

# **The study on exact *nature* and *location* of active sites for Beckmann rearrangement of cyclohexanone oxime to caprolactam.**

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## **Introduction**

Beckmann rearrangement of cyclohexanone oxime to caprolactam is one of the industrially important reactions. The caprolactam is a high demanding raw material for the synthesis of nylon 6 fibers and resins in the polymer industries. Conventional route for the synthesis of caprolactam is from benzene using sulphuric acid as catalyst. High toxicity, non reusability and high yield of byproduct (ammonium sulphate) associated with sulphuric acid, made it an unattractive Process[1]. In order overcome the following problems heterogeneous solid acid catalysts have been designed and developed for the following reaction. Beckmann rearrangement is an acid catalyzed reaction, a large number of heterogeneous solid acid catalysts like SAPO-11, zeolite L, Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>, ALPO-5, amorphous SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> tin oxide, Cs exchanged phosphotungstic acid, WO<sub>x</sub>/SBA-15 , Nb MCM-4 have been applied .

Among the following catalysts zeolites are one of the promising catalysts for Beckmann rearrangement. A bunch of work has been done using zeolites like MFI, ZSM-5, Silicalite-1 and beta, with high activity for the Beckmann rearrangement. Even though lot of research is done, the exact nature and location of active sites required for the Beckmann rearrangement is uncertain. There is still a strong argument for the location of active site in zeolite. Whether reaction takes place inside the zeolite pore, on the surface of zeolite or at the pore mouth of zeolite. Many researchers have reported the relationship between the vapor phase Beckmann rearrangement and nature of acid sites of the catalyst. Based on that, the nature of active sites required is also not clear, should it be strong, medium, weak or very weak acid sites.hence an overview over the following topic is presented in the following paper.

Study on non-zeolitic catalysts like Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> [2], SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>[3], WO<sub>3</sub>/SiO<sub>2</sub>[4], B<sub>2</sub>O<sub>3</sub> on support like ZrO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>[5] has been discussed and nature of active is determined in all the case. Study of Beckmann rearrangement over various zeolites like ZSM-5[6], Silicalite[6], USY[7] Mordenite has been illustrated and focus is put to clarify the nature and location active sites

## Experimental

### 1. Materials Preparation

$\text{WO}_3/\text{SiO}_2$  is prepared by adding 80-200 mesh silica gel to 0.5 mmol of  $\text{WCl}_6$  per gram of silica in carbon tetrachloride. The solid product is treated with the 1M nitric acid, then washed with deionized water and finally dried in flow of air at 200°C.

Boria on alumina is prepared by wet impregnating alumina and appropriate boric acid dissolved in warm distilled water to give 2,5,7,10,14,29 wt% boria loadings. After stirring for 2 hr, excess water is evaporated and the slurry was dried at 120 C. Finally all catalysts were calcined for 3 hr at 350C.

Boria on alumina is also prepared by the chemical vapor deposition of boron ethoxide at 200-350°C for 1-10 hr.

The boria supported over  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  are prepared by incipient wet impregnation method using aqueous solution of boric acid. the supports were calcined at 500C for 8 hr before loading of boria. details of catalyst are given in reference.

$\text{Ta}_2\text{O}_5/\text{SiO}_2$  (IMP) is prepared by impregnation of silica with 1M HCl solution containing 1wt%  $\text{TaCl}_5$ . preparation method in case of  $\text{Ta}_2\text{O}_5/\text{SiO}_2$ (ALk) is same instead of  $\text{TaCl}_5$ , tantalum alkoxide solution is added to the silica.

$\text{SiO}_2$  supported  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  are prepared by chemical vapor deposition of tetraethyl silane.

The high siliceous zeolite is synthesized by is synthesized by solid phase method and Homogeneous phase method according to literature.

### 2. Catalyst characterization

The Phase purity and crystallinity of catalysts are done by X Ray Diffractometer (XRD). The Acidity measurement is carried out using temperature programmed desorption (TPD) Method. The Catalyst morphology on the surface of catalyst is measured by Scanning Electron microscopy. The binding energy of the material on support will be measured by XPS instrumentation. Different kind of Silanol groups present on zeolite is determined by FTIR spectroscopy. The product analysis is done gas chromatography.

### 3. Catalytic reaction

The Beckmann rearrangement is carried out in vapor phase down flow reactor with carrier liquid (alcohols) at temperature range of 300°C to 400°C. But 350°C is found to be optimized temperature for the reaction. The Other Reaction conditions like Weight of catalyst, WHSV, Reactant: alcohol ratio are set in such way to get high conversion and selectivity for the reaction.

## Results and discussions

### a. Beckmann rearrangement over the non zeolitic catalysts;

The acidity of  $WO_3/SiO_2$  catalyst measured by calorimetric and adsorption analysis showed presence of strong Brönsted acid sites, generated during anchoring of tungsten moiety over silica. Due to strong acid sites high activity and selectivity is obtained for the Beckmann rearrangement. During the 24 hr of reaction time, the conversion remained almost constant 99%, but the selectivity decreased gradually leading to deactivation of catalyst. The deactivated catalyst is regenerated in air at  $500^\circ C$  for 6 hr. The regenerated catalyst failed to show the performance as that of fresh catalyst. The results of fresh and regenerated catalyst are given in table-1.

TABLE-1.

Reaction time	<u>Fresh catalyst</u> Selectivity of caprolactam	<u>Regenerated catalyst</u> Selectivity of caprolactam
10 hr	90%	85%
10-20 hr	78%	69%
20-24 hr	60%	53%

The decrease in selectivity for the fresh catalyst is due to the formation of coke precursors. Elemental analysis of catalyst after reaction showed the presence of 9.3% carbon and 1.1% of nitrogen which suggest might have formed by the pyrolysis and polymerization of caprolactam. The formation of coke over the catalyst slowly blocks the strong Brönsted acid sites leading to the lower selectivity. This indicates strong acid sites are responsible for high selectivity of the caprolactam in Beckmann rearrangement, but not the weaker one. The reason for low selectivity in regenerated catalyst is due to loss of active sites during the calcination step. The SEM images showed the calcinations of catalyst at  $500^\circ C$  leads to agglomeration of tungsten moieties over the silica during which active sites of the catalyst are killed. The SEM images of fresh and regenerated catalyst is as shown in figure 1.

