

**New synthesis routes for production of  $\epsilon$ -caprolactam  
by Beckmann rearrangement of cyclohexanone oxime  
and ammoximation of cyclohexanone over different  
metal incorporated molecular sieves and oxide catalysts**

Von der Fakultät für Mathematik, Informatik und  
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Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek online verfügbar.

Dedicated to my Parents

This work reported here has been carried out at the Institute for Chemical Technology and Heterogeneous Catalysis der Fakultät für Mathematik, Informatik und Naturwissenschaften in the University of Technology, RWTH Aachen under supervision of Prof. Dr. Wolfgang F. Hölderich between June 2005 and August 2008.

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## Abbreviations

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Part from chemical symbols the following abbreviations were used in the text:

| Abbreviation | Full Name                                               |
|--------------|---------------------------------------------------------|
| CHO          | cyclohexanone oxime                                     |
| CL           | $\epsilon$ -caprolactam                                 |
| HMS          | hexagonal mesoporous silica                             |
| XRD          | X-ray powder diffraction                                |
| BET          | Brunauer- Emmett-Teller                                 |
| ICP-AES      | inductive coupled plasma - atomic emission spectroscopy |
| TG           | thermogravimetry                                        |
| DTA          | differential thermal analysis                           |
| FT-IR        | fourier transmission infra red                          |
| DR-UV-Vis    | diffuse reflectance UV-Vis                              |
| MAS NMR      | magic-angle spinning nuclear magnetic resonance         |
| TPD          | temperature programmed desorption                       |
| TPR          | temperature programmed reduction                        |
| SEM          | scanning electron microscopy                            |
| XPS          | X-ray photoelectron spectroscopy                        |
| TOS          | time on stream                                          |
| WHSV         | weight hourly space velocity                            |
| GC           | gas chromatography                                      |
| GC-MS        | gas chromatography - mass spectroscopy                  |

## **1. Introduction and Objectives**

### **1. Introduction and Objectives**

In recent years the protection of environment has increased in the public and economical world, as quality of life is strongly connected to a clean environment. Current calculations show that, there were 2.26 billion pounds of approximately 300+ hazardous substances released to the environment [1]. Most of the chemical waste and hazardous substances were released into the environment from the chemical industries by use of wide range of inorganic or mineral acids as the catalysts in liquid phase reactions. In these processes during the isolation of the products, necessarily to neutralization with bases resulted in enormous quantity of salt waste. In order to control the legislation on the emission of hazardous pollutants the industry is driving toward the implementation of innovative “clean technology” including the use of alternative heterogeneously catalyzed processes [2-3]. The processes can be changed towards to “clean technology” by replacing homogeneous catalysts with heterogeneous catalysts to eliminate production of wastage [4-5]. Today, catalytic technology plays a key role in the economic development and growth of the chemical industry and contributes to around 20% of the world Gross National Product. Furthermore, in chemical industry, 60% of the chemicals and 90% of chemical processes have been developed by catalysis methods [6-7]. Heterogeneously catalyzed processes are widely used in petrochemical industry, bulk chemicals and fine chemicals production.

The Beckmann rearrangement of cyclic ketooximes to lactams is an important process step for production of polyamides. For example, Beckmann rearrangement of cyclohexanone oxime (CHO) produces  $\epsilon$ -caprolactam (CL) which is an important monomer for synthesis of Nylon 6 polyamide. The Nylon 6 polymers and resins have a

## 1. Introduction and Objectives

big influence on modern society. Due to the importance, a lot of demand is to production of Nylon in industrial manner. In a classical method CL was industrially produced in presence of sulfuric acid as catalyst. In general a perceived disadvantage of the applied route is the large amount of ammonia sulfate as side products [8-10]. This reaction is an excellent example of a new benign process by heterogeneous catalysis with 100% theoretical atom economy [11].

This thesis provides an overview of the types of catalytic processes that have shown some progress in creating clean technology and likely through continued materials improvements to lead to new environmentally benign processing. Our goal is to discuss the catalysis as technology for primary prevention i.e. minimizes waste production. The development of new heterogeneous catalysts as well as their analytical characterization and the catalytic activity results will be presented.

This thesis is composed of two projects, the first project is examining the synthesis of caprolactam via gas phase Beckmann rearrangement of cyclohexanone oxime to caprolactam over different Nb incorporated mesoporous and microporous molecular sieves such as Nb-MCM-41, Nb-SBA-15, Nb-HMS, Nb-Beta zeolite. In addition, Nb impregnated on  $\text{SiO}_2$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  supported materials. All these catalyst materials were characterized by various physical-chemical characterization techniques and finally catalytic activity tests were carried out by vapor phase Beckmann rearrangement of cyclohexanone oxime to caprolactam.

Second part of this thesis examines the single step synthesis of caprolactam from cyclohexanone by ammoximation reaction in presence of hydrogen peroxide and ammonia over different heterogeneous catalysts. This route would provide a more

## 1. Introduction and Objectives

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economical and environmentally friendly process. Moreover, this single step procedure leads to minimize the consumption of energy and is a time saving process.

In this single step reaction, the effect of temperature, effect of  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio,  $\text{NH}_3$ /cyclohexanone molar ratio, solvents and stirring speeds were evaluated over different catalysts such as Nb-MCM-41, Al-MCM-41, B-MFI, B-Al-MFI and B-Ti-Al-MFI etc. In addition, the influence of different oxidizing agents and reactions pressure were also discussed.

## **2. General Part**

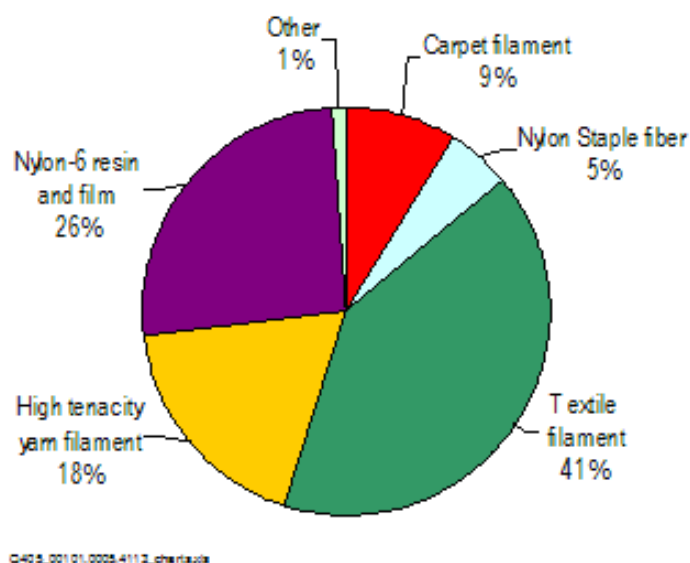
## **2. General Part**

### **2.1 General Back ground about Caprolactam and Nylon 6**

$\epsilon$ -Caprolactam is the main precursor for synthesis of Nylon 6, polyamide fibers.  $\epsilon$ -Caprolactam was first described in the 19<sup>th</sup> century by, among others, S. Gabriel and T. A. Mass in 1899, who synthesized caprolactam by the cyclization of  $\epsilon$ -aminocaproic acid. Also, O. Wallach prepared it via the Beckmann rearrangement of cyclohexanone oxime. Nylon 6 and nylon 6, 6 were the first two commercial polyamides and are still the most important polyamides with respect to their production volumes. Both nylon 6, 6 and nylon 6 were developed in the 40's of the last century, respectively by Wallace Carrothers at DuPont and by Paul Schlack at I.G. Fabens. Together, these polyamides account for more than 95% of the total amount of nylon used in the world, and nylon 6 is responsible for 59% of this quantity. It has a big influence on modern society. Besides the value for today's life, synthetic polyamides are also of the highest importance for the development of polymer and material science. Today, nylons are still important engineering plastics and well known for their fiber applications. Nylon is the first synthetic, semi-crystalline polymer that is not strongly temperature sensitive in comparison with other polymers [10]. Nylon 6 is being used in the manufacture of carpeting, textiles hosiery, knitted garments and also manufacture of large variety of threads, ropes, filaments, nets, tire cords etc. Carpeting is the highest volume segment. The other key application is nylon 6 engineering resins; this segment is driven by under-the-hood automotive components. In addition to nylon 6 fibers and resins, a small volume of caprolactam is used globally in a variety of small tonnage fine and specialty chemicals.

## 2. General Part

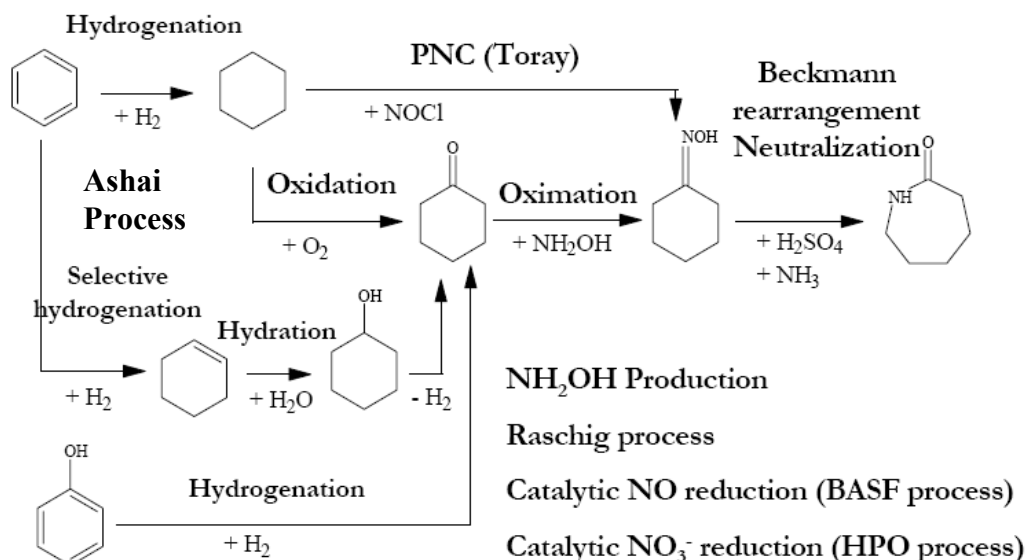
Well-known commercial products are brush bristles, textile stiffeners, film coatings, synthetic leather, plastics, plasticizers, paint vehicles, and cross-linking for polyurethanes. The distribution of global caprolactam demand by end use is shown in Figure 1.



**Figure 1: Global Caprolactam Demand by End Use, 2005**

The global market for caprolactam had reached nearly 4 million metric tones for each year by end of 2004. Although the global market is forecasted to grow an average expected to reach around 5 million metric tones by the year of 2015, Asia has experienced the most rapid demand growth.

Caprolactam can be produced from three hydrocarbon feedstocks: cyclohexane, phenol, and toluene. Approximately 68% of the world's caprolactam is produced from cyclohexane. It is mostly produced from benzene through three intermediates: cyclohexane, cyclohexanone and cyclohexanone oxime as shown in Scheme-1 [8-9].



**Scheme 1: Current caprolactam production processes.**

Cyclohexanone is mainly produced in an industrial scale by oxidation of cyclohexane with air. However, also small part of it is obtained by the hydrogenation of phenol. It can also be produced through selective hydrogenation of benzene to cyclohexene, subsequently hydration of cyclohexene and dehydrogenation of cyclohexanol.

## 2.2 Other synthesis methods of $\epsilon$ -Caprolactam

There are a large number of synthesis routes for the synthesis of CL exist. A review article by Prof. Hoelderich has described very widely about all the possible synthesis routes [11]. According to this review caprolactam synthesis routes have been divided in two main groups. The first group contains processes in which cyclohexanone oxime is used as the intermediate product. The second group contains all processes using different intermediates or different process steps.

---

### 2.2.1 Synthesis of caprolactam from cyclohexanone oxime

#### *(I). Synthesis of Cyclohexanone*

The economically most important routes for synthesis of cyclohexanone were described in Scheme-1. A new process to cyclohexanol starting from benzene was developed by Asahi (Scheme-1). By this method 60,000 tons/year of cyclohexanone were produced since 1990, a new 200,000 ton/year plant has been announced [9, 12-13].

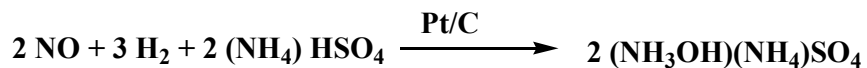
#### *(II). Synthesis of cyclohexanone oxime from cyclohexanone by ammoximation reaction:*

The reaction of cyclohexanone with hydroxylamine is a well known method for production of cyclohexanone oxime. The hydroxylamine is used in its sulfate, or phosphate form. This formation of cyclohexanone oxime by ammoximation method was attempted by different ways. The main process methods are described below.

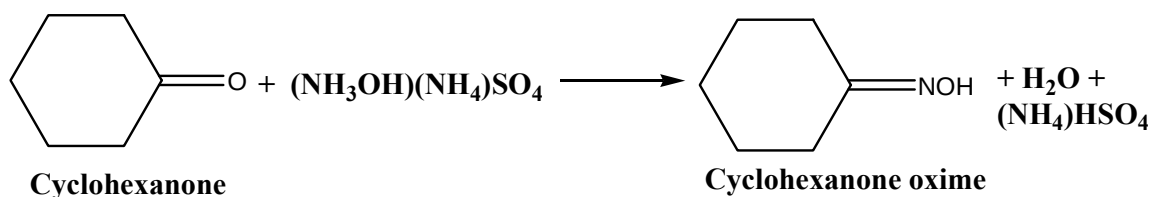
The **BASF process** (Scheme-2) is the production of hydroxylammonium sulfate solution by the hydrogenation of nitric oxide over a platinum catalyst in the presence of dilute sulfuric acid. The solution is the reduced with cyclohexanone and ammonia. This reaction is conducted at 85-90 °C with through mixing in a weak acidic solution from which the cyclohexanone oxime is obtained [9].

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**Step 1:**



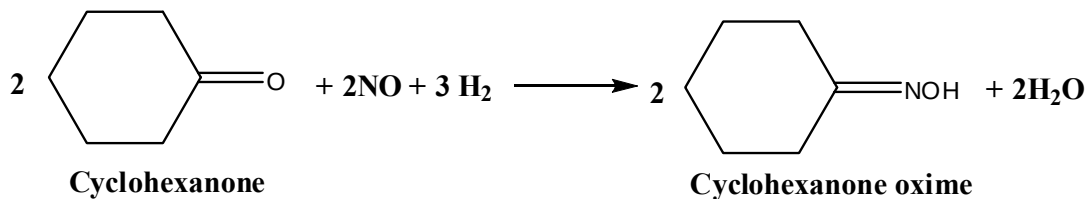
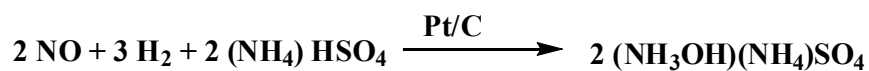
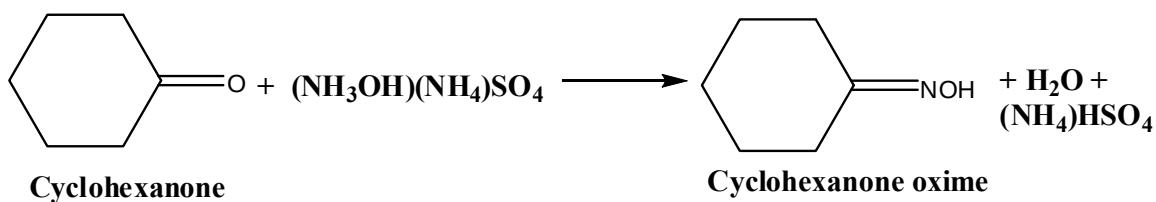
**Step 2:**



**Scheme-2: BASF Process**

A second process developed by BASF is the **acidic oximation process** (Scheme-3). The first step of this process is the catalytic hydrogenation of nitric oxide in an ammonia hydrogen sulphate solution over platinum on graphite. In a second step cyclohexanone is reacted to cyclohexanone oxime with ammonium hydroxylammonium sulfate. Complete conversion of cyclohexanone is achieved with a classic after-oximation reaction. In this process 0.1 ton of ammonium sulphate per ton of cyclohexanone oxime is formed as a by-product [9].

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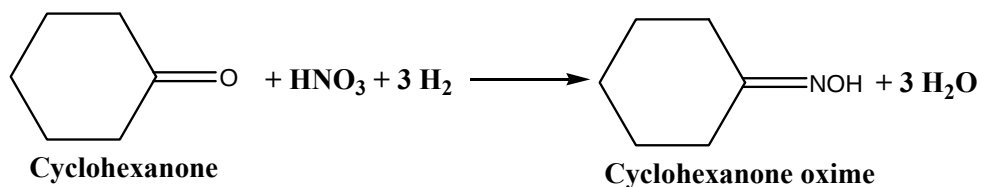
**Overall reaction:****Step 1:****Step 2:****Scheme-3: Acidic oximation process**

DSM developed the **HPO process** (hydroxylamine-phosphate-oxime) (Scheme-4). In this process the ammoximation reaction is conducted in a hydroxylamine phosphoric acid buffer solution. The first step is the reduction of the phosphoric acid/ammonium nitrate buffer solution with hydrogen and the formation of hydroxylammonim phosphate: This reaction is catalyzed with palladium on graphite or

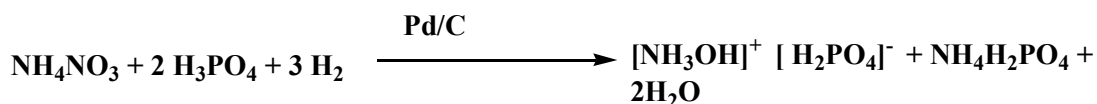
## 2. General Part

alumina carrier. The second step is the formation of the oxime. In the third step, after separation of the cyclohexanone oxime, the nitrite ions consumed are replaced by the addition of 60% nitric acid solution [9].

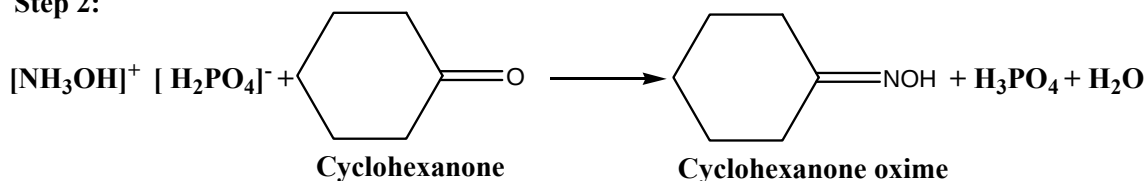
**Overall reaction:**



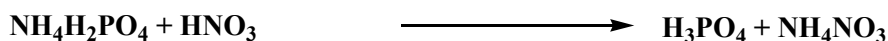
**Step 1:**



**Step 2:**



**Step 3:**



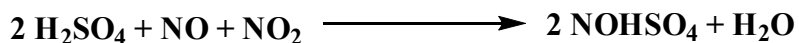
**Scheme-4: HPO process**

Toray developed the **PNC process** (photonitrosation, Scheme-5) based on the already known photonitrosation. Here, the cyclohexanone is reacted with nitrosyl chloride, thus forming cyclohexanone oxime hydrochloride. The nitrous gases necessary for the process

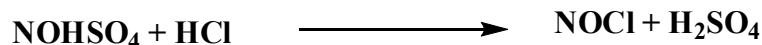
## 2. General Part

are produced in an ammonia burner and cooled, after which they reacted with sulfuric acid to form nitrosylsulfuric acid. The gaseous nitrosyl chloride/hydrogen chloride mixture is passed through liquid cyclohexane. The conversion to oxime dihydrochloride is carried out in a photo reactor with actinic light from cooled mercury immersion lamps. In the PNC Torry process 1.55 tons of ammonium sulfate is produced per ton of caprolactam [9]. The major drawback of this process is the highly energy consumption.

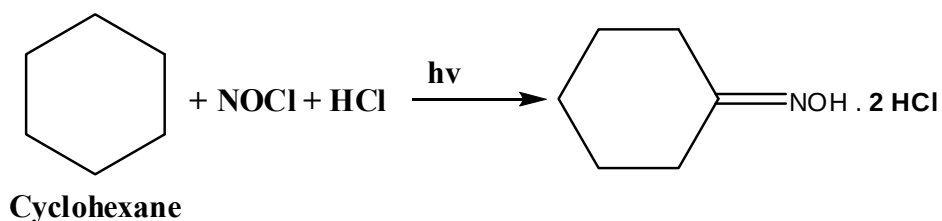
**Step 1:**



**Step 2:**

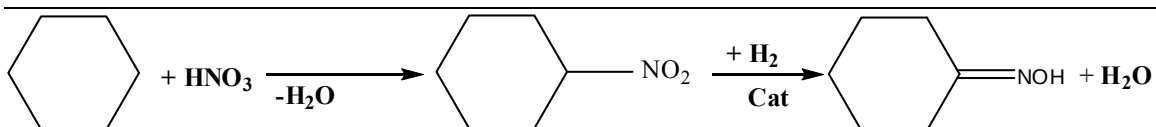


**Step 3:**

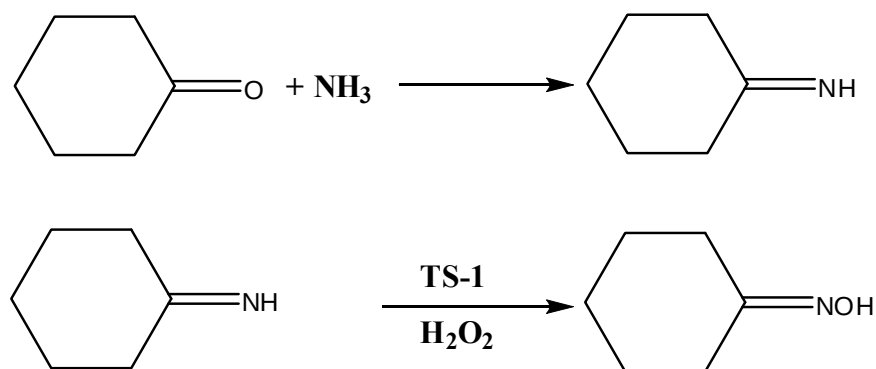


**Scheme-5: PNC process.**

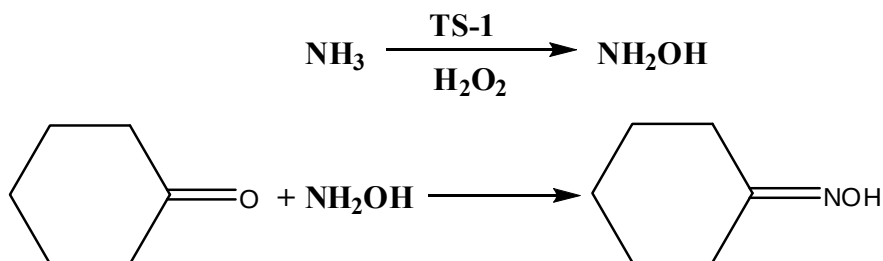
DuPont developed the **Nixan process** (Scheme-6), which was used in 1963-1967. To introduce nitrogen into the cyclohexane, a nitration with  $\text{HNO}_3$  in the liquid phase or with  $\text{NO}_2$  in the gas phase was used. Consequently, nitrocyclohexane was catalytically hydrogenated to the oxime [9].

**Scheme-6: Nixan process.**

However, **EniChem** recently developed a new environmentally benign process for synthesis of cyclohexanone oxime from cyclohexanone over TS-1 catalyst in presence of  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$ . This reaction operates in the liquid phase under mild conditions and proceeds very high yield. Moreover, this process has 100% theoretical atom economy [14-15]. EniChem has built a 12000 tons/year demonstration plant, which has been running successfully since 1994 [16]. In the EniChem process two reaction pathways have been proposed for formation of cyclohexanone oxime. According to Reddy et al. [17](Scheme-7) ammonia reacts in a first step with the ketone, forming the corresponding imine, the latter is then oxidized by hydrogen peroxide inside the pores of TS-1, giving rise to the formation of the oxime.

**Scheme-7: Ammoximation process.**

In a second pathway, according to Zecchina et al. (Scheme-8) ammonia reacts inside the pores of TS-1 forming the hydroxylamine that reacts immediately with the ketone, resulting in the formation of oxime [18].



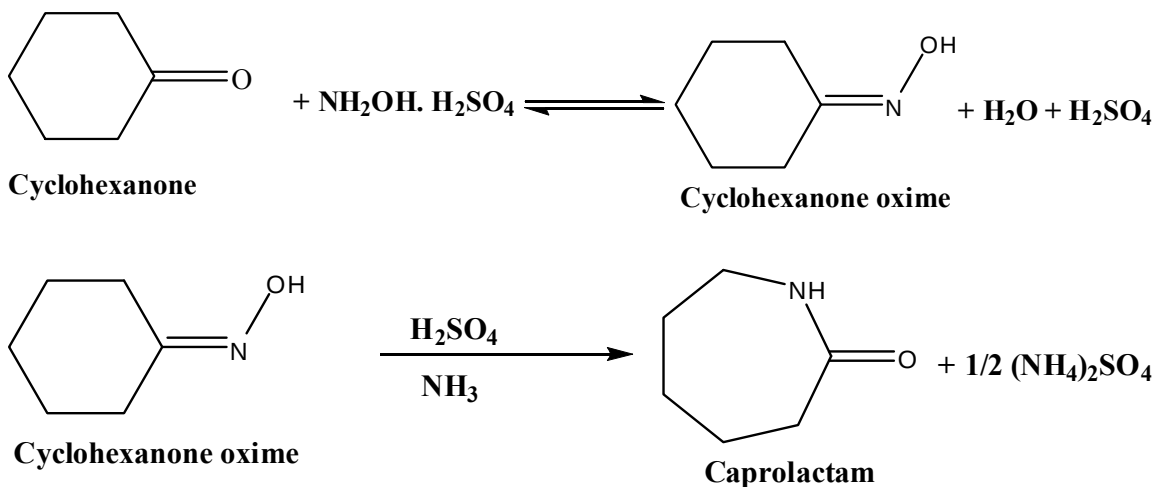
**Scheme-8: Ammoximation process.**

*(III). Beckmann rearrangement of cyclohexanone oxime to caprolactam*

The Beckmann rearrangement (Scheme-9) is a well known organic reaction and was reviewed several times [19-21].

On an industrial scale, caprolactam is produced under liquid phase reaction conditions by using stoichiometric amounts of concentrated sulfuric acid or oleum as a catalyst. In this method caprolactam is synthesized in two steps. In the first step, ammoximation of cyclohexanone with hydroxylammonium sulphate to form cyclohexanone oxime takes place, while in the second step cyclohexanone oxime is rearranged to caprolactam over sulfuric acid and oleum catalysts. This process has certain disadvantages, e.g., large amounts of base are required for neutralization of the product. In this process the main by-product is ammonium sulphate. To obtain 1 kg of caprolactam up to 4.5 kg of by product are formed [11, 22]. However, the produced

$(\text{NH}_4)_2\text{SO}_4$  could be used as a valuable fertilizer today. Moreover, in this liquid phase reaction system some other disadvantages also being considered. The main disadvantages are (1) separation of the product being too difficult and (2) corrosion of reactors by using concentrated acids as catalysts.



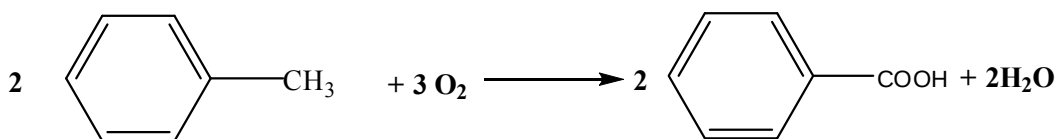
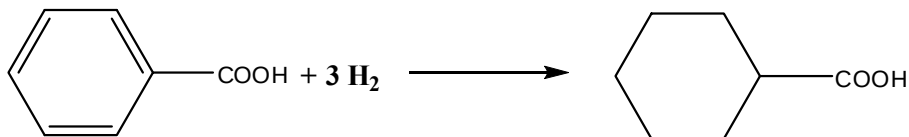
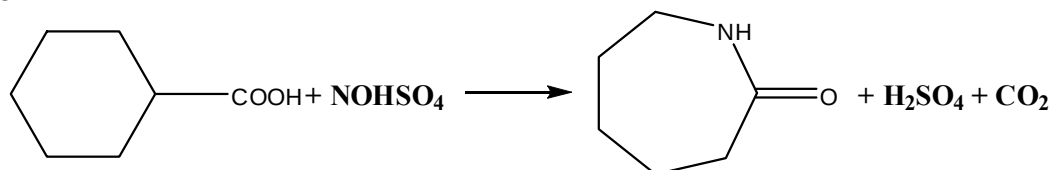
**Scheme -9: The equilibrium of the cyclohexanone ammoxidation with hydroxyl ammonium sulphate and the Beckmann rearrangement of cyclohexanone oxime to CL.**

### ***2.2.2 Synthesis of caprolactam without cyclohexanone oxime as an intermediate***

*In order to find new synthesis routes for production of caprolactam without cyclohexanone oxime as an intermediate, different companies have attempted for new synthesis routes.* The four most important processes are Snia Viscosa process, the UCC caprolactam process, the TechniChem Nitrocyclohexanone process and the BP hydrogen peroxide process.

*(I) Snia Viscosa process*

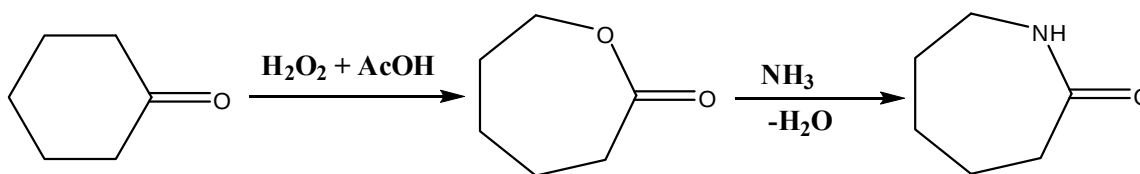
In this process (Scheme-10) toluene is converted in the liquid phase to benzoic acid at 160-170 °C and 0.8-1.0 MPa on a Cu catalyst with 30% conversion and 92% selectivity for benzoic acid. The benzoic acid is subsequently hydrogenated to cyclohexanoic acid at 170 °C and 1.0-1.7 MPa over a Pd/charcoal catalyst.  $\text{NOHSO}_4$  (prepared via  $\text{NH}_3$  oxidation and treatment with  $\text{H}_2\text{SO}_4$ ) is then added to the carboxylic acid in cyclohexane (80 °C). This process avoids the Beckmann rearrangement common to the previous processes. However, some ammonium sulfate (4 tons/ton of caprolactam) is still produced. As of 1980, it is estimated that 8% of the world production of caprolactam proceeded by this route. There are two plants, one plant in Italy (100,000 tons/year) and one in the former Soviet Union (80,000 tons/year) [9]. With the help of nitrosylsulfuric acid in oleum, cyclohexanoic acid can be converted to a mixed anhydride at reaction temperature of 80 °C.

**Step :1****Step: 2****Step :3**

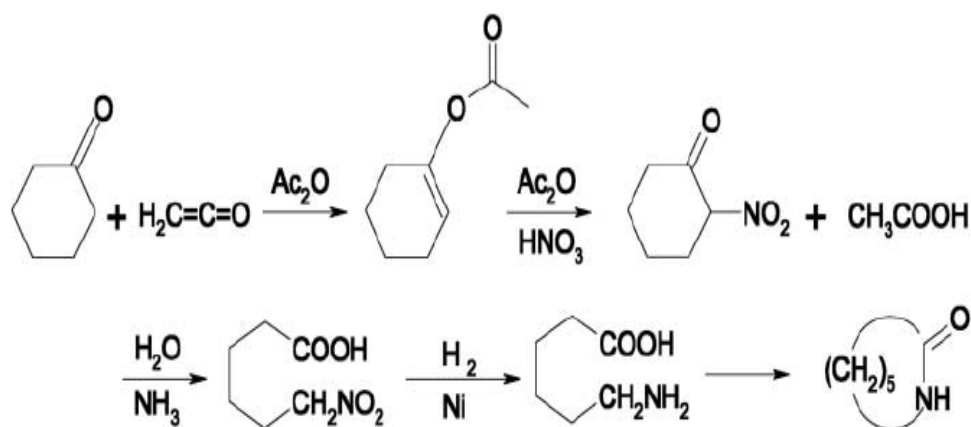
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**Scheme-10: Snia Viscosa Process.**
*(II) UCC Process*

In the UCC process (Scheme-11), cyclohexanone is oxidized with peracetic acid according to a Baeyer-Villiger oxidation to caprolactone at 50 °C and ambient pressure with selectivities of 90%. The caprolactone is then converted to caprolactam at 17 MPa and 300-400 °C. The selectivities achieved for the complete process are about 70%.

**Scheme-11: UCC process.***(III). Techni Chem Process*

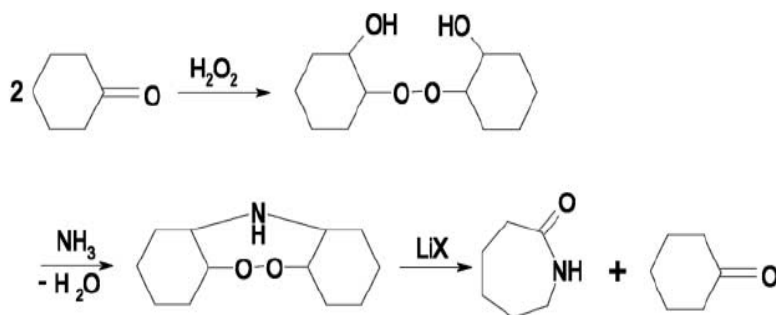
In this process (Scheme-12) cyclohexanone is converted to cyclohexeneacetate in the presence of a mixture of ketene and acetic anhydride. Subsequently, it is nitrated to be 2-nitro-cyclohexanone, during this step acetic acid is formed, which, again is reconverted to acetic anhydride with the ketone. A hydrolytic ring opening forms nitrocaproic acid, which is hydrated to the  $\epsilon$ -aminocaproic acid. This acid can be converted to caprolactam at 300 °C and 17 MPa. The main disadvantage of this process is the use of the expensive ketene. This process was never used on an industrial scale by reason of high costs of the production of acetic anhydride and ketene, although it was the first process free of by-products [9].



Scheme-12: TechniChem Process.

*(IV) BP Chemical process*

According to BP chemical process (Scheme-13), cyclohexanone is reacted with hydrogenperoxide (2:1 mixture) to form a 1,1-dihydroxydicyclohexylperoxide in the presence of an organic solvent and stabilizer. In a second step, the 1,1-dihydroxydicyclohexylperoxide reacts with ammonia to 1,1-peroxydicyclohexylamine, which is transformed to caprolactam and cyclohexanone with the help of lithium halogenides [23-25]. The great advantage of this process is that no by-products are formed. However, this process was not commercialized until now.



Scheme-13: BP 1,1-dihydroxydicyclohexylperoxide process.

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### 2.3. New synthesis methods

As caprolactam is an intermediate product with growing demand, there is an extensive research ongoing for new synthesis processes, which are economically favorable and environmentally friendly. The main aim of the research in the new synthesis methods is avoidance of the production of large amount of ammonium sulfate, which can be achieved by prevention of the formation of any salt or by the replacement of ammonium sulfate by a more valuable ammonium salt.

#### 2.3.1. *The catalytic gas phase Beckmann rearrangement reaction*

To overcome by-product formation and reactor corrosion problems, more economic and environmentally friendly process technology has been developed. In 1938, DuPont proposed a process in which cyclohexanone oxime vapor was passed over catalysts such as silica, alumina titania or magnesia, preferably in the presence of ammonia, at a temperature of 250-350 °C [26]. In the early 1950's, Dawydoff (Leuna-Werke) showed that boron oxide catalysts gave high yields in the vapor-phase Beckmann rearrangement [27]. The gas phase Beckmann rearrangement reaction was also carried out over different solid acid catalysts [28-29]. Previous studies showed that solid acids such as tungsten oxide [30], silica-tantalum oxide [31], titanium oxide [32], and boron-silica [33] are active catalysts. However, the application of all these catalysts results in low selective for CL and exhibited fast deactivation for the reaction. Recently, zeolites have been used as solid acid catalysts for Beckmann rearrangement reaction have been used [11, 22, 34-40]. Several potential materials along with all these materials such as TS-1 [41], SAPO 11,[42], Beta, Y [43-44] ZSM-5, and monolithic silicalite [22, 35-36, 40, 45-47] catalysts were applied for this reaction under gas phase as well as in liquid

phase conditions. In addition, mesoporous materials such as Si-MCM-41, Al-MCM-41 [48], silica alumino phosphate [49] and SBA-15 also lead to promising results [50]. Particularly, Prof. Hoelderich has developed very potential catalysts such as high silica zeolites (B-MFI and Beta) for this reaction and an extensive study was performed over these catalysts [11, 22, 43, 45].

### *Acidity and location of active centers of various catalysts*

The Beckmann rearrangement reaction is believed to be a typical acid-catalyzed reaction. Although, catalytic performance over solid acid catalysts under vapor phase conditions has been tested, the nature and position of the active sites in the catalysts remain controversial.

Costa et al. reported in 1980 on the Beckmann rearrangement of cyclohexanone oxime on alumina orthophosphate/ $\gamma$ -alumina catalysts [28]. They found that the reaction was catalyzed by Lewis acid and Brønsted acidic centers and that the formation of caprolactam and 5-cyanopent-1-ene were competitive reactions. A review on the influence of acidity on yields was published by Prof. Hoelderich [51].

Herrero et al [52] examined the Beckmann rearrangement to caprolactam over several medium pore (ZSM-5, ZSM-11) and large pore zeolites (Y, Beta) as well as over montmorillonite and pillared interlayer clays. The influence of silica-alumina ratio on both the conversion and selectivity were discussed. The lower the aluminum content, the higher the selectivity to caprolactam.

Yaashima et al.[53] examined a range of different catalysts such as H-ZSM-5, silicalite-1, silicagel, H-mordenite, H-ferrierite, Ca-A, Na-A, and clinoptinolite for Beckmann rearrangement. They conclude that weaker acidic sites showed a high

## 2. General Part

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selectivity for caprolactam. In presence of stronger acid sites multitude side reactions of ring opening, decomposition and polymerization was observed.

In contrast to above results, Corma and Kob et al. believed that the strong acid sites on crystalline silica-alumina are favorable for gas phase Beckmann rearrangement [30, 38, 54].

However, the research group of Prof. Hoelderich investigated the rearrangement of cyclohexanone oxime to caprolactam over high siliceous zeolites with the MFI structure in fixed bed and fluidized bed reactors to determine the nature of the active centers on the catalysts [11, 22, 45, 55-57]. According to Prof. Hoelderich, extremel weakly acidic silanol nests and vicinal silanol groups on the external surface of the highly siliceous ZSM-5 zeolites were found to be the most suitable for the Beckmann rearrangement [45]. Recent articles of in-situ analysis of FT-IR and NMR are in good agreement with the findings of Hoelderich et al. [58-60].

In addition, the Beckmann rearrangement of cyclohexanone oxime was carried out over modified B-beta-type zeolites. Upon the calcination in an air atmosphere, most of the boron was extracted from the framework, resulting in the formation of extremely weakly acidic silanol nests and vicinal groups. These mentioned hydroxyl groups were responsible for the high selectivities of up to 97% [43].

However, discrepancies exist as to the location of the reaction sites inside the micropores, at the pore aperture or at the external surface of zeolite crystals [40, 61] Sato et al. [62-63] reported in 1989 that an important factor enhancing the selectivity to caprolactam in the Beckmann rearrangement was the external surface area of the zeolites, such as ZSM-5. They conclude that reaction over high siliceous ZSM-5 proceeds on an

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external surface and therefore, does not suffer from diffusional resistance in the pores, thus preventing the side reactions.

Yashima et al. [64] compared H-ZSM-5, H-ferrierite, H-mordenite, Ca-A, H-borosilicate and H-SAPO-5. The catalysts with smaller pore window size than the molecular size of cyclohexanone oxime showed high selectivity to caprolactam. It was concluded that the selective formation of caprolactam occurred at the active sites on the external surface of zeolite materials.

Furthermore, Herrero et al. [52] reported on the use of medium and wide pore zeolites concluded that for medium pore zeolites, the active centers have to be on the outer surface, due to the diffusional transport limitation of the reagents and products and steric hindrance of the transition state. For wide pore zeolites, with increase of active sites on an external surface (e.g., in cavities and structure defects), the reaction proceeded with higher selectivities, reaching 60% conversion and 68% selectivity.

Hoelderich et al. [43] reported use of beta zeolites in the Beckmann rearrangement and found that, in contrast to the MFI structure in beta zeolite it was possible to form the caprolactam inside the elliptic pores, but that the chance for a migration of the lactam out of the pores was comparably low. With consecutive reactions to polymeric residuals in the pores, a starting point for the deactivation of the outer surface is formed. It was proposed that the reaction takes place mostly on the outer surface and most probably at pore mouth in a small shell of the zeolite crystal.

Albers et al. [65] analyzed both fresh and spent B-MFI catalysts with secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS). They demonstrated that by-products and products of consecutive reactions like nitriles and

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polymeric species are formed in the pore system close to the outer surface, causing a blockage of the pores, thus confirming to the theories of both Herrero and at the research group of Hoelderich .

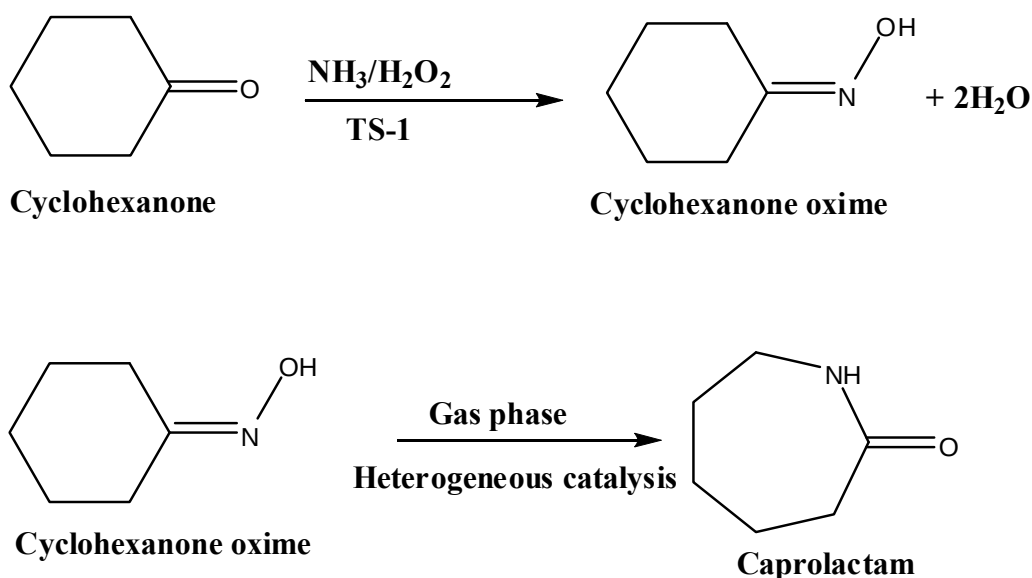
The research article of Kath et al. [40] proposed that the Beckmann rearrangement also takes place inside the pores. To prove this assumption, sorption experiments with cyclohexanone oxime and caprolactam were undertaken at 85 °C, and 140 °C, respectively. It could be shown that cyclohexanone oxime and caprolactam could enter the pore structure in time span of 3-10 min. But these findings could not be verified.

