

A Review on CO₂ Capture over Novel Adsorbents: Progress in Robust Zeolite Adsorbent Development

H. U. Hambali^{1*}, T. Jimoh^{1*}, T. L. Peng², A. A. Umar³, B. T. Mutiullah¹, J. A. Okolie⁴

¹Department of Chemical Engineering, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria.

²Department of Chemical Sciences, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

³Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

⁴Engineering Pathways, Gallogly College of Engineering, University of Oklahoma, Norman, OK73019, USA.



ABSTRACT: Indubitably, the combustion of fossils fuels has really hampered the preservation of the environment as it raises the content of CO₂ in the atmosphere which consequentially results in global warming. Adsorption process remains the popular technique owing to its cost-effectiveness, faster reaction rates and flexible design. This review detailed the research progress in preparation of modified zeolite-based and novel adsorbents towards enhanced CO₂ capture. In addition, the review presents an overview on available techniques of capturing CO₂ and mechanism of reaction. Large surface area, distinctive mechanical characteristics and uniform dispersion of the exchangeable cations in the porous framework is prerequisite for high adsorption capacity and stability over zeolite materials. Novel nanostructured and polymeric zeolite composite materials seem promising because they offer solutions to energy-related problems while also contributing to environmental preservation. It is anticipated that this review could offer a conclusive roadmap in the pursuit of a cost-effective, industrially potent adsorbent suited for enhance CO₂ capture.

KEYWORDS: CO₂ capture, Adsorbents, Zeolite, Adsorption, Porous

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I. INTRODUCTION

The increasing world's population and industrialization have resulted in high demand for energy, which is a necessity for continued economic development (Jimoh *et al.*, 2023). The high demand for energy has resulted in release of more carbon-dioxide (CO₂) from different sources which led to skyrocketing CO₂ amount available in the atmosphere, and has considerably aided in contributing to global warming; the most demanding problem of the 21st century (Chang *et al.*, 2022; Zhu *et al.*, 2023). The global CO₂ emissions from various sectors are schematically shown in Figure 1. It was reported that the release of CO₂ has greatly increased since industrialization in the 19th century; its concentration rises by 1.5–2 ppm on average per year. When compared to the level before industrialization, the CO₂ concentration in 2011 rose by 40% (Rashid & Rafey, 2023). A group of researchers ran a test on the global CO₂ concentration; the result revealed that a progressive rise in the average global CO₂ emission in the past decade. The CO₂ concentration peaked during this time at 398.2 ppm in 2015, and it averaged at 409 ppm in 2019 (Zhu *et al.*, 2023). It can be perceived that the concentration of CO₂ in the atmosphere is on the increase. As a result, immediate CO₂ emission reductions are required.

According to the Paris climate accord of 2015 which stipulate that, an inevitable action to save the menace is retaining the global warming to 1.5°C by 2100 while striving to keep it to 2°C (Fawzy *et al.*, 2020). Thus, it is crucial to

investigate carbon capture technology in order to reduce releases of CO₂ gases from anthropogenic activities for example the power generation industries, which is capable of reducing fingerprints of hazardous CO₂ by 50% by in the year 2050 (Chang *et al.*, 2022). It is worth noting that if several techniques for CO₂ capturing and storage are ignored, the price of reducing the gases emissions could drastically rise by nearly 140% (Moen, 2023). Carbon capture and storage (CCS) is universally adjudged as a feasible option in reducing CO₂ emission. It is an approach that has shown promising result in mitigating global warming effectively (Singh *et al.*, 2023). CCS entails separating the produced carbon dioxide in the transportation and industrial sectors and then moving it to an appropriate place that is fit for storage. The use of CCS was reported to have great effect on the price of energy production and the rate at which the technology might quickly enter the commercial market. The necessity for a successful technology of capturing CO₂ from power industries as one of the major sources of CO₂ is crucial as a result of global dependence of on fossil fuels (Rabiu *et al.*, 2017; Rashid & Rafey, 2023). Almost 90% of the emitted CO₂ from power industries can now be absorbed by the majority of CCS technology. Unfortunately, the majority of power generating industries with CCS process requires higher energy than the conventional counterparts (Chang *et al.*, 2022; Zhu *et al.*, 2023). This additional energy is needed mostly for the process of CO₂ capturing and compression, which raises the energy need of power generating industries by 10% to 40% (Jimoh *et al.*, 2023). Table 1 presents

*Corresponding author: hambaliuh313@gmail.com

an overview of various techniques for CO₂ capture. The CCS technique is capable of reducing the amount of CO₂ in the

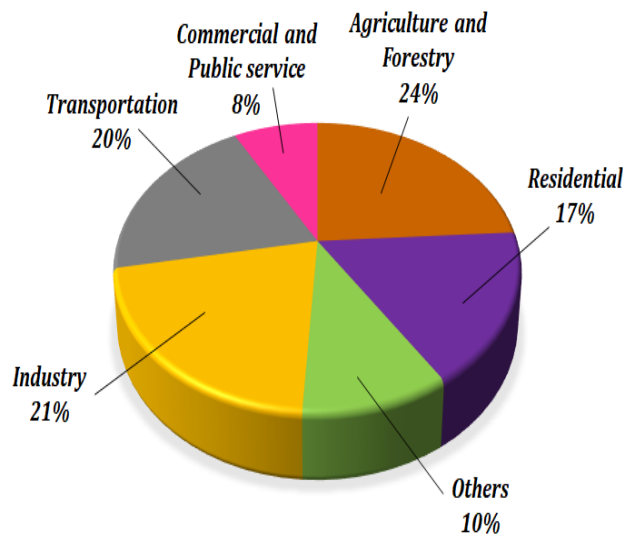


Figure 1. Global CO₂ emissions from various sectors

being cheaper than post-combustion capture. It is characterized by its CO₂ concentrations which ranges are 15–40% and its relatively high operating pressure of near 4 MPa (Jimoh *et al.*, 2023; Rashid & Rafeq, 2023). Solvents such as methanol and dimethyl ethers of propylene carbonate are normally employed to capture CO₂ in the pre-combustion method, this lowers the needed pressure and then results in less energy usage (Vega *et al.*, 2020). For oxy-combustion, thorough combustion is witnessed because the fuels are burned in oxygen instead of air. Water vapor and nearly pure CO₂ (usually 90%) make up the exhaust stream. Nitrogen and oxygen are removed from the air during this process. The biggest challenge with this method is separating oxygen from the air. Typically, this is accomplished via cryogenics, which is energy-intensive (Osman *et al.*, 2021).

The primary post-combustion capture technique is gas absorption. This basically entails sending flue gases into a CO₂ absorption unit immediately they exit a power generation unit, where about nine-tenth of the CO₂ will be removed from the flue gases by an absorbent solution (Ayeleru *et al.*, 2023). The absorbed CO₂ is then removed with the aid of steam so as to ensure the reusability of the absorber.

Table 1: Some existing techniques for CO₂ capture

Technology	Operating conditions	Strength	Weaknesses	Existing Plants	Reference
Absorption	-Low temperature. -High partial pressure.	-Industrially mature. -Suitable for retrofitting.	-Equipment corrosion. -High cost of regeneration. -High CO ₂ loading capacity.	Petroleum, natural gas and coal fired power industries.	(Ayeleru <i>et al.</i> , 2023)
Adsorption	-Low temperature. -High pressure.	-Low energy requirement. -Good adsorption capability. -Ease of handling and recovery.	-Low CO ₂ selectivity. -Scalability limitation due to unstable pressure.	Gas-fired power plant.	(Dong <i>et al.</i> , 2023)
Cryogenic	-Low temperature.	-Chemical reagent is not required. -Regeneration process is not required.	-Capital expenditure is high. -Removal of gases and other traceable components to impede blockage of equipment.	Natural gas plant.	(Wu <i>et al.</i> , 2020)
Membrane separation	-Permeability, and selectivity of the gases.	-Low capital and maintenance cost. -Regeneration process is not required. -Chemical reagent is not required.	-Low membrane material selectivity. -Limited membrane lifetime. -Limitation of operating temperature.	Natural gas plant.	(Ibrahim <i>et al.</i> , 2018).

environment by about 80% to 90% provided the CO₂ is appropriately absorbed and stored (Vega *et al.*, 2020).

The three fundamental approaches for carbon capture are: (1) post-combustion (2) oxy-fuel combustion and (3) pre-combustion capture (Mamoori *et al.*, 2017). As summarized in Table 2, the pre-combustion method ensures that carbon is eliminated from the fuel prior to combustion so as to guarantee that no CO₂ emission during the combustion. Through natural gas reforming or the coal gasification, fossil fuels or biomass are transformed into CO₂ and hydrogen mixture. The hydrogen can then be applied as fuel, while the CO₂ is subsequently removed and collected. This method has the advantage of

Table 2: Typical carbon capture and storage (CCS) technology condition. (Kumar *et al.*, 2020)

CCS Technology	Operating pressure (bar)	Temperature (°C)	Concentration (CO ₂ , %)
Post-combustion	1	40-60	3-20
Pre-combustion	14-70	200-450	15-60
Oxy-combustion	1	-55	17-70
Direct air capture	1	25	~0.04

Unlike the pre-combustion technique, this process is known for its low pressure and 10-20 % CO₂ concentration (Wu *et al.*, 2020). Recently, the main CO₂ post-combustion

technique adopted is the chemical solvent method. Monoethanolamines (MEA), Diethanolamines (DEA), and Methyldiethanolamines (MDEA) were used in the past for CO₂ capture (Karnwiboon *et al.*, 2019; Ochedi *et al.*, 2020). These solvents have been used to successfully separate carbondioxide from hydrogen during the synthesis of ammonia (Osman *et al.*, 2021).

