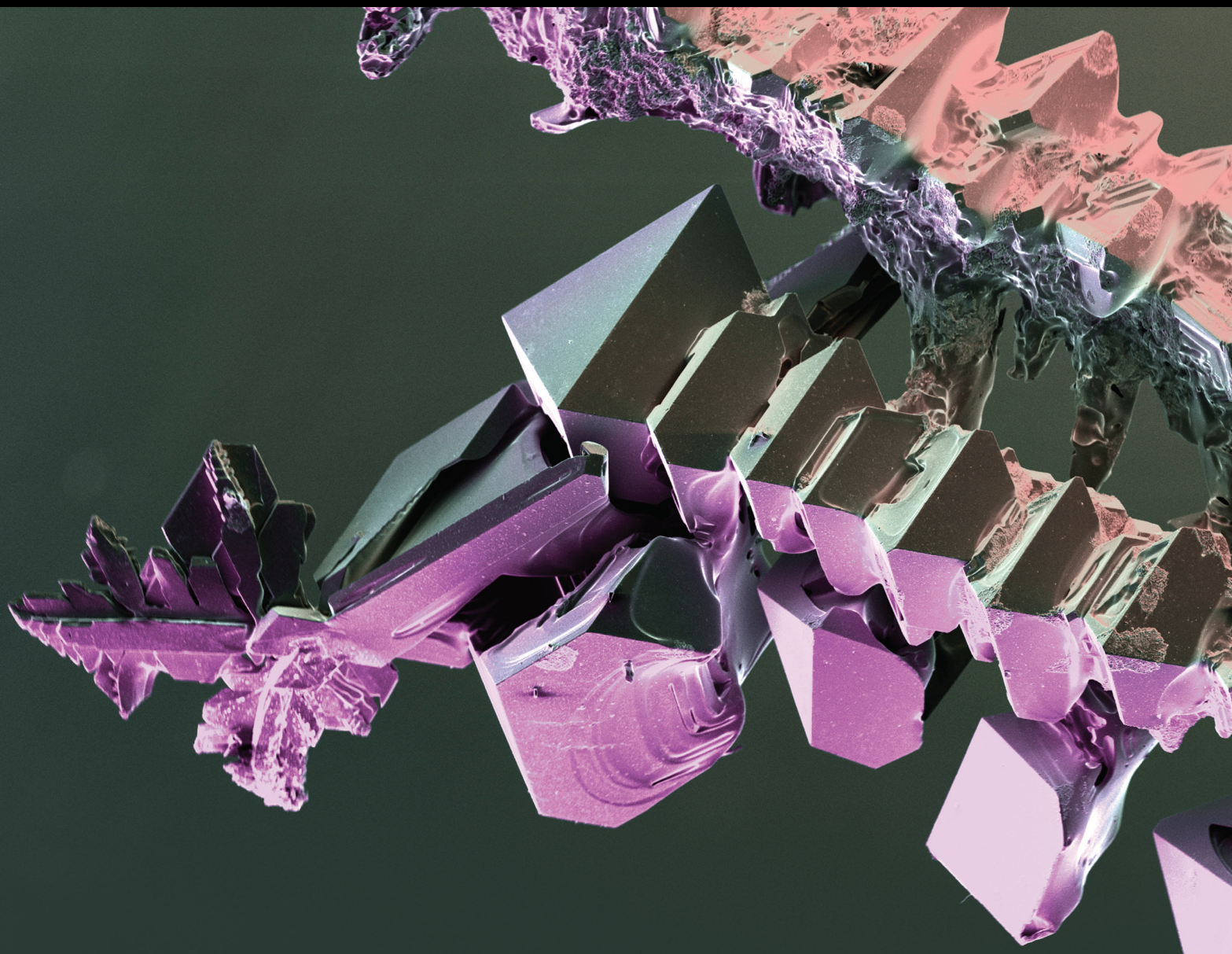# Innovative Carbon Capture Technologies for Sustainable Engineering and Environment

Lead Guest Editor: Eshorame Samuel Sanni
Guest Editors: Emmanuel Rotimi Sadiku, Michael Daramola, Oluranti Agboola, Moses Eterigho Emetere, and Emeka Emmanuel Okoro

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Contents

Review Article

Advances in the Use of Nanocomposite Membranes for Carbon Capture Operations

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The adoption of nanodoped membranes in the areas of gas stream separation, water, and wastewater treatments due to the physical and operational advantages of such membranes has significantly increased. The literature has shown that the surface structure and physicochemical properties of nanodoped membranes contribute significantly to the interaction and rejection characteristics when compared to bare membranes. This study reviews the recent developments on nanodoped membranes, and their hybrids for carbon capture and gas separation operations. Features such as the nanoparticles/materials and hybrids used for membrane doping and the effect of physicochemical properties and water vapour in nanodoped membrane performance for carbon capture are discussed. The highlights of this review show that nanodoped membrane is a facile modification technique which improves the membrane performance in most cases and holds a great potential for carbon capture. Membrane module design and material, thickness, structure, and configuration were identified as key factors that contribute directly, to nanodoped membrane performance. This study also affirms that the three core parameters satisfied before turning a microporous material into a membrane are as follows: high permeability and selectivity, ease of fabrication, and robust structure. From the findings, it is also observed that the application of smart models and knowledge-based systems have not been extensively studied in nano-particle-/material-doped membranes. More studies are encouraged because technical improvements are needed in order to achieve high performance of carbon capture using nanodoped membranes, as well as improving their durability, permeability, and selectivity of the membrane.

1. Introduction

The carbon dioxide (CO_2) volume in the atmosphere has increased since the industrial age, and this can be attributed to the anthropogenic activities. CO_2 is an effective greenhouse gas from the literature, due to its ability to absorb Earth's surface infrared radiation emission. The higher the concentration of carbon dioxide in the atmosphere, the more infrared accumulates and the average temperature of the lower layers of the Earth's atmosphere increases. This process is called global warming [1]. Carbon Capture Utilization and Storage (CCUS) technology is evolving in response to global warming and climate change. CCUS is the process of extracting CO_2 from a variety of high-temperature treatment plants and processes using a variety of technologies [2]. Along with the introduction of CCUS technology, CCU aims to use CO_2 as a source of carbon to create value from readily available raw materials [3].

Carbon capture technologies can be applied at different process stages and these include precombustion, postcombustion, and oxyfuel combustion. Technologies used in postcombustion CO_2 capture are as follows: absorption by chemical solvent, pressure/vacuum swing adsorption, adsorption by solid sorbent, cryogenic separation, membrane separation, and more recently microbial/algae separation [4]. Although cryogenic separations are energy-intensive, chemical absorption and physical adsorption are becoming increasingly important, while most membrane separation

technologies are progressively developing. Those of precombustion include absorption by chemical solvents, absorption by physical solvents, and adsorption by porous organic frameworks [4]. Oxyfuel combustion technologies from the literature include chemical looping combustion, combustion in pure oxygen, and chemical looping reforming. Some issues affecting carbon capturing technology efficiency include low adsorption capacity at high temperatures, poor absorption, low mass transfer coefficient, and so on [5].

Nanotechnology is being used to enhance and optimize the efficiency of the existing membrane technologies for CO_2 capture [6]. The part of nanomaterials in CO_2 capture shows great potential because of its large surface area and excellent performance. This study reviews the application of nanocomposites in different process stages, trends in the absorption and adsorption of CO_2, influence of physicochemical properties, nanoparticle/material type, and water vapour on carbon capture efficiency; moreover, an emphasis is placed on the use of nanodoped membranes in carbon capture. Finally, it highlights the challenges in nanodoped membrane technology for carbon capture process and therefore proposes areas for future research.

2. Carbon Capture Background

Precombustion technology captures CO_2 before the combustion process occurs resulting in cleaner fuel through the combustion process and eases the separation of CO_2 after the operation; thus, producing less CO_2 emissions [7]. Two (2) examples are ammonia production and gasification of coal in power plants. In ammonia production, the CO_2 coformed with hydrogen through the steam reforming process are detached before the ammonia synthesis occurs [8]. In the gasification process, fuels such as natural gas are converted directly into syngas by reforming. Precombustion technologies include absorption by chemical solvents such as amine-based solvents, which for instance are alkali compounds [9].

In oxyfuel combustion, inert gases are removed from the flue gas combustion. In this technique, fuel is burned with highly pure oxygen as a substitute of air to achieve complete combustion. This results in the formation of high concentrations of carbon dioxide and a small amount of water vapour in the flue during combustion. Currently, the oxygen used in the combustion process is provided by cryogenic air separation equipment. In the cryogenic air separation unit, oxygen is separated from the air by cryogenic condensation at low temperatures [10]. As shown in Table 1, oxygen fuel alternatives include chemical looping combustion and remodeling. Both use metal oxides to selectively transmit oxygen to the combustion chamber from the air. As chemical looping remodeling uses less stoichiometric oxygen volume, it produces syngas; thus, it can be seen as a suitable technique for syngas production or generation. One challenge, however, is to use the system at the high pressure required to realize the efficiency comparable to modern oxyfuel or postcombustion capture processes [8].

The postcombustion method is based on the separation of CO_2 after the fuel is burned. This approach is feasible because it can be installed in existing industries without excessively changing its operating structure. The technology of carbon dioxide capture after combustion is principally based on fluid absorption, solid adsorbent adsorption, and membrane separation [4]. Between these knowledge, the utilization of solid adsorbents for capture sequestration is considered cheaper and easier than the scientifically advance fluid absorption process. However, chemical absorption is reported to be the most appropriate physical adsorption method for postcombustion capturing of carbon dioxide in power plants [11]. The choice of adsorbent is vital in determining the final efficiency of the adsorption technology used to selectively remove and capture CO_2. Various types of adsorbents have been exploited for carbon dioxide, such as zeolites, activated carbon, and organometallic frameworks [5].

Changes in temperature or pressure promote adsorption, leading to temperature oscillation (TSA) adsorption and pressure oscillation (PSA) adsorption, respectively [7]. The main focus in this direction is on porous materials, including microporous, mesoporous, zeolites, carbonate materials, organometallic frameworks, and related amino-functionalities. Zeolite has a high adsorption capacity for higher CO_2 partial pressure, when compared with other adsorbents. However, due to competitive adsorption, low CO_2 adsorption capacity in the presence of water is often observed due to high affinity of these materials for water [12]. Membranes, on the other hand, provide better performance due to their properties and processability, but efforts to improve permeability are usually made to the detriment of selectivity and vice versa [7]. Membrane separation is a comparatively new technology for CO_2 separation. It uses different gas solubility, diffusion coefficient, adsorption, and absorption differences of various materials for separation.

Membrane separation is one of the most efficient separation methods where high-purity products are not required, as they are highly efficient contrasted with other separation systems. Membrane separation is currently being studied in detail due to its many merits in terms of technical aspects, in addition to cost factors, compared to other separation methods. In addition, its application is very flexible because it can be used in precombustion and postcombustion approaches [7]. The main limitation of separation after combustion by membrane technique is the need for very high selectivity for the extraction of relatively low CO_2 concentrations from exhaust gases. Therefore, the development of a suitable membrane material is very important to meet the requirements set by the International Energy Agency (IEA). Therefore, selectivity is very important and low selectivity is a serious problem in the commercialization of this process, as membrane properties such as porosity, wettability, and pore size are vital to the process efficiency [13].

According to the literature, nanomaterials are considered more effective due to their excellent properties, which highlights them to be used in doping membranes as potential for CO_2 capture technique with its thermal stability advantages [14, 15].

TABLE 1: CO_2 capture membranes.

Type of membrane	Membrane preparation	Temperature range (°C)	Area of application
Polymer-based	Phase inversion process	<100	CO_2 capture from natural gas, biogas, and flue gas
Dual-phase	Etching method	400–700	CO_2 and oxygen from various gas mixtures
Oxygen ion-conducting ceramics	Sequence of extrusion, and sintering technique	>700	CO_2 separation after combustion
Membrane contractors	Extrusion, and sintering technique	<100	CO_2 absorbed in a solvent
Carbon-based	Vacuum-assisted coating process	<100	Separation of CO_2 from biogas
Air liquid hollow fiber	Interfacial polymerization technique	<100	CO_2 capture from flue (stack) gas
Single-layer graphene	Ozone functionalization-based etching and pore-modification chemistry	—	Postcombustion CO_2 capture
Thermal rearranged polymer	Crosslinked thermally rearranged polymer	<100	CO_2 removal
Polymers of intrinsic microporosity	Polymerization reaction based on a double-aromatic nucleophilic substitution mechanism	<100	CO_2 removal
Perfluoro-polymer	Impregnation and coating	>70	CO_2 removal from raw natural gas treatment
Zeolite-based inorganic	In situ hydrothermal synthesis method	>100	CO_2 separation and removal
Mixed matrix	Spin coating	<100	CO_2 separation and removal

Experimental synthesis of various nanoparticles has been proven to effectively capture carbon dioxide at high temperatures, and various nanocomposite materials have been used in membrane separation processes to optimize carbon capture efficiency. Figure 1 shows the carbon capture technology, and the analysis is based on three identified carbon capture process paths [14].

One of the main problems with postcombustion combustion is the separation of relatively low CO_2 concentrations (usually about 3–15% by volume) from large amounts of nitrogen in the exhaust. The process also requires a lot of energy for solvent regeneration. The largest postcombustion operating unit has a capacity of about 800 tones CO_2 per day [15]. Several postcombustion CO_2 exist, amongst which include absorption (which is the most widely used in oil and chemical industries and involves use of solvent to remove the CO_2 from the flue gas) and membrane (involving physical or chemical interactions between membrane material and gases) [16]. In precombustion process, the CO_2 content is in the range of 15–60 mole percentage at high pressure. Precombustion technique is used for hydrogen large-scale production to manufacture fertilizer and ammonia manufacture. This capture technique is more efficient, but the base gasification process's capital costs are often more expensive because of its complicated installation than the traditional pulverized coal power plants [17]. Oxyfuel combustion usually results in gas with high CO_2 concentration, often higher than 80% by volume. This technique often entails the separation of oxygen from air with an estimated oxygen purity greater than 95%. The oxyfuel combustion system is still being proven.

The choice of technical conception is largely determined by the conditions of the process under which it must operate. Higher collection efficiency can be achieved, although this will considerably require larger separation devices and more energy and cost. Theoretically, oxyfuel combustion systems can capture nearly all the CO_2 produced. This capture technique needs additional gas treatment systems to remove nitrogen and sulfur pollutants [18].

3. Membranes

Membrane engineering is a physical process that often involves the use of a semipermeable barrier in containment and permeability flows to separate gas mixtures of two or more components. Membrane separation allows certain molecules to pass through while blocking some specific molecules from passing through the membrane (Figure 2) [19]. Membrane technology in carbon capture and storage (CCS) has advantage over other technologies because of ease of installation, and compatibility (such as offshore). In addition, it offers flexibility of operation and maintenance, reduced capital cost and energy consumption, and it requires less chemicals when related to other separation processes.

In membrane engineering, the desired components selectively permeate, and unwanted components are retained, thus, separating the mixture. Various membranes have been developed for the capture of CO_2 with energy efficiency and low cost to mitigate carbon emission [20], and the membrane separation technology has been identified as one of the most efficient solutions for carbon sequestration. Ji and Zhao [21] highlighted that gas stream separation using membrane technology is still evolving and has attracted intensive research into CCS in recent years. The selectivity of a particular membrane with respect to the gas stream ratio of permeabilities is dependent on the type of membrane, molecular weight and size, affinity to membrane material, membrane thickness, and so on [22].

Membrane material has their strengths and shortcomings in terms of material cost, separation properties, and durability. To reduce carbon recovery costs, it is important
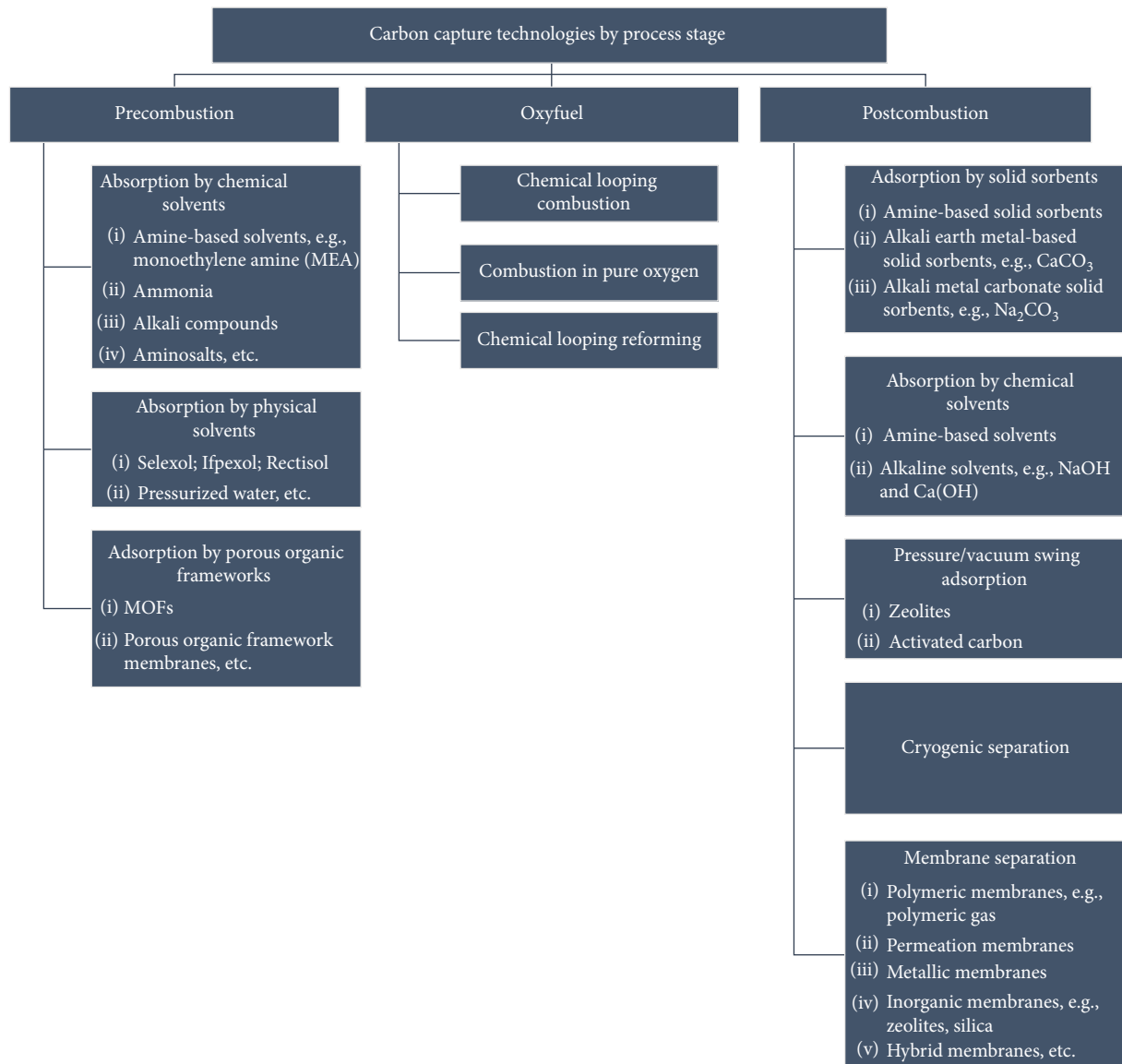
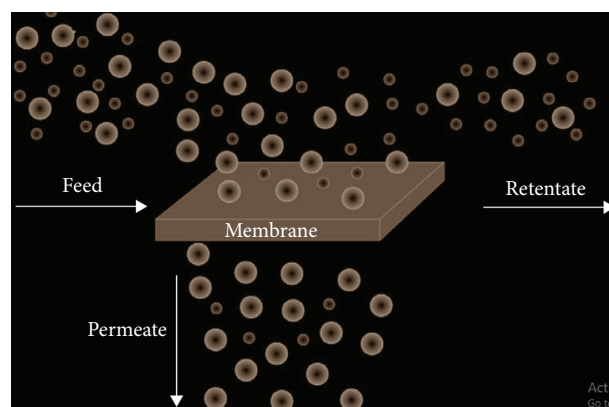Figure 1: Carbon capture technologies by process stage.

Figure 2: Membrane for gas stream separation.

to develop advanced membrane materials to increase profitability. Various membranes such as polymer films, carbon molecular sieve membranes, mixed matrix technology, microporous organic polymers, and inorganic membranes (metal, zeolite) can be used for separation of CO_2-associated gas streams [23]. To achieve a high flow rate, the supply gas is compressed and the permeable gas is combined with a vacuum to achieve an advanced driving force. Subsequently, the membrane is only a few hundred nanometers to a few micrometers thick, and most membranes in their natural form cannot resist the force of the pressurized feed gas [24]. Therefore, the membrane is generally coated or doped on a thick and permeable substrate to obtain sufficient mechanical strength. Some of the membrane features are that it must have minimal flow resistance and contain large pores to allow free flow of gas through the cover layer [25].

Koros and Mahajan [26] used the mechanism of separation to classify gas separation membranes into sorption diffusion, complex sorption diffusion, and ion-conducting membranes. Most commercial gas separation membranes are currently cheaper to produce than inorganic materials and offer some attractive properties, such as flexibility in both flat and hollow fibers. Organic membranes or polymeric membranes are the mainstream. In practice, it has been shown in the literature that polymeric membranes used operate mainly according to the solution diffusion mechanism [27]. By this mechanism, the gas molecules in the feed stream are first absorbed by the membrane, diffused through the membrane matrix, and then absorbed from the permeable side. Dense/tight membranes are often used as a selective barrier between the supply stream and the permeable gas stream. The efficiency of a membrane selectivity depends on the matrix of the membrane diffusibility and solubility. In order to obtain the desired properties, the material for synthesizing the type of membrane to be adopted must be selected correctly [28]. For this reason, different types of membranes have been specially designed for CO_2 removal.

Table 1 shows the different types of membranes for separating CO_2-related gas streams before or after combustion processes and their temperature ranges. The literature shows that ceramic membranes can be used for higher temperature in catalytic membrane reactors [29, 30]. He et al. [31] developed a single-layer graphene membrane that exceeds postcombustion capture targets by some margin. The functionalized CO_2-selective polymer chains in the nanoporous graphene allowed for the production of CO_2-selective membrane thickness on the order of nanometers. The two-dimensional nature of the membrane significantly increases the permeability to CO_2, which makes the membranes even more attractive for carbon capture. Siagian et al. [19] conducted a review on membrane gas separation and contactor. Their study compared both technologies that use features, such as carbon capture performance, characteristics, and techno-economic assessment. They highlight the need to develop novel generation of membrane with optimal pressure, temperature, and mechanical stability, as well as high selectivity and permeability. In order to prepare membranes for separation, two aspects should be

considered: the morphology of the developed film and the nature of the material used (whether inorganic or organic).

The selective membrane must not only be able to process organic vapors at high temperatures, but all other components within the module must also be durable. A number of separations problems have been clearly shown in the literature to deviate from isothermal conditions and therefore cannot be ignored [32]. When the carbon dioxide is separated from the gas stream, the temperature of the permeate drops as a direct result of the Joule–Thomson (JT) effect. The temperature drop observed on the high-pressure side is an indirect result of the JT effect, which is caused by mass permeation through the membrane as heat is transferred through the membrane along with the enthalpy due to the mass passing through the membrane. It can be seen that the temperature change in the unit depends largely on the stage cut and the concentration of CO_2 in the feed. In some cases, a gas mixture containing more CO_2 in the supply will have a larger temperature difference than the supply in the rest of the unit. This is because the composition of the raw material not only changes the amount of osmotic gas passing through the membrane wall, but also the thermodynamic properties of the residue and the gas mixture in the filtrate [33]. It is generally assumed that the value of gas permeability is temperature independent and separates the effects of gas phase composition and gradual cuts on temperature changes caused by expansion. However, the temperature variation in the unit is observed to vary greatly. Most membranes undergo thermal degradation in a wide temperature range.

