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Carbon Dioxide Capture and Storage: A General Review on Adsorbents

Mohammad Songolzadeh , Maryam Takht Ravanchi , Mansooreh Soleimani

***Abstract*—**CO_2 is the primary anthropogenic greenhouse gas, accounting for 77% of the human contribution to the greenhouse effect in 2004. In the recent years, global concentration of CO_2 in the atmosphere is increasing rapidly. CO_2 emissions have an impact on global climate change. Anthropogenic CO_2 is emitted primarily from fossil fuel combustion. Carbon capture and storage (CCS) is one option for reducing CO_2 emissions. There are three major approaches for CCS: post-combustion capture, pre-combustion capture and oxyfuel process. Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them.

There are several post combustion gas separation and capture technologies being investigated, namely; (a) absorption, (b) cryogenic separation, (c) membrane separation (d) micro algal bio-fixation and (e) adsorption. Apart from establishing new techniques, the exploration of capture materials with high separation performance and low capital cost are paramount importance. However, the application of adsorption from either technology, require easily regenerable and durable adsorbents with a high CO_2 adsorption capacity. It has recently been reported that the cost of the CO_2 capture can be reduced by using this technology. In this paper, the research progress (from experimental results) in adsorbents for CO_2 adsorption, storage, and separations were reviewed and future research directions were suggested as well.

***Keywords*—**Carbon capture and storage, pre-combustion, post-combustion, adsorption

I. Introduction

CARBON dioxide is the major greenhouse gas, which is the largest contributor to global warming. The emission of carbon dioxide to the atmosphere has been identified as a major contributor to global warming [1-4]. Sources of carbon dioxide are divided into two categories: natural source and human source.

Natural sources of carbon dioxide are more than 20 times greater than sources due to human activity, but over periods longer than a few years natural sources are closely balanced by natural sinks [3]. Main human source is the combustion of fossil fuels such as coal, natural gas or petroleum, and industrial processes such as power plants, oil refining and the production of cement, iron and steel [4-7]. Carbon dioxide has been already used in petrochemical industries for production of limited chemicals such as urea [1].

Since the beginning of the industrial age in ca. 1800, the CO_2 concentration in atmosphere has increased from 280 to 390 ppm in 2010 [8-9]. Carbon capture and storage (CCS) will play a crucial role to attain the required greenhouse gas (GHG) emissions reduction [10].

M.Songolzadeh is with Amirkabir University of Technology, No.424, Hafez Ave., Tehran, Iran, (e-mail: songol8571013@aut.ac.ir).

M. Takht Ravanchi is with Petrochemical Research and Technology co. Iran, (e-mail:. maryamravanchi@gmail.com)

M.Soleimani is with Amirkabir University of Technology, No.424, Hafez Ave., Tehran, Iran, (Tel. & Fax: +98(21) 66405847; E-mail: Soleimanim@aut.ac.ir

CCS can be defined as the separation and capture of CO_2 produced at stationary sources, followed by transport and storage in geological reservoirs or the ocean [11-12]. There are three major approaches for CCS: post-combustion capture, pre-combustion capture and oxyfuel process.

In pre-combustion, the fossil fuel is reacted with air or oxygen and is partially oxidized to form CO and H_2 (syngas). Then in a gasification reactor, it is reacted with steam to produce a mixture of CO_2 and more H_2. CO_2 is then separated, and resulting in a hydrogen-rich fuel which can be used in many applications. Oxy-combustion is when oxygen is used for combustion instead of air, which results in a flue gas that consists mainly of pure CO_2 and is potentially suitable for storage. The post combustion capture is based on removing CO_2 from flue gas after combustion. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates/captures most of the CO_2 [3, 13-14].

Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them. This makes post-combustion capture easier to implement as a retrofit option (to existing power plants) compared to the other two approaches. Therefore, post-combustion capture is probably the first technology that will be deployed [15].

Among the various separation technologies such as absorption, adsorption, cryogenic, membrane and micro algal bio-fixation, adsorption may be considered as a competitive solution. Its major advantage is the ease of the adsorbent regeneration by thermal or pressure modulation [3, 14, 16].

