

**Investigation of the Pore Structures of Hierarchical
Y and ZSM-5 Zeolites for Fluid Catalytic Cracking
Catalyst via Experimental and Computational
Approaches**

BY

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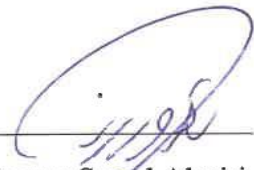
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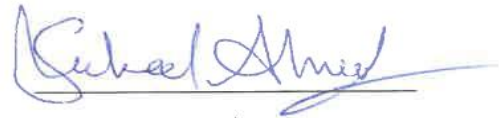
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Dedicated to Allah Almighty and My Beloved Parents

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Praise to Allah Almighty, Lord of the Universe

I am forever thankful to Allah Almighty for blessing me with all the good things in my life. Above all, I sincerely thank my parents for being a pillar of strength throughout my life and academic career with their unfailing love, support, and encouragement. This work would not have been possible if they had not believed in me.

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LIST OF ABBREVIATIONS

FCC	:	Fluid Catalytic Cracking
VGO	:	Vacuum Gas Oil
MAT	:	Micro Activity Testing
CTAB	:	Cetyltrimethylammonium bromide
USY	:	Ultra Stable Y zeolite
TOS	:	Time on Stream
LCO	:	Light Cycle Oil
HCO	:	Heavy Cycle Oil
MY	:	Modified Y-zeolite
HY	:	Hierarchical Y-zeolite
MD	:	Molecular Dynamics
MC	:	Monte Carlo
GCMC	:	Grand Canonical Monte Carlo
CVFF	:	Consistent Valence Force Field
BET	:	Brunauer-Emmett-Teller
GCMC	:	Grand Canonical Monte Carlo

BJH	:	Barrett-Joyner-Halenda
PSD	:	Pore Size Distribution
SEM	:	Scanning Electron Microscopy
XRD	:	X-ray Diffraction
TPD	:	Temperature Programmed Desorption
EDX	:	Energy Dispersive X-ray

|

ABSTRACT

Full Name : [Nida Tasneem]

Thesis Title : [Investigation of Pore Structure of Hierarchical Y and ZSM-5 Zeolites via experimental and computational approaches for Fluid Catalytic Cracking Process]

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The microporous structure, shape selectivity, ion-exchange capacity, and strong acidity of zeolites and similar crystalline molecular sieves have made them widely used in various industrial processes and reactions. However, the narrow channels and small pore size that prevent bigger molecules from diffusing generally limit their practical applicability. Therefore, hierarchical zeolites have been recently investigated as catalysts by a micro-mesoporous framework to improve the physical transport of large reactant molecules by eliminating the diffusion limitations. This study focuses on developing FCC catalysts using hierarchical Y-zeolite and ZSM-5 to enhance the production of propylene and light olefins from VGO feedstocks. Acid/base leaching and surfactant templating with Cetyltrimmoniumbromide (CTAB) created different kinds of hierarchical zeolites with controlled mesoporosity. Using XRD, TGA, SEM, NH₃-TPD, EDX, and N₂-ads/desorption techniques, the physico-chemical properties of the parent (Na-Y and ZSM-5) and hierarchical samples were thoroughly examined. An amorphous matrix and modified zeolites were added to FCC catalyst compositions. Kaolin, a silica sol binder, and amorphous silica-alumina made up the matrix. The FCC catalysts underwent hydrothermal treatment by steaming for six hours at 810°C before testing. To ascertain the yields of gasoline, LCO, HCO, propylene, light olefins, and coke, catalyst performance was assessed

at 550°C. In a fixed-bed Micro Activity Test (MAT) equipment, catalyst testing was carried out using the feedstock of vacuum gas oil (VGO). Catalytic testing showed that hierarchical ZSM-5-based FCC catalyst improved VGO conversion from 60% to 69% and significantly enhanced propylene yield to 12 wt%, while maintaining good gasoline yields. However, FCC catalysts containing hierarchical Y and ZSM-5 exhibited lower conversion and increased HCO yield, attributed to reduced acidity and catalytic activity. Overall, introducing mesoporosity into zeolites improved diffusion, enhanced product selectivity, and optimized catalytic performance, offering a promising strategy for future advancements in FCC catalyst design. In addition, Atomistic models of hierarchical Y-zeolite structures with varying pore sizes were developed using Materials Studio and characterized through sorption simulations. Sorption analysis revealed the formation of mesoporosity, with clear hysteresis observed for structures with pore sizes of 32 Å and 41 Å, confirming the development of secondary porosity. The computational results, including adsorption isotherms, pore size distribution, surface area, and pore volume, were validated through experimental results. Integrating computational design with experimental validation proved vital in optimizing hierarchical zeolite structures, demonstrating a promising strategy for rationalizing next-generation FCC catalysts. |

ملخص الرسالة

الاسم الكامل: ندى تسنيم

عنوان الرسالة: الهرمي باستخدام الأساليب التجريبية والحاسوبية ZSM-5 و Y دراسة بنية المسام في زيوليت لعملية التكسير التحفيزي السائل

التخصص: الهندسة الكيميائية

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الهيكل الميكروي المسامي، والانتقائية الشكلية، وقدرة التبادل الأيوني، والحموضة القوية للزيوليت والمنخّلات الجزيئية البلورية المماثلة جعلتها تُستخدم على نطاق واسع في مختلف العمليات والتفاعلات الصناعية. ومع ذلك، فإن القنوات الضيقة وحجم المسام الصغير، التي تمنع الجزيئات الكبيرة من الانتشار، غالبًا ما تحد من قابليتها للتطبيق العملي. ولذلك، تم مؤخرًا دراسة الزيوليتات الهرمية كمحفزات ضمن إطار ميكروي-ميسوبوري لتحسين النقل الفيزيائي للجزيئات المتفاعلة الكبيرة من خلال التخلص من قيود الانتشار. يركز هذا الدراسة على تطوير محفزات التكسير لتعزيز إنتاج البروبلين والأوليفينات الخفيفة من ZSM-5 الهرمي و Y باستخدام الزيوليت (FCC) التحفيزي السائل وقد تم إنشاء أنواع مختلفة من الزيوليتات الهرمية ذات المسامية المتحكم بها باستخدام الترشيح VGO المواد الخام (CTAB) الحمضي/القاعدي وتقنية القوالب السطحية باستخدام مركب سيتيل ثلاثي أمونيوم بروميد والهرمية بدقة باستخدام تقنيات حيود (ZSM-5 و Na-Y) تم فحص الخواص الفيزيائية-الكيميائية للعينات الأصلية وبرمجة (SEM) والمجهر الإلكتروني الماسح (TGA) والتحليل الوزني الحراري (XRD) الأشعة السينية وامتزاز/إزالة امتزاز النيتروجين (EDX) وتحليل طاقة التشتت (NH₃-TPD) امتزاز/إزالة الامتزاز للألمونيا، تكونت المصفوفة من الكاولين. FCC تمت إضافة مصفوفة غير بلورية وزيوليتات معدلة إلى تراكيب محفزات (N₂) إلى معالجة مائية حرارية FCC ومادة رابطة من السيليكا سول، والسيليكا-ألومينا غير البلورية. خضعت محفزات قبل الاختبار °C بالبخر لمدة ست ساعات عند درجة حرارة 810

،(HCO) والديزل الثقيل ،(LCO) لتحديد نواتج البنزين، والديزل الخفيف °C تم تقييم أداء المحفزات عند 550 والبروبلين، والأوليفينات الخفيفة، وفحم الكوك. أجريت اختبارات المحفزات باستخدام جهاز اختبار النشاط الميكروي أظهرت الاختبارات التحفيزية أن محفز (VGO) وباستخدام مادة التغذية من زيت الغاز الفراغي (MAT) الثابت من 60 % إلى 69 %، ورفع بشكل ملحوظ إنتاج البروبلين VGO الهرمي حسن تحويل ZSM-5 المعتمد على FCC التي تحتوي على FCC إلى 12 %وزنيًا، مع الحفاظ على معدلات جيدة لإنتاج البنزين. ومع ذلك، أظهرت محفزات. ويُعزى ذلك إلى انخفاض الحموضة والنشاط التحفيزي، HCO الهرمي تحويلًا أقل وزيادة في ناتج ZSM-5 و Y بشكل عام، فإن إدخال المسامية المتوسطة في الزيوليتات حسن الانتشار، ورفع الانتقائية للمنتجات، وحقق أداءً تحفيزيًا مستقبلاً FCC أمثل، مما يوفر استراتيجية واعدة لتصميم محفزات الهرمية ذات أحجام مسامية مختلفة باستخدام برنامج Y بالإضافة إلى ذلك، تم تطوير نماذج ذرية لهياكل الزيوليت وتمت دراستها من خلال محاكاة الامتزاز. كشفت تحليلات الامتزاز عن تكوّن المسامية، Materials Studio واضح في الهياكل ذات الأحجام المسامية 32 أنغستروم و41 (hysteresis) المتوسطة، حيث لوحظ وجود تخلف أنغستروم، مما يؤكد نشوء المسامية الثانوية.

،تم التحقق من صحة النتائج الحاسوبية، والتي شملت متساويات الامتزاز، وتوزيع حجم المسام، والمساحة السطحية وحجم المسام، من خلال النتائج التجريبية. وقد أثبت دمج التصميم الحاسوبي مع التحقق التجريبي أنه أمر بالغ الأهمية في تحسين هياكل الزيوليت الهرمي، مما يبرز استراتيجية واعدة لتطوير الجيل القادم من محفزات التكسير التحفيزي (FCC) السائل.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Catalysis is one of the most crucial branches of chemistry that significantly affects any community's environmental preservation and economic development. Zeolites are microporous aluminosilicate minerals essential to several petrochemical industry operations, including esterification, oligomerization, isomerization, alkylation, acylation, and oil refining (including fluid catalytic cracking or FCC) because of their exceptional hydrothermal stability, high specific surface area, strong Brønsted acidity, and affordability [1]. Their distinct characteristics, such as large specific surface area, strong Brønsted acidity, outstanding hydrothermal stability, and affordability, make them very useful in applications such as phase separation, catalysis, and adsorption, especially FCC [1],[2]. The fluid catalytic cracking process is crucial for refining crude oil due to its ability to yield high-value products, moderate working conditions, and feed adaptability. Between 2021 and 2030, petrochemical demand is expected to expand at a compound annual growth rate (CAGR) of 5.1% globally. The demand for petrochemicals grew by more than 50% between 2010 and 2020, and the global market is estimated to be worth USD 453 billion. The primary method used to produce propylene is the thermal steam cracking of naphtha. This process uses a lot of energy and produces many carbon dioxide emissions because it

runs at a high temperature. Furthermore, the process produces twice as much ethylene as propylene since it does not allow for control over the propylene-to-ethylene ratio. Constant modifications to the crude oil cracking process have led to the development of the FCC for producing light oils, especially propylene [3]. These days, the FCC is a very important source of reasonably priced propylene due to its financial advantages. The heavy oil, like vacuum gas oil (VGO) and atmospheric residual, is broken down into a light fraction, like naphtha, in the FCC unit using an FCC catalyst. Light olefins are produced when hydrocarbon feedstock with at least one crystalline microporous molecular catalyst comes into contact with the feed during catalytic cracking. The naphtha is then split into light gases using the ZSM-5 additive. The propylene to ethylene selectivity is significantly higher than that of thermal steam cracking. Consequently, it would be crucial to increase propylene production using the FCC method to meet the growing market demand. Because it is simple to alter the operating parameters, such as the addition rate of fresh catalyst, the addition of ZSM-5 additive, the reaction temperature, etc., the FCC is a versatile process for adjusting feed oil properties and desired product yield. Certain FCC procedures focusing on producing propylene have been created and put into production [4]. Unquestionably, the petro refinery sector, which transforms crude oil into fuels and petrochemicals, is integral to the global economy and energy supply. The FCC process, which employs zeolite-based catalysts might reach >40 percent oil conversion in the petroleum refining sector. The market's demands for certain products (such as gasoline, propylene, olefins, etc.) have significantly changed over the past few decades, resulting in changes to FCC catalysts. Y-zeolite has been considered a primary cracking component in the FCC catalyst since 1964. ZSM-5, which was invented in 1973, is used as a second FCC

catalyst. It has the main application in the enhancement of the propylene yield. Propylene is a minor product with only 4–6% of the total weight of gasoline in a conventional FCC unit. However, this trend has changed, and the maximum amount of propylene could be increased to about 20%, which would be very advantageous. ZSM-5 is a crucial part of an FCC catalyst that produces a lot of light olefins. The gasoline range ZSM-5 may break down olefins to mostly propylene and butenes [1]. Zeolites usually have micropore sizes between 0.25 and 1 nm, which limits the diffusion of reactants and products. As a result, feedstock and product molecules have diffusional limits, and their adsorption and catalytic efficiency suffer. Consequently, the restricted accessibility of active sites within the zeolite components controls the mass transfer capabilities of FCC catalysts [5]. Additionally, the formation and accumulation of heavy compounds within the zeolite micropores result in pore blockage, which causes deactivation. As a result, several techniques have been used to enhance the zeolites' pore properties and alter the selectivity toward target products [1]. Numerous strategies have been investigated to overcome the limitations of micropores. However, because of their reduced activity or the difficult synthesis method, these substitutes have not yet been able to replace zeolites as catalysts completely. Significant efforts have been made to develop and create hierarchical porous materials that combine various porosity scales, often in the range of nanometers to several hundred nanometers, to solve such diffusion problems. Recently, hierarchical zeolites have attracted interest in developing cracking catalysts and other applications [6],[5]. By adding mesopores to the structure of microporous zeolites, hierarchical zeolites are produced that improve reactant and product transport through small channels. This method also minimizes the impact of coke deactivation and lowers mass-transfer diffusion resistance [7]. There are two ways to

synthesize hierarchical zeolites: post-synthesis techniques and crystallization process control. Nevertheless, aggregation is a common drawback in the latter strategy and is not cost-effective. For post-synthetic treatments, numerous strategies, such as dealumination, desilication, and templating procedures, have been investigated to obtain hierarchical zeolites. For large-scale industrial applications, the most practical techniques are alkali/acid solution treatment and high-temperature steam treatment [8]. Acid treatment (dealumination) is the most often employed post-treatment technique to raise the silica-alumina ratio and produce mesoporosity, particularly for Y zeolites with a low $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. Several researchers have utilized this method to produce micro-mesoporous Y-zeolite, which is subsequently applied in numerous industrial applications [9],[6],[1],[10],[11],[12]. Processing parameters such as reaction temperature, duration, acid source, and concentration influence hierarchical zeolites' porosity and textural characteristics. Strongly acidic inorganic acids, such as hydrochloric and nitric acid, perform well to etch aluminum frameworks. Nevertheless, the dealumination process frequently decreases crystallinity and the breakdown of the zeolite structure [13]. So, it is advised to synthesize a hierarchical Y zeolite by combining post-treatment with soft templating and steaming. This zeolite can be employed in several processes, especially in fluid catalytic cracking catalysts [1]. Soft templating appears more versatile and, most importantly, its ability to provide controlled mesoporosity inside the zeolite structure [9]. One important thing is the connection between intracrystalline mesopore formation and zeolite micropore size. It is suggested that the surfactant species' 12-membered ring pores in Faujasite are reachable, facilitating the formation of long-range mesopores during the surfactant-based mesostructuring process. A method that can generate controlled

mesoporosity inside the crystalline structure of zeolite is highly useful and has a huge effect on the catalytic side, as in FCC. The two primary parts of a contemporary FCC catalyst are usually a matrix and a zeolite. In FCC processes, zeolites are largely in charge of catalytic activity and product selectivity, often accounting for 15–45% of the catalyst composition. Since the fresh catalyst does not precisely reflect its commercial performance, steaming is an essential stage in activating and assessing FCC catalysts. By simulating the deactivation circumstances seen during industrial operation, hydrothermal treatment offers a more accurate evaluation of catalyst behavior. A Micro Activity Test (MAT) apparatus employing vacuum gas oil (VGO) as the feedstock was used to assess the produced catalysts. All MAT tests must be run at a 550 ° C temperature and time on stream (TOS) of 30 sec [9].

Computational modeling and simulation play a pivotal role in the modern development of catalytic materials, such as hierarchical zeolites. These methods are instrumental in unraveling complex molecular interactions and processes that are often challenging to observe directly through experimental techniques alone. Molecular simulation effectively investigates atomistic-level structural characteristics and features of microporous and mesoporous materials [14]. Computational modeling gives researchers important insights into structure-property correlations at an atomistic level while saving resources and time by eliminating the need for costly and time-consuming experimental techniques. Simulations make important predictions regarding adsorption, diffusion, and transport characteristics; these predictions are critical for processes like separation and catalysis. Specifically, simulation tools like Molecular Dynamics (MD) methods provide profound insights into zeolites' adsorption and diffusion behaviors, facilitating a deeper

understanding of how molecular phenomena influence catalytic performance. Computational modelling is also essential in studying zeolite-based catalysts, especially when examining the pore structure and transport characteristics directly bearing on catalytic activity [15]. Materials Studio, a powerful molecular modelling and simulation platform, allows for the construction of zeolite models, the prediction of pore sizes, and the simulation of gas adsorption isotherms using different modules. Monte Carlo (MC) and molecular dynamics (MD) simulations are widely used to investigate the adsorption, diffusion, and interactions of reactant molecules with the zeolite framework at the atomistic level. While MD simulations offer time-resolved trajectories that disclose diffusion mechanisms inside microporous environments, GCMC simulations allow for the prediction of adsorption isotherms [16]. These methods produce crucial metrics for connecting structural characteristics with catalytic action, such as self-diffusivity, activation energies for diffusion, and adsorption enthalpies. Nevertheless, these simulations are computationally demanding for larger hierarchical systems and are usually restricted to nanoscale domains.

1.2 Research Objectives

This study aims to assess how hierarchical ZSM-5-based FCC catalysts and modified Y-zeolite-based catalysts can enhance conversion rates, gasoline selectivity, total olefin yield, and propylene output. Furthermore, hierarchical Y-zeolite's pore structure is computationally investigated using molecular modeling tools, which are verified against experimental data.

The specific objectives of this research work are:

- Mesoporosity generation in conventional Y-zeolite and ZSM-5 using simple chemical treatment to reduce diffusional limitations of heavy FCC feed molecules.
- Detailed characterization of modified Y-zeolite and ZSM-5.
- Performance evaluation of FCC catalysts in the MAT unit to study the effects of hierarchical zeolite-based FCC catalysts on VGO cracking for the enhancement of propylene and light olefins.
- To construct hierarchical Y-zeolite (FAU) models and characterize their structural and textural properties using computational techniques.
- To verify and match the computational results with the relevant experimental data. |

CHAPTER 2

LITERATURE REVIEW

2.1 Fluid Catalytic Cracking

The need for petrochemicals is expected to keep growing soon. Petrochemicals' oil demand is expected to increase by roughly 4 Mb/d per year over the next 20 years, making up 34% of the world's oil market by 2040 instead of the current 15%. The primary products of crude oil refineries are transportation fuels, such as kerosene, diesel, and gasoline. Additionally, they produce commercially significant by-products, primarily light olefins and BTX, essential for the petroleum industry [17]. More than 60% of the 400 million tons produced by the petrochemical sector are light olefins, which are recognized as the fundamental building blocks for various chemical goods, including plastics and pharmaceuticals. Because of the increased global population and improving living conditions, there is a constant need for light olefins and their derivatives. Ethylene and propylene are the most in-demand chemicals, and by 2027, market growth is projected to reach 5.85% annually [18]. One of the most crucial procedures in an oil refinery is Fluid catalytic cracking (FCC). It is used in most oil and gas industries to convert low-value hydrocarbons such as heavy gas oil, residue, and Vacuum gas oil into high-value products, i.e., gasoline and light olefins. Vacuum distillation derivatives, VGO, and atmospheric residue (AR), are the feedstocks typically upgraded in FCC units. The reactor, the distillation/separation section, and the catalyst regenerator are the three primary components of a conventional FCC unit, though many different commercially available FCC unit designs exist. The reactor-

regenerator system, the heart of the FCC process, transforms heavy crude oil fractions into useful products including liquefied petroleum gas (LPG), diesel, and gasoline [19]. The reactor can be further separated into a riser and a stripper. When the feedstock touches the heated, regenerated catalyst at the riser intake, it vaporizes in the riser. Subsequently, the vaporized hydrocarbons split into smaller molecules on the catalyst's surface within the riser [20]. A powdered fluidized catalyst breaks high molecules into shorter molecules by contacting the feed. The FCC reactor's temperature and pressure conditions are 550 ° C and 1.72 bar gauge, respectively. Concurrently, one of the by-products, namely coke, coats the catalyst's surface. Furthermore, the catalyst's activity diminishes because coke obstructs access for reactions with other molecules. The catalyst and the hydrocarbons are separated once they exit the riser. After that, the regenerator receives the used catalyst, and all hydrocarbons are directed to the main fraction for further separation. Using combustion with air in the regenerator, the coke on the catalyst surface becomes reactive. Finally, the heated catalyst that has been renewed is returned to the riser inlet. The reactor and regenerator have different functions; the reactor is made for reactions that break, and the regenerator replenishes the catalyst [21]. Since the FCC process involves many following reactions, the production of chosen products, can be thought of as intermediate products that can be made easier by using down-flow configuration to improve the distribution of residence time inside the reactor. The FCC process has numerous technological advantages over other methods, including continuous operation and a heat source for hydrocarbon cracking. Moreover, a significant quantity of heat is produced during the burning of the coke [22]. This heat powers the reactor's endothermic cracking processes and feedstock

vaporization. A variety of parameters influence propylene generation in an FCCU, but the primary ones are reactor temperature, catalyst type, C/O ratio, and total pressure [24].

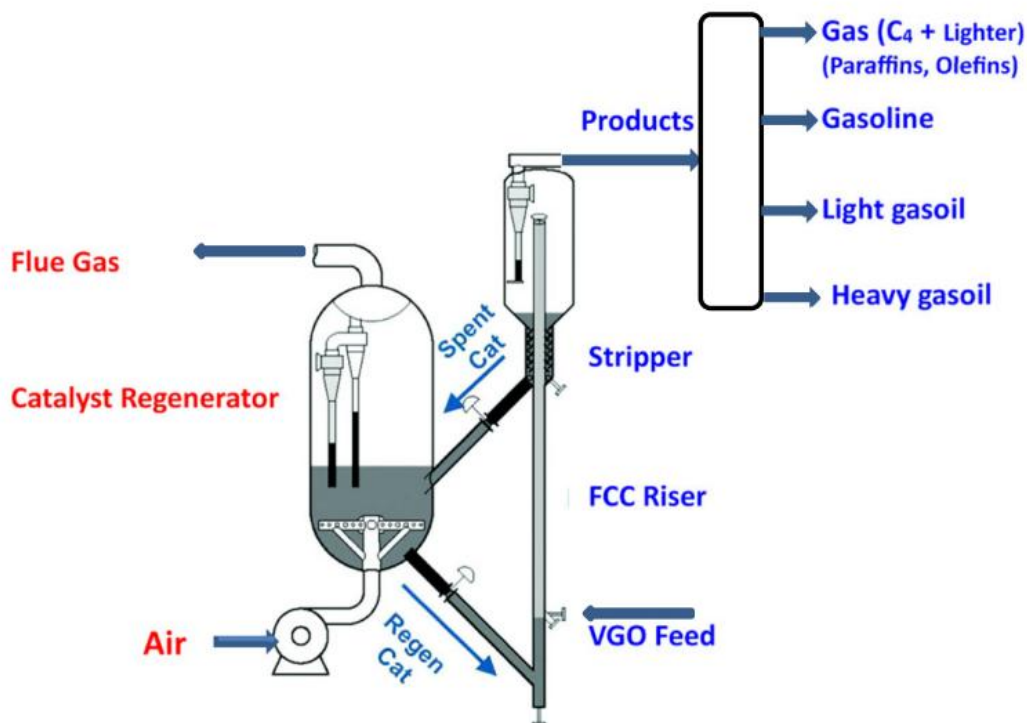


Figure 2.1: An elaborate diagram illustrating a fluid catalytic cracking unit [23].

FCC units are essential to modern refineries because they play a major role in propylene manufacturing, as a feedstock for the petrochemical industry, and in high-octane gasoline. Currently accounting for 30% of global propylene output, FCC is the second-largest source of alkenes after steam cracking [25].

2.1.1 Fluid Catalytic Cracking Catalyst

Since the first amorphous cracking catalysts, significant advancements have been made in creating catalysts and catalytic additives to upgrade conventional and unconventional FCC (Fluid Catalytic Cracking) feedstocks. The catalysts selected for the process impact the FCC unit's design and operation.

An important turning point was the crucial addition of zeolites to FCC catalysts in the 1960s, which resulted in a sharp rise in their catalytic activity [26]. Ultra-stable Faujasite Y (USY) remains the fundamental component in industrial FCC catalysis, even after exploring other zeolites. Because of its 0.74 nm diameter and three-dimensional pore structure, Y-zeolite stands out among the other zeolites used in the industry and attracts much attention. Y-zeolite, which has more active sites than other catalysts, is widely used in the oil refining industry and is essential to FCC catalysts [27]. Commercial FCC (Fluid Catalytic Cracking) catalysts comprise active or inactive matrix-supported Y zeolite crystals. These catalysts also comprise different additives, binders, and fillers, all of which have unique effects on the composition and performance as a whole [28]. Clay is used as filler and for heat capacity reasons. Many sources of silica and alumina are used to make a meso-macroporous FCC matrix that pre-cracks the larger feed molecules. Nowadays, almost all catalysts contain Y zeolite or one of its variations. Zeolites' distinct crystalline structure and acidity are two characteristics that support their catalytic activity in chemical reactions. The four tetrahedrally oriented 12-membered ring apertures constituting the Y zeolite's pore system led to the supercage, a bigger center cavity. The supercage has a diameter of 1.2 nm, while the pore aperture is 0.74 nm in diameter [29].