In addition, experiments with different crystal sizes were undertaken, showing an increase in conversion and selectivity with decreasing crystal size as already found by the group of Hoelderich [22]. Possible approaches to minimize diffusion limitations include either decreasing crystal size, thereby reducing the intercrystalline diffusion path length, or increasing the fraction of transport pores by introducing mesopores in a microporous material. The creation of mesopores in zeolitic materials has been shown to have a significant effect on their catalytic performances [66].

It can be concluded that outer surface and, at most, the pore mouth and a small part of the outer regions of the crystal seem to take part in the reaction. For the Beckmann rearrangement, the outer surface of the catalyst particles seems to be the most probable place. The comparison of MFI zeolites with large pore zeolites showed the superiority of the MFI type materials. With traces of the reactants and notable amounts of by-products were formed only in the outer layers of the zeolite crystal.

Sumitomo Chemicals Co has carried out gas phase investigations in the presence of silicalite zeolites [67-69]. As the first company, Sumitomo Chemicals Co., Ltd. has

industrialized the process for synthesis of caprolactam by using heterogeneous catalysts in 2003. This process combines Enichem's direct ammoxidation of cyclohexanone with the vapor phase Beckmann rearrangement of cyclohexanone oxime to caprolactam (Scheme-14). This plant has been operating successfully on 60,000 tons per year scale [37]. This new process has 100% theoretical atom efficiency, while the classical caprolactam production method has only 36%.

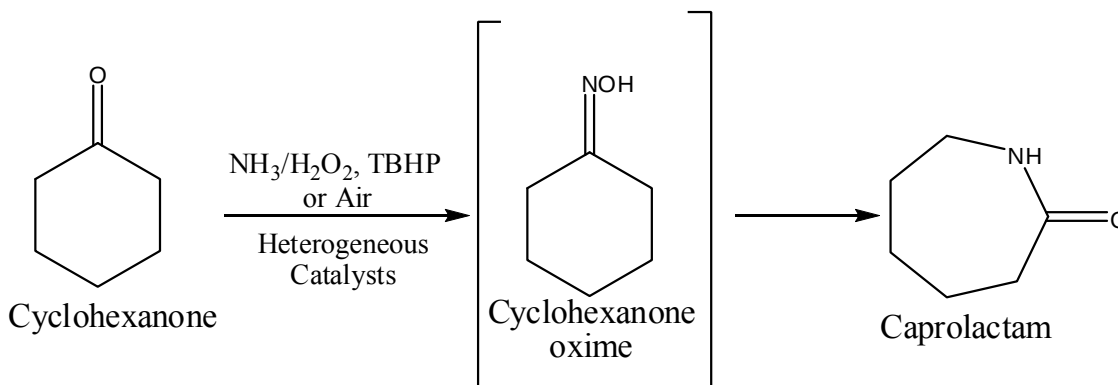


**Scheme -14: New catalytic process of the cyclohexanone ammoxidation with TS-1 catalyst and the Beckmann rearrangement of cyclohexanone oxime to CL.**

### ***2.3.2 Synthesis of caprolactam from cyclohexanone in a “one pot” reaction***

A number of reviews have been written on caprolactam, indicating alternative processes [11]. The essence of the route investigated by us was to avoid the use of the intermediate cyclohexanone oxime. This direct incorporation of ammonia into a ketone

by oxidation with either hydrogen peroxide or air over heterogeneous catalysts is called ammoximation (Scheme-15). So far, several attempts have been examined to develop a synthesis of caprolactam from cyclohexanone in a one pot method.



**Scheme-15: Synthesis of caprolactam by ammoximation process.**

In 1982 Amor et al. [70-73] first demonstrated a direct gas phase route to synthesis of caprolactam from cyclohexanone over  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts. Since, acidic catalysts are known to catalyze the vapor phase rearrangement of oxime to caprolactam, an experiment was carried out to feed ketone/ $\text{NH}_3$  and air over two successive catalyst beds. The first bed contained a  $\text{SiO}_2\text{-Al}_2\text{O}_3$  active for ammoximation at 220 °C, while the following bed contained a rearrangement catalyst at 250 °C. In this manner, they have achieved a conversion of cyclohexanone of 53% and selectivities of cyclohexanone oxime and caprolactam of 24% and 25% respectively.

Moreover, the same author has reported ammoximation reaction over different other potential catalysts such as gallium and several silica gel with different pore volumes. Caprolactam selectivity of 14% as well as oxime selectivity of 45% with 93% cyclohexanone conversion was observed [74-75].

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In 1996 Prasad et al. [76] described the ammoximation reaction in presence of nitric oxide and ammonia over  $\text{TiO}_2$ , Ti-peroxo catalyst, fireclay and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts in liquid phase reaction conditions. A maximum conversion of 47% cyclohexanone with a maximum yield of 38% and selectivity of caprolactam of 81% is achieved at cyclohexanone:NO:NH<sub>3</sub> molar ratio of 1:2.9:1.7 and a temperature of 75 °C. Also, same reaction was applied over  $\text{Al}_2\text{O}_3$  supported titanium silicalites [77]. Nevertheless, in presence of these catalysts maximum selectivity for oxime of 80% was found.

Raja et al.[78] published a single step caprolactam synthesis from ammoximation reaction in the liquid-phase, using oxygen (as air) and ammonia over bi-functional catalysts such as  $(\text{M}^{\text{II}}\text{M}^{\text{III}})\text{AlPO-36}$  ( $\text{M} = \text{Co}, \text{Mn}$ ) without any solvents. The maximum conversion for cyclohexanone was 23% with 36% and 45% selectivities for oxime and caprolactam respectively, over  $\text{Mg}^{\text{II}}\text{Co}^{\text{III}}\text{AlPO-36}$  in presence of  $\text{H}_2\text{O}_2$  as an oxidant at 75 °C for 20h of reaction time.

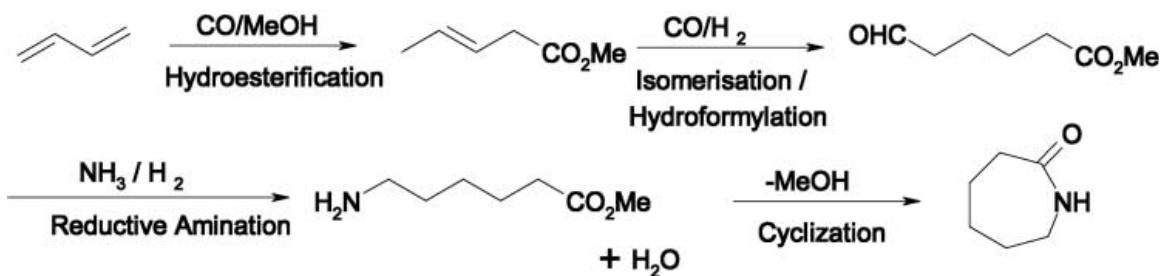
Recently, the same group of Thomas [79-80] reported a laboratory scale single step, solvent free process of producing caprolactam using a family of designed bifunctional, heterogeneous, nanoporous catalysts containing isolated acidic and redox sites. The advantage of such designed heterogeneous catalysts, and their application to a range of other chemical conversions, are also adumbrate. The maximum conversion was obtained over  $\text{Fe}_{0.02}\text{Mg}_{0.02}\text{Al}_{0.96}\text{PO}_4$  catalyst under 35 bar air pressure at 80 °C. The cyclohexanone conversion was 71.9% with 11.5% oxime selectivity and 72% caprolactam selectivity. The same work was reviewed by same authors or others in

different research articles. They have described the importance of this new single step process [81-83].

### 2.3.3 Caprolactam processes without cyclohexanone oxime as intermediate product

#### (I) Hydroesterification

The industrially most important alternative to the heterogeneous process is the production of caprolactam based on butadiene. According to data published by SRI consulting [84], it is possible to produce caprolactam with lower cost than existing processes. That route was investigated when market price of butadiene was low.



**Scheme-16: Butadiene to caprolactam: hydroesterification route.**

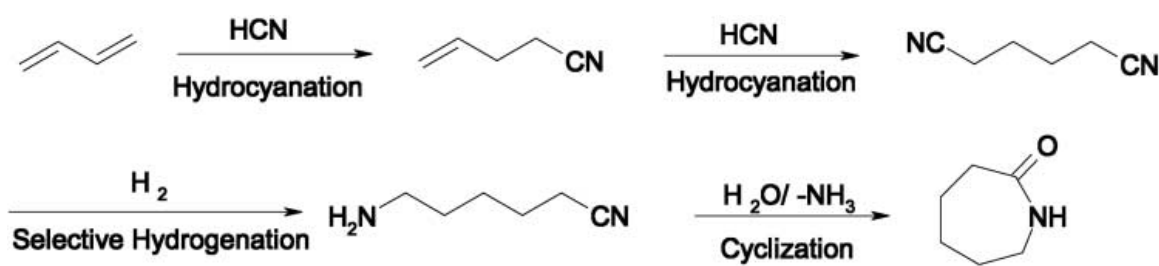
In this process, in the first step hydroesterification of butadiene to methyl-3-pentenoate is performed with carbon monoxide and methanol in presence of a cobalt complex catalyst [85] or Pd complex catalyst [86]. The next step in the described synthesis is the hydroformylation. The catalyst in the BASF process is the assembly the same octacarbonyldicobalt(0)-pyridine complex, whereas the catalyst in the DSM process is rhodium-hydride-carbonyl complex with bis-(phosphorus-triarylesters) [87]. For the hydroformylation, an isomerization of methyl-3-pentenoate to methyl-4-pentenoate is

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conducted [88-90]. In the hydroformylation step, the methyl-4-pentenoate is then directly converted into methyl-5-formylvalerate, which is the starting compound for the next step, or the product of the hydroesterification, the methyl-3-pentenoate is directly hydroformylated after an “insitu” isomerization to methyl-4-pentenoate. The third step of the synthesis is the reductive amination and cyclization to caprolactam, for which two routes are described. In the first route, the methyl 5-formylvalerate is reductively aminated to 6-aminohexanoate be followed by a cyclic amidation of 6-aminohexanoate to caprolactam. In the second route, the methyl-5-formylvalerate is hydrolyzed to 5-formyl-valeric acid followed by the reductive amination to 6-aminohexanoic acid and the subsequent cyclic amidation to caprolactam. With these, yields of 5-formyl-valeric acid of 74% are obtained over cation exchanged resin catalysts, followed by reductive amination to 6-aminohexanoic acid on Raney Ni catalyst with yields of 57% [91]. Finally, 6-aminohexanoic acid is cyclized to caprolactam without a catalyst at 300 °C with yields of 95%.

### *(II) Hydrocyanation*

The hydrocyanation of butadiene is a well established process based on homogeneous nickel phosphane catalysts (Scheme-17).



**Scheme-17: Butadiene to caprolactam: hydrocyanation route.**

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The first step in this process is hydrocyanation of butadiene to hexanedinitrile. It was developed by DuPont for the production of hexanedinitrile, which is precursor for hexamethylenediamine, the monomer for nylon 6, 6 [92]. In a second step, selective partial hydrogenation of hexanedinitrile to 6-aminohexanenitrile followed. According to DuPont, the hexanedinitrile is hydrogenated with molecular hydrogen at 6.9 MPa and 80 °C on a Raney nickel catalyst in liquid NH<sub>3</sub> [93]. The selective hydrogenation of hexanedinitrile to 6-aminohexanenitrile is performed over Raney nickel catalyst in the presence of 1,6-hexanediamine and KOH with a conversion of 81% and a 60.3% yield [94]. The last step in this synthesis route is the cyclization of 6-aminohexanenitrile to obtain caprolactam.

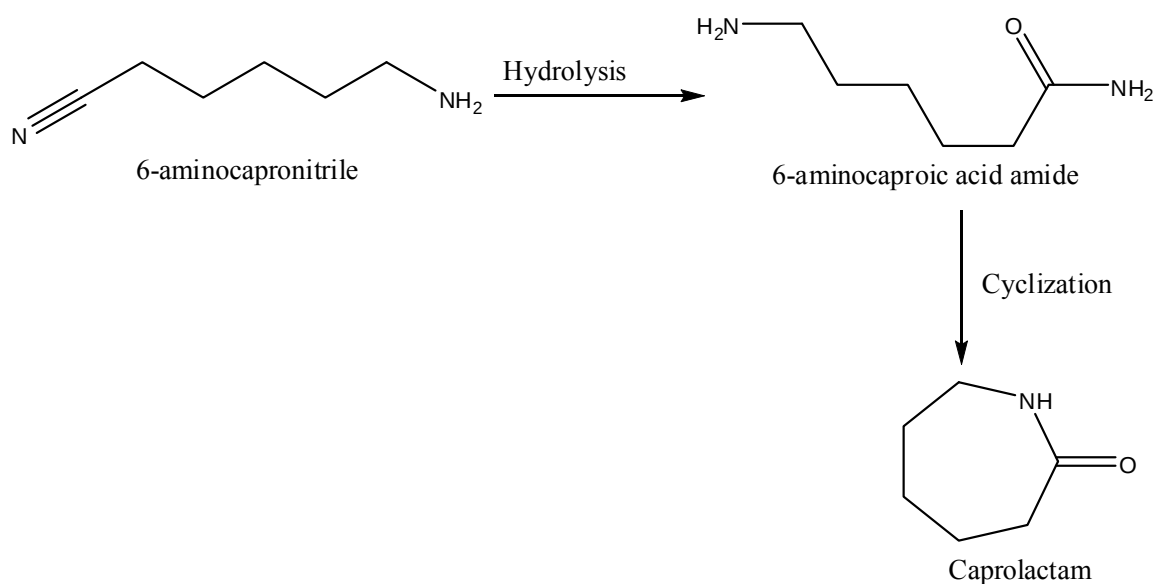
However, in the butadiene based caprolactam routes several separation and recycling steps of the products and by-products are necessary. It seems that the hydrocyanation of butadiene to caprolactam is more likely for an industrial realization than the route via hydroesterification.

### *(III) Caprolactam from 6-aminocapronitrile*

Nevertheless, the production of caprolactam from 6-aminocapronitrile by cyclization (Scheme-18) in presence of water at elevated temperature and the presence or absence of a catalyst and a solvent is also promising process. A patent from BASF [95] described a method of production of caprolactam from 10% 6-aminocapronitrile solution in water that was heated to 300 °C, in a tube reactor, the average residence time being 1 h. All of the 6-aminocapronitrile was converted during this process and needed to be recycled, thus, a yield of 93% caprolactam could be achieved. In addition, Vogel et al. described the results from this reaction in supercritical water [96-97]. 6-aminocapronitrile

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conversion of 70% and a selectivity of 66% were obtained at 350 °C and 250 bar with a residence of time of 240 s. Recently, C. Yan has reported [98] this reaction in continuous synthesis at high-temperature water. They have achieved 90% yield of caprolactam and conversion of 94% 6-aminocapronitrile at 400 °C with residence time of 96 s and 400 bar.

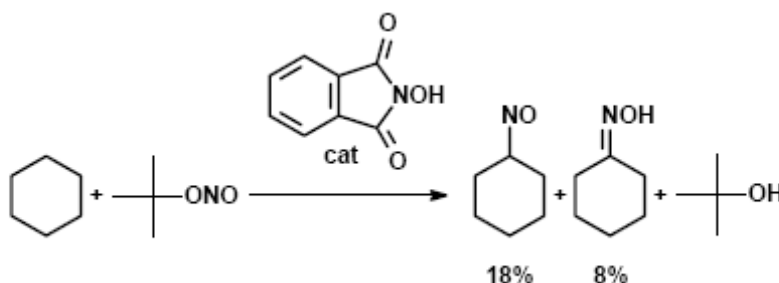


**Scheme-18: Production of caprolactam from 6-aminocapronitrile.**

### *(IV) Caprolactam from cyclohexane*

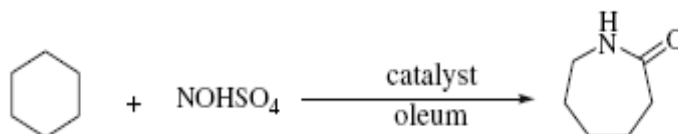
Several research groups have been attempted to synthesis of caprolactam from cyclohexane. In 2006, Y.Ishii research group has reported first time in synthesis of caprolactam from cyclohexane and t-butyl nitrite by using N-hydroxyphthalimide as key catalyst (Scheme-19) [99-100]. In this article first cyclohexane is reacted with N-hydroxyphthalimide (NHPI) catalyzed nitrosation with t-butyl nitrite (tBuONO) to give nitrocycloalkanes, and then treatment of nitrocycloalkanes with Et<sub>3</sub>N in EtOAc forms

cyclohexanone oxime. Formed cyclohexanone oxime reacts with cyanuric chloride in 1,1,1,3,3,3-hexafluoro-2-propanol produced caprolactam with 43% yield.



**Scheme-19: Nitrosation of cyclohexane with *tert*-butyl nitrite.**

Recently, K. You et al. reported a one-step formation of caprolactam from cyclohexane and nitrosyl sulfuric acid catalyzed solid vanadium phosphates composites (Scheme-20) [101]. These authors have been observed 26% cyclohexane conversion and 35% caprolactam selectivity over Mn and Co introduced Al-VPO composite catalysts.



**Scheme-20 The liquid phase nitrosation of cyclohexane and nitrosyl sulfuric acid.**

## 2.4 General introduction about heterogeneous catalysts

Porous solids have extensive commercial applications as adsorbents, catalysts and catalyst supports due to their high surface areas. According to IUPAC definition [102] porous materials have been divided into three types based on their pore dimensions.

| Type        | Pore size (Å) |
|-------------|---------------|
| Microporous | : <20         |
| Mesoporous  | : 20-500      |
| Macroporous | : >500        |

Well known microporous materials are zeolites [103] and zeolite-like materials. Zeolites are inorganic polymeric frameworks of tetrahedral alumina ( $\text{AlO}_4^{-1}$ ) and silica ( $\text{SiO}_4$ ) units. The  $\text{SiO}_4$  unit has no net charge while the  $\text{Al}^{3+}$  substitution creates an overall negative charge on the  $\text{AlO}_4^{-1}$  unit. The negative charge from aluminum substitution causes the zeolite surface to have an overall negative charge. To balance this charge, a cation,  $\text{M}^+$ , reside within the zeolite. The cation can be either inorganic (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ) or organic (e.g., quaternary ammonium compounds). Other hetero atoms besides Al, such as B, Ga, P, V, Ti, Zn, Mo, Sn, Fe and Nb, can also incorporated into the zeolite matrix [104-107].

Among the large number of synthetic zeolite structures, MFI proves to be the most versatile towards isomorphous substitution. The most important factor in changing the isomorphous substitution with metal ions is acidity. The factors affecting the acid strength per site include Si/T ratios and type of T- atoms (T= other transition metal). The acidity of the well studied ZSM-5 zeolite is decreased according to the different hetero atoms sequence is  $\text{Al} > \text{Ga} > \text{Fe} > \text{B}$ . In this way the acidity spectrum ranges from the mildly acidic borosilicate to the strongly acidic sites in aluminosilicates with high Si/T ratios. Hoelderich had given an extensive review on such type of materials and their application in organic synthesis e.g. alkylation of aromatics, production of linear

alkylbenzenes, production of cyclohexanol etc [108-109]. TS-1 is another example of Ti introduced into the framework of zeolites of the MFI structure. TS-1 demonstrates redox catalysis, quite distinct from conventional aluminosilicates zeolites [110].

### 2.5 Nb catalysts and background

Niobium (Nb) belongs to group VA in a periodic table. Nb containing materials have shown remarkable activity in heterogeneous catalysis research for synthesis of fine chemicals. An extensive research had been carried out in presence of Nb compounds as catalysis; also it can be used as promoters, support, solid acid catalysts and/or redox materials [111-112].

Nb containing materials have shown very good activity in selective oxidation and epoxidation of organic compounds in mild conditions [113-115], hydrodesulphurization [116], hydrogenation [117], oxidative dehydrogenation [118], ammoxidation [119], alkylation [120] reactions. Particularly, Nb contain molecular sieves materials such as niobium incorporated in mesoporous materials, micropore zeolites have shown great interest in this specified research field.

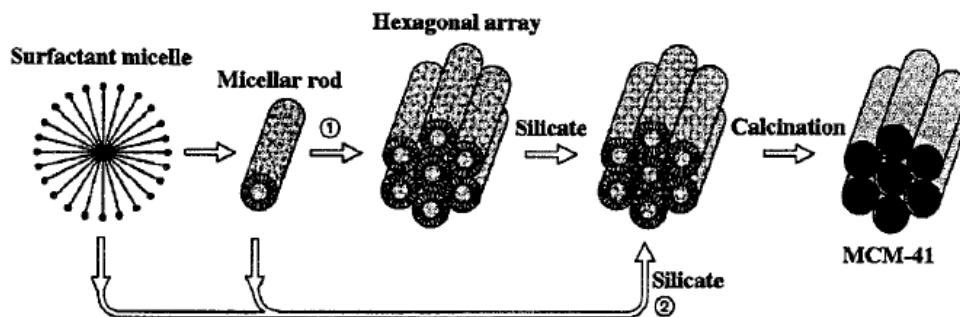
A new area in synthesizing mesoporous molecular sieves by templating method was developed by Beck et al. in 1992 [121-122]. M41S mesoporous silicate family has attractive advantages as catalyst support materials, because of high surface area ( $>1000 \text{ m}^2/\text{g}$ ) and uniform pore size (15-100 Å). A great amount of research has been devoted to the well-defined mesoporous molecular sieves that belong to the M41S family [123-125].

One form of this series, MCM-41, which possessed a uniform arrangement of hexagonally shaped mesopores of diameter varying from 20 to 150 Å, has gained great

attention in material science and catalysis. The advantage of the large pore size of these materials will facilitate the flow of reactants and products very easily through the pore system. However, materials such as Si-MCM-41 have some limitations in reactant transformation due to few active sites on its amorphous SiO<sub>2</sub> wall. Hence, framework substituted molecular sieves were examined for better catalytic performance. Such framework substituted molecular sieves with different transition metals has shown different mechanisms for the formation of the hexagonal phase.

The understanding about the synthesis of these materials and the corresponding mechanism has opened up a new aera of molecular engineering. The most outstanding feature of the preparation of these materials is the role of the templating agents. The formation of mesoporous materials with a variety of crystallographically well-defined frameworks has been made possible via a generalized “liquid-crystal templating” (LCT) mechanism. The surfactants (act as templates) are large organic molecules (amines) having a long hydrophobic tail of variable length (e.g. alkyltrimethylammonium cations with formula  $C_nH_{2n+1}(CH_3)_3N^+$ , where  $n > 8$ ) and a hydrophilic head.

Two possible pathways have been proposed for the LCT mechanism which are schematically shown in Fig. 2.



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**Figure -2: Possible mechanistic pathways for the production of MCM-41: (1) liquid crystal phase initiated and (2) silicate anion initiated.**

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In the first pathway, it is considered that, there is a formation of the surfactant hexagonal liquid-crystal phase around which the growth of the inorganic materials is directed. The  $C_nH_{2n+1}(CH_3)_3N^+$  surfactant micelles aggregate to form hexagonal arrays of rods. Silicate anions present in the reaction mixture interact with the surfactant cationic head groups. Condensation of the silicate species leads to the formation of an inorganic polymer.

It has been proposed including a liquid crystal templating mechanism bases on the specific type of electrostatic interaction between inorganic precursor (I) and surfactant head group (S). The most popular liquid crystal mechanism could be described by different pathways such as  $S^+I^-$ ,  $S^+X^-I^+$  ( $X^-$  is a counter anion) and  $S^-M^+I^-$  ( $M^+$  is a metal cation) [126]. In addition, these siliceous mesoporous molecular sieves have been post synthesis modified with different transition metals via cation exchange, impregnation etc. Another possibility is the interaction of transition metal between silicon-oxygen tetrahedral building the walls of mesostructure called isomorphous substitution of silicon. Therefore, isomorphous substitution of silicon with a transition metal is an excellent strategy in creating catalytically active sites and anchoring sites for reactive molecules in the design of heterogeneous catalysts [127].

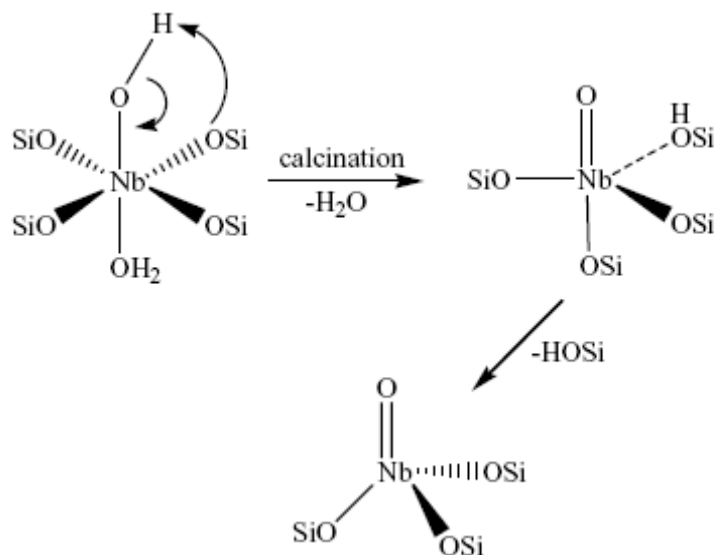
A mesoporous niobium-containing silicate of the MCM-41 type was prepared for the first time by Ziolek et al.[128] Also, the same authors were reported first time in synthesis of Nb containing mesoporous silica which were synthesized by using different triblock copolymers as templates [129-130].

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Nb was incorporated into molecular sieves zeolites (MFI) by Prakash and Hartmann et al. [131-132].

In addition, mesoporous Nb<sub>2</sub>O<sub>5</sub> was first synthesized by Antonelli et al. [133]. The main leading problem of Nb incorporated micropore zeolites is often limited by slow diffusion of reactants and products through the small pores, the accessibility of bulky organic compounds through the pores of the catalyst by reason of their small kinetic diameter (<6 Å) and the mass transfer through the catalytic active centers located within micropores can be very slow. There is an ambiguity about isomorphous substitution of transition metals in zeolite frame work. Based on Pauling's ionic radii criterion and lack of many transition metal tetrahedral oxides, isomorphous substitution is very difficult [131]. However, later studies have shown that such a substitution takes place in several metallosilicate molecular sieves for well known example is TS-1. Many characterization techniques were revealed the nature of location of Ti in a silica frame work [110]. Nb incorporated mesoporous material has shown potential applications in various reactions on account of high surface area (1000 m<sup>2</sup>/g) and uniform pore size (15-100 Å). Also, Nb active centers are much more accessible in Nb containing mesoporous materials.

In Fig-3, initially, the incorporation of Nb into the framework the oxidation number +5 with octahedral geometry. It is possibly bound to four siloxane groups, one hydroxyl and one water molecule. After calcination, dehydration will takes place and leading to the formation of a Nb=O which is assuming tetrahedral geometry [134].



**Figure-3: Possible way of Nb incorporation into silica framework.**

## 2.6 Aims of the thesis

It is evident from the literature survey that the development of new synthesis routes for production of caprolactam by an environmentally benign process is very essential from the point of view of chemical industrially.

The existing catalytic process of gas phase Beckmann rearrangement process has some limitations. Among the main problems with this processes are the catalysts, as they were deactivated within short time on stream. Indeed, catalysts have to be regenerated after certain reaction time under air in a fluidized bed reactor in a fluidized bed unit with continuous regeneration. Such catalyst regeneration process after short reaction time is industrially very energy consuming process and therefore, very costly industrial manner.

The principle objective of this present study deals with finding new catalysts which are more active and selective for a long reaction time under gas phase reaction conditions. In addition, in order to reduce the cost and save energy, reactions have been

## 2. General Part

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carried out in fixed bed reactor where catalysts regeneration and reactions were pursued in one reactor.

In order to achieve our goal, Nb containing catalysts with different structures have been prepared and all these catalysts have applied for the reaction. All niobium modified catalysts were characterized by various physical-chemical characterization techniques. Catalyst acidity was measured by ammonia TPD and pyridine FT-IR methods. All the catalyst activity tests were carried out in fixed bed reactors. The influence of temperature, WHSV, solvents, feed ratios, pressures, time on stream study and catalysts regeneration studies were very well studied and catalytic activity results were correlated with catalytic characterization results in a structure/performance correlation.

The second part of this thesis deals with the synthesis of caprolactam in a one pot liquid phase reaction from cyclohexanone in presence of hydrogen peroxide and ammonia over heterogeneous catalysts. This route provides a more economical and environmentally benign process. More over, this single step procedure leads to a minimization of the consumption of energy and is a time saving process.

The ammoximation reactions were carried out over transition metals incorporated mesoporous catalysts and zeolitic structured catalysts. The influence of temperature,  $\text{NH}_3$ /cyclohexanone,  $\text{H}_2\text{O}_2$ /cyclohexanone, stirring speeds, pressures etc were studied over different catalysts and reaction results interpreted with catalyst characterization results.

**3. Gas phase Beckmann rearrangement of  
cyclohexanone oxime to caprolactam.**

## **3. Gas phase Beckmann rearrangement of cyclohexanone oxime to caprolactam**

This chapter describes the catalyst characterization results of Nb containing different structured catalysts with various physical and chemical characterization techniques and the catalytic activity results of gas phase Beckmann rearrangement reaction. The chapter has been divided into two parts. (I) Catalyst characterization results, (II) Gas phase Beckmann rearrangement of cyclohexanone oxime to caprolactam.

### **3.1. Physico-chemical characterization of catalysts**

#### **3.1.1 XRD results**

XRD patterns of as-synthesized and calcined mesoporous Nb-MCM-41 (Si/Nb 16-128) samples were shown in Fig-1-2. The XRD patterns of Nb-MCM-41 sample, before and after calcination show the hexagonal MCM-41 phase in the sample. A typical low angle X-ray diffraction of MCM-41 shows 4 peaks, the first intensive peak appears approximately at  $2\theta=2^\circ$  (miller indices 100) and other three peaks appear at  $2\theta=3-8^\circ$  (miller indices 110, 200 and 210) [135]. In case of Nb incorporated MCM-41 molecular sieves, the XRD peaks of the as-synthesized and calcined samples exhibit an intense signal at about  $1.9 - 3^\circ$ , and additional peak at  $3.5-5^\circ$  (miller indices 100, 110) with low intensity and other peaks did not appear. The disappearance of miller indices 200 and 210 in the calcined samples may due to reduction of structure organization during the calcinations [134]. The increase of the XRD intensity after calcination is observed very clearly. Moreover, the intensity of XRD signal is increased with increasing the Nb

### 3.1. Catalysts characterization results and discussion

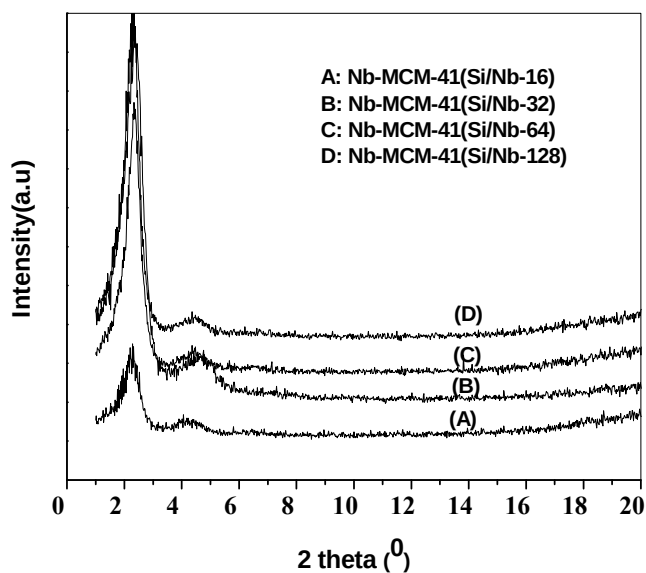
content in the samples from Si/Nb-128 to 16. It clearly indicates the incorporation of Nb into the framework MCM-41 structure. A similar kind of change was observed by Ziolek et al. [136].

After calcination the peak positions shifts to higher  $2\theta$  values due to pore size contraction. Furthermore, the absence of diffractions at higher  $2\theta$  range corresponding of metal oxides, indicating that, metal ions were either well dispersed in the framework of MCM-41 or attained an amorphous form outside of the framework. The characterization techniques XRD and BET show that all the materials had the well-ordered hexagonal mesoporous structure of MCM-41 type with one system of pores (around 4 nm pore diameter) and very high surface area ( $1000 \text{ m}^2/\text{g}$ ). Table-1 summarizes the  $d_{100}$  spacing and lattice parameter ( $a_0$ ) calculated as per literature from XRD and low-temperature nitrogen adsorption isotherms experiments. It can be seen that, upon introducing the Nb metal into the mesoporous MCM-41, the unit cell parameter calculated by  $a_0=2d_{100}/\sqrt{3}$  and  $d_{(100)}$  increased. It could be due to the larger ionic radius of  $\text{Nb}^{+5}$  ( $0.64 \text{ \AA}$ ) and longer Nb-O bond length ( $1.69 \text{ \AA}$ ). However, a decrease of the unit cell parameter and  $d_{(100)}$  spacing was also observed at higher Nb content sample, e.g. Si/Nb-16. That could be because of strong interaction of Nb with the inner silica walls, dispersion of high surface Nb concentration. Similar results were observed in case of other transition metals such as V incorporated on mesoporus silica MCM-48 structured material and Nb-MCM-41 molecular sieves [137, 138].

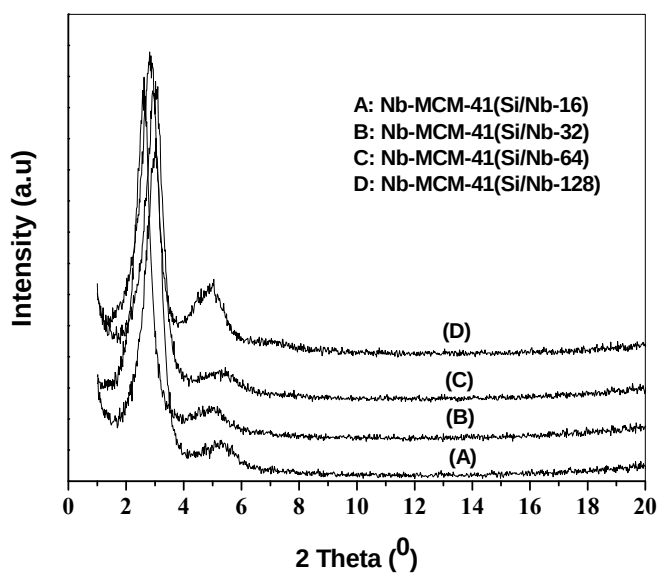
According to Zhang et al. [137] the Nb incorporation into framework occurs by two different steps. In first step, the loosely bonded silica gel has the accessibility of incorporation heteroatom at room temperature. In second step, Nb is fully condensed into

### 3.1. Catalysts characterization results and discussion

the framework silica under high temperature at hydrothermal conditions. However, in this present investigation we assume that the second mechanism occurred in the synthesis procedure.



**Fig-1: As synthesized samples**



**Fig-2: Calcined samples**

### 3.1. Catalysts characterization results and discussion

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**Fig.1-2. XRD patterns of as-synthesized and calcined mesoporous Nb-MCM-41 molecular sieves (a) Si/Nb-16 (b) Si/Nb-32 (c) Si/Nb-64 (d) Si/Nb-128**

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The purity and crystallinity of Nb-Beta zeolite, Nb mesoporous material and Nb impregnated on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> materials were characterized by XRD analysis. The low angle XRD patterns of calcined Nb-SBA-15 and Nb-HMS samples (Fig-3) exhibit strong peak in the 2 $\theta$  region of 1.0 to 1.5° due to 100 reflection and small peaks at 2 $\theta$  value 2-3° are due to higher order 110, 200 and 210 reflections indicating, formation of well order hexagonal mesoporous structure [134]. In case of Nb-HMS sample the peak corresponding reflection 100 is very broad, and it is indicating material has wormhole structure [139]. However, in Nb-HMS material, the reflection peaks related to 110, 200 and 210 did not appear. The disappearance of these peaks in the calcined samples is due to reduction of structure organization during the calcinations. In the XRD patterns of Nb-SBA-15 and Nb-HMS no diffraction peaks observed at higher 2 $\theta$  value demonstrates that absence of Nb species. The unit cell parameter ( $a_0=2d_{100}/\sqrt{3}$ ) of Nb-SBA-15, and Nb-HMS are presented in Table-2. The unit cell parameter of Nb-SBA-15 is much higher than the Nb-HMS. The XRD patterns of Nb-Beta zeolite, Nb impregnated on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> samples are shown in Fig-4. The Nb-Beta zeolite exhibits the most intensive peaks in the range 2 $\theta$ =20-30° confirming Beta structure as well as high crystallinity nature [140]. In case of Nb impregnated on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts, the reflection peaks appeared only for SiO<sub>2</sub> matrix.

### 3.1. Catalysts characterization results and discussion

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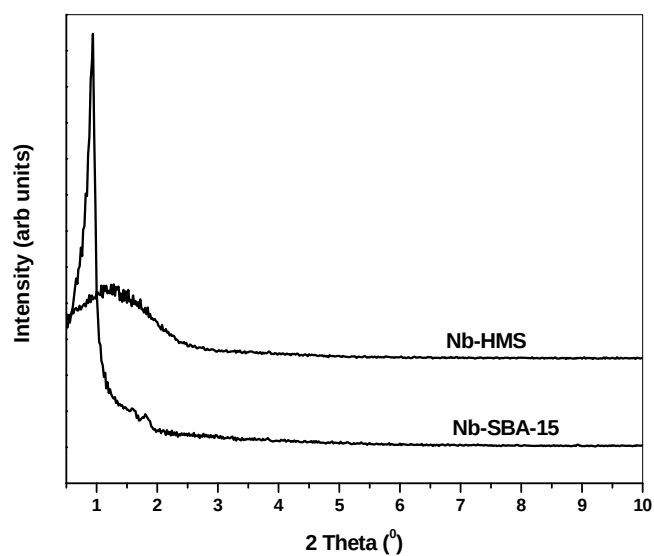


Figure-3: XRD of calcined Nb-mesoporous samples.

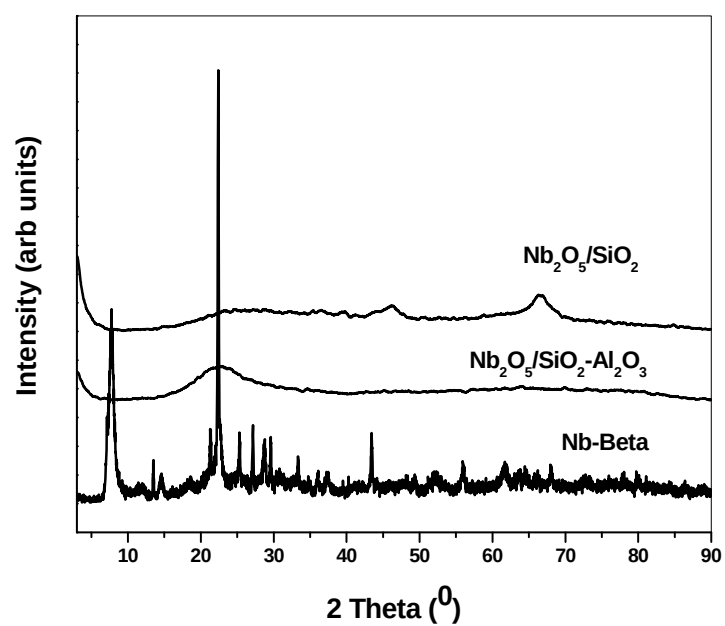


Figure-4: XRD of calcined Nb Beta and supported oxides

### 3.1. Catalysts characterization results and discussion

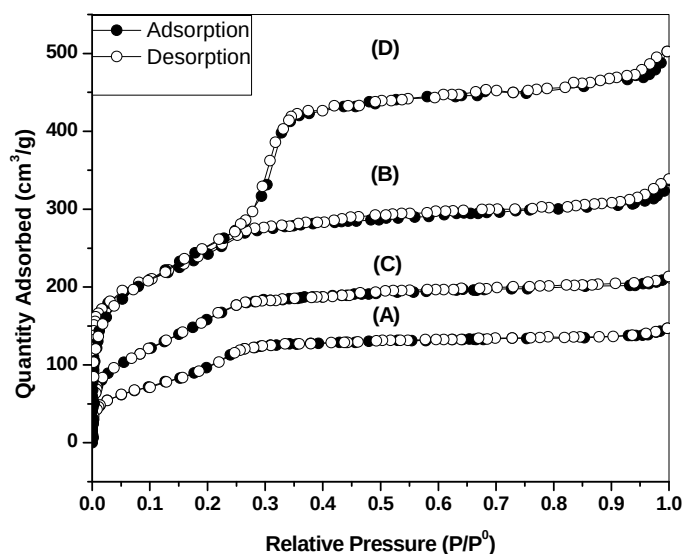
#### 3.1.2 N<sub>2</sub> Physisorption

Specific surface area, specific pore volume and pore diameter (BJH method) for calcined materials are presented in Table-1. N<sub>2</sub> isotherm of all calcined samples show type IV isotherm, (Fig-3) which is typical for mesoporous materials. The isotherm shows well-defined stages, and they coincide with those already reported in literature [141]. However, the isotherm of sample Nb-MCM-41(Si/Nb-16) has already lost the characteristic mesoporous solid shape and its surface area decreased sharply to 417 m<sup>2</sup>/g. The surface area of the catalysts decreased in the order Nb-MCM-41(Si/Nb-128)>Nb-MCM-41(Si/Nb-64)>Nb-MCM-41(Si/Nb-32)>Nb-MCM-41(Si/Nb-16). The decrease in the surface area and pore volume with increasing Nb loading can be attributed to the formation of Nb<sub>2</sub>O<sub>5</sub> species within the mesopores, which might parallely block the pores of the mesopore structure. Thus, the incorporation of higher amounts of Nb disrupts the quality of Nb-MCM-41 material. Similarly, pore volume decrease in the same order due to the presence of textural mesoporosity [142].

