Caprolactam Synthesis using Ce-MCM-41Catalysts

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Abstract

Siliceous MCM-41 was synthesized by hydrothermal method using sodiummetasilicate as a source. Cerium ion incorporated Si-MCM-41 was synthesized by hydrothermal method using Cetyltrimethylammonium bromide as template. 2, 3 and 4 weight percentage of Ceria was loaded over MCM-41 by wet impregnation method. The synthesized catalysts were characterized using FT-IR, DRS-UV-Vis, XRD and SEM techniques. The catalytic activity of the cerium ion incorporated and ceria impregnated MCM-41 was evaluated in the synthesis of caprolactam from cyclohexanone oxime in the liquid phase condition. At high temperature all the catalyst showed high conversion. In that 4 wt.% Ce impregnated Si-MCM-41 produced high conversion (76.2%) and percentage yield (66.4%). The impregnated catalyst may contain more number of cerium present in the pores, so the lewis acid sites will be more and the conversion of cyclohexanone oxime into caprolactam will be high.

Keywords: Ceria, MCM-41, Caprolactam and Hydrothermal method.

1. Introduction

The workhorses in many chemical industries are catalysts. High stability, selectivity, easy regeneration and low production cost are the important requirements of a good catalyst. In that sense catalysis is an essential technology in the manufacture of industrially important chemicals. Zeolites, Zeotype molecular sieves, M41S are used as heterogeneous catalysts. They are classified based on the pore size. Zeolites are the crystalline microporous materials that are widely applied as a catalyst in oil refining, petrochemical and fine chemical industries. They exhibit unique properties with respect to both selectivity and activity, providing low surface area. These are the limitations of zeolites are Pore dimensions (5 to 7Å) are not accommodate broad spectrum of molecules, pore sizes are not tunable and diffusion constraints associated with small pore Heterogeneous catalysis occurs when the catalysts and reactants are in the different phase. Heterogeneous catalyst offers several intrinsic advantages over homogeneous counterpart. Ease of product separation, catalyst reusability, high selectivity, easy work-up, environmental friendliness, increased surface area, non hazardous in nature, work in a continuous reaction mode [1-3].

Reports in 1992 about the discovery of M41S, a new class of silica based mesoporous materials by researchers of mobile company have boosted researchers in to the application of active phases inside the mesoporous present in these materials [4]. The typical mesoporous silica molecular sieves such as MCM-41 and MCM-48 (MCM denotes

Mobile Composition of Matter) where as the numbers 41 and 48 are merely batch numbers. The formation mechanism of these molecular sieves had been proposed in various ways, which are briefly discussed in the following sections. The liquid crystalline mesophase or micelles act as a template rather than single individual molecules or ions. Accordingly, the final product is a silicate skeleton that contains voids that mimics this mesophase resulting in the final product as a silicate skeleton. In the first path way the presence of liquid-crystal mesophase prior to the addition of the inorganic species i.e, pre-existence of surfactants aggregates (rod like micelles), followed by the migration and polymerization of silicate anions results in the formation of MCM-41 structure. In the second, the silicate spices added to the reaction mixture may influence the ordering of isotropic rod like micelles to the desire liquid crystal phases. Salient features of MCM-41 are high surface area (>1000 m^2/g), high porosity (50-500 Å), pore size are narrowly distributed, excellent thermal stability during heating to 1173 K in dry air, hexagonally arranged uniform pore structure, ore size are tunable.

Cyclohexanone oxime rearrangement is an important process for the production of caprolactam, a starting material for the manufacture of Nylon 6. The conventional rearrangement carried out industrially in fuming sulphuric acid is well known as an environmentally unfriendly process. This is particularly owing to a large amount of ammonium sulphate produced as a by-product from the subsequent neutralization of the oleum. Hence there has been interest to design and develop eco-friendly catalyst [5]. A huge number of heterogeneous catalysts have been developed and applied to the vapour phase cyclohexanone oxime rearrangement [6]. Sumitomo chemical has recently industrialized the vapour phase beckmann rearrangement using silicate-1 as catalyst [7]. Chaudhari *et al* synthesized Al-MCM-41 for cyclohexanone oxime rearrangement [8]. Ngamcharussrivichai *et al* synthesized mesoporous molecular sieves for the conversion of cyclohexanone oxime to caprolactam in liquid phase [9, 10]. Arenesulfonic acid functionalized mesoporous silica used as a novel acid catalyst for the liquid phase Beckmann rearrangement of cyclohexanone oxime to caprolactam [11]. To solve the problem of a rapid deactivation of the catalyst a fluidized bed system is employed. Alternatively, this problematic disadvantage might be overcome by carrying out the rearrangement in the liquid phase at lower temperature to get high conversion, selectivity and improved catalyst lifetime. Cerium based MCM-41 used in various types of organic transformation reaction [12-24], so we attempted the Beckmann rearrangement using ceria impregnated and incorporated MCM-41.

