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Encapsulation of gases in powder solid matrices and their applications: a review

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Abstract

Gas encapsulation in solid matrices can be an important means to sequester harmful or greenhouse gases and to store useful gases for their subsequent release for a targeted application. In this review, recent developments, the characteristics and gas adsorption capacity of non-organic and organic solid powder matrices (e.g. activated carbons, carbon nanotubes, zeolites, metal-organic frameworks, and cyclodextrins); and potential applications of their complexes in various fields (energy, environment protection, nano-device production, medicine, and food and agriculture productions) are described.

Keywords: gas encapsulation, activated carbons, carbon nanotubes, zeolites, metal-organic frameworks, cyclodextrins.
1. Introduction

Dry atmospheric air consists of approximate volumes of 78.09% nitrogen (N$_2$), 20.95% oxygen (O$_2$), 0.93% argon (Ar), 0.03% carbon dioxide (CO$_2$) and minute traces of neon (Ne), helium (He), methane (CH$_4$), krypton (Kr), hydrogen (H$_2$), xenon (Xe) and ozone (O$_3$) [1]. Some of these gases (such as carbon monoxide (CO), CO$_2$, CH$_4$ and nitrous oxide (N$_2$O)) originate from the incomplete burning of fuels (oil, coal, wood, or natural gases), the widespread use of nitrogenous fertilizers and the industrial manufacturing of nylon. These are the major greenhouse gases which contribute to global warming [1], [2], [3]. Other gases such as sulfur hexafluoride (SF$_6$) and tetrafluoromethane (CF$_4$) produced from industrial process are considered as super greenhouse gases having extremely high stability and with the highest potential impact to atmosphere. A gram of SF$_6$ is climatically equivalent to 24 kg of CO$_2$ [4], [5]. Other types of gases having high potential hazard as exposure include SO$_2$, chlorinated volatile organic compounds, and tetrahydrothiophene odorants [6], [7].

Numerous kinds of gases have been used individually, to achieve controlled and selective gaseous atmospheres in a wide range of industries in biology, medicine, science, technology, agricultural and food fields [8]. Methane has been proposed as a possible source of clean energy [9]. Hydrogen is a promising gas in the design of energy-rich fuel-cell devices [10]. Oxygen possesses great importance in diverse areas such as medicine and steel making. Nitrogen is the most commonly used inert gas in biological and food applications, space aircraft and in the ammonia (NH$_3$) production. Nitrogen, together with Ar and He, is extensively used for running analytical equipment (e.g. gas chromatography) [8], [11]. Nitrogen and CO$_2$ are also be used to modify the atmosphere in order to control the rate of respiration of agricultural products such as fruits and vegetables to extend their self-life and retard the growth of undesirable organisms during storage [12]. Nitrous oxide (N$_2$O) is extensively used in anesthesia while nitric oxide (NO) serves as an important messenger in signal
transduction processes in smooth muscle cells and neurons [13], and has antithrombotic effects [14]. Nitrous oxide is also used in canister sprays such as cooking vegetable oil and whipped cream [15], [16]. Carbon dioxide is used as a bubble-creating agent in many kinds of beverage to enhance their organoleptic properties [17], helps to extend the shelf-life and improves the quality of dairy products [18] and orange juice [19], and benefits in blood circulation improvement, blood-vessel dilation and in the activation of gastrointestinal movement [20]. Ethylene (C₂H₄) is also recognized as a useful phytohormone to trigger ripening processes, enhance color development of some types of fruits, degreen citrus fruits and promote germination of many non-dormant seeds (e.g. mung bean sprouts) [21], [22]. By contrast, 1-methylcyclopropene (1-MCP) is an anti-ethylene gas which is used for extending shelf-life and quality of agricultural products [23]. Interestingly, hydrogen sulfide (H₂S) which is the cause of bad smell (especially in rotten eggs) and acid rain [2], is found to be useful for modulating cellular functions [24]. Chlorine dioxide (ClO₂) is used to disinfect objects contaminated by microorganisms (Bacillus anthracis) [25]. Ozone (O₃) is used in water treatment and sanitization of raw fruits and vegetable products [26]. The applications of various gases are illustrated in Table 1.

Nevertheless, the use of many of these gases in diverse industries, research and development sectors has many limitations because of their inherent properties. Firstly, the solubility of most of the gases in water and their diffusion in solid materials are usually very low, and are highly dependent on the pressure and temperature. It is therefore very difficult to maintain them with high concentration in solution or solid matrices in desired conditions. Moreover, gases are normally stored and transported in a very high-pressure compressed form in metal cylinders which might be prone to explosion during utilization and transportation. Entrapment of gases in solid matrices would minimize these disadvantages because this can offer safer methods to store for further use and in energy production or emission control. Furthermore, gas encapsulation in powder, granules or pellet form of solid matrices is quite useful in the cases in which a small amount of gas is required.
Entrapment or encapsulation of gases by physical interactions with the host molecules is naturally occurring. It can also be undertaken artificially using man-made solid substrates. In nature, metal-gas interactions, hydrogen bonds and cavity effects exist in many proteins that bind gases [8]. Ability to selectively binding oxygen (O$_2$) and carbon monoxide (CO) by hemoglobin and myoglobin molecules is a good example of natural physical interactions between gases and the host molecules. Beside iron-gas interactions, the strong hydrogen bonds are also formed between oxygen and the distal histidine of hemoglobin and myoglobin [27]. Entrapment of oxygen in the blood and fixation of nitrogen in leguminous plants are well known examples of gas entrapment in biological systems [27]; [28]. In these systems, the interactions used to form the resultant complexes are noncovalent bonds with weak forces, thus reversible. These forces could be a combination of hydrogen bonding, hydrophobic forces, van der Waals, π-π interactions and electrostatic effects [29].

For the entrapment or encapsulation of gases in artificial solid matrices, numerous attempts are being made to adsorb them artificially in solid matrices for fuel, emission control and ease of use. However, either the concentrations of gas on those matrices are not yet high enough for a commercial interest or the gas does not remain stable in the matrices at the required or desirable conditions. In this review, we present the current status of entrapment or encapsulation of various gases in various artificial solid matrices, and the mechanism of gas adsorption. We will compare the gas storage capacity of various solid matrices. Furthermore, adsorption isotherms, release properties and potential applications of resultant complexes in various fields are discussed. Although there are several solid matrices have been used for gas entrapment, this review focuses mainly on promising solid matrices, namely activated carbons, carbon nanotubes, zeolites, metal-organic frameworks and cyclodextrins.
2. Mechanism of gas adsorption in solid matrices and measurements

2.1. Mechanism of gas adsorption in solid matrices

When gas molecules come in contact to solid matrices, they interact with binding sites on the surface or in cavities of the solid. This process is known as “adsorption” which is completely different with the “absorption” process in which gases directly dissolve into the bulk of the solid. Based on the nature of interactions formed between gases and solid matrices, adsorption is categorized into physical adsorption (physisorption) and chemical adsorption (chemisorption).

In physisorption gas molecules are loosely held by physical forces (dipole-dipole, apolar, electrostatic, hydrophobic associations or Van der Waals). These interactions involve a low sorption energy (8-41 kJ mole\(^{-1}\) gas); therefore physisorption is generally reversible and is found in applications in which the useful gases are trapped in solid matrices for their subsequent release for a targeted application. In contrast, in chemisorption the sharing or rearrangement of electron between the adsorbate and the adsorbent can lead to formation of a new substance [30]. The chemical bonds between the gas and the solid surface will have a high sorption energy (62-418 kJ mole\(^{-1}\) gas). Thus, an extra energy is required to remove adsorbed gases when they are chemisorbed [24], [31]. The chemisorption is useful in applications where permanently trapping of harmful gases is required. The solid matrices cannot be reused after desorbing gases. For example, lime, limestone or soda limes which produce strong alkali hydroxyls (e.g. Ca(OH)\(_2\), KOH, Mg(OH)\(_2\) or NaOH) in the presence of moisture can interact chemically with acid gases (CO\(_2\), NO\(_2\) or SO\(_2\)) [32], [33]. The differences between physical and chemical adsorption are summarized in Table 2.

Two main factors which govern gas encapsulation in solid matrices are temperature and pressure. In most cases (mainly in physisorption) high pressure is used to push gas molecules to contact at binding sites on the surface or pores of solid matrices. An increase in pressure enhances the adsorption
capacity. The effect of temperature on the adsorption capacity depends greatly on the structure of solid matrices and type of sorption. For instance in hydrogen adsorption on carbon nanotubes, adsorption capacity is higher at lower temperature [36]. In contrast, gas adsorption on zeolite is increased at elevated temperature because the enlargement of pore openings and higher kinetic energy of the gas molecules at high temperature allow gas molecules to diffuse more easily into cavities of solid matrices [37]. Therefore, it is possible to vary the pressure-temperature conditions to optimize the adsorption capacity of solid matrices.

In order to determine the equilibrium absorption capacity for a particular solid matrix, an adsorption isotherm is plotted between the amounts of adsorbed gases as a function of pressure at a constant temperature. The amount of adsorbed gases are expressed in various units, namely weight percentage (wt%); mass, moles or volume per unit mass ([g], [mole] or [cm$^3$] of gas per [g] of solid matrix respectively); or volume per volume basis (cm$^3$ of gas per cm$^3$ of solid matrix) [38]. These adsorption isotherms provide information about adsorption parameters such as surface properties as well as adsorption capacity of a solid matrix [39]. Adsorption behavior of gases on solid matrices is normally described in five general types, as initially proposed by Brunauer et al. (1945) [40], and they can be fitted by many empirical or theoretical models. The most common models are two-parameter models (Langmuir, Freundlich, Dubinin-Raduskevish, Temkin, Flory-Huggins, or Hill), three-parameter models (Sips, Redlich-Peterson, Toth, Khan, Koble-Corrigan, or Radke-Prausnitz), and multilayer physisorption models (Brunauer-Emmett-Teller (BET), Frenkel-Halsey-Hill (FHH), or MacMillan-Teller (MET)) [41]. Depending on the nature or properties of absorbent and adsorbate, one isotherm is better to describe mechanism of adsorption process than others because each of them is constructed based on a different theory or assumption. Table 3 illustrates characteristics of common adsorption isotherms.
2.2. Methods for adsorption/desorption measurements

The amount of gas adsorption/desorption on solid matrices in both single and multicomponent system can be determined by volumetric, gravimetric, oscillometry, thermal desorption or dielectric methods. For studying multicomponent coadsorption, a combination of two or more of these methods is recommended [46], [47], [48], [34]. The theory, experimental setup, examples, advantages and disadvantages of these methods are well described in the books published by Keller and Staudt (2005) [34] and Broom (2011) [49], and are briefly summarized in the proceedings of 2nd Pacific Basin conference on adsorption science and technology (2000) [50]. Therefore, this review only presents the main principles related to these methods.

