

**THE AROMATIZATION OF LIGHT NAPHTHA
VIA MODIFIED FIBROUS SILICA ZSM5 WITH
GALLIUM AND ZINC**

BY

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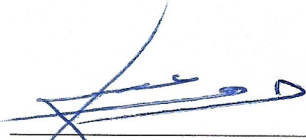
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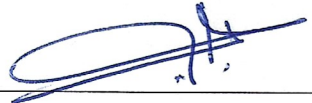
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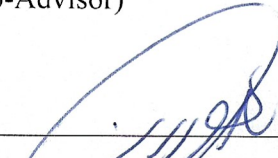

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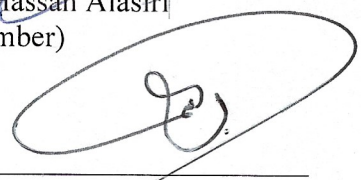
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This thesis is dedicated to my beloved family, whose unwavering support and encouragement have been the foundation of my journey.

To my mentors and professors, whose guidance and wisdom have profoundly shaped my academic and professional growth.

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LIST OF ABBREVIATIONS

LSR	:	Light Straight Run Naphtha.
ZSM-5	:	Zeolite Socony Mobil Five
WHSV	:	Weight Hour Space Velocity
BTX	:	Benzene, Toluene, Xylene
XRD	:	X-Ray Diffraction.
BET	:	Brunauer-Emmett-Teller
BJH	:	Barrett Joyner Halenda
SEM	:	Transmission Electron Microscopy
TEM	:	Scanning Electron Microscopy
TPD	:	Temperature Programmed Desorption
PIONA	:	Paraffin, Iso paraffins, Olefins, Naphthenes, Aromatics
DHA GC	:	Detailed Hydrocarbons Analysis Gas Chromatograph
FID	:	Flame Ionization Detector
MFI	:	Mordenite framework inverted
DI	:	Deionized
TEOS	:	Tetraethyl orthosilicate

ABSTRACT

Full Name : RASHEED HAMID MOHMMMAED IBRAHIM
Thesis Title : [The aromatization of light naphtha via modified fibrous silica ZSM5 with Gallium and Zinc]
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Light naphtha aromatization has garnered increasing interest in the petrochemical industry as a means to upgrade low-value streams into valuable aromatic hydrocarbons, offering economic and environmental advantages. In this research, two types of zeolite catalysts were synthesized and evaluated: nano-sized ZSM-11 (NZ11) with varying silica-to-alumina ratios (35 and 70) prepared via hydrothermal synthesis, and fibrous silica ZSM-5 (FSZSM-5) synthesized using microwave-assisted methods. Both catalysts were modified with gallium (Ga) and zinc (Zn) through incipient wetness impregnation. Comprehensive characterization was conducted using XRD, BET, SEM, TEM, and NH₃-TPD. The NZ11(70) catalyst exhibited higher crystallinity and a more uniform particle size distribution, while FSZSM-5 demonstrated enhanced surface area and crystallinity with larger, uniformly sized particles. Catalytic performance was assessed in the aromatization of light naphtha using a micro-scale continuous-flow fixed-bed reactor operated at 550 °C and atmospheric pressure, with weight hourly space velocities (WHSV) of 1 h⁻¹ for NZ11 catalysts and 2 h⁻¹ for FSZSM-5 catalysts. All catalysts achieved high naphtha conversions ranging from 97% to 99%. The unmodified NZ11(70) catalyst yielded 40.7% aromatics, which increased to 77.8% upon modification with gallium. Similarly, the unmodified FSZSM-5 catalyst produced 35.9% aromatics, with gallium modification enhancing the

BTX (benzene, toluene, and xylene) yield to 53.2%. The superior performance of Ga-modified NZ11(70) and FSZSM-5 catalysts was attributed to their structural properties, which provided increased surface area and shortened diffusion paths, facilitating better access to active sites and improved mass transfer. The incorporation of gallium introduced additional dehydrogenation sites, promoting the conversion of alkanes to olefins key intermediates in aromatization. The highly interconnected pore structures of the catalysts facilitated selective adsorption and reaction of hydrocarbons while minimizing undesirable side reactions.

ملخص الرسالة

الاسم الكامل: رشيد حامد محمد ابراهيم

عنوان الرسالة: عملية تحويل النفط الخفيفة الى المركبات الهيدروكربونات العطرية باستخدام ZSM-5 السيليكا الليفية المعدلة بالغاليوم والزنك

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أثارت عملية تحويل النفط الخفيفة الى المركبات الهيدروكربونات العطرية اهتمامًا متزايدًا في صناعة البتروكيماويات كوسيلة لترقية التيارات منخفضة القيمة إلى هيدروكربونات عطرية قيمة، مما يقدم مزايا اقتصادية وبيئية. في هذا البحث، تم تخليق وتقييم نوعين من محفزات الزيوليت ZSM-11: النانوي (NZ11) بنسب مختلفة من السيليكا إلى الألومينا (35 و 70) تم تحضيرها عبر التخليق الحراري المائي، و ZSM-5 السيليكا الليفية (FSZSM-5) التي تم تخليقها باستخدام طرق بمساعدة الميكروويف. تم تعديل كلا المحفزين بالغاليوم (Ga) والزنك (Zn) من خلال تشريب الرطوبة الابتدائية. تم إجراء توصيف شامل باستخدام حيود الأشعة السينية (XRD)، والمجهر الإلكتروني الماسح (SEM)، والمجهر الإلكتروني النافذ (TEM)، وتحليل مساحة السطح باستخدام طريقة برونور-إيميت-تيلر (BET)، وامتصاص الأمونيا المبرمج حراريًا (NH₃-TPD). أظهر المحفز (NZ11(70) بلورية أعلى وتوزيعًا أكثر انتظامًا لحجم الجسيمات، بينما أظهر FSZSM-5 زيادة في مساحة السطح والبلورية مع جزيئات أكبر ومتساوية الحجم. تم تقييم الأداء التحفيزي في عملية أرومة النفط الخفيفة باستخدام مفاعل سرير ثابت بتدفق مستمر على المقياس الميكروي يعمل عند 550 درجة مئوية وضغط جوي، مع سرعات فراغية وزنية (WHSV) تبلغ 1 ساعة⁻¹ لمحفزات NZ11 و 2 ساعة⁻¹ لمحفزات FSZSM-5. حققت جميع المحفزات تحويلات نفثا عالية تتراوح بين 97% إلى 99%. أنتج المحفز (NZ11(70) غير المعدل 40.7% من المواد العطرية، والتي زادت إلى 77% عند التعديل بالغاليوم. وبالمثل، أنتج المحفز FSZSM-5 غير المعدل 35.9% من المواد العطرية، مع تعزيز تعديل الغاليوم لإنتاج BTX (البنزين، التولوين، والزيلين) إلى 53.2%. نُسب الأداء المتفوق لمحفزات (NZ11(70) و FSZSM-5 المعدلة بالغاليوم إلى خصائصها الهيكلية، التي وفرت زيادة في مساحة السطح وتقليل مسارات الانتشار، مما سهل الوصول الأفضل إلى المواقع النشطة وتحسين نقل الكتلة. أدخل تضمين الغاليوم مواقع إضافية لنزع الهيدروجين، مما يعزز تحويل الألكانات إلى أوليفينات وهي وسيطة رئيسية في الأرومة. سهلت الهياكل المسامية المترابطة بشكل كبير للمحفزات الامتزاز الانتقائي وتفاعل الهيدروكربونات مع تقليل التفاعلات الجانبية غير المرغوب فيها مثل تكوين الكربون. أدى التأزر بين أنواع الغاليوم والمواقع الحمضية للزيوليتات إلى تحقيق كفاءة تحويل عالية وانتقائية نحو الهيدروكربونات العطرية.

CHAPTER 1

INTRODUCTION

1.1. Background

The increasing need for high-performance fuels and enforcing stringent environmental standards drive the need to improve gasoline to achieve higher octane ratings. Enhancing engine efficiency and minimizing emissions is paramount [1–3]. There has been an increasing focus on converting light straight run naphtha (LSRN) to aromatics benzene, toluene, xylenes (BTX) to tackle these challenges such as undesirable gasoline blending component, low octane number, and high vapor pressure. The LSRN is a feedstock derived from the refinery process of crude oil and mainly contains C_5 to C_6 hydrocarbons, including paraffin, naphthene, and a minor quantity of aromatics with a boiling range of 35–93 °C[4–6]. Utilizing catalytic reforming of naphtha to increase its aromatic content is a viable method for meeting stricter fuel regulations. Converting LSRN results in aromatic production that greatly enhances the octane rating of gasoline, hence enhancing the quality of combustion and ensure adherence to more stringent fuel quality rules. Recent gasoline regulations have introduced stricter limits on olefin concentrations, alongside established sulfur standards, due to olefins tendency to form carbon particulates during combustion, contributing to the formation of harmful particulate matter PM 2.5 [1,7]. At the same time, the conversion of naphtha to aromatics has become increasingly vital, as these products serve as essential feedstocks in the petrochemical industry, supporting the production of high-demand materials and chemicals. This dual focus on cleaner

fuel and efficient naphtha conversion underscores the growing importance of both processes in addressing environmental concerns while meeting industrial needs [4–6,8]. The first successful dehydrocyclodimerization of light naphtha into BTX was carried out by Csicsery in the year 1970[9,10]. This process was known at the time as dehydrocyclodimerization, it refers to the process of converting hydrocarbons with less than six carbon atoms into aromatic compounds involves a series of steps including dehydrogenation, oligomerization, and cyclization [11], as illustrated in **Figure 1**. The process of dehydrocyclodimerization requires the utilization of both high temperatures and bimetallic zeolite catalysts to be successful. On the other hand, Csicsery's catalytic process showed benefits over catalytic reforming in terms of converting a bigger percentage of paraffins into aromatics There are seven different kinds of reactions that occur during the process of catalytic reforming include dehydrogenation, isomerization, hydrocracking, cyclization, hydrogenolysis, aromatization, and coke formation, clearly represented by **Figure 2** [12].

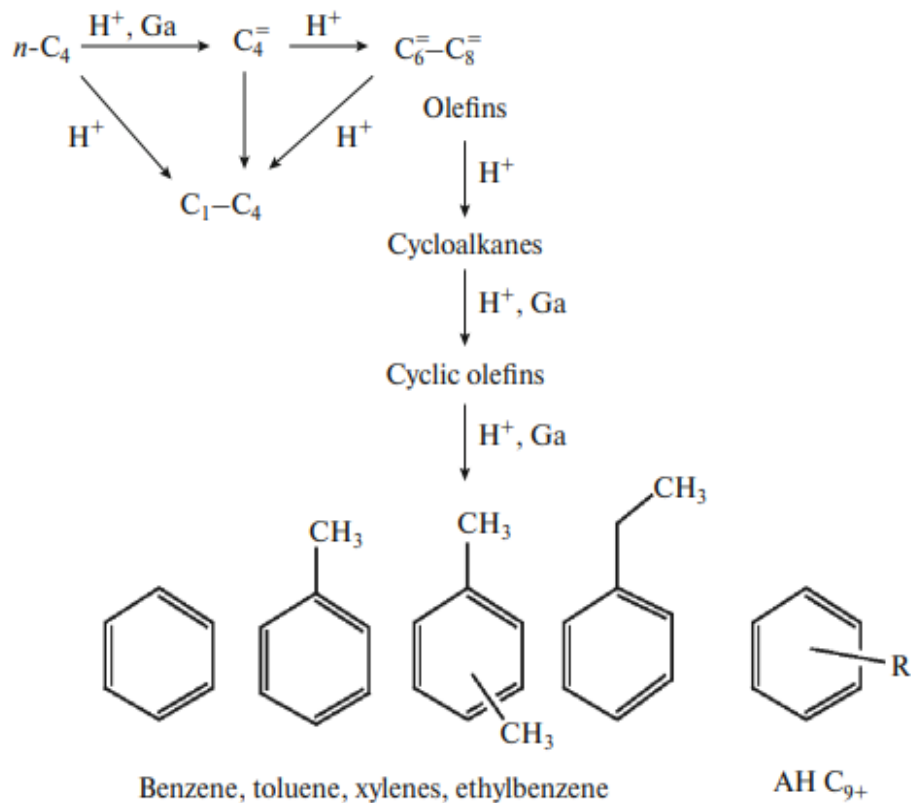


Figure 1 : The dehydrocyclocondimerization reaction[11]

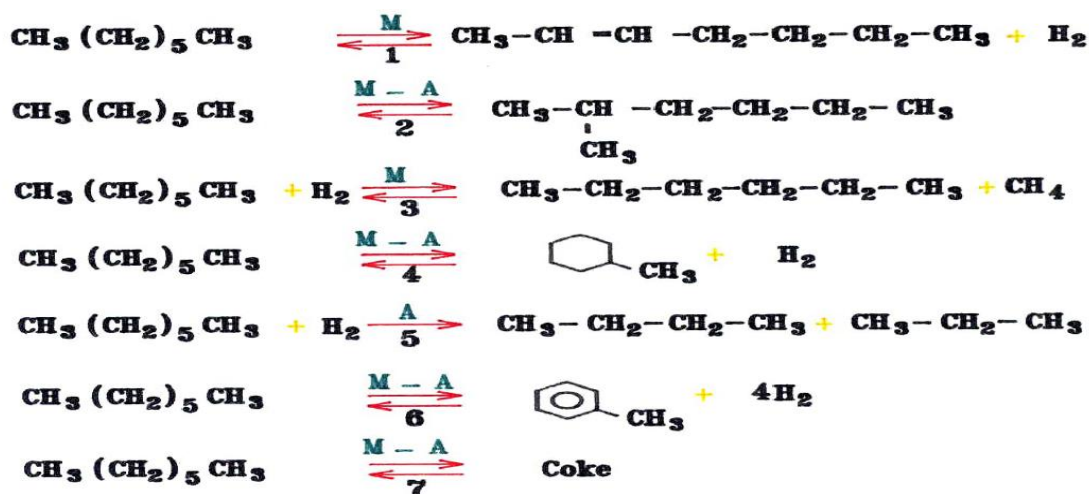


Figure 2: illustrates a typical set of reactions that occur in the Catalytic Reforming Process [12].

Aromatics, especially BTX, are essential feedstocks for producing polymers, resins, films, pharmaceuticals, and high-quality chemicals. This emphasizes their crucial significance in many industrial applications [13]. Due to the growing demand for these substances, the chemical engineering industry focuses on converting light naphtha into BTX aromatics. This advancement attracts interest from the business industry sector and academia[14]. In 2021, the global consumption of BTX aromatics exceeded 130 million metric tons. Benzene and *para*-xylene accounted for 50 million metric tons, while toluene comprised 30 million metric tons [6]. To fulfill this criterion, refineries must use the normal naphtha reforming process. This procedure involves subjecting middle naphtha with relatively low octane ratings ranging from 35 to 50 to elevated temperatures ranging from 450 to 480 °C. This approach meets the increasing need for BTX aromatics, while producing high-octane gasoline with ratings ranging from 70 to above 100. It does this by exerting hydrogen pressures ranging from 5 to 45 atm. Furthermore, it incorporates the whole supply chain, beginning with the processing of raw materials and concluding with the production of the end product [15,16].

The catalytic aromatization process encompasses many essential activities, including cracking, dehydrocyclization, dehydrogenation, and isomerization. These reactions are facilitated by bifunctional catalysts[17]. The process starts with the dehydrocyclization of paraffin, essential for augmenting the aromatic component of fuels. Furthermore, alkyl cyclopentanes undergo conversion into cyclohexane, which is further subjected to dehydrogenation to produce aromatics. This process leads to an elevated concentration of aromatic compounds. Simultaneously, linear paraffins undergo isomerization, a process that transforms them into *iso*-paraffins, enhancing the fuel's combustion properties. In addition, the process of cracking paraffin and naphthene molecules results in the conversion of larger molecules into smaller,

more valuable ones, hence enhancing refining efficiency. The catalysts have metallic and acidic sites, each performing distinct roles in the chemical processes. The metallic function, often embodied by a noble metal, provides essential active sites for hydrogenation-dehydrogenation reactions. Conversely, the acidic properties of solid support materials such as alumina facilitate isomerization and cracking processes. The outcome of these reactions is contingent upon the precise acidity level of the substrate [18,19]. The dual functionality of catalysts enhances the efficiency of the reforming process. This enables a meticulous equilibrium of chemical pathways that optimize the generation and caliber of the resultant hydrocarbons. Over the years, catalysts have evolved to include more configurations, such as bi-metallic and tri-metallic supported catalysts. These designs are exceptionally engineered to enhance the catalytic activity and selectivity required for specific hydrocarbon conversions. The advancements in catalyst design not only improve the efficacy of converting substances and the ability to generate desired products but also significantly contribute to the refining process's long-term sustainability and economic viability.

Catalysts such as Pt–Re–Al₂O₃, Pt–Sn–Al₂O₃, and Pt–Cl–Al₂O₃ are employed to optimize the synthesis of aromatic compounds, specifically BTX, achieving yields of up to 70 wt.% under specific reaction conditions [20,21]. Despite their significant effectiveness, these catalysts have the disadvantage of being expensive due to using precious metals. Due to economic constraints, the sector has seen improvements like Mobil's M2-Forming process. This procedure employs an parent H-ZSM-5 to transform light alkanes into BTX [22,23]. Unfortunately, the unmodified H-ZSM-5 deactivates quickly and has significant cracking activity, resulting in a high selectivity for C₁ and C₂ chemicals. Nevertheless, the issue may be resolved by using activating agents, namely transition metals like Cu, Cr, Mo, Pt, Ni, Zn and Ga [24,25]. This approach aligns

with the prevailing patterns where the transformation of hydrocarbon streams with low value into BTX aromatics is accomplished through different established methods, such as BP and UOP's Cyclar, Chevron's Aromax for C₆-C₈ hydrocarbons, GTC's process for C₄-C₈ hydrocarbons, and Asahikasei's Alpha process for C₄-C₆ streams[26,27]. These procedures include using zeolites such as ZSM-5, Beta, Y, and Mordenite. **Figure 4.** depicts the downstream products derived from three major aromatic hydrocarbons: benzene, toluene, and xylenes (BTX). Each compound serves as a precursor for various industrial chemicals and materials. This chart illustrates the crucial role of BTX aromatics in the chemical industry, underpinning the production of plastics, synthetic fibers, resins, and a range of specialized chemicals essential for modern applications.

Figure 3 illustrates the energy contributions (in PJ) of various chemical products Biomethane, BTX, Methanol, Hydrogen, and Ethylene across low, medium, and high scenarios for 2020 and 2030. BTX, represented by the red segment, shows a minor contribution in 2020 across all scenarios, with Biomethane dominating the energy share. However, BTX's contribution grows significantly by 2030, particularly in the "Medium" and "High" scenarios, where its share becomes more noticeable, though still secondary to Biomethane. This trend highlights the increasing importance of BTX in future energy production strategies as demand rises under higher production scenarios.

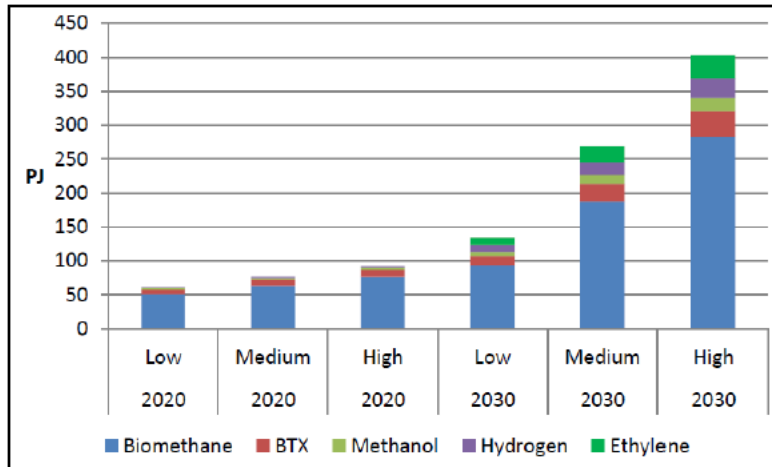


Figure 3: Expected petrochemicals growth for 2020 and 2030 aromatics (BTX).

