Int. J. Environ. Sci. Technol.
DOI 10.1007/s13762-016-1008-1

REVIEW

Feasibility of CO_2 adsorption by solid adsorbents: a review on low-temperature systems

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Received: 6 September 2015 / Revised: 23 March 2016 / Accepted: 3 May 2016

Abstract In the last few decades of industrialization, the concentration of CO_2 in the atmosphere had increased rapidly. Different organizations have invested considerable funds in research activities worldwide for CO_2 capture and storage. To date, significant work has been done and various technologies have been proposed for CO_2 capture and storage. Both adsorption and absorption are promising techniques for CO_2 capture, but low-temperature adsorption processes using solid adsorbents are the prevailing technique nowadays. In this review paper, a variety of adsorbents such as carbonaceous materials, dry alkali metal-based sorbents, zeolites, metal–organic frameworks (MOFs) and microporous organic polymers (MOPs) have been studied. Various methods of chemical or physical modification and the effects of supporting materials have been discussed to enhance CO_2 capture capacity of these adsorbents. Low-temperature (<100 °C) adsorption processes for CO_2 capture are critically analyzed and concluded on the basis of information available so far in the literature. All the information in CO_2 adsorption using different routes has been discussed, summarized and thoroughly presented in this review article. The most important comparative study of relatively new material MOFs and MOPs is carried out between the groups and with other sorbent as well.

Keywords CO_2 · CO_2 adsorption technologies · Adsorption · Adsorbent · Low-temperature adsorption

Introduction

Recently, the needs of energy for world economic and social development have increased tremendously. In the run of fulfilling these needs, carbon dioxide and greenhouse gases (GHGs) emissions have shown an increasing trend. This has threatened our world in the form of global warming and many other environmental issues, such as extreme weather, acid rain, unequal distribution of food, migration of animals and disturbed nutrition for plants and animals (Lesley 2014). It has been predicted that the mean global temperature will increase approximately 2 °C in year 2100. This increase will indirectly increase the amount of CO_2 in atmosphere. According to the geologist and environmental experts, lots of CO_2 locked in the permafrost of Arctic (Northern Hemisphere) (Rydberg et al. 2010; Yang et al. 2008) and CH_4 in the form of methane clathrate ($CH_4 \times 5.75\ H_2O$) in small cages of ice under the high pressure of ocean water (Sundquist and Visser 2014). If the average temperature of the world increased as usual scenario, CO_2 in permafrost and CH_4 in the ocean will get its way to open atmosphere and will increase the GHGs in atmosphere. Climate changing simulation designs show that the tipping point is 2–4.5 °C increase in the average temperature worldwide (Dulal and Akbar 2013; Lesley 2014).

Nowadays, most of the world population uses the conventional sources of energy. Burning of fossil fuel, solid

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waste and agricultural sectors are more responsible for emission of CO_2. Power generation and transportation are the two main sectors that contribute enormously to atmospheric CO_2 (France World Energy Outlook 2012; USA. Center for climate and energy solutions 2013). According to the World Bank statistics, 4.9 metric tons of CO_2 per capita was added to the atmosphere each year. This is the reason the atmospheric concentration of CO_2 has increased by 30.01 % since industrialization from levels of 280 ppm to about 400 ppm today. The prediction of International Panel on Climate Change (IPCC) shows that this level will increase to 570 ppm by the year 2100 (Lee et al. 2014; Yang et al. 2008). From the ice cores through proxy data analysis, it has been concluded that the CO_2 level in atmosphere is higher than at any time during the last 0.65 million years. Figure 1 shows the trend of global carbon emission from year 1900 to 2012. To estimate the carbon dioxide, multiply the carbon emission estimates by 3.667. International Energy Agency (IEA)-World Energy Outlook (WEO) in November 2013 revealed that by 2030 the emission of CO_2 in the atmosphere will attain 63 % from today's level, which is roundabout 90 % higher than those of 1980s (Carbon Dioxide Information Analysis Center 2012; Ganesh 2013).

Although carbon dioxide (CO_2) is removed from the atmosphere through plants in the biological CO_2 cycle, large amount of current and future anticipated CO_2 is beyond the capacity of our greens (Sundquist and Visser 2014). In addition, this natural cycle fall short when eventually plants and animals decay and begin to release captured CO_2 into the atmosphere, making an ineffective natural cycle (Dulal and Akbar 2013; Harsono et al. 2013). Numerous choices are there to reduce CO_2 emissions in the atmosphere such as improving power plant efficiency, replacement of coal by natural gas, introducing higher thermal efficiency combined cycles of steam and gas for power generation, shifting to renewable resources and CCS (Lee et al. 2014; Wall 2007). Generally, these techniques are not applicable to the large number of existing fossil fuel-fired power plants and other power-consuming units. Currently, 90 % of global energy is from fossil fuels consumption and this source of energy cannot be weeded out rapidly. Fossil fuels will be relied on as the primary source of energy for the next several decades. Therefore, an extensive research effort would be needed to improve the CO_2 capture and storage technologies (Zhao et al. 2013).

CO_2 capture technologies

Currently, three different technologies are used for CO_2 capture; i.e., pre-combustion, post-combustion and oxy-fuel. In these processes, up to 90 % of CO_2 capture is possible to be achieved. This percentage can be increased, but elevated cost is the main constraint (European Technology Platform 2014). In the pre-combustion capture of CO_2, the fuel is decarbonized prior to combustion. Using this technology in coal-powered plants, a stream of almost pure oxygen is produced in the air separation unit. The oxygen is then reacted with pulverized coal to form syngas. In a water–gas shift reaction (WGSR), steam is added to the syngas converting CO to hydrogen and CO_2. After physical wash, CO_2 is separated and dehydrated from the gas stream leaving H_2 behind, which is a clean source of energy (Jin and Zhang 2011; Yu et al. 2012). Oxy-fuel technology burns fuel and pure oxygen instead of ambient air. The main content of air nitrogen is removed, making a pure stream of O_2. After burning fuel and pure O_2, the flue gases are re-circulated in a burning unit to increase the concentration of CO_2 in flue gases by complete combustion of the content. Further, CO_2 is captured from the flue gases and stored. Chemical looping combustion (CLC) is related to oxy-fuel technique. CLC is relatively new concept that integrates energy conversion and CO_2 separation. In this

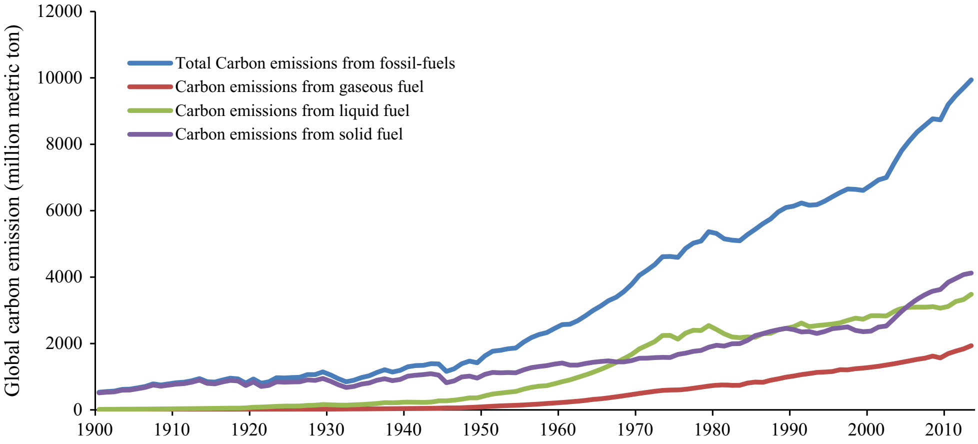

Fig. 1 Global carbon emission in million metric tons for year 1900–2012 (Thomas 2012)

technique, a solid material generally metal oxide is used as O_2 carrier containing O_2 for combustion of fuel. The O_2 carrier solid material must be re-oxidized for new cycle to complete the loop. The third one is post-combustion technology; it can be retrofitted to existing and future power plants. In this process, the fuel and air are blasted in the furnace, which produces heat and flue gases. Heat is used where it is needed, while flue gases goes to section where small particles called “fly ash” and sulfur are removed from it. Furthermore, CO_2 is removed by absorption or adsorption. For regeneration, the sorbent is moved to desorber, where it is heated to release the captured CO_2. The CO_2 can also be removed from flue gases via chemical solvent scrubbing method (Guo et al. 2013; Jin and Zhang 2011; Webley 2014; European Technology Platform 2014). Figure 2 briefly explains the CO_2 capture technologies and processes.

Most of the CO_2 capture technologies are in experimental stages. Chemisorption of CO_2 in monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) are used commercially in natural gas industry (Drage et al. 2009a, b; Kaithwas et al. 2012; Rao and Rubin 2002; Stewart and Hessami 2005). However, high degree of equipment corrosion, greater amount of energy for regeneration, large volume of absorber and low contact area between gas and aqueous solution make this process a less preferred approach (Rochelle 2009). The same way, conventional wet solvent processes are also not efficient. These processes have been examined for CO_2 capture at pilot-scale, but this technique is costly, requires pre-treatment, and produces large amount of wastewater and sludge. In adsorption process, the added advantages of those solid adsorbents are easy to handle and do not give rise to corrosion problems (Plaza et al. 2009; Thiruvenkatachari et al. 2009).

Adsorption

Solid surfaces show strong affinity toward gas molecules that come in contact with the surface. The process of trapping or binding of molecules to the surface is called adsorption. Based on the nature of interactions, adsorption can be classified into two types: (1) physical adsorption and (2) chemical adsorption. In physical adsorption, the molecules are physisorbed because of physical forces (dipole–dipole, electrostatic, apolar, hydrophobic associations or Van der Waals) where the bond energy is 8–41 kcal mol^{-1}, while in chemical adsorption, molecules chemisorbed (chemical bond; covalent, ionic or metallic) and the bond energy is about 60–418 kcal mol^{-1} (Ho et al. 2014). The adsorbent sample used in physisorption can be regenerated by simple degassing method. Chemisorption is useful where permanent binding and trapping of harmful gas is required, but after chemisorption, the regeneration of solid matrices is very challenging. For instance, lime, soda lime or limestone, which generates strong alkali hydroxyls [e.g., NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$] in the presence of moisture, interact chemically with acid gases (CO_2, SO_2, NO_2) (Ishibe et al. 1995; Ho et al. 2014).