Volumetric (also known as manometric) and gravimetric techniques are quite similar in operating principle by which both are used to measure the relationship between the amount of gas uptaken by solid matrices and pressure [49]. However, manometric technique is based on the changes in pressure of gas in chamber with known volume containing solid matrices while the gravimetric method is performed by measuring change in the mass of solid matrices kept in a gas chamber with a very sensitive balance [51]. The use of these methods to study gas adsorption equilibrium of various solid matrices has widely been reported [7], [52], [53], [54], [55], [56], [57], [58], [59], [60], [61], [62], [63].

Oscillometry is another technique developed by Keller (1995) for the measurement of gas adsorption on highly porous materials by observing the slow oscillations of a rotational pendulum that attaches the sorbent materials and fixed to a suspension wire. The amount of adsorbed gas is calculated from the frequency and logarithmic reduction of damped oscillations of the pendulum in vacuum and in gas [64], [65]. This technique allows to measure gas uptake at very high temperature and pressure (up to 2,000°C and 100 MPa), even with corrosive gas [50], [34]. The combination of oscillometry with a
volumetric or gravimetric method has also been reported to measure the gas adsorption by swelling polymeric materials [50], [66].

In order to measure the desorption of gas from solid matrices, temperature-programmed desorption (TPD) technique can determine the amount of gas released as a function of temperature by measuring the weight changes of solid matrices under ultra-high vacuum conditions. The gas concentration released from solid materials can be measured by mass spectrometry [64]. This technique includes various analogues such as thermogravimetric analysis (TGA) and thermal desorption spectroscopy, and is well reported for studying the release kinetics of trapped gases (TDS) (TDS) [49] [67], [68], [69], [70], [71], [72], [73].

Another technique for adsorption measurement of gases which have permanent (CO or H₂O) or induced (N₂, Ar or CH₄) dipole moments on porous solids is the dielectric method. The alignment to direction of magnetic field of these gases under an external electric field results in the increase of their dielectric capacity. This technique measures the differences in capacitance of a capacitor filled by solid materials in the chamber with and without gas supply[34]. Many studies on the physisorption equilibria of gases on porous solids using dielectric measurement technique have been reported [74], [75], [76], [77], [78].

Moreover, in order to measure gas adsorption/desorption on water soluble solid matrices such as cyclodextrins, the gas chromatography (GC) measurement is an alternative method. In this method, dissolution of complexes into water in an air-tightly container will release gas into headspace whose composition is subsequently determined by GC. This method was proved to be an effective way to study encapsulation of C₂H₄ into α-cyclodextrin and its release from C₂H₄-α-cyclodextrin complexes [79], [80]. A more practical and cheaper way which can replace for GC to measure gas composition in headspace is the use of gas meters. In present study, we have established a CO₂ measuring system
using CO₂ probe for study adsorption and desorption of CO₂ into cyclodextrins. This system requires fans for air circulation and magnetic stir for agitation. The experimental results show that the CO₂ concentration measured by this system is quite close that determined by GC (data no shown).

3. Solid matrices used for gas encapsulation

3.1. Types of solid matrices

The composition of solid matrices used for gas encapsulation is the major determinant factor of the physical and chemical properties of resultant complexes. Therefore, the ultimate application of complexes is a prerequisite for selecting a solid matrix to adsorb gas. These properties include ability to form interactions with gases, stability of adsorbed gases in the complexes under the operating conditions, gas release characteristics on exposure to a stimulus condition, and cost [81]. A high gas adsorption capacity of solid matrices is required for gas storage while selectivity of a given gas over another is preferred to gas separation. The controlled release of the adsorbed gas molecules is more important in most biomedical, agriculture, horticulture and food applications. An ideal solid matrix should show high storage capacity and it should interact strongly enough with gas to prevent their unintended release due to effects of surrounding environment conditions (especially temperature or humidity) during storage. But the interaction should not be so strong that it is difficult to release the gas in a desired condition for a particular application [13]. In addition, the matrices will be required to be non-toxic, biodegradable, or biocompatible if they are intended to be used in food, pharmaceutical or agriculture systems.

There are numerous types of solid matrices for gas adsorption reported in the literature. These matrices are extremely different in their framework structure composition and properties. Based on their molecular composition, solid matrices can be categorized into non-organic and organic systems [38]; [82]. In addition, they can also be classified depending upon their molecular structure if they are
crystalline or non-crystalline complex matrices. Table 4 provides a classification of the types of matrix material. The non-organic matrices can also have metal ions as binding sites for gas molecules, and are more flexible to tailor gas adsorption capacity than organic systems. There have been a number of attempts made to store various gases by entrapping them in the nanopore or mesopore structures of non-organic or organic systems for fuel and emission control, but encapsulation of gases in biocompatible compounds which is of interest for their unrestricted applications in pharmaceutical, medicine, cosmetics, agriculture and food applications is still in an infant stage in terms of development and application. There are only a few recently published research papers. The reason might be due to the low amount of entrapped gases and instability of inclusion complexes in standard conditions. Furthermore, based on the structure, solid matrices can be classified into an ordered structural group (crystalline) with well-defined pore size (e.g. zeolites and carbon nanotubes), and a disordered structural one (non-crystalline) with a wide range of pore diameters. The structure of materials is well characterized by X-ray diffraction techniques. The level of porosity can be predicted by this X-ray diffraction method and BET adsorption study [83].

3.2. Characteristics of various solid matrices

3.2.1. Activated carbons

3.2.1.1. Molecular structure and mechanism of gas-matrix complexation

Activated carbons (ACs), which are also called activated charcoals or activated coals are prepared from a wide range of high carbon content raw materials such as coal, vegetable, coconut shells, petroleum, wood, polymeric precursors and other agricultural by-products [84]. There are two common ways of producing activated carbons, known as physical and chemical activation. In physical activation two processing steps are involved at high temperature (~973 K), first carbonization of the starting material in an inert atmosphere followed by exposure of this material to an oxidizing atmosphere (steam or
oxygen). In chemical activation, the starting materials are impregnated with a chemical such as H$_2$SO$_4$, H$_3$PO$_4$, ZnCl$_2$ or alkali metal hydroxides, then carbonized at moderate temperature (673-873 K) [85]. Generally chemical activation is easier and faster to achieve [6].

Activated carbons have an extremely porous structure with a wide range of pore diameters and surface area. The surface area is from 500 to 3000 m$^2$ g$^{-1}$ depending on the process of activation (physical or chemical activation) [86]. Ranges of porosity are found in the activated carbons, macropores (>500 nm), mesopores (4-500 nm) and micropores (<4 nm) whose proportions can vary significantly according to starting materials (Figure 1). During activated carbon production, macropores are firstly created due to oxidation of weak-interaction groups on the external surface of starting materials, followed by mesopores’ formation along the walls of the macropores, and then generation of micropores throughout the structure of the raw material [87]. Under an electron microscope, individual particles of activated carbon not only display various types of porosity, but also show many areas where the graphite-like flat surfaces of particles are intercalated with an interparticulate space of only a few nanometers in which gas molecules can be adsorbed (Figure 2) [88].

### 3.2.1.2. Gas adsorption property and loading

Activated carbons can exist in various forms including powders, granules, cylindrical extrudates, spherical beads, polymers and fibres. They are the most significant adsorbent materials used to separate and purify gas mixtures, or remove hazardous gases in chemical and petrochemical industries. The findings of these research works summarized in Table 5 indicates that gas adsorption capacity of activated carbons depends essentially on the activation conditions, starting material properties, and concentration of adsorbed gases. At low temperature and pressure (about 0.101 MPa and 273-298 K) activated carbons can adsorb 0.41 g 100g$^{-1}$ of SO$_2$ [82]; 7.00-35.42 g 100g$^{-1}$ of CO$_2$ [55], [90], [91]; 11, 0.18-0.25, and 14.96 g 100g$^{-1}$ of ClO$_2$, chlorpyrifos, and CF$_4$ respectively [5], [25], [92]. When
Increasing in adsorption pressure, some types of activated carbons show quite impressive increase in adsorption capacity such as Maxsorb and coal-based activated carbon which can entrap 143.00 and 80.90 g 100g⁻¹ of CO₂ at about 3.30 MPa respectively [7], [60]. For gas adsorption, the use of activated carbon has many benefits over other techniques such as wet or dry scrubbing using lime or limestone as absorbents in terms of cost-effectiveness, energy requirement and applicability over a wide range of temperatures and pressures [42], [84]. The mechanism of gas absorption of lime or limestone will be discussed in 3.2.6.

Due to a disordered and energetically heterogeneous internal porous structure, activated carbons’ efficiency of gas adsorption in nanospaces can be low [93], especially for large-size gas molecules because they might get stuck at macropore or mesopore channels, making them unable to reach to binding sites in micropores. The heterogeneity of pores can be reduced, and binding sites can be enhanced via modification of activated carbon preparing conditions by a selection of a tailoring method according to the nature of absorbed gases. For example, CO₂ is a Lewis acid therefore removal or neutralization of acidic functionalities of activated carbons by replacing acidic groups with appropriate basic groups (such as basic nitrogen functionalities), can significantly enhance its CO₂ adsorption capacity. The surface modification of activated carbon at various conditions for controlling carbon dioxide adsorption is well reported by many researchers [90], [94], [95], [96], [97] and is reviewed by Shafeeyan et al. (2010) [98].

3.2.1.3. Gas release property of the complex

For releasing gases adsorbed in activated carbons, combination of increase in temperature and/or reduction in pressure is used, which are opposite conditions of adsorption. In the process called “temperature swing adsorption” (TSA) [104] in which gas adsorption is carried out at low temperature, and regeneration of activated carbons is performed by increasing in temperature; however in “pressure
swing adsorption” (PSA) process, regeneration is done by decreasing in pressure [55], [105]. Of these TSA typically requires a longer time to regenerate [106]. Electrothermal swing adsorption which involves direct application of electricity to saturated CO \(_2\) activated carbons, has been found more efficient and easier for desorbing carbon dioxide from activated carbon than by TSA and PSA methods [107]. While the mechanism of gas adsorption on activated carbons are well described by adsorption isotherm models shown in Table 3 [7], [42], [43], [44], [62], just a few of models was proposed to study desorption kinetics. Gay and Do (1989) [108] developed a theoretical model, which is a combination between bimodal (macropore and micropore) diffusion control with a Freundlich isotherm acting at the micropore mouth, to describe gas desorption in a single particle with different geometry and particle size. This model was used to predict SO \(_2\) desorption from activated carbon particles [109].

