# Declaration

This is to certify that

i) The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Nirma University and has not been submitted elsewhere for a degree.

ii) Due acknowledgement has been made in the text to all other material used.

**Zeel Vinodkumar Kothari**

# Certificate

This is to certify that Major Project entitled "An Environment Friendly Approach: Use of Spent FCC catalyst for carbonation reactions" submitted by Ms Zeel Kothari (15MCHE02), towards the partial fulfilment of the requirements for the degree of Master of Technology in Chemical Engineering (Environmental Process Design) of Nirma University, Ahmedabad, is the record of work carried out by her under our supervision and guidance. In our opinion, the submitted work has reached level required for being accepted for examination. The results embodied in this major project to the best of our knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

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# Abstract

In refineries, the FCC unit for the production of gasoline uses large amount of heterogeneous catalysts. The activity of catalyst decreases with time and hence requires regeneration. At certain point, it is impossible to regenerate a catalyst and often deactivated catalysts are discarded as a solid waste. Considering its quality and quantity, an alternative use of spent FCC catalyst was carried in order to utilize the waste effectively.

The spent FCC catalyst, an inexpensive source of alumina and silica source was used as raw material to synthesize zeolite X by hydrothermal method. Various parameters were changed to reach its acceptable level. Those parameters include varying methods, synthesis time, aging and temperature. The prepared catalyst was characterized by BET surface area, X-ray diffraction (XRD), inductively coupled plasma optical emission spectrometry (ICP-OES), Fourier transform infrared spectroscopy (FT-IR) and thermo gravimetric analysis (TGA) analysis.

This catalyst was used in synthesis of five membered cyclic carbonate and its activity was also compared with commercial NaX which has never been reported previously. The path chosen for the preparation of cyclic carbonate is eco-friendly which not only utilizes the carbon dioxide but also replaces the toxic chemical like phosgene. The conversion of carbon dioxide ($CO_2$), an abundant renewable carbon reagent, into cyclic carbonates is of academic and industrial interest. Cyclic carbonate serves as green solvent and has some outstanding properties such as a high boiling point and low toxicity. An enhanced styrene carbonate yield of 31% was obtained under mild conditions of 120ºC, 5 h and 14 bars $CO_2$ pressure. The influence of various parameters like amount of catalyst, reaction time and temperature were investigated carefully. The heterogeneous catalyst was readily separated after the reaction and reused without affecting the selectivity and yield of the product.

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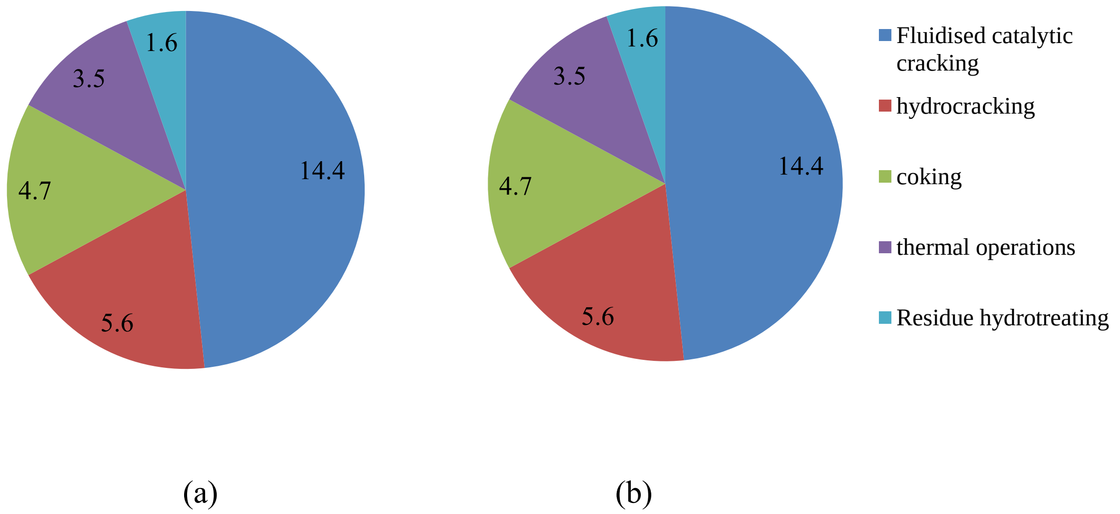
# Chapter 1    Introduction

In refineries, high valuable product like gasoline is produced mainly by catalytic cracking in fluidized bed reactor. For this purpose large amount of heterogeneous catalysts are used. The activity of catalyst decreases with time and hence requires regeneration. The catalyst is regenerated by burning off the deposited coke with air blown into the regenerator. At certain point it is impossible to regenerate catalyst and deactivated catalyst is often discarded as a solid waste [1]. The rate of deactivation depends on the quality of catalyst used and operation severity. Due to stringent environmental regulations for handling and disposal of solid waste, considerable attention has been given for recycling and reuse of spent FCC catalyst. The amount of spent catalyst discharged from different processing units depends largely on the quantity of fresh catalyst used, their lifespan as well as consequence of reaction conditions like temperature and pressure, quantity and kind of the deposits formed during use[2]. Major portion of spent catalyst comes from hydroprocessing because of the deposition of coke and metals like Mo, V, Ni and Co [3]. However reactivation is not possible in case of thermal degradation and phase separation. Although FCC catalyst is spent, it has acidic properties as well as defined crystalline structure which can be modified/reform/converted as per requirement for other applications. Stepping towards a new technology, Green Chemistry, which not only reduces the use and generation of hazardous substances but it also reduces the total cost of the process [4]. Due to stringent environmental regulations for disposal and handling of spent catalyst, research on the process of recycling and reutilization of spent FCC catalyst has achieved considerable attention [5].

In the year of 2014, on an average only 300 Fluidized Catalytic Cracking units were in operation out of total 646 refineries [6]. Other than FCC, units like hydrocracking, thermal operations and residue hydro treating also contributes to oil refineries for conversion process. Figure 1 provides an outline of the different conversion processes in use in refineries, expressed as both the number of barrels of crude oil processed per day and the number of refineries utilizing the processes [6].



(a) (b)

Figure 1(a) worldwide conversion process in refineries in barrels per day and (b) No. refineries where conversion technologies are available

Numerous conversion technologies are used in refineries and some of them even have more than one FCC unit producing gasoline, propylene and to some extent raw materials for petrochemical processes. It is expected that yearly around 840000 metric tons of spent catalysts are produced and about 2300 metric tons are produced daily [6]. The leading worldwide FCC catalyst producers are W. R. Grace, Albemarle and BASF, while local producers like CCIC in Japan and Sinopec and Petrochina in China have smaller market shares [6].

## 1.1 Environmental Impact

Environmental laws concerning the disposal of spent heterogeneous catalyst have become increasingly more crucial in recent years. The spent catalysts from petroleum refineries are considered as hazardous waste as per the Hazardous Waste (Management and Handling) Third Amendment Rules, 2010[7]. The most important hazardous characteristics of spent refinery catalysts are their toxic nature. Chemicals like V, Ni, Mo and Co present in the catalyst can be leached out by ground water after their disposal and pollute the environment. Besides the formation of leachates, spent catalyst when in contact with water, can liberate toxic gases. The release of the HCN gas from the coke deposited on catalyst comprises a considerable amount of nitrogen has been reported [5].

The hazardous nature of the spent catalyst is drawing the attention of regulatory authorities in many countries and the refiners are experiencing burdens from environmental authorities for safe handling of spent catalysts. A few option strategies, for examples landfilling, recovery of precious metals, regeneration or rejuvenation and reuse and utilization as raw materials to produce other valuable products are accessible to the refiners to manage the exhausted catalysts. The decision between these alternatives relies on technical feasibility and financial considerations.

## 1.2 Reuse of Spent Catalyst

### 1.2.1 Conversion of polymer into fuels over spent catalyst

Due to poor biodegradability and land availability, recycling of plastics is an important from environment point of view. The pyrolysis is one of the better options rather than incineration or landfilling. This can be done by two methods, thermal cracking and catalytic cracking [8]. The thermal cracking would require the high temperature in range of 400-900°C, which increases the cost and hence is unfeasible. The catalytic degradation provides numerous advantages compared to thermal cracking. The use of large number of catalysts like amorphous silica-alumina, zeolite Y, ZSM-5 and various acidic catalysts has been reported for catalytic cracking [9, 10, 11]. There is no doubt that the yield and selectivity achieved by the use of these catalysts are excellent but from the practical point of view and considering overall cost of the process, it restricts the recycling of plastic treatment. Therefore, a lot of researches are going on for the use of cheap catalyst. The use of spent FCC catalyst is considered as a good choice considering its availability and also shows promising results as it contains mixture of zeolites. Considering the facts that they are less active than alumina-silica or mesoporous catalyst, they still possess enough activity with high selectivity for hydrocarbon products. The moderate acidity of spent catalyst minimizes the formation of secondary reactions of hydrogen transfer and also restricts the formation of aromatics and paraffin. One the report claims degradation of high density polyethylene by utilizing exhausted catalyst gives high yielded products like gasoline ($C_5$-$C_{11}$) and olefins ($C_2$-$C_4$) [12].

### 1.2.2 Removal of trace olefins from aromatics streams

In refinery, aromatics streams are mainly acquired from catalytic reforming and thermal cracking while these streams typically encompass objectionable trace olefins such as mono-olefins, multi-olefins and styrene [13].The removal of trace olefins is essential as it shows negative effects on aromatics. It can be done by two methods i.e. using particulate clay and catalytic hydrogenation treating. The removal with clay treatment shows drawback of limited lifetime considering the fact that it cannot be reused again rather than discarding as a waste [14]. Another method uses the prepared catalyst and it benefits in many ways as it prolongs the lifetime compared to clay. The applications of spent FCC catalyst in elimination of trace percent of olefins from aromatics compounds are of great interest. The pre-treatment should be given for the spent catalyst used for this purpose like calcination (for removal of coke depositions) and some acidic washing in ultrasonic reactor. Later it shall be dried and should further modify with metal halides and thus, the resultant material obtained can be used for the removal of trace olefins from aromatics.

### 1.2.3 Applications in Construction industry

The fascinating properties of spent FCC catalyst have grabbed its attention in construction industry as a partial replacement of cement and sand, reducing the production cost of the process. Substitution of few percent of spent catalyst with sand and cement shows high compressive strength with no detrimental effect on environment [15].Whiteness is the most important of white Portland cement which is measured as the powdered material having a reflectance value ("L* value") in excess of 85%. The calcination is to be done in order to remove black particles of carbon. Cement with 20% replacement of white Portland cement by calcined spent catalyst shows reflectance value in range of 91-93 which meets the minimum requirement of white Portland cement [16].

### 1.2.4 Rejuvenation of spent catalyst by metal removal

The spent FCC catalyst contains metal contaminations like V, Ni, Mo and Fe on its surface. The deposited metals not only decrease the selectivity but also take part in dehydrogenation reactions. The coke formation on the catalyst can be removed by calcination but for metal removal, demetallization also called Demet process is to be done. This process removes the Nickel and vanadium deposition on the catalyst and is converted to chlorides which are then removed with catalyst. Advantages of this process are that it reduces the disposal of catalyst and also addition of fresh catalysts in the process.

