CHAPTER II

LITERATURE REVIEWS

2.1 Zeolite

Zeolites are crystalline microporous aluminosilicates with three-dimensional structures composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked by sharing oxygen atoms. There are several structural types with various cavity sizes, typically 0.3 to 1.0 nm, formed by linking pore openings of specific sizes within the tetrahedral framework. The presence of $[AlO_4]^{5-}$ tetrahedra results in the framework's negative charge, which requires a charge-balancing cation. The general formula of zeolite is $M_{a/n}[(AlO_2)_a(SiO_2)_b]\cdot cH_2O$, where M represents charge-balancing cation of alkali or alkaline earth metal, n denotes the valence of the metal cation, c indicates the number of water molecules per unit cell, and a and b represent the total number of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra in the zeolite's unit cell, respectively (Lakiss et al., 2020). The ratio b/a varies from 1.0 to 5.0 but can be adjusted depending on the zeolite's structure.

Zeolites are generally classified into two main categories: natural and synthetic zeolites. While natural zeolites are abundant, more emphasis is now placed on synthesizing zeolites because they can be produced in pure form, offer improved ion exchange capabilities, and have uniform particle sizes. They are also utilized as adsorbents, catalysts or molecular sieves, removal of heavy metals, gas capture, and various other applications (Khaleque et al., 2020) due to their porosity and ion-exchange capabilities (Yilmaz and Müller, 2009). Recently, significant attention has been focused on synthesizing zeolites from low-cost materials (Table 1). Rice husk, rice husk ash, fly ash, paper sludge, kaolin, and other silica- and alumina-rich materials can serve as raw materials for zeolite synthesis.

Table 1 The benefits and limitations of various raw materials in synthetic zeolite production (Abdullahi et al., 2017).

Raw materials	Chemical composition (%)	Advantages	Disadvantages	Zeolite	Ref.
RHA	80% SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and K_2O, and others	Low cost, ultrafine size, highly porous and chemically reactive.	Pre-treatment of RHA and waste glasses increase the cost.	ZSM5, T, NaY	C. Zhang et al. (2019) Kamseu et al. (2017)
Clay materials (kaolin, smectite)	SiO_2 46.5, Al_2O_3 41.18, Fe_2O_3 0.19, TiO_2 0.13, MgO 0.04, K_2O 0.13, Na_2O 0.18, ZrO_2 0.01, SO_3 0.15, P_2O_5 0.03, LOI 16.25	Availability, convenient source for producing low silica zeolites like Y, use of kaolin waste for zeolite synthesis reduces the cost of reagents.	High energy consumption processes like grinding, calcination, fusion required. Raw materials mining destroys the natural landscape.	NaA, mordenite, faujasites, and, NaP	Tavasoli et al. (2014)

Table 1 (Continued) show benefits and limitations of various raw materials in synthetic zeolite production (Abdullahi et al., 2017).

Raw materials	Chemical composition (%)	Advantages	Disadvantages	Zeolite	Ref.
Coal fly ash	SiO_2 38.3, Al_2O_3 34.8, CaO 11.0, Fe_2O_3 8.1, Others 7.8	The primary Main constituents are silica and alumina, which offer the potential of converting it to zeolite, Produce low price zeolite with high purity, no harmful effect.	Effect of the impeller type and agitation during the hydrothermal treatment stage of the process.	X, Na-P1, A, Y	Amoni et al. (2019)
Silica gel waste	SiO_2 99.71	High composition of silica, uniform porous structure.	Limited alumina content	A and Y	Khaosomboon et al. (2018)

Several silica sources in zeolite synthesis include silica derived from waste materials such as rice husk and coal fly ash. A particularly promising waste source for

silica is silica gel waste, which contains a high silica content, 99.71% (Khaosomboon et al., 2018). This work presents the synthesis of zeolites LTA (NaA) and FAU (NaX and NaY) using silica gel waste as a silicon precursor.

