactam under the experimental conditions.

III. Effect of Concentration of Cyclohexanone Oxime

In order to understand the effect of the concentration of oxime in the feed, a series of experiments were conducted at reaction temperature of 400°C and at a flow rate of 4 mL h^{-1} by varying the oxime concentration from 2 to 8% (w/v). It can be seen from table 5.3 that the dilution of cyclohexanone oxime in benzene improves the conversion of oxime. At low oxime concentration (2%) the yield of caprolactam is high (63.77%). As the concentration increases the yield of ε-caprolactam decreases. At high oxime concentration the formation of by-products is high.

Table 5.3 Influence of oxime concentration on oxime conversion

and product selectivity

Oxime concentration in benzene (%)	Conversion of Oxime (wt%)	ε-caprolactam		cyclohexanone	
		Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)
2	100	63.77	63.77	15.99	15.99
4	99.05	51.97	51.47	18.43	18.25
6	97.06	48.54	47.11	20.08	19.49
8	91.36	41.16	37.60	21.44	19.59

Amount of catalyst: 0.5 g STMn(3), Flow rate: 4 mL h^{-1}, Reaction time: 3 h,

Reaction temperature: 400°C

IV. Effect of Solvent

Solvents with varying polarities (like benzene ethanol and acetonitrile) are utilized to investigate their influences on the catalytic activity and the product selectivity. Both the oxime conversion and ε-caprolactam selectivity are affected by the nature of the solvent. Roseler *et al.*[20] have reported the deactivation of MFI borosilicate in the Beckmann rearrangement of

cyclohexanone oxime using different organic solvents and found that the degree of deactivation depends on the kind of solvent used. This is due to the difference in the polarity of solvents.

Table 5.4 shows the influence of solvent for the reaction of cyclohexanone oxime on STMn(3) catalyst. There is not any appreciable change in the conversion, but the selectivity of ε-caprolactam is influenced by the type of solvent used. The selectivity increases as the dipole moment of the solvent increases. The selectivity in presence of benzene (dipole moment = 0) was low (48.54%), selectivity in presence of ethanol (dipole moment = 1.44) was 54.79% while selectivity in presence of acetonitrile (dipole moment = 3.92) was high (59.21%). The most likely reason for this is that the polar solvents increase the desorption rate of lactam, decreasing its contact time on the catalyst surface, thus lowering the likelihood for acid catalyzed opening of lactam to form polymers and the coke precursors on the catalyst surface. Chung *et al.*[21] studied the solvent effects in the liquid phase Beckmann rearrangement of oxime over H-Beta catalyst. The nature of the solvent determines the performance of the reaction. The stronger the solvent-adsorption site interaction, the more difficult will be the access of the reactant to the active sites. This may lead to a decrease in the catalytic activity.

According to Ko *et al.*[22] ethanol dehydrates to ethylene, diethyl ether and water over the Al-MCM-41 catalyst under the reaction conditions and, during the reaction, the water produced suppresses the formation of coke on the catalyst surface. Our studies also show the formation of water during the reaction, when we use ethanol as the solvent. The positive effect of water on preventing deactivation was verified in the oxime conversion using B-MFI zeolites[20]. Komatsu *et al.*[23] have reported that the solvent with medium polarity was preferable for this reaction on silicalite-1. In our studies solvent effect is not much pronounced, as the selectivity does not vary much among the different solvents.

Table 5.4 Influence of various solvents for oxime conversion
and product selectivity

Solvent	Conversion of Oxime (wt%)	Selectivity (%)		
		ε-caprolactam	cyclohexanone	others
Acetonitrile	98.56	59.21	22.95	17.84
Ethanol	97.95	54.79	21.40	23.81
Benzene	97.06	48.54	20.08	31.38

Amount of catalyst: 0.5 g STMn(3), Flow rate: 4 mL h^{-1}, Reaction time: 3 h, Reaction
temperature: 400°C, oxime concentration in feed: 6 % in the solvent

V. Effect of Time on Stream-Deactivation study

To establish the stability of the systems towards deactivation, a continuous
7 h run was carried out over various catalysts and the products were analyzed
after every one hour. From figure 5.3, it is clear that the oxime conversion
remains almost constant until 5 h of reaction time in the case of T and ST.