### 1.2.5 Conversion to zeolites

As the FCC catalyst contains silica and alumina, it can be used to prepare zeolite based materials. Many articles are reported about the conversion of spent catalyst to Zeolite A, Zeolite X and Zeolite Y after undergoing various treatments [17]. The methods for the synthesis of zeolites are aqueous, Hydrothermal, Sol-gel, Microwave and Ultrasonication.

## 1.3 Scope and Outline of the thesis

Present study is aimed at exploring the effective route to utilize spent FCC catalyst. Attempt have been made to convert FCC catalyst into zeolite X. Various synthesis parameters are explored such as aging time, seeding, synthesis temperature and time to get optimized recipe for zeolite X synthesis.

As prepared zeolite X is explored for catalytic application in carbonation reaction. Solid catalyst is used for the preparation of styrene carbonate from styrene oxide and carbon dioxide. The cyclic carbonate is generally made by using toxic chemicals like phosgene. Our approach is phosgene free and eco-friendly.

This study demonstrates the environmental friendly approach as shown below:

1. Conversion of spent FCC catalyst into catalyst for carbonation reactions gives value addition to waste stream.

2. Phosgene free synthesis of cyclic carbonate is eco-friendly approach.
3. Utilization of carbon dioxide.

# Chapter 2 Literature Review

## 2.1 Zeolite X

Zeolites are crystalline structure of micro porous having alumina and silicates which consist of tetrahedral units producing open frameworks [18, 19]. From 1949 through the early 1950s, the commercially significant zeolite A, X and Y were discovered by Milton and Breck at the Tonawanda, New York, laboratories of the Linde Air Products Division of Union Carbide Corporation [19]. The only difference in zeolite X and zeolite Y is Silica: Alumina ratios, zeolite X has ratio 2-3 while that of Y type has greater than 3. Ten years later, in 1962, the synthetic type of Zeolite X were started to use as catalyst in many petrochemical industries by improving the efficiency in the existing process. The Zeolite X possesses a faujasite type structure which is shown in a Figure 2. It is a natural occurring mineral but rare mineral whose general formula is $M_{n/x}(AlO_2)_n(SiO_2)_{192-n}$, where n =77-96 and x= valence of M.

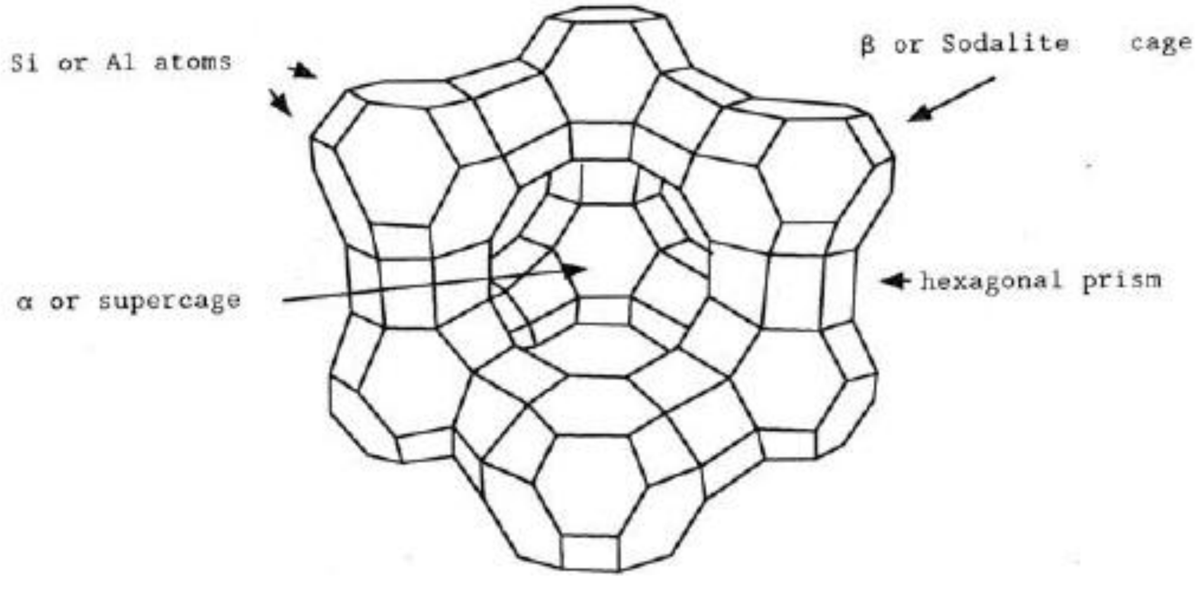


Figure 2 Structure of Zeolite X

The structure consists of ten cages linked by hexagonal prisms or double six-ring (D6R) units. The beta cages are often called sodalite cages because the structure of the zeolite sodalite contains eight of these truncated octahedral connected through the four rings. This structure transcribes a sphere of about 12Å known as the supercage. The 12 ring apertures to the supercage are about 7.4Å in diameter that allows only certain molecules to be adsorbed by the zeolite.

## 2.2 Synthesis of zeolites

### 2.2.1 Hydrothermal Synthesis

This is the most common method used for the synthesis of zeolite due to its advantageous property that it operates at low temperature. The hydrothermal method involves heating the reactants in a closed container (an autoclave). An autoclave is constructed from thick stainless steel and fitted with safety valves. Typically it is lined with a non-reactive material such as Teflon [13]. The autoclave is heated to above its normal boiling point; the pressure is increased and is called 'super-heated water'.

### 2.2.2 Microwave synthesis

The molecules or ions in a liquid or say solid are not free to rotate and the alternating electric field of the radiation:

1. Oscillating electric current is produce if any charged particles are present in molecule. The energy is transferred by the heat conduction to the surrounding by the resistance of movement.
2. If particles are absent which can freely move, but molecules or units with dipole moments are present, then the electric field acts to align the dipole moments which are dielectric heating. This is the type of heating that acts on water molecules in food. The electric field of the microwave radiation is oscillating at the frequency of the radiation, but the electric dipoles in solids do not change their alignment instantaneously, but with a characteristic time, t [20, 21]. The oscillating electric field changes its direction rapidly so that the time between changes is much smaller than the dipoles cannot respond fast enough and do not realign (lags behind). The solid

absorbs some of the microwave radiation and the energy is converted to heat depending on the dielectric constant and the dielectric loss [20, 21]. To use microwave heating, at least one component of the reaction mixture must absorb microwave radiations.

In this method microwave radiations are used to provide energy to reaction mixture to accelerate nucleation followed by crystallization. This method is very fast and energy efficient compare to conventional hydrothermal method.

### 2.2.3 Ultrasonication

The Ultrasonication make use of the ultrasound (high intensity) is a superficial and useful tool for the synthesis of microporous and nano particles [22]. Ultrasonic cavitation is the phenomenon whereby the principle of ultrasonic cleaning can be understood. The ultrasonic waves are generated to agitate the particles present in liquid samples. These waves are mainly generated by an opposite electronic ultrasounds generator and a special transducer suitably mounted under the bottom of a stainless steel tank, produce compression and vacuum waves at a very high speed, the speed depending on the working frequency of the ultrasounds generator. They normally work at a frequency between 28 and 50 kHz [23]. The pressure and vacuum waves in the liquid cause the phenomenon known as "ultrasonic cavitation". This enables reaction at faster rate and with minimum energy compare with conventional hydrothermal synthesis.

## 2.3 Zeolite as catalyst

### 2.3.1 Zeolite as a catalyst in Industries

Zeolites have quickly found out its application in industries based on its structural, morphological and compositional characteristics. More than 85% of total zeolites are used in petroleum industries for the various processes like fluidized catalytic cracking, Hydrocracking, Gasoline desulfurization, Light paraffin isomerization and reformate upgrading [20, 21]. The other zeolite based operation includes hydroxylation, alkylation, oximation and epoxidation [21]. The zeolites are also used in drug production in pharmaceutical industries

### 2.3.2 Zeolite as Catalysts in Environmental Application

The increasing environmental awareness has greatly benefited the use of zeolites. Replacement of sodium polyphosphate with zeolite is setting a good example which also shows its value in detergent market. In order to reduce emissions of $NO_x$, it is used as catalyst in selective catalytic reduction as it can withstand at high temperatures[20].The zeolites are used for the purpose of cations exchange e.g. removal of Strontium and Cesium from ‘‘dump waters’’ of nuclear power stations; industrial ‘‘water softeners’’, to prevent lime-scale blocking up cooling pipes in manufacturing facilities; removal of heavy metals like lead zinc, copper, mercury, cadmium from the environment [23].

## 2.4 Carbon dioxide and its effect

Carbon dioxide is one of the major greenhouse gases is increasing day by day in earth’s atmosphere. It is mainly generated from natural as well as human activities. Natural activities like ocean release, respiration and decomposition while human activities include deforestation, burning of fossil fuels and some industrial processes. The abundant amount of carbon dioxide in atmosphere will lead to increase in temperature and hence results in global warming and thus the increase in carbon dioxide should be control. Several ways to reduce carbon dioxide from the environment are reducing emission, carbon dioxide capture storage and its utilization. The possible strategies to reduce emission are replacing the source releasing high carbon energy carrier to less carbon rich source e.g. replacing coal by natural gas or oil. Carbon dioxide utilization, a feasible option to convert it into value added products. Some of its routes are heavily used by the industries.

## 2.5 Reactions with Carbon Dioxide to value added products

The carbon dioxide fixation in chemical reaction for value added product is one of the suitable routes for reducing concentration from atmosphere. Moreover, carbon dioxide is cheap, abundant, easily available and economical. The possible reactions with carbon dioxide are shown below:

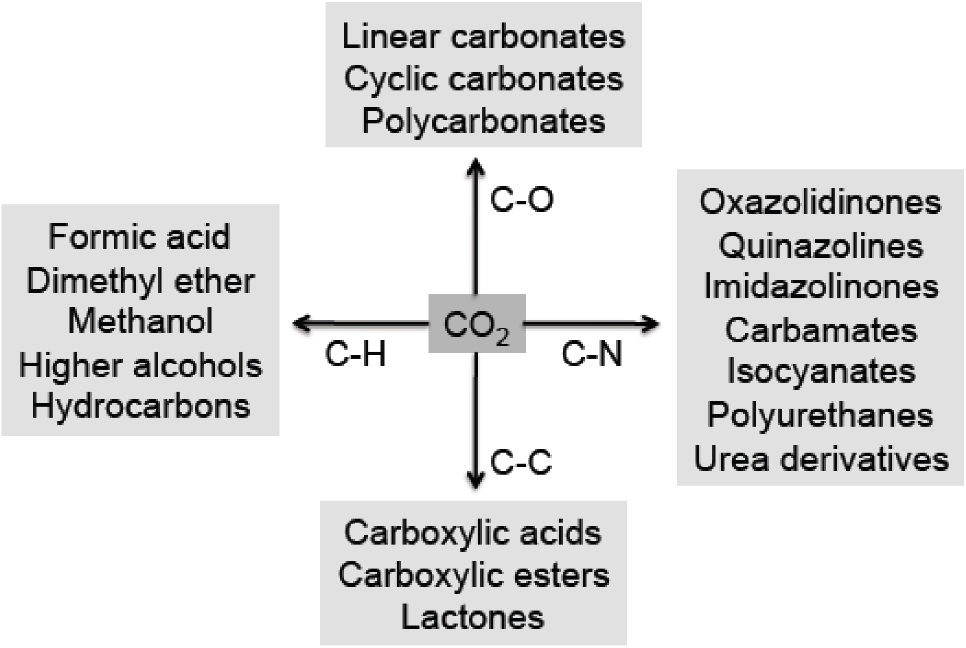


Figure 3 Possible Reactions with Carbon Dioxide

The formation of C-N bond takes place by the insertion of carbon dioxide which involves the nulceophillic attack of nitrogen. By this the nitrogen based products are synthesized. Carboxylic acids and esters are major products forming C-C bond when it attacks the weak electrophillic carbon centre of the molecule. Complex acids, alcohols and hydrocarbons are formed fixation of carbon dioxide in M-H bond. Present study deals with the formation of C-O bond by insertion of carbon dioxide in M-OR bonds.