2. Experimental

2.1. Materials

The chemicals used for the synthesis of Si-MCM-41 and Ce-MCM-41 were sodiummetasilicate ($Na_2SiO_3.5H_2O$), ceriumnitrate hexahydrate ($Ce(NO_3)_3).6H_2O$, benzonitrile (C_6H_5CN), cyclohexanone oxime ($C_6H_{11}NOH$), cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)3N^+Br^-$) and sulfuric acid ($H_2SO_4$). All chemicals used were A.R. grade.

2.2. Characterization Techniques

The X-ray diffraction (XRD) patterns, textural properties and surface morphology of the catalysts were recorded on a PANalytical X'Pert Pro X-ray diffractometer, Micromertics ASAP 2020 volumetric adsorption analyzer, scanning electron microscope (SEM) SEM-JEOL JSM-5600 model and High resolution transmission electron microscope JEOL, JEM model. The diffuse reflectance UV-Visible spectra (shimadzu) of all the catalysts were recorded between 200nm-800nm using barium sulphate covering the entire UV-Visible region.

In the present study all the reactions were carried out in liquid phase reactor set-up. The rearrangement of cyclohexanone oxime in the liquid phase was carried out at 80 $^{\circ}$C, 100 $^{\circ}$C and 130 $^{\circ}$C over catalysts in the presence of benzonitrile as a solvent. In the actual procedure the 0.1g of catalyst and 1g of cyclohexanone oxime and 10ml of benzonitrile is taken in the round bottom flask and stirred in oil bath at various temperatures by attaching a condenser fixed with nitrogen balloon at the top. The mixture was then stirred for 5 hours and a portion of it was withdrawn at the end for GC analysis. The samples were analyzed by Hewlett packed 5890, a gas chromatograph equipped with capillary column and FID detector. Nitrogen was used as a carrier gas at a flow rate of 20ml/min.

2.3. Synthesis of Si-MCM-41 and Ce-MCM-41

Si-MCM-41 and Ce-MCM-41 (50 and 75) samples were synthesized hydrothermally using a gel composition of SiO_2: x CeO_2: 0.2 CTAB: 0.89 H_2SO_4: 120 H_2O. Sodiummetasilicate and cerium nitrate were used as the sources for silicon and cerium, respectively. Cetyltrimethylammonium bromide (CTAB) was used as the template for the mesoporous nature. Sodium meta silicate (28.4 g) was added in water then cerium nitrate hexahydrate (1.76 g) added to the above solution and the solution pH was maintained to 10.5 by adding 1 M H_2SO_4 with constant and vigrous stirring to form a gel. After 45 min, an aqueous solution of cetyltrimethylammonium bromide (7.29 g) was added to the gel mixture further stirred for 2 h at room temperature. The mixture was then transferred into stainless steel autoclave, closed and heated in a hot air oven at 145 °C for 48 h. After cooling to room temperature, the product was filtered and washed with deionised water. The materials were dried and calcined at 550 °C for 1 h in nitrogen atmosphere [25].

2.4. Synthesis of Ceria Impregnated MCM-41

Ceria was supported on Si-MCM-41 by wet impregnation method. One gram of predried Si-MCM-41 was dispersed in 20 ml of deionised water with constant and vigorous stirring. Cerium nitrate hexahydrate (1.76 g) was added in to the above mixture. The dispersion was stirred for 10 h and then evaporated to dryness, and the resulting solid was dried 24 h at 96 °C, followed by calcination at 550 °C for 5 h in air. Three Ce (x%)/MCM-41 catalysts, where x% is the respective Ceria content of 2, 3 and 4 wt.%, were prepared according to the above procedure.