Depending on the type of membrane separation process, operating conditions may include hydraulic pressure, osmotic pressure, feed cross flow velocity, and temperature. Operating conditions can affect both solute rejection and permeate flux. Between these parameters, the filtrate flow is very sensitive to the temperature of the feed material. The filtrate flow increases as the feed temperature increases. This is mainly due to the decrease of feed viscosity with an increase in the raw material temperature. More specifically permeate flux typically increases as temperature increases in a linear relationship with viscosity. Furthermore, under fixed temperature condition, the concentration ratio has a fixed distribution Coefficient-Ostwald coefficient [34]. The literature has shown that temperature has a great influence on permeability coefficient, that is, with a rise in feed gas stream temperature, the permeability coefficient of the membrane material increases. This relationship is so, because with an increase of temperature, the kinetic energy of gas molecule becomes greater, so also the diffusion coefficient and moreover the solubility coefficient also becomes greater with the increase of temperature [34]. Since the permeability coefficient is obtained as a function of solubility coefficient and diffusion coefficient, it naturally increases with increasing temperature, which affects the penetration process. Normally, the solubility decreases with increasing temperature and the diffusion coefficient increases.

Various membrane designs have been proposed as cost-effective CO_2 capture options [35, 36]. To improve the performance of polymeric membranes, various resolutions have been proposed with particular importance on

exploiting the selectivity size or shape provided by dispersed nanoporous materials in combination with the polymer processability and mechanical stability. To this end, various polymers were modified with inorganic fillers to evenly disperse the filler particles in a polymer matrix to give a mixed matrix membrane (MMM) [12]. Glassy-polymers generally lead to MMMs with improved release characteristics, while highly permeable and poorly selective gummy polymers are unlikely to be effective as MMMs when inorganic fillers are used. Some of the limitations of MMM are the porosity of the polymer blocked filler, filler and polymer poor compatibility, and segregation of the filler.

Porous inorganic microporous membranes have generated considerable interest in the investigation of H_2 separation in both experimental and potential industrial applications. The main inorganic microporous membrane transfer mechanisms in the literature are as follows [4]:

(1) Knudsen diffusion due to collisions between different gases,

(2) Surface diffusion, due to gas adsorption on the pore walls, and

(3) Molecular sieve, where small molecules pass through and large molecules are blocked by the sieve.

Silica membranes have the potential to be applied at industrial stage due to their high selectivity, optimum temperature stability, and their low cost. As a general rule, membranes based on silicon dioxide obtained by chemical vapour deposition or chemical vapour phase impregnation have an H_2/CO_2 selectivity of up to 50, which is significantly higher than the Knudsen values [37, 38].

One of the drawbacks of silica membranes is their susceptibility to large amounts of water vapour, as this contributes to reduced performance. New research focuses on the creation of hybrid silica membranes that can improve hydrothermal stability and separation efficiency in the presence of significant water vapour [39]. Niobium-doped silica membrane shows enhanced hydrothermal stability in almost practical conditions. Silica membranes doped with about 17% or 33% niobium gave stability of 300 hours in the presence of water vapour while maintaining H_2/CO_2 selectivity of about 1500 [40]. Carbon membranes are produced by carbonization at extreme temperatures (700–1200 K) in an inert atmosphere, creates a microporous membrane that acts as a molecular sieve that provides surface diffusion [3]. According to Favvas et al. [41], this leads to a significant improvement in selectivity and permeability.

The carbon molecular sieve membrane obtained by carbonizing the hollow fiber copolyamide membrane BTDA-TDI/ MDI (R84) has a H_2/CO_2 selectivity of 17. Numerous endeavors have been made to improve the chemical and hydrothermal steadiness of the layer [42]. Metal membranes are best suited for CO_2 separation prior to combustion due to their infinite selectivity. Metal membranes are often palladium-based, and the hydrogen separation process is accomplished by hydrogen decoupling chemisorption at the membrane surface. Hydrogen then diffuses through the wire mesh due to the partial reduction in pressure on the opposite side of the film [8].

Disadvantages, such as embrittlement of the membrane because of low temperature phase transitions, can reduce the effectiveness of the membrane for large-scale operations. Mixed matrix membranes contain microstructures with inorganic material in the form of nanoparticles in a discrete phase, embedded in a continuous polymer matrix [43]. This concept combines the strong points of each stage: alluring mechanical properties, efficient interaction capacity of polymers, and high selectivity of the dispersed fillers. Usually, inorganic materials are added to a polymer matrix, which helps to enhance on the thermal and mechanical properties of the membrane hence increasing its adaptability in changing chemical and physical environments.

The applicability of membrane technology in carbon capture can be achieved at three stages, at the precombustion, postcombustion stage, and oxyfuel combustion stage. During the precombustion phase, these membranes are used to separate carbon dioxide from the exhaust gases before entering the combustion chamber [44]. In this process, the gaseous fuel is converted to a mixture of syngas (H_2 and CO) and CO_2, and then a gas-water substitution reaction is performed to reduce the CO content (equation (1)). The remaining H_2 and CO_2 is then separated using membrane technology:
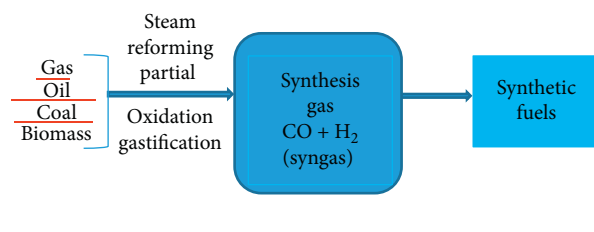
$$\tag{1}$$

The temperature range for precombustion membrane application is between 300 and 700°C and pressures of up to 80 bar. During postcombustion, these membranes are used to separate CO_2 after fuel combustion has occurred [45]. The flue gas often consists mainly of CO_2, N_2, and H_2O. Postcombustion membranes separate CO_2 and N_2 gas at moderate temperatures and ambient atmosphere pressures. This is the most widely applicable CO_2 separation method [46]. Some postcombustion membranes that have been commercially applied in CO_2 include polymer-based and mixed matrix membranes. Oxyfuel combustion involves the utilization of pure O_2 for combustion instead of air [47]. The flue gas composes mainly of CO_2, water vapour, and SO_2 impurities. Condensation process is used to eliminate the water and other process impurities. Examples of membranes used for oxyfuel combustion include fluorite-based and perovskite-based membranes.

The performance of membrane technology for gas separation is generally measured by its selectivity and permeability [48]. In order realize the anticipated performance (that is, high selectivity and permeability), appropriately selection of membrane material is vital. To achieve good mechanical strength, nanoporous membranes can be coated with a thick and porous substrate [49]. The supporting substrate should have large pore sizes to allow free gas flow through and offer low flow resistance. Kim et al. [50]

highlighted that multistage membrane process is needed to capture and recover high-purity CO_2 from off-gas with low CO_2 concentrations with "no-mixing-loss."

3.1. Membrane Gas Separation Selectivity and Permeability.

The purity of the product and recuperation rate are two key necessities for pragmatic gas separation. Ding [51] concluded that high membrane penetrability has restricted effect for applications in practical scenarios, while the same report highlighted the basic requirement for high membrane selectivity. For gas separation sets, practically all information points are underneath the clear line called "upper limit" in majority of the penetrable gas selectivity and permeability log-log plots (Figure 3). As new materials are created, the upper bound is raised. The upper bound theory generally shows that there is a hedge between selectivity and membrane performance. A highly penetrable membrane will in general be less selective and vice versa. The capacity to control the thickness of the partition layer and the conduct of the membrane material in the presence of impurities assumes a significantly more important part in the selection and improvement of new commercial membranes [52].

Equation (2) shows that membrane productivity is indirectly related to the thickness of the membrane layer. To manage the reduction in pressure across the film, it is in some cases important to build the thickness of the membrane division layer to decrease the productivity of the membrane, thus diminishing the measure of gas coursing through the cartridge. In addition to the pressure reduction on the gas supply side, the filtrate pressure accumulates on the permeate side of the membrane. This may be enough to have a serious impact on the performance of the membrane [53]:

$$J = S \times D \times \frac{\Delta P}{l} = P \times \frac{\Delta p}{l}, \qquad (2)$$

where ΔP represents the transmembrane differential pressure, P is the coefficient of permeability, l is the membrane thickness, D is the diffusivity coefficient, and S is the solubility coefficient.

For a region with limited membrane selectivity, the process of membrane separation will significantly benefit from a high selectivity, while in the region of limited pressure ratio, the advantage of high membrane selectivity is limited [51]. The design membrane process can be controlled by limiting concentration by separating the separations into stages. If the required gas concentration exceeds the critical concentration and the membrane selectivity is high enough, a single-stage unit can be used. If the needed gas concentration is below the limit, it becomes advisable to divide the process into two stages. The membrane in the first stage treats the gas up its limiting concentration, and then in the second stage, the membrane treats the gas to the desired purity. The first step is in the area of limited selectivity and can greatly benefit from the high selectivity of the membrane. The second step is a limited range of pressure ratios, and a membrane with moderate selectivity can be applied [54].
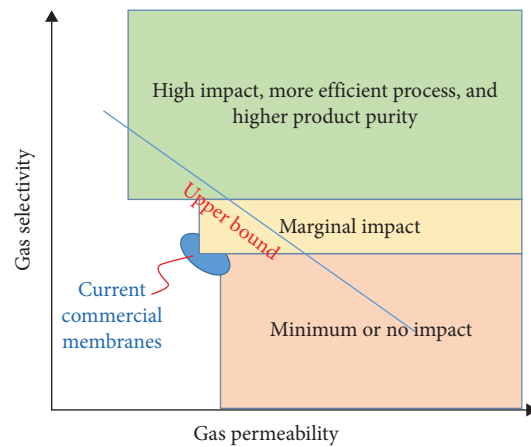
FIGURE 3: Relationship between membrane gas separation selectivity and permeability [51].

Poly (ethylene oxide) (PEO) containing polymeric membranes are highly CO_2-selective and thus attractive for the separation of CO_2-bound gases. However, the development of a membrane with a high PEO content is often difficult due to its low mechanical properties, the high tendency for PEO to crystallize and form a barrier to gas transport in the membrane [55]. The copolymers are considerably more stable mechanically, than those without pentiptycene and effectively suppress the crystallization of PEO due to the mechanism of amplification of the supramolecular chain and the exclusion of interactions caused by the structure of pentiptycene, leading to completely amorphous structure. The transportation of gas in PEO containing polymeric membrane depends on both the weight content of the PEO and the length of the PEO chain. Due to the competition between dissolution and diffusion coefficients, a nonlinear correlation is observed between CO_2 permeability and PEO mass content, producing a copolymer that changes from solubility to size-selective [55].

In the case of multicomponent membranes, the detailed morphology of the microparticles, such as the shape of each phase and the dimensional arrangement (that is, connectivity), determines the properties of the membrane, which are sensitively influenced by the copolymer composition, the segment sequence length, and the interaction between the components [56]. Compared to diffusion-controlled transport, the solubility-selection process is mainly thermodynamic, with polymer affinity permeation interactions and penetration concentrate dominating the transport process. Despite the fact that the membrane for the most part provides the surface area for mass exchange, it has a significant effect on the execution of the process. Since the entire mass exchange occurs in the pores of the film, porosity and pore size enormously impact the productivity [57].

3.2. Selectivity Mechanism of the Membranes towards CO_2 Separation.

Membrane separation process has several advantages over other conventional separation methods. Firstly, the membrane process is a viable and energy-efficient alternative to carbon capture because it does not require

phase conversion. Secondly, the required processing equipment is very straightforward and has no moving parts and it is compact, relatively simple to operate and handle; in addition, it is easily expandable [58]. The gas permeability of the membrane is a function of the properties of the membrane (physical and chemical structure), the properties of the permeable particles (size, shape, and polarity), and the interaction between the membrane and the permeable particles [59]. The first two, which are the properties of the membrane and the properties of the penetrating particles, determine the diffusion properties of a particular gas passing through a particular membrane. The third property, the interaction between the membrane and the permeable material, refers to the adsorption capacity or solubility of the gas in the membrane [60].

There are four main transport mechanisms that can be employed to calculate gas separation using porous membranes [61]. The basis of this molecular weight transfer (Knudsen diffusion) must be separated by surface interaction (surface diffusion and capillary condensation) and molecular size (molecular sieving). The movement of molecules within the thin pore channels of the membrane material occurs because the diffused molecules collide with the surface (wall) and not with each other. Since the partial pressure of the gas is the driving force of the transfer, the Knudsen transfer can be caused by concentration or by a pressure gradient. The relative permeability of every segment is not directly related to the square root of its molecular weight [62]. In the surface diffusion mechanism, the diffusing gas is adsorbed on the pore walls of the film and afterward transported easily over the surface towards diminishing the surface concentration. Various models have been utilized to portray the transport mechanism in thick membranes, for example, the solution diffusion model [63, 64], the pore flow model [65], and the thermodynamic irreversible model [66]. The solution diffusion model is by all accounts recognized by a greater part of membrane researchers. In this model [67], the process of mass transport consists of the three following steps; (1) sorption of gas from raw material to the membrane; (2) molecular diffusion of gas in the membrane; and (3) removing gas from the membrane on the downstream side of the membrane. In addition, the solution diffusion model is commonly used to describe the transport mechanism of polymer membranes. In polymer membranes, one very vital parameter is penetrating condensation. Normally, penetrants with higher critical temperatures are easily condensable and, in this way, more soluble in polymers. The diffusion coefficients are usually less than the solubility coefficients of penetrants in most polymeric membranes. Thus, the relative gas permeability coefficients in these membranes are dictated by the gas dissolvability and not by the gas diffusion coefficient, except if the penetrant is a little molecule whose diffusion coefficient is sufficiently high to make up for its lower solubility.

To achieve high separation ratios in systems such as CO_2, the interaction between one of the gases in the feed stream and the membrane surface can be caused by chemical modification of the separation layers. Chemical modification creates stronger base centers in the membrane, which leads to a stronger binding of CO_2 to the modified surface, rendering the surface partially irreversible [68]. The more bound CO_2 is less mobile, and this results in a lower permeability of CO_2 through the membrane. Cho et al. [69] concluded that surface diffusion can be used as a separation mechanism in a membrane when the membrane pore size is very small and the temperature is low. Kusakabe et al. [70] observed a decrease in separation factors and permeability with increasing penetration temperature. Furthermore, the CO_2 molecules adsorbed on the surface of the membrane micropore synthesized by the zeolite prevented penetration during the separation process.

Stern et al. [71] found that the permeability properties of a given penetrant can be notably enhanced by replacing an appropriate functional group in the polymer that will incite specific interactions with the penetrant. Such interactions mostly increase the solubility of the penetrant in the polymer.

4. Membranes Doped with Nanocomposites

Membrane technology has emerged as one of the promising approaches for efficient purification, and the use of hybrid materials and interfacial control are the main mechanisms used to improve filtration optimization efficiency [72]. Wang et al. [73] emphasized that the changes in the properties and structure of the membrane due to the presence of nanoparticles depend on the dispersion of nanoparticles in the casting solution. Gao et al. [74] noted that modifying the membrane surface (i.e., changing the structure and properties of the surface) can further enhance its filtration performance. One of the routes for further improvement in membrane performance is the development of multifunctional materials, whereby the structure of these unique materials will naturally combine with the surface reactive moieties [75]. Incorporating nanoparticles or nanomaterials into host framework using substitution doping is an effective strategy to modulate the features of a membrane [76]. Ideal materials need to have an optimal surface area, tailorable porous structure, high thermal stability, and easy surface functionality [40]. Figure 4 shows a pictorial explanation of polymer nanocomposite membrane for gas stream separation.

Membrane-based gas separation has shown great potential in carbon capture owing to its merits of high energy efficiency, low capital cost, and small environmental footprint. However, the development of novel membrane materials with a combined high selectivity and permeability is in demand [77]. He [23] also concludes in his research that significant improvements on membrane material performance, process efficiency, and module are needed for advancement of membrane technology in CO_2 capture. The adoption of nanocomposite-doped membranes has significantly increased due to their reduced operational footprint, high removal efficiency, and relatively low energy intensity. Researchers have devoted efforts to improve these membranes' performance by introducing new materials, novel nanoadditives, and developing new processes [78]. Copper oxide, carbon nanotube, polymeric nanoparticles, zinc
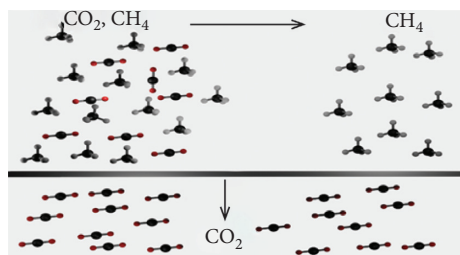
FIGURE 4: Polymer matrix forming nanocomposite membranes with enhanced gas permeability.

oxide, aluminum oxide, silicon oxide, zirconium dioxide, and titanium dioxide, for example, are among the nanoparticles/materials used for surface modification to overcome fouling issues [79]. However, poor dispersibility has been identified as one of the drawdowns in using the metal or metal oxides nanoparticles as a membrane surface modifier.

The membrane gas separation performance is dependent on several factors including membrane material, structure, thickness, and configuration (for example, hollow fiber and flat film), as well as module/system design. Various materials have been developed for CO_2 capture membrane, including organic, inorganic, and organic-inorganic compounds, each with their own typical advantages and disadvantages [80]. Thus, Arumugham et al. [81] proposed the use of hybrid nanomaterial/particles as a modifying agent due to their extraordinary physicochemical properties, improved interfacial interaction, thermal stability, and mechanical strength. These hybrid nano-based particles/materials are receiving ever-growing attention in membrane separation process technique. Two commonly used control strategies for regulation and optimization of membrane layer channels include crosslinking adjacent sheets to reduce interlayer spacing to the size of a molecular sieve and functionalizing interlayer channels to increase physicochemical affinity or introduce light transport carriers [77]. Additional crosslinking or intercalating agents are generally required to achieve channel optimization. In addition, the literature has identified interlayer channel size as another dominant parameter that governs membrane separation efficiency [82].

Membranes can be synthesized by using a variety of methods, depending on the physical and chemical properties to be achieved and the resources available. Processes that include minimal product loss, controlled operating conditions, simple or flexible parameter control, high reaction rates, economical, and environmentally friendly conditions are desirable [83].

4.1. Nano-Based Particle/Material-Doped Membranes.
Nanodoped membrane has shown a good efficiency in most cases for CO_2 capture or separation approach from flue gas streams. These nanoparticles/materials play a vital part in the formation of an efficient gas transport path in the membrane so as to increase solubility. According to Sreedhar et al. [7], there are three ways to reduce CO_2 emissions, and they include improved carbon capture and sequestration,

reducing carbon footprint, and energy intensity. Julian [84] observed that the widely applied material for CO_2 removal or separation for membrane technology in the industry is polymer-based. The choice of polymer is because their manufacturing processes are not complex when compared to other materials, and the material cost is relatively inexpensive. The incorporation of nanosilica into polymeric membrane showed a significant increase in permeability which did not decrease the membrane selectivity [85]. This phenomenon can be attributed to the gas-permeable nanospace formed by the addition of the nanosilica particles. Wu et al. [86] improved molecular sieving efficiency of polyimide membrane by embedding nanocomposites. This was achieved by using organic polymer and inorganic material to develop an inexpensive membrane that provides molecular sieving efficiency.

Monocrystalline magnetite nanoparticles can respond to an external magnetic field, allowing for potentially easy placement/retrieval, thus reducing the need for separation energy and material consumption. Furthermore, magnetite is abundant and relatively stable in the environment. According to Li et al. [84], magnetic-based nanocomposites were also developed and evaluated for their sorption properties with respect to CO_2 removal. Under high pressure, every magnetic nanocomposites showed a huge improvement in CO_2 adsorption limit, due to sorption processes of both the functional groups (from the carbon substrates) and the iron oxide nanoparticles. When contrasted with other high selectivity membranes, the nanocomposite-doped membranes, having more well characterized structure, and can keep up their selectivity under high pressure and ultrahigh gas penetration properties [87].

Copolymer-doped nanocomposite membranes were studied at various feed pressures and compared to other membranes. According to Sreedhar et al. [7], the observed results were very positive and the resistance to contamination by these membranes makes them a good option for real systems. When compared to a typical membrane, the inclusion of nanomaterial/particle has been widely reported to significantly change the physicochemical properties of the membrane (hydrophilicity, porosity, charge thickness, layer toughness, warm, compound, and mechanical soundness) and has extraordinary potential in settling the compromise between permeability and selectivity. Despite significant advances in development of nanocomposite membranes, some problems must be solved before its practical large-scale applications. These problems include poor dispersibility of nanomaterials in polymer-based membranes, aggregation and weak chemical interactions between the nanocomposites and polymer matrix, incompatibility of nanomaterials with the polymer, and control alignment of nanocomposites in the active layer [7]. Several innovative approaches have been proposed to resolve these challenges, such as the modification of the nanocomposite surfaces or optimization of the embedding process, the development of new nanocomposite with specific pore structure/charge properties, and the optimization of the loading concentration and the durability of the nanocomposites membranes.

The selection and use of suitable nanocomposite for the production of nanocomposite-doped membranes must depend on the technical properties of the feed to be processed, since there is no universal application of nanocomposites to dope any existing membrane for all types of applications. Membrane technology has a multidimensional character, which implies a high mass transfer rate and high selectivity in relation to a particular gas. In spite of the synthesis and assessment of hundreds, maybe even thousands of new materials, over 90% of the present commercial membranes are produced using less than 10 membrane materials, and the vast majority of which have been utilized for decades [88]. The literature has also shown that freshly prepared thin composite membranes usually lose 25% of their permeability in a few days and another 25% in the next week or two. In manufacturing useful membranes, one of the most important trade-offs is the choice between product purity and recovery. A single-pass membrane process can have a high-purity product or high product recovery, but achieving both requires a decent comprehension of the process. In some cases, chemical stability is an issue, while physical stability is more normal. Multilayer composite membranes contain many layers of various polymers. This is valuable on the grounds that the backing membrane makes up the most of the membranes and can be made of a relatively cheap material. How gases and vapors infiltrate through membranes is dependent upon the layer material and the structure of the gas. In the pore flow model, gases go through the layer through small pores and gas combinations are isolated by some type of molecular filtration; while the solution diffusion model expects that there are no lasting pores and that the gas dissolves in the membrane material as in a fluid. The dissolved gas at that point diffuses through the membrane by random diffusion in the concentration gradient [89]. Using a nanocomposite as a filler, Son et al. [91] created a new type of TFN membrane, into which a substrate with CNT was incorporated. The CNTs were first functionalized by oxidation before adding the polymer to the solution to form a support layer mixed with the CNTs. The interfacial polymerization process was used to create an active polyamide layer for the development of TFN membranes. Kononova et al. [92] emphasized that PI nanocomposites filled with silicate nanotubes and carbon nanofibers have shown a higher elastic modulus with an increase in the volume concentration of the nanocomposites without a catastrophic decrease in elongation at rest.

The effect of several nanoparticles, such as carbon nanofibers, nanocones/discs, halloisite hydrosilicate nanotubes, and yttrium-doped quasispherical zirconia particles, embedded in the Ultem-1000 polyetherimide was investigated by Gofman et al. [93]. The introduction of nanocomposites into a polymer increases the modulus of elasticity and the elastic limit of the base materials relative to unfilled polymeric material. Polyimide nanocomposite films (PI-PM), obtained from poly (amino acid) which has an optimized concentration of nanocomposites showed an increase in the modulus of elasticity with an increase in the concentration of nanocomposites of the order montmorillonite > SNT > ZrO_2. PI-PM films with 10% by volume SNT and ZrO_2 showed higher fracture strains of the sample compared to PI-PM/montmorillonite films. This effect suggests that SNT and ZrO_2 could more effectively improve the ductility of polyimide nanocomposites when relatively brittle polyimide montmorillonite films are not suitable [91]. The results confirm our expectations that the morphology of nanocomposites and, in particular, their height-to-width ratio strongly influence the viscoelastic properties of nanocomposites in solid and liquid state.