**Table-1: Physical properties of Nb-MCM-41 molecular sieves.**

| Catalyst | Si/Nb<br>gel<br>ratio | ICP    | d100<br>(Å) | a0<br>(Å) | BET<br>Surface<br>area<br>(m <sup>2</sup> /g) | Pore<br>volume<br>(cm <sup>3</sup> /g) | Pore<br>diameter<br>(Å) | Wall<br>thickness<br>(Å) |
|----------|-----------------------|--------|-------------|-----------|-----------------------------------------------|----------------------------------------|-------------------------|--------------------------|
| A        | 16                    | 15.54  | 33.98       | 39.24     | 417                                           | 0.28                                   | 24.64                   | 14.6                     |
| B        | 32                    | 28.31  | 49.08       | 56.67     | 612                                           | 0.26                                   | 30.48                   | 26.18                    |
| C        | 64                    | 54.72  | 41.67       | 48.12     | 632                                           | 0.36                                   | 23.68                   | 24.44                    |
| D        | 128                   | 121.66 | 38.08       | 43.97     | 929                                           | 0.94                                   | 29.27                   | 14.25                    |

### 3.1. Catalysts characterization results and discussion



**Figure-5: N<sub>2</sub> adsorption and desorption isotherm of Nb-MCM-41 samples.(A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.**

The isotherms of the calcined samples were measured at liquid nitrogen temperature (77 K). The N<sub>2</sub> isotherms for Nb mesoporous materials were depicted in Fig.6. These isotherms exhibited a type IV isotherm which is typical for mesoporous materials [141]. Adsorption at low pressure ( $p/p_0 < 0.3$ ) is attributed for thin layer of the adsorbed gas on the mesoporous walls. As the relative pressure increases ( $p/p_0 > 0.3$ ), the isotherms exhibit a sharp inflection characteristic of capillary condensation within the mesopores, and the  $p/p_0$  position of an inflection point is related to the diameter of the mesopore. The N<sub>2</sub> isotherm of Nb-HMS sample showed a large hysteresis loop at  $p/p_0 > 0.9$  which indicates that the larger pores are filled at relative high pressures and formation of macropores. N<sub>2</sub> isotherm for Nb-Beta and Nb impregnated on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were represented in Fig-7. The N<sub>2</sub> isotherm of Nb- Beta zeolite is of Type I isotherm. Nb supported SiO<sub>2</sub> shows Type II isotherm. The similar results were

### 3.1. Catalysts characterization results and discussion

observed by Gao et al. [143] in case of Nb-MCM-41 materials and Nb supported on oxides. Specific surface area, pore volume and pore diameter (BJH method) for calcined Nb materials are presented in Table.2. The pore size distributions for mesoporous Nb are very different than the Nb impregnated SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> materials. Nb mesoporous materials, particularly, Nb-MCM-41 exhibited a much smaller pore size and a narrower pore size distribution than the other Nb mesoporous materials. In contrast, Nb-Beta zeolite exhibited much smaller pore size distribution than the other catalysts.

**Table -2: Physical properties of Nb materials**

| Catalyst                                            | Si/Nb<br>Gel<br>ratio | ICP   | d100<br>(Å°) | a0<br>(Å°) | BET<br>Surface<br>area<br>(m <sup>2</sup> /g) | Pore<br>volume<br>(cm <sup>3</sup> /g) | Pore<br>diameter<br>(nm) | Wall<br>Thickness<br>(Å°) |
|-----------------------------------------------------|-----------------------|-------|--------------|------------|-----------------------------------------------|----------------------------------------|--------------------------|---------------------------|
| Nb-SBA-15                                           | 32                    | 33.33 | 61.35        | 70.84      | 807                                           | 0.83                                   | 4.3                      | 30.54                     |
| Nb-HMS                                              | 32                    | 29.53 | --           | 58.62      | 842                                           | 2.23                                   | 3.83                     | --                        |
| Nb-Beta                                             | 32                    | 27.49 | --           | --         | 389                                           | 0.089                                  | 4.47                     | --                        |
| Nb/SiO <sub>2</sub>                                 |                       | 29.72 | --           | --         | 288                                           | 1.39                                   | 15.16                    | --                        |
| Nb/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> |                       |       | --           | --         | 434                                           | 0.95                                   | 7.03                     | --                        |

### 3.1. Catalysts characterization results and discussion

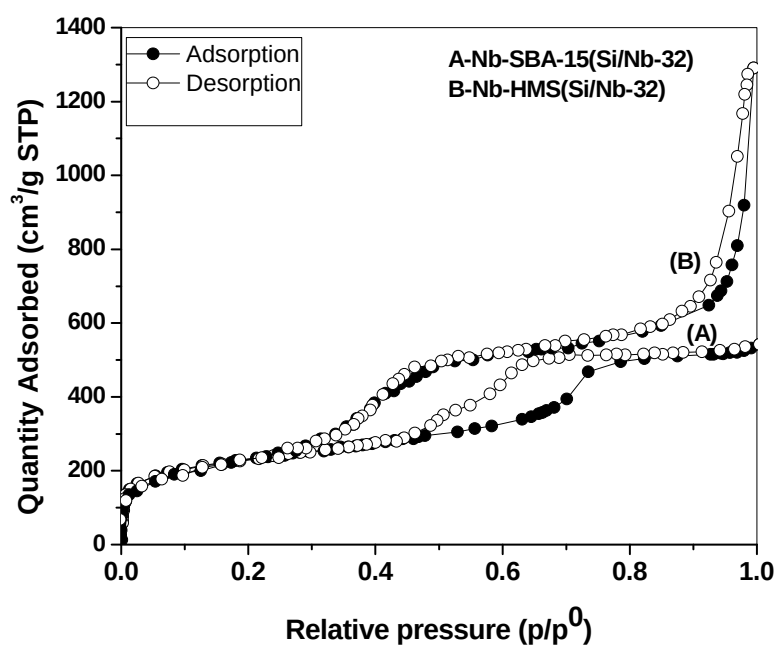


Figure-6: N<sub>2</sub> isotherm of Nb mesoporous materials

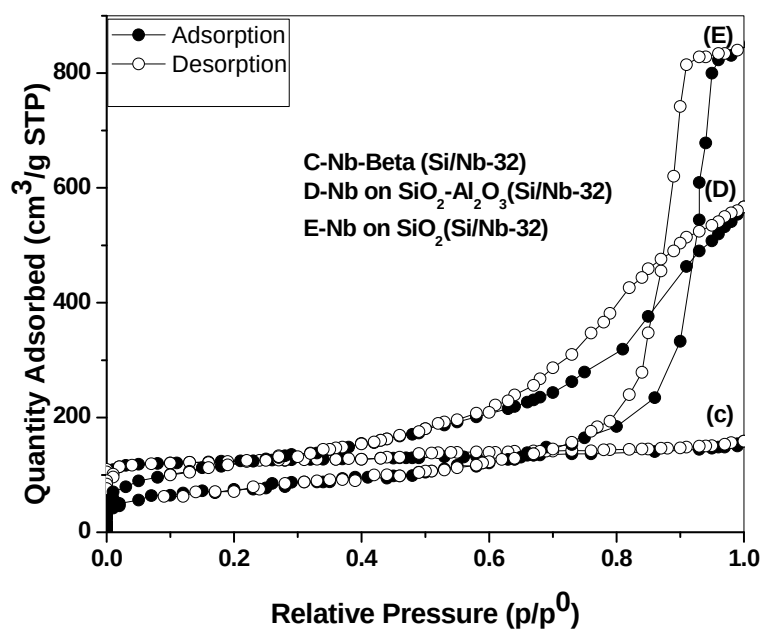


Figure-7: N<sub>2</sub> isotherm of Nb-Beta and supported oxides.

### 3.1. Catalysts characterization results and discussion

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The ICP analysis of calcined samples are presented in Table:1 and 2. The data clearly shows that the amount of metal after calcination is close to the initial gels.

#### 3.1.3. TG and DTA results of Nb-MCM-41

The results of thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of the as-synthesized Nb-MCM-41(Si/Nb-16-128) catalysts in air are illustrated in Figures 8-9. The data of TG-DTA analysis of Nb-MCM-41 samples exhibit four main steps. The first step, below temperature of 200 °C is associated with physically adsorbed water (2% weight loss). The second part of the TG curve at 200-300 °C is related to the thermal removal of template and contribute to around 35% of total weight loss. This can be attributed to the release of tetradecyltrimethyl ammonium bromide in two ways either by desorption or decomposition, accompanied by an endothermic peak in DTA at 300 °C or by oxidation of tetradecyltrimethyl ammonium bromide. The third part at 400-500 °C is attributed to decomposition and oxidation of remaining template and is accompanied by an exothermic peak in the DTA curve at 450 °C (5% weight loss). Finally, the step above 400 °C can be assigned mainly due to the dehydroxylation of SiOH groups (<1% weight loss) [142]. The percentages of weight loss are found about 28, 35, 30 and 33% for Nb-MCM-41(Si/Nb-16), Nb-MCM-41(32), Nb-MCM-41(Si/Nb-64) and Nb-MCM-41(Si/Nb-128) respectively.

### 3.1. Catalysts characterization results and discussion

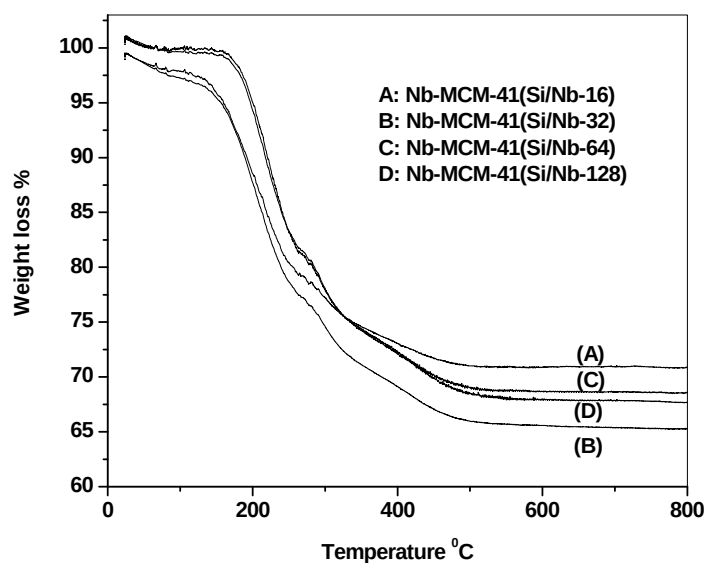


Figure-8: TGA analysis of Nb-MCM-41 molecular sieves (A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.

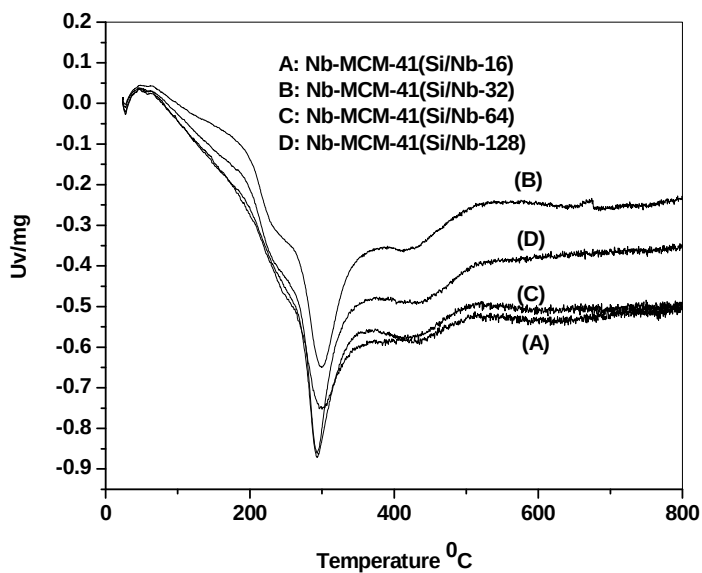
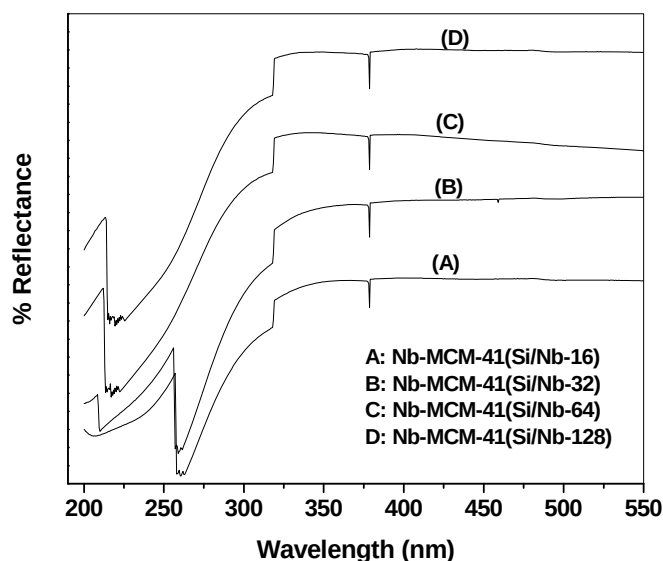


Figure-9: DTA analysis of Nb-MCM-41 molecular sieves.(A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.

### 3.1. Catalysts characterization results and discussion

#### 3.1.4. Diffuse reflectance UV-Vis spectra

Fig-10 shows the UV-Vis spectra of all calcined Nb-MCM-41 samples. These spectra have an intense band around 220 nm which can be assigned to Nb tetrahedrally coordinated to silica surfaces. The intense band at 260 nm in the spectra of samples with higher niobium loading such as (Nb-MCM-41 Si/Nb-32 and 16) is attributed to micro particles of  $\text{Nb}_2\text{O}_5$  [131, 144] which could be formed by leaching of niobium from the frame work. In these materials, niobium is coordinated to four oxygen atoms or interacted with  $\text{H}_2\text{O}$  molecule leading to be distorted tetrahedral environment. Also, Gallo et al. [135] described the mechanism of the +5 oxidation state of niobium species incorporated in the framework of MCM-41 with octahedral geometry and change the coordination by niobium species leaching during the calcination step. The intense band at 320 nm which can be assigned to Nb octahedrally coordinated to silica surface [145].

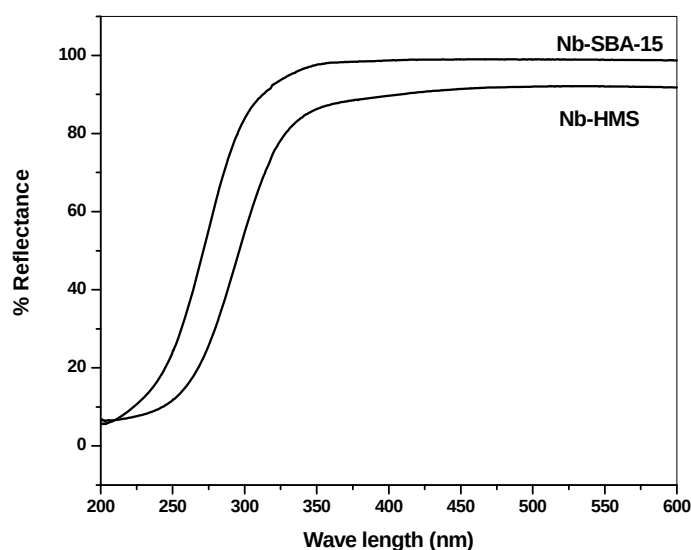


**Figure-10: UV-Vis spectra of Nb-MCM-41 molecular sieves.(A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.**

### 3.1. Catalysts characterization results and discussion

DR-UV-Vis results of Nb-SBA-15 and Nb-HMS samples are illustrated (Fig-11) the reflection peaks at 230 nm is due to tetrahedral Nb species with silica. The UV-Vis reflectance bands overlapping maxima at about 350nm are assigned to the transition of octahedral coordinated Nb species.

DR-UV-Vis results of Nb-Beta and Nb impregnated on oxides samples present (Fig-12) an intense band around 220 nm. This is assigned to tetrahedrally coordinated Nb on the silica surface. However, in case of Nb impregnated on  $\text{SiO}_2$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  supports broadness of band to 410 nm is suggested that niobium species in the samples are aggregated to form micro particles of  $\text{Nb}_2\text{O}_5$  possessing energy band structure [146]. Therefore, we can conclude that in all the samples, tetrahedrally and octahedrally coordinated Nb species are present.



**Figure-11: UV-Vis spectra of Nb-SBA-15 and Nb-HMS.**

### 3.1. Catalysts characterization results and discussion

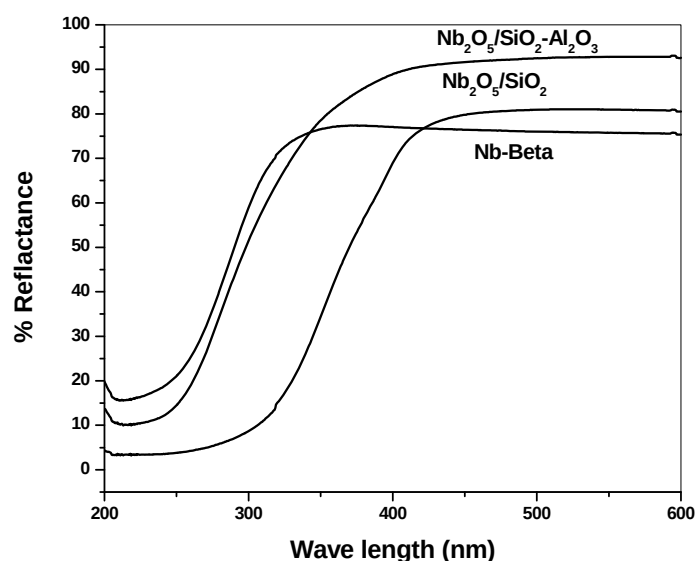


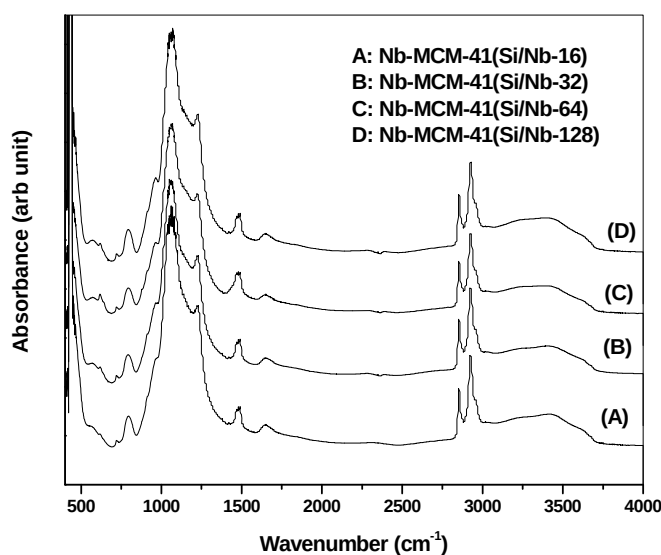
Figure-12: UV-Vis spectra of Nb-Beta and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> & SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

#### 3.1.5 FT-IR spectroscopy results

The IR-spectra of Nb-MCM-41 samples with different Si/Nb ratios of as-synthesized and calcined samples are performed in Fig-13 and 14. In the as-synthesized as well as in the calcined samples, the broad peak at 3500 cm<sup>-1</sup> is attributed to the O-H stretching of water, surface hydroxyl groups, and bridged hydroxyl groups. The peaks in the spectra of as-synthesized samples below 3000 cm<sup>-1</sup> are due to symmetric and asymmetric stretching of CH<sub>2</sub> group of the template. Their corresponding bending mode is observed at 1400 cm<sup>-1</sup>. In the spectra of the calcined samples, the symmetric and asymmetric stretching modes of CH<sub>2</sub> groups of the template are absent. This indicates complete removal of surfactant molecules from the matrix. This spectrum is in resemblance with previous reported results [147-148]. The major peaks at 1220, 1080,

### 3.1. Catalysts characterization results and discussion

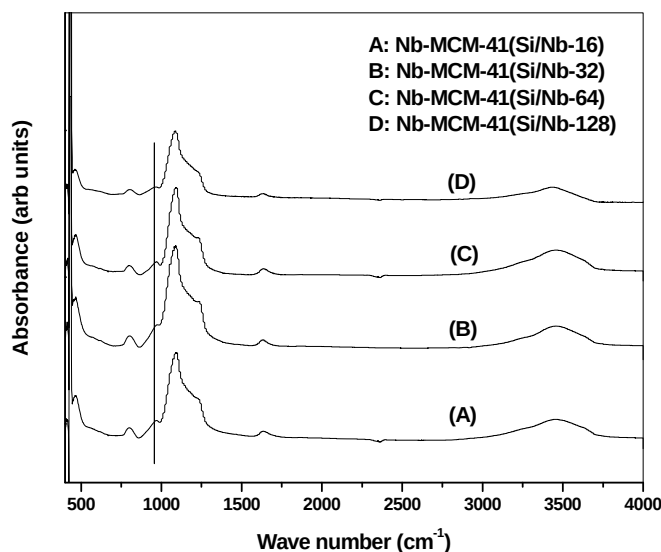
794 and 464  $\text{cm}^{-1}$  are assigned to symmetric and asymmetric stretching of Si-O-Si vibrations. The characteristic band at  $\sim 970 \text{ cm}^{-1}$  is attributed to the (Si-O-Nb) vibration [149]. However, in case of the Si-MCM-41 sample, the band at 960  $\text{cm}^{-1}$  is attributed the (Si-OH) vibration [150] Indeed, 970  $\text{cm}^{-1}$  band cannot be taken as a characteristic band for the incorporation of Nb in the framework of Nb-MCM-41 samples. Nevertheless, a slight shift in the bands corresponding to the internal vibrations of  $\text{TiO}_4$  units can be observed. Therefore, this shift may be taken as an indication of the transition metal incorporated in framework. Similar results are observed with incorporation of Ti and V on mesoporous silica sample [151].



**Figure 13: FT-IR spectra of Nb-MCM-41 molecular sieves as-synthesized samples.**

**(A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.**

### 3.1. Catalysts characterization results and discussion



**Figure 14: FT-IR spectra of Nb-MCM-41 molecular sieves calcined samples. (A) Si/Nb-16, (B) Si/Nb-32, (C) Si/Nb-64, (D) Si/Nb-128.**

FT-IR spectra of Nb-HMS and Nb-SBA-15 are presented in Fig-15 and results are similar as Nb-MCM-41 samples. In case of Nb-HMS and Nb-SBA-15 the IR band at  $960\text{ cm}^{-1}$  was appeared which is assigned for Nb-O-Si bond. The FT-IR results of Nb-Beta, Nb impregnated on  $\text{SiO}_2$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  are exhibited in Fig-16. IR spectra of crystalline Nb-beta is different from the mesoporous Nb molecular sieves and Nb impregnated on  $\text{SiO}_2$  or  $\text{SiO}_2\text{-Al}_2\text{O}_3$  samples. The infrared spectrum of Nb-Beta shows clearly an identical spectrum of H-Beta zeolite. The IR peak at  $960\text{ cm}^{-1}$  attributed the framework incorporation of  $\text{Nb}^{+4}$  ions; however, the peak intensity is very weak. The similar results indicate incorporation of V ions in Beta zeolite [152]. The IR spectrum of Nb mesoporous molecular sieves are similar to the amorphous Nb on  $\text{SiO}_2$  samples indicating similarities in their local atomic arrangements. Nevertheless, the IR spectra of Nb on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  spectra is different than other samples. For silica-alumina support the main

### 3.1. Catalysts characterization results and discussion

peak assigned at  $\sim 1095\text{ cm}^{-1}$  with shoulder at  $1200\text{ cm}^{-1}$  asymmetric stretching ( $\text{Si-O}^-$ ) groups. The weak peak at  $\sim 910\text{ cm}^{-1}$  is due to the reaction of niobium with  $\text{Si-OH}$  forming  $\text{Si-O-Nb}$  bonding [153].

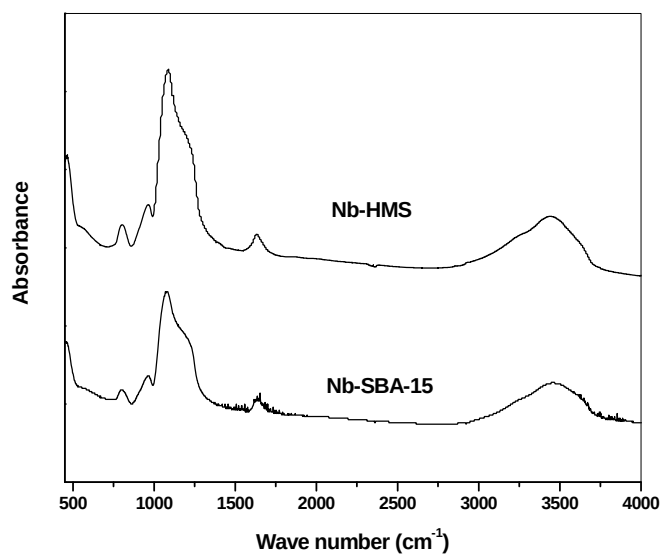


Figure-15: FT-IR spectra of Nb-HMS and Nb-SBA-15

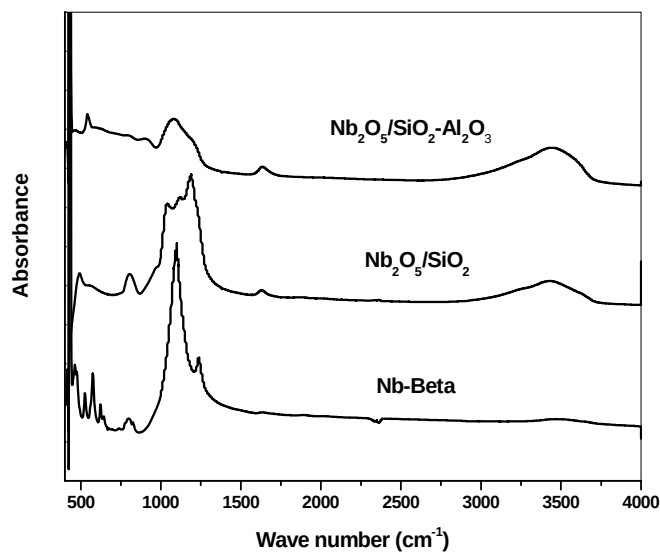


Figure-16: FT-IR results of Nb-Beta,  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  and  $\text{Nb}_2\text{O}_5/\text{SiO}_2\text{-Al}_2\text{O}_3$

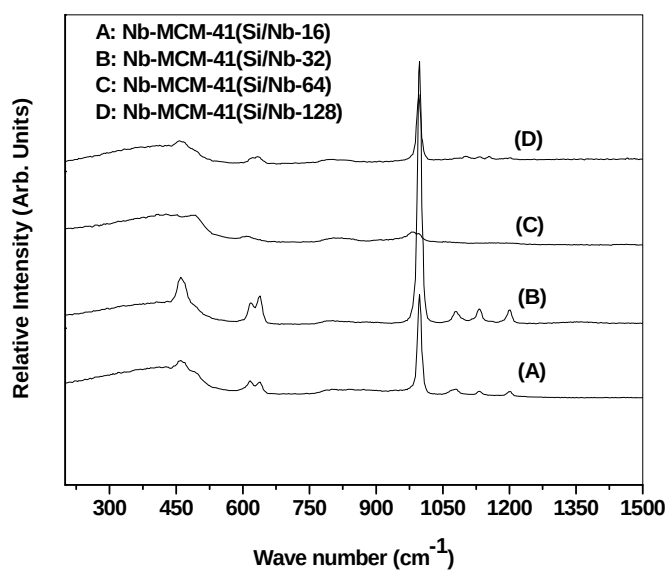
### 3.1. Catalysts characterization results and discussion

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#### 3.1.6. FT-Raman spectroscopy results

The Raman spectra of calcined Nb-MCM-41 samples with different Si/Nb ratios are presented in Fig-17. All Nb samples possess a strong Raman band at  $\sim 990\text{ cm}^{-1}$  which is assigned to Nb=O stretching vibration of isolated NbO<sub>4</sub> species. A weak Raman band could be observed at  $810\text{ cm}^{-1}$  which is a characteristic peak of tetrahedral niobium with four oxygen atoms [154-155]. Additional niobium bands in the Raman spectra of these samples observed at 650,  $\sim 610$ , and  $470\text{ cm}^{-1}$  are similar to Raman bands of Nb<sub>2</sub>O<sub>5</sub>\*nH<sub>2</sub>O which may be attributed to the presence of similar type of hydrated Nb species [156]. In addition, it is observed that with increasing the Nb loading (Si/Nb 32and16) the intensity of band increased at  $607\text{-}650\text{ cm}^{-1}$ , characteristic of the stretching mode of Nb-O-Nb polymerized bands [157]. Indeed, it shows some Nb<sub>2</sub>O<sub>5</sub> species are present at higher Nb loading samples. Additionally, some weak Raman bands appeared at  $\sim 1090\text{ cm}^{-1}$ ,  $\sim 1140\text{ cm}^{-1}$  and  $\sim 1200\text{ cm}^{-1}$ , in case of higher Nb loading samples (Si/Nb 16and32), which could be due to polymeric Nb species. Hence, Raman spectra indicate the presence of two kinds of niobium species present in the samples, first niobium species in the framework, and second polymerized niobium species on the surface. These results are in agreement with previously reported results [154].

### 3.1. Catalysts characterization results and discussion

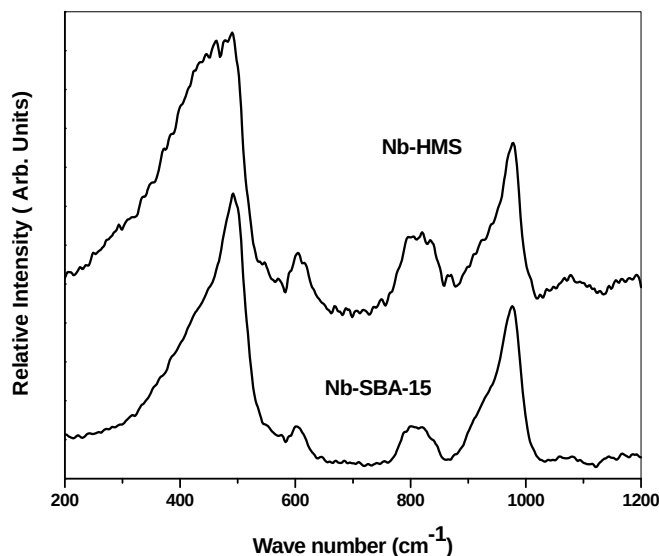


**Figure 17: Raman spectroscopy results of Nb-MCM-41 molecular sieves. (a) Si/Nb-16, (b) Si/Nb-32, (c) Si/Nb-64, (d) Si/Nb-128.**

FT-Raman results of Nb on mesoporous materials are illustrated in Fig-18. All Nb mesoporous molecular sieves show a band at  $\sim 990\text{ cm}^{-1}$ , which is a characteristic band for Nb=O stretching vibration of isolated  $\text{NbO}_4$  species [153, 156]. Another weak band is observed at  $\sim 810\text{ cm}^{-1}$ , which is due to Nb tetrahedral coordinated with four oxygen atoms. A weak Raman peak at  $\sim 610\text{ cm}^{-1}$  represents due to bulk  $\text{Nb}_2\text{O}_5$  species and strong band at  $\sim 400\text{--}480\text{ cm}^{-1}$  which is assigned to the vibration of amorphous  $\text{SiO}_2$  [148]. Nb on microporous molecular sieves (Nb-Beta), Nb impregnated on  $\text{SiO}_2$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  are depicted in Fig-19. The crystalline Nb-Beta zeolite has shown different Raman spectra than the other samples. Nb-Beta zeolite, bands observed at  $\sim 704\text{ cm}^{-1}$  and  $\sim 475\text{ cm}^{-1}$  due to presence of  $\text{NbO}_2$  species, indicate that Nb is tetrahedral co-ordinated [155]. Nevertheless, Raman bands at  $\sim 830$ , and  $331\text{ cm}^{-1}$  are attributed to the Nb-O symmetric

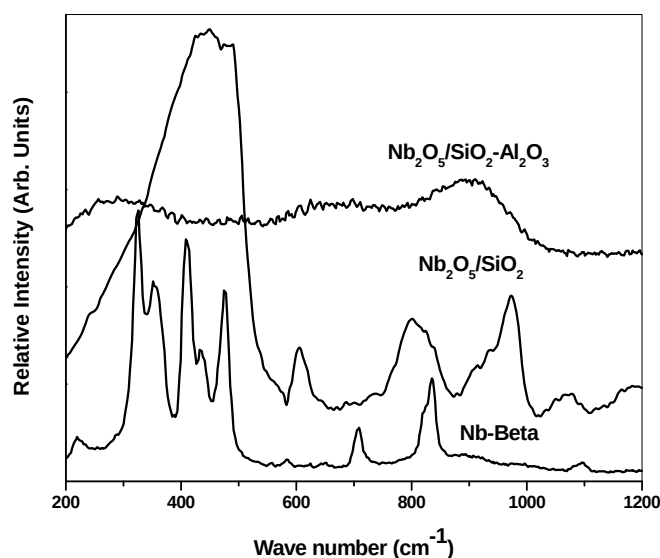
### 3.1. Catalysts characterization results and discussion

modes of the tetrahedral  $\text{NbO}_4$  species [154]. A medium band observed at  $\sim 838 \text{ cm}^{-1}$  could be ascribed to be dehydrated surface niobium oxide species with distorted octahedral  $\text{NbO}_6$  structures with longer terminal  $\text{Nb}=\text{O}$  bonds [157]. The Raman bands of Nb impregnated on  $\text{SiO}_2$  have shown similar bands as Nb incorporated on mesoporous molecular sieves indicating that similar Nb species are present. However, in case of  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  sample, the Raman band at  $\sim 990 \text{ cm}^{-1}$  splits into two bands at  $\sim 990$  and  $\sim 960 \text{ cm}^{-1}$  could be due to the dehydration of the sample [154]. In case of Nb impregnated on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  sample, the Raman bands are broad and weak since alumina is not Raman active due to low polarizability. A weak Raman band appears at  $\sim 915 \text{ cm}^{-1}$  which is related to symmetric stretching of terminal  $\text{Nb}=\text{O}$  bonds of highly distorted  $\text{NbO}_6$  species on the surface [153]. The band at  $630 \text{ cm}^{-1}$  is associated with stretching modes of polymeric Nb species. Nevertheless, in our invention we have observed that in all the samples two types of niobium species are present, the first tetrahedrally co-ordinated framework species and the second one is polymeric surface niobium species.



**Figure 18: Raman spectroscopy results of Nb-HMS and Nb-SBA-15**

### 3.1. Catalysts characterization results and discussion



**Figure 19: Raman spectroscopy results of Nb-Beta,  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  and  $\text{Nb}_2\text{O}_5/\text{SiO}_2\text{-Al}_2\text{O}_3$**

#### 3.1.7. $\text{H}_2$ –TPR results

The temperature programmed reduction ( $\text{H}_2$ -TPR) of calcined Nb-MCM-41 with different Si/Nb ratios are depicted in Fig-20. The  $\text{H}_2$ -TPR profile of different Si/Nb ratios samples shows more than one reduction peak indicating the presence of different niobium species in all the samples. The higher reduction temperature has been observed for all the samples attributed to the reduction of  $\text{Nb}^{5+}$  species present in close vicinity with Si in the framework. The lower temperature reduction peak may be due to the reduction of free  $\text{Nb}^{5+}$  species present on the outer surface of the framework. The TPR profile of Nb-MCM-41 samples with different Si/Nb ratios clearly indicate that with increasing the Nb content the low temperature reduction peak shifted to high temperature. Thus, may be due to the solid state interaction between siliceous matrix and extra framework niobium species [159]. The high temperature reduction peak is more pronounced at low Nb

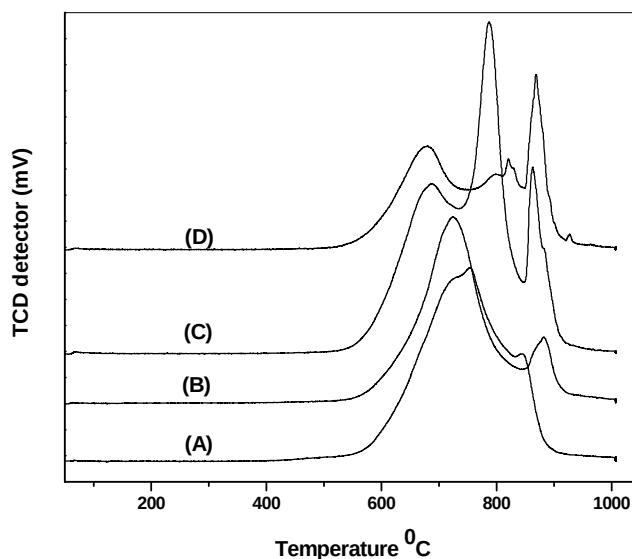
### 3.1. Catalysts characterization results and discussion

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content sample than the high Nb content samples. These results revealed that the low temperature reduction peak is due to the reduction of extra framework niobium species and reduction peak at high temperature assigned for reduction of framework niobium species. In the high temperature region, various reduction peaks can be observed in case of Si/Nb-64 and 128 samples. These various reduction peaks at high temperature may be due to the reduction of different framework niobium species. In case of Si/Nb-16 sample, reduction peak with shoulder at low temperature (725 °C) attributed the reduction of niobium species, which are formed as solid-state interaction between siliceous matrix and extra framework niobium species. These results are in good agreement with Ziolek findings [159]. These authors observed only one sharp reduction peak at low temperature when NbCl<sub>5</sub> was used as the niobium source. Nevertheless, in our present investigation, the reduction peaks at low temperature and high temperature are pronounced very clearly. From our present results, we can conclude samples with low Nb content have more framework niobium species, and samples with high niobium content have more extra framework niobium species. The reduction peaks about 850 °C are assigned to NbO<sup>-</sup> and Nb<sup>+</sup> species connected with the silica tetrahedra [160-161].

### 3.1. Catalysts characterization results and discussion

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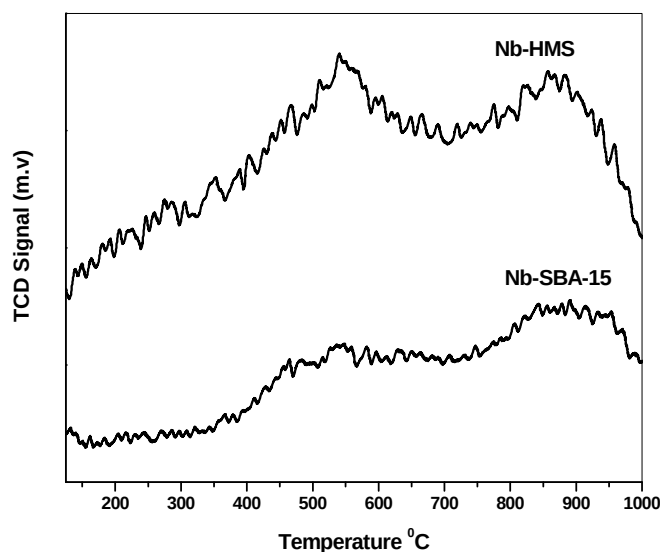


**Figure 20: H<sub>2</sub>-TPR results of Nb-MCM-41 molecular sieves. (a) Si/Nb-16, (b) Si/Nb-32, (c) Si/Nb-64, (d) Si/Nb-128.**

TPR profiles of Nb-HMS and Nb-SBA-15 indicate (Fig-21) two reduction profiles, one is at low temperature and second one is at high temperature. The TPR profile results of Nb-HMS and Nb-SBA-15 are similar as Nb-MCM-41 samples. The low temperature reduction profile is due to the extra framework Nb species and reduction peak at high temperature is assigned for reduction of framework niobium species. However, Nowak et al. Observed that materials synthesized with NbCl<sub>5</sub> as the niobium source exhibit a much larger extra-framework niobium species than the other niobium sources materials [160]. In contrast to these results, in present case of study we have observed equal distribution of extra-framework and framework niobium species. Mesoporous molecular sieves containing niobium catalysts exhibit both kinds of TPR profiles: one at low temperature with a very broad signal which is responsible for

### 3.1. Catalysts characterization results and discussion

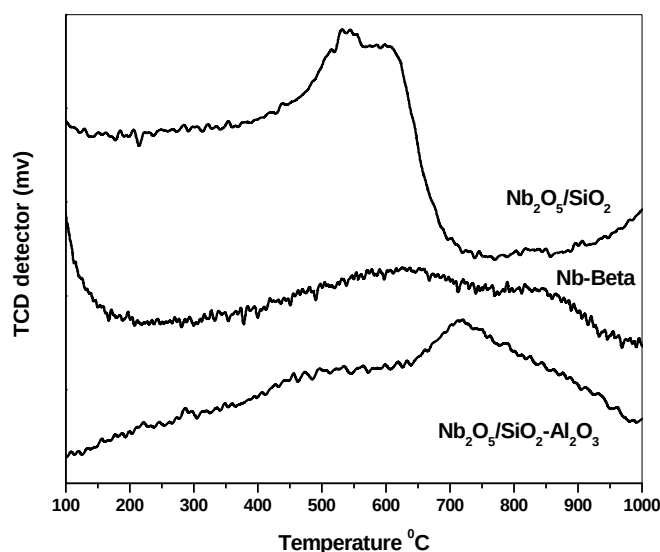
reduction of extra framework niobium species and other peak at high temperature with the domination of the first one which is due to framework niobium species reduced (Fig-21).



**Figure 21: H<sub>2</sub>-TPR results of Nb-HMS and Nb-SBA-15**

The TPR profile of Nb-Beta, Nb<sub>2</sub>O<sub>5</sub> on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> are illustrated in Fig-22. In case of Nb impregnated on SiO<sub>2</sub> only low temperature reduction peak is observed. The peak at low temperature has a shoulder. This indicates that niobium is solid state interaction with silica matrix. In case of Nb-Beta sample exhibited two reduction peaks, one at low temperature and second one is at high temperature reduction peak. The TPR profile of Nb-Beta is similar with Nb impregnated in mesoporous molecular sieves. However, the TPR profile of the Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample performs only one reduction peak at around 750 °C.