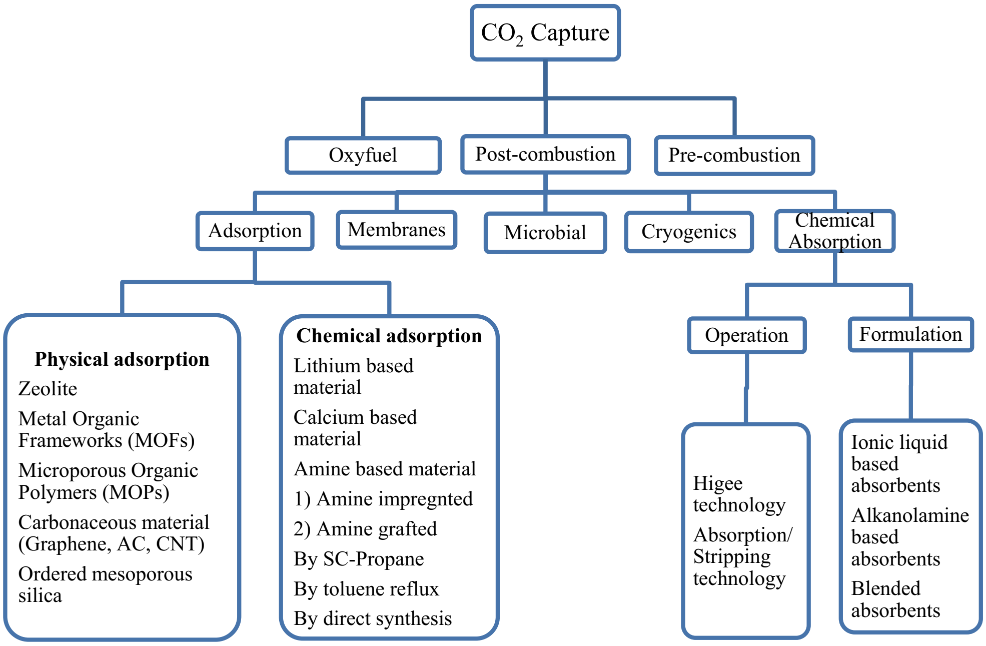

Fig. 2 Different technologies for CO_2 capture

In the process of gas adsorption, the molecules of the gas temporarily depart from the gas phase when it comes to the vicinity of the solid surface and undergoes an interaction with it. Molecules in this new condensed state remain for a short period and then return to the gas phase. The duration of this stay depends on the characteristic of the adsorbing surface and the adsorbate, the number of gas molecules that encounter the surface, their kinetic energy and other factors such as capillary forces, surface heterogeneities. Besides the characteristics of adsorbates and adsorbents, the adsorption temperature and pressure also play an important role in gas encapsulation in solid matrices. The effect of temperature on the adsorption capacity depends greatly on the nature of solid matrices and type of adsorbing gas. For example in hydrogen adsorption on carbon nanotubes, lower temperature favors adsorption. On the other hand, gas adsorption on zeolite increased at relatively high temperature because of the pores enlargement and higher kinetic energy of the gas molecules, which allows molecules to diffuse more easily into the cavities of solid matrices (Goetz et al. 2006; Ho et al. 2014; Yoon and Heo 1992). Mainly in physisorption, high pressure is used to push gas molecules to have contact at binding sites on the surface and pores of solid matrices that enhance the adsorption capacity (Anson et al. 2004). Adsorbents such as activated carbons, mesoporous silicates and zeolites, carbon fiber monolith, alumina, metal–organic framework, microporous organic polymers and metal oxides have been broadly used for CO_2 adsorption. In the following section, we will discuss a few of them.

Adsorption equilibria and kinetics important parameters to evaluate the performance of an adsorbent, which is required for designing a scaled-up adsorption process for a new material. Apart from CO_2 adsorption capacity, the kinetics and regeneration ability of the adsorbents should also be considered (Wang et al. 2010). Fast adsorption/desorption kinetics are essential for efficient CO_2 adsorption process under the operating conditions. It gives a sharp CO_2 adsorption breakthrough curve in which the effluent CO_2 concentration is measured as a function of time, while slow kinetics gives a gradual breakthrough curve. Thus, the kinetics of adsorption and desorption controls the cycle time and the amount of adsorbent required in the adsorption system. The faster an adsorbent can adsorb/desorbed CO_2, the less amount of adsorbent will be needed to capture a given volume of CO_2 (Samanta et al. 2011; Yu et al. 2012). It has been reported that the overall kinetics of CO_2 adsorption is influenced by functional groups present, as well as the pore size and distribution in the support. LTA zeolites of the similar particle sizes and Si/Al ratios showed the faster CO_2 adsorption kinetics for Meso-LTA than Micro-LTA, which must be attributed to its mesoporosity that led to rapid gas transport inside the zeolite framework (Chen and Ahn 2014).

Carbonaceous material-based adsorbents

Inorganic porous carbons are common for the CO_2 adsorption. The group of carbonaceous material-based adsorbents encompasses a large variety of materials that include activated carbon obtained from a range of materials, graphene, mesocarbon and carbon nanotubes (CNTs) (Ghosh et al. 2008; Saha and Deng 2010). Almost all carbonaceous materials of sufficient strength, low organic volatile content and high in elementary carbon can be converted into CO_2 adsorbent (David and Kopac 2014). The low cost, high surface area, wide availability, easy pore structure modification, surface functionalization and ease of regeneration make the carbonaceous material very significant adsorbent for CO_2. Recently, the development has been made in carbon capturing and storage (CCS) using carbonaceous adsorbents in integrated gasification combined cycle (IGCC) for hydrogen production and energy generation in the form of syngas or through methanation process (Drage et al. 2009a, b).

Most of the CO_2 adsorption processes are a combination of physisorption and chemisorption. Physisorption occurs due to weak van der Waals forces between adsorbates and adsorbents molecules, while chemisorption occurs due to chemical interactions between the adsorbate and the surface functional groups of adsorbents (Su et al. 2009). However, the weak van der Waals forces in physisorption make these adsorbents very sensitive to high temperature and poor in selectivity. The CO_2 adsorption capacity decreases significantly at temperature higher than 50 °C. For most of the adsorbents, room temperature was noticed as the best operating temperature for adsorption (Andres et al. 2013; Plaza et al. 2009). Previous research showed that adsorption at atmospheric pressure is effective only when the pore size is less than the molecular size of the adsorbate (Maroto-Valer et al. 2005). Adsorption on carbonaceous material is favored at high partial pressure of adsorbate. Hence, the CO_2 capture capacity in a real industrial process, where CO_2 is diluted with other flue gases, will be lower than achieved in pure CO_2 in laboratory work (Arenillas et al. 2005; Plaza et al. 2009). To increase adsorption capacity for carbonaceous materials, different modifications can be made through physical or chemical processes. Varieties of precursors (especially, metal oxides, alkali metals) are used to increase the surface area and tune the pore size for CO_2 capture. However, at some activation conditions, microporosity decreases with the increase of surface area due to the internal wall breakage. Therefore, it is not necessary that the CO_2

adsorption will increase with the increase of surface area (Maroto-Valer et al. 2005; Reddy et al. 2015). The other approach is to form structures of single-walled carbon nanotubes (CNTs), multi-walled CNTs, graphenes, ordered mesoporous carbon, microporous carbon (Yu et al. 2012). In Table 1, different reagents and their general effects on CO_2 adsorption in carbonaceous material-based adsorbents are summarized.

Naturally, CO_2 is acidic and increasing the alkalinity of the adsorbents by surface modification is very helpful for CO_2 adsorption. This can be achieved by impregnation of polyethylene glycol (PEG) and 3-chloropropylamine-hydrochloride (3-CPAHCl) or nitrogen functional group into the carbon framework (Samanta et al. 2011; Wang et al. 2010). Plaza et al. (2009) reported that an increase of nitrogen contents in the carbon-based adsorbents would enhance the adsorption capacity of CO_2. It is essentially introduced into the carbon framework either by carbonization of nitrogen-containing precursor or by the post-modification. Enhancement of nitrogen functionalities in adsorbents is referred as amination. Amination is carried out in the presence of N-containing species (i.e., gaseous ammonia, urea, cyanide, urea, melamine, polyacrylonitrile) at a specific temperature (Rufford and Jurcakova 2013). To date, naturally occurring nitrogen-containing precursors such as aminoacids, amino-carbohydrates, proteins, polymers (chitosan, glucosamine) and N-ionic liquids have been reported as agent for amination (White et al. 2011). Hao et al. (2011) used amination method to synthesize an efficient nitrogen-doped carbon adsorbent named monolith. Monolith reported to have CO_2 adsorption capacity of 3.13 mmol g^{-1} at room temperature and 1 bar pressure. Generally, the incorporation of nitrogen functionalities has increased the basicity of carbon adsorbent, but not in all circumstances. It depends on the type of incorporated group and the arrangements in the carbon matrix (Rufford and Jurcakova 2013).

