

# Advancements in Zeolite Catalysis for Efficient Oil Refining and Sustainable Energy Production

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## Abstract

*Fossil fuels remain the primary reliable and cost-effective energy source for maintaining the desired product quality. This dominance stems from advancements in petrochemistry and oil refining, driven by substantial investments in research and innovation. The exceptional efficiency of oil refining is largely attributed to the use of zeolites as catalysts, a breakthrough regarded as one of the most significant achievements in modern chemistry. Their applications span across several catalytic processes, including fluid catalytic cracking (FCC), hydrocracking, alkylation, isomerization, and reforming, all of which are vital for the production of high-value fuels and petrochemical intermediates. This paper explores various types of zeolites in their role as solid acids and highlights their structural and compositional advantages in catalytic processes. Special attention is given to emerging modifications of zeolite catalysts, such as hierarchical structures and metal incorporation, which enhance their catalytic activity, stability, and resistance to deactivation. The final section presents future perspectives on the field, highlighting improvements in transportation fuel quality, the increasing integration of biofuels into oil streams, and the potential of zeolite catalysts in alternative energy applications such as biomass conversion. This review aims to provide fundamental insights into zeolite applications in catalysis, especially in the context of growing global energy demand and the transition towards more sustainable refining technologies.*

**Keywords:** Zeolite Catalysts Fluid Catalytic Cracking (FCC) Petrochemical Refining Hierarchical Zeolites Biomass Conversion

## INTRODUCTION

These materials exist in both natural and synthetic forms. The discovery of zeolites dates back to 1756 when a Swedish mineralogist observed the release of vapor upon heating a stone now known as stilbite, recognizing it as a new type of mineral. The 19th century revealed that natural zeolites exhibited similar behavior, with certain cations capable of being exchanged for others. Additionally, natural chabazite demonstrated selective adsorption, effectively capturing water, methanol, ethanol, and formic acid vapor, while failing to adsorb substances like acetone, diethyl ether, or benzene. These properties led to the widespread use of natural zeolites as adsorbents and desiccants, later expanding into applications for air separation and purification.

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Efforts to synthesize silicates under hydrothermal conditions began in the mid-19th century, leading to the first successful synthesis of quartz in an autoclave. Significant advancements in zeolite synthesis were made in the 1940s, when research focused on converting known mineral phases using strong salt solutions at high temperatures.

In the late 1940s, hydrothermal crystallization techniques enabled the synthesis of zeolites A (LTA),

X (FAU), and P (GIS) at relatively low temperatures and alkaline conditions. By 1953, a total of 20 different zeolites had been synthesized, 14 of which had no natural equivalent, marking the beginning of zeolite technology. Between 1954 and the early 1980s, significant progress was made in zeolite production, particularly in the exploration of low, medium, and high silica-to-alumina ratio (SAR) zeolites, which revolutionized industrial applications. The synthesis of zeolite Y, with improved thermal stability and acidity, played a critical role in hydrocarbon conversion catalysis. Further developments in the 1960s led to the commercial use of zeolites A, X, and Y as selective adsorbents and catalysts. The introduction of structure-directing agents, commonly referred to as templates, significantly advanced zeolite synthesis, enabling the production of high-silica zeolites. An example of this is the synthesis of ZSM-5 (MFI) using the tetrapropylammonium (TPA) cation, which played a crucial role in shaping modern zeolite technology.

### STRUCTURE OF ZEOLITE

Zeolites are seen in a succinctly form as crystalline aluminosilicates that possess a uniform crystal structure which are identified by a large number of regular small cavities interconnected by a large number of even smaller rectangular channels. The Structure Commission (SC) of the International Zeolite Association (IZA) has been given the IUPAC authority to classify and name the different zeolitic topologies; “zeolitic” topologies have been discovered first as aluminophosphates or  $\text{SiO}_4$  and later on as aluminosilicates. The definition can broaden to materials that contain a framework of tetrahedral elements that share every vertex once and only once with four neighbors, and which have a density “significantly lower” than the corresponding “dense” phases. For instance, the SOD topology, first discovered in the aluminosilicate sodalite, actually exists also as pure silica,  $\text{AlPO}_4$  zincosilicate, beryllosilicate, beryllioarsenate, beryllio germanate, and many other compositional variants (Dyer, 2001).