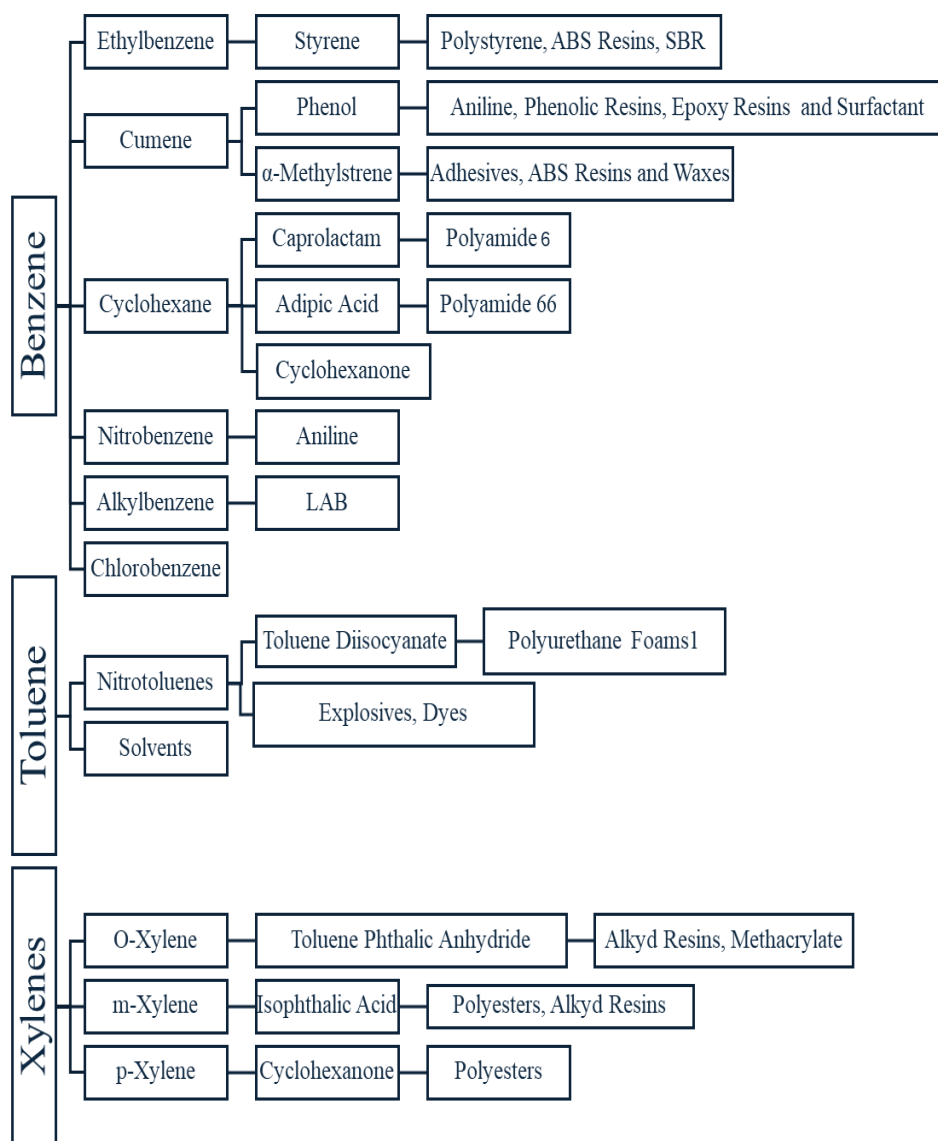


Figure 4: Chemicals product from BTX [28]

1.2.Catalyst:

The use of a catalyst is one of the most critical challenges that must be overcome in order for C1-C6 aromatization technology to be successfully commercialized. ZSM-5, Y, mordenite, and beta zeolite are some of the several types of catalysts that are currently being researched.[29]

1.2.1. Zeolites

Acidic sites are necessary for the catalysis of the aromatization process[30]. Zeolites represent a very accessible category of solid acidic substances. Zeolites are materials composed of aluminosilicates that exhibit a high degree of structural order and possess a microporous nature. The primary advantage of microporosity is in its ability to hinder the formation of large polyaromatic molecules. In an ideal catalyst, monoaromatics would be able to traverse the pores, whereas the formation of bigger compounds would be impeded by limitations in size [31].

These zeolites are highly regarded for their acidity, thermal stability, unique structures, and ability to synthesize certain compounds [33–35]. These zeolites are highly regarded for their acidity, thermal stability, unique structures, and ability to synthesize certain compounds [33–35]. ZSM-11 stands out among these choices due to its two-dimensional intersecting straight channels, The straight, two-dimensional channels in ZSM-11 presented significant advantages over ZSM-5 zeolites with sinusoidal channels. These linear pathways facilitated easier and faster diffusion of molecules, reducing diffusion resistance and enhancing reaction kinetics[36]. This structural feature minimized obstacles for reactant and product molecules, leading to improved access to active catalytic sites and better mass transfer. Additionally, the straight channels diminished the likelihood of heavy hydrocarbon accumulation and coke formation, thereby prolonging catalyst life and maintaining activity over extended periods [37]. The uniform pore structure favored the formation of desired products by providing consistent reaction environments, which reduces side reactions and enhanced selectivity These characteristics made ZSM-11 a robust and efficient catalyst suitable for various industrial applications, where performance and longevity were essential, which make it very appropriate

for aromatization. The effectiveness of ZSM-11 is improved by adding metals to its structure, which increases selectivity by aligning the zeolite's acidic cracking events with the dehydrogenation processes at the metal sites. The presence of these metal sites is crucial to produce olefin intermediates, which play a vital role in a variety of complex processes such as cracking, isomerization, or cyclization. These reactions eventually lead to the production of profitable BTX aromatic compounds [38,39].

The ZSM-5 (MFI) catalyst is highly effective in the process of aromatization due to its adjustable acid strength, distinctive pore structure, and acid distribution. ZSM-5 exhibits excellent selectivity towards BTX due to their unique properties such as high thermal stability, large surface area, strong acidity, and shape-selectivity. MFI zeolites are widely used as solid acid catalysts in refining and petrochemical industries. ZSM-5 is a commercially accessible zeolite characterized by its narrow pore size. The structural composition of ZSM-5 includes pores that are characterized by a 10-membered ring, with a diameter of around 5.6 Å. The diameter in question is deemed adequate for the synthesis of monoaromatic compounds, as it strikes a balance between being wide enough to facilitate their creation and small enough to impede the development of polyaromatic compounds [46].

ZSM-11(MEL) stands out among these choices due to its two-dimensional intersecting straight channels. The straight, two-dimensional channels in ZSM-11 presented significant advantages over ZSM-5 zeolites with sinusoidal channels. These linear pathways facilitated easier and faster diffusion of molecules, reducing diffusion resistance and enhancing reaction kinetics[36]. This structural feature minimized obstacles for reactant and product molecules, leading to improved access to active catalytic sites and better mass transfer. Additionally, the straight channels diminished the likelihood of heavy hydrocarbon accumulation and coke

formation, thereby prolonging catalyst life and maintaining activity over extended periods [37]. The uniform pore structure favored the formation of desired products by providing consistent reaction environments, which reduces side reactions and enhanced selectivity. These characteristics made ZSM-11 a robust and efficient catalyst suitable for various industrial applications, where performance and longevity were essential, which make it very appropriate for aromatization. The effectiveness of ZSM-11 is improved by adding metals to its structure, which increases selectivity by aligning the zeolite's acidic cracking events with the dehydrogenation processes at the metal sites. The presence of these metal sites is crucial to produce olefin intermediates, which play a vital role in a variety of complex processes such as cracking, isomerization, or cyclization. These reactions eventually lead to the production of profitable BTX aromatic compounds [38,39]. The aromatization process starts by generating alkenes by the cleavage of C-H and/or C-C bonds, subsequently accompanied by the transfer of hydride ions. This establishes the foundation for subsequent events, including oligomerization, cracking, activation of alkanes/alkenes, isomerization, and cyclization [35,40–42]. The process takes place on zeolites where Brønsted acid sites facilitate the first phases of olefin cracking and cyclization. Dehydrogenation and further aromatization processes, including hydrogen transfer, take place on Lewis acid sites [29,43–45].

Both MFI (ZSM-5) and MEL (ZSM-11) zeolites belong to the pentasil family. Their crystal structures are built from doubled secondary building units called SBU 5-1 (**Figure 5**), which assemble into linear chains. In MFI zeolites, these linear chains form layers. In contrast, MEL zeolites form layers via four- and six-membered rings. [47]

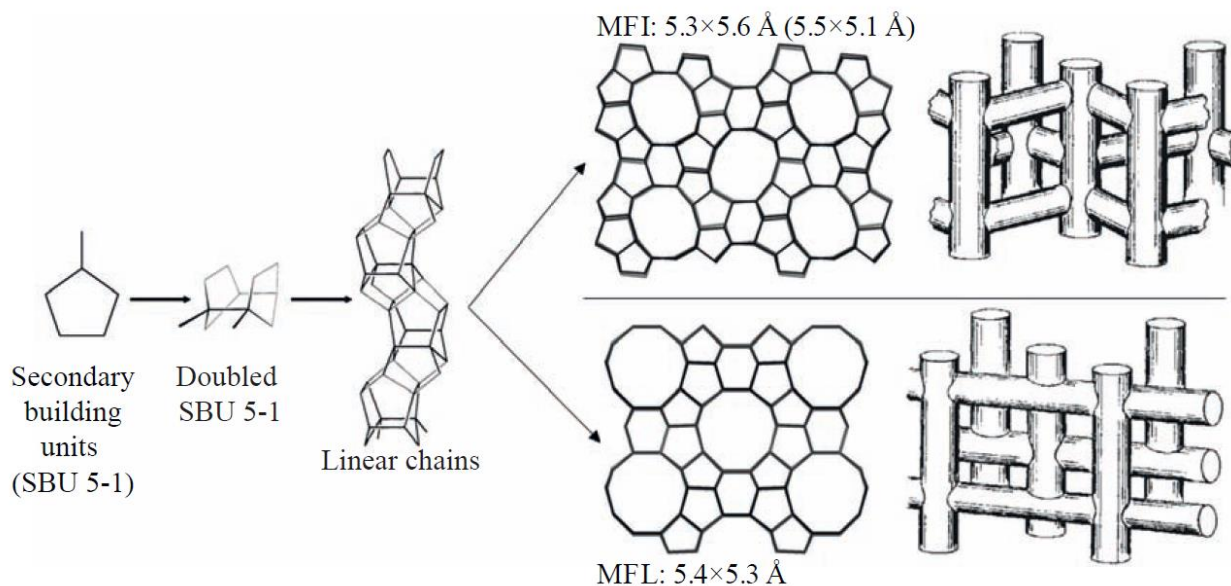


Figure 5: MFI and MEL structures formation from secondary building units 5-1.[47]

1.2.2 Metal loading

The presence of dehydrogenating sites, in addition to acidic sites, positively impacts the catalyst's ability to aromatize naphtha. These sites can be developed by incorporating metals such as Platinum, Zinc, and Gallium[30]. Metals can be incorporated into a system through various techniques, including ion exchange, chemical layer deposition, and wet impregnation[48,49].

1.3 Mechanism

The aromatization process starts by generating alkenes by the cleavage of C-H and/or C-C bonds, subsequently accompanied by the transfer of hydride ions. This establishes the foundation for subsequent events, including oligomerization, cracking, activation of alkanes/alkenes, isomerization, and cyclization [35,40–42]. The process takes place on zeolites where Brønsted acid sites facilitate the first phases of olefin cracking and cyclization. Dehydrogenation and subsequent aromatization reactions occur at Lewis site [29,43–45]. The aromatization process on H-ZSM-5 catalysts, often promoted with metal, proceeds in three distinct steps, as shown in **Figure**

6. The initial stage comprises the conversion of alkane via two primary pathways: cracking and hydrogen transfer, the latter frequently referred to as dehydrogenation. The hydrogen transfer mechanism involves a chemical interaction between alkanes and the resulting alkenes, which are subsequently adsorbed onto the acid sites of the zeolites.

This interconversion process encompasses multiple phases, including isomerization, oligomerization, and cracking. During the final stage, the aromatization of alkenes is achieved, primarily facilitated by H-ZSM-5, involving cyclization and dehydrogenation to form aromatic compounds [51].

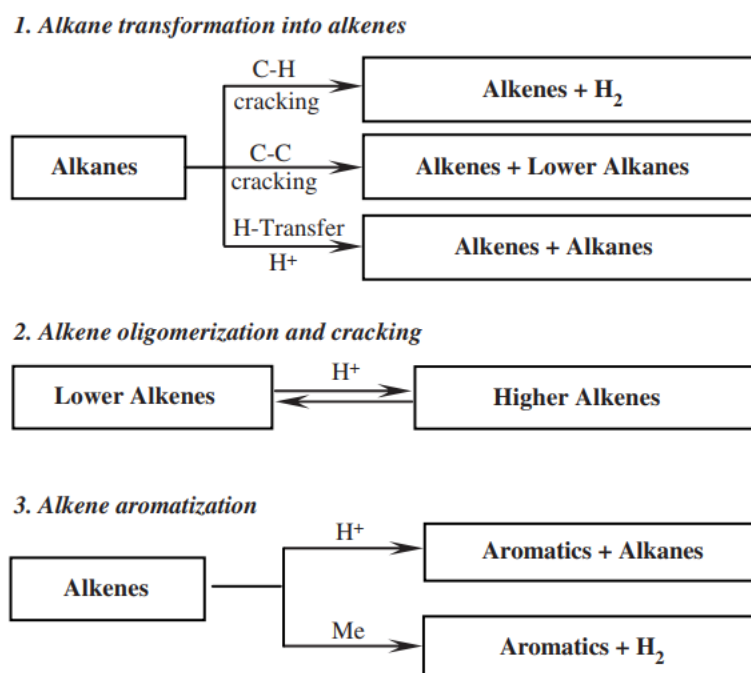


Figure 6: Mechanism of alkane aromatization on H-ZSM-5 catalysts promoted with metal.

1.4. Thesis Scope

In the second chapter, a comprehensive literature review is presented, focusing on the aromatization process. This review provides valuable insights and background information on the catalysts and various additives employed in enhancing the process. It discusses previous studies

and advancements in the field, offering a foundation for understanding the mechanisms and optimization strategies associated with light naphtha aromatization.

The third chapter delves into the specifics of the feedstock used in this study for the aromatization reaction. It provides a detailed overview of its composition and suitability for the process. Furthermore, the chapter outlines the catalysts employed in this research, detailing their synthesis steps, including both the support materials and metal-supported catalysts prepared using the wetness impregnation method. Additionally, the chapter highlights the characterization techniques utilized in this study, such as those commonly referenced in the literature, to evaluate catalyst properties and performance.

The fourth chapter focuses on the evaluation of catalytic performance in the aromatization of light naphtha. This assessment was carried out using a micro-scale continuous-flow fixed-bed reactor operated under precise conditions: a temperature of 550 °C, atmospheric pressure, and weight hourly space velocities (WHSV) of 1 h⁻¹ for NZ11 catalysts and 2 h⁻¹ for FSZSM-5 catalysts. Alongside the performance testing, extensive characterization of the catalysts was conducted using advanced analytical techniques, including X-ray diffraction (XRD) for structural analysis, Brunauer-Emmett-Teller (BET) for surface area and porosity measurement, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for morphological evaluation, and Ammonia Temperature-Programmed Desorption (NH₃-TPD) for acidity profiling. These analyses provide a comprehensive understanding of the catalysts' structural and functional properties, contributing to the interpretation of their performance in the aromatization reaction

CHAPTER 2

LITERATURE REVIEW

There are numerous variables that influence the efficiency of aromatization catalysts, including acidity, catalyst pore shape, and the distribution of metals on the support. Numerous studies have been conducted to examine the impact of various metals on zeolites, in particular H-ZSM-5 on aromatization performances, which receive a lot of attention due to the extraordinary qualities that they possessed. Notably, the use of H-ZSM-5 (MFI) helps to decrease coke formation and assures the activity will continue for a long time. Many researchers showed that Ga and Zn are considered the effective metals for naphtha aromatization.

2.1 Aromatization over ZSM-5 & ZSM-11 based catalyst:

Ellouh et al. investigated ZSM-5 synthesis combining Platinum with several modifying elements (Zn, Fe, La, and Ga) using a wet co-impregnation approach. The catalyst was synthesized by incorporating these elements into ZSM-5 [Si/Al=30]. The research investigated the light paraffinic naphtha into aromatization. They observed that Pt-Ga/ZSM-5 catalyst had a selectivity of 60 wt% towards total aromatics. Furthermore, they studied delved into the short-term stability (over 24 hours) of the most effective catalyst identified, Pt-Ga/ZSM-5[29].

In a notable study, Ummer A C et al explored the application of desilication on the H-ZSM-5 support. This approach was primarily aimed at generating an increased meso-porosity. Moreover, the active metal, Gallium, was incorporated into the process through the wetness impregnation method, which is gaining traction as an effective incorporation technique. The modified catalyst had selectivity to BTX around 62.4%. [26].

Ziyouddin S. Qureshi¹ et al. examined Light paraffinic naphtha's aromatization using the modified Mo–M/MFI catalysts (where M represents Fe, Ce, Pt, Ga, and Zn) using the wet co impregnation technique. These experiments were conducted under specific conditions, including 1 atm, 550 °C, and a WHSV of 0.81 h⁻¹. In comparison with the base MFI catalyst, the modified bimetallic versions, especially Mo–Ga/MFI and Mo–Zn/MFI, showcased a superior catalytic performance. Impressively, these bimetallic catalysts achieved a commendable selectivity of 62 wt% towards BTEX compounds, which comprise benzene, toluene, ethylbenzene, and xylenes. Additionally, the production of C₉+ aromatics ranged between 5.4 to 0.6 wt%, with the toluene to benzene ratios recorded at 0.5 and 0.6 respectively for the two catalysts[52].

Tshabalala et al explored n-Hexane aromatization over H-ZSM-5 either unmodified or modified with metals like gallium (Ga), molybdenum (Mo), and zinc (Zn). Conversion reached as high as 88% over the parent H-ZSM-5 catalyst and remained stable. However, modified catalysts conversion of under 80%. The Zn/H-ZSM-5 and Ga/H-ZSM-5 catalyst selectivity to aromatic around 40% and 35%. During TOS experiment, it was noticed that when temperature was raised to 600 degrees Celsius. At the same time, there was a reduction in the degree of selectivity towards aromatic products. [53].

Ying Shi et al investigated the impact of alkali metals on n-heptane aromatization. They utilized hierarchical Pt/Beta-Me catalysts for their investigation. The researchers conducted a study where they modified Beta zeolite using ion-exchange with (Li, Na, K, and Rb). They then utilized these modified zeolites in aromatization of n-heptane. The use of this method effectively prevents carbonaceous deposition and cracking reactions. Additionally, it promotes the dehydroaromatization of alkanes, leading to improved catalytic stability and selectivity for

aromatization in Pt/Beta-Me. The Pt/Beta-Rb catalyst demonstrating a 78.2% selectivity among other promoters [54].

Dan Xu et al. conducted a study on n-heptane aromatization. The Pt/KL catalysts exhibited excellent performance in converting n-heptane into aromatics, demonstrating a remarkable selectivity of toluene 67.3% and selectivity CH₄ 0.9%. This impressive performance was achieved despite the catalyst containing an extremely low Pt loading of just 0.21 wt%. The strong interaction between platinum (Pt) and KL showed high stability[55].

Jarvis et al. conducted a study on the transformation of LSRN and CH₄ to aromatic. Researchers have reported that a Pt-Zn/HZSM-5 catalyst can effectively minimize cracking and enhance the BTX production when converting naphtha into aromatics in the presence of methane. When the Pt-Zn combination is used in conjunction with HZSM-5, it can achieve a of 94.4% selectivity of BTX. The excellent performance of this performance can be attributed to the proper distribution of acid sites and the ability of Zn to reduce coke formation. The use of a combination of Pt and Zn resulted in a 22.4% increase in the yield of BTX, compared to incorporating alone Pt (yield of 13.1%) or Zn (yield of 13.4%)[4].

Akhtar et al. conducted a study on converting n-hexane into aromatic compounds using a catalyst termed Pt-loaded mesoporous HZSM-11, which was further improved by adding gallium. This catalyst was explicitly engineered to regulate the meso-porosity by desilication, reducing the necessary contact time for reactions by enhancing the accessibility of supplementary Ga species located outside the framework. Consequently, Pt/mesoporous GaZSM-11 substantially enhanced selectivity and conversion [56]. Zhang L et al. conducted a study on converting 1-hexene into aromatics using ZSM-11, The C₇ and C₈ aromatics are produced easily from ZSM-11 zeolite

compared to ZSM-5 zeolite, attributed to the straight channel structure of ZSM-11[57]. Furthermore, Anunziata et al. did research to investigate the influence of zinc and gallium modifications on the aromatization of 1-hexene and 1-pentene using H-ZSM-11. They observed that the unmodified ZSM-11 exhibited a conversion efficiency of 99.5% and a BTX yield of 50% when 1-hexene was used as the feedstock. Zinc (H-Zn-ZSM-11) led to a substantial increase in BTX production, reaching 62%. By contrast, the addition of gallium (H-Ga-ZSM-11) led to a yield of 57% aromatics, demonstrating the efficacy of zinc as a catalyst in the aromatization process. The trials with 1-pentene showed that the Zn-modified ZSM-11 showed much superior performance compared to the unmodified. This led to a BTX yield of 54.8% for the Zn-modified ZSM-11, whereas the unmodified variation only achieved a yield of 28.5% [58]. This research emphasizes the critical need for altering catalysts to optimize the efficiency of generating aromatic chemicals.