### 3.1. Catalysts characterization results and discussion



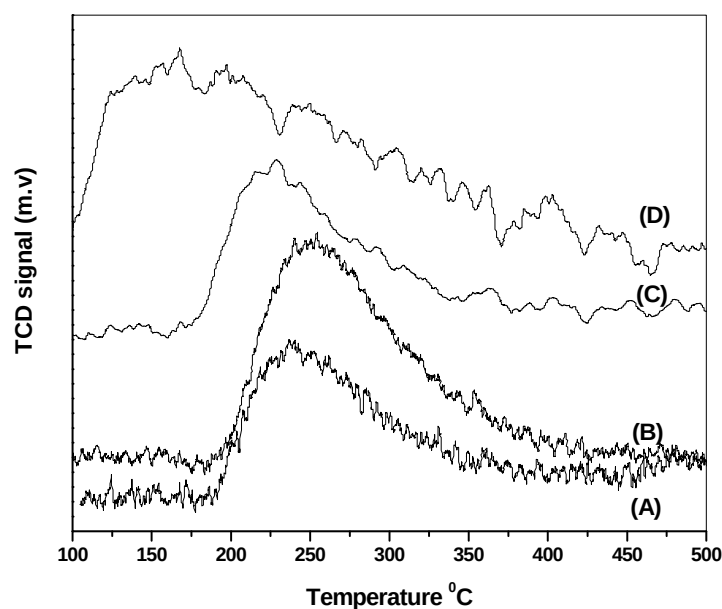
**Figure 22: H<sub>2</sub>-TPR results of Nb-Beta , Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>**

#### 3.1.8 Ammonia TPD results

The ammonia TPD profiles of the catalysts with different Si/Nb ratios are presented in Fig.23. TPD results clearly show a broad desorption signal in the region of 150-300 °C, for all the samples. Results reveal that the desorption peak shifted to higher temperature with increasing the Nb concentration (Si/Nb-128 to 16). Over all an increase in concentration as well as strength of acid sites is indicated. In addition, the acid strength increases from weak to medium with increasing the Nb concentration [162]. The acid strength enhancement of Nb-MCM-41 samples may be due to the formation of Si-O-Nb species in the framework and formation of extra framework Nb<sub>2</sub>O<sub>5</sub> species that is observed in the high Nb content samples. At a lower Nb content sample has shown weak acid sites which can be assigned to surface hydroxyl groups.

### 3.1. Catalysts characterization results and discussion

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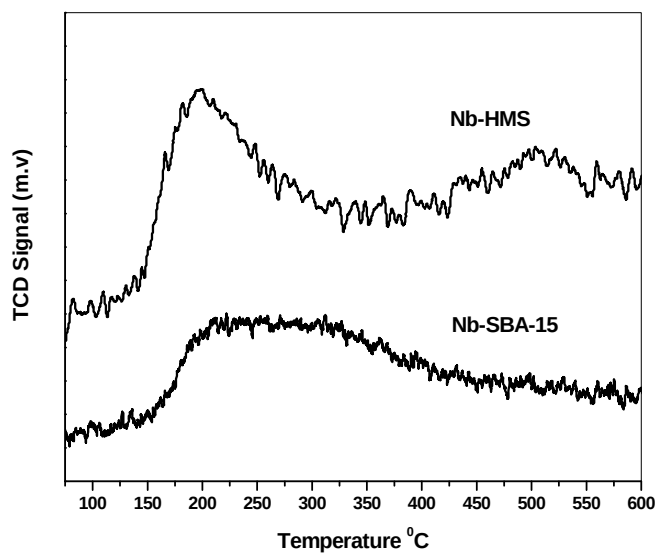


**Figure 23: Ammonia TPD of Nb-MCM-41 molecular sieves. (a) Si/Nb-16, (b) Si/Nb-32, (c) Si/Nb-64, (d) Si/Nb-128.**

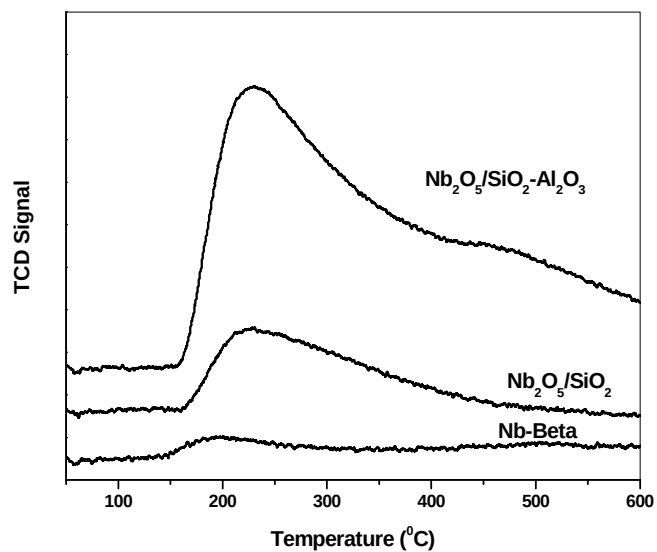
Ammonia TPD results of Nb-HMS and Nb-SBA-15 are illustrated in Fig-24. A broad desorption peak at 250 °C indicates medium acid strength. In addition, Nb-HMS sample has shown one more desorption peak at 500 °C, which is due to strong acid strength of the sample. Ammonia TPD results of Nb-Beta, Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> are demonstrated in Fig-25. The Nb-Beta sample shows the desorption peak at 200 °C with very low amount of ammonia desorption, indicating that Nb-Beta has very weak acid strength. Nb impregnated on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> samples show medium acid strength. However, in case of Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample depicted a small desorption peak at high temperature indicates the sample has strong acid sites, which might be created by alumina.

### 3.1. Catalysts characterization results and discussion

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**Figure 24: Ammonia TPD of Nb-HMS and Nb-SBA-15.**

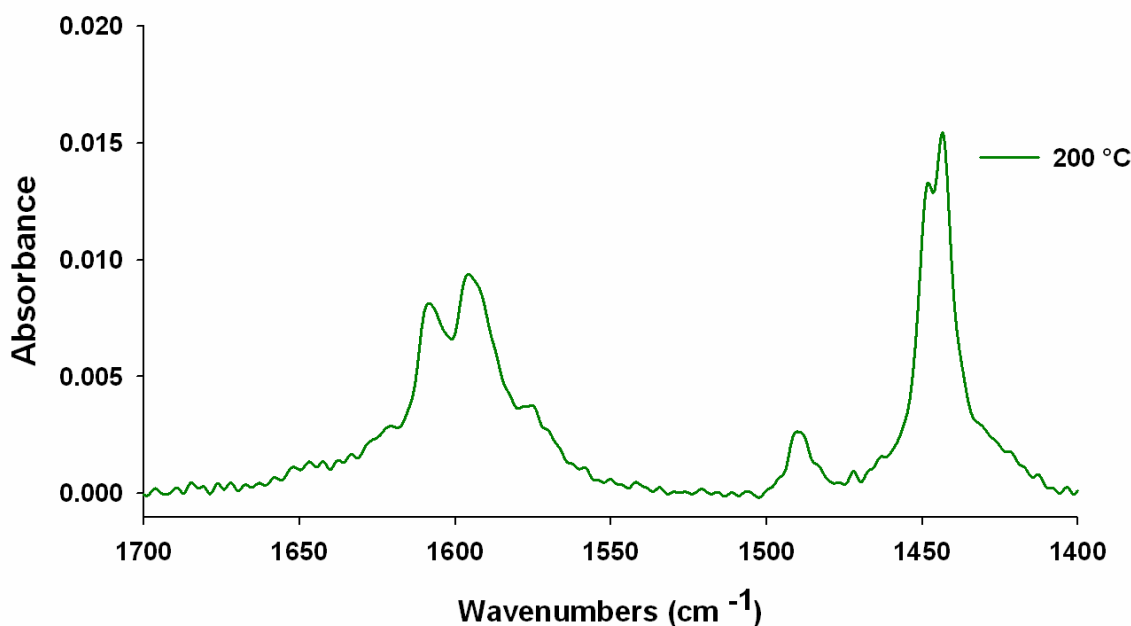


**Figure 25: Ammonia TPD of Nb-Beta, Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.**

### 3.1. Catalysts characterization results and discussion

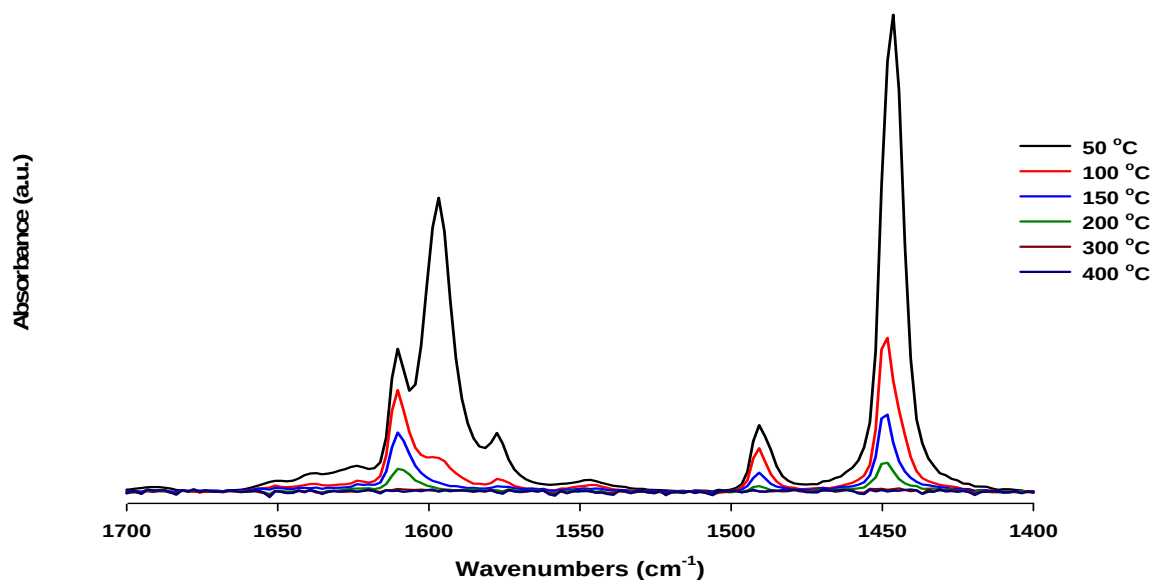
#### 3.1.9. Pyridine FT-IR

The acidity of calcined Nb-MCM-41 (Si/Nb-32) material was measured by pyridine FT-IR spectroscopy by using pyridine as probe molecule. The desorption of pyridine occurs at 200 °C. The results are indicated in Fig-26. The main peaks can be assigned to the Lewis acid-bound (1450, 1575 and 1623  $\text{cm}^{-1}$ ). Brønsted acid-bound (1545 and 1640  $\text{cm}^{-1}$ ) and both Lewis and Brønsted acid-bound (1490  $\text{cm}^{-1}$ ) to pyridine. It is also worthwhile to note that at this desorption temperature, Brønsted acid peaks are weak. Ziolek et al. [161] observed only the presence of Lewis acid sites at desorption temperature 150 °C. However, the present result indicates that Nb-MCM-41 molecular sieves have both Brønsted and Lewis acid sites, which are formed by Nb incorporation in framework.



**Figure 26: Pyridine FT-IR of Nb-MCM-41 molecular sieves (Si/Nb-32) at 200 °C.**

### 3.1. Catalysts characterization results and discussion



**Figure 27: Pyridine FT-IR of Nb<sub>2</sub>O<sub>5</sub>/ SiO<sub>2</sub> .**

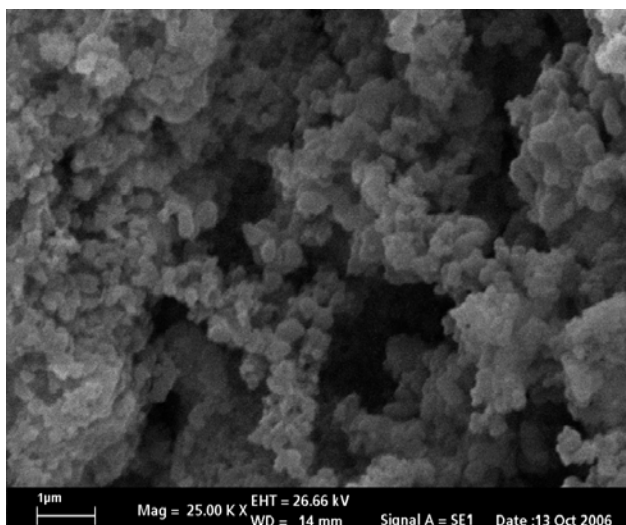
The acidity of calcined Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>, (Fig-27) indicated pyridine bonds with Lewis acid sites giving IR characteristic bands at 1620 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>. A band at 1545 cm<sup>-1</sup> is attributed pyridine adsorbed on Brønsted acid sites. A band at 1480 cm<sup>-1</sup> is a characteristic band for either Lewis or Brønsted acid sites. Hence, sample Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> indicate the presence of weak Lewis acid sites and negligible Brønsted acid sites. The Lewis acid site is attributed to the surface exposed coordinatively unsaturated Nb<sup>+5</sup> or extra frame work Nb species. By increase the temperature desorption of pyridine was complete, illustrating the weakness of acid sites in this material.

#### 3.1.10. Scanning Electron Microscopy

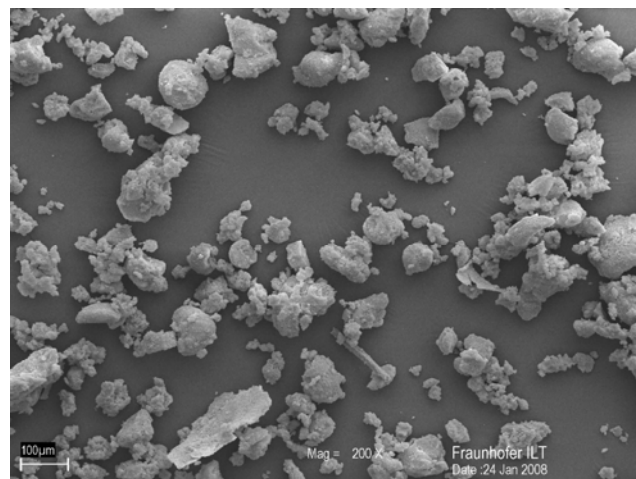
The SEM images of Nb contain different structured materials is presented in Fig.28. The morphology of Nb-MCM-41, is typical for the mesoporous metallosilicates and showed that they are formed as short spherical particles with diameters between 1.5

### 3.1. Catalysts characterization results and discussion

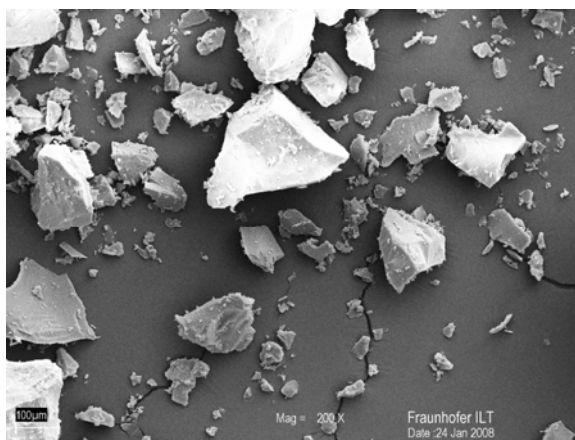
and 2.5  $\mu\text{m}$  and lengths between 10 and 20  $\mu\text{m}$ . The SEM images of Nb-HMS and  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  samples have shown irregular morphology. However, in case of NB-beta sample, uniform square shapes are observed.



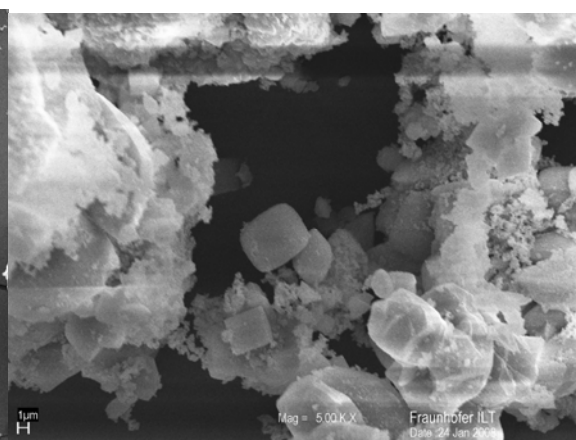
(A)



(B)



(C)



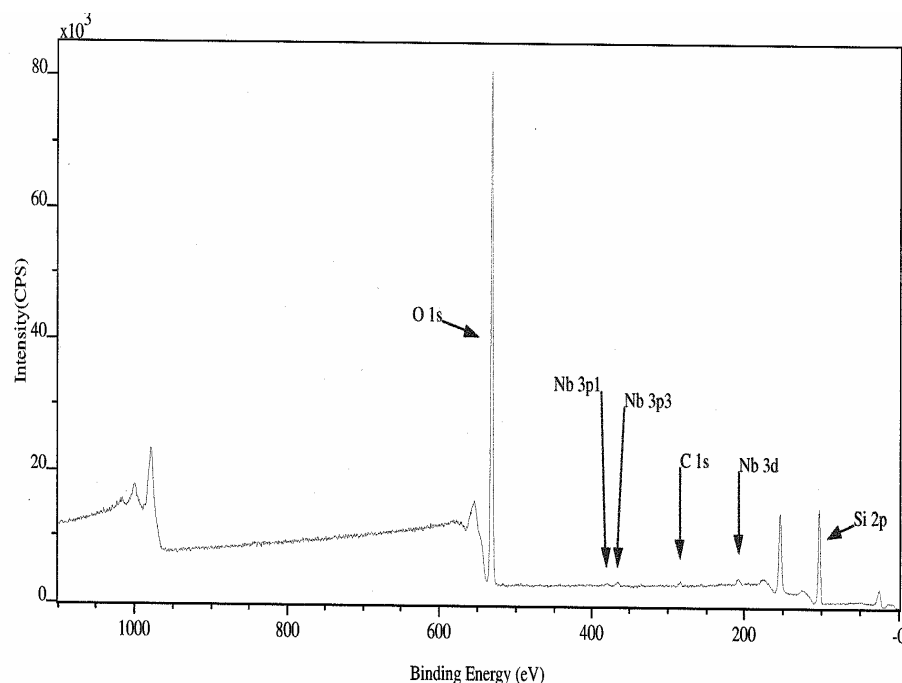
(D)

**Figure 28: SEM picture of (A) Nb-MCM-41 (Si/Nb-32) (B) Nb-HMS (C)  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  (D) Nb-Beta.**

### 3.1. Catalysts characterization results and discussion

#### 3.1.11. XPS

The XPS spectra of a calcined Nb-MCM-41(Si/Nb-32) sample primarily showed the energy absorption from Si, Nb and O elements (Fig-29).



**Figure 29: XPS spectra of Nb-MCM-41 molecular sieves (Si/Nb-32)**

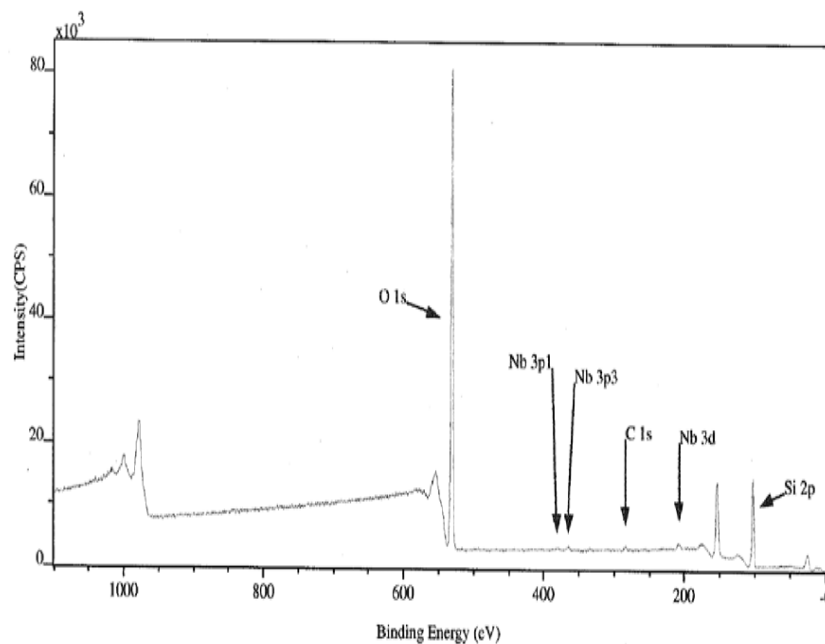
The binding energy values of two spin-orbit components of Nb 3d are 207.75 and 209.92 (Table-3). These values are similar to previously reported binding energy of  $\text{Nb}_2\text{O}_5$  [163]. The energy difference between binding energy of two spin components of Nb ( $3d_{3/2}$ ) and ( $3d_{5/2}$ ) is 2.2 eV which indicates that the niobium atoms are very well dispersed into the mesoporous matrix and are attached to silica by Si-O-Nb linkage [135, 164].

### 3.1. Catalysts characterization results and discussion

**Table 3: Binding energy of Nb-MCM-41 (Si/Nb-32) sample**

|                         | Binding<br>Energy eV | FWHM | Area |
|-------------------------|----------------------|------|------|
| Nb (3d <sub>5/2</sub> ) | 207.75               | 0.84 | 28.2 |
| Nb (3d <sub>3/2</sub> ) | 209.92               | 0.80 | 13.9 |

The XPS results of the calcined 3.15 wt% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> sample are presented in Fig-30. Table 4 lists the corresponding binding energy of Nb<sub>2</sub>O<sub>5</sub>. The O 1s binding energy peaks at 532.8 and 531.0 eV, for oxygen bonded to Si and Nb atoms [164].



**Figure 29: XPS spectra of 3.12 wt% Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>.**

### 3.1. Catalysts characterization results and discussion

**Table 4: Binding energy of Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> sample**

|                         | Binding<br>Energy eV | FWHM | Area |
|-------------------------|----------------------|------|------|
| Nb (3d <sub>5/2</sub> ) | 207.70               | 1.26 | 87.5 |
| Nb (3d <sub>3/2</sub> ) | 210.41               | 1.21 | 47.5 |

#### 3.1.12. <sup>29</sup> Si-MAS NMR

The MAS-NMR spectra of calcined Si-MCM-41, as well as of as-synthesized and calcined Nb-MCM-41 (Si/Nb-32) sample (Fig-31) shows three signals corresponding to the Q<sup>4</sup> Q<sup>3</sup> and Q<sup>2</sup> groups, at -113, -102 and -90 ppm corresponding to Si(OSi)<sub>4</sub>, Si(OSi)<sub>3</sub>OH, and Si(OSi)<sub>2</sub>(OH)<sub>2</sub>, respectively. Table-5 summarizes the relative integral intensities of Q<sup>4</sup>, Q<sup>3</sup> and Q<sup>2</sup>. In the present synthesis, we have observed the increase of Q<sup>4</sup> sides very significantly (50 to 78) at the expense of Q<sup>3</sup> and Q<sup>2</sup> during the calcination. Thus, un calcined sample exhibites a higher fraction of incompletely cross-linked silica (Q<sup>3</sup> and Q<sup>2</sup>). Therefore, calcination leads to be higher level of silica condensation [151]. However, in case of the low niobium content samples (Si/Nb-64 and 128) the increase of Q<sup>4</sup> sides is noteworthy in contrast to Si-MCM-41. These results are attributed that niobium is incorporated in the silica framework and promotes the condensation of silanol sites. Same observation was found with other transition metals such as Ti and V incorporation in mesoporous silica framework [165-166]. Nevertheless, in contrast to the above mentioned results, the Q<sup>3</sup> intensity also appeared more with increment of niobium content in the sample. It could be that Si(OSi)<sub>3</sub>ONb is shifted to a low field in

### 3.1. Catalysts characterization results and discussion

comparison to  $\text{Si}(\text{OSi})_4$ . The same behavior was observed in case of alumina-substituted zeolites [167]. According to this, it might be that  $\text{Si}(\text{OSi})_3\text{ONb}$  appears in a same shift range as  $\text{Si}(\text{OSi})_3\text{OH}$ . Indeed, we assume that the increase of intensity in the range of  $Q^3$  sites is attributed to  $\text{Si}(\text{OSi})_3\text{ONb}$ . This would also prove that Nb is incorporated in the framework.

**Table 5:**  $^{29}\text{Si}$ - NMR data of MCM-41 samples

| <i>Sample</i>           | <i>Si/Nb ratio</i> | <i>I (%)</i>    |                  |                  |
|-------------------------|--------------------|-----------------|------------------|------------------|
|                         |                    | $Q^2$ (-90 ppm) | $Q^3$ (-102 ppm) | $Q^4$ (-113 ppm) |
| Si-MCM-41               |                    | 7               | 16               | 77               |
| Nb-MCM-41<br>uncalcined | 32                 | 15              | 35               | 50               |
| Nb-MCM-41               | 16                 | 4               | 30               | 68               |
| Nb-MCM-41               | 32                 | 6               | 16               | 78               |
| Nb-MCM-41               | 64                 | 6               | 14               | 80               |
| Nb-MCM-41               | 128                | 7               | 7                | 86               |

### 3.1. Catalysts characterization results and discussion

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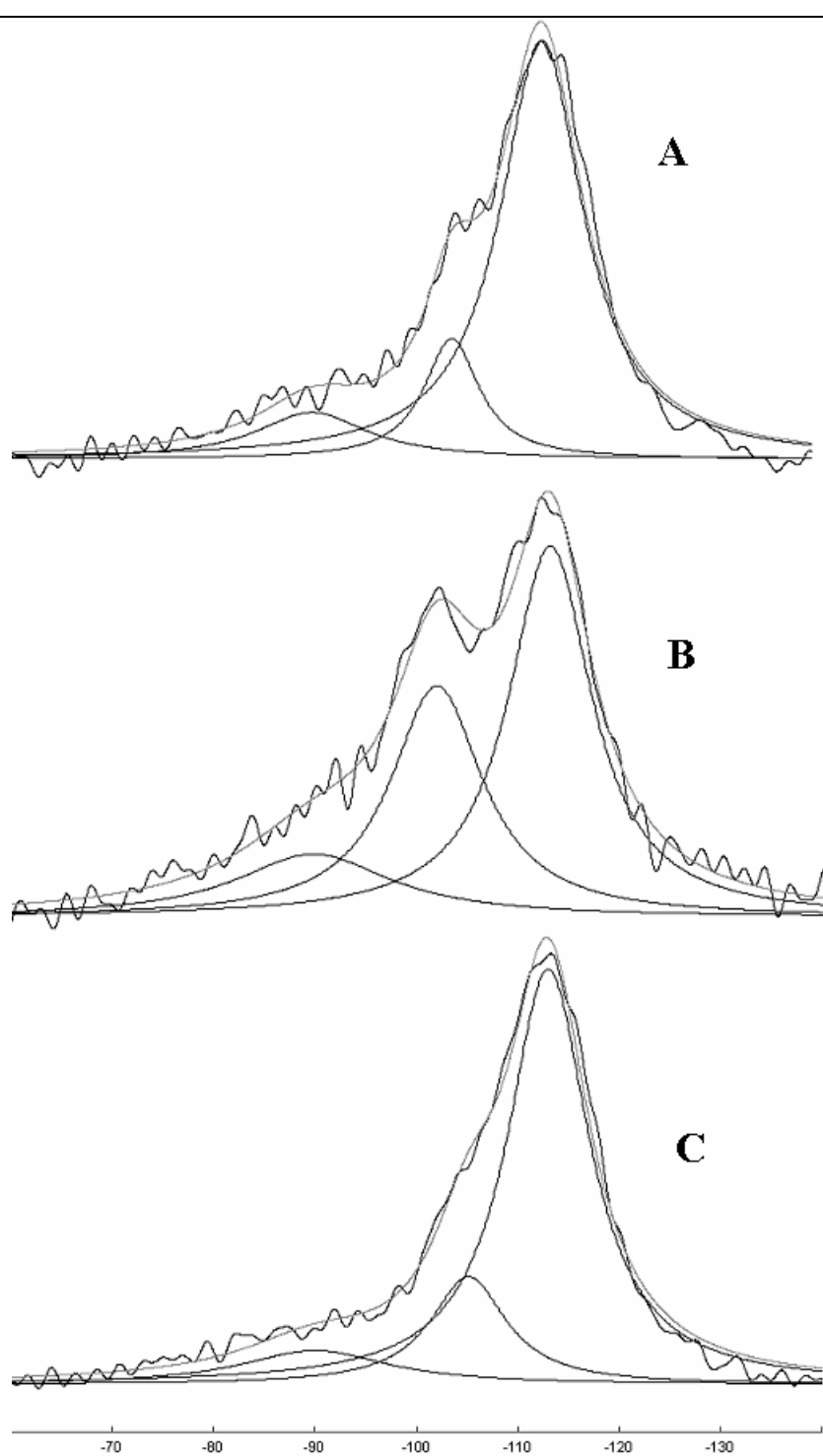


Figure 31:  $^{29}\text{Si}$  MAS NMR of (A) Si-MCM-41 (B) as-synthesized Nb-MCM-41(Si/Nb-32), (C) calcined Nb-MCM-41(Si/Nb-32).

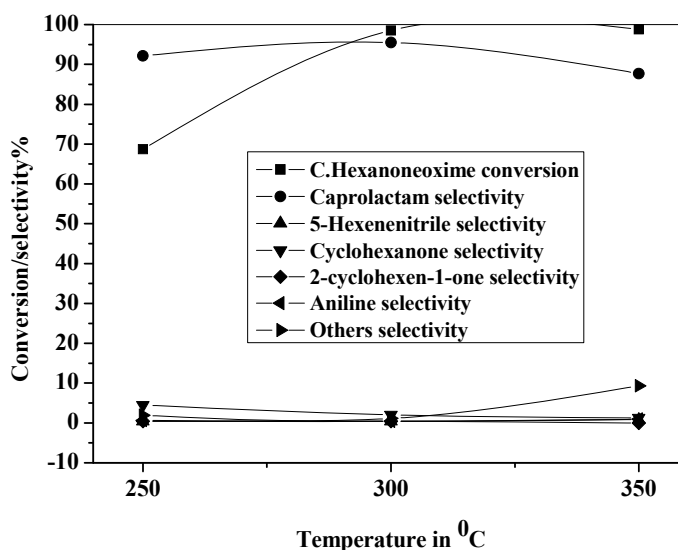
### 3.2 Gas phase Beckmann rearrangement of cyclohexanone oxime to caprolactam

#### 3.2.1 Influence of reaction temperature

The product distribution and catalytic activity were strongly dependent upon the reaction temperature. The influence of reaction temperature over Nb-MCM-41 (Si/Nb-32) the catalyst was studied at 250 °C, 300 °C, and 350 °C and the results are depicted in Fig-32. The reactant feed ratio (cyclohexanone oxime (CHO): ethanol) was kept at 1:9 wt% and WHSV was 0.3 h<sup>-1</sup>. The CHO conversion and CL ( $\epsilon$ -caprolactam) selectivity increased with increasing reaction temperature from 250-300 °C. CL was formed more selectively than the other compounds at higher temperatures. At lower reaction temperature, cyclohexanone was main by-product which is formed by decomposition of CHO. The desorption is not fast enough at lower temperature. Therefore, the intrinsic residence time is high and causes decomposition of CHO. At 300-325 °C temperature, the CHO conversion and CL selectivities are (98.5 and 95.5%) higher due to the lower oligomerization of CHO. However, at higher temperature (350 °C) the CL selectivity (87.7%) decreased because the ring opening reaction of CL to the hexenenitrile occurs and constant CHO conversion (98.7%) is still observed. These results indicate that at 300-325 °C the main reaction was Beckmann rearrangement to CL. Also, thermodynamic data clearly illustrated that a slight increase of  $\Delta_r G^\circ$  with temperature may indicate that lower temperatures are favorable for Beckmann rearrangement reaction. At high temperature the side-product formation in thermodynamic equilibrium would be strongly favored [168]. Nevertheless, 300-325 °C is somewhat higher temperature than in the case of deboronated pentasil type catalyst, where optimum reaction temperature was about

### 3.2. Catalytic results and discussion

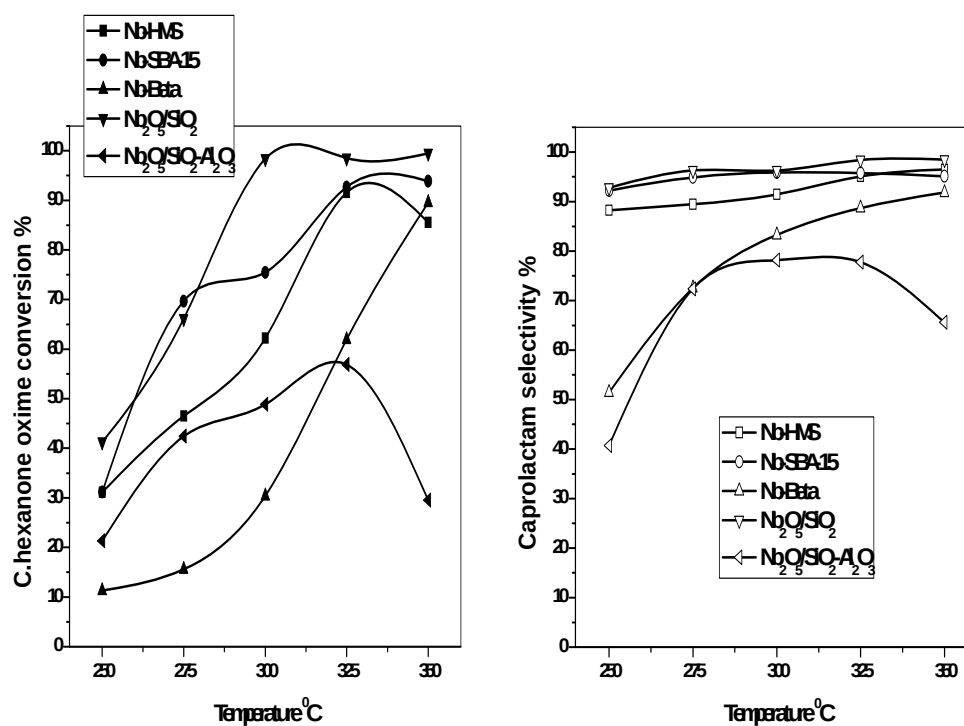
280-300 °C [11, 43, 57]. Recently, Conesa et al. [49, 169] observed that 425-450 °C is optimum reaction temperature for obtaining higher CL selectivities in gas phase Beckmann rearrangement in presence of mesoporous silicaalumino phosphate and Al-B-MCM-41 catalysts. Nevertheless, in our present investigations almost 100% conversion of CHO and above 95% selectivity for CL were achieved at around 300 °C.



**Figure 32: Effect of temperature on the conversion and selectivity over Nb-MCM-41 (Si/Nb-32) catalyst. Conditions: 0.1 bar, time =4 h, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2 l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%.**

The influence of temperature over Nb containing different structured catalysts is illustrated in Fig-33. An increase of reaction temperature from 250 °C to 325 °C, the enhancement of CHO conversion was observed. The maximum conversion reached at 325 °C. The CHO conversion with different catalysts at 325 °C follow the order, Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>>Nb-SBA-15~Nb-HMS>Nb-beta>Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

### 3.2. Catalytic results and discussion



**Figure 33: Effect of temperature on the conversion and selectivity over Nb containing different structured catalysts. Conditions: 0.1 bar, time =4 h, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2 l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%.**

The CHO conversions are 98.52%, 91.56%, 92.67%, 61.91% and 56.96% respectively. With increase the reaction temperature from 325 °C to 350 °C, the CHO conversion rates have decreased from 91.5% to 85.5% and 56.9% to 29.5% in case of Nb-HMS and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts respectively. However, in case of Nb-beta zeolite the maximum CHO conversion of about 90% is achieved at 350 °C.

The CL selectivity over different temperatures indicated that, with increasing reaction temperature an increase of CL selectivity is found over all the catalysts. The maximum CL selectivity is obtained at 350 °C. The CL selectivities over different catalysts at 350 °C follow the order Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>>Nb-SBA-15~Nb-HMS>Nb-

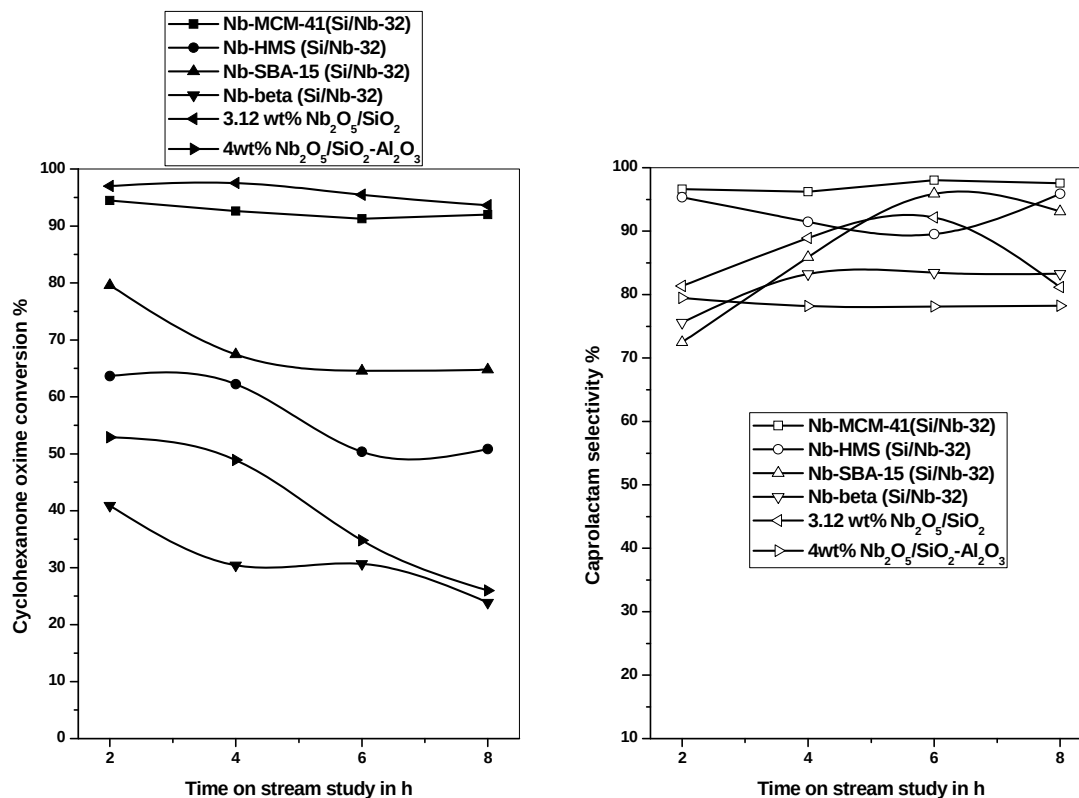
### 3.2. Catalytic results and discussion

$\beta$ - $\text{Nb}_2\text{O}_5/\text{SiO}_2\text{-Al}_2\text{O}_3$ . The CL selectivities are 98.48%, 96.53%, 95.13%, 91.82% and 65.63% respectively. Similar results were observed by Röseler et al. in presence of B-MFI catalyst [170]. In contrast to these results, Nb-MCM-41 catalysts have confirmed at high temperature (350 °C) the caprolactam selectivity was decreased [171-172]. Nevertheless, in case of  $\text{Nb}_2\text{O}_5/\text{SiO}_2\text{-Al}_2\text{O}_3$  catalyst, the caprolactam selectivity decreased from 77.74% to 65.63% by increasing the temperature from 325 °C to 350 °C. These results indicate that, the temperature about 300-325 °C is the main reaction temperature for Beckmann rearrangement of cyclohexanone oxime to caprolactam.

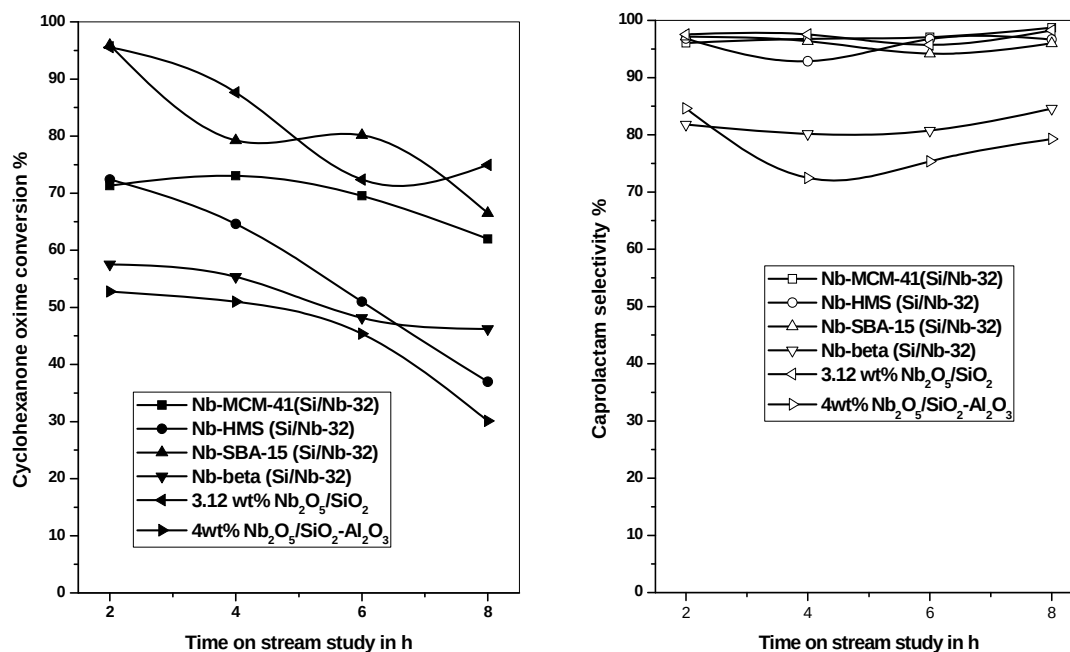
#### 3.2.2 Influence of feed ratio

The influence of feed ratios in the reaction is presented in Fig-34. This study is undertaken with 1:3, 1:6 and 1:9 wt% CHO : ethanol in the presence of Nb containing catalysts. The reactions were carried out at 300 °C and WHSV = 0.3 h<sup>-1</sup> for 10 h. The higher the dilution feed such as CHO : ethanol = 1:9 wt% the higher the conversion of CHO was observed in presence of Nb-MCM-41(Si/Nb-32) and  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  catalysts. In contrast to other catalysts, Nb-SBA-15 has shown more conversion rates in presence of low feed ratios such as 1:6 and 1:3 wt%. An increase the CHO concentration in the feed i.e. feed ratios 1:6 and 1:3 wt%, all the catalysts show fast deactivation with time on stream of 8 h. However, the CL selectivity was constant at all chosen feed ratios. The higher catalytic activity in presence of high concentration of ethanol in the feed seems to be due to the enhancement of CL desorption from the catalyst active centers.