$$\text{M}_x/\text{n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O} \quad (1)$$

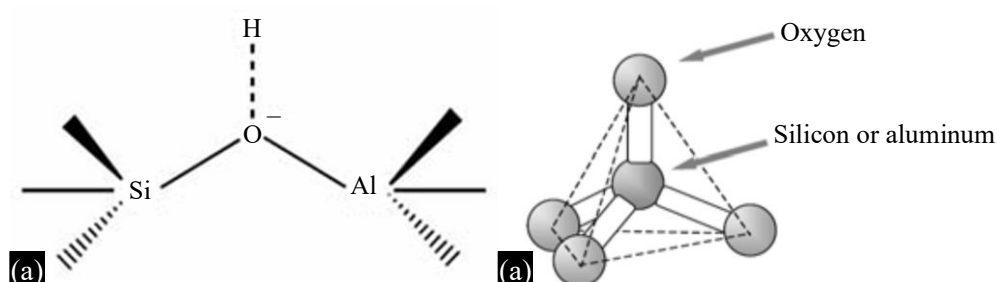
Where M represents the extra-framework cation of valance n, w is the number of water molecules and x and y are integers such that  $y/x \geq 1$ . The expression enclosed in the square brackets shows the anionic framework composition. The very regular structure and pore sizes give these materials a sponge-like appearance [1–5].

### Framework Structure of Zeolite

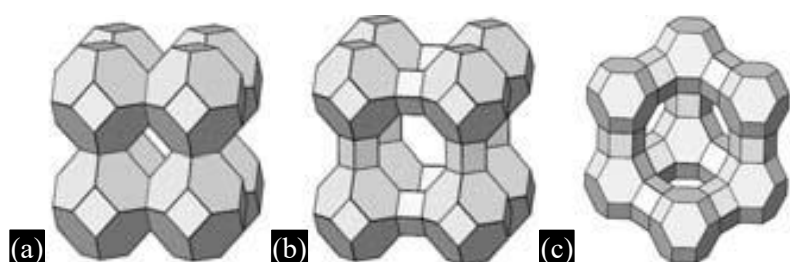
The primary building unit for zeolites is the tetrahedron and the secondary building units (SBUs) are the geometric arrangements of tetrahedra. The SBUs may be simple polyhedra such as cubes, hexagonal prisms, or cubo-octahedra (Basina *et al.*, 2018). The structures can be formed by repeating SBUs and according to them zeolites can be classified into eight groups. Figures 1(a) and (b) presents components of the structure of zeolite.

### Nomenclatures

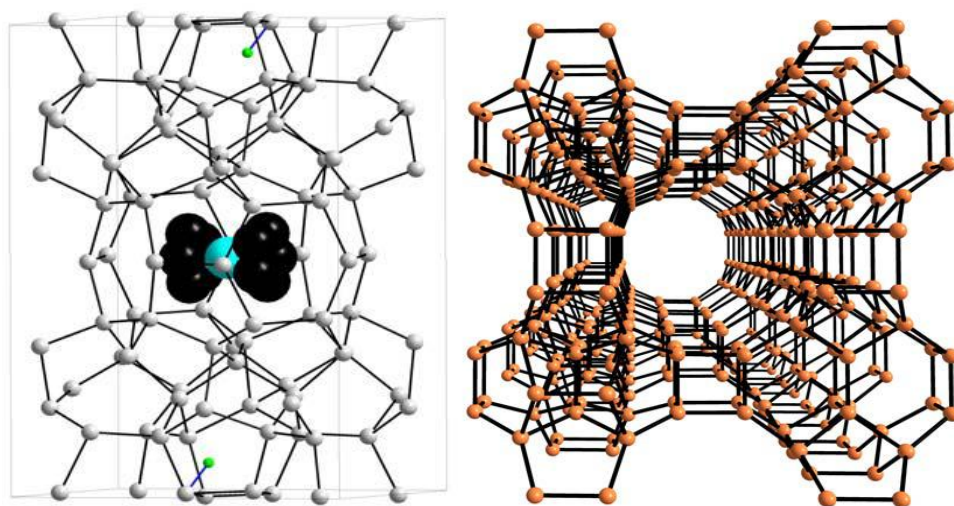
The wide variety of possible zeolite structures is due to the large number of ways in which the SBU can be linked to form various polyhedra. These polyhedra create networks of regular channels and cavities. One such polyhedron is the truncated octahedron; better known as the sodalite cage. Each sodalite cage consists of 24 linked tetrahedra which are further linked to form different zeolites with