Flue gases of current power plants are a mixture of nitrogen, oxygen, carbon dioxide, SO_2, NO_x and water plus other minor contaminants [12, 14]. The concentration of CO_2 in the flue gas is typically only 10–15% (around 12%) depending on the fuel used [17-18]. Flue gases are normally at atmospheric pressure but the temperatures might be between 320 K and 400 K, depending on the extent and type of contaminant removal [19]. The flue gas conditions have created many problems for CO_2 capture.

In addition to cryogenic process, absorption and membrane technology, adsorption is a separation technology, potential to reduce the cost and energy of post-combustion capture compared to other technologies. Adsorption processes for gas separation via selective adsorption on solid media are also well-known, and it can produce high purity streams with low energy consumption [5, 10, 20-23].

II. Adsorption

Adsorption is a physical process that involves the attachment of a gas or liquid to a solid surface. Adsorption can reduce energy and cost of the capture or separation of CO_2 in post-combustion capture. However, the success of this approach is dependent on the development of an easily regenerated and durable adsorbent with high CO_2 selectivity and adsorption capacities [1-4].

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In general, the CO_2 adsorbent must have high selectivity and adsorption capacity, adequate adsorption/desorption kinetics, remain stable after several adsorption/desorption cycles, and possess good thermal and mechanical stability [17, 24].

Adsorbents which could be applied to CO_2 capture include activated carbons, carbon fibres, silica gel, ion-exchange resins, zeolites, and porous silicates (SBA-15, MCM-41, etc.), activated alumina, metal oxides (CaO, MgO, K_2O, Li_2O), metal-organic frameworks (MOFs), organic–inorganic hybrid sorbents and other surface-modified porous media. However, zeolites, porous silica, and MOFs show negligible CO_2 adsorption at high temperature [9, 15, 25-26]. The adsorbents are used for CO_2 capture placed into two categories: physical and chemical adsorbents.

A. Chemical Adsorption

Chemisorption is a sub-class of adsorption, driven by a chemical reaction occurring at the exposed surface. Chemical adsorbents are mostly metal compounds. Metal compounds in two forms are used for CO_2 adsorption: metal oxides and metal salts. A wide range of metals have been studied, metal oxides (e.g. CaO, MgO, etc.), lithium metal oxides (e.g. Li_2ZrO_3, Li_4SiO_4, etc.), metal salts from alkali metal compounds (i.e. lithium silicate, lithium zirconate) to alkaline earth metal compounds (i.e. magnesium oxide and calcium oxide), hydrotalcites and double salts [24, 27].

In general, one mole of metal compound can react with one mole of CO_2 with a reversible reaction [27]. The process consists of a series of cycles where metal oxides (such as CaO) at 650 °C are transformed into metal carbonates form (such as $CaCO_3$) at 850°C in a carbonation reactor, and then decarbonated in a decarbonation reactor allows to regenerate the sorbent and to produce a concentrated stream of CO_2 suitable for storage [28-29].

Considerable attentions were paid to calcium oxide (CaO) as it has a high CO_2 absorption capacity and high raw material availability (e.g. limestone) at a low cost. Lithium salts recorded a good performance in CO_2 absorption, but it gained less focus due to its high production cost [27].

Hydrotalcite (HT) contains layered structure with positively charged cations and is balanced by negatively charged anions. HTI-K–Na adsorbed CO_2 at 1.109 mol/kg under wet condition at 300 ^{O}C and total pressure of 1.34 bar (CO_2 partial pressure of 0.4 bar). The measured loss of capacity was only 6.7% after 50 cycles of operation [24].

Although double salts can be easily regenerated due to low energy requirement, their stability has not been investigated. The long-term stability and performance of alkali metal-based sorbents under actual flue gas conditions remains to be established [27-28].