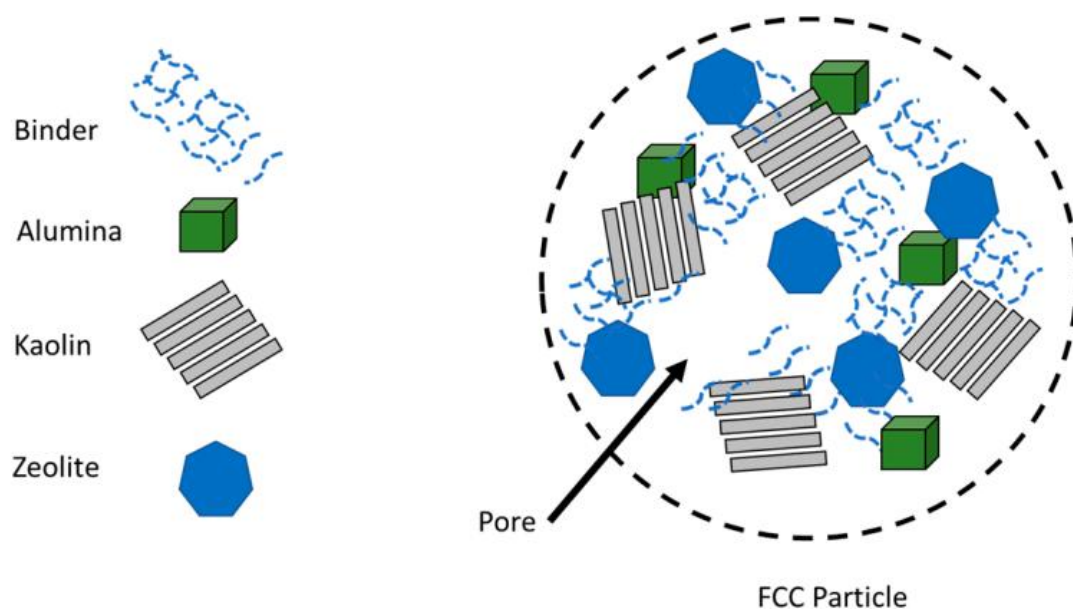


Figure 2.2: Structural Composition of FCC Catalyst [30].

Reactant molecules must diffuse through the porous structure of the catalyst particles to access the active sites, which are primarily located within the microporous framework of the zeolite. These micropores serve as the environment for adsorption and subsequent catalytic reactions. Both the exterior surfaces and the internal pore structure of these crystallites have catalytic active sites. Molecules must move into the zeolite crystals through the matrix's large pores for reactions. Diffusion in catalysts frequently occurs under the Knudsen regime, in which the zeolite pore walls greatly influence the diffusing molecules' motion. Conversely, diffusion within zeolites often operates in what is known as the “configurational regime,” defined by the hydrocarbon molecules being almost the same size as the zeolite's inner channels. As a result, the molecules inside the pores encounter significant restrictions that hinder them from evading one another. Diffusion

limitations within the pore system make it extremely difficult for bulky molecules, which are frequently found in FCC feedstocks, to enter internal locations. However, if the matrix is active, these bigger molecules could shatter on or outside of zeolite crystals. As a result, the end products of these reactions have an easier time diffusing inside the micropores [17]. Y zeolite's unique microporosity, acidity, and hydrothermal stability make it well-suited for FCC applications. By carefully crafting the catalyst, one may control the product's activity and selectivity [31]. Zeolite, crucial to the catalytic activity of FCC processes, makes up 15–40% of most FCC catalysts. Catalytic activity decreases at zeolite concentrations below 15%, while the attrition rate increases at concentrations above 45%. Sustained improvements in Y-zeolite are the best way to produce advanced FCC catalysts and get better yield performance. Alkenes are produced from gasoline molecules obtained via primary cracking, thanks to the shape selectivity and increased activity of zeolite Y. These catalysts should ideally be used with additives to maximize propene production. ZSM-5 is the additive of choice for increasing propene and butene production. ZSM-5 is the second most used zeolite in catalytic cracking applications after USY. ZSM-5 was first added in modest amounts to promote gasoline production and increased propylene production. ZSM-5 swiftly consumes the carbenium ions, preventing them from entering the mechanism of the hydrogen transfer reaction. Without ZSM-5, these carbenium ions would participate in hydrogen transfer activities, reducing the amount of olefins produced. Nonetheless, approximately 25% of the total composition of the FCC catalyst should be added [4].

2.1.2 Catalytic Cracking Reactions

The cracking reactions combine thermal and catalytic reactions, where catalytic reactions are more important. During the reactions, pre-cracking of the large molecules occurs in the amorphous silica-alumina matrix before entering into the micropores of the zeolite. These reactions are thought to occur at the acid sites of the zeolite catalyst. Numerous intricate chemical processes occur within the FCC riser. In addition to many side reactions like hydrogen transfer, concurrent thermal and catalytic cracking processes also occur. Furthermore, a range of hydrocarbon mixtures that make up the FCC feedstock combine to form a combination of many chemical species that react and evaporate at various rates. The acidity is mediated via zeolites and matrix particles, including Brønsted and Lewis acid sites [32]. The chain reaction responsible for the catalytic cracking of hydrocarbons is believed to be governed by the carbonium ion theory. The mechanism consists of three stages: initiation, propagation, and termination.

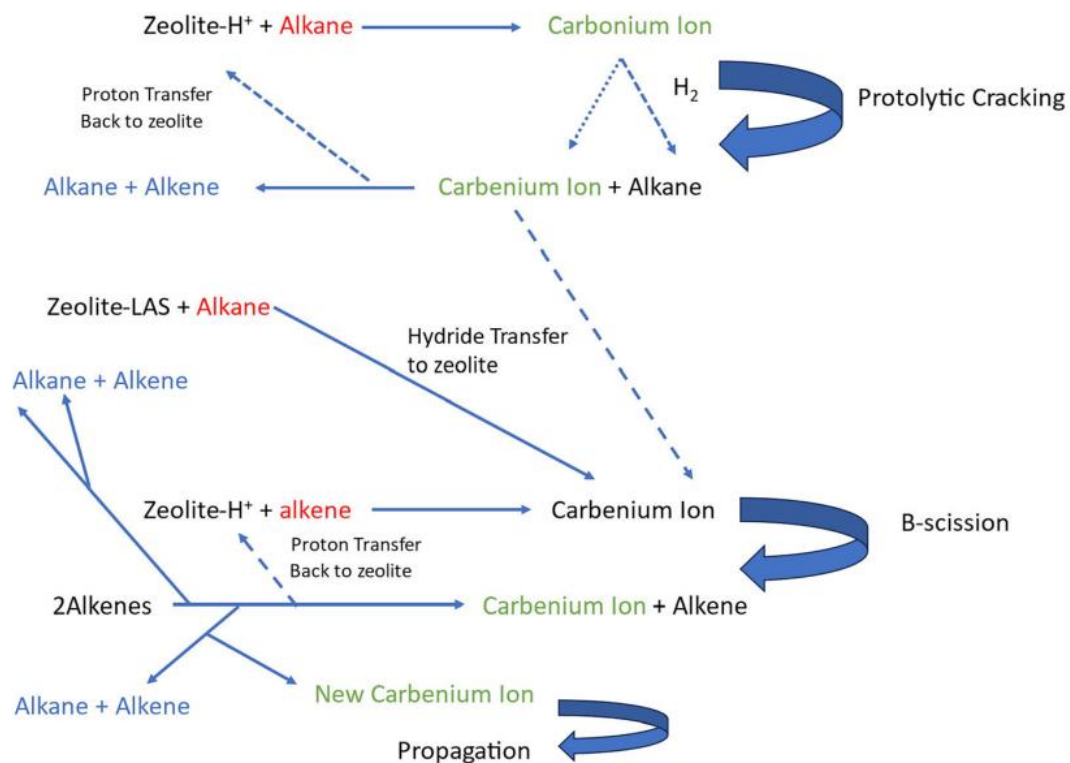


Figure 2.3: Reaction pathways involving zeolite-based acid catalysts in the cracking of hydrocarbons [17].

Figure 2.3 illustrates how hydrocarbons catalytically crack over zeolite-based acid catalysts. These consist of carbonium formation, carbenium formation by proton and hydride transfers, and β -scission, which produces a primary carbenium. The alkane first bonded to the acid site may desorb if the primary carbenium ion abstracts a hydride from a bigger alkane molecule. Alternatively, it might experience β -scission, leaving a carbenium ion on the zeolite acid site and producing ethene, allowing the reaction to proceed. An alpha-alkene can also be formed by the main carbenium ion transferring a proton to the zeolite [33]. Figure 2.4 briefly overviews the FCC cracking reactions from feedstock to gasoline and gasoline products.

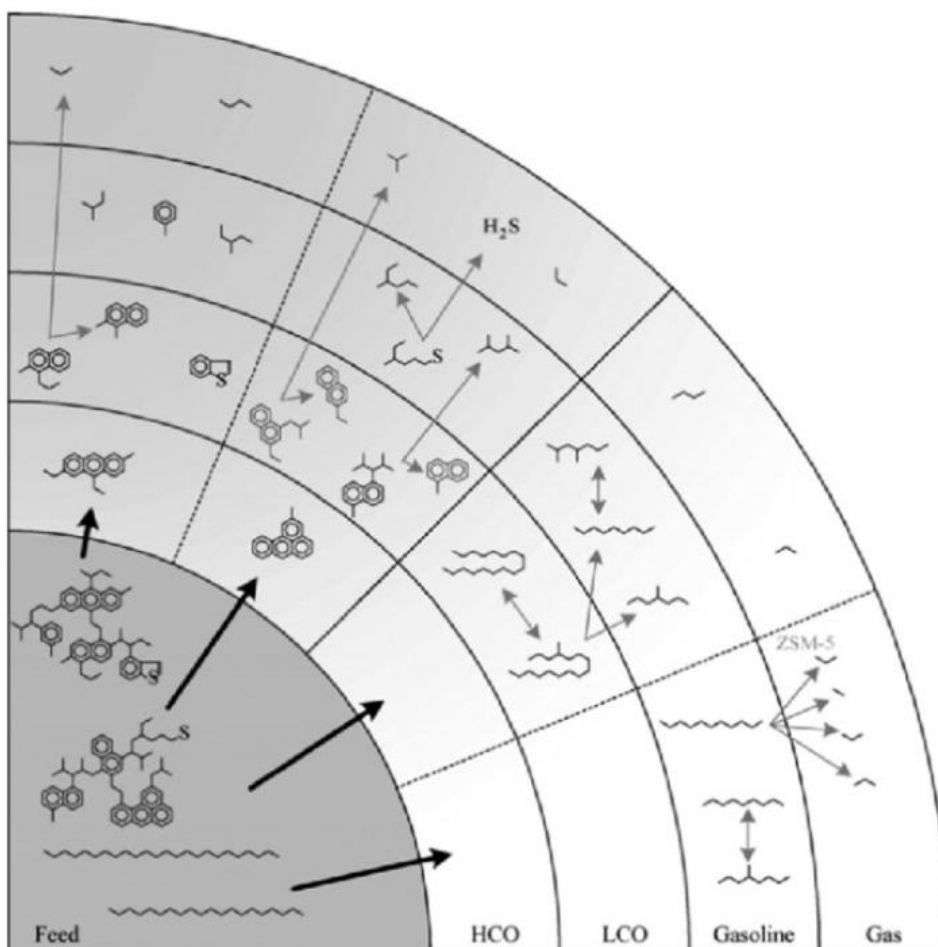


Figure 2.4: A series of cracking reactions of heavier feedstock leads to the FCC products [9].

Maintaining the residence duration of molecules inside zeolite pores below a certain threshold is necessary to stop unwanted reactions. Achieving a shorter residence time requires either decreasing the diffusion routes by synthesizing nanocrystals (smaller crystals) or increasing the net diffusion rate of molecules within the crystals through hierarchization (designing pores of different sizes). Mesoporous structures can be added to ZSM-5 to improve catalyst accessibility and decrease unwanted reactions like hydrogen transfer. As a result, work has begun to create hierarchical zeolites that display secondary

porosity, primarily in the mesopore range (IUPAC defines mesopore as having pore sizes between 2 and 50 nm). This strategy aims to maintain the zeolites' acidity and crystallinity while improving the accessibility of the bigger reagent molecules to the material's active centres [34]. Scientists are still having difficulty producing hierarchical zeolites with secondary porosity. New and improved techniques are being developed to synthesize microporous and mesoporous materials. Crucially, further porosity shouldn't risk the microporous structure; instead, these materials should maintain the distinctive characteristics of zeolites.

2.2 Hierarchical Zeolites

Zeolites are highly crystalline aluminosilicates composed of SiO_2 and AlO_4 tetrahedra, which are arranged to form well-defined porous structures. These tetrahedral units can be connected in various ways, resulting in materials with specific topologies. Zeolites are extensively used in multiple heterogeneous catalytic processes, such as isomerization, alkylation, and catalytic cracking. Strong acid sites, large specific surface areas, high ion exchange capacities, and hydrothermal stability—all of which are influenced differently by exposure to steam or hot liquid water—are some of their distinctive qualities that are thought to be responsible for their effectiveness [35]. Zeolites have various drawbacks despite their many benefits and important functions in chemical reactions. One of the main problems is that when reactant molecules are the same size or larger than the zeolite's micropores, diffusion limitations result in limited accessibility to active sites [36]. Because of this, molecular diffusivity in zeolites rapidly decreases in a variety of regimes, including "intercrystalline" diffusion, which takes place outside the catalyst, "Knudsen" diffusion, which is predominant in mesopores, and "configurational" diffusion, which occurs inside

micropores. Although it is advantageous for shape selectivity, the zeolite crystal's intrinsically slow molecular transport can also encourage undesirable secondary reactions. Micropore blockage and catalyst deactivation may result from these side reactions, which may also decrease product selectivity and produce coke precursors. Furthermore, because catalytic activity is frequently limited to the outside shell, leaving the inside areas relatively inactive, diffusion constraints limit the zeolite's efficient use [34]. Several strategies have been developed to overcome these issues. One method is ordered mesoporous materials like MCM-41, KIT, SBA-type structures, and hexagonal mesoporous silica (HMS). The well-defined mesoporosity of these materials has drawn attention to their potential as adsorbents and solid acid catalysts. Their wider use is constrained by their amorphous form, which results in decreased hydrothermal stability and generally weaker acidity. Another tactic is to create zeolites with bigger pores, usually bigger than 12-membered rings (MRs). To create more open structures, these extra-large pore zeolites are frequently made by combining materials like Germanium into the framework and employing complicated organic structure-directing agents (SDAs). Unfortunately, these materials have weak (hydro)thermal stabilities, high production costs, and decreased acidity [37]. A third tactic is to minimize zeolites' crystal size to the nanometer range. This shrinking improves molecular transport and the conversion of bulky reactants by greatly increasing the exterior surface area and shortening diffusion routes. Despite these encouraging benefits, nano-zeolites have several disadvantages, such as difficulty in separating them from reaction products and the difficulty of their production processes [38].

Creating hierarchical zeolites is an additional successful strategy for overcoming diffusion constraints. The intrinsic microporous structure of these materials is complemented and

interconnected by an extra network of mesopores and/or macropores (>50 nm). These secondary pore systems, which can be created between crystal particles (intercrystalline porosity) or within individual crystals (intracrystalline porosity), increase molecular diffusivity. Numerous techniques have been developed to create hierarchical zeolites. Nevertheless, the development of hierarchical zeolites may also impact other important characteristics of the crystal, especially its acidity. The distribution or strength of acid sites may change depending on the modification approach selected, which affects catalytic activity. Because these effects might also result from changes in acidity, it is crucial to be cautious when blaming the introduction of mesopores alone for changes in catalytic behavior. Jamil et al. illustrated this by adding mesoporosity to a self-synthesized ZSM-22 zeolite using a diluted hydrofluoric acid (HF) solution. When n-hexane was subjected to steam catalytic cracking (SCC), the resulting hierarchical catalyst showed a greater initial conversion. However, rather than the increased mesoporosity, this improvement was mostly ascribed to the zeolite's higher acidity [39]. Likewise, hierarchical ZSM-5 was demonstrated by Liao et al. to be an efficient catalyst for the monomolecular dealkylation of 4-propylphenol [40]. Numerous studies have thoroughly examined the superiority of mesoporous-structured ZSM-5 catalysts over standard ZSM-5 in fluid catalytic cracking (FCC) processes, especially in increasing light olefin yields [17].

2.3 Methods of Synthesis of Hierarchical Zeolites

Various techniques have been developed over the past few decades to produce hierarchical zeolites.

1. Top-down approach
2. Bottom-up approach
3. Nano-zeolites and Their Assembly

They are further classified into various types.

Top-down approach

- Dealumination
- Desilication
- Dissolution-Recrystallization

Bottom-up approach

- Soft-Templating
- Hard Templating
- Template-free

2.3.1 Dealumination

One of the first techniques used to add mesoporosity to zeolites was dealumination. It has been applied in industry to improve the steam and hydrothermal stability of high-alumina microporous zeolites since the middle of the 1960s. This method changes the acidity and the Si/Al ratio by eliminating aluminum from the zeolite structure. These days, dealumination is mostly utilized in the industrial manufacturing of ultra-stable Y (USY) zeolites, which are extensively employed in hydrocracking and fluid catalytic cracking (FCC). In a water vapor environment, steam treatments are usually performed at

temperatures higher than 500 °C. This causes the Al–O–Si bonds to break down and structural flaws to emerge inside the zeolite framework. After steam treatment, a modest acid treatment—known as an "acid wash"—is frequently performed to clear debris and open up the mesopores created during steaming. From a parent Y zeolite, USY zeolites with different pore volumes and acidity levels can be produced by altering the steaming temperature and the number of acid wash cycles [41]. Severe acid treatments, which causes aluminum to be extracted from the zeolite structure immediately. This method creates mesopores and raises the Si/Al ratio without requiring an additional acid wash. The type of zeolite and the particular acid employed are some variables that affect how effective these treatments are [42]. Nevertheless, dealumination procedures have many serious disadvantages to creating mesopores in zeolites. The partial amorphization, which results in a decrease in relative crystallinity, is one significant problem. Furthermore, the mesopores and holes created are frequently isolated inside the zeolite framework and unconnected to the outside, reducing their ability to improve molecular transport. Moreover, the produced mesopores usually have a wide and irregular distribution of pore sizes [43]. A sequential steaming–alkaline leaching method has been suggested by recent research for ZSM-5 modification. This successive process was used, for instance, by Wang et al. to create mesoporous ZSM-5 with intracrystalline mesopores that range in size from roughly 2 to 4 nm [40]. Another study examines the effects of silicon flaws on the dealumination-induced mesopore development in Y zeolites. The study demonstrates that Si-defects improve the material's porosity by promoting mesopore development [44]. Time and energy usage are two primary disadvantages of traditional dealumination techniques. Abdulridha et al. developed a method for creating mesoporous zeolite materials called

microwave-assisted chelation (MWAC) to overcome this. In this method, aluminum was extracted from the Y-zeolite framework by complexation using ethylenediaminetetraacetic acid (EDTA) as a chelating agent. Microwave irradiation greatly improved the process by speeding up and intensifying the chelation reaction. The resultant material achieved high and stable activity with a constant conversion rate of 97 percent, demonstrating the proper acidity for catalyzing the cracking of 1,3,5-triisopropylbenzene (TIPB). This proves that the MWAC approach is economical, time-efficient, ecologically benign, and possibly sustainable for industrial uses [45]

2.3.2 Desilication

Mesopores are created, and silicon is preferentially removed from the framework when a zeolite is treated with an alkaline solution, such as diluted NaOH, which selectively hydrolyzes Si–O–Si bonds [46]. Interconnected mesopores may form during desilication, but the zeolite's initial microporous structure is mostly preserved. The zeolite structure may degrade significantly if overly concentrated alkaline solutions are utilized, resulting in a major material loss and a sharp decline in microporosity. It is observed that the optimum alkali (NaOH) concentration for the huge quantity of mesopores without affecting the material's crystallinity was 0.2M for a time of 30 to 120 sec. At the same time, a high concentration of sodium hydroxide > 1M affects the crystallinity of the material [47]. Aqueous NaOH desilication of parent ZSM-5 zeolites is one of the most used techniques for producing mesoporous ZSM-5 structures [48]. HZSM-5 with different Si/Al₂ ratios was varied with Mn and alkaline treatment and tested as an FCC catalyst additive to increase the yield of light olefins. Due to the formation of a hierarchical micro–mesoporous structure, alkaline-treated HZSM-5 showed noticeably greater light olefin yields than the

original HZSM-5. Notably, under ideal desilication conditions, an equilibrium catalyst (E-Cat) including alkaline-treated HZSM-5 with a Si/Al₂ ratio ranging from 80 to 280 obtained a maximum light olefins yield of roughly 28.3 weight percent [49]. To improve the desilication of ZSM-5, some changes to the conventional NaOH treatment have recently been investigated. Certain additions have been shown to dramatically increase mesoporosity in the NaOH solution, facilitating the more efficient production of hierarchical structures. The impact of NaOH treatment with and without other additions was examined by Smail et al. It has been demonstrated that organic additives improve the desilication process by encouraging the development of more homogeneous mesopores. The inclusion of organic compounds resulted in increased pore diameters. Still, NaOH alone created the smallest mesopores (~3.7 nm) among the treatments: The largest pores, measuring around 15.2 nm, were made by the combination of CTAB/TPAOH with NaOH, followed by the ~11.1 nm pores produced by NaOH with TPAOH and the ~14.9 nm pores produced by NaOH with CTAB [50]. Ultrasound is another way to alter the conventional NaOH desilication process. The introduction of ultrasound during the NaOH alkaline treatment increased mesoporosity in a study that used rice husk ash as the silica source. Compared to zeolites changed using only traditional NaOH treatment, the resultant material showed better catalytic cracking activity for light naphtha, which was explained by the increased mesopore development [51]. Gorzin et al. used different concentrations of NaAlO₂ and TPAOH to study the desilication of very siliceous ZSM-5 zeolite. The zeolite framework was shielded from excessive base leaching by the presence of TPAOH. Without substantially changing the initial Si/Al ratio, they generated homogenous and narrow mesopores by optimizing the NaAlO₂/TPAOH ratio and performing an acid wash. The

methanol-to-propylene reaction's catalytic performance significantly improved due to this treatment [52]. A comparison of mesoporous ZSM-5 and conventional ZSM-5 showed a notable improvement in the generation of light olefins in a study by [25]. The mesoporous ZSM-5 produced a much greater yield of 24.0 weight percent of ethylene and propylene than the conventional ZSM-5, which produced 13.7 weight percent. This indicates the positive impact of mesoporosity on catalytic performance.

2.3.3 Dissolution-Recrystallization

A top-down method for creating hierarchical zeolites is recrystallising a partially dissolved zeolite. There are two primary steps in this procedure. The zeolite structure is first partially dissolved, usually with an alkaline solution. In the second stage, the dissolved and scattered species are reassembled into a mesoporous structure using hydrothermal treatment with a surfactant present. The properties of the resulting hierarchical zeolite, which permits the creation of different mesostructured materials, depend on the degree of dissolution and subsequent recrystallization. This method is also known as surfactant-templated recrystallization. In 2004, the first patent application was filed to generate mesoporosity inside zeolites using this method. Cetyltrimethylammonium chloride or bromide is frequently employed as a surfactant to provide carefully regulated mesoporosity to various zeolites. This technique has fewer disadvantages than the desilication process, including less silica loss and less harm to the zeolite crystal structure. The initial procedure involved modifying USY zeolite ($\text{Si/Al} = 15$) over 10–20 hours at 150°C using a CTAB solution in 0.37M ammonium hydroxide. After that, calcination was used to eliminate the CTAB

templates. Figure 2.5 illustrates a crystal rearrangement technique to introduce well-defined mesoporosity inside zeolites [1].

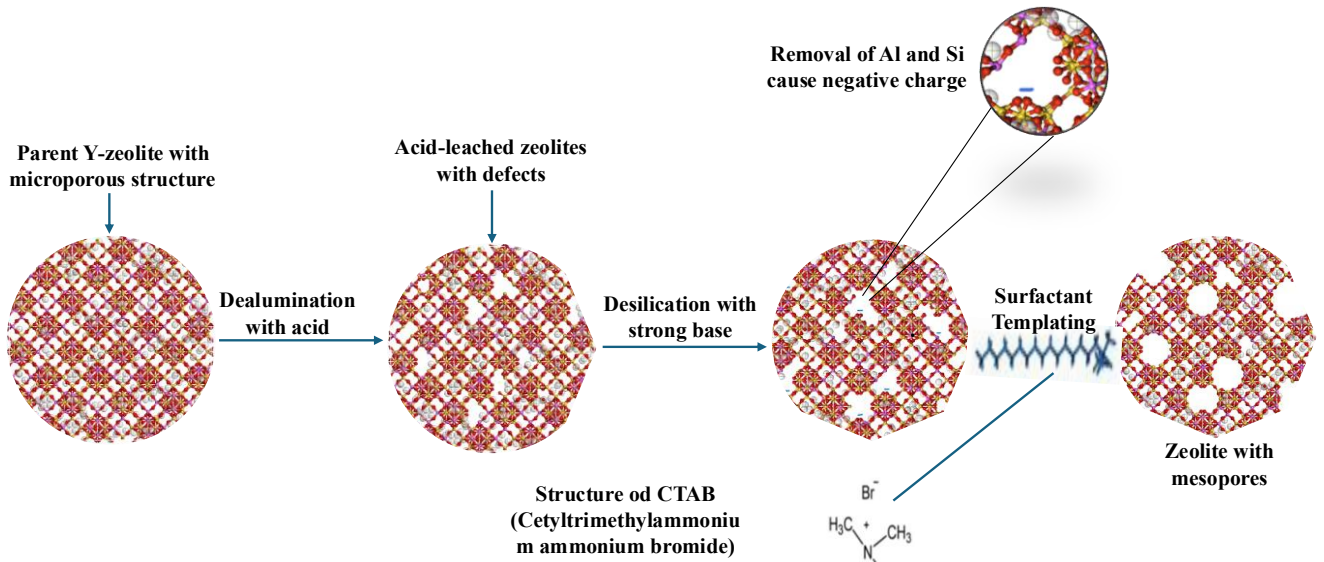


Figure 2.5: Mechanism of surfactant-templated mesopores formation

This method prohibits the dissolution of zeolite crystals and allows for useful interactions between surfactants and zeolite. Typically, complete recovery of mesostructured material is achieved after the process. Figure 2.5 describes the schematic demonstration of the mechanism of mesopore formation inside zeolite by using the surfactant. First, acidic solutions are used to treat the parent zeolite. This process produces acid-leached zeolites with structural flaws and an increased silica-to-alumina ratio by eliminating framework aluminum atoms, especially from the tetrahedral positions. The acid pre-treatment step breaks some of the Al-O bonds, which creates some vacancies and wears out the rigidity of the alumina structure. A strong base, NaOH or TPAOH, is applied to the dealuminated

zeolite. Particularly in high-silica areas, this eliminates silicon atoms from the framework in a selective manner. It dissolves portions of the crystalline structure, creating mesopores and causing the loss of Si and Al, which results in negative framework charges. The end product is a partially amorphized, faulty zeolite with more pore heterogeneity. Through electrostatic contact, surfactants are drawn to these negatively charged areas. CTAB is a cationic surfactant; the positively charged ammonium head interacts with the negatively charged zeolite surface, while the lengthy hydrophobic tail encourages self-assembly. Within the zeolite structure, surfactant molecules arrange themselves to form micelles or liquid crystalline phases. These micelles serve as a "soft mold," guiding the development of mesopores. Following surfactant templating, calcination eliminates the organic surfactant from the material, forming hierarchical zeolite. Subhan et al. produced mesostructures using NaOH and CTAB that resembled Al-MCM-41 and showed enhanced adsorptive desulfurization efficiency [53]. Other organic bases have also been investigated for this process. For instance, upon post-synthetic modification, tetraethylammonium hydroxide (TEAOH) behaves similarly to TPAOH. Zhang et al. treated extremely siliceous ZSM-5 with TPAOH and tested the methanol-to-propylene (MTP) reaction of the resulting mesoporous ZSM-5, which had pores in the 2–3 nm range. They found substantial improvement in the service time [54]. The dissolution–recrystallization method has also been used recently when a binder is present. Zhou and colleagues successfully created a hierarchical monolithic ZSM-5 that is entirely zeolitic. Binder crystallization was generated by adding n-butylamine (as a structure-directing agent) and a binder to cylindrical ZSM-5 pellets that were steam-treated. At the same time, the recrystallization process produced mesopores. Compared to a commercial counterpart, the resultant catalyst

showed noticeably improved catalytic performance in the methanol-to-hydrocarbons (MTH) process [55]. Sachse et al. elaborated on this by formulating a thorough mechanism for CTAB's function in the desilication process. A mild alkaline treatment of FAU-type zeolites causes the base to hydrolyze Si–O linkages, creating negatively charged defect sites that draw CTA^+ ions. Micelles start to develop and clump inside the zeolite crystals as the process progresses, directing the reassembly of surrounding silica fragments. An organized mesoporous structure is the end outcome. This surface-templating technique avoids substantial dissolution. Rather, it provides a more precise and regulated synthesis method by directly inducing mesostructuring inside the crystalline framework under milder alkaline conditions [56].