Although ZSM-11-based catalysts are valued for their unique pore structures and acidity, they have faced several limitations, including diffusion constraints due to their purely microporous architecture, rapid deactivation from coke deposition during hydrocarbon processing, limited hydrothermal stability under harsh conditions, challenges in precise acidity control, and difficulties in achieving high selectivity for desired products. To address these issues, we synthesized nano ZSM-11 catalysts with hierarchical pore structures by introducing mesopores alongside the inherent micropores, enhancing the diffusion of larger molecules and improving catalytic activity and selectivity for bulkier reactants. Metal ions such as gallium or zinc were incorporated into the nano ZSM-11 framework to modify the electronic and acidic properties, which reduced coke formation and enhanced resistance to deactivation. A novel synthesis method was developed to improve hydrothermal stability, optimizing synthesis parameters and post-synthesis treatments to

maintain structural integrity under severe reaction conditions. Acidity was fine-tuned through controlled incorporation of aluminum and strategic placement of acid sites, allowing for better performance in reactions requiring specific acidity levels. Additionally, active sites and pore environments were tailored to favor reaction pathways, achieving higher selectivity toward desired products while minimizing side reactions. These advanced synthesis techniques and structural modifications effectively overcame the inherent limitations of traditional ZSM-11 catalysts, resulting in catalysts with superior performance for targeted catalytic applications.

2.2 Fibrous Silica ZSM-5 (FSZM-5) applications:

Fibrous silica ZSM-5 is a zeolite material that possesses a distinctive fibrous structure. It possesses the characteristics of both silica and ZSM-5, which is a widely recognized zeolite known for its large surface area and high acidity. The combination of factors present in FSZM-5 makes it a highly promising material for a wide range of applications.

Hambali et al conducted an investigation on the process of methane dry reforming. A unique catalyst consisting of fibrous spherical ZSM-5 supported by nickel has been produced utilizing the microemulsion process. The ZSM-5 support has been modified with several promoters, including Ca, Ta, Ga, and Mg. This catalyst has been developed specifically for methane dry reforming. The distinctive configuration of the structure aids in the containment of Ni particles, hence enhancing catalytic performance via the mitigation of coke deposition. The bimetallic nickel-tantalum catalyst exhibited the most significant methane (CH_4) and carbon dioxide (CO_2) conversion rates, reaching 93% and 98% respectively. The acid sites presence and the synergistic effect of bimetallic Ni-Ta catalyst components contribute to an enhanced interaction, which effectively inhibits coke deposition and metal sintering. The catalyst known as Ni-Ta/FZSM-5 exhibits sustained activity over an extended period when subjected to a temperature of 800°C [59].

Firmansyah et al investigated the hydrocracking of cumene utilizing fibrous silica ZSM-5 (FZSM-5) that was synthesized by microemulsion. The FZSM-5 catalyst in its spherical form has notable characteristics, including a substantial surface area of 554 m²/g, a large pore diameter, a significant number of acid sites, and a pronounced catalytic activity in the process of cumene hydrocracking. The product distribution resulting from cumene hydrocracking exhibits an equal proportion of propylene and benzene, with particle sizes ranging from 2 to 20 nm. At a temperature of 573 K, the Pt/HFZSM-5 catalyst demonstrated a yield of 89.5%. In comparison, the other catalysts, namely FZSM-5, HZSM-5, HFZSM-5, and Pt/HZSM-5, exhibited yields of 12.1%, 79.8%, 69.8%, and 65.8% respectively. The Pt/HFZSM-5 catalyst exhibited notable catalytic stability, with a conversion rate of 88% being sustained over the course of 100 cumene doses. In contrast, the Pt/HZSM-5 catalyst had a decline in conversion rate of 15% under the same conditions, which may be attributed to a comparatively lower level of coke deposition. The use of dendrimeric silica fiber resulted in an augmentation of both the overall quantity and effectiveness of acid sites, hence resulting in a boost in catalytic activity.[60].

Hambali et al studied propylene production for methanol using mesostructured fibrous silica@ZSM-5 synthesized by microemulsion. The catalyst exhibited a significantly higher propylene selectivity of 56% and demonstrated remarkable stability for a duration of 80 hours while in operation compared to commercial catalyst. The HSi@ZSM-5 catalyst has the ability to inhibit coke deposition and minimize unwanted side reactions. This leads to increased propylene production, which is a crucial factor in commercial MTO processes[61].

Afiq et al explored the olefin production from methanol over a fibrous morphological zeolite catalyst (FZSM-5) has been successfully prepared using microwave assisted hydrothermal methods followed by ruthenium loaded by impregnation method. The BET surface area was

improved from 470.43 m²/g to 474.60 m²/g for HFZSM-5 and Ru/HFZSM-5 respectively. The metal incorporation to the HFZSM-5 catalyst enhanced acidity of Ru/HFZSM-5 indirectly increased the conversion of methanol to olefin from 88.60% to 95.14% and yielded 93.93% of olefins [62].

The previous study concluded that the addition of Zn and Ga increases selectivity. Additionally, fibrous silica has shown promising results in other applications.

2.3. Problem statement

The effectiveness of light naphtha aromatization faces significant hurdles, primarily stemming from two key issues. Firstly, there is a challenge related to the low selectivity of aromatic compounds in the conventional aromatization process employing the ZSM-5 catalyst, as it often generates undesired byproducts alongside the desired aromatics, negatively impacting economic viability and overall process efficiency. Secondly, the catalyst experiences rapid deactivation due to factors such as coke buildup and other deactivation mechanisms, resulting in diminished activity and a shortened operational lifespan. This frequent need for catalyst replacement or regeneration contributes to increased operational costs and downtime. To address these critical challenges, there is an urgent necessity for modifications to enhance the ZSM-5 catalyst's selectivity towards aromatic products and extend its active lifespan.

2.4. Objectives

The aim of this research is to develop a catalyst which is stable and capable of achieving a high conversion of naphtha into light aromatics. The specific objectives are as follows:

1. To Prepare nano ZSM-11 & fibrous silica ZSM-5 catalyst promoted with Ga, Zn.

2. Characterization of the nano ZSM-11 & fibrous ZSM-5 catalyst to relate structural and morphological properties to the catalyst activity.
3. Evaluate the nano ZSM-11 & fibrous silica modified ZSM-5 catalysts to measure its selectivity to aromatic and compare it to unmodified catalyst.

CHAPTER 3

Material and Methods

3.1.Experimental

3.1.1. Catalyst preparation and modification of nano ZSM-11 zeolite

ZSM-11 zeolites were synthesized hydrothermally utilizing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 35 and 70 as shown in **Figure 7**. The structure-directing agent used was tetrabutylammonium hydroxide (TBAH, 40%, Sigma-Aldrich). The silicon source used was tetraethyl orthosilicate (TEOS) from Sigma-Aldrich, whereas the aluminum source was aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) from Baker's. This synthesis used sodium hydroxide (NaOH, 98%, BDH) and deionized water. The reaction took place in Teflon-lined autoclaves that were dynamically agitated. During a standard synthesis process, 51 g of TEOS were gradually added to a water-based mixture comprising either 5.24 g or 2.62 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. This was done in order to produce the necessary $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 35 and 70, respectively. Additionally, 26 g of water were added to the mixture. Subsequently, a precise amount of 0.51 g of NaOH dissolved in 21.4 g of water was added drop by drop, followed by the addition of 77 g of TBAH to each combination. The mixtures were then rapidly agitated at ambient temperature for a duration of three hours. The zeolites underwent crystallization in Teflon-lined autoclaves with continuous rotation at a constant temperature of 170 °C for a duration of six days. After reaction, solid nano zeolite products were then separated by filtering, extensively rinsed with 0.5 liters of distilled water, and dried for an overnight at a temperature of 90 °C. A calcination condition was 550 °C 8 hours, 1 °C per minute. In order to transform synthesized NaZSM-11 into its protonic form, a series of three ion-exchange treatments were conducted. These treatments included utilizing a 1.0 M NH_4NO_3 solution, which was stirred at a temperature of 80 °C for a duration of 4.5 hours each time. Following these treatments, a final calcination process was carried out in static air at a temperature of 550 °C for a

period of five hours. The synthesized nano ZSM-11 was further modified by impregnating it with Zn and Ga metals. These catalysts included 2 wt% Ga and 1 wt% Zn. The alterations were accomplished by incipient wetness impregnation utilizing aqueous solutions of gallium (III) nitrate hydrate and zinc nitrate hexahydrate, respectively. The solution was maintained at 50 °C under stirring until the deionized water evaporated, followed by drying at 100 °C overnight. This was then followed by calcination at 550 °C for five hours. This procedure was carried out to ensure the proper integration of metal ions into the structure of the zeolite, preparing them for their intended function in catalytic applications. The synthesized catalysts were designated according to their $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, denoted as nano ZSM-11(35) [NZ11(35)], nano ZSM-11(70) [NZ11(70)], nano Zn/ZSM-11(70) [Zn/NZ11(70)], nano Ga/ZSM-11(70) [Ga/NZ11(70)], and nano GaZn/ZSM-11(70) [GaZn/NZ11(70)], where the numbers 35 and 70 indicate the specific $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios.

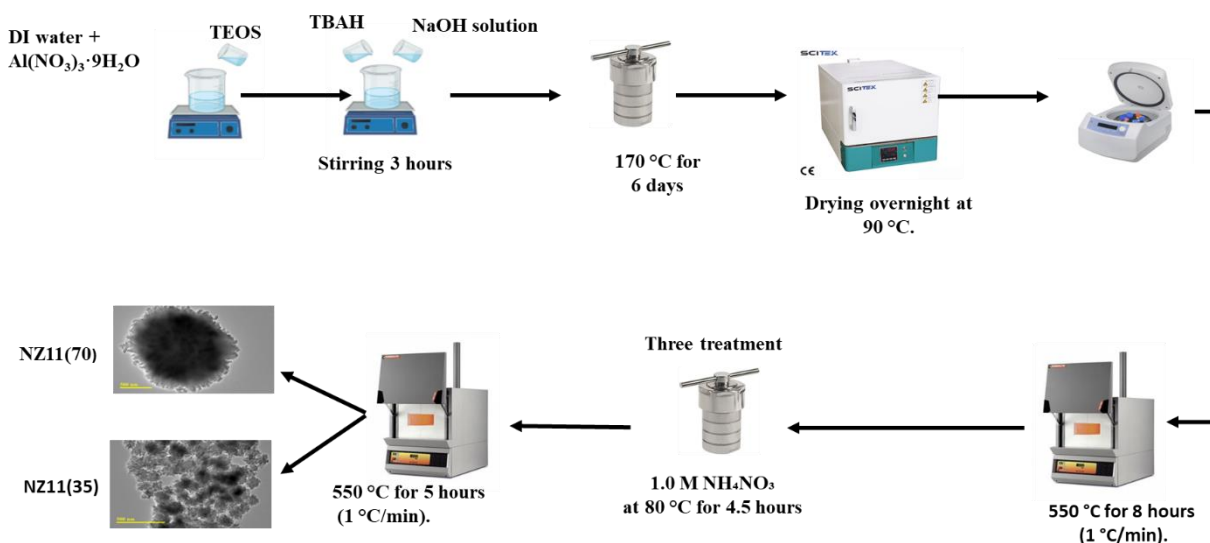


Figure 7: Preparation method for synthesizing nano ZSM-11 utilizing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 35 and 70.

3.1.2. Catalyst Preparation and modification of Fibrous Silica ZSM-5 Zeolite

The catalyst was prepared by combining 4.8 g of Urea with 8.03 g of Cetyltrimethylammonium bromide (CTAB) and dissolving the mixture in 238.58 g of water. The initial solution was subsequently mixed with a secondary solution, which was created by blending 9.71 g of n-butanol with 207.86 g of Toluene. Following the amalgamation of these two solutions, the resultant mixture underwent agitation for a duration of 25 minutes, while maintaining a regulated temperature of 25 °C. Following that, 3.98 g of Zeolite Socony Mobil-5 (ZSM-5) was introduced into the resulting mixture and agitated for a duration of 2 hours. Subsequently, a quantity of 17.04 g of Tetraethyl orthosilicate (TEOS) was added and continuous stirring for a prolonged period of 4 hours. Subsequently, the mixture underwent thermal treatment for a duration of 8 hours, maintaining a temperature of 120 °C. In the concluding stage, the mixture was subjected to a calcination process at a temperature of 550 °C for a duration of 8 hours as shown in **Figure 8**.

The FSZSM-5 modified with Ga and Zn metals using a wet impregnation procedure. Various precursors were used in the synthesis process, including gallium (III) nitrate hydrate and zinc nitrate hexahydrate. These precursor materials were utilized in the preparation of various types of zeolites, specifically the M-ZSM-5 zeolite (M=Ga and Zn). A 3 g batch was prepared by mixing the support ZSM-5 with S/A 30:1 in a specific quantity of deionized water and allowing it to stir for a period. Subsequently, the precursor dissolved in a small quantity of deionized water and added to the mixer under stirring to achieve a homogeneous distribution. Subsequently, the solution exposed to temperature of 70°C for till all DI water evaporated, followed by a drying process overnight at 100°C. The sample crushing and calcination for a duration of 5 hours at a temperature of 550 °C with a ramp rate of 5°C per minute.

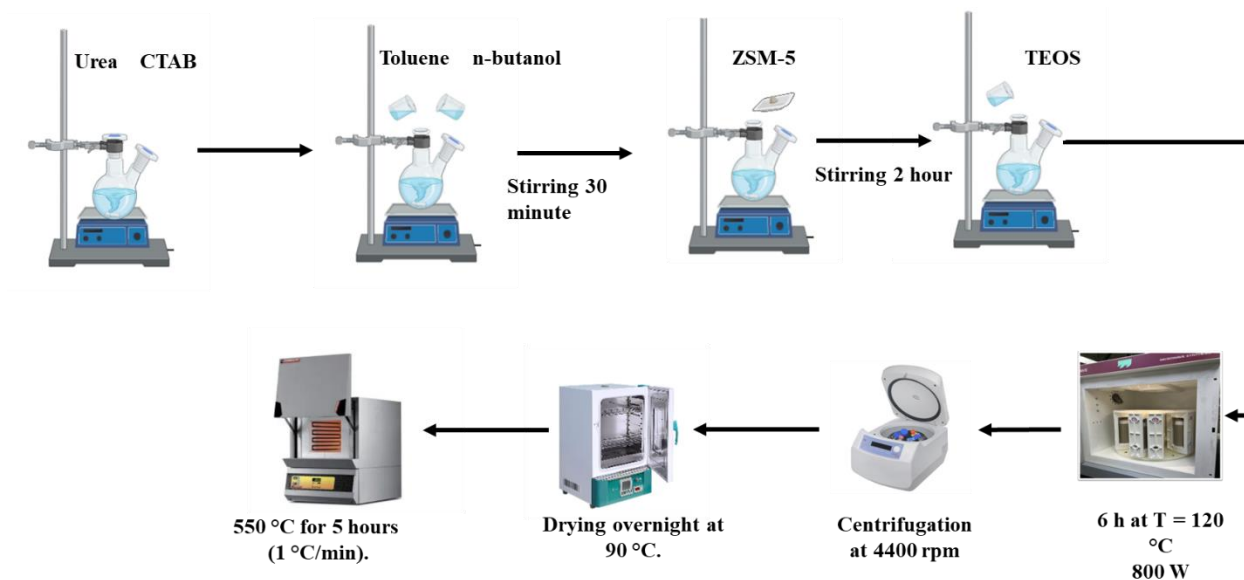


Figure 8: Preparation method for synthesizing FSZSM-5.

3.2.Catalyst characterizations

A wide range of analytical methods were used to examine the physical and chemical characteristics of nano ZSM-11 & FSZSM-5 zeolites and their modified forms. X-ray diffraction (XRD) was utilized to investigate the crystalline structures of the samples. This analysis was conducted using a Rigaku Miniflex II desktop diffractometer equipped with copper K-alpha radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected over a 2θ range from 5° to 80° , with the instrument operating at 40 kV and 15 mA, providing high-resolution insights into the phase purity and crystallinity of the zeolites. The textural properties, including surface area, pore volume, and pore size distribution, were assessed through nitrogen adsorption-desorption isotherms measured at 77 K using an ASAP-2020 Micromeritics instrument. Prior to analysis, the samples were degassed under vacuum conditions to remove any adsorbed moisture or contaminants, ensuring accurate measurement of adsorption characteristics. To accurately determine the acidic properties of the catalysts, ammonia temperature-programmed desorption (NH_3 -TPD) was performed using a BELCAT system. In this procedure, the catalyst samples were first pretreated by heating them in

a flow of helium gas to 500 °C for 110 minutes to eliminate any pre-adsorbed species. After cooling the samples down to 100 °C, they were exposed to a gas mixture of 5% NH₃ in helium at a flow rate of 50 mL/min for one hour to allow ammonia adsorption onto the acid sites. Excess ammonia was then removed by purging it with helium. The desorption of ammonia was monitored by increasing the temperature from 100 °C to 610 °C at a rate of 10 °C/min, and the amount of desorbed ammonia was detected using a thermal conductivity detector (TCD). This method provided detailed information on the strength and quantity of acidic sites present in the catalysts. The morphological characteristics of the zeolite samples were examined using scanning electron microscopy (SEM). SEM analysis was carried out on a JEOL JSM-6610LV instrument operating at an acceleration voltage of 20 kV. For sample preparation, the zeolite particles were mounted onto copper adhesive tape and then coated with a thin layer of gold using a sputter coater. This gold coating enhanced the electrical conductivity of the samples, minimizing charging effects during imaging and improving the clarity of the micrographs. Additionally, transmission electron microscopy (TEM) was employed to investigate the internal structure and nanoscale features of the zeolite particles. TEM analysis was conducted using a JEOL JEM-200F microscope operating at an accelerating voltage of 200 kV. Samples for TEM were prepared by dispersing the zeolite powders in ethanol and subjecting the suspension to ultrasonication to achieve a uniform dispersion of particles. A drop of this suspension was then placed onto a carbon-coated copper grid, and the samples were dried at 60 °C overnight to remove any residual solvent and ensure stability under the electron beam.

3.3. Catalyst evaluation

Conversion of light naphtha into aromatic compounds was conducted in a small-scale continuous-flow fixed-bed reactor operating at temperatures up to 550 °C, and atmospheric pressure. The

reactor was loaded with 0.5 g of catalyst (30 - 40 mesh size). The catalyst activation was performed in situ by maintaining a nitrogen flow rate of 20 mL/min at 550 °C for an additional two hours. Following activation, the light straight-run naphtha feedstock was introduced into the reactor at a specified WHSV of 1 h⁻¹. Reaction progress was monitored over the active catalyst for a reaction period of 1-5 hours. During the reaction, the reactor effluent containing both the liquid and gas phases were periodically injected together into the Shimadzu DHA GC to monitor the reaction progress having one FID (Rtx[®]-100-DHA, 100 m × 0.5 µm × 0.25 mm ID) and one TCD (MS-13X, 45/60×9 ft×2.0 mm ID×1/8 in OD) detector for analysis of feed along with reaction products (gas and liquid). The general diagram of reaction experiment is shown in **Figure 9**.

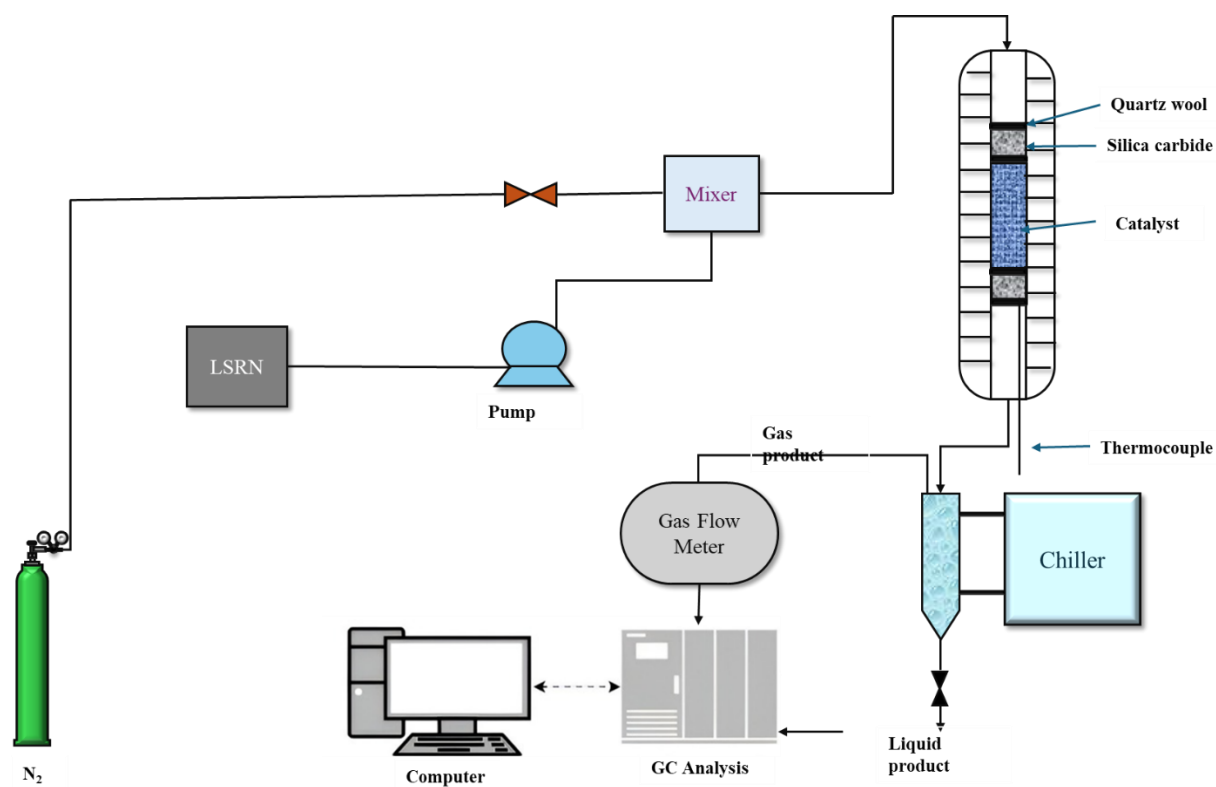


Figure 9: The experimental reaction setup.