## 2.6 Applications of Cyclic Carbonates

Five-membered cyclic carbonates are polar, and for this reason are excellent solvents. They are also important for extractive separation of mixtures and additives for hydraulic fluids. The hydrolysis of five-membered cyclic carbonates produces high yield of 1,2diols. The cyclic carbonates have found extensive use as excellent aprotic polar solvents, precursor for polycarbonates and other polymeric materials and chemical intermediates in pharmaceuticals industry [24, 25]. Some specific applications of cyclic carbonates are given in Table 1.

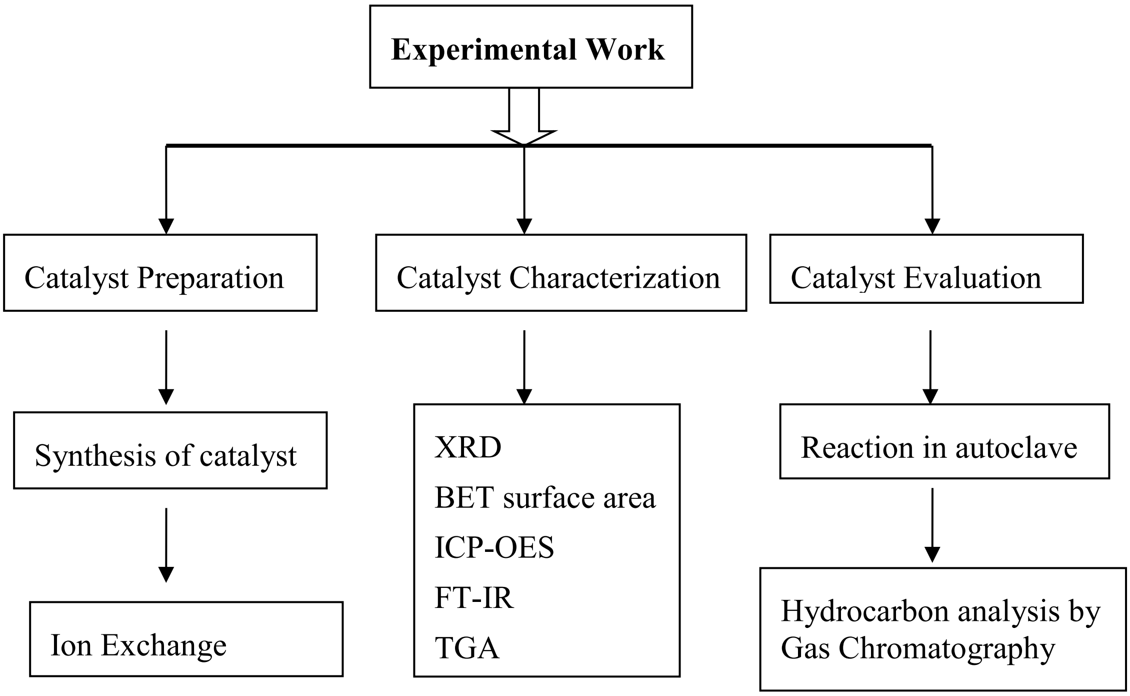
Table 1: Applications of Cyclic Carbonates

| Sr. No | Purpose | Application |
|---|---|---|
| 1. | Curing of Phenol-Formaldehyde (PF) Resins | Synthetic resins are used for the making plywoods. Phenolic resin curing slowdown in alkaline pH but accelerated in presence of esters and carbonates. Compared to ester, cure acceleration of carbonates are faster due the fact that it gives more phenolic nuclei. |
| 2. | Acceleration of Epoxy Curing | Cyclic carbonate can be used as reactive diluents for epoxy resins. Its use results in decrease in gel time due to lower viscosity and higher polarity of the medium |
| 3. | Thermosetting resin | Resins are obtained by polymerization of cyclic carbonate with isocyanate compounds in presence of fluoride catalyst. |
| 4. | Recording Materials | Cyclic carbonate compounds having an electron donating compound and accepting compounds are valuable as thermal recording materials. |

| | | |
|---|---|---|
| 5. | Electrolytes | Carbonate employed as an organic solvent in electrolytes for batteries and capacitors due to its good solvent properties The use of cyclic carbonates extends the life of capacitor. |

# Chapter 3 Experimental

This chapter highlights the experimental procedure performed in the present study and have been categorized into three parts: catalyst preparation, catalyst characterization and catalyst performance evaluation for carbonation reaction. Also this section addresses the details of raw materials used for the process.



However the laboratory catalyst preparation was carried out by synthesis of zeolite from spent catalyst. Various experiments were performed by changing synthesis parameters like percentage seeding, temperature and aging period to get optimized recipe. The prepared material was characterized by different techniques like XRD and Surface Area analyser and was compared with the commercial catalyst. The prepared zeolite X was then proceed for ion exchange with few metals i.e. Lithium, Cesium and iron. For catalyst evaluation, cycloaddition reaction of styrene oxide and carbon dioxide to styrene carbonate using the prepared catalyst was done. The progress of the reaction was carried out using GC chromatography. Later the kinetics studies were carried out for better selectivity and yield.

The performance of the catalyst was checked out by reaction and product was analysis in Gas Chromatography.

## 3.1 Raw materials

Commercially available chemical reagents like styrene oxide and DMF (AR Grade, Sigma Aldrich and Labort Fine Chem Pvt. Ltd) are of high purity and were used directly without further purification. The spent catalyst received from Reliance Industries Limited, Jamnagar from was used in this study. It mainly contains Zeolite Y, ZSM-5, additives and clay binders. Metal analysis of spent catalyst was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using microwave digester and data are presented in Table 2.

Table 2 Chemical Composition of Spent Catalyst

| **Sr. no.** | **Elements** | **Unit** | **Content** |
|---|---|---|---|
| 1. | Al | % | 33.36 |
| 2. | Ti | % | 0.2 |
| 3. | V | mg/L | 230 |
| 4. | Cr | mg/L | 59 |
| 5 | Mn | mg/L | 15 |
| 6. | Fe | % | 1.0 |
| 7. | Co | mg/L | 5 |
| 8. | Ni | % | 0.18 |
| 9. | Cu | mg/L | 18 |
| 10. | Zn | mg/L | 3 |
| 11. | Mo | mg/L | 3 |
| 12. | Pb | mg/L | 0 |

| | | | |
|---|---|---|---|
| 13. | Na | mg/L | 0.1 |
| 14. | K | mg/L | 172 |
| 15. | Ca | mg/L | 284 |
| 16. | Mg | mg/L | 182 |
| 17. | Si | % | 52.9 |

## 3.2 Catalyst Preparation

Zeolite X synthesis was carried out using hydrothermal method. Zeolite NaX can be synthesized using wide range of batch composition as noted by Breck at different temperatures (60-120°C). It can be made from different sources alumina and silica.

Hydrothermal crystallization was performed varied temperature from 90-120°C and aging from 24-96 hours.

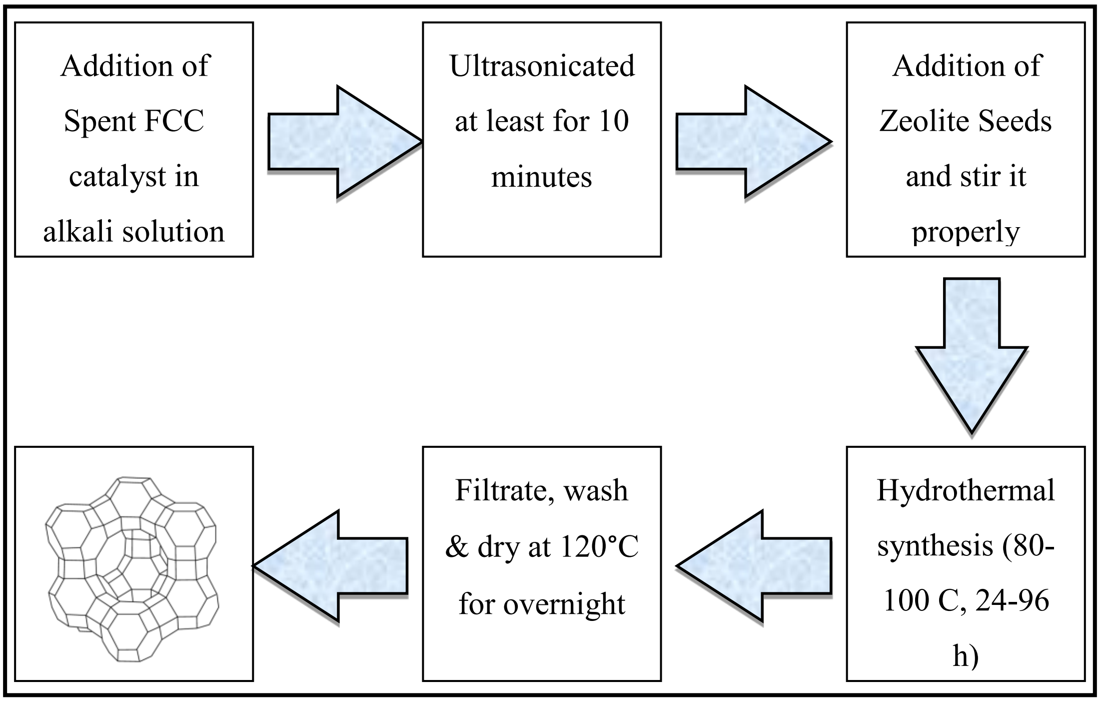


Figure 4 Hydrothermal Synthesis of Zeolite X

The alkaline solution added in the beginning of the reaction was prepared in order to reach the molar ratio $Na_2O/Al_2O_3$ = 2:1 and $SiO_2/Al_2O_3$ = 2:1. The optimized method for the preparation of catalyst is as follow:

**Batch preparation:**

1. Alkali solution was prepared by adding 10 grams of sodium hydroxide (NaOH) to 100 mL of deionized water, mixed gently until NaOH got completely dissolved.