Yudin et al. [94], considered the inclusion of magnesium hydrosilicate NT in the polymer films enhanced their mechanical properties without significant increase in the brittleness. An increase in mechanical properties was also observed for composites containing up to 15% by weight of NT magnesium, along with an increase in thermal stability. Nanocomposite-doped membranes with improved performances such as high selectivity, fluxes, and good surface morphology have been achieved by integrating nanocomposites into a polymer matrix [94]. The modified membrane can exhibit excellent stability, high selectivity for target feed streams, and high molecular weight penetrant flux with low driving force under a wide scope of process conditions. The right decision of material for the matrix and sifter stages is fundamentally significant [95].

4.2. Hybrid Nanocomposite-Doped Membrane.

Current studies have focused on developing hybrid membrane and application of nanoparticles/materials in the polymer matrix for gas separation and CO_2 removal. Progress in improving membrane output with this hybrid theory is an idea for gas separation and morphological investigations of prevailing asymmetric and composite slim membranes [96–98]. Kusworo et al. [37] proposed the mix of UV illumination, thermal annealing, and ethanol-$CH_3)_2CO$ to improve the exhibition of PES-TiO_2 nanohybrid membrane for carbon capture. The experimental results showed that the nanohybrid-PES-nano-TiO_2 with a 0.5% loading by weight of nanoparticles had the best properties in terms of gas permeability [99, 100]. The results also informed the fact that the combinations of UV irradiation, immersion in a mixture of ethanol-acetone, and combined thermal annealing treatments have shown the best performance.

Li et al. [101] highlighted the progress made in nanocomposite/hybrid CMS membranes for gas separation, and the hybrid nanoparticles were dispersed in a solvent to obtain a suspension by ultrasonic treatment. Hybrid ferrocene/PAA CMS membrane showed a higher gas permeability than pure CMS membrane due to the difference in the developed pore structure as a result of incorporation and pyrolysis of ferrocene. It was also observed that gas permeability improved as selectivity decreases with increasing ferrocene content. The best gas separation property in these hybrid ferrocene/PAA SMD membranes was observed with a precursor ferrocene content of 15% by weight, which has a gas permeability 22 times higher than that of a pure CMS membrane. In addition to surface modification and technology optimization, multicomponent composite and hybrid nanocomposites are becoming increasingly popular in

membrane manufacturing due to the different options and properties offered by different combinations of nano-composites. In terms of filtration performance, the hybrid nanocomposite membrane exhibited superior flux and solute repellency for mixed feed streams [102].

Some critiques indicate that hybrid nanocomposites commonly used in membrane manufacturing have high intrinsic costs for their raw materials and manufacturing technologies. Thus, more research is still needed to reduce the cost of hybrid nanocomposites and identify new hybrid nanocomposites at lower manufacturing costs.

5. Physicochemical Properties of Membranes

The characterization of a membrane to evaluate various properties is of great importance in research and development, since the design of various processes and membrane systems depend on reliable data on the properties of the membrane. Different membranes have various constructions that are answerable for their extraordinary functionality. The decision of a membrane for a particular partition process can be made dependent on its construction, porosity, surface movement, surrenders, mass exchange properties, morphology, compound design, and mechanical properties [7]. Porous micro/ultrafiltration membranes are ordinarily described by membrane flux, pore size and pore circulation, and molecular weight limit. Some physical and physicochemical properties of nanodoped membranes include surface area, density, interconnectivity, temperature, porosity, morphology, carbon capture sites, adsorption capacity, ability to withstand stress/strain, flexibility, selectivity, defects, and CO_2 reduction performance are discussed below. Porosity is one of the main considerations which directly impacts the CO_2 adsorption performance of the membranes [40]. Zainab et al. [40] built up a successful spider web like polyamide/carbon nanotube composite nanofibrous membrane impregnated with poly-ethyleneimine (PEI) for CO_2 capture. The physicochemical properties were characterized using N_2 adsorption/desorption, scanning electron microscopy (SEM), thermal gravi-metric analysis (TGA), and Fourier transform infrared spectroscopy (FT-IR) techniques. The resultant nanofibrous membrane showed composite structure comprising of fine nanofibers and nanonets. This composite construction acts as a vessel for the storage of CO_2 while the $-NH_2$ sites of CNTs act as a device to pull in and catch CO_2. The created membrane was then impregnated with PEI to upgrade the quantity of the CO_2 capturing sites (that is, $-NH_2$) on the surface. Notwithstanding, the presence of PEI-hindered inter- and intrafiber pores prompting decreased surface area and total pore volume. The integrated nanofiber composite membrane showed phenomenal mechanical qualities as well as remarkably tough adaptability contrasted with delicate sorbents [103].

Aside from single atom doping, heteroatom doping can essentially improve CO_2 reduction performance because of the synergistic impact of various heteroatoms. The dopants cause variety in control thickness of the nanosheets that upgrade synergist action [76]. Among various polymers

utilized for corrosive gas partition, the polyvinyl amine (PVAm) has the most promising potential. Because of the presence of large amine gathering and high level of hy-drophilicity, it provides high permeability and selectivity for CO_2 [104]. Thermodynamic properties of polymers assume a crucial part in the separation performance of membranes. Flory–Huggins hypothesis depicts the thermodynamics of polymer blends and solutions. It is a cross-section model that clarifies the nonideality of polymer combinations.

The 2D material membranes with very much charac-terized interlayer nanochannels possess extraordinary po-tential for precise molecular separation, where the size and surface synthetic property of the channel decide the sepa-ration effectiveness. The currently reported 2D material membranes for efficient CO_2 separation are primarily built by introducing cross linkers or intercalators into the in-terlayer channel. The unique breathing effect and size-sieving effect jointly contribute to the high membrane separation performance with CO_2 permeance of 150 GPU and CO_2/CH_4 selectivity of 33 [78]. The high selectivity of LDH membranes can be explained by the synergy of breathing effect to CO_2 and size-sieving mechanism. For most membranes, the separation factor of mixed gas is typically lower than the ideal selectivity of single gas due to the competitive sorption effects or CO_2 plasticization, but the LDH membranes instead exhibit slightly higher gas selectivity for mixed gas separation [78]. The higher selec-tivity in CO_2/CH_4 mixture of LDH membranes is attributed to the intrinsic breathing effect of LDH material towards CO_2 which renders the preferential adsorption and trans-portation of CO_2, thereby hindering the transport of another component in gas mixtures [105].

The development of gas transmission channels using channel-like assembly such as nanoparticles has increased nanoparticle concentration reliance and MMM dependence on CO_2 permeability without compromising CO_2/N_2 se-lectivity and also increased overall performance. The sig-nificance of the surface-modified structures has been investigated by comparing other silica nanoparticles without dendritic structures. The Maxwell model calculation first revealed the ultrahigh permeation of CO_2 via the nanospace on the surface of the nanoparticles. MMMs are composed of gas-permeable nanoscale particles with excellent potential as large-scale and highly efficient CO_2 separation membranes [106]. Surface modifications of the dendritic nanoparticle are another important approach to enhance their properties, which include but not limited to hydrophobic nature or hydrophilic or affinity between the substituent of the surface and CO_2. Therefore, nanoparticles play an important role in the formation of efficient gas transport channels in poly-meric membranes or in their interaction with CO_2 and are expected to be significantly more soluble than other gases. The proposed approach for determining the nanostructures and physicochemical properties of nanosheets is believed to provide an alternative to the creation of membranes based on 2D gas separation materials [107].

Recently, a novel class of polymers, so-called "polymers of intrinsic microporosity (PIMs)," has emerged as a promising membrane material for gas separation. PIMs

possess high free volumes and high surface areas, which can be mainly ascribed to their rigid and twisted aromatic ladder-like structures.

6. Structure-Property Relationship in Membranes

Expanding the structural variety of nanoparticles/materials is desirable to better understanding the structure-property relationships. Particle-shaped sorbent materials have been identified from the literature as a potential energy-efficient carbon capture and separations technology [76]. In addition, transformation of nanomorphologies on the membrane surface has been highlighted as novel approach for permeability improvement [108]. The performance of membranes is affected by the operating conditions such as temperature and pressure. Wu et al. [109] proposed a combination of covalent organic frameworks and mixed matrix membranes to improve the selectivity of membrane during gas separation process. The experimental results showed an enhancement of 116% in CO_2 permeability and 27.6% improvement in selectivity of CO_2/CH_4 stream. The literature has also shown unselective pore in some mixed matrix membranes, and this has been attributed to an agglomeration of inorganic materials which can be disadvantageous in gas separation efficiency.

The agglomeration of nanoparticles deforms the active surface of the membrane due to the creation of a nonselective void that occurs between the polymeric material of the membrane and its inorganic particles. These cavities were created as a result of detachment from the surface of the nanoparticles and matrix. The void causes a Knudsen diffusion mechanism with a high permeability, but the selectivity is poor. Thus, inclusion of inorganic particles in the membrane (organic) is a crucial step for gas separation [110]. Rezakazemi et al. [111] and Zou et al. [112] observed that thermal annealing process helps both the inorganic particles and polymer membrane material to unify, thus improving the overall membrane performance in terms of selectivity and permeability. Kusworo et al. [85] also observed that UV light does improve the surface structure of membrane by reducing the available nonselective voids present between the inorganic particles and polymer materials. The exposure time also contributes to the selectivity output of the produced membrane; that is, the longer the irradiation time of the UV rays, the greater the likelihood of rearranging the existing surface structure of the membrane.

For idea morphological structure when considering some class of nanodoped membranes, a joint solvent that will increase the formation of a bridge between the inorganic and polymer compounds might be needed to provide much better permeability performance. Maxwell's model showed that dense filled membranes with fillers (such as nanomaterials/particles) will decrease gas permeability through some nanohybrid membrane [113]. According to observation by Suleman et al. [114], high concentration of nanoparticles/materials can decrease nanodoped membrane selectivity, while membranes doped with optimal concentrations of nanoparticles will most likely have a more stable

membrane structure and surface dimensions that will improve its performance. Liu et al. [99] observed that avoiding the tendency of direct particle-particle contact will simplify separation processes for material collected and recycling as well as saving energy. Brinkmann et al. [115] described the temperature dependence of the transport properties of various multilayer membranes. Temperature affects both selectivity and permeability because permeability increased with temperature increase, whereas selectivity decreased.

The impact of membrane structure and thickness has been studied by Schuldt et al. [116]. Their study showed that at higher CO_2 volatility (above 8 bar), membrane swell with CO_2 leading to a selectivity decrease. Brinkmann et al. [115] examined pressure distribution in the membrane modules with membrane separation layers. Experimental data from previous work were compared with simulations based on modular flow trends and the free-volume model. For different operating conditions, different types of integrated membrane modules were used to simulate a virtual power plant. The energy consumption of the entire process was evaluated, and the membrane separation process could only compete with absorption when a 70% recovery and a 95% CO_2 purity were required and when a counter-current jacket design is applied. Another important issue that must be addressed before using membrane materials to separate gases is physical aging.

Aging process is common in glassy-polymers with defective chain packing structures, where the unbalanced elements having excessive free volume become encapsulated between the chains and act as a driving force for physical aging [117]. After aging, the collapsed membrane material chain structure contains less interstitial free volume for carbon atoms to move through. The aging-resistant properties of nanocomposite-doped membranes can be verified by the pure-gas permeation test over time, to observe the changes in normalized CO_2 permeability of membranes upon aging. The most common way to address this problem is to use covalent bonds to cross the polymer network. Specific methods include thermal crosslinking, ultraviolet crosslinking, esterification, azide-based crosslinking, and carbon-induced crosslinking [118]. These methods often require special chemical modifications of the polymer with crosslinked functional groups. However, the introduction of small molecular fragments reduces the free volume of the polymer matrix that forms the rigid skeleton, which adversely affects the permeability of the membrane [119]. Thermal rearrangement polymer (TR) is a special case that increases the rigidity of the polymer chain through an intramolecular cyclization reaction. The resulting membrane exhibits a strong antiplasticization property. However, it often comes at the expense of mechanical stability, especially ductility. The incorporation of an inorganic filler into the polymer matrix to form a hybrid membrane is a promising alternative to improving the plasticization resistance of the membrane [120].

7. Effect of Water Vapour on the Membrane Performance

A membrane performance is quantified by its permeance, selectivity, and permeability. The permeability (P_A) depends

on the sorption coefficient (S_A) and the diffusion coefficient (D_A) according to a simple relationship for the membrane material:

$$P_A = S_A D_A. \tag{3}$$

It has also been found that fabrication parameters and water vapour strongly affect membrane performance. The presence of moisture and other contaminants will affect the performance of the membrane, thereby affecting the operating costs of the plant and this may affect the separation efficiency of the membrane [121]. Scholes et al. [122] applied a commercial membrane at a coal-fired power plant for carbon capture. The flow rate of the dry flue gas entering the membrane module at 45°C was 3.5 kg/h. Water condensation was observed on the membrane during the operation. After several hours of membrane operation, the permeability and selectivity decreased dramatically, which was attributed to the plasticization of the membrane and the membrane swelling due to the presence of water vapour. After some time, the permeability and selectivity recovered but did not reach their initial values [123]. Thus, humidity is one of the biggest challenges in the membrane transport properties.

The membrane used for gas stream separation process often suffers from membrane wetting, and as such, membrane for carbon capture is no exception. These phenomena severely limit membrane performance and the application of predictions based on ideal scenarios. Wetting the membrane significantly increases the resistance to mass transfer and leads to a significant decrease in the absorption capacity [124]. Liquid inlet pressure is commonly used to estimate the wettability of an absorbent liquid on a membrane [125]. Methods for reducing membrane wettability include using hydrophobic membranes, a dense surface layer composite membrane, selecting high surface tension liquids, and operating at a pressure lower than the liquid inlet pressure [126]. Saeed et al. [104] in their research improve the water affinity and mechanical properties of PVAm membranes to enhance CO_2 separation at pressures that are moderately high. A PVAm matrix was incorporated with CNC in order to get results that are beneficial. The composite membrane used for CO_2 permeation testing was specially designed with ability to work at moderately high pressure under humid conditions.

8. Membrane Reusability and Capture Efficiency

Membrane fouling is highly dependent on the membrane material, its structure, and the properties of the filtered suspension. This is considered more serious if the streams contain solid particles, such as traces of fly ash in the gas [127]. In comparison to membrane wetting, membrane fouling effect on performance is however less significant. Alharthi et al. studied the effect of fly ash in flue gas flow [128], and the results of studies show that the influence of fly ash on membrane performance is inconsequential compared to moisture presence in the gas stream. It was reported that moisture can cause a significant decrease in permeability, while exposure to dry fly ash only slightly increases the pressure drop across the membrane. In addition to high sorption capacity, sorbents with excellent regenerability (recoverability) are technically and economically preferred to go through various adsorption/desorption cycles. In general, by controlling fluctuations in pressure or temperature, regeneration of absorbents can be achieved. The temperature change process can be used to check the suitability of the materials to be treated during CO_2 sorption/desorption and also used to regenerate sorbents.

Li et al. [86] studied the CO_2 recyclability of magnetic nanocomposites and observed a slight drop in the CO_2 sorption capacity compared to the initial capacity. In general, the excellent regenerability of PEI-magnetic nanocomposites can be explained by the low volatile nature of PEI, good thermal stability, and excellent interaction between PEI and magnetic nanocomposites, [129, 130]. Yuan et al. [131] defined capture rate as the fraction of the CO_2 amount captured from the feed stream. In practice, the capture rate can be zero, which corresponds to the membrane unit bypass scenario. This assumption would not be numerically practical for a given set of mass balance equations for a membrane. Parametric studies have shown that moderate selectivity and high permeability are desirable properties of the capture membrane after combustion [132]. The performance, reusability, and efficiency of nanocomposite membranes can also be improved by introducing dehydration unit or process to ensure that only dried flue gas fed to the membranes (Figure 5).

9. Significant and Scalable Strategy

Different membrane types have been developed for specific industrial applications yet cannot come around owing to setbacks arising in scale-up of such membranes to modular configurations which is a very challenging task. In the membrane stage process, there are many variables to consider, such as feed conditions, form pressure at feed and permeate, process design, and driving force strategy. Numerous articles have presented the effects of these variables and have suggested configurations that are useful based on optimization and parametric studies [133, 134]. Sandru et al. [135] developed a pilot scale membrane assembly with fixed carrier separation layers. The flue gas fed to the membrane unit contained CO_2 (12%) O_2 (6%), approximately 200 mg/m^3 of NO_x and SO_2. The permeability values obtained for CO_2 were in the range between 0.2 and 0.6 m^3 (STP)/(m^2 bar h), and the selectivity for CO_2/N_2 was in the range between 80 and 300. Choi et al. [136] launched a pilot-membrane separation system connected to a liquefied natural gas boiler. The hollow fiber membrane module separation layers were polyethersulfone, and the modules were initially tested with a model CO_2/N_2 mixture. The membrane separation was divided into four stages. The permeability to CO_2 through the membrane used reaches 40 GPU. Under these operating conditions, 90% of the CO_2 was captured with a purity of 99%.
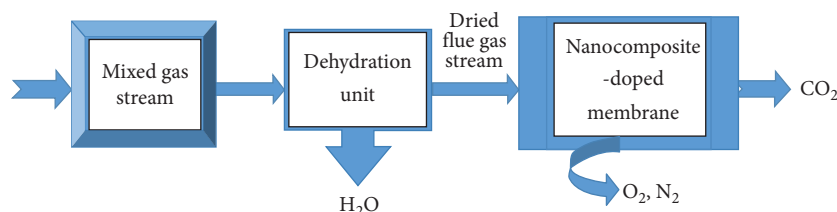
FIGURE 5: Flow diagram for proposed nanocomposite-doped membrane separation process.

Yuan et al. [131] highlight two key properties of the membrane that have a direct effect on the energy and mass balance during the separation process, and they are CO_2 permeability and CO_2/N_2 selectivity. The permeability is determined by the gas permeability of the membrane and defined as the average permeability over the thickness of the membrane. Membrane selectivity is the ability to penetrate one species over another (that is, ratio of permeabilities of the two species). Huang et al. [137] highlighted that the area of the membrane required for a specific separation objective decreases with increasing permeability for more permeable gases. On the contrary, the desired membrane area increases with increasing selectivity. A larger membrane area is required as selectivity increases so that a positive pressure difference is maintained between the feed and permeate sides by the less permeable gases. A majority of the membranes applied in CO_2 capture are still at the laboratory stage of development and testing. However, several membranes have been developed and tested at a pilot scale level by many companies and a few applied for use in full-scale capacity [138]. The application of membrane technology in CO_2 capture is currently a technologically feasible and yet small-scale industrial practice worldwide.

However, due to certain economic constraints, there is still uncertainty about how easy it is to use membranes in certain industries. The CO_2 capture system designed in a laboratory scale could be scaled up, but some of the challenges for large-scale membrane application in CO_2 capture are due to high membrane manufacturing cost for large-scale applications, lack of incentives, and membrane performance affected by operating conditions such as temperature and pressure [138]. Researchers have developed and tested some membranes for their potential in large-scale industrial applicability. Polymeric membranes such as Polyactive® and Polaris™ are now commercially available. They are operated at lower temperatures and have good thermal and mechanical strength. Table 2 shows that Memfo group at the NTNU developed a flat sheet fixed site carrier membrane which showed stable performance for six months when tested on a pilot scale by EDP power plant in Sines (Portugal) [139]. The Poly Active™ membranes developed by Helmholtz-Zentrum Geesthacht have been tested on a pilot scale with a 12.5 m^2 membrane area to capture CO_2 in real flue gas [140].

Lin et al. [141] evaluated Polaris TM thin film composite membrane for CO_2 separation from syngas. The membrane system processed about 227 kg/h of syngas and reported 95% of liquid CO_2 produced. Possible design variables in scaling membrane activities are the permeability and selectivity of the membrane, surface area of the membrane, and performance of vacuum pumps, compressors, expansion valves, and heat exchangers. The scalability and significant of the design variables are based on their effect on the objective function.

From this study, it was observed that both nanocomposite- and hybrid nanocomposite-doped membranes have not been extensively applied at the industrial scale.

The balance and optimization of some parameters such as the purity requirements, compressor cost, gas rejection specifications, and gas flowrates that are highly process-specific are required for the design of a membrane. Aside from permeability/selectivity trade-off, there are other challenges such as membrane aging that significantly affect the membrane industrial viability [142]. Membrane aging slows over time because the driving force for physical aging is gradually decreased by the presence of excess free volume. Thus, the aging of the membrane will lead to a decrease in gas permeability and a change in other physical properties, which depend on the thickness of the membrane [143]. There are many ways to configure these membranes, but the number of membrane modules, compressors, and the configuration of these systems usually depend on the flow rate desired. Polymer membranes over the last three decades have developed into a feasible gas separation industrial process. During this time, several polymers have been identified as conventional gas separation membranes. Polysulfone is one of the most heat-resistant and chemically stable thermoplastic polymers. Thus, due to its excellent mechanical properties, it is an important industrial membrane material for gas separation [144]. In addition, aromatic polyimide has high intrinsic selectivity and high gas permeability combined with desired physical properties that makes them attractive membrane materials for various gas separation applications. Thermally rearranged polymer is another promising high-performance membrane material for gas separations [145].

As membrane technology research continues to grow, the range of applications also expands. However, in the case of olefin/paraffin separation, finding an actual polymeric material of high performance that will operate under practical feed condition is essential [146]. Economical study by Peters et al. [147] and He et al. [148] to compare the membrane technology with amine scrubbing for natural gas purification of gas feed containing up to 10 mol% of CO_2 showed that amine scrubbing can be replaced by membranes for gas feeds containing 10 mol% CO_2 and lower.

10. Application and Compatibility

The membrane technology is highly flexible for applications in industries, as it can be used both before and after combustion. The main setback for postcombustion

TABLE 2: Summary of pilot and industrial scale used membrane.

Membrane	Industry applied	Scale	CO_2 purity (%)	Membrane surface area	Duration of application	No. of stages	Reference
Flat sheet FSC membrane	Cement plant	Pilot	70	18 m^2	6 months	2 stages	[106]
Polyactive™	Coal-fired power plant	Pilot	60–70	12.5 m^2	740 h	1 stage	[107]
Polyethersulphone (PES) hollow fiber	LNG fired flue gas plant	Pilot	90	(2 in, 3 in)		4 stages	[76]
Polaris polymeric FSC membrane	Cement plant	Large	99	94400 m^2 41300 m^2 10300 m^2		2-3 stages	[28]
Polaris membrane	Natural gas combined-cycle power plant	Pilot	90	8 in diameter	1000 h	2 stages	[35]
FCE electrochemical membrane	PC flue gas power plant	Large	90	11.7 m^2	9 months	1 stage	[34]
Nanoporous superhydrophobic membrane contactor	Coal-fired plant	Pilot	93.2 2580 GPU	3161 cm^2		1 stage	[42]
Polaris™	Coal gas power plant	Lab Pilot Large	95	30 cm^2 1–4 m^2 20 m^2	2000 h	2 stages	[33]
DOW nanofiltration membrane	Flue gas lignified power plant	Pilot	764 GPU	7.5 m^2 5 m^2	5 h 20 h	1 stage	[90]

separation is the high selectivity requirement to recuperate relatively low CO_2 concentrations from flue gases [149]. Therefore, the development of a membrane separation system that is suitable is very important to meet IEA requirements. Hence, a major challenge in the commercialization of this process is the low selectivity, and since selectivity is important, membrane properties such as porosity, pore size, and wettability also play a vital role in separation efficiency of carbon dioxide [150]. Although the membrane acts only as a supplier of the mass transfer surface, it has a significant impact on the performance of the process. Since all mass exchange occurs in the pores of the membrane, pore size and porosity have a large impact on performance [151]. Membrane can be a composite polymer wherein the cover layer is a thick selective layer clung to a cheap nonselective membrane. The partial pressure between the feed stream and the permeate area functions as a driving mechanism for the permeation of gases through the membrane [152]. The principle issue with permeation technology is the compromise among selectivity and penetrability. Indeed, this restricts the wide utilization of polymeric membranes for carbon capture before combustion because of their low H_2/CO_2 selectivity [153].