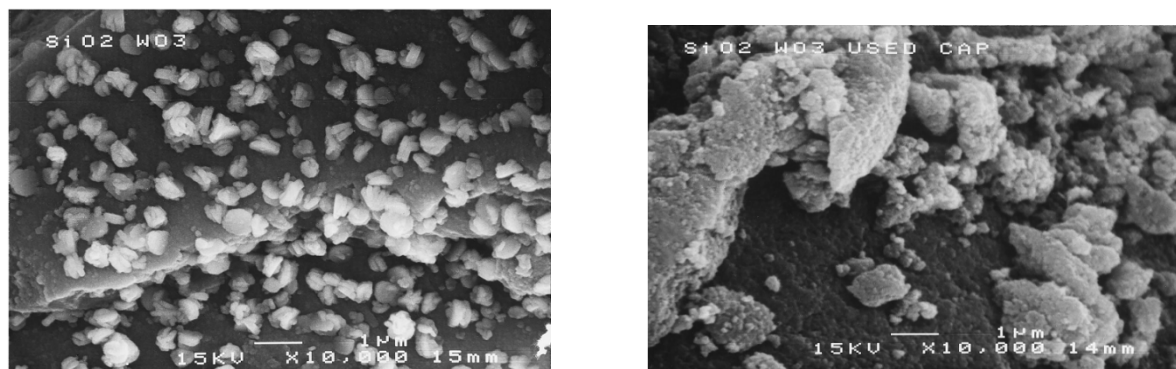


Fig-1. a) Fresh catalyst b)Regenerated catalyst.

Curtin et al studied Beckman rearrangement over  $B_2O_3/Al_2O_3$  catalyst prepared by impregnation method, and proposed the medium acid strength sites are required for the reaction. The increased boria loading on  $Al_2O_3$ , continuously shifted the desorption peak maximum to higher temperature, indicating increase in acid strength with increase amount of boria on alumina, as seen from TPD profile of ammonia (fig-2 B)

The conversion of cyclohexanone oxime decreased with time on stream for all the loading of boria on alumina catalyst. The alumina with 20% of boria loading, gave high conversion and selectivity as compared to lower loadings of boria. The decrease in conversion was rapid in case of lower loadings due to presence of weak acid strength which can be seen from the fig-2 (A).

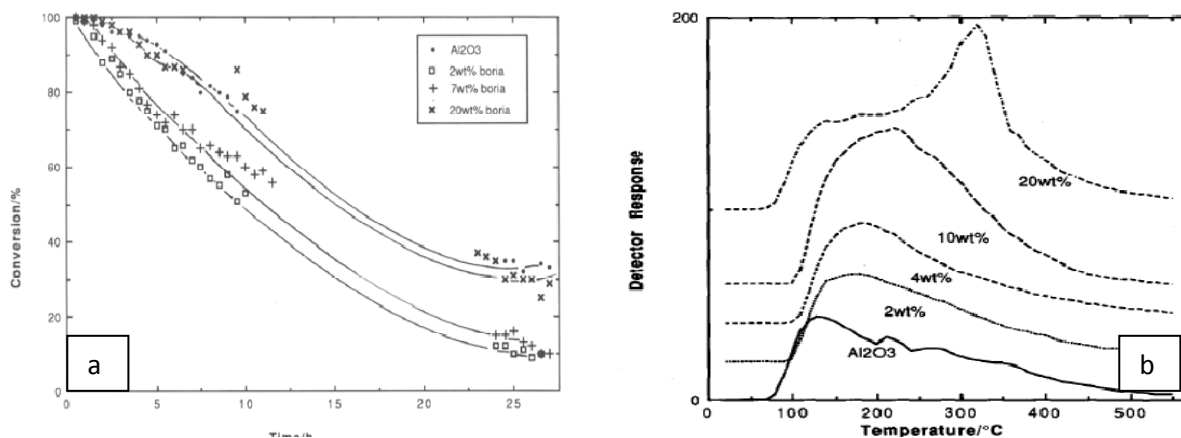


Fig-2 a) Conversion Oxime with time. b) TPD profile of ammonia.

The high conversion and selectivity for 20 wt% boria loaded alumina is attributed to the presence of medium acid strength sites and increased number of acid sites. The reaction is carried out using different boria loaded alumina catalyst for 27 hour and catalyst is analyzed for the coke content by measuring weight loss of catalyst heated over temperature 20-700°C. The results are as shown in Fig-3

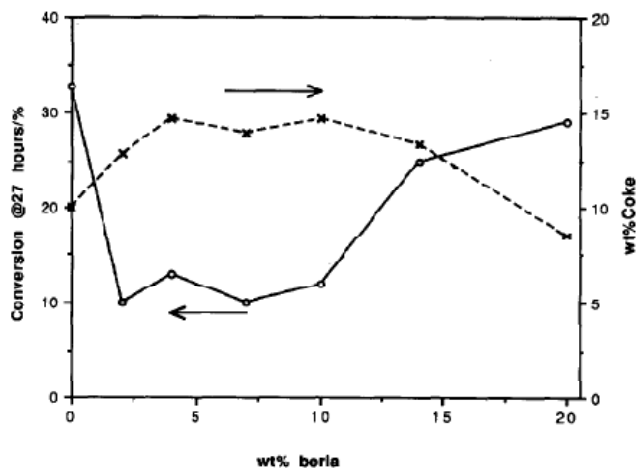


Fig-3 Formation of coke over different boria loaded alumina catalyst.

From the fig-3, it is clear that higher loading of boria on alumina showed less coke formation indicating high stability of  $B_2O_3/Al_2O_3$  catalyst for coke formation. In contrast Sato .etal prepared the same catalyst by chemical vapor deposition method using boron alkoxide as precursor .The results found to be different than the catalyst prepared by impregnation method. The comparison of activity of  $B_2O_3 /Al_2O_3$  prepared by impregnation (filled points) method and chemical vapor deposition (empty points) are as shown in the below Figure- 4 (a)

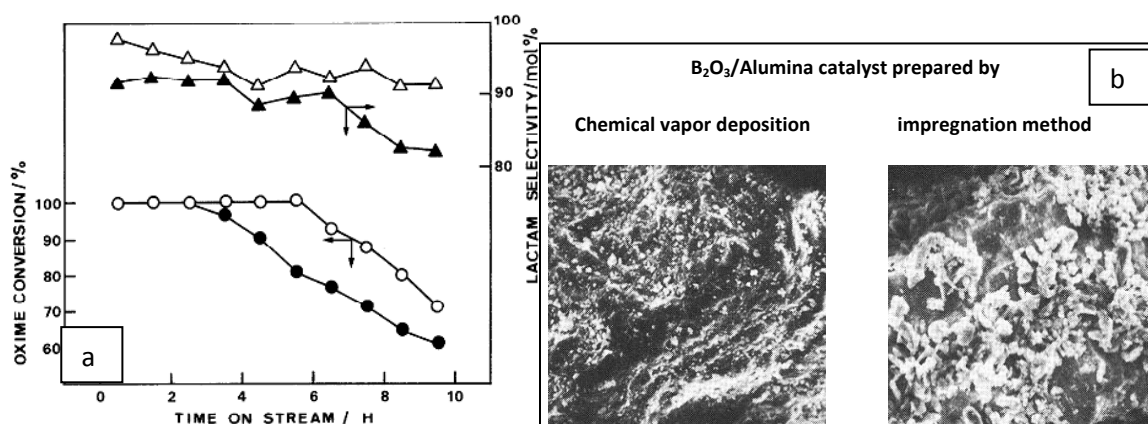


Figure- 4 a) Time on stream graph b) SEM images of  $B_2O_3/Al_2O_3$

Up to 12 wt% of boria loading on alumina will give rise to strong bronsted acidity due to formation of surface mixed oxide between alumina and boria. Hence reaction over the following catalyst leads to formation more side products like cyclohexanone and nitriles. But the reaction carried out over catalyst of 25wt %  $B_2O_3/Al_2O_3$  gave high conversion and selectivity for the reaction, with intermediate acid strength as measured by titration and TPD of pyridine .At high loadings of boria the strong acid sites will be covered by the free layers of  $B_2O_3$ , which induce intermediate acid strength in a catalyst. SEM images as shown in figure -4 (b) will solve the difference in activity of the catalyst prepared by CVD and impregnation methods. The deposition of boria on alumina by chemical vapor deposition is more uniform compared to the impregnation method leading to formation of medium acid strength.