Suitability of CO₂ capturing process has been convincingly investigated. Generally, capture of CO₂ is achieved by absorption or adsorption or membrane separation, and cryogenics. Cryogenics is suitable for oxy-fuel and pre-combustion carbon capture, whereas adsorption, absorption, and membrane technologies are excellent for post-combustion techniques (Wu *et al.*, 2020). In comparison to other mechanisms, adsorption offers advantages like a lower energy requirement, cost-effective regeneration, and excellent loading capacity at ambient circumstances. Ease of operation, can be easily maintained, high tolerance to flue gas contaminants, and good mechanical and chemical stability are additional benefits (Lai *et al.*, 2021; Singh *et al.*, 2023). This indicates that it has a promising future in CO₂ collection. It is one of the most researched mechanisms with the potential to be used as an emission cleanup technique shortly. Solid sorbents are used in this method to remove CO₂ from exhaust gases by physical or chemical adsorption. During the desorption cycle, a clean stream of CO₂ is obtained, and the adsorbent can be regenerated (Lai *et al.*, 2021).

Adsorbents such as activated carbon, zeolite, mesoporous metal oxides, polymeric composites, nanoporous carbons and MXene and chemical adsorbents (mixture of calcium oxide (CaO), solid amines sorbents, and lithium metal-based) were reported to possess robust CO₂ capture capacity (Arifuzzaman *et al.*, 2023; Dziejarski *et al.*, 2023; Musa *et al.*, 2023; Pang *et al.*, 2023; Wang *et al.*, 2023). Zeolites are aluminosilicates, both natural and artificial, that have a microporous crystal structure. The $[\text{Si}_{1-x}\text{Al}_x\text{O}_2]^{-x}$ negatively charged frameworks in natural zeolites form rather large cavities in which the balancing cations are located (Hambali *et al.*, 2022). The channels that connect these cavities provide a microporous structure that is essential for separation techniques. Zeolites can be classified using a variety of criteria, with pore aperture being of primary concern (Bai *et al.*, 2022). According to Phung *et al.* (2014), pristine zeolites are categorized into four types: small-pore zeolites, which has a pore diameter of 4 with its channel delimited by eight membered-rings; medium-pore zeolites, it has a pore diameter of 5-6 with its channels delimited by ten membered-rings; large-pore zeolites have pore diameter of near 7 with its channels delimited by twelve membered-rings; and extra. This is only a rudimentary classification because pore structure is a very important factor. Another zeolite criterion is proven by the channels' dimensionality, as zeolitic materials can have one-, two-, or 3 dimensional pore architecture depending on the arrangement of the channels (Madhu *et al.*, 2022).

In addition, zeolitic materials could be categorized according to the amount of silica (Si/Al atomic ratio) present; high-silica (>10), intermediate-silica (<10), and low-silica (< 1) (Ji *et al.*, 2017; Opanasenko *et al.*, 2016; Rajaura *et al.*, 2018). Low-silica zeolites are hydrophilic because of their

strongly negatively charged frameworks with presence of a lot of protons (Hambali *et al.*, 2020). However, highly siliceous zeolite materials display hydrophobic behavior owing to the predominance of Si-O-Si bonds (Zagho *et al.*, 2021). Zeolite is characterized by strong adsorption affinity, large surface area, high ion exchange potential and hydrophilicity. Hence, zeolites are commonly used in gas adsorption (Madhu *et al.*, 2022). Recently, zeolites were applied for adsorption of CO₂ and separation in flue gas successfully. Its gas adsorption properties are largely dependent on fast reaction kinetics, charge density and uniform spread of the exchangeable cations in the surface (Aziz *et al.*, 2020; Zagho *et al.*, 2021). However, pristine zeolites have some shortcomings such as low CO₂ adsorption, stability and a slow rate of reaction in the process of regenerating zeolites since their powders are suspended or aggregated easily (Usman *et al.*, 2022). This review discusses the research progress in preparation of zeolite-based adsorbents for enhanced CO₂ capture. The review begins by highlighting the current progress in CO₂ capture, storage, and utilization technologies that can be used to mitigate global warming. This is followed by highlights on advantages as well as disadvantages of each CO₂ capture techniques. Emerging trends in developments of robust zeolite adsorbents for capturing carbon dioxide while highlighting its tremendous features such as structural variety, high porosity, high stability, strong chemical reactivity and ultra-small pores. The final section provides summary on performance of various zeolite-based adsorbents under similar conditions and also in investigating their CO₂ capture capacity.

II. ADSORPTION PROCESS FOR CO₂ CAPTURE

Numerous technologies are established for CO₂ capture for example membrane separation, cryogenics, adsorption, and absorption (Jimoh *et al.*, 2023). As conclusively reported in literatures (Chang *et al.*, 2022; Oyehan *et al.*, 2023; Zhu *et al.*, 2023), adsorption remains the most economical method to capture liquid and gaseous compounds. The adsorption system is desirable because it requires little total maintenance, produces less secondary waste, is stable over time, has a lower adsorbent heat capacity, and does not extract moisture from flue gas (Singh *et al.*, 2023).

Basically, an ideal adsorbent should possess large surface binding sites and surface area which are responsible for fast reaction kinetics, high selectivity and adsorption capacity (Osman *et al.*, 2021). It is desirable that CO₂ adsorbent has properties which includes but not limited to cost-effectiveness, easy regeneration, high CO₂ adsorption rate, high surface area, high CO₂ selectivity, tunable porosity, tolerance to moisture and impurity and high availability (Madhu *et al.*, 2022). These adsorbents could be physical (for example silica, metal oxides, activated carbon, zeolites, MOF, porous carbon) or chemical (such as binary eutectic mixture (KNO₃ and Li NO₃), ionic liquids (ILs), and aqueous amine) (Lai *et al.*, 2021).

Adsorption is a method that achieves separation by adsorbing a particular component(s) from a liquid/gas stream unto the surface of the adsorbent material (Ji *et al.*, 2017; Opanasenko *et al.*, 2016; Rajaura *et al.*, 2018). The solid particles adsorb gas components as the gas molecules are

passed via the bed. Due to exothermicity of the process, there is need to raise the temperature so as to regenerate the adsorbents through desorption (Lai *et al.*, 2021). Generally, the post-combustion capture technique using adsorption process is categorized as swing processes namely pressure, temperature, electric or vacuum swing processes depending on the regeneration principles. These classifications set different demands and restrictions on the adsorbent and the process (adsorption), and each is explained separately below (Chao *et al.*, 2021).

A. Pressure Swing Adsorption Process

The Pressure Swing Adsorption (PSA) is referred to a cyclic adsorption technique which selectively removes the targeted component from a single and/or mixture of gaseous flow in their bulk and continuous phase under intermittent pressure changes (Zhu *et al.*, 2019). The CO₂ from a single and/or mixture of gaseous streams flowing via the packed-bed at low temperature and elevated operating pressure is adsorbed onto the adsorbents' surface during the adsorption process. Heat addition will then cause gas desorption to take place at a higher temperature. The regenerated bed is then cooled before a further series of adsorption under the regeneration temperature to guarantee stability of both the adsorbate and adsorbent (Mukherjee *et al.*, 2019).

B. Vacuum Swing Adsorption Process

Another adsorption process is the Vacuum Swing Adsorption (VSA) method, which has over the years been employed in industry for separation process of CO₂ for a number of decades due to its low energy need, simplicity, and potential for an extended use of the adsorbent (Perez *et al.*, 2019). However, VSA process in comparison with PSA involves adsorption, followed by desorption (under vacuum condition). The high desorption in VSA results in more separation capacity and yield which permits the application of a single adsorption and desorption unit (Chao *et al.*, 2021).

Since they do not utilize process valves, feed air filtering systems, feed air or associated dryers, VSA applications do not use several of the standard PSA systems' operational modules. Due to its simplicity, the single-vessel VSA system improves efficiency, lowers costs, and requires less maintenance by removing many issues with the development of a two-bed PSA (Chao *et al.*, 2021). VSA systems have low tendency for dust deposition (in adsorbent bed) because of lesser magnitude of the pressure swings. In contrast to a PSA, which typically calls for re-packing of the sieve material in three to five years' time, the lower operating pressures also give greater molecular sieve regeneration, allowing operation in humid settings and increasing service life (Rajagopalan & Rajendran, 2018).