Table 2 reveals that CO_2 adsorption capacity of virgin carbonaceous material could be improved from 0.5 to 8 mmol g^{-1} for modified carbonaceous material. Grafted or impregnated carbonaceous material with suitable chemicals, such as amine group, has attracted great interest of research community. Amine-grafted carbonaceous material, derived from glucose samples, showed significant uptakes of CO_2 that is 4.3 mmol g^{-1} at 20 °C and 1 atm (Zhao et al. 2010). Activation of carbonaceous material at high temperature and for extended time would enhance the uptake of CO_2 for anthracite-based AC. In Table 2, paulownia sawdust-derived AC (activated with KOH and heated at 800 °C) exhibited the highest CO_2 adsorption capacity of 8 mmol g^{-1}. This study revealed that KOH activation and amination were observed as significant processes for the enhancement of CO_2 adsorption capacity. In contrast, CO_2 adsorption capacity of carbonaceous

Table 1 Reported chemicals for modification of carbonaceous material-based adsorbents and their general effects

Chemicals	Effects	References
NH_3 heat treatment	Surface area development and the introduction of alkaline nitrogen groups increase CO_2 adsorption	David and Kopac (2014)
Monoethanolamine (MEA)	Surface area decreases, but the introduction of alkaline nitrogen groups increases CO_2 adsorption	David and Kopac (2014)
Amines	Amine impregnation increases the basicity, nitrogen content and microporous volume of the activated carbon. CO_2 capture does not vary linearly with surface area. The CO_2 adsorption capacities are resulted from the reaction with amine groups. Amine impregnation exhibited different results for different carbonaceous materials	Lee et al. (2013), Maroto-Valer et al. (2005), Kong et al. (2015)
KOH	One of the best activating reagents for increasing CO_2 adsorption etches the soft components of carbonaceous material and increases the number of pores and surface area	Zhu et al. (2014), Heidari et al. (2014)
H_3PO_4	Surface area and number of mesopores (2 nm < diameter < 50 nm) increase, while the size of CO_2 is 209 pm due to which CO_2 adsorption increases slightly	Heidari et al. (2014)
$ZnCl_2$	$ZnCl_2$ increases surface area and mesoporosity where mesopores are not compatible with CO_2 size. Thus, CO_2 adsorption increases very slightly	Heidari et al. (2014)
NaOH	Surface area decreases as compared to virgin AC, but CO_2 adsorption increases due to the oxygen-containing functional groups and the formation of basic surface sites for CO_2 chemisorption	Andres et al. (2013), Xing et al. (2014)
Metal Oxide	Relatively, CO_2 adsorption capacity is small for carbonaceous material impregnated with metal oxide. The reason is the large molecular size of metal oxide that blocks the pores	Somy et al. (2009)

Table 2 CO$_2$ adsorption capacity of carbonaceous material-based solid adsorbents

Sorbent	Temperature (°C)	Pressure (atm)	Capacity (mmol g^{-1})	Experimental procedure	References
AC	25	1	2.61	PSA	Siriwardane et al. (2001)
AC	25	0.1	0.57	GC-TCD	Lu et al. (2008)
AC (in N$_2$ atm.)	20	1	3.75	Ads. isotherm	Zhang et al. (2010)
AC (with KOH)	30	1	4.10	Static volume method	Heidari et al. (2014)
Anthracite-based AC[e]	30	P_{atm}	1.38	TGA	Maroto-Valer et al. (2005)
Anthracite-based AC[f]	30	P_{atm}	1.33	TGA	Maroto-Valer et al. (2005)
AC[a]	25	1	2.25	–	Radosz et al. (2008)
AC[b]	25	1	1.53	–	Radosz et al. (2008)
Sewage sludge-derived AC	25	P_{atm}	1.27	TGA	Andres et al. (2013)
AC (paulownia sawdust)	0	1	8.00	Ads. isotherm	Zhu et al. (2014)
AC-A35/4	20	1	2.00	Flow desorption	Park et al. (2006a, b)
AC-F30/470	15	1	2.86	Vol. analysis	Berlier and Frere (1997)
AC Norit RB1	40	0.15	0.50	TPD	Foeth et al. (1994)
AC Norit RB1	21	1	2.46	Gravimetric analysis	Vaart et al. (2000)
Rapeseed oil cake/walnut shell	25	P_{atm}	1.55	TGA	David and Kopac 2014)
Spent coffee-derived AC	0	0.2	2.0–3.8	Toth model simulation	Gonzalez et al. (2013)
		1.2	2.5–5.0[h]		
Bamboo-derived AC[c]	2	2	0.54	Vol. analysis	Wang et al. (2008)
Bamboo-derived AC	2	2	3.00	Vol. analysis	Wang et al. (2008)
Leather-derived AC	0	1	>2.0	TG/DTA	Bermudez et al. (2013)
Glucose-derived AC[d] (amine-rich)	–20	1	4.3	TGA	Zhao et al. (2010)
Celtuce leaves-AC (with KOH)	25	P_{atm}	6.04	TGA	Wang et al. (2012)
Coconut shell based AC	50	–	0.44	Static volume method	Li et al. (2010)
Olive stones	25	–	2.43	TGA	Plaza et al. (2009)
Oil fly ash (amine functionalized)	40	1	5.45	TGA	Yaumi et al. (2012)
PSAC (AMP)	25	P_{atm}	1.45	Breakthrough curve	Lee et al. (2013)
SWCNT	35	1	4.02	Ads. isotherm	Cinke et al. (2003)
CNTs	50	–	1.08	Ads. isotherms	Su et al. (2009)
CNTs (APTS)[g]			1.52		
Carbon Monolith (N$_2$-doped)	0	1	4.9	–	Hao et al. (2011)
Meso-Carbon	25	1	1.50	Ads. isotherm	Saha and Deng 2010)
Graphene	−78	1	2.41	Ads. isotherm	Ghosh et al. (2008)

[a] Activated carbon without acid treatment

[b] Activated carbon with acid treatment

[c] Bamboo activated carbon with water loading

[d] Grafting with oligo-amine moieties at room temperature

[e] Activated at 850 °C for 3 h

[f] Activated at 850 °C for 2 h

[g] Modified with 3-aminopropyl-triethoxysilane (APTS)

[h] Activated with NCLK3

material would be reduced when it was treated with acid as shown in Table 2. The CO$_2$ acidity is the main reason for the drop of adsorption capacity. It has also been reported that CO$_2$ adsorption will not follow a linear relationship with the surface area due to the presence of ineffective pore size in the material for CO$_2$ adsorption. Besides other preparative tools, the heat treatment is found to be one of the essential parameters for making efficient carbonaceous adsorbents. Most of the research work has shown 600–800 °C as optimum heat treatment temperature and 1–3 h as optimum dwelling time. However, high temperature and prolong dwelling time have decreased the hardness of the carbonaceous adsorbents. This is supposed to be because of continual loss of volatile matter from the carbon matrix that makes the material highly porous and create void spaces in the sample. Carbonaceous material-based adsorbents have a great potential for CO_2 adsorption, but the production cost and further activation cost are high because of high-temperature heat treatment. In future, innovative researches are needed to develop highly cost-effective production and activation processes of carbonaceous material-based adsorbents.

Dry alkali metal-based sorbents

Recently, chemical adsorption of CO_2 with a dry regenerable alkali metal-based solid sorbent immerged as a stronger option for CO_2 adsorption with the advantage of retrofitting and integrating to existing power generation plants. This process would produce more than 90 % pure CO_2 sequestration. The reaction is shown below:

$$M_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \leftrightarrow 2MHCO_{3(s)} \qquad (1)$$

$$\Delta H_r^\circ = \begin{cases} -32.24\,\mathrm{kcal\,mol^{-1}} & \text{for } M = Na \\ -33.68\,\mathrm{kcal\,mol^{-1}} & \text{for } M = K \end{cases}$$

In the reaction above, M is any alkali metal element, such as sodium (Na) and potassium (K) (Hoffman and Pennline 2001; Zhao et al. 2013). The forward step reaction is for CO_2 removal or carbonation, and the reverse direction reaction is for the sorbent regeneration (Dong et al. 2012; Chen et al. 2012). Carbonation is predominantly exothermic process, while decarbonation or regeneration is endothermic. Carbonation process will slow down after sometime due to the heat accumulation during adsorption in fixed-bed and fluidized-bed reactor. Hence, for continuous removal of CO_2, the incorporation of cooling system that transfers heat from the reactor is of great importance. For smooth transfer of exothermic heat, alkali metal-based sorbents were coated on metal support, which has high heat conductivity (Kondakindi et al. 2013; Liang et al. 2004). Alkali metal-based sorbents form bicarbonate ($MHCO_3$) at temperature below 100 °C and high partial pressure of CO_2 in the presence of water. At high temperature, $MHCO_3$ converted to carbonate (M_2CO_3), which is more stable at wide range of pressure and temperature (Zhao et al. 2013). It has been suggested that the phase transition temperature for $MHCO_3$ to M_2CO_3 is above 100 °C.

Normally, alkali metal-based sorbents are prepared by impregnation of alkali metal precursor on catalyst supports such as activated carbon (AC), Al_2O_3, SiO_2, TiO_2, MgO and zeolites. These catalyst supports are used to increase the surface area and porosity of the alkali metal-based CO_2 sorbents (Park et al. 2006a, b). If an appropriate sorbent and proper operation conditions are chosen, continuous removal of CO_2 up to 80 % can be achieved with ease under favorable economics (Zhao et al. 2013; Park et al. 2006a, b). Various metal oxides such as Na-, K- and Li-based materials are considered to be efficient for the CO_2 adsorption operation, but the seriousness of diffusion resistance has hindered their commercial consumption (Iwan et al. 2009; Yu et al. 2012). The attrition or abrasion resistance affects the CO_2 capture. Unfortunately, it is difficult to fully understand the attrition behavior of these sorbents (Zhao et al. 2011). Additionally, the raw material for alkali metal-based sorbents and supporting materials are cheap, but the need of large amount of sorbent has elevated the cost of this technology quite significantly. Therefore, regeneration is an essential tool in this technology to minimize the large amount of wastage. In order to align regeneration reaction with carbonation reaction in a continuous CO_2 adsorption operation, it is necessary to understand reaction rate and thermodynamic of both reaction thoroughly. However, the kinetics information of these reactions is very limited (Seo et al. 2007; Lee et al. 2008a, b; Dong et al. 2012). This technology has many hurdles ahead in launching it in a full-scale commercial level. Still a range of alkali metal-based sorbents have been carefully investigated by researchers for CO_2 adsorption. Notable of these sorbents are sodium-based sorbents and potassium-based sorbents.