**Figure 1.** (a) Chemical structure of zeolite, (b) primary building unit of zeolite structure.



**Figure 2.** Framework topologies of: (a) Sodalite; (b) Zeolite A/ZK-4; (c) Zeolite X/Y.



**Figure 3.** Typical structures of zeolites.

distinct framework topologies as depicted in Figure 2. Figure 3 presents the general framework topologies of zeolites A/ZK4 and zeolites X/Y, and that of sodalite,  $\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{12}$ . The small face sharing  $\beta$ -cages characteristic of sodalite are linked through double four ring and six ring units in zeolites A/ZK4 and zeolites X/Y, respectively, to produce larger cages. Each type of zeolite has specific uniform pore size, for instance, 3.5-4.5 Å for zeolite LTA, 4.5-6.0 Å for ZSM-5 and 6.0-8.0 Å for zeolite X, Y type [6].

### Main Structure

Characteristics of the framework type of a zeolite alone can explain many of the observe properties of a zeolite.

### Microporous and Mesoporous Materials

Porous materials are classified based on their pore sizes into microporous and mesoporous materials. Microporous materials have pore diameters of less than 2 nm and are widely used in laboratory environments for gas exchange while preventing contamination. These materials trap airborne particles such as mold spores and bacteria, ensuring a sterile environment. Zeolites are a significant example of this class. Their large surface area provides numerous sites for sorption processes, making them valuable in catalysis, separation, and various other applications. The synthesis of mesoporous materials is an area of continuous research, aimed at tailoring specific properties.

### Molecular Sieves

Over the past five decades, materials with diverse elemental compositions have been explored. Zeolite-like materials share structural similarities with zeolites but incorporate elements beyond silicon, aluminum, and oxygen. Their defining characteristic is the ability to precisely regulate pore sizes, allowing only molecules smaller than the pore diameter to pass through while excluding larger ones—hence the term “molecular sieves.” Zeolites, silicalites, and aluminophosphates fall under this category.

**Table 1.** Differences between molecular sieves and zeolites

| Molecular Sieves                                                          | Zeolites                                                                        |
|---------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Composition varies and distinguishes materials on the basis of their size | Special class of molecular sieves with aluminosilicates as skeletal composition |
| May be crystalline, non-crystalline, para-crystalline or pillared clays   | They are highly crystalline materials                                           |
| Variable framework charge with porous Structure                           | Have anionic framework with microporous and crystalline structure               |

**Table 2.** Physio-chemical properties of zeolite and molecular sieves.

| Property                      | Range                                                                   |
|-------------------------------|-------------------------------------------------------------------------|
| Pore size                     | ~4-13 Å                                                                 |
| Pore shape                    | Circular, elliptical                                                    |
| Dimensionality of pore system | 1-D, 2-D, 3-D.                                                          |
| Pore configuration            | Channels, cages                                                         |
| Surface properties            | Hydrophilic, hydrophobic (high silica)                                  |
| Void volume                   | Less than ~50%                                                          |
| Framework oxide composition   | Si, Al, P, Ga, Ge, B, Be, Zn: minor<br>Ti, Fe, Co, Cr, V, Mg, Mn: minor |

**Table 3.** Physical properties of four types of zeolite.

| Type | Isotopes               | Pore window (free diameter) | Si/Al ratio                | Pores (channels)                                               |
|------|------------------------|-----------------------------|----------------------------|----------------------------------------------------------------|
| LTA  | A zeolite              | 8-ring: 0.41 nm             | ~1                         | 3D spherical 1.14 nm cavities                                  |
| FAU  | X zeolite<br>Y zeolite | 12-ring: 0.74 nm            | 1 - 1.5 (X)<br>1.5 - 3 (Y) | 3D spherical 1.18 nm cavities                                  |
| MOR  | Mordenite              | 12 ring: 0.70 nm            | 5–20                       | 2D spherical 0.70 nm channels                                  |
| MHI  | ZSM-5<br>Silicate-1    | 10-ring: 0.60 nm            | ~30(ZSM-5)                 | 3D spherical 0.60 nm channels with 0.90 intersection cavities. |

Zeolite molecular sieves possess uniform pore sizes ranging from 0.3 to 2.0 nm, enabling selective adsorption based on molecular size and polarity. This property, combined with high adsorption capacity under various conditions, makes them highly effective in industrial applications. In the petroleum industry, zeolite molecular sieves are commonly used for drying, purification, and separation of liquids and gases. Their use helps prevent undesirable side reactions, ensures compliance with product specifications, and mitigates equipment corrosion and freezing issues. Examples of molecular sieves include carbons, glasses, and oxides. The key differences between molecular sieves and zeolites are outlined in the table below [8].

