

A SYSTEMATIC REVIEW **ON** ADSORBENTS FOR CARBON CAPTURE AND STORAGE **TECHNIQUES**

Abstract

The rise in Industrialization all over the world today has been matched with an equivalent rise in the amount of CO₂ being released to the atmosphere. The deleterious effect of CO₂ ranging from global warming, ocean acidification, sea-level rise, and climate change has inspired researchers to seek ways of ameliorating this negative effect and has led to extensive research on possible adsorbents for carbon dioxide capture. Currently, amine-based CO₂ capture processes are widely used in most process plants for capturing CO₂, however it is prone to so many disadvantages such as high energy cost for absorbent regeneration, corrosion, and loss of amine due to degradation and evaporation during the on-stream period which generates pollutants. This necessitates the need for more research into other possible efficient and less costly **adsorption** materials. This work takes a review on some of these other adsorbents that **have** being extensively studied such as metal salts, metal oxides, hydrotalcites, double salts, carbon, metal-organic frameworks, covalent organic frameworks, carbon nanotubes and mesoporous silica. Parameters noted for these materials are CO₂ adsorption capacity, selectivity, thermal stability, chemical stability, and mechanical stability.

Keywords: **CO₂ capture processes**, *mechanical stability*, *thermal stability*

1.0 Introduction

As more countries industrialize and use more energy to power their economies, the demand for energy worldwide has gradually risen in recent years. The majority of the time, cheap fossil fuels like coal, crude oil, and natural gas are used to meet this energy demand [1]. However, it has been determined that using carbon-intensive fuels to produce electricity is a substantial atmospheric emitter of greenhouse gases such CO₂, SO_x, H₂S, and NO_x. Thus, calls for a reduction in the world's use of fossil fuels have been made repeatedly in the public by civil society organizations, international development organizations, and environmental non-governmental organizations. However, the depiction of the continual rise in crude oil and natural gas consumption throughout the decades indicates that this decline in the consumption of carbon-intensive fuels has not been attained **(Fig.1)** [2]. This is because alternative energy sources have not yet been able to satisfy the world's energy needs, which has allowed for a rise in the use of carbon-intensive fuels.

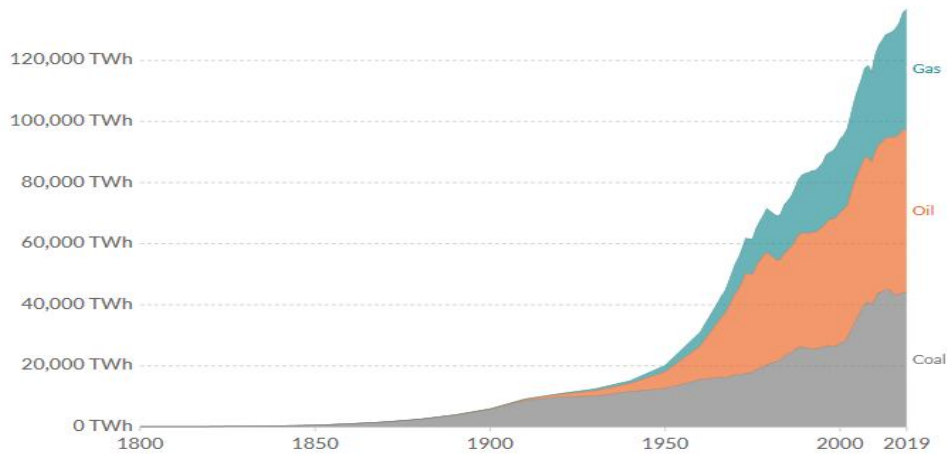


Fig. 1. Global Carbon intensive fuel consumption.

The constant burning of fossil fuels has resulted in the release of significant volumes of CO₂, which is known to be the main greenhouse gas causing climate change [3, 4]. Unfortunately, this upward trend is expected to continue over the next few decades as the EIA notes that worldwide CO₂ emissions from the energy sector will continue to rise by 0.6% from 2018 to 2050 [5]. As a result, this would intensify the global warming effect that already makes extreme weather events like hurricanes, wildfires, melting of the polar ice caps, and biodiversity loss more likely. The statistics released by NOAA, which showed that in October 2020, the global CO₂ concentration stood at 411.29 ppm [6] as opposed to pre-industrial levels of 220 ppm [7], supports the notion of rising atmospheric CO₂ concentration. Since environmental degradation and extreme weather events are more common, it is important to limit the emission of the dangerous gas and lower its atmospheric concentration. Diverse technical approaches are being investigated in this area to lower CO₂ emissions into the atmosphere. They include (i) reducing energy consumption through improved energy efficiency (ii) using hydrogen and other renewable energy sources (iii) enhancing the use of natural gas and other less carbon-intensive energy sources (iv) enhancing the use of natural carbon sinks (forests and soils), and (v) capturing CO₂ from commercial and industrial systems using Carbon Capture and Storage (CCS) technologies.

The majority of CCS plants use absorption technology to capture CO₂ and their operation involves the use of solvents such as amines, ionic liquids, micro encapsulated solvents, phase change solvents, etc. Owing to the fact that absorption technology has a high CO₂ capture effectiveness of over 90% and is a well-established technique that has been used for years in the oil and gas industry to sweeten acidic gas, it is widely used for carbon capture. However, the energy required to regenerate the solvent in the regeneration column for reuse in the absorption column means that absorption technology has the disadvantage of high energy consumption. It is therefore vital to look into remedies that address this issue, enable minimal energy usage, and guarantee energy efficiency. It has been demonstrated that

adsorption technology uses lower regeneration energies than absorption technology does, and this has made it a popular research topic [8]. The adsorption method for CO₂ would be highlighted in the next part due to the low energy of regeneration and other qualities like high surface area, porosity, and stability, etc. In addition, various industrial processes that show promising applicability for these adsorbents would be highlighted in accordance with a detailed discussion of the various state-of-the-art adsorbents used for carbon capture. This is particularly due to the fact that such thorough review work on carbon capture by adsorption is still hard to find in the literature.

1.1 Carbon capture by adsorption (CCA)

Adsorption is a surface phenomenon and interaction caused by mass transfer that takes place between an adsorbate and an adsorbent [9]; it is fuelled by the varied properties of the adsorbate and adsorbent and can thus alter desorption between the various constituents, highlighting its reversibility [10]. Adsorption, which is defined as the adhesion of atoms, ions, or molecules from a liquid, gas, or solid to the surface of a solid, takes place when a film forms between the adhered atoms, ions, or molecules and the adsorbent's surface. This film prevents the superficial atoms of the adsorbent from being encapsulated by the adsorbent atoms that are still present. Adsorbates can therefore cling to gaps created by this; however, this is not the case when the bulk volume of the material is being absorbed. Due to the imbalanced forces present at the surface where adsorption occurs, surface energy is typically produced between the constituents as the adsorbate's atoms satisfies the adsorbent's need for bonding. This type of bonding is usually influenced by the type of constituents involved in the interaction and it occurs in two forms – physical bonding (physisorption) and chemical bonding (chemisorption, a process that can be irreversible and reversible). Physisorption is driven by weak intermolecular forces (van der Waals forces, <40KJ/mol) while chemisorption occurs by covalent bonding and electrostatic attraction >40 KJ/mol [11]. Physisorption usually occurs at low temperature, low heat of adsorption and fast adsorption; also, the energy of adsorption is usually small hence the adsorbate and adsorbent are easily separated without using high energy for regeneration [12]. Chemisorption, on the other hand, is driven by processes such as surface complexation, precipitation, and ionic exchange and entails greater heats of adsorption and activation energies. Despite the fact that physisorption and chemisorption typically take place simultaneously [13], these two processes differ from one another (Table 1) [12].

Table 1. Differences between Physisorption and Chemisorption

	Physisorption	Chemisorption
1	The force of adsorption is the Van der Waal's forces	The force of adsorption is the chemical bonding force (covalent bonding and electrostatic attraction)
2	Has a non-selectivity	There is a selective process of

	process of adsorption	adsorption
3	Has a single /multiple layered adsorption	Characterized by single layered adsorption
4	Posses low heat of adsorption	Characterized by a high heat of adsorption
5	The rate of adsorption is Fast	The rate of adsorption is slow
6	The process is unstable	The process is stable

Carbon **capture** by **adsorption** has been extensively explored in order to aid its industrialisation and commercialization due to the capacity of adsorption to permit low energy induced carbon capture processes. The ensuing part will cover several chemisorbent and physisorbent types for CO₂ capture, as it is well documented that adsorption (chemisorption and physisorption) is applicable and suitable for CO₂ collection at post combustion settings. Additionally, new developments with novel sorbents will be emphasized.

2.0 Adsorbents for carbon capture and storage

This section would describe several chemisorbent and physisorbent types utilized for post combustion CCA. The chemistry, thermodynamics, and appropriateness of these sorbents for CO₂ adsorption will be the main topics of discussion. More crucially, technological advancements in designing these materials for better CO₂ capture would also be addressed.

2.1 Chemisorbents

2.1.1 Amine-based adsorbents

Amine-based adsorbents, also known as amino-solids, are porous structures created from amino-compounds and solid sorbents in order to maximize the characteristics of the pristine components for increased CO₂ adsorption capacity and selectivity, decreased energy use and equipment corrosion, and chemical stability in the presence of contaminants like SO_x and NO_x [14]. Diverse amine-based adsorbents exist as a result of the various types of amino-compounds and solid sorbents that are available; some of them include amine modified mesoporous silica, zeolites, activated carbon, metal-organic frameworks (MOF), and carbon-based solids. The higher CO₂ adsorption capacity of amine-based adsorbents in the presence of moisture [15] —a vital component constantly present in flue gas streams from industrial and process systems—increases their viability for process application. This increased CO₂ adsorption capacity is caused by the creation of bicarbonate, which is indicated in Eq. (1), by the allocation of hydroxide (OH⁻) to CO₂ from water, skipping the reaction step shown in Eq. (2) that entails the elimination of hydrogen (H⁺) obtained in CO₂ capture reactions happening in non-

humid circumstances, which results in the formation of carbamate. This process raises theoretical efficiency ($\text{molCO}_2/\text{mol amine}$) to within the range of 0.5 – 1 as against dry CO_2 capture that is limited to 0.5 or below [16]. It is important to note that the kinetic inefficiency of bicarbonate production is the reason why its efficiency is not close to one.