Deactivation rate is different for different systems. The conversion of oxime
already began to decrease at a time on stream of 5 h in the case of T and ST.
On the other hand, the complete oxime conversion was maintained until 5 h over
the metal loaded sulfated titania. Fe, Co, Ni, Cu and Zn loaded systems show an
initial increase in conversion for the first 3 h and after 5 h of reaction time they
deactivates slowly. Two main mechanisms have been suggested for the
deactivation of solid acid catalysts in the rearrangement of oxime, namely the
formation of coke[2,24,25] over the catalyst surface and/or the irreversible adsorption
of basic reaction by-products[10]. Corma and co-workers[9,10] reported that organic
bases such as pyridine suppress the conversion of cyclohexanone oxime on
H-Na-Y zeolites. Ushikubo[26] reported that the total pore volume and pore volume
of fine pores decreased considerably due to coke formation. Ko *et al.*[22]
characterized the used catalysts (Al-MCM-41) and found a small variation in their

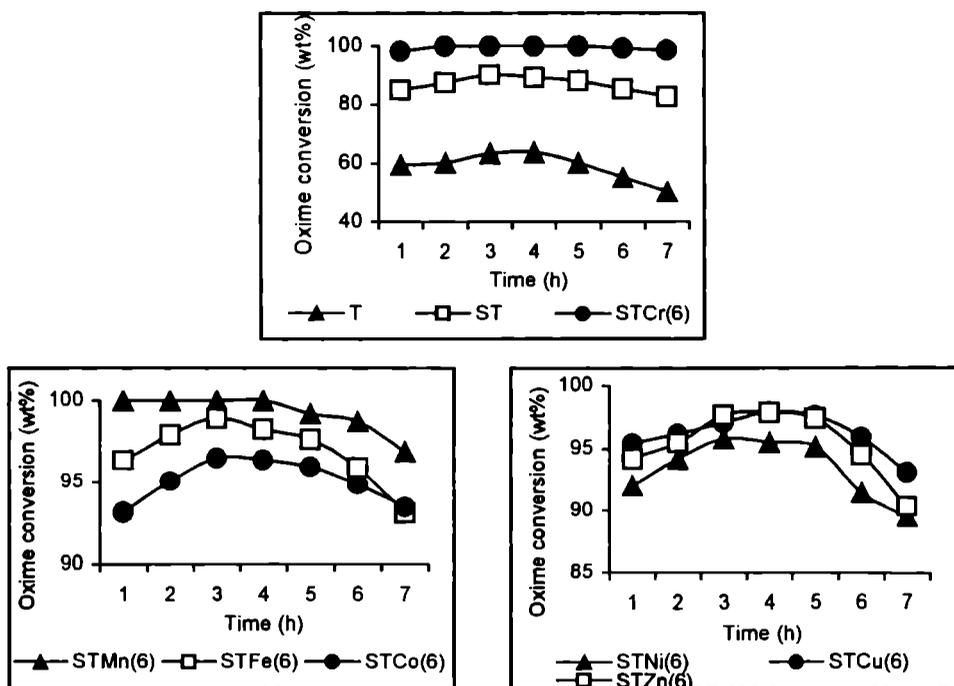acidities and a decrease in he surface area and pore volume, which may be due to pore blockage by coke formation.

Figure 5.3 Deactivation studies on oxime conversion over different systems

Amount of catalyst: 0.5 g, Reaction temperature: 400°C, Flow rate: 4 mL h^{-1}, oxime concentration in feed: 6 % in benzene

The present investigation is consistant with the possibility of coke formation over the catalyst surface, which can be correlated with the significant decrease of oxime conversion over 7 h. The coke deposition may be due to the eventual formation of carbonaceous deposits resulting from the reaction between the side products or arise from the polymerization of caprolactam[27]. The colour of the catalysts changed to dark grey or black due to coke deposition on the surface of the catalysts. The catalytic activity reached an equilibrium level after 3 to 4 h and hence all the experimental data were obtained after the stabilization of the activity.