Linde Type A (LTA) zeolite, commonly known as zeolite A, has a Si/Al ratio ranging from 1.0 to 1.5. Faujasite (FAU) zeolites exist in two forms based on their Si/Al ratio: zeolite X, with a ratio of 1.0 to 1.5, and zeolite NaY, which has a Si/Al ratio greater than 1.5. The pore diameter of LTA is 4 Å, while FAU has a larger pore diameter of 7.4 Å. Both zeolite types possess high surface areas, enhancing their adsorption capacity.

Among the various classes of zeolites, LTA and FAU are the most well-known for CO_2 capture due to their structural characteristics and Si/Al molar ratios. Figure 1 illustrates the structural units of LTA and FAU zeolites.
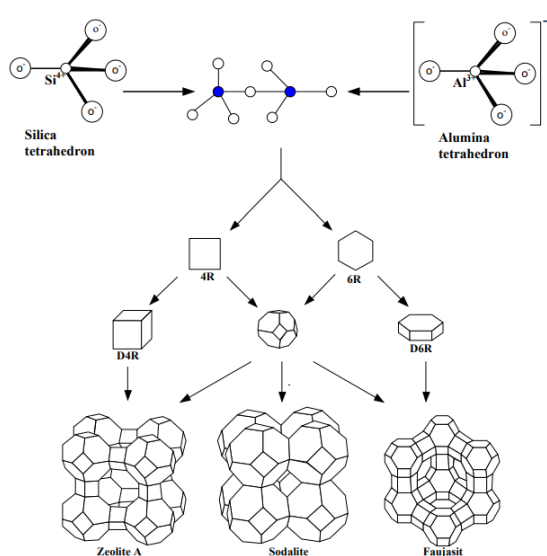

Figure 1 Structure of the LTA and FAU Zeolite Units (Masoudian et al., 2013).

2.2   Adsorption CO_2 in zeolites

The applications of zeolites are largely due to their unique properties. While zeolites are used in various fields, this research specifically focused on the use of synthesized zeolites for CO_2 adsorption.

Zeolites possess tunable channels within a rigid framework, granting them outstanding shape selectivity and efficient interaction capabilities with carbon dioxide (CO_2) molecules, the primary greenhouse gas. Large-scale CO_2 capture and utilization

are achieved through Carbon Capture, Utilization, and Storage (CCUS) technology. CO_2 capture is the process of separating and concentrating CO_2 from various emission sources using techniques like absorption, adsorption and membrane separation.

The fundamental principle of zeolite adsorption is that molecules, such as CO_2, with diameters smaller than the pore size of the zeolite, can enter and be adsorbed within the crystal. Table 2 shows a comparison of the adsorption capacity of CO_2 in zeolites.

Table 2 Comparison of CO_2 adsorption capacities in various zeolite types (Davarpanah et al., 2020).

Sample	Condition pretreatment (K)	CO_2 adsorption capacity (mmol g^{-1})	Ref.
13X	593	4.6	Khraisheh et al. (2020)
ZSM-5	573	1.6	Li et al. (2013)
	373	0.9	Wang et al. (2017)
4A	523	1.65	Siriwardane et al. (2001)
NaY and KY	393	4.4-5.18	Walton et al. (2006)
NaA from sugarcane bagasse (SCBA)	300 ℃, 3 h under vacuum	1.56	Keawkumay et al. (2024)
NaA-P from SCBA	300 ℃, 3 h under vacuum	4.30	Keawkumay et al. (2024)
NaA-PS from SCBA	300 ℃, 3 h under vacuum	4.10	Keawkumay et al. (2024)
Commercial NaA	300 ℃, 3 h under vacuum	4.38	Keawkumay et al. (2024)
Y	No treatment	2.18	Gouveia et al. (2020)

Table 2 (Continued) Comparison of CO_2 adsorption capacities in various zeolite types (Davarpanah et al., 2020).

