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Research Article

Catalyzing Organic Reactions Using Environmentally Friendly Green Catalysts: An Applied Study on Alkylation Reactions

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Abstract:

Amid the global shift towards green chemistry and the growing demand to reduce the environmental impact of chemical processes, this study investigates the effectiveness of a modified natural zeolite catalyst as a sustainable alternative to conventional, toxic alkylation catalysts such as aluminum chloride. A series of controlled laboratory experiments were conducted to compare the green and traditional catalysts in terms of reaction yield, product purity, ease of catalyst separation, environmental safety, economic feasibility, and catalyst reusability.

The experimental results revealed that the green catalyst achieved a yield of **84% ± 1.2** compared to **88% ± 1.5** for aluminum chloride. The product purity was **91% ± 0.8** with the green catalyst versus **93% ± 0.6** with the conventional catalyst. Additionally, the green catalyst demonstrated excellent ease of recovery and could be reused for up to **three consecutive cycles** with only a **3–4% decrease in activity**. Analytical techniques including Gas Chromatography–Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR), and Proton Nuclear Magnetic Resonance (^{1}H-NMR) confirmed the identity and purity of the reaction product, ethylbenzene.

This research highlights the practical potential of natural zeolite-based catalysts in promoting greener chemical synthesis. The findings support the adoption of green catalytic systems as viable, eco-friendly alternatives for industrial organic transformations, particularly in alkylation reactions.

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Introduction

Alkylation reactions are among the most important transformations in organic and industrial chemistry, widely applied in the production of pharmaceuticals, fine chemicals, and petrochemicals. They enable the functionalization of aromatic compounds, improving physicochemical properties and expanding their industrial utility. Traditionally, these reactions are catalyzed by strong Lewis acids such as aluminum chloride ($AlCl_3$) or concentrated mineral acids. While effective, such catalysts present significant drawbacks: high toxicity, corrosiveness, generation of hazardous acidic waste, and poor reusability, all of which limit their environmental and economic sustainability.

In line with the principles of green chemistry, research has increasingly focused on developing eco-friendly and recyclable catalytic systems. Natural and modified zeolites, in particular, have emerged as promising heterogeneous catalysts due to their high surface area, tunable acidity, and thermal stability. Recent studies have reported zeolite-based catalysts achieving yields comparable to $AlCl_3$ while reducing waste and enabling catalyst reuse (Li et al., 2019; Zhang et al., 2022). Other approaches include the use of plant-derived catalysts (Ruslan et al., 2021) and advanced solid frameworks such as metal-organic frameworks (MOFs), which offer high porosity and selectivity (Dechamorphy & Garcia, 2014). These green alternatives not only improve reaction efficiency but also align with global sustainability goals by minimizing hazardous by-products and lowering energy consumption.

This study aims to evaluate the catalytic performance of a modified natural zeolite in the alkylation of benzene with ethyl chloride, compared to the conventional $AlCl_3$ catalyst. Particular attention is given to reaction yield, product purity, catalyst recyclability, and environmental impact, with the goal of assessing the practical feasibility of natural zeolite as a green alternative for industrial alkylation processes.

Significance of the Research

This work contributes to the global shift toward sustainable chemical processes by evaluating natural zeolite as a green alternative to conventional Lewis acid catalysts in alkylation. Conventional systems such as $AlCl_3$ are efficient but hazardous, producing corrosive waste and posing disposal challenges. Developing biodegradable and non-toxic catalysts addresses both environmental and economic concerns. This study therefore provides practical insights into the performance of zeolite under laboratory conditions and supports the search for scalable, eco-friendly catalytic systems.

Research Problem

Although green chemistry has been widely discussed, its translation into practical catalytic systems for alkylation remains limited. Many reported green catalysts suffer from reduced selectivity or stability compared to $AlCl_3$. This research addresses the gap by experimentally testing a modified natural zeolite and evaluating its yield, purity, and reusability under controlled reaction conditions.

Research Questions

1. Can modified natural zeolite catalyze aromatic alkylation with efficiency comparable to $AlCl_3$?
2. How do yield and product purity differ between the two catalysts?
3. To what extent is the zeolite catalyst reusable compared with $AlCl_3$?
4. What environmental trade-offs are associated with replacing $AlCl_3$ with zeolite?
5. Does zeolite offer a cost-effective and sustainable option for broader industrial application?

Research Objectives

1.Quantitatively compare the catalytic performance of $AlCl_3$ and modified zeolite in benzene alkylation.
2.Assess yield, selectivity, and purity of products using GC-MS, FTIR, and ^{1}H-NMR.
3.Examine catalyst separation and reusability over multiple cycles.
4.Evaluate environmental and economic benefits and limitations of the green catalyst.
5.Provide preliminary recommendations for extending zeolite use to industrial processes.

Research Hypotheses

1.Modified natural zeolite can deliver yields and purity comparable to $AlCl_3$.
2.Zeolite is safer to handle and generates less hazardous waste.
3.Optimal reaction conditions enhance the catalytic efficiency of zeolite.
4.The use of zeolite does not compromise product quality.