## 3. Results and Discussion

3.1. X-ray Diffraction Studies

The X-ray diffraction pattern of the synthesized mesoporous Ce-MCM-41 shows the signals at (111), (220) and (311) planes are shown in the Figure 1a. The Ceria impregnated MCM-41(4 wt.%) shows the same signal at (111), (220) and (311) plane are shown in the Figure 1b. This confirms that there is no free CeO_2 present in the Si-MCM-41 and the structure of the Si-MCM-41 was not disturbed. Further it indicates that the long range order structure is achieved and the structure is retained after the introduction of cerium ions in the framework.
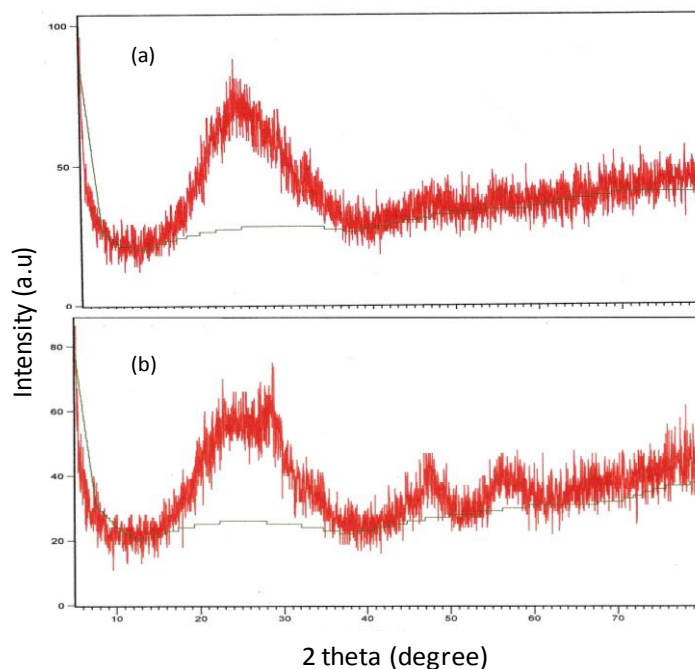
**Figure 1. XRD patterns of Ce-MCM-41 and CeO$_2$-MCM-41**

3.2. FT-IR Spectroscopy

The Infrared spectra of calcinated Si-MCM-41 and Ceria impregnated Si-MCM-41 are shown in the Figure 2 (a & b). The board peak around 3450 cm^{-1} is due to the -OH stretching of water, surface hydroxyl group and bridged hydroxyl groups. The symmetric stretching and bending modes of Si-O-Si produces signals around 800 cm^{-1}. The peak around 460 cm^{-1} is due to the bending mode of Si-O-Si, Ceria impregnated MCM-41 shows broad peak at 1085 cm^{-1} with shoulder around 1200 cm^{-1} which is characteristic of silica. The shoulder around 960 cm^{-1} is increased when the loading weigh is increased, this is the characteristic of asymmetric stretching of Si-O-M bond are shown in the Figure 2b. The asymmetric stretching of Si-O-Si produces a peaks around 1633 and 1096 cm^{-1}. The infrared spectra of Ce-MCM-41 (Si/Ce = 50) shown in the Figure 2c. All the peaks are similar to that of Ceria impregnated MCM-41, except the asymmetric stretching of Si-O-M bond which extended to higher wave number around 970 cm^{-1}. This is due to presence of cerium in the frame work.
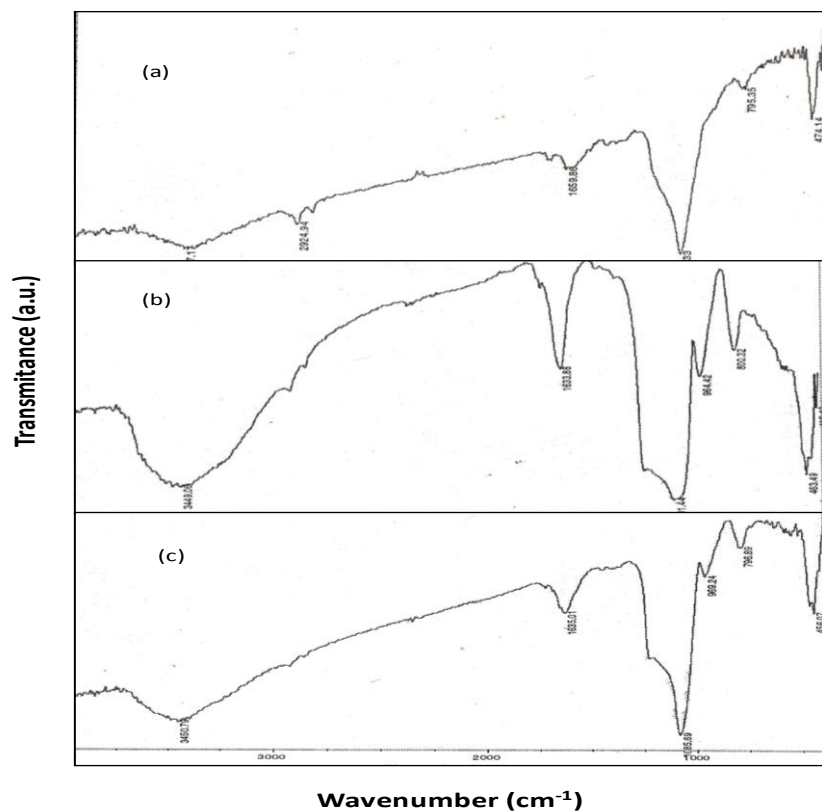
Figure 2. FT-IR spectra of (a) Si- MCM-41, (b) CeO$_2$-MCM-41 and (c) Ce-MCM-41