Curtin et al depicted from TPD profile [fig -2(b)], that the acid strength increases with increase in loading of boria on alumina. But in contrast sato .etal observed reverse order i.e. high acidity on 12 wt% of boria loading and medium acidity for boria loading above 12 wt%. The only difference in the following catalysts is preparation methods and use of alumina support having different surface area.

Study of  $B_2O_3$  over different oxides like  $SiO_2$  , $Al_2O_3$ , $ZrO_2$ , $TiO_2$ , $MgO$  is applied for Beckmann reaction. The  $B_2O_3/ZrO_2$  is found to be a prominent catalyst among the other catalyst with high caprolactam yield for the Beckmann reaction. The activity and selectivity of all the boria loaded catalyst over different oxides is as shown in the graph 5a and 5b.Very slow deactivation of  $B_2O_3$  catalysts supported on alumina,

silica and zirconia is noticed. In case of titania and ZSM-5 deactivation was found to be rapid, which is clear from the fig-5(a).

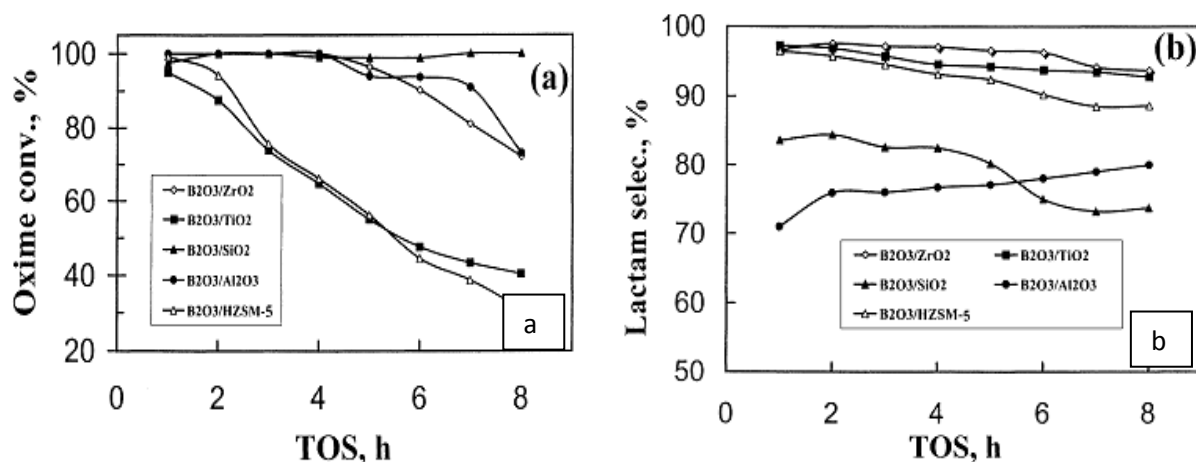


Fig-5 a) Oxime conversion b) lactam selectivity over different metal oxides

Improvement of the B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst is made by optimizing the borica loading from 0-20 wt%.

The both oxime conversion and lactam selectivity over different borica loading is shown in the below Fig-6

(a)

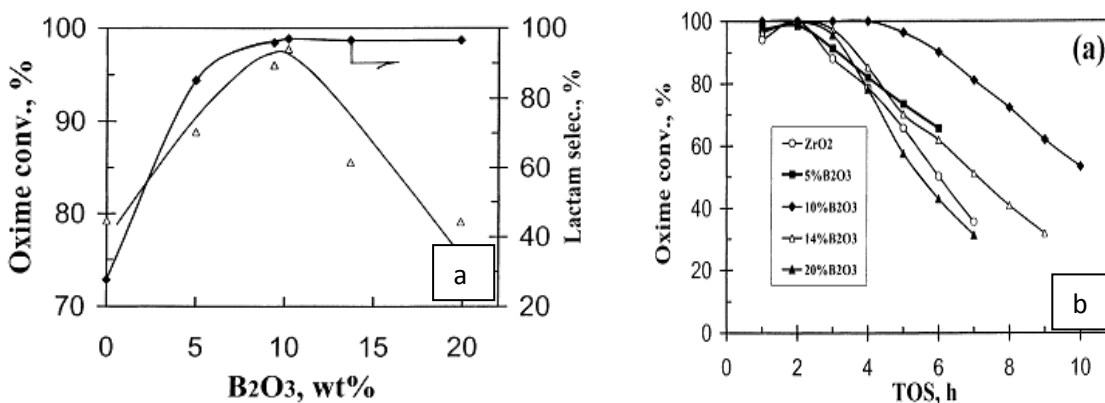


Fig-6 a) effect of different loadings of borica on activity b) oxime conversion for 10 hr of reaction time

Initially increase in Borica loading over zirconia increased the activity and selectivity, up to 10 wt% of borica loading maximum conversion and selectivity is observed. Further increase of borica loading decreased the conversion. The optimized 10wt% of borica on zirconia not only increase the caprolactam yield but also found to be more stable than its other loadings of borica over zirconia as shown in the fig -6 (b)

The TPD profiles of ammonia adsorbed on B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts showed presence intermediate strength as shown in fig-7

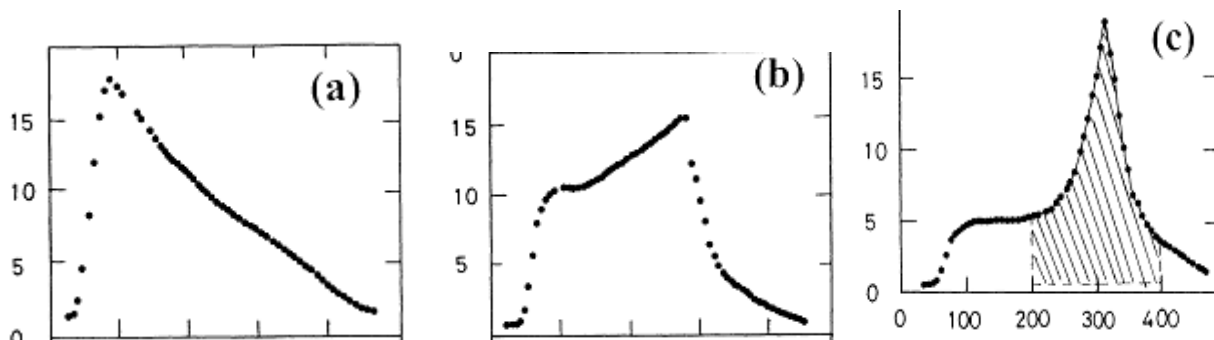


Fig-7 TPD profiles of  $B_2O_3/ZrO_2$  with a) 5 wt% b) 10 wt% c) 20 wt% of boria

The 5Wt%, 10Wt%, 20Wt% of boria loading over zirconia generated weak, medium and relatively strong acid strength in the catalyst. Among these three catalyst  $B_2O_3$  (10wt %) / $ZrO_2$  resulted on high performance of the Beckmann rearrangement.

