CHAPTER II
LITERATURE REVIEWS

2.1 Zeolite

The first scientific report of a zeolite was published by Cronstedt in 1765, when he described the mineral stilbite as "boiling stones." The name "zeolite" is created from the Greek terms called "zeo," which means "to boil," and "lithos," which means "stone." In 1862, St. Claire Deville produced zeolites in a laboratory (Zimmermann & Haranczyk, 2016). However, the most crucial early developments in the industrial synthesis of zeolites were achieved in the 1950s by Milton and Breck at Union Carbide.

Zeolites are crystalline and hydrated aluminosilicates that were characterized by the structural framework made from silica and alumina tetrahedra interconnected by shared oxygen atoms. This framework includes distinct channels and cavities filled with ions and water molecules, giving zeolites unique physical and chemical properties. Based on TO4 tetrahedra (where T can be either an aluminum or silicon atom), zeolites are valuable for various applications, such as ion exchange, molecular sieves, gas adsorption, and catalysis. Zeolite LTA (Linde Type A) has a cubic zeolitic framework that features sodalite cages (SOD-cages), formed by linked single four- and six-membered rings. In the LTA framework, zeolite A contains an **α**-cage made up of eight cuboctahedra connected by twelve cuboids. Each SOD cage in LTA is correlated with its six closest neighboring SOD cages through double T4-rings (D4R).

Regarding energy consumption, the carbon economy, and production costs, researchers have paid great attention to seeking cheap raw materials to replace high-cost pure synthetic materials in the synthesis of zeolite A. Clay minerals, coal ashes, natural zeolites, municipal solid wastes, and industrial sludge are known as alternative raw materials for the synthesis of zeolite A owing to their low cost and available

abundance in nature and industry. Among available raw materials, bentonite minerals with Si and Al sources have been recognized as highly promising precursors for the synthesis of zeolite A. Bentonite is a natural clay used in many industries, including bonding, plasticizing, and suspending. Bentonite is made from silica tetrahedral sheets and one central alumina octahedral sheet (J. Wang et al., 2017). The theoretical composition of Bentonite contains 71.62% of SiO_2, 15.22% of Al_2O_3, and 13.17% of water. Thus, Bentonite can be used as the starting material for the synthesis of zeolite since its SiO_2/Al_2O_3 ratio (around 4.7) is in a suitable range with that of synthesis zeolite A.

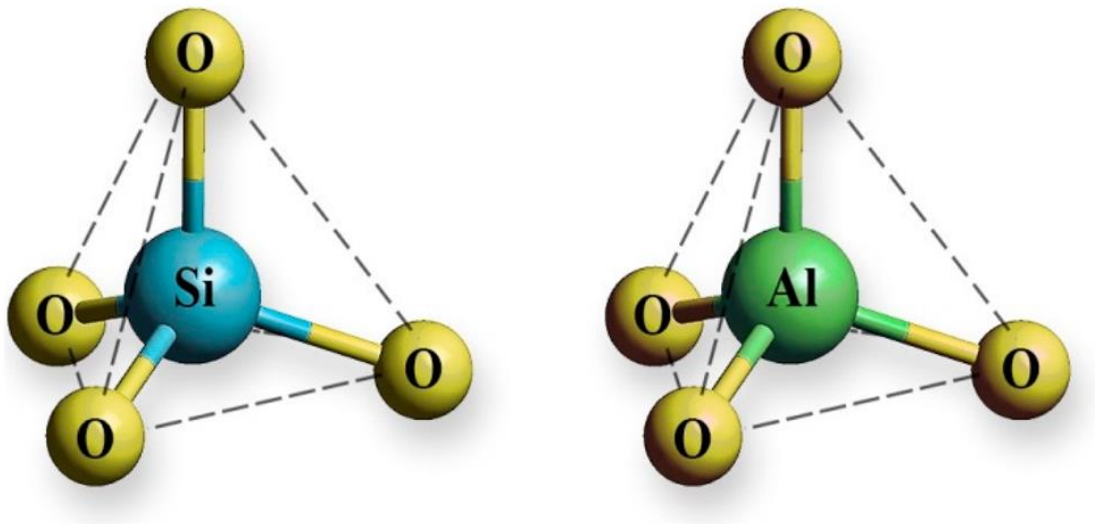

Figure 2.1 Representation of $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ tetrahedral

(Pavlović & Rajić, 2023)

Zeolites are crystalline aluminosilicates that possess microporous structures, with pore sizes between 3 and 7 Å. The latest Atlas of Zeolite Framework Types has cataloged approximately 176 different framework structures. The key attributes of these solid materials include their clearly defined structures, large surface areas,

effective adsorption of small molecules (acting as molecular sieves), and ion-exchange capability. Zeolites are composed of TO4 tetrahedra (T = Si, Al), which integrate oxygen atoms to form a 3D network. The extra framework cations can be ion-exchanged with other cations, for instance, alkali metals, alkaline earth metals, and transition metals. Besides, the Al content within the framework can vary from Si/Al≈1 to ∞ depending on the synthesis conditions. Moreover, Al or Si can be inserted into the framework during the post-synthesis modification process. Meanwhile, a higher Si/Al ratio of the framework can enhance both hydrophobicity and hydrothermal stability. Zeolite frameworks contain cages of different shapes, such as a spherical cage, which can be interconnected by channels with diameters determined by the number of T atoms as n-member rings. Large pore zeolites are constructed of 12-member rings (d > 7Å), medium pore zeolites contain 10-member rings (5Å < d < 6Å), while small-pore zeolites contain 6- or 8-member rings (diameter d: 2.8Å < d < 4Å. The Structure Commission of the International Zeolite Association (IZA-SC) assigns a three-letter code to each framework type. Table 2.1 illustrate essential zeolites with three-letter codes based on the Si/Al ratio or phosphate content

Table 2.1 Nomenclature and specifications of important zeolites

Low silica		**Intermediate Silica**		**High Silica**		**Other elements**	
Si/Al ≤ 2		**2 < Si/Al ≤ 5**		**5 < Si/Al**			
IUPAC name	Example	IUPAC name	Example	IUPAC name	Example	IUPAC name	Example
ANA	Analcime	BHP	Linde Q	BEA	Zeolite β	AEI	AlPO4-18
BIK	Bikitaite	FAU	NaY	FER	Ferrierite	AEL	AlPO4-11
CAN	Cancrinite	FER	Ferrierite	MEL	ZSM-11	AFN	AlPO4-14
EDI	Edintonite	LTL	Linde L	MFI	ZSM-5	AFR	SAPO-40
FAU	NaX	MAZ	Mazzite	MFS	ZSM-57	AFX	SAPO-56
FRA	Franzinite	MEI	ZSM-18	MSO	MCM-61	CAN	Tiptopite
LTA	Linde A	MER	Merlinoite	MTF	MCM-35	CHA	SAPO-47

Table 2.1 Nomenclature and specifications of important zeolites (Continued)

Low silica		**Intermediate Silica**		**High Silica**		**Other elements**	
Si/Al ≤ 2		**2 < Si/Al ≤ 5**		**5 < Si/Al**			
PHI	Phillipsite	MOR	Mordenite	MTT	ZSM-23	FAU	SAPO-56
SOD	Sodalite	OFF	Offretite	MWW	MCM-22	OSI	UiO-6
THO	Thomsonite	STI	Stilbite	ZSM	ZSM-48	SAV	Mg-STA-7

Low-silica zeolites, also known as aluminum-rich zeolites, have a nearly saturated aluminum content, with a molar ratio of Si/Al≈1. This structure allows for the maximum possible aluminum content in the tetrahedral framework (as seen in zeolites A and X). Low-silica zeolites contain the largest cation-exchange sites among zeolites, providing a strong hydrophilic surface selectivity. These zeolites have the largest pore volumes among known types, giving them a significant economic advantage in applications that require bulk separation and purification, where high capacity is essential.

Intermediate-silica zeolites were first developed at Union Carbide Laboratories in the early 1950s to provide enhanced thermal, hydrothermal, and acid stability. During production, these zeolites achieved significant commercial success as both adsorbents and hydrocarbon-conversion catalysts. The surfaces of these zeolites remain heterogeneous and demonstrate high selectivity for water and other polar molecules. Intermediate zeolites characterized by 2 < Si/Al < 5 in natural forms such as mordenite, erionite, clinoptilolite, and chabazite, also synthetic variants such as omega, mordenite, Y, and L. Within this Si/Al range, these materials retain hydrophilic properties.

High-silica zeolites are characterized by a silicon-to-aluminum (Si/Al) ratio greater than 5. This results in increased hydrophobicity and organophilicity, fewer intense Brønsted acidic sites, and enhanced thermal and hydrothermal stability. These materials can be synthesized directly by incorporating organic components into

aluminosilicate or silicate gels. Besides, they can be produced via post-synthesis modifications, such as hydrothermal steaming or treatment with aqueous (NH4)2SiF6, SiCl4, or F_2. Additionally, dealumination, which involves the removal of framework aluminum can improve catalytic properties and enhances thermal stability.

Many elements have been correlated with the zeolite framework, with the substitution of phosphorus by silicon within the zeolite structure. This led to the silica-aluminophosphates (SAPOs), which possess cation-exchange properties. Aluminophosphates (AlPOs) are composed of alternating AlO_2^- and PO_2^+ units to form a neutral, organophilic, and non-acidic framework. The incorporation of additional elements such as Si, Mg, Fe, Ti, Co, Zn, Mn, Ga, Ge, Be, Li, As, and B into the tetrahedral sites of AlPOs gives a vast number of element-substituted molecular sieves (MeAPO, MeAPSO, SAPO), which are essential heterogeneous catalysts.

Zeolites are widely used across multiple industries such as detergents, gas separation, desiccation, and catalysis. With lower cost, Natural zeolites are primarily utilized in bulk mineral applications. In 2008, the consumption of natural zeolites was estimated at 1.27×10^6 t. The second-largest application of zeolites is as catalysts, accounting for 17% by volume and over 55% of the market value, reflecting the higher cost of zeolites used in catalysis. Zeolite Y constitutes more than 95% of total zeolite catalyst consumption, primarily in the Fluid Catalytic Cracking (FCC) process. Smaller quantities are used in petrochemical synthesis and hydrocracking. In 2008, catalyst consumption was estimated at approximately 0.3×10^6 t. Zeolites also serve as adsorbents for drying and purifying petrochemical streams (such as ethylene and propylene), natural gas, and for bulk chemical separations (including normal paraffin and xylenes). Additionally, they are used in air separation industries to produce oxygen via pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA). In 2008, about 0.18×10^6 t (10%) of zeolite was used as an adsorbent. Other applications include the transformation of photochemical organics, sensor manufacturing, odor removal, paper fillers, solar energy conversion, plastic additives, soil conditioners and

fertilizers, pozzolanic cement and concrete, lightweight aggregates, and dietary supplements in animal nutrition. Global production of natural zeolites in 2008 was estimated at 3.0×10^6 t. China and Cuba are the largest consumers of additives used to enhance cement strength. Zeolite prices vary considerably depending on the application. In the United States, natural zeolite for bulk applications is priced between 0.04 and 0.25 USD per kilogram, whereas industrial adsorbent applications range from 1.5 to 3.5 USD per kilogram. For catalyst applications, prices range from 3 to 4 USD per kilogram for fluid catalytic cracking (FCC) and reach approximately 20 USD per kilogram for specialty catalysts. Adsorbent prices are generally 5 to 9 USD per kilogram, while detergent prices are around 2 USD per kilogram.