### 3.2. Catalytic results and discussion

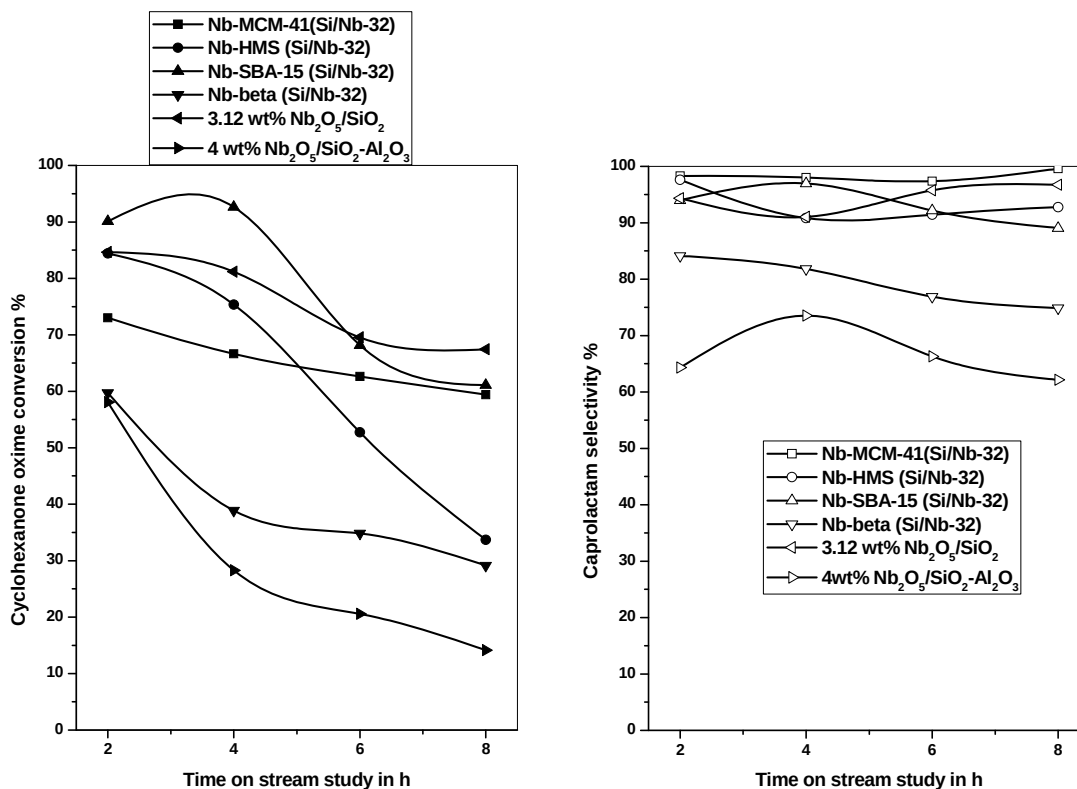


(A) Conversion and selectivities at feed ratio 1:9



### 3.2. Catalytic results and discussion

#### (B) Conversion and selectivities at feed ratio 1:6



#### (C) Conversion and selectivities at feed ratio 1:3

**Figure 34: Effect of feed ratio on the conversion and selectivity over Nb containing different structured catalysts. Conditions: 300 °C, 0.1 bar, carrier gas = 2 l/h N<sub>2</sub>, WHSV= 0.3 h<sup>-1</sup>.**

#### 3.2.3 Influence of solvents

The product selectivity and catalyst stability are strongly dependent upon the type of solvent being used in the reaction. The influence of different solvents in the gas phase Beckmann rearrangement of CHO was previously studied by using non-polar solvents such as benzene, toluene and polar solvents such as acetonitrile, chloroform and some alcohols such as methanol, ethanol, isopropanol and cyclohexanol [170, 173]. Kitamura

### 3.2. Catalytic results and discussion

et al. studied the effect of alcohols over the reaction [174]. Among all mentioned solvents we could demonstrate that ethanol is a promising solvent for the reaction.

The effect of solvents over the reaction and kinetic measurements were also investigated by Komatsu et al. [175]. In this investigation study, he was used different dipole moment solvents from 0 (benzene) to 3.92 (acetonitrile). They have observed maximum yield of caprolactam at medium dipole momentum of solvent such as ethanol with 1.44. These findings were explained by desorption of CL due to the attack of a solvent molecule on the active sites being the rate determining step.

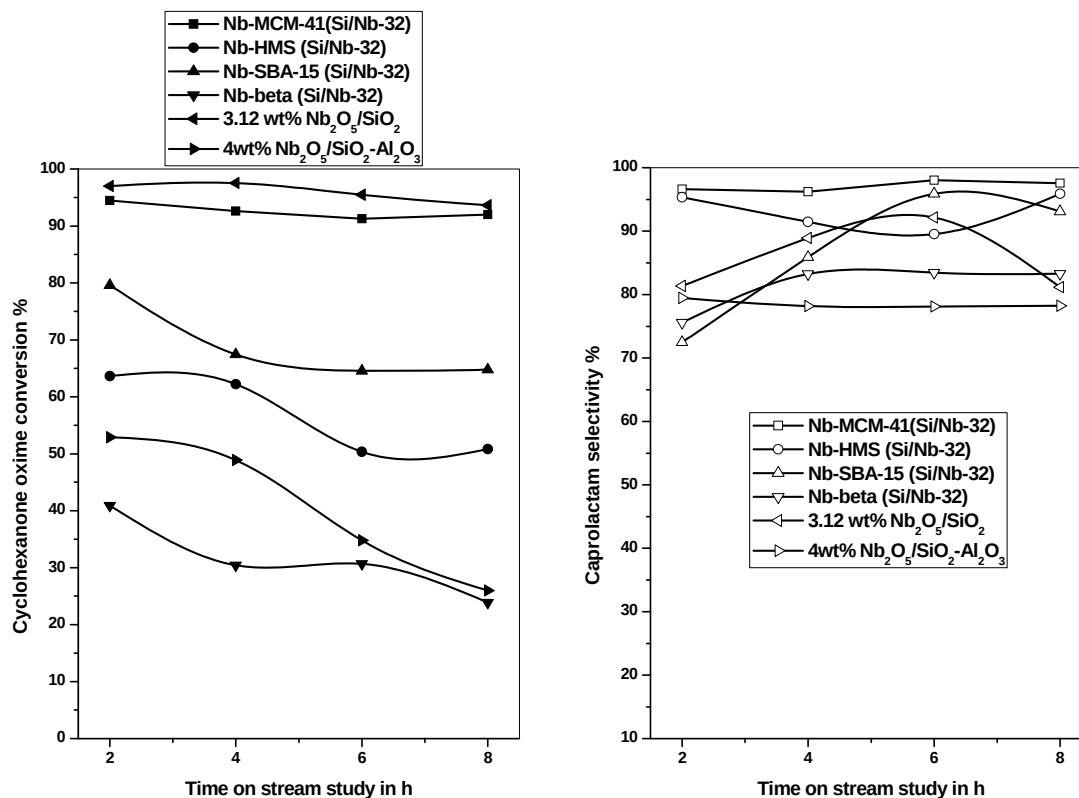
In presence of ethanol as the solvent the catalytic activity and selectivity for CL increased. Fig-34 shows the effect of the solvents such as methanol, ethanol and benzene respectively. In presence of ethanol as the solvent, the CHO conversion and CL selectivity over Nb-MCM-41 and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> did not change significantly with time on stream for 8 h indicating that these two catalysts have shown good stability under these reaction conditions. In presence of ethanol as the solvent, other catalysts have shown decrease the activity significantly with time on stream study. In presence of methanol as a solvent, except Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> all other catalysts have shown less activity. However, in presence of non polar solvent such as benzene, all catalysts result in poor performance. Moreover, it is also note to worth that the deactivation rate is faster in presence of benzene as a solvent.

The catalytic activity follows in the order ethanol>methanol>benzene. Takahashi et al. observed that the CL selectivity is higher by using methanol as a solvent than in presence of benzene [176]. Surprisingly, in contrast to Takahashi findings, our former results and our present investigations demonstrate almost 100% CL selectivity when

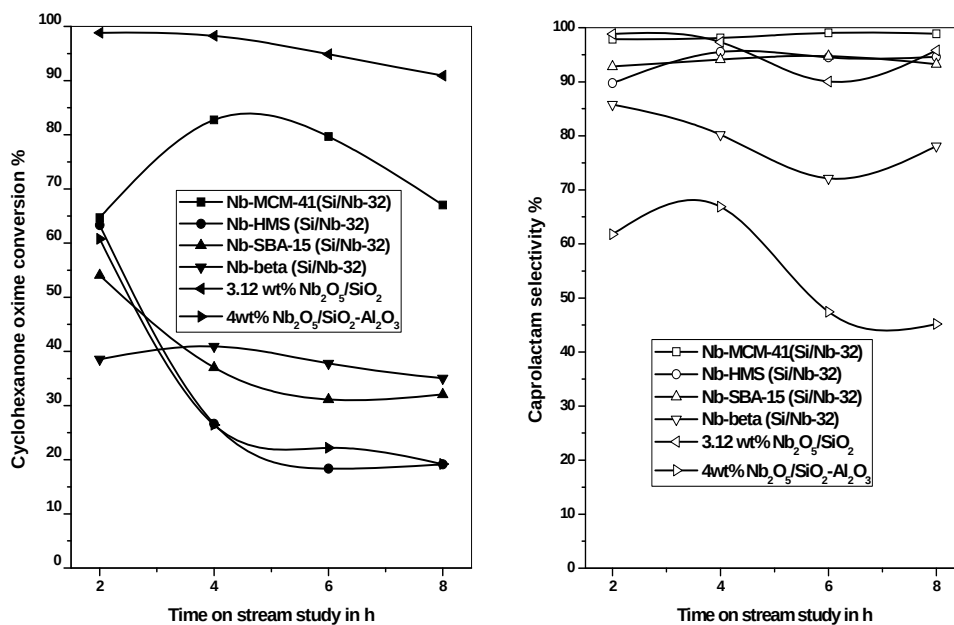
### 3.2. Catalytic results and discussion

benzene is used as a solvent over Nb-MCM-41 catalyst. In addition, in presence of methanol as a solvent, the conversion started decreasing with time [170, 177]. Nevertheless, Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalyst has performed constant activity in presence of methanol and ethanol as solvents. According to Kitamura et al. [173] in presence of silicalite catalyst, the terminal or neutral silanols are reacted with alcohol vapors to form silylether complexes. These terminal or neutral silanol groups are not active sites for rearrangement reaction. By blockage of these, silanol groups are responsible for augment of catalytic activity in presence of alcohols as solvents. Furthermore, the dielectric constant and polar nature of these low molecular weight alcohol solvents are favorable for 1,2-hydrogenshift during the rearrangement [178]. However, in present investigation the effect of ethanol over Nb catalysts is not quite clear yet. The dehydration of ethanol to ethylene is most probably not taking place as we have observed in case of B-MFI as well as Nb-MCM-41 catalysts [170].

### 3.2. Catalytic results and discussion

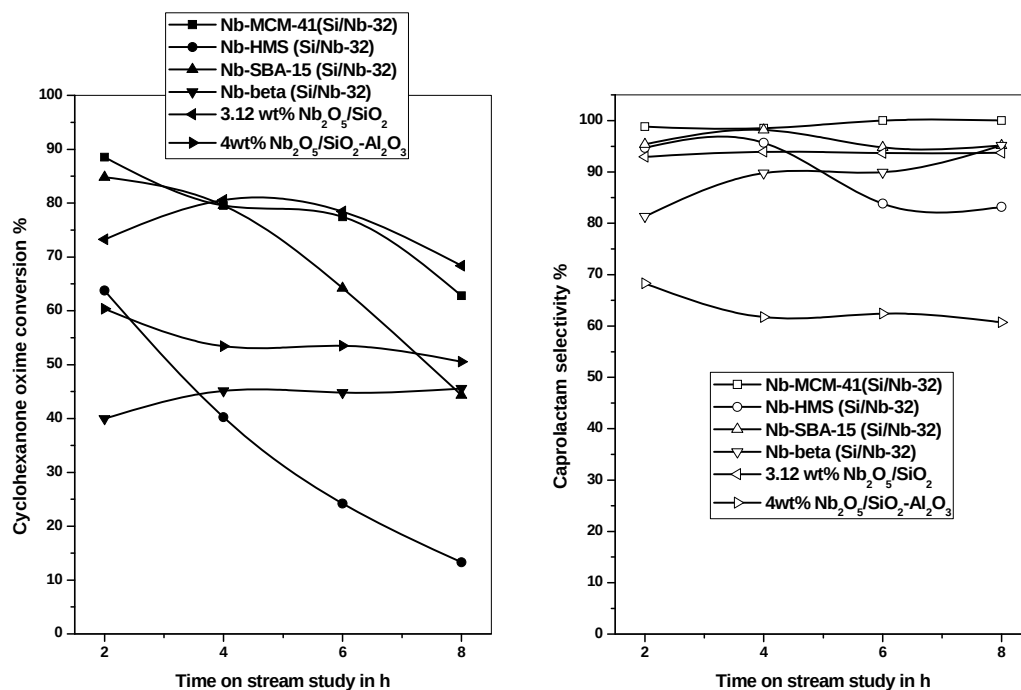


**(A) Conversion and selectivities at ethanol as the solvent.**



**(B) Conversion and selectivities at methanol as the solvent.**

### 3.2. Catalytic results and discussion



(C) Conversion and selectivities at benzene as the solvent.

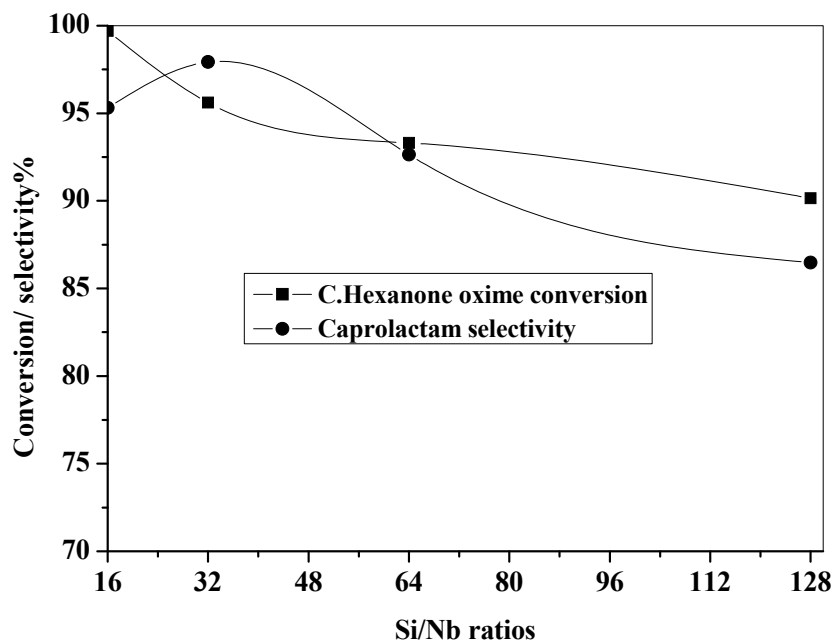
Figure 34: Effect of solvents on the conversion and selectivity over Nb catalysts.

Conditions: 300 °C, 0.1 bar, carrier gas = 2 l/h N<sub>2</sub>, WHSV= 0.3 h<sup>-1</sup>, solvent:substrate ratio-9:1 wt%.

#### 3.2.3 Influence of Si/Nb ratios over Nb-MCM-41 catalysts

The effect of different Si/Nb ratios in the MCM-41 materials on catalytic performance is shown in Fig-35. The CHO conversion and CL selectivity decreased with increasing Si/Nb ratios (with low amount of Nb loading) of the sample. The CHO conversion rates and CL selectivities follow the order Nb-MCM-41(Si/Nb-16)> Nb-MCM-41(Si/Nb-32)> Nb-MCM-41(Si/Nb-64)> Nb-MCM-41(Si/Nb-128).

### 3.2. Catalytic results and discussion



**Figure 35: Effect of Si/Nb ratios of different Nb-MCM-41 molecular sieves on the conversion and selectivity. Conditions: 300 °C, 0.1 bar, TOS = 4h, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2 l/h N<sub>2</sub>, oxime : EtOH=1:9 wt%.**

These catalytic activity results were correlated to the ammonia TPD profiles of the sample. The main reason for higher activity of samples with higher Nb containing content could be due to the medium acidic sites. Ammonia TPD profiles clearly indicated that with increasing Nb loading the strength of acid sites increased from weak to medium. Thus, these results demonstrate that the CHO conversion is strongly dependent on the amount and strength of the acid sites. The spectroscopic analysis of DR-UV-Vis, FT-Raman spectroscopy and H<sub>2</sub>-TPR results suggested that, with increasing Nb loading, extra framework Nb<sub>2</sub>O<sub>5</sub> species are appeared in the samples. It could be that these extra framework Nb<sub>2</sub>O<sub>5</sub> species also responsible for such strong activation of this reaction.

### 3.2. Catalytic results and discussion

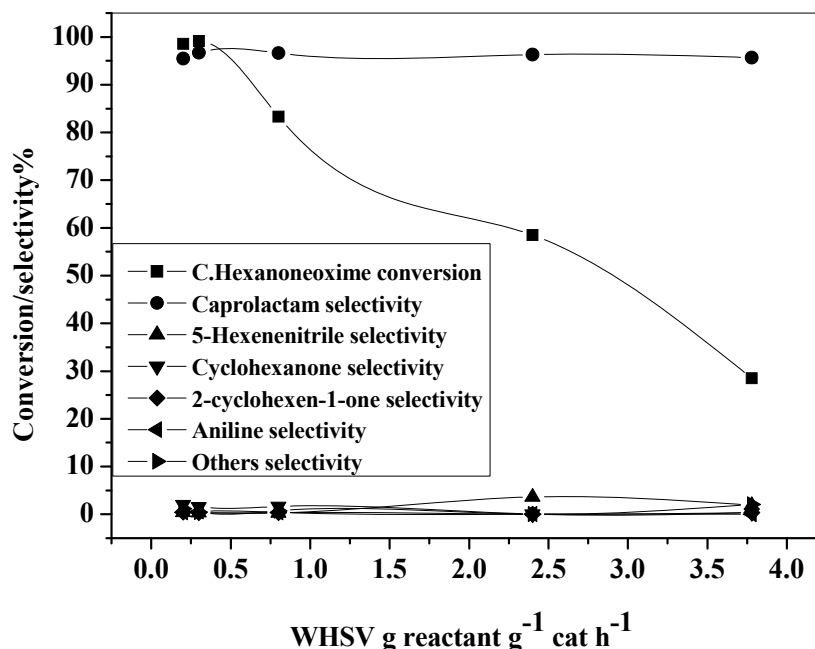
However, many researchers have reported the catalytic activity relationship with acidity of the catalysts. Kob et al. assumed that strong acid sites were more favorable for the reaction than the weak acid sites [30]. In contrast, Hoelderich et al. reported that, weakly acidic vicinal silanol groups and nest silanol sites are the active sites for the formation of very high CL selectively [11, 22, 43, 45]. These findings are confirmed by recently solid-state NMR studies [59-60]. In addition, Beckmann rearrangement proceeds on Brønsted sites. Pyridine FT-IR spectra results of Nb-MCM-41(Si/Nb-32) catalyst has shown presence of both Brønsted and Lewis acid sites with distribution of weak to medium acid sites. All Nb-MCM-41 catalysts with different Si/Nb ratios perform very good conversion rates of almost 100% with high selectivities for CL of >95%.

#### 3.2.4 Influence of weight hourly space velocity (WHSV)

The influence of WHSV of the feed on the conversion and selectivity of the products over Nb-MCM-41 (Si/Nb-32) catalyst is illustrated in Fig-36. While the catalyst weight is kept at 2 g, the contact time was varied by changing the feed rate i.e. WHSV = 0.2-4 h<sup>-1</sup>. A continuous decrease of CHO conversion from 100 to 30% is observed with increasing WHSV of the feed. The maximum yield of CL with 95.9% is found at WHSV of 0.3 g<sub>reactant</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.

However, in the present investigations, with increasing the WHSV from 0.2 to 2.5 h<sup>-1</sup>, the selectivity for 5-hexenenitrile is slightly enhanced, but we couldn't observe significant change in the selectivity of CL and other products by variation of WHSV.

### 3.2. Catalytic results and discussion



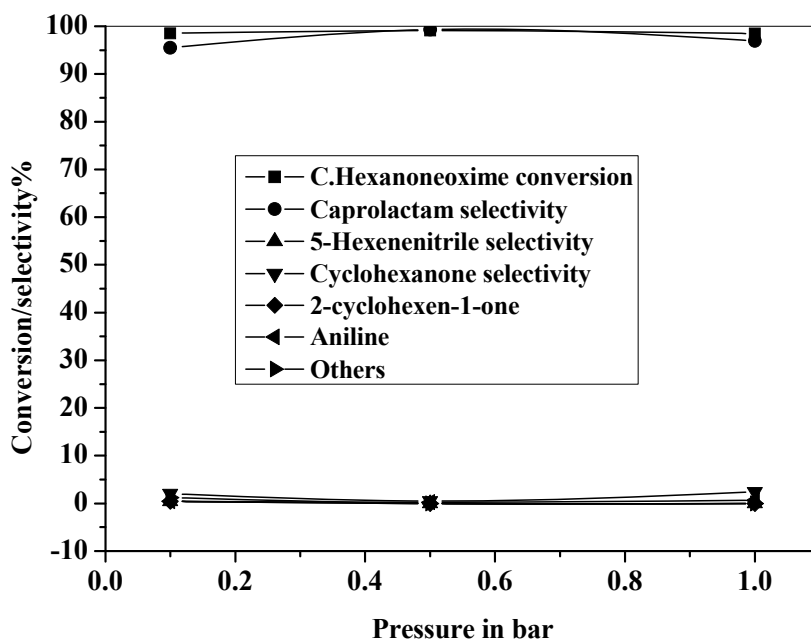
**Figure 36: Effect of WHSV on conversion and selectivity over Nb-MCM-41 (Si/Nb-32) catalyst. Conditions: 300 °C, 0.1 bar, TOS = 4h, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%.**

#### 3.2.5 Influence of pressure

Previous studies by our group have shown that reduced pressure led to a significant improvement of the CHO conversion and CL selectivity in the reaction [22, 43, 45]. In order to see the influence of the pressure the reactions were carried out over Nb-MCM-41 (Si/Nb-32) catalyst under different pressures 0.1, 0.5, and 1.0 bar at 300 °C. The results with respect to CHO conversion and CL selectivity are presented in Fig.37. In the pressure range from 0.1 to 0.5 bar the conversion of CHO and CL selectivity reached up to 100%. By an increase of the pressure from 0.5 to 1 bar the conversion and selectivity

### 3.2. Catalytic results and discussion

started to drop slightly. These results clearly indicated that with an increment of pressure from 0.1 bar to 0.5 bar, the products desorption rate from the catalyst surface is enhanced.

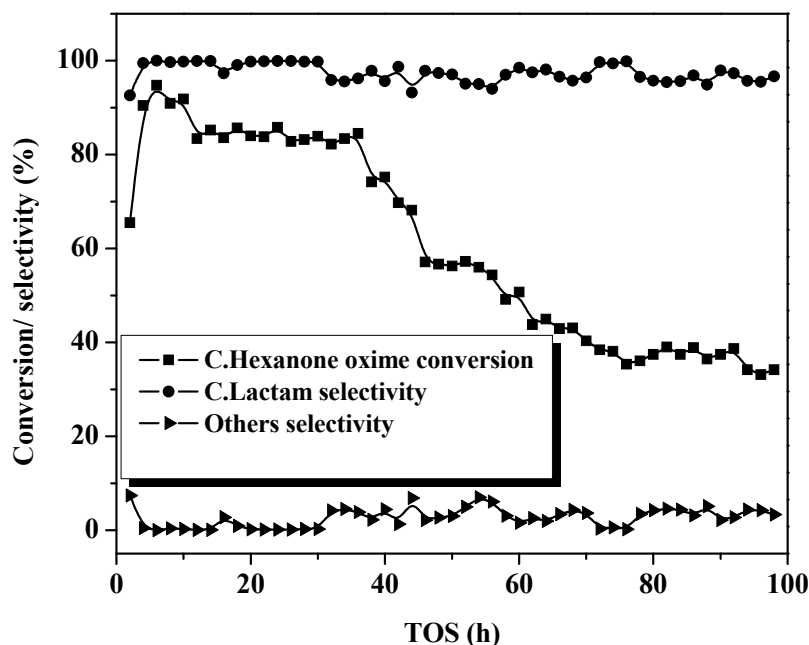


**Figure 37: Effect of reduced pressure on the conversion and selectivity over Nb-MCM-41 (Si/Nb-32) catalyst. Conditions: 300 °C, WHSV= 0.3 h<sup>-1</sup>, TOS = 4h, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%.**

#### 3.2.6 Time on stream study

The time on stream activity study of Nb-MCM-41 (Si/Nb-128) is presented in Fig-38. Reaction was carried out for 100 h for study the deactivation of the catalyst. The results revealed that the catalyst shows very good activity in the CHO conversion and CL selectivity respectively for 40 h. Afterwards, the CHO conversion began to decrease. The conversion declined to 40% after 100 h of time on stream. However, the selectivity for CL was found almost constant at 97% during 100 h time on stream.

### 3.2. Catalytic results and discussion



**Figure 38: Time on stream study of the catalyst Nb-MCM-41 (Si/Nb-128).**

**Conditions: 300 °C, pressure =0.1 bar, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%.**

The catalyst deactivation proceeds most probably via poisoning of the active sites. These results are in good agreement to those previously reported in case of H-MCM-22 catalyst [172]. Whereby, the catalytic stability can be divided into two periods: Period I up to 40 h exhibiting stable conversion and period II, up to until 100 h with rapid aging of a catalyst. It is well known that catalysts deactivation for Beckmann rearrangement of CHO by formation of aliphatic oligomers on the catalyst surface [65]. Moreover, it was observed that when higher acidic sites of MFI zeolite are present for this reaction, ring opening reaction occur and formation of more oligomer precursors on the catalyst surface takes place [65]. Surprisingly, in our present study we did not observe significant

### 3.2. Catalytic results and discussion

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increase of the selectivity to ring opening reaction products such as hexenenitrile compounds.

Furthermore, to elucidate the type of deposits formed on the catalyst surface, after 100 h, the spent Nb-MCM-41 (Si/Nb-128) catalyst was investigated by means of XPS analysis. These data showed (Table-6) that the C 1s signal at binding energies of 284.8-285.5 eV, which is an indication that presence of aliphatic carbon on the catalyst surface [179-180] and not for carbon of aromatic or SP<sup>2</sup>- character [181-182]. In addition, the XPS depth profile shows that nitrogen had penetrated into the material as well. The N 1s binding energy at about 399-400 eV, which is corresponding due to the aminofunctional and ammonium-like species present on the surface [183]. This might be a evidence that hexane nitrile compounds are formed and subsequently oligomerized or polymerized, resulting in the blockage of the pores. Comparable results were observed in case of B-MFI catalysts and it was intensively investigated in both fresh and deactivated catalysts by secondary ion mass spectroscopy (SIMS) and x-ray photoelectron spectroscopy (XPS) [65].

### 3.2. Catalytic results and discussion

**Table 6: Results of the XPS data of Nb-MCM-41(Si/Nb-128) after 100 h**

| Surface concentration | Given in atomic percent | Binding energy in eV |
|-----------------------|-------------------------|----------------------|
| C 1s                  | 21.21                   | 285.5                |
| O 1s                  | 55.19                   | 533                  |
| N 1s                  | 3.32                    | 399.5                |
| Si 2p                 | 20.28                   | 104.5                |
| Nb 3d                 | traces                  | --                   |

In order to reveal the reason for the deactivation of Nb-MCM-41(Si/Nb-128) catalyst in the gas phase Beckmann rearrangement of CHO to CL, the catalyst was analyzed by N<sub>2</sub> adsorption method after 100 h TOS. Table-7 shows the decrease of pore diameter and surface area of used catalyst in comparison with the fresh catalyst. This behavior is attributed to catalyst active sites being uniformly blocked by side-products and consecutive reaction products like nitriles and polymeric species.

### 3.2. Catalytic results and discussion

**Table 7: Surface area and pore diameter for Nb-MCM-41(Si/Nb-128) before and after reaction.**

| Catalyst             | Surface Area (m <sup>2</sup> /g) | Pore Diameter (Å) |
|----------------------|----------------------------------|-------------------|
| Nb-MCM-41(Si/Nb-128) | 929                              | 29.27             |
| Fresh                |                                  |                   |
| Nb-MCM-41(Si/Nb-128) | 414                              | 20.8              |
| After 100 h          |                                  |                   |

#### 3.2.7 Catalyst regeneration study under air or under non-oxidative gas

Sato et al. examined the regeneration of non-zeolitic catalyst such B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst by burning off the coke in air at 500 °C for 3 h and found that while CHO conversion was completely recovered, CL selectivity was poorer [184]. On the other hand, our group has developed a regeneration method for deactivated B-MFI catalysts in a fluidized bed reactor [185-186] and investigated the long-term regeneration stability of specially modified B-MFI catalysts as well as MCM-22 catalysts over 40 days. The catalyst was regenerated at 500 °C for 16 h under air after 6 h reaction time [187, 170]. Also, they found that the regeneration could be carried out in a non-oxidative atmosphere such as N<sub>2</sub> [185].

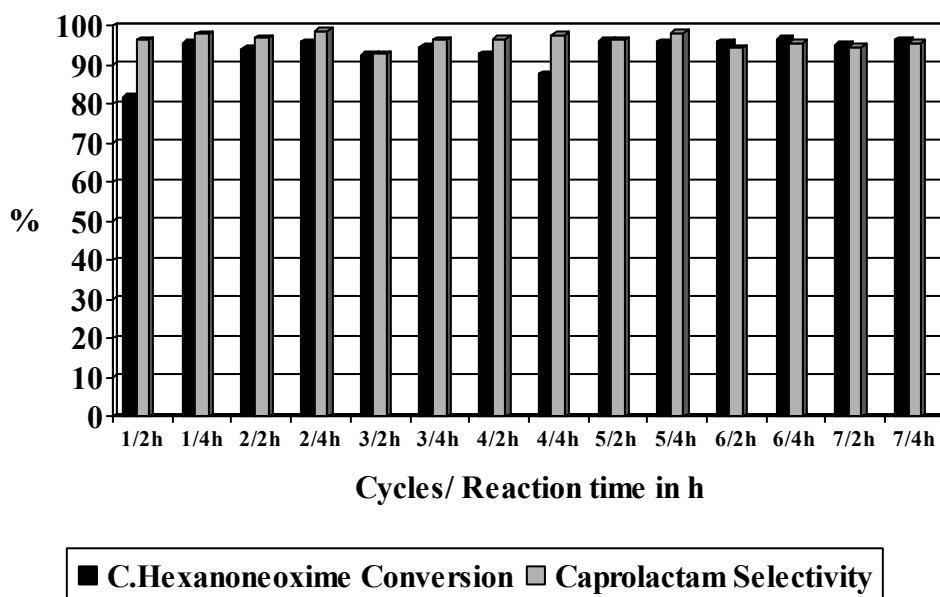
The present regeneration study was conducted on a deactivated Nb-MCM-41(Si/Nb-32) catalyst under air or non-oxidative gas such as N<sub>2</sub> for five or more cycles. The results based on CHO conversion and CL selectivity are illustrated in Fig-39 and 40. In both the cases the catalyst could be regenerated five or even more cycles without any

### 3.2. Catalytic results and discussion

considerable activity loss. The regeneration study under air has shown almost constant activity for seven cycles. When the catalyst was regenerated in the presence of air at 500 °C for 4 h, the original activity was completely recovered.

In contrast, when the regeneration was performed under N<sub>2</sub> gas at 500 °C for 4 h, CHO conversion started to decrease after five cycles from 100 to 85%, the CL selectivity, however, increased to almost 100% by the end of five cycles.

Based on the above results it is concluded that the pore blockage by aliphatic oligomers, is the main reason for deactivation of the catalyst. These oligomers, which are formed by ring opening reaction, can be desorbed or rinsed out with nitrogen or other oxidative gases as we found before [185]. Moreover, the regeneration studies under air and N<sub>2</sub> concluded that the deactivation is reversible.

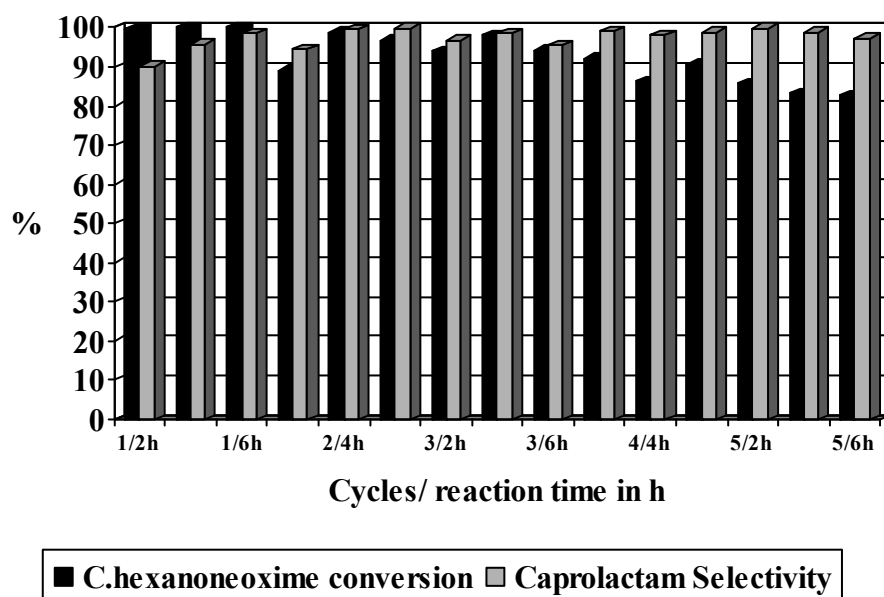


**Figure 39: Catalyst recycle studies under air with Nb-MCM-41 (Si/Nb-32).**

**Conditions: 300 °C, 0.1 bar, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2 l/h N<sub>2</sub>, oxime :**

**EtOH=1:9 wt%, regeneration conditions under air at 500 °C for 4h.**

### 3.2. Catalytic results and discussion



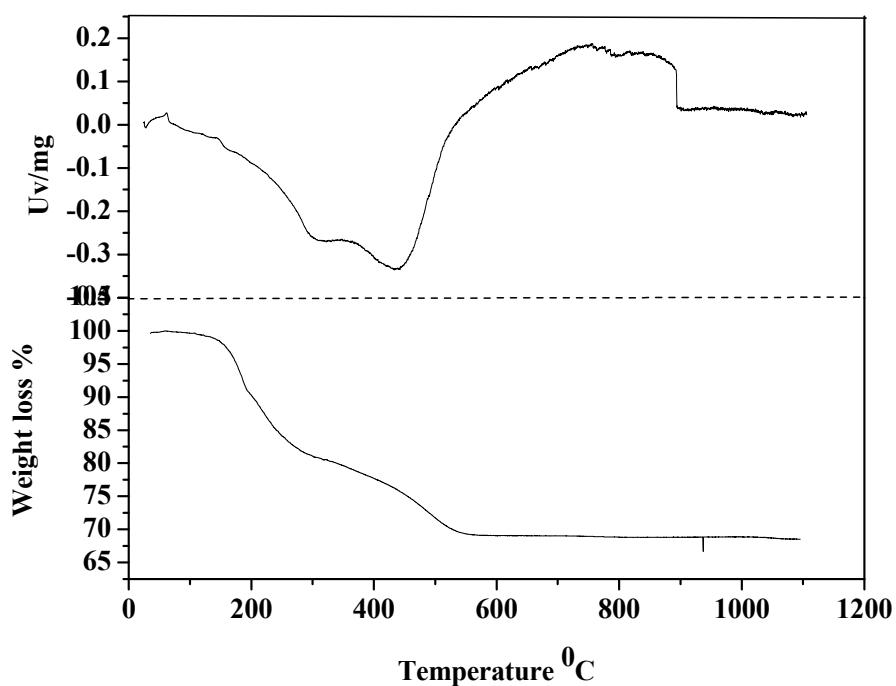
**Figure 40: Catalyst recycle studies under N<sub>2</sub> with Nb-MCM-41 (Si/Nb-32).**

**Conditions: 300 °C, 0.1 bar, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2l/h N<sub>2</sub>, oxime :**

**EtOH=1:9 wt%, regeneration conditions under N<sub>2</sub> at 500 °C for 4h.**

After the reaction, we observed that catalysts changed to become black, suggesting that catalyst is at least partly covered with coke. Consequently, the amount of coke formation on the spent catalysts is measured by TG & DTA analysis. After five regeneration cycles of the catalyst under nitrogen, the catalyst was investigated by means of TG and DTA analysis. It is observed that, after TG analysis, the white color of the catalyst was restored as results of coke combustion. The relation ship between amount of coke formed on the catalyst surface and combustion temperature depicted in Fig 41.

### 3.2. Catalytic results and discussion



**Figure 41: TG& DTA analysis of Nb-MCM-41 (Si/Nb-32) catalyst after five cycle regeneration under N<sub>2</sub> gas.**

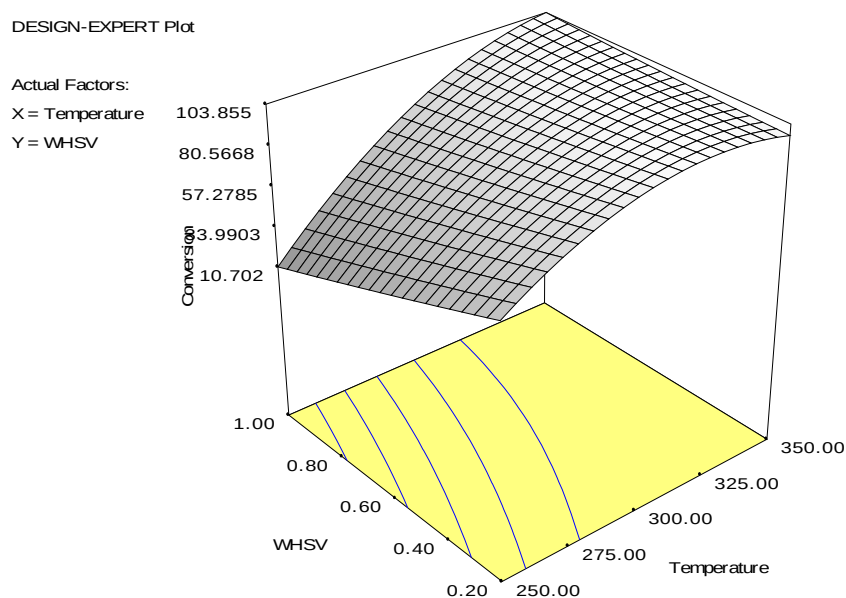
TG & DTA analysis results of a spent catalyst revealed that all the coke from the catalysts surface can be removed at 300-500 °C. The combustion of the coke caused sudden decrease of TGA signal at 300 to 500 °C. The weight loss is approximately 35% observed. Thereby, the strong exothermic peak at around 450 °C and shoulder peak at 300 °C are attributed for combustion and removal of coke from the catalyst.

#### 3.2.8 Reaction results by following Design Expert

In order to determine the optimum reaction conditions reactions are carried out using response surface design for Nb-MCM-41 (Si/Nb-32) catalyst. From above studies it

### 3.2. Catalytic results and discussion

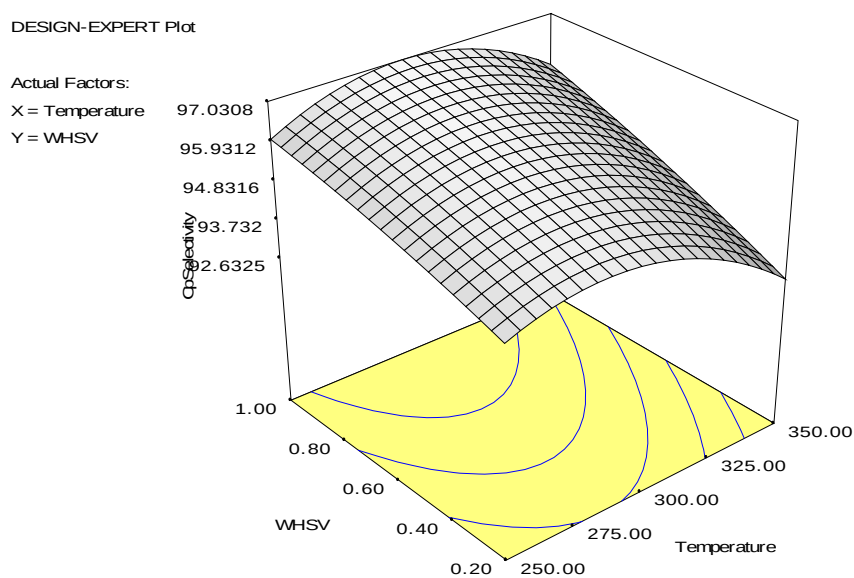
was found that the reaction temperature and WHSV play the major role in conversions and selectivities. Indeed, the reactions are carried out by changing these two factors in contrast the other reaction conditions such as feed ratio, reduced pressure and carrier gas flow are maintained constant.



**Figure 42: CHO conversion over Nb-MCM-41(Si/Nb-32)**

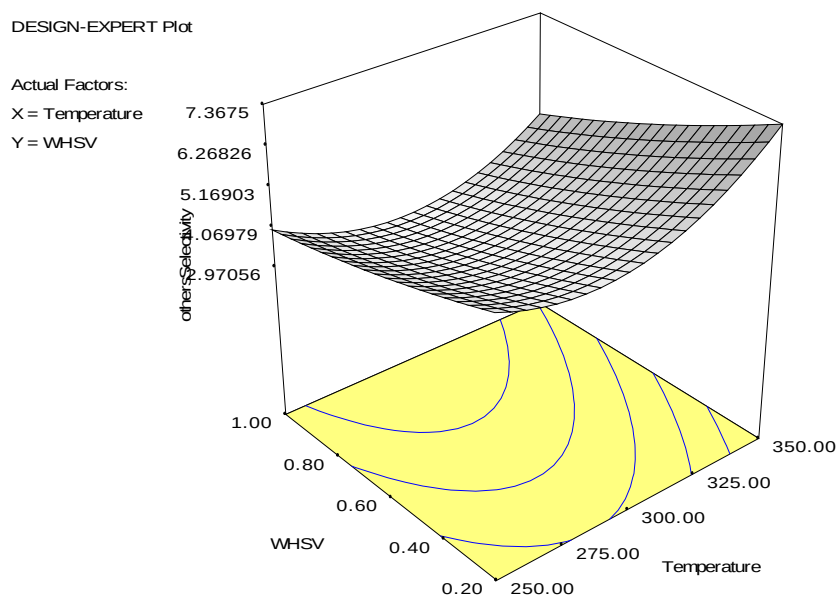
**Condition: 0.1 bar, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%, TOS= 4h.**

### 3.2. Catalytic results and discussion



**Figure 43: CL selectivity over Nb-MCM-41(Si/Nb-32)**

**Conditions: 0.1 bar, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:9 wt%, TOS= 4h.**



**Figure 44: Selectivity of other products over Nb-MCM-41(Si/Nb-32)**

**Conditions: 0.1 bar, carrier gas = 2l/h N<sub>2</sub>, CHO: EtOH=1:9 wt%, TOS= 4h.**

### 3.2. Catalytic results and discussion

Design-Expert model results are shown in Fig.16-18. Results clearly illuminate that at high temperatures of around 300 °C-325 °C, and at high WHSV of around 0.4 h<sup>-1</sup> values, 100% CHO conversion can be achieved. At lower temperature 250 °C, the conversion reached maximum about 30%. The CL selectivity is increased with reaction temperature from 250-300 °C and WHSV value from 0.2 to 0.4 h<sup>-1</sup>. With further increase the reaction temperature from 300 °C to 350 °C and WHSV values from 0.4 to 1 h<sup>-1</sup> the CL selectivity is decreased. At the same time the selectivity for other by-products are started to increase. As a result we can conclude that 300 °C and a WHSV = 0.4 h<sup>-1</sup>, are best suitable to achieve 100% CHO conversion and more than 95% CL selectivity.

