

**SYNTHESIS, CHARACTERISATION AND
EVALUATION OF ZEOLITES FOR HYDROCARBON
CONVERSION**

A project report

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BONAFIDE CERTIFICATE

This is to certify that the thesis entitled “**SYNTHESIS, CHARACTERISATION AND EVALUATION OF ZEOLITES FOR HYDROCARBON CONVERSION**” submitted by Abu Taher Ali (R670215002), to the University of Petroleum and Energy Studies, for the award of the degree of **Master of Technology** in Chemical Engineering with Specialization in Process Design is a bonafide record of project work carried out by him under our supervision. The results embodied in this project review report are based on experimental work done at BPCL R&D. BPCL R&D reserves all rights to patent, publish and present the data as this work has been performed at BPCL R&D.

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ABSTRACT

Zeolite catalysts play a key role in refinery processes by converting petroleum fractions into high-grade fuels and lubricants. Zeolites are microporous zeolite frameworks consisting of silica and alumina frameworks. However the sole presence of micropores in these materials often imposes intracrystalline diffusion limitations, rendering low utilisation of the zeolite active volume in catalyzed reactions thus lowering the conversion of reactants and selectivity of products. In view of this, it is of outmost importance to develop frameworks where there is a good balance of microporosity and mesoporosity for achieving higher catalytic activity as well as better accessibility and diffusion within the zeolite channels. The combination of microporosity and mesoporosity in hierarchial zeolites could lead to better accessibility for reactants and products, leading to increased yield patterns at high throughput level.

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LIST OF EQUIPMENTS

S.No	Name of Equipment	Purpose
1.	Batch Reactor	Mixing /Gel formation
2.	Fixed bed reactor	Hydroisomerisation
3.	Gas Chromatograph Online	Separating compounds, checking purity
4.	Micromeritics ASAP 2020	BET Surface area, pore volume, pore size etc.
5.	Altamira TPD	Acidity
6.	X-ray diffraction	Phase, structure etc
7.	Magnetic Stirring	Heating and Mixing
8.	Calcination Unit	Removing Templates, making H ⁺

LIST OF SYMBOLS

°C	Celcius
Å	Angstrom (1×10^{-10})
Nm	Nanometer (1×10^{-9})
µm	Micrometer (1×10^{-6})
cm	Centimeter (1×10^{-2})
cm³	Cubic Centimeter
mg	Milligram
g/l	gram /liter
g/cm³	gram/centimeter cube
M	Molar
meq/100g	Milliequivalents/100gram

LIST OF ABBREVIATION

SDA	Structure Directing Agent
hr	Unit of Time in hour
ZSM	Zeolite Soconie Mobil
MTT	Mobil Twenty Three
SiO ₄	Silica oxide
AlO ₄	Aluminium Oxide
Al ₂ O ₃	Alumina
NaOH	Sodium Hydroxide
KOH	Potassium Hydroxide
FWHM	Line width at half the maximum
DMF	Dimethyl Formamide
TEOS	Tetraethyl Orthosilicate
H ₂ O	Water
Si	Silica
Al	Alumina
Na	Sodium
TPAOH	Tetrapropyl Ammonium Hydroxide
TBAOH	Tetrabutyl Ammonium Hydroxide
XRD	X-ray Diffraction
TPD	Temperature Programmed Desorption
BET	Braunaur, Emette and Teller
FCC	Fluid Catalytic Cracking
PBU	Primary Building Umit

SBU	Secondary Building Unit
OH ⁻	Hydroxyl Ion
GC	Gas Chromatograph

CHAPTER ONE

INTRODUCTION

1.1 Historical Background

The government has emphasized on improving environmental quality through better management particularly in air and water quality, solid waste management and as well as the utilization of cleaner technology. Zeolites can contribute to cleaner and safe environment in a great number of ways. In powder, detergents, zeolites have replaced the harmful phosphate builder, which have been banned in many countries due to the water pollution risks. In petroleum and hydrocarbon industry, the chemical process can be more efficient with zeolite as the catalyst, thus saving the energy and indirectly reduced the pollution. The processes can be carried out in fewer steps and minimizing unnecessary waste and by products. Furthermore, zeolite can act as the solid acids which could reduce the need for corrosive liquid acids and as redox catalyst and sorbents where they can remove atmospheric pollutants such as engine exhaust gases. Zeolite can also be used to separate harmful organics from water and removing heavy metal ions including those produced by nuclear fission from water.

Basically, Zeolites are hydrated aluminosilicates of the alkaline and alkaline earth metals with fully cross- linked open framework structures made up of corner sharing SiO_4 and AlO_4 tetrahedra. There are about 40 natural zeolites which have been identified during the past 200 years and more than 150 zeolites have been synthesized. The most common of natural zeolites are anaclime, chabazite, clinoptilolite, erionite, modernite, and phillipsite while as for synthetic zeolites; the most common are zeolites A, X,Y and ZSM-5. Both natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieves and catalytic properties.

1.2 Importance of research

A considerable research and development effort is being made to produce tailor made zeolite synthesis. This is because natural zeolites are rarely pure and contaminated to varying degree with other mineral like quartz, SO_4^- and amorphous glass. Thus for this reason natural zeolites are excluded from many important commercial applications where uniformity and purity are

essential. On the other hand synthetic zeolites could be manufactured in a uniform phase-pure state. Furthermore it is possible to produce desirable structure of synthetic zeolites like zeolite A, ZSM-5, Y, Mordenite, Beta, ZSM-22. ZSM-23 etc.

By better understanding on the mechanism responsible for zeolite formation from its precursor, tailor made zeolites can be manufactured. It is necessary to know the mechanism process since a desirable structure zeolite can be engineered as per to its application. The change made in synthesis process can affect the structure and type of zeolite produced. As an example, the varying degrees of Si concentration and the source of Si used can produce a different type of zeolite. Therefore, it is necessary to have a vast knowledge on its fundamental process because a specific tailor made zeolite depend on its application whether used as ion-exchanger for water and waste water treatment or as catalyst used in hydrocarbon industry.

1.3 Objective of the research:

The aim of the research is to synthesise zeolites and carry out their post synthesis modification To achieve this, following activities will be carried out:

- i. To synthesise zeolites from sodium aluminosilicate solution via hydrothermal solution gel process.
- ii. To carry out post synthetic modification of the synthesised zeolites.
- iii. To examine the characteristics of the synthetic zeolite produced (i.e morphology, physico-chemical, acidity, isomers and phase identification)
- iv. To evaluate the potential of the modified zeolite on hydrocarbon conversion.

1.4 Scope of the research:

The major aim of the work presented in this thesis is to investigate the synthesis of zeolite from sodium aluminosilicate solution and modification of synthesized zeolite,. The synthesis will be carried out under the confined hydrothermal conditions at certain temperatures for a particular period of time. In this study the sodium aluminosilicate solution was prepared by using silicate solution, aluminate solution (amount of alumina remains constant) and alkali. The alkali is a very good mineralizing agent and helps in creation of monomeric silica and alumina precursors which react to give the final zeolite. The solid is separated by filtration, washed

several times with distilled water and then dried over night in oven at 120°C. At the end, the solid product was recovered for further characterization and analysis.

In this study, the investigation on the post synthetic modification has been carried out by treating the zeolite with varying alkali concentration (0.2 to 0.6M). The alkali extracts the silica from the framework and the amount extracted depends on the time and temperature of the alkali treatment. Studies on surface morphology of the zeolite produced are carried out by SEM, while the identification of zeolite phases are carried out by using XRD. The surface area and acidity are obtained by using BET and TPD techniques.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The properties of hierarchical zeolites, i.e those combining the intrinsic microporosity with an auxiliary framework of mesopores, have sparked intense effort to improve the zeolite utilization in catalysis[21,22]. Among the numerous methods available to prepare the mesoporous zeolites, desilication by alkaline treatment is one of the most widely applied, established as a simple and effective approach [23,24]. Furthermore, the increasing number of zeolite families, prepared in hierarchical form by alkaline treatment (MFI [26], MTW [27], MOR [28], BEA [29], AST [30], FER [31], MWW [32], IFR [33],CHA [34], FAU [35], and TON [36]).

Desilication was first prepared by Groen et al. [38,39], who identified by applying NaOH treatment on MFI zeolites at a fixed condition, that a confined molar framework Si/Al ratio (25 to 50) for optimal intracrystalline mesopore formation exists. At higher Si/Al ratios, uncontrolled Silicon extraction occurs, resulting in the formation of larger pores. For low Si/Al ratio, silicon extraction is hampered resulting in limited extra mesoporosity. Consequently, framework aluminum was coined as ‘pore-directing agent’ (PDA), due to its regulatory effect on silicon leaching. Apart from Al³⁺, other trivalent heteroatoms in lattice positions (Fe³⁺, Ga³⁺, B³⁺) also proved successful in exerting the role of PDA [40].

Apart from optimization of the desilication treatment, significant progress concerning the in-depth characterization and categorization of hierarchical zeolites has been achieved. The final hurdle to achieve full compositional flexibility in the preparation of mesoporous MTT zeolites by desilication requires tackling the low Si/Al range. To date, mesoporous Al-rich zeolites are mostly prepared via Top Down and Bottom Up approaches [20].