## USES AND APPLICATION OF ZEOLITE

Zeolites have extensive applications across multiple industries due to their unique ion-exchange, adsorption, and catalytic properties.

### Commercial and Domestic Applications

Zeolites are commonly used in domestic and commercial water purification systems, including ion-exchange beds for water softening. In analytical chemistry, they serve as molecular sieves, allowing the selective passage of specific molecules for separation and analysis [9]. Additionally, zeolites have potential applications in gas separation, including the removal of H<sub>2</sub>O, CO<sub>2</sub>, and SO<sub>2</sub> from low-grade natural gas, as well as the separation of noble gases, N<sub>2</sub>, O<sub>2</sub>, freon, and formaldehyde. However, their full potential in gas handling remains underexplored (Wise, 2013).

### Petrochemical Industry

These reactions often involve quantum-chemical Lewis acid site interactions, making zeolites highly efficient catalysts in petrochemical transformations (Boaventura et al., 2022).

### **Nuclear Industry**

Zeolites are utilized in nuclear waste reprocessing due to their microporous structure, which enables the selective adsorption of specific ions while allowing others to pass through. This property facilitates the efficient removal and permanent trapping of fission products from nuclear waste. Additionally, zeolites' alumino-silicate composition offers exceptional durability and resistance to radiation. Once loaded with radioactive waste, zeolites can be hot-pressed into durable ceramic blocks, effectively immobilizing hazardous materials. A notable example of zeolite application in nuclear remediation was the use of zeolite sandbags to adsorb radioactive cesium from seawater near the Fukushima nuclear plant (Jiao et al., 2020).

### **Heating and Refrigeration**

Zeolites are employed in solar thermal collectors and adsorption refrigeration systems due to their high heat of adsorption and reversible hydration-dehydration properties. Their ability to absorb and release heat while maintaining structural stability makes them valuable for harvesting waste heat and solar energy in thermal applications (Jiao et al., 2020).

### **Detergents**

The largest single application of zeolites is in the global laundry detergent industry. In 1992, the annual consumption of anhydrous zeolite A in detergent formulations reached approximately 1.44 million metric tons (Jiao et al., 2020).

### **Construction**

Synthetic zeolites are incorporated into warm-mix asphalt concrete to reduce the production and laying temperature, leading to lower fossil fuel consumption and reduced emissions of CO<sub>2</sub>, aerosols, and vapors. This application, which began in Germany in the 1990s, also facilitates easier compaction and enables cold-weather paving and longer transportation of asphalt mixtures [10]. In Portland cement, zeolites function as pozzolanic additives, reducing chloride permeability, improving workability, moderating water content, and enhancing break strength by promoting slower drying (Jiao et al., 2020).

### **Agriculture**

Clinoptilolite, a natural zeolite, is utilized in agriculture as a soil amendment that provides a slow-release source of potassium. When preloaded with ammonium, it similarly offers a controlled release of nitrogen. Additionally, zeolites act as water reservoirs, capable of adsorbing up to 55% of their weight in water and gradually releasing moisture in response to plant demand. This property helps prevent root rot and mitigates drought stress, thereby enhancing soil moisture management in agricultural practices (Jiao et al., 2020).

### **NATURAL ZEOLITE**

However, naturally occurring zeolites are rarely pure, often containing impurities such as other minerals, metals, quartz, or different zeolite types. Due to these impurities, natural zeolites are unsuitable for many commercial applications that require high purity and uniformity.

### **Artificial or Synthetic Zeolite**

In the late 1940s, Richard Barrer studied the transformation of mineral phases under the influence of strong salt solutions and high temperatures (170–270°C). Some of the resulting materials were later identified as zeolites. Robert Milton advanced this field by utilizing more reactive starting materials, such as freshly precipitated aluminosilicate gels. In 1961, the range of reactants expanded further with the introduction of quaternary ammonium cations, leading to a significant increase in the number of known synthetic zeolites, including ZSM-5 (Jiao et al., 2020).