2. 10 grams of spent catalyst was added to the reaction mixture and ultrasound it for 10 minutes in order to break the structure.

3. To this, 0.5 grams of Zeolite X was added as seeds under stirring conditions. Stirring continues till overnight.

**Crystallization:**

1. Vessel: 250mL polypropylene bottle (sealed)

2. Incubation: Not required

3. Temperature: 90°C

4. Time: 48 hours (The turbid gel phase was observed to diminish in height as the reaction proceeds, accelerating rapid in the final stages of the crystallization, leaving a clear supernatant above the crystalline phase observed.)

**Product recovery**

1. Resultant product was removed from the heat source and cooled to room temperature.

2. Vacuum filtration was done using wattman filter paper 41 to recover solids and washed with deionized water until filtrate pH measured below 8.

3. Final product was dried at 120°C.

## 3.3 Catalyst Preparation by varied parameters

Various experiments were performed on the withdrawn catalyst to reach its acceptable level by changing some of its parameters. Those parameters include varying methods, aging time and temperature. The summary of the experiments are as shown in the Table 3:

Table 3: Parameters for the synthesized material

| Sr. No | Method | FCC | Time (hr.) | Temperature (ºC) | Seeding (%) |
|---|---|---|---|---|---|
| 1. | Aqueous | Uncalcined | 24 | 90 | 5 |
| | | | 48 | 90 | 5 |
| 2. | Aqueous | Uncalcined | 48 | 90 | 5 |
| | | | 48 | 90 | 5 |
| 3. | Hydrothermal | Uncalcined | 24 | 90 | 5 |
| | | | 48 | 90 | 5 |
| | | | 48 | 90 | 7 |
| | | | 72 | 90 | 7 |
| | | | 96 | 90 | 7 |
| | | Calcined | 24 | 90 | 5 |
| | | | 48 | 90 | 5 |

## 3.4 Ion exchange of synthesized Zeolite 13X

The manner in which metal is introduced to a support will influence its dispersion as well as the nature of the metal-support interaction. Supported catalyst with low concentration of metal are generally prepared by impregnation (or in some case ion-exchange). The choice of precursor salt is made on both, solubility in water or preferred solvent and for its ability to disperse throughout the support. The ion exchange capacity of a certain type of zeolite depends mainly on Si/Al ratio. The more Al in zeolite framework structure, the more ion exchange it can undergo. In general ion exchange depends on the size of cation, size of pores in the zeolite structure and temperature. The procedure of ion-exchange is simply carried out by mixing zeolite based structure with a solution of salt of the targeted cation at room temperature or higher temperatures if the exchange rate is to be enhanced. The prepared catalyst was exchanged with Lithium, Cesium and Iron and respective molar solution was prepared from Lithium Chloride, Cesium Chloride and Ferrous Ammonium Sulphate.

**Procedure:**

1. 25g of Zeolite X sample was taken and 500 ml of 0.1 M ion solution was added.
2. Ion exchange was carried out under reflux condition for 6h.
3. The above procedure was repeated for 3 times. After that, the sample was washed several times with distilled water, followed by drying at 120ºC for 6-8 h.

## 3.5 Catalyst Characterization

The characterization of the catalyst is an important aspect in order to obtain information about molecular nature, structure of the active component to prepare the catalyst and also helps in optimizing industrial catalytic processes. No single technique is available to get the complete information about the surface structure of the active component and it is an impossible task to a single discipline of the subject to get comprehensive overview of the molecularities of the surface. Characterization of heterogeneous catalyst refers to the textural properties which are responsible for its performance in the given reaction. Several analytical and spectroscopic techniques were employed to characterize synthesized zeolite X samples. The details are given below.

### 3.5.1 X-ray Diffraction Spectrophotometer

XRD patterns were recorded on Bruker Advance D8 to obtain crystallographic structure and chemical composition of solids. The patterns were recorded for all synthesized samples in order to verify the formation and nature of structure. The XRD patterns of the support and the prepared catalysts were obtained using a Cu (Ka) radiation source (1.5418 Å) and operated at 40 kV and 30 mA. The catalysts were crushed to fine powders prior to measurement. X-ray diffraction is a technique to identify the crystallinity of catalysts. This technique is based on the knowledge that each compound in catalyst has a characteristic diffraction pattern. The crystallinity can be determined by comparing the intensity of a number of particular peaks to the intensity of the same peaks obtained by standard samples.

Figure 5: Brunker Advance D8 XRD

The diffraction pattern is plotted based on the intensity of the diffracted beams. These beams represent amp of reciprocal lattice parameter, known as Miller index (hkl) as a function of 2θ, which satisfies Bragg equation: $n\lambda = 2d \sin\theta$ where n is an integer number; λ is the wavelength of the beam, d is interplanar spacing and θ is a diffraction angle. Powder XRD pattern were recorded for all the samples in order to verify the formation and structure of various micro porous materials. The diffraction patters were recorded in the 2θ range of 5-80°. The scan speed and step size were 2.5° min-1 and 0.02°, respectively.

### 3.5.2 BET surface area

BET analysis is aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of powders, solids and granules, the values are expressed in meter square per gram. Clean solid surfaces adsorb surrounding gas molecules and Brunauer, Emmett and Teller theory (BET) provides a mathematical model for the process of gas sorption.

Figure 6: Micromeritics ASAP 2020

This physical adsorption of a gas over the entire exposed surface of a material and the filling of pores is called physisorption and is used to measure total surface area and pore size analysis of nanopores, micropores and mesopores. The BET surface area measurement is crucial in understanding the behaviour of a material, as material reacts with its surroundings via its surface, a higher surface area material is more likely to react faster, dissolve faster and adsorb more gas than a similar material with a lower surface area. Typical analysis would include: Specific surface area BET surface area analysis using Nitrogen, or Krypton for low surface area materials.

### 3.5.3 FT-IR

FT-IR spectroscopy is used to probe the structure of zeolites and monitor reactions in zeolite pores. Analysis of all synthesized materials and prepared catalyst for catalysis application were performed by using FT-IR (Nicolet 6700) using KBr pellets. Specifically, structural information can be obtained from the obtained from vibrational frequencies of the zeolite lattice observed in the range between 200-1500 cm$^{-1}$.

### 3.5.4 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) measures weight changes in a material as a function of temperature or time under a controlled atmosphere. Its principal uses include measurement of a material's thermal stability and composition. Analysis of spent zeolitic materials was done in order to check the weight loss during recycle studies. The temperature is kept from the range of 20°C to 850°C with the ramp of 20°C/minutes in the oxygen atmosphere.

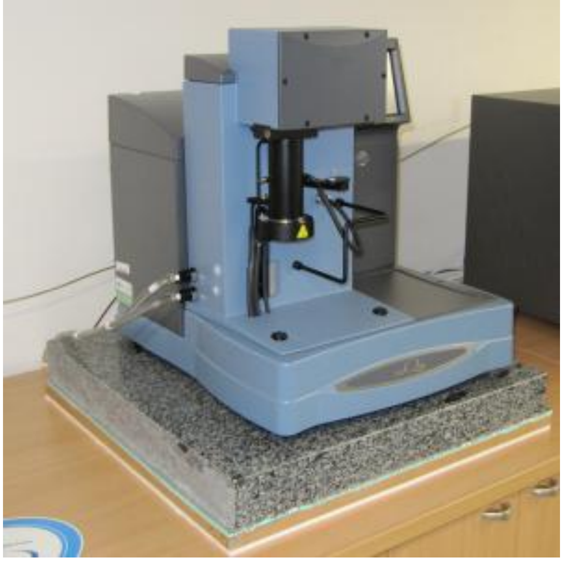


Figure 7 TGA Instrument

### 3.5.5 Inductively Coupled Plasma-Optical Emission Spectroscopy

ICP-OES (Perkin-Elmer, 4300 DV) analysis aims to identify trace elements presence in the aqueous samples. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Single element measurements can be performed cost effectively with a simple monochromator/photomultiplier tube (PMT) combination, and simultaneous multielement determinations are performed for up to 70 elements with the combination of a polychromator and an array detector. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.

In this instrument, Argon plasma generates excited atoms and ions; these emit characteristics radiation which detected by CCD detector by following steps of analysis.

Sample Preparation: Zeolitic samples require extraction or acid digestion in order to keep metals in solution.

Nebulization: Liquid samples are converted to Aerosol and are transported to plasma. A spray chamber is placed between the nebulizer and ICP torch to remove large droplets from aerosols.

Desolvation/Vaporization: Water is driven off, and remaining solid and liquid portions are converted to gases.

Atomization: Gaseous molecules are broken into atoms. Plasma temperature & inert chemical environment are important at this stage.

Excitation/Emission: Atoms gain energy from collisions and emit light of a characteristic wavelength

Separation/Detection: A grating disperses light that is quantitatively measured by CCD detector

Figure 8: ICP-OES

## 3.6 Catalyst Performance

The evaluation was carried out using the carbonation reaction in the Parr reactor 4848. The batch reactor of 300 ml (stainless steel Autoclave) was used for this purpose.

Figure 9 Parr Reactor 4848

The reactor was filled with the 10mmol styrene oxide and 100ml solvent i.e. DMF. Required amount of catalyst was loaded in the reactor. Prior to the performance reaction start, the carbon dioxide was supplied into reactor at 8 bars and hold for a 2 minutes, it was flushed out three times. After the vessel is pressurized by carbon dioxide, the temperature was slowly increased and the impeller was at required rpm of 250. The liquid products were analysed by a gas chromatograph equipped with a flame ionization detector and capillary column.

### 3.6.1 Hydrocarbon analysis by GC

The most widely used technique for analysis of hydrocarbon is gas chromatography (GC). The gas chromatography is a separation technique consists of injector, column and detector. The sample is injected with carrier gas stream, mainly hydrogen and allowed to flow throughout the column of the different molecules at different rates. The MDGC, Bruker 450 was used in the present study for monitoring. The injector temperature is always high which convert liquid sample to vaporized form. The split ratio is maintained at the injector in order to reduce the sample amount and also avoids the overloading of column and subsequent separation problems. The cross-linked and non-polarmethylsiloxane column gives an elution times which is nearly to the order of increasing boiling point. The column having internal diameters of 0.1–0.5 mm and the length of the column ranges from 30 to 100 m. The detector kept at the end generates and identifies a signal proportional to the concentration of each hydrocarbon as the components exit the column. It functions by accumulating (by an electrode) the ions of the flame created during combustion of the hydrocarbons. The sample to be detected is approximately proportional to the weight of carbon present, which significantly abridges quantitative analysis. The detector temperature is always higher than the injector temperature in order to avoid the condensation while sample reaches near to the detector. The rate of sample transport through the column is totally reliant on the velocity of carrier gas, injector pressure and the oven temperature. The lightest hydrocarbons (methane and ethane) are transported very rapidly through the column and separation requires low temperature (ambient). On the other hand, the heaviest aromatics need a high temperature of 200°C or even more in order not to adsorb strongly at the column front. The column material, its length, the detector temperature, the carrier gas type, and the split flow rate also affect the separation. In the present study, the GC used is armed with a flame ionization detector and a capillary column of RTX-5. The analysis takes 50minutes.The temperature program for GC analysis heated samples from 90 to 220°C at 6°C/min, split ratio of 42 and carrier gas flow was maintained at 2.3 mL/min. Inlet and detector temperatures were set constant at 230°C and 240°C respectively. The yield of product can be estimated as percentage weight by weight on styrene carbonate.