In thermal reactivation or regeneration of saturated activated carbons the complex is dried firstly at low temperature (about 378 K), followed by pyrolysis at 773-973 K in an inert atmosphere to desorb gas, and then gasification with oxidizing gases (steam or O \(_2\)) at a higher temperature (about 1,173 K) to eliminate residual gas completely [110]. The high temperature can burn off about 5-15 (wt\%) of the carbon bed for each cycle leading to a loss of adsorption capacity [111]. This process can also transfer the contaminants and change the pore size distribution of activated carbons [112]. In spite of being the most widely described method, thermal reactivation requires a high energy and cost to operate. Alternative approaches, which are believed to lessen the drawbacks of thermal reactivation, are well reported, including wet oxidation [113], electrochemical [112], chemical and solvent [114], ultrasound [115], supercritical [116], and bio-regeneration [117] methods.

3.2.2. Carbon nanotubes

3.2.2.1. Molecular structure and mechanism of gas-matrix complexation
Another solid matrix whose main chemical make-up is similar to that of activated carbons is carbon nanotube. It was discovered in 1991 by Iijima as a tube-like material made of carbon. The tube typically is several micrometers in length and a few nanometers in hollow cavity [118]. A tube can be scrolled by one or several graphene sheets to form the single-walled nanotubes or multi-walled nanotubes respectively (Figure 3) [119]. The both ends of pristine tube are generally locked by fullerene-like half spheres consisting of five- and six-membered carbon rings, limiting the gas molecules’ penetration and interaction with binding sites inside of tubes [120]. However, it has been demonstrated that heat treatment in the presence of air leads to open caps at both ends of tubes, improving the gas adsorption capacity significantly [121]. Levesque et al. (2002) compared hydrogen adsorption capacity between a parallel bundle of closed and open carbon nanotubes having the same diameter; and found that for closed carbon nanotubes, adsorption capacity is reduced by a factor of 10 for a nominal diameter (d) of nanotube of 3.4 Å, and by a factor of 2 for d = 6.0 Å [122].

The multi-walled nanotubes with many graphene layers can exist in a wider variety of configuration and shapes with an interlayer spacing of approximately 0.34 nm [123]. Figure 4 illustrates some possible structures of the multi-walled nanotubes. The structure of “Russian doll” (Figure 4a) or “hexahedral prisms” (Figure 4b) include a set of single-walled cylinders or hexahedral prism tubes arranged coaxially one into another respectively, therefore the inner spaces of these structures are out of reach for gas molecule penetration. In contrast, gas molecules can easily access into inner spaces of the multi-walled nanotubes with the structures shown in Figure 4c: papier-mache, which has small graphene fragments assembly, and Figure 4d: scroll, which has a single sheet of graphite rolled in around itself [124]. The gas adsorption of carbon nanotubes has become an integral part for fundamental research, as it has offered a wide range of potential applications including energy storage, emission control, gas separation and nano-electrical devices. The carbon nanotubes have a very high gas storage capacity, because of their compact structure in bundles (Figure 5a) and the existence of
numerous binding sites for interactions with gas molecules (Figure 5b). The binding sites are located inside the nanotubes, on external surfaces of nanotubes, or on spaces among the nanotubes (e.g. interstitial or on the groove that is the space between two or three tubes respectively) [125]. In general, gases adsorbed on the inside and inter-space binding sites are much strongly bound than that on the surface of carbon nanotubes [126]. Shi and Johnson (2003) who studied CH₄, Ar, and Xe adsorption on homogenous (e.g. the same-diameter tubes) and heterogeneous (e.g. a wide range of different-diameter tubes) bundles of carbon nanotubes found that these gases are not adsorbed into the interstitial channels of homogeneous bundles, but do adsorb on interstitial channels of heterogeneous bundles as the latter situation consists of structures with multi-packing defects with relatively large interstitial channels [127].

3.2.2.2. Gas adsorption property and loading

Carbon nanotubes have been found to adsorb a wide variety of gases such as CO₂, Ar, H₂, N₂, tetrafluoromethane (CF₄) and others (Table 6). Interaction between the nanotube surface and gas molecule is based on physical adsorption because of the nonspecific van der Walls interactions [5]. The gases can be highly compressed reaching the density of a solid phase because high pressure results into densification and condensation of the gas inside the pores enhancing the storage capacity significantly. Encapsulation also results in an enhancement of the flexural strength within the nanotube structure due to the presence of a solid or compressed gas inside the tube core. The findings of these research works summarized in Table 6 indicates that in many cases (e.g. CO₂ adsorption) the gas encapsulation capacity of carbon nanotubes is not as high as that of activated carbons, but carbon nanotubes have been demonstrated to be effective solid matrices to entrap many high molecular weight gas molecules. Carbon nanotubes encapsulated 47.68, 55.14, and 34.36 g 100g⁻¹ of CCl₄, Xe and Kr respectively, at very low pressure and temperature conditions ((1.1-2.7)x10⁻⁴ MPa and 77-224
K) [57], [128]. At higher pressures and temperatures, carbon nanotubes were predicted to entrap about 119.77 and 21.12 g 100g\(^{-1}\) of SF\(_6\) and CF\(_4\) respectively [5], [129]. The adsorption capacity also varies on the treatment of the nanotubes. As a result attempts have been made to modify the nanotubes to increase the high yield of gas storage in nanotubes, such as by creating aligned dense arrays of nanotubes like stack of bamboo structure [130] or by attaching functional amine groups in the side wall of the nanotubes which are able to adsorb carbon dioxide [131]. Dramatic changes in the electronic and transport properties of the carbon nanotubes have been observed after adsorbing charge acceptor gases (O\(_2\) or NO\(_2\)), which are essential in manufacturing nano-electronic devices, chemical probes or biosensors [126].

There are some characteristics of the carbon nanotubes that limit their gas adsorption capacity and hinder their further application. Firstly, difficulties in purification during synthesis lead to impurities resulting from the residue of metal catalysts in carbon nanotubes [119]. These impurities, together with water insolubility and non-biodegradable ability has constrained applications of carbon nanotubes in biomedical or food fields to date [132].

### 3.2.2.3. Gas release property of the complex

Temperature and pressure are two well-known factors for gas desorption from carbon nanotube complexes. Liu et al. (1999) found that at room temperature 73.8\% (3.3 g 100g\(^{-1}\)) of the adsorbed hydrogen amount (4.20 g 100g\(^{-1}\)) on single-wall carbon nanotubes was released as the pressure was reduced from 10 MPa to atmospheric pressure, and the remaining adsorbed hydrogen (0.9 g 100g\(^{-1}\)) was only desorbed when the complex was heated up to 473 K [136]. The combination of changes in pressure and temperature to increase the rate of gas release from carbon nanotubes was also reported by Hsu et al. (2010). The time required to release all of the CO\(_2\) adsorbed onto multiwalled carbon nanotubes modified by 3-aminopropyl-triethoxysilane (3.7 g 100g\(^{-1}\) of CO\(_2\) at 333 K, 0.101 MPa) was
25 minutes by thermal treatment at 393 K, and was 30 minutes by vacuum suction at 0.014 MPa. However, when these two methods were combined, the time for CO$_2$ release declined significantly to 5 minutes. Interestingly, after 20 cycles of adsorption-regeneration for both treatment ways, the CO$_2$ adsorption capacity and main properties of multiwalled carbon nanotubes (pore structure and surface functional groups) were almost unchanged [143]. This was also reported for the adsorption capacity of H$_2$ onto Li- or K-doped carbon nanotubes [141]. One method used to study desorption kinetics of gas from carbon nanotube complexes is thermal desorption spectroscopy (TDS) [144], from which the binding energy and desorption activation energy are determined. For example, by using this method the binding energy of Xe on single-walled carbon nanotube bundles was found about 27 kJ mole$^{-1}$ [144]; the hydrogen desorption activation energy from open- and closed-structure multiwalled carbon nanotubes were -16.5 and -18.5 kJ mole$^{-1}$ respectively [145], from Ni nanoparticle-dispersed multiwalled carbon nanotubes was 31 kJ mole$^{-1}$ [146] and 30.8 kJ mole$^{-1}$ [147]. Unfortunately, no reports on modeling of gas desorption from carbon nanotubes is found. However, gas desorption kinetics from a graphite surface, which is similar to carbon nanotube surface, is well described by zero order models [148], [149].

3.2.3. Zeolites

3.2.3.1. Molecular structure and mechanism of gas-matrix complexation

Zeolites are microporous, 3-D crystalline and hydrated aluminosilicates, in a completely linked framework of tetrahedra. The general empirical formula of zeolites is expressed as $M_{x+y}O^\ast [(AlO_2)_{x}(SiO_2)_{y}]^\ast mH_2O$ in which n is the valence of the cation (M), m is the number of water molecules, x and y are the total number of tetrahedra per unit cell (normally x : y = 1-5) [150]. The “tetrahedron” is a basic building unit and includes cations (typically Si$^{4+}$ or Al$^{3+}$) in the centre and O$^{2-}$ in the corners. They are linked together via highly-flexible apical oxygen interactions to form a more
complex building unit called a “ring”. Normally, the number of tetrahedra in a ring determines its name and diameter. A ring built by 10 or 12 tetrahedra is known a 10-ring or 12-ring, and their diameter is 0.56 or 0.73 nm, respectively [151]. The next level of zeolite structure is created via the arrangement of rings in various ways to form a “cage”. This cage can be occupied by water molecules and cations (K⁺, Na⁺, Ca⁺ or others). These water molecules and cations have considerable freedom of movement resulting in reversible dehydration and ion exchange respectively [152]. The formation of zeolite structure is illustrated in Figure 6.

There are four common types of cages found in zeolite frameworks namely α-, β-, ε- and super-cage [151]. The β-cage (sodalite cage) and ε-cage (cancrinite cage) are formed by both 4-rings and 6-rings in different arrangements while the α-cage and super-cage are created by connecting 8-rings and 12-rings, respectively. Moreover, the cages can be arranged in cage-to-cage chains to form one-, two- or three-dimensional channels which allows gas molecules to diffuse along their pore [151]. The arrangement of tetrahedra in a large number of ways produces different possible zeolite structures [153]. More than 200 types of zeolites including natural and artificial ones have been identified and their porous networks as well as some properties are clearly described in databases such as “The Database of Zeolite Structures”[154] and “Zeolites and Microporous Structures Characterization” (ZEOMICS) [155].