3.4. Composition of feed light straight run naphtha

The feed LSRN used in this investigation comprises a range of hydrocarbon classifications, encompassing *n*-paraffins, *iso*-paraffins, naphthenes, and aromatics. The composition provides a comprehensive breakdown of the weight percentages of these hydrocarbons in various carbon chains, namely C₅, C₆, and C₇. The most significant category in composition is *iso*-paraffins, which make up 59.5 wt%, followed by *n*-paraffins, which account for 28.8 wt%. The mixture's composition of naphthenes and aromatics is 8.1 wt% and 3.3 wt%, respectively as shown in **Figure 10**. An in-depth feed analysis is essential for evaluating its appropriateness and responsiveness during aromatization. This analysis affects the selection of catalysts and reaction conditions to maximize the yield and quality of the final product.

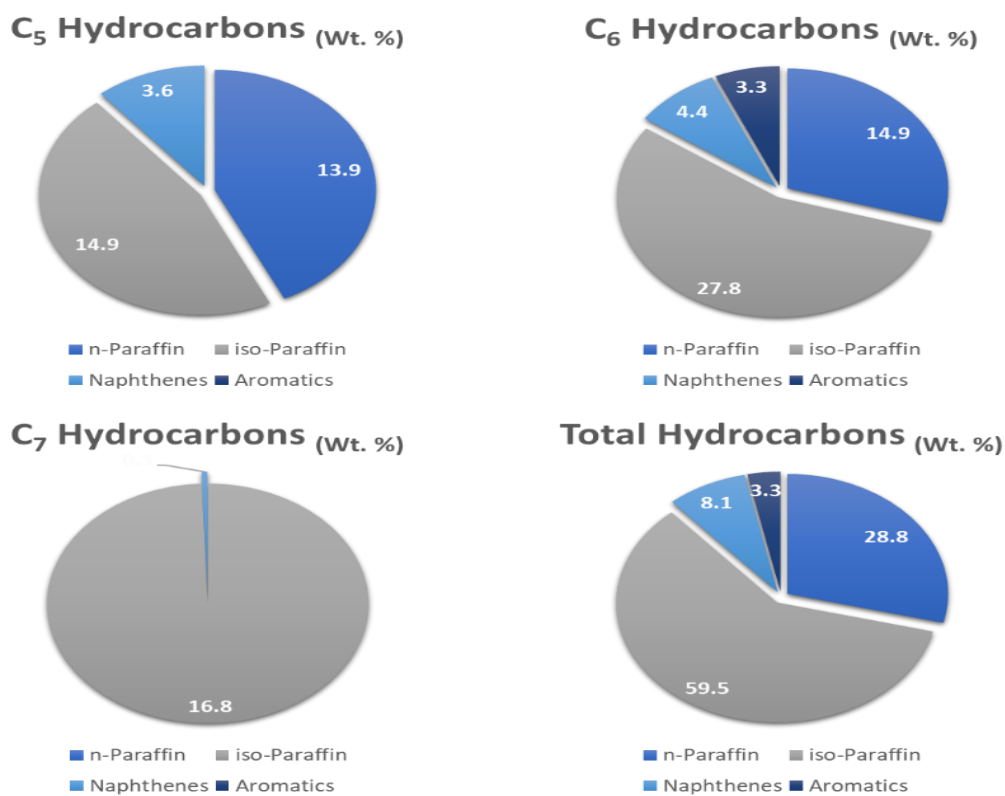


Figure 10. Composition of feed light straight run naphtha.

CHAPTER 4

Results and Discussion

4.1. Results and Discussion for nano ZSM-11

4.1.1. Physiochemical properties of catalysts

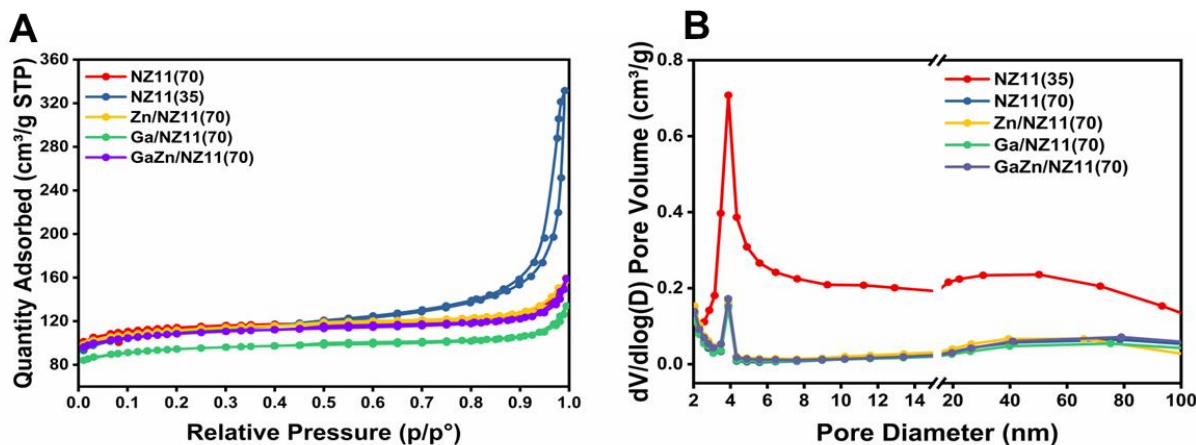
A. Structural analysis via N₂ isotherm and pore size distribution

The structural features of synthesized nano ZSM-11 zeolites, both unmodified and modified with metals such as Ga, Zn, and GaZn, were better understood by analyzing nitrogen adsorption-desorption isotherms and pore size distribution as displayed in **Figure 11**. The samples have Type I isotherms, which propose that they are microporous materials with a high affinity for adsorption at low relative pressures. The NZ11(70) exhibits a slightly greater BET surface area (347 m²/g) in comparison to the NZ11(35) (337 m²/g) as shown in **Table 1**. The addition of metals leads to noticeable modifications in the structure: although, Zn/NZ11(70) maintains a high surface area similar to the original NZ11(70). However, Ga/NZ11(70) undergoes a substantial decrease in surface area, either owing to pore blockage or structural changes produced by the inclusion of gallium. The GaZn/NZ11(70) sample demonstrates a synergistic interplay between Ga and Zn, leading to a marginal reduction in surface area compared to the unaltered parent NZ11(70).

The examination of pore size distribution provides more clarity on these structural alterations. NZ11(35), has a distinct peak at around 4 nm, indicating a well-defined microporous structure with a moderately large pore volume. On the other hand, NZ11(70) displays a broader peak, suggesting a reduction in small pores and a slight increase in medium-size pores. Metal alterations subtly impact the pore structure: Zn/NZ11(70) retains a distribution comparable to unmodified NZ11(70), but Ga/NZ11(70) exhibits a modest widening of the range of pore sizes, indicating the formation of mesopores.

Table 1. Textural properties of parent and metal modified nano ZSM-11 zeolites.

Textural Property	NZ11(70)	NZ11(35)	Ga/NZ11(70)	Zn/NZ11(70)	GaZn/NZ11(70)
BET Surface Area (m^2/g)	347	337	288	342	331
Total Pore Volume (cm^3/g)	0.11	0.40	0.21	0.24	0.25
Average Pore Diameter (nm)	5.46	13.43	7.48	6.74	7.66

**Figure 11.** N₂ isotherm (A) and pore size distribution (B) of NZ11(35), NZ11(70), Ga/NZ11(70), Zn/NZ11(70) and GaZn/NZ11(70) zeolites.

B. X-Ray Diffraction analysis of catalysts

The X-ray diffraction (XRD) patterns shown in **Figure 12** provide an examination of the structural properties of NZ11(70) zeolite samples, both for parent and after modification with gallium (Ga), zinc (Zn), and a mixture of both metals (GaZn).

Figure 12 presents the XRD patterns of NZ11(35), NZ11(70) metal-modified NZ11(70) with Ga and Zn. The X-ray diffraction (XRD) analysis revealed significant differences in the crystallinity and structural characteristics of the NZ11 zeolites under different conditions and metal modifications. The samples exhibit characteristic diffraction peaks often seen in materials with the MEL topology, namely at 2θ values ranging from 7 to 9 degrees and 22 to 25 degrees. These peaks provide evidence that the ZSM-11 framework has been maintained. The parent NZ11(70) (**Figure 12 (A)**) shows a has distinct and well-defined peaks, especially at crystallographic planes [501] and [303] as in **Figure 12 (C)** [63,64].

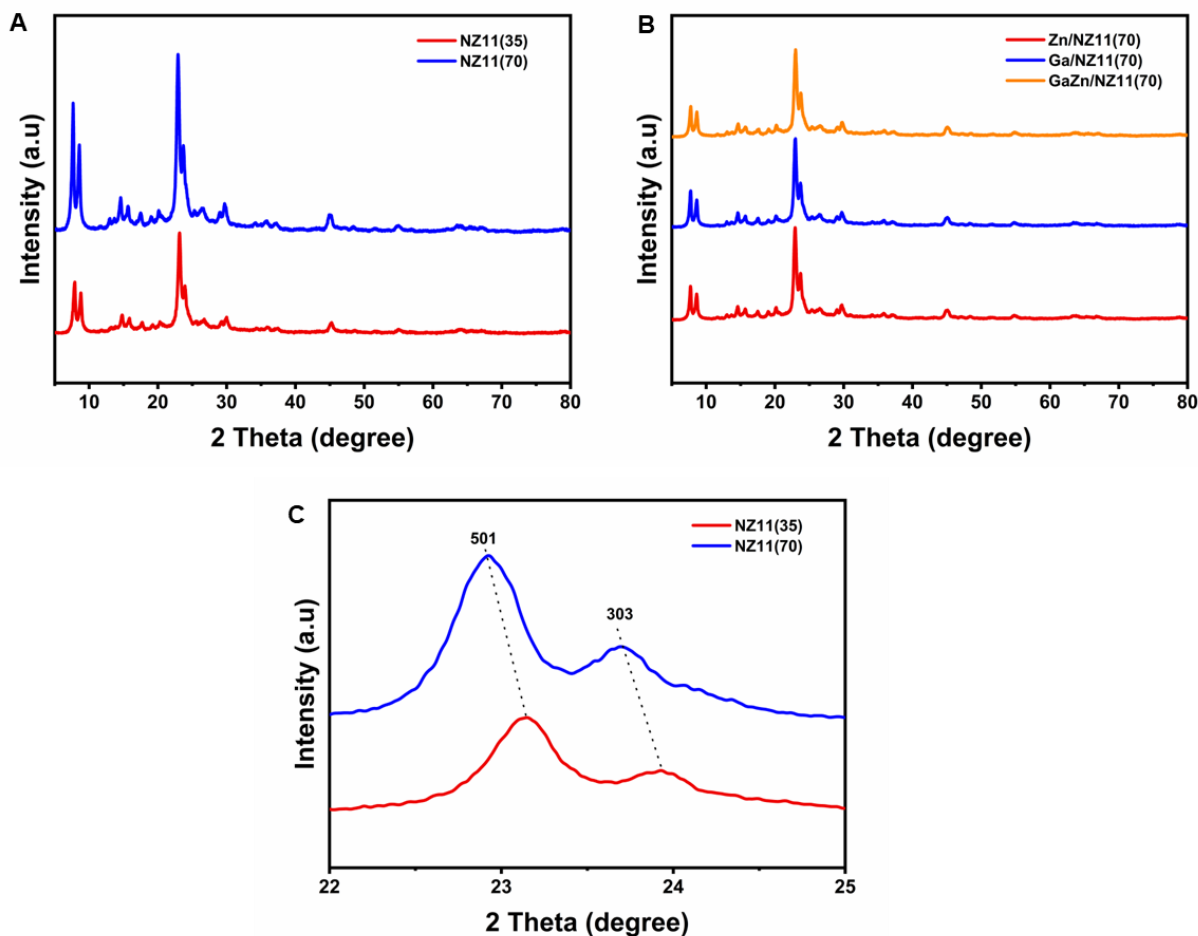


Figure 12: X-ray diffraction patterns of NZ11(35), NZ11(70), Ga/NZ11(70), Zn/NZ11(70) and GaZn/NZ11(70) zeolites.

The comparison between NZ11(35) and NZ11(70) indicated that NZ11(70) exhibited sharper and more defined peaks, suggesting a higher degree of crystallinity compared to NZ11(35), although both samples maintained similar peak positions, reflecting an unchanged fundamental crystal structure. This increase in crystallinity is likely attributed to the different preparation conditions. **Figure 12(A)**, Upon modification with zinc, gallium, and both metals (Zn/NZ11(70), Ga/NZ11(70), and GaZn/NZ11(70)), the XRD patterns (**Figure 12(B)**) showed that the metal incorporation indicate that there is no significant metal or metal oxide peaks are identified due to highly dispersion of metal on the surface of zeolite[63,65] did not significantly shift the peak

positions, indicating that the zeolite's crystal framework remained largely intact. However, notable differences in peak intensities and sharpness were observed. The GaZn/NZ11(70) sample exhibited the sharpest and most intense peaks, indicating enhanced crystallinity, while Zn/NZ11(70) displayed broader peaks, implying a potential reduction in crystallinity due to zinc incorporation. These findings suggest that while single metal modifications influence the crystallinity of NZ11(70), dual metal incorporation, particularly with gallium and zinc, leads to an even higher degree of crystallinity, making GaZn/NZ11(70) potentially more suitable for applications requiring highly ordered structures. The observed variations in crystallinity among the different samples underscore the impact of both preparation conditions and metal modifications on the structural properties of zeolites. The GaZn/NZ11(70) sample, which has been changed in two ways, exhibits the most significant decrease in peak intensity and the highest level of peak widening compared to all other samples.

These findings indicate that the combination of gallium and zinc results in a substantial rise in structural disarray and a further decline in crystallinity. Although changes have been made, the fundamental structure of ZSM-11, known as the MEL topology, remains intact. This suggests that the framework of NZ11 stays stable even when a significant amount of metal is added. The combination of this solid structural stability and the decreased crystallinity that was found emphasizes the careful equilibrium between preserving the zeolite framework and incorporating metal-induced alterations for possible uses in catalysis.

C. Acidic profile of catalysts via NH₃-TPD analysis

The ammonia temperature-programmed desorption (NH₃-TPD) in **Figure 13** profiles provide a comprehensive understanding of the acidic properties of nano ZSM-11 zeolites, both in their original state and after being modified with gallium (Ga) and zinc (Zn). The NH₃-TPD profiles exhibit two distinct desorption peaks: one in the lower temperature range (100 – 400 °C), which corresponds to weak acid sites [32,41], and a second in the higher temperature range (400 – 600 °C), representing Medium to strong acid sites, which are associated with the hydroxyl groups surface in ZSM-5 and may include Brønsted sites, are probably decreased by the presence of basic metal oxide particles. [32,42,43]. For the unmodified zeolites, NZ11(70) and NZ11(35), the total acidity is relatively low, at 0.23 mmol/g and 0.24 mmol/g, respectively as shown in **Table 2**. NZ11(35) exhibits a slightly higher concentration of weak acid sites (0.18 mmol/g) compared to NZ11(70) (0.15 mmol/g), which may contribute to increased catalytic activity in reactions favoring weaker acid sites, such as isomerization. However, both exhibit limited concentrations of strong acid sites, indicating reduced effectiveness in reactions that require high-temperature activation, such as cyclization and dehydrogenation. The Ga-modified zeolite, Ga/NZ11(70), stands out with a substantial increase in both total acidity (0.85 mmol/g) and a notable presence of strong acid sites (0.43 mmol/g). This higher concentration of medium and strong acid sites, as evidenced by the significant peak in the 400 – 600 °C range, directly enhances the catalyst's dehydrogenation and cyclization activities, making it highly efficient in aromatization reactions. The balance between weak (0.42 mmol/g) and strong acid sites in Ga/NZ11(70) suggests an optimized environment for both cracking and aromatization processes, contributing to its superior catalytic performance. Zn/NZ11(70) exhibits a higher total acidity (0.81 mmol/g) than the unmodified NZ11(70), with a moderate increase in both weak (0.36 mmol/g) and strong acid sites (0.45 mmol/g). This indicates that zinc may enhance the catalytic activity by increasing the number of available acid sites, though

not to the same extent as gallium. Zn-modification shows improved performance compared to the base zeolite but is less effective than the Ga-modified counterpart, likely due to the lower strong acid site concentration. The bimetallic GaZn/NZ11(70) catalyst shows the highest total acidity (0.87 mmol/g) and a balanced distribution of weak (0.40 mmol/g) and strong acid sites (0.47 mmol/g). The higher strong acid site concentration compared to Ga/NZ11(70) indicates a potential for increased cracking activity, which could lead to a more diverse product distribution, as observed in hydrocarbon conversions. The combination of gallium and zinc results in a catalyst with both enhanced dehydrogenation capabilities from gallium and improved cracking performance.

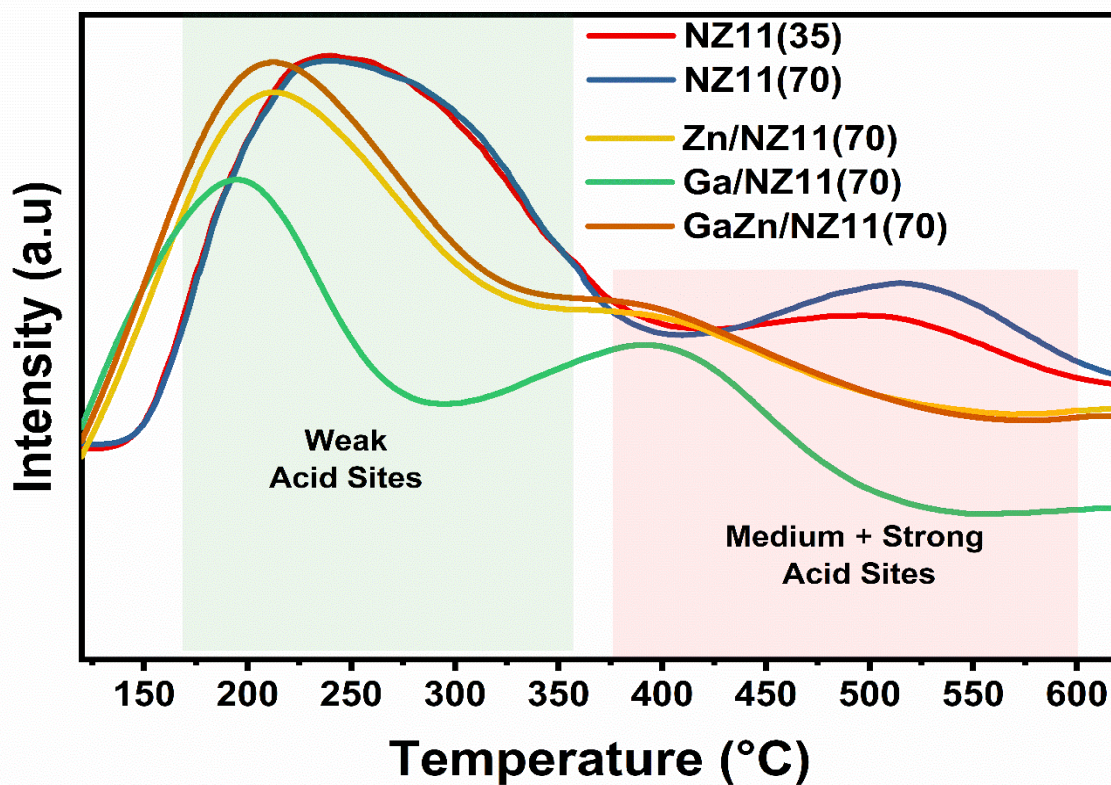


Figure 13: NH₃-TPD profile of NZ11(35), NZ11(70), Ga/NZ11(70), Zn/NZ11(70) and GaZn/NZ11(70) zeolites.