One way for improving adsorption efficiency is using nanomaterials for CO_2 adsorption. Nanomaterials are materials with at least one dimension equals or less than 100 nm [27]. The nanocrystalline Li_2ZrO_3 achieved 27 wt% absorption capacity in 5 min compared to the normal Li_2ZrO_3 that need 24h to achieved 18 wt% adsorption capacity. The sorbent was also more stable in CO_2 adsorption/desorption process and maintained the capturing capacity after 7 cycles.

Essaki et al [30] investigated flue gas removal using packed-bed lithium silicate pellets. CO_2 adsorption capacity was reported 5.0 (mol CO_2/kg sorbent at 600 ^{O}C) which was relatively low compare to the lithium silicate nanoparticles [27].

However, nanomaterials are always related to high production cost with complicated synthesis process. The disadvantages of chemical adsorbents are difficult regeneration, and usage of these adsorbents need more studies for finding new adsorbents.

B. Physical Adsorption

Physisorption, also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption.

The major physical adsorbents reported for CO_2 adsorption include activated carbons, inorganic porous materials such as zeolites, hydrotalcites [4, 9, 28, 31]. If the CO_2 adsorption capacity of solid adsorbents reaches 3 mmol/g, the required energy for adsorption will be less than 30–50 % energy for absorption with optimum aqueous mono-ethanolamine (MEA) [32].

Coal is one of the adsorbent suggested for CO_2 capture. Sakurovs et al. [33] found an approximately proportional relationship between the maximum sorption capacity of a coal for gases and their critical temperature. The critical temperature of carbon dioxide is greater than methane; therefore carbon dioxide is adsorbed more strongly than methane on the coal.

Results of Sakurovs et al. [33] showed that the ratio of maximum sorption capacity between carbon dioxide and methane decreases with increasing carbon content. The average CO_2/CH_4 sorption ratio is higher for moisture-equilibrated coal and decreases with increasing coal rank [34].

The total amount of CO_2 that can be adsorbed in coal depends on its porosity, ash and affinity for this molecule. Ratios between CO_2 and CH_4 adsorption capacities vary from 1.4 for high rank coals to 2.2 for low rank coals [8].

Activated carbon (AC) has a number of attractive characteristics, such as its high adsorption capacity, high hydrophobicity, low cost, and low energy requirement for regeneration [35]. Activated carbons present a series of advantages as CO_2 adsorbents: they are inexpensive, insensitive to moisture, has high CO_2 adsorption capacity at ambient pressure and, moreover, they are easy to regenerate, and they have well developed micro and mesoporosities [10, 22, 27, 36].

Siriwardane et al. [37] studied the adsorption of CO_2 on the molecular sieve 13X, 4A and activated carbon. The molecular sieve 13X showed better CO_2 uptake than molecular sieve 4A. At lower pressures activated carbon had a lower CO_2 uptake than the uptakes of the molecular sieves, but at higher pressures the adsorption was higher for activated carbon than molecular sieves [37].

However, activated carbon CO_2/N_2 selectivities (ca. 10) are relatively low. Zeolitic materials, on the other hand, offer CO_2/N_2 selectivities 5-10 times greater than those of carbonaceous materials [28].

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The capacity of NaKA zeolite to adsorb CO_2 was similar to the capacity of NaA zeolite, 3.88mmol/g. A very high ideal CO_2/N_2 selectivity (172 times) and a high CO_2 adsorption capacity (3.2 mmol/g) were observed at an optimal K^+ content of 17 atoms% rendering NaKA [38].

In physical adsorption, the size and volume of the pores are important. Micropores are defined as pores, 2 nm in size, mesopores between 2 and 50 nm, and macropores, 50 nm in size. The micropores make better selective adsorption of CO_2 over CH_4 [26, 39-41].

Carbon nanotubes (CNTs) are most famous among nano-hollow structured materials with their dimension ranges from 1 to 10 nm in diameter and 200 to 500 nm in length. Cinke et al. investigated purified single-walled carbon nanotubes (SWNTs) adsorbed CO_2 better than unpurified SWNT. In addition, Multi-walled carbon nanotubes (MWNTs) showed stability for 20 cycles of adsorption and regeneration [27]. Lu et al. compared the adsorption capacity of MWCNTs with granular activated carbon (GAC) and zeolite. Under the same adsorption condition, MWCNTs recorded CO_2 adsorption capacity as 1.57 mol CO_2/kg sorbent while activated carbon and zeolites adsorbed 1.65 mol CO_2/kg sorbent and 1.44 mol CO_2/kg sorbent, respectively [27].