2.1.1 Zeolite A

Zeolite A or Linde Type A (LTA) is one of the most widely researched and applied synthetic zeolites. It possesses a highly crystalline aluminosilicate framework composed of interconnected TO_4 tetrahedra (where T = Si or Al) arranged in a cubic symmetry. The substitution of Si^{4+} by Al^{3+} in the framework generates negative charges that was balanced by exchangeable cations such as Na^+, Ca^{2+}, or K^+. This feature imparts zeolite A with remarkable cation-exchange capacity, therefore, it suitable for different applications. The framework of zeolite A is characterized by its three-dimensional pore system, featuring uniform pore openings of approximately 4.1 Å (for the NaA form), which enables selective adsorption and molecular sieving. Depending on the exchanged cation, the pore size can be adjusted; for example, the CaA form has an effective pore opening of ~5 Å, leading to the commercial terms 4A, 5A, and 3A zeolites. The unique structure of zeolite A has led to its extensive use in adsorption and ion-exchange processes. Its high affinity for polar molecules, particularly water, makes it an effective desiccant and drying agent in industrial processes. Additionally, the cation-exchange ability is exploited in water softening, where zeolite A efficiently removes calcium and magnesium ions, thereby reducing hardness. In environmental applications, zeolite A has been studied for the removal

of heavy metals, ammonium, and other toxic cations from contaminated water. Zeolite A has tunable ion-exchange selectivity to target specific contaminants for sustainable water treatment. Zeolite A also has a potential in adsorbing volatile organic compounds (VOCs) and greenhouse gases, thereby contributing to pollution control and energy-efficient separation technologies. Even though Zeolite A is less catalytically active than high-silica zeolites like ZSM-5, it still has niche applications in catalysis, especially when modified with metal cations. In the industrial sector, zeolite A is widely used as a detergent builder, which serve as an environmentally friendly alternative to avoid harmful phosphates. Its ion-exchange capability enhances washing efficiency by binding hardness ions, which increases the cleaning power of surfactants.

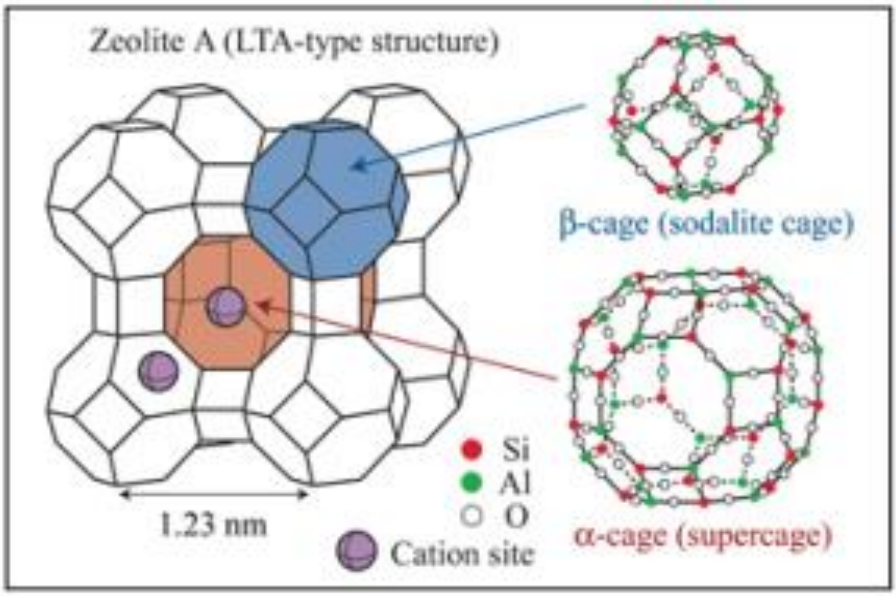

Figure 2.2 Features of the pores in zeolite A (IZA code LTA) (Petrov, 2012)

2.1.2 Zeolite properties

2.1.2.1 Zeolite as a catalyst

Table 2.2 illustrates the primary applications of zeolites as catalysts. Zeolites can be divided into three main categories: 1) Inorganic reactions,

2) Organic reactions, and 3) Hydrocarbon conversion. Zeolites exhibit several distinctive properties as catalysts, such as acidity, shape selectivity, high surface area, and structural stability. These characteristics will be discussed further in the following sections.

Table 2.2 Property of zeolites as a catalyst (Kianfar, 2020)

Inorganic reactions	**Organic reactions**	**Hydrocarbon conversion**
H_2S oxidation	Aromatisation (C4 hydrocarbons)	Allkylation
NO reduction of NH_3	Alkylation (naphthalene, benzene ethylbenzene, aniline, biphenyl, polyaromatics, etc.)	Cracking
CO oxidation, reduction	Aromatics (hydrogenation, oxidation, nitration, disproportionation, hydroalkylation, hydroxylation, oxyhalogenation, etc.)	Dehydration
Decomposition of H_2O	Chiral (enantioselective)	Fischer-Crafts alkylation
	Hydrogenation	Hydrocracking
	Cyclohexane (oxidation, isomerization, aromatization, ring opening)	Hydrogenation
		Dehydrogenation
		Hydrodealkylation
		Isomerization
		Methanol to gasoline
		Methanation
		Shape-selective reforming

2.1.2.2 Acidity and Basicity

Lewis acid is a species with electrons on its based that can be used for electron pairing. Brønsted states that acid-base contains protons, which appliable for transferring (H^+ ion) using acids as "proton donors" and bases as "proton acceptors." On solid surfaces, a Brønsted acid site can transfer a proton to an adsorbed molecule, while Lewis acid sites can accept electron pairs from those molecules. Besides, zeolites' acidity is primarily due to the presence of metal cations or hydroxyl protons in their extra-framework. In the case of aluminosilicate zeolites, the positive 4^+ charges on the silicon atoms in tetrahedral positions (T position) and the negative 2^- charges on the coordinating oxygen atoms result in neutral SiO_4 tetrahedra. Substitution of silicon atoms in the framework by aluminum atoms can change the corresponding tetrahedra charges from neutral to 1^-. These negative framework charges are balanced by extra-framework metal cations or hydroxyl protons, which form weak Lewis acid sites or strong Brønsted acid sites, respectively, and are responsible for the catalytic activity of the zeolite materials. Hydroxyl protons are found in zeolites, which are located on oxygen atoms that link silicon and aluminum atoms within the framework. Besides, the structural OH groups are referred to as Si-OH-Al groups (Figure 2.3a). Another hydroxyl group in zeolites is the silanol group (Si-OH), a terminal OH group found on the external surfaces of zeolite crystals (Figure 2.3b). The formation of these silanol groups results from dealumination of the zeolite framework via calcination, hydrothermal treatment, or strong-acid treatment. According to the specific treatment conditions, silicon migration, silanol group formation, and the generation of hydroxyl groups are correlated to an extra-framework aluminium (Figure 2.3c). In certain cases, dealumination results in the formation of Lewis acid sites at the extra-framework aluminium species and framework defects (Figure 2.3d). The proximity of these Lewis acid sites to bridging OH groups can generate superacidic Brønsted sites.

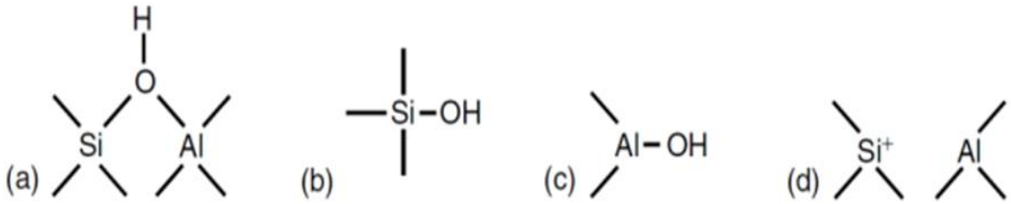

Figure 2.3 Different types of hydroxyl groups and acid sites in zeolites.
(Kianfar, 2020)

Despite the widespread use of acidic zeolites as solid catalysts in the chemical industry, relatively little attention has been given in the literature to their use as basic catalysts. These solid catalysts with basic properties have a considerable potential for several important industrial processes (e.g., Claus reaction). The nature of basic sites in zeolites is less well-defined than that of acid sites. The basic framework oxygen atoms or alkali metal cations in the zeolite framework contributes to their function as weak Lewis acid sites. The basicity of zeolites can be increased by modifying the framework's electronegativity or by incorporating basic components into their structure. Alkali-exchange of zeolites in aqueous solution or through solid-state ion exchange produces materials with basic framework oxygen atoms of relatively low base strength. Techniques such as IR spectroscopy, alkane cracking, UV-visible spectroscopy, temperature-programmed desorption of amines, microcalorimetry, and solid-state NMR spectroscopy have been used to quantify Brønsted and Lewis sites in solid-acid systems. However, these techniques do not readily distinguish between Lewis and Brønsted sites. Therefore, the combination of different characterization methods is often necessary to obtain comprehensive information.

2.1.2.3 Shape selectivity

Catalytic sites in zeolites can significantly affect reaction selectivity. Several classical concepts are valuable for catalyst designers in

understanding and predicting these influences. The size and shape of the pores, along with the properties of the reactants, determine whether molecules can be chemically activated at the active sites within the crystal structure. This phenomenon is referred to as reactant shape selectivity (RSS). When a mixture of product molecules desorbs from the intracrystalline active sites, the faster diffusing, "slimmer" molecules will be more prevalent, leading to a pseudothermodynamic equilibrium in the bulk phase. This effect is known as product diffusion shape selectivity (PDSS). Geometric constraints near the active site can hinder the formation of certain transition states, thereby affecting product selectivity. This phenomenon is known as transition-state shape selectivity (TSSS). Unlike other methods, crystallite-encapsulated sites are crucial for Reactive Selectivity and Product Distribution Selectivity (RSS and PDSS), while TSSS can also occur in half-open cages located at the ends of crystals. This phenomenon has primarily been observed in hydrocarbons and alkyl aromatics within medium-pore zeolites with 10-membered rings (10-MRs), and similar principles apply to functionalized organics and to different zeolite structures. The types of active sites extend beyond Bronsted acid sites; they also include metal and redox sites. This topic has been thoroughly reviewed in the literature. The application of these concepts implies that crystals can maintain compositional uniformity and that intracrystalline sites can display the same selectivity. It was initially suggested that factors such as pore size, tortuosity, and the pore structure defined by zeolite topology play significant roles in shaping the intrazeolitic fields and gradients. These factors, in turn, influence the rates of primary and secondary reactions and the overall selectivity. More recently, the impact of confinement on various kinetic and thermodynamic processes has been highlighted, shedding light on its effects on adsorption and diffusion. Configurational-bias Monte Carlo methods have enabled the simulation of slowly diffusing molecules confined within cages or adsorption sites in zeolite structures. This approach, which involves mapping the free-energy landscape in the intracrystalline space, overlooks the effects of local differences in site architecture or concentration on reaction selectivity. To account for several unexpected shape-selectivity phenomena observed

in long-alkane hydroconversion, the term inverse shape selectivity was coined. In zeolite pore widths of 0.65–0.74 nm, the opposite was encountered, that is, preferential formation of branched over linear hydrocarbons, viz., the formation of high yields of di-branched from n-alkanes over 10-MR zeolites like AFI (SAPO-5), the phenomenon being confirmed by adsorption experiments. The molecular basis of such effects has been attributed to purely entropic effects in monodimensional pores at high pressures, where smaller pores expel larger molecules. Several shape-selective phenomena were attributed to topology-dependent structural sites. Such nest effects resulted from tuning the curved catalyst surface to the configuration of adsorbed species, with entropic effects governing the fitting. A distinction has been established between two types of extra-framework catalysis, primarily in ZSM-22 (TON), namely pore-mouth and keylock selective catalysis. Alkanes can undergo hydroconversion to yield products that cannot be formed within or desorbed from the zeolite structure. The prevalent formation of specific molecules, such as 2-methylbranched alkanes from n-alkanes, has been attributed to transformation at a single pore mouth. In contrast, compounds like 2,4-dimethyloctane from n-decane are generated at adjacent pore mouths, with their selectivity influenced by both chain length and molecular topology.