Several types of sodium carbonate-based sorbents have been investigated extensively in the literatures due to its abundance and relatively cheap material. These types may be different on the basis of supporting material of sorbent such as AC, Al_2O_3, SiO_2, TiO_2, MgO (Park et al. 2006a, b), ZrO_2 (Lee et al. 2005) and zeolites or on the basis of process production of M_2CO_3 and $MHCO_3$. Dong et al. (2012), Chen et al. (2012) studied both the effects of supporting material and the production process of M_2CO_3 and $MHCO_3$ for CO_2 adsorption process. It was found that carbonate and calcined carbonate derived from bicarbonate are inefficient for CO_2 capture without the support of inorganic matrix. Na_2CO_3 is an impervious natured material, and it does not carbonate easily. Calcination improves the microscopic structure of Na_2CO_3, which slightly increases the CO_2 capture capacity of this sorbent. Moreover, instead of producing $NaHCO_3$ in carbonation reaction, this sorbent has generated $Na_5H_3(CO_3)_4$ as a major product. In addition, the carbonation reaction takes too much time. Alternatively, using alumina (Al_2O_3) as porous matrix or support material for both sorbents, a considerable improvement of microscopic structures was noted indicating the enhancement in carbonation characteristics. Unlike the previous experiment, the product generated is only $NaHCO_3$. This concludes that sodium carbonate and sodium bicarbonate are effective when used with a suitable inorganic matrix (Dong et al. 2012; Chen et al. 2012; Park et al. 2006a, b). Carbon adsorption results did not change significantly for calcined and non-calcined sorbents, which shows little effect of calcination temperature on the properties of the sorbents. $NaHCO_3$ decomposes to Na_2CO_3 when it is calcined at the temperature higher than 110 °C (Zhao et al. 2013).

The CO_2 uptake capacity depends on the structural characteristic of these materials. Lee et al. (2008a, b) studied the effect of particle size and shape of sorbents on CO_2 adsorption. Size distribution and defected spherical shapes such as hollow shapes, doughnut and dimple shapes can be avoided by controlling some parameters in carbonate slurry preparation. The parameters for the preparation are concentration, pH and viscosity of the slurry. In addition, organic additives such as dispersants can be added to control the preparation parameters. Results have shown that CO_2 adsorption can be improved with the increment in surface area, attrition resistance and H_2O retention capacity. High surface area and pore volume of a sorbent have increased the H_2O retention capacity indirectly. Table 3 shows process conditions and efficiency of Na_2CO_3 sorbents supported on different inorganic matrix. Mostly, alkali metal-based sorbents are used at temperature below 100 °C in chemical adsorption of CO_2. However, these adsorbents can be better used at high temperature. Siriwardane et al. (2007) developed Na/CaO sorbent for CO_2 adsorption at 315 °C, which is appropriate for high-temperature CO_2 capture applications such as coal gasification systems. Unlike carbonaceous material-based sorbents and zeolites, dry alkali metal-based sorbents can be used at a wide range of temperatures from ambient to about 500 °C.

Many researchers have studied potassium-based sorbents for CO_2 sorption in considerable detail. Lee et al. (2005) attempted to develop various potassium-based sorbent formulations and carried out basic research in CO_2 sorption. As adsorption is a surface phenomenon, research is also going on in the area of particles shape of dry alkali metal-based sorbent (Zhao et al. 2013). Both K_2CO_3- and Na_2CO_3-based sorbents have been investigated and shown almost similar results (Wang et al. 2010). The literature has revealed that inorganic matrix support has a significant effect on the CO_2 sorption. MgO support is one of the efficient support materials for alkali metal-based sorbent. Table 3 shows CO_2 adsorption range is 0.34–4.49 mmol CO_2 g^{-1} of sorbent for K_2CO_3 supported on a range of inorganic matrix. K_2CO_3/MgO could adsorb the maximum amount of CO_2 per unit of sorbent mass (more than theoretical value) as compared to K_2CO_3/SiO_2 (Lee et al. 2005). The high amount of CO_2 adsorption capacity of K_2CO_3/MgO could be explained by the fact that MgO itself, as well as K_2CO_3, could adsorb CO_2 in the presence of water vapor even at low temperatures (Lee et al. 2008a, b). Water retention capacity plays an important role in the CO_2 capture. Increasing water vapor concentration in the range of 10–20 vol % would increase the CO_2 sorption capacity. The preparation method of sorbent also slightly affects the sorption capacity. Sample obtained by wet-mixing method is more efficient than sample obtained by impregnation method (see in Table 3) (Zhang et al. 2014a, b).

It has been learned that the CO_2 adsorption capacity of sorbents such as K_2CO_3/AC, K_2CO_3/MgO, K_2CO_3/Al_2O_3 and K_2CO_3/TiO_2 is the function of number of cycle used in the process (Liang et al. 2004). Lee et al. (2005) tested regenerated K_2CO_3/AC, K_2CO_3/MgO, K_2CO_3/Al_2O_3 and K_2CO_3/TiO_2 sorbents for CO_2 capture capacity, and the results showed that K_2CO_3/AC is the only sorbent for which CO_2 capture capacity increases after the first cycle of regeneration. The sorption capacity of the K_2CO_3/TiO_2 and K_2CO_3/ZrO_2 maintained the same for other cycles and CO_2 adsorption capacity for K_2CO_3/Al_2O_3 and K_2CO_3/MgO decreased (Lee et al. 2008a, b). The decrease in the CO_2 capturing capacity of K_2CO_3/MgO and K_2CO_3/Al_2O_3 after regeneration process at temperature below 200 °C is due to the formation of $KAl(CO_3)_2(OH)_2$, $K_2Mg(CO_3)_2$ and $K_2Mg(CO_3)_2{\cdot}4H_2O$, which do not allow complete conversion to the original K_2CO_3 in regeneration process. Contrary to the K_2CO_3/MgO and K_2CO_3/Al_2O_3, in the case of K_2CO_3/TiO_2 and K_2CO_3/AC, crystals structure of $KHCO_3$ formed during carbonation. Even at moderate temperature of 130 °C, this crystal structure phase could be easily converted in original phase during regeneration process (Lee et al. 2005). This indicates that the changes in the structure of sorbent depend upon the nature of support material. Besides the number of cycle, the parameters such as gas velocity, carbonation temperature, solid circulation and water vapor content have a significant effect on CO_2 adsorption in alkali metal-based sorbents. It was noted that CO_2 removal increased when gas velocity decreased and solid circulation rate increased (Yi et al. 2007).

Literature revealed that potassium-based sorbent can be produced from various precursors of K_2CO_3, $K_2CO_3{\cdot}1.5H_2O$ and $KHCO_3$ (Zhao et al. 2009). K_2CO_3 obtained from calcination of $KHCO_3$ was found to have high carbonation rate and considerably efficient for CO_2 adsorption. The effect of calcination of Na_2CO_3 on CO_2 adsorption is not significant as compare to K_2CO_3. Stoichiometric calculations of balanced Eq. (1) revealed that

Table 3 Adsorption capacity and properties of alkali metal-based sorbents on different support

Active phase	Catalyst support	Adsorption Temp. (°C)	Regeneration Temp. (°C)	Capacity (mmol g^{-1})/ Efficiency	Experimental procedure	References
Na_2CO_3	Ceramic	60–70	120–140	0.5–3.2	TGA, fixed-bed reactor	Green et al. (2006)
	Ceramic	50–70	>135 (in N_2)	2.6 (80 %)	Bubbling bed	Seo et al. (2007)
	Ceramic	50–70	120 (in N_2)	2.3 (>80 %)	TGA	Lee et al. (2008a, b)
	Al_2O_3	60	–	>85 %	TGA	Dong et al. (2012)
	Without support (calcined at 200 °C)	60		72.87 %		
	Al_2O_3	60–70	120–200	90 %	Electro-balance and fixed-bed reactor	Liang et al. (2004)
	Al_2O_3 (calcined at 300 °C)	45	–	7.7	Fixed-bed reactor	Kondakindi et al. (2013)
	CaO	315	700	3.0	Breakthrough curve	Siriwardane et al. (2007)
K_2CO_3	Zirconium oxide (ZrO_2)	50–100	130–200	2.08	Fixed-bed, breakthrough	Lee et al. (2009)
	MgO	50–100	150–400	4.06[a] 4.49[b]	Fixed-bed, breakthrough	Lee et al. (2008a, b)
	Al_2O_3	70–90	130 (in N_2)	2.9	TGA, fixed-bed	Lee et al. (2011)
	AC, silica gel	60	200	0.34–1.7	TGA, fluidized bed	Zhao et al. (2009)
	Activated coke and silica	100	150	2.1 (80 %)	Fixed-bed and bench scale	Hayashi et al. (1998)
	TiO_2, SiO_2, CaO and zeolites	60–100	130–400	1.1–2.7	Fixed-bed, multiple cycle	Lee et al. (2005)

[a] Impregnation method

[b] Wet-mixing method

the maximum theoretical capacity of Na_2CO_3 and K_2CO_3 is 9.43 and 7.23 mmol of CO_2 g^{-1}, respectively (Samanta et al. 2011). When these materials are impregnated on ultrahigh porous matrix, the CO_2 capture capacity is higher than theoretical capacity because of the additional efficiency of porous matrix. Al_2O_3 impregnated with calcined K_2CO_3 (K_2CO_3/Al_2O_3) in particular, appeared to have large surface area, high attrition strength and high mechanical strength (Dong et al. 2012; Chen et al. 2012; Zhao et al. 2013). Alkali metal-based adsorbents used chemisorption to capture CO_2 therefore effort is needed for regeneration (Hayashi et al. 1998). For regeneration, adsorbent with captured CO_2 is transported to calcination chamber where at moderate temperature of 120–210 °C the bicarbonate decomposes and releases CO_2/H_2O mixture. The mixture is cooled down, and H_2O is separated from CO_2 by condensation (Lee et al. 2011; Zhao et al. 2013). Finally, the regenerated sorbent is returned back to the carbonation reactor and the process cycle is completed. Lee et al. (2005) suggested that potassium-based sorbents such as K_2CO_3/TiO_2, K_2CO_3/AC, K_2CO_3/MgO and K_2CO_3/Al_2O_3, which has large capacity for CO_2 adsorption, could be completely regenerated above the temperature of 130, 130, 350 and 400 °C, respectively.