Research Methodology

A laboratory-based experimental design was adopted, comparing $AlCl_3$ and modified natural zeolite under identical conditions (60 °C, 90 min, fixed catalyst loading). Reaction outcomes were analyzed in triplicate to ensure reproducibility. Product characterization was performed using **GC-MS** (identity, retention time), **FTIR** (functional group confirmation), and **^{1}H-NMR** (structural verification). Catalyst stability was evaluated through reusability tests and post-reuse characterization (XRD, SEM, BET).

Research Limits

1.Restricted to a single model reaction (benzene alkylation).
2.Only one type of natural zeolite catalyst was tested.
3.Results are limited to laboratory scale and serve as **preliminary indicators**, not industrial validation.
4.Analytical methods were limited to instruments available in the university laboratory.

Previous Studies

1. Al-Sayed, Muhammad (2020) – "Applications of Natural Catalysts in Organic Reactions – An Experimental Study"

This study, published in the Arab Journal of Green Chemistry, examined the effectiveness of several natural catalysts derived from plant sources, such as citrus peel extract and palm fiber, in accelerating alkylation and esterification reactions. The results indicated that these catalysts demonstrated good efficiency under moderate temperature and pressure conditions, achieving high reaction yields while minimizing organic waste. The study also demonstrated the possibility of reusing some catalysts for up to five cycles without a noticeable decrease in performance.

2. Al-Shammari, Nada Abdullah (2021) – "Effectiveness of Clay Catalysts in Organic Reactions with Low Environmental Impact"

In this study, published in the Journal of Applied Chemistry – University of Baghdad, Iraqi clay zeolite was used as a catalyst in alkylation and esterification reactions. The study provided locally manufactured, low-cost, and highly effective alternatives. The results showed that the local zeolite possesses good catalytic acceleration capacity with suitable thermal stability, and reduced effluent production by over 60% compared to conventional metal catalysts.

3. Corma & Garcia (2008) - "Gold Nanoparticles as Green Catalysts in Organic Reactions"

This study discussed the potential of using gold nanoparticles as green catalysts in organic reactions, particularly in alkylation reactions. The researchers demonstrated that nanogold has a high surface area that can enhance reaction speed while reducing the need for harmful temperatures. The results showed that the use of these catalysts achieves high yields with a significant reduction in effluent and gaseous waste, making them an environmentally and economically sustainable option compared to conventional heavy metal catalysts. The research also indicated that these catalysts can be reused multiple times without significant loss of efficiency, which supports industrial sustainability.

4. Dechamorphy & Garcia (2014) - "Metal-Organic Frameworks as Solid Catalysts for Alkylation Reactions"

This study examined metal-organic frameworks (MOFs) as solid catalysts with unique properties such as high porosity and large surface area. The research focused on the possibility of modifying these frameworks to improve alkylation reactions, as they provide a controllable catalytic environment through modification of the metal-organic structure. The results demonstrated that the use of MOFs reduces the use of toxic liquid catalysts and enables cleaner reaction processes with high yields and high product purity. It was also confirmed that these materials are environmentally friendly and reusable, opening new avenues for sustainable industrial applications.

1. Sheldon (2012) - "Green Chemistry and Catalysis"

In this study, the researcher reviewed the basic principles of green chemistry, focusing on the importance of catalysts in achieving these principles. He emphasized that the use of green catalysts contributes to reducing raw material consumption, decreasing hazardous waste production, and improving energy efficiency. The study also presented several examples of environmentally friendly catalysts that can be used in alkylation and other reactions, highlighting the role of catalysts in chemicals or high increasing selectivity and reducing negative environmental impacts. The study concluded that applying these principles in the laboratory and industry is essential to achieving the sustainability of modern chemistry.

2. Anastas & Warner (1998) - "Green Chemistry: Theory and Practice"

This work is considered one of the most important references that laid the foundations of green chemistry. The authors discussed the ten principles of green chemistry that aim to reduce or eliminate the use of harmful substances and minimize waste. The study highlighted the importance of designing green catalysts that allow reactions to be carried out efficiently under moderate conditions of temperature and pressure. He also pointed out that adopting these principles contributes to better environmental protection and reduces industrial costs in the long term. The study provided an important theoretical and practical framework for the development of green catalysts, including natural zeolites and plant catalysts.

3. Harra (2008) - "Review on Green Catalysts in Organic Alkylation"

This review focused on the role of green catalysts such as natural zeolites, plant extracts, and some processed mineral materials in organic alkylation reactions. The study demonstrated that these catalysts are characterized by their ability to achieve reactions with good yields and high selectivity while significantly reducing the toxic waste generated by conventional catalysts. It also demonstrated that the ease of preparation and low cost of these catalysts support their application in industrial processes. The study pointed out the challenges related to standardizing reaction conditions and the need for further research to improve the stability and efficiency of these catalysts.