Study of physiochemical properties of following catalyst showed the formation of  $BO_3$  units over  $ZrO_2$  with increase of boria loading. Initial loading will form the monolayer of  $BO_4$  units; with further increase of boria will form a secondary  $BO_3$  layer over primary  $BO_4$  sub layer. The formation of  $BO_3$  over  $BO_4$  layer given active sites with intermediate acid strength.

From the above it is clear that not only the amount of boria loading is responsible for the generation of acidity, but support also plays important rule. For example in case of 12 Wt% of boria over alumina gave rise to strong acid sites ,but same amount of boria loading over zirconia gave rise to intermediate acid strength. Not only chemical properties but physical properties like pore size, surface area and crystal size of support plays important role in deciding acid distribution in the catalyst.

A detailed study of tantalum oxide supported on silica catalyst is studied for the Beckmann rearrangement by Takashi Ushilkobo etal .A good activity and selectivity is observed for the  $Ta_2O_5/SiO_2$  (alk) synthesized using tantalum alkoxide precursor by chemical reaction method. They compared the catalytic activity of  $Ta_2O_5/SiO_2$  (alk) with  $Ta_2O_5 /SiO_2$  (IMP) prepared by impregnation method,  $Ta_2O_5$  , $Nb_2O_5$ and  $B_2O_3 /Al_2O_3$ .the details are as given in the below table -2

TABLE-2

	Catalyst	Oxime Conversion %	Caprolactam Selectivity%	Caprolactam Yield %
1	$T_2O_5/SiO_2$ (4.3 Wt%)(Alk)	96.5	97.5	94.1
2	$T_2O_5/SiO_2$ (4.3 Wt%)(IMP)	40.8	70.5	28.8
3	$B_2O_3/Al_2O_3$ (26.5 wt%)	93.4	92.1	86.0
4	$Ta_2O_5 \cdot n H_2O$	42.6	69.9	29.8
5	$Nb_2O_5 \cdot n H_2O$	21.2	67.5	14.3

The difference in the activity and selectivity for the catalyst  $Ta_2O_5/SiO_2$  (IMP) and  $Ta_2O_5/SiO_2$  (Alk) is the different in the method of preparation. Chemical preparation method has distributed tantalum moiety uniformly over Silica leading to generation medium acid strength, but in case of impregnation method non-uniform distribution of tantalum moiety over  $SiO_2$  resulted in strong Brönsted acidity. The SEM images clearly indicate the difference in the tantalum distribution over silica as shown in the graph. (fig-8)

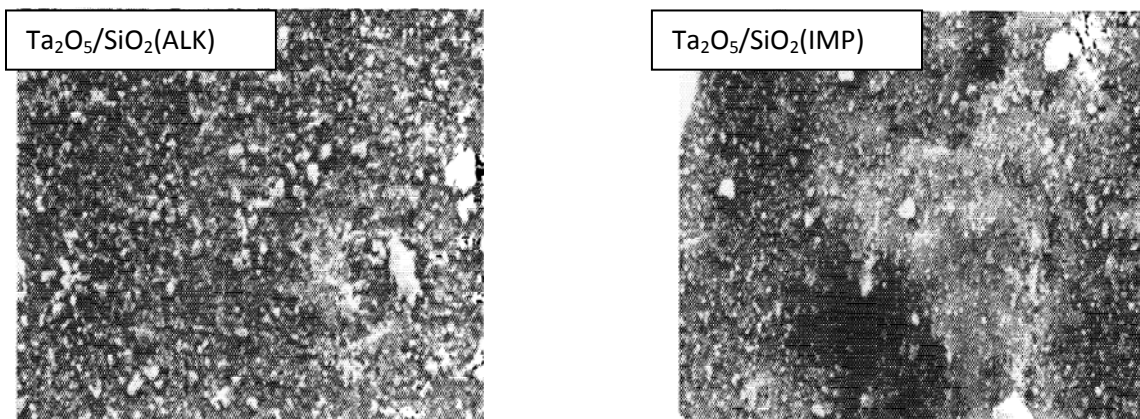


Fig-8 SEM images of a)  $Ta_2O_5/SiO_2$  (Alk) b)  $Ta_2O_5/SiO_2$  (IMP)

It is interesting to see low level conversion for the strong Bronsted acid catalyst like  $Ta_2O_5/SiO_2$ (IMP) and  $Ta_2O_5$ . The low conversion is due to adsorption of the caprolactam over the strong bronsted acidity leading to blockage active sites by coke precursor.

The formerly studied  $B_2O_3(20\text{ wt\%})/Al_2O_3$  catalyst showed the same TPD profile peak as that of  $Ta_2O_5/SiO_2$  (Alk) indicating presence intermediate acid strength. Initial decline of conversion in  $B_2O_3/Al_2O_3$  was rapid for first ten hour of reaction time, but same is not seen in case of  $Ta_2O_5/SiO_2$ .(see fig-8).The activity and selectivity for the  $Ta_2O_5/SiO_2$  remained almost constant for first ten hour .