Sample	Condition pretreatment (K)	CO_2 adsorption capacity (mmol g^{-1})	Ref.
4A	200 °C, 12 h under vacuum	3.39	Panda et al. (2019)
5A	150 °C, 12 h under vacuum	3.68	Gao et al. (2015)

Zeolite has shown strong potential as an adsorbent for CO_2 capture, with pretreatment playing a key role in enhancing adsorption performance. Specifically, the pretreatment temperature of the zeolite significantly influences its CO_2 adsorption capacity, which increases as the temperature rises (Kuceba and Nowak, 2005). This suggests that the activation temperature is an important factor in the CO_2 sorption process; the higher temperatures promote dehydration and generate additional adsorption sites (Keawkumay et al., 2024).

2.3 Mechanisms of CO_2 adsorption in zeolites

The adsorption behavior of FAU, classified as large-pore zeolites (diameter 0.60–0.80 nm), is primarily determined by electrostatic interactions. However, LTAs, classified as small-pore zeolites (diameter 0.30–0.45 nm), exhibit diffusion and size exclusion, which additionally affect adsorption behavior.

CO_2 adsorption via electrostatic interactions with the adsorbent is referred to as equilibrium separation. This interaction is influenced by factors such as the polarity and polarizability of gas molecules, as well as the electric field gradient of the zeolite surface, which becomes stronger with increased aluminum content. Despite being a nonpolar molecule, CO_2 exhibits strong adsorption on zeolites due to its significant quadrupole moment and high polarizability.

2.3.1 Mechanisms of CO_2 adsorption in zeolite FAU and LTA

The primary adsorption mechanisms proposed for medium- and large-pore zeolites are shown in Figure 2. A CO_2 oxygen atom could interact with an extra-

framework cation within the zeolite cavities (Figure 2A). Both CO_2 oxygen atoms could also bridge separate extra-framework cations (Figure 2D). Moreover, CO_2 could form carbonate species by adsorption on framework oxygen via carbon atom with interaction between CO_2 oxygen and potassium cation (Figures 2B and 2C).
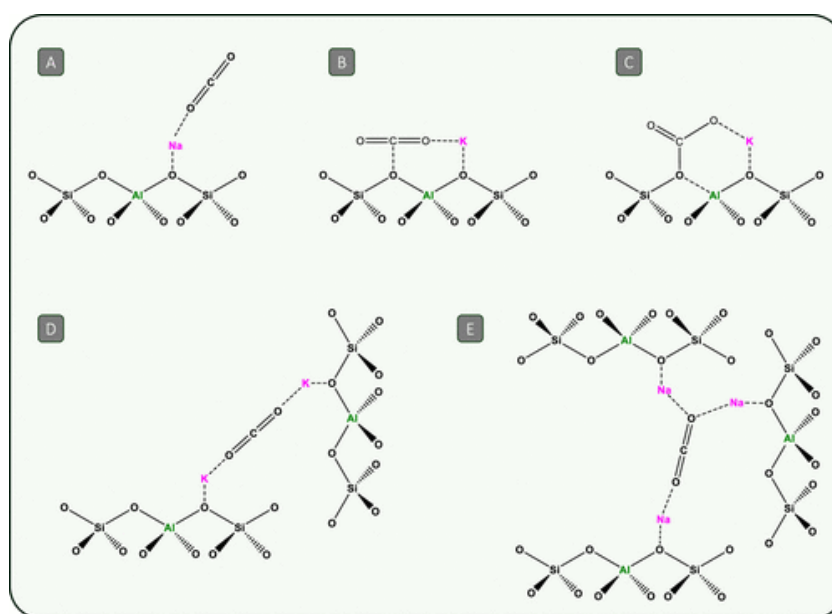

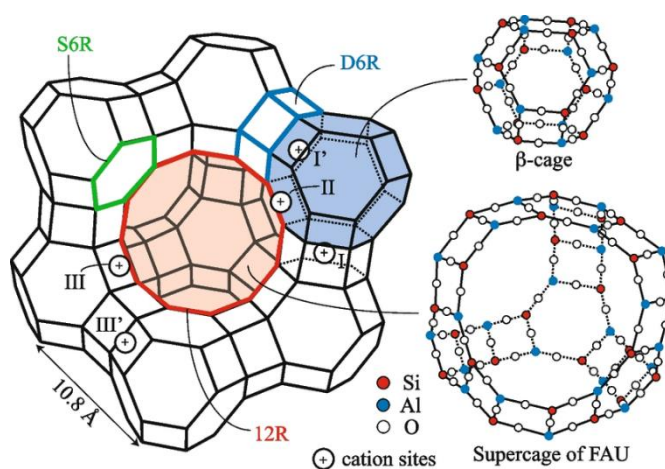**Figure 2** Mechanisms of CO_2 Interaction with zeolites (Boer et al., 2023).