4. Li, X., Wang, Y., & Chen, Z. (2019) – "Zeolite-based Catalysts for Green Organic Synthesis: A Review": This study provided a comprehensive review of the use of various types of natural and modified zeolite catalysts in organic reactions,

particularly in alkylation and oxidation processes. The researchers noted that zeolite's porous structure and moderate surface acidity make it ideal for efficient and selective catalysts, with the potential for reusability over multiple cycles. The study also recommended promoting the use of this type of catalyst in developing industries with limited environmental resources.

5. Zhang, H., Liu, J., & Zhao, F. (2022) – "Sustainable Alkylation Using Recyclable Heterogeneous Catalysts": This recent study focused on the development of reusable heterogeneous catalysts for industrial alkylation reactions, using metal bases mounted on silica materials such as SBA-15 and modified zeolite. The results showed that these catalysts achieved high reaction yields, reaching 90% in some cases, and were used in continuous flow systems without a decrease in catalytic activity. The study provided a model for applying green catalysts in a realistic industrial setting with minimal environmental impact.

Chapter One:General Concepts of Organic Reactions and Catalysis

1.1 Organic Reactions: Definition and Importance:

Organic reactions are fundamental processes in which carbon-containing compounds are transformed through bond breaking and formation, often involving functional groups such as hydroxyl (-OH), amine ($-NH_2$), or carbonyl (C=O) [1]. These transformations underpin many industrial sectors, including pharmaceuticals, polymers, agriculture, and petrochemicals [2]. With increasing emphasis on sustainability, research now focuses not only on synthetic efficiency but also on reducing environmental impact.

1.2 Main Types of Organic Reactions

Organic reactions can be broadly categorized as follows:

a) **Substitution reactions**: Replacement of one atom or group with another, as in
b) nucleophilic or electrophilic aromatic substitution [3][4].
c) **Addition reactions**: Insertion of atoms across unsaturated bonds, widely applied in alcohol and halide synthesis [5].
d) **Elimination reactions**: Removal of groups (e.g., water, HX) to generate double or triple bonds [6].
e) **Rearrangement reactions**: Structural reorganization within molecules to yield more stable or active products [7].
f) **Oxidation–reduction reactions**: Changes in oxidation state, e.g., alcohols to aldehydes or carboxylic acids [8].

These categories provide the mechanistic basis for designing new synthetic routes, optimizing selectivity, and integrating environmentally friendly approaches.

1.3 The Concept of Chemical Catalysis

Catalysis accelerates chemical reactions by lowering the activation energy barrier without the catalyst itself being consumed. By providing an alternative pathway with lower transition energy, catalysts not only increase the rate of reaction but also influence direction and selectivity [9]. Catalysis is broadly classified into:

a) **Homogeneous catalysis**, where catalyst and reactants share the same phase, typically liquid.
b) **Heterogeneous catalysis**, where catalyst and reactants are in different phases,

such as solid catalysts in petrochemical processes [10].

This concept underpins much of the modern chemical industry, allowing reactions to proceed at lower temperatures with higher efficiency and reduced waste.

1.4 Types of Catalysts

Catalysts can be grouped according to their chemical nature [11]:

a) **Acid catalysts** (H_2SO_4, $AlCl_3$) that activate C–O and C=C bonds.
b) **Base catalysts** (NaOH, K_2CO_3, amines) that generate reactive anions.
c) **Metal catalysts** (Pd, Pt, Ni) widely used in hydrogenation and coupling reactions.
d) **Enzyme catalysts** with high substrate selectivity, increasingly applied in biomanufacturing.
e) **Green catalysts**, including natural zeolites, nanoscale oxides, plant extracts, and biodegradable polymers, which combine efficiency with low toxicity and reusability.

Each category offers distinct advantages in selectivity, stability, and sustainability, making the choice of catalyst reaction-specific [12].

1.5 The Role of Catalysts in Modern Chemistry

Catalysts improve efficiency and sustainability by:

1. **Accelerating reactions**, reducing completion times.
2. **Improving selectivity**, directing reactions toward desired products.
3. **Lowering energy demands**, enabling milder operating conditions.
4. **Enhancing environmental compatibility**, particularly when green catalysts are employed [13][14].

Developing robust, recyclable, and eco-friendly catalysts has thus become a strategic goal in modern chemistry, directly addressing global sustainability challenges.

Chapter Two:Green Chemistry and Environmental Catalysts

2.1 The Concept of Green Chemistry

Green chemistry is the design of products and processes that minimize or eliminate hazardous substances, with the goal of preventing pollution at its source rather than managing it afterward [15]. Emerging in the 1990s, it integrates principles from chemistry, environmental science, and engineering to create safer and more sustainable reactions [16]. Central strategies include maximizing atom economy, employing reusable catalysts, replacing toxic solvents with biodegradable or aqueous systems, and conducting reactions under milder conditions [17]. These approaches not only support compliance with international environmental standards but also reduce the carbon footprint of chemical industries.