## 3.7 Performance testing of catalyst

Cyclic carbonates are used as an intermediate component in the pharmaceutical industries. Earlier, they were produced by phosgene. The importance of the research efforts to viable routes in the production of cyclic carbonates, independent of toxic chemical, cannot be overlooked. Styrene carbonate, which can readily be produced from Styrene oxide and Carbon dioxide in presence of catalyst, offers an interesting alternative.

A number of works have been reported in literature for the development of various catalyst systems for $CO_2$cycloaddition. The zinc complex with various bases shows the good catalytic activity even at mild parameters [26, 27, 28, 29]. The heterogeneous catalyst sometimes are less active compared to homogeneous ones like metal complexes, organic halides and ionic liquid, but the easy separation of catalyst makes the reaction more efficient and economical. Yano et al. was the first to use the metal oxide as inorganic catalyst for the epoxidation reactions giving the 60% yield of phenyl carbonate [30, 31]. Yamaguchi et al. made the use of Mg-Al for the synthesis of styrene carbonate which requires high amount of catalyst per gram of substrate and reaction time of 24 hours [31, 32]. The use of zeolite-beta based catalyst in conjunction with quaternary ammonium salt had been reported by R. Srivastava et al. [33]. Michele Aresta et al. used Zeolite 5A giving the yield of styrene carbonate of 3.1% [34]. In the present study, styrene oxide (10mmol), prepared catalyst and organic solvent (20 ml) were taken in 300 mL of Parr pressure reactor for cycloaddition reactions. The reaction scheme is shown in Figure 10.

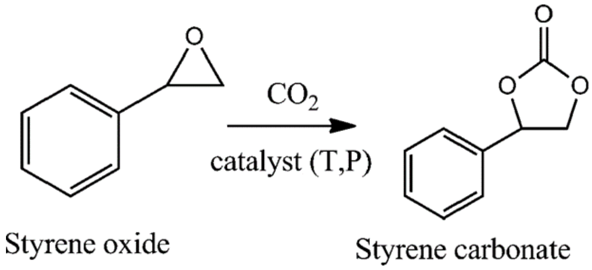


Figure 10: Synthesis of Styrene Carbonate from Styrene Oxide and $CO_2$

The procedure for the reaction is as follows:

1. Initially mix the required amount of styrene oxide, DMF and zeolite based catalyst. (catalyst used for the study was dried at 350°C)
2. Stir it properly.
3. Transfer the sample into reaction vessel.
4. Place the split-rings on the vessel.
5. Tighten the bolts with wrench.
6. Place the safety ring on it.
7. Place the safety ring screw.
8. Ensure if the bolts are tightened in order to avoid leakage.
9. Cover the reaction vessel with reactor heating furnace.
10. Rinse the vessel with Carbon dioxide gas and repeat it three times.
11. Pressurized the reactor with Carbon dioxide gas up to 14 bars.
12. Turn on the reactor.
13. Set the temperature 140°C and stirrer at 250rpm.
14. For sampling, stop the stirrer.
15. Wait for the catalyst to settle down.
16. Gently open the sampling valve and collect the sample.
17. Close the valve after sampling is done.
18. After the completion of reaction, switch off the motor and temperature controller.
19. Remove the reactor heating furnace.
20. Allow the vessel to cool down.
21. Once the reactor vessel is cooled, remove the ring by loosening the screws.
22. Remove the split-rings by loosening the bolts.

23. Take the sample.
24. Take the reactor vessel and allow it for cleaning.

The reactor was then cooled, unreacted carbon dioxide was released. The catalyst was separated by centrifugation and the products were isolated and analysed quantitatively by gas chromatography.

For comparative studies, experiments were also conducted in a similar manner using potassium hydroxide at same conditions.

# Chapter 4 Results & Discussion

## 4.1 Conversion of spent FCC catalyst to zeolite X

The spent catalyst obtained from FCC unit was converted to zeolite X by hydrothermal method. The spent catalyst contains varied components like Zeolite Y, ZSM-5, alumina and some metal impurities which were checked by XRD and ICP-OES respectively. The characterization of prepared zeolite was carried out using XRD and BET surface area and was also compared with reference sample and raw catalyst.

### 4.1.1 XRD

#### 4.1.1.1 Characterization of raw catalyst

The X-Ray diffraction of spent catalysts (calcined and uncalcined) is different (Figure 11). The uncalcined FCC catalyst with deposited coke during processing shows poor crystallinity. However, its diffractogram recorded after calcination, showed the well-defined crystalline peaks of zeolite Y and ZSM-5. Therefore, calcined FCC catalyst was used in the synthesis of the material.

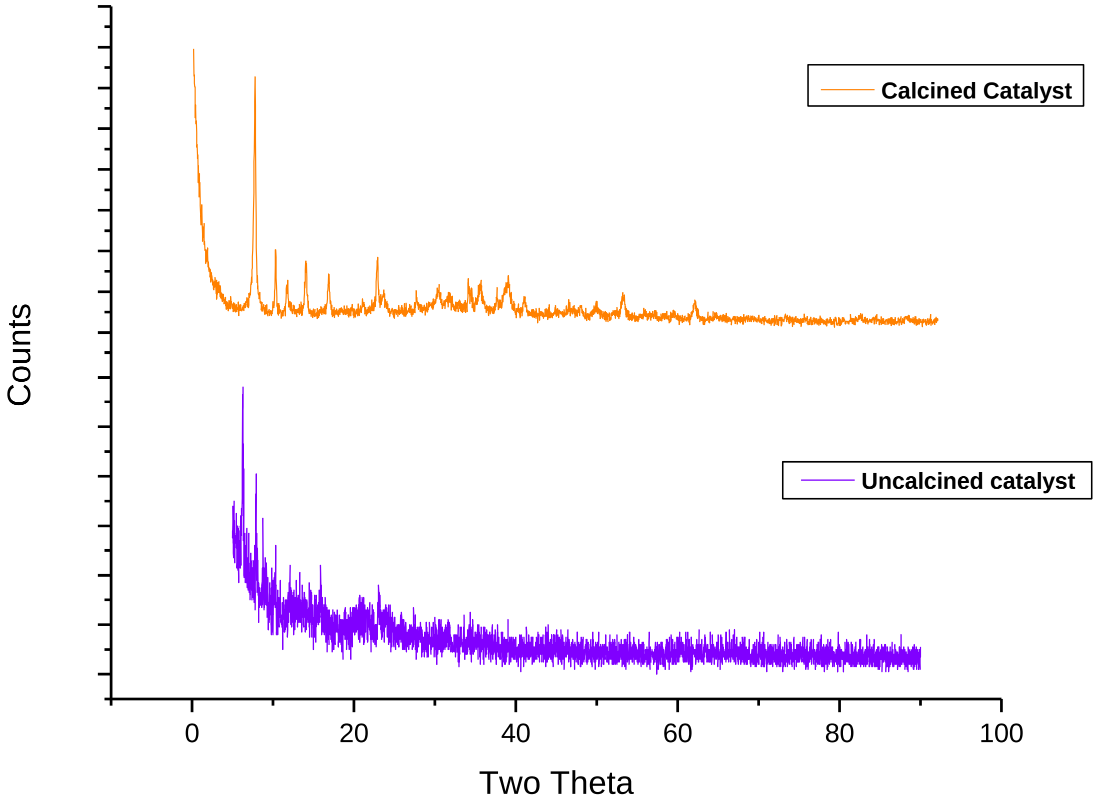


Figure 11: XRD pattern of Calcined FCC catalyst and Uncalcined FCC catalyst

### 4.1.1.2 Prepared catalyst over varied parameters

Numbers of synthesis were performed with varied parameters (Table 3) and their XRDs are shown in Figure 12. The XRD of (a) is reference sample i.e. commercial zeolite X, while that of (b-e) are synthesized samples. All the synthesized samples confirm formations of zeolite X with varying degree of crystallinity. The reaction conditions of synthesized samples are as follows (b): aqueous method and synthesis time and temperature were 48 h and 90ºC which shows amorphous structure. The reaction conditions of pattern (c) were same as pattern (b) but the temperature in this case was kept at 100ºC. The crystallinity was still very poor and in the later cases (d-f) the method was switch to hydrothermal method. The reaction conditions of (d) were24 h and 90ºC, this pattern show poor crystallinity indicating the insufficient time for crystallization. The reaction conditions of (e) were48 h and 90ºC, which shows good crystallinity of 93%. The reaction conditions of (f) were same as (e) but the synthesized time was increased to 72 h. There was not much difference between the crystallinity in the pattern of (e) and (f), so the reactions conditions of pattern (e) were considered optimized. So hydrothermal synthesis of zeolite X carried out at temperature 90ºC for 48 h are considered as optimized reaction conditions.

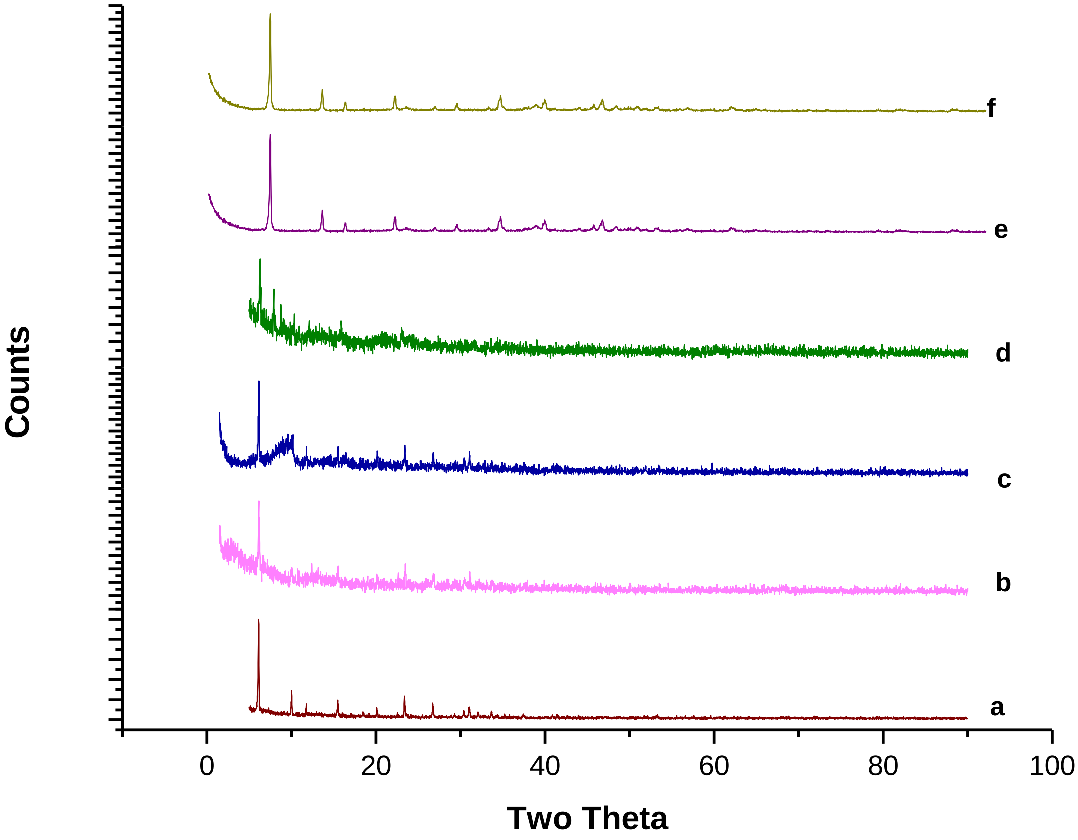


Figure 12: XRD of (a) reference sample and (b-e) synthesized sample from spent catalyst

### 4.1.1.3 Comparison of spent, commercial and prepared catalyst

The comparison of powdered XRD pattern of spent FCC catalyst, commercial Zeolite 13X and Zeolite X converted from spent FCC, which was synthesized by optimized method are shown in Figure 13. The same was compared with standard XRD pattern of commercially available Zeolite X. It can be determine that the identification peaks of zeolite X of FAU framework are at 2θ = 6.124, 10.019 and 11.758 which are also present in prepared zeolite. Thus it can be determine that structure of zeolite FAU is formed.