Figure 3 Schematic representation of the FAU-type framework structure (Nakano and Harashima, 2024).

Figure 3 shows the framework of FAU zeolites containing sodalite building blocks linked by double six-membered rings (D6Rs), resulting in the formation of a

supercage with a 12-membered ring (12MR) window. The sodalite cage is composed of 8 six-membered rings (6MRs) and 6 four-membered rings (4MRs). From the different Si/Al ratios, zeolite Y contains a lower amount of Al, leading to a reduced presence of extra-framework cations per mass of material. Figure 4 exhibits the positions of cations in the FAU structure (Rouquerol, 1999).
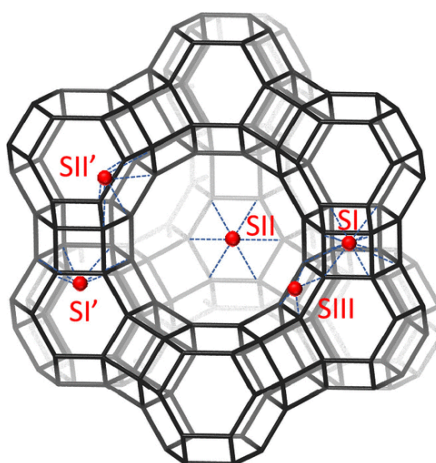

Figure 4 The potential locations of counter cations within the Faujasite structure (Norby et al., 1998).

In the FAU structure, CO_2 cannot access the cations at sites I, I′, and II′ within the D6R or sodalite cage (Figure 4). In NaX, CO_2 adsorption occurs at two sites, II and III′, within the supercage. At low CO_2 loading, CO_2 favorably interacts with site III′ cations, which is positioned slightly off from site III (site III′ is not shown in Figure 4). This may be due to the greater accessibility of these sites, as they are closer to the supercage center than site II. At higher CO_2 loading, when the type III′ sites are occupied, CO_2 additionally interacts with the cations at site II (Maurin et al., 2005). In zeolites NaY and LiY, CO_2 interacts with cations at site II because the sites III′ are unoccupied.

2.3.2 Mechanisms of CO_2 adsorption in small-pore zeolites

In small-pore zeolite A, the mechanisms are the same as medium- and large-pore zeolites. However, the accessibility of these pores becomes an important additional factor in influencing both adsorption capacity and selectivity because the pore sizes are comparable to the size of the adsorbent.

Figure 5 shows the structure of zeolite A, which is a small-pore zeolite composed of sodalite cages connected by double 4 rings (D4Rs), forming a supercage (also referred to as the α-cage, as shown in Figure 5) that can be accessed through 8-membered rings (8MRs). Figure 6 illustrates three cation sites in zeolite A. Cation site II is found within the window of the 8-membered ring (8MR) that allows access to the supercage. In NaA, the cation is positioned away from the center of the window, which does not significantly hinder the diffusion of CO_2 into the supercage (Boer et al., 2023).
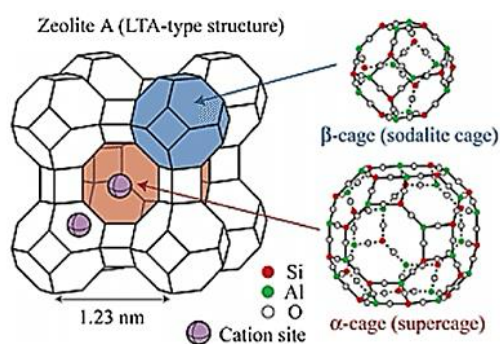