2.2 The Twelve Principles of Green Chemistry

Anastas and Warner's twelve principles (1998) form the framework for sustainable chemical design [18]. Key principles most relevant to catalysis include:

a) **Pollution prevention** through cleaner synthesis routes.
b) **Atom economy and fewer reaction steps** to minimize waste.
c) **Use of safer solvents** or solvent-free conditions.
d) **Catalysis instead of stoichiometric reagents** to improve efficiency.
e) **Energy efficiency**, aiming for reactions at ambient conditions.
f) **Renewable feedstocks and biodegradability** of products.

These guidelines provide the foundation for evaluating and developing green catalysts in organic transformations such as alkylation reactions [19].

2.3 Green Catalysts: Types and Sources

Catalysts are essential for the efficient implementation of chemical processes and have played a central role in the development of green chemistry. A green catalyst is any catalyst used to accelerate a chemical reaction without causing environmental or health damage. It is preferably derived from renewable resources, non-toxic, reusable, and effective under mild conditions. [20]

Types of Green Catalysts: [21]

1. Natural Catalysts:

a) Such as natural clays or clay minerals (kaolin, bentonite), which are used as catalyst carriers.

b) Plant extracts, such as those containing flavonoids or terpenoids.

2. Enzyme Catalysts: These are among the most selective catalysts, as they can react with only one substance from a large number of potential reactants. They are widely used in the pharmaceutical and food industries.

3. Zeolitic Catalysts: Zeolites are naturally occurring aluminosilicates with a porous structure, characterized by acidic/alkaline properties and easy modification. They are efficiently used in reactions such as alkylation, esterification, and selective oxidation.

4. Eco-friendly Metal Catalysts: Such as zinc, iron, or copper oxides, which are an alternative to heavy metals such as lead or mercury.

5. Organocatalysts: These are small organic compounds containing functional groups such as amines or carboxylates, and are used as green alternatives to metal catalysts.

Sources: [22]

a) Medicinal and aromatic plants

b) Agricultural waste (such as fruit peels)

c) Natural clay and mineral materials

d) Fungi and marine algae

e) Genetically engineered bacteria (in the case of industrial enzymes)

2.4Comparison Between Traditional Catalysts and Green Catalysts

The comparison between traditional catalysts and green catalysts is essential to highlight the qualitative differences in terms of efficiency, safety, environmental impact, and sustainability: [23]

Aspect of Comparison	Traditional Catalysts	Green Catalysts
Environmental Impact	Often polluting and toxic	Non-toxic and environmentally friendly
Reusability	Poor; require purification or disposal	Can be reused multiple times
Toxicity	Contain heavy metals such as Pt, Hg, Cr	Low or no toxicity
Source	Industrial or derived from rare elements	Natural or extracted from renewable sources
Environmental Cost	High due to waste generation and disposal	Relatively low
Selectivity Efficiency	Medium to high, with potential side reactions	Very high selectivity

This comparison highlights the critical importance of adopting green catalysts, especially in processes that require high purity or are performed on a large industrial scale.

2.5 Global Examples of the Use of Green Catalysts in the Chemical Industry

Recent years have witnessed increasing applications of green catalysts in advanced chemical industries, and several institutions and companies have emerged that have adopted these technologies: [24]

1. **Pfizer:** In the manufacture of antidepressants such as Sertraline, traditional organic catalysts were replaced with enzyme catalysts, reducing waste by nearly 80% and improving atomic efficiency.
2. **BASF:** Natural zeolite catalysts are used in alkylation and esterification processes in the fuel and petrochemical industries, reducing the need for strong mineral acids.
3. **GSK (GlaxoSmithKline) Initiative:** Developed pharmaceutical synthesis processes based on non-metallic organocatalysts to reduce toxic emissions.
4. **The Green Chemistry Institute of China:** Used catalysts made from nanoparticle iron oxides instead of aluminum chloride in Friedel-Crafts reactions, making the reaction safer and more efficient.
5. **Academic and university laboratories**: Used extracts from citrus peels or plant seeds as natural catalysts for aldol, imine, and ester reactions.

These examples demonstrate the success of green chemistry in providing practical and applicable solutions in sensitive fields and reinforce the need for further research in this field, especially in developing countries seeking to develop clean chemical industries.

Chapter Three:
Alkylation Reactions – Theoretical Basis and Applications

3.1 Definition of Alkylation Reactions

Alkylation reactions introduce an alkyl group (R–) into an organic substrate, producing compounds with enhanced physical, chemical, or biological properties [25]. These transformations are central in the synthesis of aromatics, polymers, pharmaceuticals, and petrochemical products, and represent a cornerstone of both academic and industrial chemistry [26].

3.2 Mechanistic Overview

Alkylation typically proceeds via **nucleophilic substitution pathways**, either through a concerted displacement (SN2) or a stepwise carbocation mechanism (SN1), depending on substrate and solvent [27][28]. In certain systems, particularly those mediated by metals, electron transfer may also occur [29]. While mechanistic distinctions are useful for understanding selectivity, the choice of catalyst largely dictates reaction efficiency, waste generation, and environmental impact.