## 3.3. Scanning Electron Microscopy
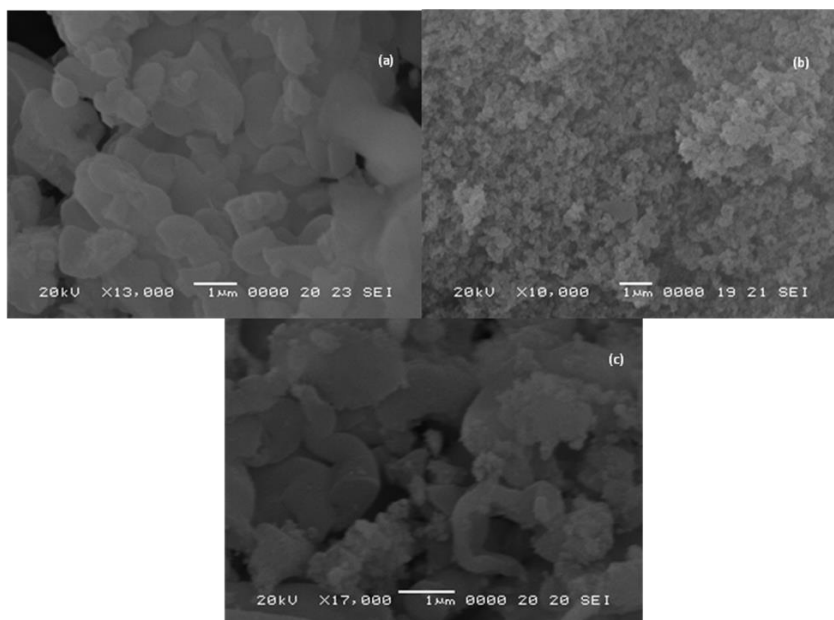
Figure 3. SEM images of (a) Si-MCM-41, (b) Ce-MCM-41 and (c) CeO$_2$-MCM-41

The SEM images of Si-MCM-41, cerium ion incorporated MCM-41 and ceria loaded

MCM-41 are shown in **Fig. 3 (a, b & c)**. In Fig. 3a Si-MCM-41 image showed uniform particles with aggregation of particles. Cerium ion incorporated MCM-41 also showed structure similar to MCM-41 (Fig. 3b). Ceria loaded MCM-41showed the uniform loading of ceria particles over MCM-41 in Fig. 3c.