Figure 5 Schematic representation of the LTA-type framework structure (Abdullahi et al., 2017).
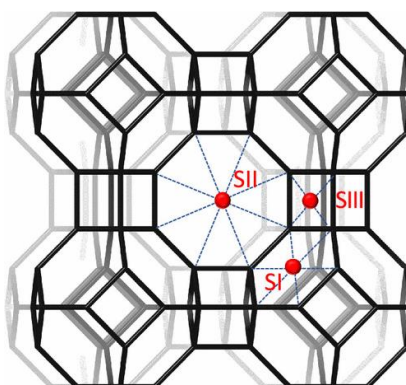

Figure 6 Cation sites for CO_2 in the LTA zeolite (Zukal et al., 2011).

2.4 Factors influencing CO_2 adsorption in zeolites

2.4.1 Type of Framework

Zeolite classifications are based on the distinct size and geometry of their channels and cages. The framework structure plays a crucial role in defining key material properties, including the number of T atoms (T = Si or Al) within the rings

and the corresponding pore size (Å). For effective CO_2 diffusion, the pore aperture must be at least 3.3 Å, meaning the framework should consist of an 8-membered ring (8MR) or larger, as smaller rings have apertures that are too restrictive. Additionally, pore size can be adjusted by incorporating alkali or alkaline earth metals, which in turn can influence the adsorption mechanism (Boer et al., 2023).

The pore structure, along with the size and geometry of a zeolite, plays a crucial role in governing adsorbate diffusion and ultimately affects its effectiveness as an adsorbent.

2.4.2 Si/Al Ratio

The Si/Al ratio in zeolites plays a crucial role in determining their adsorption capacity and selectivity for polar and polarizable molecules. Zeolites with lower Si/Al ratios have higher aluminum content, resulting in an increased number of extra-framework cations that act as active adsorption sites. A lower Si/Al ratio leads to a greater number of adsorption sites per unit mass, thereby enhancing CO_2 adsorption capacity. Additionally, silicoaluminate zeolites contain Lewis base sites originating from oxygen atoms adjacent to aluminum. As aluminum content increases, the density of these basic sites also rises, strengthening interactions with acidic CO_2 molecules and improving adsorption efficiency (Barthomeuf, 1984).

However, the Si/Al ratio also affects the available pore volume, as each aluminum site requires a charge-balancing cation. In zeolites with a low Si/Al ratio, the abundance of cations per unit mass can create steric hindrance, potentially limiting the accessible pore space and reducing overall adsorption capacity.

2.4.3 Extra-framework Cations

The adsorption properties of zeolites can be tailored by exchanging extra-framework cations, typically Na^+, with other mono- or multivalent cations. This cation substitution influences the acid–base characteristics of the zeolite. The acidic sites are associated with the exchangeable cations, while the basic sites correspond to oxygen atoms bonded to aluminum within the framework (Barthomeuf, 2003). The strength of these basic sites increases as the electronegativity of the cation decreases, as a less electronegative cation enhances the negative charge on the oxygen atoms in the zeolite framework.

The basicity of zeolites exchanged with alkali cations follows the order: Cs^+ > Rb^+ > K^+ > Na^+ > Li^+. Zeolites with higher basicity exhibit stronger interactions with acidic CO_2, leading to enhanced adsorption capacity and selectivity. Furthermore, as the ionic radius increases (Li^+ < Na^+ < K^+ < Rb^+ < Cs^+), the polarizing power of the cations decreases, weakening interactions with CO_2 for larger cations.

2.4.4 Diffusion of Adsorbates through the Zeolite Frameworks

The diffusion rate of adsorbates via zeolite pores is crucial for achieving rapid adsorption equilibrium. Additional factors that significantly impact the diffusion of adsorbates through zeolite pores include partial blockage of micropores by cations and the interaction between the adsorbate and these cations (Boer et al., 2023).

2.4.5 Influence of Water

In zeolites A and zeolite X, the CO_2 adsorption capacity could be reduced significantly by the presence of small amounts of water vapor. The reduction is due to competition between CO_2 and H_2O for the same adsorption sites, with H_2O strongly interacting with the zeolite's sites due to its dipole moment.