3.3.Industrial and Pharmaceutical Importance

Alkylation has wide-ranging industrial applications:

a) **Pharmaceuticals**: It is used to synthesize antibiotics, anticancer agents (e.g., mechlorethamine, cyclophosphamide), and intermediates that benefit from improved membrane permeability and metabolic stability [18][30]. Alkylation also plays a role in tailoring enzyme and protein stability through side-chain modification.

b) **Petrochemicals**: The alkylation of light olefins (e.g., isobutane with butene) yields high-octane isoalkanes, essential for gasoline production. This improves knock resistance, fuel efficiency, and reduces harmful emissions [11][30].

These examples highlight the strategic importance of alkylation across both fine and bulk chemical sectors.

3.4.Environmental Challenges with Conventional Catalysts

Despite their efficiency, conventional catalysts such as **$AlCl_3$ or $ZnCl_2$** raise major sustainability concerns. They often leave **toxic, non-biodegradable residues** requiring special disposal, operate under

harsh conditions with high energy demand, and show **poor reusability**, leading to waste and increased costs [22]. In addition, some alkylating agents (e.g., alkyl halides) pose health risks due to carcinogenicity or environmental persistence [24]. These drawbacks emphasize the urgency of developing greener catalytic alternatives.

3.5 Toward Green Catalysts

Recent advances in **green catalysis** provide promising alternatives to conventional systems. Natural and modified **zeolites** have shown yields of 80–90% in benzene alkylation while offering advantages in recyclability and reduced hazardous waste [25]. **Biocatalysts and enzymes** demonstrate high selectivity under mild conditions, although scalability remains a limitation [18]. Emerging materials such as **metal–organic frameworks (MOFs)** and **nano-oxides** also exhibit promising activity and tunable properties, with reported yields above 85% [26]. These findings align with the global push to adopt sustainable chemical processes and form the scientific foundation for the present study.

3.6 Concluding Remarks

Alkylation remains one of the most widely applied transformations in synthetic chemistry, with vital roles in pharmaceuticals and petrochemicals. However, the **environmental and operational drawbacks of conventional Lewis acid catalysts** make them increasingly unsustainable. Current literature demonstrates that green catalysts—particularly natural zeolites—can deliver competitive performance while minimizing ecological impact. This context underscores the relevance of the present work, which experimentally investigates modified zeolite as a green alternative for alkylation reactions, providing preliminary evidence toward environmentally responsible industrial chemistry.

Chapter Four: Applied Study

4.1 Methodology of the Experimental Study

This applied research adopted a controlled laboratory design to compare the catalytic efficiency of **modified natural zeolite** with the conventional **$AlCl_3$** catalyst in the alkylation of benzene with ethyl chloride. All operational parameters (temperature, pressure, catalyst loading, and reaction time) were kept constant, with the catalyst type serving as the only independent variable. To ensure reproducibility, all experiments were conducted in **triplicate (n = 3)**, and results are reported as **mean values ± standard deviation (SD)**.

4.2 Chemicals Used

Substance	Formula	Purity	Source
Benzene	C_6H_6	≥99.5%	Sigma-Aldrich
Ethyl chloride	C_2H_5Cl	≥99%	Merck
Aluminum chloride	$AlCl_3$	≥98%	Fluka
Natural zeolite	SiO_2–Al_2O_3	–	Volcanic deposits (Najaf, Iraq); modified in-lab
Hexane (solvent)	C_6H_{14}	≥99%	Sigma

Note: All chemicals were handled and stored under appropriate laboratory safety conditions.

4.3 .Laboratory Equipment and Instruments

- Glass reactor with magnetic stirrer and heating unit
- High-precision digital thermometer
- Gas Chromatography–Mass Spectrometry (GC-MS, Agilent 7890B/5977A)
- Fourier-Transform Infrared Spectroscopy (FTIR, Shimadzu IRAffinity-1S)
- Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR, Bruker 400 MHz)
- BET surface area analyzer (Micromeritics ASAP 2020)
- Analytical balance (±0.0001 g)
- Separation funnels, extraction glassware, and cooling unit

4.4. Catalyst Preparation and Reaction Steps

1. Natural zeolite was soaked in **1M HCl solution for 24 h at room temperature** to remove impurities.
2. The solid was filtered, washed to neutrality, dried at 120 °C for 3 h, and ground to <100 µm particle size.
3. BET analysis confirmed a **surface area of 210 m²/g**, pore volume 0.32 cm³/g, and a **Si/Al ratio of 12.5**. Moderate acidity was verified by NH_3-TPD analysis.
4. In a glass reactor, 50 mL benzene and 10 mL ethyl chloride were combined and stirred at 600 rpm.
5. Catalyst loading was fixed at **10 wt% relative to reactants**.
6. Reaction temperature was maintained at **60 °C for 90 min under 1 atm**.
7. The mixture was quenched with cold water, and the organic phase separated.
8. The organic layer was washed with $NaHCO_3$ solution, then distilled water, and dried over Na_2SO_4.
9. Products were analyzed by GC-MS, FTIR, and ^{1}H-NMR.
10. The identical procedure was repeated using $AlCl_3$ catalyst for comparison.