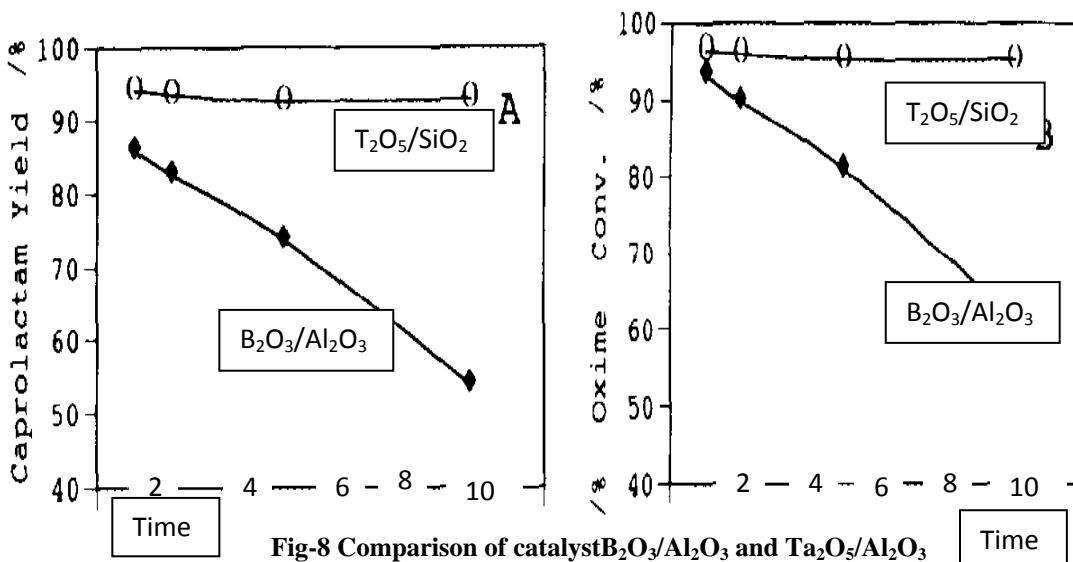


Fig-8 Comparison of catalyst  $B_2O_3/Al_2O_3$  and  $Ta_2O_5/SiO_2$



TPD profile of all catalysts and their activity showed that intermediate acid strength sites are best for the Beckmann rearrangement. TPD profiles of all the Catalysts are as show in fig-9

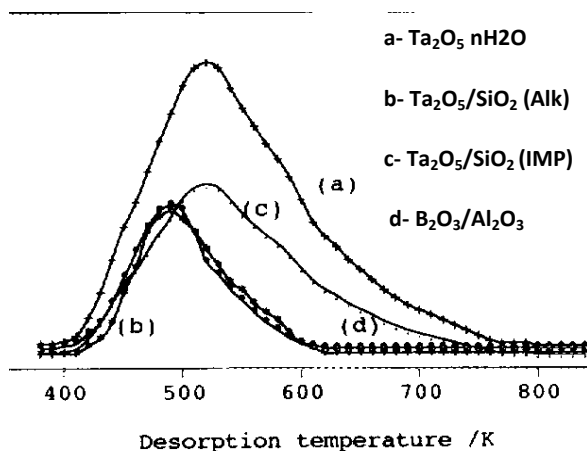


Fig-9 comparison of acid strength of different tantalum catalysts

The Chemical vapor deposition of silica on the oxides of  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$  generated weak Brönsted acidity which are responsible for the smooth run of Beckmann reaction. The acidity generated is almost same over all the silica deposited  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ . Increase in the activity of the reaction increases with the amount of silica deposition up to 12 wt% , the activity of the catalyst and the deposition of silica over  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$  are presented as shown below figure -10.

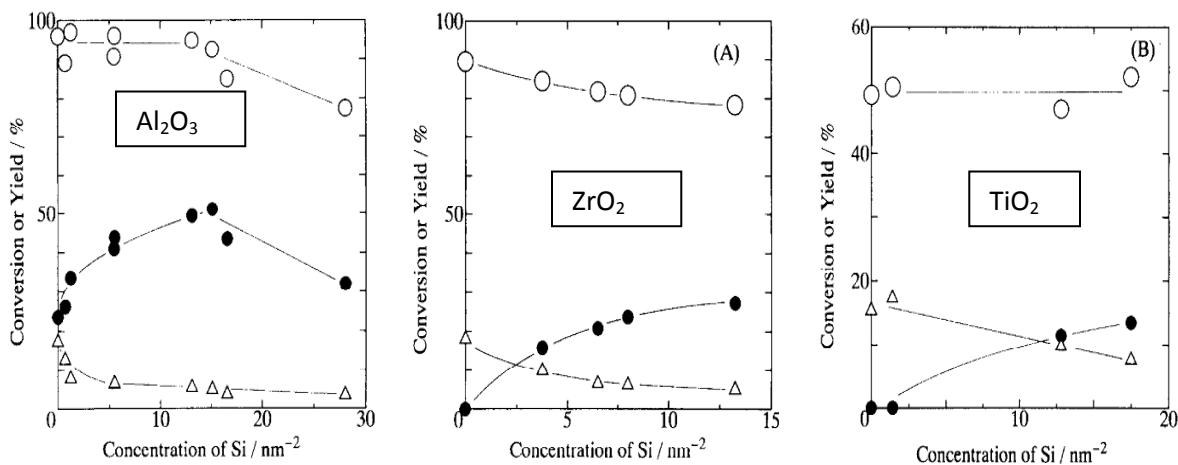


Fig-10 . Conversion of cyclohexanon oxime (O), yield  $\epsilon$ -caprolactam (●) and yield of cyclohexanon ( $\Delta$ )

The acidity in the following catalysts is predicted by the run of test reaction. The test reaction carried out is isomerization of butene which need very weak Brönsted acidity. Since caprolactam yields are very small; it seems, the weak acid sites are not suitable for the following reaction. The study on measurement of acidity of the following catalysts by TPD measurements, catalyst regeneration and effect of solvent is still area of research to be clarified.

The catalytic investigation of all the above catalysts indicated the strong and weak acid strength are not suitable for the Beckmann rearrangement, instead moderate acid strength are best for the reaction. The presence of strong acid sites adsorbs the reactant/product so strong that desorption of those molecule become difficult leading to pyrolysis to form a carbon and byproducts. The weak one is not having the acid strength to adsorb the reactants/products hence leading to low activity and selectivity. With Intermediate acid strength both the disadvantages can be ruled out.

Another interesting point to be noted is, preparations methods will effects the distribution of acid sites in the catalyst, which intern affects the catalytic activity of the reaction. For better catalytic performance more attention and care should be given for the catalyst preparation to get homogeneity in non zeolitic oxide materials.

Since the non zeolitic oxide materials applied are not crystalline and also doesn't possess the high porosity in their structure .The location of active sites for the reaction will be the surface of catalyst. The nature and location of the active sites in case of non zeolitic catalysts for Beckmann rearrangement are acid sites with Intermediate acid strength, present on the surface of catalyst.

#### **b. Beckmann rearrangement over crystalline zeolitic catalysts;**

The study of crystalline zeolitic materials for Beckmann rearrangement is quite interesting in terms of nature and location of acid sites required, as compared to non-zeolitic catalysts.

Break through work on Beckmann rearrangement over zeolites is carried out by the Sato .etal from Sumitomo Company, Japan. They studied the Beckmann rearrangement over zeolites with different Si/Al ratios and concluded the very weak acid sites are required for the smooth run of the reaction.

They also resolved, not only the natures of acid sites are important but other parameters like crysatallinity, density of acid sites and preparation methods of zeolites have direct effect on the reaction. The high siliceous Zeolites were prepared by use of two different silica precursor i.e. one with sodium silicate and other with Tetra ethyl ortho silicate(TEOS).