During the early 1990s, new families of zeolite-like materials were discovered, including mesoporous phases such as the M41S and SBA series, which were synthesized using surfactant molecules or

processes involving centrifugation, washing, and drying. The microporous framework of these materials is primarily composed of silicon (Si) and aluminum (Al), introduced in oxide form through amorphous precursors containing Si-O and Al-O bonds. The crystalline structure of zeolites features Si-O-Al linkages, and their synthesis is typically kinetically controlled, often yielding metastable products.

The sol-gel method is a widely used synthesis approach, where additional elements such as metals or metal oxides can be incorporated. Hydrothermally synthesized silicalite sol exhibits remarkable stability, making it a preferred method for scalable zeolite production (Naraki et al., 2017).

### ZSM-5 ZEOLITE

In 1967, Argauer and Landolt established synthesis parameters for pentasil zeolites, defining key molar ratios, including  $\text{OH}^-/\text{SiO}_2 = 0.07\text{--}10$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5\text{--}100$ , and  $\text{H}_2\text{O}/\text{SiO}_2 = 1\text{--}240$ . Their method successfully produced relatively pure ZSM-5 zeolite only when organic amines, such as tetrapropylammonium compounds, were used as structure-directing agents (Dyer, 2001). Subsequent research introduced alternative synthesis methods that eliminated or replaced these expensive, toxic, and flammable organic amines (Liu et al., 2022). These efforts aimed to improve the reactivity of the silica and alumina starting materials while mitigating the risk of zeolite structure degradation due to thermal decomposition of the amines.

ZSM-5 (Zeolite Socony Mobil) is an aluminosilicate molecular sieve with a high silica-to-alumina ratio, making it ideal for catalytic, adsorption, and membrane applications. The first patent for ZSM-5 synthesis described its formation with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ranging from 20 to 120 (Dyer, 2001; Liu et al., 2022). This ratio significantly impacts the material's acidity and surface properties, necessitating careful control during synthesis. Due to their high thermal stability, shape selectivity, and superior catalytic activity, ZSM-5 zeolites are widely utilized in petrochemical processes, oil refining, and environmental applications, including catalytic cracking, isomerization, aromatization, and alkylation.

In its anhydrous state, the general molecular formula of ZSM-5 is:



Here, M represents a cation with valence n, commonly an alkali metal or an organo-ammonium cation, typically a mixture of sodium and tetraalkyl ammonium cations with alkyl groups containing 2 to 5 carbon atoms. The term “anhydrous” refers to the absence of molecular water in this formulation. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in ZSM-5 can vary widely, with some aluminum-free versions existing where silica serves as the primary framework component, containing only trace aluminum impurities (Dyer, 2001).

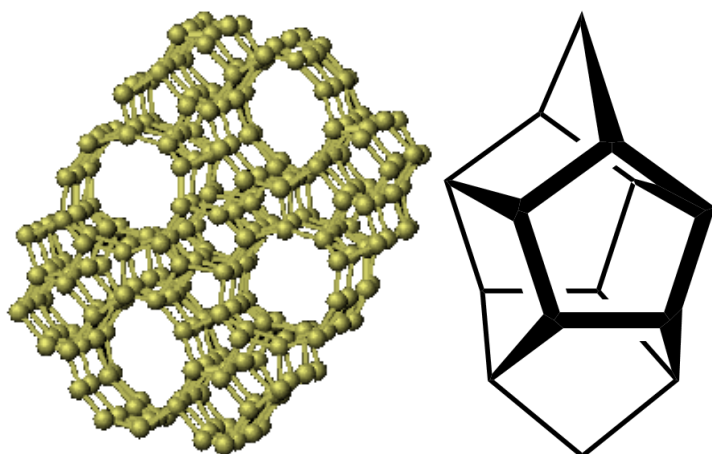
### Structure of ZSM-5 Zeolite

ZSM-5 consists of pentasil units interconnected by oxygen bridges, forming pentasil chains. Each pentasil unit comprises eight five-membered rings, where silicon or aluminum atoms serve as the vertices, with oxygen atoms bonded between them. These pentasil chains assemble into corrugated sheets containing ten-membered ring pores. Figures 4 and 5 Similar to the pentasil units, each ten-membered ring features silicon or aluminum vertices with oxygen atoms forming the bridges. The corrugated sheets link via oxygen bridges, producing a framework with straight ten-ring channels parallel to the corrugations and sinusoidal ten-ring channels perpendicular to the sheets (Liu et al., 2022) [11–14].