3.2.3.2. Gas adsorption property and loading

Zeolites known as “molecular sieves” are extensively used in various branches of industry such as the petrochemical and petroleum-refining industries for gas emission control, or gas separation and storage (Table 7) because of their unique properties. The uniformity and wide range of the pore dimensions are determined by the location, size and coordination of the extra-framework cations as well as the arrangement of tetrahedra. They can have a high selective adsorption ability because different forms of
cation can lead to significant differences in the adsorption ability for a particular gas. The pore sizes of zeolite cavities are fixed and are usually small, which reduces their efficiency as adsorbent of large gas molecules such as tetrafluorocarbon. The characteristic sizes of the cage pores and channel apertures have a thermal dependence [150], [151]. At elevated temperatures, the increased thermal vibrations of the atoms in the zeolite framework result in an enlargement of the pore openings. In addition, an increase of kinetic energy of the gas molecules at higher temperature allows gases to diffuse through zeolite apertures [156]. In this case, the encapsulation process includes the forcing of gases into the cavities of zeolite crystals at high temperature and pressure, and consequently gases would be trapped inside when gas-zeolite matrices are cooled to ambient temperature [93]. This might be called as “encapsulation mechanism”. However, in the case of encapsulation of gases whose diameter is much smaller than cage aperture size of zeolites, (e.g. Kr in zeolite 5A), another encapsulation mechanism known as “chemifixation mechanism” can be observed. In the latter mechanism, gas molecules are blocked in cavities of zeolites through closure of aperture of the channels under hydrothermal treatment at very high temperature (> 823 K for Kr) which can covert the zeolite structure from a crystal to amorphous state due to thermal reaction of zeolite components [157].

The zeolites can be modified by ion exchange to facilitate the adsorption of some gases. The difference in cation size can affect pore width and consequently the adsorption capacity of zeolites. Weitkamp et al. (1995) investigated the hydrogen adsorption capacity of A-type zeolite as a function of cations. Using Na-A zeolite, they performed ion-exchange with solutions of potassium, rubidium and cesium chloride with degree of 95% for K-A, and 53% for Rb-A and Cs-A respectively, and found that at 573 K and 10 MPa almost no hydrogen was encapsulated in the Cs-A zeolite while the adsorption amount for K-A, Rb-A and Na-A zeolites was 0.051, 0.040 and 0.028 g 100g$^{-1}$ respectively [169]. The degree of ion exchange can also lead to a reduction in adsorption capacity; for example hydrogen adsorption capacity in a Na-A zeolite approached zero when the degree of cesium exchange reached 55%; while
adsorption capacity was not affected as degree of cesium exchange was 20% [169]. Similarly, Shang et al. (2010) also found that adsorption capacity for nitrogen and methane by chabazite modified with K⁺, Na⁺ and Ca²⁺ was significantly affected although there was no remarkable difference in their crystal structure. Ionic K⁺ with large size (0.133 nm) causes pore blockage, resulting in preventing gas molecules from diffusing through the window while this phenomenon is not detected with small size Ca²⁺ (0.099 nm) and Na⁺ (0.097 nm) ions [63]. Selection of cation type as well as degree for ion exchange process will depend on the nature of encapsulated gases.

The basic frameworks of zeolites are nontoxic materials with high chemical and biological stability, and can form reversible interactions with many molecules including gas molecules [14]. Therefore, zeolites (especially natural zeolite such as clinoptilolite) can be used in medicine for drug delivery [170], for treat stomach ulcers and fasten injury healing process; in agriculture for animal dietary supplement and crop yield enhancement [171]. However, inhalation of zeolite dust can result in respiratory problems [172] and the possible leaching of metal ions present in zeolites into aqueous solution [173] might limit their applications. More extensive studies are needed to ensure that use of zeolites, especially synthesized zeolites for these applications does not cause any problems.

### 3.2.3.3. Gas release property of the complex

Gas encapsulation process in zeolites is reversible, but it requires either high temperature to open cage apertures again to release gases, or treatment with water or acid [156]. Kalinnikova et al. (1986) proposed two ways to effectively decapsulate N₂ and O₂ from KNaA zeolite by heating the gas-zeolite complexes up to 400-500 K, or by blowing with moist gas at milder temperature (330-350 K) [158]. Release of hydrogen entrapped in NaA, KA and RbA zeolites was almost complete at 480 K, and depends on types of metal ions exchanged into zeolites. At the same temperature (especially at high temperature, >450 K), the H₂ release rate of KA zeolite was significantly higher than that of RbA.
zeolite, and was double that of NaA zeolite [169]. Moreover, gas release trigger factors from zeolite complexes are also determined by mechanism of gas-zeolite interactions’ formation. Matsuoka et al. (1986) found that when Kr molecules that were fixed into zeolite-types 3A and 5A by “encapsulation mechanism” released remarkably when the Kr-zeolite complexes were immersed in water at room temperature. By moistening the gas-zeolite complexes, the zeolite cations can move easily; resulting in widening cage apertures and subsequent release of the encapsulated gases. However, in cases in which Kr-zeolite complexes were formed by the “chemification mechanism”, an extremely high temperature (> 1,073 K) was required to recrystallize the amorphous Kr-zeolite matrices, causing release of gases [157]. Furthermore, these authors also concluded that diffusion coefficients of Kr in zeolites which were obtained from Ficks’law can be used for predicting amounts of Kr released from Kr-zeolite complexes in dry air [157]. The activation energy for diffusion of N₂, CO₂, and Ar in 3A zeolite was reported to be 72.38, 54.39 and 66.11 kJ mole⁻¹ respectively [67]. In addition, release control for entrapped molecules is also obtained via surface modification by functional groups [174], and altering of zeolite-shell thickness [175].

3.2.4. Metal-organic frameworks

3.2.4.1. Molecular structure and mechanism of gas-matrix complexation

Metal-organic frameworks (MOFs) were discovered by Hoskins and Robson in 1989 [176]. They are crystalline materials composed of metal ions or clusters linked by organic bridging ligands via strongly covalent interactions to form 1-, 2- or 3-dimensional infinite network structures [177]. The structure formation of metal-organic frameworks is shown in Figure 7. The 3-D metal-organic frameworks are of most interest because their voids can accommodate guest molecules for many applications including catalysis, sensor devices, or gas storage and separation [178]. These frameworks are ideal solid matrices for gas separation, storage and purification because of their high uniform pore size typically
ranging from 0.3 up to 4.8 nm and extremely high surface area (6240-10,400 m² g⁻¹ for MOF-210 for example, significantly higher than maximum surface area of zeolite (904 m² g⁻¹ for zeolite Y) and activated carbon (2630 m² g⁻¹)). They also have high porosity (void volumes up to 90%) [179]. They are flexible and easy to modify their structure and properties with respect to the desired application through the changes of the metal centres and/or the organic linkers [180]. There are a wide range of metal ions (Cu⁺, Cu²⁺, Ag⁺, Cd²⁺, Zn²⁺, Co²⁺, Li⁺, Mg²⁺ or Ni²⁺) and organic linkers (polycarboxylates, phosphonates, sulfonates, imidazolates, amines, pyridyl or phenolates), which can be selected for designing and synthesizing of metal-organic frameworks [181].

The synthesis of metal-organic frameworks can be accomplished either in liquid phases (water or organic solvent) in a closed vessel at room temperature [183] for heat-labile starting materials, or at high temperature to accelerate the rate of reaction between starting materials, known as hydrothermal [184], solvothermal [185], and microwave-assisted synthesis [186]; or in solid state to control reactivity towards to high yield formation [187]. Moreover, it is also possible to amend their structure for specific purposes after they are synthesized. This can be done by introducing metal ions or desired functional groups into the metal-organic frameworks (in their cavity, organic linker groups or open metal sites). Some examples are replacement of the coordinated molecules by highly polar ligands to enhance adsorption selective capacity for carbon dioxide over nitrogen [188]; coordination of polyethyleneimine into metal-organic frameworks (MIL-101) to accelerate CO₂ adsorption capacity [189]; imprisonment of boron nitride into MIL-53 channels to improve adsorption capacity of H₂ and CO₂ [190]; or changes of N₂, H₂ or CO₂ adsorption capacity of MIL-53 with the introduction of isocyanate and isothiocyanate groups into their structure [191]; or improvement of adsorption selectivity towards to CO₂ over CH₄ of MOF-5 by adding lithium metal (Li) [192]. There are a large number of ways to create numerous types of metal-organic frameworks. This diversity might lead to stability and potential toxicology issues of metal-organic frameworks for biological applications. The
reasons are differences in structure and composition. For example ZIF-8, UiO-66 and MIL-100(Fe) are quite stable in water while MOF-5 degrade in presence of water; and in phosphate buffer (pH = 7.4), Bio-MIL-1,1 and MIL-101(Fe) dissolve quickly while M-CPO-27 remains intact [181]. Therefore, it is very difficult to predict the stability of a particular metal-organic framework based on its structure, which can affect controlled-release property. Moreover, although some preliminary research about toxicology of metal-organic frameworks (Fe-MIL-88 and Fe-MIL-101) on rats did not show any harmful effects; and iron fumarate, with the same chemical composition as metal-organic frameworks Fe-MIL-88A, has been approved as an iron supplement [193]. Similar to zeolites the presence of ion metals in structure may pose potential problems for biological applications because of potential for their leaching.

3.2.4.2. Gas adsorption property and loading

Unlike zeolites in which metal ions are always available to form interactions with gas molecules, the metal ions in metal-organic frameworks are tightly held in pores by covalent interactions with organic bridging ligands, or solvent molecules during their synthesis. Removal of the solvent molecules, termed activation of metal-organic frameworks, can be performed by heat treatment [194] or solvent exchange [195]. This results in a structure of metal-organic frameworks with metal ions which may not be coordinatively saturated, known as open or coordinatively unsaturated metal sites. These sites are important in the enhancement of the gas adsorption capacity [196], [197], [198]. Some selected research publications on the adsorption of various types of gases and vapours in several MOFs solid matrices are summarized in Table 8. Furthermore, a number of published papers have reviewed and compared the adsorption capacity of numerous types of metal-organic frameworks for CO₂ capture, and for CH₄ and H₂ storage [197], [198], [199], [200].