5.3 COMPARISON OF DIFFERENT SYSTEMS

A comparative evaluation of the catalytic activity of various sulfated titania systems in the vapour phase Beckmann rearrangement is given in this section. After analyzing the optimization results, catalytic activity of the systems were studied under the following conditions, temperature - 400°C, flow rate - 4 mL h^{-1}, oxime concentration - 6% in benzene and time on stream - 3 h. Sulfation and metal loading improved the activity of tiania to a considerable extent. An attempt to correlate the surface acidity with oxime conversion and ε-caprolactam selectivity is also done. Tables 5.5 and 5.6 present the results of the vapour phase Beckmann rearrangement of cyclohexanone oxime over different transition metal loaded sulfated titania systems.

Table 5.5 Influence of the type of metal loaded in the vapour phase
Beckmann rearrangement of cyclohexanone oxime

Systems	Conversion of Oxime (wt%)	ε-caprolactam		cyclohexanone		Selectivity to others (%)
		Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	
T	63.45	20.43	12.96	16.97	10.77	62.60
ST	90.36	41.13	37.17	24.65	22.27	34.22
STCr(3)	98.41	54.41	53.54	19.43	19.12	26.16
STMn(3)	97.06	48.54	47.11	20.08	19.48	31.38
STFe(3)	96.23	42.08	40.49	20.85	20.06	37.07
STCo(3)	94.14	43.84	41.27	19.18	18.06	36.98
STNi(3)	92.00	47.92	44.09	22.77	20.95	29.31
STCu(3)	95.08	46.53	44.24	17.64	16.77	35.83
STZn(3)	95.69	45.00	43.06	18.24	17.45	36.76

Amount of catalyst: 0.5 g, Flow rate: 4 mL h^{-1}, Reaction time: 3 h, Reaction temperature: 400°C, oxime concentration in feed: 6 % in benzene

From the results of NH_3-TPD as well as cyclohexanol decomposition reaction, it is understood that the catalysts possess acidic character. These acid sites are strong enough to catalyze Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. From table 5.5, it is clear that titania in the pure form is much less active in this rearrangement. Also it results in the formation of unwanted products to a greater extent. Sulfated titania and transition metal loaded sulfated titania systems are very active towards the reaction along with increased selectivity for ε-caprolactam.

Table 5.6 Influence of the amount of metal loading in the vapour phase Beckmann rearrangement of cyclohexanone oxime

Systems	Conversion of Oxime (wt%)	ε-caprolactam		cyclohexanone		Selectivity to others (%)
		Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	
STCr(6)	100.00	57.88	57.88	22.25	22.25	19.87
STMn(6)	100.00	56.10	56.10	26.16	26.16	17.74
STFe(6)	98.93	46.84	46.34	24.23	23.97	28.93
STCo(6)	96.55	50.32	48.58	23.54	22.73	26.14
STNi(6)	95.84	52.21	50.04	25.14	24.09	22.65
STCu(6)	97.10	51.89	50.39	25.59	24.85	22.52
STZn(6)	97.68	51.10	49.91	25.3	24.78	23.53
STCr(9)	89.56	50.84	45.53	23.58	21.12	25.58
STMn(9)	89.03	49.08	43.70	21.93	19.52	28.99
STFe(9)	88.36	44.03	38.90	18.18	16.06	37.79
STCo(9)	86.81	44.92	39.00	25.11	21.80	29.97
STNi(9)	86.59	46.83	40.55	19.47	16.86	33.70
STCu(9)	87.14	46.00	40.08	21.59	18.81	32.41
STZn(9)	87.95	45.73	40.22	19.42	17.08	34.85

Amount of catalyst: 0.5 g, Flow rate: 4 mL h^{-1}, Reaction time: 3 h, Reaction temperature: 400°C, oxime concentration in feed: 6 % in benzene