3.4. DRs-UV Spectroscopy

UV-Visible spectroscopy has been extensively used to characterize the nature and the coordination of the inner transition metal ion in the substituted molecular sieves .The DR-UV-Visible spectral analyzing of Ce-MCM-41 was shown in the Figure 4 reveals that broad band in the UV region between 200 and 400 nm, which is attributed to the low energy charge transfer between the oxygen ion and central Ce^{4+} ion in the molecular sieves.
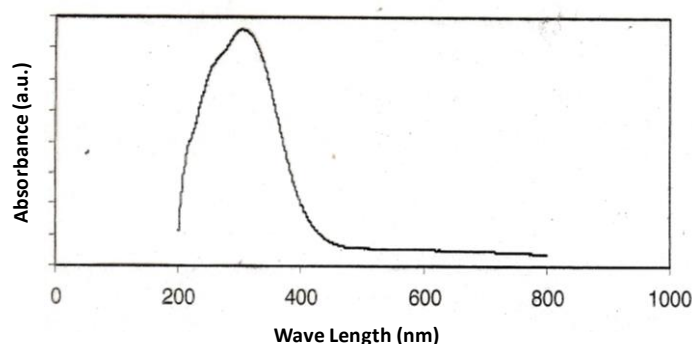

Figure 4. DRs-UV-Vis Spectrum of Ce-MCM-41

3.5. Catalytic Activity

The rearrangement of cyclohexanone oxime was studied at 80, 100 and 130 ^{o}C at 5 hours. The products were caprolactam and cyclohexanone. Cyclohexanone oxime conversion, the yield and selectivity of the products are present in the Tables. The conversion also increased from 80 to 130 ^{o}C. The yield of caprolactam increased from 80 to 130 ^{o}C. At 130 ^{o}C we get the maximum yield of caprolactam. Results are shown for the catalytic performing material from the synthesized catalysts 2, 3 & 4 wt% Ceria Impregnated MCM-41 (Table 1,2 & 3).

Synthesis of caprolactam cerium ion incorporated MCM-41 and ceria loaded MCM-41 are summarized in **scheme 1**.

cyclohexanone oxime   CeO$_2$-MCM-41 / Ce-MCM-41   Caprolactam   Cyclohexanone
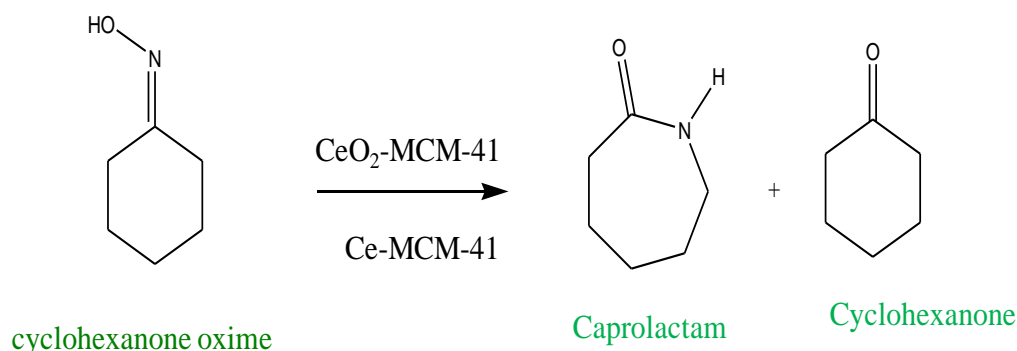
Scheme 1. Caprolactam synthesis using CeO$_2$-MCM-41 and Ce-MCM-41

Table 1. Effect of Temperature on the Synthesis of Caprolactam over 2 wt% Ceria Impregnated MCM-41 (Weight of the catalyst: 0.1g, Cyclohexanone oxime: 1g, Benzonitrile: 10ml, Duration: 5hours

Temperature (^{o}C)	Conversion (wt. %)	Product selectivity (wt. %)		Product yield (wt. %)
		Caprolactam	Cyclohexanone	Caprolactam
80	34.6	71.8	26.7	24.8
100	42.1	82.3	15.8	34.7
130	54.5	88.2	11.8	48.1

Table 2. Effect of Temperature on the Synthesis of Caprolactam over 3 wt% Ceria Impregnated MCM-41 (Weight of the catalyst: 0.1g, Cyclohexanone oxime: 1g, Benzonitrile: 10ml, Duration: 5hours

Temperature (^{o}C)	Conversion (wt. %)	Product selectivity (wt. %)		Product yield (wt. %)
		Caprolactam	Cyclohexanone	Caprolactam
80	39.7	68.7	32.2	27.2
100	52.1	86.4	12.7	45.1
130	60.1	92.6	7.4	55.7