3.2.4.3. Gas release property of the complex
Gas release from metal-organic frameworks can be carried out by decreasing pressure, increasing temperature, or exposing to moisture; and the release rate of guest molecules depends considerably on the size of cavities, rigidity, and solvent solubility of metal-organic frameworks [24]. By using thermal desorption spectroscopy (TDS) method, Panella et al. (2008) found that both metal-organic frameworks Cu-BTC and MOF-5 have two types of size-different cavities (0.5 & 0.9 nm for Cu-BTC, and 0.11 & 0.15 nm for MOF-5) which are binding sites for hydrogen while metal-organic framework MIL-53 possess only one 0.85 nm-size cavity. It was found that hydrogen adsorbed in the larger pore size of metal-organic frameworks required the higher temperature to desorb [73]. Water solubility of metal-organic frameworks also affects the release rate of adsorbed molecules. McKinlay et al. (2008) found that the metal-organic frameworks Co-MOF and Ni-MOF loaded with NO can stable over time at dry atmosphere, but significantly release NO when exposing to moisture, even at only 11 %RH [13]. The replacement of water molecules into the coordinated NO in metal-organic frameworks causes desorption of NO. However, at the similar moisture condition, NO-HKUST-1 complexes release a very small amount of NO [193]. Moreover, the release rate of NO from metal-organic frameworks is also affected by type of metal ions. The NO-Ni-MOF complexes release NO much faster than the NO-Co-MOF complexes [13].

3.2.5. Cyclodextrins

3.2.5.1. Molecular structure and mechanism of gas-matrix complexation

Cyclodextrins are starch derivatives and belong to a group of cyclic oligosaccharides composed of α-(1,4) linked glucopyranose units. These compounds have been recently researched to encapsulate gases although such encapsulation potential was reported in early 1960’s [213]. Typical cyclodextrins constitute of 6, 7 and 8 glucopyranose units, known as α-, β-, and γ-cyclodextrins respectively (Figure 8); and their common properties are presented in Table 9. The construction units of cyclodextrins have
a toroidal-like shape with the larger and the smaller openings of the toroid at upper and lower faces exposing to the secondary and primary hydroxyl groups respectively [214].

The interior of the cyclodextrin toroids is considerably less hydrophilic than the aqueous environment, and thus able to host hydrophobic molecules including solids, lipids and gases. In contrast, the exterior is sufficiently hydrophilic to impart cyclodextrins water soluble [217]. The water solubility of γ-cyclodextrins is highest (23.2 g 100mL⁻¹), being significant higher than that of α- and β-cyclodextrins about 1.5 and 20 times (14.5 and 1.85 g 100mL⁻¹) respectively [217]. The water solubility of cyclodextrins are significantly dependent on temperature, and models expressing a relationship between water solubility and temperature for each type of cyclodextrin was developed by Astray et al. (2009) [218]. Engulfment of the hydrophobic groups of the guest molecules inside the cavity has been found to improve guest molecules solubility in water [219]. Studies on the toxicity of cyclodextrins have shown that orally administered cyclodextrins are non-toxic due to lack of absorption from the gastrointestinal tract [220]. It is hard for cyclodextrins to permeate biological membranes because of their high molecular weight and the presence of many hydrogen donors and acceptors in their structure [221]. Moreover, cyclodextrins (α-, β-, and γ-types) are categorized as GRAS (Generally Recognized As Safe) in the USA, “natural products” in Japan, and as “novel food” in Australia and New Zealand. Therefore, cyclodextrins are being used in food, pharmaceutical, and chemical industries, as well as agriculture and environmental engineering to encapsulate many hydrophobic compounds aiming to solubilize or stabilize them at expected rate and conditions [221], [222], [223].

Cyclodextrin complexes can be formed either in solution which is used for nearly all guest molecules, or in the crystalline state by forming a paste with water [224]. In solution, cyclodextrin apolar cavities are always occupied by water molecules via energetically unfavourable polar-apolar interactions, and these water molecules are easily displaced by less polar guest molecules [214]. Therefore, the main
driving force for the formation of inclusion complexes is the substitution of the high-enthalpy water molecules in cyclodextrin cavities by hydrophobic guest molecules [218]. There is a difference between cyclodextrin and the previously mentioned solid matrices in that this is an aqueous process, whereas the others were direct gas adsorption.

3.2.5.2. Gas adsorption property and loading

Among three forms of cyclodextrins, α-cyclodextrin has the smallest interior cavity (0.47 - 0.53 nm) and is found to be most suitable for forming complexes with organic guests having less than five carbon atoms in their molecules because the smaller cavity will offer the more interaction and better binding force between the guest molecule and walls of cavity [228]. Most common gases have low molecular weight and small size, which can easily fit to the cavity of α-cyclodextrin [226]. Therefore, a number of researchers have reported encapsulation of gases into α-cyclodextrin (Table 10).

The first report about encapsulation of gases into α-cyclodextrin was published by Cramer & Henglein (1956) [213]. Various gases (CH₄, C₂H₆, C₃H₈, Kr, 1-methylcyclopropene, Xe, CO₂ and C₂H₄) were bubbled into α-cyclodextrin solution at controlled pressure (0.7-12 MPa) and temperature (293.15 K) which resulted in encapsulated gas content ranging from 1.04-10.27 g 100g⁻¹ in crystallized complexes which were collected after 5-7 days of encapsulation [227]. By studying the dynamics of Xe inside α-cyclodextrin cavities, Dubois et al. (2004) [229] found that binding constant of dipolar interactions between Xe and interior cavity was 23±5 (M⁻¹), which close to the value reported by Bartik et al. (1995) [230] of 22.9±6.1 (M⁻¹). In a study by Neoh et al. (2006) [20] they attempted to complex carbon dioxide, a non-polar gas, into α-cyclodextrin either in solid state with different initial moisture content (2, 10 and 30 wt%) at a pressure of 1 or 3 MPa, or in saturated solution of α-cyclodextrin under 3 MPa. The results showed that increase of encapsulating pressure from 1 to 3 MPa had significantly increase in the inclusion ratio while effects of initial moisture content of α-cyclodextrin on inclusion ratio was
not consistent. At 3 MPa, the highest inclusion ratio was observed at sample with 10% of moisture content (5.92 g of gas 100g⁻¹), higher than at 2% and 30% of moisture content with 5.06 and 4.88 g of gas 100g⁻¹ respectively. For saturated α-cyclodextrin solution, besides the lowest inclusion ratio (4.79 g of gas 100g⁻¹), yield of crystalline complexes was only about 56% after 120 hrs of encapsulation. However, complexes crystallized from saturated α-cyclodextrin solution were more stable in all storage humidity condition than complexes produced from solid state of α-cyclodextrin. An increase of storage humidity promoted diffusion of gases consequently increasing the rate of CO₂ release. Having more than 1 mole of CO₂ per 1 mole of α-cyclodextrin indicated that in some molecules of α-cyclodextrin there were more than one CO₂ molecule complexed. By using a similar technique, Ho et al. (2011) [79], [80] complexed ethylene gas in the α-cyclodextrin forming a crystalline complex. This was performed under moderate pressure range of 0.1-1.5 MPa.

As in other encapsulation system mentioned earlier, the yield (crystallized complex recovery) was dependent on the amount of the pressure and the time, in which yield increased with increasing encapsulation pressure and time and reached to equilibrium at value about 45%. In the complex powder, the gas was stable at normal atmospheric condition of temperature and pressure but was sensitive to the humidity above 45% RH. It was possible to predict the release kinetics based on the temperature and humidity of the environment condition. The amount of encapsulated gas was gas : cyclodextrin of 1 : 1 mole which is equivalent to around 2.9% by weight of ethylene (w/w). Gas molecular encapsulation process in α-cyclodextrin solution is a two-step reaction. This reaction involves dissolution of gas into aqueous phase, and formation of inclusion complex in which gas is encapsulated by crystallized α-cyclodextrin. Activation energy required for dissolution of gas will be more than that of diffusion and complexation reactions [225].
There has been no report of the use of β- and γ-cyclodextrins for gas encapsulation. However, cyclodextrins modified by cross-linking with carbonildiimidazole (known as cyclodextrin nanosponges) were found to encapsulate some types of gases because of the changes in channels between cyclodextrins or formation of porous networks during modification process, which can serve as places to occupy gases [231]. These were proved through the research results of Cavalli et al., (2010) [232], who showed that α-, β-, and γ-cyclodextrin cross-linking with carbonildiimidazole at 353-373 K for 4 hrs can also become an oxygen delivery system due to their high oxygen gas storage ability. Moreover, Trotta et al., (2011) [226] found that β-cyclodextrin nanosponges prepared by the similar method can store high amounts of O₂, CO₂ and 1-methylcyclopropene.

The physical interactions such as dipole-dipole bonds, apolar-polar interactions, hydrophobic associations or Van der Waals are found responsible for complexation between host and guest, with no evidence for forming or breaking covalent bonds [233]. Among these interactions, electrostatic and hydrogen bonding significantly affects the shape and structure of complexes. However, depending on particular inclusion complex, some interactions are more important than others. The importance and contribution of each types of bonding to complex formation can be well interpreted via multivariate quantitative structure-activity relationship (QSAR) analyses [234].

In most cases, the complexes are obtained in crystalline form. Followed by the complexation, cyclodextrin inclusion complexes can crystallize in two basically different patterns, the cage and the channel (tunnel) types [235] (Figure 9). The cage type results in when cyclodextrins are packed crosswise or side-by-side, in layers and adjacent layers are displaced by about one half molecules. In each of this molecular arrangement, the internal cavity of a cyclodextrin is locked on both sides by neighboring cyclodextrins further entrapping the guest molecules. On the contrary, channel complexes are formed when cyclodextrins are stacked like coins in a roll (head-to-head or head-to-tail pattern).
therefore cavities line up to produce long channels (tunnels) holding guest molecules. It has been
difficult to identify exactly which type of fashion will be formed under a particular condition [236].
However, for α-cyclodextrin, cage type structures are usually formed with small molecular guests
while long molecular and ionic guest molecules induce channel- or tunnel-type structures [237]. The
tunnel types are generally found for β- and γ-cyclodextrins. The crystal formation is responsible for
further locking up of the guest molecule and release property of the complexed gas. Therefore,
crystallized complexes were found to be stable for months at normal condition although the storage
capacity of gas complexes and obtained yield might not be high enough for actual applications [20],
[226], [79]. The hydrophilic cavities of cyclodextrins are not generally able to entrap polar gases such
as ammonia (NH₃), sulfur dioxide (SO₂) or hydrogen sulfide (H₂S).