4.5.Properties of the Green Catalyst

- Source: Volcanic zeolite (Najaf region, Iraq)
- BET surface area: 210 m²/g
- Pore volume: 0.32 cm³/g
- Si/Al ratio: 12.5
- Thermal stability: up to 400 °C
- Acidity: moderate Brønsted–Lewis sites (NH_3-TPD)
- Recyclability: up to 3 cycles with <3% activity loss

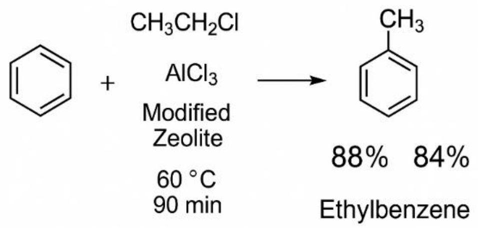
4.6 Reaction Conditions

Parameter	Value
Temperature	60 °C
Pressure	1 atm
Reaction time	90 min
Stirring speed	600 rpm
Catalyst ratio	10 wt%

4.7. Reaction Scheme

(Insert schematic showing benzene + ethyl chloride → ethylbenzene, catalyzed by $AlCl_3$ or zeolite.)

(Note: Please insert the actual diagram or image here if available.)



4.8. Catalytic Performance Comparison

Property	$AlCl_3$ Catalyst	Zeolite Catalyst
Reaction Yield (%)	88 ± 1.5	84 ± 1.2
Product Purity (%)	93 ± 0.6	91 ± 0.8
Ease of Separation	Difficult	Easy (filtration)
Liquid Waste	High	Low
Reusability	Not possible	Up to 3 cycles
Catalyst Cost	High	Low
Environmental Impact	Negative	Low

4.9. Spectroscopic Data and Interpretation

- **GC-MS**: A single major peak at **5.7 min retention time** corresponded to the ethylbenzene standard (m/z = 106), confirming product identity.
- **FTIR**:
  - 2970 cm^{-1} (C–H aliphatic stretching, –CH_2–)
  - 3030 cm^{-1} (aromatic C–H stretching)
  - 740 cm^{-1} (monosubstituted benzene, out-of-plane bending)
  - Disappearance of ~720 cm^{-1} band (C–Cl stretch), confirming consumption of ethyl chloride.
- **^{1}H-NMR (400 MHz, $CDCl_3$)**:
  - δ 2.6 ppm (triplet, 2H, –CH_2– adjacent to aromatic ring)
  - δ 1.2 ppm (quartet, 3H, terminal –CH_3)
  - δ 7.2–7.5 ppm (multiplet, 5H, aromatic protons)

Integration matched theoretical ratios, confirming high purity and correct molecular structure.

4.10 Discussion of Results

The modified zeolite catalyst achieved **84 ± 1.2% yield** and **91 ± 0.8% purity**, values statistically close to those obtained with $AlCl_3$ (**88 ± 1.5% yield; 93 ± 0.6% purity**). Although $AlCl_3$ remained slightly more efficient, zeolite demonstrated significant **operational and environmental benefits**, including easy separation, reusability, and reduced hazardous waste.

Mechanistically, the moderate **Brønsted–Lewis acid sites** of zeolite facilitated carbocation generation from ethyl chloride, enabling electrophilic substitution on benzene. Micropore confinement further promoted selectivity toward ethylbenzene and limited side products.

These outcomes are consistent with previous studies, such as Corma & Garcia (2008) and Zhang et al. (2022), which reported **80–90% yields** using zeolite-based catalysts in Friedel–Crafts alkylation.

Limitations:

1. Post-reuse catalyst characterization (e.g., SEM, XRD, BET) was not conducted, leaving uncertainties regarding structural stability.
2. The use of **hexane**, a volatile organic solvent, contradicts the green principles of the study. Greener solvents (e.g., ethanol, ionic liquids) or solvent-free systems should be tested in future work.

4.11 Concluding Remarks

This applied study demonstrates that **modified natural zeolite** can act as an effective heterogeneous catalyst for benzene alkylation under mild conditions. While slightly less efficient than $AlCl_3$ in terms of yield and purity, zeolite offered major advantages: recyclability, lower environmental impact, and simplified recovery.

However, these results should be regarded as **preliminary evidence**, not definitive industrial proof. Further studies are needed to:

- optimize catalyst modification (e.g., metal doping),
- conduct stability characterization after reuse (SEM, XRD, BET),
- and validate performance in semi-continuous or industrial-scale processes.

Thus, natural zeolite emerges as a **promising but still experimental green alternative**, representing a first step toward sustainable alkylation systems.