Even though there have been so many synthetic strategies proposed and demonstrated to obtain hierarchical zeolite structure, they can be classified into two major categories namely “Top Down” and “Bottom Up” approaches. The top down approaches starts with microporous zeolites that are then post synthetically modified to create hierarchical zeolite structures. Dealumination and desilication represents the two most frequently investigated post synthesis routes for the top down approach. Alternatively, the bottom up approach builds hierarchical zeolites through the engineering of microporous and mesoporous domains. The bottom up

approach is considered to be more synthetically challenging as it often involves complicated templating routes, such as hard and soft templating.

In general, conventional zeolites are crystalline materials constructed typically 6,8,10 or 12 tetrahedral atoms (T-atoms) arranged as rings with pore sizes less than 1 nm. These are termed as small, medium and large pore zeolites, terms identified from the perspective of their microporous region. For these microporous zeolites, the active sites becomes inaccessible when reactants with size greater than the dimension of the pores are present due to the strong diffusion limitations resulting from the relative rigid zeolite framework. The diffusion limitation also increases the possibility of coking which deactivate the catalysts and also shorten their catalytic life.

To alleviate these limitations, hierarchical zeolites were conceived with the aim of adding secondary porosity to traditional zeolites. Generally hierarchical zeolites should facilitate access of bulky reactants to catalytically active sites while simultaneously preserving the acidity and crystallinity of the original conventional zeolites.

2.2 Structures

Zeolite structure contains two types of building units namely primary and secondary. A primary building unit (PBU) is simpler building compared to secondary one. This is because in PBU a tetrahedron of (TO₄) of 4 oxygen ions surrounding a central ion of either Si⁴⁺ or Al³⁺. These PBU are linked together to form a three dimensional framework and nearly all oxygen ions are shared by two tetrahedra. Zeolite framework is based on an extensive three dimensional network in which the polyhedral sites, usually tetrahedral are linked by oxygen atoms.

Different combinations of the same secondary building unit (SBU) may give numerous distinctive structural polyhedra formed from smaller ring units. The net negative charge on the framework is balanced by the presence of cations in most cases Na or K which are situated in cavities within it. The zeolite framework is almost structurally independent of the (Na, Ca, K) cations and as the later do not fill all the cavities. Figure 1 shows the basic structure of zeolite framework. The complexity of zeolite structure is due to the various ways in which the tetrahedral groups are linked by the common sharing of oxygen ions to form polynuclear complexes.

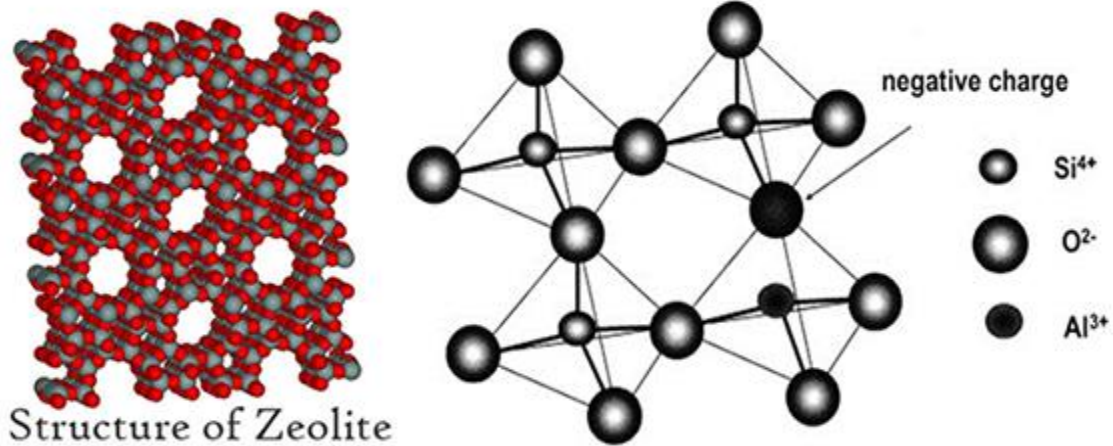


Figure 1 Basic structure of Zeolite framework

2.3 Properties

Zeolites have unique properties which are dependent upon its crystal structures and thus the inner cavities such as the pores, their size and form. Many of these properties are especially desirable for environmental protection, such as cation exchange capacity, adsorption properties, acid stability, ammonium capacity and wet attrition resistance. Table 1 shows broad range of physico-chemical properties of zeolite and other molecular sieves.

Table 1: Properties of zeolites

Property	Range
Pore size	~4 to 50 Å
Pore shape	Circular, Elliptical
Dimensionality of pore system	1-D, 2-D, 3-D
Pore configuration	Channels, Cages
Surface properties	Hydrophilic, Hydrophobic (High Silica)
Void volume	Less than ~50%
Framework oxide composition	Si, Al

2.4 Synthesis of Zeolites:

Occurrence of natural zeolites has inspired scientists to develop synthetic approaches. The processes by which zeolites were formed have been replicated and modified in order to obtain the same or different materials, sometimes, with totally different properties as a final product.

Synthetic zeolites on the other hand, hold some advantages over their natural analogs. The synthetic zeolites can, of course, be manufactured in a uniform phase-pure state. It is also possible to manufacture desirable structure which does not appear in nature such as zeolite A. Since the principal raw materials required to manufacture are silica and alumina, are among the abundant mineral components on earth. Finally zeolite manufacturing processes engineered by human kind requires significantly less than 50 to 50,000 years as prescribed by nature.

2.4.1 The Hydrothermal Method

The hydrothermal concept is defined as “heterogeneous reactions to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions”. Hydrothermal methodologies, as the name suggests, usually are carried out using water under relatively high pressure levels (1-100 MPa), generally autogenous, and at high temperature (100-200 °C). Although a more recent definition states that hydrothermal procedures are carried out above ambient temperature and 1 bar. In this method the pressure increases as a consequence of temperature, the pressure at the interior of the reactor is rarely known but the value that is taken as reference corresponds to the vapour pressure at that temperature. Sometimes when a different solvent is replacing water the method is generically called solvothermal. Some scientists have gone further, calling the process according to the solvent used, for instance; glycolthermal and ammonothermal.

A hydrothermal environment requires the presence of alkaline media in the form of basic solutions. The fundamental species needed for the formation of zeolites in laboratory are: a source of silica (SiO_2), a source of alumina (Al_2O_3), an alkaline media, an organic template and water. All are put together to react under high temperature conditions to achieve the crystallisation after an ageing period. A typical process for the zeolitic materials production following the hydrothermal method:-

1. Amorphous sources of silica and alumina are dissolved in highly alkaline solutions containing NaOH or KOH. The sources selection is vital since the formation process involves the dissolution and remineralisation of silica and alumina species.
2. Heat is applied to previously formed mixture which often takes place inside of a sealed autoclave. The purpose of this is the generation of pressure to accelerate the formation of products.
3. The crystallization starts after an initial induction period, during which the process of dissolution and remineralisation of silica and alumina species takes place.
4. After the induction time, gradually almost all the material is converted into crystals, this stage is the known as the crystallisation period.
5. Final stage occurs after crystallisation, the recovery is done by filtration, washing and drying. If templates were used, calcination process at high temperature is carried out to remove them.

All scientific and technological developments in the zeolite field have been achieved thanks to the manipulation and exploration of several key factors. In general, the main factors to consider in zeolite and zeolite-like synthesis are composition, reaction variables (such as time and temperature). These concepts are described below:

2.4.2 Factors affecting Zeolite Synthesis

Following factors influences the crystalline zeolite structure

1. Composition of the reaction mixture.
2. Nature of reactants and their pretreatments.
3. Initial and final pH of the system.
4. Temperature of the process and its variation with time (if any).
5. Time allowed for the reaction to take place, including the calcination time.
6. Mixture, whether homogeneous or heterogeneous.
7. Seeding.
8. Template molecules (if any).

2.4.3 Composition of the Reaction Mixture:

The composition of the reaction mixture is one of the most important factor governing the product properties. These includes:

- i. Silica to alumina ratio.
- ii. OH ion concentration.
- iii. Inorganic cations.

i. $\text{Si O}_2 / \text{Al}_2 \text{O}_3$ in the gel phase constraints the framework composition of the zeolite. The ratio often determines the candidate frameworks in exploratory zeolite crystallization. The hydrophobic / hydrophilic nature of the zeolite is also affected by this ratio as Al is hydrophilic and Si is hydrophobic. Also, high Al contents can give higher acidic sites, which are useful for many applications. Zeolites with higher silica / alumina ratio are used for catalytic applications in cracking and isomerization. As the Al content is increased the acid resistance & thermal stability of the zeolite reduces. These effects can be summarized as follows:

Increasing the silica / alumina ratio affects following physical properties of the zeolite:

- a. Increases acid resistance.
- b. Increases thermal stability.
- c. Increases hydrophobicity.
- d. Decreases affinity for polar adsorbents.
- e. Decreases cation content.

Decreasing the silica / alumina ratio affects following physical properties of the zeolite:

- a. Increases hydrophilicity.
- b. Increases cation exchange properties.
- c. Decreases the pore size for same numbered ring, as Al has lower atomic radius than Si.