To obtain better reproducibility and standard conditions for the reaction, the design expert model has given 9 predicted reaction conditions with durability of one. Table-8 presented the predicted values of conversion and selectivity with different temperature and WHSV values.

**Table: 8-Design-Expert model solutions**

| S.No | Temperature<br>(°C) | WHSV<br>(h <sup>-1</sup> ) | C. Oxime<br>Conversion<br>(%) | C.Lactam<br>Selectivity<br>(%) | Others<br>Selectivity<br>(%) | Dura<br>bility |
|------|---------------------|----------------------------|-------------------------------|--------------------------------|------------------------------|----------------|
| 1    | 297.47              | 0.27                       | 96.62                         | 95                             | 5                            | 1              |
| 2    | 326.93              | 0.49                       | 99.99                         | 95                             | 5                            | 1              |
| 3    | 304.99              | 0.30                       | 98.35                         | 95                             | 5                            | 1              |
| 4    | 316.59              | 0.39                       | 99.61                         | 95                             | 5                            | 1              |
| 5    | 273.99              | 0.26                       | 83.15                         | 95                             | 5                            | 1              |
| 6    | 268.73              | 0.28                       | 77.67                         | 95                             | 5                            | 1              |
| 7    | 325.84              | 0.48                       | 99.96                         | 95                             | 5                            | 1              |
| 8    | 276.98              | 0.25                       | 85.77                         | 95                             | 5                            | 1              |
| 9    | 328.09              | 0.51                       | 100                           | 95                             | 5                            | 0.99           |

### 3.2. Catalytic results and discussion

For checking the durability, reactions were carried out according to the reaction conditions predicted from solutions of Desing-Expert model (Table-6: S.No-3, 5 and 7). Reaction results were summarized in Table-9. These results clearly illustrate that experimental results are nearly same as the predicted values of design expert model.

**Table: 9-comparision of reaction results with predicted results:**

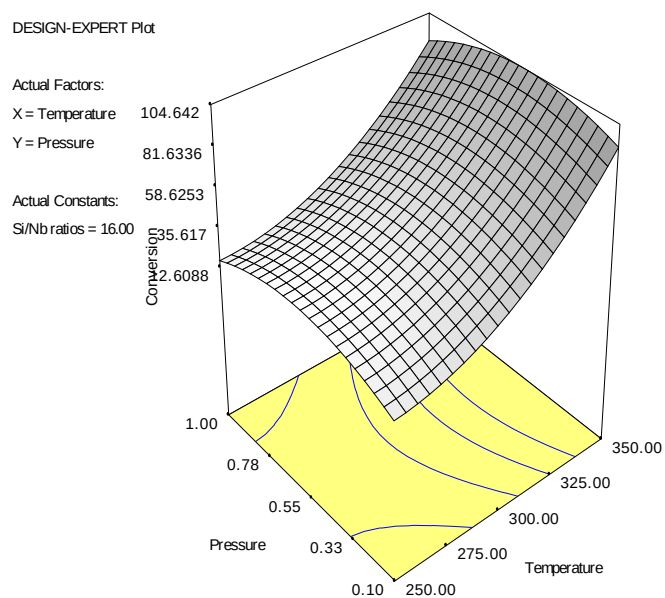
|                                    | Temperature<br>( <sup>0</sup> C) | WHSV<br>(h <sup>-1</sup> ) | C. Oxime<br>Conversion<br>(%) | C.Lactam<br>Selectivity<br>(%) | Others<br>Selectivity<br>(%) |
|------------------------------------|----------------------------------|----------------------------|-------------------------------|--------------------------------|------------------------------|
| <b><i>Predicted</i></b>            | 304                              | 0.30                       | 98.3                          | 95                             | 5                            |
| <b><i>Achieved<br/>results</i></b> | 300                              | 0.3                        | 99.1                          | 96.7                           | 3.3                          |
| <b><i>Predicted</i></b>            | 326                              | 0.48                       | 99.9                          | 95                             | 5                            |
| <b><i>Achieved<br/>results</i></b> | 326                              | 0.5                        | 96.1                          | 97.4                           | 2.5                          |
| <b><i>Predicted</i></b>            | 274                              | 0.26                       | 83.1                          | 95                             | 5                            |
| <b><i>Achieved<br/>results</i></b> | 274                              | 0.25                       | 82.3                          | 91.4                           | 8.5                          |

#### *Reaction results with Nb-MCM-41 (Si/Nb-16)*

From previous results it is clear that among with temperature and WHSV, the feed ratios and pressure also have strong influence in CHO conversion and CL selectivity. In order to find the right temperature and pressure reactions are carried out in presence of Nb-MCM-41(Si/Nb-16) catalyst. Also, the main concern thereby is the obtained 100 % CHO conversion and 97% CL selectivity, at WHSV-2 h<sup>-1</sup> and, a feed ratio of CHO:ethanol(1:3), which are harsh conditions for catalyst deactivation.

### 3.2. Catalytic results and discussion

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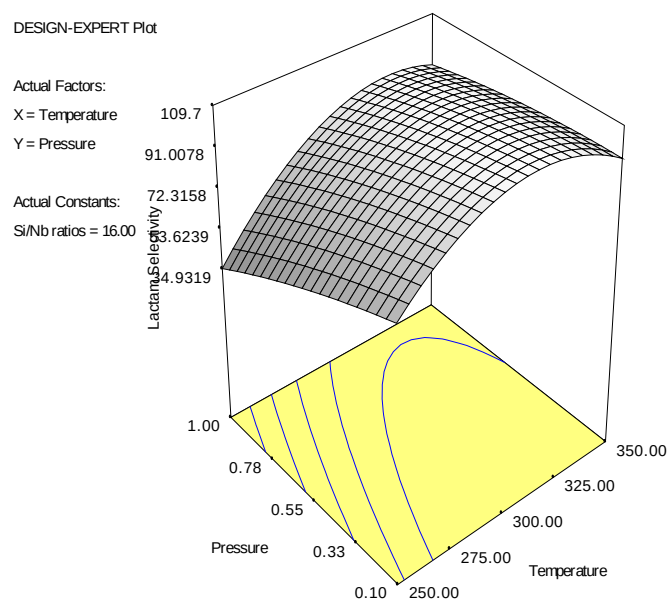


**Figure 45: CHO conversion over Nb-MCM-41(Si/Nb-16)**

**Condition: 0.1 bar, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:3 wt%, WHSV-2h<sup>-1</sup> TOS=**  
**4h.**

### 3.2. Catalytic results and discussion

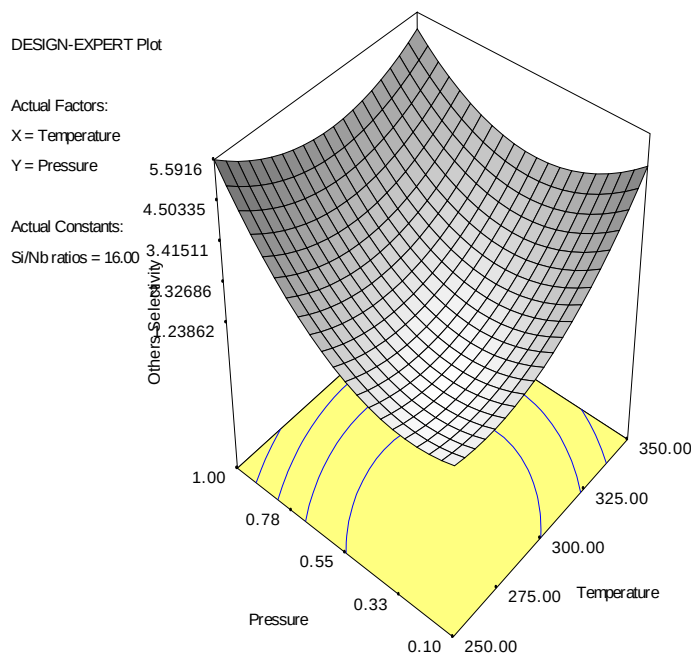
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**Figure 46: CL selectivity over Nb-MCM-41(Si/Nb-16)**

**Condition: 0.1 bar, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:3 wt%, WHSV-2h<sup>-1</sup> TOS= 4h.**

### 3.2. Catalytic results and discussion



**Figure 47: Others selectivity over Nb-MCM-41(Si/Nb-16)**

**Condition: 0.1 bar, carrier gas = 2l/h N<sub>2</sub>, CHO : EtOH=1:3 wt%, WHSV-2h<sup>-1</sup> TOS= 4h.**

Fig 45-47 shows that the conversion and selectivity over temperature vs pressure in presence of Nb-MCM-41(Si/Nb-16) catalyst. Results clearly indicate that the CHO conversion and CL selectivity are mainly depended on temperature and pressure. With increasing the reaction, temperature from 250 °C to 325 °C and pressure from 0.1 bar to 0.55 bar the conversion of CHO 100 % and selectivity of CL above 97% are obtained. However, with further increment of reaction temperature from 320 to 350 °C and pressure from 0.55 to 1 bar the conversion and selectivity decreased. These results clearly indicate that at lower temperature the formation of cyclohexanone is dominant and at higher temperature formation of others (oligomers

### 3.2. Catalytic results and discussion

of caprolactam) increased. However, in this study we clearly observed that catalyst was deactivated within 6h of time on stream.

The design expert model has given six solutions with durability of nearly one for checking the reaction conditions. The following table-10 shows the solutions and experimental results.

**Table-10: Design-Expert model solutions:**

| <b>Solutions</b> | <b>Tem</b> | <b>Pre</b> | <b>Si.Nb</b> | <b>Con</b>  | <b>CP sel</b> | <b>5-Cy sel</b> | <b>C.Hn one sel</b> | <b>C.H e sel</b> | <b>An i sel</b> | <b>Oth e sel</b> | <b>Desirability</b> |
|------------------|------------|------------|--------------|-------------|---------------|-----------------|---------------------|------------------|-----------------|------------------|---------------------|
| <b>1</b>         | 341        | 0.2        | 128          | 86.5        | 97.6          | 0               | 2.5                 | 0                | 0.7             | 0                | 0.9                 |
| <b>2</b>         | 341        | 0.3        | 128          | 87.1        | 97.6          | 0               | 2.5                 | 0.02             | 0.7             | 0                | 0.9                 |
| <b>3</b>         | 340        | 0.3        | 128          | 88.3        | 98.9          | 0               | 1.2                 | 0.1              | 0.8             | 0                | 0.9                 |
| <b>Exp</b>       | <b>340</b> | <b>0.4</b> | <b>128</b>   | <b>88.9</b> | <b>97.6</b>   | <b>0.1</b>      | <b>0.4</b>          | <b>0.40</b>      | <b>0.3</b>      | <b>0.33</b>      |                     |
| <b>4</b>         | 343        | 0.4        | 128          | 93.8        | 99.7          | 0               | 0.3                 | 0.24             | 1.0             | 0                | 0.9                 |
| <b>5</b>         | 337        | 0.5        | 16           | 90.8        | 97.6          | 0.8             | 0                   | 0.17             | 0.3             | 3.02             | 0.9                 |
| <b>6</b>         | 338        | 0.5        | 16           | 92.4        | 97.7          | 0.8             | 0                   | 0.21             | 0.3             | 3.06             | 0.9                 |
| <b>Exp</b>       | <b>338</b> | <b>0.5</b> | <b>16</b>    | <b>93.7</b> | <b>98.6</b>   | <b>0.4</b>      | <b>0.3</b>          | <b>0.03</b>      | <b>0.2</b>      | <b>0</b>         |                     |

#### 3.2.9 Catalytic activity tests over Ta-MCM-41 and Nb-Ta-MCM-41

Catalytic activity results of Ta-MCM-41 (Si/Ta=50) and Nb-Ta-MCM-41(Si/Nb+Ta=64) were shown in Table-11. Reactions were carried out at 300 °C for 6 h. From these results it can be notice that both the catalysts have demonstrated considerable catalytic activity in respective of CHO conversion and CL selectivity. Nb-Ta-MCM-41 catalyst has performed high selectivity for CL than the Ta-MCM-41. Nevertheless, the activity of Nb-Ta-MCM-41 is less as comparision with the Nb-MCM-41 catalysts.

### 3.2. Catalytic results and discussion

**Table 11: Catalytic activity results of Ta-MCM-41 (Si/Ta=50) and Nb-Ta-MCM-41 (Si/Nb+Ta=64). Conditions: 300 °C, 0.1 bar, WHSV = 0.3 h<sup>-1</sup>, carrier gas = 2 l/h N<sub>2</sub>, oxime : EtOH=1:9 wt%.**

| Feed ratios<br>(ethanol:CHO) | CHO<br>conversion% |              | CL selectivity<br>% |              |
|------------------------------|--------------------|--------------|---------------------|--------------|
|                              | After<br>2 h       | After<br>6 h | After<br>2 h        | After<br>6 h |
| Ta-MCM-41                    | 88.8               | 72.8         | 60.1                | 75.0         |
| Nb-Ta-MCM-41                 | 87.3               | 78.7         | 93.8                | 98.2         |

## 4. Summary and Outlook

## 4. Summary and Outlook

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### **4. Summary and Outlook**

The objective of this work was to incorporate niobium into the mesoporous and microporous molecular sieves framework such as Nb-MCM-41, Nb-SBA-15, Nb-HMS and Nb-Beta. In addition, Nb was impregnated on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported materials. The preparation of such materials was to be fully characterized by various analytical techniques and tested in gas phase Beckmann rearrangement reaction of cyclohexanone oxime to caprolactam.

These analytical results provide strong evidence that Nb has incorporated into the mesoporous and microporous silica framework. All samples have well ordered mesoporous structure with uniform pore size. The XRD results confirmed the structure and phase purity of the samples. N<sub>2</sub> sorption studies revealed that all Nb incorporated mesoporous molecular sieves have type IV isotherm and Nb-Beta has shown type I isotherm, which are characteristic isotherm for such materials. In addition, with increasing Nb content in the MCM-41 materials, partial loss of the mesoporous structure occurred.

Raman and DR UV-Vis spectroscopy results revealed that Nb molecular sieves contain two types of niobium species, one is tetrahedrally coordinated Nb species in framework and the other is polymerized hydrated Nb<sub>2</sub>O<sub>5</sub> species on the outer surface of the materials. These outer surface niobium species were observed particularly at high Nb content samples.

FT-IR spectroscopy results indicated a band at 960 cm<sup>-1</sup>, which is a characteristic peak for Nb-O-Si linkage. In addition, Si- MAS NMR and XPS spectroscopic results

#### 4. Summary and Outlook

indicated the presence of Si-O-Nb linkage confirming the Nb incorporation into Si framework.

H<sub>2</sub> TPR profiles of Nb content samples have shown two different reduction peaks, one at low temperature and other one at high temperature. A low temperature reduction peak is assigned for extra framework niobium species and high temperature reduction peaks are attributed due to the framework niobium species. However, Nb impregnated samples have shown different TPR profiles compared with the Nb incorporated molecular sieves.

SEM images of Nb-MCM-41 showed that they are formed as short spherical particles with diameters between 1.5 and 2.5  $\mu\text{m}$  and lengths between 10 and 20  $\mu\text{m}$ . The SEM images of Nb-HMS and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> samples have shown irregular morphology. Nb-beta zeolite has shown uniform spherical shaped crystals.

Ammonia TPD results indicated that all Nb containing different structured materials have shown weak to medium acid sites. Moreover, the acid strength of the samples is increased with increase the amount of the Nb content. Pyridine FT-IR spectroscopy results revealed that samples have both Brønstead and Lewis acid sites.

The catalytic activity of Beckmann rearrangement of CHO to CL over different Nb containing catalysts has performed very good conversion and selectivity. The effect of reaction temperature over different catalysts show optimum temperature at about 300-325 °C for gas phase Beckmann rearrangement. At low temperature, the cyclohexanone conversion and caprolactam selectivities were low. At 325 °C, cyclohexanone oxime conversion and caprolactam selectivity over different catalysts follow the order: Nb-MCM-41~Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>>Nb-SBA-15~Nb-HMS>Nb-beta>Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. The poor

#### 4. Summary and Outlook

catalytic performance Nb-Beta catalyst may be due to the narrow pore size distribution and small pore volume ( $0.089 \text{ cm}^3/\text{g}$ ) of the sample. The low activity of  $\text{Nb}_2\text{O}_5/\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  catalyst could be due to the strong acid strength of the sample and these strong acid sites might have created by Al.

The catalyst deactivation by using different feed ratios follows the order of  $1:3 > 1:6 > 1:9 \text{ wt\%}$ . Catalysts Nb-MCM-41 and  $\text{Nb}_2\text{O}_5/\text{SiO}_2$  have shown constant activity in respect oxime conversion and caprolactam selectivity at a high ethanol content feed ratio (1:9). The high activity at 1:9 feed ratio could be due to the easier product desorption from the catalyst active centers.

The reaction results over different solvents revealed that solvent strongly affected the activity, selectivity and stability of the catalysts. Medium polar solvents such as ethanol have shown constant activity, while the conversion decreased markedly with time on stream when other solvents, such as methanol and benzene were used. It is concluded that ethanol is the most effective solvent, which expel CL from the active sites in order to accelerate the Beckmann rearrangement reactions.

Time on stream studies indicate that the catalyst maintained constant activity for up to 40 h, afterwards, the conversion started to decrease. Nevertheless, constant CL selectivity was observed during the 100 h time on stream. It clearly indicates that catalyst deactivates due to the poisoning of catalyst active sites either by coke or by oligomers. In addition, the decrease of surface area and pore diameter was observed after 100 h reaction time.

The regeneration study revealed that catalysts can be regenerated in oxidative or even non-oxidative gas such as  $\text{N}_2$ . The reaction can be carried out without significant

#### 4. Summary and Outlook

loss of the catalytic activity. The TG& DTA analysis of a spent catalyst regenerated under N<sub>2</sub> show around 35 wt % loss of activity after the 5 th cycle. All the coke could be removed from the catalyst surface by heating the samples at 500 °C for 4 h under N<sub>2</sub> or air.

Design-Expert model results revealed that temperature of 325 °C, WHSV-0.4 h<sup>-1</sup>, and pressure 0.5 bar are optimum reaction conditions for obtaining 100% CHO conversion and above 95% CL selectivity.

#### **Out look**

Until now, zeolitic materials have been played a pivotal role in the synthesis of  $\epsilon$ -caprolactam from gas phase Beckmann rearrangement of cyclohexanone oxime. Also, from these findings we can notice that Nb incorporated mesoporous molecular sieves such as Nb-MCM-41, Nb-SBA-15 and Nb-HMS have given promising results for gas phase Beckmann rearrangement of CHO to CL. Although, significant achievements have been obtained over zeolitic materials and mesoporous materials, the main problems lead to expensive of these materials and synthesis procedure for these materials is time consuming process. In addition, non-zeolitic materials also have been attempted for this reaction. For instance, tantalum-silica, boron-silica, boron-alumina, tungsten-silica catalysts are applied for this reaction. However, the application of all these catalysts resulted in low selective for CL and exhibited fast deactivation for the reaction. Moreover, all these catalysts activity is not efficient in commercial manner. Now surprisingly we have observed a cheap non-zeolitic material such as Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> is very active and selective for this reaction.

#### 4. Summary and Outlook

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Amazingly, contrast to zeolites and mesoporous materials, this catalyst has the following significant advantages: 1) high atom efficiency and no production of toxic waste materials, 2) cheap and easy way to synthesis of catalysts, 3) high active, selective and reusability of the catalyst, 4) high stability as commercialized catalyst.

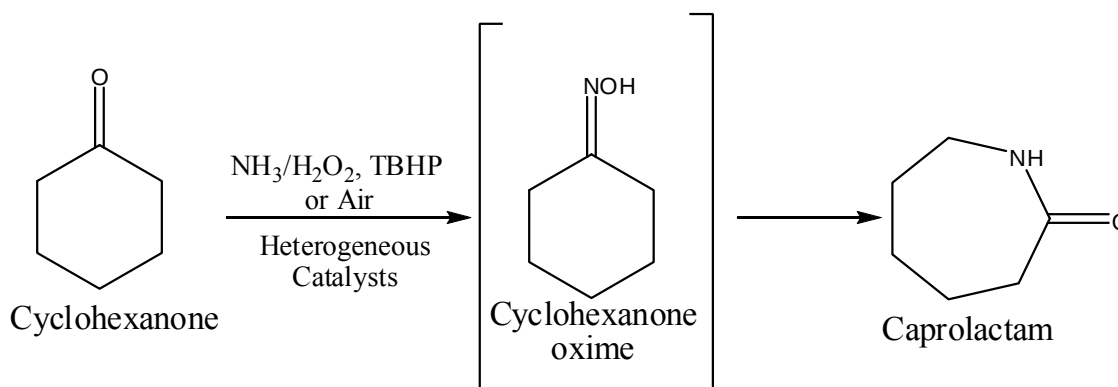
In future, this catalyst can be used as a potential catalyst for Beckmann rearrangement of cyclohexanone oxime to caprolactam under gas phase conditions. In order to commercialize this catalyst, more reactions have to be carried out in fixed bed as well as continuous flow reactors under different reaction conditions. Also, detailed investigations have to be done for understanding the role of the catalyst active centers and control the deactivation of the catalyst.

**5. “One pot” liquid phase ammoximation of  
cyclohexanone to caprolactam over heterogeneous  
catalysts**

## 5. Liquid phase ammoximation reaction

### 5. “One pot” liquid phase ammoximation of cyclohexanone to caprolactam over heterogeneous catalysts

The main aim of this work deals with the synthesis of caprolactam in a one pot liquid phase reaction from cyclohexanone in presence of hydrogen peroxide and ammonia over heterogeneous catalysts. This route provides a more economical and environmentally friendly process. Moreover, this single step procedure leads to minimize the consumption of energy and is a time saving process (reaction scheme-1).



**Reaction scheme-1**

Our strategy is outlined in reaction scheme-1. In order to achieve our goal, reactions have been carried out in liquid phase reaction conditions over different home made heterogeneous catalysts. All catalysts used for this reaction, were synthesized by hydrothermal method. Reactions have been carried out in batch reactors under ambient pressure and under pressure conditions in autoclave reactors.

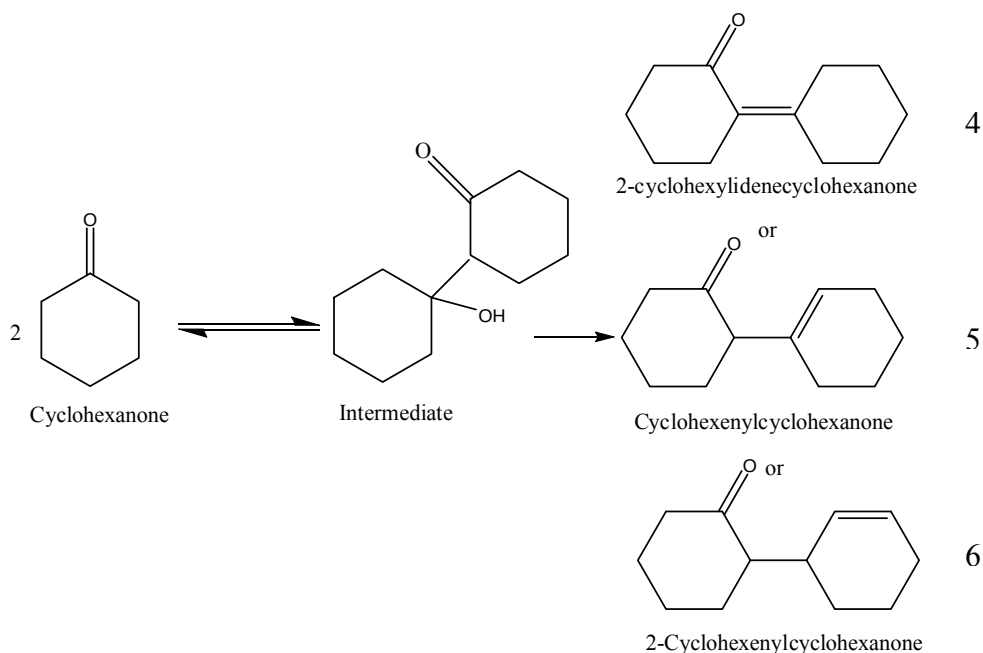
## 5. Liquid phase ammoximation reaction

### *Other products in ammoximation reaction*

In the reaction among with cyclohexanone oxime and caprolactam formation, other products have been observed too, some of these by-products were confirmed by GC-MS analysis. The possible by-products and side reactions are described below.

#### *i). Cyclohexanone condensation reaction*

The self condensation of cyclohexanone in presence of acid catalysts are described in prior art [188-190]. The condensation of cyclohexanone products finally land up with there isomeric mixture namely, 2-(1-cyclohexen-1yl) cyclohexanone, (4) cyclohexylidenecyclohexanone (5) and 2-cyclohexenylcyclohexanone (6). Reaction scheme-2 is shown below.

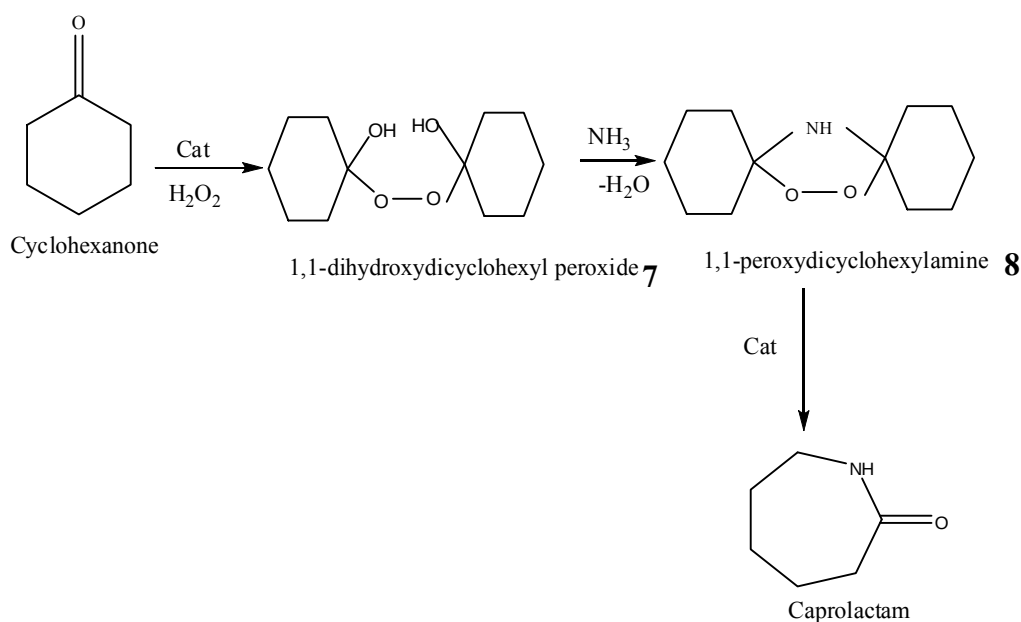


**Reaction scheme-2**

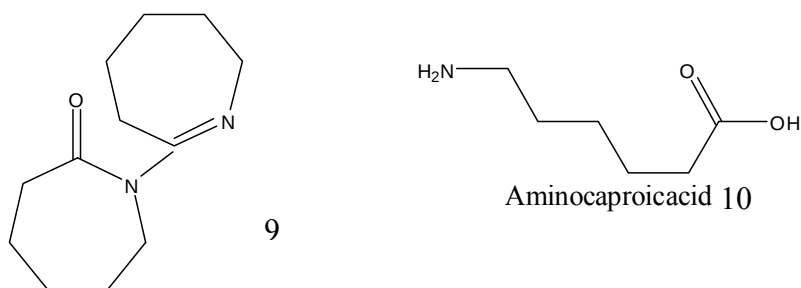
## 5. Liquid phase ammoximation reaction

### ii) Oligomerisation of caprolactam

Caprolactam oligomers can be formed by condensation of caprolactam or 1-1 peroxydicyclohexylamine (8). 1-1 peroxydicyclohexylamine can be formed by cyclohexanone reaction with hydrogen peroxide and ammonia. BP Chemicals has discussed in their patent in 1976 for synthesis of caprolactam from 1-1 peroxydicyclohexylamine [23]. GC-MS results also confirmed the presence of oligomers compounds in the reaction mixture. Possible oligomers are shown in reaction scheme-3.



Other products from caprolactam:

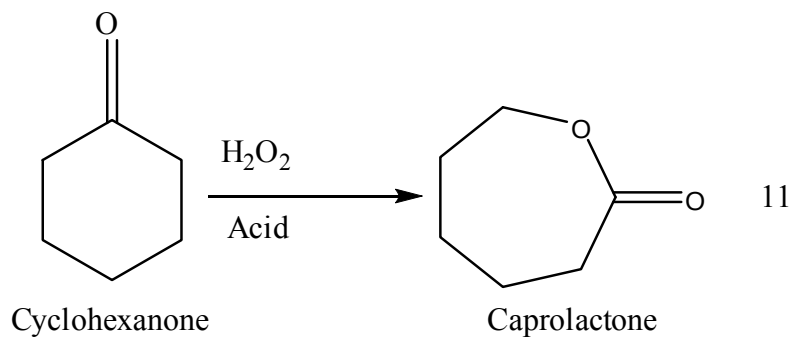


Reaction scheme-3

## 5. Liquid phase ammoximation reaction

### iii) Baeyer-Villiger oxidation of cyclohexanone to caprolactone

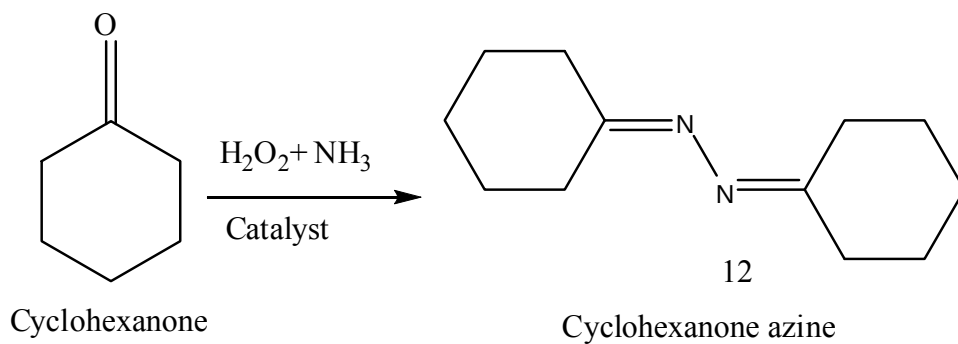
As it is well known, the Baeyer-Villiger oxidation reaction can also take place in presence of acid catalysts [191-192]. In the present reaction conditions, in presence of an acid catalyst and hydrogen peroxide this Baeyer –Villiger reaction product can be formed easily.



**Reaction scheme-4**

### iv) Cyclohexanone azine formation

Cyclohexanone azine (**12**) can be derived from the oxidation of the cyclohexanone imine (**16**).

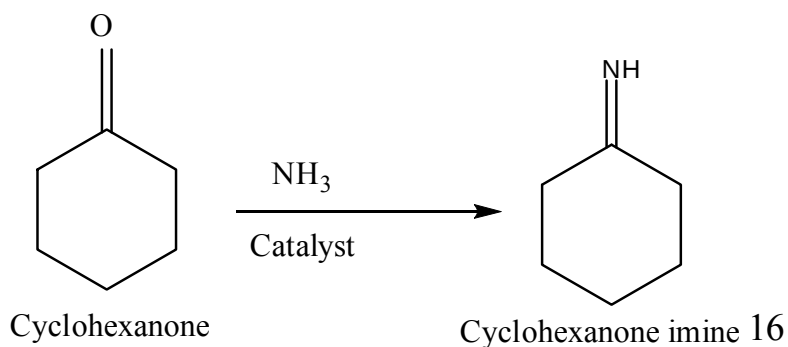
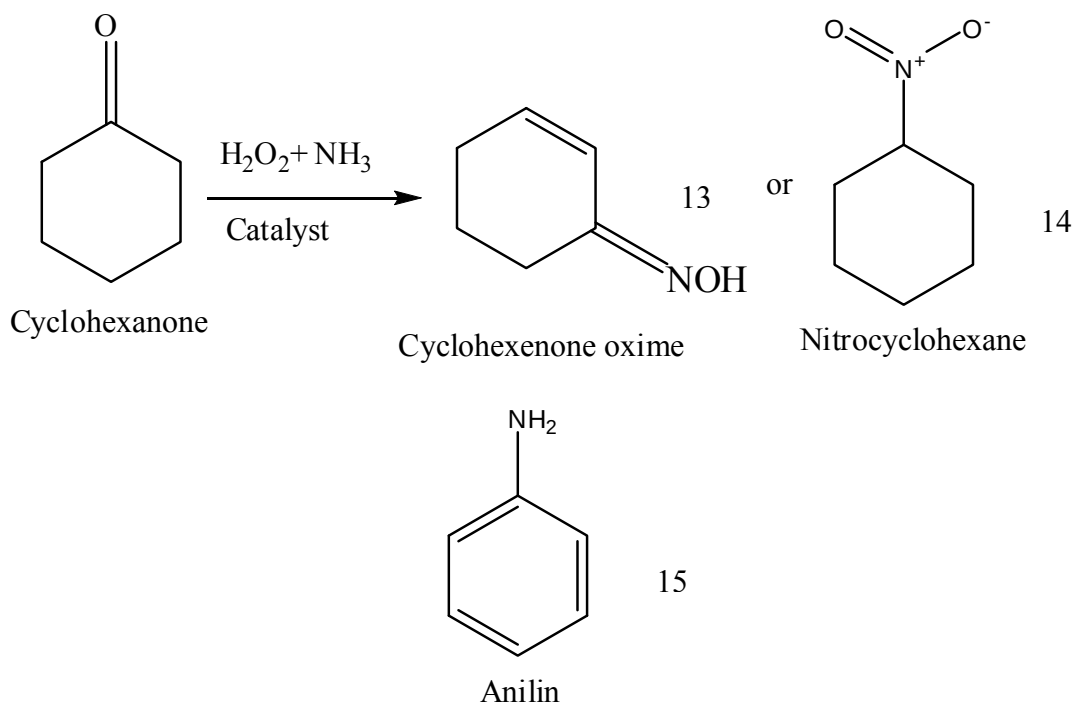


**Reaction scheme-5**

## 5. Liquid phase ammoximation reaction

### v) Nitrocyclohexane and cyclohexenone oxime formation

Nitrocyclohexane (**14**) and cyclohexenone oxime (**13**) might be either derived from consecutive oxidation reactions of cyclohexanone oxime (**2**) or from side reaction of cyclohexanone (**1**). Among with all these by-products aniline also observed as a by-product which might have formed from cyclohexanone imine (**16**).



Reaction scheme-6

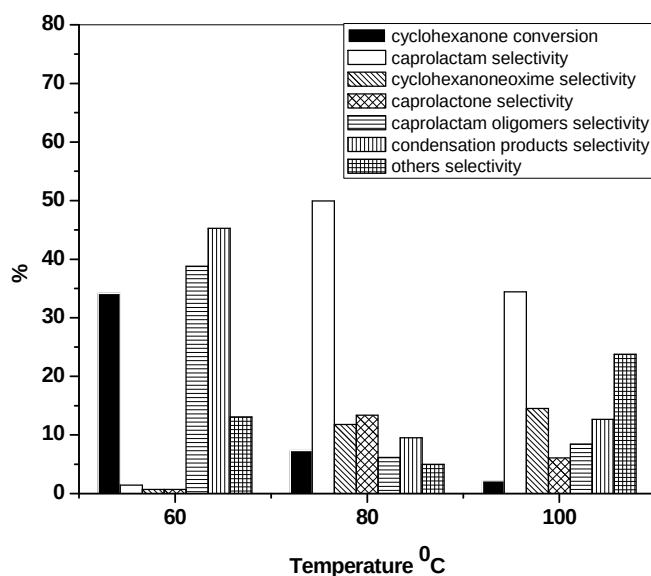
## 5. Liquid phase ammoximation reaction

All reactions by-products which are formed by reaction iv) and v) are included in the other product list. From here onwards others selectivity means composition of all these products.

### 5.1 Reaction results over Nb-MCM-41 catalysts in batch reactor

#### 5.1.1. Influence of reaction temperature

The effect of reaction temperature of cyclohexanone ammoximation reactions over Nb-MCM-41 catalysts was carried out at 60 °C, 80 °C, and 100 °C. Reaction results are shown in Fig-1.



**Figure 1: Effect of reaction temperature over Nb-MCM-41 (Si/Nb-32).**

Conditions: cat weight-0.2g,  $\text{NH}_3$ : ketone = 1.94 (molar ratio);  $\text{H}_2\text{O}_2$ : ketone = 1.32 (molar ratio), solvent-ethanol (10 wt %), stirring speed 900 rpm, reaction time-4h

The reaction temperature shows significant influence on the ammoximation of cyclohexanone over Nb-MCM-41 catalyst. As shown in Fig-1, the conversion of

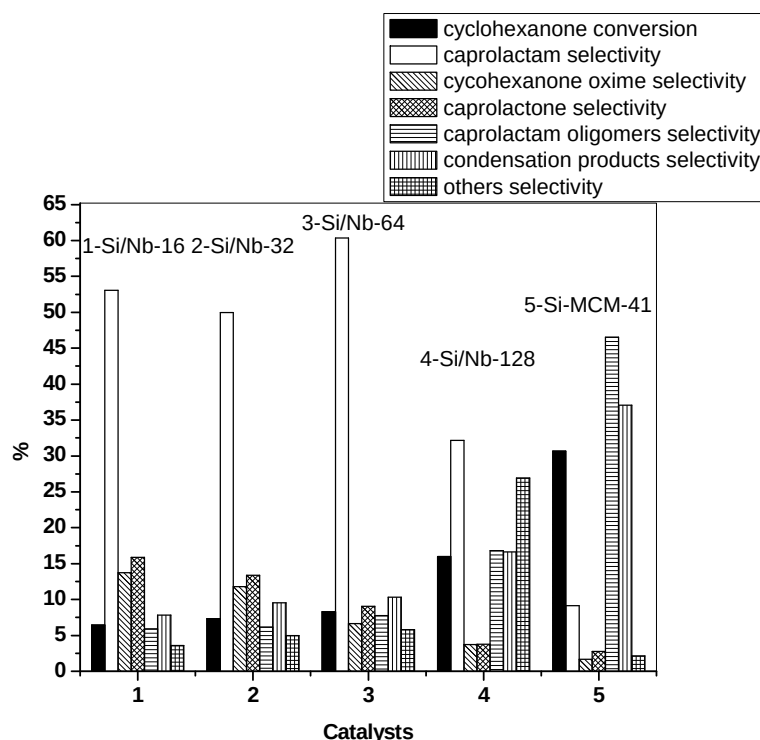
## 5. Liquid phase ammoximation reaction

cyclohexanone decreased with increasing temperature from 60 °C to 80 °C from 35% to 8%, whereas the selectivity for caprolactam increased to about 50%. With further increase of the temperature to 100 °C, a rapid decrease in the conversion of 3% and the selectivity of caprolactam of 35% was observed. However, the selectivities of others, at low temperature, the selectivity for caprolactam oligomers (**7**, **8**, **9** and **10**) and cyclohexanone condensation products (**4**, **5** and **6**) are high. A decrease of these products selectivities was observed with increasing reaction temperature from 60 °C to 80 °C. At the same time the selectivity for caprolactam was increased. It seems that at 80 °C caprolactam oligomers (**7**, **8**, **9** and **10**) are decomposed to form caprolactam (**3**). Surprisingly, with increasing the temperature from 80 °C to 100 °C, cyclohexanone oxime selectivity increased as well. The decrease in the conversion of cyclohexanone at high temperature is partially attributed to easier vaporization such as NH<sub>3</sub> and/or decomposition of hydrogen peroxide.

### 5.1.2. Influence Nb content

A series of Nb-MCM-41 catalysts with different Si/Nb ratios (Si/Nb=16-128) were prepared and used in the ammoximation of cyclohexanone. The reactions were carried out at a same weight ratio of catalysts, hydrogenperoxide/cyclohexanone and ammonia/cyclohexanone molar ratios. All the reactions were carried out in presence of ethanol as solvent. In all these cases the ethanol has taken 10 wt% of all the reactants mixture.

## 5. Liquid phase ammoximation reaction



**Figure 2: Effect of Nb content.**

Conditions: temp- 80 °C, cat weight-0.2g,  $\text{NH}_3$ : cyclohexanone = 1.94 (molar ratio);  
 $\text{H}_2\text{O}_2$ : cyclohexanone = 1.32 (molar ratio), solvent-ethanol (10 wt %), stirring speed 900 rpm, reaction time-4h

The cyclohexanone conversion increased with less Nb content in the sample (Fig- 2). However, simultaneously the selectivity for caprolactam decreased. The maximum caprolactam selectivity obtained was 60% in presence of Nb-MCM-41 (Si/Nb-64). In case of Nb free Si-MCM-41 catalyst the selectivity of caprolactam oligomers and cyclohexanone condensation products are more than 40%. These results clearly indicate that in presence of very weak acid catalysts such as Nb free Si-MCM-41 and Nb-MCM-

## 5. Liquid phase ammoximation reaction

41 (128) the conversion of cyclohexanone is high but at the same time selectivity for condensation products and caprolactam oligomes are preferably formed.