As the metal loading increases from 3 to 6% the oxime conversion is found to increase (Tables 5.5 and 5.6). However it is found that high metal content of 9%, decreases the oxime conversion. Among all the catalysts, the maximum selectivity to ε-caprolactam formation is 57.8% for system with 6% chromia loading. All the sulfated systems show more than 85% conversion. In the case of STCr(6) and STMn(6) the conversion reaches 100%.
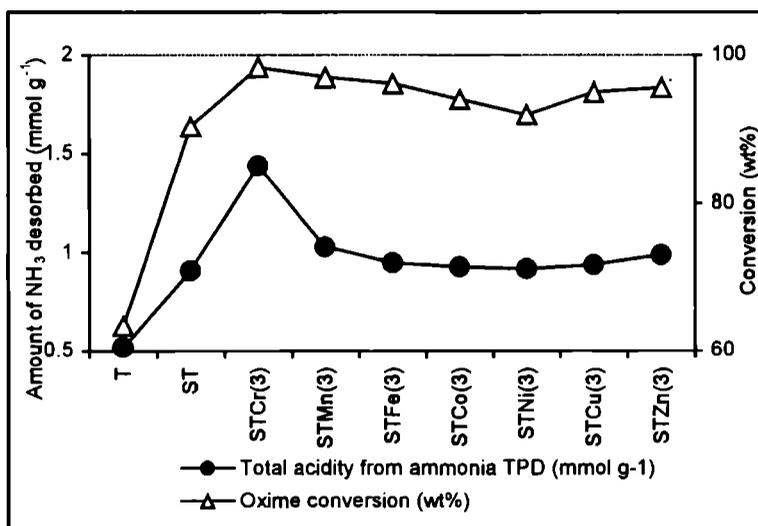

Figure 5.4 Correlation between oxime conversion and total acidity

As Beckmann rearrangement is considered as an acid catalysed reaction, an attempt has been made to obtain a correlation between the acidity and the oxime conversion. As seen from NH_3-TPD studies, the metal loading affects their acidity remarkably. The concentration of acid sites (per m^2 of catalyst) on the surface and the extent of metal loading show a direct relationship. As the metal content increases, the total concentration of acid sites increases initially, but at high loadings acidity decreases. Activity results revealed that a maximum oxime conversion was obtained at a loading of 6 wt% and lactam selectivity got saturated when the metal loading was more than 6 wt%. These results suggested that the activity and selectivity of the catalysts

depend on their acid strength distribution. Figures 5.4 and 5.5 show the correlation between oxime conversion and total acidity obtained from NH_3-TPD.
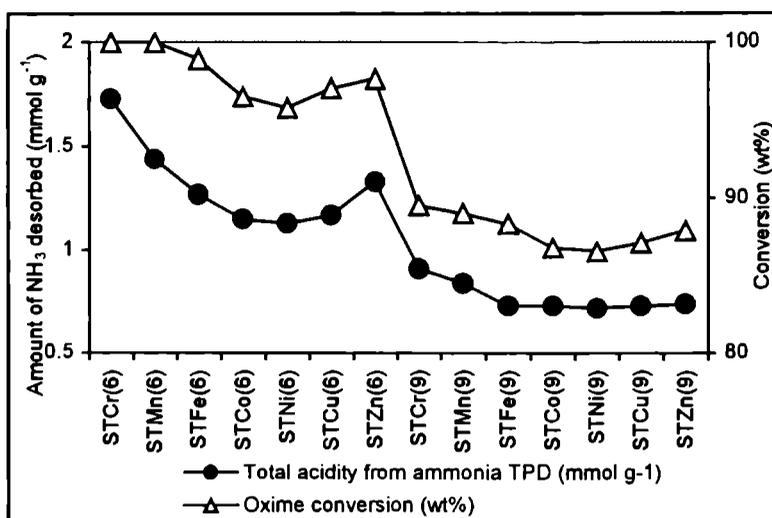