Also depending on the phase diagram, this ratio can vary the nature of the final zeolite.

ii. **Hydroxide ion concentration:** It functions as structure director through control of the degree of polymerization of silicates in solution. OH ion modifies the nucleation time by influencing transport of silicates from the solid phase to solution. It enhances the crystal growth and controls the phase purity. In a study⁷ it was found that the OH/Si ratio influences the pore size. i.e. higher the ratio, wider were the pores.

iii. **Role of Inorganic Cations:** Inorganic cations are defined as species, upon addition to the reaction mixture, crystallization is induced of a specific zeolite structure that could not be formed in the absence of the agent. These cations are used in the zeolite synthesis for following reasons:

- a. They act as structure directing agents.
- b. They balance the framework charge.
- c. They govern the morphology of the zeolite.
- d. They affect the crystal purity
- e. They also affect the product yield.
- f. These agents determine which of the competing frameworks is actually formed.

2.4.4 Nature of Reactants

The sol-gel synthesis is carried out with inorganic as well as organic precursors. It is seen that the properties of the product zeolites are influenced by the precursor. The final compound has approximately the same chemical composition, but the crystalline structures of the two products, using inorganic and organic precursors, were substantially different. The inorganic precursors yielded more hydroxylated surfaces whereas the organic precursors easily incorporated the metals into the network. This is a very important observation from the viewpoint of the catalysis and separations.

2.4.5 Process Temperature

The rate of crystallization is directly proportional to temperature while the rate of nucleation is inversely proportional to temperature. As both the processes undergo simultaneously for large period of time, the operating temperature need to be optimized for maximum zeolite yield. The reaction mixture, being in disordered state, is at higher entropy than the crystalline, ordered state.

Usually, zeolites are synthesized below 350°C, with some exceptions. Higher temperatures generally yield more condensed phase species. Temperature influences several factors in zeolite synthesis; it can alter the zeolite phase obtained as well as change the induction period before the start of crystallization. This induction period decreases with increasing temperature.

2.4.6 Reaction Time

In the sol-gel processing of zeolites, the reaction mixture forms gel very quickly. This gel, after some time phase separates into two phases, solid and liquid, with increase in the mixture density. The solid precipitates from the gel. This solid is the crystalline material, the zeolite. These observations indicate that the reaction mixture forms a metastable state, which splits into two stable states, one of which is the crystalline solid phase. It is very important to control the time, because the same reactants may yield different products at different times at same process conditions.

The optimization of time is very important in the industrial manufacturing of the zeolites. When only one phase is obtained, optimization is maximization of the crystallization over short period of time. But difficulties arise when more than one metastable zeolite (or non zeolite) phases are observed. Crystallization parameter must be adjusted to minimize the production of the other phases while also minimizing the time needed to obtain the desired crystalline phase.

2.4.7 p^H of the reaction mixture

The zeolite synthesis via sol-gel process is carried out in alkaline p^H (> 10). The p^H of the reaction mixture does not relate directly to the total OH content of the system, but p^H does appear as an important parameter in the synthesis of the zeolites in terms of the presence of free OH in the system.

A marked change in pH is noted to accompany crystal formation. A simultaneous increase in p^H of the system can be observed with crystallization. This increase in pH is the indication that the SiOH in colloidal state incorporates in the framework in the form of SiO₂. This is due to SiOH being acidic in nature.

The p^H of the system is also very important to stabilize the sol. It also controls the particle size.

2.5 Preparation of Hierarchical micro-mesoporous zeolite by hydrothermal treatment:-

Hierarchical porous materials are defined as materials containing two or more porosity levels in its structure.. Hierarchical materials are also those that contain different particle size ranges within the same body. The classification of the hierarchical zeolitic materials within three categories: a) hierarchical zeolite crystals, b) zeolite with nanosized crystals and c) supported zeolite. A graphical description is shown in figure 2.

The desirable configuration of a hierarchical porous structure is having the best features of three porosity levels –micro, -meso, -macro i.e an enhanced activity, increased internal and external surface area, high exchange capacity, an improved mass transport through the materials interior, high crystallinity and also therefore higher stability.

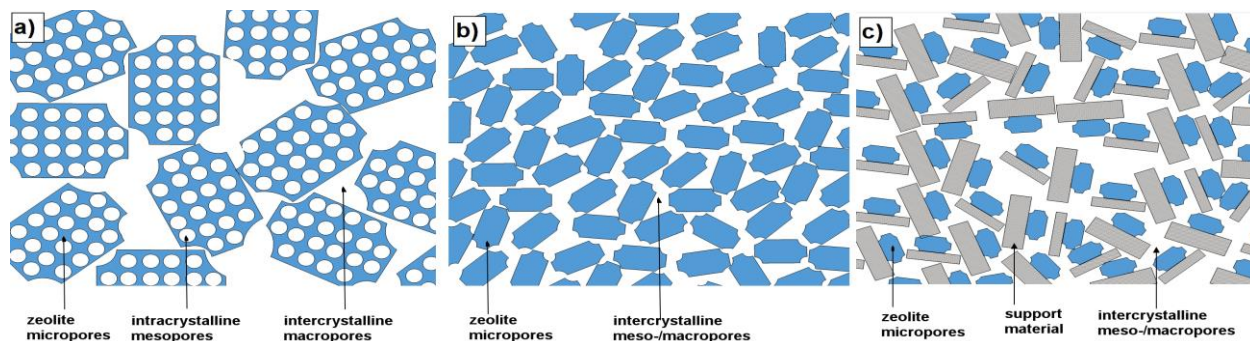


Figure 2: Three different zeolite hierarchical configurations a) Hierarchical zeolite structure , b)nanosized zeolite crystal and c) supported zeolite crystals.

2.5.1 Different Strategies in Zeolites Hierarchization:-

Different methods have been developed for synthesizing hierarchial zeolites: a) Constructive and b) Destructive approaches routes include the modification of the synthesis protocol resulting in zeolite nanocrystals, zeolites including a secondary template for mesopore formation, or synthesis of zeolite composites.

2.5.1.1 Destructive zeolite synthesis strategies:-

In general, top down synthesis approaches begins with existing microporous zeolites that are then post synthetically modified to create hierarchical zeolite structure. Dealumination is a well known post synthetic treatment for zeolites that are first reported by Barrer et al in the early 1960s to extract alumina from clinoptilolite with mineral acids[41]. Mesopores may be

introduced into the zeolite crystals by a destructive chemical post-synthesis modification by means of selective extraction of structure atoms from the zeolite framework. As zeolites are commonly aluminosilicates, the most studied demetalation methods are dealumination and desilication.

Dealumination:- Dealumination accounts for the most useful and widely used demetalation process in industry [44–49]. It can be achieved by hydrolysis of the Al-O-Si bonds of the zeolite framework through calcination,[50–52] steaming, acid leaching,[53, 54] or chemical treatment. Originally, dealumination treatments were performed to control the acid-site concentration and strength by increasing the Si/Al ratio of low-silica zeolites. It has been shown, however, that during this process, defects appear to form new mesoporosity. More detailed literature review on the generation of mesopores in zeolites by various dealumination methods and detailed characterization, as well as its impact on catalysis are discussed in a review by Van Donk et al [42].

Dealumination by calcinations:- For zeolites synthesized by use of an organic template, the calcinations under oxygen is the first post-synthesis treatment that needs to be performed to obtain an active stable zeolite. Depending on the calcination conditions and the zeolite type, part of the aluminum atoms can be removed from the framework to form extra-framework aluminum (EFAI).[50–52] The bulk Si/Al ratio does not change, as the aluminum species remain in the zeolite channels, whereas the framework Si/Al ratio increases. A mild acidic treatment can be applied to dissolve EFAI to establish the final micro- and mesoporosity without further extraction of framework aluminum.[81, 55]

Dealumination by acid leaching:- Generally, a mild acid leaching is used after calcination or steaming to remove amorphous materials in the form of soluble oxo-anions from the pores.[53, 54, 82, 57] However, more concentrated aqueous acids are also efficient hydrolyzing agents of the Si-O-Al bonds and can extract aluminum directly from the zeolite framework, leaving defects in the porous structure.[52, 58, 60–63]. In both cases, mineral acids, such as nitric, hydrochloric, or sulfuric acid are used, as well as organic acids, such as oxalic, acetic, or tartaric acid. Clearly, the nature of the acid and the zeolite structure can be of great influence on the effectiveness of this method. Calcined mordenite treated with oxalic acid shows a higher bulk Si/Al ratio and

fewer mesopores than if treated with HCl. [53]. Lee et al.[59] showed the importance of pH during dealumination of zeolite NaY with hydrochloric acid. Above a pH of 2.3, dealumination did not occur, whereas below a pH of 0.5 dealumination was completed.