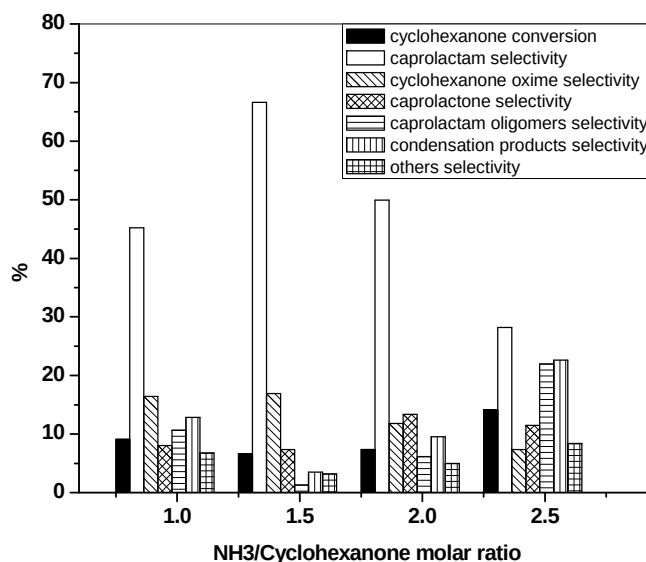
The acidity of the Nb samples was measured with ammonia TPD (temperature programmed desorption) method. TPD results clearly show a broad desorption signal in the region of 150-300 °C, for all the samples. The results reveal that the desorption peak shifts to higher temperature with increasing the Nb concentration (Si/Nb-128 to 16) in the sample. The acidic strength of the single sites in the materials with less Nb is stronger than in the materials with high Nb content. Similar features are known for zeolitic materials [10]. In addition, the acid strength increased from weak to medium with increasing the Nb concentration. The acid strength enhancement of Nb-MCM-41 samples may be due to the formation of Si-O-Nb species in the framework and formation of extra framework Nb<sub>2</sub>O<sub>5</sub> species that is observed in case of the high Nb content samples. At lower Nb content, the samples have weakly acidic sites which can be assigned to surface hydroxyl groups. These results suggests that, high Nb content samples, Nb-MCM-41 (Si/Nb 16, 32 and 64) yield caprolactam selectivity than samples with less Nb content such as Si/Nb-128 and Nb free Si-MCM-41. The high selectivity of caprolactam at high Nb content samples may be due to the medium acid strength of these samples.

### 5.1.3. Effect of NH<sub>3</sub>/cyclohexanone molar ratio

The effect of the NH<sub>3</sub>/cyclohexanone molar ratios on ammoximation is shown in Fig-3. With increasing the NH<sub>3</sub> concentration in the reaction mixture from 1.0 to 1.5 molar ratios, the selectivity of caprolactam increased to 65% but cyclohexanone conversion was only 7%. Further increment of NH<sub>3</sub> concentration form 1.5 to 2.5 the

## 5. Liquid phase ammoximation reaction

cyclohexanone conversion increased to 15% but at the same time the selectivity for condensation products and oligomers increased. The high cyclohexanone conversion obtained in an excessive amount of  $\text{NH}_3$  was probably due to a partial loss of  $\text{NH}_3$  by vaporization. In addition, at high  $\text{NH}_3$ /cyclohexanone molar ratio, the selectivity of others increased. It could be that in presence of an ammonia excess in the reaction mixture, cyclohexanone reacts with ammonia to form a cyclohexanone imine (**16**). This imine further reacts with ammonia to lead to higher selectivity of condensation products and others.



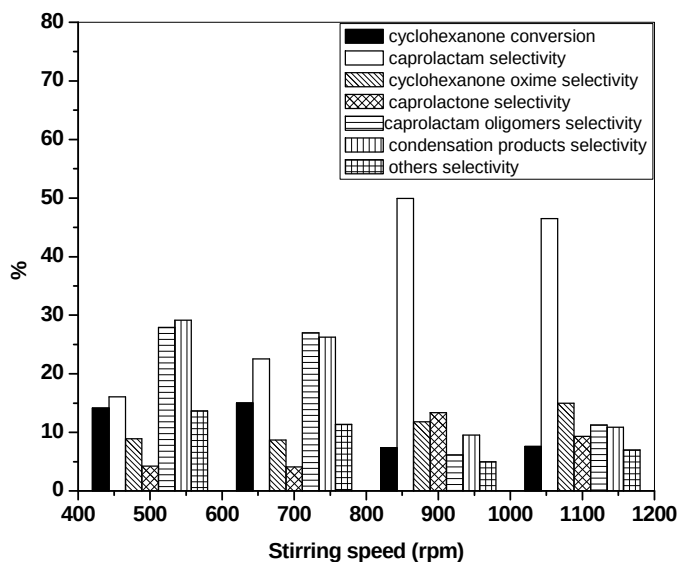
**Figure 3: Effect of  $\text{NH}_3$ /cyclohexanone molar ratio over Nb-MCM-41 (Si/Nb-32).**

Conditions: temp- 80 °C, cat weight-0.2g,  $\text{H}_2\text{O}_2$ : ketone = 1.32 (molar ratio), solvent- ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h

## 5. Liquid phase ammoximation reaction

### 5.1.4. Effect of stirring speed

In order to see the effect of stirring speed over Nb-MCM-41 (Si/Nb-32), reactions were carried out at 500 rpm, 700 rpm, 900 rpm and 1100 rpm, and results are depicted in Fig-7. At low stirring speed (500 and 700 rpm) the cyclohexanone conversion rates are about 12%. Surprisingly, with increasing stirring speeds from 700 to 900 rpm, cyclohexanone conversion decreased and caprolactam selectivity increased. In contrast at high stirring speed, the selectivity for condensation products and caprolactam oligomers decreased. The maximum caprolactam selectivity (50%) was obtained at 900 rpm. Presumably, at high stirring speed the products desorption from the catalyst surface is facilitated.



**Figure 4: Effect of stirring speed over Nb-MCM-41 (Si/Nb-32).**

Conditions: temp- 80 °C, cat weight-0.2g, NH<sub>3</sub>: ketone = 1.94 (molar ratio), H<sub>2</sub>O<sub>2</sub>: ketone = 1.32 (molar ratio), solvent-ethanol (10 wt %), reaction time-4h

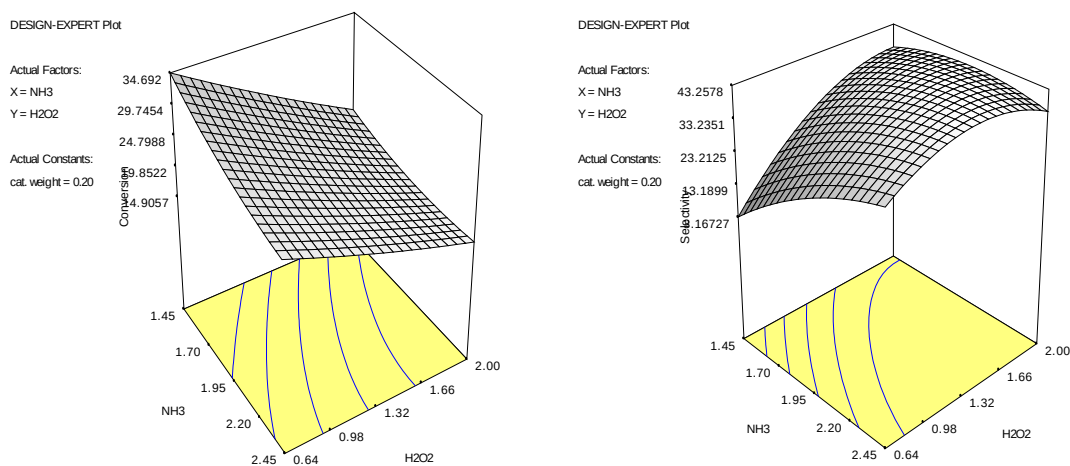
## 5. Liquid phase ammoximation reaction

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### 5.1.5. Effect of H<sub>2</sub>O<sub>2</sub>/cyclohexanone and NH<sub>3</sub>/cyclohexanone over Al-MCM-41 catalyst

In order to find the optimum reaction conditions in the liquid phase, the reactions were carried out by following Expert-Design model in presence of Al-MCM-41 catalyst. According to our previous studies, 80 °C is an optimum temperature for this reaction. Indeed, temperature and catalyst weight kept constant and reactions were carried out by changing H<sub>2</sub>O<sub>2</sub>/cyclohexanone and NH<sub>3</sub>/cyclohexanone molar ratios. Fig-5 shows the conversion and selectivity for caprolactam over H<sub>2</sub>O<sub>2</sub>/cyclohexanone and NH<sub>3</sub>/cyclohexanone molar ratios. Results revealed that the molar ratio of H<sub>2</sub>O<sub>2</sub>/cyclohexanone about 1.0 and the molar ratio of NH<sub>3</sub>/cyclohexanone about 1.45 the maximum cyclohexanone conversion of 34 % achieved. The selectivity of caprolactam reached maximum of 43 % at these conditions. Design-Expert model shows optimum reaction conditions are the catalyst weight of 0.26 g, H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio 1.42 and NH<sub>3</sub>/cyclohexanone molar ratio 2.13.

## 5. Liquid phase ammoximation reaction



**Figure 5: Conversion and caprolactam selectivity over Al-MCM-41.**

Conditions: temp-80 °C, solvent-ethanol (10 wt%), cat weight-0.2 g, stirring speed-900 rpm, reaction time-4h

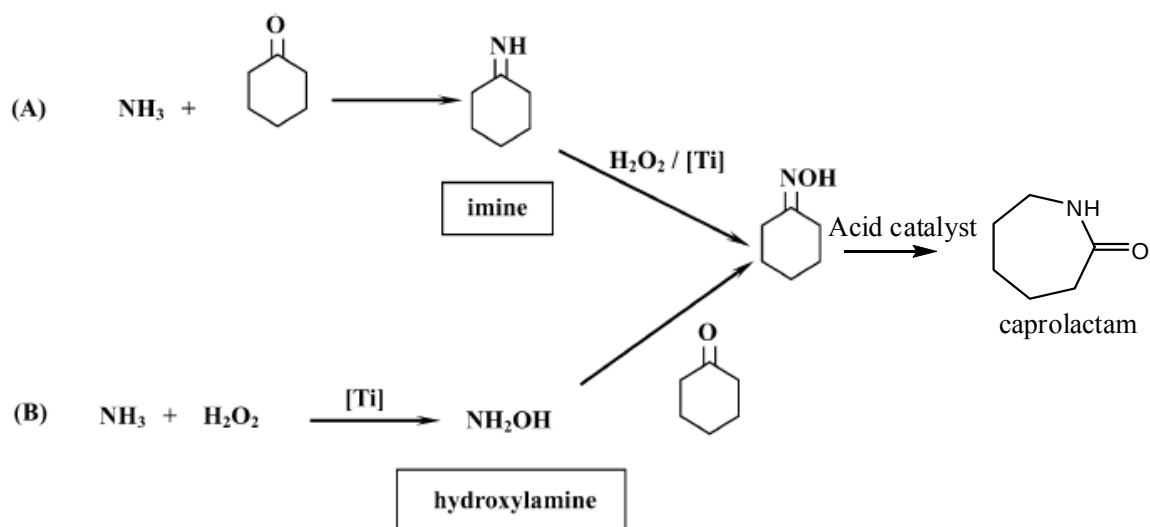
### 5.2. Reaction results over B-MFI, B-Al-MFI, B-Ti-MFI and B-Ti-Al-MFI catalysts in batch reactor

#### 5.2.1 Reaction results over different catalysts

The TS-1 catalysts are well known as active and selective catalysts for cyclohexanone oxime formation in the cyclohexanone ammoximation reaction. B-MFI catalyst is very active and selective for gas phase Beckmann rearrangement reaction. Ammoximation was considered to proceed through a TS-1 catalyzed oxidation of an intermediate of cyclohexanone imine (**16**) formed by the either in presence or absence of catalysts. The formation of hydroxylamine in the reaction by oxidation of ammonia with hydrogen peroxide on the Ti sites. The oximation of cyclohexanone with hydroxylamine

## 5. Liquid phase ammoximation reaction

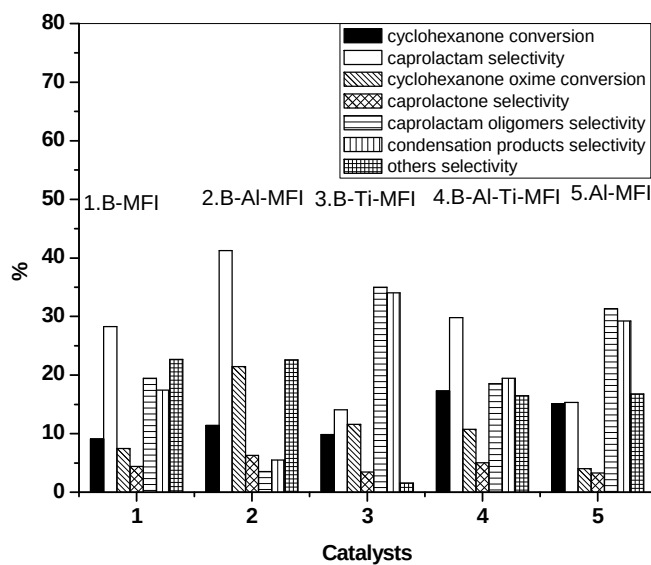
to oxime (reaction scheme-9). More over, in presence of acid catalysts, rearrangement reaction could occur and the cyclohexanone oximeformed as intermediate might be converted to caprolactam.



**Reaction scheme-7**

In order to see the effect of different metals in cyclohexanone ammoximation reaction, different metal atoms modified MFI zeolites such as B-MFI, Al-MFI, B-Ti-MFI, B-Al-MFI and B-Ti-Al-MFI were applied for this reaction. The results are shown in Fig-6.

## 5. Liquid phase ammoximation reaction



**Figure 6: Cyclohexanone conversion and products distribution over various MFI zeolites**

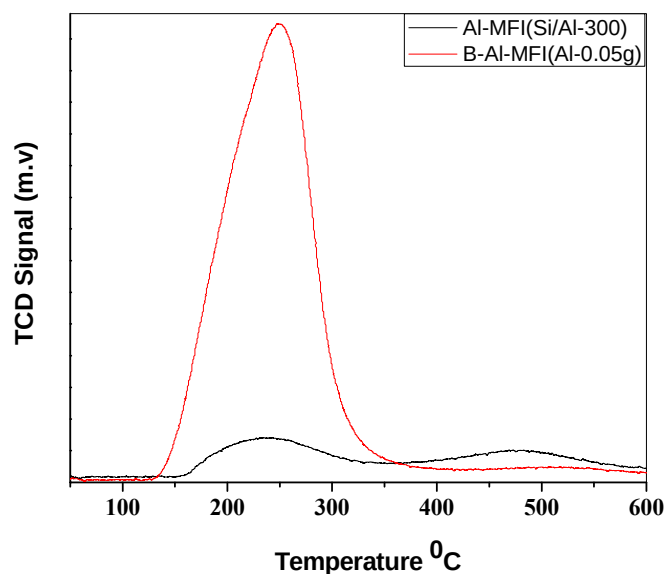
Conditions: temp- 80 °C, cat weight-0.2g,  $\text{NH}_3$ : ketone = 1.94 (molar ratio);  $\text{H}_2\text{O}_2$ : ketone = 1.32 (molar ratio), solvent-ethanol (10 wt %), stirring speed 900 rpm, reaction time-4h.

The ammoximation of cyclohexanone over different MFI catalysts clearly indicates that when the reactions are carried out in presence of the weak acid catalyst such as B-MFI, the cyclohexanone conversion was about 10% and caprolactam selectivity was about 28%. In presence of bi-metallic catalysts such as B-Al-MFI and B-Ti-MFI catalysts, an increase of cyclohexanone conversion was observed. In addition, the selectivity for caprolactam also increased to 40% in presence of B-Al-MFI catalyst. In presence of B-Ti-MFI catalysts, the selectivity for condensation products increased to 34%. Nevertheless, in presence of tri-metallic catalyst B-Al-Ti-

## 5. Liquid phase ammoximation reaction

MFI is applied for this reaction, the conversion of cyclohexanone increased to 17%. But, at the same time, the caprolactam selectivity was only 30%. When the reactions are performed in presence of Al-MFI catalyst, about 15% cyclohexanone conversion and 15% caprolactam selectivity were observed. This catalyst has shown high selectivities for caprolactam oligomers and condensation products. These results clearly indicate that with increasing acid sites from weak to medium the conversion rates and selectivities for the desired products were increased. With increasing the acid sites from medium to strong acid sites, the formation of oligomers, condensation products and others increased.

The acidity of B-Al-MFI and Al-MFI samples was measured with ammonia TPD (temperature programmed desorption) method. The ammonia TPD profiles of these catalysts are presented in Fig.7.



**Figure 7: Ammonia TPD of B-Al-MFI and Al-MFI**

## 5. Liquid phase ammoximation reaction

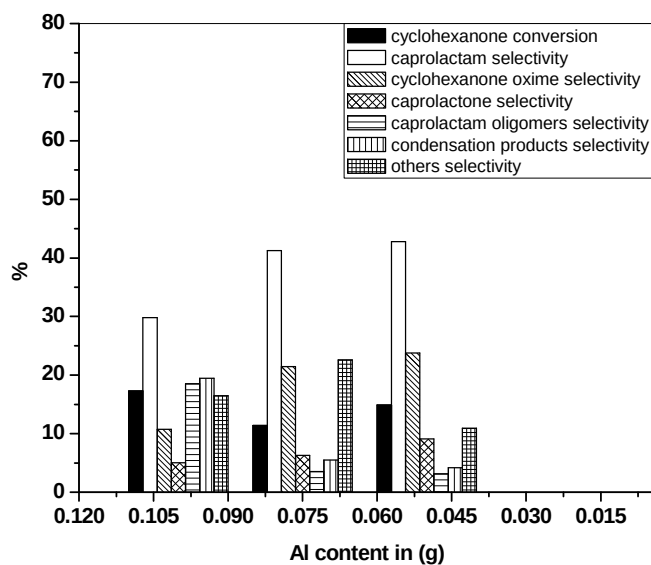
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In case of Al-MFI, ammonia desorption at 250 °C indicating the existence of weak acid sites and at higher temperature at 480 °C indicating that the sample has strong acid sites. In case of B-Al-MFI catalyst, the strong desorption peak 250 °C indicates that sample has medium or even low acidic strength.

### 5.2.2 Effect of Al content in the catalysts

Previous results clearly illustrated that the acid strength is playing a major role in conversions and selectivities. Acid strength can increase by adding alumina content in the sample. In order to determine the effect of alumina, reactions were carried out in presence of different Al content samples. The effect of Al content over cyclohexanone conversion and products distribution are presented in Fig-8. From these results, we can see that there is no significant effect of Al concentration on cyclohexanone conversion. However, with decreasing the Al concentration, caprolactam selectivity increased. At high alumina content the sample, high selectivity for oligomers, condensation products and others was observed, which is due to the strong acid sites of the samples.

## 5. Liquid phase ammoximation reaction



**Figure 8: Effect of Al content in MFI structured zeolites.**

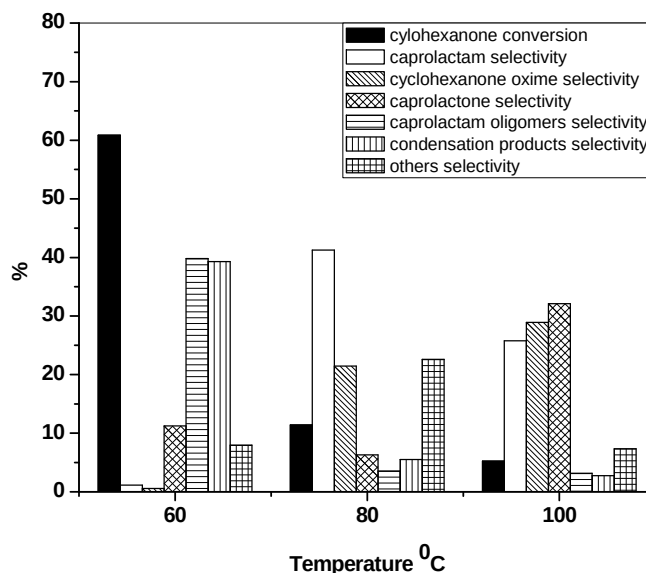
Conditions: temp- 80 °C, cat weight-0.2g, NH<sub>3</sub>: ketone = 1.94 (molar ratio); H<sub>2</sub>O<sub>2</sub>: ketone = 1.32 (molar ratio), solvent-ethanol (10 wt %), stirring speed 900 rpm, reaction time-4h

### 5.2.3 Effect of temperature over B-Al-MFI (Al-0.05) and (Al-0.075) catalysts

The influence of reaction temperature over different alumina content samples B-Al-MFI –Al-0.05 and 0.075 are shown in Fig-9-10. Reactions are carried out at 60 °C, 80 °C and 100 °C. The conversion of cyclohexanone was very high at lower temperature for both catalysts. However, with increasing the temperature from 60 to 80 °C cyclohexanone conversion decreased from 60% to 10% in presence of B-Al-MFI (Al-0.075) and from 50% to 17% in B-Al-MFI (Al-0.05). However, the increase of caprolactam was observed in both catalysts to 40% and 29% respectively. With further enhancement from 80 to 100 °C the conversion as well as selectivities for desired

## 5. Liquid phase ammoximation reaction

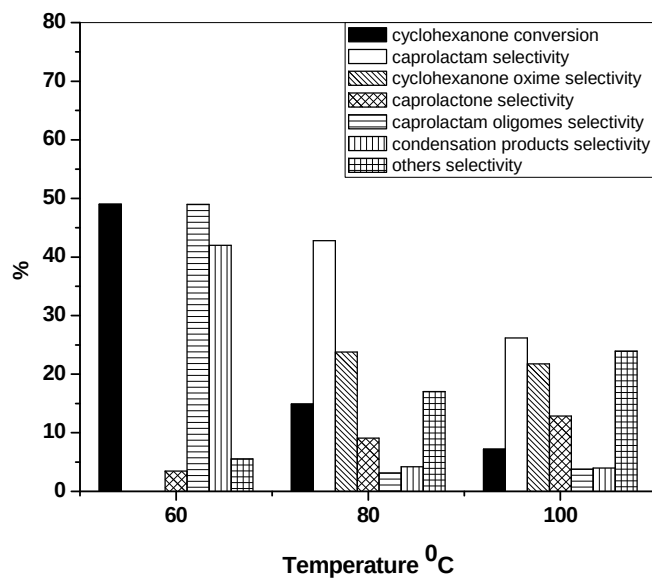
products started to decrease in presence of both catalysts. That could be due to the decomposition of the  $\text{H}_2\text{O}_2$  as we have seen before in presence of Nb-MCM-41 catalysts. Nevertheless, in presence of B-Al-MFI (Al-0.075) at 100 °C, the selectivity for caprolactone increased to 30%. These results clearly demonstrate that at 100 °C, Baeyer-Villiger oxidation reaction also takes place. In case of B-Al-MFI (Al-0.05) catalyst, at lower temperature, only caprolactam oligomers and condensation products were dominant in the product distribution. However, with increasing the reaction temperature from 60-80 °C, caprolactam selectivity increased. Further increase of temperature to 100 °C the selectivity for other compounds increased. In the low alumina content sample (Al-0.05) the selectivities for oligomers and condensation products are high. The high selectivity for others at a low alumina content sample may be due to the weakly acidic strength of the sample. Similar results have been found in presence of weakly acidic samples such as Nb-MCM-41 (Si/Nb-128) catalyst.



**Figure 9: Effect of temperature over B-Al-MFI (Al-0.075).**

## 5. Liquid phase ammoximation reaction

Conditions: cat weight-0.2g,  $\text{NH}_3$ : ketone = 1.94 (molar ratio);  $\text{H}_2\text{O}_2$ : ketone = 1.32 (molar ratio), solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h

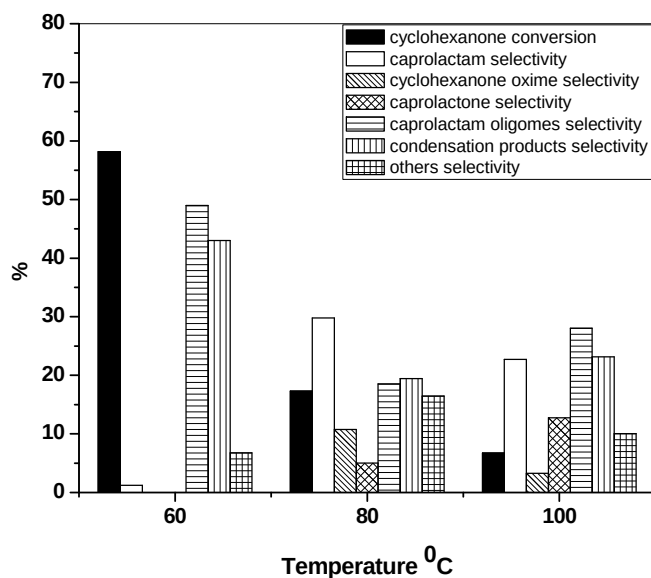


**Figure 10: Effect of temperature over B-Al-MFI (Al-0.05).**

Conditions: cat weight-0.2g,  $\text{NH}_3$ : ketone = 1.94 (molar ratio);  $\text{H}_2\text{O}_2$ : ketone = 1.32 (molar ratio), solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h

## 5. Liquid phase ammoximation reaction

### 5.2.4 Effect of temperature over B-Al-Ti-MFI catalyst



**Figure 11: Effect of temperature over B-Al-Ti-MFI.**

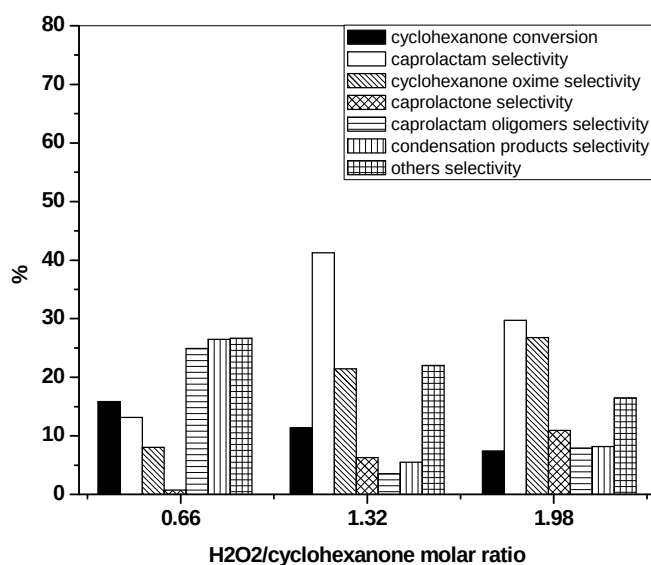
Conditions: cat weight-0.2g,  $\text{NH}_3$ : cyclohexanone = 1.94 (molar ratio);  $\text{H}_2\text{O}_2$ : cyclohexanone = 1.32 (molar ratio), solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h

The effect of temperature over B-Al-Ti-MFI catalysts is presented in Fig-11. The reaction results are similar as seen before. At low temperature the cyclohexanone conversion is very high up to 58%. With increasing the reaction temperature the conversion decreased and selectivity for caprolactam increased. With further increase of the reaction temperature from 80 °C to 100 °C, the conversion as well as selectivity for caprolactam decreased. However, at 100 °C, the caprolactone selectivity is increased, which is formed by Baeyer-Villiger oxidation reaction. Thus, at high temperature (100 °C) Baeyer-Villiger oxidation is taken place.

## 5. Liquid phase ammoximation reaction

### 5.2.5 Effect of $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio over B-Al-MFI (Al-0.075)

The effect of  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio was studied over B-Al-MFI (Al-0.075) catalyst. All reactions were carried out at 80 °C and under maintaining constant the other reaction parameters such as catalyst weight, stirring speed,  $\text{NH}_3$ /cyclohexanone molar ratio.



**Figure 12: Effect of  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio over B-Al-MFI (Al-0.075).**

Conditions: temp- 80 °C, cat weight-0.2g,  $\text{NH}_3$ : cyclohexanone = 1.94 (molar ratio);  
solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h

The effect of  $\text{H}_2\text{O}_2$ /cyclohexanone ratio on B-Al-MFI (Al-0.075) is exhibited in Fig-12. With increasing the  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio, the cyclohexanone conversion decreased. The decrease of conversions at high  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio could be due to the existence of too much free  $\text{H}_2\text{O}_2$  in the reaction system

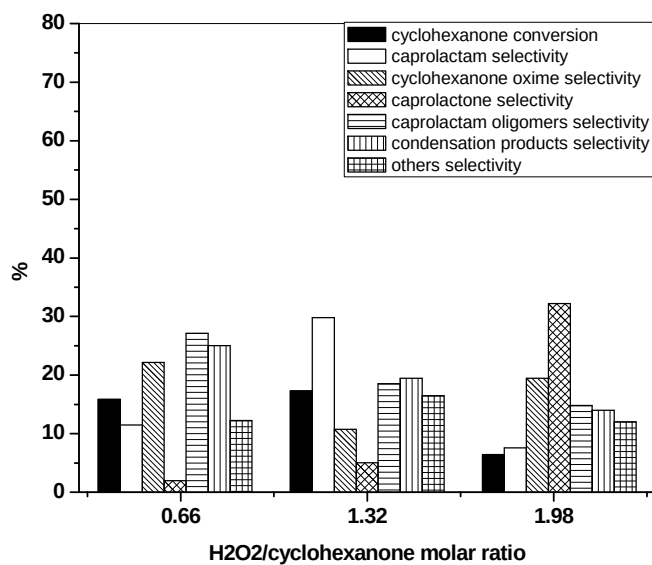
## 5. Liquid phase ammoximation reaction

accelerated the cyclohexanone oxime back to the cyclohexanone. However, at high  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio, the selectivity for cyclohexanone oxime and caprolactone increased. Thereby, at higher  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio ammoximation reaction and Baeyer –Villiger oxidation reactions are taking place competitively.

### 5.2.6 Effect of $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio over B-Al-Ti-MFI catalyst

The effect of  $\text{H}_2\text{O}_2$ /cyclohexanone on B-Al-Ti-MFI is shown in Fig-13. At a low molar ratio of  $\text{H}_2\text{O}_2$ /cyclohexanone, the conversion of cyclohexanone was about 16 %. With increasing the molar ratio from 0.66 to 1.32, the conversion of cyclohexanone slightly increased. Nevertheless, at a low molar ratio the selectivities for caprolactam oligomers and condensation products are high. With increasing the molar ratio, increase of caprolactam selectivity and a decrease of other products are observed. Thus, in presence of high molar ratio, the self condensation reaction of cyclohexanone appears to be less. However, with further increment of  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio from 1.32 to 2, the selectivity for caprolactone increased. In addition, the decrease of cyclohexanone conversion was observed simultaneously. These results suggest that adding an excess amount of  $\text{H}_2\text{O}_2$ , the concentration of unreacted  $\text{H}_2\text{O}_2$  is high in the reaction mixture. This excess  $\text{H}_2\text{O}_2$  would have further oxidized the oxime (**2**) back to cyclohexanone (**1**).

## 5. Liquid phase ammoximation reaction



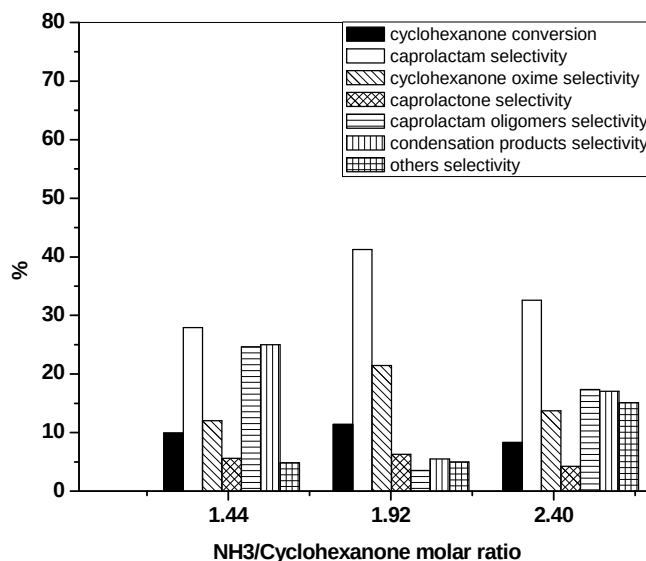
**Figure 13: Effect of  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio over B-Al-Ti-MFI.**

Conditions: temp- 80 °C, cat weight-0.2g,  $\text{NH}_3$ : cyclohexanone = 1.94 (molar ratio);

solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h.

## 5. Liquid phase ammoximation reaction

### 5.2.7 Effect of $\text{NH}_3$ /cyclohexanone molar ratio over B-Al-MFI (Al-0.075)



**Figure 14: Effect of  $\text{NH}_3$ /cyclohexanone molar ratio over B-Al-MFI (Al-0.075).**

Conditions: temp- 80 °C, cat weight-0.2g,  $\text{H}_2\text{O}_2$ : cyclohexanone = 1.32 (molar ratio);

solvent-ethanol (10 wt), stirring speed 900 rpm, reaction time-4h

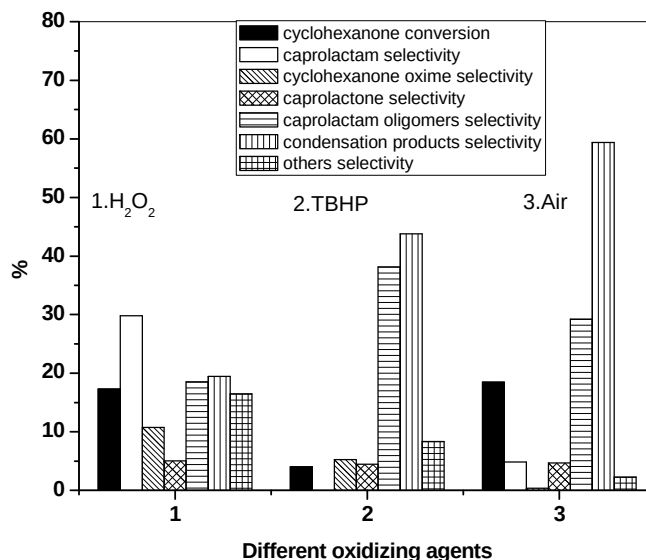
The effect of  $\text{NH}_3$ /cyclohexanone over B-Al-MFI catalyst is depicted in Fig-14. With increasing the  $\text{NH}_3$ /cyclohexanone molar ratio from 1.44 to 1.92, the conversion for cyclohexanone is almost constant 10%. However, the caprolactam selectivity is increased due to the increase of the  $\text{NH}_3$ /cyclohexanone molar ratios. With further increment from 1.92 to 2.4 molar ratio the conversion as well as caprolactam selectivity decreased. This could be due to a partial loss of  $\text{NH}_3$  by vaporization. Also, at high  $\text{NH}_3$ /cyclohexanone molar ratio the selectivity for the other compounds also increased, too. This behavior is

## 5. Liquid phase ammoximation reaction

attributed to that at high molar ratio the intermediate compound; cyclohexanone imine (**16**) is further reacting to form cyclohexanone azine (**12**) very easily.

### 5.2.8 Effect of different oxidizing agents over B-Al-Ti-MFI

In order to see the effect of oxidizing agents over B-Al-Ti-MFI catalyst, reactions were carried out in presence of hydrogen peroxide, tertiary butyl hydroperoxide and air as oxidizing agents. When air used as oxidizing agent, pressure conditions have been applied and all the reactions were carried out at 80 °C. Reaction results are illustrated in Fig- 15.



**Figure 15: Effect of different oxidizing agents over B-Al-Ti-MFI.**

Conditions: temp- 80 °C, cat weight-0.2g, NH<sub>3</sub>: cyclohexanone = 1.94 (molar ratio);  
H<sub>2</sub>O<sub>2</sub> or TBHP/cyclohexanone = 1.32; solvent-ethanol (10 wt %), stirring speed 900 rpm,  
reaction time-4h

## **5. Liquid phase ammoximation reaction**

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In presence of hydrogenperoxide, the cyclohexanone conversion was about 17% and caprolactam selectivity was around 30%. When tertiary butyl hydroperoxide was applied, very low cyclohexanone conversion with 4% was observed. Also, we couldn't see any caprolactam formation in the reaction mixture over tertiary butyl hydro peroxide. Only selectivities for caprolactam oligomers and condensation products have been observed. Reactions under pressure conditions in presence of air have shown more favorable for formation of condensation products. The condensation products selectivity was 60% under these conditions. Very low caprolactam selectivity and low conversion rates of cyclohexanone were observed in presence of air.

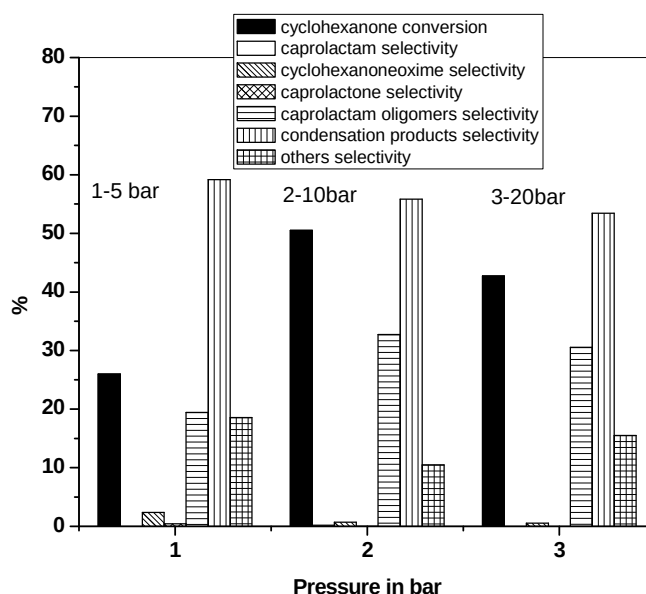
### **5.3 Reaction results under pressure condition**

In order to see the effect of pressure in the ammoximation of cyclohexanone to caprolactam, reactions were carried out in autoclaves. Reaction pressure was maintained by using either air or oxygen for 2 h.

#### **5.3.1 Effect of O<sub>2</sub> pressure over Al-MCM-41**

Reactions were carried out with O<sub>2</sub> as an oxidizing agent. The conditions are 5 bar, 10 bar and 20 bar at 80 °C.

## 5. Liquid phase ammoximation reaction



**Figure 16: Effect of O<sub>2</sub> pressure over Al-MCM-41.**

Conditions: temp- 80 °C, cat weight-0.2g, NH<sub>3</sub>: cyclohexanone = 1.94 (molar ratio);

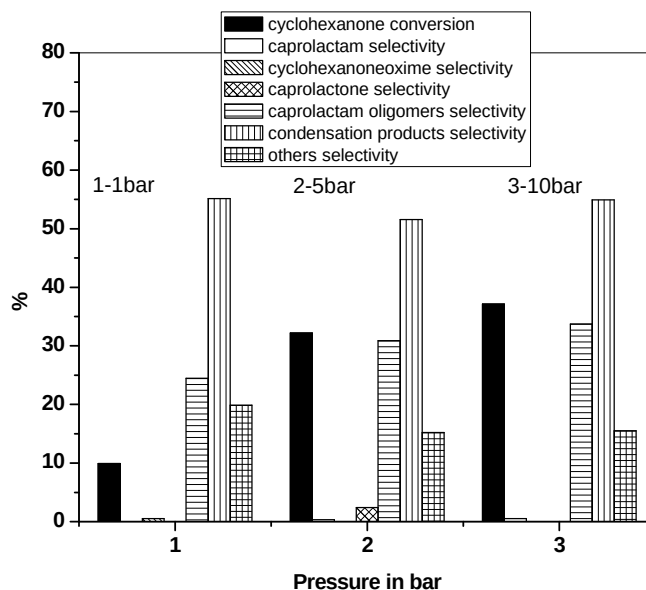
solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-2 h

Figure-16 shows the effect of pressure over the Al-MCM-41 catalyst. Results clearly indicate that the conversion of cyclohexanone was high and increased by pressure. With increasing pressure from 5 to 10 bar the conversion increased to 50%. Surprisingly, under these pressure conditions we couldn't observe any caprolactam formation. In contrast to very high selectivity for condensation products (60%) and also increasing oligomers formation. Results clearly illustrate that under pressure conditions, cyclohexanone condensation reactions become dominant.

## 5. Liquid phase ammoximation reaction

### 5.3.2 Effect of air pressure over Al-MCM-41

The effect of air pressure over Al-MCM-41 catalysts carried out under 1 bar, 5 bar and 10 bar at 80 °C. The reaction results are presented in Fig-17.



**Figure 17: Effect of air pressure over Al-MCM-41**

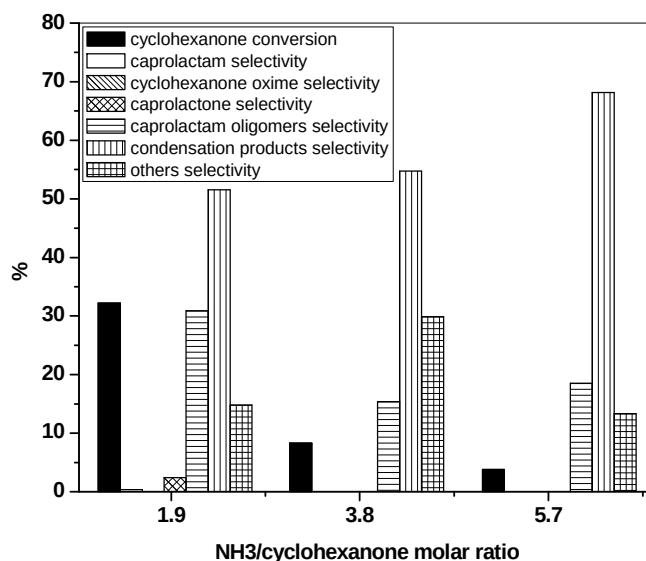
Conditions: temp- 80 °C, cat weight-0.2g, NH<sub>3</sub>: cyclohexanone = 1.94 (molar ratio);  
solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-2 h

The obtained results indicate that with increasing pressure from 1 to 5 bar, the cyclohexanone conversion increased from 10 to 35%. With enhancing of pressure from 5 to 10 bar a less steep increment of cyclohexanone conversion was observed. However, under these conditions only extremely low caprolactam selectivity of 0.5% was obtained. These results are similar to the results under O<sub>2</sub> pressure conditions. In presence of some strong acid catalysts such as Al-MCM-41 high selectivities for by-products are obtained which have been formed by condensation and consecutive oxidation reactions.