3.2.5.3. Gas release property of the complex

The interactions of guest molecules within the host cyclodextrin are not permanent but rather a
dynamic equilibrium [224]. These are the reasons why gases are easily released from complexes. The
important environmental factors which have been proved to be effective ways for controlling the
releasing rate of gases are humidity and temperature. Increase in humidity and temperature would
accelerate the release rate of gases from cyclodextrin inclusion complexes, and gases are almost
immediately released upon dissolution in water [17], [20], [80]. Neoh et al. (2006) [20] found that CO₂ release rate from CO₂-α-cyclodextrin complexes under various
relative humidity (5, 33 and 75%) was well described by Avrami’s equation although this model was
initially developed for describing crystallization of polymer [238], and that CO₂ release mechanism
was diffusion controlled whose rate was significantly enhanced by high relative humidity. Similarly, in
a study on ethylene release kinetics from ethylene-α-cyclodextrin complexes under various relative
humidity (52.9, 75.5 and 93.6%) and temperature (318, 338, 358 and 378 K), Binh et al. (2011) [80]
claimed that both Avrami’s and power law models can be used to describe ethylene release rate for all conditions, and the former was better fit to experiment data than the latter. A power law model has been commonly used to describe the release rate of solid or liquid components in pharmaceutical products [239]. Moreover, Binh et al. (2011) also found that the amount of energy required to activate ethylene release in inclusion complexes was 65.9 kJ mole⁻¹.

3.2.6. Other solid matrices used for gas encapsulation

Other solid matrices used for gas entrapment are calcium-containing inorganic materials known as lime, limestone, or soda limes. They contain or produce strong alkali hydroxyls (e.g. Ca(OH)₂, KOH, Mg(OH)₂ or NaOH) in the presence of moisture. These alkali hydroxyls interact chemically with acid gases (CO₂, NO₂ or SO₂) from industrial exhaust streams [32], [33]. Unlike previous mentioned solid matrices with high surface area and possessing regeneration possibility, these materials have low surface area with about 2-22.5 m² g⁻¹ [240] and are generally not reused because of chemical interactions with gases. Normally, lime compounds are used as adsorbents in wet, dry or semi-dry scrubber systems for removal of undesirable gases. In wet systems gas streams are sprayed together with lime solution or are forced to pass through a bulk of lime solution. In dry systems dry powder sorbents are directly injected into the reactor. For semi-dry one, absorbents are first mixed with water to form a slurry which is then injected into the reaction chamber [33]. For these systems, especially for dry and semi dry ones the relative humidity in reaction chamber is a stimulating factor for reaction. The reaction between lime or limestone with SO₂ increases 10 times as relative humidity increases from 20 to 60% [240]. Due to formation of chemical reaction, these matrices were found to adsorb a high amount of gases at normal conditions. For example, by forcing the gas mixture go through a column packed with soda lime for 20 mins, NO₂ and CO₂ adsorption capacity were found about 3.86
and 24.5 g 100g$^{-1}$ respectively [32]. However, these matrices are only used for sequestering harmful gases without recycling, and gas entrapment into these matrices generates waste products (solid salts).

Furthermore, encapsulation of gas molecules in the inner spaces of other cavitands (container shaped molecules), (hemi) carcerands and capsules are also reported. In the cavitand groups of molecules (including cyclodextrins which are discussed in the 3.2.5 section), various cavitand matrices are also being reported to encapsulate a number of gas molecules. One of the examples is the calix[4]arene, which are bowl-shaped molecules with shallow clefts and large lattice voids which can encage many gas molecules such as CH$_4$, CF$_4$, C$_2$F$_6$, CF$_3$Br and H$_2$ [241], [242]. The carcerand and hemi-carcerand (cyclic oligomers) are other nano-container molecules which are hollow inside and able to entrap gases [243]. The gas entrapment in carcerand is almost permanent and happens during carcerand synthesis process. Encapsulated gases could not be released from carcerand complexes (also known as carceplexes), even at very high temperature. In contrast, complexes of hemicarcerands (also known as hemicarceplexes) are quite stable at normal conditions and guest molecules are easily released from hemicarceplexes at high temperature [244]. The hemicarcerands and their cavities form reversible noncovalent interactions with gas molecules. For example, cryptophane-A, a type of hemicarcerand, with cavity volume of 0.095 nm$^3$ can fit easily CH$_4$ (0.028 nm$^3$) and Xe (0.042 nm$^3$) gases [245].

Leontiev et al. (2007) reported a water-soluble hemicarcerand containing two hemispheres connected by methylene bridges with a molecular cavity of around 0.44 x 0.7 nm between two spheres, which was wider than the kinetic diameter of low molecular chain hydrocarbons (0.38-0.43 nm). This makes it possible for an easy flow of the gas or solvent dissolving the gas in and out. Hemicarcerands are water soluble, easy to incorporate gases and also form strong complexes. For example, a simple bubbling of butane gas in a solution of hemicarcerands in water can form around 40% complex [246]. Gas encapsulation can also occur on capsule matrices made up of self-assembly of dimers (e.g. 4,4'-
bis(dimethylamino) benzils or dihydroxytartaric acid disodium salt) which surrounds gas molecules (CH₄, C₂H₄ and Xe) through hydrogen-bonding [247]. The gas adsorption mechanism of these matrices and other synthetic cavities are well reviewed by Rudkevich and Leontiev (2004) [2], [8], [248].

4. Applications of gas-solid matrices

Surprisingly, there are very few actual applications reported on the stored gas in solid matrices to date although promising research works have been published. The reasons might be low adsorption capacity, inappropriate rate of gas release at desired conditions, and toxicity of solid matrices (especially for food, agriculture and pharmaceutical applications). Published research has shown that the storage of gases in solid matrices has high potential for applications in clean energy production, environment protection (emission control and removal of hazardous gases or vapors), nano-devices production, food and agriculture production and pharmacy (Table 11).

4.1. Clean energy production

After the Kyoto Protocol came into effect on 16 February 2005, the development of alternative clean energy sources, instead of fossil fuel, to reduce the amount of emission gases releasing to the air has become an urgent issue for many countries. Some natural gases, such as methane and hydrogen, can be ideal clean energy sources for vehicles because they are lightweight, abundant and almost environmentally harmless [249]. Burning these gases produces very much less amount of toxic gases. However, storage capacity of these gases in solid matrices at expected conditions is still low, although several types of solid matrices (e.g. activated carbons, zeolites and metal-organic frameworks and carbon nanotubes) under various adsorption conditions have been tested (Tables 5, 6, 7, 8 and 10). According to the Energy Efficiency & Renewable Energy (2013), by 2015 and 2017, a single-use
hydrogen storage system (2.0 wt% H\(_2\))\(^{(1)}\) for portable power applications and onboard automotive hydrogen storage system (5.5 wt% H\(_2\))\(^{(2)}\), respectively will be developed [250].

As presented in Tables 5, 6, 7, 8 and 10, hydrogen storage of some potential solid matrices can meet these targets however adsorption conditions (temperature and pressure) are far away from expected situations. In zeolite-gas system, based on theoretical calculation, the highest storage ability of hydrogen at 0 K and zero pressure was found for FAU and RHO zeolite types with about 2.86 wt% loading capacity. However, experimental results at atmospheric pressure (0.10 MPa and 77 K) gave loadings which were lower than those figures, with only 1.3 wt% [168]. Interestingly, metal-organic frameworks MOF-177 can adsorb up to 7.50 wt% of hydrogen at 77 K and 7 MPa, which is much higher than the FCTO target [208]. However, decrease in absorption pressure to normal condition (~0.101 MPa) results in significant reduction in absorption capacity of MOF-177, to only 1.52 wt% [207]. Among all solid matrices described above, carbon nanotubes are likely to be the most effective one to store hydrogen because their hydrogen adsorption capacity is very high, especially at low temperature (77-80 K) and high pressure (>7 MPa) which ranged from 4.50 wt% to 8.00 wt% (as shown in Table 6), and simulation results at 77 K and 7 MPa indicated that triangular array open single walled nanotubes can store up to 33 wt% of hydrogen. Nevertheless, increasing the adsorption temperature would lead to decline markedly in hydrogen storage capacity of carbon nanotubes. For example, at room temperature (~298.15 K), even at high pressure (>10 MPa), hydrogen storage capacity was found only 0.90-4.20 wt%. Carbon nanotubes doped with alkali metals such as lithium (Li) or potassium (K) ion have shown extremely high hydrogen uptake capacities at ambient pressure and 313 K or 673 K which was 14 or 20 wt% respectively [141], which are well above the FCTO target. The explanations for this phenomenon might be catalytic effects of alkali metals (Li or K) as

\(^{(1)}\) & \(^{(2)}\): These values are on a solid matrix weight basis
well as open-ends and layer-structure of carbon nanotubes. However, releasing hydrogen from these samples required much higher temperatures [141].

For methane, in order to be used as a clean energy source its storage capacity should be as high as compressed natural gas capacity (35 wt%) [38], and therefore almost no present solid matrices can meet that requirement (Tables 5, 6, 7, 8 and 10). Among activated carbon types, the highest methane absorption capacity was found only 21.65 wt% and 23 wt% for Maxsorb (3.3 MPa & 273 K) and coal-based activated carbon (8.5 MPa & 284.3 K), respectively [7], [60]. At similar adsorption conditions (3.65 MPa & 298 K), metal-organic frameworks IRMOF-6 can adsorb about 17.1 wt% [204], which is the maximum value among all types of metal-organic frameworks. The methane storage ability of zeolite and carbon nanotubes is much less than that of activated carbon and metal-organic frameworks. Carbon nanotube adsorbed only 7.62 wt% at 1.72x10⁻³ MPa and 78.7 K [128] while zeolite 3A was predicted to store about 6.90 wt% methane at extremely high temperature and pressure (410 MPa & 623 K) [156]. As shown in Table 7, methane adsorption capacity of the other types of zeolite is quite well below this value.

In summary, in order to be practically used for clean energy, further improvement in storage capacity is required. It is known that gas adsorption capacity of solid matrices depends primarily on number of factors such as surface area, free volume, framework density and heats of adsorption [38]. These will be the basis for further improvements.