Incorporation of multi walled carbon nanotube (MWCNT) into HKUST-1, $[Cu_3(C_9H_3O_6)_2\ (H_2O)_3]\cdot xH_2O$, $(Cu_3(btc)_2$; btc = 1,3,5- benzene-tricarboxylate) have been reported by Zhonghua et al. [42]. Unmodified $[(Cu_3(btc)_2]$ and $[CNT@(Cu_3(btc)_2]$ have showed CO_2 capacity of 295 and 595mg /g, at 298 K and 18 bar, respectively. MIL-101 or $Cr_3(F,OH)(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3\cdot nH_2O$ ($n \approx 25$), is one of the metal organic framework with Lewis acid sites that can be activated by removal of guest water molecules. Anbia and Hoseini [31] have incorporated MWCNTs into MIL- 101 to synthesize a hybrid composite and denoted it as MWCNT@MIL-101. MIL-101 and MWCNT@MIL-101 show CO_2 adsorption capacities of 0.84 and 1.35 mmol/g at 298 K and 10 bar, respectively (CO_2 adsorption capacity enhanced about 60%) [31].

Liu et al. indicated that zeolite 5A has higher volumetric capacities and less heat effect of the zeolite 13X [43]. Chabazite zeolites were prepared and exchanged with alkali cations – Li, Na, K and alkaline-earth cations – Mg, Ca, Ba, were studied to assess their potential for CO_2 capture from flue gas by vacuum swing adsorption. It was found that NaCHA and CaCHA hold comparative advantages for high temperature CO_2 separation whilst NaX showed superior performance at relatively low temperatures [44].

The average values of heat adsorption on zeolites (36 kJ/mol) is larger than for AC (30 kJ/mol), confirming the mentioned affirmation. Moreover, this carbon was easily regenerated completely and it did not shown capacity decay after 10 consecutive cycles [10].

The presence of several impurity gases ($SO_x/NO_x/H_2O$) greatly complicates the CO_2 separation processes. Therefore, conventional adsorption-based CO_2 capture processes rely on using a pre-treatment stage to remove water, SO_x and NO_x, which adds considerably to the overall cost [23].

Yi et al. showed that the adsorption capacities follows the order $SO_2 > CO_2 > NO > N_2$ on both zeolites (5A and 13X). Compare two different adsorbents, the better separation efficiency can be realized by 5A zeolite [45].

Due to the increase cost of raw materials, growing research interest has been focused on producing AC from agricultural waste. Some of the agricultural wastes include the shells and stones of fruits, wastes resulting from the production of cereals, bagasse and coir pith [46].Rosas et al. prepared hemp-derived AC monolith by phosphoric acid activation.

The porosity of ACs derived from hemp stem is highly depended on the activation temperature, whereas the activation time has a minor influence. The hemp stem derived carbons are microporous materials and therefore suitable materials for hydrogen storage and CO_2 capture [46].

More recently, nano-systems researchers have synthesized and screened a large number of zeolitic-type materials known as zeolitic imidazolate frameworks (ZIFs). CO_2 capacities of the ZIFs are high, and selectivity against CO and N_2 is good. As there is a great deal of flexibility in the kinds of ZIF structures that can be synthesized, it is likely the new materials with even better adsorption selectivity and capacity can be developed in this way [28].

Recently, gas adsorption by activated carbon fibres and carbon fibre composites has been identified as a promising alternative. Lately, structured porous monolith materials made from carbon fibres, which have the ability to selectively adsorb. The results of some researchers (Burchell and Judkins, Dave et al., Yong et al.) indicate that the CO_2 adsorption efficiency of the honeycomb monolith is twice that of activated carbon and 1.5 times greater than ZIF material [3].