Based on their technique of manufacture and the type of bond produced between amino-functional groups and sorbent materials, these various amine-based adsorbents are divided into three classes (Class 1, 2 and 3 amino-solids) [17].

While selectivity is typically assessed using the well-known Ideal Adsorbed Solution Theory (IAST) or Henry's Law, the adsorption capacity of adsorbents, including amine-based adsorbents, is typically determined via equilibrium/dynamic adsorption study (using adsorption isotherms) and heat of adsorption (using Clausius Clapeyron Equation) (also referred to as single component isotherms). Adsorbents' suitability for industrial use is heavily influenced by these two factors (adsorption capacity and selectivity) [18]. As a result, amine-based adsorbents must have improved adsorption capacity, heat of adsorption, and selectivity at lower CO_2 concentrations that can be found in flue gas streams. The ease with which CO_2 molecules pass through layers of amines in the framework to access amine moieties connected to the adsorbent is what determines the adsorption capacity of amine-based adsorbents [19]. In this regard, a rise in temperature would lower diffusional barriers and boost the sorbent's overall capacity for adsorption; however, once CO_2 molecules bind to the adsorbent, kinetics become less important. By this time, the adsorption capacity is thermodynamically controlled [19], which causes the uptake of CO_2 to decrease as temperature rises. Temperatures between 70 and 75 °C have been found to be the ideal for amine-based adsorbents to achieve their highest adsorption capacities. Above this range, thermodynamic equilibrium would facilitate desorption, which would lower adsorption capacity [20]. The curve below reveals a distinctive form that is impacted by both chemical and physical adsorption, according to analysis of adsorption isotherms of amine-based adsorbents explored by numerous researchers. The type of adsorbent used for amino-functional group support affects the sorbent's adsorption capacity at regions of higher partial pressure, and also illustrates the diminishing influence of chemisorption at higher partial pressures just as physisorption does at regions of low loadings. This is demonstrated in Fig.2 [14].

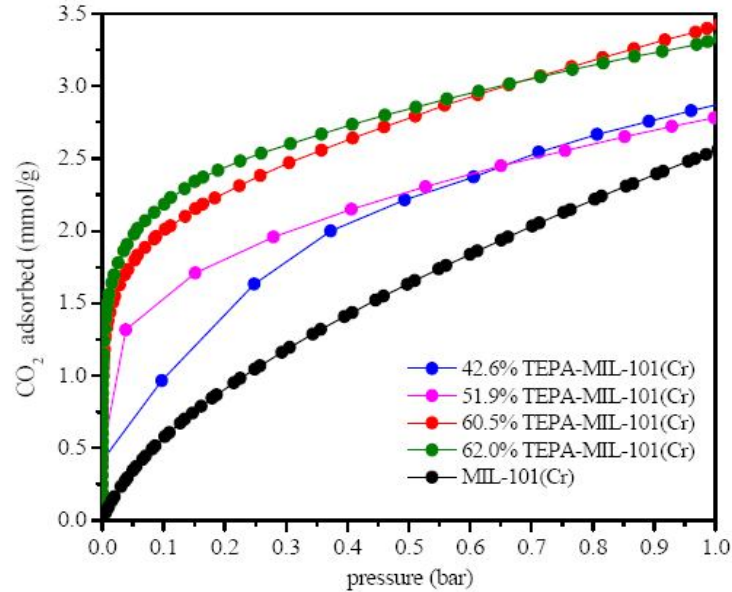


Fig 2. Adsorption isotherms of TEPA-MIL-101(Cr), an amine-based adsorbent shows curve that is influenced by chemical and adsorption; initial high CO₂ uptake at low loading and increased uptake at higher pressures.

All classes of these sorbents must be inert and stable in the presence of various reactants in process systems since the cyclic stability of amine-based adsorbents is essential to their industrial and commercial use (especially in presence of other gases found in practical flue gas mixtures). But this is not the case with Class 1 amine-based adsorbents; this group of sorbents has been found to produce urea because, under certain post-combustion conditions, covalent bonding is absent (typical industrial temperatures above 135°C). Additionally, it has been claimed that this urea production can take place in dry conditions at temperatures as low as 65°C even when there is little CO₂ present in the gas combination [21]. Due to the loss of strong covalent bonds needed for an enhanced reaction when using amines of low molecular weight, Class 1 amine-based adsorbents experience loss of amino-functional groups from the support (leaching) [22]. As a result, high molecular weight amines become desirable for Class 1 amine-based adsorbents, but use of these amines has the drawback of slow diffusion [23]. Aminosilanes and short-chained amines are preferable for Class 2 and 3 amine-based adsorbents because they produce powerful covalent bonds that make them more process-efficient than Class 1 amine-based adsorbents. As a result, it has been shown that these kinds of amine-based adsorbents exhibit stability after numerous sorption cycles. In this regard, MOF MIL-101(Cr) wet-impregnated with TEPA demonstrated stability and continued to possess its original CO₂ adsorption capability [14].

Selected amine-based sorbents previously used are highlighted in Table 2 with a focus on parameters such as adsorption capacity, selectivity, heat of adsorption (critical parameter that determines

regeneration energy and cost of operation), and stability due to their promising potential for CO₂ capture at post combustion conditions.

Table 2. Properties of selected amine-based adsorbents for CO₂ capture

Amine-based adsorbent	CO ₂ uptake			Stability	Adsorbent support	Heat of ads. (KJ/mol)	Ref.
	Ads. Cap. (mmol/g)	T (K)	P (bar)				
MMSV(a)-PEI-60%	4.73	363	-	After ten sorption cycles, good stability		-	[24]
PEI-423/MPS	4.5	348	-	Retained adsorption capability after 5 sorption cycles.		64.3	[23]
SBA-15-NH ₂	0.95	298	-	-	Silica	34.3	[25]
Zn ₂ (dobpdc)(i-2)(i-2-CO ₂)	4.8	298	1	-	MOF	83	[26]
PD-TEPA Monolith	2.23	298	1	After 5 cycles, there was minimal loss of initial adsorption capacity.	Silica	-	[27]
AEEA-55/SiO(OH) ₂	4.54	298	0.1	Following 12 adsorption cycles, a 12% reduction in the initial adsorption capacity was observed.	Nanoporous silicic acid (SiO(OH) ₂)	29.9	[28]
MPS-LA-120	3.86	323	1	After 120 sorption cycles, the amount of pristine adsorption capacity lost was negligible.	Silica	68	[29]
SynA50	1.75	298		Three sorption cycles were the maximum for stability in humidity.	Silica	-	[30]
PD-MAPS_2	0.54	318	-	After five sorption cycles, there was minimal loss of adsorption capacity.	Silica		[31]
0.29EH/PEI-PAM-65	2.93	323		After 50 sorption cycles, adsorption capacity dropped from 2.93 mmol/g to 2.66 mmol/g	Polyacrylamide (PAM) composite beads	56.8	[32]

PEHA-PO-1-2/50S	2.4	358	Epoxide was added to the sorbent, increasing its resistance to oxidation.	Silica	72	[33]
MP-50	2.75	358	After 10 sorption cycles, the adsorption capacity decreased from 2.75 mmol/g to 2.66 mmol/g.	Mesoporous silica nanotubes	-	[34]

2.1.2 Metal Oxides

The integration of CO₂ collection into Integrated Gasification Combined Cycle (IGCC) Plants is being impeded, according to [35], by the unavailability of a cost-effective adsorbent. Other adsorbent substances including zeolites, hydrotalcites, metal-organic frameworks, etc. are the subject of extensive research. Due to its high CO₂ sorption capacity (17.8 mmol/g) and availability in the form of limestone, calcium oxide is emerging as a promising sorbent in the metal oxide class. Because it can adsorb CO₂ at high temperatures, calcium oxide can reduce costs by avoiding the need to cool the gas during CO₂ capture [35]. The reaction between the metal oxides and CO₂ results in the formation of thermodynamically stable carbonates, such as calcium oxide (CaO) and magnesium oxide (MgO). The metal carbonates renew the oxides when heated and release a stream of CO₂ gas. A cyclic process is created by the interaction of exothermic carbonation and endothermic regeneration reaction. In the end, the produced pure CO₂ gas can either be buried or utilised to improve oil recovery [36].