Table 2: Acidity NZ11(35), NZ11(70), Ga/NZ11(70), Zn/NZ11(70) and GaZn/NZ11(70) zeolites.

Property	NZ11(70)	NZ11(35)	Ga/NZ11(70)	Zn/NZ11(70)	GaZn/NZ11(70)
Total Acidity (NH ₃ mmol/g)	0.23	0.24	0.850	0.81	0.87
Peak I (100 - 400 °C)	0.15	0.18	0.42	0.36	0.40
Peak II (400 - 600 °C)	0.08	0.06	0.43	0.45	0.47

D. Catalysts imaging using SEM and TEM

The SEM and TEM images in **Figure 14 & 15** of NZ11(70) and NZ11(35) were distinctly influenced by their SiO₂/Al₂O₃ ratios, leading to notable differences in particle size and morphology. NZ11(70) exhibited a particle size of approximately 950 nm, with nanorod-like crystals aggregated into larger structures. The individual nanorods, contributing to the catalyst's unique mesoporous nature and potentially enhancing mass transport. In contrast, NZ11(35) displayed a significantly smaller particle size of 189 nm, with aggregated nanorods the reduction in the SiO₂/Al₂O₃ ratio correlated with a decrease in both particle and nanorod dimensions, likely contributing to a higher surface area and improved diffusion pathways. Both materials showed intercrystalline mesoporosity, particularly in NZ11(35), where the smaller nanorods and reduced crystallinity were more pronounced. This mesoporous structure, assembled from aggregated nanorods, is expected to enhance catalytic efficiency by facilitating reactant access to active sites, while the reduced crystallinity may have made the nanorods more susceptible to interaction with OH⁻ anions, forming empty pores. The SEM image reveals the nanostructured morphology characteristic of the Ga/NZ11(70) framework, with agglomerated particles forming a distinct, irregular shape. The surface appears to be covered with nano-sized clusters.

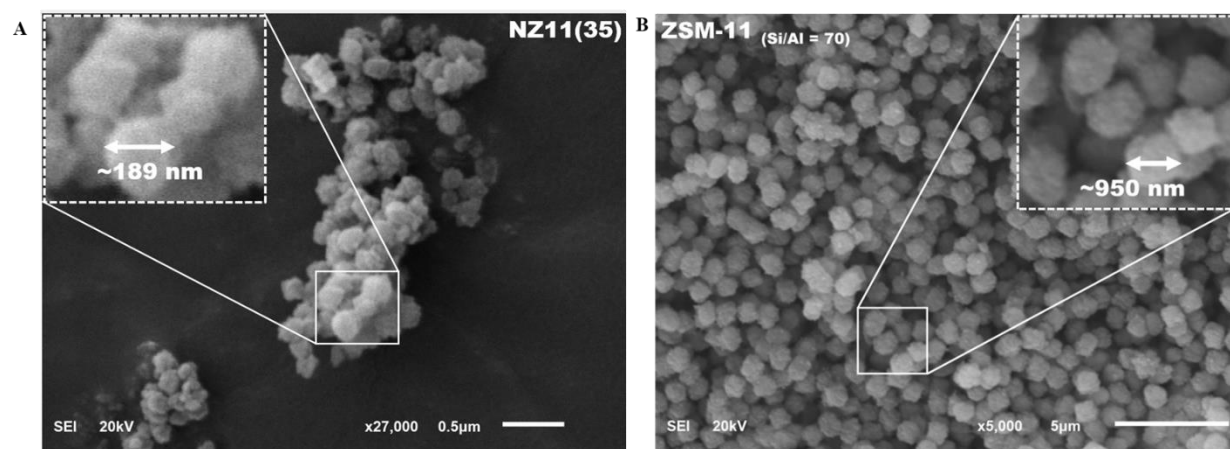


Figure 14: SEM images of NZ11(35), NZ11(70) zeolites and EDS analysis of Ga/NZ11(70), Zn/NZ11(70) and GaZn/NZ11(70) zeolites.

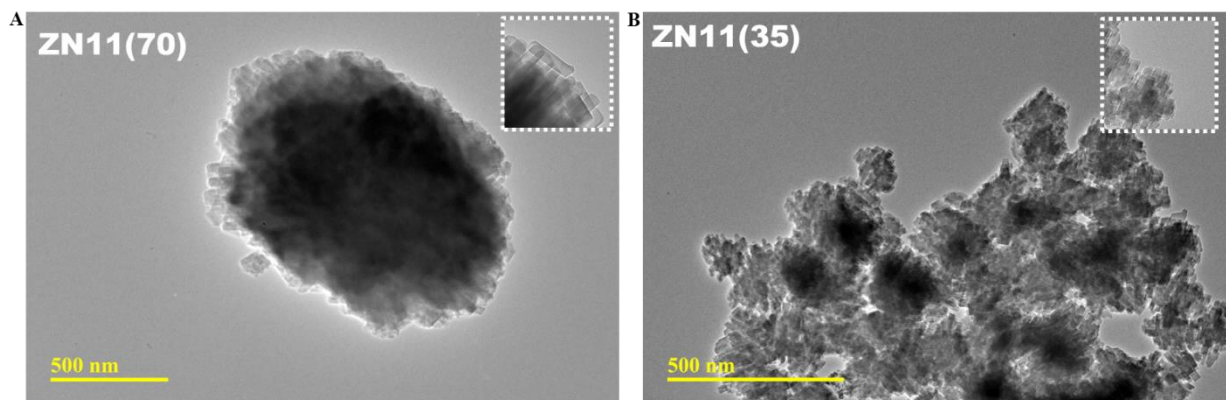


Figure 15: TEM image of NZ11(35), and NZ11(70) zeolites.

Conversely, the NZ11(70) has a more organized and crystalline arrangement. The TEM pictures show distinct nanorods with finely aligned lattice fringes in a unidirectional manner, indicating a high level of crystallinity. The heightened structural organization indicates that the enhanced silica content diminishes imperfections and improves stability within the framework. The NZ11(70) sample has a homogeneous and layered structure that can potentially hinder the accessibility of catalytic sites. This is because the crystals are densely packed, which may hamper the diffusion of reactants. However, this improved structural organization can potentially boost selectivity in aromatization.

4.1.2. Catalytic Performance Tests

The catalytic performance of synthesized nano ZSM-11 zeolites was investigated for converting LSRN into aromatic compounds at a temperature of 550 °C. The catalysts were examined unmodified and after being modified with metals, including gallium, zinc, and a mixture of both. The catalytic performance information is summarized in **Figure 16**. Both parent nano ZSM-11 catalysts achieved near-complete conversion rates of 97–99%. Notably, the slight superiority of ZSM-11(70) was attributed to its higher silica content, which influenced the acidity and pore structure of the zeolite. In terms of aromatic selectivity, ZSM-11(70) achieved a total aromatic yield of 40.7% compared to 38.3% for ZSM-11(35). Notably, ZSM-11(70) demonstrated increased selectivity toward heavier aromatic hydrocarbons (C_9^+ aromatics), suggesting that its pore structure and acidity profile favored secondary reactions leading to the formation of higher-molecular-weight aromatics. The straight channel system of ZSM-11 facilitated the diffusion of larger hydrocarbon intermediates, promoting oligomerization and cyclization reactions that contributed to the synthesis of heavier aromatics. Both catalysts exhibited minimal methane (C) and ethane yields, with negligible differences between the two ratios, suggesting that the SiO_2/Al_2O_3 ratio had little influence on cracking reactions that generate lighter hydrocarbons. The catalyst with a SiO_2/Al_2O_3 ratio of 70 produced slightly higher yields of C_3+C_4 and total P&O compared to the catalyst with a ratio of 35, indicating that increased SiO_2 content enhances selectivity for medium-chain hydrocarbons and paraffin/olefin production. This could be attributed to reduced acidity associated with higher SiO_2/Al_2O_3 ratios, which moderates cracking activity while favoring oligomerization and dehydrogenation pathways (**Figure 16B**).

The introduction of metal species into the ZSM-11(70) framework significantly influenced both conversion rates and product distribution. The Zn/ZSM-11(70) catalyst achieved complete LSRN

conversion (100%) and markedly increased yields of benzene and toluene, resulting in a cumulative BTEX selectivity of 67.8% (**Figure 16A**). Zinc incorporation enhanced dehydrogenation activity by introducing additional Lewis acid sites, which facilitated the initial dehydrogenation of alkanes to alkenes crucial intermediates in the aromatization pathway. Gallium-impregnated ZSM-11(70) (Ga/ZSM-11(70)) also reached full conversion and exhibited the highest yield of total aromatic 77.8%, with a pronounced increase in toluene selectivity (**Figure 16C**). Gallium species acted as effective dehydrogenation centers, promoting dehydrocyclization reactions that favored the formation of aromatics, particularly toluene and xylene. Ga/ZSM-11(70) exhibited a significant increase in total acidity (0.850 mmol NH₃/g) compared to the unmodified NZ11(70) (0.23 mmol NH₃/g), indicating a higher density of active sites crucial for catalytic reaction like dehydrogenation and cyclization essential in aromatic formation. The catalyst showed a balanced distribution of acid sites, with nearly equal contributions from weaker acid sites and medium & stronger acid sites. The Ga/ZSM-11(70) enhanced the aromatization by facilitating the initial dehydrogenation of light hydrocarbons into olefins, intermediates necessary for aromatization. Simultaneously, promoted cyclization and hydrogen transfer reactions leading to aromatics [32,44], Thus, the combination of high total acidity and an optimal balance of acid site strengths in Ga/NZ11(70) directly contributed to its superior performance in enhancing the yield of aromatics. Gallium promotes the selective conversion of olefins to aromatics by removing hydrogen atoms via acid sites that activate C–H bonds allowing these sites to regenerate without forming cracking products while gallium and zinc act as catalysts facilitating the re-combinative desorption of hydrogen atoms formed during acid-catalyzed C–H bond activation [26]. The bimetallic GaZn/NZ11(70) catalyst maintained complete conversion and displayed selectivity outcomes intermediate between the Zn and Ga single-metal catalysts, suggesting a synergistic

interaction between gallium and zinc ions, where gallium enhanced dehydrocyclization while zinc contributed to dehydrogenation efficiency, collectively optimizing the aromatization reaction. When gallium was combined with zinc in the GaZn/NZ11(70) catalyst, the aromatic yield was lower than with Ga/NZ11(70) alone. This reduction can be attributed to the interaction between gallium and zinc within the zeolite framework, which likely altered the distribution and strength of acid sites critical for aromatization. Zinc's presence could have modified the catalytic environment, partially inhibiting gallium's effectiveness in promoting dehydrocyclization and cyclization reactions. Additionally, zinc may have facilitated alternative reaction pathways, like increased dehydrogenation, leading to the formation of lighter hydrocarbons or olefins and thus reducing intermediates available for aromatic formation. The anticipated synergy from combining gallium and zinc did not enhance the aromatization activity beyond gallium alone, resulting in a lower aromatic yield with the GaZn/NZ11(70) catalyst compared to Ga/NZ11(70). Examining the selectivity toward lighter hydrocarbons, Ga/NZ11(70) exhibited a reduced yield of C₃ and C₄ hydrocarbons compared to unmodified NZ11(70), indicating that gallium favored the conversion of intermediates into aromatics rather than lighter alkanes (**Figure 16D**). Both Zn/ NZ11(70) and GaZn/ NZ11(70) further decreased the yields of C₃ and C₄ hydrocarbons.

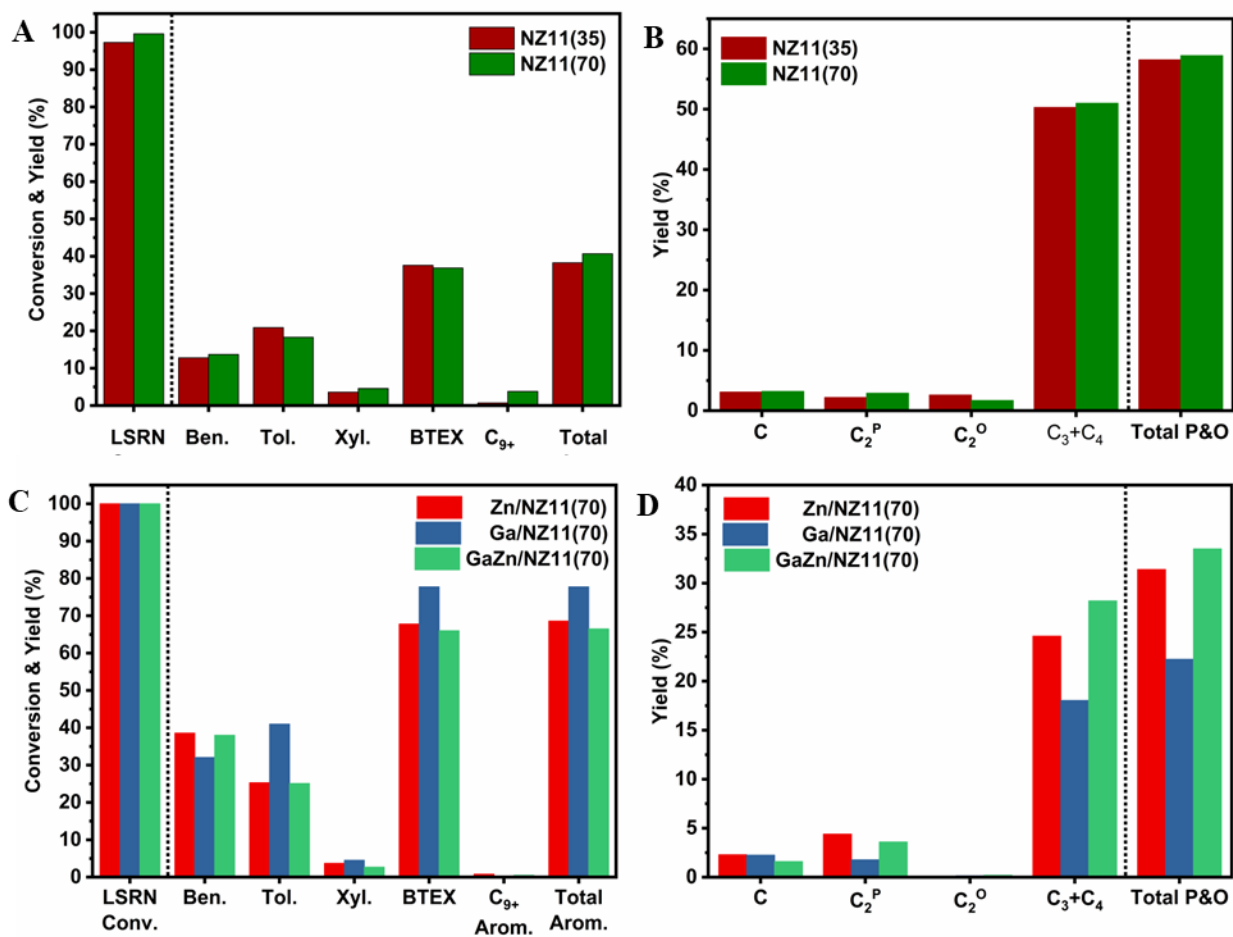


Figure 16: Comparative analysis of conversion and selectivity performance of nano ZSM-11 catalysts with different SiO₂/Al₂O₃ ratios for the aromatization of LSRN. A and C depict conversion and yield of liquid products, C and D illustrate the yield of gaseous.

4.2. Results and Discussion for fibrous silica ZSM-5

4.2.1. Catalyst characterizations:

A. Structural Analysis via N₂ Isotherm and Pore Size Distribution:

Table 3 summarized the BET analysis for the ZSM-5, FSZSM-5, Ga/FSZSM-5, and Zn/FSZSM-5 zeolite catalysts. The incorporation of fibrous silica in ZSM-5 significantly increased the BET surface area of FSZSM-5 to 427 m²/g, compared to 342 m²/g in the parent ZSM-5, primarily due to a marked increase in the t-Plot external surface area, which more than doubled to 318 m²/g. This enhancement suggests an extensive development of mesoporosity, as evidenced by the mesopore volume, which rose from 0.058 cm³/g in ZSM-5 to 0.328 cm³/g in FSZSM-5. However, this modification concurrently reduced the t-Plot micropore area and volume, indicating a partial loss of the microporous framework. The incorporation of gallium and zinc into the FSZSM-5 structure (Ga/FSZSM-5 and Zn/FSZSM-5) resulted in a slight reduction in the BET surface area to 389 m²/g and 359 m²/g, respectively, while the mesopore volume further increased, particularly in Zn/FSZSM-5, which exhibited a substantial mesopore volume of 0.563 cm³/g

The pore size distribution analysis in **Figure 17** revealed that ZSM-5 exhibited a minor peak around 4 nm, indicating its predominantly microporous nature with minimal mesopore presence. In contrast, FSZSM-5 showed a sharp peak near 3.5 nm, suggesting an increased contribution from mesopores, likely due to structural modifications introducing secondary porosity. Ga/FSZSM-5 displayed a similar profile to FSZSM-5 but with the peak slightly shifted toward larger pore sizes, indicating a broader distribution of mesopores that could facilitate the diffusion of larger molecules. Zn/FSZSM-5 presented a broader pore size distribution with significant mesopore volume in the 4–8 nm range, an enhancement attributed to the incorporation of zinc, which would accommodate larger molecules in catalytic reactions.

Table 3: The textural characteristics of ZSM-5, FSZSM-5, Zn/FSZSM-5, and Ga/FSZSM-5 zeolite catalysts.

Property	ZSM-5	FSZSM-5	Ga/FSZSM-5	Zn/FSZSM-5
Surface Area				
BET Surface Area (m ² /g)	342	427	389	359
t-Plot Micropore Area (m ² /g)	210	108	116	110
t-Plot External Surface Area (m ² /g)	133	318	274	249
Pore Volume				
Total Pore Volume (cm ³ /g)	0.17	0.38	0.45	0.62
t-Plot Micropore Volume (cm ³ /g)	0.11	0.05	0.06	0.06
Mesopore Volume (cm ³ /g)	0.06	0.33	0.39	0.56
Average Pore Diameter (nm)	5.05	4.05	5.60	8.07

ZSM-5 demonstrated the lowest nitrogen adsorption capacity as shown in the nitrogen adsorption-desorption isotherms **Figure 18**, consistent with its low mesopore volume and microporous structure, as evidenced by limited adsorption at higher relative pressures. FSZSM-5 exhibited increased nitrogen uptake at elevated relative pressures, indicative of enhanced mesoporosity, aligning with the observed increase in mesopore volume and external surface area from the textural data **Table 3**. Ga/FSZSM-5 showed similar adsorption behavior to FSZSM-5 but with a slightly higher capacity at higher pressures, suggesting a higher mesopore volume and possibly larger mesopores. Notably, Zn/FSZSM-5 had the highest nitrogen adsorption capacity, especially at higher relative pressures, which was consistent with its substantial mesopore volume (0.56 cm³/g), and large average pore diameter (8.073 nm) indicated in the textural properties. These modifications in porosity had significant implications for catalysis. The introduction of metal oxides (gallium and zinc) and FSZSM-5 led to substantial alterations in pore structure. The increased mesoporosity observed in FSZSM-5, Ga/FSZSM-5, and particularly Zn/FSZSM-5 was advantageous for catalytic applications involving larger molecules that could not access the micropores of ZSM-5. The presence of larger pores and higher mesopore volumes would improve molecular diffusion and potentially reduce deactivation due to pore blockage. Zn/FSZSM-5,

possessing the highest mesopore volume and pore diameter, was expected to exhibit superior catalytic activity in reactions requiring larger pore channels, such as the catalytic cracking of heavy hydrocarbons. The nitrogen adsorption isotherms supported these conclusions, reflecting the impact of zinc incorporation on the pore structure.