Alcaniz-Monge et al. [47] studied CO_2 adsorption performance on a honeycomb adsorbent made from cellulose and pitch. Petroleum pitch-1 based honeycomb monolithic composite captured 97% of CO_2 present. Kimber et al. indicated the selectivity of CO_2 decreased with increase in burn-off [3].

Metal-organic framework (MOF) materials are crystalline with two- or three-dimensional porous structures that can be synthesised with many of the functional capabilities of zeolites.

They are formed due to the coordination bonds between metal salt and multidentate ligands. MOFs are promising candidates as separation materials for CO_2 capture [5-6, 9, 31, 41].

Several MOFs have been proposed as adsorbents for CO_2 separation processes, and among these Cu-BTC [polymeric copper(II) benzene- 1,3,5-tricarboxylate] proved to be endowed with CO_2 adsorption performances that are higher than those of typical adsorbents such as 13X zeolite [48].

Millward and Yaghi [49] investigated CO_2 isotherms for a cross-section of framework characteristics such as square channels (MOF-2), pores decorated with open metal sites (MOF-505 and $Cu_3(BTC)_2$), hexagonally packed cylindrical channels (MOF-74), interpenetration (IRMOF-11), amino- and alkyl-functionalized pores (IRMOFs-3 and -6), and the extra-high porosity frameworks IRMOF-1 and MOF-177.

Their results indicated that adsorption capacities of CO_2 varies from 3.2 mmol/g for MOF-2 to 33.5 mmol/g for MOF-177 at ambient temperature and pressure of 45 bar [41].

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Zirconium-metal organic frameworks (Zr-MOFs) were synthesized with or without ammonium hydroxide as an additive in the synthesis process.

Adsorption tests showed that Zr-MOF presented much higher CO_2 adsorption than CH_4.Zr-MOF exhibited CO_2 and CH_4 adsorption of 8.1 and 3.6 mmol/g, respectively, at 273 K, 988 kPa [41].

Zhang et al. focused on the effect of water vapour on the pressure/vacuum swing adsorption process. The selected adsorbents in this study were CDX (an alumina/zeolite blend), alumina and zeolite 13X as these adsorbents will be either the pre-layer for water adsorption or the main CO_2 adsorption layer in the packed bed [23].

The MCM-41 material is one of the mesoporous products made by the hydrothermal method. Lu et al. showed the mesoporous silica spherical particles (MSPs) can be synthesized using low-cost Na_2SiO_3, thus they can be a cost-effective adsorbent for CO_2 greenhouse gas capture from flue gas [6, 50].

The adsorption capacities of various zeolite adsorbents are summarized in Table I.

TABLE I
CO_2 ADSORPTION CAPACITIES OF DIFFERENT ZEOLITES [5].

Zeolite type	T [K]	p_{CO2} [bar]	q [mmol.g-1]	Cycle
13 X	393	0.15	0.7	-
5 A	393	0.15	0.38	-
4 A	393	0.15	0.5	-
WEG-592	393	0.15	0.6	-
APG-II	393	0.15	0.38	-
Na-Y	273	0.1	4.9	-
Na-X	373	1	1.24	2
NaX-h	323	1	2.52	2
NaX-h	373	1	1.37	2
Na-X-c	323	1	2.14	2
Na-X-c	373	1	1.41	2
Cs-X-h	323	1	2.42	2
Cs-X-h	373	1	1.48	2
Cs-X-c	323	1	1.76	2
Cs-X-c	373	1	1.15	-

Layered double hydroxides (LDHs) have the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2][X^{q-}_{x/q}.nH_2O]$ with x typically in the range between 0.10 and 0.33. These materials can be readily and inexpensively synthesized with the desired characteristics for a particular application. A CO_2 adsorption capacity of 3.55mmol g^{-1} was achieved by Ca–Al LDH with ClO_4^- anion at 330 ^{O}C and 1 bar [32].