2.3.4 Soft Templating Methods

To encourage the creation of intracrystalline and/or intercrystalline mesopores, organic substances can be used as mesoporous templates in the synthesis mixture. For this, a range of templates can be used, such as block polymers, amines, surfactants, organosilanes, and organic ammonium salts. For example, soft templates can serve as the physical scaffolding mesopores grow around by creating micelles. They might also engage in chemical interactions with the growing zeolite phase, which would further affect the structure and creation of the mesoporous network [46]. Mesoporegen can be readily eliminated by calcination following zeolite production, and mesopores are then formed at the mesoporegen positions. To endure synthesis conditions, zeolite synthesis templates must be hydrothermally stable. However, care must be taken because using some templates can create amorphous mesoporous materials instead of the intended crystalline hierarchical zeolites. Soft templates are a novel and elegant way to control pore topologies in zeolites.

Still, because of the high cost of the templates, this method is frequently linked to greater economic expenses, which makes it less feasible for large-scale industrial applications. Furthermore, the removal of soft templates may cause harmful gases to be released, raising safety and environmental issues [41]. In a study, Meso ZSM-5 was created using block copolymer and tested against conventional ZSM-5 for catalytic cracking of Vacuum gas oil. Propylene yield was more than quadrupled over Meso-Z, which has an MFI topology but includes intrinsic mesopores and a highly accessible pore structure, at a gasoline penalty comparable to that of the ZSM-5 addition [57]. Customized soft templates are expensive, frequently preventing them from being used in catalytic applications. However, Meng et al. successfully created mesoporous ZSM-5 by combining diethylamine (DEA) with a mono-quaternary ammonium surfactant, which is inexpensive. The final catalyst's catalytic performance was on par with a catalyst made with a more costly quaternary ammonium surfactant [58]. In a different work, Xing et al. used silicon and aluminum from acid-treated kaolin clay in conjunction with organosilanes. The mesopore-forming hexadecyltrimethoxysilane was used in a steam-assisted crystallization (SAC) process. Compared to commercial ZSM-5, the resultant catalyst performed better in the methanol-to-aromatics process [59].

2.3.5 Hard Templating Methods

Hierarchical zeolites can be synthesized by combining hard templates with structure-directing agents (SDAs). During synthesis, the microporous zeolite forms solid materials with a rigid structure around these templates, such as carbon compounds. The hard template is usually removed by calcination or chemical dissolution after synthesis, leaving meso- or macropores in its stead. Hard templates provide excellent control over mesopore size, are varied, and are chemically inert. They are usually simple to remove, but doing so frequently calls for high temperatures, which could cause product loss. Their relative hydrophobicity may limit their application. Furthermore, the hydrothermal and mechanical stability of hierarchical zeolites made using hard templates is generally weaker, and the resulting mesopores frequently have little interconnectivity [60]. The use of hard templates to create mesoporous MFI-type zeolite crystals has been thoroughly investigated in later research. Other hard templates and synthesis techniques have surfaced in recent years, and there is a rising movement to use bio-derived hard templates as more economical and ecologically friendly substitutes [36].

2.3.6 Template Free Synthesis

Without mesoporogens, template-free techniques provide an alternate means of creating hierarchical zeolites that may be more economical and ecologically beneficial. One such technique is seed-assisted synthesis, which entails adding tiny proto-zeolitic units to the synthesis gel created during the initial crystallization phases. Although the underlying process is unclear, this approach improves crystallinity and enables mesoporosity adjustment. Structure-directing agents (SDAs) can be added to seed-assisted synthesis for additional control. Furthermore, hierarchical zeolites can be created by carefully

controlling the crystallization process without the need for templates. Zeolites with customized mesoporosity and regulated active site accessibility and distribution can be produced by carefully regulating nucleation and crystal development [61]. The template-free synthesis of mesoporous ZSM-5 often relies on the SAC method. Using the SAC technique, Ge et al. used trace amounts of TPAOH to successfully synthesize mesoporous ZSM-5 with an abundance [62]. In the multicomponent reaction comprising propanol, formaldehyde, and ammonia, the material demonstrated outstanding catalytic performance, with an impressive 95% selectivity toward 3,5-dimethylpyridine. This demonstrates how well the synthesized zeolite Y without a template works in intricate catalytic reactions [63].

2.3.7 Nano zeolites and Their assembly

Because of their unique advantages over traditional zeolites, nano zeolites—zeolite crystals with diameters in the nanometer range—have garnered much interest for catalytic applications. They have shorter diffusion routes and a greater exterior surface area due to their smaller crystal size. They also have more accessible active sites and a high external-to-internal atom ratio, which improves their overall catalytic effectiveness. In catalytic applications, these characteristics result in increased activity, higher performance, and a longer lifespan. Numerous techniques exist for synthesizing nano zeolites, both with and without structure-directing agents (SDAs). Some approaches include seed-induced synthesis, milling followed by recrystallization, limited space growth, and alternative methods, including microwave-assisted or ultrasonic irradiation. Zeolite production can be limited to the nanoscale, producing nano-sized zeolite crystals by carefully regulating the kinetics of nucleation and crystal development [64].

2.4 Computational Insights into Hierarchical Zeolites

Using computer methods, it is currently standard practice to investigate zeolites' structural stability, characteristics, and technological uses. It is essential to comprehend the sorption and thermodynamics of zeolite molecules to use them as ion exchangers, shape-selective catalysts, and sorbents. The application of computational methodologies in new fields of zeolite chemistry research has been stimulated and expedited by the exceptional effectiveness of theoretical methods in forecasting and interpreting experimental results. The capabilities of current computer methods in zeolite study are extensive. These include predicting the physical and chemical characteristics of zeolite crystals, simulating X-ray diffraction patterns, evaluating their stability at different pressures and temperatures, and molecular modeling of framework structures—all of which allow for the prediction of novel structures. These techniques also make it possible to calculate the sorbent's and sorbate's vibrational characteristics, examine the adsorption and diffusion of guest molecules, and forecast the reaction routes in catalytic processes. Molecular mechanics and lattice energy minimization are two well-known approaches to the static simulation technique. Individual molecule systems are better modeled using molecular mechanics, but solid-state crystal structures are mainly simulated using lattice energy minimization. The Monte Carlo simulation method is well-suited for studying molecules adsorbed in zeolites. While the approach shares similarities with static simulation methods, it differs by incorporating the flexibility of statistical mechanics—randomly moving atoms and molecules to explore all relevant configurations and ensure a thorough investigation of potential adsorption sites [65]. The two M.C. techniques currently unknown are the grand canonical ensemble and the metropolis approach. Yashonath et al.'s simulation research

[66] looked at the temperature dependency of methane's binding and mobility within zeolite Y to better understand the behaviour of adsorbed methane. The methane molecule and the zeolite framework were treated as rigid entities in the computations, which were performed assuming a zero-coverage limit. M.C. simulation on methane adsorption in the zeolites Faujasite, mordenite, and ZSM-5 was carried out by Smit and den Ouden [67]. The low-occupancy sorption of alkanes in silicalite was effectively predicted by June et al. [29] using the Metropolis Monte Carlo approach [68]. The typical Metropolis algorithm was also used by Pickett et al. to model the behavior of para-xylene and benzene in zeolite theta-1. According to their research, para-xylene exhibited no rotational motion at 150 K and above temperatures, while benzene only displayed one form of rotation [69]. Freeman created a hybrid technique incorporating energy minimization, Monte Carlo, and molecular dynamics techniques to determine adsorbed molecules' minimum global energy site. The sorption behavior of butene isomers in ZSM-5 was effectively investigated using this integrated technique [70]. Molecular dynamics (M.D.) simulation is considered one of the most powerful computational tools for studying time-dependent properties of molecular or atomic motion within zeolite crystals. It provides both thermodynamic data and detailed insights into the dynamics of sorption and diffusion processes. However, its major limitations include difficulties in modeling the diffusion of larger adsorbed molecules and accounting for electronic polarizability due to the high computational time and memory demands. Nevertheless, advancements in supercomputing and computational resources are increasingly making full-scale M.D. simulations in zeolite research more practical and accessible. Newton's equations of motion must be explicitly solved numerically to use molecular dynamics (M.D.) techniques. Initial coordinates, randomly assigned velocities

for each particle, and potential energy functions that characterize their interactions are necessary for these simulations. At each tiny time step, the configuration of the system and associated forces are changed using a numerical integration method. To steer the system toward equilibrium, particle velocities are given randomly and then scaled over subsequent time steps [65]. Methane and small hydrocarbons in silicalite have been the subject of several noteworthy molecular dynamics (M.D.) modeling investigations by Catlow [71] and Goodbody [72].

2.4.1 Sorption Studies in Faujasite

The Faujasite structure consists of sodalite cages connected by twin rings of six members. Due to the successful synthesis of Faujasite structures with extraordinarily high silicon-to-aluminum (Si/Al) ratios, simulation studies are now using a completely siliceous version of Faujasite. This study [73] uses Grand Canonical Monte Carlo simulations to show that a force field obtained from ab initio computations accurately simulates methane–zeolite interactions across various Faujasite compositions (Na-Y and Na-X). The method helps design zeolites for methane storage or separation in environmental and petrochemical applications by precisely reproducing experimental adsorption data and exposing CH₄ adsorption mechanisms. Grand Canonical Monte Carlo simulations and experimental methods integrating gravimetry, manometry, and microcalorimetry were used to study the adsorption behavior of pure CO₂, CH₄, and their equimolar combination in model zeolite Na-Y. To better understand the intricate adsorption mechanisms, this work sought to thoroughly characterize gas–zeolite interactions and contrast mixed adsorption with single-component adsorption [74]. The loading-dependent diffusion of benzene in zeolite Na-Y was examined in the study using Grand Canonical Monte Carlo (GCMC), and molecular

dynamics (MD). Key features of the adsorption sites were revealed by the realistic structural model of the sorbate–sorbent system produced by GCMC simulations. The results found two preferred adsorption sites for benzene molecules within the zeolite framework [75]. A realistic model for xenon adsorption in sodium-Y zeolite is demonstrated using molecular dynamics simulation [76]. Propane adsorption in sodium and calcium forms of FAU-type zeolites X and Y is investigated using Grand Canonical Monte Carlo (GCMC) simulations. Because these cations generate more adsorption sites and enhance capacity, the results indicate that propane adsorption rises with increasing non-framework cation density [77]. Methane and nitrogen adsorption on FAU zeolites with Si/Al ratios of 1, 2, and 3 were investigated using MD simulations using the COMPASS force field [78]. The diffusivities and computed adsorption isotherms were verified using experimental data. Under all circumstances, methane selectivity stayed above 2, and stronger absorption was noted at lower Si/Al ratios. Using verified molecular simulations, the adsorption thermodynamics of N₂ and O₂ on FAU zeolites with different Si/Al ratios were examined under a wide range of temperature and humidity settings pertinent to PSA-based oxygen production [79]. Using molecular simulations, this work intends to investigate the diffusion of methyl mercaptan in Na-X zeolite under various pressures and temperatures and the adsorption of methyl mercaptan and methane, both as single components and in mixtures. The findings demonstrate that the COMPASS force field model of methyl mercaptan adsorption closely matches experimental data and exhibits Langmuir behavior [80]. With a low ratio of Si to Al because of their high cation density, FAU zeolites have substantial CO₂ adsorption capabilities, which makes them interesting for CO₂ capture. According to Wang et al.'s investigation of FAU samples (SAR = 1.18

and 1.01), adsorption enhancement rose with CO₂ loading but decreased with increasing coverage. The relevance of framework composition on CO₂ uptake behavior was confirmed by Monte Carlo simulations that used a verified force field and XRD-derived structures to provide molecular-level insight into the formation of the adsorption complex [81]. In the gas industry, ethyl mercaptan's selective extraction from natural gas continues to be a major obstacle. For this reason, nanoporous zeolites with different topologies have demonstrated great promise as efficient adsorbents. GCMC simulations have been used to forecast the adsorption behavior of ethyl mercaptan, both in its pure form and in combination with methane, under challenging experimental settings. On siliceous zeolites, adsorption isotherms at 298 K and pressures up to 100 kPa showed that adsorption capacity is correlated with pore diameter, with FAU showing the maximum uptake [82].

2.4.2 Progress in Simulating Micro-Mesoporous Materials

Molecular simulation effectively investigates atomistic-level structural characteristics and features of microporous and mesoporous materials [14]. Computational modeling gives researchers important insights into structure-property correlations at an atomistic level while saving resources and time by eliminating the need for costly and time-consuming experimental techniques. Simulations make important predictions regarding adsorption, diffusion, and transport characteristics; these predictions are critical for processes like separation and catalysis. Researchers attempted to mimic various zeolites in a study by Zhou et al. [83], a hexagonal model of MCM-41 was built, and a GCMC simulation was used to study the adsorption of CO₂, N₂, and flue gas on MCM-41. Chen et al. [14] The Materials Visualizer module was used to build a ZSM-5-MCM-41 model to investigate toluene adsorption and analyze structural data. The calculated adsorption isotherm closely

matched the experimental findings and followed the Langmuir model. Cao et al. [84] used the Tjatjopoulos–Feke–Mann (TFM) potential to examine the interactions between fluid molecules and the MCM-41 pore wall in their GCMC simulations of nitrogen adsorption on MCM-41. Maddox and associates used the Grand Canonical Monte Carlo approach to study fluid adsorption in Buckytubes through molecular simulation [85]. Various Lennard-Jones (LJ) parameters were applied to the O₂-N₂ interactions in each sector to describe the heterogeneity. The adsorption and transport of a basic adsorbate in hierarchical porous solids with interconnected microporosity (~1 nm) and mesoporosity (>2 nm) are demonstrated by molecular simulations in a recent paper [86]. Baoyu Liu et al. [87] performed the molecular simulation of a mesoporous ZSM-5 type molecular sieve and used the benzene and toluene adsorption model. Molecular modeling has mostly been done on purely mesoporous or microporous materials, but mostly for MCM-41. Until now, few attempts have been made to model micro-mesoporous materials [88]. Various research studies have mostly relied on experimental methods to study the behavior of micro-mesoporous Y-zeolite; however, there is still a lack of computational research on this topic. The literature review indicates that no considerable attempt has been made to model hierarchical Y-zeolite (FAU structure) with different pore sizes to investigate their adsorption isotherms and characterize them to obtain microscopic insights using molecular simulations. So, there is a need to model the hierarchical FAU structure. The adsorption behavior of these hierarchical porous materials is still unknown, even though the benefits of combining different porosity scales have been shown in different catalysis and phase separation applications. Despite extensive research on hierarchical Y-zeolites, a fundamental gap remains in accurately characterizing their pore structures and adsorption

behavior at the atomistic level. While experimental techniques provide valuable insights, they are often limited in resolving nanoscale details. Computational modeling offers a powerful alternative to explore these structures in greater depth, yet existing studies lack comprehensive models that accurately replicate hierarchical FAU zeolites with varying pore sizes.

The foremost objective of this study is to develop and analyze atomistic models of hierarchical FAU zeolites using computational techniques. Using Materials Studio software, we constructed hierarchical FAU models with different pore diameters and investigated their structural and adsorption properties. This study systematically examines pore size and volume distribution, multilayer adsorption behavior, self-diffusivity, and adsorption isotherms, providing a detailed understanding of their morphological and structural characteristics. We establish models that accurately represent hierarchical zeolite structures by directly comparing computational simulations and experimental results. These validated models bridge the gap between theoretical and experimental approaches, serving as predictive tools for adsorption behavior in micro-mesoporous zeolites. Our findings provide a fundamental framework for future studies involving hierarchical zeolites in catalysis and adsorption applications

Another goal is to investigate and assess the catalytic performance of modified Y-zeolite and ZSM-5-based catalysts in the FCC process and check their synergistic effects. It aims to increase the yield of light olefins, particularly propylene, improve conversion rates, and improve gasoline selectivity. A surfactant-templating technique creates hierarchical Y-zeolite and ZSM-5 to add regulated mesoporosity to the zeolite structure. Optimizing

catalyst performance is important from an industrial and economic standpoint since the petrochemical industry's need for lighter, high-value hydrocarbons continues to grow. This research aims to create more effective FCC catalysts by bridging the gap between theoretical and experimental approaches. This will provide insights into the logical design of hierarchical zeolites for sophisticated catalytic applications in petrochemical and refining processes.

CHAPTER 3

RESEARCH METHODOLOGY

This chapter will demonstrate the experimental and computational methodology used in the studies to modify Y-zeolite and ZSM-5 for FCC catalysts. It also presents a detailed synthesis of experimental procedures and techniques to characterize zeolites. The MAT unit's evaluation procedure for testing FCC catalysts is also discussed.

3.1 EXPERIMENTAL METHODOLOGY

An outline of the modified zeolites (Y-zeolite and ZSM-5) used in this research is provided in this chapter, along with information on the FCC catalyst used and its detailed characterization. Additionally, it explains how the Micro Activity Test (MAT) unit works. The basic ideas behind the analytical tools used for product analysis are finally covered.

3.1.1 Materials

The following materials were utilized for the modification of Y-zeolite and ZSM-5, as well as for preparing FCC catalysts.

- Na-Y zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.6$) was obtained from CATAL (CT-421).
- ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) was obtained from CATAL (CT-405).
- Sodium hydroxide (NaOH pellets $\geq 98.0\%$) was supplied by Sigma Aldrich.
- Cetyltrimethylammonium bromide (CTAB), Ammonium nitrate, Kaolin, Ludox AS-30, Citric acid (Citric acid Monohydrate 99.5 % m/m), Nitric acid, and Sulphuric acid were also obtained from Sigma Aldrich.

- Siral 40 (40% Al₂O₃, 60% SiO₂) was obtained from CONDEA
- Vacuum gas oil (VGO) was obtained from a domestic refinery

3.1.2 Post-treatment of Y-zeolite

Commercial Na-Y zeolite (Si/Al = 2.56) was purchased from the CATAL company. The modification of Y zeolite to obtain the hierarchical zeolite was adapted from previous method [1] with some changes in the process conditions. The changes in process conditions are mentioned at the end of this experimental procedure. The present post-treatment method prepared a slurry by mixing 10 g of commercial Na-Y-Zeolite (Si/Al = 2.56) with 100 ml of water. The pH of the slurry was close to 10 and was adjusted to 5.5-5.7 by adding a few drops of diluted nitric acid (5 % dilute). Afterwards, the slurry was stirred with 10% citric acid solution (0.05M, 0.1M and 0.15M) for 1 hr at ambient temperature. Different amounts of citric acid were added as the pore-expanding reagents. Then, treated Y-zeolite was recovered by vacuum filtration and washed three to four times with deionized water. The solid is dried for some time at 80 °C. Further, it was re-slurried in distilled water (100 ml) containing 0.24M of sodium hydroxide (NaOH) and 0.03M of cetyltrimethylammonium bromide (CTAB). The mixture was then stirred for 20 minutes. Next, the solution was treated under hydrothermal conditions in a Teflon-lined autoclave at 120 ° C for 12 hr. After this, the treated zeolite was recovered using vacuum filtration, washed with deionized water, and dried overnight at 110 ° C. A modified zeolite sample was calcined at 550°C for 7 hr to remove the impurities and the organic template. The calcined sample was placed in a desiccator at 100 °C temperature until it was cooled to room temperature. The obtained modified zeolites were denoted as MY-0.05M, MY-0.1M, and MY-0.15M, respectively. The modified zeolites were exchanged three times with an

ion exchange of 0.1M ammonium nitrate solution at 80°C for 3 hr to obtain the H-form of zeolite. For each gram of zeolite, 15 ml of 0.1M ammonium nitrate solution was used for ion exchange. Finally, drying overnight and calcination for 2 hr for 2 hr was performed to remove the last traces of moisture. Amin Talebian-Kiakalaieh et al. [1] use 150 °C reaction temperature for hydrothermal treatment. The author used only one concentration of acid for modification. Also, pH adjustment was not mentioned in this work. Further, 1M ammonium nitrate was used for a three-time ion exchange without mentioning the liquid-to-solid ratio.

3.1.3 Post-treatment of ZSM-5

For ZSM-5, desilication, dealumination, and soft templating procedures were used to add mesoporosity to the produced ZSM-5 zeolite. The initial treatment involved treating around 10 g of the commercial ZSM-5 in 100 ml of deionized water. Then, heat it with NaOH solution (0.5M and 1M) to vary the desilication process at 80 °C for 1 hour. Stir the solution at 500 r.p.m. The desilicated ZSM-5 was obtained by filtering and drying the product at 80°C for a whole night after thoroughly washing it. The next step was to perform acid-leaching on desilicated ZSM-5. Solutions of sulfuric acid with varying concentrations (0.4 M, 1.2 M, and 1.6 M) were prepared to modify the extent of the dealumination process. Dried ZSM-5 was added to each solution, and the mixtures were stirred at 80 °C for 3 hours. After the stirring process, the samples were filtered, thoroughly washed with deionized water, and then dried for a period of time. After that, CTAB was used as the surfactant in a soft templating stage. This was completed by dissolving 10 g of the desilicated and dealuminated ZSM-5 in 100 ml of 0.3 M NH_4OH solution that contained 2.5 g of CTAB. Stir the solution at room temperature for 20 min. The combination was

then hydrothermally treated for 12 hours at 150°C. The solution was filtered, dried overnight, and calcined at 550 °C for 6 hr. After that, three consecutive ion-exchange cycles were performed on the resultant hierarchical ZSM-5 (HR/ZSM-5) using a 0.1 M NH₄OH solution at 80°C for 1 hour to get the H-form of ZSM-5. The material was filtered, cleaned, and dried at 80°C at the end of each cycle. The catalyst powder was then prepared for use in FCC applications by calcining it for five hours at 550°C.

To assess how various acid concentrations (0.4 M, 1.2 M, and 1.6 M) affected the formation of mesoporosity, we first altered the dealumination phase in our experimental protocol. Zeolites with the following labels were produced: ZSM-5-0.4M A, ZSM-5-1.2M A, and ZSM-5-1.6M A. In a follow-up series of studies, mesopore production was further examined by adjusting the desilication process using different base concentrations (0.15M, 0.5 M and 1 M). The corresponding samples were identified as ZSM-5-0.25M B, ZSM-5-0.5M B and ZSM-5-1M B. Lastly, ZSM-5-1M B was used as an additive in FCC testing. The reasons are described in detail in the results and discussion.

3.1.4 Preparation of FCC catalysts using hierarchical Y-zeolite and ZSM-5

Four FCC catalysts were prepared using Y-zeolite, ZSM-5, and a matrix. The matrix of FCC catalysts consisted of amorphous silica-alumina, silica solution, and clay, which were chemically obtained from Siral40, Ludox AS-30, and kaolin, respectively. All five components, HY-zeolite, Ludox AS-30, Siral 40, kaolin, and ZSM-5, were mixed in water with percentages in Table 3.2. The slurry was heated to 70 °C with continuous magnetic stirring until it dried. The resulting mixture was then placed in an oven and dried overnight at 110 °C. The dried product was subsequently crushed and calcined at 550 °C for 6 hours.

Finally, 10 grams of each prepared sample were subjected to 100% steam treatment at 810 °C for 6 hours.

Table 3.1: Specification of FCC catalysts.

Name of the Catalyst	Specification
NFCC-Y-Z	FCC catalyst with Y zeolite and ZSM-5
NFCC-HY-Z	FCC catalyst with HY (MY-0.1M) and ZSM-5.
NFCC-Y-HZ	FCC catalyst with Y zeolite and modified ZSM-5 (ZSM-5-1M B).
NFCC-HY-HZ	FCC catalyst with HY zeolite (MY-0.1M) and modified ZSM-5 (ZSM-5-1M B)

The steamed catalyst was sieved before the micro-activity test unit to ensure particle size. After steaming, the modified FCC catalyst names were NFCC-Y-Z, NFCC-HY-Z, NFCC-Y-HZ, and NFCC-HY-HZ. The details of these names are given in Table 3.1. The scheme for modifying zeolites and preparing FCC catalysts is given in Figure 3.1.

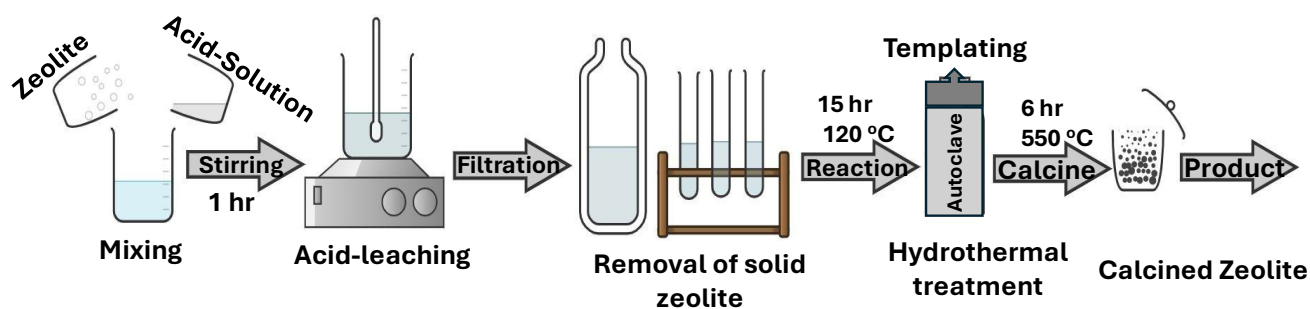
Table 3.2: Chemical composition of FCC catalysts.