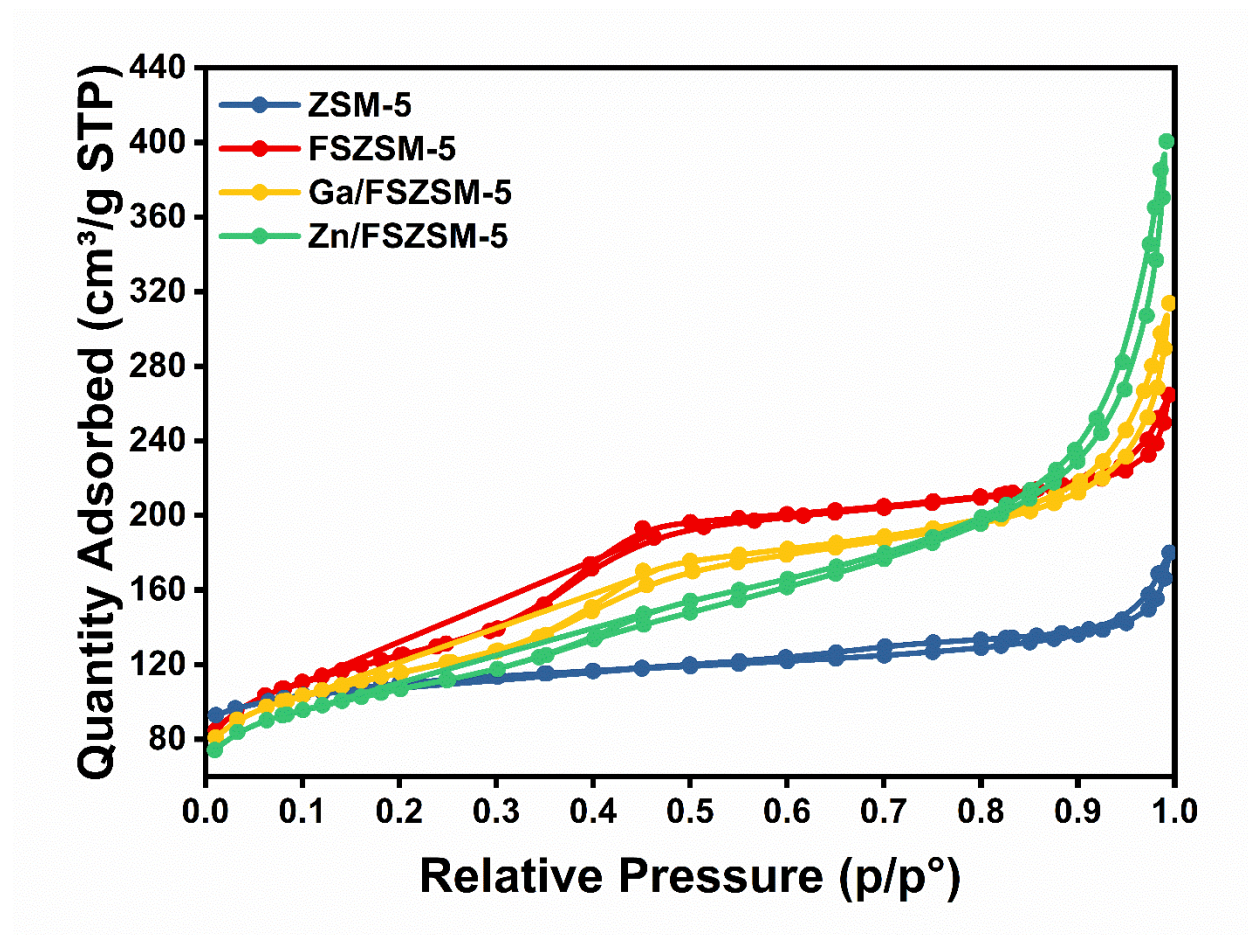


Figure 17: N_2 isotherms plot of ZSM-5, FSZSM-5, Ga/FSZSM-5 and Zn/FSZSM-5 zeolite catalysts.

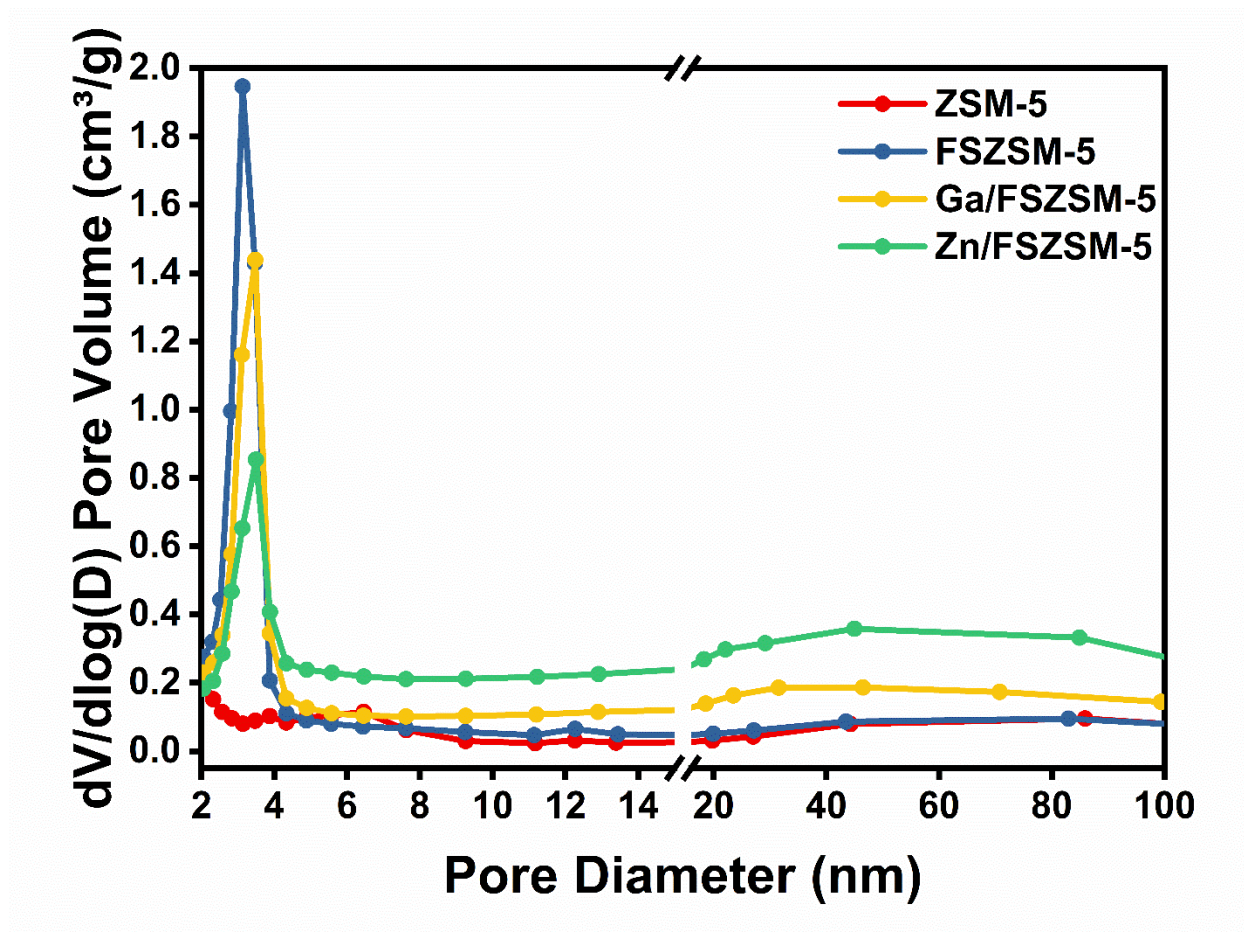


Figure 18: Pore size distribution of ZSM-5, FSZSM-5, Ga/FSZSM-5 and Zn/FSZSM-5 zeolite catalysts.

B. X-Ray Diffraction Analysis of Catalysts

The X-ray diffraction (XRD) patterns of ZSM-5, fibrous ZSM-5 (FSZSM-5), Ga/FSZSM-5, and Zn/FSZSM-5 zeolite catalysts provided significant insights into their structural integrity and phase compositions, as shown in **Figure 19**. The XRD analysis demonstrated that all samples retained characteristic peaks corresponding to the MFI framework of ZSM-5. All FSZSM catalysts exhibited similar peak diffraction patterns to the parent material at 2θ values of $7-9^\circ$ and $22-25^\circ$, confirming that the MFI framework's structural integrity was maintained despite modifications. Among these, the ZSM-5 sample displayed the highest peak intensities, reflecting its high

crystallinity. In contrast, the modified catalysts, such as FSZSM-5, showed slightly reduced peak intensities compared to the parent ZSM-5. This reduction may be attributed to the incorporation of silica species during the dendrimeric silica fiber formation process[66,67]. Additionally, the modified catalysts FSZSM-5, Ga/FSZSM-5, and Zn/FSZSM-5 exhibited broader peaks and slightly reduced intensities, indicating a modest decrease in long-range order and crystallinity. This reduction in crystallinity likely resulted from the dispersion of nano-sized particles into the parent ZSM-5 structure. Furthermore, no significant peaks corresponding to metal or metal oxide species were detected in the modified samples [29,68]. Notably, Zn/FSZSM-5 showed the most pronounced peak broadening and intensity reduction, which could be attributed to significant structural modifications arising from the larger ionic radius of zinc or increased mesoporosity. Quantitative analysis further substantiated these observations. The peak intensities for ZSM-5 were the highest, with sharp and well-defined diffraction peaks around $2\theta \approx 23^\circ$, reflecting a well-ordered crystalline structure. FSZSM-5 exhibited a decrease in peak intensity compared to ZSM-5, confirming the introduction of mesoporosity and the presence of structural defects. Ga/FSZSM-5 and Zn/FSZSM-5 showed even greater reductions in peak intensities indicating that the incorporation of gallium and zinc into the zeolite framework led to more pronounced distortions in the crystalline lattice. Specifically, Zn/FSZSM-5 demonstrated the broadest peaks among the samples, suggesting that zinc incorporation resulted in the formation of smaller crystalline domains or a more significant alteration of the ZSM-5 framework. This finding was consistent with previous nitrogen adsorption data, which showed increased mesoporosity in Zn/FSZSM-5, leading to broader XRD peaks due to heightened structural disorder within the material.

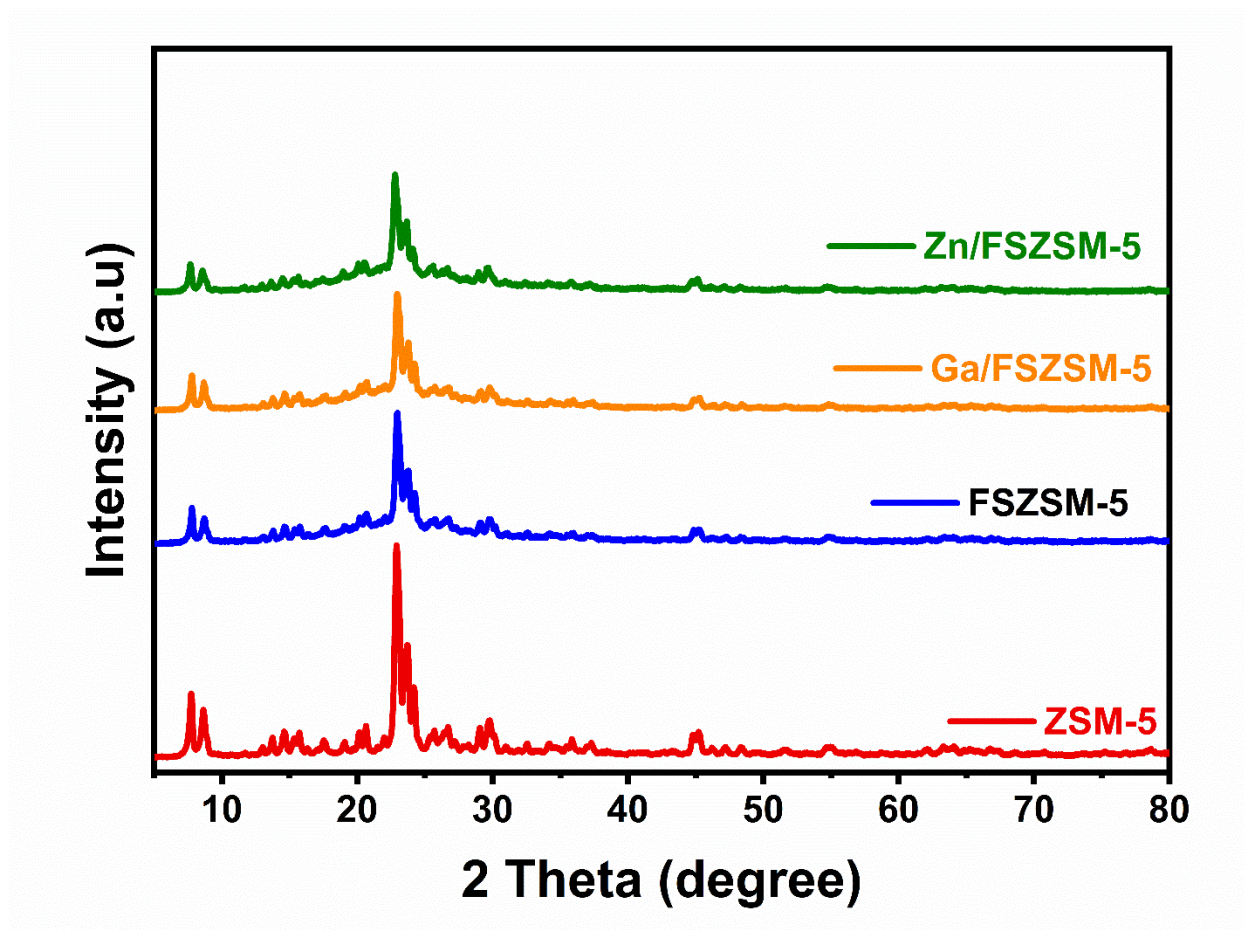


Figure 19: XRD pattern of ZSM-5, FSZSM-5, Ga/FSZSM-5 and Zn/FSZSM-5 zeolite catalysts.

C. Ammonia Temperature-Programmed Desorption (NH₃-TPD).

The overall acidity and acid strength of the catalysts ZSM-5, fibrous ZSM-5 (FSZSM-5), and modified FSZSM-5 were evaluated using NH₃-TPD. In the TPD profiles **Figure 20**, two distinct peaks of ammonia desorption were observed: one belongs to weak to medium acid sites at temperatures between 100 and 300 °C, and another associated with strong acid sites ranging from 300 to 600 °C. However, the impregnated non-acidic zinc and gallium oxides may reside within the zeolite micropores, obstructing the acid sites and rendering them inaccessible for NH₃ chemisorption. The ammonia adsorbed on the weak acid sites corresponds to the low to medium temperature peak, which effectively influences proton mobility. The high-temperature TPD peak, related to stronger adsorption sites belonging to surface hydroxyl groups in the zeolite, may include

Brønsted sites originating from non-framework aluminum facing the mesopores. This peak diminishes with increasing metal loading, suggesting that stronger acid sites are suppressed by the basic metal oxide particles. The unmodified ZSM-5 catalyst exhibited the highest desorption response, particularly in the temperature range of approximately 100 – 400 °C, with a pronounced peak around 200 °C indicative of a high concentration of medium-strength acid sites. Its total acidity was measured at 1.11 mmol/g, the highest among the samples, reflecting its abundance of strong Brønsted and Lewis acid sites. In contrast, FSZSM-5 showed a significantly diminished response, with a less intense peak near 200 °C and a total acidity reduced to 0.43 mmol/g **Table 4**. This reduction suggested a decrease in medium-strength acid sites, likely due to fibrous treatment leading to framework dealumination or alterations in the acidity caused by fibrous incorporation.

Table 4. Acidity of ZSM-5, FSZSM-5, Ga/ FSZSM-5 and Zn/FSZSM-5 zeolite catalysts.

Property	ZSM-5	FSZSM-5	Ga/FSZSM-5	Zn/FSZSM-5
NH₃ TPD Results				
Total Acidity (NH ₃ mmol/g)	1.11	0.43	0.48	0.60
Peak I (100-300 °C)	0.414	0.246	0.246	0.455
Peak II (300-600 °C)	0.7	0.18	0.236	0.144

The Ga-modified FSZSM-5 displayed an intermediate desorption profile, with a moderate peak around 200 °C and a total acidity of 0.48 mmol/g. Gallium incorporation appeared to partially restore the medium-strength acid sites lost in FSZSM-5. The Zn-modified FSZSM-5 catalyst exhibited a more pronounced peak at approximately 200 °C and a total acidity of 0.60 mmol/g, indicating that zinc modification was more effective in enhancing the acidity of the catalyst. Additionally, Zn/FSZSM-5 showed a distinct secondary peak above 400 °C, suggesting the presence of stronger acid sites, albeit in smaller amounts compared to unmodified ZSM-5. This enhancement in both medium and strong acid sites suggested that Zn/FSZSM-5 could perform well in reactions requiring such acidic environments.

Overall, the modifications applied to ZSM-5 had significant impacts on acidity and acid site distribution. The fibrous modification to produce FSZSM-5 led to a substantial decrease in total acidity and a reduction in both medium- and strong-strength acid sites. The subsequent incorporation of gallium and zinc into FSZSM-5 partially restored the catalyst's acidity, with zinc proving more effective than gallium.

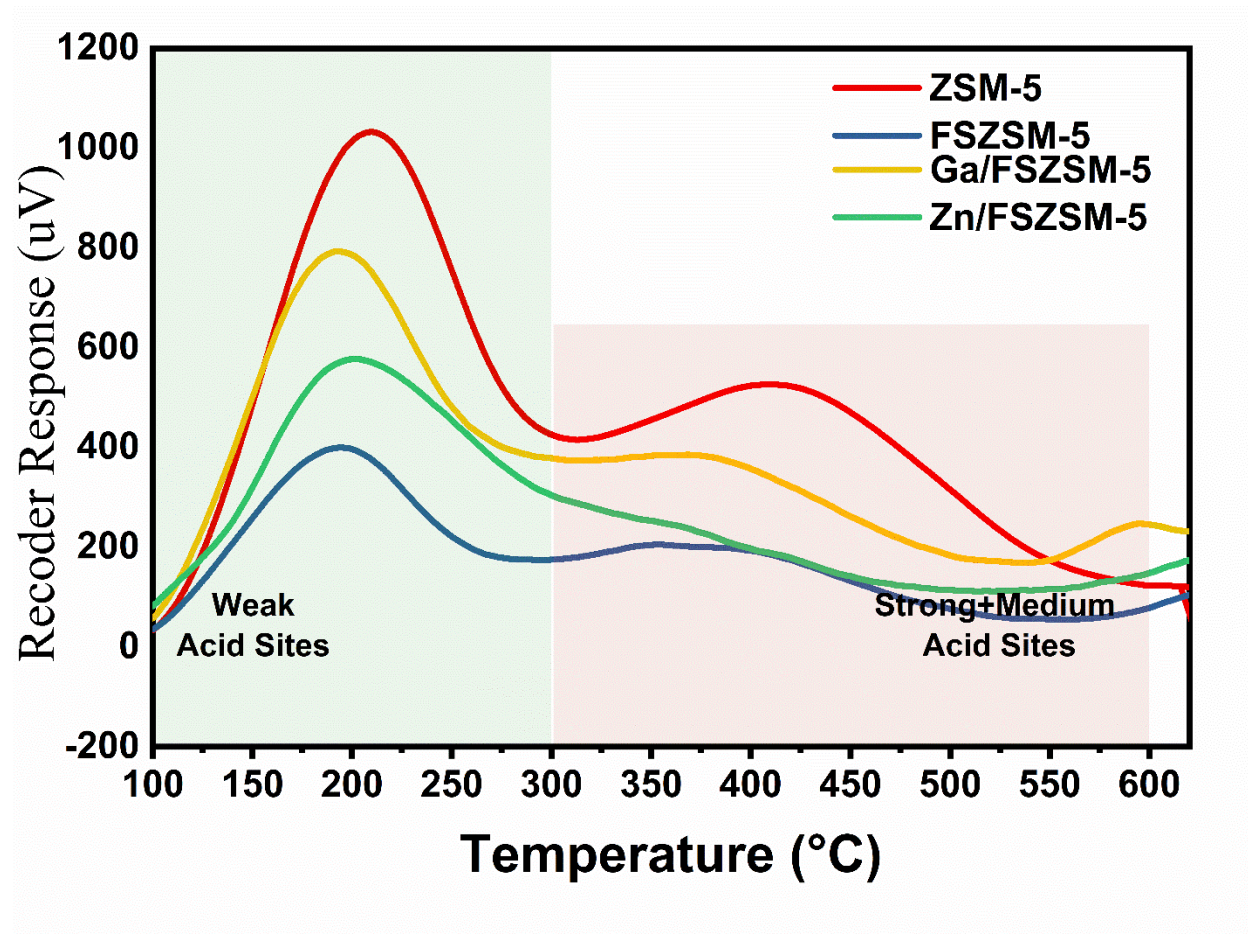


Figure 20: NH3-TPD profile of ZSM-5, FSZSM-5, Ga/ FSZSM-5 and Zn/FSZSM-5 zeolite catalysts.

D. Scanning electron microscopy (SEM) images:

SEM images of ZSM-5, FSZSM-5, Ga/FSZSM-5, and Zn/FSZSM-5 catalysts revealed that all samples exhibited a highly agglomerated and irregular morphology **Figure 21**. The particles appeared amorphous and lacked distinct shapes or crystalline facets at the magnification used. Despite modifications with fibrous, gallium, or zinc, there were no significant changes in particle shape or morphological features compared to the unmodified ZSM-5. The particle size distribution was broad across all samples, ranging from sub-micron particles to larger clusters, indicating heterogeneous sizes resulting from the synthesis process. The high degree of agglomeration formed loosely packed aggregates with visible voids and spaces between particles, which might influence catalytic behavior by affecting surface area and reactant accessibility.