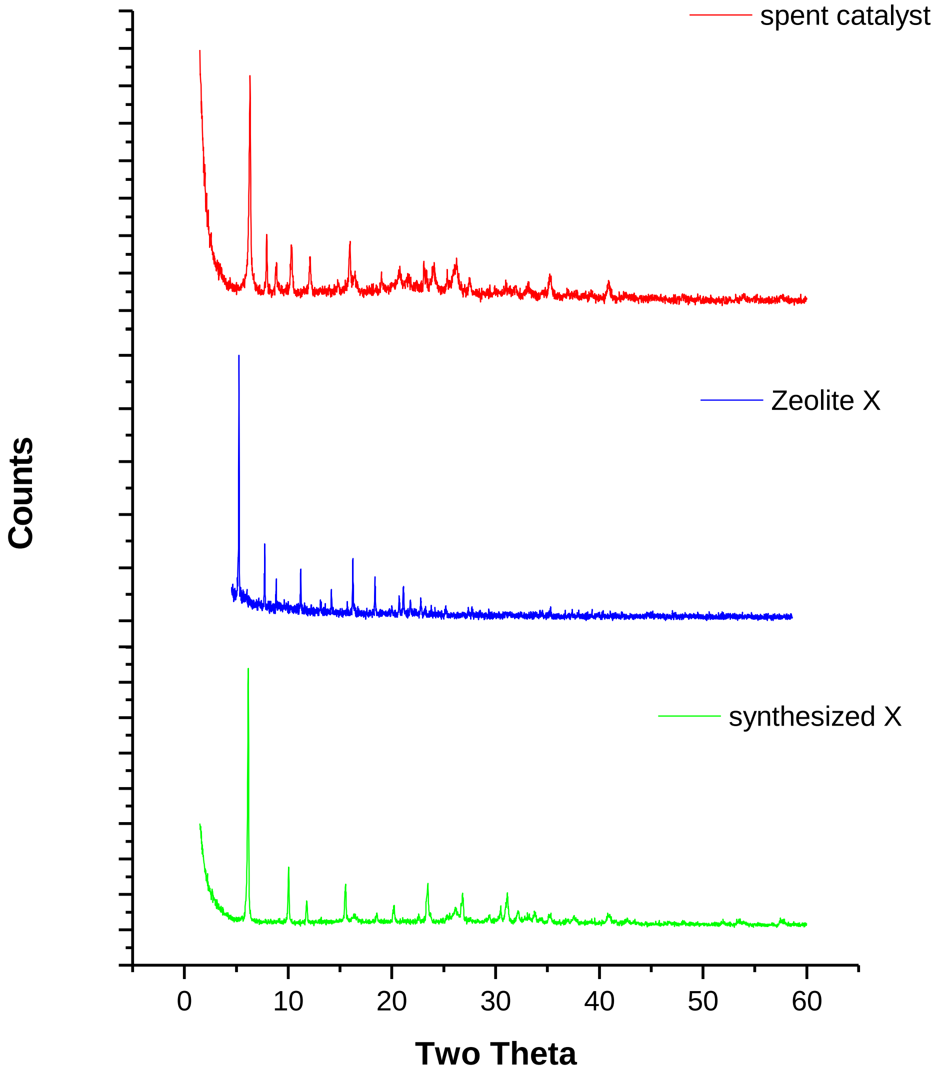


Figure 13: Comparison of Zeolite 13X, prepared catalyst and spent FCC catalyst

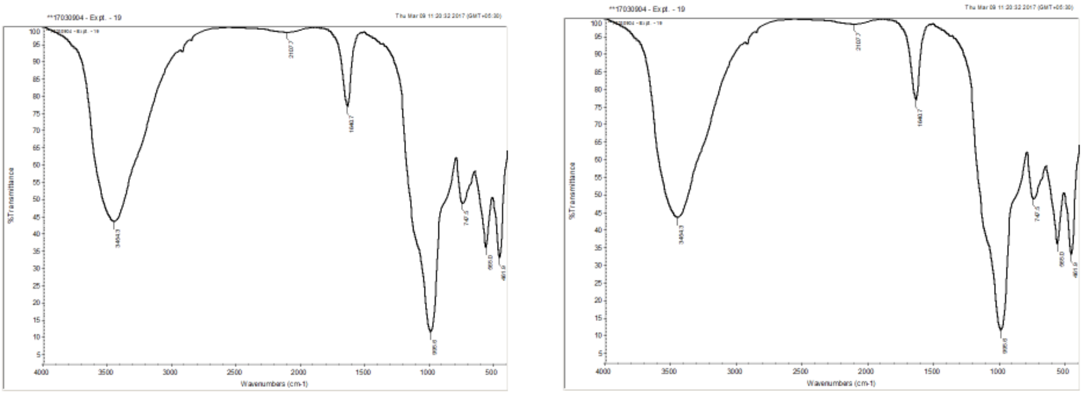
### 4.1.2 BET Surface Area

The surface area was carried out using the Micromeritics ASAP 2020. BET surface of the synthesized samples were compared with commercial catalyst and raw material are presented in Table 4. From the results, it can be easily concluded that the surface area of the synthesized samples is more than the Spent FCC catalyst. However it is slightly less than commercial sample, suggesting the presence of some amorphous phase which leads decrease in surface area.

Table 4: Surface Area of Samples

| Sr. No. | Catalyst | BET Surface Area ($m^2/g$) |
|---|---|---|
| 1. | Zeolite 13X | 727 |
| 2. | Spent FCC (uncalcined) | 180 |
| 3. | Spent FCC (calcined) | 184 |
| 4. | Synthesised zeolite X | 457 |

### 4.1.3 FT-IR



(a) (b)

Figure 14: FT- IR spectra of (a) commercial zeolite X and (b) Prepared Catalyst

Figure 14 shows the comparison of the FT-IR spectra between as synthesized conventional zeolite NaX and as synthesized zeolite X and raw spent catalyst. It can easily be concluded from the figure that the vibration bond T-O bending at 565 $cm^{-1}$, external linkage band in the range of 748 cm-1 and asymmetric stretch in the range of 955 to 1640 $cm^{-1}$ ascertain formation of zeolite structure. The above mention bands are found in all the three samples. Absorption band at 460 to 560 $cm^{-1}$reveals high crystallinity which confirms the XRD results.

## 4.1.4 ICP-OES

The elemental analysis of prepared material was performed using Inductively Coupled Plasma- Optical Emission Spectroscopy using microwave digester for sample preparation. The results are shown in the Table 5. The presence of Titanium, Iron and Sodium are high, clearly indicating that these impurities were carried forward during synthesis from spent catalyst.

Table 5: Elemental Analysis of Prepared Catalyst

| Sr. no. | Elements | Unit | Converted NaX |
|---|---|---|---|
| 1. | Al | % | 0.66 |
| 2. | Ti | % | 0.35 |
| 3. | V | mg/L | 144.40 |
| 4. | Cr | mg/L | 52.50 |
| 5. | Mn | mg/L | 4.40 |
| 6. | Fe | % | 0.32 |
| 7. | Co | mg/L | 44.24 |
| 8. | Ni | % | 0.20 |
| 9. | Cu | mg/L | 10.20 |
| 10. | Zn | mg/L | 52.50 |
| 13. | Na | % | 0.44 |
| 14. | K | mg/L | 345.60 |
| 15. | Ca | mg/L | 177 |
| 16. | Mg | mg/L | 101.11 |
| 17. | Si | % | 0.22 |

## 4.2 Zeolite Preparation using Filtrate of previous synthesis

In order to make effective use of alkali, the first filtrate of prepared catalyst was collected and titrated against oxalic acid to evaluate its strength. Part of filtrate was also tested by inductive coupled plasma optical emission spectroscopy (ICP-OES) to check amount of alkali. Based on strength of alkali, the balanced required amount of NaOH was added to the filtrate and used in the second batch of conversion of spent FCC catalyst by following same procedure. Product collected was filtered and washed with water. After drying at 120°C, the X-ray diffraction was studied. The second use of filtrate enables to save 50% of NaOH and 75 % water required for the conversion of zeolite X from spent FCC catalyst.

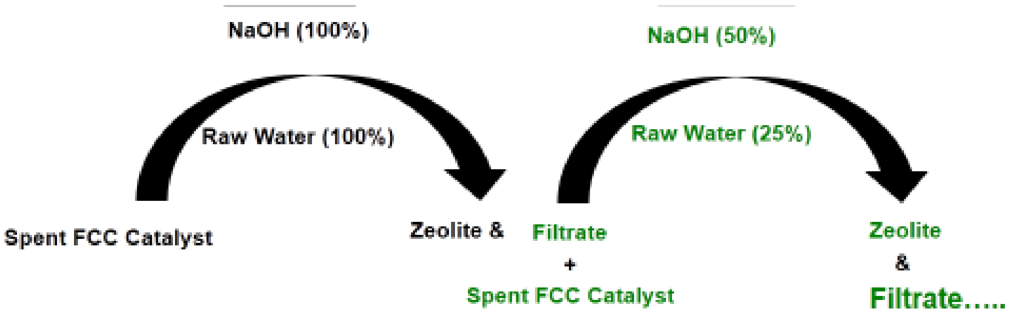


Figure 15 Reuse of filtrate to convert spent catalyst

The elements that are present in the filtrate are listed in Table 6.