Table 3. Effect of Temperature on the Synthesis of Caprolactam over 4 wt% Ceria Impregnated MCM-41 (Weight of the catalyst: 0.1g, Cyclohexanone oxime : 1g, Benzonitrile: 10ml, Duration: 5hours)

Temperature (^{o}C)	Conversion (wt. %)	Product selectivity (wt. %)		Product yield (wt. %)
		Caprolactam	Cyclohexanone	Caprolactam
80	45.7	73.3	26.4	33.5
100	73.2	84.4	11.3	61.7
130	76.2	86.7	10.3	66.4

The synthesis of caprolactam is not appreciatively catalyzed by the surface silanol sites of Si-MCM-41 because of the insufficient acid strength. The impregnation of CeO_2 in the pores of the Si-MCM-41 and incorporation of the Ce in to the silicate frame work of mesoporous material generates acid sites which are considerably more active and selective to the lactam. Liquid phase rearrangement of cyclohexanone oxime produced mainly caprolactam and cyclohexanone. The conversion of cyclohexanone oxime and the percentage yield of the caprolactam were observed to be high at 130 ^{o}C. At that temperature 4 wt.% Ceria impregnated MCM-41 produced high conversion (76.2%) and percentage yield (66.4%). Both conversion and percentage yield are found to be high with this catalyst. Ce (3 wt.%) impregnated Si-MCM-41 produced only 60.1% conversion, 2 wt.% Ce impregnated Si-MCM-41 produces only 54.5%.

3.5.1. Synthesis of Caprolactam using Ce-MCM-41

The rearrangement of cyclohexanone oxime was studied at 80, 100 and 130 ^{o}C at 5 hours. The products were caprolactam and cyclohexanone. Cyclohexanone oxime conversion, the yield and selectivity of the products are present in the Tables. The conversion also increased from 80 to 130 ^{o}C. The yield of caprolactam increased from 80 to 130 ^{o}C. At 130 ^{o}C we get the maximum yield of caprolactam. Results are shown for the catalytic performing material from the synthesized catalysts, Ce-MCM-41 (Si/Ce = 50 & 75) (Table 3 &4).

Ce-MCM-41 (Si/Ce=50 and 75) gave only less conversion but high selectivity. The impregnated catalyst may contain more number of cerium present in the pores, so the lewis acid sites will be more and the conversion of cyclohexanone oxime into caprolactam will be high. The lower conversion in incorporated catalyst might be due to its framework acidity is not adequate enough to catalyse the rearrangement reaction. Hence ceria impregnated catalysts are found to be favourable for the synthesis of the caprolactam.

Table 4. Effect of Temperature on the Synthesis of Caprolactam over Ce-MCM-41(Si/Ce = 50) (Weight of the catalyst: 0.1g, Cyclohexanone oxime : 1g, Benzonitrile: 10ml, Duration: 5hours)

Temperature (^{o}C)	Conversion (wt. %)	Product selectivity (wt. %)		Product yield (wt. %)
		Caprolactam	Cyclohexanone	Caprolactam
80	15.2	90.7	8.5	13.8
100	26.3	86.3	12.7	22.7
130	39.7	84.0	16.0	33.2