Industrial applications of CO_2 separation membranes require reliable test conditions. The membranes used to capture CO_2 prior to combustion and removal of sulfur from natural gas require high-pressure conditions. However, CO_2 separation before and after combustion requires high-temperature operations. It is also important to conduct research at a high operating pressure because of the condensable nature of CO_2, and at a higher operating pressure, adsorption of CO_2 begins to plasticize the membrane, which leads to a decrease in membrane selectivity [121]. Physical aging is a thermodynamic phenomenon that manifests itself, especially in polymers with low chain packing, due to relaxation and convergence of chains, which leads to a

decrease in the fraction of the free volume of the membrane. The performance of nanodoped membrane can further be improved through the development of multifunctional thermal and chemical resistance composite materials, whereby the unique properties of the nanocomposite may be combined to surface reactive moieties, leading to other activities [154]. The number of commercial membranes that can be used to separate carbon dioxide after postcombustion is limited. Most of the commercial membranes have been tested in coal-fired power plants [44].

White et al. [155] applied a pilot-membrane sized system to separate a flue gas stream that contained about a ton of CO_2/day corresponding to approximately 0.05 MWe of a carbon source fired power plant. The technological design is made use of a two-step separation process. It first used in the first stage a combination of light feed compression and permeate vacuum to achieve a pressure and capture ratio of approximately 50% of CO_2 in the inlet gas stream. The second step used combustion air as a purge gas to increase CO_2 recovery to about 90%. Pohlmann et al. [140] used simulation results published by Brinkmann et al. [156] to develop a pilot scale unit consisting of envelope modules containing separation layers, with effective membrane area of about 13 m^2. Flue gas stream containing 14.6% CO_2, 6.7% O_2, 51–100 ppm SO_2, 75–91 ppm NO_x, and 14.5% of H_2O was used, while the input and permeate pressures were 1.265 and 0.05 bar, respectively. The authors highlighted the need to pretreat the gas stream before entering the membrane. This pretreatment stage includes removal of condensates, water vapour, and dust from the gas stream. There are several factors that can affect a membrane performance in a gas permeation process, they include, but are not limited to, changes in feedstock composition which affect directly the adsorption phenomenon or the swelling degree at the gas film interface as envisage by sorption/diffusion principles. Since the diffusion of gas components in the membrane

depends on the concentration or solubility of the components, feed stock composition greatly influences the permeation properties. Interaction effects between two or more species can occur in multicomponent feeds, which can greatly affect selectivity [157].

Carbon capture and storage involves CO_2 separation from energy-related industrial sources, transportation to storage sites, and long-term segregation from the atmosphere. The isolated carbon dioxide can then undergo compression and transported to suitable storage sites such as in geological formations, oceans, carbonate minerals, and oil and gas reservoirs, or used in industrial processes. CO_2 stockpiling plays an important role in the CCS chain and falls into two distinct categories: collection using geological infrastructure and marine base infrastructure. Geological infrastructure includes coal reserves, gas fields, oil fields, groundwater production, and sedimentary and fresh water resources [158]. The choice will depend on technology maturity, cost, diffusion, overall capacity, and technology transfer. Thus, potential technical storage of CO_2 includes ocean storage, geological storage, and industrial conversion of CO_2 to inorganic carbonates [159]. For geological storage, essential physical trapping mechanism such as caprock is necessary, in order to prevent CO_2 from migrating to the surface. The potential for industrial use of CO_2 is low, and there is relatively little experience in the literature with combining CO_2 capture, transport, and storage into a fully integrated CCS system [160]. Although the geological storage seems to be a more reliable method for large storage of CO_2, however, the orientation of both the formation pores and mineral grains or fracture along a preferential direction can also constitute barriers to flow resulting in different elastic response. Therefore, quantifying geological heterogeneity will affect the challenges of deploying large-scale carbon dioxide storage facilities in geological formations, which will affect microscopic fluid displacement and tire integrity [161]. CO_2 is also used in greenhouses to improve plant growth. Today, many companies are developing new ways to use capture CO_2, including its use for the enhancement of concrete, chemicals and fuels, polymers for plastics, carbon fiber, and carbon materials.

The efficiency of the membrane gas separation process largely depends on the transport characteristics of the membrane, that is, its permeability and selectivity in relation to specific gases in the mixture. Materials used or used for gas separation membranes cover the entire spectrum of organic and inorganic substances, from polymers to ceramics, metals, and other inorganic materials on the one hand [162]. Inorganic membranes generally exhibit better mechanical, chemical, pressure, and thermal stability compared to other polymer membranes.

11. Considerations for Future Research

(1) Evaluating of the Knudsen diffusion mechanism in membranes by using knowledge-based systems, developed from artificial intelligence techniques to improve performance and carbon capture efficiency.

(2) Application of smart models in simulating steady state process associated with membranes selectivity and permeability trends in carbon capture.

(3) Identifying optimal and appropriate nanomaterials/ particles for low-cost membrane fabrication and doping.

(4) Application of less dense hybrid nanocomposites that will avoid membrane poisoning and increase membrane performance in terms of selectivity and permeability.

(5) Doping phase incompatibility and morphological defects should be considered in developing novel nanohybrid particles/materials for membrane doping (that is, optimizing compatibility between the different constituent composites).

(6) Development of hybrid nanocomposites that can break the permeability-selectivity trade-off for practical carbon capture and gas separation.

(7) The effect of physical aging on long-term polymeric-based membrane doped with nanocomposites should be evaluated.

12. Conclusion

Different membrane materials have different separation characteristic properties, thermal and chemical stabilities, mechanical strengths, and costs of production, and they have their different own suitable uses. Carbon capture with gas separation membranes has attracted great interest over the last ten years; however, there are still problems associated with postcombustion CO_2 capture membranes, such as limited membrane separation performance (with most polymer membranes, there is a trade-off between permeability and selectivity), membrane stability, and durability. Therefore, the membranes for carbon capture applications must be specifically developed with high performance and relatively low manufacturing costs. The choice of a suitable membrane material for a particular application depends primarily on the properties of the membrane material, the composition/impurities of the feed gas, the operating conditions of the process, and the separation requirements. Recently, the efficiency of membrane separation has been greatly improved due to the great efforts of researchers.

From this study, it was observed that both nanocomposite- and hybrid nanocomposite-doped membranes have not been extensively applied on the industrial scale. Some critiques indicate that hybrid nanocomposites commonly used in membrane manufacturing have high intrinsic costs for their raw materials and manufacturing technologies. Thus, more research is still needed to reduce the cost of hybrid nanocomposites and identify new hybrid nanocomposites at lower manufacturing costs.

Data Availability

No data were used to support the findings of this study.

Conflicts of Interest

Acknowledgments

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Research Article

Alumina Support for Cobalt Catalyst in a Methane Dry Reforming Reaction: The Role of Water Content in a Solvent Medium

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This study aimed to synthesize alumina from an inorganic aluminum nitrate precursor in various binary solvent systems of ethanol and water using the sol-gel self-assembly (SSA) method, employing a triblock copolymer, pluronic P123, as the pore-directing agent. The resulting materials were implemented as a support for the cobalt (Co) catalyst in a methane dry reforming (MDR) reaction at 1073 K under 1 atm. Regardless of the water percentage used in the support synthesis, the methane dry reforming reaction over Co catalysts on alumina supports showed the negligible change in conversion during the 12 h reaction. Moreover, there was evidence of large quantities of amorphous carbon and graphitic carbon on the spent catalyst surface. However, the low oxidation temperature of these deposited carbons could help maintain the balance between the carbon formation and the carbon elimination processes on the catalyst surface during the reforming reaction, hence prolonging the lifetime of the catalyst. The high conversion of methane (CH_4) from 64.6% to 82.8% and carbon dioxide (CO_2) from 70.7% to 86.6% for the MDR reaction over the as-prepared alumina-supported Co catalyst demonstrated a significant improvement in catalyst production for the MDR reaction from the viewpoint of large-scale applications.

1. Introduction

The increase in the average temperature and climate change caused by greenhouse gases has become serious global issues. The human activities such as the burning of oil, coal, and gas, as well as deforestation, are associated with energy-related carbon dioxide (CO_2) emissions in the atmosphere. Therefore, in addition to the need to find new eco-energy sources, the use of mineral resources in an ecological and environmental approach is also a significant concern. Consequently, the methane dry reforming (MDR) method has emerged as a potential approach for producing syngas from CO_2 and methane (CH_4), which is a significant feedstock for downstream petrochemical processes [1–6]. Although this approach could have environmental and economic benefits, the catalyst limitations have impeded it from wide-ranging applications in large-scale industrial production.

Noble metals, such as rhodium (Rh), ruthenium (Ru), and platinum (Pt), have significant catalytic activity for the MDR process in terms of conversion and coking inhibition [7]. However, the unavailability and expensive cost of these catalysts are major drawbacks preventing their use in industrial applications. To date, cobalt- (Co-) based catalysts have garnered considerable attention since they possess comparable catalytic activity and higher stability against temperature variations in comparison to noble metals [8, 9]. Moreover, different metal oxides have been evaluated as the support for a Co-catalyzed MDR reaction, such as oxides of the alkaline Earth elements, including magnesium oxide

(MgO), calcium oxide (CaO) [8], ceric dioxide (CeO_2) [10], lanthanum dioxide (LaO_2) [11], strontium oxide (SrO) [12], aluminum oxide (Al_2O_3) [13–16], and Santa Barbara Amorphous-15 (SBA-15) [17–19]. Among of these materials, mesoporous alumina (MA) has been proven to be a potential support because of its availability. Recent contributions in heterogeneous catalysis regarding porous support and mesoporous structure materials have been widely used as catalyst supports since they can facilitate the dispersion of the catalysts and confine the active particles inside their matrix, preventing them from aggregating during the reaction [17, 19–21]. Mesoporous alumina support is one of the materials that has a high potential for being screened for the same effects in a MDR reaction.

Sol-gel self-assembly (SSA) is a common approach used for mesoporous Al_2O_3 production due to its easy, accessible, and reproducible characteristics in fabricating mesoporous structures [22]. Most SSA processes have been conducted by employing an organic salt precursor dispersed on a soft template dissolved in anhydrous ethanol (C_2H_5OH) [22, 23]. However, the toxicity and the high cost of organic salt and anhydrous (C_2H_5OH) ethanol have made them the most unlikely substances for this purpose. Thus, interest in using a less expensive and readily available inorganic aluminum precursor in large-scale applications is increasing. Additionally, the presence of water in the solvent has a significant influence on the pore structure of the resulting alumina materials [24], thus enabling intrapellet diffusion of the active nanoparticles in the porous framework [25]. To the best of our knowledge, only a few studies have investigated the combination of an inorganic aluminum precursor and a binary solvent mixture (C_2H_5OH in H_2O) for synthesis of alumina using the SSA method, to act as a support for a Co catalyst in an MDR reaction. Therefore, instead of using an organic salt precursor and anhydrous ethanol, the present study employed a combination of an inorganic aluminum precursor and a binary solvent mixture (C_2H_5OH in H_2O) for alumina synthesis using the SSA method. The performance of the Co catalyst on the as-prepared supports for the MDR reaction was evaluated to determine the amount of water needed in the solvent when preparing the support.

2. Materials and Methods

2.1. Chemicals.
Aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ (≥98%) and fuming hydrochloric acid (HCl) (37%) were purchased from Merck (Darmstadt, Germany). Pluronic® P-123 (MV = 5800) and cobalt (II) nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 98%) were obtained from Sigma-Aldrich (St. Louis, Missouri, US). C_2H_5OH (99.9%) was obtained from VWR Chemicals (Darmstadt, Germany). All the reagents were used directly without any further purification. All the gases, including CH_4, CO_2, nitrogen (N_2), and hydrogen (H_2), were of analytical grade and provided by Air Products and Chemicals, Inc.

2.2. Catalyst Synthesis.
Al_2O_3 was prepared by dissolving 0.98 g of P-123 in 14.6 ml of the C_2H_5OH-H_2O solvent mixture with the following proportions of water: 0%, 25%, 50%, and 75%. This solvent mixture was mixed at an ambient temperature for 30 min, followed by adding 3.68 g of $Al(NO_3)_3 \cdot 9H_2O$ and dropping 1.6 ml HCl (37%) solution. The obtained blend was additionally stirred for 60 min prior to undergoing the hydrothermal process at 373 K for 24 h in an autoclave. The obtained mixture was dried in the oven for 48 h at 333 K and then calcined in a furnace for 5 h at 1073 K.

The Al_2O_3-supported Co catalyst was prepared using the incipient wetness impregnation method. In particular, 0.28 g of the $Co(NO_3)_2 \cdot 6H_2O$ precursor was mixed with 0.25 ml of C_2H_5OH, and the resulting solution was sprayed on 0.5 g of as-synthesized alumina. The resulting mixture was dried overnight at 373 K and then calcined at 873 K for 5 h. The individual alumina support, prepared from the binary solvent system with a water content of 0%, 25%, 50% and 75%, was labelled as MA00, MA25, MA50, and MA75, respectively. Consequently, the supported Co catalysts synthesized from the abovementioned support were denoted as 10Co/MA00, 10Co/MA25, 10Co/MA50, and 10Co/MA75.

2.3. Catalyst Properties.
The phases and crystalline structure of the selected spent catalysts were determined using a Rigaku Miniflex 600 X-ray diffraction instrument, which employed a copper (Cu) target as the radiation source at the wavelength of 1.5418 Å. The test specimen was scanned from 3° to 80° with the speed of 1° min^{-1}.

The amount of deposited carbons on the spent catalysts was quantified via the thermal programmed oxidation conducted on a TA TGA Q500 equipment (TA Instruments, Newcastle, DE, USA). In particular, the sample was heated at 373 K in N_2 atmosphere for 30 min to eliminate the volatile compounds, followed by increasing the temperature to 1023 K in a mixture flow of 20% O_2 in N_2 with a ramping rate of 10 K min^{-1}. The oxidation stage at 1023 K was left for an additional 30 min prior to cooling to room temperature.

The surface morphology of the selected catalysts was elucidated using scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) detector (Hitachi Tabletop Microscope TM3030 Plus unit, Hitachi High Technologies Corp., Tokyo, Japan) and a Raman spectrometer employing 532 nm laser excitation (JASCO NRS-3100, Tokyo, Japan).

2.4. Catalytic Activity Evaluation.
The fixed-bed reactor with a 3/8 diameter was used to evaluate the MDR reaction catalyzed by the alumina-supported Co at a fixed gas hourly space velocity (GHSV) of 36 L·g_{cat}^{-1}·h^{-1}. Prior to each assessment, H_2 reduction was done in situ at 1073 K for 1 h using a mixed flow of 50% H_2 in N_2. The output products were analyzed in an Agilent 6890 gas chromatography (Agilent Technologies, Santa Clara, CA, USA). The reactant conversions (X_i with i: CH_4 and CO_2) and product yields

$(Y_{CO}$ and $Y_{H_2})$ were estimated using the following equations, respectively:

$$X_i(\%) = \frac{F_i^{in} - F_i^{out}}{F_i^{in}} \times 100\%, \tag{1}$$

$$Y_{CO}(\%) = \frac{F_{CO}^{out}}{\left(F_{CH_4}^{in} + F_{CO_2}^{in}\right)} \times 100\%, \tag{2}$$

$$Y_{H_2}(\%) = \frac{F_{H_2}^{out}}{2 \, x \, F_{CH_4}^{in}} \times 100\%, \tag{3}$$

where F^{in} and F^{out} are the inlet and outlet molar flow rates (mol s^{-1}), respectively.

3. Results and Discussion

3.1. Catalyst Assessment of the MDR Reaction

3.1.1. Effect of Different Types of Alumina Support on the MDR Reaction.
Four substrates, prepared using a mixed-solvent of C_2H_5OH and different proportions of H_2O (0%, 25%, 50%, or 75%), were applied as a support for the Co catalyst, and the catalytic performance of the substrates for the MDR reaction was evaluated at a stoichiometric feed ratio and temperature of 1073 K. As seen in Figures 1–4, the conversion of the reactants and the product yield were unchanged within the 12 h reaction, indicating the firm stability of the four catalysts under MDR reaction conditions. The conversion of CO_2 and CH_4 in the MDR reaction showed a decreasing trend from 86.6% to 70.7% and from 82.8% to 64.6%, respectively, in the order of 10Co/MA00 > 10Co/MA25 > 10Co/MA50 > 10Co/MA75 catalysts. This decrease in catalyst performance along with an increase in the water concentration in the solvent for the support preparation could be due to the modification in the support's pore structure, which was caused by the increase in the water content. Thus, the MDR reaction performance strongly depends on the support's features and the active Co metal properties, such as crystal size and dispersion [26]. Furthermore, it has been reported that the percentage of water in the solvent mixture has a significant impact on enlarging the pore diameter of MA produced using the SSA method [23], hence facilitating the generation of active metals with an appropriate size and enhancing the intrapellet diffusion of both the reactants and the products [25].

The effectiveness of the MDR reaction was consolidated via the time on stream (TOS) plot of the H_2 and CO formation yields, as seen in Figures 3 and 4. The support in catalyst activity was observed to play a significant role in both the CO and H_2 yields. In particular, the H_2 and CO yields were highest in the case of the 10% Co/MA00 catalyst; they were about 62.4–68.7% and 71.2–76.0%, respectively. When the MDR reaction was conducted with the 10% Co/MA75 catalyst, the CO yield decreased by approximately 10–20% and the H_2 yield decreased by approximately 20–30%. Regardless of the type of support, the H_2/CO ratio was always <1, thus proving the coexistence of the reverse water-gas-shift process in the MDR reaction [27].

3.1.2. Effect of CH_4 and CO_2 Partial Pressure on the MDR Reaction.
To evaluate the partial pressure influence of CH_4 (P_{CH_4}) and CO_2 (P_{CO_2}) on MDR, the reactions over the 10% Co/MA00 catalyst were conducted with P_{CH_4} and P_{CO_2} in the range of 10–40 kPa at a temperature of 1023 K. Figure 5 shows the correlation between the CH_4 and CO_2 conversions with the change in P_{CH_4} at P_{CO_2} of 20 kPa (Figure 5(a)) and the change in P_{CO_2} at a fixed P_{CH_4} of 20 kPa (Figure 5(b)). The CH_4 conversion gradually decreased by approximately 15.0% as P_{CH_4} increased from 10 kPa to 40 kPa (see Figure 5(a)). This decrease in the CH_4 conversion was due to the upsurge in carbon formation caused by extreme CH_4 cracking in the surplus of the CH_4 feedstock. The formed carbon induced active sites blocking and hindering the catalytic performance of the MDR reaction [28]. In contrast, the CO_2 conversion increased and reached 80.6% when the P_{CH_4} increased from 10 kPa to 40 kPa.

Thus, the increase in P_{CH_4} resulted in superior CH_4 adsorption on the catalyst, therefore improving the CO_2 consumption through the MDR reaction [29]. A similar trend was also observed for the MDR reaction over the CeO_2-supported Co catalyst [28].

However, the CH_4 conversion showed continuous improvement to 82.7% when P_{CO_2} increased from 10 kPa to 40 kPa, while P_{CH_4} was kept at 20 kPa (see Figure 5(b)). This behaviour can be linked to the enhanced elimination of the deposited carbon, as depicted in equation (4) [30], and the coinciding existence of the CH_4 steam reforming process that was due to the increase in H_2O via the reverse water-gas-shift process, as follows [31]:

$$CH_4 \xrightarrow[-H_2]{} C_xH_{1-x} \xrightarrow[+CO_2]{} H_2 + CO \tag{4}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{5}$$
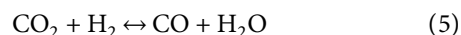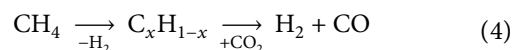
A decrease in the CO_2 conversion was found when P_{CO_2} increased from 10 kPa to 40 kPa (see Figure 5(b)), which could be due to the deficiency of CH_4 in reacting with the CO_2-rich feedstock. Furthermore, the presence of excess CO_2 in the reactor could intensify the possibility for active Co particles to be oxidized as follows, which resulted in a decrease in CO_2 adsorption [27]:

$$3Co + 4CO_2 \longrightarrow Co_3O_4 + 4CO \tag{6}$$
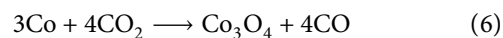
3.2. Characterization of the Spent Catalyst

3.2.1. XRD Analysis.
The XRD spectrum of the synthesized 10% Co/MA00 after 12 h MDR reaction at 1073 K is shown in Figure 6. The peaks at 2θ of 37.6°, 45.6°, and 67.0° were assigned to the Al_2O_3 phase (JCPDS card no. 04-0858); the signals at 31.7°, 37.5°, and 44.6° corresponded to the Co_3O_4 crystalline phase (JCPDS card no. 74-2120). Moreover, the metallic Co presence was verified via the detection of a peak at 51.6° (JCPDS card no. 15-0806). The copresence of Co metallic and oxide particles in the 10% Co/MA00 sample indicated the occurrence of the redox cycle of the Co species during the MDR reaction. Notably, a broad peak at 2θ from
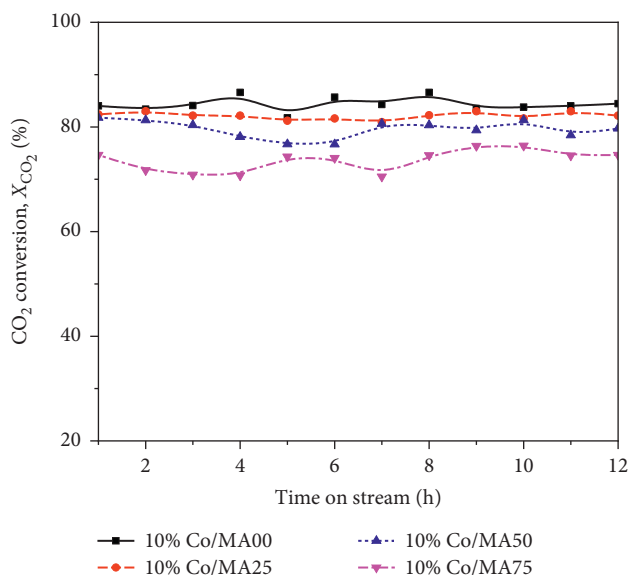
FIGURE 1: Time on stream conversion of CO_2 in MDR over different catalysts at 1073 K.
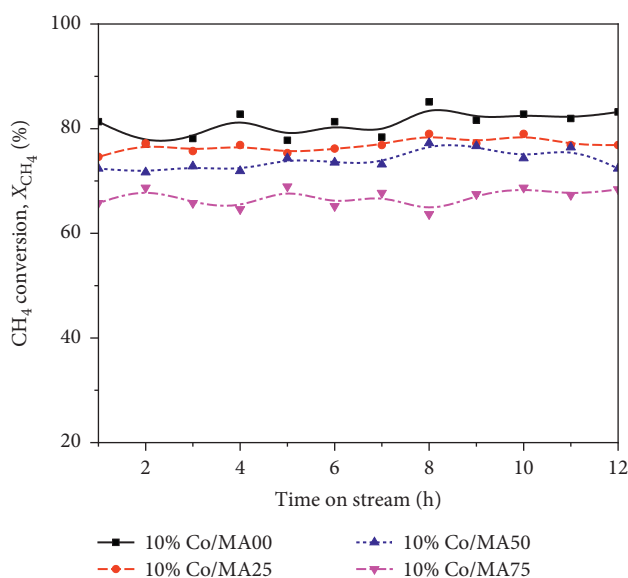
FIGURE 2: Time on stream conversion of CH_4 in MDR over different catalysts at 1073 K.

15.0° to 30.0° was deconvoluted into two separate diffraction signals, denoted as α and β, and displayed in a small inserted picture in Figure 6. The α peak represents amorphous carbon, and the β peak represents graphitic carbon [32].