Zeolites-based adsorbents

Zeolites are synthetic or naturally occurring microporous crystalline aluminosilicates mineral with an identical pores structure. Zeolites have a honeycomb or cage-like structure, which has been identified as the world's only mineral with naturally occurring negative charge (Yang et al. 2008). Conventional zeolites have interlocking tetrahedron of silicate and aluminate in various regular arrangements through shared oxygen atoms. Substitution of Si with Al (or other metals) leads to a negative charge on the framework. The charge is balanced by exchangeable cations usually alkaline or alkaline-earth metals (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) (Wang et al. 2010). These cations are located in the channels and cavities throughout the pores structure. Furthermore, the electric field and basicity of this material normally vary inversely with the Si/Al ratio. Lower ratio of Si/Al has higher basicity. Basicity increases the specific interaction between CO_2 and zeolites that resulted in high value of CO_2 adsorption (Bonenfant et al. 2007; Ertan 2004). The channel diameter of zeolites ranges from 300 to 1000 pm, while kinetic diameter of CO_2 is about 209 pm. As a result, zeolites can also separate CO_2 by molecular sieving effect (Yang et al. 2008; Zhang 2013).

The polarity and the presence of pores make the zeolite an efficient shape-selective sorbent for a broad range of separation applications. Relatively large energetic dipole and quadrupole moment in the molecules is also one appealing factor for selective adsorption of gases in zeolites (Pham et al. 2014). Gases having large quadrupole moment and polarizability interact more easily with the electric field created by the structural cations of zeolites (Na^+, K^+, Ca^{2+}, Mg^{2+}), which favors adsorption of CO_2 on zeolites. The order of adsorption capacity of gases on zeolites is $CO_2 > N_2 > CH_4 > H_2$. This pattern can be explained by the fact that CO_2 has greater quadrupole moment (4.30×10^{-26} esu cm^2) and polarizability (2.65×10^{-24} cm^3) than N_2 (quadrupole moments: 1.52×10^{-26} esu cm^2; polarizability: 1.76×10^{-24} cm^3) and CH_4 (quadrupole moment: 0; polarizability: 2.60×10^{-24} cm^3) (Hudson et al. 2012; Jiang et al. 2013).

Zeolites adsorption properties depend on the electrostatic properties of each molecule that takes part in the adsorption process. Adsorption of gases decreases on a solid sorbent with the increase of process temperature. Due to the high exothermic nature of CO_2 adsorption, selectivity of the CO_2 is low as compared to N_2, CH_4 and H_2O on above 30 °C and become negligible after 200 °C. On the other hand, the linear structure and small size of CO_2 make the adsorption of CO_2 in different zeolites considerable at low temperature (Poshusta et al. 2004).That is why, CO_2 preferentially pervades in CO_2/CH_4, CO_2/N_2 and CO_2/H_2 mixtures relatively at low temperatures. Gases adsorption by zeolites adsorbents depends on composition and structure of the framework, size and shape, purity, cationic form and molecular polarity (Samanta et al. 2011). Zeolites are generally considered to have strong adsorption behavior for moisture. Sometimes, the moisture contents of zeolites reach 20 % of its own weight. The presence of moisture content significantly decreases adsorption capacity of cationic zeolites by favoring the formation of bicarbonates and decreasing strength and heterogeneity of the electric field. Additionally, CO_2 adsorption capacity increases with the gas phase pressure and decreases with the rise in adsorption temperature. This trend can be observed in Table 4 (Bonenfant et al. 2007; Kamiuto et al. 2002; Li et al. 2013; Yu et al. 2012). The study of Siriwardane et al. (2003) suggested that natural zeolites with the highest surface area and sodium (Na) content yield the highest adsorption capacity for CO_2.

Zeolites can be synthesized by hydrothermal method or by calcination at high temperature (Yoo et al. 2009). Crystallization temperature, aging temperature and time affect the synthesis of zeolites. Mostly, the literature revealed aging time range from 1 h to 3 days and aging temperature from room temperature to 600 °C. Increasing the aging time maximizes crystallinity and decreases the crystalline particle size in zeolites. Furthermore, crystallinity and nanoparticles exhibit promising performance for CO_2 adsorption (Ginter et al. 1992; Jiang et al. 2013). Some of the physical properties of the zeolites are listed in Table 4. In this table, Zeolite 13X and NaX give maximum adsorption capacity in the range of 6–7 mmol g^{-1} at room temperature and high phase pressure. Summing up all the parameters and comparison exhibit that zeolites are relatively more efficient than carbonaceous materials-based adsorbents, but regeneration needs relatively more efforts. Contrary to carbonaceous material-based adsorbents and MOFs, the CO_2 adsorption capacity of zeolites increases with the limited increase in the adsorption temperature. The reason of elevated CO_2 uptake is the opening and enlargement of pores in zeolites with moderately high adsorption temperature (Ho et al. 2014; Yoon and Heo 1992). The study of zeolites revealed that there are 50 types of natural and 150 types of synthetic zeolites. The presence of impurity in naturally occurring zeolites makes them less favorable for adsorption of CO_2. Chabazite in naturally occurring zeolites and 13X in synthetic zeolites are better adsorbents for CO_2 separation from mixture of gases. As the industrial units emit the flue gases at high temperature therefore in upcoming days, the research must be focused to develop a mechanism for zeolites that may adsorb CO_2 at high temperature. For optimization of this technology, the regeneration after adsorption of CO_2 also needs more research.

Selective adsorption of CO_2 by metal–organic frameworks (MOFs)

Zeolites, membrane and amine solution have been reported in selective capturing of CO_2 for gas purification. However, regeneration of such system and desorption of CO_2 require considerable amount of energy, which makes these system low energy efficient and costly. A new class of hybrid nanoporous materials named metal–organic frameworks (MOFs) have been introduced for selective CO_2 adsorption processes, gas storage and catalysis (Britt et al. 2009; Li et al. 1990). These materials are a combination of inorganic clusters that are spread apart by organic linkers. The organic linkers form the edges of the cubes, and the inorganic clusters form the vertexes (Chen et al. 2015; Liu et al. 2012). Table 5 shows the possible organic linkers and inorganic clusters in different MOFs. These small units are assembled in a nanometer scale and make highly porous framework (surface area, 10,000 m^2 g^{-1}) which can separate different gases and can store a lot of gas in this framework (Arnold et al. 2013). Millward and Yaghi (2005) reported that a container filled with MOF-177 could capture nine times the amount of CO_2 in the container

Table 4 Physical properties and adsorption capacity of different zeolites

Sorbent	Temperature (°C)	Pressure (atm)	Ads. capacity (mmol g^{-1})	Experimental procedure	References
NaX	32	0.28	5.71	Gravimetric analysis	Bonenfant et al. (2007)
NaX	30	P_{atm}	4.20	GC	Li et al. (2013)
NaX (binderless)	25	0.5	4.80	Gravimetric analysis	Yu et al. (2012)
NaX (binderless)	25	0.4	4.50	Gravimetric analysis	Yu et al. (2012)
CaX	30	P_{atm}	3.40	GC	Li et al. (2013)
CaX (binderless)	25	1	4.90	Gravimetric analysis	Yu et al. (2012)
CaX (binderless)	25	0.4	3.50	Gravimetric analysis	Yu et al. (2012)
KX (binderless)	25	1	5.00	Gravimetric analysis	Yu et al. (2012)
KX (binderless)	25	0.4	4.50	Gravimetric analysis	Yu et al. (2012)
CaA	30	P_{atm}	2.60	GC	Li et al. (2013)
NaA	30	P_{atm}	2.40	GC	Li et al. (2013)
NaY	32	1	5.50	Gravimetric analysis	Choudhary et al. (1995)
NaM	25	1	2.95	Gravimetric analysis	Choudhary et al. (1995)
Zeolite 13X	20	0.15	2.63	Fluidized bed	Harlick and Tezel (2004)
	22	1.5	4.90		
Zeolite 13X	22	1	4.61	Fluidized bed	Cavenati et al. (2004)
Zeolite 13X (Binderless)	40	5	4.70	GC	Silva et al. (2014)
Zeolite 13X	25	1	4.66	Fluidized bed	Cavenati et al. (2004)
Miso-LTA	25	1	5.45	TGA	Chen and Ahn (2014)
Micro-LTA			4.77		
Silicalite	30	0.15	0.48	Calorimeter-volum. apparatus	Dunne et al. (1996)
Silica zeolite (CHA)	0	1	4.40	GCMC simulations	Pham et al. (2014)
Na-ZSM-5	30	1	0.75	GC	Katoh et al. (2000)
Molecular sieve 13X	25	1	2.8–3.6^{a}	PSA	Siriwardane et al. (2001)
Molecular sieve 13X	20	0.15	2.18	Fluidized bed	Kamiuto et al. (2002)
Molecular sieve 4A	25	1	2.3–3.1^{a}	PSA	Siriwardane et al. (2001)
Molecular sieve 4A	20	0.15	1.65	–	Kamiuto et al. (2002)
T-type zeolite	15	1	4.01	GC	Jiang et al. (2013)
Erionite (ZAPS)	17	0.26	3.00	–	Bonenfant et al. (2007)
Mordenite (ZNT)	17	0.26	1.80	–	Bonenfant et al. (2007)
Clinoptilolite (ZN-19)	17	0.26	1.70	–	Bonenfant et al. (2007)
NCW^{b}	5	0.4	2.08	Vol. and Isothermal ads.	Ertan (2004)
13X	5	0.9	6.30	Vol. and Isothermal ads.	Ertan (2004)
5A	5	0.7	5.46	Vol. and Isothermal ads.	Ertan (2004)
HY-5	22	1	1.13	Fluidized bed	Harlick and Tezel (2004)
HZSM-5-30	22	1	1.90	Fluidized bed	Harlick and Tezel (2004)
HiSiv 3000	22	1	1.44	Fluidized bed	Harlick and Tezel (2004)
ZSM-5^{c}	40	0.1	0.32	GC	Li et al. (2013)
ZSM-5	30	1	1.60	GC	
H-SSZ-13	25	1	3.98	Gravimetric analysis	Hudson et al. (2012)