Graphite nanoplatelets (GNP) were prepared by acid intercalation followed by thermal exfoliation. Functionalized graphite nanoplatelets (f-GNP) were prepared by further treatment of GNP in acidic medium.

Palladium (Pd) nanoparticles were decorated over f-GNP surface by chemical method. Results of Mishra et al. were showed that maximum adsorption capacities of Pd-GNP nanocomposite and f- GNP (at 25 ^{o}C and 11 bar) were 0.0051 and 0.0043 mol/g, respectively, (at 50 ^{o}C and 11 bar) were 0.0045 and 0.0038 mol/g, and although (at 100 ^{o}C and 11 bar) were 0.0041 and 0.0033 mol/g [51].

C. Adsorbent Modification

The role of CO_2 as a weak Lewis acid is well established. According to the nature of carbon dioxide, the surface of the physical adsorbents can be modified by adding basic groups, such as amine groups and metal oxides [26, 28, 36, 40]. Three different methods for production of these adsorbents were investigated: activation with carbon dioxide, heat treatment with ammonia gas (amination and ammoxidation) and heat treatment with polyethylenimine (PEI) [7, 22, 36]. However, it has been suggested that amine modification can produce better and cheaper CO_2 adsorbents. Recently, the improvement of the adsorptive properties of activated carbons using metallic species, such as copper oxides, has been reported to be effective for carbon dioxide adsorption [40, 52].

The templated type of activated carbons exhibit a high CO_2 adsorption rate, a good adsorption capacity (~ 3.2 mmol CO_2/g at 25 ^{O}C), a good selectivity for CO_2/N_2 separation (~ 6.5) and they can easily be regenerated [26]. Furthermore, unlike typical commercial adsorbents such as zeolites, TRI-PEMCM-41 is tolerant to moisture in the feed and is highly selective towards acid gases in mixtures with nitrogen, oxygen, hydrogen and methane even at very low concentrations [7, 53].

Possible techniques for enhancing the adsorption capacity include loading amines onto various types of supports such as mesoporous silicas, including SBA-12 (Zelenak et al.), SBA-15 (Hiyoshi et al.; Zelenak et al.; Zukal et al.), microspheres (Araki et al.). Alternative supports include zeolites (Su et al.; Zukal et al.), MCM-41 (Zelenak et al.) and MCM-48 (Huang et al.; Kim et al.) [32].

Xu et al. designed selective 'molecular basket' by grafting poly-ethylenimine (PEI) uniformly on MCM-41. CO_2 adsorption capacity of the sorbent was 24 times higher than MCM-41 and 2 times higher than PEI [27].

The addition of ammonium hydroxide resulted in the Zr-MOF with a slight lower adsorption of CO_2 and CH_4, however, the selectivity of CO_2/CH_4 is significantly enhanced. Results of Abid et al. showed the selectivity of CO_2/CH_4 on Zr-MOF is between 2.2 and 3.8, while for Zr-MOF-NH4 selectivity is between 2.6 and 4.3 [41].

A nitrogen-rich carbon with a hierarchical micro-mesopore structure exhibited a high CO_2 adsorption capacity (141 mg/g at 25 ^{O}C, 1 atm), excellent separation efficiency (CO_2/N_2 selectivity is ca. 32) and excellent stability [53].

Amine modified layered double hydroxides (LDHs) have been prepared by several different methods. Park et al used dodecyl sulfate (DS) intercalated LDH as precursor and added (3-aminopropyl) triethoxysilane (APTS) together with N-cetyl-N,N,N-trimethylammonium bromide (CTAB). Wang et al. [32] investigated the synthesis of amine modified layered double hydroxides (LDHs) via an exfoliation and grafting synthetic route is reported. The highest adsorption capacity for CO_2 was achieved at 1.75 mmol/g by MgAl N_3 at 80 ^{O}C and 1 bar [32].

Meng et al. [25] reported that porous carbons with well-developed pore structures were directly prepared from a weak acid cation exchange resin (CER) by the carbonization of a mixture with Mg acetate in different ratios.

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The porous carbons exhibited the highest CO_2 adsorption values of 164 mg/g at 1 bar and 1045 mg/g at 30 bar.