3.2.2. Raman Measurements. Figure 7 shows the Raman spectrum of the 10% Co/MA00 after 12 h MDR reaction at 1073 K. Four active Raman peaks at 473.9 cm^{-1}, 517.7 cm^{-1}, 609.7 cm^{-1}, and 678.5 cm^{-1}, illustrated in the embedded picture, were assigned to the corresponding Co_3O_4 symmetric vibrational modes of E_g, F_{2g}, F_{2g}, and A_{1g}. The signal at 678.5 cm^{-1} represents the vibration of the octahedral site, and the E_g and F_{2g} modes are likely related to the mixed vibrations of the octahedral site and the tetrahedral oxygen

movements [33]. These typical peaks were observed in the Raman spectra of the spent catalyst, suggesting that the reduced Co^0 species in the H_2 pretreatment were reoxidized to Co_3O_4 during the MDR reaction. Two peaks at 1338.5 cm^{-1} and 1573.5 cm^{-1} demonstrate the heterogeneity of the surface carbons including ordered carbon-like graphite (G-band) and amorphous carbon (D-band). The D-band was attributed to amorphous carbon or carbon nanofibers, while the G-band arises from the stretching of the C-C bond in graphitic carbon [34].

3.2.3. Surface Morphology Analyses. The SEM-EDX measurements of the 10% Co/MA00 catalyst after MDR at 1073 K suggest the presence of filamentous carbons or
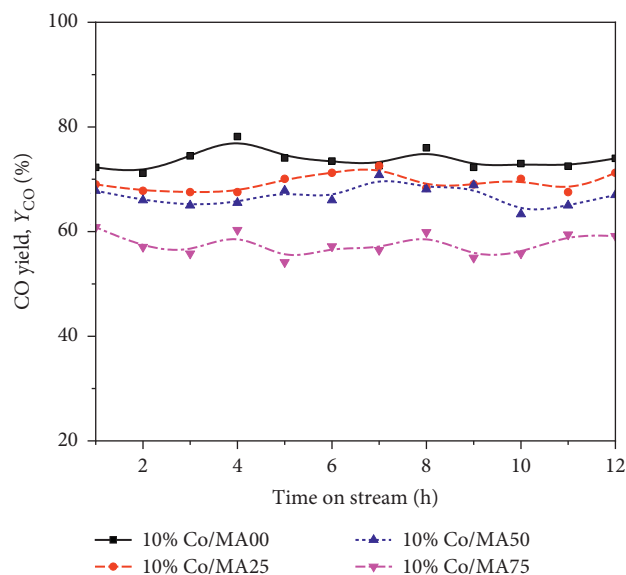
FIGURE 3: Time on stream yield of CO in MDR over different catalysts at 1073 K.
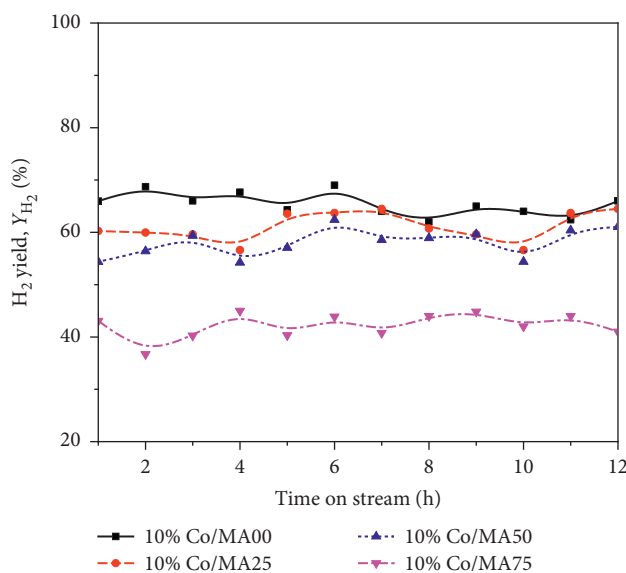
FIGURE 4: Time on stream yield of H_2 in MDR over different catalysts at 1073 K.

carbon fibers, as shown in Figure 8. The percentage of total carbon in the catalyst was around 64.03% based on the normalized EDX results. This could be due to the fact that the alumina-supported Co catalyst is known to boost the formation of filamentous carbon in a CH_4 atmosphere at high temperature [35].

3.2.4. TPO Measurements. Thermal-programmed oxidation (TPO) was performed to quantify the sum of the carbon deposits on the 10% Co/MA00 catalyst after MDR at 1073 K. As seen in Figure 9, about 77.1% weight of the sample was

lost after the oxidation at temperatures ranging from 700 K to 850 K, which is in agreement with the EDX results (see Table 1). The differences in the results obtained from the two analytical methods could be due to the decomposition of the other elements in the TPO measurement.

Moreover, the low oxidation temperature of the deposited carbon at temperatures ranging from 750 K to 820 K, as determined from the derivative weight curves, suggest that all the deposits were well gasified in the reforming conditions; hence, they did not cause a loss of intrinsic catalyst activity or lengthen the lifetime of the catalyst [13].
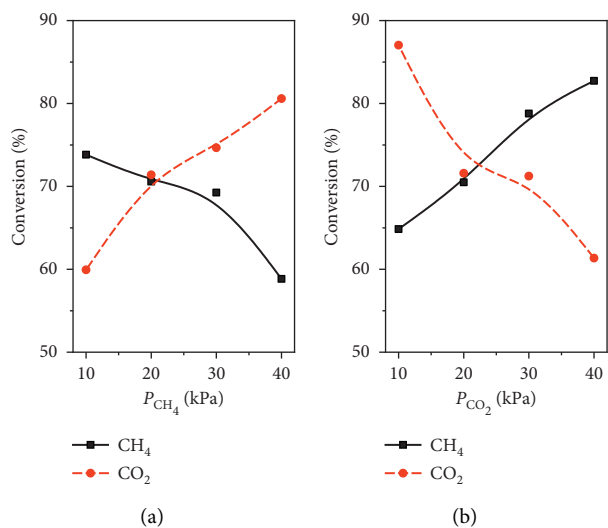
FIGURE 5: Influence of P_{CH_4} and P_{CO_2} on the CH$_4$ and CO$_2$ conversions in MDR over 10% Co/MA00 at 1023 K.
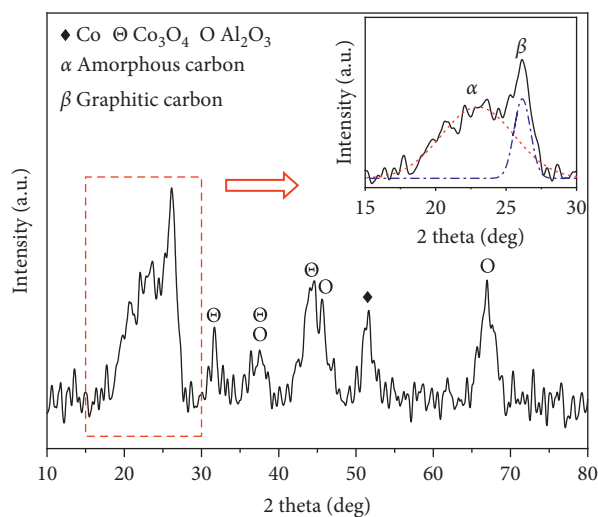
FIGURE 6: XRD spectra of spent 10% Co/MA00 after MDR at a stoichiometric feed ratio of 1 and 1073 K.
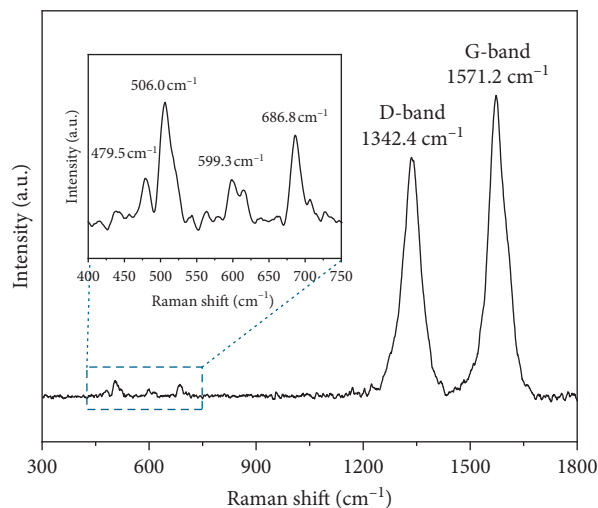
FIGURE 7: Raman spectra of the spent 10% Co/MA00 after MDR at 1073 K and stoichiometric feed ratio of 1.
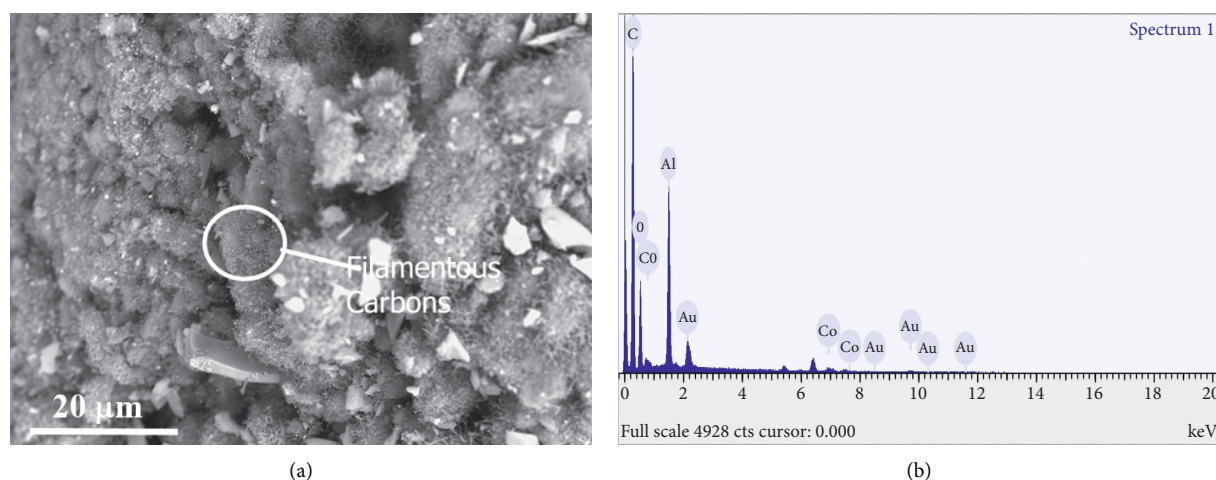
FIGURE 8: (a) SEM image and (b) EDX analysis of the 10% Co/MA00 catalyst after MDR at 1073 K and a stoichiometric feed ratio of 1.
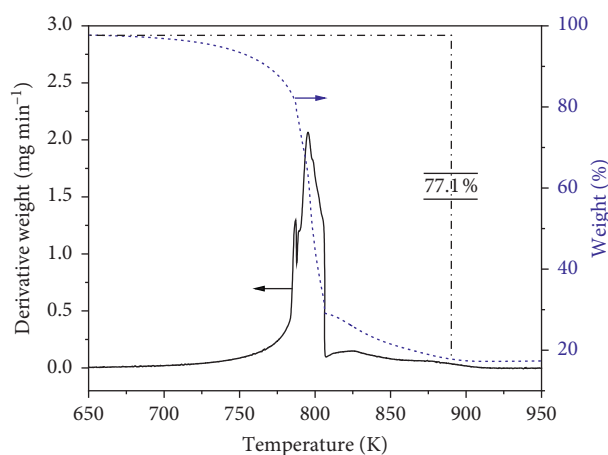
FIGURE 9: The weight loss and the derivative of weight loss profile of the 10% Co/MA00 catalyst after MDR at 1073 K and stoichiometric feed ratio of 1.

TABLE 1: EDX measurement of the 10% Co/MA00 catalyst after MDR at 1073 K.

Element	Weight (%)
Carbon (C)	64.03
Oxygen (O)	27.81
Aluminum (Al)	7.30
Cobalt (Co)	0.86

4. Conclusions

The performance of the Co catalysts supported on MA for the MDR reaction was investigated in terms of the support contribution. The water content in the solvent mixture applied for the Al_2O_3 support synthesis plays a crucial role in assembling the structure; hence, it influences the catalytic activity in the MDR reaction. Regardless of the type of support used, the Co catalysts showed good stability under 12 h MDR reaction. Notably, the 10% Co/MA00 catalyst demonstrated the highest activity for the MDR reaction with a carbon monoxide yield of 71.2–76.0%, and the deposit on the spent 10% Co/MA00 catalyst surface was found to consist of both amorphous carbon and graphitic carbon possessing low-oxidation temperature property and hence easily be eliminated in situ the reaction process. Moreover, the reactant partial pressure was found to have a significant impact on the CO_2 and CH_4 conversions as well as the product yields when the MDR reaction was conducted at 1023 K.

Data Availability

All experimental data used to support the findings of this study are available within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Review Article

Novel Systems and Membrane Technologies for Carbon Capture

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Due to the global menace caused by carbon emissions from environmental, anthropogenic, and industrial processes, it has become expedient to consider the use of systems, with high trapping potentials for these carbon-based compounds. Several prior studies have considered the use of amines, activated carbon, and other solid adsorbents. Advances in carbon capture research have led to the use of ionic liquids, enzyme-based systems, microbial filters, membranes, and metal-organic frameworks in capturing CO_2. Therefore, it is common knowledge that some of these systems have their lapses, which then informs the need to prioritize and optimize their synthetic routes for optimum efficiency. Some authors have also argued about the need to consider the use of hybrid systems, which offer several characteristics that in turn give synergistic effects/properties that are better compared to those of the individual components that make up the composites. For instance, some membranes are hydrophobic in nature, which makes them unsuitable for carbon capture operations; hence, it is necessary to consider modifying properties such as thermal stability, chemical stability, permeability, nature of the raw/starting material, thickness, durability, and surface area which can enhance the performance of these systems. In this review, previous and recent advances in carbon capture systems and sequestration technologies are discussed, while some recommendations and future prospects in innovative technologies are also highlighted.

1. Introduction

The continuous increase in gaseous emissions is a major environmental challenge that bedevils our planet as well as the global populace. Climate change and global warming are resultant effects of the release of CO_2, CH_4, chlorofluorocarbons (CFCs), O_3, and NOx into the atmosphere [1, 2]. The greenhouse gas contributions of chlorofluorocarbons/methane are far higher than those of CO_2 when compared on the basis of unit mass [2]. However, due to the release of CO_2 from fossil fuels, which is the primary source (98%) of the global energy demand, most of the efforts to combat the menace of greenhouse gases are concentrated on CO_2 capture technologies [3]. In the year 2013, the high greenhouse gas concentrations in the earth's atmosphere were quite alarming; also, the CO_2 concentration was 396 ppm (i.e., about 142% of the estimated CO_2 concentration in the preindustrial era [4]. Findings from the Global Atmosphere Watch (a greenhouse gas bulletin) showed that CO_2 concentration experienced the highest increase between 2012 and 2013, compared to those reported for previous years. However, this was judged to have been caused by the reduction in CO_2 uptake in the biosphere. From 2013 to date, the increase in greenhouse gas emissions caused by a rapid rise in population density, industrial activities, and anthropogenic activities has given rise to unprecedented repercussions/effects ranging from environmental pollution to health deterioration, water contamination/pollution, eco-destruction, loss of aquatic life, and undesirable climate change. At a climate conference held in Paris (i.e., the COP21) in December 2015, a total of 195 countries instituted a resolution on the first-ever-historic legal-binding agreement on climate issues, where it was commonly agreed that the global temperature would be kept at an average increase of less than 2^oC, which is slightly above what was obtainable in preindustrial times.

The resultant rise in the world's fossil fuel reserves alongside the rapid change in energy demands has led to the unavoidable global expansion of some existing plants, as well as the construction of new ones in order to boost production capacities as a preparatory measure to absorb the global energy shocks. This situation has extended into further years owing to the current state of industrial development and economic growth in different parts of the world, especially in the developed nations. According to the information provided by the Energy Information Administration (EIA), an arm of the US Department for Energy, while fossil fuels were projected to be the world's leading source of energy (80% of the world's energy) in the next two decades, energy consumption was predicted to also rise by 56% by 2040. According to the literature, the CO_2 emissions from power plants were predicted to rise by 46% in 2010 [5]. Furthermore, according to EIA reports, the combined CO_2 emissions from India and China from the use of coal are expected to triple that of the US by the year 2030 [6].

Three strategies are employed in trapping CO_2 emissions from fossil fuel-powered plants; the methods include oxy-, pre-, and post-combustion capture of CO_2 [7]. In pre-combustion capture, the gas is trapped from the parent mixture prior to undergoing combustion. Oxy-combustion capture has to do with capturing CO_2 during combustion, i.e., while burning gas in the air. In postcombustion capture, the gas is trapped from flue gas (a mixture of constituents such as nitrogen, water vapor, and oxygen), in a downstream unit retrofitted with a carbon capture system within the plant. The challenges associated with this process include low CO_2 partial pressure, high flue gas temperature, and the high amount of CO_2 in the flue gas [7, 8]. This also confirms why coal-fired power plants have been reported to be one of the largest stationary point sources of CO_2 emissions [9].

In the United States, policy implementation for CO_2 reduction exists at the local and state levels [10]. However, requests to build new coal-fired power plants are being denied regularly due to their lack of CO_2 controls at inception as well as their medium to high tolerance for CO_2 emission [11]. In 2009, 44.5% of US electricity was generated from coal, whereas, in 2008, CO_2 emissions from electricity generation accounted for about 40 and 34% of the global anthropogenic and GHG emissions [12, 13]. Globally, 31.2 Gt CO_2 emissions were told to have been released from fossil fuel combustion and cement production [14]; this value dropped by 1.3% in 2009 [15].

1.1. Some Related Reviews on Carbon Capture.

In the study of Leung et al. [16], various aspects of carbon capture systems and some current state-of-the-art technologies for CO_2 capture, transport, separation, storage, leakage phenomena, monitoring, and life cycle analysis were discussed. They asserted that the choice of a specific CO_2 capture technology depends on the nature of the CO_2-generating plant and fuel source. Based on their discussions, absorption is the most preferred method for capturing CO_2 and according to them, it is due to the higher efficiency and cost-effectiveness of the process. Vakharia et al. [17] scaled up the performances of synthetic amine-doped thin-film composite membranes for CO_2 capture from flue gas, where they recorded CO_2 permeance > 700 GPU (1 GPU = 10^{-6} cm^3 (STP)/(s cm^2 cmHg)) with corresponding CO_2 selectivity above 140 at 330 K. Aaron et al. [18] carried out a review of some existing CO_2 capture technologies; they concluded that the most viable method for CO_2 capture is absorption using MEA. Other liquid absorbents, i.e., piperazine and anionic liquids, have also been discussed as potential candidates for carbon capture [19]. However, piperazine which flows and reacts faster with CO_2 than MEA has been proposed owing to its larger volatility relative to MEA; hence, its usefulness in CO_2 absorption is quite expensive and which is the reason for its noncommercialization [20]. The review conducted by Brunetti et al. [21] compares CO_2 separation involving membranes and other separation technologies, i.e., adsorption and cryogenic separation of CO_2. They highlighted that membranes are strongly affected by low CO_2 concentration and pressure from flue gas, which is a major hurdle in applying this technology.

Chemical absorption or scrubbing process is currently the technology most likely to be implemented in the near future but is rather energy-intensive. In recent years, membrane-based CO_2 separation appears to be a competitive substitution for conventional chemical absorption technologies. Wang et al. [22] reviewed the basic process design techniques for some CO_2 absorption processes using chemical solvents and membranes; they also highlighted the need to optimize some operational parameters, techniques for process modification, membrane module types, etc., in which the energy requirements and economic implications of both CO_2 capture technologies were scrutinized. However, they asserted that membrane-based separation lacks obvious advantages, in terms of energy requirement and cost, over MEA-based absorption where 90% CO_2 capture is feasible.

Based on the review carried out on carbon capture and utilization (CCU) by Koytsoumpa et al. [23], commercial applications of the thermal power and industrial sectors of pre- and postcombustion captured carbon were discussed. The focus of CCU is for the trapped CO_2 to serve as fuel or as a means of generating heat and power. Hence, they asserted that CCU combined with energy storage is an evolutionary approach for instilling the power to fuel concept, which in turn guarantees high market supplies of fuel and other chemicals. Furthermore, recent advances in supercritical CO_2 cycles for heat and power production were also presented.

Owing to the different types of absorption, adsorption, membrane, and cryogenic processes available for carbon capture operations, absorption still stands out as the most widely used method in commercial applications. Based on the content and composition of treated gas samples, different physical and chemical methods of adsorption are available for carbon dioxide and sulfur species removal from process streams [24–27]. For mixtures containing low amounts of carbon dioxide, chemical solvents are preferred to physical solvents; however, physical solvents give better results at high partial pressures. In addition, the thermal energy

requirement for gas separation processes involving chemical solvents is much higher compared to those of physical solvents due to the addition of heat via the reboiler attached to the stripper column [25]. This is because, according to Henry's law, the loading capacities of physical solvents have a virtual linear relationship with the partial pressures of the components to be removed, which in turn allows for easy solvent regeneration by pressure throttling. The dissolution of carbon dioxide in the physical liquid solvent is attributed to the van der Waals or electrostatic interaction and is optimal at high pressure and low temperature, hence the need to optimize the process conditions for optimum CO_2 capture.

A review of the development of novel carbon capture technologies was conducted by Lockwood [28], where their energy requirements and cost implications were compared in terms of efficiency-penalty, cost of power, cost of the CO_2 capture process, and the current developmental status of new technologies. For operations that actually factor in the cost of CO_2 capture into the power generation process, chemical loop combustion or the oxyfuel-based Allam cycle offers great potentials to meet the economic requirements of the overall process. For retrofit designs, high performance is often associated with CO_2 capture. According to them, in the US, the post-, pre-, and oxyfuel combustion research programmes present some ambitious targets for new technologies to achieve a CO_2 capture cost of about $20 per tonne. Novel solvents are seen to tilt towards lower-cost involvements in terms of energy regeneration requirements as compared to those associated with conventional amine solvents, phase-change systems, ionic liquids, other nonaqueous solvents, and enzyme-activation systems which are all promising technologies. Alternatively, other commercial gas separation technologies involving solid sorbents, membranes, and cryogenic separation have also been widely investigated. Although there are obvious cost implications for postcombustion capture applications, these techniques may offer some measurable benefits to precombustion capture systems, especially in areas where higher CO_2 partial pressures are desired. Hence, the integration of the CO_2 capture step and the water gas-shift reaction occurs within the adsorbents or membranes. In oxyfuel combustion, pressurised systems have shown a high tendency for efficiency improvements within the supercritical CO_2 cycle at some unique conditions of combustion. Ceramic membranes for oxygen production were also recommended as a means of lowering costs relative to those obtained for cryogenic air separation. Dramatic energy saving can also be achieved via chemical looping strategies, as a result of the inherent avoidance of the possibility of a gas separation step. This technology offers significant scale-up options to companies and research institutes, where the focus is on low-cost oxygen carriers. Raza et al. [29] reviewed the various processes involved in the reduction of CO_2 emissions where it was mentioned that carbon capture and storage techniques hold high promises for reducing the global carbon footprint. Their thought pattern focused on a CCS technology that deals with the capture and storage of CO_2 in deep geological formations for the regulation of the earth's temperature.

Some basic guidelines/principles for long-term CO_2 sequestration and storage were also discussed with considerations for the processes and mechanisms (buoyancy, pressure gradient, reservoir heterogeneity, dispersion, diffusion, mineralization, phase trapping, and adsorption by organic materials) involved alongside the various interactions stimulated by supercritical CO_2 injection into the subsurface of geological sites. According to the authors, the selection of apt geological sites for CO_2 storage is informed by the physical characteristics of CO_2 and its phase change tendencies as influenced by CO_2 transport/hydraulic pressure and temperature variation. Although CO_2 can exist as liquid, solid, or gas, it often exists as a supercritical fluid at geological formations whose depths are greater than 800 m and this is as a result of an increase in pressure and temperature at such depth [30, 31]. According to the review conducted by Sood and Vyas [32], CO_2 can be trapped from process facilities and transported to sedimentary basins, saline aquifers, and coal reservoirs for storage. The basic techniques highlighted include oxy-, pre-, and post-combustion strategies. Based on the storage capacities of the CCS technique, it is obvious that the storage capacities of CCS systems make them the most prospective candidates for carbon capture and storage owing to the huge tons of CO_2 storage capacities of the aforementioned sites. However, issues that bother on safety are paramount, especially when these sites are overburdened by excessive pressures that may subsequently result in hazards.