Desilication by alkaline leaching:-

Desilication is another well-known demetallation approach, which consists of the selective extraction of silicon atoms from the zeolite framework. Recent reviews give a good state of the art summary on the subject.[43, 64] This technique has been known for a long time to yield lower Si/Al ratios with only small changes in framework acidity,[65, 66] but only recent studies have demonstrated the possibility to obtain mesoporous zeolites, more or less controllably, depending on the mineralizing agent.[67–70] Extraction of silicon atoms leads to a significant amount of extra porosity, preferentially initiated at boundaries or defect sites of the zeolite crystals,[67, 83, 84] with preserved structural integrity. Moreover, it has been demonstrated that there exists an optimal Si/Al ratio for this method, which, in the case of ZSM-5, was proven to be in the range of 25–50 (Figure 3).[43, 67, 72, 73] The results indicate that the charge on the lattice aluminum prevents the extraction of neighboring silicon of the zeolite framework, as suggested by Cizmek et al [66]. Hence, the presence of high concentrations of Al in ZSM-5 prevents the extraction of Si from the framework; on the other hand, for ZSM-5 with a Si/Al ratio higher than 50, no selective extraction and, therefore, no selective mesopore formation occurs. With NaOH treatment, surface areas up to 250 m²/gm and a broad pore size distribution around 10 nm can be obtained.[73]

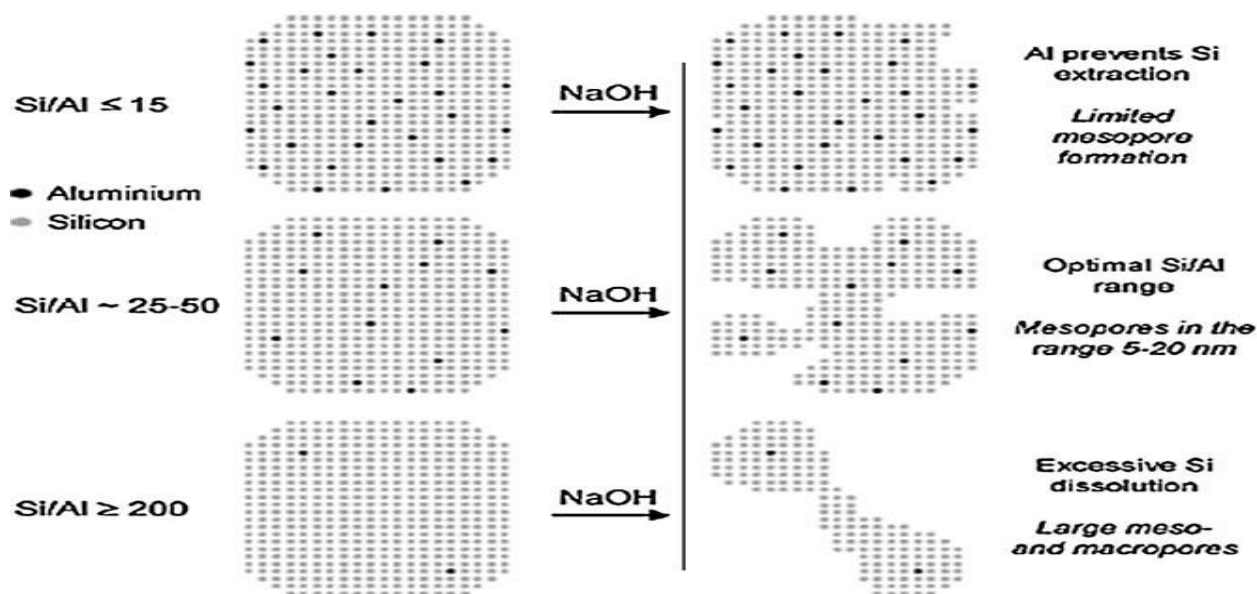


Figure 3. A simplified representation of the influence of the Al content on the desilication

Desilication by alkaline leaching in the presence of organics:-

Hierarchical zeolites combining micro and meso porosity were successfully prepared by desilication of ZSM-5 [72,74] and Beta [75] in aqueous solution of organic bases such as tetrapropyl ammonium hydroxide (TPAOH) and tetra butyl ammonium hydroxide(TBAOH). These are intrinsically less reactive and less selective towards silicon dissolution than inorganic hydroxides. Thus, treatments required higher temperatures and/or longer duration for the formation of significant mesoporosity allowing a high control of the dissolution process. High Al leaching was observed, relative to NaOH treatments and therefore high Si/Al ratios in the resulting mesoporous zeolites were reached. Moreover, the use of organic hydroxides directly produced the protonic form of the meoporous zeolites after calcinations avoiding the need for ion-exchange with NH_4NO_3 [85].

2.5.2 Constructive zeolite synthesis strategies:-

After the discovery of mesoporous materials by the Mobil researchers, a great deal of work was done to increase the low acidity and the poor hydrothermal stability of these amorphous materials, notably trying to induce a full zeolitic order inside the mesopores wall. Improvement through the aluminum incorporation and post synthetic treatments with, in particular zeolite

molecular templates or nano crystals, modified mesoporous materials still remained in zeolites, often due to segregated crystalline and amorphous phases [77-76].

In recent years, various new techniques exemplifying the constructive synthesis approach have been developed [78,79] A range of innovative propositions have been made for the introduction of zeolite microporosity in the amorphous walls of mesoporous materials or so called 'zeolitization' of mesoporous materials. Furthermore, direct or two-step synthesis routes have been explored with the use of multiple, soft as well as hard, templates.

Hard templates build hierarchical zeolites through engineering microporous and mesoporous domains often with template materials. Due to their versatility and availability, carbon materials are often used as hard templates, including carbon black, carbon nanotubes/nanofibers, carbon aerogel, and various ordered mesoporous carbon replicas [86-67]. Carbon templates have the advantage in that they can produce a wide variety of mesoporous structures, from being highly ordered and highly networked, to being isolated and not interconnected, depending upon how the templates themselves are structured or aligned during the synthesis process.

The use of solids as hard templates can be divided into two: a) sacrificial solids, materials that are removed after synthesis, and b) non-sacrificial solids, materials that actually remain after synthesis. In the latter case, composites are formed , i.e. two different materials in one body.

Sacrificial Solids

In hard templating, solid materials with specific size, from 2 to 50 nm for mesopores and larger than 50 nm for macropores, are utilised as hard templates. Generally, the template removal generates an extra porosity level with a geometrical correspondence. Figure 4 gives a schematic of synthesis of hierarchical zeolites using sacrificial solid templates. A common method using solid templates is the so-called confined space. In this procedure the zeolite crystallisation is carried out within a meso- or macro- porous system provided by a non-reactive matrix

One of the main disadvantages using solid matrices is the cave-like mesopores formation which are closed to external phases and being inaccessible for large molecules.

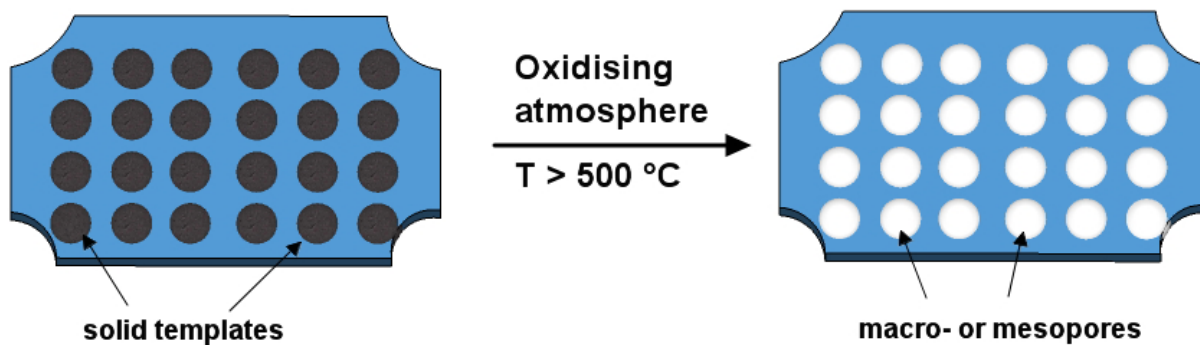


Figure 4: Schematic of Sacrificial solid templates

Non-Sacrificial Solids

Templates that remain after synthesis support zeolite crystals forming composites. In these materials, the additional porous structure is based on the support characteristics. Different materials have been employed as zeolite particles supports such as metals, polymers, ceramic clays and carbons. In particular, carbon has been explored as it is low cost and has both chemical and thermal stability in a non-oxidising environment. Nevertheless, hydrophobic characteristics on the carbon surface do not favour the interactions between zeolite particles or precursor gels and carbons. In order to overcome these problems, several methods have been proposed: the deposition of zeolite seeds on carbon prior to zeolite growing process, the use of binder with hydrophilic features such as SiO_2 , Al_2O_3 . The disadvantage of using seeds is that it is not always possible to control the zeolite amount and/or zeolite-layer thickness. Also, certain supports do not resist hydrothermal conditions leading to partial or complete scaffolds collapse. The use of binder, generally in the fabrication of membranes, causes structural defects originating from thermal stresses.

Soft templates Templates are large molecules that can be cationic surfactants. The strategy is based on the formation of micellar aggregate solutions, i.e. molecules with surfactant properties that self assemble in different shapes and dimensions depending on their miscibility properties. This also is known as dual template approach and has its principle in the size of molecules that control the crystal growth in the zeolite precursor but do not form part of the final framework. In the crystallization of zeolitic materials, templates interact directly with the silica species due to

their hydrophilic behaviour. Examples of soft templates include surfactants, ionic liquids and block copolymers. A general method of synthesis is shown in Figure 5

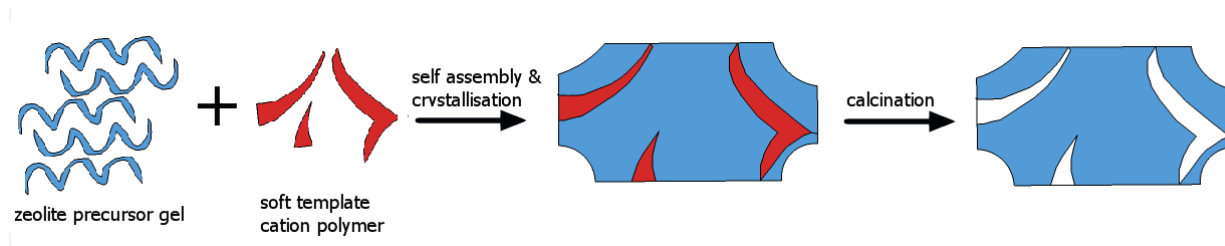


Figure 5: Mesopores are formed by the use of cationic polymers as soft templates

Thus, the soft template synthesis approach, however, brings about the same before-mentioned HSE issues and the synthesis cost constraints related to the necessity of large quantities of the organic mesopore-directing agent. Remarkably, the approach developed by Wang et al.[87, 88] applies an excess of TPAOH as single template for the synthesis of composite materials combining microporous ZSM-5 zeolites with an amorphous mesoporous matrix.