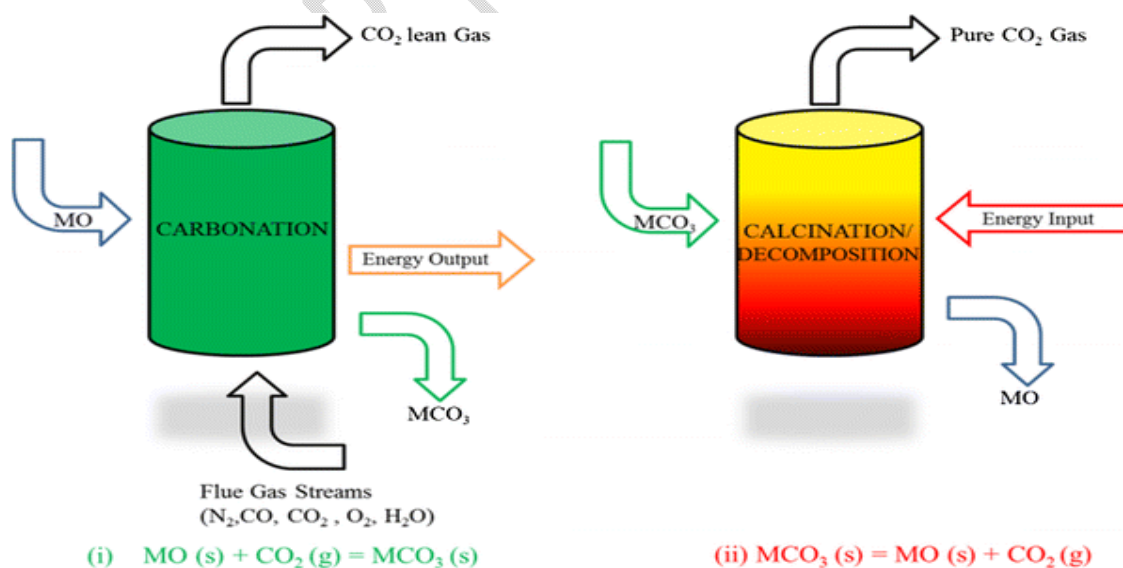


Fig 3: cyclic CO₂ capture process for metal oxides (MgO) and metal carbonates (MCO₃)

Magnesium oxide is an attractive candidate for pre-combustion CO₂ capture due to its favourable temperature window (200-500 °C) [37]. Due to their abundance in nature, low cost of manufacture,

and decreased toxicity, metal oxides are regarded as attractive chemisorbents for CO₂ collection. They work well for CO₂ collection when combined with the basic sites of a few chosen metal oxides that have lower charge or radius ratios, increasing their ionic nature and site basicity [38]. Additionally, research into the use of metal oxides for CO₂ capture has been popular due to their adaptability in a broad range of temperatures, from ambient to roughly 700°C .[39]. The process efficiency of metal oxides in capturing CO₂ is constrained in process applications due to the impact of sintering [38] which lowers sorbent performance, particularly at high temperatures when metal oxides are recycled frequently for best performance. This reduction is made possible by a reduction in pore size, a corresponding alteration in pore shape, and even the closing of microscopic pores during the heating process of recycling. Additionally, it has been shown that the structure of metal oxides has a bimodal pore size distribution as a result of sintering; in this instance, bigger pores are seen [40]. Once more, this is made possible by the recycling process's reduction in surface energy, which causes microscopic pores to enlarge in size.

2.1.2.1 Selection criteria for metal oxides

The selection criteria for metal oxide is usually based on the pre and post combustion technologies and conditions in the power plants. This includes only those solid materials that maybe suited as CO₂ sorbent candidate and further considered for experimental validation, provided they meet the criteria of lowering the energy cost for both the capture and regeneration process and can be operated at desired conditions of CO₂ pressure and temperature.

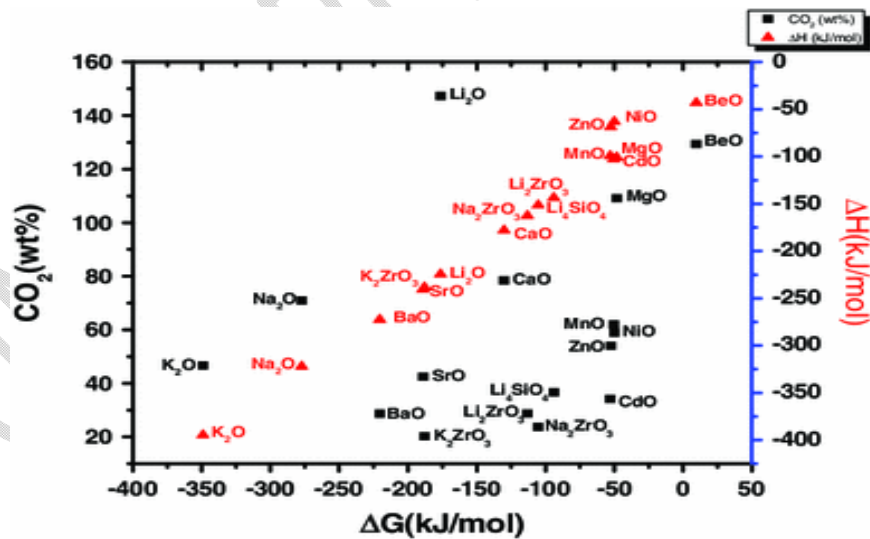


Fig 4: Thermodynamic properties and CO₂ wt% absorbed by different metal oxides at 300K

The thermodynamic characteristics and CO₂ weight percentage absorbed by various metal oxides are shown in the Fig 4 [36]. The figure shows that BeO has favourable thermodynamics, however due to the risks associated with beryllium dust or powder, this system is not a good option for CO₂

collection. It is significant to remember that a strong exothermic forward reaction between the metal oxide and CO_2 necessitates a high temperature for oxide regeneration. To handle the high volume of flue gas stream at any fossil fuel burning plant, a low CO_2 wt% (about 40–50) will call for a significant number of the solid materials. So, a significant energy or carbon emission penalty can be mitigated by a high regeneration temperature and low CO_2 weight percentage. Furthermore, these oxides may not be appropriate for CO_2 capture in any plant because they eventually have a substantial impact on power costs. The optimal sorbents should function to separate CO_2 from H_2 within the pressure and temperature ranges mentioned above in order to minimize energy usage.

Due to the restrictions listed above, only a small number of oxides were selected for experimental validation since they appear promising. Considering their accessibility and advantageous thermodynamics, the two alkaline-earth metal oxides CaO and MgO receive an abundance of attention [36]. The oxides of magnesium, aluminium, chromium, copper, tantalum, iron, barium, cesium, rubidium, potassium, sodium, and lithium are some other metal oxides that have drawn attention but are not covered in this study.

2.1.2.1.1 Magnesium Oxide (MgO) based adsorbent

Magnesium carbonate (MgCO_3) results through the reaction between MgO and CO_2 . At room temperature, MgCO_3 is in a stable thermodynamic state. Kumar and Saxena [36] in their work showed that 0.92 tons of MgO is required to capture 1 ton of CO_2 and as a result, every power plant site will need a significant quantity of MgO in order to remove CO_2 . MgO is a good option for pre- and post-combustion capture systems due to its low regeneration temperatures, $T_2 = 287^\circ\text{C}$ (post-combustion) and $T_1 = 447^\circ\text{C}$ (pre-combustion) [41]. Other advantages include the availability of cheap precursors, the ease of regeneration using temperature swing adsorption, and a moderate selectivity in the presence of steam. Pure magnesium oxide is found in abundance in nature, but it has considerable disadvantages, such as a limited adsorption capacity, a sluggish reaction rate, and poor thermo-mechanical stability [42]. Despite the fact that these disadvantages have reduced the effectiveness of magnesium oxide as an adsorbent, several investigations have been carried out to find solutions.

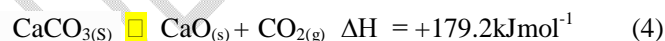
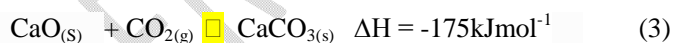
“With regards to adsorption mechanism, the adsorption of CO_2 on MgO is a surface phenomenon which involves acid-base type of reaction. The acidic CO_2 molecules react with the basic O^{2-} sites to form different types of complexes” [37]. Carbonates (monodentate, bidentate, and bridging), carbonate ions, and bicarbonates are among the complexes that can form depending on the circumstances and environment of capture. Monodentate carbonates typically develop at low temperatures due to quick physical adsorption. Because chemical adsorption occurs rather slowly at higher temperatures, the bidentate carbonates are primarily found there [43]. Surface geometry at the atomic level has a significant impact on the strength of basic sites. Low coordination numbers are found in the oxygen atoms near the crystallographic corners and edges of MgO . These atoms are less

complex than those found in basal planes. Thus, at these low coordinated spots, CO₂ will be absorbed more effectively .[42]

The initial stage of adsorption causes a carbonate layer to build on the surface, which prevents additional CO₂ molecules from being absorbed making pure magnesium oxide to perform poorly. Another factor is the pure magnesium oxide's small surface area. Therefore, recent research has been focused on creating magnesium oxide-based adsorbents with improved performance, employing various methods. One of these methods is the synthesis of mesoporous magnesium oxide. Another is the use of a support matrix to help magnesium oxide nanoparticles disperse more effectively. A third method is the synthesis of modified magnesium oxide from molten salts. A fourth method is the use of mixed metal oxides. These performance enhancement strategies were covered in the work of Bhatta et al. [37]. MgO/Al₂O₃ sorbent for CO₂ capture at low temperatures was examined in a fixed bed by Li et al. [44] and the sorbent was shown to have a maximum CO₂ capture capacity at a MgO loading of 10 wt%, which came about as a result of the equilibrium between the sorbent's physical adsorption and chemical absorption. The CO₂ collection capacity with the water vapour initially rose and then decreased. With water vapour concentrations of 0 and 13 vol%, the total CO₂ capture capabilities were generally as high as 0.97 and 1.36 mmol/g at 60 °C respectively. Water vapor's contribution in raising MgO activity is well studied and known now.

2.1.2.1.2 Calcium Oxide (CaO) based adsorbent

According to Eqs. (3) and (4), the reaction of CaO with CO₂ is reversible. CO₂ is adsorbed by CaO in an exothermic carbonation reaction between 500 and 800 °C. The converse endothermic desorption of CO₂ occurs between 800 and 950 °C. Decarbonation or calcination is the term for this [37].