Table 6: Elements in Filtrate

| Elements | Ppm | Total amount in Filtrate (mg) |
|---|---|---|
| Al | 6.082 | 170.2 |
| Ti | 0.016 | 0.448 |
| V | 0.74 | 20.72 |
| Cr | 0.002 | 0.06 |

| | | |
|---|---|---|
| Mo | 0.009 | 0.25 |
| Pb | 0.002 | 0.06 |
| Na | 501.5 | 14042 |
| K | 0.465 | 13.02 |
| Li | 0.002 | 0.06 |
| Sr | 0.023 | 0.64 |
| La | 1.485 | 41.58 |

## 4.3 Catalyst Preparation

The prepared zeolite X undergone exchanged with Li and Cs. The elemental analysis of exchanged sample was carried out with ICP-OES and later the amount of exchange was calculated with respect to sodium leaching from zeolite. The commercial zeolite X also undergone exchanged with Fe and Ni, in order to check the performance as a promoter which is discussed in sub section 4.6. The percentage exchange of all these samples is shown in the Table 7.

Table 7: Ion Exchange of Prepared Zeolite

| Sr. No. | Catalyst | % exchange |
|---|---|---|
| 1. | Li-exchanged with converted X | 71.8 |
| 2. | Cs-exchanged with converted X | 2.9 |
| 3. | Fe-exchanged with Zeolite X | 0.01 |
| 4. | Ni-exchanged with Zeolite X | 0.15 |

## 4.4 Catalyst Evaluation for Styrene Oxide to Styrene Carbonate Reaction

The cycloaddition reaction contains styrene oxide of 10 mmol, DMF of 20 ml and synthesized zeolite X of 250 mg. Initially the pressure of carbon dioxide was kept at 7 bars and then the temperature was slowly increased to 140°C.Initially reaction was carried out using converted NaX as catalyst, followed by Li and Cs exchanged converted zeolite X to check the effect of different metal on the said reaction. Table 8 shows performance of these catalysts towards carbonation of styrene oxide. Results shows converted NaX shows better results compared to Li and Cs counterparts. Hence converted NaX was further used for kinetic study for said reaction to get optimized parameter

Table 8: Catalyst Evaluation of synthesized and ion exchanged catalyst

| Sr. No. | Catalyst | Conversion | Yield |
|---|---|---|---|
| 1. | Converted NaX | 19.8 | 10.7 |
| 2. | Li-exchanged with converted NaX | 10.5 | 4.3 |
| 3. | Cs-exchanged with converted NaX | 18.5 | 2.8 |

Among the Li and Cs, the desired results were obtained by converted NaX achieving the yield of 10.7%. Therefore, the converted NaX was selected for further study.

### 4.4.1 Reaction Mechanism of styrene oxide to styrene carbonate

Carbonation reactions are of two types, one involves carbon dioxide at high pressure and releases when pressure is reduced and second, which converts it into chemical compounds. The present study discusses the chemical fixation of carbon dioxide to value added products using heterogeneous catalyst. The synthesis of cyclic carbonate via cycloaddition of carbon dioxide to epoxide is one of the effective routes for the chemical fixation of carbon dioxide [35]. The reaction mechanism is shown below:

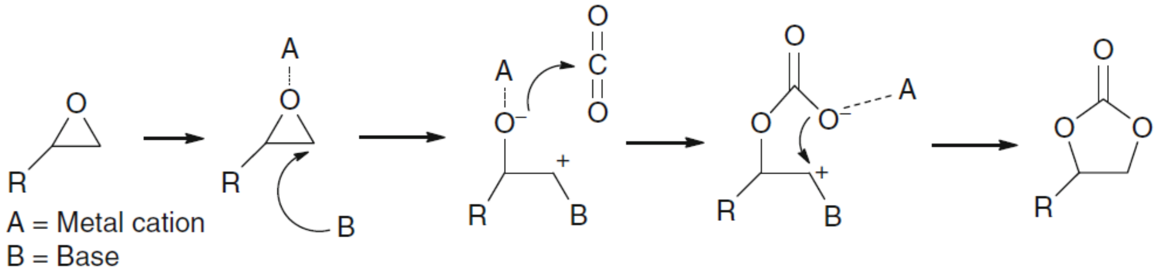


Figure 16 Reaction mechanism of $CO_2$ to Epoxide

The Lewis acidic centre of metal cation would intact with the oxygen molecule of the epoxide, and the base would assault the less hindered carbon atom of the epoxide ring. Such supportive activation of the epoxide would make the ring opening easier, being the reason for the promotional effects of the base. It is also possible that base activates a $CO_2$ molecule. In the absence of organic bases, the oxygen atoms on the metal oxide surface would act as Lewis base, but it would be less effective than organic base [31].

## 4.5 Kinetic Study

### 4.5.1 Effect of amount of catalyst

The effect of catalyst loading was studied using varied quantity of synthesized catalyst like 150 mg, 250 mg and 350 mg at 140°C and 14 bars pressure at 250 rpm. It is evident from the Table 9, that both, conversion of styrene oxide and yield of styrene carbonate achieved at 250 mg were comparatively higher than under other two operating conditions. We also observed that an increase in catalyst loading resulted in an increase in Styrene oxide conversion. Since yield of styrene carbonate was the major criteria for proceeding the reaction, 250 mg was selected for further evaluation.

Table 9: Effect of amount of catalyst

| Amount of Catalyst (mg) | Conversion (%) | Selectivity (%) | Yield (%) |
|---|---|---|---|
| 150 | 30.9 | 46 | 14 |

| | | | |
|---|---|---|---|
| 250 | 43.6 | 70.6 | 31 |
| 350 | 41.4 | 40.5 | 16.8 |

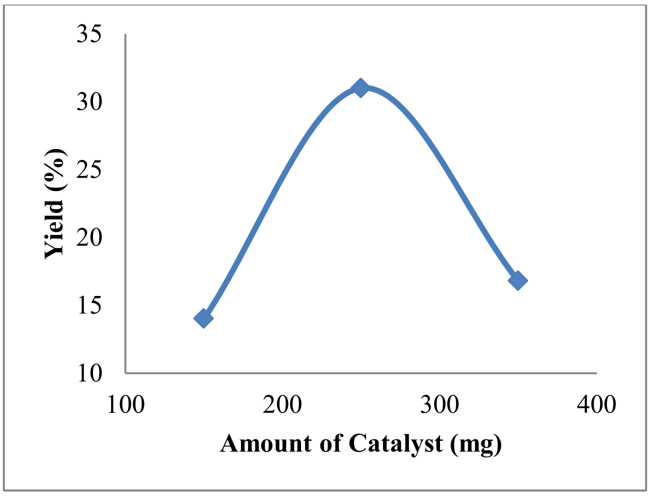


Figure 17: Optimizing amount of catalyst

### 4.5.2 Effect of Temperature

Four reactions were carried out using 250 mg of catalyst at 100°C, 120°C, 140°C and 160°C at 250 rpm. Styrene oxide conversion was found highest at 160°C, slightly higher at 140°C. However, the yield of Styrene carbonate was nearly similar at 140°C and 160°C. Hence 140°C temperature was considered optimum and used for further evaluation. The conversion of oxide increases with the increase in temperature as expected.

Table10: Effect of Temperature on carbonation reaction

| Sr. No. | Temperature (ºC) | Conversion (%) | Selectivity (%) | Yield (%) |
|---|---|---|---|---|
| 1. | 100 | 4 | 35 | 1.4 |
| 2. | 120 | 17.5 | 51.5 | 9 |

| | | | | |
|---|---|---|---|---|
| 3. | 140 | 44 | 70.5 | 31 |
| 4. | 160 | 80.2 | 40.9 | 33 |

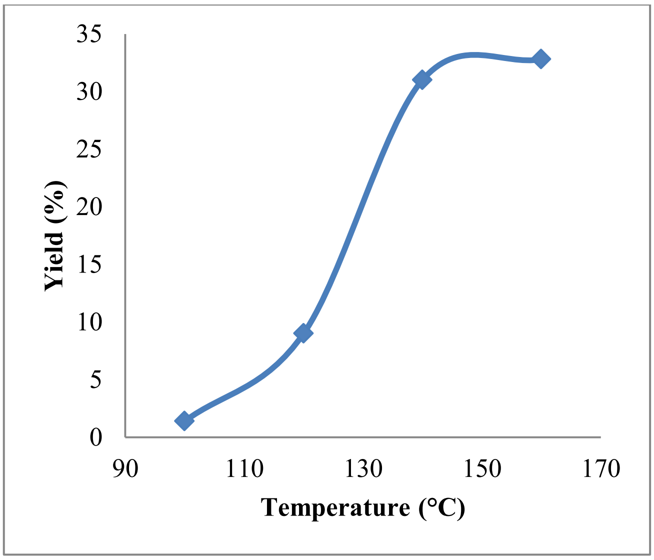


Figure 18: Effect of Temperature on carbonation reaction

### 4.5.3 Effect of Time

The reaction was monitored over a period of seven hours. The other reaction conditions were 120ºC, 12 bars and 250 rpm. The samples were analysed by Gas Chromatography at 3 h, 5 h and 7 h. Initially no catalytic activity was observed till 3 h. However, after 3 h, slowly the conversion started. Since there was no significant improvement in conversion of styrene oxide after 5 h and 7 h reaction time, the reaction time of 5 hours was kept as optimum for further study.

Table11: Effect of Reaction time

| Reaction Time | Conversion (%) | Selectivity (%) | Yield (%) |
|---|---|---|---|
| 0 h | 0 | 0 | 0 |
| 3 h | 9 | 70 | 6.5 |

| | | | |
|---|---|---|---|
| 5 h | 17 | 73 | 13 |
| 7 h | 18 | 77 | 14 |

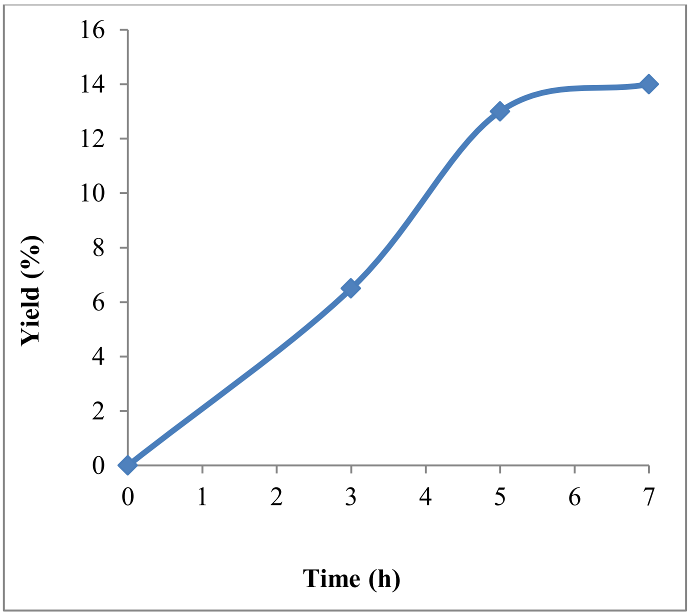


Figure 19: Effect of reaction time on carbonation reaction

### 4.5.4 Recycle Studies

The recyclability test was done by reusing the catalyst after its each cycle. After the reaction, the catalyst was collected, washed with acetone and dried at 120°C in oven for 24 hours. The catalyst before its use was activated at 550°C in order to remove the coke deposition (2.8 %, Figure 22). The catalyst was successfully recycled at least 3 times without any change in crystallinity. However, the yield decreased in second cycle up to 20% but later it remained constant in remaining cycles studied. The reason could be the content of sodium in synthesized catalyst was washed out to some extent in the second cycle which was enhancing the reaction.