Name of catalysts	HY-zeolite (wt%)	ZSM-5 (wt%)	Siral 40 (wt%)	Ludox AS-30 (wt %)	Kaolin (wt%)
NFCC-Y-Z	15	15	9	17.2	43.6
NFCC-HY-Z	15	15	9	17.2	43.6
NFCC-Y-HZ	15	15	9	17.2	43.6
NFCC-HY-HZ	15	15	9	17.2	43.6

3.1.5 Characterization of Catalysts

The following techniques describe all Y-zeolite (un-modified and modified) samples' physical and chemical characteristics and ZSM-5 (un-modified and modified).

Modification of Zeolite



Preparation of FCC Catalyst

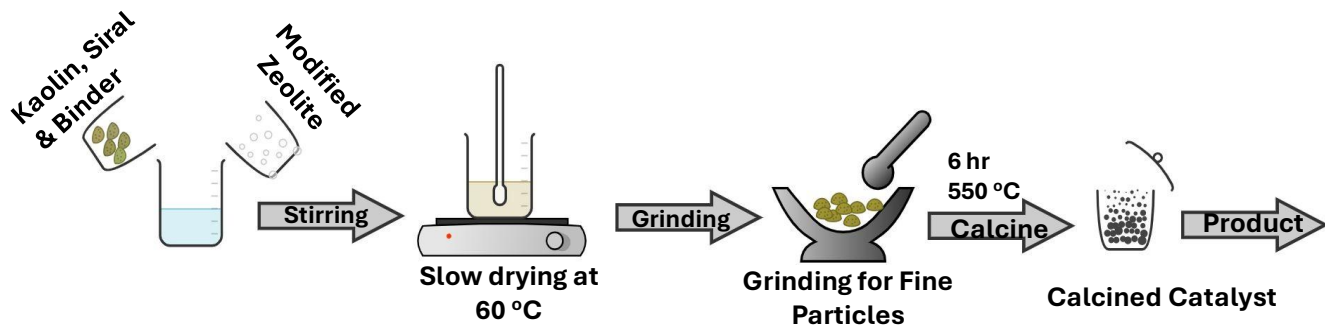


Figure 3.1: Scheme for modification of zeolite and preparation of FCC catalysts.

a) X-ray Diffraction

The structural crystallinity of hierarchical zeolite samples was examined by X-ray Diffraction (XRD) using a Rigaku Mini flex II with nickel-filtered CuK α radiation having a wavelength of $\lambda = 1.5406 \text{ \AA}$ at 30mA and 40kV operating parameters. A diffraction pattern was generated for 2θ angles from 5° to 80° with a scan rate of $2^\circ/\text{min}$.

b) BET surface area and pore size distribution

The specific surface area, pore volume, and pore size distribution were determined using a Micromeritics ASAP-2020 sorption analyzer with the help of nitrogen adsorption at 77 K. A 100 mg calcined sample was taken to measure the BET surface area and pore volume. Before nitrogen physisorption, the samples were degassed under a vacuum (10^{-5} torr) at 350°C for 3 hr. The nitrogen adsorption and desorption isotherms were measured in the relative pressure range of 0 to 0.99. The Brunauer–Emmet–Teller model (BET) was used in the $0.005 < P/P_0 < 0.030$ range to determine the specific surface area. The micropore volume and mesopore-specific surface area were determined using the t-plot method, while the average mesopore diameter was calculated using the Barrett–Joyner–Halenda (BJH) model.

c) Scanning Electron Microscopy

Scanning electron Microscopy (SEM) on a TESCAN instrument developed by Oxford and an EDX analyzer was used to analyze the crystals' morphology and size.

d) Temperature-programmed desorption

Acidity measurements in BELCAT equipment were performed using ammonia temperature-programmed desorption (TPD). A 50 ml/min helium flow rate (He) was used

to pre-treat the calcined sample (50 mg) for one hour at 300°C. The sample was then allowed to cool to 100 °C and exposed for 30 minutes to an NH₃/He mixture. Ammonia gas was eliminated using He purges for an hour to measure TPD. The temperature was then raised to 600 °C at 10 °C per minute while maintaining the same He flow. A TCD detector was employed to track the desorbed NH₃ gas.

3.1.6 Evaluation of Catalysts

All FCC catalysts were evaluated in the MAT unit based on the product yield of gasoline, LCO, HCO, and coke at 550 °C using VGO as feed.

a) Micro activity test procedure

The cracking behavior of vacuum gas oil was investigated using a fixed-bed reactor called the Micro Activity Test (MAT) unit (Sakuragi Rikagaku, Fukuoka, Japan), as shown in Figure 3.2. The properties of HT-VGO are listed in Table 3.3. Following the ASTM D-3907 standard procedure, the MAT unit assessed the FCC catalyst activity. The reaction was carried out for 30 seconds on stream at a system temperature of 550°C. 4.0 g of catalyst and 1.0 g of vacuum gas oil were used in each experiment. After the reaction, nitrogen gas was used to strip the products for nine minutes at a flow rate of 30 cc/min. The conventional ice-water trap was replaced with a low-temperature circulating bath because of the high volatility of the liquid products. A burette attached to the liquid receiver's outlet collected gas products during the reaction and stripping stages. The syringe was weighed before and after the reaction to precisely measure the volume of vacuum gas oil added to the system. The MAT operating conditions are summarized in Table 3.4.

Table 3.3: Properties of MAT Feed Oil.

Property	Value
Density (g/cm ³)	0.88
Nitrogen (ppm)	172
Sulfur (ppm)	298
Aromatics (wt %)	42
Residue (wt %)	0.9
Saturates (wt %)	60
Initial boiling point	310
5 (%)	345
25 (%)	375
50 (%)	422
90 (%)	510
Final boiling point	565

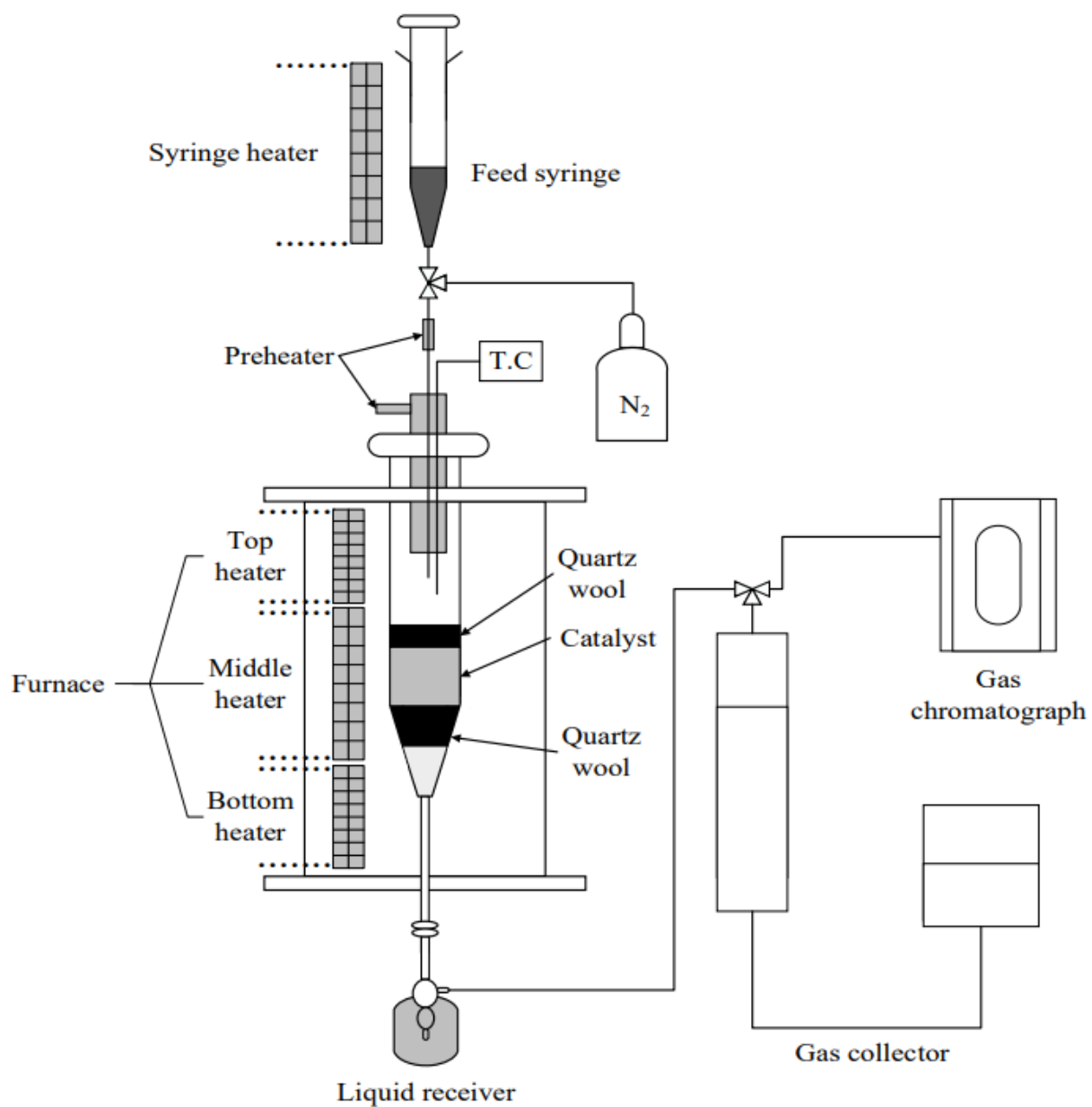


Figure 3.2: Micro activity test (MAT) unit.

b) Analysis of MAT products

A liquid phase, a gaseous phase, and coke deposited on the spent catalyst are the end products of the MAT process. An adequate mass balance was defined as 95–103% of the injected vacuum gas oil feed. All MAT products undergo a thorough gas chromatographic examination to ascertain the yield distribution and get information about the behavior of the feedstock on the catalyst. A Micro GC Agilent 3000A system was used to examine the gaseous products.

Table 3.4: MAT operating conditions.

Property	Value
Feed weight injected	1 g
Catalyst weight	4 g
Feed injection time	30 s
Feed injector temperature	5°C higher than the reaction temperature
Liquid receiver temperature	-9°C

This device made it possible to identify and measure fixed gases, hydrogen (H₂), and light hydrocarbons up to C₄ and C₅ paraffin. Every hydrocarbon from C₁ to C₄, as well as C₅ paraffin, was precisely measured. Hydrocarbons heavier than C₄ were added to the weight of the liquid product following analysis, whereas the total weight of light hydrocarbons up to C₄ was added up. The carbon content, represented as a percentage of the catalyst's weight, was computed using the generated data. An infrared analyzer was used to quantify the combustion gas (CO₂) generated during the coke analysis process. A Shimadzu GC 2010 gas chromatograph with a simulated distillation setup was used to analyze liquid products by the ASTM D-2887 technique. Light cycle oil (LCO), heavy cycle oil (HCO), and gasoline were the three primary fractions into which these liquid products were divided. The combined yield of gasoline, total gases, and coke were used to compute the

conversion of vacuum gas oil. Unconverted fractions of the feedstock were defined as components like HCO and LCO with boiling temperatures higher than 221 °C.

3.2 Computational Methodology

Molecular simulations based on first-principal, GCMC, and molecular dynamics (MD) are frequently employed to partially compensate for the experiment's limitations. MD simulations have been widely used to examine various systems. They are especially useful for examining how molecules behave in different environments, including adsorption processes in porous materials like zeolites [90]. A GCMC simulation, which operates at a constant chemical potential (μ), volume (V), and temperature (T), can be employed to determine an isotherm for gas adsorption [91]. The GCMC simulation represents an open system in equilibrium with an endless bulk fluid reservoir. The ensemble average number of adsorbate molecules (N) as a function of pressure is used to determine the adsorption isotherm for a particular nano-porous adsorbent. GCMC simulation is particularly suitable for studying single-layer and multilayer adsorption [92]. All the simulations in this study were carried out using BIOVIA Materials Studio 2023. A simulation box was constructed using the Materials Studio to simulate an infinite system, and periodic boundary conditions were imposed in all three dimensions.

3.2.1 Zeolite Structure and Composition

Na-Y zeolites are made of sodium, silicon, oxygen, and aluminum and are naturally occurring Faujasite minerals with different Si/Al ratios and composition of $\text{Na}_x\text{Al}_x\text{Si}_{192-x}\text{O}_{384}$ ($0 \leq x \leq 96$). Periodic simulation boxes of FAU zeolite structures were constructed to depict microporous and mesoporous configurations. The schematic structure of FAU is given in Figure 3.3. The Si/Al ratio for the parent structure was optimized to

match that of experimental Na-Y zeolite, ensuring an accurate representation of its natural composition. To create the model of an FAU structure with a particular Si/Al ratio, Al atoms were arbitrarily swapped out for a Si atom using the Löwenstein rules to stop Al–O–Al bonds from forming [14]. The resulting structure has a Si/Al ratio of 2.55, close to the experimental value of 2.56. Incorporating Na⁺ ions compensates for the negative charges introduced by the substitution. Using Materials Studio's Cation Locator module, the necessary sodium ion concentration was calculated and then added to the FAU structure. The Cation Locator module was used to insert cations into the zeolite structure, utilizing the CVFF to ensure accurate placement of the ions [89].

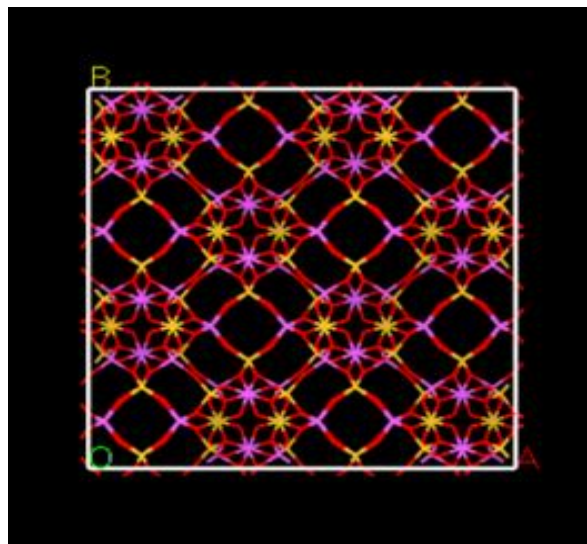
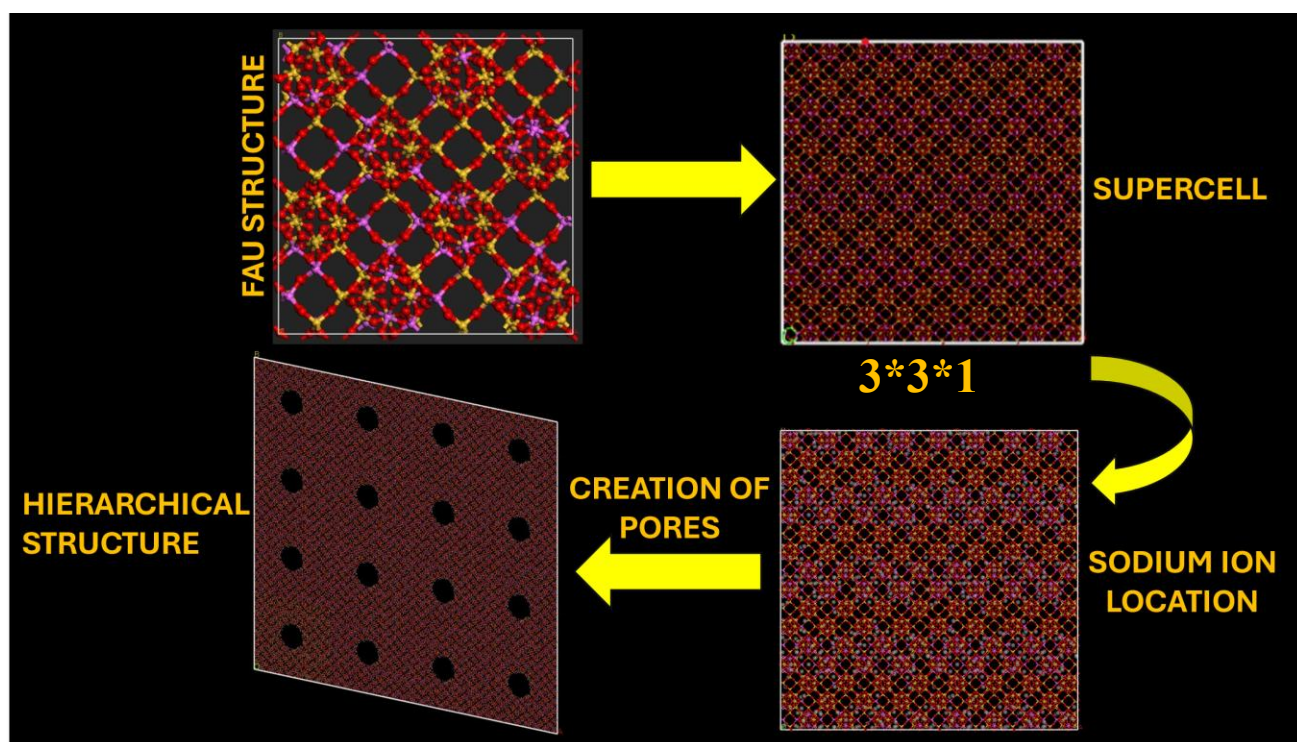


Figure 3.3: Schematic structure of FAU zeolite:
red: O, yellow: Si, and purple: Al.

Atomic charges are chosen as $q_{\text{Na}} = +1$, $q_{\text{Si}} = +2.4$, $q_{\text{O}} = -1.2$ and $q_{\text{Al}} = +1.4$ [86]. In the GCMC technique, the charges are applied using the QEq method. Since Vlugt and Schenk showed that framework flexibility has a negligible impact on adsorption properties, zeolite is considered rigid [77].

3.2.2 Construction of Hierarchical Zeolite Models for Simulation

Three different models of micro-mesoporous materials were built. The structure of mesoporous zeolite features a similar arrangement of mesopores integrated within a zeolite-like microporous crystalline aluminosilicate framework. The initial structure of FAU was introduced into the Materials Studio packages' Materials Visualizer module. The FAU zeolite unit cell was enlarged to create a supercell. A 3x3x1 supercell was used for this purpose. Then, a cylindrical pore was carved into the FAU structure. A clearly defined pore is created in the structure's centre by removing atoms from the framework's core region. Different pore diameters were obtained by varying the carved cylindrical channel's radius. Three other structures with different pore diameters, ranging from small to large, were created and simulated to investigate the impact of pore size on the zeolite's adsorption performance. MFAU-1, MFAU-2, and MFAU-3 are computational models with pore diameters of approximately 2 nm, 3 nm, and 4 nm, respectively. It was possible to compare the computational and experimental results meaningfully since these sizes were selected to resemble the average pore sizes found experimentally for hierarchical zeolites (MY-2.5, MY-4.5, and MY-6.5) (explained in section 3.1).



[Figure 3.4: Schematic Diagram of Modelling Process..]

The influence of varying pore sizes on the adsorption isotherm behaviour and other key features of the hierarchical zeolite will be evaluated with the aid of these simulations. Figure 3.4 shows the detailed schematic diagram of the complete modeling process. During the construction of pores, unsaturated Si and O atoms were generated. According to the procedure described in previous work [87], O and H atoms were added to saturate the cleaved bonds: (i) silicon atoms with fewer than four bonds to oxygen neighbors are saturated with oxygen atoms, and (ii) oxygen atoms with fewer than two bonds to Si atoms had their vacant bonds filled with hydrogen atoms. As a result, hydroxyls were randomly introduced to the pore surface. After removing every silicon atom connected to three

hydroxyls, the system is once more saturated with hydrogen atoms. The pores and internal surface were saturated with hydrogen by the Hydrogen Adjust Module.

This procedure was used to prevent the formation of Si–H groups on the interior surface and to guarantee that the simulation box maintained charge neutrality and that none of the silicon and oxygen atoms had dangling bonds [86],[14]. Because atoms are removed during construction, the Si/Al ratio changes. Table 3.7 provides a comprehensive description of the simulation parameters for all structures. Next, the Forcite module of the Materials Studio packages was used to optimize all the structures geometrically. The Forcite Module is a tool for several molecular mechanics computations, including molecular dynamics, geometry optimization, and single-point energy calculations [90]. It makes use of simulation methods based on classical force fields. The Geometry Optimization task improved the structure's geometry until the relative distances between a collection of atoms stabilized. Geometry optimization was performed using CVFF Forcefield to ensure the structure was stabilized and reached its lowest energy configuration. The convergence quality was fine: energy was $0.00002 \text{ kcal mol}^{-1}$, maximum force was $0.001 \text{ kcal mol}^{-1} \text{ per } \text{\AA}$, and maximum displacement was $0.00001 \text{ \AA}$. This is accomplished by an iterative process that involves adjusting the atomic coordinates and, potentially, the cell parameters until the structure's overall energy is reduced. A conjugate Gradient algorithm was chosen. By doing this, the structure can accept the added modifications—like adding mesopores or replacing atoms—without undergoing any irrational bond lengths, angles, or distortions. By fine-tuning the atomic arrangement, geometry optimization makes the modified structure physically realistic and appropriate for further simulations or studies. After geometry optimization, the sodium cation density was adjusted to correspond to the

aluminum density within the zeolite framework to maintain charge balance. The ball and stick structure of all three models is presented in Figure 3.5. An infinite lattice with a mesoporous zeolite structure was produced by applying P1 symmetry and periodic boundary constraints to the unit cell.

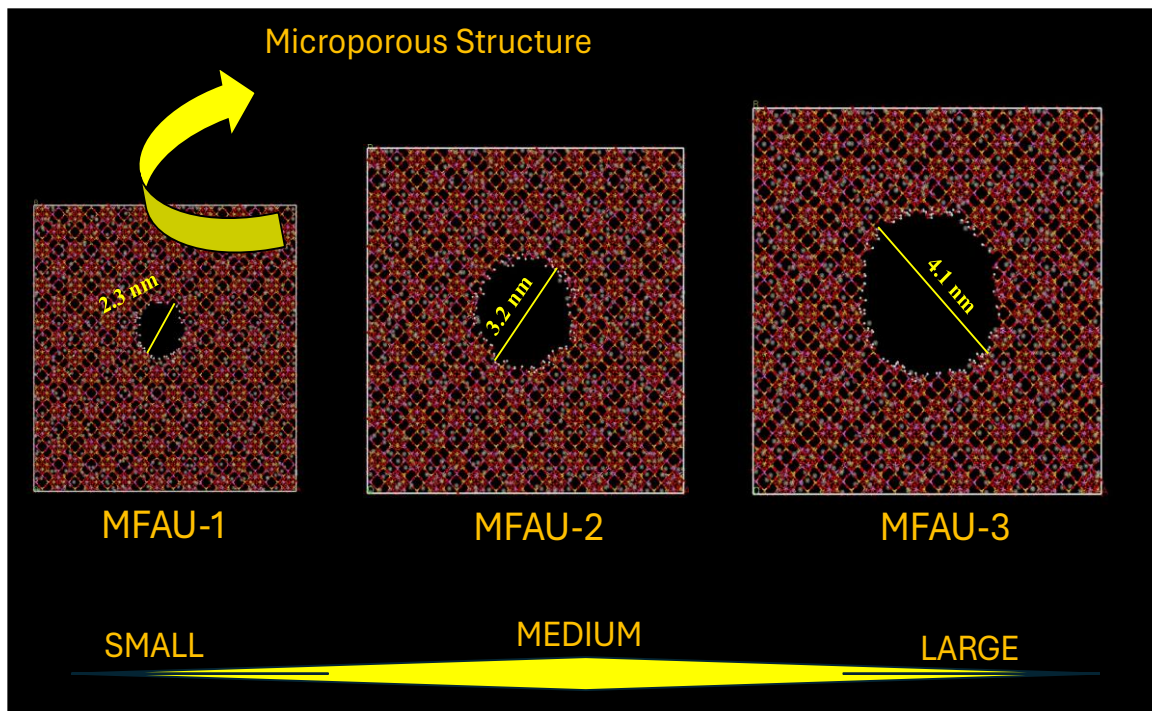


Figure 3.5: Hierarchical FAU models with different pore diameters.

3.2.3 Adsorption Simulation Technique

Grand Canonical Monte Carlo (GCMC) simulations with periodic boundary conditions were employed to evaluate adsorption isotherms and the isosteric heat of adsorption. Following the first configuration of a zeolite framework devoid of adsorbates, subsequent configurations were generated using the Metropolis algorithm. This algorithm uses variations in the system's energy to determine if the adsorbate's creation, disappearance, rotation, and translation should be accepted or rejected [90]. GCMC simulations were conducted using the Sorption module in Materials Studio software (2023). Nitrogen

adsorption at 77K on both parent and micro-mesoporous FAU structures was simulated using this method with periodic boundary conditions throughout a pressure range that closely resembles experimental circumstances. The pressure range is chosen from 1 kPa to 100 kPa. The nitrogen adsorption isotherm at 77 K is frequently used to describe an adsorption behavior because capillary condensation takes place at extremely low pressure, resulting in the fluid trapped inside the micropores becoming filled [84].

Table 3.5: Simulation Parameters of FAU Hierarchical Models.