The surface texture across all catalysts was rough and porous, likely due to the agglomerated nature of the particles. Although large pores were not visible at the magnification used, the roughness suggested the presence of porosity at smaller scales, essential for catalytic reactions. The absence of segregated phases indicated that the fibrous and metal modifications were well dispersed throughout the materials, maintaining a relatively homogeneous structure. Furthermore, the structural integrity of the zeolite framework was largely retained after modification, as evidenced by the similarity in morphology between the modified and unmodified samples. These observations implied that the synthesis and modification procedures produced catalysts with expected structural features conducive to catalytic applications, without introducing significant anomalies.

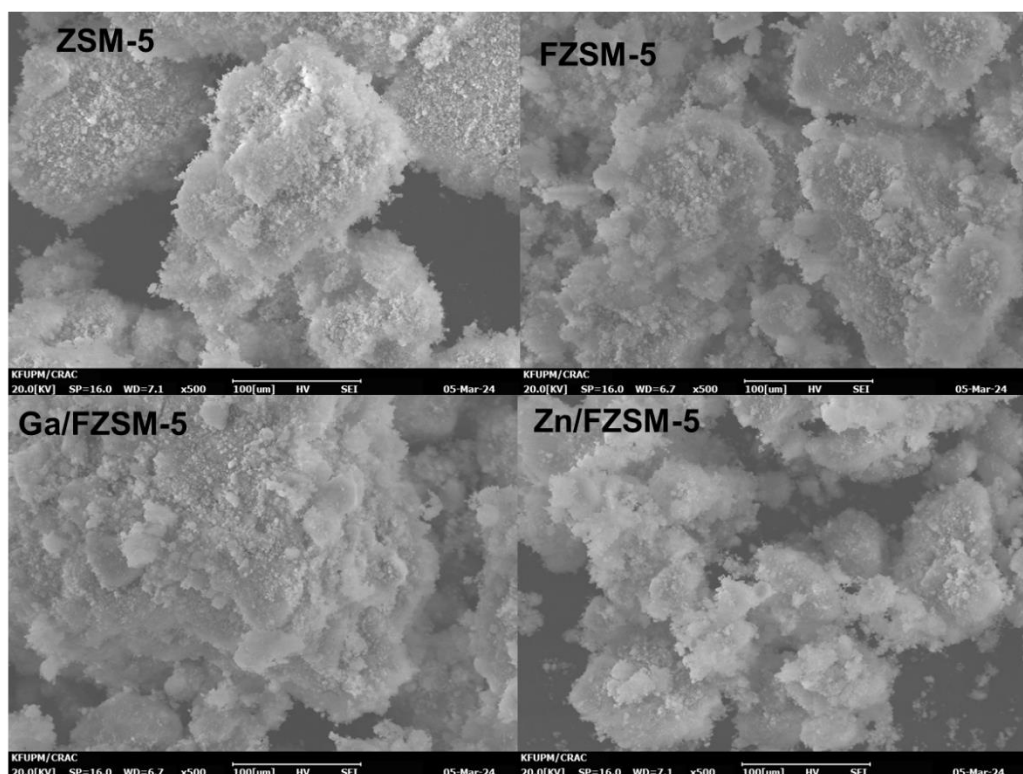


Figure 21: SEM image of ZSM-5, FSZSM-5, Ga/ FSZSM-5 and Zn/FSZSM-5 zeolite catalysts.

E. Transmission electron microscopy (TEM)

The transmission electron microscopy (TEM) images provided detailed insights into the morphological characteristics of conventional ZSM-5 (**Figure 22A**) and fibrous silica-modified ZSM-5 (**Figure 22B**). The conventional ZSM-5 exhibited a compact and crystalline structure, where particles aggregated into dense clusters with limited interstitial spaces. This morphology suggested a relatively low external surface area and restricted accessibility to internal active sites. The tightly packed structure likely impeded the diffusion of reactant molecules into the zeolite's micropores, potentially limiting its effectiveness in catalytic applications that require efficient mass transport. In contrast, the fibrous silica-modified ZSM-5 displayed a markedly different morphology characterized by a network-like architecture of interconnected fibrous structures. This highly porous framework indicated a significantly increased surface area compared to the conventional ZSM-5. The interconnected fibers created larger pore channels and void spaces,

enhancing the accessibility of reactant molecules to the active sites within the zeolite framework. This porous morphology was advantageous for applications demanding efficient mass transport and diffusion, as it facilitated the movement of larger molecules that might otherwise be hindered by the microporous structure of unmodified ZSM-5. The structural differences between the two materials underscored the critical role of morphology in tailoring zeolite-based catalysts for specific applications. The fibrous silica modification effectively altered the textural properties of ZSM-5, enhancing its suitability for diffusion-sensitive processes. For instance, in catalytic reactions involving bulky hydrocarbons or in adsorption processes requiring rapid mass transfer, the fibrous silica ZSM-5 would likely demonstrate superior performance due to its enhanced porosity and surface accessibility. These findings highlighted the significant impact of synthesis approaches on the microstructural evolution and functional properties of zeolite materials. By introducing fibrous silica during the synthesis of ZSM-5, it was possible to engineer the catalyst's morphology to meet specific performance criteria. The increased mesoporosity and altered pore connectivity in fibrous silica ZSM-5 not only improved mass transport but might also influence the distribution and strength of acid sites, which are crucial for catalytic activity. Furthermore, the enhanced surface area and porosity could lead to a higher dispersion of active sites and improved interaction between the catalyst and reactant molecules. This structural modification might result in increased catalytic efficiency and selectivity, particularly in reactions where diffusion limitations are a significant concern. The fibrous silica framework could also provide additional pathways for heat and mass transfer, potentially improving the overall stability and longevity of the catalyst under reaction conditions. The comparison between conventional and fibrous silica-modified ZSM-5 emphasized the importance of tailoring catalyst morphology to optimize performance for targeted applications. It demonstrated that strategic modifications at the nanoscale

could lead to significant improvements in macroscopic properties and functionalities. Such insights are valuable for the development of advanced catalysts in the petrochemical industry, environmental remediation, and other fields where zeolite materials play a pivotal role.

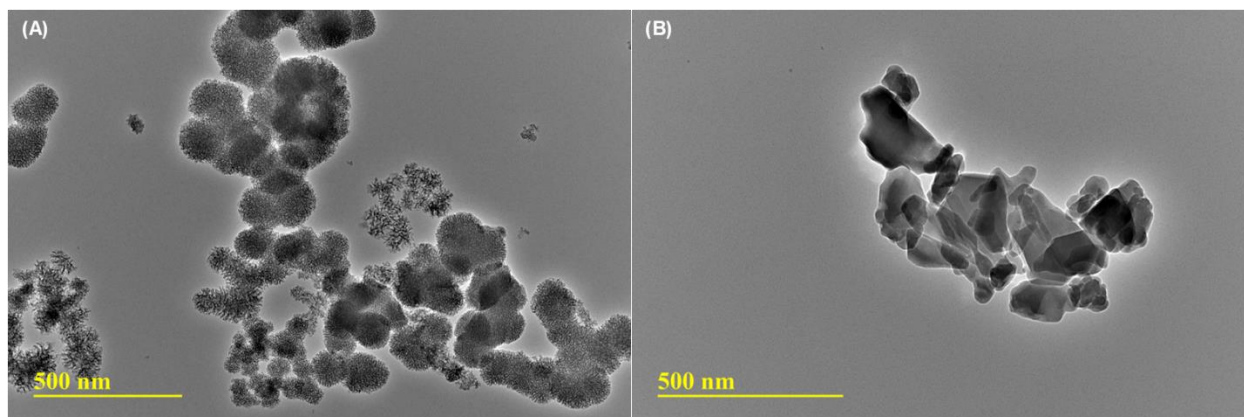


Figure 22: TEM image of ZSM-5, FSZSM-5 zeolite catalysts.

4.2.2. Catalytic Performance Tests

Figure 23 presented the yield performance of ZSM-5, fibrous silica-modified ZSM-5 (FSZSM-5), and FSZSM-5 further modified with gallium (Ga) and zinc (Zn), offering insights into how different catalysts influenced aromatic hydrocarbon production. The standard ZSM-5 catalyst demonstrated a high total aromatic yield of 47.3 wt.%, with substantial contributions from benzene (17.3 wt.%) and toluene (20.5 wt.%). The xylene yield was moderate at 6.8 wt.%, and heavier aromatics (C9+A) accounted for a minor fraction of 2.6 wt.%. These results suggested that the microporous structure of ZSM-5 favored the formation of smaller aromatic molecules like benzene and toluene but limited the production of larger ones such as xylenes and C9+A due to pore size constraints restricting their diffusion and formation.

Modification of ZSM-5 with fibrous silica to create FSZSM-5 led to a reduced total aromatic yield of 35.9 wt.%. There were notable declines in the yields of benzene (8.3 wt.%) and toluene (16.7 wt.%). However, the yield of heavier aromatics (C9+A) increased to 5.7 wt.%, indicating that the alteration of the zeolite framework affected the catalyst's acidity and diffusion properties. The introduction of fibrous silica likely altered the pore structure, possibly creating mesoporosity or changing the connectivity of the micropores, which facilitated the formation and diffusion of larger aromatic molecules at the expense of lighter ones. This shift in selectivity towards heavier aromatics suggested that the modified catalyst allowed for greater molecular mobility, enabling larger molecules to access active sites that were previously inaccessible in the unmodified ZSM-5 as shown in **Figure 23A**.

Further modification of FSZSM-5 with gallium (Ga/FSZSM-5) resulted in the highest total aromatic yield observed in the study, reaching 53.2 wt.%. This catalyst excelled in xylene production, achieving a yield of 13.2 wt.%, while maintaining high yields of benzene (17.0 wt.%) and toluene (20.9 wt.%), and minimizing the production of heavier aromatics (C9+A) to 2.0 wt.%. The incorporation of gallium into the zeolite framework likely enhanced the catalyst's dehydrogenation activity, promoting the aromatization of hydrocarbons and favoring the formation of xylenes and other lighter aromatics. Gallium is known to introduce additional Lewis acid sites and facilitate dehydrogenation reactions, which are critical in the formation of aromatic rings from aliphatic hydrocarbons. The improved performance of Ga/FSZSM-5 suggested that gallium played a significant role in modifying the electronic properties of the catalyst, enhancing its ability to produce valuable aromatic compounds like xylenes. In contrast, modification of FSZSM-5 with zinc (Zn/FSZSM-5) led to the lowest total aromatic yield among the catalysts studied, at 33.9 wt.%. The yields of benzene and toluene decreased to 14.7 wt.% and 12.3 wt.%

respectively, and the xylene yield was modest at 5.7 wt.%. The production of heavier aromatics (C9+A) was also low at 1.2 wt.%. These observations suggested that zinc modification may have reduced the catalyst's acidity or altered its active sites in a manner that was less favorable for aromatic hydrocarbon production. Zinc is often associated with hydrogenation and dehydrogenation activities, but in this context, it may have shifted the reaction pathways towards non-aromatization routes or increased the formation of light gases and olefins instead of desired aromatics.

Comparing the performance of the different catalysts, it was evident that the incorporation of gallium into FSZSM-5 significantly enhanced both the total aromatic yield and the selectivity towards xylenes, making Ga/FSZSM-5 the most effective catalyst for aromatic hydrocarbon production in this study. The results highlighted that gallium's presence enhanced the dehydrogenation steps necessary for aromatization, thereby boosting the formation of valuable aromatic compounds while suppressing the formation of heavier, less desirable by-products.

The modification with fibrous silica alone (FSZSM-5) altered the catalyst's properties in a way that shifted the product distribution towards heavier aromatics. This change could be attributed to modifications in the pore structure and acidity profile of the zeolite. The creation of additional mesoporosity or changes in pore connectivity might have allowed larger hydrocarbon intermediates to participate more readily in reactions leading to heavier aromatics. Additionally, changes in the acidity could have affected the rate and selectivity of cracking and dehydrogenation reactions.

The reduced performance of Zn/FSZSM-5 underscored the complexity of catalyst modification and the need for a nuanced understanding of how different elements interact with the zeolite

framework. While zinc can enhance certain catalytic activities, its incorporation in this case did not favor the production of aromatic hydrocarbons, possibly due to unfavorable changes in acidity or active site availability.

These findings emphasized the critical role of catalyst composition and structural modifications in determining the yield and selectivity of aromatic hydrocarbons. The ability to tailor catalyst properties through modifications such as metal incorporation and structural alteration provides a valuable tool for optimizing catalytic processes. Specifically, the enhanced performance of Ga/FSZSM-5 suggested that targeted modifications could be employed to maximize the production of desired products like xylenes, which are important precursors for industrial applications such as polyester production.

The gas product as shown in **Figure 23 B**, the unmodified ZSM-5 catalyst exhibited the highest methane (C1) yield at 22.5 wt.% and a moderate production of ethane and ethylene (C2+C2=) at 18.8 wt.%. However, its yields for propane and butane (C3+C4) and higher paraffins and olefins (P&O) were relatively limited, at 4.5 wt.% and 2.8 wt.% respectively. This distribution suggested that ZSM-5 favored the formation of lighter hydrocarbons, likely due to its microporous structure and strong acidity promoting cracking reactions that produce smaller molecules.

The incorporation of fibrous silica into ZSM-5 to form FSZSM-5 led to a substantial reduction in methane yield to 11.0 wt.% and a moderate decrease in ethane and ethylene production to 14.9 wt.%. Concurrently, there was a significant enhancement in the yields of propane and butane (9.0 wt.%) and paraffins and olefins (10.2 wt.%). This shift indicated that the fibrous silica modification altered the catalyst's properties, possibly by introducing mesoporosity and modifying the acidity profile, which in turn affected the diffusion of reactants and products within the catalyst

framework. The increased production of heavier hydrocarbons suggested that secondary cracking reactions were suppressed, allowing for the accumulation of larger hydrocarbon molecules.

Further modification of FSZSM-5 with gallium to produce Ga/FSZSM-5 resulted in an even lower methane yield of 6.9 wt.% while maintaining balanced yields of propane and butane (9.7 wt.%) and paraffins and olefins (6.2 wt.%). The decreased methane production, coupled with steady yields of heavier hydrocarbons, suggested that gallium incorporation enhanced dehydrogenation activity. Gallium is known to introduce additional Lewis acid sites and facilitate dehydrogenation processes, which promote the formation of olefins and aromatics rather than light alkanes. This modification likely shifted the reaction pathways toward the production of more valuable hydrocarbons.

Among all the catalysts studied, Zn/FSZSM-5 exhibited the lowest methane yield at 5.6 wt.% but achieved the highest production of ethane and ethylene (28.6 wt.%) and propane and butane (24.8 wt.%). This significant increase in medium-chain hydrocarbons indicated that zinc modification effectively promoted the formation of C₂–C₄ hydrocarbons, particularly olefins, which are valuable intermediates in petrochemical processes. The enhanced production of ethylene and propylene suggested that zinc sites facilitated dehydrogenation and oligomerization reactions, leading to higher olefin yields. Zinc's role in enhancing aromatization and dehydrogenation reactions is well-documented, and its incorporation into FSZSM-5 appeared to optimize these pathways.

These observations underscored the profound impact of structural modifications and metal incorporation on hydrocarbon selectivity. The fibrous silica modification altered the textural properties of the catalyst, likely increasing mesoporosity and affecting the distribution and strength

of acid sites. These changes influenced the diffusion of reactants and intermediates, as well as the accessibility of active sites, thereby affecting the reaction mechanisms and product distribution.

The incorporation of gallium and zinc introduced additional active sites that promoted specific reactions. Gallium enhanced dehydrogenation activity, favoring the formation of olefins and aromatics, while zinc promoted reactions leading to the production of light olefins and liquefied petroleum gas (LPG) components. Zn/FSZSM-5, in particular, excelled in olefin and LPG production, highlighting its potential for applications requiring high yields of medium hydrocarbons. This catalyst demonstrated superior performance in promoting medium-chain hydrocarbon formation, which is crucial for the production of key petrochemical feedstocks.

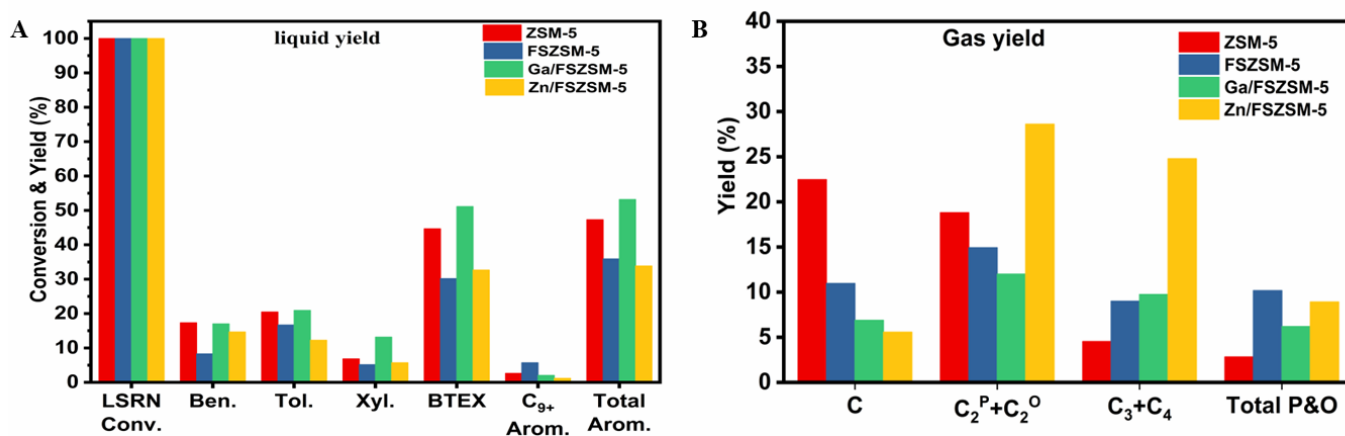


Figure 23: Comparison of the percent yield of the conversion of LSRN at 550 °C and 1.0 h⁻¹ WHSV with of ZSM-5, FSZSM-5 and modified FSZSM-5 zeolite catalysts

CHAPTER 5

Conclusion and Recommendation

5.1. Conclusion

The study of modified zeolite catalysts for the conversion of light naphtha into valuable hydrocarbons revealed significant insights into the effects of structural and compositional alterations on catalytic performance. Nano-sized ZSM-11 zeolites with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (35 and 70) effectively transformed low-value petrochemical streams into lucrative BTX aromatics. Detailed characterization using TEM, SEM, XRD, NH_3 -TPD, and BET analyses established a clear correlation between the catalysts' structural features such as surface morphology, crystallinity, acidity, and porosity and their catalytic efficiency. The addition of gallium to ZSM-11 with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 70 through incipient wetness impregnation markedly enhanced the catalyst's effectiveness, achieving nearly complete conversion of light naphtha (97–99%) and a remarkable aromatic yield of 77.8 wt% at 550°C and 1 atm. This underscores the exceptional performance of Ga-modified ZSM-11 and provides valuable guidance for the rational development of advanced catalysts aimed at producing high-quality gasoline and essential petrochemical components more economically and sustainably.

Similarly, the evaluation of ZSM-5, fibrous silica-modified ZSM-5 (FSZSM-5), and their metal-modified variants (Ga/FSZSM-5 and Zn/FSZSM-5) highlighted the profound impact of catalyst modification on the production and selectivity of aromatic hydrocarbons and gaseous products. The unmodified ZSM-5 catalyst favored the formation of lighter aromatics such as benzene and toluene, a result attributed to its microporous structure and strong acidity promoting cracking reactions that yield smaller molecules. However, it proved less effective in producing larger

aromatics like xylenes due to pore size limitations. Modification with fibrous silica to create FSZSM-5 altered the pore structure and acidity of the catalyst, leading to a reduction in total aromatic yield and a shift in selectivity towards heavier aromatics (5.7 wt%). The introduction of fibrous silica likely increased mesoporosity or changed micropore connectivity, facilitating the formation and diffusion of larger aromatic molecules while suppressing secondary cracking reactions. This resulted in decreased methane production and enhanced yields of propane, butane, and higher paraffins and olefins. The incorporation of gallium into FSZSM-5 (Ga/FSZSM-5) significantly enhanced both the total aromatic yield to 53.2 wt% and the selectivity towards xylenes to 13.2 wt%, establishing it as the most effective catalyst for aromatic hydrocarbon production in this study. Gallium's presence enhanced dehydrogenation activity, promoting aromatization processes that favored the formation of valuable lighter aromatics while minimizing heavier by-products. In terms of gaseous products, Ga/FSZSM-5 further reduced methane yield while maintaining balanced yields of heavier hydrocarbons, indicating a shift towards more valuable hydrocarbon formations. In contrast, zinc modification of FSZSM-5 (Zn/FSZSM-5) resulted in the lowest total aromatic yield and reduced production of benzene, toluene, and xylenes. This suggests that zinc may have unfavorably altered the catalyst's acidity or active sites, possibly shifting reaction pathways towards non-aromatization routes or increasing the formation of light gases and olefins. However, Zn/FSZSM-5 excelled in producing ethane and ethylene (28.6 wt%) as well as propane and butane (24.8 wt%), indicating its effectiveness in promoting the formation of medium-chain hydrocarbons particularly valuable olefins used in petrochemical processes. These findings highlight the critical role of tailored catalyst design in optimizing hydrocarbon conversion processes. Adjusting structural properties and incorporating specific metals into zeolite frameworks can significantly influence the yield and selectivity of desired products. The enhanced

performance of gallium-modified catalysts in producing high yields of aromatics, especially xylenes, offers valuable insights for developing advanced catalysts. Such catalysts hold promise for more efficient and sustainable production of high-quality fuels and key petrochemical intermediates, aligning with industry goals for economic viability and environmental stewardship.