Figure 5.5 Correlation between oxime conversion and total acidity

Xu et al.[29] reported that the active sites for Beckmann rearrangement are the medium and strong acid sites on the surface of B_2O_3/ZrO_2 catalysts. Dai et al.[30] studied the catalysis of H-USY zeolites and showed that an appropriate amount of relatively weak acid sites of H-USY was effective for a high selectivity of lactam. The results of our investigation also show that the oxime conversion depends on the total acidity of the systems, while the lactam selectivity depends on medium acid sites as obtained from NH_3-TPD method. Figures 5.6 and 5.7 show the correlation between ε-caprolactam selectivity and medium acidity obtained from NH_3-TPD. Medium acid sites govern the formation of ε-caprolactam. The good agreement between NH_3-TPD results and conversion suggests that all the surface acid sites irrespective of their strength, take part in the rearrangement reaction. The higher conversion of the sulfated titania and metal loaded sulfated titania catalysts may be due to the substantial amount of strong acid sites on the surface.
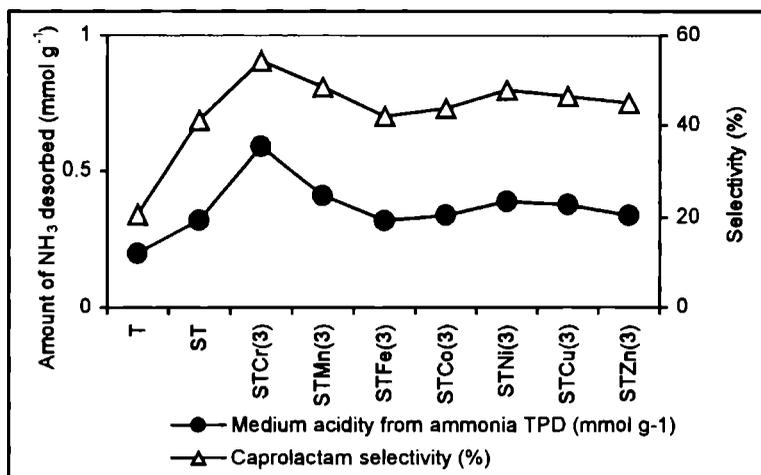
Figure 5.6 Correlation between ε-caprolactam selectivity and medium acidity
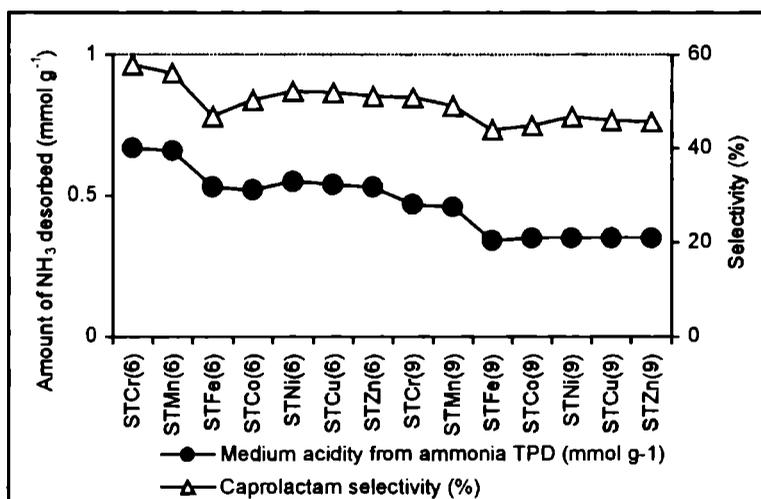
Figure 5.7 Correlation between ε-caprolactam selectivity and medium acidity