Despite all the efforts put into the well-appreciated past reviews as highlighted in some of the documented literature, it is evident that none seems to have looked into the collection of research works that have do with the application of hybrid systems/novel solvent systems and membrane technologies as the best potential candidates for carbon capture in lieu of the excellent properties they offer in those combinations. This then served as one of the major motivators for this study. Others include the scarcity of literature on the capture of several other carbonaceous compounds and the ill conceptualization of carbon capture in the light of CO_2 capture only.

To date, a lot of attention has been given to CO_2 capture due to its very high concentration in the earth's atmosphere relative to other gases; this has also led to the minimal attention received by other greenhouse gases, hence another motivation for this research, which serves to advocate for the focus on hybrid technologies for the trapping of CO_2 and other carbonaceous substances rather than paying attention to CO_2 only. Also, researchers are still searching for better strategies for curbing the global carbon footprint by trying out new measures that are not only highly efficient but also cost-effective and environmentally friendly. This is because, while a lot of the existing techniques are targeted at CO_2 capture, a myriad of these techniques lack high CO_2/carbon selectivity, stability, durability, etc. Hence, this paper seeks to uncover some of the advances made in carbon capture research, as well as consider possible ways of improving on the current technologies, all aimed at optimizing their performances towards ensuring a clean environment. Although somewhat efficient, the known/aforementioned CO_2 capture

technologies are quite expensive, thus giving an estimate of about 70–80% of the overall cost of a full CCS system, capture, transport, and storage [33]. Therefore, significant R&D efforts are currently focused on the reduction of operating costs and energy penalties which must be borne out of strategic selection of the choice materials, such as hybrid technologies, without a compromise for low quality while optimizing the process conditions towards ensuring high carbon selectivity and separation. All of these alongside discourses on the use of modified hybrid systems/MOF-ionic liquid systems for multigas (CCl_3, CCl_4, CH_4, H_2Cl_2, CFCs, etc.) capturing are barely available with major attention given to conventional absorption/adsorption processes alongside oxy, pre-, and postcombustion capture processes for CO_2 sequestration because the term carbon capture is often seen to be limited to CO_2/CH_4 capture as evidenced by the available literature. Also, any carefree attitude in this regard/the neglect of other greenhouse gases will gradually result in the accumulation/build-up of these gases to the point that they begin to constitute serious problems.

1.2. Categories of Carbon Sequestration Technologies. The existing carbon capture technologies can be grouped into the following categories.

1.2.1. Physiochemical Absorption

(1) Physical Absorption: Selexol, Rectisol, Fluorinated Solvents, and Ionic Liquids. Physical absorption involves the reversible/nonreversible use of solvents that have high affinity for carbonaceous substances; these solvents include methanol, propylene carbonate, dimethyl ethers of polyethylene glycol, fluorinated solvents, and the most recent group known as ionic liquids. Ionic liquids (ILs) are liquid salts of cations and anions; they have boiling points of less than $100°C$ and have the ability to trap CO_2 from a mixture of gases [34–36] owing to their inherent properties, such as low volatility, high CO_2 solubility, thermal stability, and their susceptibility to structural tuning that allows for the attainment of certain advantageous properties [37–39]. Several studies involving ILs have been devoted to determining the extent of CO_2 solubility, selectivity and IL performance, as well as their thermal/chemical stability [34, 40]. Some advances on the use of amine-modified ILs or task-specific ILs (TSILs) [41, 42] have shown that these liquids have high affinity for CO_2. Although the literature has recorded some significant advances in the production of low-viscosity ILs, one common challenge associated with the use of TSILs/ILs is the high viscosity of the fluids after CO_2 entrainment during gas separation processes. Another solvent trapping process for CO_2 capture is the Rectisol process. The Rectisol process (Figure 1) uses cold methanol to trap acid gases such as CO_2 from contaminated gas streams [43–45]. The Fluor process employs propylene carbonate ($C_4H_6O_3$) and CO_2 partial pressure for removing CO_2, while the Selexol process makes use of dimethyl ethers of

polyethylene glycol in trapping CO_2 at pressures ranging from 2.07 to 13.8 MPa.

The use of Purisol, Rectisol, Selexol, etc., is common in the oil and gas industry, and they are often preferred over chemical solvents at high acid gas partial pressures. Choosing the right solvent for natural gas sweetening seriously depends on factors such as gas composition, temperature, and partial pressure of gas, as well as the product specs. The works of Tennyson and Schaaf [46] and Kohl and Nielsen [45] are recommended for due consultation by readers. Over a wide range of conditions, aqueous amines are suitable for acid gas absorption from natural gas; however, these solvents still have some serious shortcomings, which include high energy costs for solvent regeneration [47], low CO_2/H_2S selectivity, corrosivity, and high volatility. This, however, sparked off the need for other viable alternatives which in turn ushered in the era of ionic liquids. Considering the past few decades, a huge chunk of studies have discussed the solubility of CO_2 relative to other acid gases in several ionic liquids [34, 48]. However, evidence has shown that, for high gas absorptivity of CO_2 in ILs, CO_2 solubility is trivial relative to the selectivity because the latter gives more credence to the degree of separation obtained from an absorption process [48]. In clear terms, considering the opinions of experts, despite the essentiality of both parameters, CO_2 selectivity is more dependable relative to its influence on the absorptivity of ILs. In another study, CO_2 absorption-desorption rates in polyionic liquids (hybrid system) were reported to be much faster compared to those of ionic liquids and the processes are totally reversible [49–51]. The absorptive potentials of ionic liquids, monomeric and polymeric materials, rely on the chemical and molecular structure of the ions/anions that make up the polar ends of the liquids [50]. Generally, ILs are characterized by low vapor pressures, nonflammability, chemical/thermal stability, tunable polarity, reliable electrolytic properties, and easy recycling [52].

A method to determine the bubble-point pressures of CO_2 and CH_4 at temperatures of 303.15 and 363.15 K and at pressures up to 14 MPa using the Peng–Robinson Equation of state and the van der Waal's mixing rule, in ionic liquids, was established by Ramdin et al. [53]. The solubility of CH_4 was estimated to be 10 times lower than that of CO_2 on a mole fraction basis. Furthermore, Henry's constants for CO_2 and CH_4 for all the ionic liquids (ILs) were used to determine the ideal CO_2/CH_4 selectivities which gave values comparable to those obtained for the Selexol, Purisol, Rectisol, Fluor, and sulfonate solvents. The estimated CO_2/CH_4 selectivity decreased at increased temperature and molecular weight. Genduso and Pinnau [54] also carried out a study that deals with the estimation of the sorption, diffusion, and plasticization properties of cellulose triacetate polymer films in a mixed-gas (CO_2/CH_4) environment.

(2) Chemical Absorption: Methanol Amine (MEA), Caustic Alkali, and NH_3. The Warrior Run coal-fired power station in the United States has a CO_2 capture capacity of about 150 t/d. Amongst the choice solvents for CO_2 capture, MEA is the most widely used amine amongst other members of
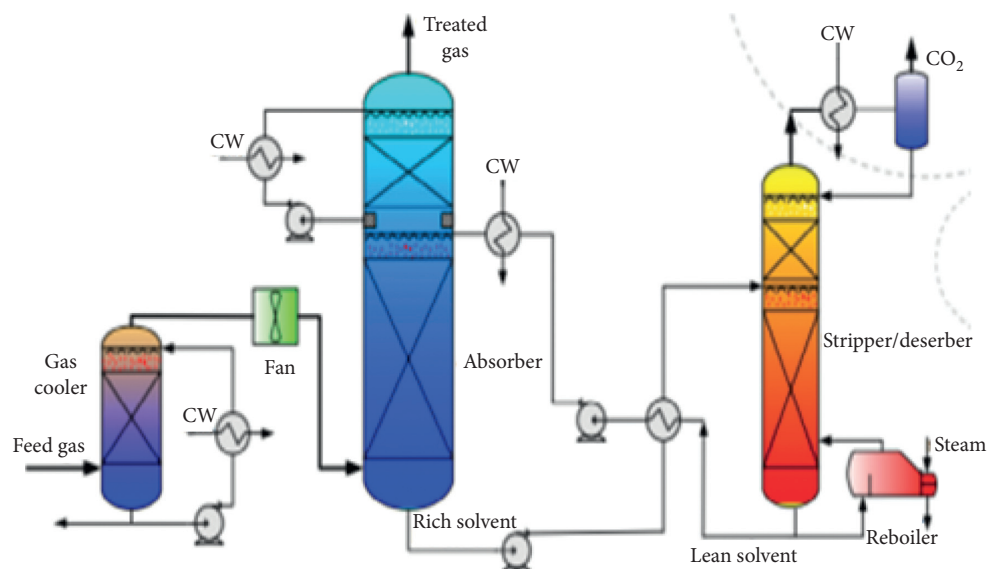
Figure 1: The Rectisol process for gas treatment (reprinted from Sanni et al. [27] and Salako et al. [43]).

the amine family because the CO_2 recovery rate and product purity are as high as 98% and 99%, respectively. However, one major demerit of this method is the tendency for MEA degradation when it is in contact with the oxidising environment of flue gas, whereas the energy requirement for the regeneration of the spent solvents can reduce energy costs by about 40% when compared with the cost incurred from using conventional MEA solvents. Hence, alternative solvents such as sterically hindered amines have been proven to possess good absorption and desorption features with minimal degradation or low solvent loss during carbon sequestration [27].

Till date, the most widely adopted technique for CO_2 capture from postcombustion processes/flue gas involves the use of aqueous solvents such as (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) as well as hybrid systems which comprise of a mixture of more than one amine [55–57] or blends of amines and chemical solvents such as $Ca(OH)_2$ (Figure 2). Gas scrubbing, using alkanol amines, is one of the most widely adopted cost-effective strategies available on commercial scale for postcombustion CO_2 capture [58].

In order to overcome the limitations posed by amine-based solvents for stripping CO_2 from flue gas, they can (i) be doped with 0.1 M $Ca(OH)_2$ + 27.3–30% DEA at pressures of 2–2.7 bar for optimum CO_2 capture of about 98.3–99.6% (Figure 3) or (ii) be replaced with aqueous ammonia for CO_2 separation owing to its inherent lower heat of absorption. In addition, liquid ammonia (NH_4OH) is known to be able to trap impurities such as NO and SOx that are present in the gas stream. However, one major setback associated with the use of ammonia-based solvents is the recurring need of lowering the flue gas temperature prior to it being introduced in to the absorption column; this helps to abate the ammonia losses that would have ensued if the flue gas was introduced into the absorption column at higher temperature. High gas temperature increases the energy

requirement of a large volume of flue gas that is yet to be treated [59]. Another limitation associated with the use of liquified ammonia for CO_2 capture is that the chilled ammonia may foul heat exchangers as a result of the deposition of ammonium bicarbonate from saturated liquids [7].

1.2.2. Cryogenic Separation. Cryogenic separation of CO_2 from a gaseous mixture is done via simultaneous cooling and condensation. Cryogenic separation is commercially adopted for streams with >90% CO_2 concentrations; however, the process is not economical for more dilute CO_2 streams. One major limitation of cryogenic separation of CO_2 is the amount of energy required to enforce refrigeration, especially for dilute streams. Also, dehydration of the gaseous stream is a necessary step prior to cooling because it helps to prevent plugging/blockages. In lieu of the aforementioned limitations, cryogenic separation of CO_2 engenders the production of liquid CO_2 as a transport fuel for ships [60]. Cryogenic operations are often compatible with highly pressured/concentrated gaseous mixtures, such as in precombustion or oxygen-fired combustion processes.

To date, cryogenic sequestration of CO_2 is deemed unrealistic owing to the high cooling costs incurred from the process; hence, there is a need for new developments/methods for cutting down the huge costs associated with cooling the gas. The work of Knapik et al. [61] suggests that the cold duty for a CO_2 separation protocol must come from an integrated liquefied natural gas (LNG) regasification or cryogenic air separation system, which takes advantage of an attached CO_2 liquefaction and separation module that helps to ensure the efficient denitrification of natural gas towards ensuring low energy consumption. Natural gas denitrification is a subject that is poorly addressed by the current body of literature; this then flags the extent of the urgency of research works that qualitatively address the subject matter. According to Knapik et al.
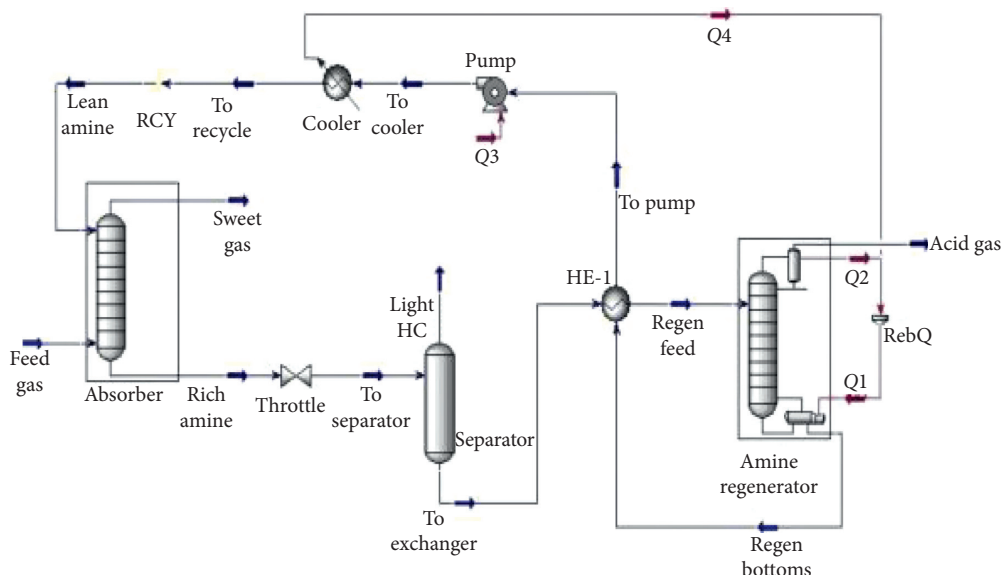
FIGURE 2: Process flow diagram for a DEA-Ca(OH)$_2$ gas scrubbing plant (adapted from Sanni et al. [27]).
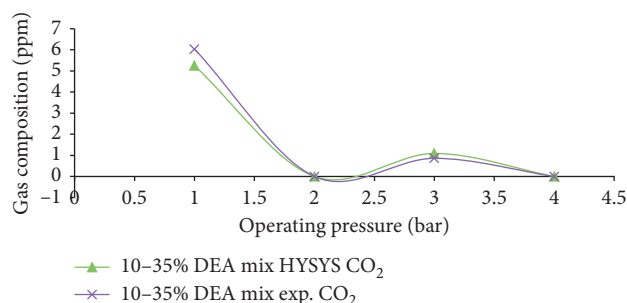
FIGURE 3: Operating pressure vs. CO$_2$ absorption using 0.1 M Ca(OH)$_2$ + 10–35% DEA (adapted from Sanni et al. [27]).

[61], the cryogenic separation of CO$_2$ considers the separation of liquid CO$_2$ from flue gas generated from oxy-fuel combustion. The outlet N$_2$ stream transiting from an N$_2$ removal unit (NRU) serves as the cold stream from the condenser that helps to liquefy CO$_2$. As a result of the low temperature generated from nitrogen expansion, the inclusion of an external refrigeration cycle is not required, and this makes the process somewhat economical. The amount of trapped CO$_2$ from the process is a function of the flue gas composition and operating pressure. Based on their findings, 83.07% CO$_2$ of 99.17% purity can be captured in this process. The energy required for separating the liquified CO$_2$ is 0.125 kWh/kg CO$_2$ or 449 kJ/kg CO$_2$. This novel CO$_2$ separation unit offers a unique opportunity to produce liquified CO$_2$ at moderate conditions; the integration of both cryogenic processes is technically and economically advantageous. Xu and Lin [62] successfully carried out the cryogenic separation of CO$_2$ from flue gas generated from natural gas. They asserted that the hybrid NRU-CO$_2$ capture installation is an innovative concept with good commercialization potential. The optimization of a cascaded thermodynamic system for separating CO$_2$

from liquified natural gas has been investigated [63], while the effect of multiple cryogenic desublimation on the dehydration and decarbonization of natural gas was studied by Ali et al. [64]. Song et al. [65] carried out a study that bothers on the cryogenic separation of CO$_2$ on Stirling coolers via heat integration.

1.2.3. Membrane Separation/Absorption. The performance of membranes for carbon capture processes is measured by the ease with which the component of interest adsorbs onto the surface of the membranes whilst allowing the permeation of other components. Membrane types include porous inorganic membranes, palladium-based, ceramic, polypropylene, polyphenylene oxide/polydimethylsiloxane (for gas separation), polymeric, zeolite, and MOF membranes, which cannot give high degrees of separation, and thus would require the integration of multiple stages and/or recycle streams. In lieu of this, problems such as process complications, energy consumption, and high costs often arise. Hence, solvent-assisted membranes are being developed to combine the best features of membranes and solvent scrubbing. Much development is required before membranes could be used on a large scale for carbon capture in power stations [44].

Polymeric membranes (Figure 4(a)) are classified as dense membranes which include polyimides, polysulfones, and cellulose acetate as well as their derivatives. Another group is one that comprises fixed-site carriers (FSC) (Figure 4(b)); they are made by coating polyvinyl amine on several supports. These membranes ensure high CO$_2$ selectivity and gas permeation/rejection by means of an integrated carrier within the membrane. The third group includes membranes fused with low-vapour-pressure liquids (e.g., K$_2$CO$_3$ or diethanolamine) as supports for housing the immobilized carrier within the membrane pores (Figure 4(c)). The three mechanisms (diffusion, sieving, and
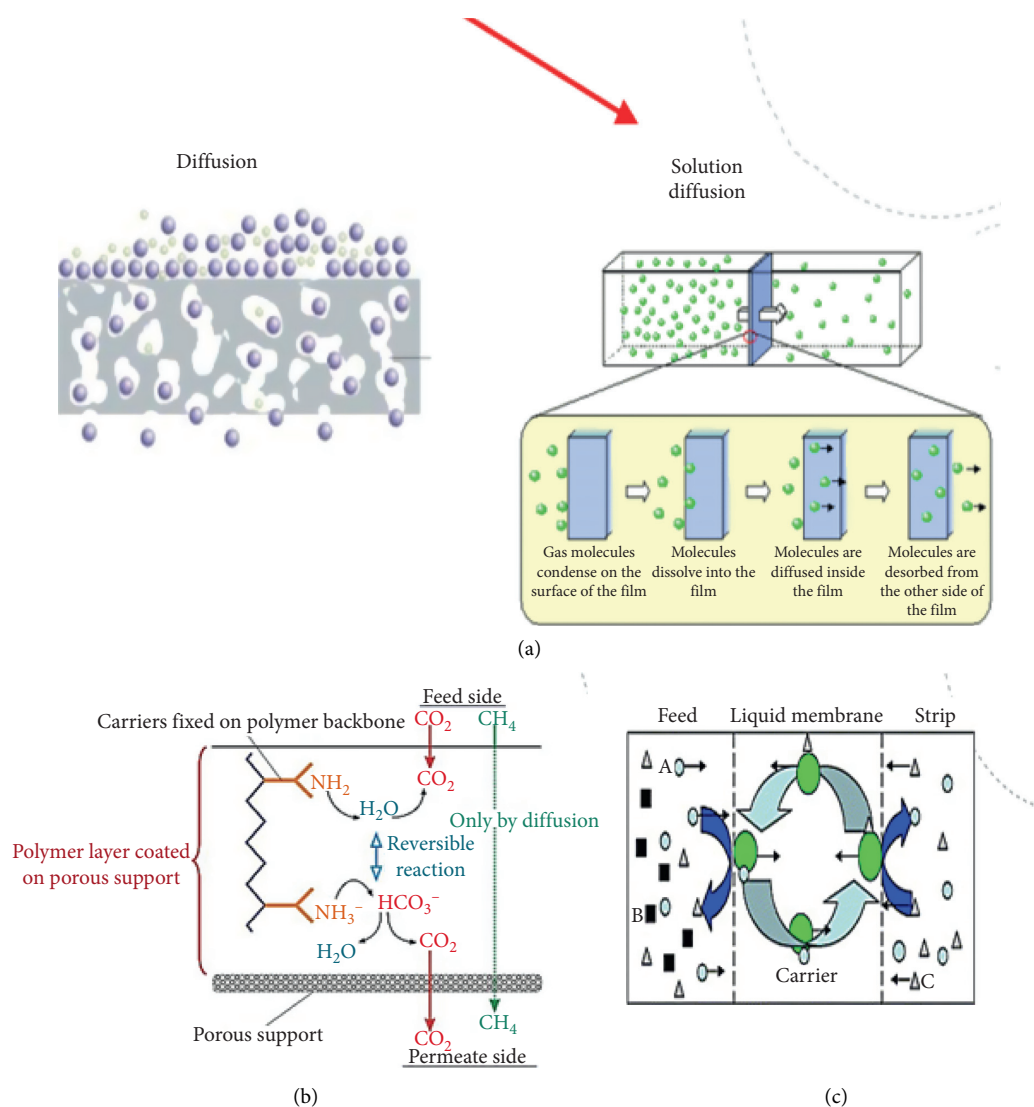
FIGURE 4: Schematic view of (a) dense polymeric membrane, (b) fixed-site carrier membrane, and (c) supported liquid membranes (adapted from Bolland [44]).

solution diffusion) responsible for gas adsorption in polymeric membranes are as illustrated in Figure 5.

In the study carried out by Tan et al. [66], a flexible microporous organic polymer (MOP) tagged BOP-1 was synthesized and functionalized using Cl and NH_2 moieties. Their findings revealed higher CO_2 uptake within a pressure limit of 1 bar, thus giving CO_2-trapped concentrations of 3.94 and 1.60 mmol/g at 273 and 298 K, respectively. At 273 K, the polymer selectivity for CO_2/CH_4 was abrupt, i.e., 568 at 0.02 bar. Considering the experimental and theoretical validations, they asserted that the –CH_2–NH– linker within the polymer framework played a significant role in enhancing CO_2 polymer binding and was thus responsible for the flexibility of the entire framework. Amongst the diverse CO_2/CH_4 sequestration technologies, porous materials are very ideal candidates owing to their high energy efficiencies and low operating costs [67].