The Zeolite prepared by using TEOS showed high crystallinity, large external surface area and almost no acidity as compared to zeolite synthesized by sodium silicate precursor. Both conversion and selectivity

were almost constant for the silicalite prepared by TEOS but the same prepared by sodium silicate source showed increase in the conversion and selectivity with increase of crystallinity as shown in the following graph (figure- 11 .a)

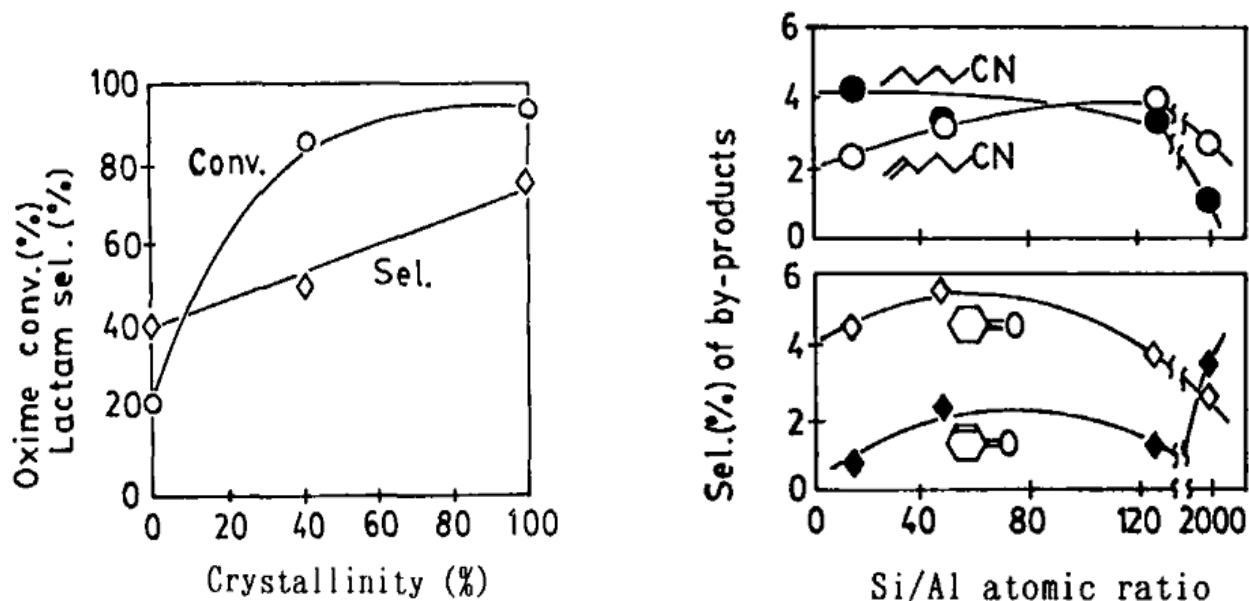


Fig-11 a) effect of crystallinity on the reaction 2) effect of Si/Al ration on byproducts

The graph in figure-11 indicates increase in Si/Al ratio decreased the byproducts like cyclohexenone, cyclohexanone, hexane nitrile and 1 hexene nitrile. Hence improvement of selectivity is observed for high Si/Al due to presence of weak acid sites, it is clear that weak acid sites have positive contribution for the Beckmann rearrangement rather than the strong acid sites (lower Si/Al). To determine the nature of active site, reaction is carried out over zeolites having different external surface areas (ESA) and correlation is obtained between ESA and yield for the caprolactam as given in fig-12 (a),

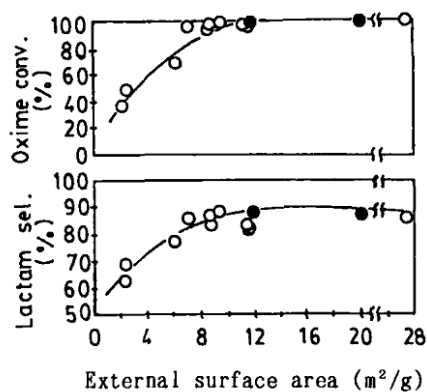
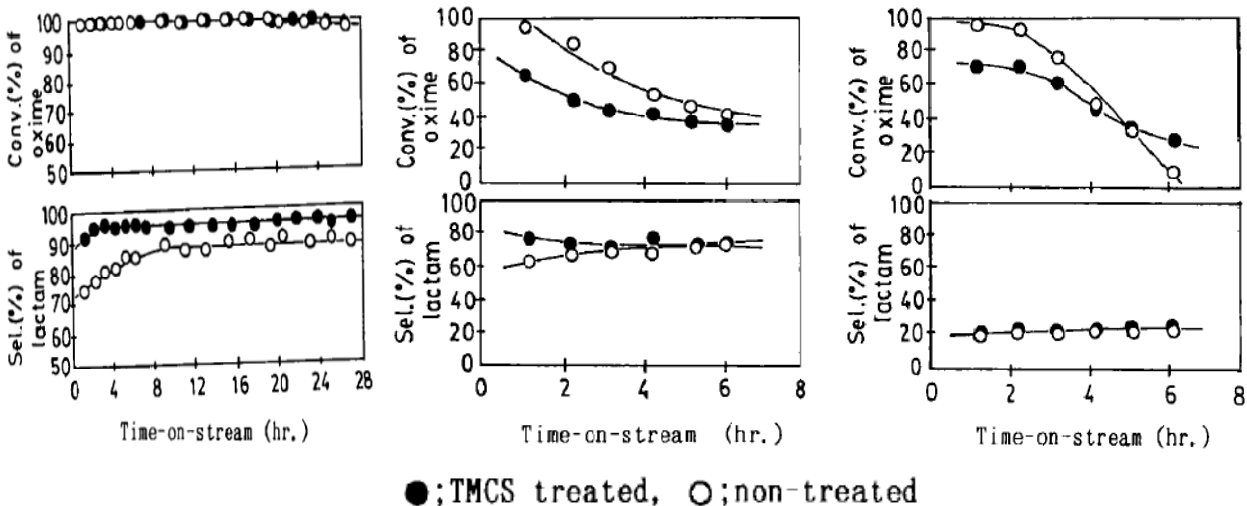


Fig -12 a) influence of external surface area on catalytic performance.