Shape-selective catalysis varies based on the different dimensions of reactants, products, or intermediate molecules, and the pore size. Molecules with dimensions less than a critical size can enter the pores and react on the internal catalytic sites. However, molecules can leave the pores in the final product. Thus, shape-selective catalysis can be utilized to enhance the yield of desired products and prevent undesired products formation. Besides, shape selectivity is influenced by the pore-size constraints that govern the entry of reactant molecules, the diffusion or removal of product molecules from the pores, and the formation of specific transition states. These three factors may overlap, including:

1) Reactant selectivity

2) Product selectivity

3) Restricted transition state selectivity

Reactant selectivity is the ability to push material molecules pass through the zeolites' pores, while excluding larger molecules compared to pores size. In other words, only starting materials with specific sizes and shapes can penetrate the zeolite pores (see Figure 2.4a). This characteristic of zeolites is often described as a "molecular sieve." Table 2.3 compares kinetic molecular diameters of reagents with the pore openings of different zeolites. The analysis provides useful guidance for selecting an appropriate zeolite for a given starting material. However, the kinetic diameter offers only an approximate measure of molecular size, as molecules are not rigid structures. An example of reactant selectivity in zeolites is the dehydration of butanol over the CaA zeolite. The straight-chain alcohol is dehydrated much more quickly compared to iso-butanol, which has a larger molecular diameter. Product selectivity in zeolites occurs when the size of the molecule formed inside the pores is too large to diffuse out. Well-known examples of product selectivity in zeolites include the methylation of toluene and the disproportionation of toluene over the ZSM-5 zeolite. In both cases, all three isomers, including ortho, meta-, and para-xylene, are generated within the pores. Although the thermodynamic equilibrium corresponds to a p-xylene fraction (as the desired product) of only 24%, it can be obtained with a selectivity of more than 90%. This is because p-xylene has smaller dimensions and a diffusion rate that is 104 times faster than that of the other two isomers. In other words, although all isomers form relatively quickly within the zeolite cavity, p-xylene diffuses out of the cavity at a much faster rate.

Table 2.3 Pore sizes of zeolites and molecule diameters (Kianfar, 2020)

Zeolite	Pore size (Å)	Molecule	Kinetic diameter (Å)
KA	3.0	He	2.5
SAPO-34	3.8	NH_3	2.6
NaA	4.1	H_2O	2.8
CaA	5.0	N_2, SO_2	3.6
Erionite	3.8 x 5.2	Propane	4.3
ZSM-5	5.3 x 5.6	n-Hexane	4.9
Beta	5.6	Isobutane	5.0
CaX	6.9	Benzene	5.3
Mordenite	6.7-7.0	p-Xylene	5.7
NaX	7.4	CCL_4	5.9
AlPO-5	7.3	Cyclohexane	6.2
VPI-5	12.7	o-, m-Xylene	6.3

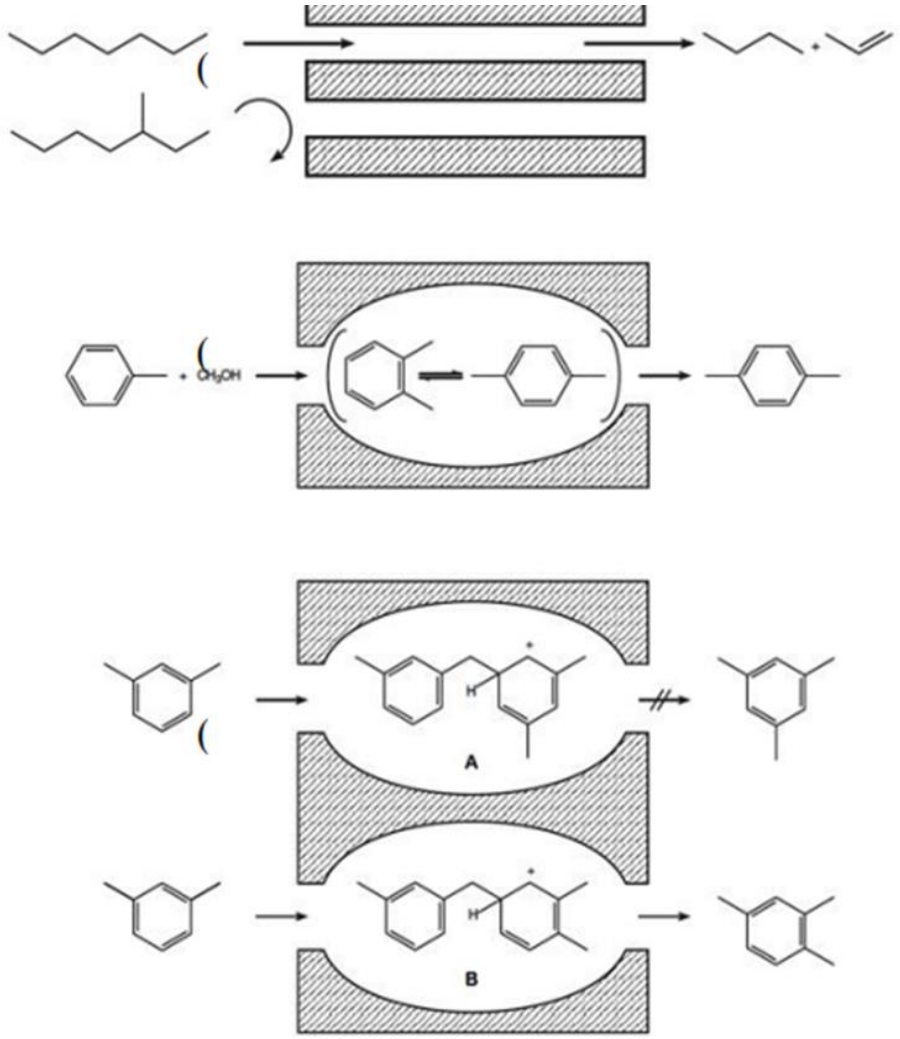

Figure 2.4 Shape selectivity of zeolites with examples of reactions: (Kianfar, 2020)

a) Reactant selectivity: cleavage of hydrocarbons,

b) Product selectivity: methylation of toluene

Since the Restricted transition-state selectivity depends on the available space within the zeolite's cavities or pores, the chemical reaction pathway is altered because specific reactions are prevented by the lack of space required for their corresponding transition states. Thus, intermediates with a geometrical fit to the zeolite

cavities can be formed during catalysis, and reactions that require smaller transition states can proceed with no hindrance. In practice, it is often difficult to distinguish between product selectivity and restricted transition state selectivity. Alkylation of benzene with ethylene over ZSM-5 to produce ethylbenzene exemplifies restricted transition-state selectivity. By limiting competing side reactions, the process can achieve high selectivity toward ethylbenzene.

2.1.2.4 Adsorption of zeolite

Zeolites are crystalline aluminosilicate minerals characterized by a highly ordered microporous framework consisting of interconnected channels and cavities. This unique structure endows them with exceptional adsorption properties, making them widely used in environmental remediation, gas separation, and catalysis. The adsorption behavior of zeolites arises primarily from their uniform pore size distribution, high surface area, cation-exchange capacity, and tunable hydrophilic/hydrophobic character. The adsorption capacity of zeolites is closely linked to their crystalline framework. The presence of tetrahedrally coordinated Si and Al atoms, connected via oxygen bridges, generates a negatively charged lattice that is balanced by the presence of extra-framework cations, such as Na^{+}, Ca^{2+}, or K^{+}. These cations not only stabilize the framework but also act as active sites for adsorption through ion-dipole interactions. The pore sizes of zeolites (typically ranging from 3 to 10 Å) provide molecular sieving ability, enabling selective adsorption of molecules based on size and shape. The structure of zeolites is made up of silicon-oxygen and aluminum-oxygen tetrahedra linked together by oxygen atoms. Zeolites can be classified based on their SiO_2/Al_2O_3 ratio into three categories: low siliceous zeolites (Si/Al mole ratio = 1–2), medium siliceous zeolites (Si/Al mole ratio = 3–10), and high siliceous zeolites (Si/Al mole ratio = 10^{+}). Low siliceous zeolites contain a high amount of AlO_4 units and Si–O–Al bonds, while high siliceous zeolites contain a lower amount. The Al–O bond consists of approximately 40% covalent and 60% ionic characteristics, whereas the Si–O bond is covalent. As a result, the Si–O–Al bond is much more polar

compared to the Si–O–Si bond. Highly polar water molecules (H_2O) interact more strongly with polar surfaces or groups than with relatively nonpolar ones. Therefore, the zeolites with a low SiO_2/Al_2O_3 ratio are generally more hydrophilic than those with a high SiO_2/Al_2O_3 ratio. Some typical zeolites with different types, Si/Al mole ratios, and water vapor adsorptions. The amount of water adsorbed on zeolites is strongly dependent upon the Si/Al ratio. In addition, there is little difference in water vapor adsorption between zeolite 3A and zeolite 13X with a similar Si/Al ratio, which indicates that water vapor adsorption (hydrophilicity) of zeolite is highly correlated with the Si/Al ratio rather than the zeolite type. For gas adsorption, zeolites have been widely studied for their gas adsorption capabilities such as CO_2, CH_4, and N_2. Studies have shown that zeolite A and zeolite X exhibit high selectivity for CO_2 due to their quadrupole moment and strong electrostatic interaction with the cations within the zeolite pores (Helfferich, 1985). The adsorption equilibrium and kinetics are influenced by the framework composition (Si/Al ratio) and the type of cation. For instance, NaA zeolite demonstrates superior CO_2 adsorption compared to CaA due to stronger interactions between CO_2 molecules and Na^+ sites. Beyond gas adsorption, zeolites are highly effective in adsorbing organic molecules such as dyes, phenols, and pesticides from aqueous media. The hydrophilic nature of low-silica zeolites favors the adsorption of polar molecules, while high-silica zeolites exhibit hydrophobicity, making them suitable for the removal of non-polar organic contaminants (S. Wang & Peng, 2010). For example, zeolite Y and ZSM-5 have been successfully applied in the removal of volatile organic compounds (VOCs). In contrast, zeolite A has demonstrated a strong affinity for methylene blue dye adsorption in wastewater treatment. Moreover, zeolites possess a significant ion-exchange capacity, which enhances their ability to adsorb heavy metal ions, such as Pb^{2+}, Cd^{2+}, and Cu^{2+}, from water. Natural zeolites, particularly clinoptilolite, have been widely studied for their application in water purification due to their low cost and high selectivity for divalent cations (Mumpton, 1999). The efficiency of adsorption depends different cation present types, the solution pH, and

the presence of competing ions. Surface modification of zeolites using surfactants or functional groups can further improve their affinity for specific pollutants.

Factors Affecting Adsorption Performance

1) Si/Al ratio: A Low Si/Al ratio can increase cation density, enhancing hydrophilicity and ion-exchange capacity, while a high Si/Al ratio improves hydrophobicity and thermal stability.

2) Cation type and exchange: Different cations alter the electrostatic field within the zeolite pores, thereby affecting adsorption affinity and selectivity.

3) Temperature and pressure: Adsorption of gases generally decreases with increasing temperature but increases with pressure.

4) Surface modification: Functionalization with organics or impregnation with metals enhances adsorption specificity toward target pollutants.

2.1.2.5 Modification of zeolites

The structure and composition of zeolites can be customized for specific applications through two main approaches: (1) Direct synthesis and (2) Post-synthetic treatment and modification. Direct synthesis is the primary method used to create zeolites. Several factors significantly influence the zeolite structure, including the composition of the synthesis mixture, synthesis temperature, reaction time, solution pH, aging and seeding conditions, as well as the directing agent or template used. However, in many cases, direct synthesis does not yield zeolites with the desired properties for their intended applications. To overcome this limitation, post-synthetic treatments such as ion exchange, the preparation of metal-supported zeolites, dealumination, the reinsertion of heteroatoms (such as boron, gallium, germanium, or aluminum) into the zeolite framework, and other modification methods offer practical alternatives to adjust zeolites for improved framework compositions and other properties. For instance, in the catalytic cracking process using HY zeolite, it is essential

to have strong acid activity along with high thermal and hydrothermal stability. It is well established that a higher SiO_2/Al_2O_3 ratio contributes to greater stability of the zeolite structure. However, few zeolites can be prepared using SiO_2/Al_2O_3 ratio through direct synthesis and this ratio is limited to a maximum value of around six. Dealumination in this case is a useful way to increase the SiO_2/Al_2O_3 ratio. Three dealumination methods have been used to produce the desired properties

1) Hydrothermal treatment (e.g., steaming).