Table 4 continued

Sorbent	Temperature (°C)	Pressure (atm)	Ads. capacity (mmol g^{-1})	Experimental procedure	References
Cu-SSZ-13	25	1	3.75	Gravimetric analysis	Hudson et al. (2012)

[a] Cyclic tests

[b] Natural zeolite tuff washed with distilled water

[c] SiO_2/Al_2O_3 ratio = 280

Table 5 Possible candidate for linkers and clusters

Organic linkers	Inorganic clusters
1,4-benzenedicarboxylate	Zn_4O
2,5-dihydroxyterephthalic acid	Nickel acetate tetrahydrate
N,*N*-dimethylformamide	Magnesium nitrate hexahydrate
2,5-Thiophenedicarboxylic acid	Cobalt(II) nitrate hexahydrate
Polytetrafluoroethene	Iron(II) nitrate hexahydrate
1,3,5-benzenetristetrazolate	$AlO_4(OH)_2$
1,3,5-benzenetricarboxylate	
Biphenyldicarboxylate (BPDC)	
2-aminoterephthalic acid	

compared to that without the MOF-177 at 35 bar pressure and 25 °C.

Mainly three mechanisms are functional for separation of gases in MOFs: (1) the molecular sieving mechanism, (2) thermodynamic separation mechanism and (3) the kinetic separation mechanism (Zhang 2013). In molecular sieving mechanism, MOFs adsorb the gases based on channels size and kinetic diameter of gas molecules is referred as molecular sieving effect. In kinetic separation mechanism, the difference in the gases diffusion rate plays an important role, while in thermodynamic separation mechanism, different affinities of various components in the gas mixture and the surface of MOFs are the main controlling tool (Lee et al. 2007; Sumida et al. 2011). Due to the large number of MOFs topology, metal nodes and linkers, more than 20,000 MOFs have been reported in the literature. Various physical and chemical properties of MOFs have been developed. For example, MOFs can be produced with low densities (0.2–1 g cm^{-3}), large surface areas (500–10,000 m^2 g^{-1}), well-defined porous volume, good thermal and mechanical stabilities as well as with special chemical functionalities. These functions make MOFs a potential candidate for CO_2 adsorption (Uzun and Keskin 2014; Yazaydın et al. 2009).

Table 6 shows physical properties and adsorption capacity of different types of MOFs. Adsorption of CO_2 in MOFs depends on the attachment sites in the linkers. Liu et al. (2012) studied eight different positions on linker of IRMOF-1 and three orientations of CO_2. The finding revealed that the hydrogen in the linker's edge is the most favorite adsorption site for CO_2 when the attachment is parallel. The linkers and guest molecules interaction maybe increased through chemical modification, such as adding functional groups, increasing the size of linker as well as Li-doping. However, the later one is relatively new technique and not much work has been reported until now. Functionalizing the pores of MOFs with coordinatively unsaturated metal ions or Lewis basic groups (e.g., amine and hydroxyl groups) increase the CO_2 capture capacity and adsorption selectivity (Masoomi et al. 2014). The main interaction force between the linkers and CO_2 is van der Waals and electrostatic force induced by the cluster. This is the reason MOFs adsorption is high at low temperature (<40 °C). Adsorption pressure also plays an important role in adsorption of CO_2. The high pressure pushes gas molecules to have more contact at binding sites on the surface and pores of solid matrices of MOFs that enhance the adsorption capacity (see in Table 6) (Anson et al. 2004; Xu et al. 2014). Furthermore, higher adsorption energy indicates stronger interaction between the linkers and guest molecules. Compared to other gases like H_2, N_2, CO and CH_4, the affinity for CO_2 is relatively much higher because of its strong quadrupole electronic structure (Agueda et al. 2015; Lou et al. 2014; Xu et al. 2014).

The incorporation of functional groups in metal–organic frameworks (MOFs) changes the surface chemistry and allows modifying their adsorption properties. For instance, Wu et al. (2012) reported the amino-functionalization of MIL-68(In) that resulted higher sorption enthalpies for CO_2. In addition, combining amine functionalities to the linker of IRMOF-1 converts it to IRMOF-3 and little improves CO_2 adsorption. On the other hand changing the metal from Zn to Co, Ni and Mg in the framework enormously increases CO_2 adsorption. Lowering atomic weight of the metal in the framework increases the uptake of CO_2 per metal atom for Mg, Ni, Co and Zn (Yazaydin et al. 2009). However, the lower atomic weight of metal does not completely explain the enhanced capacity of MOFs. The relative humidity in the gases or the exposure of MOFs to water has substantial influences on the adsorption of CO_2 (Cho et al. 2012). However, there would be no apparent changes in the powder X-ray diffraction (PXRD) patterns for the water-exposed samples, but the BET surface area

Table 6 Physical properties and adsorption capacity of different MOFs

MOFs	Temperature (°C)	Pressure (atm)	Ads. capacity (mmol g^{-1})	Experimental procedure	References
MOF-5	25	35	22	N/A	Liu et al. (2012)
MOF-177	25	35	33.5	Vol. adsorption	Millward and Yaghi (2005)
Ni-MOF-74	25	10	7.5	Ads. isotherms	Chen et al. (2015)
	50		6.2		
	75		5.3		
UTSA-16	25	35	5.2	GC	Agueda et al. (2015)
	40		4.8		
	65		4.3		
Mg/DOBDC	23	1	8.1	Ads. isotherms	Caskey et al. (2008)
Co/DOBDC	23	1	6.9		
Ni/DOBDC	23	1	5.4		
Zn/DOBDC	23	1	5.1		
MOF-14	25	20	10.8	Ads. isotherms	Karra et al. (2013)
Fe(II)-MOF-74	25	10	6.45	Ads. isotherms	Lou et al. (2014)
Fe(II)-MOF-74[a]			4.38		
Fe_2(DOBDC)	25	1.1	7.20	Ads. isotherms	Queen et al. (2014)
Co-MOF-74	25	1	6.55	TGA	Cho et al. (2012)
Acylamide MOF	0	1	1.48	N/A	Xu et al. (2014)
MIL-101	30	<50	40.0	Ads. isotherms	Llewellyn et al. (2008)
MIL-101[b]	25	0.15	4.20	Ads. isotherms	Lin et al. (2013)
	−50		3.40		
MIL-53(Al)[c]	15	20	6.50	Breakthrough curve	Couck et al. (2009)
TMU-4	−78	1	6.68	TGA	Masoomi et al. (2014)
TMU-5			6.24		
bio-MOF-1[d]	0	1	4.50	Ads. isotherms	An and Rosi (2010)

[a] Modified by oxidation

[b] Polyethyleneimine (PEI) incorporated

[c] Amine functionalized

[d] Cation exchange with TEA

was extensively reduced up to 50 % (more than 50 % in the case of Cu-BTC and Mg-MOF-74). The partial collapse of pores upon water exposure might be the reason for decrease in BET surface area. The small pores size (1100–1300 pm) and open-metal sites of MOFs lead to high selectivity of CO_2 compare to other gases (Karra et al. 2013; Liu et al. 2012; Uzun and Keskin 2014).

It has been noted from the literature that each type of MOF has specific optimum condition that applies to CO_2 capturing. Thus, CO_2 adsorption capacity for MOF-17 will not be the same for UMCM-150 at same process conditions. In addition, MOFs with high capacity for CO_2 at high pressure will not often perform well at low pressure (Yazaydin et al. 2009). Series of metal–organic frameworks M(DOBDC) (M = Mg, Mn, Fe, Co, Ni, Cu and Zn; dobdc^{4-} = 2,5-dioxido-1,4-benzenedicarboxylate) has a great potential for adsorption of CO_2 (Queen et al. 2014). Mg/DOBDC is one of the most efficiently known CO_2 adsorbents at the low to moderate CO_2 partial pressure but has some difficulties in regeneration for cyclic operation (Choi et al. 2012). CO_2 adsorption can be physisorption or chemisorption in MOFs. It has been learnt that magnesium oxide (MgO) exothermically chemisorbs CO_2 to form magnesium carbonate ($MgCO_3$). On basis of this, it has been suggested that the adsorption capacity of Mg/DOBDC may be attributed to relatively higher ionic character of Mg–O bond rather than chemisorption. This is obvious from literature that CO_2 absorption capacity increases with decreasing M–O bond length in the framework of M/DOBDC. The series for bond lengths is Mg–O (1.969 Å) < Ni–O (2.003 Å) < Co–O (2.031 Å) < Zn–O (2.083 Å) which complies with the CO_2-capturing capacity (Caskey et al. 2008; Yazaydin et al. 2009).

Concluding the work of different researchers on MOFs in Table 6 revealed that MIL-101, MOF-5 and MOF-177 has higher CO_2 adsorption capacity at room temperature and relatively at high pressure than the benchmark adsorbents reported before including the amine-functionalized ones. These three types should be considered in future at lower temperature and high pressure. MOFs as adsorbents for post-combustion CO_2 capture are expected to have high adsorption capacity but require understanding suitable flue gas conditions (Samanta et al. 2011).