PSA and VSA systems' behaviors are influenced by a several variables, such as flue gas impurities, applied pressures, feed gas temperature, type of adsorbents, and CO₂ concentration (Mukherjee *et al.*, 2019). Rajagopalan & Rajendran (2018) showed that if VSA was fed at a temperature of 40 °C, about 70% of CO₂ will be recovered. Flue gas impurities, which comprise 68 to 75 % N₂, 10 to 15 % CO₂, 5 to 10 % H₂O, 2 to O₂ of 5 % and minute levels of SO_x and NO_x, have a huge impact on PSA and VSA as it increases the overall

capture cost. Hence, a pretreatment stage needs to be made available to eliminate these mentioned impurities (Perez *et al.*, 2019).

C. Temperature swing Adsorption Process

Another adsorption process is the Temperature Swing Adsorption (TSA) adsorption technique for capture of volatile organic compounds (VOCs) present in the air. By adjusting the operating temperature, CO₂ adsorption and desorption in TSA happen cyclically. TSA uses numerous vessels that are interconnected and adopt either mobile, stationary or fluidized beds. There are numerous benefits of TSA: (1) flue gas impurities have minimal effect on the process and are removed at a temperature of around 160°C; (2) TSA is easily integrated into existing power generation units; It is a low-risk, quick-to-implement approach; (3) It can be easily maintained because it runs on a low pressure (4 bar); (4) TSA has a significant initial cost but is frequently cheap to operate (Zhao *et al.*, 2019).

Due to the high energy consumption of the TSA systems (cooling and heating units), research has been done to reduce this high consumption of energy by enhancing the capturing, energy integration, and developing low-temperature adsorbents. Because of presence of low-grade heat, operating expenses in power industries are greatly reduced. Heat regeneration is mostly conducted on-site as practiced in the lime and cement plants. The cost of CO₂ capture will be greatly impacted if an extra heat generator is employed (Chao *et al.*, 2021).

Another adsorption-desorption technique for cyclic CO₂ capture is the Temperature Vacuum Swing Adsorption (TVSA). It combines both TSA and vacuum swing adsorption process. A hybrid TVSA method with a decreasing desorption temperature can be used to increase productivity and decrease energy usage. It is necessary to look into the balance between the consumption of heat and electricity (Mukherjee *et al.*, 2019). In TVSA, the adsorbent is preloaded to its maximum extent in the first column. Thereafter, the adsorption is done in two-columns arrange in series to filter the waste air stream (Sharma & Maréchal, 2019). Following adsorption, adsorbent regeneration is started to desorb CO₂ from the adsorbent at the selected regeneration temperature. As the adsorbent is cooled to the temperature of adsorption for the second sequence of the adsorption/desorption cycle, the effluent CO₂ is supplied back into the input gas stream (Lai *et al.*, 2021). This technique seems better than PSA and TSA because of its high productivity (Lai *et al.*, 2021), lesser energy consumption, high CO₂ recovery of 97%, and shorter CO₂ desorption time, (Sharma & Maréchal, 2019)

D. Electrical Swing Adsorption Process

This ESA technique was first used to capture carbon dioxide in 1977. For ESA, the Joule effect immediately heats the adsorbent bed while the adsorbents are supplied a low voltage electric current so they can regenerate, thereby decreasing the cost of energy for CO₂ collection without applying heat to the adsorption unit (Regufe *et al.*, 2020). ESA differs from PSA and TSA in that it requires less heat, heats up more quickly, and has better desorption kinetics. Materials made of semi-conductive activated carbon fiber are so

appropriate for using the Joule effect to directly heat the adsorbent (Perez *et al.*, 2019). Luo *et al.*, (2006) correlated the topologies of activated carbon adsorbents as fiber fabric, monoliths, and beads. Interestingly, the monoliths were found to have the lowest pressure drop, cheapest, and maximum permeability closely followed by activated carbon fiber composites. These benefits dramatically lower capital expenditures and operating expenses.

The key factor contributing to ESA's cost advantages is the energy savings that result from using the Joule effect exclusively on the adsorbent bed during the desorption stage. In order to improve the process with a better focus on energy efficiency, research is conducted on the desorption's operating conditions, such as the current/voltage and energy intensity, carrier gas flow rate, and the preheating period. The electric conductivity still rates highly among the characteristics of adsorbents for ESA process, even if only limited CO₂ adsorbents could apply the Joule effect (Pereira *et al.*, 2022).

III. FABRICATION OF ZEOLITE ADSORBENTS FOR CO₂ CAPTURE

In 1756, Axel Fredrik Cronstedt invented the nomenclature "zeolite". They are microporous material applied for a number of areas such as adsorption, catalysis, purification, drug administration, and separation because of their unique chemical makeup and porous structure (Derakhshankhah *et al.*, 2016). They are also frequently used as molecular sieves for adsorbing CO₂ because of their pore sizes and customizable cavities (Wang *et al.*, 2022). Zeolites are used in air separation set-ups owing to their strong interactions among their cation and the robust quadruple moment of N₂ in contrast to O₂. In the presence of moisture and pollutants (for example SO_x and NO_x) in the gas, because more energy is needed to desorb the water vapor from zeolites, zeolites have a poorer adsorption efficiency and a slower response rate during the regeneration of zeolites (Krishna & van Baten, 2022). Zeolite outperforms other adsorbents in terms of performance, particularly in the low-pressure zone, and also has better CO₂/N₂ selectivity (Lee *et al.*, 2022). Zeolite-based materials will be discussed below coupled with their preparations and their adsorption performance. The hydrothermal approach is used to synthesize crystalline zeolites in a basic aqueous media employing an alumina source, a silica source, and an inorganic and/or an organic structure-directing agent (Rajaura *et al.*, 2018). Mesoporous zeolites are produced by the transformation of microporous zeolites (Opanasenko *et al.*, 2016).

A. Zeolite 13X

Zeolite 13X is commonly produced by hydrothermally processing of natural clays like 13X-B (bentonite material), 13X-C (commercial), 13X-F (feldspar material) and 13X-K (kaolin material) as depicted in Figure 2 (Karka *et al.*, 2019). The raw materials were mixed with sodium hydroxide solutions (1 to 3M), homogenized at room temperature, and aged for various amounts of time to create the modified zeolites. The aged samples were autoclaved at autogenous pressure (72 hours and 65°C). The prepared material were

afterwards washed to attain pH of 9 then dried for 12 hours at temperature of 90°C (Garshasbi *et al.*, 2017).

Generally, zeolite 13X can be made from natural kaolin (13X-K) sources. Freundlich, Langmuir, Langmuir–Freundlich, BET, and Toth models were examined for adsorption of CO₂. Interestingly, Langmuir–Freundlich model provided superior fit (Kumar *et al.*, 2020). Hybrid (meso-13X-PEI) with considerable CO₂ capture capability results from the impregnation of mesoporous zeolite 13X (meso-13X) and polyethyleneimine (PEI) (Chen *et al.*, 2015). Its larger pore volume makes it better at capturing CO₂ than PEI-modified zeolite 13X (Karka *et al.*, 2019).

To generate amine-grafted zeolite 13X, Bezerra *et al.* (2014) used increasingly concentrated methanolic MEA solutions. Its adsorption capacities were low in contrast to pristine zeolites; nevertheless, its adsorption capacity incline as temperature rises. Although they have similar adsorption properties, amine-grafted zeolites offer more distinctive adsorptive characteristics than pure zeolites owing to availability of greater adsorption sites, and this may open up new study fields (Regufe *et al.*, 2020).

Yuan *et al.* (2022) prepared composite materials from the impregnation of MCM-41 and Zeolite 13X via single- and double-step crystallization techniques. The formed composites (MCM-41/13X) is found to have an excellent adsorption capacity in that it is nearly double in contrast to that of MCM-41. Interestingly, incorporation of mesopores into zeolites boosted adsorption efficiency of the manufactured composites while lowering the deactivation rate, hence, their demand has been on the increase (Yuan *et al.*, 2022).

High-performance cation exchanged zeolites are now possible thanks to Chen *et al.* (2015) use of molecular simulations to model the cationic exchange of zeolites (13X) with various concentrations of Ca²⁺, K⁺, Li⁺. The zeolite separation performance results using their energy, CO₂/N₂ selectivity, pore volume, isosteric heat, and adsorption isotherm; LiX-80 sample was found to have the greatest potential for CO₂/N₂ separation. Novel polymetallic ged zeolites were produced via mixing Ag⁺ and Pd²⁺ with LiX-80 (Chen *et al.*, 2015). Remarkably, LiPdAgX zeolite showed better CO₂/N₂ selectivity and CO₂ loading than 13X and LiX-80 samples (Girimonte *et al.*, 2017).

The performance of Ceca-13X zeolites were inspected using concentration pulse chromatography and constant volumetric method to examine the isotherms of respective binary mixtures and pure gases (Regufe *et al.*, 2020). The results were related with the binary projected behaviors adopting the 'extended Langmuir model'. The findings proved that the binary systems under study, for which equilibrium phase-diagrams were produced using experimental isotherms, could only be roughly described by this model. More so, Ceca 13X's significant CO₂/CH₄ and CO₂/N₂ selectivity during thermodynamic consistency tests suggested that it might be used to purify landfill gas and remove CO₂ from natural gas, flue gas streams, or ambient air (Mulgundmath *et al.*, 2012; Jadhav *et al.*, 2007).