For MOFs, some major limitations in their use include the high energy requirement of the solvent regeneration process, thermal stability of the amine system during regeneration, and the presence of impurities that are present in the flue gas stream, which may have some significant effect on the chemical stability and sorption capacity/potential of the solvent [68, 69]. MOFs are a class of porous materials comprising of a network of metal ions/clusters of nodes connected by organic ligands; they have a wide application in gas separation processes [70, 71]. These materials have very high surface areas, ultrahigh porosity, and flexibility, which is imposed by the presence of ligands/connectors [70, 72–78]. One major merit of MOFs over other solid adsorbents lies in their adaptability to pore size tuning and framework functionalization, which are premeditated by carefully selecting suitable ligands, functionality/surface enhancers, metal ions, and the mode of activation. The limitations of MOFs are more pronounced in humid environments and this has led to a probe into understanding their mechanisms of operation during gas adsorption, which has further stimulated the development/integration of novel
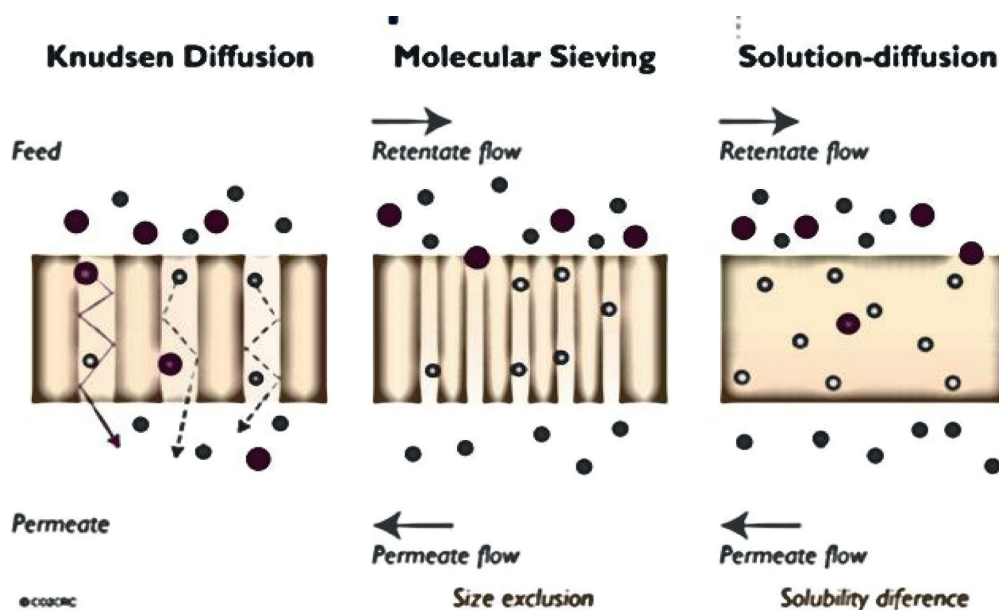
FIGURE 5: Mechanism of diffusion of gas through membrane pores (adapted from Bolland [44]).

structures, hybrid systems, and technologies as means of improving their adaptation to such environments. The strategies adopted in improving the performance of MOFs include the following.

(1) The Opening up of Metal Sites. This involves the removal of solvent molecules connected to metal nodes by the creation of a vacuum or application of heat after synthesizing the metal framework during chemical activation. The presence of open metal sites in MOFs impacts their CO_2 selectivity and the binding energy between adsorbed CO_2 molecules and the MOF surface. This helps to open metal centers/binding sites where CO_2 molecules can become attached and bind the pore surface via dipole-quadrupole interactions. A method that helps gain insight into the interactions between trapped CO_2 and the ionic force field generated by open metal sites in MOF-74 has been developed. The procedure adopted allows for the accurate estimation of the adsorption isotherms that enhance the subsequent evaluation of the hypothetical open metal sites in MOFs [79]; the findings corroborate the results of Kong et al. [80]. Some widely used MOFs include HKUST-1, M-MIL-100, M-MIL-101, and M-MOF-74, where M represents the metal site. In order to accurately determine the influence of open metal sites in MOFs, it is expedient to isolate the effects contributed by the organic ligand, the synthetic route, and the nature of the inherent functional groups present in the MOF framework. For M-MOF-74 subjected to low pressures, some authors have confirmed the suitability of light metal sites for its surface area enhancement alongside its CO_2 uptake [81]. An examination of the effect of metal centers in M-MOFs was done using a computational approach [81–83] that portrays Rh, Pd, Os, Ir, and Pt as ideal candidates for enhancing CO_2 capture within MOFs. Casey et al. [84] carried out an investigation on the adsorption mechanism and electrostatic force field created by metal centers comprising of Mo, Ni, Zn, Fe, Cu, and Cr in the isomers of HKUST-1. They observed that divalent metals such as Mg^{2+} helped to improve the binding potential of CO_2 which in turn enhanced CO_2 selectivity. It was also observed that the mode of activation of the metal matrix also influenced the MOF's affinity for CO_2; their results also support the findings in the work of Llewellyn et al. [85], in which they confirmed the effect of different activation methods on CO_2 loading using MIL-100 and MIL-101. The interaction of CO_2 and unsaturated Cr(III), V(III), and Sc(III) metal sites in MIL-100 framework was studied using variable-temperature infrared spectroscopy. The estimated adsorption enthalpies for Cr(III), V(III), and Sc(III) were −63, −54, and −48 kJ/mol, respectively; these are the highest ever-recorded CO_2 adsorption enthalpies on MOFs with open metal centers [86]. The work of Sumboon et al. [87] involves the synthetic characterization of M-DABCO metal series (M = Ni, Co, Cu, and Zn), in which they systematically tested the effect of different metal centers on surface area, pore volume, and CO_2 uptake. They asserted that, of all the tested metals, Ni-DABCO possessed the highest pore volume and specific surface area as a result of the high charge density concentration at the metal center. A close comparison of the M-DABCO with MIL-100(Cr) and an activated carbon (AC) sample showed that the presence of the unsaturated cations gave CO_2 uptake of $180 \, cm^3/g$ as compared to the values obtained for the Cr and AC samples which are $60 \, cm^3/g$ and $30 \, cm^3/g$, respectively [88].

(2) Presynthetic Modification of Organic Ligands. Organic ligands/linkers are the functional bridges that help connect a network of metal nodes; hence, they are responsible for the final outlook of the framework structure, pore volume/pore window, and surface area, which are highly essential for the successful sequestration of CO_2. Ligand functionalization infuses some active functional groups into MOFs which

subsequently ease the organic ligand modification by the inducement of strong covalent interactions. Torrissi et al. [89] modelled the impact of some functional groups attached to ligands using the density functional theory (DFT). The inclusion of amine functional moieties in organic ligands has also been proven to have positive effects on open nitrogen sites within MOF frameworks [90]. The work of Keceli et al. [91] bothers on an amide modification of four biphenyl ligands. However, it was observed that varying the length of the alkyl amide group had a significant impact on the porosity, surface area, and CO_2 containment of the MOF. The activation procedure was also found to have influenced the surface area of the MOF, which was allotted to have been caused by solvent removal from the MOF framework. Yang et al. [92] synthesized three amino-functionalized MOFs from 2-aminoterephthalate (ABDC), Mg, Co, and Sr. The produced MOFs had low surface areas of 63, 71, and 2.5 m^2/g for Mg, Co, and Sr, respectively, which also culminated in low CO_2 uptake of about 1.4 mmol/g at 1 bar and 298 K. However, the MOFs demonstrated high selectivities for CO_2 with the highest being 396 as recorded for the Mg-ABDC, which also corresponds to a high heat of adsorption [92]. Shimizu et al. [93] made use of 3-amino-1,2,4-triazole ligands in designing a 3D MOF structure of characteristic area, pore volume, and CO_2 uptake of 782 m^2/g, 0.19 cm^3/g, and 4.35 mmol/g, respectively, at 1.2 bar and 273 K. Furthermore, the estimated enthalpy of adsorption of the Mg-ABDC was 40.8 kJ/mol at zero coverage, which is very close to the value (48.2 kJ/mol) obtained for a commercial zeolite (NaX) sample. Xiong et al. [94] employed nitrogen atoms and methyl functional groups supported on 5-methyl-1H-tetrazole ligands in synthesizing UTSA-49 framework. The synthesized MOF gave a CO_2 uptake and enthalpy of 13.6 wt.% at 1 bar, 298 K, and 27 kJ/mol, respectively. The results obtained from testing the effects of the triazolate ligands were found to be in close agreement with the findings of Gao et al. [95]. Hence, it becomes very pertinent to gain good insight into the mechanisms behind the synergistic effects offered by the pore-surface-imposed functional groups as well as their size exclusion effects owing to their potential in optimizing the performance of functionalized MOFs.

(3) Postsynthetic Functionalization of MOF-Metal Matrices. Postfunctionalization of MOFs helps guide against the limitations imposed by presynthetic functionalization. However, an accurate control of the process conditions is required, which is aimed at retaining the service life and stabilities of the unstable functional groups during solvothermal synthesis. In addition, the infusion of other functional groups into the synthetic mix may result in the distortion of the metal framework as a result of the improper mixing and steric hindrance that occur during crystallization, thus yielding undesired products. The insertion of functional groups at metal sites at the presynthetic stage of the framework casting may adversely affect the building blocks of the MOF, which may in turn lead to the structural deformation of the crystal lattice of the MOF [96–98]; hence, postsynthetic functionalization is considered a viable approach for combatting the highlighted shortcomings

towards capacitating the resulting MOFs for high carbon/CO_2 capture. Some amine-moiety-modified solid adsorbents [99–102] and MOFs [103, 104] have shown improved CO_2 sorption over their unmodified counterparts. Lee et al. [105] grafted 16.7 wt.% diamine into MOF-74/Mg(dopbdc) at room temperature. The modified MOF exhibited a CO_2 uptake of 13.7 wt.% at 0.15 bar, while McDonald et al. [106] reported a CO_2 uptake of 12.1 wt.% for N, N′-dimethyl ethylenediamine grafted into Mg(dopbdc). The isosteric enthalpy of adsorption of CO_2 ranged from 49 to 51 kJ/mol, thus confirming chemisorption of CO_2 molecules, whose kinetics was determined by the formation of carbamic acid as identified using the Fourier transform infrared (FTIR) spectroscopy. The multicycle adsorption evaluation of the engrafted Mg(dopbdc) only revealed a 3% loss of CO_2 uptake after the 5th cycle; however, the MOF was found to be hydrologically stable with a high CO_2 uptake. The work of Chernikova et al. [107] bothers on the synthesis of a nanoporous fluorinated MOF named "SIFSIX-3-M," where M = Zn, Cu, or Ni, which encompasses a periodic arrangement of fluorine moieties in an enclosed one-dimensional (1D) channel; the synthesized MOF was seen to have a remarkable CO_2 selectivity over CH_4 and H_2 in several gas mixtures. Tables 1 and 2 consist of properties of some MOFs measured at high and low pressures, respectively. Comparing the results in both tables shows that higher selectivities are somewhat guaranteed at low pressures than at high pressures. The highest recorded selectivity was obtained for UTSA-49 in Table 2, with a selectivity of 95.8% at 1 bar and 298 K.

Since studies on the sequestration of other carbonaceous substances are rare in the literature, the three processes itemized in "(1), (2), and (3)" can be tried for the different MOFs discussed in line with their capacities to trap CH_4, $CHCl_3$, CCl_4, CH_2Cl_2, and their compatibilities with the substances.

Reports have it that polymers of intrinsic microporosity (PIM) are also prospective starting materials for the synthesis of ultrapermeable thin-film composite (TFC) membranes. This is because PIMs are known to provide advantages including high fractional free volume (FFV), good mechanical and film-forming characteristics, and excellent processability which provide for high CO_2 selectivity of the material [135]. In lieu of the aforementioned properties, pristine PIMs are usually associated with shortcomings ranging from physical aging to low CO_2/N_2 selectivity (<20) which limit their industrial application. The detrimental aging effect of PIMs is somewhat evident in TFC assemblies, especially in situations where a 90% drop in CO_2 permeance was clearly ascribed to the physical aging of the composite material [136, 137]. In order to offset the aging problem associated with TFCs, a TFC membrane codoped with a polymer of intrinsic microporosity such as the PIM-1 was hybridized with nano-MOFs (i.e., MOF-74-Ni and NH_2-UiO-66 nanoparticles) and adopted for postcombustion CO_2 capture [138]. The design of the TFC membrane comprised of three layers, i.e., (i) a PIM-1@MOF mixed matrix CO_2-selective layer; (ii) an ultrapermeable polydimethylsiloxane (PDMS) gutter layer impregnated

TABLE 1: Properties of MOFs and MOF-based membranes measured at pressures of 8.5–224.99 bar.

| Nomenclature/ molecular formula | Feed composition ($CH_4/CO_2/H_2$) | X ($CO_2:CH_4:H_2$) (wt.%) or as given | High-pressure separation data | | | | | | | |
			BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Adsorptive capacity (%)	P (bar)	T (K)	S_{CO2}	Q	Ref.
UiO(bpdc)	—	79.7 : 12.2 : 5.7	2646	2965	72.5	20	303			[108]
ZJU-32	—	49	3831	49	40		300			[109]
UPG-1	—	72 : 69 cc/g	410	514	11.9	9.8	298	24	24	[110]
Cu3 (H2L2) (bipy)2 .11H2O	—	77 cc/g			6.4	8.5	298			[111]
Cu_3 (H_2L_2) (etbipy) 2 .24H2O	—	77 cc/g			4.7	9.6	298			[111]
NU-111	—	350 : 284 cc/cc feed	4932		61.8	30	298		23	[112]
HTS-MIL-101	—	1112 mg/g	3482		52.8	40	298			[113]
DGC-MIL-101	—	1112 mg/g	4198		59.8	40	298			[113]
UTSA-62a	30/20/5	189 : 270 cc/cc of feed	2190		43.7	55	298		16	[114]
ZIF-7		10.3	312	355	20.9	10	298		33	[115]
{Ag3[Ag5(l3-3,5-Ph2tz)6] (NO3)2}n	—	0.025 : 0.35 mmol/g			12.3	10	298	10.5	19.1	[116]
Basolite® C 300	99.9%	16 mmol/g	1706.42		41.9	224.99	318		18	[117]
Basolite® F300	99.9%	16 mmol/g	1716.46		24.1	224.99	318		19	[117]
Basolite® A100	99.9%	8 mmol/g	1524.8		26.9	224.99	318		9	[117]
MIL-101(Cr)	99.99%	1.17 mmol/g	2549		24.2	30	303			[118]
HKUST-1	99.99%	1.82 mmol/g	1326		26.3	30	303			[118]
DMOF	—	2.5 mol/kg	1980		38.1	20	298	12[a]	20	[119]
DMOF-cl2	—	2.15 mol/kg	1180		26.4	20	298	17	21	[119]

$^*X = CO_2$ uptake

with MOF nanosheets that provides for CO_2 permeance in the range of 10,000–11,000 gas permeation unit (GPU), thus allowing for less CO_2 transport resistance relative to the pristine PDMS gutter layers; and (iii) a third porous polymeric substrate-layer. Furthermore, by blending the nano-sized MOF particles into the PIM-1, the resulting TFC membrane assembly gave high permeation of CO_2 in the region of 4660–7460 GPU with CO_2/N_2 selectivity ranging from 26 to 33 as compared with that of the pristine PIM-1, which gave CO_2 permeance of 4320 GPU with corresponding CO_2/N_2 selectivity of 19. In addition, the PIM-1–MOF-based TFC membrane was seen to exhibit enhanced resistance to aging effect, thus maintaining a constant CO_2 permeance in the region of 900–1200 GPU with CO_2/N_2 selectivity of 26–30 after 8 weeks.

Other works on PIM for CO_2 capture include the work of Bhavsar et al. [139] where ultrapermeable PIM thin-film nanocomposite membranes were anchored on microporous polyacrylonitrile (PAN) supports for effective CO_2 capture. Borisov et al. [136] also carried out an investigation of gas (CO_2/N_2) selectivity in thin-film PIM-1 composite membranes where they established the potential of the membrane for adsorbing both gases. However, it was also observed that the selectivity of the membrane for each gas decreased over the aging period of the membrane. Liang et al. [140] also allotted the performance of multilayer PIM composite hollow fibers to their intrinsic microporous multilayer gutters. In addition, the studies conducted by Tiwari et al.

[141] and Swaidan et al. [142] bother on the examination of the aging period, plasticization, and CO_2 adsorptive performance of a synthetic thin-film and rigid PIM-1 membranes, respectively.

Three-phase mixed matrix membranes comprising of poly (ether-block-amide (PEBA), polyethylene glycol (PEG), and nanozeolite X were produced; the effects of the PEG and/or the nanozeolite on CO_2 and CH_4 permeabilities and CO_2/CH_4 selectivity of the membranes were examined. The CO_2 permeability and selectivity of the membranes were seen to increase with feed pressure and PEG loading. However, at a pressure of 8 bar, the PEBA membrane doped with 30% PEG and 10% nanozeolite X gave the best performance with CO_2 permeability and CO_2/CH_4 selectivity 95 Barrer and 45, respectively [143].

Synthetic ionic liquid (3-di-n-butyl-2-methyl-imidazolium chloride (DnBMCl)) was used in modifying a sample Pebax 1657 surface as a means of strengthening the carbon-carbon bond in the mixed polymer matrix [144]. By the coating method, ZIF-8 nanoparticles produced from different precursor ratios were doped in the matrix of the IL-Pebax 1657 system in order to fabricate the mixed matrix membranes (MMMs). Tests such as SEM, DSC, FTIR, 13C NMR, TGA, and gas permeation analysis were used to characterize and evaluate the performance of the MMMs. Based on the results of the gas permeation tests conducted, increased CO_2/CH_4, CO_2/N_2, and CO_2/H_2 selectivities were observed for the modified DnBMCl-MMM relative to the

TABLE 2: Properties of MOFs and MOF-based membranes measured at pressures of 0.91–1.01 bar.

Nomenclature/ molecular formula	Feed condition ($CO_2:N_2$)	X ($CO_2:CH_4:H_2$) uptake (wt.%)	Low-pressure separation data							Ref.
			BET surface area (m²/g)	Langmuir surface area (m²/g)	Adsorptive capacity	P (bar)	T (K)	S_{CO_2}	Q (kJmol^{-1})	
rht-MOF-pyr		112 : 17 cc/g	2100		12.7	1	298		28	[120]
rht-MOF-1		90 : 16.4	2100		11	1	298		29	[120]
JLU-Liu22		170 cc/g	1487		15.6	1	298		30	[121]
SIFSIX-3-Co	15 : 85	62.6 cc/g	223		10	1	298		47	[122]
SIFSIX-3-Ni	—	64.5	368		10.3	1	298		59	[122]
$\{[H_2N(CH_3)_2]4 [Zn9O_2 (BTC)6 (H2O)_3].3DMA\}cn$	—	99 : 63 cc/g	844	1132	10.9	0.91	298		29	[123]
$\{[NH_2 (CH_3)_2, Cd(BTC)].DMA\}n$	—	32 : 23 cc/g	406	539	6.4	0.91	298	30	34.7	[123]
Ni-DOBDC		2.30 mol/kg	798		18.2	1	298			[124]
Py-Ni-DOBDC		1.64 mol/kg	409		12	1	298		16	[124]
UiO(bpdc)	—	8	2646	2965	8	1	303			[108]
ZJU-32	—	0.1 : 0.01	3831		4.8	1	300			[109]
Zn(5-mtz) (2-eim).(guest) [ZTIF-1]		49 : 13.16 cc/g	1430	1981	8.2	1	295	81	22.5	[125]
Zn(5-mtz) (2-pim).(guest) [ZTIF-2]		29.3 cc/g	1287	1461	3.8	1	295		20	[125]
UTSA-49 10 : 90; 15 : 85; 20 : 80		69 cc/g	710.5	1046.6	13.6	1	298	95.8		[126]
ZJNU-40 5 : 95		108 cc/g	2209		16.4	1.01	296		18.4	[127]
UPG-1	—	22	410	514	2.1	1	298	24	24	[110]
UiO-66(Zr100)		2.2 mmol/g	1390	1644	6.2	1	298		26	[128]
UiO-66(Ti32) and UiO-66(Zr/Ti)		2.3 and 4 mmol/g	1418	1703	6.4	1	298		28	[128]
UiO-66(Ti44)	—	2.3 cc/g	1749	2088	7.2	1	298		34	[128]
JLU-Liu1	—	34.7 : 0.5 cc/g	145	221	5.9	1	298		47.7	[129]
UTSA-62a 30/20/5		189 : 270 cc/ cc of feed	2190		8.1	1	298		16	[114]
Zn-DABCO	60–100 mg	1.87 mmol/g	1870	1902	7.2	1	298		22.4	[87]
Ni-DABCO	60–100 mg	2.17 : 0.51 mmol/g	2120	2219	8.1	1	298		25.8	[87]
Co-DABCO	60–100 mg	1.02 : 0.57 mmol/g	2022	2095	4.1	1	298		29.8	[87]
Mg/DOBDC	40 : 60 v/v	180 cc/g	1415.1		25	1	298		47	[88]
$\{Ag_3[Ag_5(l3-3,5-Ph_2tz)_6](NO_3)_2\}n$	—	7-8 CO_2 molecules/ unit adsorbent (0.39 mmol/ g)			1.6	1	298	10.5	19.1	[116]
$\{Ag_3[Ag_5(l3-3,5tBu_2tz)_6](BF_4)_2\}n$	—	0.37 mmol/g			1.6	1	298	14	15	[116]
Basolite® C 300		2 mmol/g	1706.42		9.4	0.95	318		18	[117]
Basolite® F300		0.5 mmol/g	1716.46		2,4	0.95	318		19	[117]
CPM-5			2187		8.8	1	298	16.1	36.1	[130]
ZIF-68 15 : 10 : 75 ($CO_2:SO_2:N_2$)		1.6 mol/kg	1220		41.3	0.9	298	30	33.3	[131]
Zn_4(bpta)2-1 -		41.95 cm³/g		51	8.2	1.2	298	23	34.82	[132]
Cu_2L (DMA)$_4$ UHP-grade	UHP-grade 99.99%	160 cm³/g	1433		22.2	1	296	41.6	35	[133]
bio-MOF-11	10 : 90 ($CO_2:N_2$)	147 cm³/g	1148		22.2	1	273	123	33.1	[134]
bio-MOF-14	10 : 90 ($CO_2:N_2$)	44.8 cm³/g		17	8	1	273	Extremely high	—	[134]

MM and pristine Pebax 1657 membranes. Also, they asserted that the inferior CO_2 separation ability exhibited by the MMMs in the mixed-gas condition compared to the situation where pure gas was adopted for the test was influenced by the effect of plasticization in the MMMs. In addition, the modified DnBM-Pebax 1657-ZIF-8 MMMs exhibited superior CO_2/CH_4 and CO_2/N_2 selectivities at feed pressures of 2 and 4 bar, respectively. The study by Sutrisna et al. [145] involves the comparison of the operational stability of Pebax modified with ZIF-8 for gas separation with flat sheet and composite hollow Pebax fibre membranes. Also, the modified ZIF-8 was found to be stable alongside the pristine ZIF-8 due to the hydrogen bonds and the polyamide chains present in both samples, and these were reported to have improved the stiffness of the linear glassy polymer chains, thus ensuring good operational stability of the membranes at high pressure for the flat sheet and hollow fibre membranes. In addition, the outstanding long-term stability of the hollow fibre membrane suggests that the ZIF-8/Pebax coating improved the aging resistance of the poly[1-(trimethylsilyl)-1-propyne] (PTMSP) gutter layer. The poly (ether-block-amide) (Pebax) mixed matrix membranes (MMMs) were prepared using size-tunable nanoparticles of ZIF-8 nanofillers (40, 60, 90, and 110 nm, i.e., ZIF-8-40, ZIF-8-60, ZIF-8-90, and ZIF-8-110) synthesized from 98% zinc acetate dehydrate ($Zn(COO)_2 \cdot 2H_2O$) and 98% 2-methylimidazole (Hmim, C_4H6N_2) [146]. The ZIF-8 nanofillers were produced in microemulsion by controlling the ratio of Zn^{2+} to Hmim (1 : 16, 1 : 8, 1 : 5, and 1 : 2). They were then uniformly distributed in the Pebax matrix without visible agglomerations/defects at loadings of 0–20 wt.% as confirmed by FESEM. Based on the results, the ZIF-8 significantly improved the CO_2 permeability and CO_2/N_2 selectivity of the MMM. The enhanced permeability of the MMM was attributed to the induced free/pore volume of the polymer caused by the integration of larger sized ZIF-8. The resulting increase in the selectivity of the MMM was allotted to the high surface area of the ZIF-8 nanofillers, which provided more active sites for CO_2 capture with improved resistance to mass transfer for N_2. For 5 wt.% loading of the ZIF8-90, the MMM had the best CO_2 separation performance with a permeability of 99.7 Barrer and CO_2/N_2 selectivity of 59.6, which both gave a marginal increase of about 25% when compared to the pristine Pebax membrane.