The adsorbents were prepared based on the central composite design (CCD) with three independent variables (i.e., amination temperature, amination time, and the use of pre-heat treated (HTA) or pre-oxidized (OXA) sorbent as the starting material). Shafeeyan et al. demonstrated that the optimum conditions for obtaining an efficient carbon dioxide adsorbent is usage of a pre-oxidized sorbent and amination at 425 ^oC for 2.1 h [35].

Gargiulo et al. showed CO_2 adsorption capacity of PEI-functionalized TUD-1 (Technische Universität Delft) silica is about 3 mmol/g, if not better than those relative to similar substrates [48].

Jang et al. [40] studied the adsorption behaviours of nickel oxide loaded activated carbons for CO_2 capture. The maximum CO_2 adsorption capacity was found to be 49.9 cm^3/g at the 10 min-NiO–ACs that is higher than ACs of 41.2 cm^3/g at 25 ^oC.

Table III compares CO_2 adsorption capacities and stability of different absorbents, which were studied for post-combustion CO_2 capture.

III. Different Cycle for Co_2 Adsorption

Four different regeneration strategies were compared in a single-bed CO_2 adsorption unit: pressure swing adsorption (PSA), temperature swing adsorption (TSA), vacuum swing adsorption (VSA), electric swing adsorption (ESA) and a combination of vacuum and temperature swing adsorption (VTSA).

For the single-bed cycle configurations, the productivity and CO_2 recovery followed the sequence:

ESA < TSA < PSA < VSA < VTSA.

Values of productivity up to 1.9 mol kg^{-1} h^{-1} and a maximum CO_2 recovery of 97% were reached [10, 20, 48]. The performances found in the literatures of PSA, VSA and ESA processes for CO2 capture are reported in Table II.

IV. Conclusion

CO_2 emissions have an impact on global climate change. Many various technologies such as membrane separation, absorption, cryogenic distillation and adsorption can be used for CO_2 capture. The adsorption is the ideal way to achieve efficient CCS. Conventional solid adsorbents include activated carbons, zeolites, ion-exchange resins and meso-porous silicates, activated alumina, metal oxides, and other surface-modified porous media.

In this work, the application and efficiency of different adsorbents were compared together. It can be concluded that the choice of the best adsorbent depends on the operating conditions of the process. The $CaO–MgAl_2O_4$ and nano CaO/Al_2O_3 are the best chemical adsorbents. Although the chemical adsorbents have high adsorbent capacity and selectivity, but their regeneration is difficult.

At higher pressure (above 4 bar) activated carbons are more efficient than zeolites. The energy and cost of adsorption for activated carbons is nearly half of that of zeolites. On the other hand, zeolites (particularly 13X and 5A) have high selectivity for CO_2, and they are suitable for application in the CO_2/N_2 separation process. Generally, Zeolite 5A may have better adsorption efficiency at co-adsorbing SO_2, NO and CO_2 than zeolite 13X. Using the pre-layer was suggested by researchers because of the presence of materials such as H2O, SO_x and NO_x in flue gas.

TABLE II
Comparison between Several Adsorption Cycles for Co_2 Capture Process [20]

Process	CO_2 purity (%)	CO_2 recovery (%)
ESA	23.33	92.57
VPSA	99	53-70
PTSA	99	90
2-bed-2-step PSA	18	90
VPSA	99.5-99.8	34-69
PSA	99.5	69
PSA/VSA	58-63	70-75
VSA	90	90
PSA/VSA	58	87
PSA/VSA	82.7	17.4
3-bed VSA	90-95	60-70
TSA	95	81
ESA	89.7	79
PSA	16	89

In order to achieve more selective separation CO_2 from flue gas the modified adsorbent surface was considered. Furthermore, the most modified adsorbents are highly selective towards acid gases in mixtures including of nitrogen, oxygen, hydrogen and methane even at very low concentrations, and also the presence of moisture in the feed does not affect its performance. New adsorbents such as honeyncomb monolith, MOFs, CHAs (NaCHA and CaCHA), PMO (MCM and SBA) and MSPs (Na_2SiO_4) are suitable adsorbents for selective CO_2 separation but they require more researches and studies.