Because they can directly collect CO₂ from high-temperature flue gas and are affordable as well as having outstanding adsorption capability, calcium-based adsorbents have garnered a lot of interest. A severe decline in adsorption performance will result from the calcium-based adsorbents' propensity to sinter after repeated adsorption-desorption cycles [45]. The reversible reaction between CaO and CO₂ forms the basis of the concept called calcium looping. Several other terminologies are also used in the literature for this concept, including carbonate looping, regenerative calcium cycle and Ca-looping. Almost all kinds of CO₂ removal routes could benefit from the use of calcium looping. Calcium looping has several benefits, including the following: (i) reduced efficiency penalty in power plants, (ii) simple application in industry-scale circulating fluidized beds, which is an energy-efficient mature technology, (iii) it can be economically integrated with other carbon-intensive industries (for instance,

cement), (iv) it uses extremely cost-effective, low-risk adsorbent (limestone or dolomite) and (v) it is environmentally friendly and readily available. In light of this, the calcium looping concept is applicable to a wide range of carbon dioxide collection strategies with varied degrees of technological maturity. The calcium looping (CaL) cycle (Fig. 5); [46], is a promising CCS method based on the alternating uptake (in a carbonator) and release (in a calciner) of CO₂ from calcium-based sorbent, most commonly limestone because of its affordability and abundance. The CO₂ in the flue gas generated from a combustion plant is captured by CaO in the carbonator at around 650–700 °C following an exothermic reaction (Fig. 5) [46]. As a result, the carbonator generates a stream of used sorbent, which is a combination of CaCO₃ and CaO, as well as a CO₂-depleted flue gas. Eventually, the used sorbent is fed into the calciner, where endothermic regeneration is conducted at temperatures between 850 and 950 °C. This method regenerates the CaO-based sorbent and produces a CO₂-rich flue gas that is ready for further processing and storage. In order to prevent dilution of the CO₂-rich stream created in the calciner, the heat needed to maintain the endothermicity of the calcination process is often provided by burning auxiliary fuel in the calciner in an oxy-firing mode. In order to provide the calciner with oxygen, this alternative involves coupling the CaL plant with an Air Separation Unit (ASU). If a solid auxiliary fuel, like coal, is utilized, there is an additional problem because the regenerated sorbent must first be separated from ash residues before being recycled to the carbonator. The most common reactor configuration for calcium looping is a Dual Interconnected Fluidized Bed (DIFB) reactor setup, which makes it simple to transport solids between reactors and provides an ideal environment for the development of heterogeneous gas-solid interactions [46].

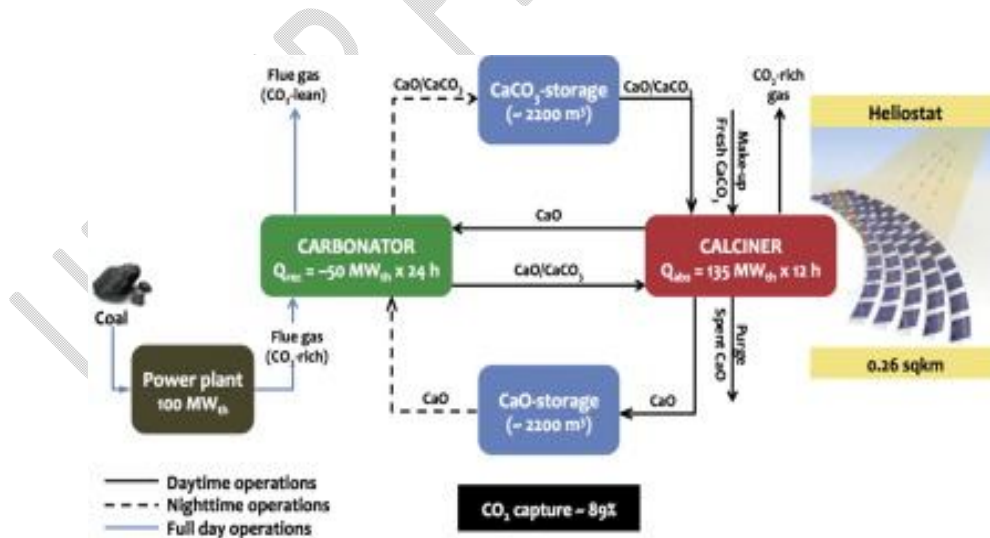


Fig 5. The calcium looping process. source

The stoichiometric adsorption capacity is very high, equating to 78.6 wt% CO₂. However, due to a number of parameters, such as the nature of the precursors, adsorbent particle size, and shape, the real

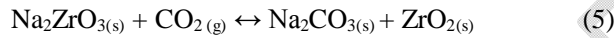
capacity is rather low. Although natural adsorbents like dolomite and limestone are fairly inexpensive, they have a serious attrition problem. The attrition resistance of synthetic calcium oxide-based adsorbents is substantially higher, although they are not as cost-effective as natural ones. Additionally, the cumulative sulphonation process in the presence of SO₂ reduces adsorption capability [47].

2.1.3 Lithium-based sorbents

Lithium based sorbents has been considered for use in CO₂ capture due to their ionic mobility and affinity for CO₂ [48]. These compounds are quite promising and have been thoroughly investigated for their CO₂ adsorption properties. Notably among them are LiFeO₂, Li₂CuO₂, Li₂ZrO₃, Li₈SiO₆ and Li₄SiO₄ [49]. Among these materials, Lithium Orthosilicates (Li₄SiO₄) has serious potential given its higher CO₂ sorption capacity, cyclic stability than LiFeO₂, Li₂CuO₂, and Li₈SiO₆, and lower cost than that of Li₂ZrO₃ [50]. “Additionally, the regeneration temperature of Li₄SiO₄ material is much lower when compared with the calcium-based CO₂ sorbents, indicating that lower energy consumption is required for its regeneration” [50]. Research also shows that the addition of dopants such as Al, Fe, Na, K and Cs increases the CO₂ Uptake of lithium orthosilicate. In an experiment carried out by Walther-Dario et al. [51] using steel metallurgical slags as silica source with and without addition of 10-30wt% K₂CO₃, he observed that the CO₂ Capture efficiency improved with the addition of K₂CO₃ because of the formation of a eutectic phase between K₂CO₃ and Li₂CO₃, which facilitated CO₂ diffusion into the material bulk. The best capture capacity value (104mg CO₂/g material) was obtained using the material produced from steel metallurgical slag with 20wt% K₂CO₃. Also, Olivares-Marin et al. [52] reported that K-doped Li₄SiO₄ obtained using fly ash as source of SiO₂ exhibited a capacity of 101 mg g⁻¹ under optimum conditions (at 600 °C with 40 mol% K₂CO₃). Further studies is focused on decreasing the precursor particle size or choosing more sintering-resistant precursors to result in a smaller product grain size. Such is evident by the recent research done by Rajesh Belgamwar et al. [53] who synthesized lithium silicate nanosheets which showed a high CO₂ capture capacity (35.3wt% CO₂ capture using 60% CO₂ feed gas close to the theoretical value) with ultra-fast kinetics and enhanced stability at 650⁰C. He opined that the nanosheet morphology of the Lithium silicon nanosheets allowed for efficient CO₂ diffusion to ensure reaction with the entire sheet as well as providing extremely fast CO₂ capture kinetics (0.22 g g⁻¹ min⁻¹). It was also reported that the LSNs were stable for at least 200 cycles without any loss in their capture capacity or kinetics and neither formed a carbonate shell unlike conventional lithium silicates which are known to rapidly lose their capture capacity and kinetics within the first few cycles due to thick carbonate shell formation and also due to the sintering of sorbent particles.

2.1.4 Sodium based sorbents

The CO₂ capture properties of certain sodium-based compounds was first reported by Lopez-Ortiz et al. [54] who stated that Na₂ZrO₃, Na₂SbO₃, and Na₂TiO₃ could absorb CO₂ in the temperature range of 600-700 °C. and that reactivity followed the order Na₂ZrO₃ > Na₂SbO₃ > Na₂TiO₃. Sodium Meta Zirconate (Na₂ZrO₃) exhibited better adsorption rate and inferior regeneration performance compared to Li₄SiO₄ and Li₂ZrO₃. With a CO₂ adsorption capacity of 23.75wt% and a lower cost compared to other sodium-based sorbents, Na₂ZrO₃ has gained attention as a good CO₂ adsorbent. They can operate at higher temperature plus a higher reaction rate has also been observed compared to lithium-based adsorbents [54]. Though Na₂ZrO₃ is able to adsorb CO₂ even at room temperature, the best temperature for CO₂ adsorption on Na₂ZrO₃ is said to be 600°C [54]. The adsorption reactions is as shown in Eq. (5).



2.1.5 Hydrotalcites

Hydrotalcites, broadly classified as layered double hydroxides (LDHs), have some distinct characteristics preferred in CO₂ capture technology; the speed with which it attains chemical equilibrium as well as a high regenerative limit contrast with normal calcium oxides [55]. According to temperature tolerance range levels, LDHs are classified as intermediate-temperature adsorbents, with sorption/desorption temperatures reaching 200-400 °C [56]. It is generally denoted as $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{x+} \left[(\text{I}^{n-})_{\frac{x}{n}} (\text{OH})_2 \right]^x$, where: M²⁺ and M³⁺ are divalent M²⁺ (Mg²⁺, Cu²⁺, Zn²⁺, Ni²⁺, etc) and trivalent cations M³⁺ (Al³⁺, Fe²⁺, Cr³⁺, etc), respectively, and Iⁿ⁻ is an anion of valency n which occupies the interlayer region, and maintains electrical neutrality of these materials. The anions range can be further explained as (Iⁿ⁺ = NO₃²⁺, SO₄²⁺, etc), y= 1-(3x/2) and x is the M³⁺/(M²⁺ + M³⁺), with a ratio of (0,14 < x ≤ 0,33) [9,10,11].