In the work of Beni and Shahrak [147], pristine zeolites (ZIF-8 and ZIF-90) were synthesized and compared with samples of both zeolites functionalized with Li, K, and Na cations. Based on the CO_2 adsorption tests conducted, the Li-functionalized zeolites gave the highest CO_2 uptake for both zeolites and these they allotted to have been enhanced by the interactions (i.e., electrostatic and dispersion interactions) that occurred between the adsorbate and adsorbent molecules which gave rise to higher binding energies. Simulation results also revealed that, at 1 bar and 298 K, the CO_2 uptakes for the Li-functionalized ZIF-8 and ZIF-90 increased by 7 and 9 times over their pristine counterparts, thus giving values of 6 and 9 mmol/g CO_2 uptake, respectively. The Li-functionalized-ZIFs

exemplified chemisorption as informed by their calculated heats of adsorption which also provides vital information for efficient regeneration of the adsorbents in pragmatic situations.

1.2.4. Microbial and Algal Seed Coats: Contextualizing Regenerative Agriculture. Along farmlands on the East Coast of Australia, efforts are being put in place by farmers to test modern approaches of combatting climate change. One of such measures involves planting seeds that are coated with fungi and bacteria with the intent of capturing CO_2 from air [148]; according to reports, the plan is to sink billions of tons of carbon into farmlands. There are also speculations that the coated seeds exhibit a higher carbon capture potential than a carbon capture plant. A start-up firm, known as the Soil Carbon Company, is working on a modern technology whose origin is traceable to the University of Sydney where the annual projections on the carbon sequestration potential of the technology are 8.5 gigatons carbon or one-fourth of the global annual CO_2 emissions in a year. There are also projections that this technology can store trapped carbon for a longer time than some regenerative agricultural carbon capture technologies. Injecting microbes into crops on a farmland/plantation enhances the carbon storage capacity of plants since all plants make use of atmospheric carbon dioxide in their normal carbon cycles during photosynthesis; the absorbed carbon traverses the plant roots before ending up in the soil. However, some of the trapped carbon is fairly lost in the surrounding air. This then informed the idea of coating plant seeds with fungi and bacteria that can convert the trapped carbon into a form that can be stored much longer in soils over a long period of time, say hundreds of years. This technology is promising but is yet to gain full support for commercialization. Based on some findings, the process will enrich the soil and reduce the need for high amount of fertilizers.

Another technology that bothers on the use of microbes is microbial electrolytic carbon capture (MECC) which employs microbial electrolytic cells during wastewater treatment. The process/treatment brings about net negative carbon emissions from wastewater by simply converting the inherent CO_2 in water to calcite/limestone (CaCO3) [149] with the release of high amount of hydrogen gas that can be harnessed for other profitable ventures. CO_2 from anthropogenic sources contributes significantly to the regional dynamics of climate change as a result of the greenhouse gases released into the atmosphere from such processes. Most CO_2 mitigation practices are fossil fuel-based, which give off other compounds such as SOx and NOx during combustion. No doubt, a nation's economic growth relies on its capacity for energy generation and how energy efficient it is, i.e., in terms of energy production for transportation and production of industry goods and services. CO_2 from wastewater processing contributes a small percentage (i.e., about 15%) to the global greenhouse gas emissions [150]; presently, about 3% of the total electricity generated within the US is channeled to wastewater treatment facilities which have a capacity of 12 trillion gallons of wastewater per year.

MECC contributes significantly to sustainable energy practice, owing to the fact that it takes advantage of the properties of the organic constituents of wastewater for eliminating carbon-based compounds/CO_2 in order to produce a precipitate (calcite) alongside H_2 [151]. Operators of wastewater treatment facilities are held accountable for their greenhouse gas emissions during wastewater treatment by the Greenhouse Gas Protocol Initiative. For instance, the process is energy-intensive as it requires energy for the aeration process, which in turn releases volatile compounds from wastewater, during the agitation and transportation of polluted and recycled fluids within the entire process. The electricity used in wastewater treatment gives carbon dioxide, methane, and NOx gases; the aerobic treatment step gives off N_2O and CO_2, whereas the sedimentation and activated sludge steps produce CO_2 and CH_4.

1.2.5. Adsorption: Packed Beds (Alumina/Activated Carbon/ Zeolite), Graphene, and Monolith-Molecular Sieves (Carbon-Coated Substrate and Carbon-Carbon Fibre Monolith). Solid adsorbents such as zeolite/activated carbon can be employed in trapping CO_2 from gaseous mixtures at high pressures/temperatures. During pressure swing adsorption (PSA), gas flows through one or more packed beds of adsorbent at high pressure until the concentration of the gas progressively attains equilibrium (Figure 6). Thereafter, the bed is regenerated by reversing the pressure, whereas, in temperature swing adsorption (TSA), sorbent regeneration or gas desorption occurs by an increase in temperature. The adsorption of CO_2 onto solid adsorbents is not considered economically viable for the recovery of large volumes of CO_2 from flue gas, due to the low capacity of these adsorbents as well as their CO_2 selectivities [152, 153]. However, hybrid systems or a combination of several carbon capture technologies may become necessary in order to make these processes economically viable.

Zeolites are aluminosilicates with well-defined micro/ ultrasmall porous structures, thermal stability, recyclability, and chemical reactivity [154]. They are rated as high-performing adsorbents [155–158]. Some zeolite networks have been tested for their abilities to trap CO_2 under different humid conditions, and the adsorption process was simulated using the Monte Carlo simulation [159]. Although under wet conditions, a rise in CO_2 uptake of pure zeolites has not been confirmed experimentally, however, there are speculations that the CO_2 uptake of some zeolite structures is expected to rise under moist conditions [12]. For porous adsorbents such as zeolites, CO_2 storage is predominately seen to be caused by adsorbate-adsorbate interactions [159], which is in contrast to the case of selective CO_2 sequestration that is largely influenced by adsorbent-adsorbate interactions or their chemical affinity for CO_2 at low pressures [160].

No doubt, zeolites are potential adsorbents for CO_2 capture; however, their adsorption efficiencies are usually influenced by their chemical constituents/composition, charge density, and pore size. Highly crystalline zeolites with three-dimensional pores and high surface areas can be obtained by controlling the Si/Al ratio in the zeolite matrix.

The notable influence of the presence of alkali/alkaline earth cations in zeolite matrices is another subject yet to be fully explored; thus, optimizing the composition of a sample zeolite may somewhat alter its CO_2 adsorption capacity, which is also justified by the work of Balashankar and Rajendran [161], who optimized a zeolite screening process for postcombustion trapping of CO_2 under vacuum swing adsorption in order to determine the optimal conditions for high efficiency. In lieu of the myriad of approaches adopted for increasing the CO_2 adsorptive capacities of zeolites, they still present some shortcomings which include their relatively low CO_2/N_2 selectivity when compared with their CO_2 adsorption potentials/high hydrophilicity, especially in feed mixtures containing both gases. Nonetheless, the CO_2 absorptive capacities of zeolites may likely decrease especially in situations where the CO_2/N_2 mixtures are entrained with moisture. Also, upon adsorption, zeolite regeneration is only achievable at temperatures (>300 °C) [162].

The CO_2 capture potential of zeolites has been widely discussed owing to their molecular sieving abilities and strong dipole-quadrupole/electrostatic interactions that exist between CO_2 and the alkali/alkali-earth-metal cations (Li, Na, and Al) in the zeolite matrices [163]. These cations influence the heat of adsorption of CO_2, such that it increases with a corresponding increase in the monovalent charge density of the inherent negative charges in the material [164, 165]. Zeolites 13X and 5A have been reported to give high CO_2 retention/performances in the range of 3–25 wt.% at room temperature and a CO_2 pressure of 100% [3, 166–168]; they also recorded a CO_2 capture of 2–12 wt.% at room temperature and a CO_2 partial pressure of 15% [169–171]. Cavenati et al. [172] demonstrated the ability of zeolite 13X as a suitable adsorbent for CO_2; they recorded a CO_2 capture of 28.7 wt.% and CO_2/N_2 separation capacity of 3.65 at 298 K and 10 bar. The work of Jadhav et al. [173] bothers on the modification of zeolite 13X using monoethanolamine (MEA) impregnation in order to improve its CO_2 trapping capacity. The CO_2 adsorption capacity of the modified zeolite 13X was seen to be better than that of the pristine zeolite by a factor of about 1.6 at 303 K, while at a temperature of 393 K, the efficiency was seen to improve by a factor of 3.5. However, in lieu of the reduction in pore volume and surface area that ensued from the MEA impregnation, they asserted that the improved capacity of the modified zeolite 13X was due to the chemical interactions between CO_2 and the infused amine groups. Zeolites 13X and 5A impregnated with LiOH (LEZ-13X and LEZ-5A) were used to trap CO_2 under ambient conditions. Based on the BET analysis, the surface areas of the LiOH-doped sorbents were much smaller than those of the undoped zeolite. Also, the LiOH-doped zeolites gave higher CO_2 adsorption relative to the bare zeolite when in contact with air/oxygen. An optimization of the optimum moisture content for maximum CO_2 removal was carried out by correlating the measured relative humidity (RH) with CO_2 uptake [174].

Some recent advances in the use of graphene have also shown its potential as a suitable adsorbent for GHGs/CO_2. Graphene is a 2D super carbon-based allotrope with Sp^2
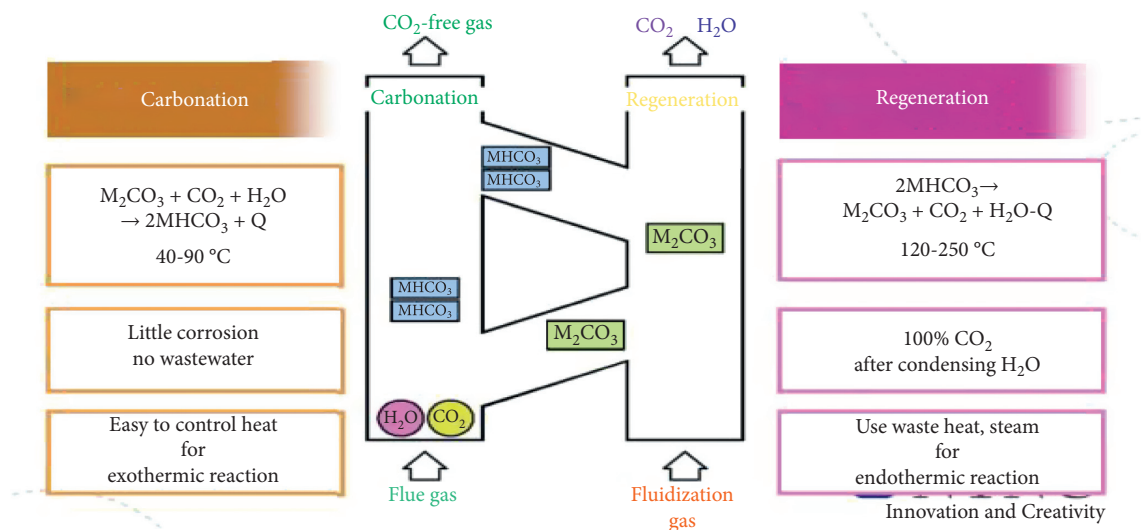
FIGURE 6: Dry sorbent CO_2 capture with fluidized beds and adsorbent regeneration (adopted from Bolland [44]).

hybridized atomic layers [175]. Graphene and its derivatives are potential materials for effective CO_2 capture [176–181]. According to Kemp et al. [182], this happens by reason of the grafting of compatible functional groups onto graphene layers, thus giving rise to highly stable N-doped graphene composites with surface areas in the region of $1336 \, m^2/g$ and reversible CO_2 capacity of 2.7 mmol/g at 298 K and 1 atm for repeated adsorption cycles. Oh et al. [183] studied the performance of borane-modified graphene; they reported a CO_2 uptake of 1.82 mmol/g at 1 atm and 298 K. New hybrid systems such as mesoporous graphene oxide (mGO)-ZnO nanocomposite [184], mesoporous TiO_2-graphene oxide nanocomposites [185], Mg-Al layered double hydroxide (LDH) graphene oxide [186], MOF-5-aminated graphite oxide (aGO) [187], UiO-66-graphene oxide composites [188], as well as MIL-53(Al)-graphene nanoplates (GNP) [189] have shown improved CO_2 adsorptive properties over their nonhybrid counterparts. Table 3 gives a summary of the advances made in different categories of carbon sequestration technologies.

The certification of materials as good adsorbents for CO_2 separation from flue gas depends on the following criteria:

(i) Adsorptive capacity: this gives information on the quantity of CO_2 that can be trapped on the surface of the solid adsorbent. It is defined as the gravimetric or volumetric uptake of CO_2 per unit mass of adsorbent (i.e., grams or volume of CO_2/grams of adsorbent). This dictates the amount of sorbent as well as the size of the adsorbent/packed bed required for a particular operation. The adsorptive capacity of a solid adsorbent determines the energy required during the adsorbent regeneration step.

(ii) Selectivity: this is defined as the CO_2 uptake ratio with respect to another gas (i.e., N_2 during post-combustion CO_2 capture or CH_4 in CO_2 sequestration from natural gas). The adsorbent selectivity for carbon-based compounds has a resultant effect on the purity of the adsorbed gas [190]. The simplest approach for estimating the selectivity of a solid adsorbent is to evaluate its adsorption profile based on the single-component adsorption isotherms of CO_2 and N_2.

(iii) Enthalpy of adsorption: this is the amount of energy required to regenerate the solid sorbent, which in turn impacts the cost of the regeneration process. It also measures the affinity of the material for CO_2/target-substance in relation to the strength of the adsorbate-adsorbent interactions.

(iv) Chemical, physical, and thermal stabilities: excellent solid adsorbents must be able to demonstrate high stability when in contact with the contaminated streams, especially during the adsorption-regeneration cycle [191].

(v) Hydrostability: essentially, hydrosorbent stability is a necessary requirement for the sustainable performance of solid adsorbents in contact with water vapour. Furthermore, the thermal capacity and conductivity of the adsorbent are also essential properties for solid adsorbents during mass transfer operations.

(vi) Adsorption-desorption kinetics: the time taken for adsorption and adsorbent regeneration greatly relies on the profile of the adsorbate adsorption-desorption kinetics, which is determined by breakthrough curves. Adsorbents that adsorb and give off adsorbates with ease upon regeneration are more often preferred, owing to the fact that these can be achieved within shorter cycle times for small quantities of adsorbents, which in turn influences the overall cost of trapping the adsorbate.

(vii) Cost of adsorbent: since several adsorbents that exhibit excellent sorption attributes are readily available at low costs, they are rather deemed the most ideal candidates for CO_2 capture. In lieu of the advantages gained from the cheap nature of these

TABLE 3: Summary of advances made in the categories of carbon sequestration technologies.

S. no.	Categories of carbon sequestration technologies	Process type/solvent	Trapped carbonaceous gas	Refs.
		Physical absorption		
		Selexol: ethers of polyethylene glycol	CO_2	[36]
			CO_2	[44]
		Rectisol: (CH_3OH)	CO_2	[34]
		Fluorinated solvents: ($C_4H_6O_3$)	CH_4	[53]
1	Physiochemical absorption	Purisol ionic liquids	CO_2/CH_4	[27, 53]
		Chemical absorption		
		Monoethanolamine (MEA)	CO_2	[55]
		Diethanolamine (DEA)	CO_2	[27]
		Methyl diethanolamine (MDEA)	CO_2	[56, 57]
		$Ca(OH)_2$+DEA	CO_2	[27]
2	Cryogenic separation	*Air separation system*	CO_2	[60, 61]
		Adsorption		
		MOP: (BOP-1) functionalized with Cl and NH_2 moieties	CO_2/CH_4	[66, 67]
3	Membrane separation	MOFs: (i) With open metal sites	CO_2	[70, 71, 81, 82]
		(ii) With presynthetic modification of organic ligands	CO_2	[91–93]
			CO_2	[99, 102, 107]
		(iii) Postsynthetic functionalization of MOF-metal matrices	CO_2 and CH_4	[107]
4	Microbial and algal seed coats	*Regenerative agriculture* (MECC)	CO_2 and CH4	[151]
		Zeolite/activated carbon	CO_2	[44, 152, 153]
		Graphene		
		(i) Pristine graphene	CO_2/GHGs	[181]
		(ii) N-doped	CO_2	[182]
		(iii) Borane-modified graphene	CO_2	[183]
5	Adsorption	(iv) Mesoporous graphene oxide (mGO)-ZnO nanocomposite	CO_2	[184]
		(v) Mesoporous TiO_2-graphene oxide	CO_2	[185]
		(vi) Mg-Al layered double hydroxide (LDH) graphene oxide	CO_2	[186]
		(vii) MOF-5-aminated graphite oxide (aGO)	CO_2	[187]
		(viii) UiO-66-graphene oxide composites	CO_2	[188]
		(ix) MIL-53(Al)-graphene nanoplates	CO_2	[189]

materials, the environmental impact of their synthetic routes is a major hurdle that needs to be overcome. As previously mentioned, some solid adsorbents that have been adopted for the trapping of carbonaceous substances/CO_2 include activated carbon (AC), single/multiwalled carbon nanotubes (CNTs), and graphenes. ACs are inexpensive, porous-amorphous structures, which possess high specific surface areas that serve as gas traps for greenhouse gas (GHG)/CO_2-uptake [192–194]. Unlike zeolites, one of the basic ills associated with the use of ACs for CO_2 adsorption is that there are no active sites for the gas to bond with the adsorbate as orchestrated by the presence of cations in zeolite. Weak interactions result in low enthalpies of adsorption and sorbent regeneration. ACs give very low CO_2 uptake at reduced pressures due to the absence of electric fields on the surfaces of ACs. Kacem et al. [195] carried out a study to test the capacity of ACs and zeolite for CO_2 separation from N_2 and CH_4 based on their regeneration potential, reusability, and adsorptivity. They observed that the CO_2 uptake for ACs was far higher than that of zeolites at pressures above 4 bar. The amount of CO_2 recovered at the AC regeneration stage was purer compared to that recovered from the zeolite samples. In addition, the ACs were found to be more stable in the presence of water vapor, thus resisting any framework collapse [196].

To improve the performance of ACs for CO_2 adsorption, amines have been found to be very effective [197–200]. Maria et al. [201] modified the surface of a microporous AC of 80% active surface via the simultaneous grafting of amine and an amide onto its surface. The work of Gibson et al. [202] bothers on the impregnation of polyamine within the pores of carbon, where the CO_2 adsorption was seen to be 12 times that of the undoped carbon. CO_2-uptake by AC has been enhanced by direct impregnation with chitosan and triethylenetetramine onto AC surface, where about 60 and

90% increment in CO_2 uptake were recorded at 298 K and 40 bar. The performance of NH_3-modified ACs have been investigated at 1 atm and within a temperature range of 303 to 333 K [203]; reports from the investigation showed that the calculated enthalpies of CO_2 adsorption for the modified AC and the piristine AC are 70.5 kJmol^{-1} and 25.5 kJmol^{-1}, respectively, thus indicating that the adsorption process is largely due to chemisorption. At 303 K and 1 bar, the recorded selectivity and adsorption capacity of the NH_3-modified AC gave corresponding CO_2 uptake of 3.22 mmol/g for the NH_3-modified AC and 2.9 mmol/g for the un-modified AC [203]. CNTs are very friendly with amine solvents, such that when combined, they are very efficient in the trapping of CO_2 [204–208]. Liu et al. [204] synthesized industry-grade CNTs that were functionalized with tetrae-thylenepentamine (TEPA). The effect of the amine loading on CO_2 uptake, enthalpy of adsorption, and adsorbent re-generation was investigated. The TEPA-impregnated CNTs gave a CO_2 adsorption rate of 3.09 mmol/g adsorbent at 343 K. A similar investigation was conducted using 3-aminopropyl triethoxy silane (APTES) [209], poly-ethylenimine (PEI) [206], and di-/tri-ethanolamines [210].

2. Future Considerations for Carbon Capture Systems

No doubt, in the near future, greenhouse gas emissions will continue to constitute a global menace to the earth's climate, her populace, and the ecosystem. However, over decades, the literature reveals that concerted efforts were channeled to-wards abating/controlling CO_2 emissions owing to the large volume of CO_2 released from fossil fuels. On a unit basis, the amount of other gaseous constituents can be somewhat significant, hence the need to look into trying out some of the methods developed for CO_2 capture for their likelihood of being compatible with other greenhouse gases. This then suggests that new methods or modified versions of some existing methods may become necessary in order to achieve this expectation. In addition, there is a need to have a clear understanding of the chemical structure of these gaseous constituents (HCl_3, CCl_4, H_2Cl_2, CH_4, etc.) and how porous materials can be engineered to ensure their entrapment. The framework of some choice MOFs can be tuned to make them have high selectivity with respect to a target component relative to other gases. For instance, if CH_4 is the target gas to be trapped, the matrix of a choice MOF has to be tuned to ensure its selectivity for CH_4; the same goes for membranes where high functionalities can be achieved via doping the membranes with nanoparticles or activating them with ionic liquids. This hybrid approach helps to combat the ills as-sociated with using one type of approach per operation because a hybrid system offers the combined abilities of different blends to trap these gaseous constituents. Some of the challenges associated with CO_2 capture during post-combustion capture have also been pointed out to include low CO_2 partial pressure, high flue gas temperature, and high CO_2 concentration in the gas. Also, as already dis-cussed, aqueous amines are suitable for acid gas absorption, but their shortcomings (high costs of solvent regeneration,

low CO_2/H_2S selectivity, corrosivity, and solvent volatility), these have spiked up a revolution in technological advances, where ionic liquids can be used alongside membranes or MOFs for improved adsorption of not just CO_2 but other greenhouse gases.

3. Conclusion

Carbon capture systems have proven to be very helpful in reducing the global carbon footprint of the earth. Based on the recent advances recorded in the use of membranes of high thermal, hydrological, and chemical stability, as well as ionic liquids, MOFs, and other solid adsorbents, it is clear that no one adsorbent is an all-time solution to all the greenhouse gas emissions. It then suffices to say that the best solution still lies in creating optimized hybrid capture systems comprising of one or more combinations of MOFs with methyl functionalized ligands [119] + inorganic/ionic liquids; bionanocomposite mem-branes comprising of rGO + DEA or K_2CO_3/$Ca(OH)_2$ + DEA; and zeolite + ionic liquids, etc., for effi-cient trapping of greenhouse gases.

Despite the potential of each material as a stand-alone technology, the recommendation of the novel hybrid sol-vents often drifts towards lower energy costs, low solvent loss, low fouling tendencies, and regeneration requirements compared to those associated with conventional amine solvents and this is due to the inherent phase changes that are usually associated with ionic liquids/nonaqueous sol-vents and enzyme-activation systems which are all prom-ising technologies. For mixtures of low carbon dioxide contents, chemical solvents are usually preferred to physical solvents because physical solvents give better performances at high CO_2 partial pressures.

Also, since the presence of fluorine and chlorine functional groups in polymer-/MOF-based membranes help in the adsorption of CO_2 [121], the functional groups of the adsorbents can also be tweaked in favour of their adsorptive capacities for CH_4 and other carbonaceous gases when polymers/MOFs such as polyhedral metal-organic (PMO) frameworks are being fabricated using super-molecular building blocks functionalized with halogenated solvents of chlorine and fluorine in order to boost their abilities to trap CO_2 and some light hydrocarbons in-cluding CH_4 and C_3H_8. Since a large majority of these systems have been adopted in capturing CO_2, a good in-sight of the underlying mechanisms that help to ensure carbon seizure in these systems or their modified forms will help tailor the properties of these adsorbents to suit their applications to other gases. Based on the findings of this review, better CO_2 adsorption is often recorded at lower temperatures and higher pressures. Furthermore, as a re-sult of the high solubilities of some of these gases in some ionic liquids, these liquids can be selected, functionalized, and integrated into some choice adsorbents for the basic purpose of trapping any greenhouse gas of interest. This will not only help to reduce cost but will in turn maximize the effectiveness and efficiencies of modern-day green-house capture systems.

Data Availability

All data used to support the findings of this study are available within the article.

Conflicts of Interest

The authors are sure that there are no known conflicts of interest as regards the publication of this manuscript.

Acknowledgments

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