And also, The dual solid templating route is a convenient and versatile way to tune the size, shape, and connectivity of the mesopore network in the zeolite by choosing the proper hard template. Although various solids have been used, it appears that the most general approach is to employ different types of carbon based materials as hard mesopore templates,[23] of which carbon black, carbon nanofibers, and sugar-type carbohydrates are among the cheapest, although still rather expensive.

2.6 Advantages and Disadvantages of Hierarchical Zeolites

Advantages of Hierarchical Zeolite:-

- ❖ Highly attractive properties, such as superior mass/heat transfer characteristics
- ❖ Lower restriction of the diffusion of reactants in the mesopores
- ❖ Low pressure drop
- ❖ Exhibiting both micropore and macropore volume.
- ❖ High ion exchange capacity
- ❖ Producing uniform mesopores

- ❖ Increase in adsorption capacity of bulky molecules, particularly on the external mesopores surface
- ❖ Faster intraparticle diffusion owing to shorter diffusion path lengths
- ❖ Shorter retention times of the products within the micropores, hindering the occurrence of undesirable reactions.
- ❖ Generating additional active phases (metal, metal oxides)
- ❖ Direct effect on the improvement of activity, selectivity and lifetime of the Zeolite
- ❖ Low cost (inorganic SDA)
- ❖ Higher product efficiency.
- ❖ Reuse and easy recovery

Disadvantages of Hierarchical Zeolite:-

- ❖ Reduced hydrothermal stability of Zeolite framework
- ❖ Takes more time for catalyst preparation

2.7 Applications

Zeolites have basically found a wide array of application due to their applicability in almost all fields of human life where chemical, biochemical and physico-chemical processes are taking places. They can be used for purification of gaseous as well as liquid mixtures and solution by sorption, for strong molecules, for sieving and filtering , for ion exchange purpose and also for catalysis under non oxidizing and oxidizing environment. The uses for zeolites are generally categorized into three function classifications and within each function exist a broad range of application as below.

2.7.1 Zeolite in adsorption and separation

The basis for the usage of zeolite in gas adsorption is due to the shape selectivity properties. The ability to preferentially absorb certain molecules while excluding others has opened up a wide range of molecular sieving applications. Sometimes, it is simply matter of the size and shape of pores controlling access into the zeolite. In other cases, different type of molecules enter into the zeolite, but some diffuse through the channels more quickly, leaving other stuck behind.

Cation containing zeolites are extensively used as desiccants due to their high affinity for water and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interaction with metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Thus zeolites can be used to separate molecules based on difference of size, shape and polarity. The use of zeolite in some application of adsorption and separation is stated as follows:

2.7.2 Zeolite in Ion-Exchange

The counter cations in zeolites are mobile and may easily be exchanged. This ion exchange capability is utilized in detergent and waste water purification. In detergent industry zeolite act as a water softner, i.e uptaking calcium and magnesium ions from water and releasing sodium ions.

2.7.3 Zeolite in Catalysis

One of the major uses of zeolite is in heterogeneous catalysis in the petrochemical industry. They are used as cracking catalysts (H-form of zeolite Y, faujasite) in refining and hydroprocessing applications. They are used also e.g for production of synthetic gasoline (ZSM-5) from methanol, and synthesis of fine chemicals. Zeolite catalysts give high selectivity (shape selective) and their properties may be tailored by changing the chemistry .e.g Si/Al ratio and counter cations.

2.8 Characterisation of the Synthesized Zeolites

2.8.1 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is one of the most important techniques to characterise crystalline solids. This methodology identifies the structure through the crystallographic phases of analysed material. Also it can be used to estimate the degree of crystallinity and/or the purity of a phase. XRD data can also provide information about chemical composition. The development of this technique has allowed understanding of the structural configuration of zeolites.

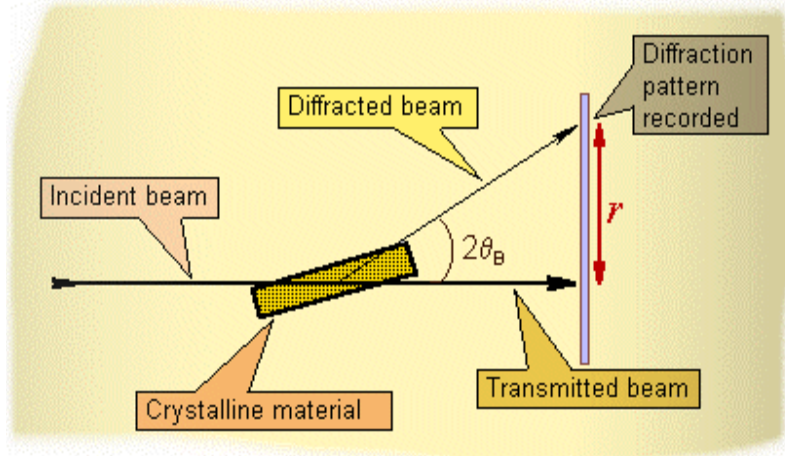


Figure 6. X-ray diffraction pattern diagram

X-ray diffraction is a non destructive techniques that is widely used for structure determination of crystalline materials (Figure 6). X-ray diffraction is widely used for analysis of crystalline powders. Each crystalline material produces a pattern of reflections, which position (in 2θ degree) reflects the distance between atomic planes in the crystals. The position and relative intensity of the lines in the x-ray diffraction pattern such as a fingerprint for a given type of crystalline material. By comparing a x-ray diffraction pattern against the patterns collected for known crystalline compounds, the composition of analysed material can be determined.

In addition to phase determination, powdered XRD patterns can be used to estimate the crystal size in a powder material. As the particale size decreases, the reflection in the XRD pattern will be broadened. This correlation is used in Scherrer's equation to calculate the particle size $\frac{K\lambda}{B\cos\theta}$ where K is the shape factor ($K=1$ for spherical particles), λ is the x-ray wave length (1.5418 \AA in the case of Cu Ka radiation), B is the line width at half the maximum (FWHM), and θ is the Bragg angle. The particle size determined using Scherrer's equation should be used with caution, as multiple factors besides the crystalline size contribute to broadening of the reflections in XRD patterns. In the case of partially intergrowth crystallites Scherrer's equation underestimate the particle size when compared with electron microscopy analysis.

2.8.2 Determination of Specific surface area (BET) and pore volume

The **BET** method most widely used to assess surface area and pore characteristics of materials with technological importance is the Brunauer-Emmet and Teller (BET) using N_2 at 77 K. In fact, it has been recognized as a standardised method. BET theory was first proposed in 1934 while working on ammonia catalysts. It is an extension of the theory proposed by Langmuir in 1916.

Adsorption of gases on the surface of a porous material provides crucial information about the surface area, pore volume and pore size distribution. The basis for adsorption measurements is physisorption of gas molecules on the surface. Physisorption is a van der Waals type of interaction (dispersion or dipolar) between the adsorbate and substrate. Physisorption interactions are weak and are of the order of 20 kJ/mol, so the gas molecules easily adsorb and desorb from the surface, and the surface coverage increases at lower temperature.

By knowing the volume of adsorbed gas, which is required to form a monolayer on the surface and the area which each gas molecule occupies, one can calculate the surface area. The adsorbates usually used for surface area measurements are nitrogen and that have a cross section of 0.162 nm^2 . In the case of zeolite material, external and total surface areas are determined by collecting a BET isotherm for the sample before and after calcinations. Internal surface area can then be calculated as the difference between the total and external surface areas.

The micropore volume of zeolite can be determined using a t-plot method, developed by Lippens and DeBoer. The total pore volume is calculated by measuring the volume of nitrogen adsorbed at p/p_0 near unity. At the relative pressure, adsorbate is assumed to be condensed inside the pores of zeolite. The measured total pore volume of zeolite is larger than the micropore volume due to the condensation of adsorbate in the intercrystalline voids between zeolite crystals or in the case of hierarchical zeolite, in the mesopores. Thus the total pore volume is often assumed to be the sum of micropores and mesopores in the case of hierarchical zeolite materials.

The distribution of pore volumes with respect to the pore size is called a pore size distribution. For pore size distributions, the pore geometry, such as cylindrical, spherical or slit shape, needs to be taken into account. BJH model for pore size distribution measurements assumes a cylindrically shaped pore. The BJH model assumes that condensation of adsorbate in

pores of smaller diameter occurs at lower partial pressures and large pores are filled with adsorbate as the pressure increases. Conversely, adsorbate desorbs from pores of larger size as the partial pressure decreases.