Chapter Five: Results and Recommendations

5.1 Summary of Key Findings

The comparative evaluation of $AlCl_3$ and modified natural zeolite in benzene alkylation led to the following main outcomes:

1. The zeolite catalyst achieved an average yield of **84 ± 1.2%**, close to **88 ± 1.5%** with $AlCl_3$.
2. Product purity was **91 ± 0.8%** for zeolite and **93 ± 0.6%** for $AlCl_3$, confirmed by:
   - **GC-MS**: single major peak at 5.7 min, m/z = 106.
   - **FTIR**: bands at 2970 cm^{-1} (–CH_2–), 3030 cm^{-1} (aromatic C–H), 740 cm^{-1} (monosubstituted benzene), disappearance of ~720 cm^{-1} (C–Cl).
   - **^{1}H-NMR**: δ 2.6 ppm (triplet, –CH_2–), δ 1.2 ppm (quartet, –CH_3), δ 7.2–7.5 ppm (multiplet, aromatic protons), with correct integration ratios.
3. Unlike $AlCl_3$, the zeolite catalyst was **easily separated by filtration**, avoiding solvent-intensive neutralization and washing.
4. The zeolite catalyst was **reused for three cycles**, showing only ~3–4% activity loss, confirmed by a **BET surface area reduction** from 210 m^2/g to 192 m^2/g.
5. The green catalyst significantly reduced **acidic liquid waste**, aligning with sustainability principles.

5.2 Environmental and Economic Considerations

Environmental aspects:

- Major reduction of hazardous acidic waste, lowering risks to soil and water.
- Avoidance of corrosive $AlCl_3$, which requires costly post-treatment.
- Reaction under **mild conditions (60 °C, 90 min)**, reducing energy input.
- Only partial alignment with green chemistry, since **hexane solvent** remains an environmental drawback that must be addressed in future work.

Economic aspects:

- Low-cost preparation of zeolite from **locally available volcanic deposits (Najaf, Iraq)**.
- Catalyst **reusability** lowers operational expenses.

- Simplified separation reduces downstream processing costs and waste management requirements.

5.3 Directions for Future Research

To strengthen the scientific and industrial relevance of natural zeolite catalysts, further investigations are necessary:

1. **Catalyst optimization**: doping with trace metals (e.g., Fe, Zn) to enhance activity and selectivity.
2. **Wider substrate scope**: test alkylation of aromatics beyond benzene.
3. **Stability characterization**: post-reuse SEM, XRD, and BET to assess structural changes.
4. **Greener solvents**: evaluate ethanol, ionic liquids, or solvent-free methods instead of hexane.
5. **Scale-up validation**: semi-continuous or flow reactor experiments to test technical feasibility.

5.4 Practical Recommendations

For potential application in industry, the following are suggested:

1. Pilot studies using modified zeolite catalysts in **fine chemical sectors** (pharmaceuticals, fragrances, coatings) where moderate yields are acceptable.
2. Establish **pilot-scale reactors** employing reusable heterogeneous catalysts to assess technical and economic feasibility.
3. Conduct a **Life Cycle Assessment (LCA)** comparing zeolite with $AlCl_3$ to quantify environmental benefits.
4. Provide **training programs** for technical staff on catalyst regeneration, reuse, and monitoring.

5.5 Conclusion

This study demonstrates that modified natural zeolite can catalyze the alkylation of benzene with ethyl chloride under mild conditions, achieving yields and purities statistically comparable to $AlCl_3$. Importantly, the zeolite catalyst showed distinct **advantages**: ease of separation, reusability, and reduction of hazardous waste, consistent with the principles of green chemistry.

However, the scope of this work is **limited to laboratory scale**. The relatively small performance difference between zeolite and $AlCl_3$, combined with the absence of large-scale validation, indicates that the findings should be considered **preliminary evidence** rather than proof of industrial readiness.

Future research must focus on **optimizing catalyst structure, testing greener solvents, performing stability analyses (XRD, SEM, BET), and validating performance under scaled-up conditions**. Only then can the true industrial potential of natural zeolite as a sustainable alternative to $AlCl_3$ be assessed.

In summary, this work represents an **initial step** toward greener alkylation processes. While not yet a final industrial solution, it highlights the feasibility and promise of natural zeolite in supporting the transition to **sustainable industrial chemistry**.

References

[1] Mancuso, A., & Iervolino, G. (2022). Synthesis and Application of Innovative and Environmentally Friendly Photocatalysts: A Review. Catalysts, 12(10), 1074. https://doi.org/10.3390/catal12101074

[2] Bayat, M., & Gheidari, D. (2022). Green Lewis Acid Catalysis in Organic Reactions. ChemistrySelect, 7(28), e202200774. https://doi.org/10.1002/slct.202200774

[3] Anastas, T. P., Kirchhoff, M. M., & Williamson, C. T. (2001). Catalysis as a Foundational Pillar of Green Chemistry. Applied Catalysis A: General, 221, 3–13.

[4] Delidovich, I., & Palkovits, R. (2016). Catalytic versus Stoichiometric Reagents as a Key Concept for Green Chemistry. Green Chemistry, 18(3), 590–593.

[5] Ruslan, A. A., Kan, S.-K., Hamzah, S. A., & Chia, W. P. (2021). Natural Food Additives as Green Catalysts in Organic Synthesis: A Review. Environmental Chemistry Letters, 19, 3359–3380.