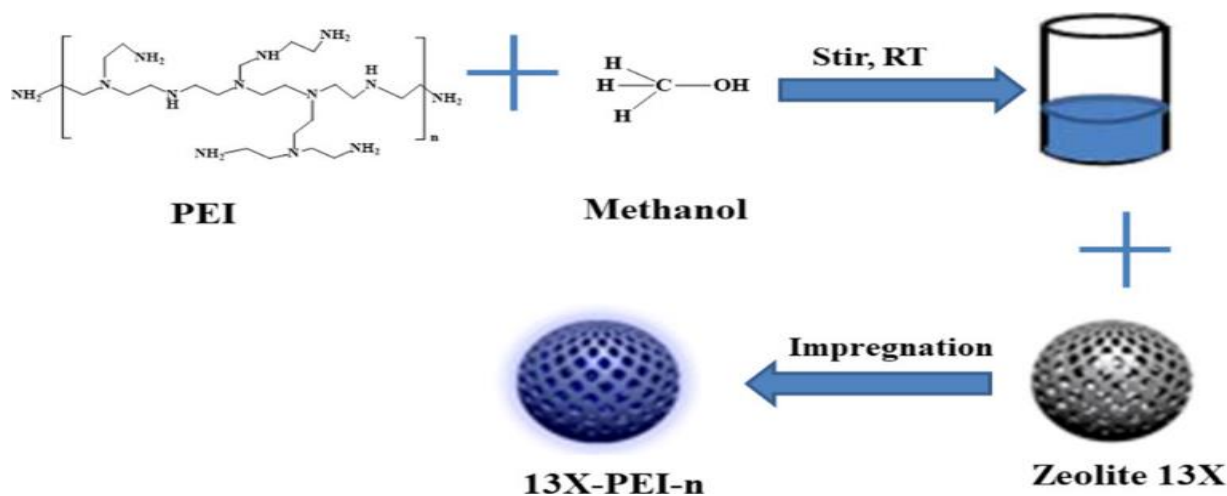


Figure 2: Schematic presentation of Zeolite13X based adsorbent (Karka *et al.*, 2019).

B. 3D-printed zeolite monoliths

Traditional extrusion methods are commonly used to create monoliths. Due to its cheap manufacturing costs and excellent productivity, 3D printing has recently become an essential technique for creating complex objects with distinctive mechanical and structural characteristics. 3D printing, as opposed to conventional extrusion methods, enables the exact production of 3D items with desired attributes and configurations (Pereira *et al.*, 2022). It has been utilized for the fabrication of monoliths with a variety of channel sizes, wall thicknesses, cross-sectional areas and exceptional mechanical qualities.

Thakkar *et al.* (2016) developed the first ever 3D-printed monoliths that has high content of zeolites. Figure 3 displays the cylindrical, square-channeled, smooth-surfaced morphology of the prepared zeolite monoliths that were 3D printed (Thakkar *et al.*, 2016). The magnified views (Figure 3b-d and 3f-h) further reveal microporous nature of the monoliths with pore sizes of 5 to 50 μm . The unique monoliths were produced applying zeolites 5A and 13X, bentonite-clay (as binder), poly (vinyl) alcohol (as co-binder), and methylcellulose (as plasticizing organic binder). Methylcellulose's hydroxyl-groups strengthened the cohesiveness of the particle aggregates, thus stability of the monolith. The distilled water and powder were carefully blended for homogeneity. In a 3 mL syringe, the paste was extruded by a 3D printer onto a template made with software (RoboCAD 4.2) after it was injected and then placed layer by layer. The monolithic structures were printed and subsequently dried at ambient temperature, and then heated to 100°C to avoid skin cracking and to increase their material strength quickly. After being oven-dried, the monoliths were calcined for 2-4 hours at 700°C. Zeolite and binder particle micro, meso, and macro-pore networks were found to constitute the monolith wall (Thakkar *et al.*, 2016).

C. Cation-exchanged ZK-5 zeolites

According to the properties associations of the cations (Li, Mg, K and Na) exchanged zeolites applied for CO₂ capturing, the NaKA zeolite absorbed CO₂ more efficiently than N₂ because the former has a higher effective kinetic diameter

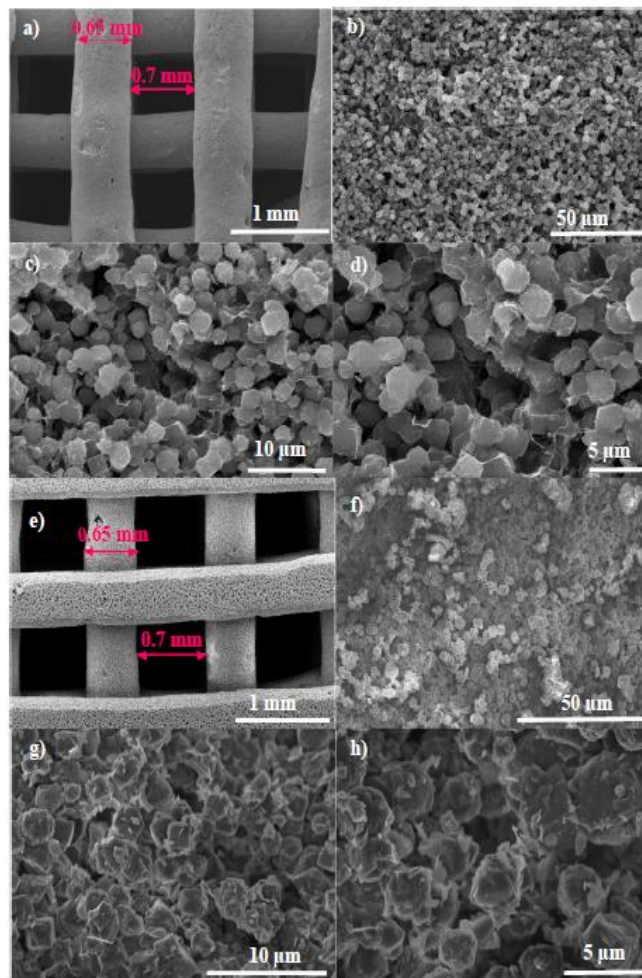


Figure 3: SEM images of 3D-printed zeolite monoliths. Adapted with permission from (Thakkar *et al.*, 2016) Copyright 2016 American Chemical Society.

(Pham *et al.*, 2017). Similarly, Lozinska *et al.* (2014) investigated the topology of cations (Na, Cs, K) exchanged zeolites (RHO) as shown in Figure 4. It was discovered that while inter-cage surface sites hindered CH₄ adsorption, they

underwent a temperature-dependent process known as "trapdoor" when CO₂ adsorption occurred. Poly(N-vinyl imidazole)/zeolite Zn-β is a novel membrane material for CO₂ separation that was fabricated by Liu *et al.* (2018).

Zeolite composite membrane adsorbents were prepared by solution casting and microwave-assisted ion exchange technique. The above-mentioned zeolite's channels were applied to model the hydrophobic aperture of reactive sites of carbonic anhydrase (CA). The prepared composite materials is consisted of Zn²⁺ in three different forms, which assisted to simulate the CA catalytic method, facilitating CO₂ transport, and improving the coupling of the poly(N-vinyl imidazole) and zeolite. The CO₂/N₂ selectivity of the poly(N-vinyl imidazole)/Zn-polysulfone prepared samples at 1 bar was 224 and its CO₂ permeance was 4620 GPU, both of which showed good separation performance (Liu *et al.*, 2018). Recently, the remarkable CO₂/CH₄ selectivity recorded for RHO zeolite has been ascribed to its pore size which successfully prevents CH₄ adsorption (Krishna & van Baten, 2022).

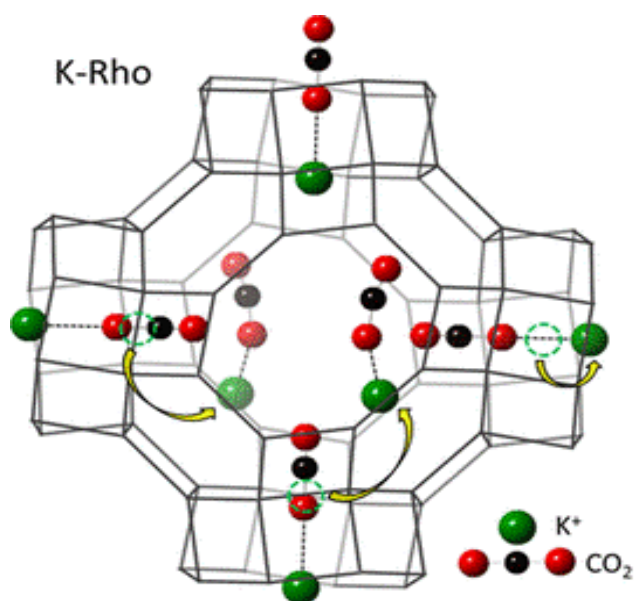


Figure 4: Schematic presentation of Adsorption of CO₂ on cation-exchanged zeolite Rho (Lozinska *et al.* 2014).