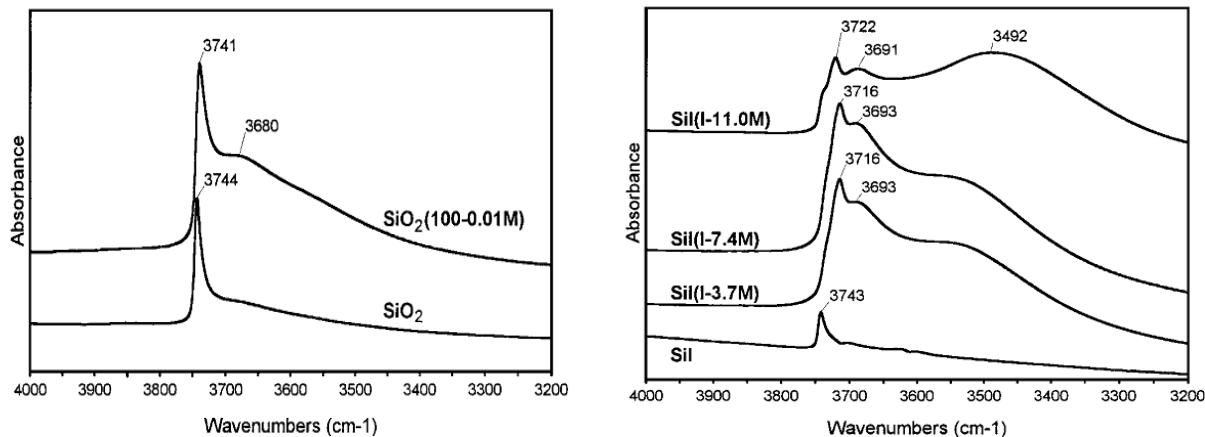
the graph clearly indicate increase in the external surface area, increased the conversion and selectivity ;showing the active sites of reaction are neutral silanol groups present on the surface of zeolite and not the internal surface of the zeolite. This can also be understood by considering molecular diameter of cyclohexenonxime (6.5~7)Å and caprolactam(7 ~7.5 Å) larger than the pore opening of zeolite (5.1 ~ 5.6 Å). If the active sites are neutral silanol groups then, amorphous silica have higher density of silanol groups than the silicalite hence, it should show high conversion and selectivity than silicalite. But the silica gel is able to give only about 25 % selectivity which is too low to be compared to silicalite (85% lactam selectivity). The above difference in the selectivity is attributed to the high density of silanol groups' and their irregular orientation present on the amorphous silica. To redistribute or to lower these silanol groups in low, high siliceous ZSM-5 and amorphous silica were treated with Trimethyl chloro silane and the results obtained as shown below



**Fig-13 Time on stream of a) high Siliceous Zeolite b) low Siliceous zeolite c) amorphous Silica**

After treatment of TMCS the selectivity of high siliceous zeolite is improved from 85% to 95% whereas, it remained almost same in case of other two catalysts. Result presented in fig-13 depicts the presence of specific silanol groups on the highly crystalline siliceous zeolite. The increase in selectivity of high siliceous zeolite is attributed to the lowering of silanol density and blocking of amorphous silanol groups present on the surface if any. The IR study on the TMCS treated/non treated of highly siliceous and amorphous silica gave some clues regarding active sites of the reaction. After silylation with TMCS the amorphous silanol groups have been decreased and hydrophobicity increased leading to easy desorption of product molecules. According to sato .etal crystalline neutral silanol groups are active sites for the reaction. To

know the exact active sites, Hölderich et al [8] studied the influence of different kind of hydroxyl group on the surface of amorphous and crystalline silicalite.



**Fig-14 FTIR spectra of SiO<sub>2</sub> and SiO<sub>2</sub>(1-0.01M)**

In the previous work we found that amorphous silica is inactive for Beckmann rearrangement. But acid treatment to amorphous silica revealed the nature of active sites. Care full observation of FTIR (fig-14) indicated presence of terminal silanol groups at 3740 cm<sup>-1</sup> in both cases and an extra peak at 3680 cm<sup>-1</sup> for acid treated catalyst is observed. The treatment of HCl solution at high temperature created some of the extra vicinal silanol groups, which are responsible for the high selectivity (80%) of the caaprolactam. It is clear that not the neutral silanol groups are not the active sites but the vicinal silanol groups are the active sites for the reaction. Further treatment of Silicalite with different concentrated ammonia solution gave rise to rapid increase in the conversion and selectivity is obtained as shown in table-4.

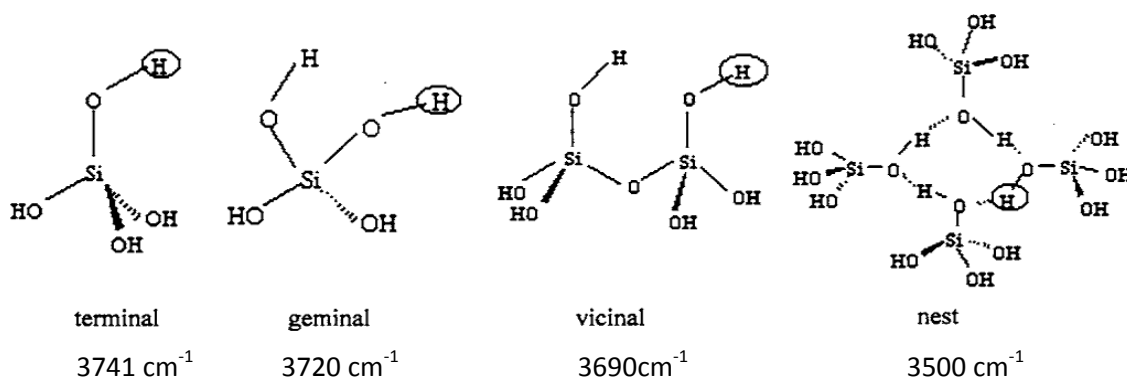
**Table-4. Catalytic results of silicalite treated with ammonia.**

	Molarity of ammonia			
	11.00M	7.4 M	3.7M	untreated
<b>Conversion(TOS 2 hr)</b>	86%	85%	93%	27%
<b>Selectivity (TOS 2 hr)</b>	97%	98%	98%	39%

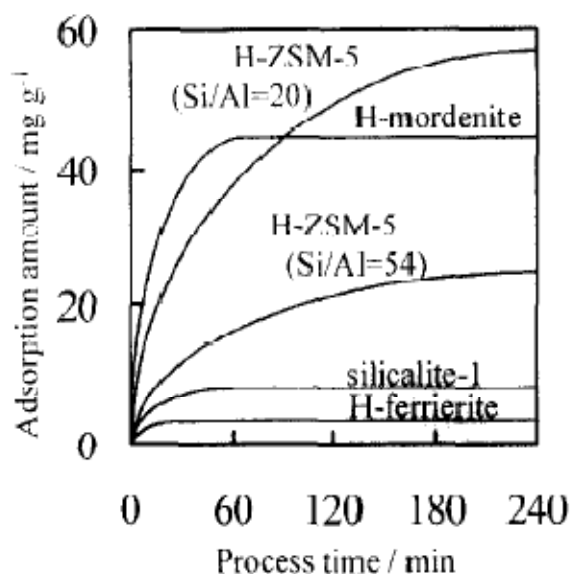
The above data shows the optimum concentration ammonia treatment to get high yield for the Beckmann reaction. The treatment of high concentrated ammonia solution leads to decrease in conversion due to redistribution of acid sites. The FTIR Study of the following catalysts is as shown in the Fig-15.