Adsorbent	FAU	MFAU-1	MFAU-2	MFAU-3
Si/Al	2.55	2.47	2.49	2.45
Unit Cell Volume (Å ³)	250841	250841	250841	250841
Density (g/cm ³)	1.3447	1.3057	1.2435	1.1668
Cell Composition	O ₆₁₄₄ Na ₈₆₄ Al ₈₆₄ Si ₂₂₀₈	H ₃₂ O ₅₉₆₄ Na ₈₃₄ Al ₈₅₆ Si ₂₁₁₈	H ₁₁₈ O ₅₆₉₁ Na ₈₀₄ Al ₈₀₅ Si ₂₀₁₁	H ₁₀₀ O ₅₃₃₈ Na ₇₅₃ Al ₇₆₆ Si ₁₈₇₈
Cell Side Length	a= b= 100.112 c=25.028	a= b= 100.112 c=25.028	a= b= 100.112 c=25.028	a= b= 100.112 c=25.028
Cell Angles	a= b= c = 90°	a= b= c = 90°	a= b= c = 90°	a= b= c = 90°
Conversion factor (molecules /UC to mol/kg)	1.96 × 10 ⁻²	2.10 × 10 ⁻²	2.49 × 10 ⁻²	3.35 × 10 ⁻²

This method will more precisely investigate the multilayer adsorption phenomena and mesoporosity impact on adsorption behavior. The ensemble average of the number of adsorbed atoms as a function of the gas reservoir pressure (P) determines nitrogen density in the pores. The COMPASS force field modeled all interactions between guest molecules (Na⁺ and N₂) and the FAU zeolite structure. With an accuracy of 0.001 kcal/mol (1 Cal = 4.184 J), the long-range electrostatic interactions were computed using the Ewald summation method [89]. The Ewald summation technique, which has an accuracy of

0.0001 kcal/mol, is used for electrostatic potential energy. The spline and buffer widths are 1.00 and 0.5 Å, respectively. Based on the finding from molecular simulations, rigid zeolite frameworks are assumed that flexible structures have a negligible impact on zeolite adsorption. The MC moves included the swap (0.39) of a guest molecule with the reservoir, translation (0.20) of a guest molecule or a Na⁺, rotation (0.2) of a guest molecule, or partial re-growth (0.02) of a guest molecule in each cycle during the simulations. The van der Waals potential energy was also calculated using an atom-based summation approach with a cutoff distance of 15.5 Å. This distribution was selected to maximize computing resources and guarantee a thorough exploration of the configuration space. The number of calculations for achieving the equilibrium was considered 2×10⁶ steps for equilibrium and 1×10⁶ steps for production. In the GCMC simulations, the fugacity (f) was specified as a stand-in for pressure to define the chemical potential (μ). The following is an expression of the connection between fugacity and chemical potential:

$$\mu = \mu^0 + RT \left(\frac{f}{f^0} \right) \quad Eq(1)$$

Where μ^0 is the reference chemical potential and f^0 is the reference fugacity. The Material Studio (MS) adsorption results are shown as molecules per unit cell (UC). Maddox and Gubbins [85] note that when creating an isotherm using molecular simulation, the number of nitrogen molecules adsorbed in a specific micropore volume must be converted into mol/kilogram. For this, the amount in the final row of Table 3.7 is needed. These figures come from Eq. (2), where Avogadro's constant is $N_{Av} = 6.022 \times 10^{23}$.

$$q \left(\frac{mol}{kg} \right) = \frac{q \left(\frac{molecule}{uc} \right)}{pV N_{Av}} \quad Eq(2)$$

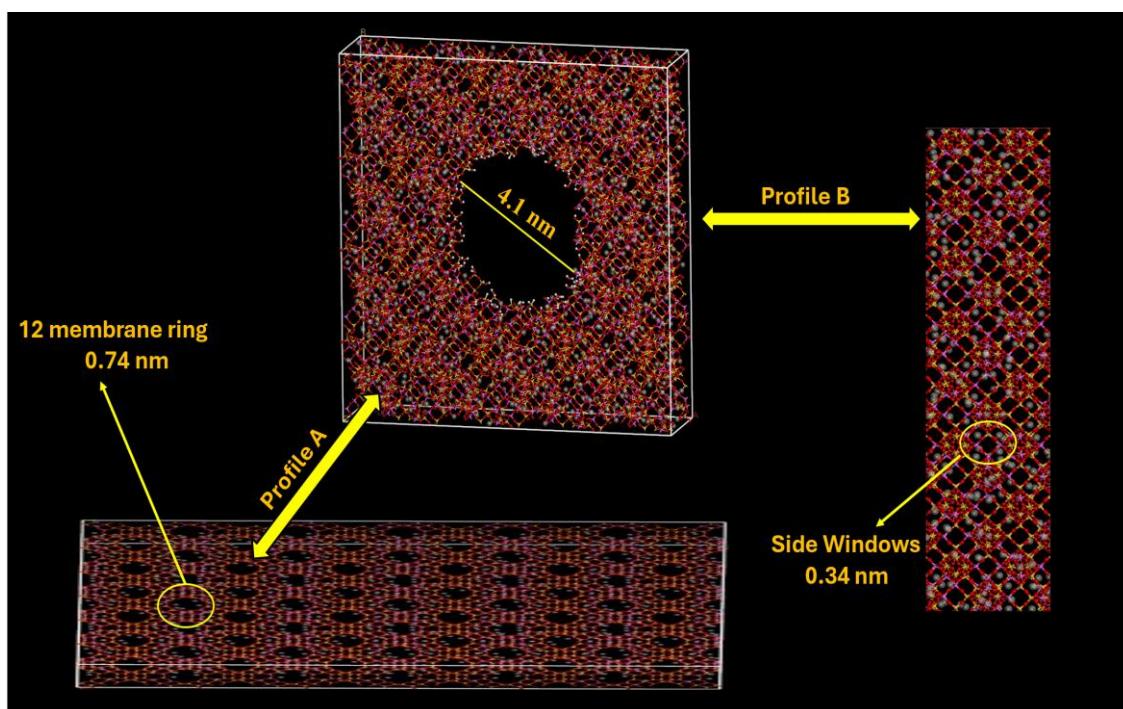


Figure 3.6: Ball and stick structure model of hierarchical FAU and profile pictures of the structure.

Figure 3.6 describes ball-and-stick structure models of hierarchical FAU and all profile pictures. All simulations were run multiple times with varying pore sizes to guarantee the outcomes' reliability and thoroughly examine the system's behavior. This method improves the precision of the results and ensures consistency. Beginning with well-equilibrated Monte Carlo configurations, molecular dynamics (MD) simulations were used to study nitrogen dynamics in the hierarchical porous materials. MD simulations provide key information regarding the dynamics of the adsorbed or confined [86]. To prevent the finite size effect, periodic boundary conditions were applied in the GCMC and MD simulations. The mean square displacement (MSD), a linear function of simulation time, is obtained through MD simulations. The MD simulations, which use a Berendsen thermostat with a

time constant of 1 ps for thermal energy exchange, begin with an initial equilibration in the NPT ensemble at a constant temperature of 77K and pressure of 100 kPa with a total simulation time of 200 ps. The atomic coordinates are saved every 200000 steps in the simulations, which employ a time step of 1 fs. After NPT optimization, the structure is subjected to an NVT ensemble with a total simulation time of 400 ps. This guarantees full optimization of the structure's energy.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Investigation of the Pore Structure of Hierarchical Y-zeolite via Experimental and Computational Approaches

4.1.1 Structural Analysis

XRD analysis was conducted in this study to monitor the structural changes that occurred in modified zeolites with different acid concentrations. Figure 4.1 demonstrates the XRD measurements of mesoporous Y-zeolites developed by treatment with acid and base in the presence of a surfactant used as a template. The figure shows that the intensity of XRD patterns for treated zeolites (MY-0.05M, MY-0.1M, MY-0.15M) decreases compared to parent zeolite (Y-zeolite) with an increase in the severity of the acid treatment conditions. The decrease in intensity of XRD patterns is related to the apparent decline in crystallinity due to the structural degradation of modified zeolites and intercrystalline mesoporosity created by such treatment. This reduction corresponds with Garcia-Martinez et al. 's report, [93], where a decrease in crystallinity and peak broadening, which signify the breaking of Al–O bonds have been documented when mesopores are introduced into the parent zeolite

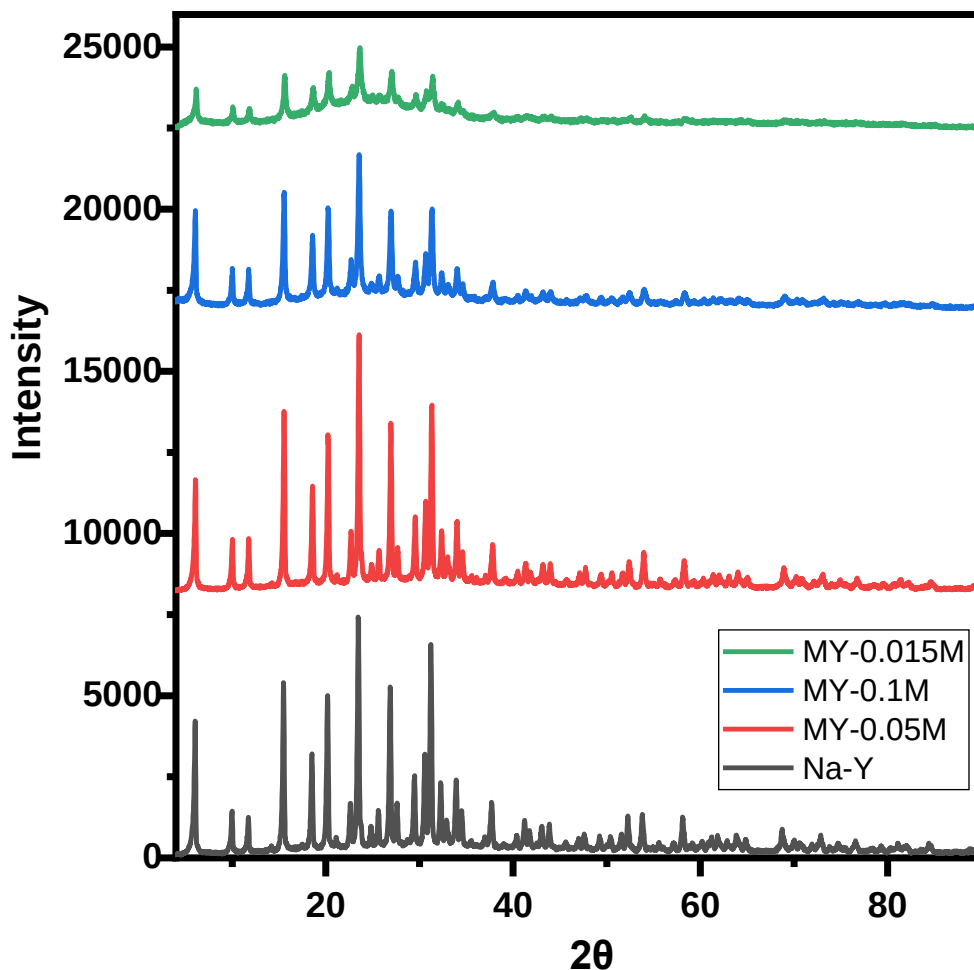


Figure 4.1: XRD analysis of Hierarchical samples of Y-zeolite.

XRD measurements also reveal that mesoporous zeolites sustain significant crystallinity under relatively mild conditions used for the post-treatment of MY-0.05M and MY-0.1M, showing no signs of extra-crystalline or amorphous phase. But for MY-0.15M, only 35% of the crystallinity is sustained [1]. The severity of this pre-treatment (e.g., acid concentration, duration, temperature) can be fine-tuned to control the extent of dealumination and the level of mesoporosity introduced during the subsequent surfactant

treatment in a basic medium. The parent Na-Y zeolite signals are closely aligned with the diffraction peaks of the modified zeolites. [94].

Table 4.1: Si/Al ratio and relative crystallinity of Y-zeolite samples.

Samples	SiO₂	Al₂O₃	Na₂O	Si/Al	R.C (%)
Na-Y	51.18	17	12	2.65	100
MY-0.05M	12.77	2.99	1.91	3.71	98
MY-0.1M	25.03	5.52	1.96	4.01	74
MY-0.15M	22.39	2.74	1.46	7.22	35

Details of the Si/Al ratio and relative crystallinity of all samples are given in Table 4.1. The increase in the Si/Al ratio for all the modified samples is observed for the hierarchical samples mentioned in the table, compared to the parent Y-zeolite, confirming that the post-treatment led to a dealumination of the structure, also reflected in a partial decrease in relative crystallinity [95]. However, the amount of Si removed may not have been significant due to the starting material's low Si/Al ratio [96],[97]. Figure 4.2 shows the surface morphology of modified zeolites (MY-0.05M, MY-0.1M, and MY-0.15M) at a scale bar of 5 μ m and 20 k magnifications. The SEM images of modified zeolite samples showed a similar morphology to that of the parent Na-Y zeolite reported in the literature [93]. Na-Y zeolite appears more compact, with less visible interparticle voids, while MY-0.1M and MY-0.15M morphology is more open and less densely packed, indicating a more

porous structure. Moreover, no major clusters were observed on the surface of the zeolites after the post-treatment.

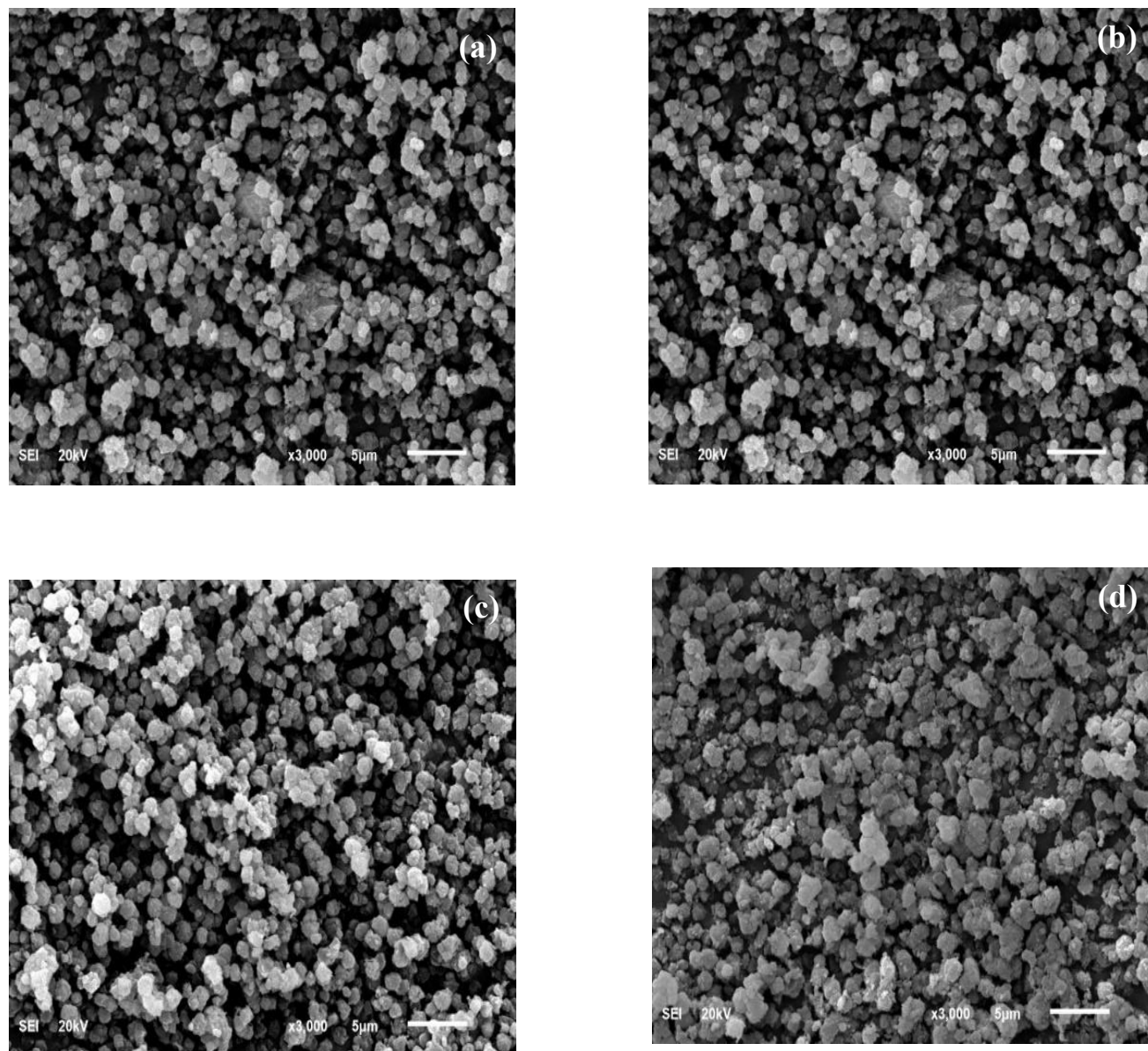


Figure 4.2: SEM images of (a) Na-Y (b) MY-0.05M (c) MY-0.1M (d) MY-0.15M.

4.1.2 Sorption Analysis

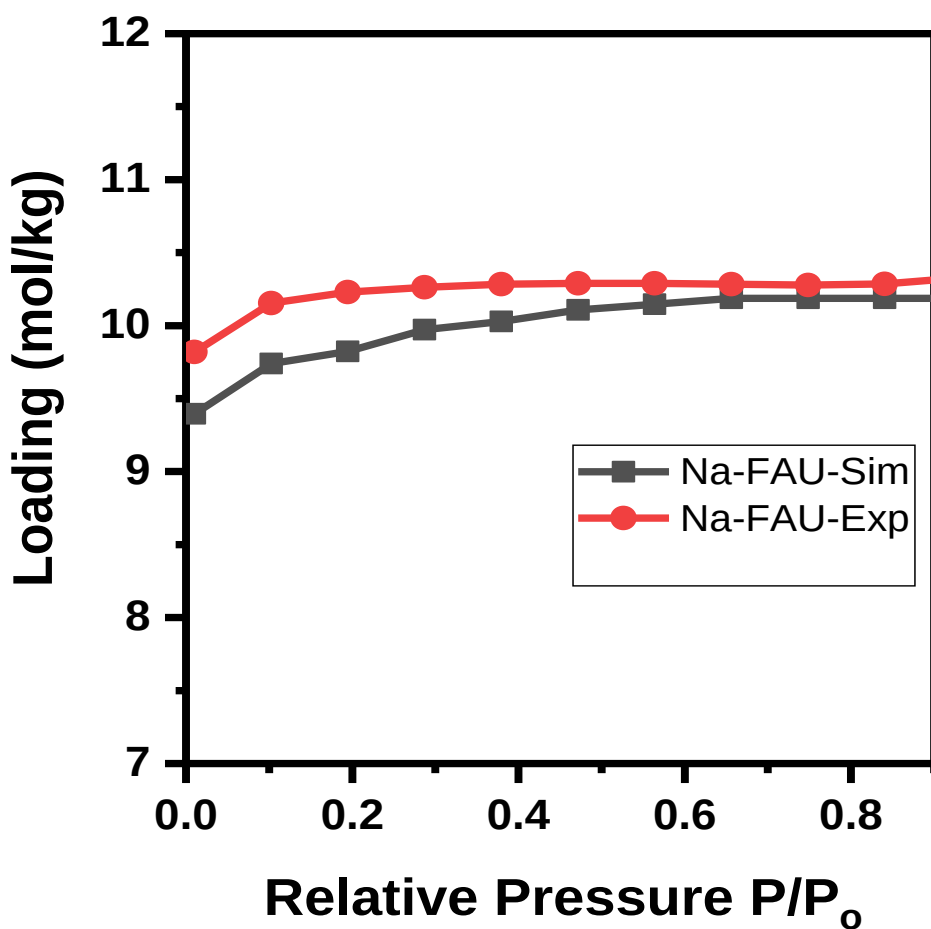
Table 4.2 shows the chemical and physical properties of the parent and hierarchical Y-zeolites in the presence of acid, base, and surfactant. BJH adsorption/desorption cumulative pore volume and average pore size were thus determined using the BJH method [84]. Furthermore, the BET-specific surface—the most widely used technique for representing porous materials—was also calculated. N₂ adsorption-desorption analysis showed that modified MY-0.05M, MY-0.1M, and MY-0.15M samples have a surface area of 677 m²/g, 840 m²/g, and 864 m²/g, as compared to 680 m²/g of parent Na-Y zeolite. The modified Y-zeolite samples' pore volume (V_p) results were extremely interesting, showing an increase in (V_p) size from 0.37 to 0.40 (8% increase), 0.58 (56% increase), and 0.76 cm³ (105%), for the MY-0.05M, MY-0.1M, and MY-0.15M samples, respectively. Micropore volume is decreased, and mesopore volume is increased for MY-0.05M, MY-0.1M, and MY-0.15M samples. For example, micropore volumes of MY-0.05M, MY-0.1M, and MY-0.15M decreased by 12%, 33%, and 56 %, respectively. On the other hand, mesopore volumes of 0.112, 0.391, and 0.61 cm³/g were observed for MY-0.05M, MY-0.1M, and MY-0.15M, respectively. The average pore diameter (D_p) for both hierarchical samples showed a notable rise. Indeed, the D_p size increased from 0.74 nm for Na-Y to 2.1 nm (183% increase) for MY-0.05M and to 2.9 nm (264% increase) and 3.8 nm (372 % increase) for MY-0.1M and MY-0.15M, respectively. The textural properties of treated zeolites depend on acid concentration, contact time, and surfactant type used in post-treatment. It is noted that mesopore volume increases with an increase in acid concentration for MY-0.05M, MY-0.1M, and MY-0.15M samples. In contrast, a large part of the micropore volume is conserved for MY-0.05M, MY-0.1M, and MY-0.15 M. A high

micropore volume decrease indicates a microporous structure loss. Increased surface area and pore volume are observed with increased pore diameter. These findings demonstrated that the soft templating method and Na-Y zeolites' acid/base treatments effectively produced hierarchical zeolites [1]. Figure 4.4 shows the N₂ adsorption-desorption isotherm data for the MY-0.05M, MY-0.1M, and MY-0.15M samples compared with the parent zeolite. It shows the Type-I isotherm for Na-Y and MY-0.05M samples with more pronounced uptake at low P/P₀, confirming the presence of microporous structures [6], [1]. For modified Y-zeolite samples, an H4-type hysteresis loop is noticed (less evident for MY-0.05M), which is related to mesoporous zeolites having a bimodal pore size distribution that highlights the presence of both micropores and mesopores [10]. The figure shows that MY-0.1M and MY-0.15M exhibit a remarkable N₂ uptake at a relative pressure greater than 0.4, showing the presence of a large mesopore compared with MY-0.05 M. The successful formation of hierarchical zeolites is demonstrated by the observed hysteresis loop between the adsorption and desorption isotherms' data, which also validates the existence of mesoporous structures and improved textures.

Table 4.2: Results of textural parameters of hierarchical Y-zeolite obtained through N₂ adsorption and desorption.

Sample	BET surface area (m²/g)	Micropore Surface Area (m²/g)	Mesopore Surface Area (m²/g)	Micropore volume (cm³/g)	Mesopore Volume (cm³/g)	Total Pore Volume (cm³/g)	Average Pore Diameter (nm)
Na-Y	680	643	39	0.33	0.04	0.37	< 2
MY-2.5	677	562	115	0.294	0.113	0.407	2.4
MY-4.5	845	425	423	0.219	0.367	0.586	2.7
MY-6.5	803	51	750	0.11	0.66	0.766	3.8

To match the findings of experiments with our simulated results, the GCMC approach was used to model nitrogen adsorption in different hierarchical Y-zeolite structures. The isotherms were measured from low to high partial pressures, corresponding to varying nitrogen concentration levels within the pore structure. First, sorption analysis is performed on an unmodified FAU structure. Figure 4.3 compares the nitrogen adsorption isotherms on Parent FAU structure from simulations and experiments to evaluate how the computational model reproduces experimental data.



[Figure 4.3: Nitrogen Adsorption isotherm of Y-zeolite by simulation and experimental approach.]

Because of the filling of micropores, the amount of N_2 adsorbed in the FAU zeolite grows quickly at low pressures and then plateaus after the pores are filled. Because of the strong confinement inside the micropores, capillary condensation is inhibited, making this process ongoing and reversible. These micropores, which are about 1 nm in size, are cages with 1.3 nm diameters and 0.78 nm apertures. [86]. The experimental and simulated results match each other with a maximum relative error of 2%. The slight discrepancy at the curve's beginning could result from minute changes to the structure's assumed parameters, which means that the model structure is organized.

The computed and experimental adsorption curves for the parent FAU structure converge at increasing relative pressures ($P/P_0 > 0.5$) and are similar. Overall, it has been observed that the COMPASS force field is suitable for accurately replicating adsorption isotherms of Y-Zeolite structures.

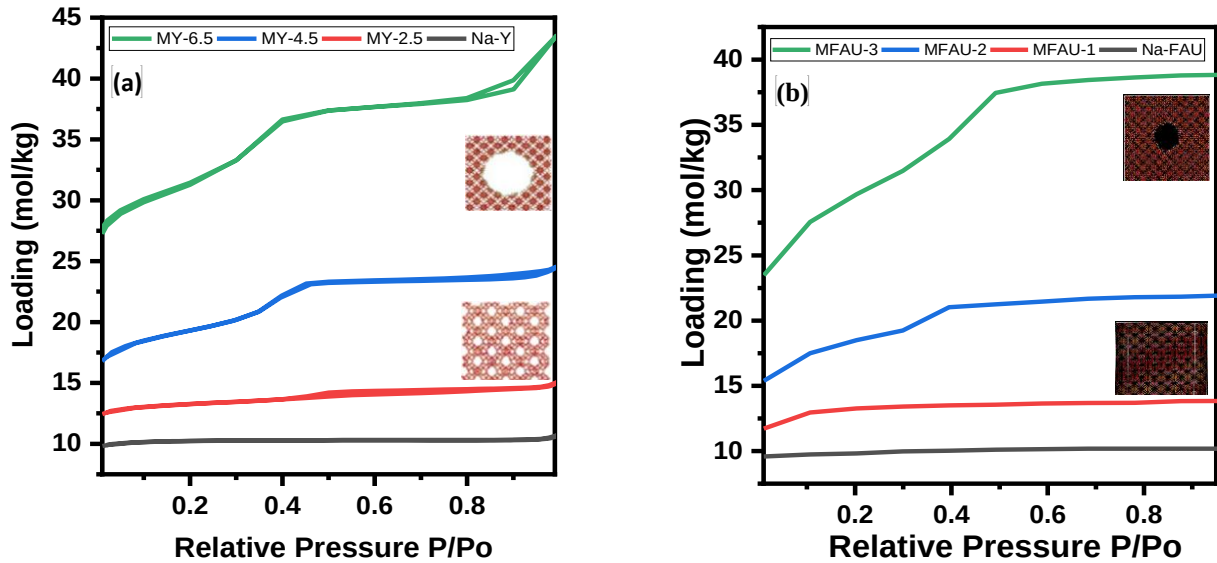


Figure 4.4: Nitrogen Adsorption Isotherm on Hierarchical Y-zeolite investigated by both (a) experiment and (b) simulation.