D. NaX Zeolite

In terms of benefit-to-cost ratio, NaX zeolite is one of the most standard adsorbents and prospective zeolitic CO₂ (Muriithi *et al.*, 2020). According to Gargiulo *et al.* (2018), it is feasible to create robust NaX zeolite that is excellent for absorbing CO₂ using waste materials that are widely accessible like rice husk ash (RHA). Similarly, Muriithi *et al.* (2020) used waste coal combustion fly ash deposits to synthesize NaA and NaX. CO₂ adsorption isotherms measured at four different temperatures indicate that NaX-RHA has superior CO₂ adsorption behaviors than comparable commercial substrate material. The semi-empirical Sips model satisfactorily showed a good fit for CO₂ adsorption by NaX-RHA sample, and the best fitting data of the model constraints showed that NaX-RHA possess the best properties for enhanced CO₂ adsorption (Gargiulo *et al.*, 2018; Oreggioni *et al.*, 2015). The Henry's law constants, pure and binary isotherms, and adsorption limiting

temperatures for CO₂ and CH₄ on prepared zeolite (CaX) were all obtained (Oddy *et al.*, 2013). The adsorption efficiency of the CaX zeolite was found to be higher than the NaX zeolite when pure isotherm data were compared. However, the latter's CO₂/CH₄ separation coefficient was higher than the former's, although the heat of CO₂ adsorption was the opposite (Oddy *et al.*, 2013).

E. RTH-type aluminosilicate zeolites

An aluminosilicate zeolite (RTH) of Al/Si ratio of 1:10 was fabricated by blending Na⁺ or K⁺ with 1,2,3-trimethylimidazolium (act as structure forming agent) in hydroxide conditions (Jo *et al.*, 2015). Also, Cu-zeolite (RTH) was prepared by stirring NH₄-RTH rigorously in a 0.01 M Cu(CH₃COO)₂ solution, thereafter drying (12 hours, 110°C) and air calcination (5 hours). In contrast to the plank-like structure of RTH zeolite crystals, the morphology of the prepared material's crystals was cuboid, with few poorly defined crystallites. While the Na-RTH zeolite's CO₂ absorption was less than that of the Na-RHO zeolite (25 °C and 1 bar), its CO₂ sorption kinetics were quicker than those of Na-RHO. Therefore, it was discovered that Na-RTH was a desirable CO₂-selective adsorbent as revealed in Figure 5 (Jo *et al.*, 2015).

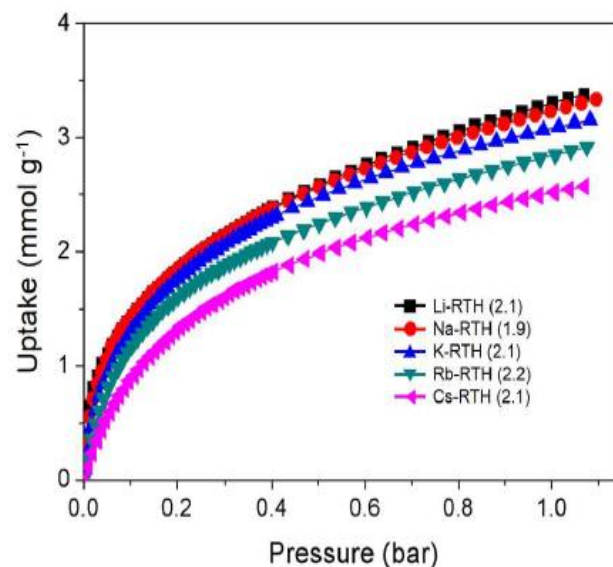


Figure 5: CO₂ adsorption isotherms for RTH-type zeolite at temperature of 298 K. Reproduced from (Jo *et al.*, 2015) with permission from the Royal Society of Chemistry.

F. MFI-type zeolite

Zeolite membranes are created on porous supports and are crystalline in nature. They are ideal for a variety of industrial separation processes since their typical pore aperture of 0.3 to 1.3 nm (0.55 nm for MFI-type zeolites) (Wang *et al.*, 2022). To create MFI type zeolites, a variety of structure-directing agents and silica can be utilized (Ji *et al.*, 2022). Zeolite membranes are typically made by hydrothermal deposition of aluminosilicates or silicate in an aqueous solution (Hambali *et al.*, 2020); but they can also be prepared on several type of porous supports via secondary growth pore plugging, in-situ crystallization and vapor-phase transfer techniques. The

secondary-growth remains the popular approach (Ji *et al.*, 2022). Despite the fact that the support was penetrated when these membranes were created by pore plugging, silicalite-1 crystals were covered by a 1.5 m thick covering. Because of the close packing of silicalite-1 crystals and their small size, more than 35% of the support's active layer was shown to be porous (Cacho-Bailo *et al.*, 2017).

G. Zeolite 4A

Hwang *et al.* (2018) used alkali fusion and hydrothermal synthesis to create a zeolite 4A-type from natural basalt rock. The basalt rock was crushed to size of 30 mm using a disk mill equipment. Iron oxide was first removed from the basalt powder by treating it with 1 M HCl for two hours at temperature of 80°C. Thereafter, drying was done (at 120°C for 12-hour). The product (alkaline in nature) was pulverized, agitated for two hours at room temperature in distilled water, and then separated by filtration after being calcined with sodium hydroxide for one hour at 500 °C. Zeolite synthesis was done for 2, 4, 8, 12, or 24 hours at 90 °C in the reactor comprising of NaOH using an aluminosilicates solution (Hwang *et al.*, 2018). The solid underwent filtering, a distilled water rinse, and a 12-hour drying period at 120 °C. Similarly, barium salt based zeolite (4A) had higher equilibrium CO₂ adsorption capacity than commercially available zeolite at 293 K and 15 bar because of its surface area, surface heterogeneity, and micropore volume (Hwang *et al.*, 2018)

H. Zeolite-chitosan (ZY-CS)

Amino and hydroxyl groups are found on the CS backbone (Jayakumar *et al.*, 2010). CS, which is primarily made from shrimp exoskeletons and crab-processing wastes is biocompatible, biodegradable, and can be applied for several biomedical and industrial applications (Kumar *et al.*, 2018). For CO₂ removal, nanoporous carbon aerogels and porous CS derivatives have been shown to have excellent morphological stability (Alhwaige *et al.*, 2016; Kumar *et al.*, 2016). More so, Kumar *et al.* (2018) used calcination and solvent exchange to synthesize ZY-CS composite. This synthesized composite has better CO₂ adsorption capacity than pure zeolite (Kumar *et al.*, 2016). Both ZY-CS and pure zeolites are non-toxic and cheap. When ZY-CS and pure zeolite were imaged using SEM, presence of nonporous shape was discovered and was evenly scattered throughout the ZY-CS biopolymer surface to create layers with voids. These findings of HTEM is in agreement with previous assertions which revealed stratified, interconnected, tubular, microporous, and mesoporous zeolite (ZY-CS) adsorbent (Kumar *et al.*, 2020).

Surface area of 22.53 m²/g was recorded for the ZY-CS composite in contrast to pure zeolite with 4 m²/g (Teimouri *et al.*, 2016). The 140% increase was as a result of formation of more adsorptive sites induced mesoporous and layered structure formation. The unmodified zeolite exhibited poor CO₂ adsorption capacity, while the prepared composite (ZY-CS) produced superior performance because of its higher surface area, well-defined, mesoporous topology. The ZY-CS composite's capacity to adsorb CO₂ exceeded zeolite due to the high amount of basic sites of the former material's amino moieties (Silva *et al.*, 2013; Kumar *et al.*, 2016).

I. Zeolite Nanoparticles

High adsorption efficiency, design of robust adsorbents with remarkable selectivity for CO₂, are the main hurdle in improving CO₂ adsorption process (Singh *et al.*, 2019). It is necessary to manufacture inexpensive zeolite-based nanoparticles that possess fast kinetics and high adsorption capacity on a wide scale for CO₂ /flue gas separation (Derakhshankhah *et al.*, 2016). Offretite and erionite form an intergrowth to form zeolite T. Though their structural arrangements differ, offretite and erionite are closely related to one another. The molecular dimension of CO₂ is 0.33 nm, while that of CH₄ is 0.38 and N₂ is 0.36 nm (Battiston *et al.*, 2022). Zeolite T has a peculiar pore size of 0.36 nm. Zeolite T nanoparticles can still only be prepared to a certain extent, though, Jiang *et al.* (2013) synthesized highly recyclable 150–200 nm zeolite T nanoparticles hydrothermally. Astonishingly, 30% increase in adsorption capacity using nanosized zeolite T in contrast to conventional micro structured zeolite.

Numerous conceptions have been put up regarding the production of zeolite nanomaterials both with and without the usage of morphology-directing materials (Saleh, 2022). Zeolite NaA nanomaterials were produced via template-free hydrothermal method (Shakarova *et al.*, 2014). Methylcellulose's thermo-gelation in the alkaline environment had a significant effect in defining the particle diameter and distribution. Contrastingly, the developed nanomaterials comprising of 100 nm sized particles produced superb CO₂ adsorption capabilities (operating condition of 100 kPa and temperature of 293 K) than the commercial NaA zeolite (Liu *et al.*, 2013).