2) Chemical treatment (e.g., reaction with EDTA, $(NH_4)2SiF_6$, $SiCl_4$, F_2 gas)

3) Combination of hydrothermal and chemical treatment (e.g., treatment with HCl, HNO_3, NaOH, KF).

The Si/Al ratio is important since the catalytic activity of a zeolite depends on the number of acidic hydroxyl (OH) groups associated with aluminum in its framework. This ratio directly influences the formation of carbonium or carbenium ions within the zeolite. Dealumination can improve the porous structure and enhance several important properties of zeolites, such as acidity, catalytic activity, thermal and hydrothermal stability, resistance to aging, and coking. However, excessive dealumination can reduce zeolite crystallinity. While dealumination is typically expected to lower zeolite catalytic activity, in some cases, if the increase in acid strength outweighs the decrease in acidic centers, dealumination can enhance catalytic activity. The increase in the acidity of hydroxyl (OH) groups is due to their interaction with aluminum species that have been displaced from the framework and are left within the cavities of the zeolite. The aluminosilicate structure of zeolites consists of ionic components, including Si^{4+}, $Al^{3+,}$ and O^{2-} ions. When Al^{3+} ions replace some Si^{4+} ions in the SiO_4 tetrahedra of the zeolite framework, this leads to the creation of an excess negative charge. To neutralize this negative charge, a compensating source of positive charge, in the form of cations, must be added. These non-framework cations

are crucial to determining the zeolite's catalytic properties. One method to incorporate cations into the zeolite is to use an aqueous salt solution, which allows the cations to enter the zeolite. Another method involves solid-state reactions between zeolites and cationic compounds intended to enter the porous structure. This approach offers several advantages over traditional liquid-phase ion-exchange processes as follow:

1) Prevention of handling large volumes of salt solutions

2) Less generation of waste salt solution

3) Introducing metal cations into narrow pore cavities where the ion exchange in aqueous solutions is not efficient.

2.1.3 Zeolite application

2.1.3.1 Microporous materials

Zeolites are crystalline aluminosilicates with three-dimensional framework of interconnected channels and cavities within the microporous range (< 2 nm). This structural feature provides them with high surface area, ion-exchange capacity, and molecular sieving ability, enabling selective adsorption and separation of molecules. Consequently, zeolites have become indispensable materials in industrial, environmental, and biomedical applications (Corma, 1997). One of the most prominent uses of zeolites is in gas separation and purification. Their uniform pore system allows them to differentiate molecules based on size and polarity. Zeolite A, in particular, possesses pore openings of approximately 0.41 nm, making it suitable for separating oxygen (kinetic diameter 0.346 nm) from nitrogen (0.364 nm). This property is utilized in pressure swing adsorption (PSA) oxygen concentrators, where nitrogen is preferentially adsorbed within the pores of the zeolite, resulting in an oxygen-enriched effluent. The efficiency and performance of such systems depend strongly on the crystallinity, purity, and adsorption capacity of the zeolite used. In addition to medical oxygen generation, zeolites are widely applied as heterogeneous catalysts in

petroleum refining and petrochemical industries, where they facilitate processes such as fluid catalytic cracking, isomerization, and hydrocracking. Their high thermal stability and shape-selective catalysis enable efficient conversion of hydrocarbons into fuels and valuable intermediates (Corma, 1995; Degnan, 2003). Zeolites also play a significant role in environmental protection and remediation. Due to their ion-exchange properties, they are utilized for water softening, removing heavy metals, and treating wastewater. Their strong adsorption capacity for gases such as CO, NH_3, and volatile organic compounds (VOCs) makes them effective in air purification and greenhouse gas mitigation (Mumpton, 1999; S. Wang & Peng, 2010). Additionally, zeolites are used as drying agents, odor absorbers, and carriers for fertilizers in agricultural applications. In the context of this thesis, the primary application of zeolite as a microporous material lies in the synthesis of Zeolite A for oxygen concentrators. Utilizing natural raw materials such as ball clay for zeolite synthesis provides a cost-effective and sustainable route for producing adsorbents that meet the growing demand for medical oxygen. This highlights the importance of zeolite's microporous framework in enabling selective adsorption processes, particularly in life-saving technologies such as PSA oxygen concentrators.

2.1.3.2 Applications of Zeolite A in Agriculture

Zeolite A has found increasing applications in agriculture because of its capability in high cation exchange, water retention ability, and environmental compatibility. While naturally occurring zeolites such as clinoptilolite are more commonly utilized, synthetic zeolite A has demonstrated comparable performance in improving soil quality, enhancing nutrient efficiency, and promoting sustainable agricultural practices (Reháková et al., 2004). One of the key agricultural applications of zeolite A is its use as a soil amendment. The porous framework of zeolite A enables high water absorption and slow release, which improves soil moisture retention in arid and semi-arid regions. This property has been particularly beneficial in countries with water scarcity, such as parts of the Middle East and Africa, where

zeolites have been applied to mitigate drought stress in crops (Karaca, 2004). Additionally, zeolite A acts as an ion exchanger, which can reduce the leaching of ammonium, potassium, and calcium, from the soil. By holding cations within its structure and releasing them gradually, zeolite A enhances fertilizer efficiency and reduces the need for repeated applications. Studies from Asia and Europe have reported that zeolite amendments improve nitrogen-use efficiency in rice and maize cultivation, thereby increasing yields while lowering fertilizer costs (Bansiwal et al., 2006; Leggo, 2000). Zeolite A has also been applied in animal husbandry and waste management. When incorporated into animal feed, it helps in binding excess ammonium ions, reducing odor emissions, and improving animal health. In regions with intensive livestock production, such as Europe and North America, zeolite A has been utilized to treat manure and control ammonia emissions, thereby contributing to environmental sustainability. Globally, the use of zeolite A in agriculture reflects its role as a multifunctional material for sustainable farming practices. Its contributions to soil improvement, fertilizer efficiency, water conservation, and waste treatment align with current global priorities in achieving food security and reducing environmental impacts. The potential for large-scale application of zeolite A, particularly when synthesized from inexpensive raw materials such as clays, further highlights its relevance for both developed and developing countries.

2.1.3.3 Applications of Zeolite A in Medicine

Zeolite A has attracted significant attention in the medical field due to its ion-exchange capability, adsorption capability, and biocompatibility. Its unique structure enables selective adsorption of ions and molecules, making it highly suitable for biomedical and pharmaceutical applications. One of the most prominent applications of zeolite A in medicine is as a drug delivery carrier. The porous structure allows for the encapsulation of therapeutic molecules, providing controlled release and enhanced bioavailability. For instance, zeolite-based systems have been used for the sustained release of antibiotics and anticancer drugs, where the zeolite framework

protects the drug from degradation and ensures targeted delivery. Zeolite A has also been reported to exhibit detoxifying effects within biological systems. Its ion-exchange properties have the capabilities to remove toxic from heavy metals and ammonium ions from the body, making it useful in therapies aimed at detoxification. Additionally, the high surface area and negative charge of zeolite A facilitate adsorption of harmful metabolites and pathogens, supporting its use as a dietary supplement in human and veterinary medicine. In wound healing and tissue regeneration, zeolite A has demonstrated potential as an antimicrobial and hemostatic agent. Studies have shown that zeolite-containing dressings can accelerate blood clotting by activating the coagulation cascade and simultaneously reducing infection risks through microbial adsorption. This dual functionality positions zeolite A as a valuable material in surgical and emergency medicine. Furthermore, zeolite A is being investigated for cancer therapy. Its adsorption properties may reduce oxidative stress and limit the proliferation of tumor cells. Some studies suggest that zeolite can enhance immune response and improve the efficacy of conventional cancer treatments (Pavelić et al., 2001). Although more clinical evidence is needed, these findings highlight its potential role in complementary oncology. Overall, the applications of zeolite A in medicine underscore its versatility as a biocompatible microporous material. Its roles in drug delivery, detoxification, antimicrobial activity, and tissue engineering continue to be the focus of research, contributing to the development of novel medical technologies.

2.1.3.4 Applications for industry

Since 2010, research has increasingly focused on using zeolite A as a supplementary cementitious material (SCM) to enhance the durability and sustainability of concrete. A key benefit is its pozzolanic activity, where it reacts with calcium hydroxide ($Ca(OH)_2$) to form calcium silicate hydrate (C-S-H) gel, which enhance the concrete matrix (Alexa-Stratulat et al., 2023). This densification leads to several improvements, for example, enhanced mechanical properties. Studies have shown that the addition of zeolite A can significantly improve the compressive strength and

flexural strength of mortars and concrete by refining the pore structure. Improved durability, achieved by using zeolite A, helps mitigate the harmful alkali-aggregate reaction (AAR), a major cause of concrete degradation, by consuming the free alkalis. Utilizing zeolite A as a partial substitute for Portland cement enhances environmental sustainability by reducing overall cement content, which consequently lowers the carbon footprint associated with concrete production. These recent findings solidify the role of zeolite A as a promising and eco-friendly additive for modern construction.

Zeolite A's unique molecular sieve properties and tunable acidity have made it a subject of extensive research in the catalyst industry since 2010. Its small pore size allows for shape-selective catalysis, controlling which molecules can enter and react within its framework.

Recent literature focuses on zeolite A's applications as both a catalyst and a catalyst support:

Catalyst Support: It serves as an excellent support for metal nanoparticles, preventing them from clumping and deactivating. This makes it a popular choice for reactions, including the selective catalytic reduction (SCR) of nitrogen oxides (NOx) from vehicle emissions (Cho et al., 2017).

Hydrogen Production and CO_2 Conversion: Zeolite-supported transition metal catalysts are being explored for hydrogen-related reactions and for the conversion of CO_2 to valuable products, addressing key challenges in clean energy (M. Liu et al., 2024).

Biomass Conversion: Researchers are utilizing zeolites to convert biomass into green fuels and high-value chemicals, a crucial step toward sustainable chemistry (Qazi et al., 2022)

2.1.3.5 Adsorption of Harmful Substances

Zeolites, crystalline aluminosilicates with a three-dimensional framework are widely studied due to their exceptional adsorption capabilities. Their unique pore architecture, high specific surface area, and ion-exchange properties make them highly effective in capturing and immobilizing harmful substances from air, water, and industrial effluents. Over the past decades, researchers have investigated natural and synthetic zeolites as adsorbents for heavy metals, dyes, organic pollutants, and toxic gases, demonstrating their versatility in environmental remediation. Zeolites possess uniform micropores (0.3–1 nm), which provide selective adsorption sites for molecules of compatible size. The negatively charged aluminosilicate framework, balanced by exchangeable cations (Na^+, K^+, Ca^{2+}), enhances their affinity toward polar and ionic species. The hydrophilic or hydrophobic nature of a zeolite depends on its Si/Al ratio, which in turn influences its adsorption capacity for water, organic compounds, and heavy metals. High thermal and chemical stability further enables their application in diverse adsorption processes. One of the most extensively studied applications of zeolites is the removal of toxic heavy metals from aqueous systems. Studies have demonstrated that clinoptilolite, a natural zeolite, effectively adsorbs Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} ions through ion-exchange mechanisms. For instance, Wang and Peng (S. Wang & Peng, 2010) reported that zeolite-based adsorbents exhibit high selectivity toward lead ions due to their ionic radius compatibility with the zeolitic channels. Modified zeolites, such as those treated with surfactants or impregnated with iron oxides, have shown improved removal efficiency for arsenic and chromium species, highlighting the importance of surface modification in enhancing adsorption capacity. Zeolites also demonstrate potential in eliminating organic pollutants, including synthetic dyes, phenols, and pharmaceutical residues. Their adsorption mechanisms often involve hydrophobic interactions, electrostatic attraction, and molecular sieving effects. Studies indicate that high-silica zeolites, such as ZSM-5, exhibit a strong affinity for volatile organic compounds (VOCs) and aromatic

hydrocarbons due to their hydrophobic pore surfaces. In the textile industry, zeolite-based adsorbents have been explored for treating dye-contaminated wastewater, with surface-modified zeolites demonstrating enhanced uptake of both cationic and anionic dyes. Beyond water treatment, zeolites play a critical role in capturing harmful gases. Zeolites 13X and 5A are widely used for removing CO_2, SO_2, and NOx from flue gases. Their well-defined pore sizes and strong interactions with polar molecules enable selective adsorption even in mixed-gas environments. Furthermore, zeolites play a crucial role in pressure swing adsorption (PSA) systems for purifying air and natural gas. Recent studies have also highlighted their role in capturing ammonia and hydrogen sulfide, demonstrating their contribution to controlling industrial air pollutants.