Table 5. Effect of Temperature on the Synthesis of Caprolactam over Ce-MCM-41(Si/Ce = 75) (Weight of the catalyst: 0.1g, Cyclohexanone oxime : 1g, Benzonitrile: 10ml, Duration: 5hours)
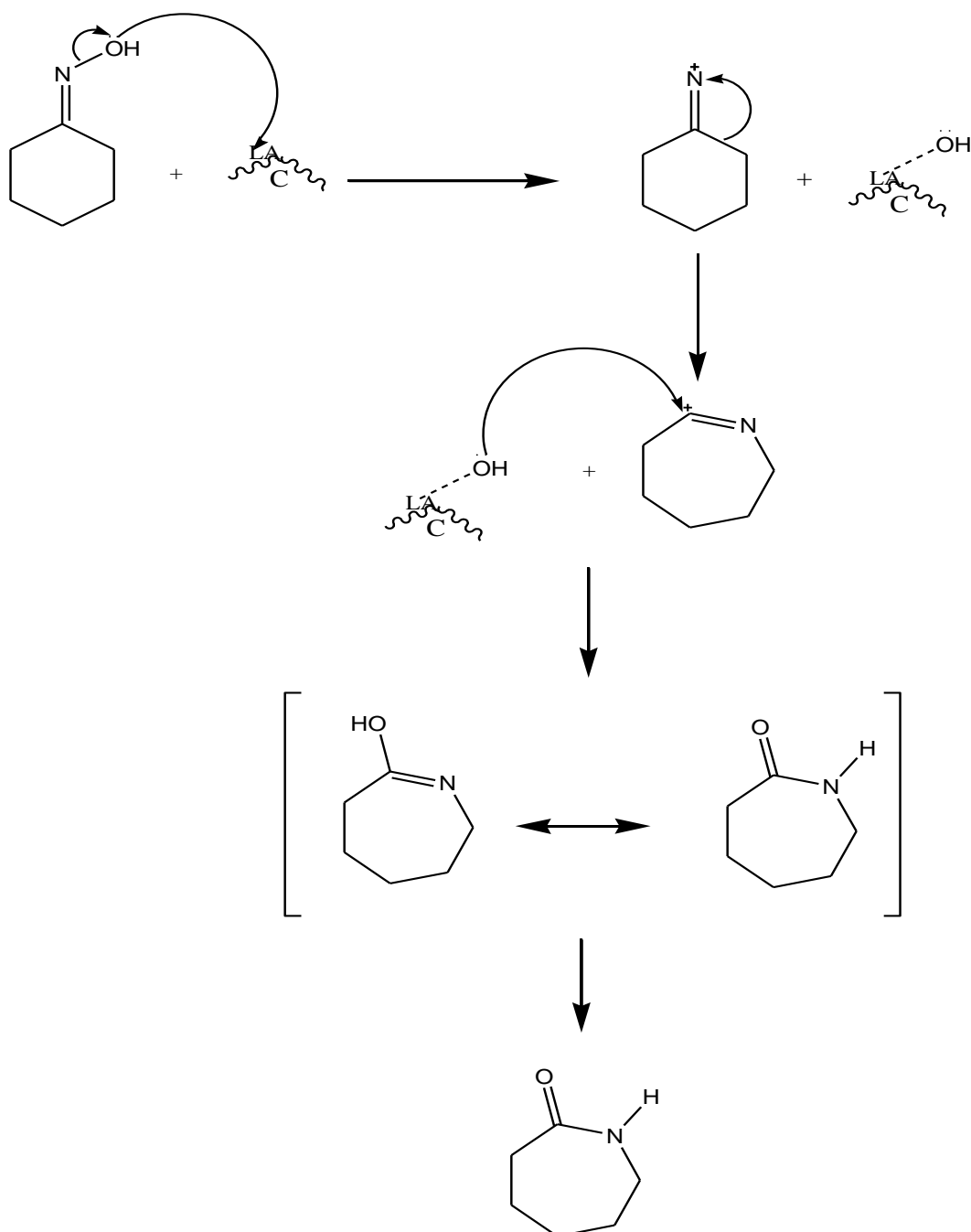
Temperature (^{o}C)	Conversion (wt. %)	Product selectivity (wt. %)		Product yield (wt. %)
		Caprolactam	Cyclohexanone	Caprolactam
80	10.5	93.7	5.7	10.5
100	16.7	92.3	7.3	15.6
130	29.2	87.3	12.5	25.4

The mechanism for the formation of caprolactam is proposed as given below.

4. Conclusions

Cerium ion incorporated and cerium loaded MCM-41 was successfully synthesized and characterized by various techniques. The framework of silica was not disturbed by incorporation of cerium ions and the ceria loading. All the synthesized catalyst showed high conversion of cyclohexanone oxime into caprolactam at 130 ^{o}C. In that 4 wt.% Ceria impregnated MCM-41 showed high conversion (76.2%) and percentage yield (66.4%) when compared to other catalysts. Because the ceria loaded catalysts contain more number of lewis acid site, which favours the percentage yield of the caprolactum. This study concluded that caprolactam could be selectively synthesized from cyclohexanone oxime over 4 wt.% Ceria impregnated MCM-41 catalysts at 130 ^{o}C using benzonitrile as solvent.

Acknowledgments

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