Table 12: Recycle Studies of the prepared Zeolite

| Sr. No. | Catalyst | Conversion (%) | Selectivity (%) | Yield (%) |
|---|---|---|---|---|
| 1. | Freshly prepared Zeolite | 45 | 60 | 28 |
| 2. | Reusing Catalyst 1sttime | 32 | 59 | 20 |
| 3. | Reusing catalyst 2ndtime | 31 | 54 | 19 |

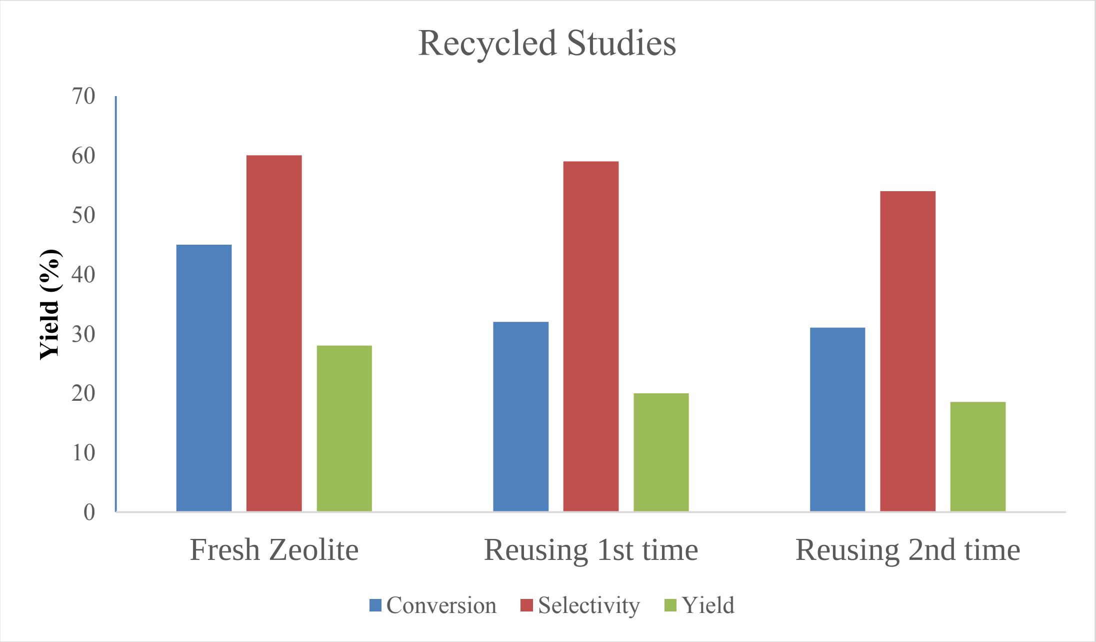


Figure 20: Recycle Studies for the prepared reaction

The catalyst was recycled successfully at least three times and there is no change in crystallinity of recycled catalyst. The XRD pattern of recycled catalyst is shown in

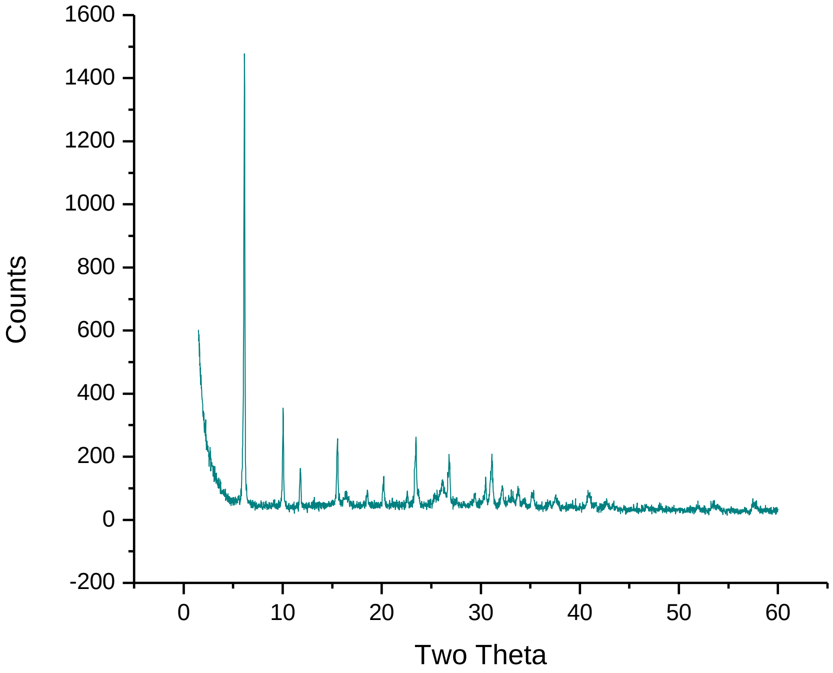


Figure 21: XRD pattern of Recycled Catalyst

TGA analysis of synthesized zeolite NaX which is used twice is shown in Figure 22. As the figure shows there was a weight loss of around 10% is observed when sample is heated from RT to 900 °C. The weight of initial 12.83 mg is decreased to 11.56 mg at the final stage of heating. There was weight loss of 6.5% (0.83 mg) and 2.8% (0.5mg) at 300ºC and 530ºC respectively. The earlier loss in weight could be due to presence of any residual reactant or solvent used during reaction and later could be due to the coke deposition on prepared catalyst.

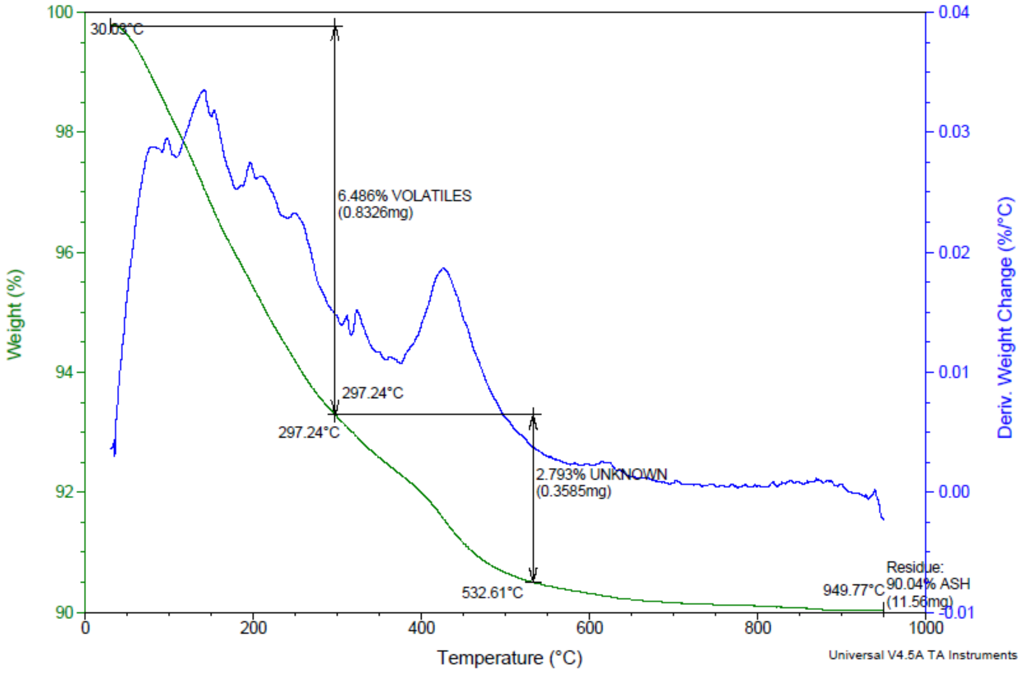


Figure 22: TGA of 2nd Cycle

## 4.6 Catalyst Evaluation by metal exchange with reference sample

The prepared catalyst showed promising results because of high surface area and presence of metal impurities which were carried forward during synthesis. If surface area was the only reason for the good catalytic activity than zeolite X could have shown the best results as it possess more BET surface area (727 $m^2/g$)than the prepared catalyst (457$m^2/g$). The metal impurity present in the prepared catalyst may be one of the reasons for this changed behaviour. In order to verify this effect, the metal impurities were deliberately added on the reference catalyst. As the prepared zeolite contains high amount of iron and nickel of 0.32 and 0.20 percent respectively (Table 5), we tried to load exactly same amount of metals with the commercial zeolite X which practically couldn’t happen (Table 7) and results are presented in Table 13.

Table 13: Performance of Metal Loading on commercial zeolite X

| Sr. No. | Catalyst | Yield (%) |
|---|---|---|
| 1. | Reference sample NaX | 12 |
| 2. | Fe-exchanged zeolite X | 7 |
| 3. | Ni-exchanged zeolite X | 10.2 |

The individual effect of metal couldn’t proceed the reaction as expected but the synergetic effects of these metals may enhances the reaction. All these depend on the amount of metal loaded, cation locations and its accessibility and alkalinity of prepared zeolite.

# Chapter 5 Conclusions

The spent FCC catalyst was effectively converted to crystalline zeolitic material using hydrothermal method. Depending on the synthesis conditions and activation treatment, it is possible to convert the exhausted catalysts into alumina rich zeolite type X. The XRD pattern of calcined and uncalcined FCC catalyst reveals the use of calcined FCC catalyst for the synthesis as it possesses more crystallinity. The results of powder XRD and BET surface area,confirms the FAU structure of Zeolite X. The XRD pattern of prepared catalyst reflects broad peaks that are identical to commercial sample. About 60-65% conversion and 93% crystallinity is obtained for zeolite X synthesized with the spent catalyst. The lowering in crystallinity is attributed to the unconverted spent catalyst. The BET surface area of synthesized X was more than spent catalyst and less than pure sample, suggesting the presence of impurities in it. The elemental analysis of synthesized catalyst by ICP-OES suggests presence of impurities like Iron, Titanium and Nickel that are carry forward from spent catalyst during synthesis.

The filtrate of previous zeolite synthesis was used in the second batch which enables to save 50% of NaOH and 75 % water required for the conversion of zeolite X from spent FCC catalyst. This not only makes the effective use of alkali, but also makes the process more eco-friendly.

The catalyst performance was checked in conversion of styrene oxide to styrene carbonate. The average yield of 31% was achieved which is substantially higher that that shown by using spent catalyst and commercial NaX catalyst showing yield of 10% and 11% respectively. Thus the catalyst preparation was simple, inexpensive and works well at low pressure and temperature.

The probable reasons of high selectivity and high yield could be due to high surface area, crystallinity and presence of impurities. The impurities may act as promoter. Addition of the individual metal impurities in catalyst however, did not show improved performance in commercial NaX catalyst. Some more experimentation is required to understand this synergetic effect of these metals which enhances reaction.

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