2.1.3.6 Zeolite molecular sieve

The year 1979 marked the twenty-fifth anniversary of the commercial introduction of molecular sieve zeolites as a new class of industrial materials. These materials were first introduced in late 1954 as adsorbents for industrial separations and purifications. Since then, the interest in and appreciation for this unique class of materials have led to a substantial amount of scientific literature. To date, there are over 15,000 scientific articles and more than 10,000 issued patents dedicated to their synthesis, properties, structure, and applications. The molecular sieve industry is projected to have grown into an estimated quarter of a billion-dollar market, serving all major segments of the chemical process industries, including significant applications in the petroleum refining and petrochemical industries. It has generated a myriad of other adsorption, catalytic, and recent ion exchange applications. In 1967, Milton examined the origins and advancement of molecular sieve zeolites. Milton states that the initial findings and synthesis of new zeolites A, X, and Y, which subsequently led to their use in various commercial roles as selective adsorbents and catalysts. This study will discuss the progression of molecular sieve materials, including their synthesis, properties, and applications from 1954 to 1979, focusing on significant milestones and trends in these areas. It will not attempt to

replicate the comprehensive studies of zeolite molecular sieves by Breck or Barrer, nor the latest review articles on the use of molecular-sieve zeolites as adsorbents, catalysts, and ion exchangers, or on the applications of natural zeolites. The success of molecular sieve zeolites discovers new materials whose properties have been engineered to enhance existing processes and support the development of new ones. The application of molecular sieve zeolite adsorbents for various separations and purifications has become well established in the chemical process industries. Purification applications generally rely on surface selectivity for polar or polarizable molecules, such as water, CO_2, or sulfur compounds, as well as bulk separations based on molecular sieving principles. For instance, pressure swing adsorption in air separation was initially conceptualized by Milton as a molecular sieving operation based on the sizing difference between oxygen and nitrogen molecules. Also, the strong specific interaction between nitrogen's molecular quadrupole and the cation, with purification applications involving molecular sieving, where the selection of the zeolite adsorbent is determined by pore size, is designed to exclude potentially co-adsorbed molecules. For example, using type 3A molecular sieve for drying cracked gas effectively prevents the co-adsorption of ethylene and heavier unsaturated hydrocarbons. The unique structure of zeolite creates a system of uniform micropores and channels that can selectively adsorb molecules based on size, polarity, and shape. Due to their highly ordered pore system, zeolites are commonly referred to as molecular sieves, with pore sizes typically ranging from 3 to 10 Å, making them suitable for separating and adsorbing small gas molecules, such as nitrogen, oxygen, and carbon dioxide. The ion-exchange capacity of zeolites, resulting from the substitution of Si^{4+} by Al^{3+} in the framework, further enhances their adsorption and catalytic properties (Jha & Singh, 2016). This feature has led to their extensive use in industrial applications, including gas separation, purification, catalysis, and environmental remediation. In gas separation technologies, molecular sieves play a central role in processes such as pressure swing adsorption (PSA), where zeolites, particularly zeolite 5A and 13X, are employed to selectively adsorb nitrogen and enrich oxygen in medical and industrial

oxygen concentrators (Sircar, 2002). Moreover, the selectivity of zeolite molecular sieves can be tailored by adjusting the Si/Al ratio, framework topology, and cation-exchange properties, making them versatile materials for advanced applications. The stability, regenerability, and environmental compatibility of zeolite molecular sieves have positioned them as a key class of microporous materials in both traditional and emerging technologies.

2.2 Zeolite synthesis method

Zeolites can be synthesized from a variety of raw materials, both mineral and man-made. However, not all raw materials are economically viable for zeolite synthesis. Therefore, suitable raw materials should possess specific properties: they must be inexpensive, readily available, have low production costs, be selective in their reactions, yield high production levels, and contain minimal foreign substances. To date, several physicochemical and solvothermal methods have been adopted and developed to produce synthetic zeolites. This includes the hydrothermal method (Sugano et al., 2005), the alkali-fusion method, the sol-gel method, and the alkali-leaching method (Shoppert et al., 2017). The choice of synthesis method depends on the specific type of zeolite to be produced, as each technique has its own advantages and limitations.

2.2.1 Hydrothermal method

The hydrothermal technique is considered the primary method for synthesizing zeolites. This approach is essentially solvothermal, where water serves as a solvent and a base act as a mineralizer at varying temperatures and pressures. Conventionally, hydrothermal synthesis needs to use a sealed vessel usually made of polypropylene and Teflon-lined (PTFE) steel autoclave (Sangeetha & Baskar, 2016). Since the hydrothermal method requires lower temperature, this method is straightforward and more cost-effective. Zeolites are typically synthesized via a

hydrothermal approach (Cundy & Cox, 2003b) due to different advantages agreed by many researchers, which include low energy consumption, high reactivity of reactants, ease of maintenance over the solution, reduced air pollution, formation of metastable phases, and unique condensed phases. Numerous factors can influence the performance of hydrothermal methods, including temperature and pressure, batch composition, silica-to-aluminum ratio, reactant materials, overall alkalinity, aging time, template conditions, and seeding (Johnson & Arshad, 2014). To date, numerous attempts have been made to synthesize zeolites using the traditional hydrothermal technique. For instance, Wang et al. demonstrated the creation of synthetic zeolite (ZSM-5) from expanded perlite (or kaolin) through this method (P. Wang et al., 2007). Another research team successfully developed various hierarchical zeolite structures (BEA, LTA, FAU) using the conventional hydrothermal process (H. Chen et al., 2011). However, recent advancements have been made in this methodology. For example, Yao et al. produced Zeolite X powder from diatomite rich in silica and alumina using an eco-friendly and simplified hydrothermal approach (Yao et al., 2018). This Zeolite X shows significant promise for applications in industry, catalysis, and adsorption technology. Additionally, many researchers have reported the synthesis of zeolite A from aluminoborosilicate glass utilizing a hydrothermal method, with acid treatment applied beforehand to enhance the formation of a single-phase zeolite A with high crystallinity. There have also been efforts to produce zeolite A from municipal waste, an economical option with a higher alumina content (Terzano et al., 2015). Moreover, zeolite K–F was synthesized from recycled amber container glass using a one-pot hydrothermal technique (Taylor et al., 2020). The advantages of this process are that it does not require pre-treatment for the activation or the removal of hazardous components. However, the conventional hydrothermal method does not satisfy the severe terms of sustainability, as it uses structural directing agents that directly integrate and fill the pore volume of synthesized zeolites, which must be removed by high-temperature combustion. Therefore, there is a significant risk of hazardous and greenhouse gas emissions impacted by high-temperature combustion. Moreover, the

generation of high autogenous pressure in the (PTFE) lined steel autoclave, caused by heating the reaction mixture, can pose a severe threat to the equipment. Also, the conventional hydrothermal synthesis approach is often viewed as a high-energy-consuming method because it takes an extended time (1–20 days) to achieve final production. In the conventional hydrothermal method, controlling nucleation is difficult due to slow mixing hence, while uncontrollable nucleation leads to the formation of larger crystal sizes (Li et al., 2006). An agitator is often used to address issues, but it primarily promotes the movement of macroscopic layers. As a result, the mixing within these layers relies on the slow diffusion of reactant molecules. To enhance the the conventional hydrothermal strategy for zeolite synthesis, researchers have developed various sustainable methods. These include the microwave-assisted hydrothermal method, the alkali-fused hydrothermal method, the microwave-digested alkali-fusion-assisted hydrothermal method, and the ultrasound-assisted hydrothermal method. The microwave-assisted synthesis method is noted for its unique "microwave effects." Katsuki et al. (Katsuki et al., 2005) emphasized the synthesis of zeolites using microwave heating can significantly reduce the zeolite production time compared to traditional hydrothermal methods. They recognized that employing microwave heating throughout the synthesis can effectively shorten reaction time. For instance, NaY zeolite was synthesized by microwave heating in 10-15 minutes, yielding high crystallinity and purity. However, synthesizing zeolites from waste raw materials results in multiphase products and requires an extended process. Therefore, alkali fusion before hydrothermal treatment can reduce synthesis time and prevent the formation of inert multiphases (Bukhari et al., 2015). Several attempts have been made to synthesize zeolite using the alkali-assisted hydrothermal method. For example, the synthesis of zeolite X has also been carried out using a low-grade bauxite raw material through a two-step synthesis method. Meanwhile, Belviso et al. (Belviso et al., 2017) explored the use of clay minerals to synthesize various types of synthetic zeolites, including sodalite, faujasite, and A-type zeolite. They employed an alkaline hydrothermal method along with pre-alkali fusion, which could be done with or

without adding alumina. Additionally, they noted that industrial waste, specifically bauxite tailings, has been utilized for the synthesis of zeolite X. Other raw materials, such as waste perlite dust, fly ash, and steel slag, have also been used to synthesize faujasite, zeolite Y, and zeolite X through hydrothermal methods. It is important to note that the alkali fusion method requires high temperatures, exceeding 800°C. To reach a higher temperature within a short period, researchers have integrated a microwave heating system into the alkali fusion hydrothermal method. Mason and Peters described a method involving fusion pretreatment and microwave-assisted hydrothermal processes to create zeolite from fly ash generated by municipal solid waste incineration (MSWI). The fusion pretreatment transformed quartz into an amorphous state, allowing it to dissolve easily in a hydrothermal solution, thus speeding up the zeolite production process. Despite its drawbacks, the hydrothermal method holds significant promise for generating faujasite, X, Y, and ZSM-5-type zeolites tailored for specific uses. In conclusion, the hydrothermal synthesis of zeolites shows considerable potential, providing various advantages.

2.2.2 Sol-gel method

The sol–gel method is a physicochemical technique in which an inorganic colloidal suspension, or “sol,” undergoes structural evolution to form a three-dimensional gel network within a continuous liquid phase, as illustrated in Figure 2.5 This process effectively facilitates the transition of a liquid solution into a solid gel. One of its key benefits is the enhanced control it provides, resulting in increased porosity and specific particle sizes. Several factors can affect the effectiveness of the sol-gel process, including (i) the rate of hydrolysis, (ii) temperature, and (iii) the rate of heating, and (iv) pH. There are many reports on this method. For example, Wu et al. (Wu et al., 2009) reported a two-step sol-gel route for the synthesis of MCM-22 zeolite regarding static hydrothermal conditions using the silica source from tetraethyl orthosilicate. Phiriyawirut et al. (Phiriyawirut et al., 2003) synthesized the MFI zeolite directly from the silatrane. The reaction temperature was varied using microwave

heating. They reported that a long aging time is more critical to achieve high crystallinity. Sathupunya et al. (Sathupunya et al., 2002) illustrated the synthesis of analcime (ANA) and gismondine-type (GIS) zeolites directly from the precursor of alumatrane and silatrane. This technique together with the microwave-assisted method and does not require specialized and expensive equipment. This method delivers high-quality, homogeneous product through molecular-level mixing. Besides various advantages, there are some limitations, such as the cost of precursors, which need to be overcome in the future.