The instrumental configuration of the porosity analyser is shown in Figure 7.

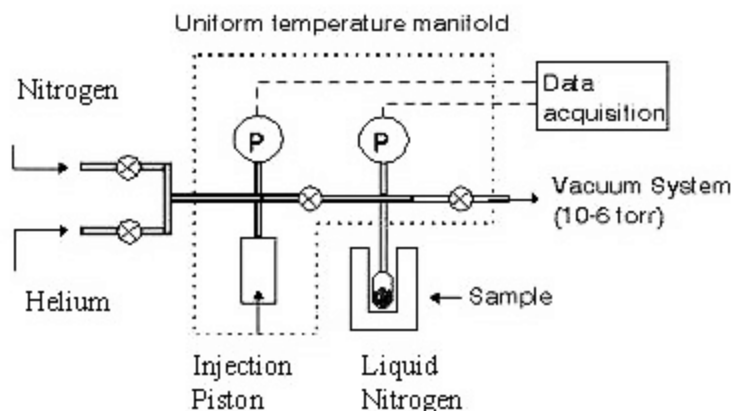


Figure 7. Diagram of surface analysis equipment

2.8.3 Determination of Acid/Base properties by Temperature Programmed Desorption (TPD)

The temperature programmed desorption (TPD) of a basic molecules such as ammonia (NH₃-TPD) is one of the most commonly used methods for measuring the surface acidity of zeolites and related materials.

As the sample is heated, pro-adsorbed gas is progressively desorbed, and sometimes decomposes. With increased temperature, the desorption rate increases, goes through a maximum, and finally goes back to zero as the surface is depleted of adsorbate. A desorption spectrum is a record of the concentration of desorbed gas as a function of temperature.

TPD of adsorbed basic probe molecules from an acidic surface may yield a profile with several desorption peak. The temperature dependence of desorption is related to the strength of acid sites which may involve either physical or chemical adsorption. In general, in TPD spectra the peak area shows the amount of acid sites, while the temperature of the peak maxima are correlated to the acid strength distribution of surface sites releasing the probe molecules. This method can only be used to roughly distinguish the various acid site strength. In addition the desorption peaks may be greatly affected by experimental conditions.

TPD consists of the following steps : (a) sample pretreatment (b) preadsorption of the adsorbate (c) evacuation or flushing with the carrier gas to remove physically adsorbed gas (d) programmed desorption of the residual chemisorbed gas into the stream of carrier gas (e) detection of the desorbed gas in the carrier and (f) trapping and analysis of the desorbed gas. The carrier gas is usually helium at atmospheric pressure, but argon and nitrogen is also used. Thermal conductivity cells can be employed as detectors which measures the composition of the effluent stream as a function of the sample temperature.

The parameters that have to be optimized in TPD analysis are: (a) flow rate of carrier gas (b) reactant gas / inert gas ratio (c) sample volume/ mass (d) the sample particle size (e) the geometry of reaction vessel (f) the heating rate (g) the signal intensity and (h) the pressure system.

2.8.4 Catalyst Evaluation (Hydroisomerisation in Fixed bed reactor):

Hydroisomerisation has been applied for producing high octane gasoline and low pour point diesel as well as for improving the viscosity properties of waxy feedstocks such as slack waxes. Isomerisation of light alkanes is an important process in oil refining. Hydrocracking and hydroisomerisation requires a metal function for hydrogenation and dehydrogenation purposes. Thus, industrial process of n- paraffin hydroisomerisation requires the presence of bifunctional catalysts, which means that two types of sites should be present in the catalyst. The main function of the metallic site is to dehydrogenate the feed alkanes and to hydrogenate the isomer alkane. In contrast the function of the acid sites is to crack or to isomerizes the paraffin. In bifunctional catalysts, the balance between the metal and acid functions has an effect on product selectivity and help to reduce unwanted side reactions.

In brief, the hydroisomerization process is divided into the following reactions steps

- Adsorption of reactant on zeolite
- Dehydrogenation of the reactant on the noble metal clusters of the catalyst
- Isomerization on the acid sites
- Hydrogenation of the products on the noble metal clusters
- Desorption of products from the zeolite

The dehydrogenation of normal alkanes into its alkene takes place on the noble metals. The alkene then transport from the metal sites to an acidic site. A protonation of the resultant alkene then takes place on the acidic site, converting the alkene to an alkyl carbonium ion intermediate. The resulting alkylcarbonium ion then goes through either a structural rearrangement. This is followed by migration and hydrogenation on a metal site to produce isomers of the initial alkane which have higher octane number and also form crack products on metal sites. Metals such as Pt or Pd are normally used because of their high activity, along with 1-dimensional zeolites like , ZSM-22, ZSM-23 etc, which have a high activity and selectivity for hydroisomerisation of n-alkanes because of their high resistance against the deactivation by coke.

CHAPTER THREE

Material and Experimental work

3.1 Reagent and Chemicals: The chemicals and reagents which are used for experiment are mentioned in table 2.

Table 2: List of chemicals used for synthesis of parent and modified Zeolite ZSM-23

SI No	Name of Chemicals
1.	Hi-Silica
2.	Sodium Hydroxide pellets
3.	Anhydrous Sodium Aluminate
4.	Hydrochloric Acid
5.	Platinum
6.	Acetic Acid
7.	Aluminium
8.	Tetrabutylammonium Hydroxide
9.	Potassium Hydroxide
10.	N,N- Dimethylformamide
11.	Diquat

3.2 Sample preparation and Experimental work

3.2.1 Synthesis of ZSM-23 by DMF template:-

The hydrothermal synthesis of ZSM-23 zeolite in the presence of DMF as template was carried out at 160 °C for 48 hrs with gel prepared as per the procedure below. HiSil-233D was used as silica source and aluminum sulfate as the alumina source. A typical synthesis procedure is described as follows: a clear solution was prepared by mixing 0.55 g aluminum sulfate, 3.6 g water, and 4.1 g DMF under stirring, at room temperature for 30 mins. The obtained clear solution was added to a mixture of 2.5 g NaOH, 37g H₂O and 16.6 g silica sol, giving the gel with a ratio of SiO₂:Al₂O₃:-NaOH:DMF: H₂O = 100:1.0:72:67:4500. After stirring for 3 h , the gel was transferred to an autoclave and crystallized at 160°C for 48 h. The product was collected by filtration, washed with deionized H₂O, and dried in air at 110°C for 24 h [20].

3.2.2 Post Synthesis modification of ZSM-23 for DMF template

The post-synthetic modifications were performed on the parent zeolite ZSM-23 synthesised using DMF as the template. The template in the as-synthesized zeolites was removed by calcination in static air at 550°C for 15 h using a heating rate of 1°C min⁻¹. Post-synthetic modifications were performed according to a protocol described elsewhere [18], and experimental conditions listed in Table 3. Prior to acidity studies and catalytic evaluation, solids were converted into the protonic form by 3 consecutive ion exchanges with 1.0M aqueous solution of NH₄NO₃ (conditions: Table 4), followed by calcination in air for 5 h at 550°C and 5°C min⁻¹. All the zeolite samples were loaded with 0.3% Platinum using tetraamine platinum nitrate as the Pt salt to obtain Platinum loaded H-form of the zeolite.

Table 3 Experimental conditions for preparation of hierarchical zeolites from ZSM-23-DMF samples

Sample code	Reagent	C M	T °C	t hr	Yield after AT gm/ml	Yield after Acid T gm/ml
MMZ-28(Parent)	–	–	–	–	–	–
MMZ-36(10gm)	NaOH	0.2	60	4	9.15	6.00
MMZ-26(9.6gm)	NaOH	0.4	60	4	7.02	5.50
MMZ-34(15gm)	NaOH	0.6	60	4	4.18	3.88
HCl	HCl	0.1	60	4		

3.2.3 Synthesis of ZSM-23 by Diquat template:-

The diquat-7 dibromide salt used to crystallize zeolite ZSM-23 was prepared by reacting 1,7 dibromoheptane and trimethylamine. 150grams (0.58moles) of 1,7 dibromoheptane (available from aldrich chemical company) was weighed out and transferred directly to a two liter, three necked reaction flask equipped with a stirrer. 300ml of absolute ethanol was added to the reaction flask while the contents of the flask stirred continuously.

Then 300grams (excess) of trimethylamine solution (25% in methanol) was transferred to the two liter reaction flask. The two liter reaction flask was fitted with a dry ice condenser to minimize $(\text{CH}_3)_3\text{N}$ loss during reflux. The reaction mixture was refluxed for about 14 hours, while crystals of diquat-7 dibromide salt were formed and separated from the reaction solutions at the end of the reflux period. The reaction flask was cooled by immersion in water-ice bath. The product was filtered and washed several times and diquat 7 crystals were dried by streams.

3.2.4 Post Synthesis modification of ZSM-23:-

The post synthesis modification for this ZSM-23 by diquat was done by same procedure as described above in for samples synthesized using DMF as template and the experimental conditions are given in Table 4.