5.2.Recommendations

Based on the observed results, the following recommendations are proposed:

1. **Industrial Application of Ga/FSZSM-5:** For processes aiming to maximize the production of valuable aromatic compounds like xylenes, Ga/FSZSM-5 is recommended due to its enhanced dehydrogenation activity and superior performance in producing lighter aromatics.
2. **Utilization of Zn/FSZSM-5 for Olefin Production:** Zn/FSZSM-5 should be considered for applications requiring high yields of light olefins and liquefied petroleum gas (LPG) components.
3. **Further Research on Catalyst Mechanisms:** Investigations into the mechanistic pathways by which gallium and zinc modifications influence catalyst activity and selectivity are recommended.
4. **Exploration of Co-Modification Strategies in nano ZSM-11& FSZSM-5:** Exploring the co-incorporation of Mo and Pt gallium and zinc or other metal promoters may yield catalysts with synergistic effects, potentially combining the benefits of enhanced aromatization and olefin production. Such studies could lead to catalysts with tailored performance profiles suitable for a broader range of industrial applications.

5. **Assessment of Catalyst Stability:** Evaluating the long-term stability and resistance to deactivation of these modified catalysts under industrial operating conditions is crucial.

References

- [1] Fan Y, Bao X, Lei D, Shi G, Wei W, Xu J. A novel catalyst system based on quadruple silicoaluminophosphate and aluminosilicate zeolites for FCC gasoline upgrading. *Fuel* 2005;84:435–42. <https://doi.org/10.1016/j.fuel.2004.09.010>.
- [2] Development of OTA technology for olefin removal of full range FCC gasoline | Request PDF n.d. https://www.researchgate.net/publication/290711938_Development_of_OTA_technology_for_olefin_removal_of_full_range_FCC_gasoline (accessed July 28, 2024).
- [3] Alabdullah MA, Gomez AR, Vittenet J, Bendjeriou-Sedjerari A, Xu W, Abba IA, et al. A Viewpoint on the Refinery of the Future: Catalyst and Process Challenges. *ACS Catal* 2020;10:8131–40. <https://doi.org/10.1021/acscatal.0c02209>.
- [4] Jarvis J, He P, Wang A, Song H. Pt-Zn/HZSM-5 as a highly selective catalyst for the Co-aromatization of methane and light straight run naphtha. *Fuel* 2019;236:1301–10. <https://doi.org/10.1016/j.fuel.2018.09.109>.
- [5] Chica A, Corma A. Hydroisomerization of Pentane, Hexane, and Heptane for Improving the Octane Number of Gasoline. vol. 187. 1999.
- [6] Akhtar MN, Aitani AM, Ummer AC, Alasiri HS. Review on the Catalytic Conversion of Naphtha to Aromatics: Advances and Outlook. *Energy and Fuels* 2023;37:2586–607. <https://doi.org/10.1021/acs.energyfuels.2c03716>.
- [7] Gallucci F, Paturzo L, Basile A. An experimental study of CO₂ hydrogenation into methanol involving a zeolite membrane reactor. *Chemical Engineering and Processing: Process Intensification* 2004;43:1029–36. <https://doi.org/10.1016/j.cep.2003.10.005>.
- [8] Cheremisinoff NP, Rosenfeld P. The petroleum industry. *Handbook of Pollution Prevention and Cleaner Production - Best Practices in The Petroleum Industry* 2009:1–97. <https://doi.org/10.1016/B978-0-8155-2035-1.10001-6>.
- [9] Zeng D, Zhu G, Xia C. Recent advances of aromatization catalysts for C₄ hydrocarbons. *Fuel Processing Technology* 2022;226. <https://doi.org/10.1016/j.fuproc.2021.107087>.
- [10] Csicsery SM. Dehydrocyclodimerization I. Dehydrocyclodimerization of Butanes over Supported Platinum Catalysts. vol. 17. 1970.
- [11] Koklin AE, Kalenchuk AN, Mashchenko N V., Lunin V V., Bogdan VI. Dehydrocyclodimerization of n-Butane into Aromatic Hydrocarbons in the Gas-Phase and under Supercritical Conditions on a ZSM-5 Zeolite in the H-Form and Modified with Ga

- or Pt. Russian Journal of Physical Chemistry B 2020;14:1277–81.
<https://doi.org/10.1134/S1990793120080035>.
- [12] Mohaddecy RS, Abghari SZ, Sadighi S, Seif Mohaddecy SR, Zahedi S, Sadighi S, et al. REACTOR MODELING AND SIMULATION OF CATALYTIC REFORMING PROCESS. vol. 48. 2006.
 - [13] Arslan MT, Qureshi BA, Gilani SZA, Cai D, Ma Y, Usman M, et al. Single-Step Conversion of H₂-Deficient Syngas into High Yield of Tetramethylbenzene. ACS Catal 2019;9:2203–12. <https://doi.org/10.1021/acscatal.8b04548>.
 - [14] Liu R-L, Hua-Qing Z, Zhi-Wei WU, Zhang-Feng Q, Wei-Bin F, Wang J-G. Foundation Item: the National Basic Research Program of China (973 Program, 2011CB201403, 2011CB201406) and National Natural Science Foundation of China (21273264). vol. 43. 2015.
 - [15] Aitani A, Akhtar MN, Al-Khattaf S, Jin Y, Koseoglo O, Klein MT. Catalytic Upgrading of Light Naphtha to Gasoline Blending Components: A Mini Review. Energy and Fuels 2019;33:3828–43. <https://doi.org/10.1021/acs.energyfuels.9b00704>.
 - [16] Talaghat MR, Karimi MS. Operation parameters effect on yield and octane number for monometallic, bimetallic and trimetallic catalysts in naphtha reforming process. Energy Sources, Part A: Recovery, Utilization and Environmental Effects 2020;42:176–93. <https://doi.org/10.1080/15567036.2019.1587064>.
 - [17] James G. The Chemistry and Technology of Petroleum FOURTH EDITION. n.d.
 - [18] Aboul-Gheit AK, Ghoneim SA-W. Catalysis in the Petroleum Naphtha Catalytic Reforming Process. Recent Patents on Chemical Engineering 2012;1:113–25. <https://doi.org/10.2174/2211334710801020113>.
 - [19] Aboul-Gheit NAK. Effect of hydrohalogenation of metal/zeolite catalysts for cyclohexene hydroconversion -Part 3- Pd/H-ZSM-5 catalysts. Journal of the Chinese Chemical Society 2007;54:1211–22. <https://doi.org/10.1002/jccs.200700172>.
 - [20] Elsayed HA, Menoufy MF, Shaban SA, Ahmed HS, Heakal BH. Optimization of the reaction parameters of heavy naphtha reforming process using Pt-Re/Al₂O₃ catalyst system. Egyptian Journal of Petroleum 2017;26:885–93. <https://doi.org/10.1016/j.ejpe.2015.03.009>.
 - [21] Pastrana-Martínez LM, Morales-Torres S, Maldonado-Hódar FJ. A Comparative Study of Aromatization Catalysts: The Advantage of Hybrid Oxy/Carbides and Platinum-Catalysts Based on Carbon Gels. C (Basel) 2021;7:21. <https://doi.org/10.3390/c7010021>.

- [22] Tshabalala TE. Aromatization of n-Hexane over Metal Modified H-ZSM-5 Zeolite Catalysts. 2009.
- [23] Xu Y, Lin L. Recent advances in methane dehydro-aromatization over transition metal ion-modified zeolite catalysts under non-oxidative conditions. *Appl Catal A Gen* 1999;188:53–67. [https://doi.org/10.1016/S0926-860X\(99\)00210-0](https://doi.org/10.1016/S0926-860X(99)00210-0).
- [24] Shu Y, Ichikawa M. Catalytic dehydrocondensation of methane towards benzene and naphthalene on transition metal supported zeolite catalysts: templating role of zeolite micropores and characterization of active metallic sites. vol. 71. 2001.
- [25] Tshabalala TE. Aromatization of n-Hexane over Metal Modified H-ZSM-5 Zeolite Catalysts. 2009.
- [26] Ummer AC, Akhtar MN, Alnaimi E, Ding L, Alasiri HS. Aromatization of Commercial Full Range Naphtha Over Modified Hierarchical ZSM-5 Catalyst. *ChemistrySelect* 2021;6:11541–50. <https://doi.org/10.1002/slct.202103033>.
- [27] Zeng D, Zhu G, Xia C. Recent advances of aromatization catalysts for C4 hydrocarbons. *Fuel Processing Technology* 2022;226. <https://doi.org/10.1016/j.fuproc.2021.107087>.
- [28] Al Ghatta A, Hallett JP. Bioderived furanic compounds as replacements for BTX in chemical intermediate applications. *RSC Sustainability* 2023;1:698–745. <https://doi.org/10.1039/d3su00038a>.
- [29] Ellouh M, Qureshi ZS, Aitani A, Akhtar MN, Jin Y, Koseoglu O, et al. Light Paraffinic Naphtha to BTX Aromatics over Metal-Modified Pt/ZSM-5. *ChemistrySelect* 2020;5:13807–13. <https://doi.org/10.1002/slct.202003492>.
- [30] Caeiro G, Carvalho RH, Wang X, Lemos MANDA, Lemos F, Guisnet M, et al. Activation of C2-C4 alkanes over acid and bifunctional zeolite catalysts. *J Mol Catal A Chem* 2006;255:131–58. <https://doi.org/10.1016/j.molcata.2006.03.068>.
- [31] Cundy CS, Cox PA. The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time. *Chem Rev* 2003;103:663–701. <https://doi.org/10.1021/CR020060I>.
- [32] Lukyanov DB, Gnep NS, Guisnet MR. Kinetic modeling of ethene and propene aromatization over HZSM-5 and GaHZSM-5. *Industrial and Engineering Chemistry Research*; (United States) 1994;33:2:223–34. <https://doi.org/10.1021/IE00026A008>.
- [33] Catlow CRA, Bell RG, Gale JD, Lewis DW. Modelling of structure and reactivity in zeolites. *Stud Surf Sci Catal* 1995;97:87–100. [https://doi.org/10.1016/S0167-2991\(06\)81877-X](https://doi.org/10.1016/S0167-2991(06)81877-X).

- [34] Colella C. Zeolites and Ordered Mesoporous Materials: Progress and Prospects. *Stud Surf Sci Catal* 2005;157:13–40.
- [35] Aitani A, Akhtar MN, Al-Khattaf S, Jin Y, Koseoglu O, Klein MT. Catalytic Upgrading of Light Naphtha to Gasoline Blending Components: A Mini Review. *Energy and Fuels* 2019;33:3828–43. <https://doi.org/10.1021/acs.energyfuels.9b00704>.
- [36] Yuan K, Jia XY, Wang S, Fan S, He SP, Wang PF, et al. Effect of crystal size of ZSM-11 zeolite on the catalytic performance and reaction route in methanol to olefins. *Chemical Synthesis* 2023;3. <https://doi.org/10.20517/cs.2023.19>.
- [37] Shen Y, Le TT, Fu D, Schmidt JE, Filez M, Weckhuysen BM, et al. Deconvoluting the Competing Effects of Zeolite Framework Topology and Diffusion Path Length on Methanol to Hydrocarbons Reaction. *ACS Catal* 2018;8:11042–53. <https://doi.org/10.1021/acscatal.8b02274>.
- [38] Al-Eid M, Ding, L, Sewdan D, AL-Shafei E, Al-Ghamdi R, Alqarawi A, et al. Effect of ZSM-5 Particle Size and Framework Silica-to-Alumina Ratio on Hexane Aromatization. *Catalysis Research* 2022;02:1–19. <https://doi.org/10.21926/cr.2204035>.
- [39] Imai H, Takada M, Ike Y. Synthesis of zeolite catalysts containing Zn and Ga for aromatization of n-hexane. *Journal of the Japan Petroleum Institute* 2021;64:293–301. <https://doi.org/10.1627/jpi.64.293>.
- [40] Lukyanov DB, Gnep NS, Guisnet MR. Kinetic Modeling of Propane Aromatization Reaction over HZSM-5 and GaHZSM-5. vol. 34. 1995.
- [41] Krannila H, Haag, WO, Gates BC. Monomolecular and Bimolecular Mechanisms of Paraffin Cracking: n-Butane Cracking Catalyzed by HZSM-5. vol. 135. 1992.
- [42] Gnep NS, Doyemet JY, Sec0 AM, Ribeiro FR, Guisnet M. Conversion of Light Alkanes into Aromatic Hydrocarbons: 1-Dehydrocyclodimerization of Propane on PtHZSM-5 Catalysts. 1987.
- [43] Xin M, Xing E, Gao X, Wang Y, Ouyang Y, Xu G, et al. Ga Substitution during Modification of ZSM-5 and Its Influences on Catalytic Aromatization Performance. *Ind Eng Chem Res* 2019;58:6970–81. <https://doi.org/10.1021/acs.iecr.9b00295>.
- [44] Mériaudeau P, Naccache C. Dehydrocyclization of alkanes over zeolite-supported metal catalysts: Monofunctional or bifunctional route. *Catal Rev Sci Eng* 1997;39:5–48. <https://doi.org/10.1080/01614949708006467>.
- [45] Ono Y. Transformation of Lower Alkanes into Aromatic Hydrocarbons over ZSM-5 Zeolites. *Catalysis Reviews* 1992;34:179–226. <https://doi.org/10.1080/01614949208020306>.

- [46] Van Duin JJB. Aromatization of Ketones over Zeolite Catalysts. 2018.
- [47] Vorobkalo VA, Knyazeva EE, Ivanova II. MEL Zeolites: Synthesis, Properties, and Catalytic Applications. *Petroleum Chemistry* 2021;61:299–324.
<https://doi.org/10.1134/S0965544121030099>.
- [48] Pornsetmetakul P, Mainewawklang N, Wattanakit C. Preparation of Metal-Supported Nanostructured Zeolite Catalysts and their Applications in the Upgrading of Biomass-Derived Furans: Advances and Prospects. *Chempluschem* 2024.
<https://doi.org/10.1002/cplu.202400343>.
- [49] Vichaphund S, Aht-Ong D, Sricharoenchaikul V, Atong D. Production of aromatic compounds from catalytic fast pyrolysis of Jatropha residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods. *Renew Energy* 2015;79:28–37.
<https://doi.org/10.1016/J.RENENE.2014.10.013>.
- [50] Tshabalala TE. Aromatization of n-Hexane over Metal Modified H-ZSM-5 Zeolite Catalysts. 2009.
- [51] Nguyen LH, Vazhnova T, Kolaczowski ST, Lukyanov DB. Combined experimental and kinetic modelling studies of the pathways of propane and n-butane aromatization over H-ZSM-5 catalyst. *Chem Eng Sci* 2006;61:5881–94.
<https://doi.org/10.1016/j.ces.2006.05.017>.
- [52] Qureshi ZS, Ellouh M, Aitani A, Akhtar MN, Jin Y, Koseoglu O, et al. Efficient conversion of light paraffinic naphtha to aromatics over metal-modified Mo/MFI catalysts. *Journal of Porous Materials* 2022;29:683–92. <https://doi.org/10.1007/s10934-022-01196-3>.
- [53] Tshabalala TE, Scurrrell MS. Aromatization of n-hexane over Ga, Mo and Zn modified H-ZSM-5 zeolite catalysts. *Catal Commun* 2015;72:49–52.
<https://doi.org/10.1016/j.catcom.2015.06.022>.
- [54] Shi Y, Zhou Q, Qin Z, Wu Z, Jiao W, Dong M, et al. Promoting effect of alkali metal on the catalytic performance of hierarchical Pt/Beta in the aromatization of n-heptane. *Microporous and Mesoporous Materials* 2022;343.
<https://doi.org/10.1016/j.micromeso.2022.112189>.
- [55] Xu D, Wu B, Ren P, Wang S, Huo C, Zhang B, et al. Controllable deposition of Pt nanoparticles into a KL zeolite by atomic layer deposition for highly efficient reforming of n-heptane to aromatics. *Catal Sci Technol* 2017;7:1342–50.
<https://doi.org/10.1039/c6cy02652d>.

- [56] Akhtar MN, Al-Yassir N, Al-Khattaf S, Čejka J. Aromatization of alkanes over Pt promoted conventional and mesoporous gallosilicates of MEL zeolite. *Catal Today*, vol. 179, 2012, p. 61–72. <https://doi.org/10.1016/j.cattod.2011.06.036>.
- [57] Zhang L, Liu H, Li X, Xie S, Wang Y, Xin W, et al. Differences between ZSM-5 and ZSM-11 zeolite catalysts in 1-hexene aromatization and isomerization. *Fuel Processing Technology* 2010;91:449–55. <https://doi.org/10.1016/j.fuproc.2009.12.003>.
- [58] Anunziata OA, Pierella LB, Marino RG. SELECTIVE TRANSFORMATION OF LIGHT OLEFINS INTO AROMATIC HYDROCARBONS OVER PENTASIL ZEOLITES. vol. 54. 1995.
- [59] Hambali HU, Jalil AA, Abdulrasheed AA, Siang TJ, Abdullah TAT, Ahmad A, et al. Fibrous spherical Ni-M/ZSM-5 (M: Mg, Ca, Ta, Ga) catalysts for methane dry reforming: The interplay between surface acidity-basicity and coking resistance. *Int J Energy Res* 2020;44:5696–712. <https://doi.org/10.1002/er.5327>.
- [60] Firmansyah ML, Jalil AA, Triwahyono S, Hamdan H, Salleh MM, Ahmad WFW, et al. Synthesis and characterization of fibrous silica ZSM-5 for cumene hydrocracking. *Catal Sci Technol* 2016;6:5178–82. <https://doi.org/10.1039/c6cy00106h>.
- [61] Hambali HU, Jalil AA, Triwahyono S, Jamian SF, Fatah NAA, Abdulrasheed AA, et al. Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol. *Int J Hydrogen Energy* 2021;46:24652–65. <https://doi.org/10.1016/j.ijhydene.2019.11.236>.
- [62] Afiq M, Aziz H, Mamat CR, Jalil AA. Synthesis of Ruthenium Supported on Protonated Fibrous Silica ZSM-5 for Methanol to Olefin Reaction. vol. 3. 2018.
- [63] Meng X, Chen C, Liu J, Zhang Q, Li C, Cui Q. Effects of zinc incorporation on hierarchical ZSM-11 catalyst for methanol conversion. *Appl Petrochem Res* 2016;6:41–7. <https://doi.org/10.1007/s13203-015-0120-3>.
- [64] Synthesis and structure of synthetic zeolite ZSM-11 1978.
- [65] Yu Q, Li C, Tang X, Yi H. One-step synthesis, characterization and catalytic performance of hierarchical Zn-ZSM-11 via facile ZnO routes † 2015. <https://doi.org/10.1039/c4ra14375b>.
- [66] Hambali HU, Jalil AA, Triwahyono S, Jamian SF, Fatah NAA, Abdulrasheed AA, et al. Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol. *Int J Hydrogen Energy* 2021;46:24652–65. <https://doi.org/10.1016/j.ijhydene.2019.11.236>.

- [67] Firmansyah ML, Jalil AA, Triwahyono S, Hamdan H, Salleh MM, Ahmad WFW, et al. Synthesis and characterization of fibrous silica ZSM-5 for cumene hydrocracking. *Catal Sci Technol* 2016;6:5178–82. <https://doi.org/10.1039/c6cy00106h>.
- [68] Zhang C, Kwak G, Lee YJ, Jun KW, Gao R, Park HG, et al. Light hydrocarbons to BTEX aromatics over Zn-modified hierarchical ZSM-5 combined with enhanced catalytic activity and stability. *Microporous and Mesoporous Materials* 2019;284:316–26. <https://doi.org/10.1016/j.micromeso.2019.04.041>.

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❖ Conference Presentation

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BTX production from aromatization of light naphtha over modified ZSM-11 with Gallium. Technical session presented at ChemIndix conference.

❖ Area of interest:

- Teaching
- Research: conversion of crude to Chemical (Heterogenous catalysis)