4.2. Environmental protection

Application of gas storage in solid matrices for environmental protection implies removal of gases which can be either greenhouse gases (CO₂, CF₄ or SF₆) or hazardous gases and vapors (SO₂, chlorinated volatile organic compounds, and tertbutyl mercaptan or tetrahydrothiophene odorants) from flue gases or exhaust to prevent their detrimental effects to the environment. For this application,
high adsorption capacity, high adsorption selectivity and high interaction energy are expected [38]. Among reported solid matrices, activated carbon seems to be the most effective matrix for this application. The first reason is its high carbon dioxide adsorption capacity. Activated carbon Maxsorb (surface area of 3250 m$^2$ g$^{-1}$) could adsorb 143 g 100g$^{-1}$ at 3.3 MPa and 273 K [60], closely followed by a coal-based activated carbon (surface area of 1342 m$^2$ g$^{-1}$) with an adsorption capacity of 80.9 g 100g$^{-1}$ [7]. The adsorption energy for these types of activated carbons is 16-26 kJ mol$^{-1}$ which indicates that interaction between carbon dioxide and activated carbons is strong enough to give reasonable stability at room temperature. Moreover, activated carbon can absorb other toxic gases such as SO$_2$, ClO$_2$, tertbutyl mercaptan (TBM) or tetrahydrothiophene (THT) odorants, chlorinated volatile organic compounds and chlorpyrifos to some extent (Table 5). Therefore, activated carbon can be used to eliminate effectively these compounds out of environment. Although carbon nanotubes shows significantly lower carbon dioxide adsorption capacity than activated carbons, they have high potential ability for entrapping other greenhouse gases such as CF$_4$ and SF$_6$, with 21 and 119 g 100g$^{-1}$ respectively; and toxic gasses such as carbon tetrachloride - (CCl$_4$) with 47.68 g 100g$^{-1}$. Cyclodextrins can adsorb up to 5.87 g 100g$^{-1}$ carbon dioxide [227], but they are unable to be used for this application as CO$_2$-cyclodextrin complexes are not stable at normal operating conditions [225]. They also release carbon dioxide easily under high relative humidity (RH > 75%).

Metal-organic frameworks have the highest surface area among solid matrices, but their carbon dioxide adsorption capacity falls behind activated carbons. At 0.10 MPa the CPO-27-Ni metal-organic framework adsorbs between 12.40 and 29.90 g 100g$^{-1}$ CO$_2$ depending on temperature (303-353 K), which is the highest amount among various types of metal-organic frameworks. Other metal-organic frameworks shown to have ability to interact with carbon dioxide are MIL-53, BNH@MIL-53, Mg-MOF-74, Zn$_2$Atz$_2$(ox), MIL-101, PEI-MIL-101, CD-MOF-2 or Zn-MOF at various degree. This proves that diversity and flexibility in modification of metal-organic frameworks structure, which
means that changes in metal ions or incorporation with other component, can result in change in the adsorption capacity. Unlike metal-organic frameworks, carbon dioxide adsorption by most zeolites occurs at a higher pressure. Zeolites 4A and 13X adsorb about 21.10 and 22.90 g 100g⁻¹ CO₂ at 2.07 MPa and 300 K respectively [55]. For zeolites 13X, when pressure was increased to 5 MPa, its adsorption capacity increased to 32.44 g 100g⁻¹ [165].

4.3. Nano-device production

Unlike other solid matrices, carbon nanotubes are an amphoteric system which means that they can be doped as an electron donor or electron acceptor once exposed to some types of gases. This charge transfer results in significant changes in the density of free charge carriers, leading to variations of electrical and/or thermal conductivity of carbon nanotubes [251]. This is the basis for production of nanotube molecular devices to detect small concentrations of various types of gases. Gases, which are known to induce charge transfer in contact to carbon nanotubes are O₂, NO₂, NH₃, H₂, N₂, He and Br₂ [251], [252], [253], [254], [255], [256]. The nano-devices detect the presence of gases through measuring electrical resistance, thermoelectric power, or local density of states as a function of exposure time and gas concentration. In order to be used for this application, carbon nanotubes should be metallic, semimetallic or semiconducting. These properties are mainly determined by their chirality, and are only observed in several groups of carbon nanotubes [257], [258].

According to the research findings of Barberio et al. (2009) there is no indication of oxygen adsorption on either clean and pristine or low energy Ne⁺ ion bombarded single-walled carbon nanotubes at 298.15 K and 1.3×10⁻¹⁰ MPa while the one irradiated with 300 eV O⁺ ions showed oxygen chemisorption [134]. In addition, Collins et al. (2000) proved that electrical properties of single-walled carbon nanotubes changed dramatically on exposure to oxygen, which indicated adsorption of oxygen on carbon tubes [259]. Kong (2000) demonstrated the advantages of chemical sensors produced from
semiconducting single-walled carbon nanotubes to detect NO\textsubscript{2} and NH\textsubscript{3} over existing solid-state sensors such as a high-performance metal oxide sensor and poly-pyrole-conducting polymer sensor at room temperature [253] in terms of sensitivity and response time. However, the use of these devices for this purpose still has room for improvement. Slow recovery is one of the limitations as the nano-devices which still require high temperature treatment to desorb gases for the next measurement [253].

4.4. Medical applications

Together with oxygen, four other gases which are proved to have beneficial medical effects are CO\textsubscript{2}, H\textsubscript{2}S, CO and NO. Carbon dioxide contributes to blood-vessel dilation, blood circulation improvement, activation of gastrointestinal movement, and controlling of blood pressure [20], [260]. H\textsubscript{2}S, CO and NO are well-known neurotransmitters, and play an essential role in the regulation of vascular operation [261]. There is no research on storage of CO\textsubscript{2} in solid matrices for medical applications to date. There are only a few studies on H\textsubscript{2}S, CO and NO but these still require further extensive studies in terms of storage ability, toxicology and release rate. For medical applications, solid matrices should be free of toxic compounds, capable of storing an appropriate amount of gas, deliver it to specific sites in the body, and release it at a desirable rate through a simple triggering mechanism [173]. Uncontrolled release such as an initial quick release or a very slow release of gases can waste valuable products and do potential harm to the patient [24]. Metal-organic frameworks with high porosity, high biodegradable ability and extremely flexibility in the modification of their structure for intended purposes can be of interest for therapeutic purposes. Moreover, zeolites and cyclodextrins have also being researched to entrap gas for this purpose.

According to Xiao et al. (2007) [173], the metal-organic frameworks HKUST-1 absorbed 3 mmol g\textsuperscript{-1} NO at normal condition (0.101 MPa and 298 K), and in contact with water vapor total amount of NO released from NO-HKUST-1 was only 2 µmol g\textsuperscript{-1}. This amount is found to be very effective in
inhibiting thrombosis formation (1 pmol min\(^{-1}\) mm\(^{-2}\) of NO) [262]. In an \textit{in vitro} experiment this complex showed significant effectiveness in thwarting thrombosis formation, even after storing this complex in inert environment for up to several weeks [173]. At similar conditions, other metal-organic frameworks Ni-MOF and Co-MOF showed much higher amount of adsorbed NO, which is about 7 mmol g\(^{-1}\) NO at 298.15 K and 0.101 MPa [13]. Total amount of NO adsorbed in Ni-MOF or Co-MOF (7 mmol g\(^{-1}\) NO) was released after 2 weeks, in which only 1% of its release was in the first hour with trigger factor of humidity of gas (11% RH). This release property is useful in biological application in desiccated environment such as delivery of NO to wound healing on the skin. In phosphate-buffered saline (similar to blood or other physiological solutions), the NO releasing rate from these complexes was much faster, and it took only several hours to release about 50% of total amount of NO absorbed. An \textit{in vitro} study in pig coronary arteries showed NO released from NO-MOFs caused relaxation of arterial tissue [13].

In zeolites, the amount of NO adsorbed is much lower than that of metal-organic frameworks, with only 1.2-1.3 mmol g\(^{-1}\) for Co-exchanged zeolite-A at room temperature and 0.101 MPa pressure [14]. The total amount of NO released from zeolite-A can reach 1 mmol g\(^{-1}\) NO. NO-releasing-zeolites have been demonstrated to potentially prevent blood clots [14].

There are some concerns for using these zeolites and metal-organic frameworks in medical applications. The first problem is non-dispersability of these systems in the aqueous phase, which may result in difficulties in controlling the release rate as well as in delivering these matrices to target sites. Another concern is the toxicology of metals in frameworks [173]. In order to overcome the first issue, polymers such as poly-tetrafluoroethylene (PTFE) or poly-dimethylsiloxane (PDMS), have been incorporated to these frameworks as binders. This incorporation has only slightly retarded the release rate of gases [14]. Ion exchange of these solid matrices with less- or non-toxic metals could be a means
to reduce concerns about toxicology of solid matrices, especially for metal-organic frameworks. For example Zn ion in Zn-MOFs has been exchanged with other less toxic metals [263].

Allan et al. (2012) studied the applicability of the Ni-CPO-27 and Zn-CPO-27 metal-organic frameworks to entrap H$_2$S for medical purposes. They found that at 0.101 MPa and 303.15 K, Ni-CPO-27 showed the highest storage capacity of 12 mmol g$^{-1}$ of gas. Following exposure to a moist atmosphere, only 1.8 mmol g$^{-1}$ of H$_2$S was released from Ni-CPO-27 and 0.5 mmol g$^{-1}$ from the Zn-CPO after 30 minutes; and H$_2$S release from both CPO-27 stopped after 1 hour with a total release of only a third amount of the adsorbed H$_2$S. These complexes were stable for more than 9 months with small loss and were still able to release H$_2$S after this storage period. In an *in vitro* study, foetal calf serum, Zn-CPO-27 incorporated with 10% PTFE polymer, only released H$_2$S after several minutes of induction. For pig coronary arteries *in vitro* study, the use of a H$_2$S-Zn-CPO-27 complex stored for 9 months caused vascular relaxation after 5 minutes of induction [211].

In the case of CO gas, although there are some reports on adsorption of CO on zeolites and metal-organic frameworks, they are not likely to be applied in biology. This is due to the very low adsorption capacity of this gas on zeolites and metal-organic frameworks at desired conditions. Britt et al. (2008) claimed that there is no adsorption capacity of CO on several types of metal-organic frameworks (MOF-5, IRMOF-3, MOF-74, MOF-177, MOF-199, IRMOF-62 and BPL carbon) [177]. Zeolite X in forms of ion exchange with Na and Ba absorbed only 2.41 and 2.67 mmol g$^{-1}$ of CO, respectively at 303.45 K and 0.76 MPa, and less than 1 mmol g$^{-1}$ at normal conditions (303.45 K and 0.101 MPa) [161]. Although cyclodextrins are extensively being used for encapsulation of solid and liquid drugs [221], only β-cyclodextrins cross-linked with carbonildiimidazole show the ability to store oxygen for potential *in vivo* application. In this case the complex is coated with silicon membrane to control release rate as well as avoid an initial burst release [226].
4.5. Food and agriculture production applications

Although there are a number of research on encapsulation of solid or liquid compounds in solid matrices for food and agriculture applications [264], gas encapsulation for this purpose is still in an early stage of development. The first application of gas entrapment on solid matrices in food fields is the use of activated carbon and/or other adsorbents such as baking soda (sodium bicarbonate powder), clays or zeolites for deodorization in food storage spaces (e.g. refrigerators, freezers, or other cold storage units) [265], [266]. In these cases, adsorbents are normally packaged into porous and nonwoven pouches, and then placed in posts on back or front panels, or suspended freely of cold storage units. They adsorb unpleasant odors produced by strong smells or spoiled foods via the circulation of air inside freezers.