Microporous organic polymers (MOPs)

Synthetic and natural polymers have a broad range of properties that make them an essential material in our daily life. The development of MOFs has expended a new area of synthetic chemistry for ordered and tunable microporous frameworks. These materials have special properties like reproducible characteristics and controlled pore size, well-defined macromolecular structure and stability in acidic and basic media, as well as good thermal and mechanical properties (Martin et al. 2011). MOPs are networks of various rings whose disorderly and inefficient packing lead to open porous configuration, while the COFs are high surface area crystalline structure prepared by controlled polymerization of boronic acids. Different families of MOPs include hypercrosslinked polymers (HCPs), conjugated microporous polymers (CMPs) and polymers of intrinsic microporosity (PIM). The multistep synthesis of MOPs requires expensive catalysts that may limit the uses for CO_2 capture in real life. However, He et al. (2015) used cost-effective one-step Friedel–Crafts reaction to achieve a series of three-dimensional framework of pre-functionalized triptycene-based polymers (TPPs).

Hypercrosslinked polymers (HCPs) exhibit apparent BET surface areas as about 2100 $m^2 g^{-1}$ that is presumably because of the network with higher degree of condensation, which are less able to collapse and densify, thus leading to higher BET surface area (Katsoulidis and Kanatzidis 2011; Martin et al. 2011). For some MOPs, the literature revealed considerably low BET surface area. For example, the BET surface area for polymer/silica-supported PEI fiber (CA-S-PEI-PI) and polybenzimidazoles (PBIs) is 23 and 200 $m^2 g^{-1}$, respectively, that is very low in comparison with other organic polymers such as intrinsic microporosity (PIM), porous aromatic frameworks (PAFs), porous polymer networks (PPNs) and COFs (He et al. 2015). However, the CO_2 uptake of PBIs is higher than that of the COFs, diimide polymers or imine-lined organic cages and comparable to CO_2-selective MOFs or zeolite tetrazolate frameworks (ZTFs). The relatively high CO_2 uptake and binding is most likely due to the functional nature of PBIs because of the amphoteric imidazole moieties and favorable interactions of the CO_2 polarizability through hydrogen bonding and dipole–quadrupole interactions that utilize the protonated and proton-free nitrogen sites of imidazole rings, respectively. Rabbani and El-Kaderi (2011) sensitized benzimidazole-linked polymer (BILP-1) by condensation reaction between tetrakis (4-formylphenyl) methane (TFPM) and 2,3,6,7,10,11-hexaaminotriphenylene (HATP), which is believed to be the most porous purely organic benzimidazole-linked polymer reported until now with the BET surface area of 1172 $m^2 g^{-1}$.

To boost the affinity between adsorbents surface and CO_2 molecules, the porous polymers can be subjected to different techniques of modification. The CO_2-philic functionalities are introduced into the porous polymers through “knitting” method in recent research studies. The functionalities include amino ($–NH_2$), acetyl ($–COCH_3$), formyl (–CHO) and nitro ($–NO_2$) groups (He et al. 2015; Lu et al. 2011). Additionally, the introduction of N_2-rich polar moieties such as carbazole and triazine groups is also an impressive route to increase CO_2 adsorption capacity. Phosphorylation also positively influences the adsorption capacity of CO_2 in these materials. Because of the pores blockage, these methods of incorporation also have an adverse effect on the surface area that can lead to low CO_2 adsorption capacity if the surface area of adsorbent is openly compromised. To avoid this issue and attain sufficient surface area after the incorporation of CO_2-philic moieties, the selection of ultrahigh porous and physicochemically stable materials is necessary. The studies have revealed that an appropriate pore size commensurate with the kinetic diameter of CO_2 molecule is one of the desirable features for improving the CO_2 adsorption at ambient temperature. The molecular size of CO_2 is 209 pm; therefore, the MOPs with small micropores are more selective for CO_2 molecules rather than the large CH_4 (414 pm), N_2 (364 pm) and H_2 (289 pm) (Amoros et al. 1996; Katsoulidis and Kanatzidis 2011; Martin et al. 2011). The CO_2 selectivity of these materials surpasses carbon-based materials and zeolites and is comparable to non-covalent porous materials (NPMs) and Bio-MOF-11. The reversibility and sensitivity in sorption/desorption trend for MOPs show that CO_2 affinities with pore walls are weak enough to allow adsorbent regeneration without applying heat. The materials that have strong acidic or basic sites usually exhibit high CO_2 interaction and require heat input to regenerate their active adsorption sites as in the case of primary alkanolamine MEA (Rabbani and El-Kaderi 2011; Zhu et al. 2013).

Aside from BET surface area and pores size, the adsorbability of MOPs depends on the presence of functional groups on the adsorbent surface. It is found that the introduction of acidic O-containing functional groups and basic N-containing groups into the polymers network help CO_2 adsorption capacity, where the former one facilitates the hydrogen bonding interactions between the adsorbent surface and CO_2 molecules. Generally, the presence of water in the gas stream negatively affects the CO_2 adsorption capacity. This is due to the formation of water layer on the surface of MOPs under humid condition because of high porosity. The adsorbed water in the empty spaces increases mass transfer resistance during CO_2 adsorption, therefore negatively affecting the CO_2 adsorption capacity to some degrees. However, in some cases the humid environment is positive to the CO_2 adsorption capacity in MOPs. Kong et al. (2015) synthesized a polymer-based adsorbent named AH-RFSA by polymeric sol–gel process that performed better in humid conditions than dry adsorption process. The same result is reported by Fan et al. (2014) for the polymer/silica-supported PEI fiber adsorbents (see Table 7). MOPs are best used in pressure swing adsorption (PSA) system for separation of different gases and adsorption of CO_2. At higher pressure, the MOPs are superior to commercial activated carbons and zeolite-based materials (zeolite NaX, zeolite 13X). The same trend is also noted for metal–organic frameworks (MOFs) at higher pressure.

Table 7 shows the adsorption data for different polymer-based adsorbents that revealed the decrease in CO_2 adsorption capacity as the adsorption temperature increased, while the opposite happened with the pressure increased. In some polymers such as PPN, the BET surface area is very high because of the macropores those are not suitable for CO_2 adsorption. Upon functionalization, the surface area of PPN decreased and the pore size progressively became smaller which is commensurate with the kinetic diameter of CO_2 molecule.

Table 8 gives a broad range of the adsorption capacities and process conditions of adsorbents mentioned in this paper. Based on the literature, it was concluded that the adsorption temperature is the dominant controlling parameter for CO_2 adsorption in the first three adsorbents, namely carbonaceous material, alkali metal-based sorbent and zeolites. For CO_2 adsorption in MOFs and MOPs, temperature as well as the adsorption pressure drastically changes the CO_2-uptake value.

Heat of CO_2 adsorption of the adsorbents

The heat of adsorption (Q_{st}) of a gas mixture is a critical variable for design of practical gas adsorption or desorption processes such as pressure swing and thermal swing process. Q_{st} is the difference of the partial molar enthalpy between the adsorbate gas phase and the adsorbed phase, which reveals the interaction strength between adsorbate and adsorbent (Martin et al. 2011). This parameter can be calculated from heat released in calorimetric experiment and from the analysis of adsorption isotherm at different temperatures. Heat of adsorption determined by the latter technique is called isosteric heats of adsorption, which is generally used in the characterization of adsorbents material for gas and liquid phase adsorption (Builes et al. 2013). Information about Q_{st} is very important, particularly during gaseous phase adsorption because the heat released upon adsorption is partially adsorbed on the adsorbent, which causes a rise in the adsorbent temperature and influences the adsorption equilibrium and kinetics and thus, as a result, the overall gas adsorption capacity of the adsorbent (Martin et al. 2011). From quantification of the CO_2 isosteric heat of adsorption, the nature of the CO_2 adsorption can be determined, where low heat of adsorption (8–41 kJ mol^{-1}) revealed physisorption and higher value of heat of adsorption (62–418 kJ mol^{-1}) indicated chemisorption. Furthermore, this parameter showed that the CO_2 interaction with the adsorbent material might be mainly an intermolecular force or hydrogen bond (Ho et al. 2014; Zhao et al. 2012).

Higher values of Q_{st} for adsorbent indicate a stronger interaction of the CO_2 molecule with the adsorbent surface, but the CO_2-uptake values dropped down because of higher adsorption temperature. Mostly, the adsorption and desorption processes are assumed to be approximately isothermal, even though in some cases the CO_2 heat of adsorption considerably changes the process temperature. For instance, the CO_2 heat of adsorption on zeolite is substantial enough to cause the rise of adsorption temperature as much as 50 °C. Thus, it has been reported that the CO_2 heat of adsorption on zeolite is ~ 10 times higher than that on activated carbon at the same temperature and pressure (Radosz et al. 2008; Zhao et al. 2012). Some of the studies revealed the same isosteric heat of CO_2 adsorption for MOPs and activated carbons, reflecting the structural similarities between the two adsorbent materials. The higher microporosity and impregnation of adsorbent material with N-functionality or carboxylic acid group elevate the heat of CO_2 adsorption for various adsorbent materials (Gadipelli and Guo 2015). Lu et al. (2011) grafted PPN with sulfonic acid and its lithium salt, which significantly increased the CO_2-uptake capacity and isosteric heat of CO_2 adsorption under ambient conditions. Multi-walled carbon nanotubes (CNTs) and amine-grafted CNT presented heats of CO_2 adsorption around 11.8 and 18.9 kJ mol^{-1}, respectively, which revealed the effect of incorporation of amine on heat of CO_2 adsorption. CNTs and carbonaceous material-based adsorbents showed lower heat of CO_2 adsorption than those found for MOFs, MOPs and many kinds of zeolites, because of its weaker interaction with CO_2 (Martin et al. 2011).