As a result, the same methodology is applied to research on micro-mesoporous models. At 77K, physisorption (van der Waals forces) is the main mechanism by which nitrogen is adsorbed on FAU zeolite, and the availability of surface area and pore volume is essential for this process. On the other hand, at elevated temperatures (near ambient temperature), adsorbate-adsorbent interactions are affected by any electrostatic interactions from ions present in the zeolite structure in addition to physical forces. As noted in the research [98], high adsorption loading is observed at high temperatures for different zeolite structures because adsorbates may overcome activation barriers with the help of the greater temperature, which could boost their capacity by enhancing electrostatic interactions with ions. To avoid the electrostatic effects caused by sodium ions and concentrate on the structural properties of modified FAU structures, we conducted our adsorption studies at 77K. Figure 4.4 displays the adsorption isotherms for the simulated mesoporous frameworks (MFAU-1, MFAU-2, and MFAU-3). These model's adsorption isotherms have properties common to both microporous and mesoporous (except MFAU-1). This shows that hierarchical models have been developed and simulated successfully. A typical Type I isotherm can be seen for the structure MFAU-1. This behavior can be attributed to the small size of the introduced pore. This aligns with our experimental results, where no pronounced hysteresis is observed for MY-0.05M, as the introduced pore size is too small to exhibit such behaviour. The MFAU-2 and MFAU-3 structures exhibit a Type IV isotherm, a clear sign of mesoporous materials. The isotherm is sigmoidal in shape and has a clear inflection point around $P/P_0 = 0.4 - 0.6$ (same in the case of experimental results), typical of a Type IV isotherm. The curve levels off at higher pressures, characteristic of combined micro-mesoporous adsorption behavior. N_2 adsorption and desorption branches

are observed in the experimental procedure, but we can only simulate the adsorption behavior in our software. As is well known, it is difficult to determine the microscopic structure of fluids because experimental observations can only record their macroscopic characteristics. However, GCMC simulations can be used to investigate the microscopic structure of fluids. Figure 4.5 shows the density distribution of nitrogen in MFAU-1 models at various pressures at 77 K. The image illustrates that adsorption mostly occurs on the microporous surface at low pressures (~ 1 kPa). The small pores fill with nitrogen as the pressure reaches 10 kPa, and no more adsorption is seen at higher pressures. The adsorption isotherm of MFAU-1 shows that multilayer adsorption is not present. This is because the narrow pore size cannot accommodate capillary condensation. As a result, the adsorption isotherm shows no hysteresis, and the structure retains its original microscopic state.

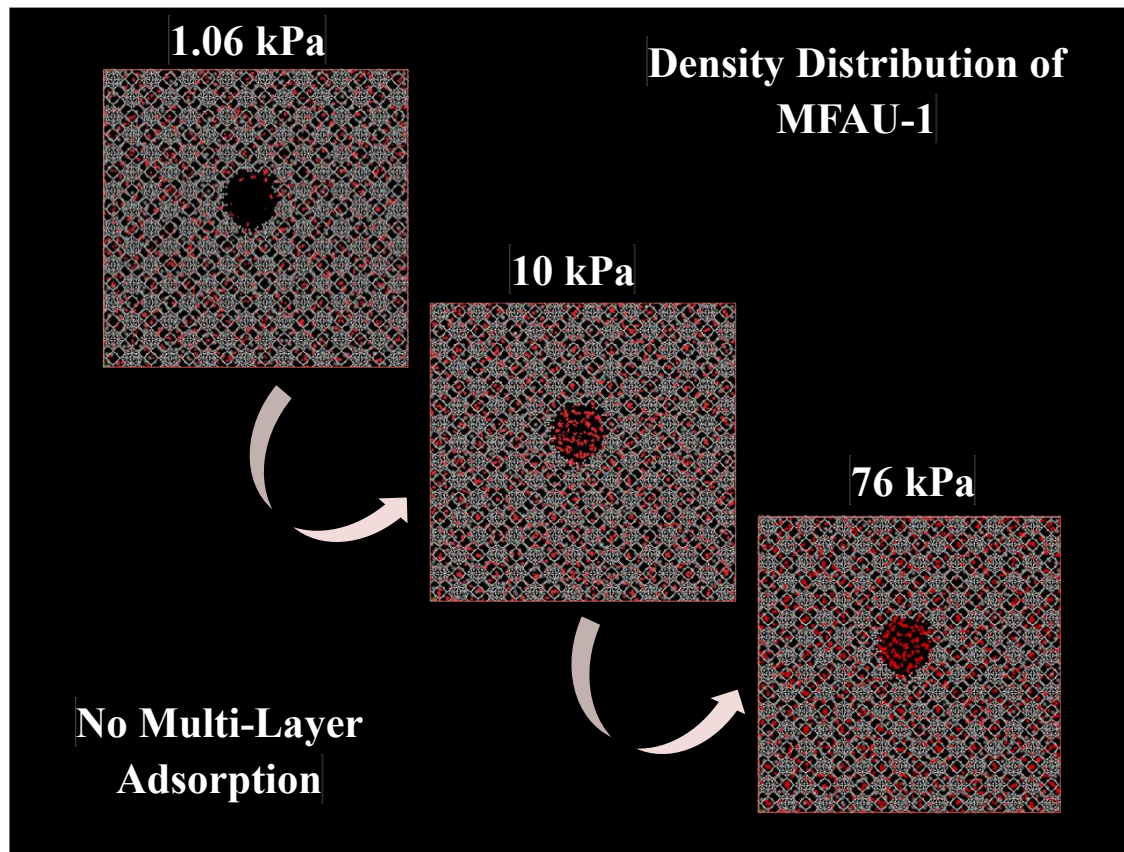


Figure 4.5: Density distribution of nitrogen in MFAU-1 structure (Dark red points represent the nitrogen molecule).

The results align with experimental evidence, which shows that microporous structures are present in minimal modification (MY-0.05M), which displays a Type I isotherm. The density distribution of two other models (MFAU-2 and MFAU-3) is depicted in Figures 4.6 and 4.7. At an extremely low pressure (< 1.06 kPa), nitrogen molecules adsorb to the surface of the modified (MFAU-2) model. As pressure increases, the contact layer of nitrogen reaches a saturated state at $p = 1.06$ kPa. At this point, the core of the mesopore remains empty due to low gas pressure. Because of adsorption on the mesopore surface, also known as the multilayer adsorption regime, the amount of adsorbed material in the hierarchical material increases with increasing pressure after the zeolite porosity is completely occupied. When the pressure reaches $p = 20$ kPa, a second adsorption layer starts forming, but the mesopore core remains largely unoccupied. This is all before the capillary condensation transition. Finally, the mesopore fills when the pressure in the MFAU-2 model reaches $p = 38$ kPa. Abruptly, confirming that capillary condensation is occurring.

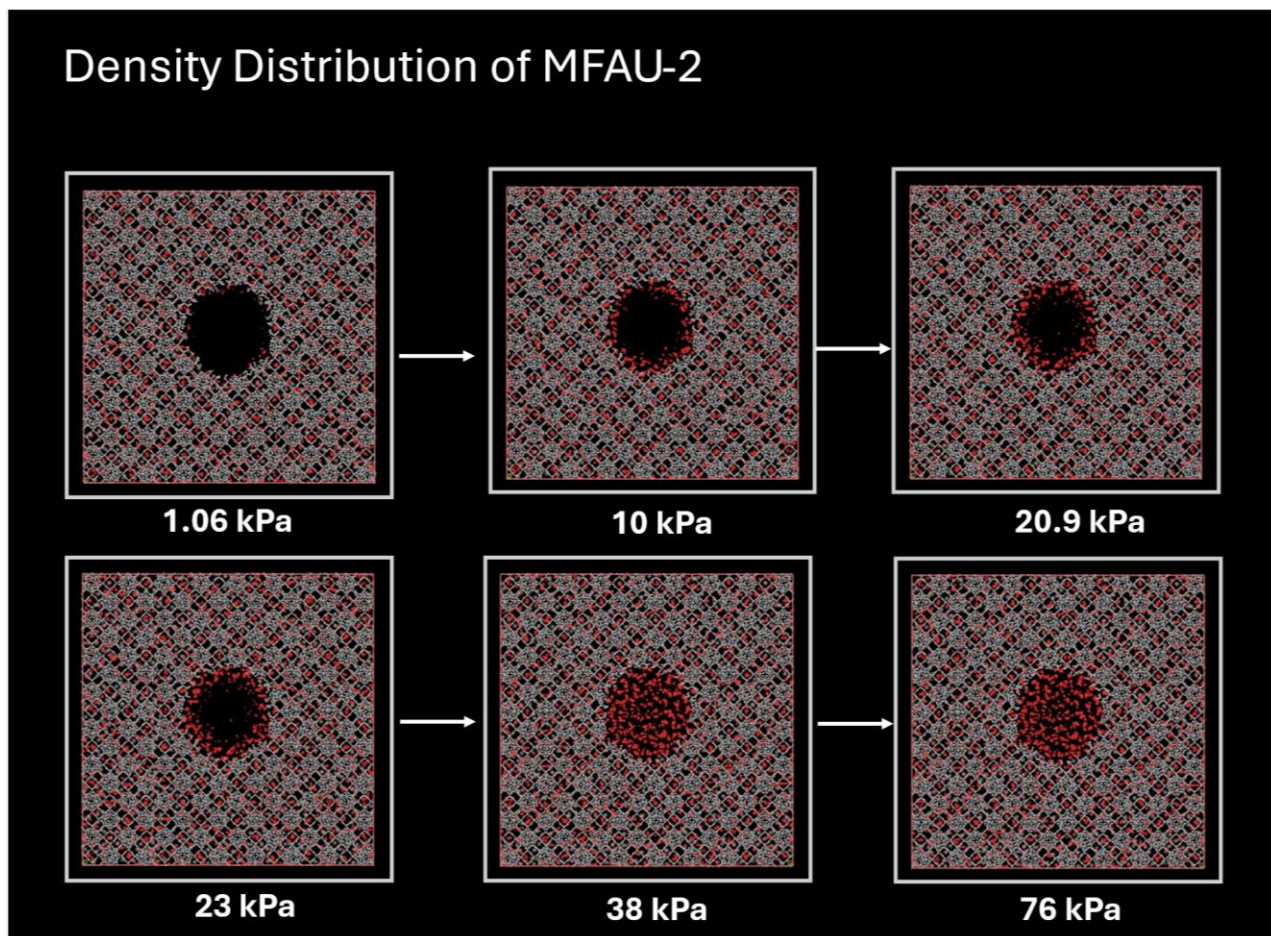


Figure 4.6: Density distribution of nitrogen in MFAU-2 structure (Dark red points represent the nitrogen molecules)

The dark region in the mesopore disappears, meaning nitrogen has condensed into a liquid-like phase inside the pore. This is consistent with the steep increase in your adsorption isotherm, showing a sudden rise in uptake. Similar results are reported in [86], [14], [89]. No further adsorption occurs beyond this point (76 kPa) because the mesopore is saturated. The same trend is observed for the density distribution of MFAU-3 in Figure 4.7. For MFAU-3, capillary condensation occurs at 48 kPa. The adsorption isotherm for this model exhibits a discontinuous and irreversible rise, corresponding to capillary condensation and

evaporation within the mesopore, similar to that observed in pure mesoporous materials at pressures significantly lower than the bulk saturation vapor pressure. The process of multilayer adsorption is also evident, as shown in the figures.

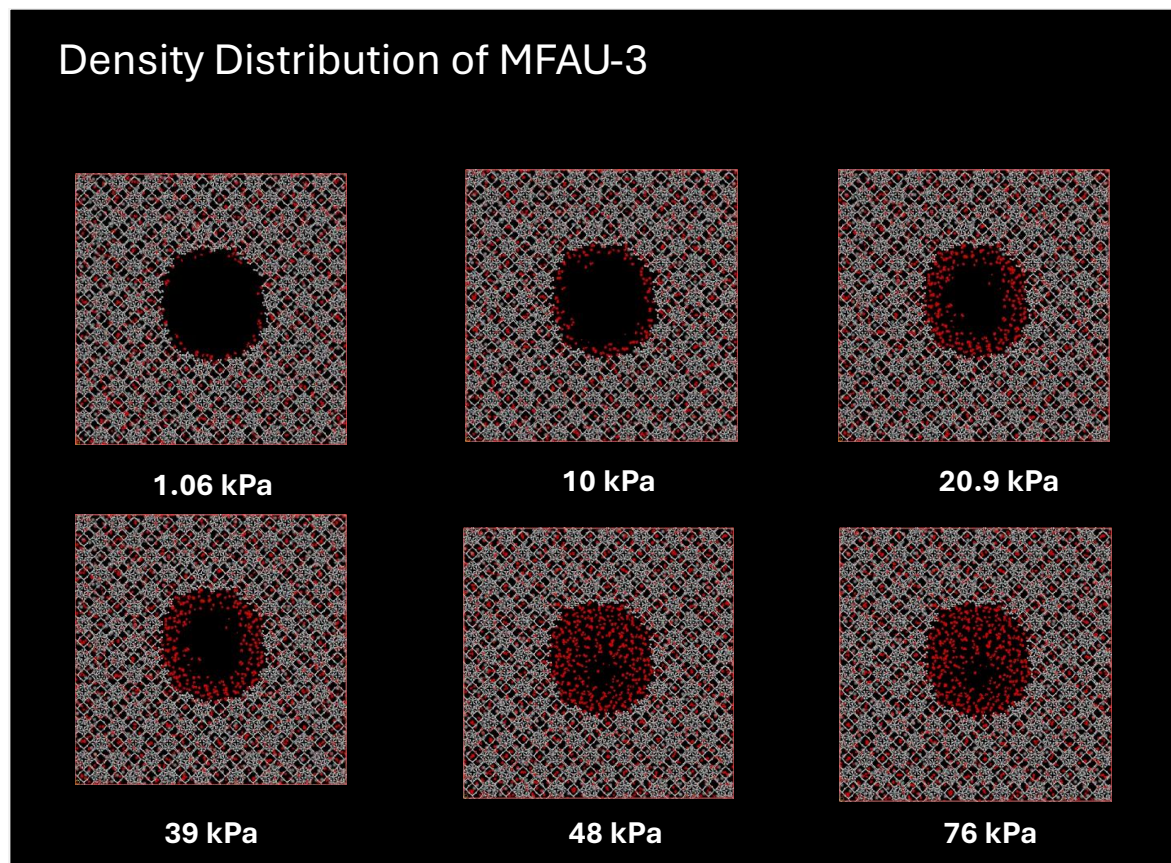


Figure 4.7: Density distribution of nitrogen in MFAU-3 structure (Dark red points represent the nitrogen molecules).

The simulated results agree with the experimental results, where higher modification results are obtained for large average pore size and type IV isotherm.

Figure 4.8 represents the probability of the distribution of energy states or adsorption energies for all FAU structures. As is typical of the original FAU structure, the sharp peaks of Na-FAU indicate a more homogenous and constrained energy environment. The peaks change and enlarge with increasing pore size. Due to pore expansion altering the local environment, this broadening of energy distribution suggests a wider range of adsorption sites or higher flexibility in energy states. With larger pores lowering overall confinement energy, the variations in peak positions indicate differences in adsorption site strength or interactions. This differing distribution will impact the interaction between gas molecules and zeolite.

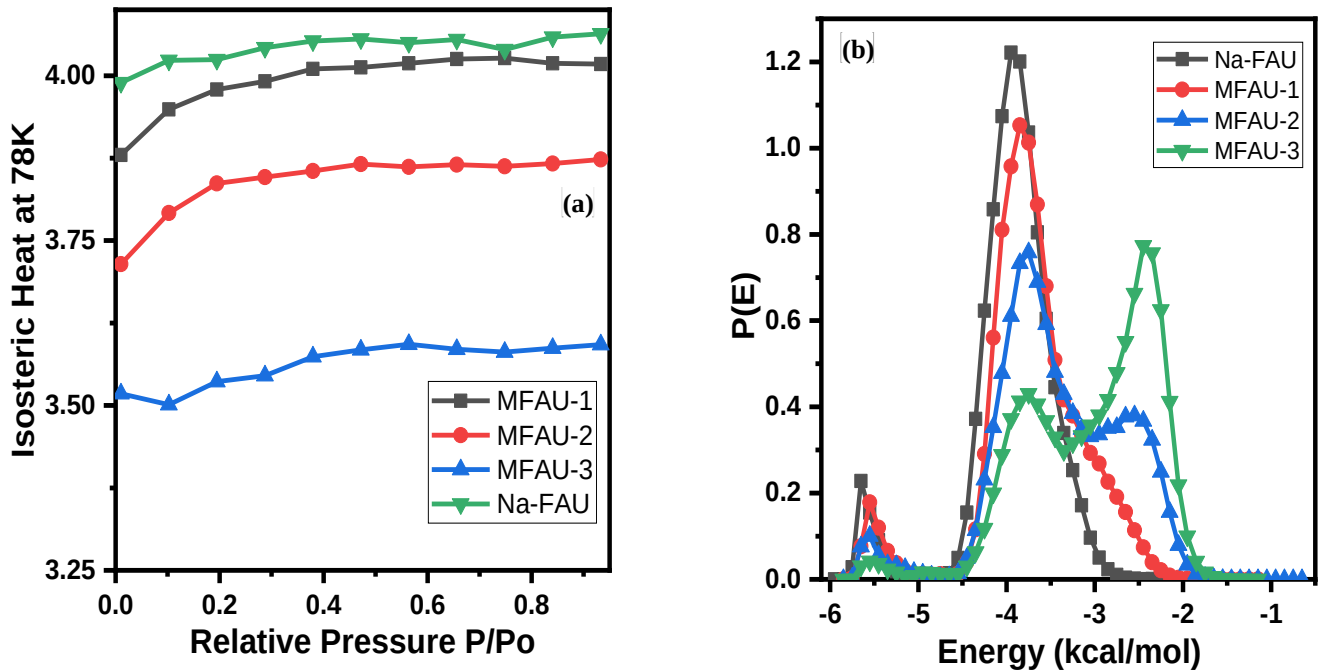


Figure 4.8: (a) Isosteric heat at 78K for nitrogen adsorption (b) The adsorption energy distribution curves: Energy probability of nitrogen interactions with FAU Models

The isosteric heat of adsorption decreases with an increase in pore size, as given in Figure 4.6. Low isosteric values for hierarchical models are likely to be due to structural or compositional modifications. Despite the low interaction strength, adsorption capacity increases with the increase in pore size. This implies that pore accessibility and structure control the adsorption mechanism rather than interaction strength. The energy shift during the adsorption process is shown in Figure 4.9. The energy variation statistics indicate that the system remains stable and in equilibrium at each step. A slight increase in intermolecular energy and decreases in Van der Waals and electrostatic energies suggest minimal interaction between the adsorbates and the FAU model. Thus, nitrogen adsorption on the FAU model is a physical adsorption mechanism

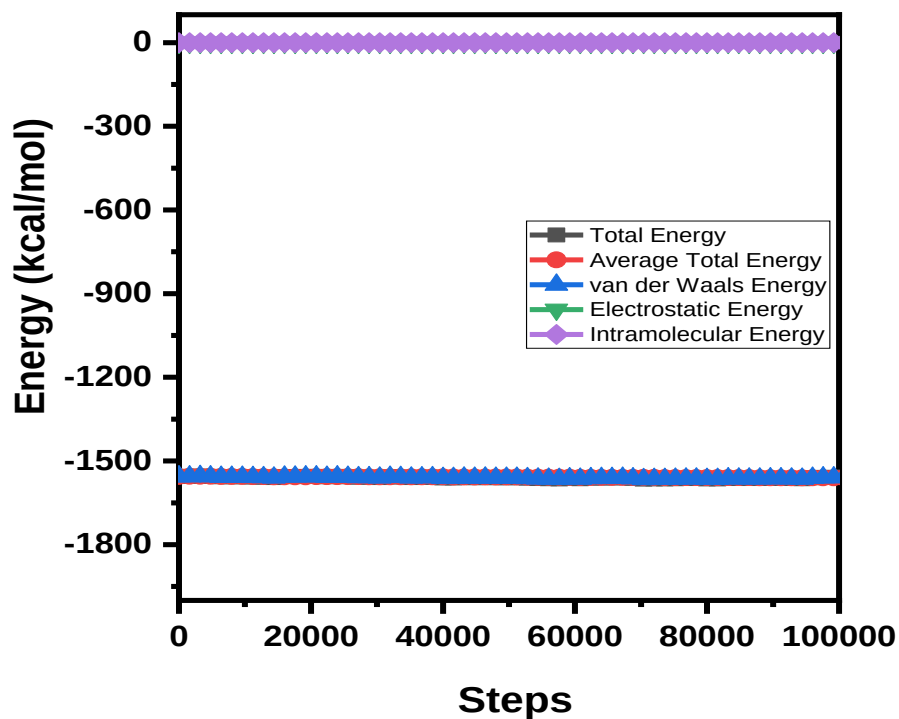


Figure 4.9: Energy Variation in the Nitrogen Adsorption Process.

The pore size distribution (PSD) and pore volume of the experimental hierarchical zeolite samples were evaluated by analyzing their nitrogen adsorption-desorption isotherms. The micropore volume slightly decreased following post-synthesis modification. Meanwhile, a significant increase in mesopore volume confirmed the successful introduction of mesoporosity [1]. The BJH adsorption pore size distribution graph is presented in Figure 4.10.

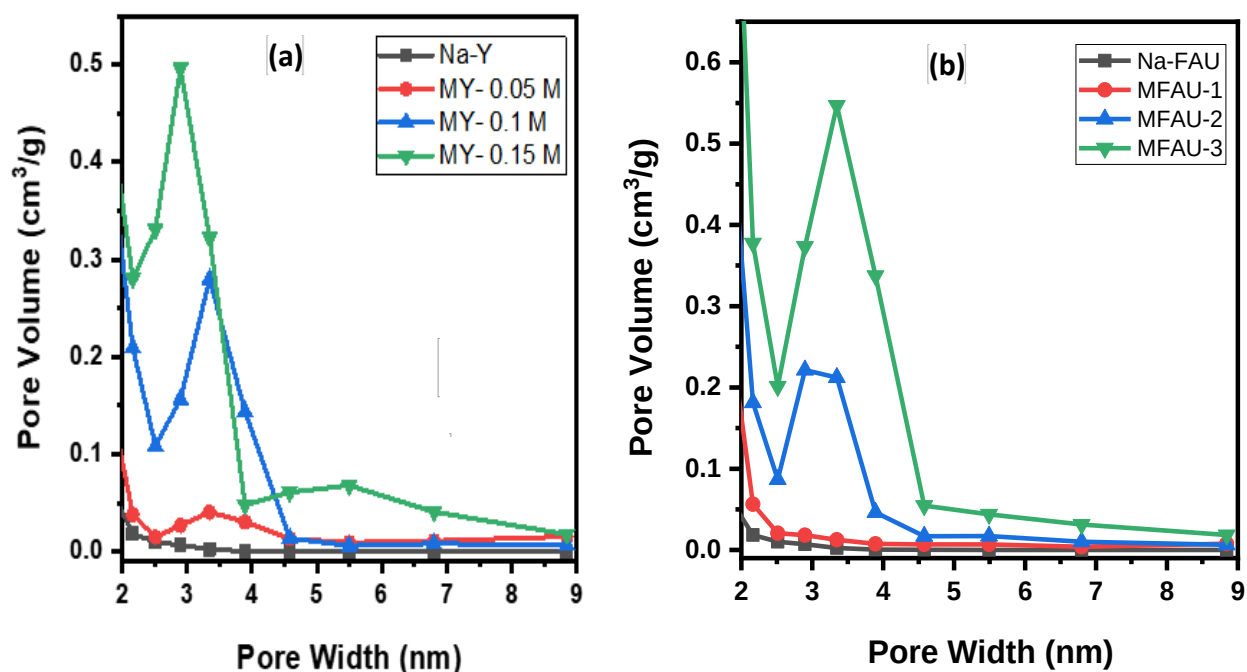


Figure 4.10: Pore size distribution is calculated using the BJH Method: (a) Experimental and (b) Simulated

The increase in pore volume with an increase in pore size was confirmed by pore size distribution. The flat profile of the unmodified Na-Y sample indicates a mostly microporous structure with a small mesopore volume. Minor textural mesoporosity could cause tiny peaks in the mesopore region. MY-0.05M sample exhibits a slightly higher mesopore volume but is still exceedingly small. A significant rise in pore volume between

3 and 5 nm for MY-0.1M suggests the presence of a hierarchical structure containing both micropores and mesopores. A bimodal pore size distribution curve is observed in the case of MY-0.15M, with a dominant peak between 2-5 nm and a small peak beyond 5 nm. This could result from a more widespread framework rearrangement or the agglomeration of smaller pores [99]. The broader distribution suggests more uniform mesoporosity. In computational analysis, the pore size distribution is investigated using two techniques. The first approach uses the method outlined in previous studies to determine the local diameter of the pores [86], [14], [87]. The distance between the hydrogen atoms at the pore surface and the pore center was measured to estimate the pore radius. The corresponding pore size distribution exhibits a mean Gaussian distribution, as depicted in Figure 4.11. According to this, the average pore size of the three modified models is 23.1 Å, 32.2 Å, and 41.6 Å, much closer to our experimental values. In the second approach, the pore size distribution curves are obtained by applying the BJH model to the adsorption isotherm data from the sorption analysis. The results are displayed in Figure 4.10.

Table 4.3: Textural Properties of Hierarchical FAU Models.

Model	Accessible Surface Area (m²/g)	Free Volume (m³)	Occupied Volume (m³)	Specific Free Volume (cm³/g)	Average pore Diameter (nm)
Na-Y	719	2.192E-26	0.30391	0.30391	0.75
MFAU-1	747	2.427E-26	0.35731	0.35731	2.3
MFAU-2	848	3.049E-26	0.49782	0.49782	3.2
MFAU-3	875	3.750E-26	0.75887	0.75887	4.1

The results are consistent with the experimental findings. In the MFAU-2 and MFAU-3 models, average pore diameters are 3.2 nm and 4.1 nm, respectively, with strong peaks between 2 and 5 nm. The adsorption capacities of nitrogen on Y-zeolite are calculated for experimental samples and simulated structures. Adsorption capacity is calculated according to the formula

$$\text{Adsorption Capacity} = \frac{n * M}{A_v * p * V} \quad \text{Eq(3)}$$

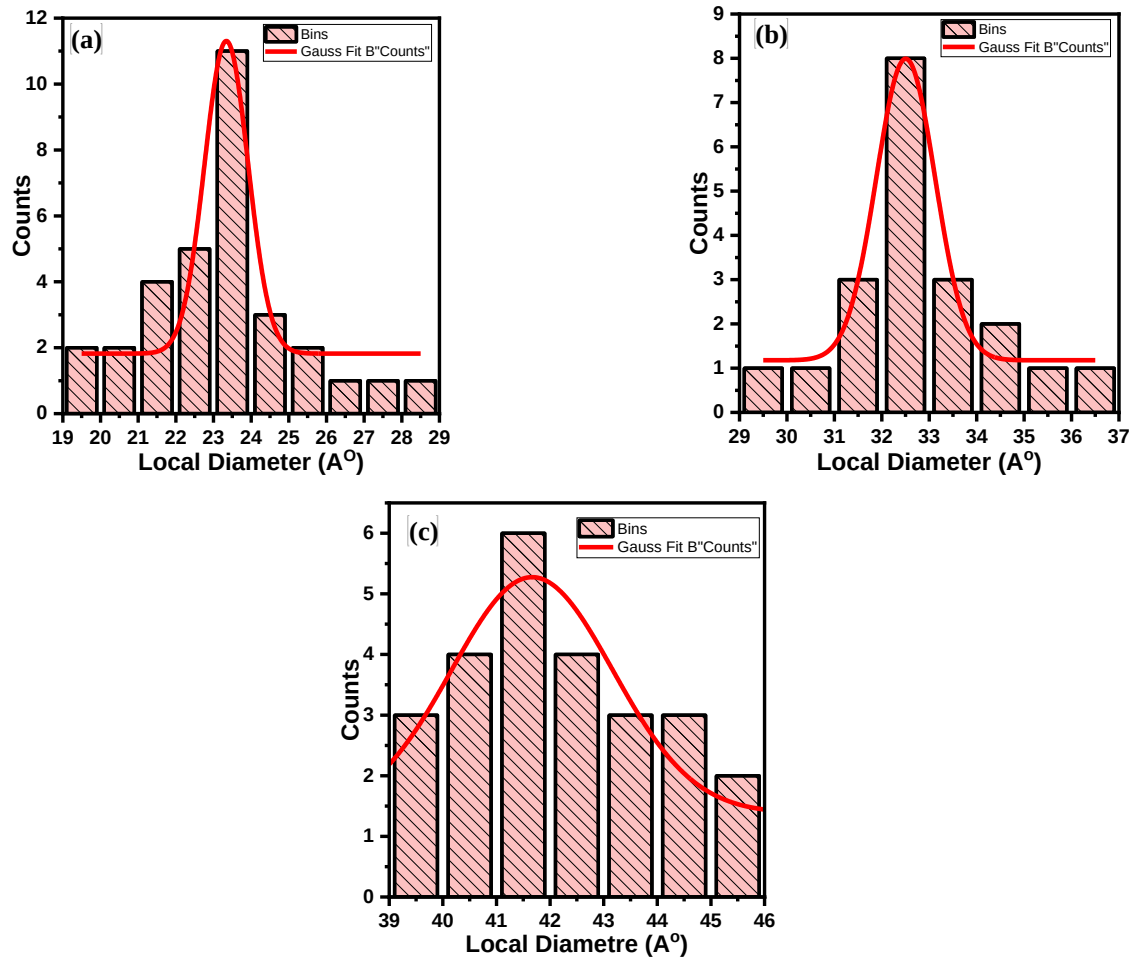


Figure 4.11: Gaussian distribution of pore size in the Hierarchical FAU models (a) MFAU-1 (b) MFAU-2 (c) MFAU-3.