Table 4: Experimental conditions for preparation of hierarchical zeolites from ZSM-23-Diquat-7 samples

Sample code	Reagent	C	T	t	Yield after AT	Yield after Acid T
		M	°C	hr	gm/ml	gm/ml
MMZ-38(Parent)		–	–	–	–	–
MMZ-39(15gm)	NaOH	0.2	60	4	10.02	9.00
MMZ-40(15gm)	NaOH	0.4	60	4	7.65	7.00
MMZ-41(15gm)	NaOH	0.6	60	4	7.02	4.45
HCl	HCl	0.1	60	4		
Ion-exchange	NH₄NO₃	1	60	24		

Where AT and Acid T are Alkali treatment and acid treatments respectively.

CHAPTER FOUR

Results and Discussions

4.1 Effect of acid and alkali treatment.

The ZSM 23 was synthesized successfully with two different templates and modified by treatment with different concentrations of inorganic bases and 0.1 molar hydrochloric acid. It is observed that there is a decrease in the yield of zeolite after alkali and subsequent acid treatment. The decrease in yield is more pronounced with increasing alkali concentration. There is a decrease in yield at every stage of treatment (alkali as well as acid).

4.2 Characterization of Synthesized and modified zeolites

4.2.1 XRD Analysis

The powder x-ray diffraction pattern of the zeolite samples were recorded on a simens D-500 X-ray powder diffractometer over 2Θ range of 5° to 35° at a scanning speed of 2Θ per minute and a step size of 0.05. The diffractometer was equipped with Ni-filtered Cu K- α radiation source (8978 eV or $\lambda = 1.5418 \text{ \AA}$). The X-ray source was operated at 45 mA and 40 kV. Sample preparation for the X-ray analysis involved gentle grinding of the solid into a fine powder and packing of approximately 0.1-0.3 g of the sample into an aluminium sample holder with light compression to make it flat and tight. The powder X-ray pattern of the parent ZSM-23 zeolites matched with those mentioned in the literature. The X-ray spectra are given in Figure 8. In case of ZSM-23 zeolite synthesized with DMF as the template, there is a collapse in the structure which is indicated by the decrease in the intensity of the peaks. There is an appearance of the impurity peaks after the acid and alkali treatment. ZSM-23 synthesised using diquat as the template was stable to treatment up to 0.4M concentration of NaOH. However there is a decrease in the intensity of the XRD peaks with higher concentrations.

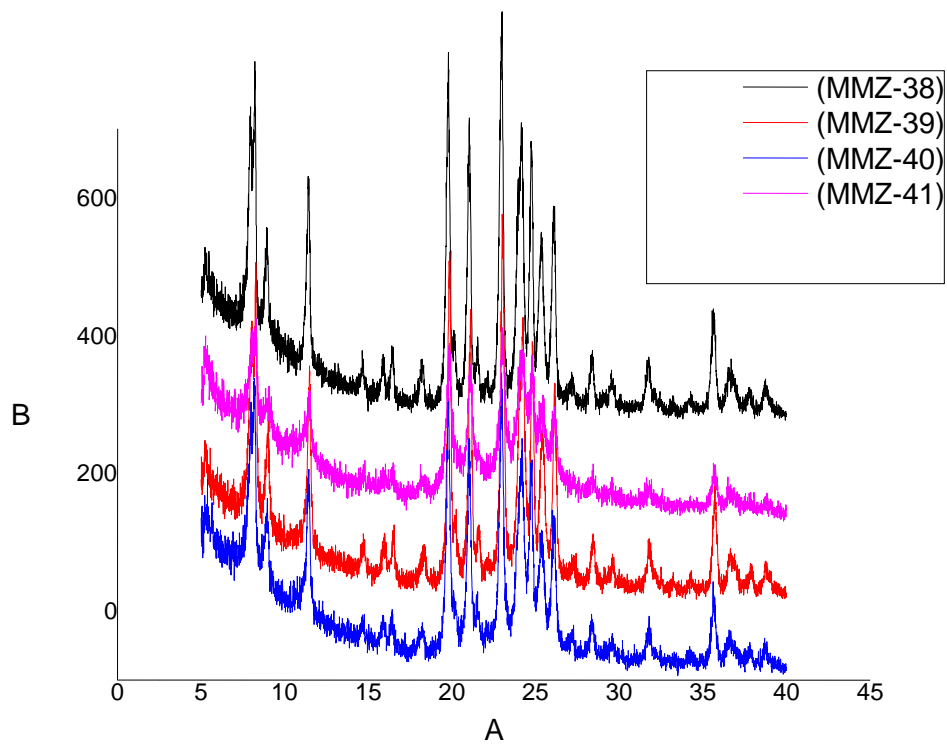
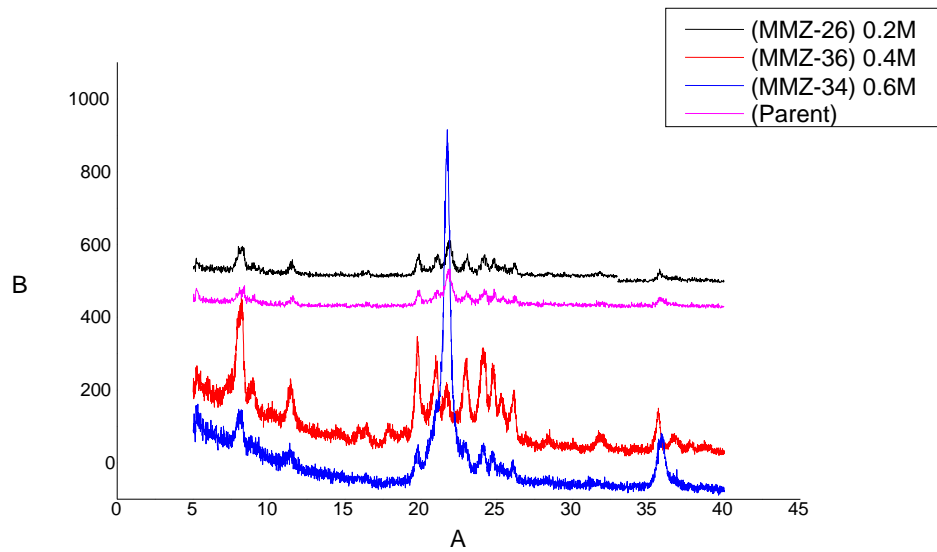


Figure 8: The X-ray diffraction of parent and Hierarchical ZSM-23 zeolite catalysts

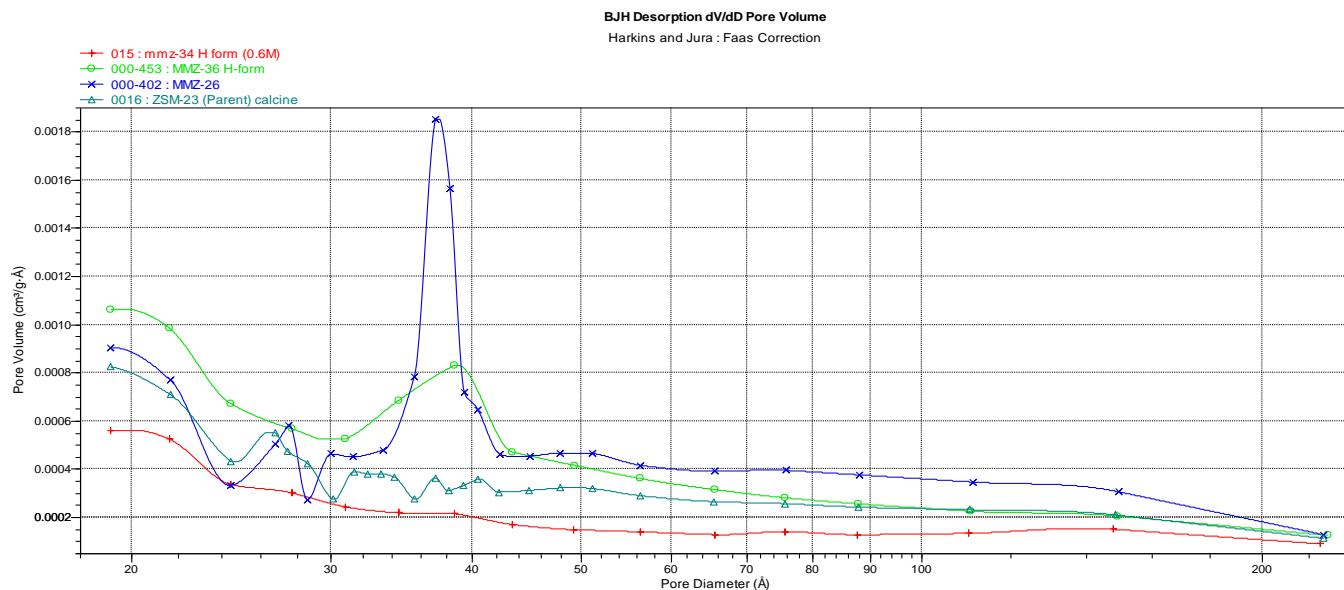
4.2.2 Specific surface are

Surface area of the parent and treated ZSM-23 for both template zeolites were measured using the BET method on a Micromeritics ASAP 2020. Typically 0.10gm of zeolite powder was degassed at 350°C overnight in vacuum. After degasing, the isotherm was then recorded and the specific surface area was calculated for the samples after calcinations in order to obtain the external S_{ext} , total surface area S_{tot} , and pore volume respectively.