Cheung *et al.*, (2013) fabricated zeolite NaKA nanoparticles, and they observed that the rate of CO₂ adsorption on the fabricated zeolite-based nanoparticles (NaA, NaKA) did not significantly increase. As previously indicated, the zeolite pore size can be customized using ion-exchange (Zagho *et al.*, 2021). When compared to zeolite NaA, the selectivity of modified zeolite (NaKA) was raised by a ratio of 5 to 10. In zeolite NaKA, CO₂ diffusion between the cages will be slowed because of the small pore dimension. Nonetheless, rate of diffusion was enhanced quadratically by reducing particle size and improving crystal quality (Ruhaimi *et al.*, 2022).

J. Zeolite-based Nanofibers

The popular and effective route to fabricate thin and continuous nanofibers is by electrospinning method (Lu *et al.*, 2022). Electrospinning allows for the creation of nanofibers with the appropriate properties, including large surface area and diameters between a few nanometers to tens of micrometers (Ji *et al.*, 2017). For instance, Calderon *et al.* (2014) showed that adding 10 wt percent of natural zeolite to acrylonitrile butadiene styrene fibers improved their gas separation ability. Zeolite ZSM-5, at a concentration of 34 weight percent, was added to poly(vinylpyrrolidone) (PVP) nanofibers to enhance the catalytic cracking of isobutene (Hambali *et al.*, 2021; Liu *et al.*, 2016).

Additionally, the step of creating zeolite/polymer nanofibers can be carried out first, and then the polymer matrix can be removed using a thermal surface etching method at

temperatures between 250 and 450°C to make zeolite nanofiber materials. Thermally etched zeolite Y nanofibers at 400°C with 816 m²/g surface area was compared with zeolite Y powder. It is noteworthy that a viable tool to fine tune zeolite Y morphology is via adjustment of thermal etching temperature which induce porosity and surface area increase (Ji *et al.*, 2017; Zhang *et al.*, 2020).

K. Zeolite-based Foams

Zeolites are a kind of microporous crystalline aluminosilicate that have potentials material for CO₂ adsorption in the fight against the menace of global warming. Traditional zeolite powders' low processability prevents them from being used in many industrial gas filtration applications (Modak & Jana, 2019). Valencia *et al.* (2019) fabricated hybrid foam by employing gelatin and nanocellulose supporting materials to get over this restriction. These foams can support extraordinarily high silicalite-1 levels of up to 90% weight without any crosslinkers. As a result, the zeolite crystals' efficiency was maintained by the dense networks of nanocellulose and gelatin without clogging their pores (Valencia *et al.*, 2019). The research on hybrid foams showed a direct relationship between high CO₂/N₂ selectivity zeolite loading and CO₂ uptake. These foams' ability to be reused showed a slight decline in adsorption effectiveness. For the 90 weight percent filled zeolite foams, this innovative design provided the optimum overall mix of adsorption and mechanical properties (Zagho *et al.*, 2021). It could be deduced that the pristine zeolite adsorbent is not perfect for CO₂ uptake, thus the need for improvements by several synthesis protocols as summarized in Figure 6.

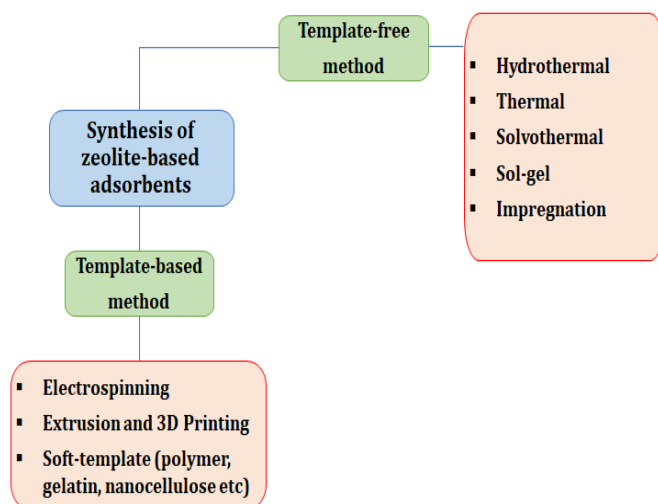


Figure 6: Major methods for development of zeolite-based adsorbents.

IV. PERFORMANCE OF ZEOLITE-BASED ADSORBENTS FOR CO₂ CAPTURE

Adsorbents like activated carbon, mesoporous metal oxides, zeolite, polymeric composites, nanoporous carbons

and MXene, ordered porous carbon, and their composites and chemical adsorbents (mixture of calcium oxide (CaO), solid amines sorbents, and lithium metal-based) are employed for capturing CO₂ (Lai *et al.*, 2021). They've been widely employed due to their adsorptive qualities, which are attributable to their internal structures, chemical nature, and distinctive shape (Ullah *et al.*, 2018). The CO₂ adsorbents' physical and chemical features have a considerable impact on their adsorption abilities (Lai *et al.*, 2021). The performance of zeolite-based adsorbents will be discussed in this section.

Zeolites (A, Y, 13X, ZSM, and chabazite) displayed good performance during separation of CO₂ from N₂ (Koohsaryan & Anbia, 2016). The superb adsorption capabilities of zeolite 13X and zeolite NaY make them popular choices for CO₂ capture via post-combustion process (Kwon *et al.*, 2022). It's interesting to note that K. Akhtar *et al.* (2018) developed series of zeolite NaX laminates which are thin and binderless using the pulsed current preparation technique. The thicknesses of the prepared materials were 310 to 750 m with widths above 50 mm. The laminates produced high CO₂ capture capacities, and selectivity for CO₂/N₂ as well as CO₂/CH₄. Amazingly, zeolites' adsorption properties can be tuned via altering their structure and external layers (Lu *et al.*, 2022).

Zeolites which can be prepared via template-based and template free methods and made up of linked channels with homogeneous pores that range in size from 0.5 to 1.2 nm (Rajaura *et al.*, 2018). Generally, the surface area of synthesized zeolites is induced by preparation protocol adopted as presented in Table 3. It was observed that surface area of zeolite-based material ranges between 340 to 940 m²/g. When aluminum (Al) is substituted for silica at the zeolite's tetrahedral site to create an anionic silicate-based network, it results in a negatively charged oxygen neighboring the substituted aluminum atom to the framework (Muraoka *et al.*, 2016). Zeolite is characterized by strong adsorption affinity, large surface area, high ion exchange potential and hydrophilicity (Wang *et al.*, 2022). Over the years, zeolites are used in gas adsorption, thus the need prepare and test several zeolite-based materials for CO₂ adsorption.

Ogawa *et al.*, (2014) discovered that zeolite LiX produced poor CO₂ adsorption capacity when operating pressure is low, but gave high performances at high pressure due to substantial CO₂ adsorption affinity. Yu *et al.* (2013) used chitosan-assisted synthesis to make binder less zeolite NaX microspheres for CO₂ adsorption. Ullah *et al.* (2018) examined different modified zeolites (zeolite-Y, zeolite, ZSM-5, and mordenite) for high-pressure CO₂ adsorption. Zeolite-Y, Zeolite, and Modernite were found to portray an equivalent adsorption capacity between 30–72 mmol g⁻¹ at operating pressure of 200 bar and (35, 50, and 65 °C) while ZSM-5 is 14–42 mmol g⁻¹ at same operating conditions.

Due to the sodium (Na) cation, 13X zeolite possess greater capability for CO₂ capture than other zeolite materials. It has a larger concentration of sodium cation in its structure, which creates a field (electrostatic) that interacts strongly with the quadrupole moments of CO₂ molecules. Zeolite materials' capacity to absorb CO₂ reduces in the presence of moisture because they are easily saturated with water (Silva *et al.*, 2014).

Table 3: CO₂ adsorption characteristics of zeolite adsorbents

Zeolite type	Preparation Method	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Adsorption activity condition (T°C, P bar)	Reference
Zeolite 13X	Hydrothermal treatment	591	0.250	(25, 1.6)	(Chen <i>et al.</i> , 2015)
3D-Printed Zeolite Monoliths	Traditional extrusion or 3D Printing	517	0.250	(25,1)	(Thakkar <i>et al.</i> , 2016)
Zeolite 4A	Alkali fusion and hydrothermal method.	559	0.250	(20, 15)	(Sowunmi <i>et al.</i> , 2018)
MFI-type zeolite	Hydrothermal deposition of precursor in aqueous media.	405	0.240	(25, 1)	(Migliardini <i>et al.</i> , 2015)
NaX Zeolites	Microwave and conventional hydrothermal method.	388	0.132	(25, 5)	(Gargiulo <i>et al.</i> , 2018)
β- Zeolites	Organic functionalization method	573	0.26	(30, 1)	(Hao <i>et al.</i> , 2018)

A. Novel adsorbents for CO₂ capture

The novel polymeric composites and nanostructured zeolite adsorbents as discussed in previous section, portrays modified properties in contrast to their commercial counterparts. Obviously, apart from zeolite-based adsorbents, potentials of other novel materials were extensively studied for CO₂ adsorption. The low performance of pristine MOF in CO₂ capture could be impeded by coupling with composites and mesostructured materials. Tuning the composition metals or linkers in the organic phase is effective in modulating the pore structure of MOF which lead to enhanced selectivity and CO₂ adsorption capability (Cui *et al.*, 2023; Wang *et al.*, 2023). Modifications of adsorption capacity of MOF could be achieved via surface functionalization protocol. The functionalization is achieved by incorporation of Lewis basic sites and polar functional groups which boosts CO₂ capture. Modifications of adsorption behavior of MOF could be achieved via surface functionalization. The functionalization is achieved by incorporation of Lewis basic sites and polar based functional groups that boost CO₂ capture (Ayelelu *et al.*, 2023; Rezaei & Taghizadeh, 2023). Basically, improved CO₂ capture over MOF based adsorbent is ascribed to its nano structured pore and channel, high surface area and storage capacity of its large void volumes (Anson-Bertina *et al.*, 2022). Similarly, high CO₂ sorption behavior was observed by immobilization of MOF onto rigid carriers (for example biochar and filler additives) (Wang *et al.*, 2021). Incorporation of biomass-based ingredients in MOF composites could further improve stability and act as secondary adsorption sites for CO₂ capture.