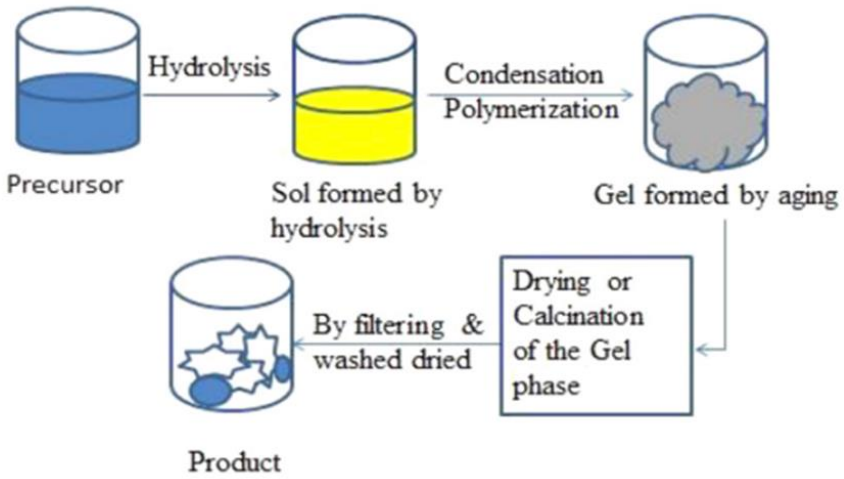

Figure 2.5 Sol-gel method for the synthesis of zeolite. (Khaleque et al., 2020)

2.2.3 Microwave method

Microwave heating is a fast, energy-efficient technique for synthesizing zeolites by applying microwave radiation. Microwaves act as high-frequency electric fields that ultimately generate heat to drive the reaction. Therefore, the energy can transfer from the microwave to the reactant material through resonance or relaxation. There are many advantages of using microwave methods. For example, it gives concise

time, which leads to small particle size and high-purity zeolite can be obtained (Fig 2.6). Factors that affect the microwave method are (i) SiO_2/Al_2O_3 molar ratio (Si/Al), (ii) alkalinity, (iii) wavelength produced from the magnetron, (iv) zeolization time and temperature, (v) crystallization time and temperature. In most cases, microwave-assisted synthesis of zeolites is combined with other methods, such as hydrothermal, solvothermal, and ionothermal methods. For example, Kim et al. used microwave irradiation to synthesize synthetic zeolite beta in fluoride media. In their experiment, they demonstrated that fluoride mineralization under microwave irradiation and seeding reduced particle size by increasing nucleation (Kim et al., 2004). Recently, a rapid microwave-heating method was developed for the liquid-phase synthesis of Y-type zeolite at high temperatures. The effects of microwave heating temperature, crystallization time, and silica-to-alumina ratio on the synthesis of Y-type zeolite are systematically investigated.

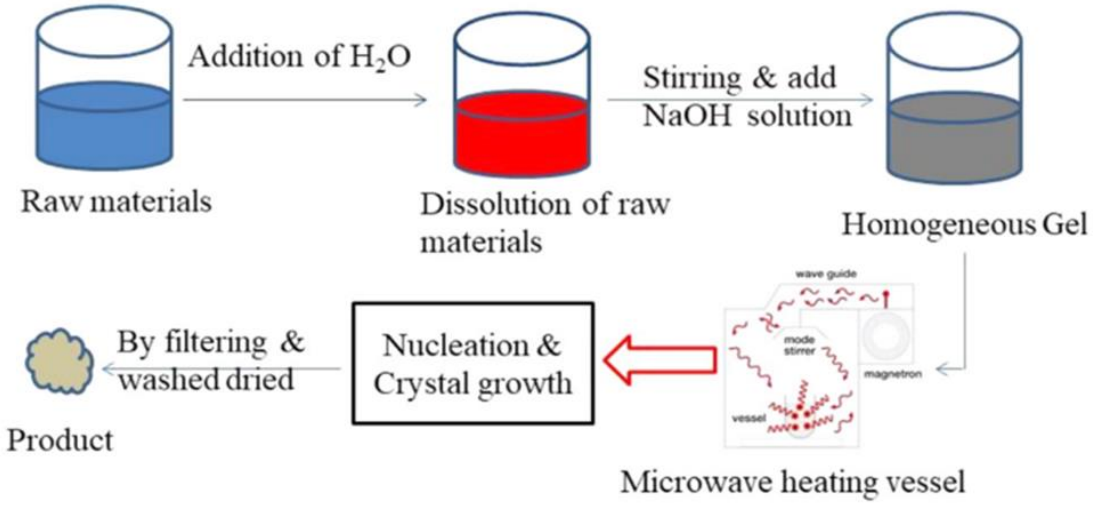

Figure 2.6 Microwave method for the synthesis of zeolite.

(Khaleque et al., 2020)

2.2.4 Ultra-sound energy method

Ultrasound with frequencies ranging from 20 kHz to 2 MHz is a branch of sonochemistry that is widely used in synthetic chemistry. Ultrasound has a significant influence on various types of synthesis cases, including the synthesis of amorphous or crystalline materials and polymerization reactions. Due to its significant influence on crystallization, ultrasound has received considerable attention in zeolite synthesis. The advantages of this method are straightforward: it has a rapid reaction, does not require complex facilities, provides a high crystal growth rate, offers a suitable particle size distribution and morphology, and allows control of the nucleation process. Ultrasound induces cavitation, the growth and explosive collapse of microscopic bubbles. Cavitation can also increase secondary nucleation rates and improve crystal purity during cooling crystallization. Owing to the various traditional and emerging applications of synthetic zeolites, the ultrasound energy method enables tunable zeolite synthesis. Temperature, time, and the molar ratio of reactants are considered the main parameters to determine the type and characteristics of the zeolite formed. Ultrasound energy methods have been used extensively to synthesize zeolites. For example, Pal et al. reported the synthesis of NaP zeolite nanocrystals at ambient temperature in a short crystallization time via ultrasound (Pal et al., 2013). Herein, sonication energy enables the formation of active radicals, which in turn lead to rapid crystallization of the zeolite phase. Synthesis of hierarchical ZSM-5 zeolites with long-term catalytic activity was also reported via ultrasound-assisted synthesis (Huang et al., 2016). Therefore, ultrasound energy-assisted methods are attractive to researchers due to their significant influence on zeolite synthesis.

2.2.5 Alkali-fusion and leaching method

In zeolite synthesis, the alkali fusion method is a general approach for decomposing materials rich in silica or alumina in the presence of alkali, which acts as an activator to form soluble aluminate and silicate salts. Solvothermal methods also use alkali (e.g., NaOH), but there are some differences between solvothermal and

alkali-fused methods. In the alkali fusion method, alkali is used to prevent multi-phase formation and is fused with the raw materials in a solid state before being introduced to any solvent. In contrast, in the solvothermal method, alkali is used in a solution state and acts as a mineralizer of the reaction medium. Generally, in the alkali-fusion method, the raw material is first fused with an alkali (e.g., NaOH) before a hydrothermal treatment (Fig2.7). During the hydrothermal treatment, the fused product is mixed with water and treated with the proper conditions, like heating at an appropriate temperature for the crystallization to form zeolite. Factors affecting the alkali-fusion methods are (i) the silicon-aluminum ratio of the raw material, (ii) concentrating the reacting alkali medium, (iii) temperature, and (iv) crystallization rate. Many studies have previously been conducted to synthesize zeolites using this method. For example, the synthesis of X-type zeolite by alkali fusion (e.g. sodium carbonate as an activator) followed by hydrothermal treatment using coal fly ash as a raw material. It was found that the alkali activator has a significant influence on the synthesis of synthetic zeolite. In addition, the alkali fusion method is usually used to synthesize zeolite A, zeolite X, and hydroxysodalite from the BFS. In a previous study, Chen et al. reported the synthesis of zeolite X from lithium slag through a hydrothermal reaction with alkali fusion. They mentioned the excellent properties of the zeolite (D. Chen et al., 2012). Moreover, in most processes, the alkali fusion technique is followed by a hydrothermal method for synthesizing zeolite. Both methods require high temperatures, time, and pressure. The primary sources for zeolite synthesis are commercial chemicals, which are very rich in alumina silicate, mineral resources in the earth's crust, and industrial by-products. By adjusting the experimental conditions, a range of zeolitic materials such as zeolite X, zeolite P, hydroxysodalite, tobermorite, and nepheline can be synthesized. This approach enables the use of low-grade raw materials without prior purification and produces high-purity anhydrous zeolites, offering a notable advantage. Alkali leaching is another approach in which the leachate maintains the silica-alumina ratio, such as with a NaOH solution. The factors that influence the alkali leaching method are (i) desalination rate, (ii) silica-alumina ratio of leachate-free solid product,

(iii) fusion temperature, (iv) concentration of leaching agent, and (v) crystallization rate. Several investigators have reported different zeolite syntheses via an alkali-alkali leaching approach. For instance, El-Naggar et al. synthesized pure zeolites using the alkaline leaching method from silica extracts obtained from fly ash. Their synthesized A-X zeolite blends showed the most significant potential for cesium ion sorption. The main benefit of this route is the production of a very efficient product at a low cost (El-Naggar et al., 2008).

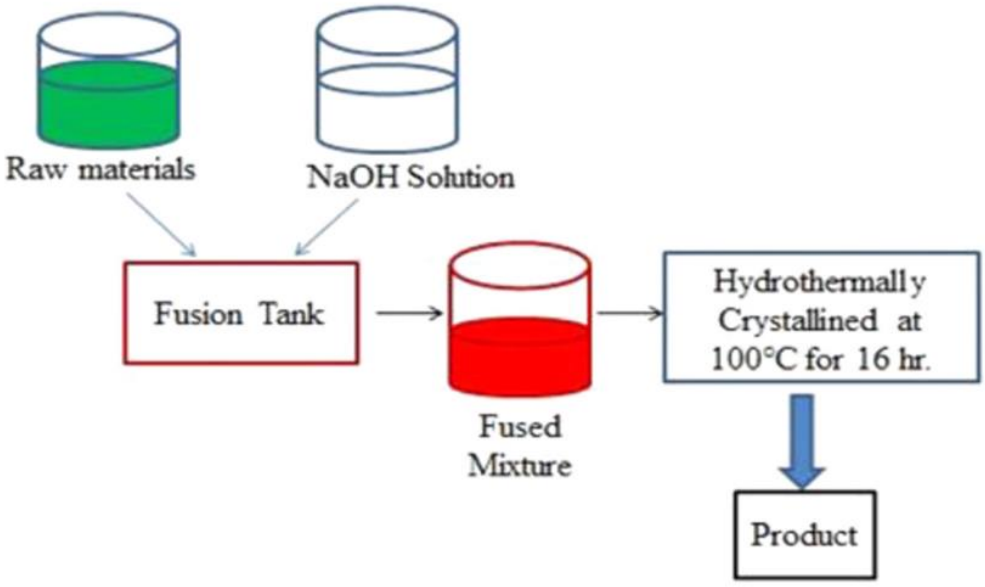

Figure 2.7 A schematic representation of zeolite synthesis via the alkali fusion method (Khaleque et al., 2020).

2.3 Ball clay

Ball clays are fine-grained and highly plastic sedimentary clays that fire to a light or nearly white color. They are used mainly in the manufacture of ceramic whiteware and are valued for their key properties of plasticity, which makes them easy

to mold, their unfired strength, and the fact that when fired, they have a light color. Normally, sedimentary clays fire to a reddish color. Some ball clays also have the ability to disperse in water to produce fluid slips (high solids aqueous suspensions). Ball clays exhibit highly variable compositions and consist not of a single mineral, as shown in Table 2.4. The clay is primarily composed of a mixture of three minerals: kaolinite, mica, and quartz. Each of these minerals contributes unique properties to the clay. Among them, kaolinite is the key component. The crystallinity, which refers to the degree of structural perfection, and the size of the kaolinite crystals present in various ball clays can significantly affect their performance in ceramics.