Where n is the number of nitrogen molecules adsorbed per cell, M is the molecular weight of Nitrogen, A_v is Avogadro's constant, and V and ρ are the Volume and density of the cell. The adsorption capacity increases linearly with an increase in pore size. Large pore sizes provide more interaction sites and space for the adsorbates. Introducing mesopores (MFAU-1 $\rightarrow$ MFAU-3) improves the connectivity between micropores and mesopores, making it simpler for adsorbate molecules to enter. The increase significantly reduces diffusional limits in adsorption capacity, which makes these materials ideal for heavy oil applications. A good agreement between the experimental and simulation results is shown in Figure 4.13. With an average relative error of 0.039, the trend between the simulated results and experimental data is comparable. Within the same pore size range, both simulated and experimental data demonstrate almost similar adsorption capacity for both modified and unmodified zeolites, demonstrating the accuracy of the computational model in predicting adsorption behavior. Surface area and free volume size are effective parameters for characterizing porous materials. The free volume and surface area were usually calculated using the Connolly surface method [100]. The accessible solvent surface area of all models was estimated using Connolly surfaces, generated with a spherical probe of 2 Å diameter. The Connolly surface represents the boundary where the probe contacts the atoms, defined by their scaled van der Waals radii, rather than the path traced by the probe center. In other words, the molecule is effectively rolled over by the probe to create a smooth, continuous outer surface [101]. Figure 4.12 displays the model's accessible area. The surface area depicted here is where a particular spherical probe in the periodic cell may reach.

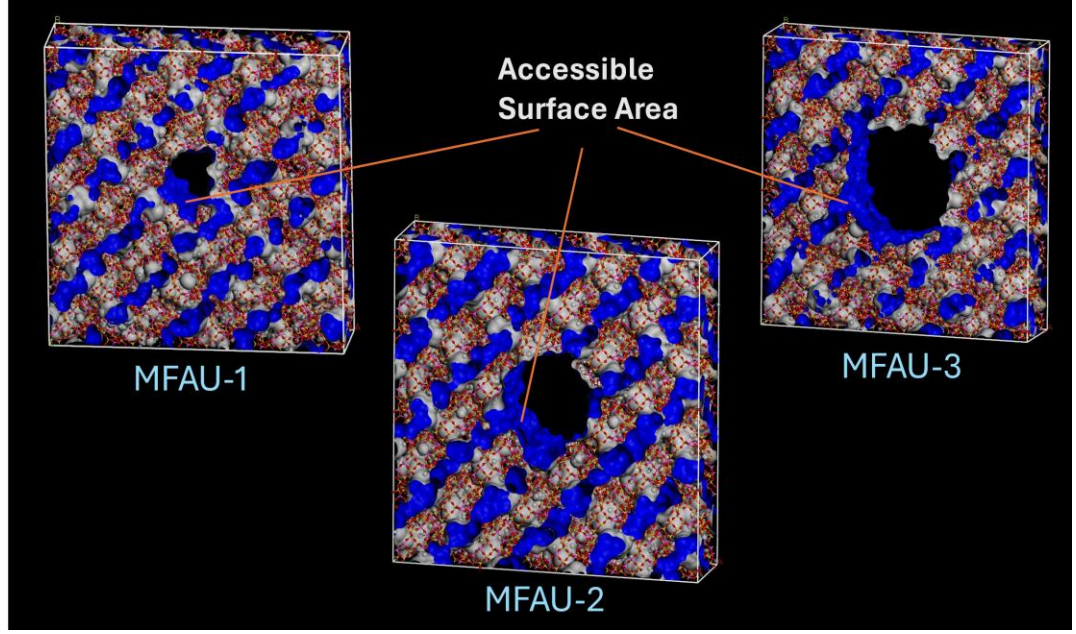


Figure 4.12: The accessible surface area of Hierarchical FAU models (depicted through the Conolly method).

The surface area of the structures using this method is slightly higher than the experimental values obtained through the BET model. The reason for this discrepancy may be that the computational models are built using a perfect Y-zeolite structure, in which the arrangement of the pores follows an ideal ordered phase. Furthermore, structural areas that might not be accessible during nitrogen adsorption in BET analysis can be accessed by Conolly's small probe diameter, which could cause differences in the measured values [87].

A key factor in adsorption is the atomic-level smoothness of a pore surface. This coefficient, λ , is defined as

$$\lambda = \frac{S_c}{2n\pi r_a l_z} \quad \text{Eq (4)}$$

was employed to illustrate the pore surface's smoothness. In eq (4), S_c is the Connolly surface area, n is the number of pores in the model, r_a is the radius, and l_z is the length along the axis. The value of λ depicts the degree of smoothness.

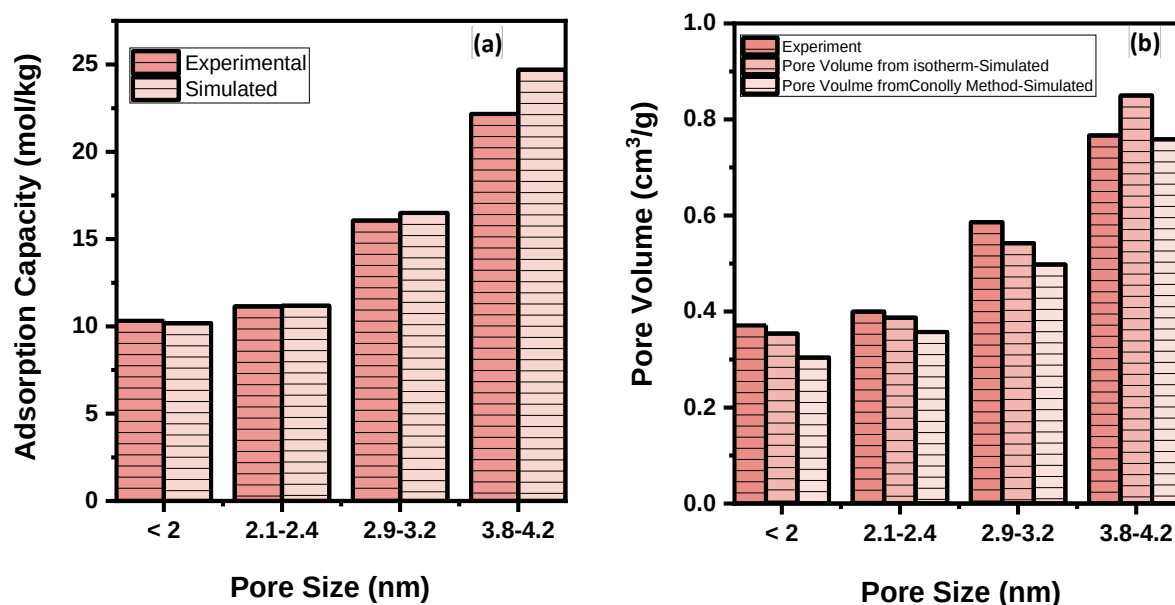


Figure 4.13: The (a) adsorption capacities and (b) pore volume vs pore size for all experimental Y-zeolite samples and FAU models

At the atomic level, a unit value denotes an ideal smooth cylindrical pore, whereas a value larger or smaller than one denotes surface corrugation. In our hierarchical FAU models, λ was found to be 3.1, 2.0, and 1.51 for the MFAU-1, MFAU-2, and MFAU-3, respectively, which implies the smoothness of the model increases with an increase in pore size. Connolly surface analysis also considers the available void space inside the framework and is used to calculate the pore volume (free volume) of all structures. Figure 4.13 shows the relationship between pore size and pore volume for experimental and computational results. Simulated pore volume is also calculated using adsorption isotherm data and is

compared with experimental data. The findings show a high degree of agreement between the simulated and experimental data, with an average relative error of 0.065 for pore volume calculated using isotherm data and 0.096 for the Conolly method. The total pore volume grows as the pore size increases because more space is available to hold guest molecules. This pattern is consistent with the fundamental principles of porous materials.

4.1.3 Diffusion Properties

The self-diffusion coefficient provides a quantitative description of diffusion, a macroscopic quantity. The time-dependent diffusion coefficient (D_{self}) is calculated using the MSD results. The self-diffusion coefficient can be used to characterize the intrinsic diffusion of particles in the pores since it represents the diffusion characteristics of gas molecules on zeolites without a concentration gradient. In MD simulation, Newton's equation of motion was iteratively solved to follow the motions of an ensemble of particles. It is necessary to compute the particle of MSD using the acquired trajectory to determine self-diffusion coefficient. The diffusion coefficient of penetrants can be calculated using the Einstein equation once the long-time limit has been achieved and the MSD is linear. The plot of MSDs for FAU and all hierarchical models is shown in Figure 4.14. Nitrogen confined in the microporous FAU structure has a self-diffusivity value of $10^{-9} \text{ m}^2/\text{s}$ and is the same as in previous research [86]. The self-diffusion coefficients of gas molecules on FAU models decrease in MFAU-3>MFAU-2>MFAU-1>Na-FAU. Pore size dependence of self-diffusion of nitrogen on all structures is shown in Figure 4.15. Nitrogen's self-diffusivity rises with increasing pore size. This is expected since bigger pores facilitate the free passage of nitrogen molecules by lowering diffusion resistance. The limited space and strong adsorptive interactions with the pore walls hinder diffusion in microporous areas.

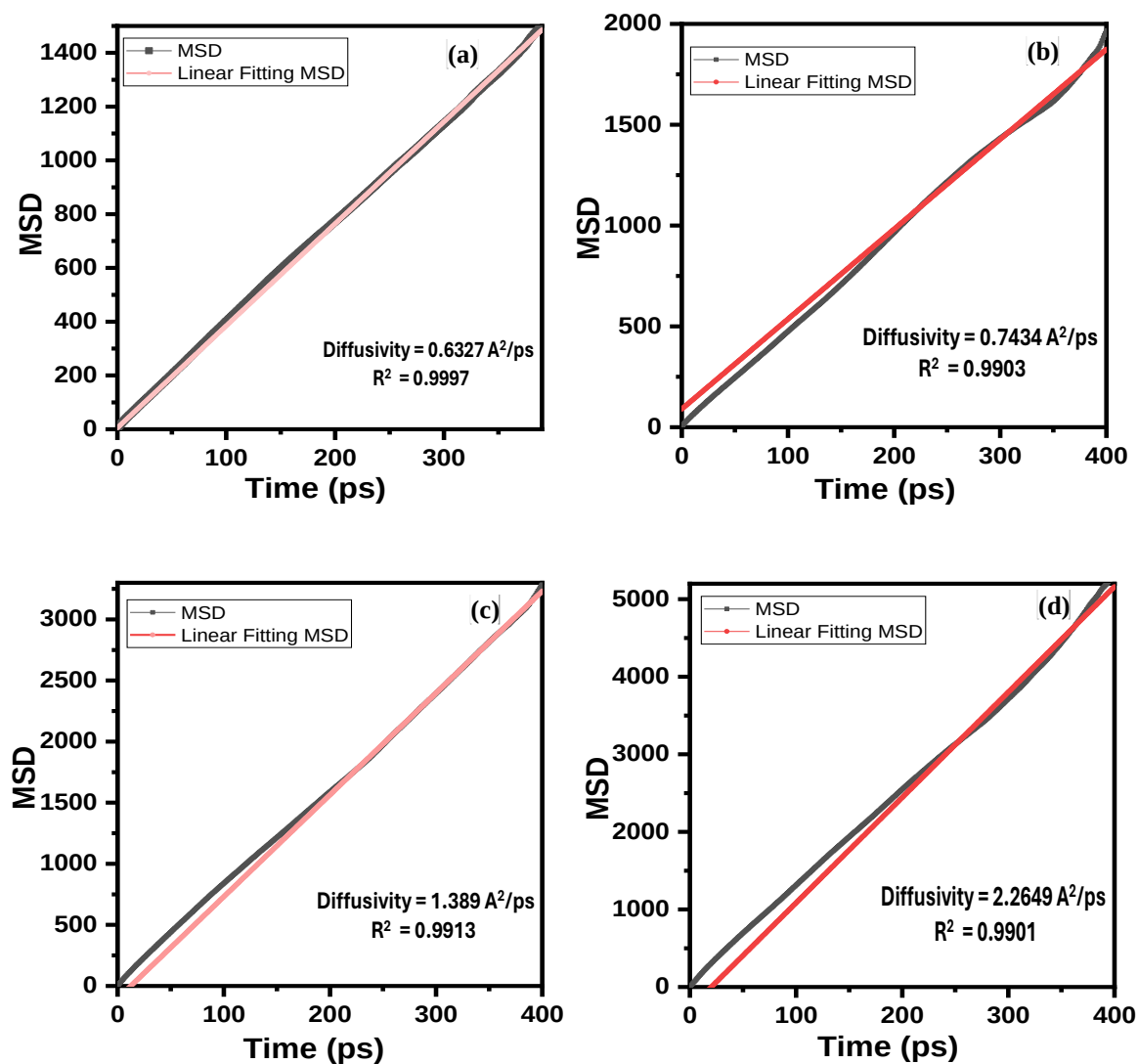


Figure 4.14: MSD of Nitrogen on FAU structures (a) Na-FAU (b) MFAU-1 (c) MFAU-2 (d) MFAU-3 versus time at 298K.

Adding mesopores improves mass transfer and total diffusion rates compared to microporous materials. This might be advantageous for processes where effective molecule transport is essential, such as adsorption, separation, and catalysis.

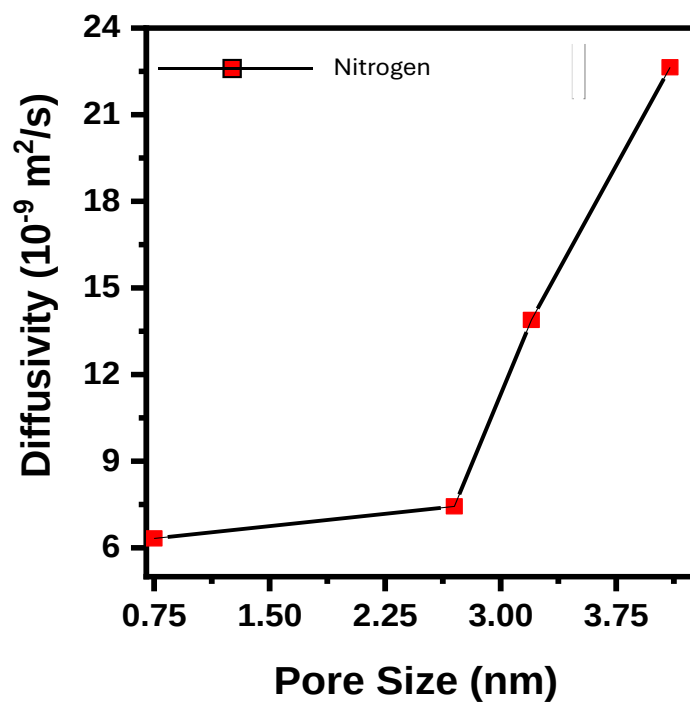


Figure 4.15: Pore size dependence of self-diffusion coefficients of nitrogen on FAU structures

4.2 Tuning the Porosity of Y-zeolite and ZSM-5 for Fluid Catalytic Cracking of Vacuum Gas Oil to Light Olefins

4.2.1 Characterization of Hierarchical Y-Zeolite and ZSM-5

Detailed characterization of hierarchical Y-zeolite and ZSM-5 is given in this section:

a) Structural Analysis

There is no indication of any other crystalline or amorphous phases in any of the XRD patterns, which shows that the produced zeolites have great crystallinity. Section 4.1.1 provides a clear explanation of the hierarchical Y-zeolite's XRD pattern. The crystallinity of the modified Y-zeolite (MY-0.1M) is good. The standard Na-Y zeolite closely matched the diffraction peaks of the hierarchical Y zeolite signals. The XRD patterns are given in Figure 4.1.

Figure 4.16 displays the XRD patterns of hierarchical ZSM-5 samples that were generated with different levels of dealumination. It is confirmed that all developed hierarchical ZSM-5 materials are pure-phase MFI-type with no extra unidentified peaks when the standard ZSM-5 peaks match the XRD patterns of the parent ZSM-5 and the hierarchical HR-ZSM-5 samples. Moreover, variations in acid content do not result in a loss of crystallinity.

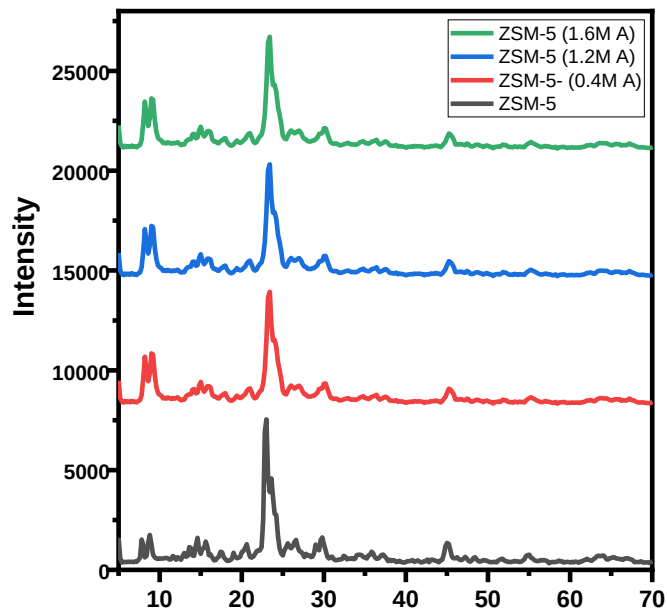


Figure 4.16: XRD patterns of parent and hierarchical ZSM-5

MFI-type ZSM-5 diffraction peaks are present in all samples, including those treated with varying base concentrations. This demonstrates that the framework structure remains intact even after the desilication procedure. As base concentration rises, relative peak intensities somewhat decline, but peak locations stay constant. This implies a slight decrease in crystallinity as the degree of desilication increases, which is common because of partial framework disruption [1]. Figure 4.17 displays the XRD patterns of hierarchical ZSM-5 samples that were generated with different levels of desilication. The remarkable structural stability of ZSM-5 is observed in the XRD patterns of the hierarchical samples. All samples maintain the distinctive MFI-type diffraction peaks with no extra or unknown reflections, confirming phase purity, even after being treated with increasing amounts of NaOH (0.25 M to 1 M).

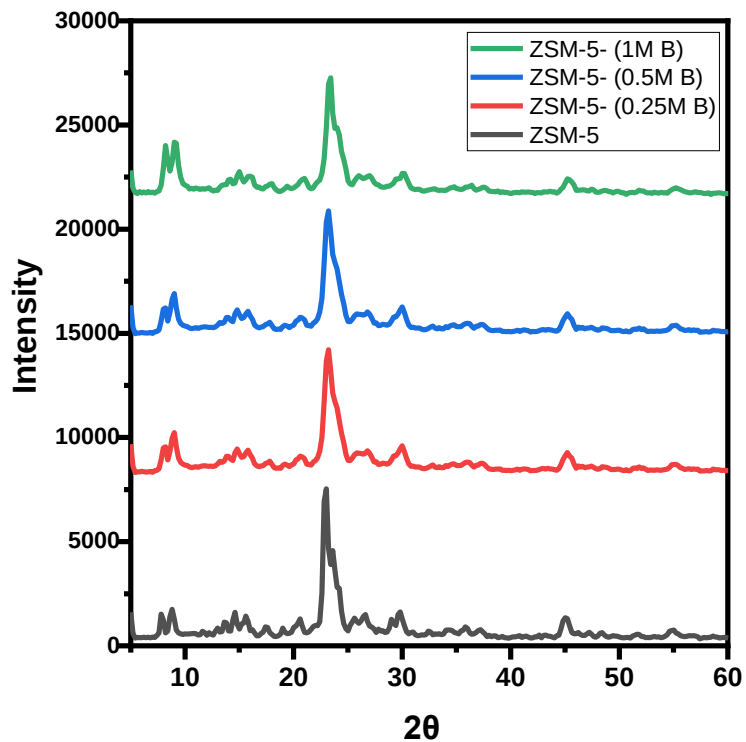


Figure 4.17: XRD patterns of parent and hierarchical ZSM-5.

b) Textural Characteristic analysis by N₂ adsorption/desorption

Figure 4.18 presents the sorption analysis of both the parent and hierarchical Y zeolite samples. A detailed interpretation of these results is provided in Section 4.1.2.

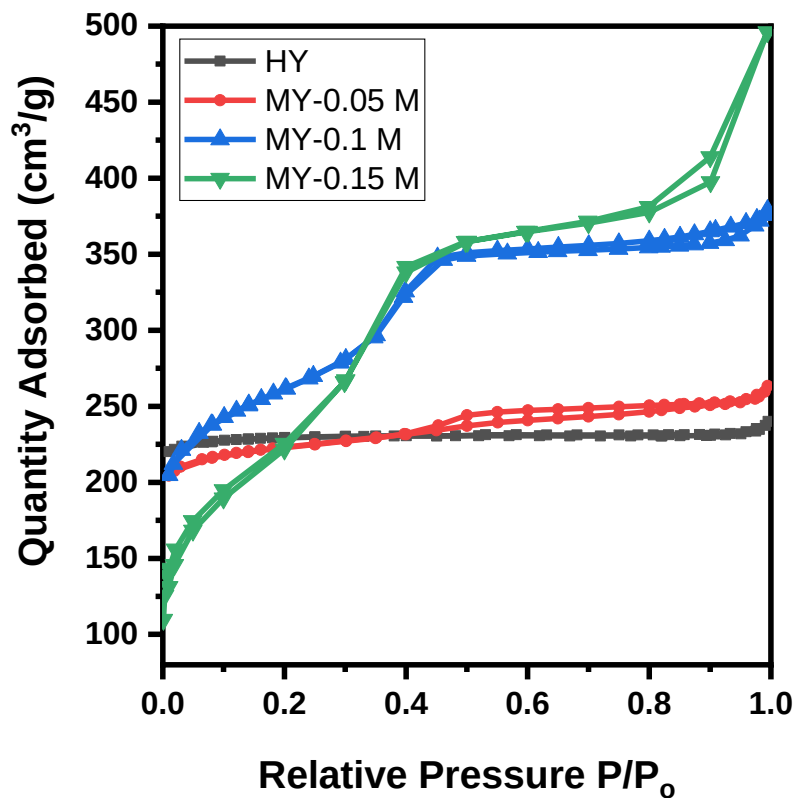


Figure 4.18: Nitrogen adsorption–desorption isotherms of hierarchical Y-zeolites..

The nitrogen adsorption–desorption isotherms of the parent ZSM-5 and hierarchical ZSM-5 samples made by dealumination with different acid concentrations (0.4 M, 1.2 M, and 1.6 M) are shown in Figure 4.19. Type IV isotherms indicate the presence of mesoporosity with a distinct hysteresis loop in all hierarchical samples. The treated samples exhibit higher nitrogen uptake at higher relative pressures than the parent ZSM-5, indicating that hierarchical structures were successfully formed.

However, the isotherm shape and adsorption capacity do not significantly alter when the acid content is raised over 0.4 M. This implies that, under the investigated conditions, more dealumination has no impact on improving mesoporosity or hierarchical character. This could be because of the ZSM-5 framework's stability or the saturation of available dealumination sites due to a high Si/Al ratio.

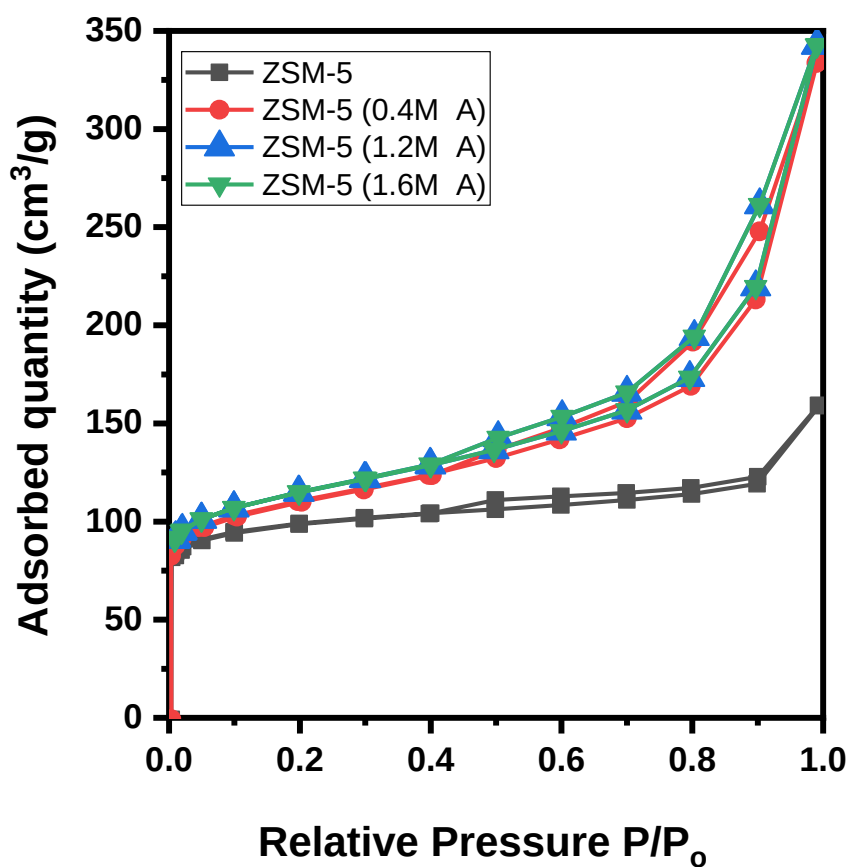


Figure 4.19: Nitrogen adsorption–desorption isotherms of hierarchical ZSM-5 zeolites.