Fig. 6 shows an adapted schematic form of LDHs.

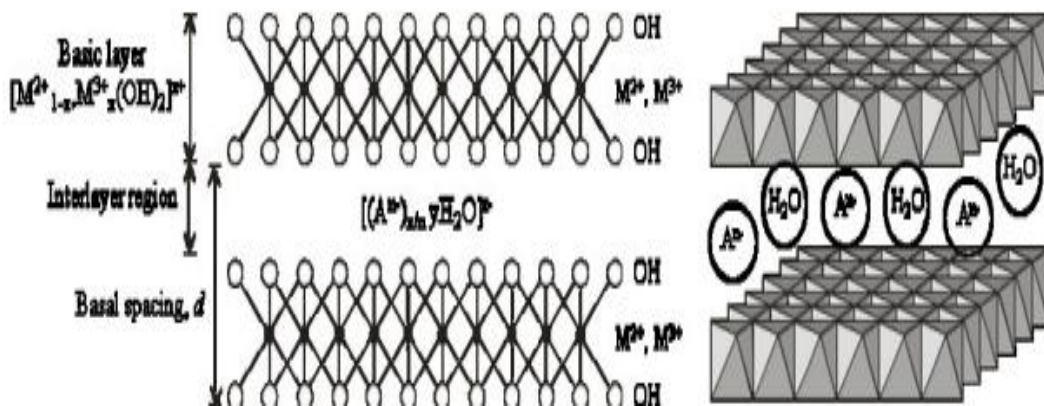


Fig. 6. Structural illustration of LDHs; M²⁺ and M³⁺ (Albuquerque et al., 2016)

Overall, the reduction of the ratio between the metals in LDHs disfavours the exchange kinetic process since it stabilizes the layers and diminishes the efficiency of ionic exchange, modifying the sorption capacity of these compounds. In the past decades, several studies have been done on the adsorption behaviour of CO₂ using layered double hydroxides, hydrotalcite-like compounds, or anionic clays. Some factors influence the sorption capacity of these materials, including type of M²⁺, M²⁺/ M³⁺ (Al³⁺) ratio, the anions present in the interlayer, the water content, the temperature, the cycle number and chemical. On a holistic view, a good performance for an efficient CO₂ sorption requires some important characteristics besides its high sorption capacity, other qualities such as a high stability and a fast sorption/desorption kinetics are equally important. Tang's group [57] concluded that "besides their characteristics, LDHs present in sorption materials are also very interesting including their speed to achieve equilibrium and their superior regeneration in relation to calcium oxides. Previous scholarly works have synthesized specific LDHs together with thermally modified for CO₂ sorption. Some examples of LDHs used for CO₂ capture, as well as their unique sorption capacities have been mentioned (Table 3)".

Table 3. Comparison of the CO₂ absorption capacities of various layered double hydroxides (LDHs), hydrotalcite-like compounds (HTlc) or anionic clays [55].

Materials	Gas Mixture	Adsorption conditions	Adsorption Capacity	Authors
K-HTlc & Mg-Al	CO ₂ /N ₂ , N ₂ and H ₂ O	673-733 K/ 0.0 - 0.7 bar	0.0 to 0.6 mol.Kg ⁻¹	[58]
K-HTlc & Calcined	H ₂ S and CO ₂	400°C and 5 bar	In multiple cycle experiments	[59]
HTlc – NiMgAl & NiMgAlFe	Flow of CO ₂	20°C at 1 atm	1.58 mmol/g	[60]
HTlc & Mg-Al	Flow of CO ₂	200°C at 1 atm	0.58-0.83 mmol/g	[57]
K-HTlc, Mg/Al & K-HTlc – 400 C/6	Ar/He/CO ₂ and H ₂	0.4 MPa	51.4 mg/g adsorbents	[61]
20 wt.% K-HTlc & Mg/Al= 0.6	CO ₂ , H ₂ O	T= 400-450°C 0.0 to 30 bar	0.0 to 1.6 mol.Kg ⁻¹	[62]
25 wt.% K-HTlc & MgAl - 400°C / 6 h	H ₂ , Argon and CO ₂	400 and 300°C / 1.2 MPa	1.01 and 0.6 mmol/g	[63]
HTlc & Mg-Al	N ₂ / CO ₂	300-400°C / 10 bar	0.52-1.21 mmol/g	[64]
SBA-15-HTc &	He / CO ₂	343 K and 1 atm	0.6-2.5 mmol/g	[65]

2.1.6 Double Salts

Double salts are formed by the chemical combination of aqueous solutions of the carbonates and bicarbonates of sodium and potassium followed by crystallization. These salts can either be in molten states or other various forms. A pioneer study carried out at the Norwegian University of Life Sciences (NMBU) facilitated a breakthrough in Carbon Capture by Salt Technology using what they termed Carbon Capture Molten Salts (CCMS) [1]. The technology operates upon the fundamental principles of Calcium-Looping (CaL) with key modification in CCMS which utilizes the CO_2 as its sorption particles and are completely or partially dissolved in molten salt, whereas in CaL, the sorption particles are in a solid phase. The melt consists of inorganic salt and alkali earth metal oxide. When testing this technology, promising results were revealed. Using CaO as sorbent dissolved in a few select mixtures of salt yielded a high CO_2 capturing rate from a gas mixture with 14 vol% CO_2 . Unlike technologies using similar capture techniques, the sorbent in CCMS does not deteriorate after a few cycles of CO_2 capture. Today the CCMS technology has mostly been tested with CaO as CO_2 -sorbent. CaO has shown promising results during CO_2 capture in CCMS; however, CaO needs large amounts of energy to be regenerated, $885\text{ }^\circ\text{C}$, after capturing CO_2 . This is due to the high reaction enthalpy of the decarbonation reaction. The high energy requirements are the main cost driver of CCMS with CaO [66].

2.2 Physisorbents

2.2.1 Carbon-based materials

Carbon belongs to group 14 of the periodic table, and it is one of the most abundant resources on earth. It is present in rocks (limestone, dolomite, marble, etc), fossil fuels (coal, petroleum and natural gas), food components and most importantly in the air with oxygen [67]. “The existence of carbon in different forms can be attributed to its unique electronic structure which allows the formation of stable chemical bonds in various configurations. Carbon unique chemical characteristics means it can form single, double or triple bonds; it can catenate (bond with one another), forming cyclic or acyclic chains as well as straight or branched chains; with non-metallic elements it is capable of forming strong bonds” [67]. Allotropy is the existence of elements in different forms but same physical state. Carbon has three allotropes: amorphous carbon, crystalline graphite and diamond. They possess diverse properties and therefore each deserves to be considered as an allotrope. The specific of the three allotropes are not discussed in this study, as they are not specific on the details of carbon capture. Furthermore, since carbon materials constituents are reactive with a wider range of elements it is safe to assume that a controlled chemical analysis can make carbon materials preferred in the

making of materials for carbon capture in the CCUS value chain. Production of innovative CO₂ capture materials based on carbon or similar elements are essential in the general low carbon emission and energy goals for production industries while phasing into renewable-based energy options. Very large amounts of CO₂ must be captured to be then used or stored. Thus, efficient carbon capture materials are instrumental to CO₂ utilisation and storage.

“Direct air capture (DAC) is another formidable challenge of capturing CO₂ directly from the earth’s atmosphere. The Glaser group at the University of Missouri-Columbia has specialised in the study and development of rubisco-inspired biomimetic approaches to the reversible capture of CO₂ air. In their contribution the group shows how the reversibility of CO₂ binding in a rubisco-based small molecule model is essentially dependent on a drop-in entropy upon capture” [66]. Two examples of carbon-based materials utilized in adsorption technology are biochar and carbon black.

2.2.2 Zeolites

These are mostly crystalline aluminium silicates which exist naturally and are also produced synthetically. They have a three-dimensional structure with pores and consist of silicon, aluminium, and oxygen ions. The silicon ions are neutrally loaded in the crystal structure. The aluminium ions cause negative areas to exist. In order to keep the load balanced, a cation (Na⁺, K⁺...) or a proton (H⁺) is placed in the pores as a counter-ion. This special characteristic makes it suitable for molecular sieves. Over 190 of this unique compound’s frameworks have been identified and just over 35 of them are naturally occurring [68]. Naturally occurring zeolites are very useful in both industrial and domestic processes. The large discovery of nearly purified zeolites in the volcanic tuffs in the western United States in 1957 led to its widespread adoption and usage. Before then, there was no standard on the use of this compound. Natural zeolites are a significant class of minerals used in industry and other applications [69]. The era of commercial natural zeolite began with the 1957 discovery of sizable amounts of relatively high purity zeolite minerals in volcanic tuffs in western United States and several other nations. Prior to it, there was no evidence that zeolite minerals with qualities suitable for use as molecular sieve materials could be found in significant concentrations. As new adsorbent materials with enhanced stability characteristics, the natural zeolites chabazite, erionite, and mordenite began to be commercialized in 1962 as molecular sieve zeolites [69]. During the 1960s, clinoptilolite was used in wastewater treatment and radioactive waste recovery due to its exceptional stability qualities as well as its strong cation exchange selectivity for cesium, strontium, and ammonium ions [69].