Table 2.4 Chemical composition of ball clay (Worrall, 2013)

Component	Wt%
SiO_2	40-60
Al_2O_3	25-40
Fe_2O_3	0.25-4.0
K_2O	0-0.75
TiO_2	0-0.4
CaO	0.0.5
MgO	0.0.3
Na_2O	0.5-4.0

Ball clays are primarily used as raw materials in ceramics. The main types of ceramic whiteware that include ball clay are sanitary ware, wall and floor tiles, and tableware. Additionally, ball clay is used in kiln furniture, enamels and glazes, building

bricks, fillers, and sealants. It is rare for ball clay to be used on its own; the amount employed varies depending on the specific product. Other key components of ceramic whiteware include kaolin, silica sand, and a flux, such as feldspar, which lowers the melting point of the other ingredients. Although it often accounts for only a small percentage of total raw materials, ball clay can be essential in certain ceramic products. Within a ceramic body, ball clay acts as a binding agent, enhancing plasticity, workability, and strength prior to firing. This allows the ceramic body to be formed and handled safely between the shaping and firing processes and also provides strength in the fired body. Some ball clays are particularly valued for their fluid and casting properties, which are important for slip-casting, especially in the manufacture of sanitary ware.

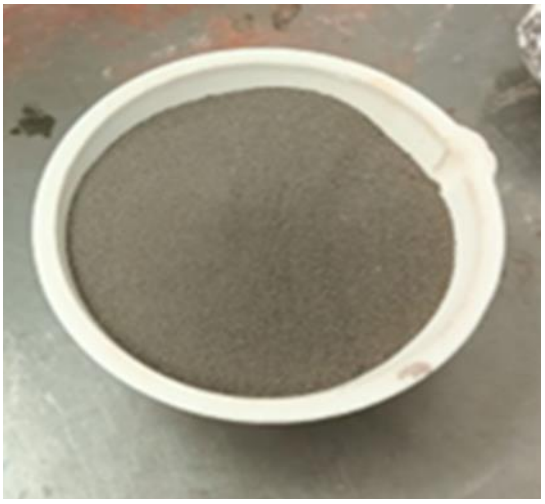

Figure 2.8 Ball Clay

2.4 Pressure Swing Adsorption Oxygen Concentrator

Air pollution is becoming a global issue that impacts both acute and chronic respiratory problems, concerning individuals and communities alike. Wearing disposable face masks has become a popular way to protect against exposure to

pollutants. However, a person with chronic obstructive pulmonary disease (COPD) could find it difficult to breathe through these masks. Consequently, there is an increasing demand for a lightweight and portable oxygen concentrator that provides a medical-grade oxygen supply with an O_2 concentration of approximately 88-92 vol%. Nowadays, oxygen concentration technologies are influenced by air separation processes, including cryogenic techniques, membrane separation, and pressure swing adsorption (PSA). These methods effectively produce enriched oxygen by utilizing ambient air as the source. Although cryogenic distillation is the leading process for air separation in industrial oxygen plants, the pressure swing adsorption (PSA) technique has the advantage of reducing energy consumption for small production scales. Compared with membrane separation methods, which require higher pressures and costly, selective, permeable materials, pressure swing adsorption (PSA), which uses nanosized zeolite adsorbents, offers a more practical approach for creating portable oxygen concentrators. The substantial microporous surface area of zeolite adsorbents enables the PSA-based portable oxygen concentrator to effectively capture nitrogen from air, producing a high-pressure stream of concentrated oxygen. The device can be regenerated by lowering the pressure, which releases the trapped nitrogen, thereby providing a continuous flow of oxygen to help individuals and increase the fraction of oxygen they inhale. Typically, this oxygen concentration system is combined with a filtration system that removes PM2.5 particles, improving the quality of the resulting gas stream. Finlayson and Sharp patented the pressure swing adsorption process in 1932 (GB Patent 365092), which describes an air separation technique involving pressurized adsorption and depressurized desorption phases (W. John Thomas, 1998). In 1958, two separate pressure swing adsorption units were patented: one that uses a fractional product purge flow during desorption, and another that employs pressure-vacuum swing adsorption (PVSA) (Sircar, 2002).

The selectivity of zeolite adsorbents for nitrogen over oxygen is attributed to the interaction between the electrostatic field of cationic zeolites and the quadrupole

moments of nitrogen and oxygen. Specifically, the quadrupole moment of nitrogen is three times greater than that of oxygen, which leads to selective adsorption on the zeolite surface (Drain, 1953). The most commonly used commercial zeolite in the oxygen concentration process is zeolite 13X, renowned for its excellent nitrogen-to-oxygen adsorption selectivity. Additionally, 13X zeolite modified through Li+ exchange demonstrates an enhanced nitrogen adsorption capacity at the active cation sites within the zeolite framework. The JLOX-101 LiX zeolite, provided by LUOYANG JIANLONG Chemical, is specifically designed for a Pressure Vacuum Swing Adsorption (PVSA) process, offering high oxygen selectivity. The Pressure Swing Adsorption (PSA) system was initially implemented in industrial plants as a cost-effective alternative to cryogenic separation plants, both in terms of capital investment and operating expenses. Over the past two decades, portable PSA oxygen concentrators have been developed, driven by advancements in the synthesis of more effective zeolites that offer higher gas adsorption capacity and selectivity. These PSA oxygen concentrators can deliver a continuous flow of oxygen by utilizing ambient air as their gas source. Two-bed or multi-bed PSA systems operate by alternately adsorbing and desorbing gases in the zeolite columns, allowing for continuous oxygen separation. For the production of medical-grade oxygen on-site, a cylinder gas source or several high-capacity air compressors are typically installed to enhance the rapid pressure swing adsorption process, thereby ensuring a consistent output of high-purity oxygen (Rao et al., 2014). Given the portable nature of small-scale concentrators, various simplified designs have been introduced to the PSA process to facilitate system miniaturization.

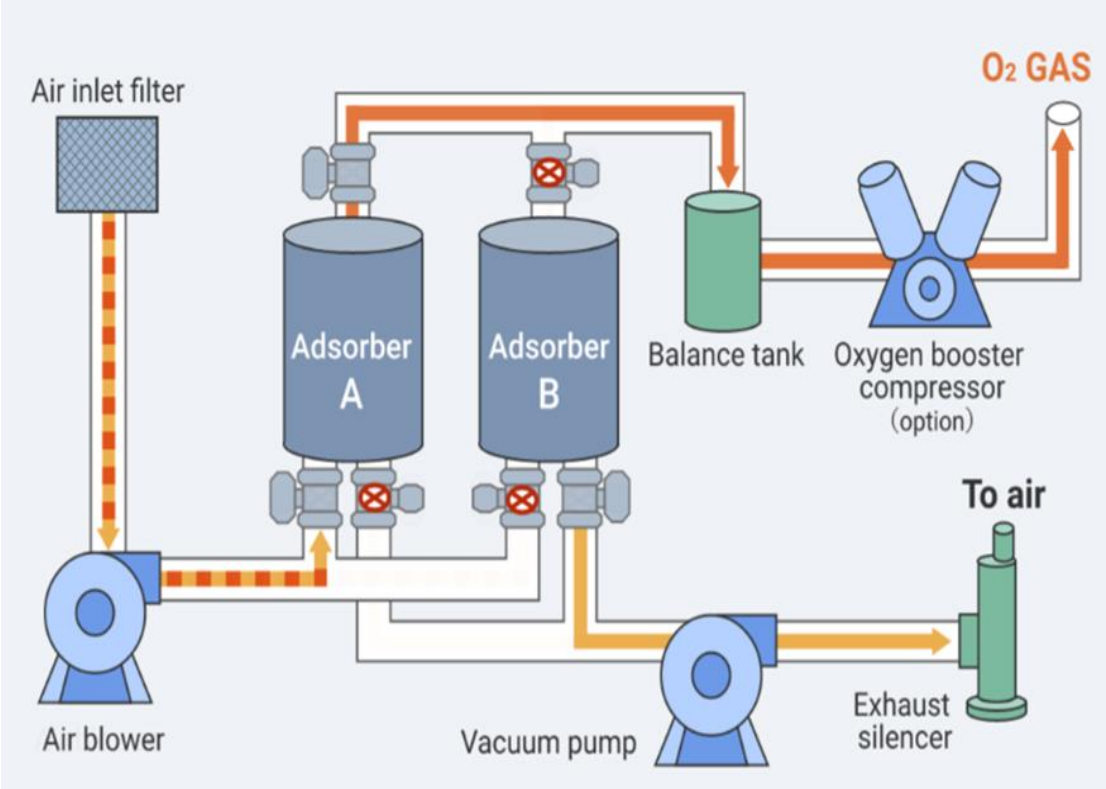

Figure 2.9 Schematics of the PSA oxygen concentrator

2.5 Research

2.5.1 Zeolite A synthesis

Mousa Gougazeh and J.-Ch. Buhl investigated the creation of zeolite materials by hydrothermally transforming natural kaolin from Jordan in sodium hydroxide (NaOH) solutions of different concentrations. This process was carried out at 100 °C over a duration of 20 hours. The mixture consisted of zeolite A, quartz, and hydroxy sodalite (HS), with zeolite A identified as the main product when NaOH concentrations were between 1.50 and 3.50 M, as evidenced by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The study demonstrated that zeolite A can be derived from natural kaolin under these conditions, indicating that metakaolinization occurs at 650 °C. The successful hydrothermal synthesis of zeolite

A used kaolin as the primary raw material, and XRD analysis showed high relative crystallinity. SEM confirmed that the surface morphology of zeolite A was cubic in shape. Thus, kaolin was proposed as a viable and cost-effective raw material for the industrial production of zeolite A. (Gougazeh & Buhl, 2014).

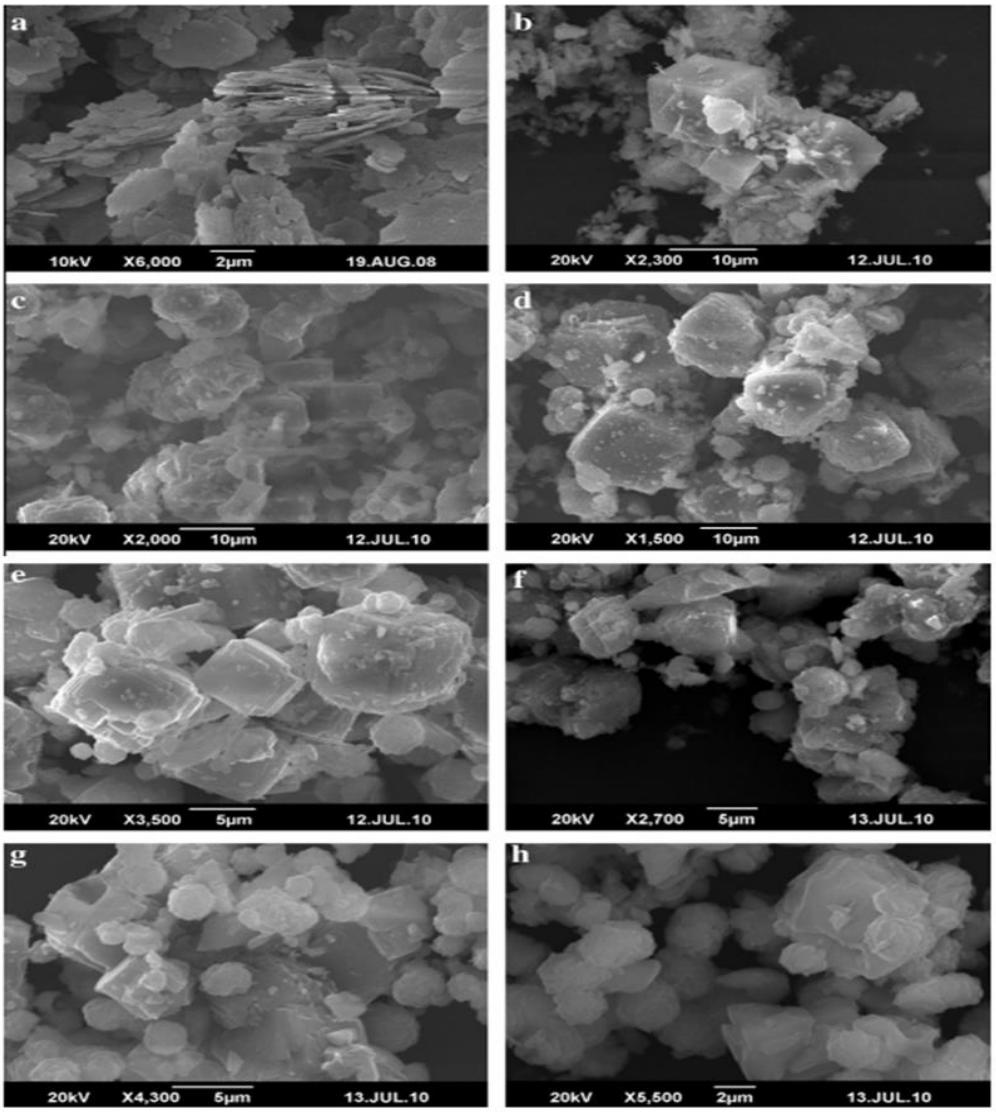

Figure 2.10 SEM micrographs illustrate the zeolite A's formation and related phases obtained through hydrothermal synthesis. In panel (a), hexagonal platy