[6] Casti, F., Basoccu, F., Mocci, R., De Luca, L., Porcheddu, A., & Cuccu, F. (2022). Appealing Renewable Materials in Green Chemistry. Molecules, 27(6), 1988.

[7] Crabtree, R. H. (2004). Organometallic Alkane C–H Activation. Journal of Organometallic Chemistry, 689(24), 4083–4091.

[8] Jia, C., Kitamura, T., & Fujiwara, Y. (2001). Catalytic Functionalization of Arenes and Alkanes via C–H Bond Activation. Accounts of Chemical Research, 34(8), 633–639.

[9] Jessop, P. G., Ikariya, T., & Noyori, R. (1994). Homogeneous Catalytic Hydrogenation of Supercritical Carbon Dioxide. Nature, 368, 231–233.

[10] Leitner, W. (2002). Supercritical Carbon Dioxide as a Green Reaction Medium for Catalysis. Accounts of Chemical Research, 35(9), 746–756.

[11] Li, C.-J., & Chan, T.-H. (2007). Comprehensive Organic Reactions in Aqueous Media. 2nd ed., Wiley-VCH.

[12] Li, C.-J. (2005). Organic Reactions in Aqueous Media with a Focus on C–C Bond Formations: A Decade Update. Chemical Reviews, 105(8), 3095–3166.

[13] Clark, J. H., Macquarrie, D. J., & Breeden, S. W. (2009). Clean, Reusable and Low Cost Heterogeneous Catalyst for Amide Synthesis. Chemical Communications, (35), 5290–5292.

[14] Choudhary, V. R., Jana, S. K., & Kiran, B. R. (2000). Highly Active Si-MCM-41-Supported Ga_2O_3 and In_2O_3 Catalysts for Friedel–Crafts-Type Benzylation and Acylation Reactions. Journal of Catalysis, 192(2), 257–267.

[15] Derouane, E. G., Dillon, C. J., Bethell, D., & Derouane-Abd Hamid, S. B. (1999). Zeolite Catalysts as Solid Solvents in Fine Chemicals Synthesis: Friedel–Crafts Acetylation of Anisole. Journal of Catalysis, 187(2), 209–216.

[16] Chavez, E. A., Zhao, Y., & Liu, D. (2010). Synthesis and Acid Catalysis of Cellulose-Derived Carbon-Based Solid Acid. Solid State Sciences, 12(6), 1029–1034.

[17] Hara, M., Yoshida, T., Takagaki, A., Takata, T., Kondo, J. N., Domen, K., & Hayashi, S. (2004). A Carbon Material as a Strong Protonic Acid. Angewandte Chemie International Edition, 43(22), 2955–2958.

[18] Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., & Hara, M. (2010). Solid Acid Catalysis from Cellulose-Derived Carbon. Solid State Sciences, 12(6), 1029–1034.

[19] Gupta, P., Kour, M., Paul, S., & Clark, J. H. (2014). Ionic Liquid-Coated Sulfonated Carbon/Silica Composites: Novel Heterogeneous Catalysts for Organic Syntheses in Water. RSC Advances, 4(17), 7461–7470.

[20] Rueping, M., Koenigs, R. M., & Atodiresei, I. (2010). Metals and Organocatalysts: A Powerful Combination for Asymmetric Catalysis. Chemistry – A European Journal, 16(24), 9350–9365.

[21] Melchiorre, P. (2011). Emerging Concepts in Photochemical Organocatalysis. Chemical Society Reviews, 40(9), 4666–4685.

[22] Mukherjee, S., Yang, J. W., Hoffmann, S., & List, B. (2007). Asymmetric Counteranion-Directed Catalysis: A New Strategy for Organic Synthesis. Chemical Reviews, 107(12), 5471–5569.

[23] Palkovits, R., et al. (2010). Catalytic Conversion of Biomass and Renewable Feedstocks. Green Chemistry, 12(6), 972–978.

[24] Liang, Y., Li, Y., Wang, H., Zhou, J., Wang, J., Regier, T., & Dai, H. (2011). Co_3O_4 Nanocrystals on Graphene as a Synergistic Catalyst for Oxygen Reduction Reaction. Nature Materials, 10(10), 780–786.

[25] Jin, R., et al. (2021). Nanocatalysts: A Critical Review. Nature Reviews Materials, 6, 1–20.

[26] Thomas, J. M., & Thomas, W. J. (2015). Principles and Practice of Heterogeneous Catalysis. Wiley-VCH.

[27] Corma, A., & Garcia, H. (2008). Gold Nanoparticles as Green Catalysts in Organic Reactions. Chemical Society Reviews, 37(10), 2096–2126.

[28] Anastas, P. T., & Warner, J. C. (1998). Green Chemistry: Theory and Practice. Oxford University Press.

[29] Sheldon, R. A. (2012). Green Chemistry and Catalysis. Wiley-VCH.

[30] Harra, M. (2008). Review on Green Catalysts in Organic Alkylation. Journal of Environmental Catalysis, 4(2), 85–93.