Excellent adsorption capacity of MXenes based adsorbents was ascribed to interlayer openings and large surface area. The major hurdle in application of MXenes is poor durability and improper reusability. Adopting a suitable preparation protocol and starting materials is beneficial towards their industrial application for CO₂ capture (Arifuzzaman *et al.*, 2023; Pang *et al.*, 2023). For further comprehension of the role of MXenes in CO₂ capture, more research efforts are required. The focus of recent researches is to find efficient and low-cost adsorbent. The features and cost

of some novel adsorbents are shown in Table 4. It can be conceived that zeolite and other biomass materials are widely available at a cheaper rate in contrast to other novel and emerging materials. The ability to produce zeolite from biomass, natural clay and other cheaper materials is an added advantage. Nevertheless, more findings are needed towards a suitable and cheaper synthesis protocol for fabrication of novel zeolite-based adsorbents. There is need to design more environmentally benign and sustainable synthesis technique towards new structured zeolite adsorbents development. In the same vein, more studies are required for large scale and economical production of novel adsorbent materials.

B. Mechanism of CO₂ adsorption on zeolite

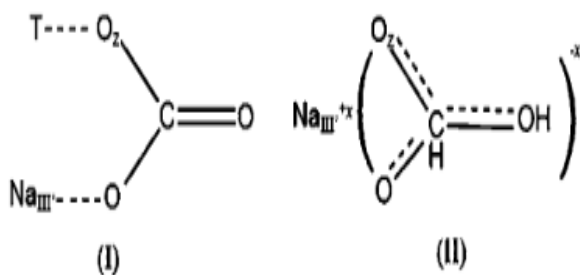
Adsorption process is a phenomenon that happens on the surface of a substance and has been conclusively investigated. Sorbent is referred to the substance/material that adsorbs another substance, while sorbate refers to the substance that is adsorbed onto the surface of the sorbent (Konni *et al.*, 2020). In general, sorption of sorbate molecules onto sorbent surface is achieved via molecular interactions and subsequent diffusion of sorbate molecules from within the sorbent material.

Ensemble of factors influence sorption, including dosage, concentration, temperature, pH, sorbate structure and topology (Xu *et al.*, 2018). To better comprehend adsorption test results, models such as Freundlich, Langmuir, Temkin and Redlich–Peterson are mostly employed. Likewise, it is crucial to compute thermodynamic properties (H°, G°, and S°) (Abd-Hamid *et al.*, 2017). Over the years, mechanism of CO₂ adsorption on zeolite-based materials has been investigated, the ion-dipole interaction is what causes physisorption of CO₂ to occur when the gas is oriented linearly (Yeung & Han, 2014). More firmly bonded carbonate species are detected in addition to physical adsorption. These adsorbed CO₂ sites are bi-coordinated and twisted, as presented in Scheme 1.

Zeolites seem excellent for pressure swing adsorption (PSA) technique and are very good at isolating CO₂ from gas mixtures. Even at this, at 30°C their adsorption abilities reduce with increasing temperature though become negligible at

Table 4: Features and cost effectiveness of adsorbents for CO₂ capture

Adsorbent materials	Features	Price (USD \$/kg)	Reference
Activated Carbon	-Widely available. -Thermally stable. -Ease of regeneration. -Require high operating pressure.	~35.1 (Merck, 2023)	(Kumar <i>et al.</i> , 2020)
Metal Oxide	-Widely available. -Low toxicity. -Require high energy for regeneration.	~32.5 (CaO, Bernd Kraft, 2023)	(Musa <i>et al.</i> , 2023)
Metal organic framework (MOF)	-Tunable pore structure. -Large surface area. -Ease of regeneration.	~527.3 (Mubarak <i>et al.</i> , 2022)	(Cui <i>et al.</i> , 2023; Wang <i>et al.</i> , 2023)
Zeolite	-Universal availability. -Thermally stable. -High surface area. -Low adsorption capacity.	~3.5 (Chemxin, 2023)	(Bai <i>et al.</i> , 2022)
Silica	-High surface area. -Thermally and mechanically stable. -Tunable pore structure. -Require high energy for regeneration.	~6.4 (ChemAnalyst, 2023)	(Dziejarski <i>et al.</i> , 2023)
MXene	- Unique electronic structure. -Large surface area. -Improper reusability. -Difficulty in large scale production.	~12.2/g (Zaed <i>et al.</i> , 2023)	(Arifuzzaman <i>et al.</i> , 2023; Pang <i>et al.</i> , 2023)

**Scheme 1: The bonded carbonate species linked with bi-coordination (Yeung & Han, 2014)**

above 200 °C. Additionally, their selectivity CO₂ over other gases is still low (Zhu *et al.*, 2019). In general, zeolites' ability to separate gases is determined by three factors: its purity, cationic form, and framework's structure and composition. Zeolites X, MFI, Y and CHA (e.g. ZAPS, ZN-19) have all been studied, notably, those that are extremely crystalline, have a large surface area, and feature three-dimensional topology as revealed in Figure 7 (Lu *et al.*, 2022).

At 25°C and 1atm CO₂ partial pressure, Siriwardane *et al.* (2001) found that zeolite adsorbents had remarkable CO₂ adsorption capacities (13X =3.64 and 4A =3.07 mmol g⁻¹). Merel *et al.* (2008) employed indirect thermal swing adsorption to do a comparative analysis on the CO₂ capturing capacities of zeolites 5A and zeolite 13X. It was revealed that the former outperformed the latter, because of robust electrostatic field within the pores and heterogeneity of the surface.

Torralba-calleja *et al.* (2013) discovered that the Si/Al ratio decreases inclination for polar molecules (like CO₂) because of the robust electronic field inside within the pores and increased surface heterogeneity.

Zeolite swapped with alkali and alkaline-earth cations is another research topic. The adsorptive characteristics of porous adsorbents can be tuned by adjusting the accessible pore volume, as well as pore in electronic field. Conversely, zeolite containing Li has the maximum CO₂ capability, according to Walton *et al.* (2006) who looked into the CO₂ adsorption properties of X and Y zeolites replaced with K, Rb, Li, Na, and Cs. In their 2008 study on the effects of Cs and Na on Y zeolites, Díaz *et al.* (2008) came to the conclusion that, at high temperature, Cs-Y is an appropriate candidate for CO₂ adsorption. Wirawan & Creaser (2006) did a comparative study to assess the adsorption capacity of cation-exchanged MZSM-5 (Rb, Na, Cs, B, Li, K, R, H, and Ba). Their result revealed that Ba/ZSM-5 adsorbed species best and has the greatest adsorption capacity.

Moisture is another challenge for zeolite-based adsorbents in practical applications. Wirawan & Creaser (2006) discovered that in the presence of H₂O molecules, process of CO₂ adsorption on zeolites (CaY and NiY) is limited since water is preferentially adsorbed on such surfaces. In the same vein, CO₂ adsorption on type X zeolite material was significantly influenced by water (Brandani & Ruthven, 2004; Rege & Yang, 2001). From a thermodynamic perspective,

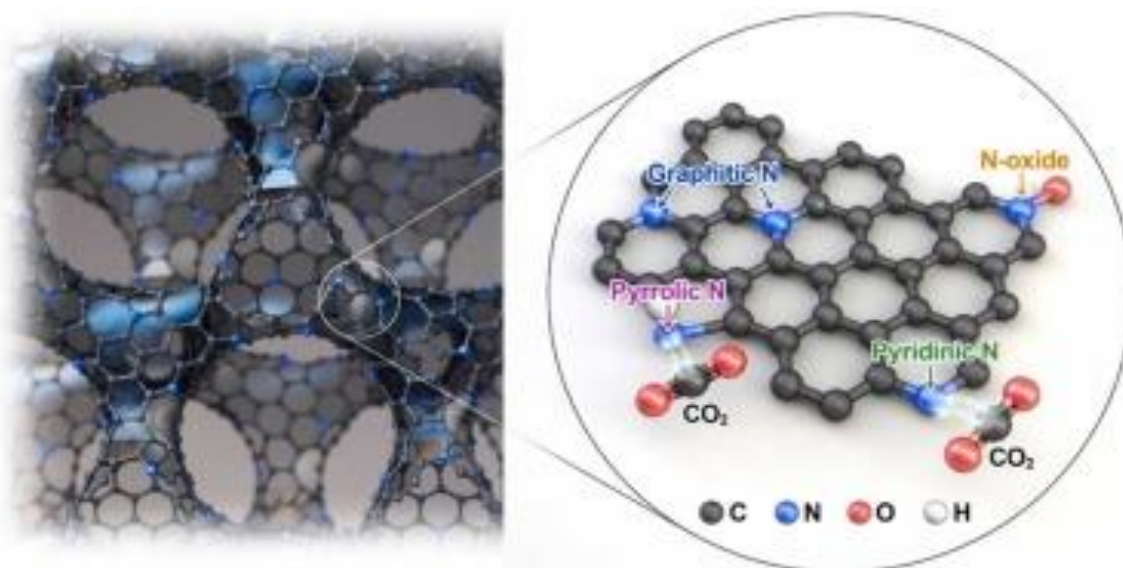


Figure 7: Structure of N-doped zeolite adsorbent Reprinted from (Lee *et al.*, 2022), Copyright (2022), with permission from Elsevier.

adsorption of CO₂ is severely hindered in presence of H₂O (Ullah *et al.*, 2018).