Table 9 displays heat of CO_2 adsorption for different adsorbent specified conditions, showing higher adsorption heat for zeolites compared to other adsorbents. Thus, CO_2

Table 7 Adsorption capacity for the MOPs

MOPs	Temperature (°C)	Pressure (atm)	Ads. capacity (mmol g^{-1})	Surface area (m^2 g^{-1})	Experimental procedure	References
Hypercrosslink organic polymer (HCPs)	25	1	1.70	1642	TGA	Martin et al. (2011)
		30	13.40			
Phloroglucinol-based POFs	0	1	4.20	917	TGA	Katsoulidis and Kanatzidis (2011)
	25		2.16			
Benzimidazole-linked polymer (BILP-1)	0	1	4.32	–	Ads. isotherm	Rabbani and El-Kaderi (2011)
	25		2.95			
PPN-6	22	0.15	1.50	4023	TGA	Lu et al. (2011)
PPN-6-SO_3H		0.15	3.60	1254		
PPN-6-SO_3Li		0.15	3.70	1186		
Monolithic AH-RFSA	30	1	3.57[a]	–	–	Kong et al. (2015)
			4.43[b]			
CA-S-PEI-PI[c]	35	–	0.51[a]	23	Ads. isotherm	Fan et al. (2014)
			1.16[b]			
TPP-1-NH2	0	1	4.17	–	Ads. isotherm	He et al. (2015)

[a] Dry adsorption

[b] Adsorption with humidity

[c] Polymer/silica supported PEI fiber

Table 8 Broad ranges of adsorption capacities and adsorption conditions based on the literature

Adsorbent	Adsorption temp. (°C)	Pressure (atm)	CO_2 adsorption capacity (mmol g^{-1})
Carbonaceous material	−78 to 50	0.1 to 2.0	0.5 to 8.0
Alkali metal-based sorbent	45 to 315	–	0.5 to 7.7
Zeolites	0 to 40	0.1 to 30	0.32 to 6.3
MOFs	−78 to 75	0.15 to 35	1.48 to 33.5
MOPs	0 to 35	1 to 30	0.51 to 13.4

adsorbs more strongly on solid adsorbents particularly on zeolites than the other gases. Normally, the heat of adsorption of gases on most of adsorbents shows this order: $H_2 < CH_4 < N_2 < CO_2$. Carbon dioxide adsorption is more selective in CO_2/H_2, CO_2/N_2 and CO_2/CH_4 mixtures at low temperatures, because of the electrostatic properties of CO_2 (Yang et al. 2008).

Regeneration and commercial viability

Adsorption is an exothermic process, and thus regeneration of the adsorbents in the form of desorption can be performed by rising the temperature (Kaithwas et al. 2012). Regeneration is an important part in the CO_2 adsorption, and the energy needed for adsorbent regeneration is the key to the economic viability of the process. For promising commercial applications, the adsorbents should demonstrate stable performance for long cyclic adsorption and complete desorption operation under the feasible industrial condition (Wei et al. 2013). The regeneration process for alkali metal-based sorbent in thermogravimetric analysis (TGA) begins at temperature above 102 °C and terminates at about 210 °C. These adsorbents have a drawback in that the reactivity always decreases with the increase in the number of operation cycles (Wang et al. 2010). Additionally, this process required large-size equipment and intensive energy for regeneration, which makes it relatively uneconomic. It is believed that the heat duty for the alkali metal-based sorbent regeneration can constitute up to 70 % of the total operating costs in a CO_2 capture plant (Yang et al. 2008). Recently, nanoporous FeOOH and $TiO(OH)_2$ were used as supports to reduce the energy input for regeneration of Na_2CO_3. It was noted that the activation energy for the decomposition of $NaHCO_3$ to Na_2CO_3 was reduced from about 80 to 44 kJ/mol and from 80 to 36 kJ/mol when the support was nanoporous FeOOH and $TiO(OH)_2$, respectively (Zhao et al. 2013).

Carbonaceous material-based adsorbents have the lowest CO_2 adsorption capacity, but the number of cycles has

Table 9 Heat of CO_2 adsorption by different adsorbents at specified conditions

Type of adsorbent	Name of adsorbent	Temperature (°C)	Pressure (atm)	Q_{st} (kJ mol^{-1})	References
Carbonaceous material	AC	25	1	3	Radosz et al. (2008)
	AC (ZL-30)	30		10.5	Guo et al. (2006)
	Leather-derived AC	35	1	8	Bermudez et al. (2013)
Zeolites	Commercial Zeolite	25	1	30	Radosz et al. (2008)
	Zeolite T	25	0.1	33.6	Salmasi et al. (2013)
	SAPO-34			39.4	
MOFs	Pd(2-pymo)$_2$	25	0.5	26	Yazaydın et al. (2009)
	Bio-MOF-1	15	1	31.2	An and Rosi (2010)
	Ni(dobdc)	25	atm	38	Queen et al. (2014)
MOPs	HCP	25	1.13	23.5	Martin et al. (2011)
	GO frameworks	25	4.0	35	Gadipelli and Guo (2015)
	AAM-silica	45	0.1	37	Zhao et al. (2012)

less effect on CO_2 adsorption, which gives extended operational life and easy regeneration (Agueda et al. 2015). The same results have been found for MOPs with higher CO_2 adsorption capacity, but the CO_2 affinities with the surface are weak enough to allow adsorbent regeneration without applying any heat (Zhu et al. 2013). Zeolite is also found a potential adsorbent for CO_2 adsorption because of its pores suitability for CO_2 entrapment, but the elevated cost of regeneration remains a major drawback (Zhang 2013). MOFs strikes the right balance between high CO_2 adsorption capacity, operational life and energy requirement for regeneration, as they have shown advantages in separation applications due to their unique structural properties, including high porosity, large surface area, low crystal density and high chemical and thermal stability.

Heat of adsorption (Q_{st}), in other term, is the amount of the energy required for regeneration of the adsorbents, which should be substantially low (Samanta et al. 2011). The higher the heat of adsorption, the stronger the interaction between the CO_2 molecules and adsorbent active sites, and thus, the higher the energy demand for the regeneration. Table 9 shows highest heat of adsorption for zeolites, while the lowest is for the carbonaceous material-based adsorbents. The same trend in the energy requirement has been observed for the regeneration of these adsorbents. Due to the balance between CO_2-adsorption capacity, operational life and energy requirement for regeneration, MOFs and MOPs seem to be a feasible option of commercialization in the future.

Conclusion

This is almost impossible to switch at once from fossil fuel to environmental friendly (low carbon footprint) renewable sources of energy because of already developed and existing fossil fuel-based processes and technologies. Fossil fuel will be the main source of energy for next few decades. To minimize the negative externalities of CO_2, searching renewable sources of energy and CO_2 capture and storage (CCS) is of equal importance. Several methods are there for CO_2 capture, where low-temperature solid adsorption has a great potential.

Low-temperature CO_2 adsorbents include carbonaceous material, zeolites, metal–organic frameworks, alkali metal-based sorbents, microporous organic polymers. In most of the research work, alkali metal-based sorbets are reported at low-temperature (≤100 °C) adsorption process. Contrary to other adsorbents discussed in this review article, alkali metal-based sorbents can be used for CO_2 adsorption up to 500 °C; therefore, retrofitting it in coal-fired power plant is more cost effective. H_2O is used as a reactant in carbonation reaction; as a result, alkali metal-based sorbents are more suitable for removal of CO_2 under moist conditions. The other four types of materials adsorb CO_2 primarily by physical interaction. These processes have good CO_2 adsorption capacities and regeneration efficiency at low temperature. The carbonaceous material-based adsorbents are easy to make, cheap, abundant, stable and easy to regenerate. However, the weak van der Waals force makes it temperature sensitive, which decreases the selectivity for CO_2. Thus, carbonaceous material-based sorbents are preferred to use at temperature lower than 60 °C. Zeolites are stable adsorbents that have a large surface area for adsorption, but after use, it requires great effort to desorb the adsorbed gas and regenerate the adsorbent. Compared to zeolites, MOFs, MOPs and carbonaceous material-based adsorbents need little effort to regenerate after adsorption. Zeolites adsorption capacity increases with a slight increase in adsorption temperature because of the pores opening, but the adsorption capacity drops down beyond 100 °C. Generally, for MOFs, MOPs, zeolites and carbonaceous material-based adsorbents, the CO_2 adsorption temperature is up to 70 °C that is lower than the real flue gases temperature (normally 90 °C). Consequently, using these adsorbents in industries for CO_2 capture is needed to cool down the flue gases or modify these adsorbents for high-temperature adsorption. Cooling flue gases is energy-consuming, so later on it should be considered in future research.

In chemisorption, the partial pressure of CO_2 does not affect the adsorption capacity of alkali metal-based sorbents considerably, while in physisorption, it is very significant for CO_2 adsorption in carbonaceous material-based adsorbents and zeolites, especially MOFs and MOPs. In the case of these adsorbents, the high pressure pushes the CO_2 gas molecules to have maximum contact at binding sites on the surface and pores of solid matrices that enhance the adsorption capacity. On the other hand, the presence of water vapor in the flue gas may negatively affect the capacity of these four adsorbents and reduces the availability of the active surface area in physisorption.

Abbreviations

AC	Activated carbon
BET	Brunauer, Emmett and Teller
BILP-1	Benzimidazole-linked polymer
CCS	Carbon capturing and storage
CLC	Chemical looping combustion
CMPs	Conjugated microporous polymers
CNTs	Carbon nanotubes
COFs	Covalent organic frameworks
DTA	Differential thermal analysis
GC	Gas chromatography
GCMC	Grand Canonical Monte Carlo
HCPs	Hypercrosslinked polymers
IEA	International Energy Agency
IGCC	Integrated gasification combined cycle
IPCC	International Panel on Climate Change
M	Na or K
MOFs	Metal–organic framework
MOPs	Microporous organic polymers
NPMs	Non-covalent porous materials
PAFs	Porous aromatic frameworks
PBIs	Polybenzimidazoles
PPNs	Porous polymer networks
PSA	Pressure swing adsorption
PSAC	Palm shell activated carbon
PXRD	Powder X-ray diffraction
Q_{st}	Heat of CO_2 adsorption
SWNTs	Single-walled carbon nanotubes
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TPD	Temperature-programmed desorption
TPPs	Triptycene-based polymers
WEO	World Energy Outlook
WGSR	Water–gas shift reaction
ZTFs	Zeolite tetrazolate frameworks

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