5.4 MECHANISM OF BECKMANN REARRANGEMENT REACTION

The mechanism of the liquid phase Beckmann rearrangement promoted by sulfuric acid is well known as a typical concerted intermolecular SN2 reaction

where the alkyl group in *anti* position migrates against the OH of the oxime group[31]. The mechanism of Beckmann rearrangement is shown in figure 5.8.
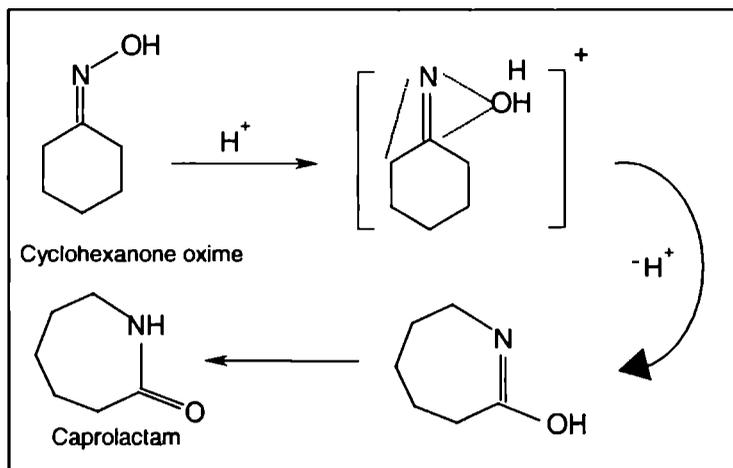

Figure 5.8 Suggested mechanism for Beckmann rearrangement of cyclohexanone oxime
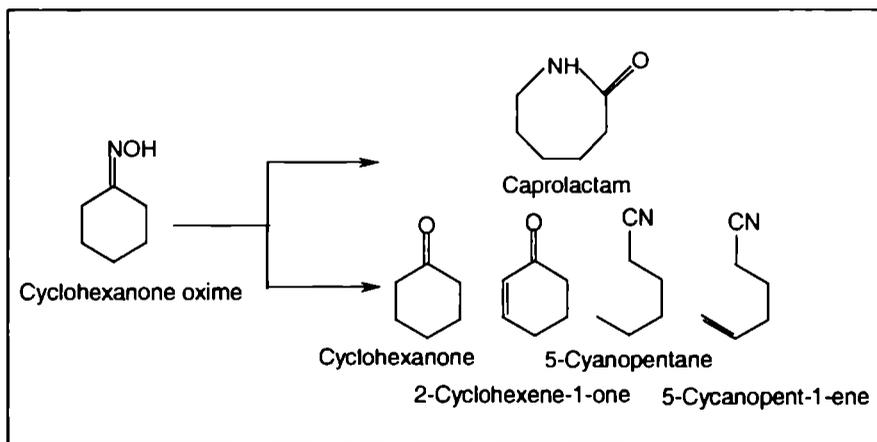

Figure 5.9 Reaction scheme for Beckmann rearrangement of cyclohexanone oxime

The reaction conditions are quite different for liquid and vapour phase. Kajikuri *et al.*[32] concluded that the mechanism of the vapour phase Beckmann rearrangement reaction is the same as in liquid phase. The major product of

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the reaction is ε-caprolactam, while minor quantities of 5-cyanopentane, 5-cyanopent-1-ene, cyclohexanone and 2-cyclohexene-1-one are also formed as side products[33] in the rearrangement of cyclohexanone oxime. The reaction scheme is presented in figure 5.9.

5.5 CONCLUSIONS

The following conclusions can be drawn from the present study.

- Transition metal loaded sulfated titania systems are found to be active for the Beckmann rearrangement reaction.

- Chromia loaded systems are found to be better catalysts than others among the investigated catalyst systems.

- Acid sites of intermediate strength play important role in the selective formation of lactam.

- Reaction variables such as reaction temperature, flow rate, solvent, reaction time and oxime concentration have strong influence on the oxime conversion and ε-caprolactam selectivity.

- Conversion of oxime increased with increase in temperature, and the highest selectivity to lactam was obtained at an optimum reaction temperature of 400°C.

- Polar solvents give higher selectivity to lactam than other solvents. Catalysts get deactivated after 5 h due to coke formation, which may block the active sites.

- The acidic and catalytic property of the catalyst was found to be affected by the percentage of metal loading. Catalysts with optimum metal loading of 6 wt%, which contained the maximum number of medium strength acid sites, shows good selectivity towards ε-caprolactam.

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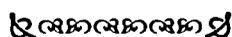
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