It can be seen among the various adsorption cycle, the productivity and CO_2 recovery of VTSA, VSA and TSA are in order TSA< VSA<VTSA.

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TABLE III
ADSORPTION CAPACITY OF DIFFERENT ADSORBENTS FOR POST-COMBUSTION CO_2. CAPTURE

Sorbent	Operating Temperature (°C)	Operating Pressure (kPa)	CO_2 Capture Capacity (mol CO_2/kg sorbent)	Regeneration Cycles, n	CO_2 Capture Capacity Remained after n cycles (%)	Researchers	References
Physical Adsorbents							
AC (4%KOH)	30	30	0.55	-	-	Guo et al.[?]	[27]
AC (EDAa + EtOH[b])	30	30	0.53	-	-	Guo et al.	[27]
AC (4%KOH + EDAa + EtOH[b])	30	30	0.64	-	-	Guo et al.	[27]
MCM-41	25	100	0.62	-	-	Serna-Guerrero et al.	[27]
MCM-41(DEA[c])	75	100	1.26	-	-	Franchi et al.	[27]
MCM-41 (50% PEI[d])	75	100	2.52	-	-	Franchi et al.	[27]
Activated carbon (AC)	30	30	0.35	-	-	Guo et al.	[27]
MCM-41 (50% PEI[d]) "molecular basket"	75	100	2.95	-	-	Guo et al.	[27]
PE[e]-MCM-41	25	100	0.50	-	-	Serna-Guerrero et al.	[27]
PE[e]-MCM-41(TRI[f])	25	100	2.85	-	-	Serna-Guerrero et al.	[27]
PE-MCM-41(DEA[c])	75	100	2.36	-	-	Franchi et al.	[27]
MCM-48	25	100	0.03	-	-	Jang et al.	[27]
MCM-48(APTS[g])	25	100	0.64	-	-	Jang et al.	[27]
ithium zirconate	400	100	5.00	-	-	Oliveira et al.	[27]
ithium orthosilicate	600	100	6.13	-	-	Oliveira et al.	[27]
alcium oxide	600	100	17.30	-	-	Oliveira et al.	[27]
nesium hydroxide	200	103	3.00	-	-	Siriwardane et al.	[27]
nesium oxide oporous)	100	100	2.27	-	-	Bhagiyalakshmi et al.	[27]
rated carbon	30	110	1.58	-	-	Mercedes et al.	[27]
M-41	25	100	0.62	-	-	Serna-Guerrero et al.	[27]
ecular basket' M-41(50%PEI)	75	100	2.50	8	96.0	Xu et al.	[27]
MCM-41(TRI)	25	100	1.80	10	94.4	Serna et al.	[21]
MCM-41(DEA)	25	100	2.90	7	96.6	Franchi et al.	[27]
NT	60	101	1.30	-	-	Hsu et al.	[18]
NT	60	101	1.70	-	-	Hsu et al.	[18]
Chemical Adsorbents							
oporous (MgO)	25	101	1.80	3	100	Bhagiyalakshmi et al.	[27]
nanopods	600	101	17.50	50	61.1	Yang et al.	[42]
derived from osized $CaCO_3$	650	101	16.70	100	22.2	Florin et al.	[27]
-$MgAl_2O_4$ (Spinel particles)	650	101	9.10	65	84.6	Li et al.	[27]
CaO/Al_2O_3	650	101	6.00	15	61.7	Wu et al.	[27]
um silicate particles	610	101	5.77	-	-	Ochoa-Fernández et al.	[27]
crystalline O_3 particles	575	101	6.10	8	100	Khomane et al.	[27]
/Al_2O_3	650	101	6.02	-	-	Wu et al.	[27]
um Silicate nano icles	600	101	5.00	-	-	Essaki et al.	[30]
HNa	300	134	1.11	50	93.3	Lee et al.	[27]

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