Zeolites were first presented in 1954 as adsorbents for industrial separations and purifications. They are presently used in a number of applications due to their distinctive porous qualities. They are employed in the building industry, agriculture, animal husbandry, petrochemical cracking, water

softening and purification, the separation and elimination of gases and solvents, and these activities [69][70]. Zeolites are crystalline aluminosilicates made of SiO_4 and AlO_4 tetrahedra connected to one another by sharing all of their oxygen atoms, resulting in regular intra-crystalline cavities and channels with molecular dimensions. Zeolites are distinguished by the fact that their frameworks are composed of 4-coordinated atoms creating tetrahedra. By joining their corners, these tetrahedra form a wide range of exquisite forms. Small molecules can access the framework structure's linked cages, cavities, or channels because they are large enough. The structure of substantial holes explains why these compounds consistently have low specific densities. The gaps of zeolites, which are utilized in a variety of applications, are connected and form long, wide channels that vary in size depending on the compound. The ions and molecules that live there can easily drift into and out of the structure thanks to these channels. The negative charge of the aluminosilicate structure attracts the positive cations that live in cages to balance the negative charge. Zeolites have more substantial cages in their structures than the majority of other tectosilicates [71]. Zeolites have found significant applications in both agriculture and environmental protection. Zeolite-filled sorption columns can be used for the treatment of wastewater containing heavy metal ions [71,72] or radioactive isotopes [73]. The removal of ammonium ions from municipal, industrial, and agricultural wastes is also possible [74]. Zeolites can be employed in agriculture as feed additives, agrochemical component transporters, and in the treatment of soil and fish [75]. Additionally, attempts have been made to change their structure so that they have catalytic [76] or antibacterial [77] qualities. After all, they are frequently utilized in several homes as pet litter.

On the other hand, because their properties are solely dependent on their crystal structure, natural zeolites have a limited range of industrial uses. The main drawback is that the channels are too tiny (clinoptilolite, the most prevalent type in nature, has a channel diameter of 0.30–4 nm [68] which prevents the adsorption of bigger gas molecules and chemical compounds. Zeolite deposits are a non-renewable resource as well. Numerous attempts were made to create zeolites in the laboratory due to the requirement for the synthesis of molecular sieves and adsorbents with highly particular characteristics. The main drawback is that the channel sizes are too small (0.30–4 nm for clinoptilolite, the most prevalent kind in nature).

2.2.2.1 Artificial zeolites

Zeolites are acknowledged as minerals with a natural origin, although there are already over a hundred different varieties of zeolite structures that can be produced artificially. Zeolites were created naturally when volcanic ash and the water in the fundamental lakes came into contact. Several thousand years passed during this process. In a lab setting, hydrothermal processes can be attempted to mimic utilizing increased pressure or temperature, natural raw materials, and/or synthesized silicates. Equipment, clean substrates, and energy are needed for the synthesis reaction. As a result,

the product's cost could be significantly greater than the cost of natural zeolite. As a result, while attempting to lower the cost of the reaction itself, research frequently focuses on the hunt for more affordable and readily available substrates for the manufacture of zeolites. Environmental factors are shaping current developments in research on the synthesis of zeolites, which implies the utilization of natural or waste raw materials for this purpose. Zeolite synthesis involves the use of volcanic glasses, such as perlite, pumice and diatomites. However, aluminosilicate waste products or expanded perlite waste are frequently used to make zeolites [78]. However, using natural raw materials to produce zeolites has economic advantages when compared to using synthetic substrates. Synthesis using raw materials with a complex chemical composition will not give the product 100 percent purity, and zeolites obtained in this way are excluded from many significant commercial applications. Zeolite material generated using the aforementioned techniques is predicted to cost in the middle of natural and synthetic zeolite. The use of one of these technologies, however, might prove to be the most cost-effective option given that costs for waste storage and utilization will definitely rise. Like natural zeolites, synthetic zeolites have a variety of structures and characteristics. Individual varieties of zeolites crystallize depending on factors such reaction duration, temperature, and pressure as well as the chemical make-up of the reaction mixture, including the reagent concentration [79]. The kinds of phases that develop in these systems are generally well understood. According to the synthesis parameters, the primary products are analcime, zeolite Na-P1 and hydroxysodalite (Fig. 7; a – c) [80].

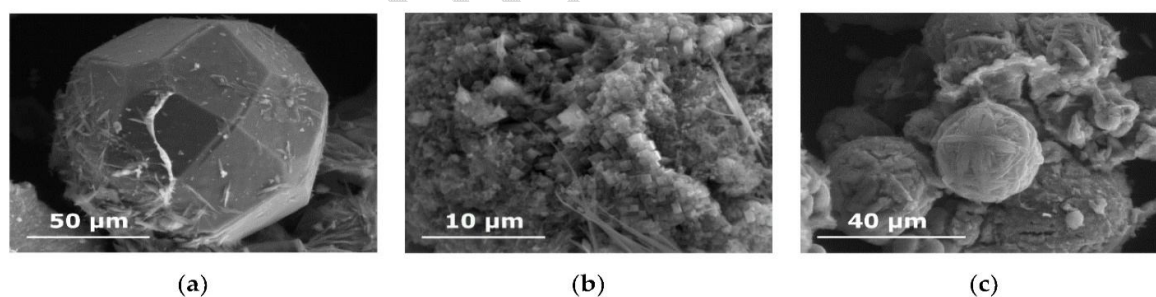


Fig. 7. Microstructures of zeolites obtained in hydrothermal conditions at elevated pressure: (a) analcime (b) zeolite Na-P1 (c) hydroxysodalite.

2.2.3 Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs) also known as coordination polymers are captivating crystalline nanomaterials made up of organic linkers (bridging ligands) and inorganic nodes (metal cations) that extend infinitely into two or three dimensions through metal-ligand bonding. They belong to a group of synthetic porous materials that have three-dimensional structures made of metal ions and organic molecules (or ligands) [81]. Like other crystalline porous materials such as zeolites, MOFs allow

outside molecules to adsorb on their pores [81]. MOFs constitute of a new class of materials, which could serve as an ideal platform for the development of next-generation CO₂ capture materials because of their large capacity for adsorption of gases and easy tunability of their structures. Their structures and properties can be tailored to meet the needs of particular applications because the pore size, pore shape, network topology, and surface functioning of MOFs can be systematically modified through chemical alteration. “During synthesis, metal ions/clusters, known as secondary building units (SBUs), are linked by organic molecules through the self-assembly of the individual components. The link/interaction is formed through strong coordination bonds between the molecules. This serves as the structural backbone of the framework” [82]. The size and shape of the organic linkers, along with the geometry of the SBUs, significantly influence the structural configuration and characteristics of MOFs. Because of this information, MOFs can be created to produce the desired crystal shape, pore size, and functional application. For instance, Zhang *et al.* [83] improved the CO₂ adsorption capacity of zeolitic imidazolate framework-8 (ZIF-8) by altering the surface basicity using ammonia impregnation and heat treatment in nitrogen and hydrogen atmospheres. The overall number of basic sites in the redesigned ZIF-8 significantly increased. The sample redesigned by ammonia impregnation had the greatest basicity, followed by those redesigned by hydrogen and nitrogen treatments. Due to CO₂'s acidic nature, the modified ZIF-8 samples had a lot of total basic sites, which enhanced CO₂ uptake. According to the results obtained by [83], the sample transformed by ammonia impregnation had the highest capacity for CO₂ adsorption, with 330 mg/g. This is a 45% increase in CO₂ adsorption over the original sample, which had a CO₂ uptake of 225 mg/g.

“In the design of MOFs, stability is an indispensable factor. To achieve the desired application, MOFs must be thermally, hydrothermally, chemically, and mechanically stable” [84]. “The stability of MOFs is influenced by the oxidation state of the compound, the metal-ligand coordination geometry, and acid dissociation constant (pKa) of the ligand. The metal ligand bond in MOFs hydrolyses in aqueous medium, which reduces their chemical stability” [85]. “However, the chemical stability of MOFs can be synthetically improved using high valence metal ions (Fe³⁺, Zr⁴⁺) and by bonding between divalent metal ions and nitrogen-containing ligands like imidazoles” [84]. There are numerous ways to produce metal-organic frameworks. Although solvothermal synthesis is the predominant method used, other methods have been employed as alternatives, including hydrothermal synthesis, microwave aided synthesis, electrochemical synthesis, sonochemical synthesis, and mechanochemical synthesis. Most MOF synthesis processes take place in liquid phase and include heating a mixture of organic linkers (bridging ligands), such as carboxylates, phosphates, sulfonates or heterocyclic compounds with a metal salt in a solvent system that contains an ionizing solvent functionality. Solvothermal and hydrothermal approaches, with typical reaction periods of several hours to days, are the most widely used methods for MOF synthesis as shown in Fig. 5. The synthesis

conditions of the different preparation routes and percentage of MOFs synthesized using the various techniques (Fig.9) [86] .

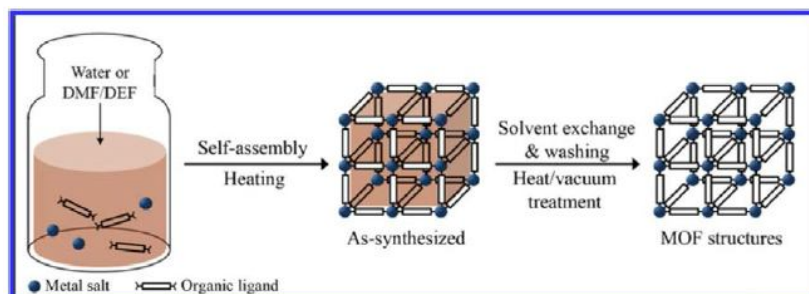


Fig. 8. Schematic diagram showing Conventional solvothermal synthesis of MOFs.