Table 5: Textural properties of parent and post synthesis treated samples are given below:

Sample	Molarity	S_{BET} m ² /g m	$S_{External}$ m ² /gm	Total Pore volume cm ³ /g m	Micro pore volume cm ³ /gm	Meso pore volume cm ³ /g m	Pore Size Å	Acidity micromo les/gm of catalyst
ZSM-23	Parent	50	25.15	0.15	0.11	0.04	30	83
MMZ-36	0.2	114	32.272	0.099	0.033	0.066	34.7372	15.3
MMZ-26	0.4	124	63.435	0.129	0.025	0.103	41.3728	31.8
MMZ-34	0.6	85	26.448	0.1129	0.028	0.084	48.67	No acidity
MMZ-38	Parent	288	61	0.172	0.088	0.084	23	260
MMZ-39	0.2	326	113	0.253	0.087	0.166	31	282
MMZ-40	0.4	420	198	0.406	0.097	0.309	39	280
MMZ-41	0.6	245	166	0.33	0.04	0.29	54	200

The textural properties of parent ZSM-23 and alkali- acid treated samples are given in table. 5 above. The parent zeolite in case of ZSM-23 synthesised with DMF as the template had a surface area of 50 m²/gm. When the parent sample was subjected to alkali treatment there was an increase in the surface area of the treated samples up to an alkali concentration of 0.4M. Along with the decrease in the surface area the sample treated with 0.6 M alkali had no acidity. Same trend was observed with alkali treatment of ZSM-23 synthesised with Diquat-7 as the template. However the ZSM-23-Diquat-7 sample was much more stable to alkali treatment than the ZSM-23-DMF template. There was an increase in the average pore size distribution and the presence of hysteresis in the isotherm is an indication of the generation of mesoporosity (figure 9).



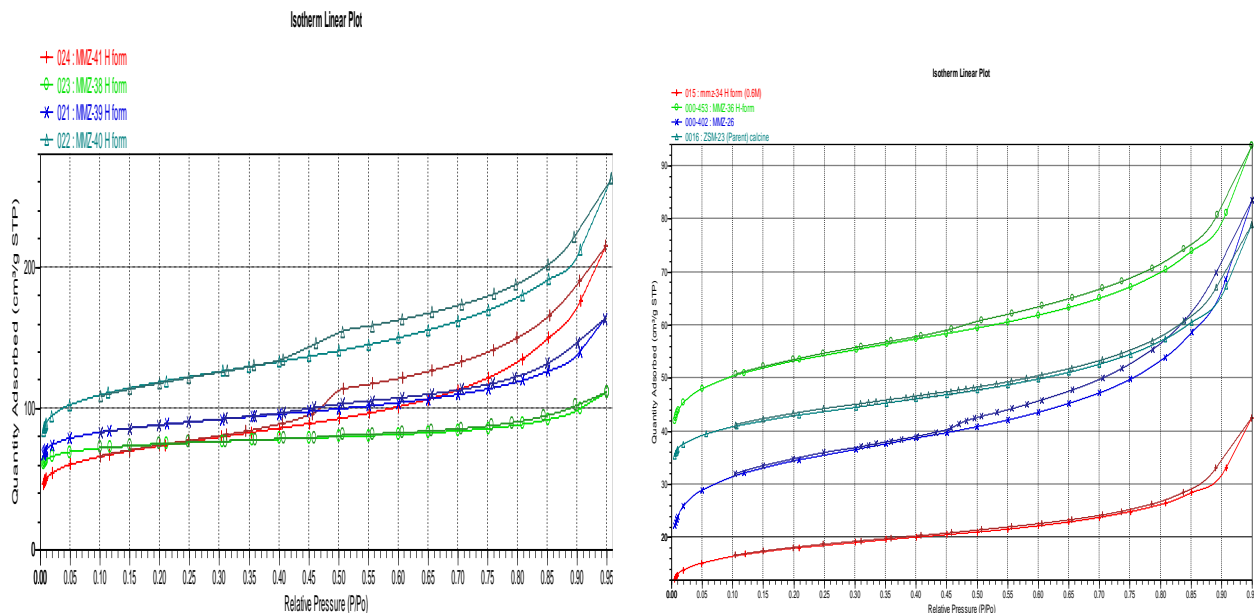


Figure 9: The BET isotherm and BJH desorption plot for parent and modified catalysts

4.2.3 TPD studies

To characterize the acidity, the temperature programmed desorption of ammonia (NH₃TPD) was carried out on AMI 200 from ALTAMIRA INSTRUMENT. Prior to NH₃ adsorption at 100°C, the samples were preheated in helium at 550°C for 1hr. The physically adsorbed NH₃ was removed in a flow of helium for 1hr, and then the adsorbed samples were heated with a rate of 10°C/min to 600°C under helium (50ml/min). The signals were recorded by monitoring the desorbed ammonia with a TPD detector respectively. The acidity values of all the samples are given in table 5.

4.2.4 Hydroisomerization reaction in Fixed bed reactor:

The reaction of n-hexadecane hydroisomerization was carried out in a continuous fixed bed reactor with an internal diameter of 11.5 mm. The extrudates of catalyst were sized in to dimensions of 1mm diameter with the length of ~2-5 mm, and loaded into the isothermal zone of the reactor. The remaining part of the reactor was filled with inert glass wools and glass beads. The catalyst was reduced in-situ before the evaluation test at 350 °C for 4 h under a H₂ flow of 100 mL/min. After the reduction of the catalyst, the reactor was adjusted to the desired reaction temperature, and then the n- hexadecane was injected into the reactor. Experimental conditions

were as follows: catalyst weight of 5.0 g; reaction temperatures of 280°C -320°C; hydrogen pressure of 60 bar; WHSV of 1.1 h⁻¹; H₂/n-C16 volume ratio of 900:1. Sampling was performed every 6 h on stream, and the products were analyzed by gas chromatography (Agilent Technologies 6890N) with a capillary HP-1 column (0.2mI.D.×50m) and FID detector.

Table 6: Conversion, yield and selectivity of isomerization of n-hexadecane over parent and hierarchical ZSM-23 at 60 bar and 1.1 whsv

Sample	Used Templates	Temperature °C	Conversion %	Yield %	Selectivity %
ZSM-23 (Parent)	DMF	300	9.73	6.69	68.75
		330	22.49	18.77	83.46
		350	57	50	87
MMZ-36(0.2M)	DMF	330	87	67	77
		333	89	67	75
MMZ-26(0.4M)	DMF	300	26.34	23.48	89.12
		330	85.97	74.62	86.79
		334	89.89	75.41	83.88
MMZ-38 (Parent)	Diquat	296	86	64	74
		298	88	63	72
MMZ-39(0.2M)	Diquat	290	86	64	74
		292	89	64	72
MMZ-40(0.4M)	Diquat	289	89	65	73
		292	92	63	68
MMZ-41(0.6M)	Diquat	289	72	53	73
		296	89	64	71
		301	94	63	67

The results of hydroisomerization of n-hexadecane are given in table 6. The parent zeolites in both cases were less active in terms of the temperature required to achieve approximately 90% conversion of n-hexadecane than the hierarchical zeolites. The higher activity of the hierarchical

zeolites is mainly because of the enhancement in diffusion of the reactants through the catalyst particle as indicated by the increase in the total surface area of the zeolite. The data given in table 5 shows that there is an increase in the mesopore volume with alkali treatment in the hierarchical zeolites. Higher temperatures were required for the hierarchical ZSM-23-DMF samples than the hierarchical ZSM-23-Diquat-7 samples to achieve equivalent conversion levels of n-hexadecane. This is mainly due to the difference in surface areas of the parent zeolites. The parent ZSM-23-DMF zeolite had a surface area of 50 m²/gm as compared to a surface area of 288 m²/gm for the ZSM-23-Diquat-7 sample. The C₁₆ isomer selectivities were higher on the ZSM-23-DMF samples (parent as well as hierarchical) than the ZSM-23-Diquat-7 samples (parent as well as hierarchical) as the total acidity of the ZSM-23-DMF samples was less than the total acidity of the ZSM-23-Diquat-7 samples. The higher acidity of the ZSM-23-Diquat-7 samples led to more cracking of the n-hexadecane molecules as compared to the ZSM-23-DMF samples. The hydrocracking of n-hexadecane and squalane was carried out over conventional and mesoporous Y zeolites [89]. It was observed that the mesoporous Y zeolite was more active by at least 20 °C than the parent Y zeolite.

CHAPTER FIVE

Conclusion and Suggestion for future work

Conclusions:

In this dissertation,

the synthesis and characterization of Pt loaded ZSM-23 and its hierarchical counterparts were carried out and tested for n-hexadecane hydroisomerisation reaction. The following conclusions can be drawn:

1. ZSM-23 was successfully synthesized using DMF and Diquat-7 as the templates. The zeolites were characterized by XRD, Ammonia TPD and BET surface area.
2. The hierarchical form of the synthesized ZSM-23 was prepared by treatment with alkali/acid for inducing mesoporosity which reduced diffusion limitations in the zeolite crystal. This is seen from the increase in the mesopore volume of the hierarchical zeolites.
3. The hierarchical zeolite was more active than the parent zeolites. This is seen from the activity studies where higher temperatures were required to achieve appreciable n-hexadecane conversion on parent zeolites than on the hierarchical zeolites.

Way forward:

1. To achieve higher selectivities in ZSM-23-diquat zeolites by further modification of the hierarchical zeolites
2. To carry out detailed electron microscopy studies of the hierarchical zeolites to check the interconnected intracrystalline cylindrical mesopores.

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