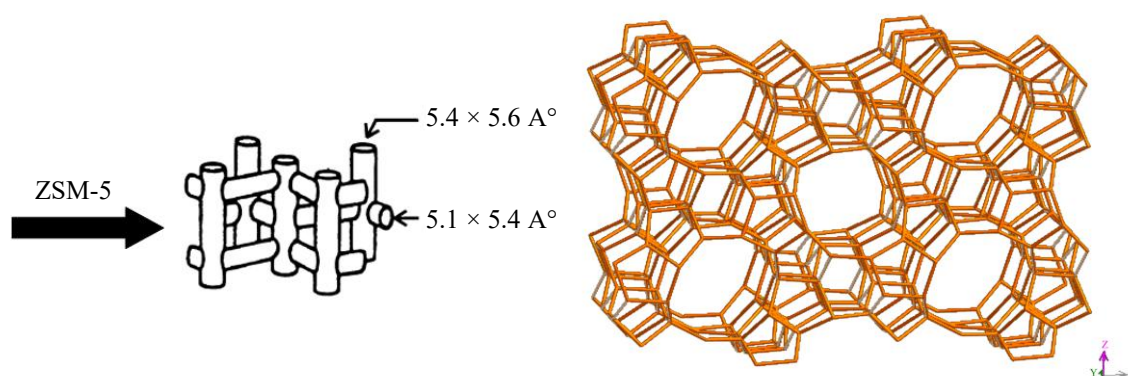
below a transition temperature, located between 300 and 350 K.

### Properties of ZSM-5

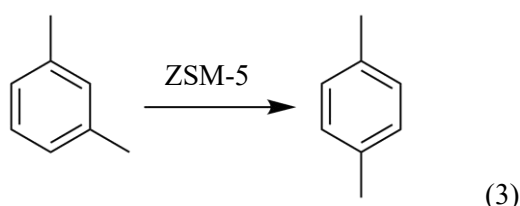
It is because of the good pore channel system of ZSM-5 that makes some organic linear molecules such as olefin and paraffin to enter to the sieve of ZSM-5, and then cracked to propylene by the concept of shape selectivity of ZSM-5. ZSM-5 has a good crystal size in a micrometer range which could influence the catalytic performance for synthesis of large molecules appropriated to a limitation of mass transfer.



**Figure 4.** Framework structure of ZSM-5 Zeolite.



**Figure 5.** The pore size of the channels in ZSM-5.



**Figure 6.** Aromatic hydrocarbon dealkylation of 1,2-dimethylbenzene (o-xylene) to benzene catalyzed by ZSM-5 zeolite.

Figure 6 illustrates the dealkylation reaction of o-xylene (1,2-dimethylbenzene) to benzene in the presence of a ZSM-5 zeolite catalyst. This transformation demonstrates the shape-selective and acidic properties of ZSM-5, which facilitates the removal of methyl groups under controlled conditions. The zeolite's microporous structure and strong Brønsted acid sites play a crucial role in breaking the C–C bonds of alkyl groups, enabling the production of high-value aromatic compounds such as benzene. Such reactions are significant in refining and petrochemical industries where the conversion of substituted aromatics to simpler, more valuable molecules enhances overall process efficiency and product yield.

## CONCLUSION

Zeolites have emerged as indispensable catalysts in the petrochemical industry, playing a pivotal role in enhancing the efficiency, selectivity, and sustainability of oil refining processes. Their unique framework structure, high surface area, and tunable acidity make them ideal for a wide range of catalytic applications, from fluid catalytic cracking to reforming. Advances in zeolite modification—such as the

development of hierarchical porosity and incorporation of metal ions—have further amplified their catalytic potential, enabling better resistance to deactivation and improved performance under harsh industrial conditions. As the energy sector undergoes a transformative shift toward cleaner fuels and sustainable technologies, zeolite catalysts are poised to support this evolution through their role in upgrading transportation fuels and integrating renewable feedstocks like biomass. This review underscores the continued relevance and versatility of zeolites in modern catalysis and highlights the importance of ongoing innovation to meet future energy and environmental challenges.