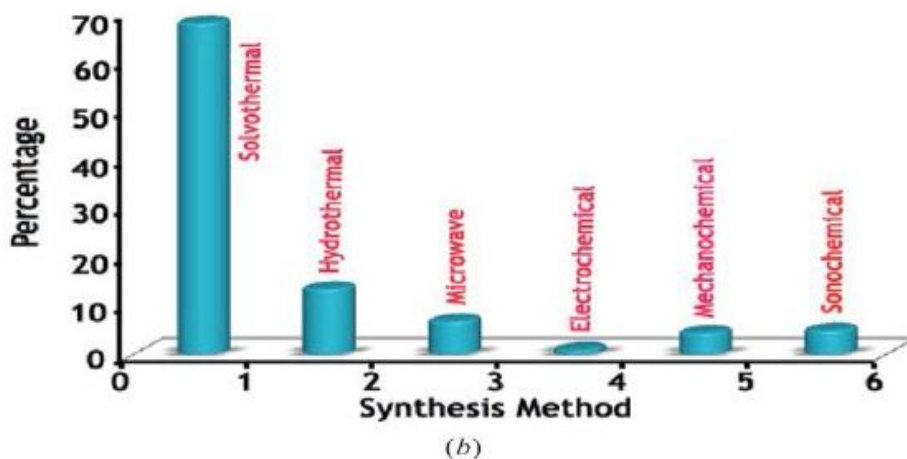
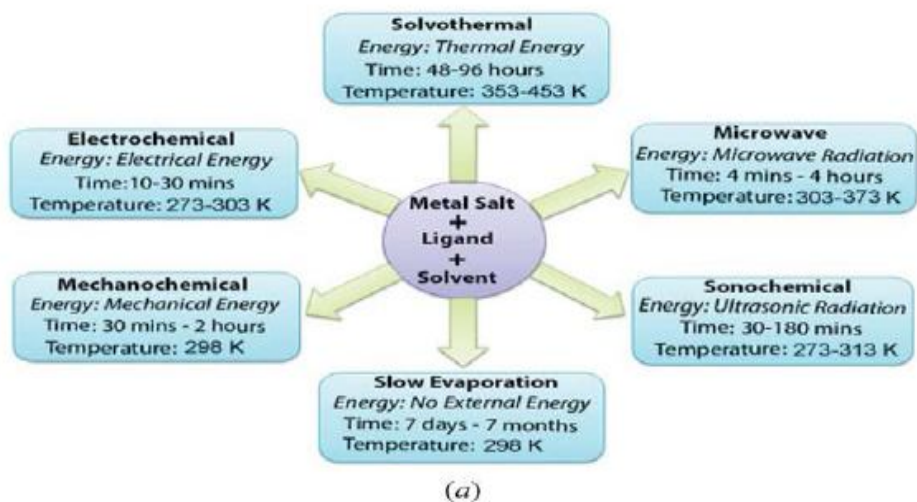


Fig. 9. (a) Synthesis conditions commonly used for MOF preparation (b) summary of the percentage of MOFs synthesized using the various techniques.

The synthesis of MOFs usually involves post-synthetic modification (PSM). When synthesizing MOFs, integration of functional groups of interest is typically challenging [87]. However, by post-synthetic modification processes, desirable functionalities can be added to MOFs. Post synthesis modification involves the addition of extra functional group(s) to MOFs that have already undergone synthesis to accomplish specific application goals. Protonation or doping of MOFs in a non-covalent interaction, coordinate interaction, or covalent interaction are two methods for post-synthetic modification [88]. The addition of numerous capabilities to the same framework and the creation of a variety of MOFs with the same topology but bearing different functionality are two major advantages of post-synthetic modification.

Due to MOFs' distinctive structural characteristics, further potential applications have recently received a lot of attention. Its outstanding gas capturing ability has been designated for the separation of numerous undesired and environmentally dangerous chemical species, which is why MOFs are becoming more and more appealing for use in environmental applications [89]. MOFs are preferred over zeolites, activated carbon and other conventional adsorbents because of their large surface area and well-defined pore properties which makes them more useful for volume specific applications such as separation, purification and adsorption processes [89]. Metal Organic Frameworks must be activated before they are used as adsorbents. Activation of MOFs involves the removal of solvent molecules from their pores to open the void spaces within the crystal lattice [90]. The synthetic MOF is heated to force solvent molecules out of the pores, which activates the structure. The active open metal sites, which exhibit Lewis acidity, acts as adsorption or binding sites where CO₂ molecules attach and coordinate to the surface of the material through electrostatic interaction [91]. Evaporation removes the majority of solvent molecules that have been encapsulated. However, activation is accomplished under vacuum at extremely high temperatures in situations when solvent molecules exhibit significant interactions with either metal ions or organic linkers.

Given their high gas adsorption capacity and porosity, metal-organic frameworks are viewed as potential candidates for catalytic CO₂ removal from flue gas. A number of metrics are used to assess how well metal-organic frameworks trap carbon dioxide. "A MOF material is typically deemed appropriate for CO₂ capture if it has a high CO₂ capture/storage capacity with quick adsorption/desorption kinetics, high selectivity or affinity to CO₂, high enthalpy/heat of CO₂ adsorption (Q_{st}) and is stable under capture and regeneration conditions" [91]. Although physical adsorbents such as MOFs, Zeolite and Carbon-based adsorbents prove to be effective CO₂ adsorbents at low temperature and high pressure, they always adsorb water vapor in preference to CO₂ and this result to low CO₂ at low pressure [92]. Therefore, these adsorbents may not be appropriate sorption materials for post-combustion gas treatment. In spite of the afore mentioned short coming, remarkable improvements have been achieved in the development of better CO₂ adsorbents such as, Amine-modified porous materials, Zeolite-Metal-Organic Frameworks. These modified porous materials have large surface area and high carbon CO₂ adsorption capacities even at low pressure. Certain structural and chemical characteristics of MOFs enable CO₂ uptake in post-combustion capture through pre- and post-synthetic alterations. These characteristics include hydrophobicity, heteroatoms, open metal sites, and SBU interactions [93]. By activating the MOF material, open metal sites, also known as coordinately unsaturated metal sites, are produced. The synthetic MOF is heated to force solvent molecules out of the pores, which activates the structure. The Lewis acidity-exhibiting active open metal sites serve as binding or adsorption sites where CO₂ molecules cling to and coordinate to the material's surface through electrostatic contact [93]. The selectivity and absorption of CO₂ are improved by metal-organic frameworks with co-ordinatively unsaturated metal sites because they

have a high heat of CO₂ adsorption at low pressures [93]. According to a study by Britt's group [94], Mg-MOF-74 effectively absorbs 8.9 wt.% of CO₂ from a gas mixture containing 20% CO₂ in methane with no discernible uptake of methane. According to a comparison study, Zn-MOF-74, which is structurally identical to Mg-MOF-74, only absorbs 0.35 wt.% of CO₂ [94]. The high CO₂ adsorption capability of Mg-MOF-74 is therefore attributed, according to the authors, to the interaction between the gas molecule and the Mg²⁺ ion. Nuclear magnetic resonance (NMR) simulations of CO₂ dynamics in Mg-MOF-74 open metal sites by [95] indicated a robust physical connection between the gas molecule and the MOF framework. "In addition, MOFs could separate CO₂ from other gases through the molecular sieving effect or size exclusion, i.e., only gas molecules with appropriate kinetic diameter can pass through the pores of the MOF. The specific surface area, pore volume and pore size distribution of metal organic frameworks are crucial factors that affect shape-selective adsorption and catalysis. Through pore- and volume-based manipulations, MOFs can be highly modular shape-selective catalysts" [96].

2.2.4 Covalent Organic Framework

"Covalent organic frameworks (COFs) are porous crystalline organic polymers synthesized by the covalent linkage of organic molecules bonded in a repeating fashion to form a porous crystal that is ideal for gas adsorption and storage. COFs are promising because of their chemical and thermal stabilities as well as synthetic versatility, giving rise to a wide variety of functional and structural designs. They are constructed by linking well-defined organic building units through strong covalent bonds such as C-C, C-N, C-O, B-O, C-N and C-Si. They are usually synthesized by reversible condensation reactions where the reversibility originates from the hydrolysis back reaction. Their synthesis includes but not limited to the following organic reactions, viz; the formation of B-O (boronate, boroxine and borosilicate), C-N (imine, hydrazine, and squaraine), C-N (triazine and imidization), B-N (borazine) and N-N (azodioxides) bond linkages" [97]. "Therefore, many synthetic strategies have been developed for the synthesis of COFs of different dimensions and with different textural properties. Compared with other crystalline porous solid adsorbents (inorganic zeolites and hybrid MOFs), COF materials possess the advantage of low density, high permanent surface areas, high chemical and thermal stability, columnar p-stacking structure, tunable pore size and structure and versatile covalent combination of building units" [97]. "All these advantages have attracted considerable interest of scientific community in COFs, thereby making the materials new candidates for important applications in gas adsorption, optoelectronics, catalysis, gas separation, proton conductivity, chemical sensor, drug delivery, energy storage and chromatographic separation" [97].

The ability of the synthesized COF materials to have the combined properties of stability, crystallinity, and porosity is one of the key issues in the field of COFs, and this needs to be considered in order to accelerate functional exploration and applications of COFs, particularly for CO₂ capture.