Figure 4.20 shows the nitrogen adsorption–desorption isotherms of parent ZSM-5 and hierarchical ZSM-5 samples that were created by employing different base concentrations (0.25 M, 0.5 M, and 1 M NaOH) to alter the degree of desilication.

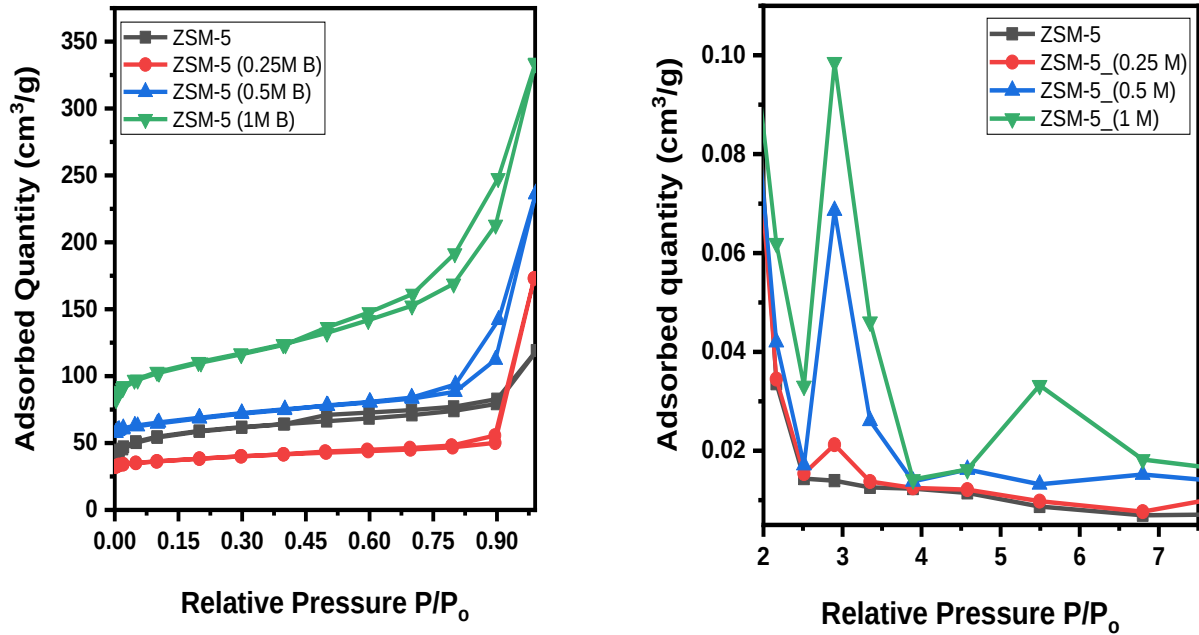


Figure 4.20: Nitrogen adsorption–desorption isotherms and pore size distribution of hierarchical ZSM-5 zeolites.

Particularly in the 0.5 M and 1 M base-treated samples, there is a definite trend showing that increasing NaOH concentrations result in noticeably higher nitrogen uptake at higher relative pressures ($P/P_0 > 0.4$). This rise, typical of Type IV isotherms with hysteresis loops, validates the desilication-induced formation of mesoporous structures. Desilication is a more successful method for hierarchical pore growth in ZSM-5 than dealumination, since it increases mesoporosity as base strength increases [97].

N₂ adsorption-desorption analysis showed that modified MY-0.25M B, MY-0.5M B, and MY-1M B samples have a surface area of 375 m²/g, 390 m²/g, and 422 m²/g, as compared

to 400 m²/g of parent ZSM-5 zeolite. The modified Y-zeolite samples' pore volume (V_p) results were extremely interesting, showing an increase in (V_p) size from 0.245 to 0.267 (8% increase), 0.364 (50% increase), and 0.516 cm³ (112%), for the MY-0.25M B, MY-0.5M B, and MY-1M B samples, respectively. Micropore volume is decreased, and mesopore volume is increased for MY-0.25M B, MY-0.5M B, and MY-1M B samples. For example, micropore volumes of MY-0.25M B, MY-0.5M B, and MY-1M B decreased by 33%, 43%, and 24 %, respectively. On the other hand, mesopore volumes of 0.179, 0.289, and 0.414 cm³/g were observed for MY-0.25M B, MY-0.5M B, and MY-1M B, respectively. The average pore diameter (D_p) for hierarchical samples showed a notable rise. Indeed, the D_p size increased from 2.1 nm for ZSM-5 to 2.8 nm (33% increase) for MY-0.25M B and to 3.8 nm (81% increase) and 5.0 nm (138 % increase) for MY-0.5M B and MY-1M B, respectively. The textural properties of treated zeolites depend on base concentration, contact time, and surfactant type used in post-treatment. It is noted that mesopore volume increases with an increase in base concentration for MY-0.25M B, MY-0.5M B, and MY-1M B samples.

Table 4.4: Textural Properties of Hierarchical ZSM-5 (via desilication).

Sample	BET surface area (m²/g)	Micropore volume (cm³/g)	Mesopore Volume (cm³/g)	Total Pore Volume (cm³/g)	Average Pore Diameter (nm)
ZSM-5	400	0.133	0.112	0.245	2.1
ZSM-5 0.25 M B	375	0.088	0.179	0.267	2.8
ZSM-5 0.5 M B	390	0.075	0.289	0.364	3.8
ZSM-5 1M B	422	0.100	0.414	0.514	5.0

All textural properties of hierarchical ZSM-5 are given in Table 4.4. Increased surface area and pore volume are observed with increased pore diameter. These findings demonstrated that the soft templating method and ZSM-5 zeolites' acid/base treatments effectively produced hierarchical zeolites.

The PSD graph in Figure 4.20 displays the distribution of pore sizes in parent ZSM-5 and hierarchical ZSM-5 samples created by desilication with varying NaOH concentrations. On the other hand, the hierarchical samples show wider distributions that reach into the mesoporous region (2–50 nm), suggesting that secondary porosity was successfully generated. The mesopore distribution's intensity and breadth increase with base concentration, particularly in the sample treated with 1 M NaOH, which exhibits a sizable mesoporous volume centered about ~5-10 nm.

c) Morphological Analysis

Upon morphological examination, the distinctive Faujasite zeolite morphology is discussed in detail in section 4.1.1. On the other hand, Figure 4.21 shows how the Hierarchical ZSM-5 sample developed a mesoporous structure by a series of acid and basic leaching steps followed by surfactant templating. The SEM pictures show how the ZSM-5 samples' morphology changed as the concentration of NaOH used for desilication increased. As is typical of microporous zeolites, the parent ZSM-5 displays distinct, dense crystals with smooth surfaces. The early generation of mesopores is indicated by the minor surface roughening that occurs after treatment with 0.25 M NaOH. This result is more noticeable in the sample treated with 0.5 M NaOH, where partial crystal etching and enhanced surface imperfections point to a hierarchical structure formation. The successful creation of a well-developed hierarchical ZSM-5 structure is confirmed by the sample treated with 1 M NaOH, which exhibits severe morphological disruption, a highly porous and fragmented appearance, and no visible aggregation.

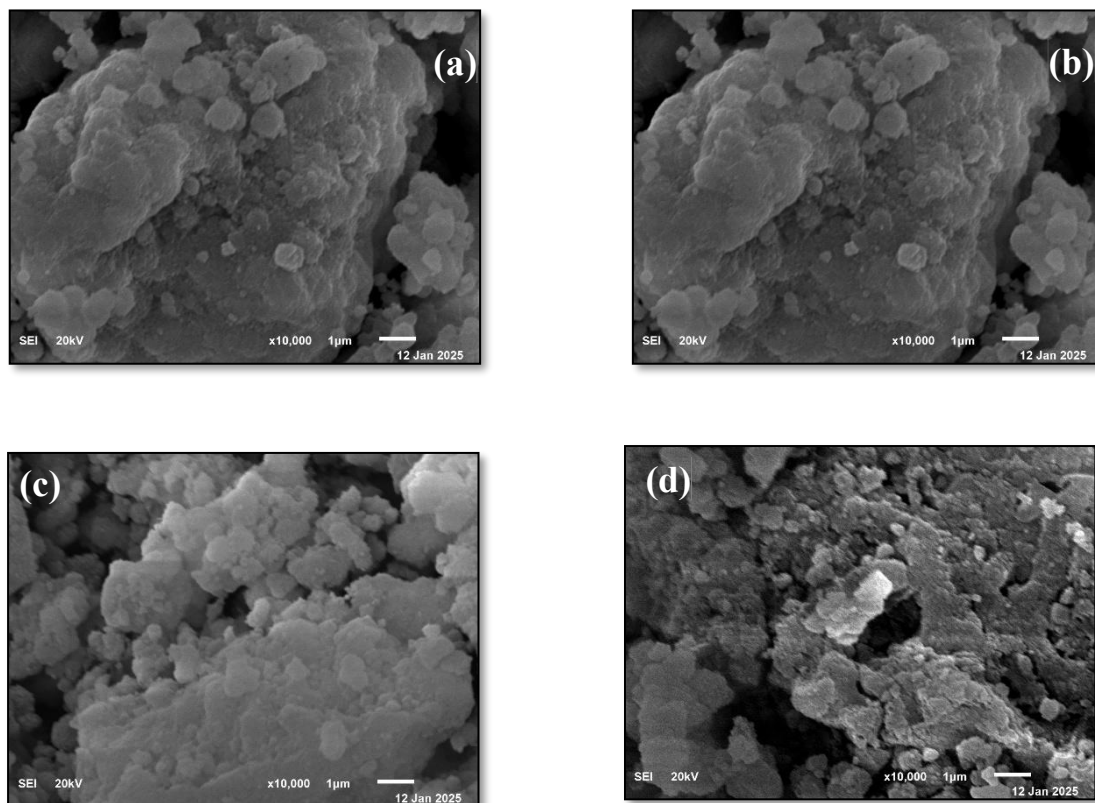


Figure 4.21: SEM images of hierarchical ZSM-5 (a) Parent ZSM-5 (b) ZSM-5-0.25M B (c) ZSM-5-0.5M B (d) ZSM-5-1M B.

After initial characterization, the hierarchical Y sample treated with 0.1 M acid (MY-0.1M) and the hierarchical ZSM-5 sample treated with 1 M base (ZSM-5-1M B) were identified as the most promising, exhibiting well-developed mesoporosity while preserving crystallinity and microporous structure. These two samples were selected for further analysis and testing.

d) Acidity analysis by NH₃-TPD

This analysis is to determine the total acidity of modified zeolite samples. Figure 4.22 shows the parent's temperature desorption peak and the zeolites' hierarchical form.

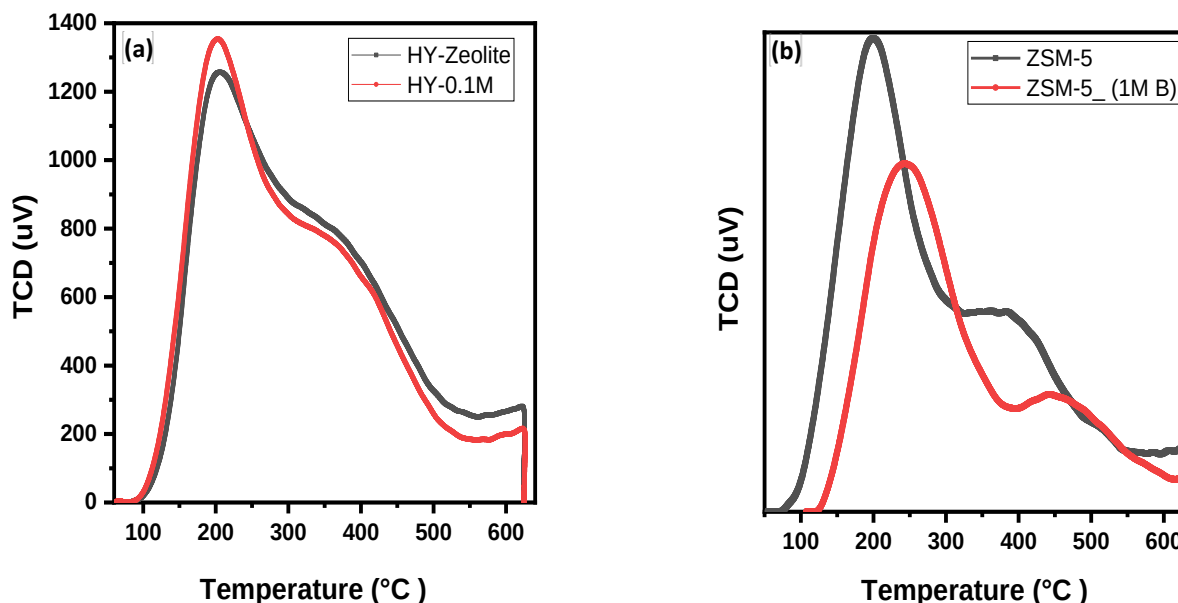


Figure 4.22: Ammonia-TPD profiles of the parent and hierarchical zeolites. (a) Y-zeolite
(b) ZSM-5

The total acidity of the hierarchical HY-0.1M sample and HY-Zeolite is 1.972 and 1.930 mmol/g, respectively, as shown in Table 4.5. This suggests that the HY-0.1M sample maintains a high level of acidity even after modest treatment. On the other hand, the total acidity of ZSM-5 is 0.972 mmol/g; in the hierarchical ZSM-5-(1M B) sample, this drops to 0.741 mmol/g. The harsher desilication conditions, which probably cause the partial loss or deactivation of acid sites in the ZSM-5 framework, are to blame for this decrease in acidity.

Table 4.5: Acidity analysis of Hierarchical zeolites.

Sample	Weak Acidity (100-300 °C)	Medium Acidity (300-450 °C)	Strong Acidity (> 450 °C)	Total Acidity (mmol/g)
HY- Zeolite	0.707	1.135	0.130	1.972
HY- 0.1M	0.794	1.014	0.122	1.930
ZSM-5	0.443	0.477	0.052	0.972
ZSM-5- 1M B	0.477	0.246	0.018	0.741

4.2.2 Evaluation of Hierarchical Zeolite-based FCC catalysts

Table 4.6 presents the distribution of product yields from VGO cracking over four steamed FCC catalysts. The conversion of VGO is defined as $100 - (\text{Light cycle oil wt\%} + \text{Heavy cycle oil wt. \%})$ since VGO contains both light and heavy cycle oil. The influence of mesoporosity of hierarchical zeolites on the activity and stability of FCC catalysts for converting VGO into value-added chemicals is examined in this section. The figure shows the catalytic performance of different FCC catalysts based on parent and hierarchical combinations of Y and ZSM-5 zeolites (referred to as NFCC-(Y-ZSM-5), NFCC-(HY-ZSM-5), NFCC-(Y-HZSM-5), and NFCC-(HY-HZSM-5). The NFCC-(HY-ZSM-5) catalyst, which integrates hierarchical ZSM-5, produces the highest overall conversion, closely followed by NFCC-(Y-HZSM-5). This suggests that mesoporosity greatly improves the cracking efficiency. All catalysts exhibit a comparatively constant gasoline yield, with NFCC-(HY-ZSM-5) and NFCC-(Y-HZSM-5) showing a little improvement. This suggests that hierarchical structures promote the synthesis of desired gasoline-range products. It is noted that conversion increases from 60 wt% for NFCC-Y-Z to 69 % for NFCC-Y-HZ. The mesoporosity generation in Y zeolite and ZSM-5 results in an increase

in VGO conversion. From Table 4.6, it is shown that the highest gasoline yield of 32 wt% was achieved for NFCC-Y-HZ compared to 30 wt% for parent NFCC-Y-Z. On the other hand, the yield of HCO was significantly decreased for NFCC-Y-HZ compared to NFCC-Y-Z. Greater HCO conversion is observed with the NFCC-Y-HZ catalyst, which is attributed to the increased pore size of the ZSM-5 component. The yields for light cycle oil (LCO) in hierarchical catalysts are marginally lower than in the parent ones, which is consistent with the hypothesis that deeper heavy molecule cracking is facilitated by

Table 4.6: Comparative MAT data of base catalyst and modified zeolite-based FCC catalysts for cracking of VGO at 550°C .

Name of catalyst	NFCC-Y-Z	NFCC-HY-Z	NFCC-Y-HZ	NFCC-HY-HZ
Feed	HT-VGO	HT-VGO	HT-VGO	HT-VGO
Cat/Oil (g/g)	4.00	4.00	4.00	4.00
Mass balance	90.90	92.70	95.17	100.64
Conversion %	60.00	64.00	69.00	58.00
Yields (wt%)				
H ₂	0.03	0.06	0.05	0.04
C ₁	0.15	0.34	0.35	0.39
C ₂	0.11	0.29	0.37	0.39
C ₂ =	0.88	1.44	1.53	1.30
C ₃	1.26	1.57	1.54	1.12
C ₃ =	8.50	10.85	12.00	9.00
iC ₄	5.40	5.86	5.46	3.93
nC ₄	0.91	1.00	0.94	0.61
t ₂ C ₄ =	2.26	2.59	2.97	1.83
1C ₄ =	1.52	1.91	2.15	1.44
iC ₄ =	3.69	4.29	4.98	3.05
c ₂ C ₄ =	1.59	1.89	2.16	1.32
1,3-BD	0.02	0.02	0.02	0.02
C ₄ in Liquid	0.32	0.23	0.27	1.46
Total Gas				
Gasoline (Liquid)	30.46	31.00	32.52	30.00
LCO	12.29	12.80	10.53	9.34
HCO	29.12	24.78	21.28	34.00
Coke	1.47	1.04	1.03	0.93
Groups (wt%)				
H ₂ -C ₂ (dry gas)	1.17	2.13	2.31	2.12
C ₃ -C ₄ (LPG)	25.49	30.22	32.34	23.77
C ₂ =-C ₄ = (Light olefins)	18.79	23.22	25.92	19.41
C ₃ =+C ₄ =	17.91	21.79	24.40	18.11
C ₄ = (Butenes)	9.40	10.94	12.56	9.12

increasing mesoporosity. The hierarchical catalysts, particularly NFCC-(HY-ZSM-5), exhibit a significantly lower heavy cycle oil (HCO) yield, indicating improved cracking performance due to improved diffusion and accessibility in the hierarchical pore.

NFCC exhibits the highest propylene yield (HY-ZSM-5), underscoring the mesoporosity benefit in producing lighter, valued olefins. A 27 % and 41% propylene increase is observed for NFCC-HY-Z and NFCC-Y-HZ zeolite compared to NFCC-Y-Z. The enhanced ability of hierarchical catalysts, particularly NFCC-(HY-ZSM-5), to break down VGO into smaller molecules is demonstrated by the increase in butylene and overall light olefin synthesis. A 23% and 38% increase in light olefins is observed for NFCC-HY-Z and NFCC-Y-HZ zeolite compared to NFCC-Y-Z. The increased cracking activity with hierarchical structures does not substantially result in over-cracking or excessive coke generation, as evidenced by the relatively low and comparable dry gas and coke yields across all catalysts. In general, adding hierarchical zeolite enhances catalytic conversion, encourages propylene production, and preserves a balanced selectivity for the manufacture of gasoline without increasing undesirable byproducts like coke and dry gas.

The NFCC-(HY-HZSM-5) catalyst shows the lowest overall conversion (58%) among all the tested catalysts. This decrease in conversion can be attributed to a reduction in acidity or excessive mesoporosity, which likely weakens the acid site density and compromises the catalytic cracking ability. The reduction in acidity, observed during the initial characterization, leads to less efficient VGO cracking.

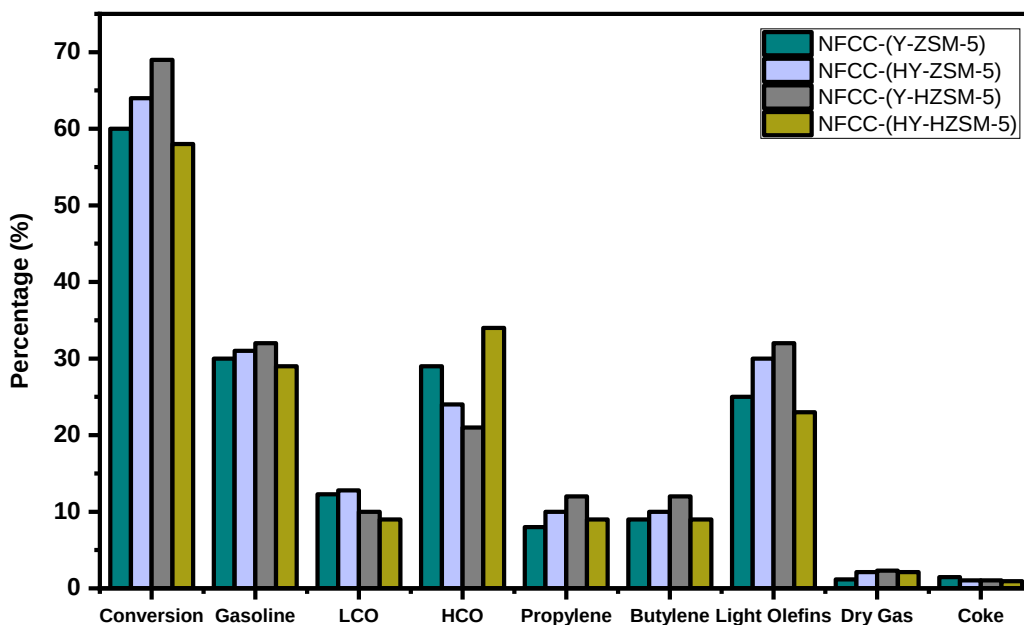


Figure 4.23: The percentage yield of various products from VGO cracking using different FCC catalysts.

LCO (light cycle oil) and HCO (heavy cycle oil) yields are relatively high, especially HCO at 34%, the highest among all catalysts. This suggests that heavier fractions are not fully cracked into lighter, more valuable products — a direct consequence of reduced acid strength and fewer active sites. Light olefin ($C_2=$ - $C_4=$) yield (19.41%) and propylene ($C_3=$) yield (9%) are both lower compared to NFCC-(HY-ZSM-5) and NFCC-(Y-HZSM-5), confirming that the catalyst is less efficient in promoting deep cracking to lighter olefins. While mesoporosity is important for improving accessibility, too much destruction of the microporous network and acid sites leads to incomplete conversion and a shift towards heavier products like LCO and HCO.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The primary objective of this study was to synthesize FCC catalysts using mesoporous Y-zeolite and ZSM-5 to enhance the production of propylene and light olefins. A second major goal was to develop hierarchical structures of Y-zeolite with the aid of computational tools, followed by their characterization and experimental validation. XRD analysis revealed that introducing mesoporosity led to a decrease in peak intensities, without the generation of amorphous material. This reduction was less evident in hierarchical ZSM-5, highlighting the exceptional structural stability of ZSM-5 zeolite. N₂ physisorption measurements demonstrated a decrease in micropore volume with increasing acid concentration for the MY-0.05M, MY-0.1M, and MY-0.15M samples, accompanied by a substantial rise in mesopore volume. Specifically, mesopore volumes of 0.367 cc/g and 0.661 cc/g were recorded for MY-0.1M and MY-0.15M, respectively, compared to only 0.04 cc/g for the parent Na-Y zeolite. In contrast, for ZSM-5, increasing acid concentration did not significantly affect mesoporosity. Therefore, desilication conditions were adjusted, and an increase in mesopore volume was observed with higher base concentrations, confirming that desilication is a more effective method for generating hierarchical ZSM-5 structures. A bimodal pore size distribution was also observed for all modified zeolites, reducing heavy molecules' diffusion limitations in heterogeneous catalysis reactions. All

modified zeolite samples were used to prepare FCC catalysts. The VGO conversion increased from 60% to 69% when using the FCC catalyst containing hierarchical ZSM-5. A noticeable improvement in gasoline yield was also observed with FCC catalysts prepared from modified zeolites. The highest propylene yield, reaching 12 wt%, was achieved with the FCC catalyst based on hierarchical ZSM-5. However, the FCC catalyst prepared with hierarchical Y-zeolite and ZSM-5 exhibited a decrease in overall conversion and increased HCO yield. This performance decline is attributed to reduced catalytic activity and acidity in the combined hierarchical catalyst.

An atomistic structure representing hierarchical Y-zeolite, with tunable pore sizes synthesized in the laboratory, was developed and employed in grand canonical Monte Carlo (GCMC) simulations. This constructed model successfully replicates the experimental adsorption isotherms for nitrogen, closely aligning with the results obtained through the BET technique. The simulated pore size distribution and surface area strongly agree with experimental data, demonstrating the model's reliability. Three atomistic hierarchical models exhibit Gaussian-like pore size distributions with average pore diameters of 23 Å, 32 Å, and 41 Å, closely matching experimental measurements. Both the adsorption capacities and pore volumes obtained from simulations are consistent with experimental results. Furthermore, nitrogen diffusivity was analyzed and found to increase with larger pore sizes, confirming expected trends. While all models accurately reflect the experimental characteristics of the hierarchical Y-zeolite, minor structural aspects still require further refinement based on experimental insights. Nevertheless, these discrepancies do not compromise the overall accuracy of describing the pore architecture of the micro-mesoporous Y-zeolite. Importantly, the methodology presented in this study

covers the way for the reasonable design of a wide range of micro-mesoporous molecular structures by systematically integrating different zeolite frameworks and mesoporous domains within a single unit cell. Ongoing research in our laboratory aims to advance this promising approach further.

5.2 Recommendations

The following are recommended for future work:

- Use of different synthesis methods for mesoporosity generation other than post-treatment of Y-zeolite, such as templating methods adopting a bottom-up approach, because of the retention of micropore volume as well as acidity of zeolites.
- Preparation of FCC Catalyst using spray dryer to achieve a suitable pellet size (50 – 90 μm) to assess the performance close to commercial conditions.
- Bio-based templates are used to generate mesoporosity in zeolites to ensure sustainability.
- Utilizing atomistic hierarchical Y-zeolite structures for the adsorption of heavy hydrocarbons. Their potential in advanced adsorption and catalytic applications will be further explored and optimized.

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