FTIR study of the ammonia treated Silicalite revealed the presence of broad peak at 3500 cm<sup>-1</sup> due to presence of hydrogen bonded neighboring silanol groups to form silanol nests. The Increase of conversion and selectivity for the ammonia treated silicalite is due to generation of acid sites from nest silanol groups.

The different types of silanol groups present on silicalite are as shown in below figure



If the location of active site is considered most of the papers support the reaction take place on the surface of zeolite and not inside the pores. To confirm the location of active sites yashima etal[9] studied the adsorption of cyclohexanone oxime over zeolites of different pore openings.



**Fig-15 Changes in adsorption amount on various zeolite with time.**

Adsorption of cyclohexanone oxime on various zeolites was measured by using a highly sensitive thermal balance. The Mordenite zeolite with 12-membered oxygen ring adsorbed the cyclohexanone oxime and reached equilibrium in very short time. The ferrite (distorted 10 member rings) also adsorbed in very short time and reached the equilibrium. However the amount adsorbed at equilibrium is too low. These result showed that oxime can be absorbed by the 10 member zeolite but the amount adsorbed indicate the adsorption taking place only on the external surface of zeolite. the same is also observed for the silicalite as shown in the Fig-15.

The use of zeolite selectivity for caprolactam is not yet reached 100% which indirectly indicate very few of Cyclohexanone oxime molecules enter the pores of zeolite with great difficulty. Sorption experiments with cyclohexanone oxime and caprolactam were undertaken at 85°C (necessary due to the high reactivity on silicalite-1) and 140°C, respectively. It could be shown that cyclohexanone oximes as well as caprolactam were able to enter the pore structure in a time span of 3–10 min. The adsorption in beta zeolite was reported to be about 20% higher than the one found for the MFI structure. and most of the work indicates that the reaction takes place on the surface and not the inside the pores of Zeolite. This Is true as we know the zeolites are having negative thermal coefficient of expansion hence at higher temperature the pores of the zeolite still get reduced in such way that oxime will not go through the pores.

The proton forms of HUSY zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of 6.3,27,62, 97, and 390 have been prepared by dealumination of Zeolite Y. As the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> increased the conversion of cyclohexanone oxime decreased and selectivity initially increased to maximum but again decreased .The conversion and selectivity for the following HUSY catalysts are shown below Table-3

No	Catalyst (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> )	Conversion		Selectivity	
		1hr	6hr	1 hr	6hr
1.	HUSY(6.3)	99.9	99.8	76.6	86
2.	HUSY(27)	99.9	99.9	88.8	93.8
3.	HUSY(62)	100	99.9	93.7	94.6
4.	HUSY(97)	89.5	56.5	85.1	87.9
5.	HUSY(309)	45.8	17.6	64.1	80.3

The less conversion for the USY(309) zeolite is due to very low weak acidity which is clear from the TPD of ammonia profile as shown in figure . The lower selectivity for the very high acidic USY (6.3) and very low acidic USY (309 and 97) zeolite is due to formation of by products. In the former zeolite cyclohexanone /cyclohexenone are the byproducts, whereas in later case nitriles are formed as byproducts. The proper mechanism of formation of cyclohexanone/ cyclohexenone is not clear, but formation of nitriles is due to hydrophobic nature of USY (309) which cannot retain the water leading to the ring opening to form nitriles. From the above data it seems that moderate amount of relatively weak acid sites on H-USY (27) and-USY (62) are suitable for the Beckmann rearrangement.

Careful study on TPD profile of both B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (20 Wt% boria) and USY (27) catalysts shows almost the same peak profile with maximum desorption peak in the range of 200-350°C. But in case of boria

catalyst it's categorized as medium strength acid site whereas in USY zeolite, it's mentioned as relatively weak acid sites. Hence a proper sorting has to be done using a standard TPD profile which is shown in the figure below. It confirms from the standard graph that, medium strength acid sites are present in USY zeolites which are responsible for the high activity of the reaction.

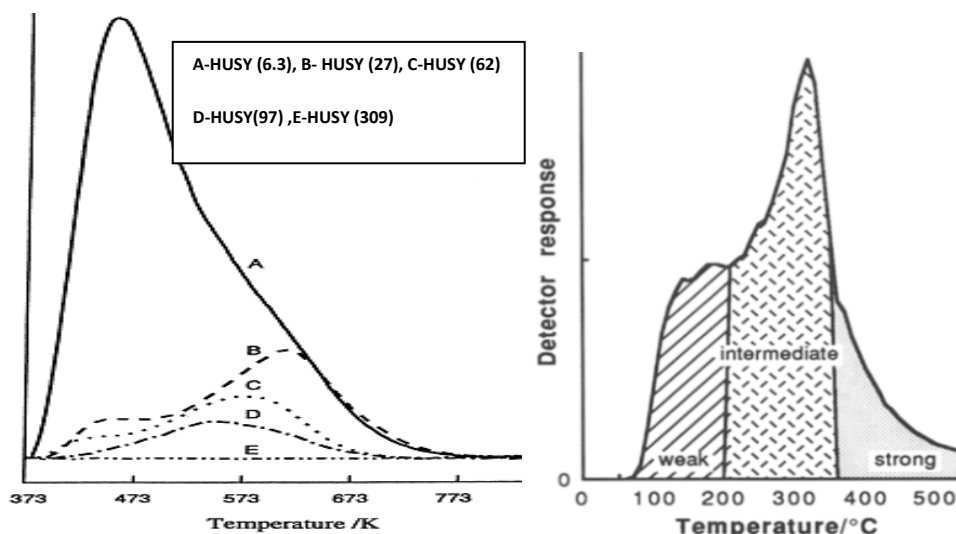


Figure-1 a TPD profile of USY Zeolites with different Si/Al 2) standard TPD profile

From the above investigation, the nature and location of the active sites in case of zeolite catalysts for Beckmann rearrangement are acid sites with weak strength (hydrogen bonded silanol groups), present on the surface of catalyst. Not only the acid strength effects the reaction but also the crystallinity of the zeolite affects.

## Conclusion

In case of non-zeolitic material  $Ta_2O_5/SiO_2$  is found to be outstanding catalyst for the Beckmann rearrangement without deactivation for first ten hours with high conversion and selectivity. The non-zeolitic oxide materials applied are not crystalline and also don't possess the porosity in their structure. The location of active sites for the reaction will be the surface of catalyst. The nature and location of the active sites in case of non-zeolitic catalysts for Beckmann rearrangement are acid sites with Intermediate acid strength, present on the surface of catalyst.

The high siliceous zeolite material with high crystallinity showed a better performance in Beckmann reaction. The nature and location of the active sites in case of zeolite catalysts for Beckmann rearrangement are acid sites with weak strength (hydrogen bonded silanol groups), present on the surface of catalyst. Not only the acid strength effects the reaction but also the crystallinity of the zeolite affects.



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