Kandambeth *et al.* [98] developed a strategy to protect the COF interior by introducing $-OH$ functionalities adjacent to the Schiff base $[=C=N]$ centers in COFs and thereby forming an intramolecular $O-H \cdots N=C$ hydrogen bonding, to enhance the chemical stability and crystallinity in 2D porphyrin COFs. This targeted COF, namely DhaTph, compared to methoxysubstituted COF (DmaTph) analogue where the hydrogen-bonding interaction has been removed, showed better chemical stability, crystallinity, and higher porosity. The S_{BET} of DhaTph ($1305 \text{ m}^2/\text{g}$) was higher than that of DmaTph ($431 \text{ m}^2/\text{g}$) as calculated. The high surface area of DhaTph was attributed to the improved crystallinity of this material due to the strong intramolecular $O-H \cdots N=C$ hydrogen bonding interactions. The CO_2 uptake of DhaTph was reported to be 128 mg/g at $273 \text{ K}/1 \text{ bar}$, while DmaTph shows lower CO_2 uptake of 73 mg/g . Chen's group [99] also reported synthetic control over crystallinity and porosity of COFs through management of interlayer interactions based on self-complementary p-electronic force. They used imine-linked porphyrin COFs, in which fluoro-substituted and non-substituted arenes at different molar ratios were integrated into the edge units. The self-complementary p-electronic force was reported to improve the crystallinity and enhance the porosity by maximizing the total crystal stacking energy and minimizing the unit cell size. Consequently, the COF consisting of equimolar amounts of fluoro-substituted and non-substituted units were reported to show the largest effect. Their study suggests a new means of designing COFs with enhanced crystallinity and porosity through management of interlayer interaction. The large surface area and tuneable pore size are important advantages for COFs to be used for gas adsorption and purification. One of the most challenging issues in the field of COFs is the combined features of stability, crystallinity and porosity in COF materials, which are important parameters for their applications in CO_2 capture. Synthetic strategies enabling the controlled synthesis of microporous crystalline structures that are hitherto of interest to CO_2 capture at $273 \text{ K}/1 \text{ bar}$ and 298 K at higher pressure are therefore of paramount importance to CCS technology.

The CO_2 uptake performance at low pressure depends on the pore width rather than the S_{BET} because the adsorption at 1 bar is believed to be a micropore diameter dominated process. The CO_2 uptake capacity of COFs at $273 \text{ K}/1 \text{ bar}$ has been reported to reveal that COFs with micropore diameter smaller than 1 nm usually possess large CO_2 uptake capacity [98]. "Also, synthesis of COFs with specific polar groups on the surface of pore is another effective way of enhancing CO_2 uptake performance at low pressure. Compared with boron-based COFs, the imine-based and triazine-based COFs show higher CO_2 uptake, which thus indicates that nitrogen groups in COFs could act as Lewis-base active sites that attract the Lewis-acidic CO_2 molecules, thus enhancing CO_2 uptake performances" [100]. "High pressure gas storage of CO_2 using porous materials is important for natural gas purification processes. Compared to the low-pressure adsorption, high-pressure adsorption of COFs is equally important to the CO_2 storage. COFs exhibit different features for CO_2 storage at high pressure in contrast to their CO_2 uptakes at low-pressure. For instance, at high-pressure, the CO_2

uptake capacities of COFs are reported to be dependent of S_{BET} and pore volume, with COF-10 exhibiting the highest S_{BET} of $1760 \text{ m}^2/\text{g}$ and largest CO_2 uptake capacity of 1010 mg/g at $298 \text{ K}/55 \text{ bar}$ [101]. Generally, for the high-pressure CO_2 uptake, the greater the BET surface area and pore volume, the larger the CO_2 capture capacity. An effective strategy to enhance CO_2 uptake performance at high pressure is to target high surface area and pore volume for COFs during their synthesis routes.

2.2.5 Carbon Nanotubes

Carbon nanotubes (CNT) comprise a large group of nanometre-thin hollow fibrous materials with different physicochemical characteristics (e.g., length to diameter ratios, atomic configuration, impurities, defects, and functionalization). With respect to their different physicochemical characteristics, properties such as electrical, optical, thermal conductivity, tensile strength, and chemical reactivity are typical of CNT [102]. Therefore, CNT has been found useful in a wide range of industrial applications, which could allow performance enhancement in products, specification alterations, gas and energy storage, additives in composite nanomaterials etc. [103]. However, their potency is based on the type of application and quality of properties in view. In this review, CNT application will be focused on its usage as an adsorbent in captured carbon storage. High amount of CO_2 emission from the world's major energy source over the years which has been the fossil fuels, has drawn detrimental consequences to the world's climatic condition. This has motivated several studies aimed at reducing the environmental carbon concentration level to acceptable standards. Of recent, the incorporation of amine functional groups to porous solid materials for enhanced CO_2 adsorption have been studied [104].

CNTs has been found useful as adsorbent for CO_2 , which could make it a viable solution in the carbon capture and storage research goal, as it is compatible with amine impregnation. The large surface area possessed by CNT with good geometric structure is a desired characteristics in the preparation of composite adsorbent for CO_2 capture. Also, they are hydrophobic, and the presence of water vapour would have no adverse effects on them [105]. This is an advantage over other solid adsorbents such as zeolites. Therefore, the hydrophobic property of CNT could be explored in finding composite adsorbents with great resistance to water, for CO_2 capture from flue gas. Two major types of CNT have been reportedly used in adsorption. These are single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs), [106]. The SWCNT are made of one single layer of graphene cylinder, whereas the MWCNT is composed of many layers of graphene cylinders nested inside each other [107]. This structural difference gives each type of CNT different properties that could be explored and exploited towards developing composite materials with high CO_2 adsorption capacity. The properties of CNTs with the selected properties all applying to SWCNT have been listed below (Table

4) [103]. Some listed properties including aspect ratio and tensile modulus are also shared by high nanotexture c-MWCNTs.

Table 4. Properties of carbon nanotubes

Properties	Values	Comments
Aspect ratio	~1 000 – 10 000	Possibly higher.
Specific surface area	~ 2 780 m ² /g	When considering both surfaces of open SWCNTs.
Tensile strength	> 45 GPa	Other values up to 100 GPa can be found in the literature.
Tensile modulus	1 to 1.3 TPa	Independent on diameter when > 1nm.
Tensile strain	> 40%	Provides toughness values higher than that of spider web.
Flexural modulus	1.2 TPa	
Thermal stability	> 3000°C	In oxygen-free atmosphere.
Electrical conductivity	10 ⁴ – 10 ⁷ S/cm	Better than copper.
Transport regime	Ballistic, up to superconductivity	T _c < 1 k
Thermal conductivity	~ 6 000 W/mk	Better than diamond
Electron emission	10 ⁶ – 10 ⁹ A/cm	Highest current density

Methods such as grafting or impregnating a surfactant onto the surface of CNT had been proven to enhance the CO₂ adsorption capacity of the composite material. [108] reported that impregnating polyethyleneimine onto MWCNT increased the CO₂ adsorption capacity of the CNT by 200%. Also, [109] made reports on the effect of grafting polyaspartamine surfactant onto the surface of MWCNTs which could result in increased the CO₂ adsorption of the material by 500%. Furthermore, MWCNT/3-aminopropyltriethoxysilane (APTS) performed better in CO₂ adsorption than amine-functionalized carbon in an experiment carried out by Su's group and the theoretical regeneration energy displayed by the composite material was lower when compared to that of amine-functionalized activated carbon [110]. In addition, [104] found out that SWCNTs showed the highest CO₂ adsorption capacity (29.97 gCO₂/kg adsorbent) compared to the MWCNTs (12.09 gCO₂/kg adsorbent), a 150% increase in adsorption capacity over MWCNTs was observed in the experiment carried out. However,

there has been limited literature on the CO₂ adsorption capacity of CNTs for CO₂ capture with respect to the use of SWCNTs.

2.2.6 Mesoporous Silica

Considering low-temperature CO₂ removal options (such as activated carbons, metal-organic framework (MOFs)-based adsorbents, zeolite) [111-114], the loading capacity of amines supported on porous solid materials have been identified as a good prospect when compared to the one of liquid amines. Also, its enhanced adsorbing capacity in the presence of water, acceptable kinetics, high selectivity, and simple synthesis have made it desirable in comparison to the conventional adsorbents. Inorganic mesoporous materials (such as silica) are suitable for this purpose in that they possess large and accessible pore volume which allows for grafting of amines without significant reduction of CO₂ mobility. Furthermore, they tend to be stable both mechanically and thermally in the presence of low-temperature post-combustion gases [113]. This implies that they can accommodate the amine molecules and provide relative advantage of high affinity of amines to CO₂ with the high surface area of a porous adsorbent [112]. Both Zeolites and MOFs are considered to have a high CO₂ capture capacity, and some of them are quite stable, however they are costly. Wide range of separation processes finds zeolite an efficient shape-selective sorbent due to their polarity and the presence of pores [115].

Studies on mesoporous silicas as adsorbents for CO₂ capture have been reported in literature including MCM-48 [116], MCM-41 [117], SBA-15 [118]. SBA-15 material was able to provide high stability, and the presence of effective **micro pores** with its meso-channels, which contribute to gas physisorption [119, 120].

Conclusion

Although much study has been done regarding these adsorbents, their application on an industrial level is still quite inchoate. Some of these sorbents still suffer from lack of stability over multiple CO₂ adsorption and desorption cycles. As a result, more work still needs to be done in increasing their CO₂ adsorption capacity, mechanical and thermal strength. Further success in CO₂ capture, storage and utilization is not just a function of the study of conventional materials, but also depends on the discovery and synthesis of novel materials with high CO₂ capture capacity, good thermal and recycling stability. These novel materials which could be advanced polymers, organic materials, inorganic materials and hybrids of organic and inorganic materials should possess a high density of basic functional groups or active sites. For catalytic applications including the water-gas shift, steam reforming and preferential oxidation reactions, high temperature CO₂ adsorbents (CaO and alkali ceramics) and intermediate temperature CO₂ adsorbents (most notably LDHs) are still subject to poor

thermal stability in the reaction temperature ranges. The expectation is that more CO₂-adsorbent enhanced catalytic reactions will be identified and studied in the future. To achieve the desired improvements in adsorption capacity and multicycle durability of CO₂ adsorbents, the acquisition and analysis of data from existing adsorption reactors, regeneration processes and integrated capture systems is vital. The development of advanced adsorbents for CO₂ capture will foster the realization of techno-economical systems that will combine cutting-edge CO₂ capture technologies and associated processes such as hydrogen generation in reforming reactions, electricity generation using hydrogen, and water treatment.

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