## REFERENCES

1. Basina, G., AlShami, D., Polychronopoulou, K., Tzitzios, V., Balasubramanian, V., Dawaymeh, F., Karanikolos, G.N., Al Wahedi, Y. 2018. Hierarchical AlPO<sub>4</sub>-5 and SAPO-5 microporous molecular sieves with mesoporous connectivity for water sorption applications. *Surface and Coatings Technology*, 353, 378-386.
2. Boaventura, K.M., Peixoto, F.C., Fernandes, H.L.S., Pessoa, F.L.P. 2022. Long-Range Investment Assessment in a Petrochemical Industry: Cost and Safety Considerations. *Computers & Chemical Engineering*, 161, 107737.
3. Buekenhoudt, A., Kovalevsky, A., Luyten, J., Snijders, F. 2010. 1.11 - Basic Aspects in Inorganic Membrane Preparation. in: *Comprehensive Membrane Science and Engineering*, (Eds.) E. Drioli, L. Giorno, Elsevier. Oxford, pp. 217-252.
4. Chen, H., Wang, W., Ding, J., Wei, X., Lu, J. 2017. CO<sub>2</sub> Adsorption Capacity of FAU Zeolites in Presence of H<sub>2</sub>O: A Monte Carlo Simulation Study. *Energy Procedia*, 105, 4370-4376.
5. Drisko, J.A. 2018. Chapter 107 - Chelation Therapy. in: *Integrative Medicine (Fourth Edition)*, (Ed.) D. Rakel, Elsevier, pp. 1004-1015.e3.
6. Dyer, A. 2001. Zeolites. in: *Encyclopedia of Materials: Science and Technology*, (Eds.) K.H.J. Buschow, R.W. Cahn, M.C. Flemings, B. Ilschner, E.J. Kramer, S. Mahajan, P. Veyssière, Elsevier. Oxford, pp. 9859-9863.
7. Feng, C., Deng, Y., E, J., Han, D., Tan, Y., Luo, X. 2022. Effects of the ZSM-5 zeolites on hydrocarbon emission control of gasoline engine under cold start. *Energy*, 260, 124924.
8. Jiao, W., Su, J., Zhou, H., Liu, S., Liu, C., Zhang, L., Wang, Y., Yang, W. 2020. Dual template synthesis of SAPO-18/34 zeolite intergrowths and their performances in direct conversion of syngas to olefins. *Microporous and Mesoporous Materials*, 306, 110444.
9. Liu, W., Long, Y., Zhang, J., Liu, S., Zhou, Y., Tong, X., Yin, Y., Li, X., Hu, K., Hu, J. 2022. Ag-Cu modified ZSM-5 zeolite to effectively eliminate NO<sub>x</sub> and slip ammonia from coal-fired flue gas: Catalytic performance and characterization. *Journal of Environmental Chemical Engineering*, 10(5), 108461.
10. Naraki, Y., Ariga, K., Nakamura, K., Okushita, K., Sano, T. 2017. ZTS-1 and ZTS-2: Novel intergrowth zeolites with AFX/CHA structure. *Microporous and Mesoporous Materials*, 254, 160-169.
11. Pinto, R.V., Pinto, M.L. 2019. Chapter 14 - Nanoporous Materials: New Generation of Nitric Oxide Donors. in: *Therapeutic Application of Nitric Oxide in Cancer and Inflammatory Disorders*, (Eds.) L. Morbidelli, B. Bonavida, Academic Press, pp. 277-305.
12. Ratel, L., Kuznik, F., Johannes, K. 2022. Open Sorption Systems. in: *Encyclopedia of Energy Storage*, (Ed.) L.F. Cabeza, Elsevier. Oxford, pp. 526-541.
13. Strathmann, H., Giorno, L., Drioli, E. 2010. 1.05 - Basic Aspects in Polymeric Membrane Preparation\*. in: *Comprehensive Membrane Science and Engineering*, (Eds.) E. Drioli, L. Giorno, Elsevier. Oxford, pp. 91-112.
14. Wise, W.S. 2013. MINERALS | Zeolites☆. in: *Reference Module in Earth Systems and Environmental Sciences*, Elsevier.