crystals of untreated kaolin are shown. Panel (b) features well-developed cubes of zeolite A alongside remnants of metakaolin. In panel (c), zeolite A appears have formed prior to hydroxysodalite (HS), as indicated by the growth of HS crystals on the surface of zeolite A. Panels (d–f) display spheroidal aggregates of HS that developed on the surfaces of the cubic zeolite A crystals, demonstrating penetration twinning. Finally, panels (g–h) depict the lepispheric morphology of HS associated with the cubic crystals of zeolite A (Gougazeh & Buhl, 2014).

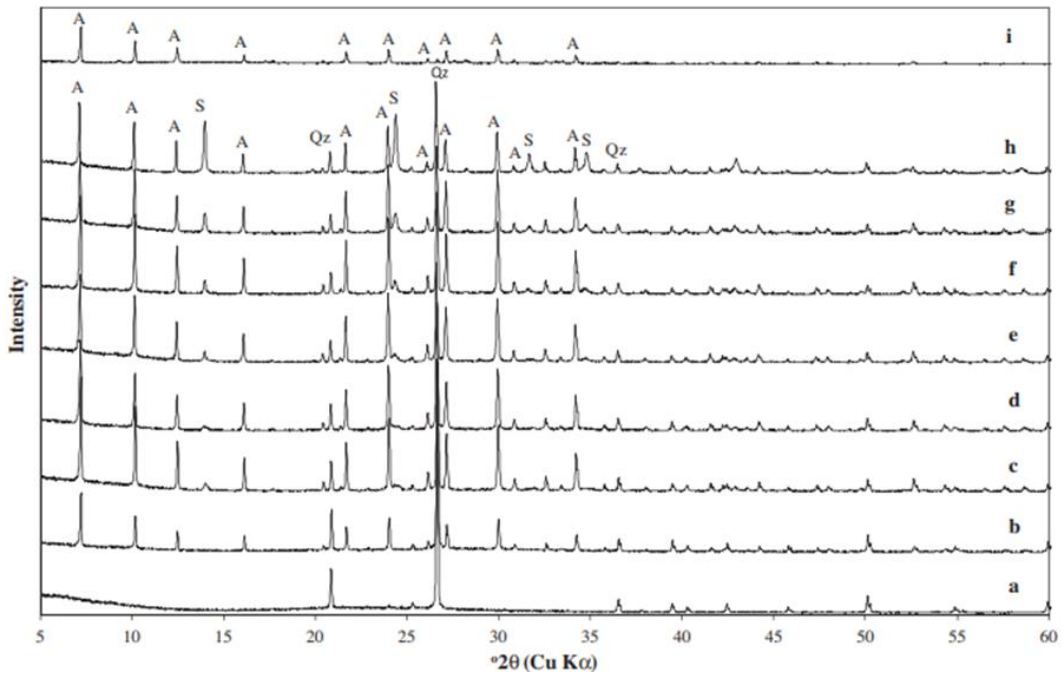

Figure 2.11 XRD patterns of zeolite A and associated phases obtained by Hydrothermal synthesis (a) unreacted metakaolin, (b) 1.0 M NaOH, (c) 1.5 M NaOH, (d) 2.0 M NaOH, (e) 2.5 M NaOH, (f) 3.0 M NaOH, (g) 3.5 M NaOH, and (h) 4.0 M NaOH, (i) commercial zeolite A. A: zeolite A, S: hydroxysodalite, Qz: quartz (Gougazeh & Buhl, 2014).

2.5.2 Ion exchange research

Lisa Price, Ka Ming Leung, and Asel Sartbaeva investigated local and average structural changes in zeolite A following ion exchange. Solid-state FTIR revealed changes to the local structure of the LTA framework upon ion exchange with NH^{4+} and Ca^{2+}. Exchange with Li^{+}, K^{+}, and Rb^{+} ions does not significantly affect the long-range crystal order. The FT-IR spectra for Li-A, Na-A, K-A, and Rb-A all display the fundamental zeolite framework vibration at Vmax/cm−1 of 959, 968, 972, and 969, respectively, corresponding to the asymmetric V(O–T–O) stretch, as shown in Figure 2.12. In addition, the framework symmetric $V_{(O-T-O)}$ stretch occurs at $V_{/cm-1}$ 684, 664, 663, and 666 for Li-A, Na-A, K-A, and Rb-A, respectively. The broad peaks at 3350–3450 cm^{-1} and the weaker peaks at 1650 cm^{-1} observed in all spectra correspond to the $V_{(O-H)}$ stretching and $\delta_{(H-O-H)}$ bending vibrations of water molecules in the hydrated samples. The only noticeable differences in the spectra are that the framework $V_{(O-T-O)}$ asymmetric stretch shifts slightly to a higher wavenumber and the $V_{(O-T-O)}$ symmetric stretch shifts slightly to a lower wavenumber, with increasing cation size, $Li^{+} < Na^{+} < K^{+}$

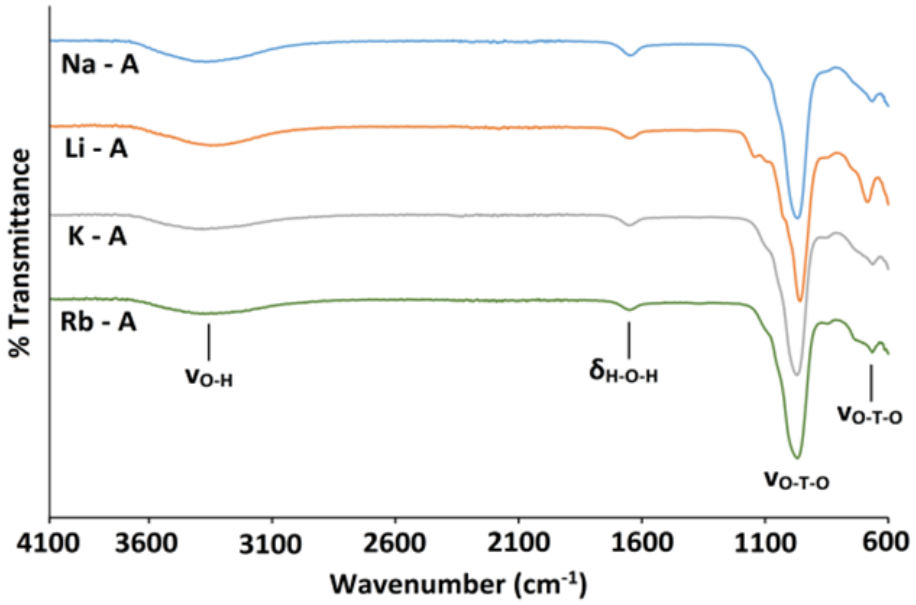

Figure 2.12 FT-IR spectra for Na-A (blue line) and cation-exchanged Li-A (orange line); K-A (grey line) and Rb-A (green line) (Price et al., 2017).

2.5.3 Spray drying research

Tuiana Shoinkhorova and her colleagues conducted a study on shaping ZSM-5-based catalysts using spray drying techniques. In their research, they explored a method for formulating catalysts through this process. They incorporated ZSM-5 zeolite, which has a silica-to-alumina molar ratio of 23, along with various commercially available clays, including kaolin, talc, montmorillonite, attapulgite, and sepiolite, into the composites. The researchers optimized the spray-drying parameters to produce particles with sizes ranging from 30 to 100 μm. They demonstrated that varying the gas flow rate, nozzle aperture, pretreating the slurry with ball milling, and adjusting the ratio of the slurry components allowed for the production of composite particles with different sizes and morphological characteristics. Among all the variables studied, the

most critical factor in the slurry formulation was the total solid content of the sprayable slurry. This content is significantly influenced by the components of the catalyst, particularly the binder and clay. Slurry dilutions below 30 wt% resulted in loosely packed, surface-defective composite materials with poor attrition resistance. In contrast, higher loadings under optimal spraying conditions produced much better-shaped particles (Shoinkhorova et al., 2019).

2.5.4 Zeolite molecular sieve

Ehsan Javadi Shokroo and colleagues conducted a comparative study examining the use of zeolite 5A and zeolite 13X for air separation through pressure swing adsorption (PSA) (Shokroo et al., 2016). The simulation results indicated that zeolite 13X exhibited a slightly higher nitrogen adsorption capacity compared to zeolite 5A. However, under the same operating conditions, zeolite 5A had a larger mass transfer zone than its counterpart. When comparing the equal volume of nitrogen adsorbed by both materials, zeolite 5A demonstrated a greater ability to desorb a larger volume of nitrogen within a specific timeframe. Additionally, to achieve oxygen purity of 96%, using zeolite 5A proved to be more cost-effective than using zeolite 13X.

2.5.5 Studies on adsorption-based air separation for medical-grade oxygen production

Various studies in the literature have examined alternative adsorption cycles and materials for air separation (Jareteg et al., 2020). Farooq et al. investigated a 2-bed, 4-step PSA method for air separation utilizing 5A zeolite through simulation and testing (Farooq et al., 1989). Kopaygorodsky et al. investigated the use of 5A zeolite in ultra-rapid PSA cycles to enhance air separation efficiency (Kopaygorodsky et al., 2004). Santos et al. tested three possible adsorbents and examined the 4-step PSA and PVSA cycles for Oxygen generation (Santos et al., 2006). A two-step pulsed PSA approach was developed by Rao et al. to investigate the potential level of shrinking in medical applications (Rao et al., 2010). A four-step rapid PSA process was developed

by Rao et al. A rapid PSA process based on LiX zeolite was developed in Refs. (Zhu et al., 2017). The process characteristics and performance measures for various literature studies are summarized in Table 2.5

Table 2.5 Literature Studies on adsorption-based air separation for medical-grade oxygen production

Adsorbent	**Cycle type**	**Duration (s)**	**Operating Pressure**		**Purity (%)**	**Reference**
			P_a	P_d		
5A zeolite	2-bed 4-StepSA	100	1.5	1.01	93.4	49
5A zeolite	2-step PSA	<3	1.52	1.01	85	50
LiX zeolite	4-step PSA	3-5	3.04-4.05	1.01	90	4
LiLSX zeolite	4-step PSA	3-9	4.0	1.0	90	53
LiLSX zeolite	5-step PVSA	7	2.4	0.6	90	54
LiLSX zeolite	4-bed 6-step VPSA	5	2.53	1.01	92	47
LiLSX zeolite	2-bed 6-step VPSA	3.8-6.8	1.95	0.43	92-93	43