Díaz *et al.* (2008) observed that adsorption of CO₂ on Y zeolites treated with Cs and Na increased, which they attributed to an increase in Bronsted acidity in zeolites following alkali treatment. Interestingly, surface acidity amplified after alkaline treatment of pristine zeolite, and the H₂O molecules may produce additional Bronsted acid sites as a result of its alignment to the Lewis sites. Furthermore, the stability of the zeolite structure may also be harmed by water. Zeolite structures may dealuminate in acidic conditions when CO₂ is present, which can lead to partial or full framework collapse (Díaz *et al.*, 2008). Similarly, Zhang *et al.* (2009) examined the impact of acid-treated zeolites on adsorption capacities, and observed that the acids cause their capacities to diminish.

SUMMARY AND PERSPECTIVES

A concise review on recent scenarios in CO₂ capture has been presented. CO₂ emissions from many sources are responsible for the continuous rise in global temperatures which led to the menace of global warming. This issue has compelled scientists to devise practical solutions to eliminate CO₂ from the atmosphere. Technologies such as CCS were deployed to eliminate GHGs, mainly CO₂. Absorption, membrane sequestration, and adsorption methods have been developed to adsorb and separate CO₂ gas utilizing novel adsorbents. Among these approaches, except adsorption, are hampered by high energy demand coupled with production of hazardous gases. Ideal adsorbent materials have the potential to be used commercially in the gas collection (CO₂, CH₄, and H₂). They are commonly employed in adsorption of CO₂ under certain conditions because of their unique properties, making them suitable CO₂ adsorbents. Zeolites prove better than its counterparts for capturing CO₂ because it is characterized by molecular sieving, large porous surface area, hydrophilicity, and strong adsorption affinity.

Remarkable efforts have been made in development of robust adsorbents for enhanced CO₂ adsorption. Conventional zeolite materials are susceptible to dealumination in acidic conditions when CO₂ is present, which lead to partial or full framework collapse. Hence, leading to low adsorption capacity, stability and a slow rate of reaction in the process of regenerating zeolites since their powders are suspended or aggregated easily. Although zeolite-based materials have good stability with a wide surface site for adsorption, desorbing the adsorbed gas and regenerating the adsorbent needs a significant amount of work. Other adsorbents such as MOFs and carbonaceous materials, on the other hand, require little effort to renew after adsorption. In comparison to the real flue gas temperature, which is often 90 °C, the optimal temperature of CO₂ adsorption over zeolite-based materials is around 70 °C. Hence, either the adsorbents need to be fine-tuned or flue gas has to be cooled to make zeolites suitable for adsorption at elevated temperatures towards industrial settings for CO₂ collection. This needs to be addressed because cooling of the flue gas consumes a lot of energy. Moreover, moisture is another challenge for zeolite-based adsorbents in practical applications. From a thermodynamic perspective, adsorption of CO₂ is severely stalled in presence of water. Thus, several syntheses approaches are crucial in improving adsorptive characteristics of zeolite and novel adsorbents.

Hydrothermal process seems a viable route to prepare robust zeolite adsorbents. Interestingly, surface acidity amplified after alkaline treatment of pristine zeolite, and the H₂O molecules may produce additional Bronsted acid sites as a result of its alignment to the Lewis sites. The negative charge produced by switching an AlO₄ for SiO₄ is countered by the placement of metals (such as Na, Cs, Ba, Li, K, Ca, and Mg) in the structure's aperture. The dispersion of these cationic metals in the pores and channels, charge density, and size had a noteworthy influence on the adsorption and gas separation capabilities of zeolites. Amine-grafted zeolites offer more distinctive adsorptive characteristics than pure zeolites owing to availability of greater adsorption sites. The incorporation of

mesopores into zeolites boosted adsorption efficiency of the zeolite composites while lowering the deactivation rate. Generally, the surface area of modified zeolite adsorbents is in the ranges between 350 to 940 m²/g. Thermally etched zeolite Y nanofibers at 400°C with 816 m²/g surface area was compared with commercial zeolite powder. It is noteworthy that a viable tool to fine tune zeolite morphology is via adjusting the thermal etching temperature led to change in porosity and surface area.

Numerous conceptions have been put up regarding the production of novel polymeric nanomaterials both with and without the usage of morphology-directing materials. Electrospinning method proved effective in fabrication of thin and continuous nanofiber zeolite with exceptional stability and CO₂ selectivity. Development of zeolite nanomaterials comprising of 100 nm sized particles was achieved via template-free hydrothermal method. It induced relatively quick CO₂ capture and higher adsorption capabilities than the commercial zeolites. Conversely, zeolite composite membrane was successfully prepared via secondary growth pore plugging, in-situ crystallization and vapor-phase transport techniques. Outstanding CO₂/CH₄ selectivity was recorded for zeolite composite membrane adsorbents which was ascribed to crystallinity and pore size which successfully prevents CH₄ adsorption. Offretite and erionite could form a beneficial intergrowth to form zeolite composites. Amazingly, 30% increase in adsorption capacity was recorded in contrast to conventional micro structured zeolite adsorbents.

Astonishingly, novel nanostructured and polymeric zeolite composites with remarkable adsorption capacities were recently developed. Unique zeolite that are extremely crystalline with large surface area, and feature of three-dimensional materials were explored for CO₂ capture from flue gases. It was established that 3D printing is an efficient technique for creating complex objects with distinctive mechanical and structural characteristics. More so, electrospinning allows for the creation of nanofibers with the appropriate properties, including large surface area and diameters between a few nanometers to tens of micrometers needed for excellent CO₂ adsorption. The low performance of pristine MOF in CO₂ capture could be impeded by coupling with composites and mesostructured materials. Tuning the composition metals or linkers in the organic phase is effective in modulating the pore structure of MOF which lead to enhanced selectivity and CO₂ adsorption capability. Conversely, modifications of adsorption capacity of MOF could be achieved via surface functionalization. Incorporation biomass-based ingredients in MOF composites could further improve stability and act as secondary CO₂ binding sites. Excellent adsorption capacity of MXenes based adsorbents was ascribed to interlayer openings and large surface area. The major hurdle in application of MXenes is poor durability and improper reusability. Adopting a suitable preparation protocol and starting materials is beneficial towards their industrial application for CO₂ capture.

It is desirable that CO₂ adsorbent has properties which includes but not limited to cost-effectiveness, easy regeneration, high CO₂ adsorption rate, high surface area, high CO₂ selectivity, tunable porosity, tolerance to moisture and

impurity and high availability. Global availability and the ability to produce zeolite from biomass, natural clay and other cheaper starting materials is an added advantage. Numerous possibilities exist in the fabrication of innovative structured adsorbents for CO₂ adsorption. Conversely, more studies are required for large scale and economical manufacture of novel adsorbent materials. Research focus on computational modelling to further understand interaction mechanisms is indispensable.

V. CONCLUSION

To circumvent low adsorption efficiency, stability and rate of reaction associated with solid adsorbents, zeolite-based materials with strong CO₂ adsorption affinity have emerged. This review discussed on novel nanostructured adsorbents with robust CO₂ adsorption. These materials deserved attention as a result of their molecular sieving, high porous surface area, distinctive mechanical and structural characteristics which is prerequisite for excellent CO₂ adsorption. Research progress in engineering novel robust zeolite materials with a wide surface site for adsorption have inspired hope for their efficient industrial application. Using suitable synthesis protocol, material composition and metals could pave way towards large scale and economic development of CO₂ capture adsorbents.

AUTHOR CONTRIBUTIONS

H. U. Hambali: Conceptualization, Supervision, Methodology, Writing – review & editing. **T. Jimoh:** Conceptualization, Methodology, Writing – review & editing. **T. L. Peng:** Conceptualization, Writing – review & editing. **A. A. Umar:** Conceptualization, Writing – review & editing. **B. T. Mutiullah:** Conceptualization, Writing – review & editing. **J. A. Okolie:** Conceptualization, Writing – review & editing.

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