## 5. Liquid phase ammoximation reaction

### 5.3.3 Effect of $\text{NH}_3$ /cyclohexanone molar ratio over Al-MCM-41 catalyst

In order to see the effect of ammonia concentration under pressure conditions, reactor pressure was maintained constant by air at 5 bar.



**Figure 18: Effect of  $\text{NH}_3$ /cyclohexanone molar ratio over Al-MCM-41**

Conditions: temp- 80 °C, cat weight-0.2g, air pressure = 5 bar; solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-2h

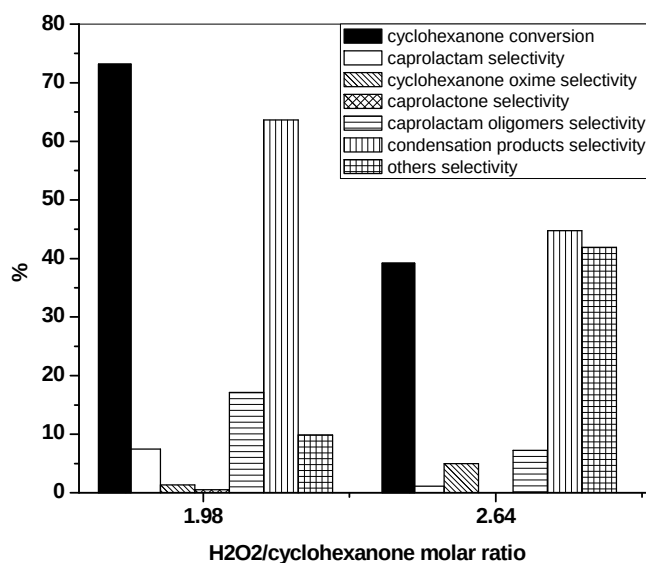
Results of Fig-18 show that with increasing  $\text{NH}_3$ /cyclohexanone molar ratio surprisingly cyclohexanone conversion decreased and the selectivity for condensation products increased. The maximum selectivity with 70% for condensation products is observed 70% also molar ratio of  $\text{NH}_3$ /cyclohexanone at 3.8, the selectivity of other products increased to 30%. With increasing the  $\text{NH}_3$ /cyclohexanone molar ratio from 1.9 to 5.7 the cyclohexanone conversion was decreased. At the same time an increase of condensation products selectivity was also noticed. However, the caprolactam oligomers

## 5. Liquid phase ammoximation reaction

selectivity was decreased with an increase of molar ratio. At low ammonia molar ratio about 2.5% caprolactone selectivity was obtained.

### 5.3.4 Effect of H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio over Al-MCM-41 catalyst

The effect of H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratios was studied under ammonia pressure of 2 bars over Al-MCM-41 catalyst.



**Figure 19: Effect of H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio over Al-MCM-41**

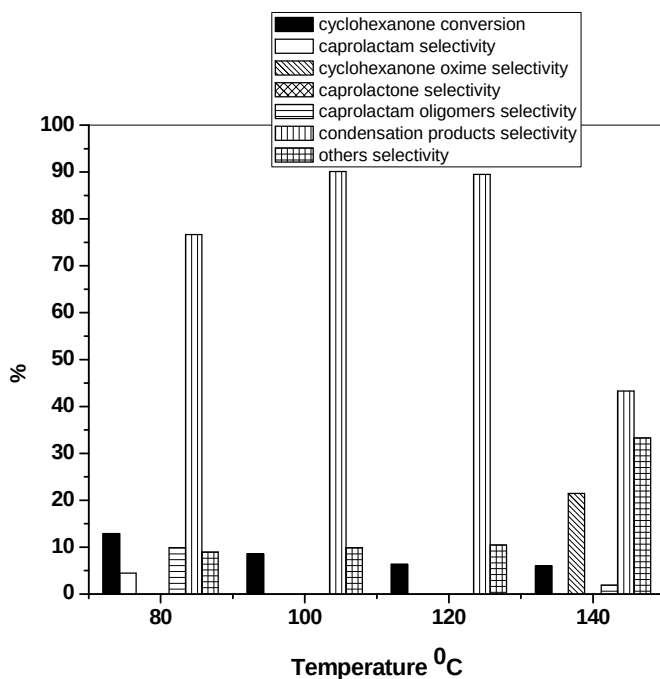
Conditions: temp- 80 °C, cat weight-0.2g, ammonia pressure = 2 bar; solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-2h.

The results show (Fig-19) that at low H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio the cyclohexanone conversion was 74% and caprolactam selectivity was only 7%. At high

## 5. Liquid phase ammoxidation reaction

$\text{H}_2\text{O}_2$ /cyclohexanone molar ratio the cyclohexanone conversion decreased surprisingly. Also, an increased selectivity of other products is observed. It could be that in presence of an excess  $\text{H}_2\text{O}_2$ / cyclohexanone molar ratio further oxidation of cyclohexanone takes place. The decrease of conversion at an excess of  $\text{H}_2\text{O}_2$  could be due to the reoxidation of cyclohexanone oxime to cyclohexanone. However, under those conditions also high selectivity for condensation products is observed. Thus, the condensation reaction is more favorable under ammonia pressure conditions.

### 5.3.5 Effect of temperature over Nb-Ta-MCM-41 catalyst



**Figure 20: Effect of temperature over Nb-Ta-MCM-41.**

Conditions: cat weight-0.2g,  $\text{NH}_3$ : cyclohexanone = 1.94 (molar ratio);  $\text{O}_2$  pressure = 20 bar, solvent-ethanol (10 wt%), stirring speed 900 rpm, reaction time-4h.

## 5. Liquid phase ammoximation reaction

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The effect of temperature under pressure conditions at 20 bar O<sub>2</sub> was studied over Nb-Ta-MCM-41 catalyst. Results are presented in Fig-20. These indicate that the conversion of cyclohexanone was below 10% except for 80 °C with about 15%. In all the cases mainly condensation products are observed in the reaction mixture. However, at 140 °C, the selectivity for cyclohexanone oxime with 20% was observed. Also, a decrease of condensation products selectivity and an increase of other compounds selectivity were found. However, at 80 °C, caprolactam was formed with 5% selectivity.

## 6. Summary and Outlook

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### **6. Summary and Outlook**

The principle aim of this work is to obtain good yields of caprolactam in a single step, one pot liquid phase reaction from cyclohexanone in presence of hydrogen peroxide and ammonia over heterogeneous catalysts.

In order to achieve this goal, we have prepared different metal incorporated mesoporous materials such as Al-MCM-41, Nb-MCM-41 and Nb-Ta-MCM-41 catalysts. In addition, microporous zeolites modified with different metals such as, B-MFI, as well as bi-metallic and tri-metallic materials such as, B-Al-MFI, B-Ti-MFI and B-Ti-Al-MFI have been synthesized and investigated for their catalytic performance. All these catalysts were proven to be active for this reaction.

Especially, the mesoporous materials Nb-MCM-41 (Si/Nb-64) and Al-MCM-41, catalysts could improve the caprolactam selectivity to some extent. The maximum caprolactam selectivity of about 60% was obtained over Nb-MCM-41 (Si/Nb-64) and 43% over Al-MCM-41 catalyst.

Studying the effect of different Si/Nb ratios of such Nb-MCM-41 catalysts, it could be demonstrated that high Nb content samples such as Si/Nb 16, 32 and 64 have shown considerable selectivities for caprolactam. The catalytic activity of these high Nb content Nb-MCM-41 materials is attributed due to the increase of acid strength from weak to medium. Ammonia TPD profiles of these samples also proved that with increasing the Nb content acid strength increased. The weakly acidic samples such as Nb-MCM-41 (Si/Nb-128) and Si-MCM-41 samples have shown high cyclohexanone conversion but low caprolactam selectivity. With these catalysts more caprolactam

## 6. Summary and Outlook.

oligomers are formed. That means the activity of these weakly acidic materials is too less to catalyze the decomposition of the caprolactam oligomers.

The effect of reaction temperature over Nb-MCM-41(Si/Nb-32) catalyst suggests that 80 °C is the optimum temperature for obtaining a considerable caprolactam selectivity (50%). At low reaction temperature, the conversion of cyclohexanone was high, however, it was accompanied by high caprolactam oligomer and condensation product formation. At high reaction temperature (100 °C) decrease of conversion and selectivity indicates easier evaporation and decomposition of the reactants.

The effect of stirring speed over Nb-MCM-41 (Si/Nb-32) catalyst illustrates that at lower stirring speeds, cyclohexanone conversion was high but very low selectivity for caprolactam was observed. In contrast with increasing the stirring speed the caprolactam selectivity went up. These results suggest that at high stirring speed, caprolactam desorption from the catalyst is facilitated.

The effect of NH<sub>3</sub>/cyclohexanone ratio over Nb-MCM-41 (Si/Nb-32) catalyst has shown maximum selectivity for caprolactam at 1.45 molar ratio. With further increase of the molar ratio from 1.45 to 2.5 an enhancement of cyclohexanone conversion was observed but caprolactam selectivity was low. At high NH<sub>3</sub>/cyclohexanone molar ratio, easier evaporation of ammonia takes place and cyclohexanone is self condensing to condensation products (**4**, **5** and **6**).

Design-Expert model results using Al-MCM-41 as a catalyst suggested optimum reaction conditions at catalyst weight-0.26 g, H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio 1.42, and NH<sub>3</sub>/cyclohexanone molar ratio 2.13 to obtain a cyclohexanone conversion of 15.9% and a caprolactam selectivity of 48%.

## 6. Summary and Outlook.

The catalytic activity of microporous zeolites (MFI structure) with respect to cyclohexanone conversion follows the order B-Al-Ti-MFI > Al-MFI > B-Al-MFI (Al-0.075) > B-Ti-MFI > B-MFI. The selectivity of caprolactam follows the order in MFI structured catalysts are B-Al-MFI (Al-0.075) > B-Al-Ti-MFI > B-MFI > Al-MFI ~ B-Ti-MFI. The high activity of the tri-metallic B-Al-Ti-MFI catalyst could be due to the presence of different active sites in the catalyst such as the reducing metal Ti and the strong acidity provider Al. We are assuming that in presence of bi-metallic and tri-metallic catalysts first cyclohexanone reacts with hydrogen peroxide and ammonia to form cyclohexanone oxime selectively. In a second step cyclohexanone oxime rearrangement reaction will take place on the acidic sites, (due to alumina) to form caprolactam selectively. However, in this stage we are not certain about the mechanism of caprolactam formation. The formation of caprolactam in ammoximation reaction is an ambiguity. Caprolactam can be formed either from cyclohexanone oxime by rearrangement or from 1-1peroxidyclohexylamine (**8**) by decomposition.

Catalysts with different alumina content samples showed that high alumina content samples (Al-MFI (Si/Al-300) and B-Al-MFI Al-0.01) result in high cyclohexanone conversion. However, the selectivity for caprolactam was too low in the presence of high alumina content samples. In contrast, high selectivities for caprolactam oligomers and condensation products were observed. The selectivities for caprolactam and cyclohexanone oxime were high at low alumina content samples (B-Al-MFI Al-0.075 and 0.05). These, findings are due to the strong acidic sites of high alumina content samples.

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Ammonia TPD profile of Al-MFI and B-Al-MFI (Al-0.05) catalysts are good agreement with the above statement. The ammonia desorption peak of Al-MFI at 250 °C indicating the existence of weak acid sites and a desorption peak at 480 °C indicated that the sample has strong acid sites. In case of the B-Al-MFI catalyst, the strong desorption peak at 250 °C indicates that the sample has medium acid strength.

The effect of reaction temperature over different bi-metallic catalysts (B-Al-MFI; Al-0.075, B-Al-MFI; Al-0.05) and tri-metallic catalysts (B-Al-Ti-MFI) reveals that at 60 °C, the conversion of cyclohexanone was high but the selectivity for oligomers and condensation products was high, too. At 80 °C, a decrease of cyclohexanone conversion was observed but simultaneously the selectivity of caprolactam increased. However, with further accretion of reaction temperature from 80 °C to 100 °C, conversions as well as selectivities decreased. That could be due to the evaporation or decomposition of the reactants, particularly  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$ . However, at 100 °C, the increase of caprolactone selectivity was observed in presence of B-Al-MFI (Al-0.075) catalyst. These results indicate that at 100 °C Baeyer-Villiger oxidation reaction is also taking place in presence of alumina containing catalysts. It is well known from the literature that alumina BEA zeolite is an active catalyst for Baeyer-Villiger oxidation reaction.

The influence of  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratios over B-Al-MFI (Al-0.075) and B-Al-Ti-MFI catalysts elucidates that at low  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio of 0.66, the conversion was high but the formation of caprolactam oligomers and condensation products are high as well. The maximum caprolactam selectivities were obtained at  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio of 1.32 in presence of both catalysts. Nevertheless, at high  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio cyclohexanone conversion was decreased over

## 6. Summary and Outlook.

both catalysts. The decrease of cyclohexanone conversion at high  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio may be due to the further oxidation of cyclohexanone oxime to cyclohexanone. However, in presence of B-Al-Ti-MFI catalyst, an increase of caprolactone selectivity was observed at high  $\text{H}_2\text{O}_2$ /cyclohexanone molar ratio. These results clarified that in presence of excess hydrogen peroxide, Baeyer-Villiger oxidation reaction occurs.

The influence of  $\text{NH}_3$ /cyclohexanone molar ratio studies over B-Al-MFI (Al-0.075) indicates that the maximum caprolactam selectivity was attained at  $\text{NH}_3$ /cyclohexanone molar ratio of 1.92. At a high  $\text{NH}_3$ /cyclohexanone molar ratio of 2.4, the decrease of cyclohexanone conversion was observed. That could be due to evaporation of ammonia. In addition, the increase of selectivities for oligomers, condensation products and other products were increased.

Reaction results using different oxidizing agents over B-Al-Ti-MFI catalyst denote that considerable cyclohexanone conversion rates and caprolactam selectivity were achieved only in presence of hydrogen peroxide as oxidizing agent. Reaction results in presence of tertiary butyl hydroperoxide show very low cyclohexanone conversion and high selectivity for oligomers and condensation products. Reaction results under air pressure conditions have indicated that results are more favorable for condensation reactions.

Reaction results with different solvents (ethanol and t-butanol) over B-MFI catalyst have shown that in presence of both solvents the cyclohexanone conversion was high and high selectivity for oligomers was observed. It seems that the reaction temperature  $60\text{ }^\circ\text{C}$  was too low for decomposition of caprolactam from oligomers.

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Reaction results under air and O<sub>2</sub> pressure conditions over Al-MCM-41 catalyst have depicted that with increasing partial pressure, cyclohexanone conversion was increased. In addition, under such conditions, high selectivity for cyclohexanone condensation products was found. These results imply that reactions under pressure accelerate the self condensation reaction of cyclohexanone.

The effect of NH<sub>3</sub>/cyclohexanone molar ratio studies over Al-MCM-41 catalyst, at 20 bar O<sub>2</sub> pressure, indicates that at high NH<sub>3</sub>/cyclohexanone molar ratio the cyclohexanone conversion decreased. Also, at high NH<sub>3</sub>/cyclohexanone molar ratio, the selectivity of condensation products was increased.

The influence of H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio at 2 bar ammonia pressure in presence of Al-MCM-41 catalyst demonstrate that with increase of H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio, the cyclohexanone conversion decreased. Simultaneously, a decrease of condensation products selectivity and increase of other selectivities was observed under these conditions. It seems that at high H<sub>2</sub>O<sub>2</sub>/cyclohexanone molar ratio, other consecutive oxidation reaction products (**12**, **13**, and **14**) are formed.

The effect of temperature under pressure conditions over Nb-Ta-MCM-41 catalyst results revealed that with an increasing the reaction temperature from 80 °C to 140 °C, cyclohexanone conversion was decreased. At the same time an increase of other selectivities was observed at high temperature. Over all temperatures, selectivity for condensation products was high. Here we have similar findings as in the case of other catalysts.

## 6. Summary and Outlook.

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### **Outlook**

These attempts for synthesis of caprolactam from cyclohexanone as a starting material has given clear idea that caprolactam can be synthesized under liquid phase conditions. All applied catalysts have shown considerable activity in respect to cyclohexanone conversation and caprolactam selectivity. Further improvements of cyclohexanone conversation and caprolactam selectivity over these metals modified bi-functional and tri-functional catalysts are possible. The more efforts should be done in order to assess the feasibility of such a process and to increase its practicability.

Reaction results are illustrated that caprolactam oligomers are forming more selectively at low temperature. Indeed, first of all all caprolactam oligomers have to be identified by analytical techniques and then, try to develop a method to synthesis of caprolactam very selectively from oligomers.

Other considerations to improve the conversions and selectivities would be carrying the reactions in continious flow reactor over metals modified bi-bunctional catalysts. The advantages of carrying the reactions in continious flow reactors are control the side products formation by decrease the reactants contact time with catalyst active centers, perticularly cyclohexanone condensation reaction.

## **7. Materials and Methods**

### **7. Materials and Methods**

This chapter describes the experimental system and procedures used in this study. The chapter divided into three parts; (1) catalyst preparation, (2) catalyst characterization, (3) reaction study. The first part (section 7.1) presents the catalyst preparation including catalyst preparation of transition metal incorporated mesoporous structured materials (MCM-41, HMS and SBA-15), microporous structured materials (MFI and Beta). The second part (section 7.2) shows the details of the characterization techniques such as XRD, BET surface area, UV-Vis, FT-IR, NH<sub>3</sub>-TPD, AAS-ICP, TG-DTA, SEM and MAS-NMR. The last part (section 7.3) illustrates the reaction set-up of gas phase Beckmann rearrangement of cyclohexanone oxime to caprolactam. Also, single step caprolactam synthesis from cyclohexanone in the presence of ammonia and hydrogen peroxide or air as oxidizing agents in liquid phase at ambient and pressure conditions.

#### **7.1 Catalyst preparation**

MCM-41 (Mobil Crystalline Material-41) is one of the members of M41S molecular sieves first synthesized by Mobil corporation [193-195]. The hydrothermal synthesis of mesoporous silicate and alumino silicate MCM-41 material from a gel consisting of silica source (sodium meta silicalite), alumina source (sodium aluminate), a structure directing agent (tetra decyltrimethyl ammonium bromide), niobium source (niobium chloride) deionized water, sulfuric acid and acetic acid (which are adjusting the pH) has been carried out in stainless steel autoclaves at 383 K under autogenous pressure for 48 h. The hydrothermal synthesis of Si-MCM-41, Al-MCM-41, Nb-MCM-41 and Ta-MCM-41 was described by following method.

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### 7.1.1 Hydrothermal synthesis of Si-MCM-41

Si-MCM-41 molecular sieves were synthesized according to following synthesis method in reference [196].

Sodium meta silicate was used as the sources for silica. In a typical synthesis method, 21.8 gm of sodium meta silicate was dissolved in 80 ml of deionized water and stirred for 10 min at room temperature by using mechanical stirrer. The resultant solution was stirred and the pH of the mixture was maintained to 10.5 by using concentrated sulphuric acid to form a gel. After that, an aqueous solution of tetradecyltrimethylammonium bromide was added drop wise, so that the gel was changed into white suspension. The molar composition of the resultant mixture was  $\text{SiO}_2$ : 0.2TDTAB:  $0.89\text{H}_2\text{SO}_4$ :  $120\text{H}_2\text{O}$ .

The suspension was transferred in to an autoclave and heated at  $120^\circ\text{C}$  for 2 days to complete crystallization. After crystallization, the product was filtered off, washed with deionized water and dried at  $110^\circ\text{C}$  for 12h. Finally dried sample was calcined at  $550^\circ\text{C}$  for 6h.

### 7.1.2 Hydrothermal synthesis of Al-MCM-41

Al-MCM-41 was prepared according to a slightly altered method of reference [197]. In a 250 ml polyethylene flask, 10.5 g tetraethylammonium hydroxide (TEAOH, 40 wt% aqueous), 0.21 g  $\text{NaAlO}_2$  and 50 g  $\text{H}_2\text{O}$  were mixed together and stirred at room temperature for 1 h, followed by the addition of 10 g tetradecyltrimethylammonium bromide. The resulting mixture was stirred for 4 h. Then, 15.23 g Ludox-HS-40 were added drop wise over a period of 1 h, following by vigorous stirring at ambient temperature for 4 h. The crystallization took place at  $105^\circ\text{C}$  for 6 days. After the third

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and fifth day, pH was adjusted at 10.2 using  $\text{CH}_3\text{COOH}$  (10 wt % aqueous). After crystallization, the solid was dried at 120 °C overnight, followed by calcination under static air at 540 °C for 6 h.

### 7.1.3 Hydrothermal synthesis of Nb-MCM-41, Ta-MCM-41 and Nb-Ta-MCM-41

Sodium metasilicate and niobium pentachloride were used as sources for silica and niobium. In case of Ta-MCM-41 catalysts,  $\text{TaCl}_5$  was used as the source for tantalum. In a typical synthesis method, 21.8 gm of sodium metasilicate was dissolved in 80 ml of deionized water and stirred for 10 min at room temperature by using mechanical stirrer. An appropriate amount of niobium penta chloride was dissolved in 25 ml of isopropanol and resulting solution was added drop wise into silica solution. The resultant mixture was stirred for 1 h and the pH of the mixture was maintained to 10.5 by using concentrated sulfuric acid to form a gel. After that, an aqueous solution of tetradecyltrimethylammonium bromide was added drop wise, so that the gel was changed into white suspension. The molar composition of the resultant mixture was  $\text{SiO}_2$ :  $x\text{NbCl}_5$ : 0.2TDTAB:  $0.89\text{H}_2\text{SO}_4$ :  $120\text{H}_2\text{O}$  ( $x$  varies with Si/Nb ratio). In case of mixed metals (Nb and Ta) mesoporous structured catalysts,  $\text{Si}/(\text{Nb}+\text{Ta})=32$  and 64 were synthesized same procedure as above.

The suspension was transferred in to an auto clave and heated at 120 °C for 2 days to complete crystallization. After crystallization, the product was filtered off, washed with deionized water and dried at 110 °C for 12 h. Finally dried sample was calcined at 550 °C for 6 h.

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### 7.1.4 Hydrothermal synthesis of Nb-SBA-15

Nb incorporated SBA-15(Si/Nb-32) sample was synthesized by hydrothermal method. 5 g of P123 (poly alkylene oxide triblock copolymer) was combined with 75 g of H<sub>2</sub>O mixed with 35 ml of 2 M HCl. Afterwards, 10 g of TEOS (tetraethylorthosilicate) and the amount of NbCl<sub>5</sub> in order to get Si/Nb atomic ratio of 32 were added and obtained mixture was allowed to react at 60 °C for 8 h. The mixture was allowed to react at 80 °C for 8 h. The precipitate was recovered by filtration, washed with distilled water and dried at 110 °C for 12 h. Finally sample was calcined at 550 °C for 6 h under air.

### 7.1.5 Synthesis of Nb on hexagonal mesoporous silica (Nb-HMS-1)

TEOS (tetraethylorthosilicate) of 0.1 mol and required amount of NbCl<sub>5</sub> was mixed in isopropanol solution. To this mixture added a solution of N-dodecyl amine (0.027 mol) and HCl (2 mol) in water (3.63 mol). The resulting gel was stirred for 5 min and aged at room temperature for 18 h. After aged at room temperature, sample was filtered off and washed with deionized water for several times. Finally obtained filtered sample was dried at 110 °C for 12 h and calcined at 500 °C for 6 h.

### 7.1.6 Synthesis of Al free Nb-Silicalite (Beta structure)

The catalyst was prepared by following the references [191]. The Nb-beta sample was obtained by hydrothermal synthesis at 140 °C for 12 days. In a container TEOS (98%) was mixed with an aqueous solution of TEAOH (35%). After 90 min stirring, a solution of metal salt solution (NbCl<sub>5</sub> was dissolved in Isopropyl alcohol.) was added and the mixture was kept under stirring until the complete evaporation of the ethanol formed

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upon hydrolysis of TEOS. Finally, HF (40 %) and, dealuminated zeolite beta seeds were added. After the required crystallization time, the autoclaves were cooled and the products were filtered and extensively washed with distilled water. Finally, sample was dried at 110 °C for 10 h and calcined at 580 °C for 8 h under air.

### 7.1.7 Synthesis of Nb impregnation on SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supports

The silica support used was DAVICAT SP 550-10021 (Surface Area = ~300 m<sup>2</sup>/g) and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (60:40) support was SASOL SIRAL-40 (Surface Area = 520 m<sup>2</sup>/g). The Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by impregnation method employing NbCl<sub>5</sub> precursor. In the preparation method first appropriate amount of NbCl<sub>5</sub> was dissolved in 100 ml isopropanol. To this solution added 10 g of SiO<sub>2</sub> support in case of Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> and 10 g of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support in case of Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst sample. The resultant mixture was stirred until the isopropanol gets evaporated at 110 °C. After impregnation, samples were dried at 110 °C for 4 h and calcined in flowing air at 400 °C for 4 h.

### 7.1.8 Synthesis of B-Al-MFI

Boroaluminosilicate catalysts were prepared by two different methods. In first method, catalysts were prepared by following the method [198]. 11.7 g of SiO<sub>2</sub>(aerosol) was dissolved in 180 g of 50 wt% aqueous hexamethylenediamines (HMD) solution and this mixture was stirred at room temperature for 3 h. Separately, in another beaker 2.2 g of Boric acid was dissolved in 9 g of HMD aqueous solution and stirred this mixture solution at room temperature for 3h. After 3 h stirring the above two solutions were

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mixed and resulting to this solution mixture added 0.1 g of aluminum hydroxide and stirred whole reaction mixture at room temperature for another 2 h before transferred into stainless steel autoclave for crystallization. The complete crystallization took place at 170 °C for 5 days. After crystallization, the product was filtered off, washed with deionized water and dried at 110 °C for 12 h. Finally, dried sample was calcined at 550 °C for 6 h.

In a second method, B-Al-MFI catalysts were prepared by hydrothermal method using tetrapropyl ammonium hydroxide as a structure directing agent and tetraethyl ortho silicate (TEOS) as silica source. To a solution of TEOS, an appropriate amount of aqueous tetrapropylammoniumhydroxide (40% aq. TPAOH solution) was added to hydrolyze the TEOS. To the resultant liquid mixture, a solution of the required quantity of boric acid and alumina sources were added. The clear liquid thus obtained was stirred for 1h in order to complete hydrolysis of TEOS and metal sources. Finally, the remaining TPAOH in double distilled water was added slowly to the above mixture. The final mixture was stirred for 3 h at room temperature to remove to alcohol. The chemical composition of the initial gel was

$Y \text{ B}_2\text{O}_3 : X \text{ Al}_2\text{O}_3 : \text{SiO}_2 : 0.36 \text{ TPAOH} : 35 \text{ H}_2\text{O}$ . Normally, in all the cases Si/Al-300 and Si/B-40 was maintained. The crystallization was carried out at 170 °C for 5 days. The solid obtained was filtered, washed with distilled water and dried at 110 °C for 10 h and finally calcined at 550 °C for 8 h under air.

### 7.1.9 Synthesis of B-Ti-MFI

B-Ti-MFI catalysts were synthesized by following second procedure of B-Al-MFI catalysts by just changing the sources. In case of B-Ti-MFI catalysts, Ti source was taken

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instead of alumina and titanium isopropoxide is the titanium source. The ratios were maintained in the gels for Si/Ti- 300 and Si/B- 40.

### 7.1.10 Synthesis of B-Al-Ti-MFI

B-Al-Ti-MFI catalysts were prepared same method as in case of B-Al-MFI second synthesis procedure. In this case additionally titanium and alumina sources were taken. The initial gel ratio for this catalyst was Si/Ti+Al = 300 and Si/B = 40.

## 7.2 Analytical methods

A number of techniques are used to characterize the synthesized catalysts. Among these, X-ray diffraction, N<sub>2</sub> physisorption, diffuse reflectance UV-vis (DR-UV-vis), fourier transmission infra red (FT-IR), atomic emission spectroscopy (ICP-AES), thermal gravimetric analysis and differential thermal analysis (TGA-DTA), H<sub>2</sub>- temperature programmed reduction (TPR), scanning electron microscopy (SEM) Raman spectroscopy, X-ray photo electronic spectroscopy (XPS), and <sup>29</sup>Si-MAS NMR (magic-angle spinning nuclear magnetic resonance) spectroscopy. Catalyst acidity was measured by (ammonia temperature programmed desorption) NH<sub>3</sub>-TPD and pyridine FT-IR techniques.

### 7.2.1 X-Ray diffraction

Powder x-ray diffraction was used to identify the structure, phase purity, degree of crystallinity, unit cell parameters and crystal size. As the powder diffraction technique is very essential tool for measuring the phase purity and percent of crystallinity of the synthesized molecular sieve can be ascertained by comparison with the standard pattern

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for the molecular sieves under investigation. XRD pattern of the mesoporous phase is exhibit peaks in the low angle region the most intense peak being (100) reflection. In the case of wall thickness of hexagonal channel is usually calculated by subtraction of the inside pore diameters obtained by gas adsorption from the unit cell dimensions determined by XRD. Isomorphous substitution of a heteroatom in the framework of the molecular sieves result in changes in the unit cell parameters and unit cell volume. This is one of the ways to confirm isomorphous substitution.

Powder X-ray diffraction (XRD) data were recorded on a Siemens Diffractometer (D 5000) operated at 45 KV and 40 mA, using Nickel filtered Cu K $\alpha$  radiation with 1.5406 Å between 1.5° and 40° (2 theta), with a scanning speed of 0.02 °/min.

### 7.2.2 BET measurements

The Brunauer- Emmett-Teller (BET) volumetric gas adsorption technique using nitrogen, argon etc is standard techniques for the determination of surface area and pore size distribution of porous samples. The relation between amount of gas adsorbed and the equilibrium pressure of the gas at constant temperature is defined by the adsorption isotherm. The wall thickness of hexagonally packed silicates (MCM-41, SBA-15 and HMS) were determined as the difference between the repeat distance of  $a=2d_{100}/\sqrt{3}$  (from XRD) and the Horvath-Kawazoe pore diameter using N $_2$  adsorption.

Nitrogen adsorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 Gas Sorption and Porosimetry System. Samples were activated at 300 °C for 3h under a vacuum, and then the adsorption-desorption was conducted by passing nitrogen into the sample, which was kept under liquid nitrogen. Brunauer–Emmett–Teller surface areas were determined over a relative pressure range from 0.05 to 0.20.

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Pore size distributions were calculated from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda method.

### 7.2.3 Thermal Analysis

Thermal analysis was widely used to study the structure stability of as synthesized forms of molecular sieves. It provides information about the temperature required for the removal of adsorbed water, decomposition of the included organic cations in the pores and channels of molecular sieves. Data obtained from TG, DTA and DTG study are useful in evaluating the thermal properties of molecular sieves.

TGA-DTA measurements were carried out on (NETZCH 209/2/E equipped with a STA-409 controller) with an alumina plate under an air atmosphere (air flow) from ambient to 1000 °C at a heating rate of 10 °C/min.

### 7.2.4 Infrared Spectroscopy

Framework infrared spectroscopy provides additional information about the structural details of the molecular sieves. It can be used to confirm acidic nature and isomorphous substitution in molecular sieves.

FT-IR spectra of samples was taken in the range of 4000-400  $\text{cm}^{-1}$  on a (Nicolet Protégé 460). Acidity of the samples was measured with pyridine adsorbed FT-IR spectroscopy (Nicolet Protégé 460) equipped with an evacuable furnace cell with KBr windows, containing sample wafer. Initially, catalyst powder was pressed into a 5 mm wafer, which was loaded into the IR chamber and heated up 400 °C over night under reduced pressure of  $10^{-3}$  mbar. After the cell was cooled down to 50 °C the background spectra was recorded. Spectra were always collected as an average of 200 runs with 0.5  $\text{cm}^{-1}$  definition. The pyridine adsorption was carried out slowly where the catalyst was

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equilibrated with pyridine vapors at 50 °C. After 60 min evacuation, a spectrum was recorded and heated stepwise scanning with IR spectroscopy.

### 7.2.5 Nuclear Magnetic Resonance

$^{29}\text{Si}$  MAS-NMR (Magic Angle Spinning Nuclear Magnetic Resonance) spectra in determining the nature and chemical environment of the atoms. This technique has been found to be very useful in understanding the structural and physicochemical properties of molecular sieves.

The solid-state  $^{29}\text{Si}$  MAS NMR spectra was recorded on a Bruker DSX 500 NMR spectrometer equipped 4-mm MAS probe head. The samples were spinning (MAS) at a rate of approximately 10 KHz. The spectra were recorded with a  $45^\circ$  pulse, a contact time of 10s and a recycle delay of 5000  $\mu\text{s}$ , with out cross polarization. Samples spectra was deconvulated by dmfit 2008 software.

### 7.2.6 Diffuse Reflectance UV-visible spectroscopy

This technique measures the scattered light reflected from the surface of samples in the UV-visible range (200-800 nm). For most of the isomorphously substituted molecular sieves, transitions in the UV region (200-400 nm) are of prime interest. This spectroscopic technique is used to determine the coordination state of transition metal ions substituted in the matrix of the molecular sieves, involving ligand-to- metal charge transfer transitions at  $\sim 200\text{-}220\text{ nm}$ .

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Diffuse-reflectance UV-vis spectra of solid samples was recorded with (Perkin Elmer Lambda 950) equipped with diffuse reflectance attachment, with BaSO<sub>4</sub> as the reference.

### 7.2.7 X-ray Photoelectron Spectroscopy (XPS)

XPS is among the most frequently used techniques in catalysis. It gives information on the elemental composition and the oxidation state of the elements. It is an important tool for the characterization of the surface of zeolites and related materials. Depth selective information can be obtained by varying the angle between the sample surface and analyzer. Mesoporous molecular sieves containing different heteroatoms such as Al, Ti, V, Nb and Ta have been analyzed by XPS technique to obtain information about the dispersion of the heteroatom in the structure.

XPS measurements were carried out in an Ultra Axis spectrometer. The samples were irradiated with monoenergetic Al K<sub>α1,2</sub> radiation (1486.6 eV) and the spectra were taken at a power of 144 W (12 kV x 12 mA).

### 7.2.8 Temperature programmed techniques

Temperature programmed techniques such as TPD (temperature programmed desorption) and TPR (temperature programmed reduction) are useful techniques in heterogeneous catalysis. For measuring the acid strength of the samples, ammonia TPD is used and reducibility of transition metals in the catalysts particles, H<sub>2</sub>TPR technique is used widely.

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NH<sub>3</sub>-TPD of samples were measured on TPDRO 1100 apparatus from CE instrument, with Thermal Conductive Detector (TCD). Initially, samples were heated at 500 °C under inert gas for removal the physisorbed water from the catalysts. Afterwards NH<sub>3</sub> was physisorbed from room temperature to 600 °C. The amount of desorbed ammonia was recorded by a thermal conductive detector (TCD) during various temperature scans.

H<sub>2</sub>-TPR of samples was carried out with TPDRO 1100 apparatus from CE instrument with Thermal Conductive Detector (TCD). First instrument lines were pretreated by passing N<sub>2</sub> (20 ml/min) at 450 °C for 1 h. After cooling to ambient temperature, the nitrogen flow was replaced by 10% H<sub>2</sub>/Ar mixture. The catalyst samples were heated in this atmosphere to 1000 °C at heating rate of 10 °C/min. The flow rate of the H<sub>2</sub>/Ar mixture was 32 ml/min throughout the experiment.

### 7.2.9 Raman spectroscopy

Raman spectroscopy is a versatile technique in heterogeneous catalysis research for measuring the type of metal oxide species present on the surface of the catalysts. This technique gives valuable information, particularly, in presence of mixed metal oxides and transition metal contain molecular sieves.

The Raman spectra of calcined samples was obtained on a (Bruker RFS 100/S) with the 1064 nm line of Nd-YAC laser.

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### 7.2.10 ICP-AES

This method allows to find the exact amount of various elements present in given samples. In case of Nb, Al, Ti, Ta and Si contain molecular sieves the ICP is used to quantify the amount of metals present.

Bulk elemental analysis was measured with Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES) on a spectroflame D (Spectro Analytic Instrument).

### 7.2.11 SEM

The morphology of crystal shape and size were measured by SEM (LEO 1455 EP Scanning Electron Microscopy) with analysis method.

### 7.2.12 Gas Chromatography

The GC analyses were carried out on a Siemens Chromatograph 5890, equipped with a flame ionization detector and a (FS-OV 1701, 50 m) a capillary column with methyl undecanoate as the internal standard.

|                      |                            |
|----------------------|----------------------------|
| GC                   | Siemens Chromatograph 5890 |
| Column               | FS-OV 1701, 50 m           |
| Column temperature   | 50-240 °C,                 |
|                      | 6 min isotherm , 8 °C/min, |
|                      | 20 min isotherm            |
| Injector temperature | 280 °C                     |

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|                      |                 |
|----------------------|-----------------|
| Carrier gas          | Helium, 1.0 bar |
| Detector             | FID             |
| Detector temperature | 280 °C          |

### 7.2.13 GC Mass spectroscopy

In the reaction mixture, unknown products were identified by GC-MS by using GC Varian Star 3400 CX with Varian MS Saturn 3 spectroscopy.

|                      |                      |
|----------------------|----------------------|
| GC                   | Varian 3400 CX       |
| MS                   | Varian Saturn 3      |
| Energy               | 70 eV                |
| Column               | 25 m SE 54           |
| Column temperature   | 50-270 °C            |
|                      | 6 min isotherm 50 °C |
| Injector temperature | 10 °/min             |
| Carrier gas          | Helium, 1.0 bar      |
| Detector             | FID                  |
| Detector temperature | 250 °C               |

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### 7.3. Catalytic Reactions

#### 7.3.1 Gas phase Beckmann rearrangement of cyclohexanone oxime to caprolactam

Gas phase Beckmann rearrangement of cyclohexanone to caprolactam reactions over Nb containing materials were carried out in fixed bed reactor by using 6mm stainless steel reactor. The flow diagram for reactor is presented in Fig-1. The catalytic reaction was carried out in a fixed-bed reactor (316 stainless, 6mm o.d.). A mixture of pelletized catalyst (ca. 1.6-1.0 mm mesh) and quartz sand (also 1.6-1.0 mm mesh) was packed into the reactor, and then heated in flowing air at 500 °C for 4h. Subsequently, the reactor was cooled to the desired reaction temperature. Before starting the reaction nitrogen gas was passed through catalyst bed for 15 min. CHO was dissolved in ethanol. The feed was injected into the reactor by a piston pump (Telab, Heidelberg) along with N<sub>2</sub> as carrier gas. The reactor outlet was connected to a cooling trap, which was immersed into isopropanol and dry ice mixture. The reactor effluent taken at specified intervals was analyzed using a Siemens Chromatograph 5890, equipped with a flame ionization detector and a (FS-OV 1701, 50 m) a capillary column with methyl undecanoate as the internal standard. Regeneration of the catalyst was done by calcination at 500 °C for 4 h under air flow. Some reactions were performed with Design Expert -5 (Start- Ease) [199] and afterwards we followed the thereby optimized conditions.

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### 7.3.2 Ammoximation of cyclohexanone to caprolactam

Ammoximation of caprolactam reactions was carried out in a batch type 3-neck glass (slurry) reactor. The batch reactor system consists of a dry round-bottomed flask equipped with a reflux cooler. The temperature was kept stable by a silicon oil bath equipped with a thermostat and a magnetic stirrer; the temperature was measured in the oil bath. The stirring speed was maintained by magnetic stirrer. Reactors are shown in Fig-2. Reactions were done after reaction medium was brought up to reaction temperature. In the reactor, required amount of cyclohexanone, ammonia, solvent and catalyst were charged. Hydrogen peroxide was introduced continuously for 2 h by slow addition into the reaction mixture under stirring for avoiding the decomposition. After 2 h addition of hydrogen peroxide, reaction was continued further 2 h. After 4 h reaction time, reaction was stopped and reactor was cooled down to room temperature. Samples were collected periodically or after reaction and centrifuged for separate the catalyst from the reaction mixture. Samples were analyzed by Gas Chromatography in order to quantify the conversion and selectivity of the products by internal standard method.

Reactions under pressure conditions were carried out in autoclaves. Such reactors consist of pressure monometer indicating the reactor pressure. Reactants were filled in glass lined autoclave. The required reaction temperature was maintained by (Eurotherm) temperature controller and reactor inside temperature was measured by thermocouple. The stirring speed of reaction was controlled by magnetic stirrer. Pressure reactors are shown in Fig-3. Required amounts of cyclohexanone, ammonia, solvent and catalysts were filled in glass lined autoclave and reactor was closed tightly. Reactor was filled by either air or O<sub>2</sub>. Filled reactors were kept in between heating coil and required reaction

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temperature was obtained by temperature controller. After reaching the temperature, reactions were performed for 2 h. After 2 h reaction time, reactor was cooled down to room temperature. Samples were collected in centrifuged samples and catalysts were separated off by centrifugation method. Samples were analyzed by Gas Chromatography with an internal standard method.

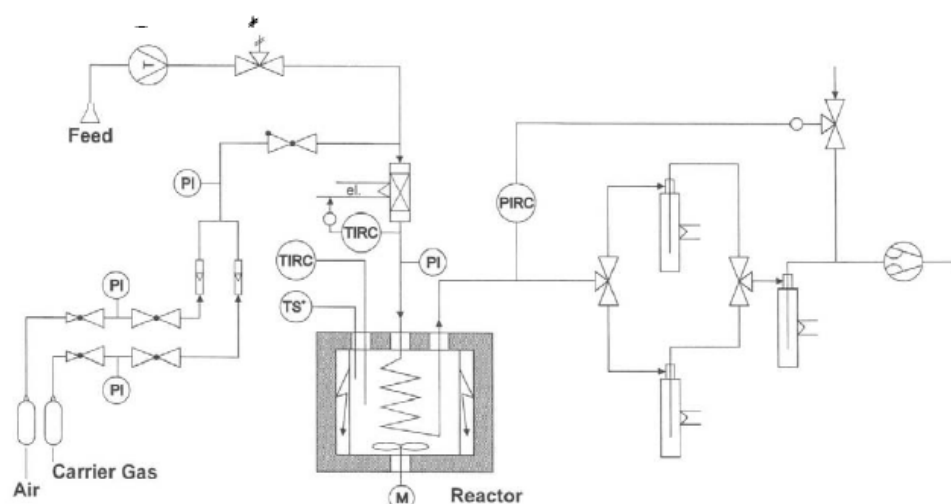


Fig. 1. Flowsheet of fixed bed reactor. PI = pressure indication, TI = temperature indication, PIRC = press. ind. registration control, TIRC = temp. ind. registration control, TS<sup>+</sup> = temperature switch (+ upper boundary), M = motor.



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**Figure: 2- Batch reactors**



**Figure: 3- Pressure reactors**

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