In cases when adsorbents contact directly to a food ingredient and become a food component, the nature of solid matrices, toxicology, biodegradability, encapsulation capacity, stability of complexes and releasing rate of gas are important criteria which need to be considered [267]. Therefore, only cyclodextrins among all of the solid matrices described earlier are qualified for entrapping gases for direct food applications. In this field, some research has been reported. Ho et al. (2011) complexed ethylene gas (C\textsubscript{2}H\textsubscript{4}) in α-cyclodextrin at a pressure range of 0.1-1.5 MPa. The amount of encapsulated gas was gas : cyclodextrin of 1 : 1 mole which is equivalent to about 2.9% ethylene by weight (w/w). The complex powder was stable at normal atmospheric condition of temperature and pressure but was sensitive to the humidity above 45% RH. The gas was almost immediately released upon dissolution in water. This inclusion complex has successfully been tested for its applicability in horticulture to promote the ripening process of mangos and germination of mung bean sprouts. Only 100 g of this powder was able to trigger the ripening of 20 tons of mangoes in a container in-transit from a farm to a market located at a long distance [79], [80]. For germination of mung bean sprouts, soaking mung
beans with this powder at a level 0.525-52.5 mg 100 mL⁻¹ water significantly improved the rate of seed germination, hypocotyl thickness and uniformity in length of mung bean sprouts [22].

Unlike ethylene, carbon dioxide gas is used in food field to retard the rate of respiration of the agricultural products. Besides, it is a bubble-creating agent in various types of beverage or a leavening agent in some food confections. Although its encapsulation in α-cyclodextrin was earlier patented in Japan in 1987 [226], this work did not lead to a commercial application probably due to the limited storage capacity achieved in applied processes. Neoh et al. (2006) showed that the level of CO₂ encapsulated was 1.25 moles per one mole α-cyclodextrin within a pressure range of 1.0-3.0 MPa, which is much lower than a theoretical value [20]. Based on the theory, the longitudinal molecular size of CO₂ is about 0.232 nm while the internal cavity size of α-cyclodextrin is roughly 0.52 nm diameter and 0.79 nm height; which means more than 2 moles of CO₂ might be entrapped by only a mole of α-cyclodextrin. A low storage capacity of CO₂-α-cyclodextrin complexes is still useful in some cases. In a recent patent, Zeller and Kim (2013) investigated use of CO₂-α-cyclodextrin complexes in cappuccino frothing. They mixed 1.5-3.0 g of complex powder (prepared at 3.4 MPa at 298.15 K for 7 days) to 11.5 g of instant cappuccino mix, and then reconstituted with 150 mL hot water (361.15 K). The froth formation ability of this sample was increased by 2-3 times compared to a sample without adding complexes. A similar result in enhancement of height of froth was observed by adding of N₂O-α-cyclodextrin complexes (encapsulated at 3.4 MPa, 298.15 K for 3 days) in hot instant cappuccino, cocoa, espresso and coffee mixes. Flavor of products with N₂O-α-cyclodextrin complexes was much better than that with CO₂-α-cyclodextrin complexes which induced carbonation and sensation flavor. The stability of froth was mainly determined by foam stabilizers present in milk protein. In another study, mixing of about 3% of N₂O-α-cyclodextrin complex into dough resulted in increasing of oven-baked pizza volume ingredient by 22% with an uniform internal foam structure [17].
Encapsulated gas has also been successfully used in the preparation of powdered soluble foamer by using a mixture of milk, caseinate, maltodextrin, lactose and sucrose [268]. This mixture was moistened to between 15% and 55%, and subjected to extrusion and spray-drying, respectively to create a porous structure which can entrap nitrogen gas at 2 MPa, 343.15 K for 20 minutes. This powder (20% by weight) was mixed with soluble coffee powder and was observed to enhance foam height by about 10 times [268].

**Conclusion**

This review updated the mechanism and methods of encapsulation of gases in solid matrices and highlighted the opportunity and importance of research in gas encapsulation. Gas encapsulation or adsorption in powder solid matrices can be an important means to sequester harmful or greenhouse gases (SO$_2$, CO$_2$, SF$_6$ or CF$_4$) and to store useful gases for their subsequent release in a targeted application (H$_2$, CH$_4$ or C$_2$H$_4$). Numerous types of solid matrices for gas adsorption have been reported in the literature, typically as activated carbons, carbon nanotubes, zeolites, metal-organic frameworks and cyclodextrins. These matrices are extremely different in their framework, structure, composition and properties, and have physical or chemical mechanism of gases on the adsorbent molecules, particle surface or molecular cavity. The gas-adsorbent interaction can be physical or chemical, thus reversible or irreversible respectively. The composition and properties of solid matrices are the major determinant factor of the physical and chemical properties of the resultant complexes. Therefore, the ultimate application of complexes is a prerequisite for selecting a solid matrix to adsorb a gas. Numerous attempts are made to store various gases by entrapping them in inorganic matrices (activated carbons, carbon nanotubes, zeolites and metal-organic frameworks) for environmental protection (harmful or greenhouse gases) and clean energy production (natural gases especially hydrogen and methane). Similarly, examples of gas encapsulation in biocompatible, biodegradable or edible powder matrices
(zeolites, metal-organic frameworks and cyclodextrins) that are significant in medicine, food and agricultural fields have also been reported.

The further application of gas encapsulated in these solid matrices is still limited by their low encapsulation capacity and stability in standard conditions. The high energy requirement for high loading of gas during complexation is another limitation. However, in some cases where a small amount of gases is required for an application, gas encapsulation can be effective due to the availability of gas in a powder format. In the powder form the use of the gas is often more safe and easy to handle, as compared to usual compressed counterpart and offers a wide range of potential applications.

Acknowledgements

The authors are grateful for the financial support of Australia Awards Scholarships.
References


[16]. Hanson, W.H. and R. Smith, Sprayable dispensing system for viscous vegetable oils and apparatus therefore, 1993, Google Patents.


Fig 1: Schematic representation of three types of pores in an activated carbon particle
(Adapted from [89])
Fig 2: The model of activate carbon with two intercalated layers of gases between single planes of graphite (Adapted from [88])
Fig 3: Illustration of single-walled (a) and multi-walled (b) carbon nanotubes
Fig 4: Illustration of various possible arrangements of multi-walled carbon nanotubes (a): Russian doll; (b): hexahedral prisms; (c): papier-mache; and (d): scroll [123]
Fig 5: A bundle of nanotubes (a) and various possible adsorption sites of a tube bundle (b)
Fig 6: Illustration of zeolite structure formation (Adapted from [151])
Fig 7: The building block of metal-organic frameworks (Adapted from [182])
Fig 8: Geometrical dimensions of α-, β-, and γ-cyclodextrin structure (CD = cyclodextrin) [215]
**Fig 9:** Schemes of possible arrangement of cyclodextrin molecules in crystalline complexes  
(Adapted from [235])
Graphical abstract

Applications of resultant complexes
1. Clean energy production
2. Environmental protection
3. Nano-device production
4. Medicine
5. Food and agriculture production
### Table 1: Examples of usage of various gases for different functions and products

<table>
<thead>
<tr>
<th>Gases</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Bubble-creating or leavening agent, extension of the shelf-life of dairy products and fruit juices, improvement of food quality, modified atmosphere in food storage, prevention of thrombus formation,</td>
</tr>
<tr>
<td>N₂</td>
<td>Modified atmosphere in food storage, space aircraft, the production of ammonia</td>
</tr>
<tr>
<td>O₂</td>
<td>Medicine, steel making</td>
</tr>
<tr>
<td>CO</td>
<td>Modified atmosphere packaging for meat products, gasotransmitter and therapeutics</td>
</tr>
<tr>
<td>H₂</td>
<td>Energy-rich fuel-cell devices</td>
</tr>
<tr>
<td>CH₄</td>
<td>Clean energy production</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>Fruit ripening and promotion for germination of seeds</td>
</tr>
<tr>
<td>N₂O</td>
<td>Canister sprays (non-stick cooking oil, whipped cream), and anaesthesia</td>
</tr>
<tr>
<td>SO₂</td>
<td>Anti-browning of fruits and vegetables</td>
</tr>
<tr>
<td>1-MCP</td>
<td>Delay ripening of fruits and vegetables</td>
</tr>
<tr>
<td>O₃</td>
<td>Water treatment, sanitisation of raw fruits and vegetables</td>
</tr>
<tr>
<td>He, Ar &amp; N₂</td>
<td>Analytical equipment (e.g. gas chromatography)</td>
</tr>
<tr>
<td>ClO₂</td>
<td>Surface disinfection</td>
</tr>
<tr>
<td>NO &amp; H₂S</td>
<td>Gasotransmitter and therapeutics (e.g. platelet aggregation inhabitation and antibacterial activity, modulating cellular functions)</td>
</tr>
</tbody>
</table>
Table 2: Differences between physical and chemical adsorption [34], [35].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature of binding</td>
<td>- Physical forces (dipole-dipole, apolar, electrostatic, hydrophobic associations or Van der Waals)</td>
<td>- Chemical bonds (covalent, metallic or ionic)</td>
</tr>
<tr>
<td></td>
<td>- Polarization</td>
<td>- Electron exchange</td>
</tr>
<tr>
<td></td>
<td>- Reversible</td>
<td>- Irreversible</td>
</tr>
<tr>
<td>Heat of adsorption</td>
<td>Low (8-41 kJ mole⁻¹ gas, i.e. ~ heat of liquefaction)</td>
<td>High (62-418 kJ mole⁻¹ gas)</td>
</tr>
<tr>
<td>Effects of temperature on adsorption ability</td>
<td>Decrease with increase in temperature</td>
<td>Increase with increase in temperature</td>
</tr>
<tr>
<td>Pressure in which adsorption occurs</td>
<td>Insignificant at low pressure and increase with increase in pressure</td>
<td>Much lower than pressure range of physisorption</td>
</tr>
<tr>
<td>Volume of absorbed gases</td>
<td>Depends on boiling point and critical temperature of gases</td>
<td>Independent on boiling point and critical temperature of gases</td>
</tr>
<tr>
<td>Saturation uptake</td>
<td>Multilayer adsorption</td>
<td>Monolayer adsorption</td>
</tr>
<tr>
<td>Activation energy for desorption</td>
<td>Low</td>
<td>Very high</td>
</tr>
<tr>
<td>Kinetics of adsorption</td>
<td>Very variable - often an activated process</td>
<td>Fast - since it is a non-activated process</td>
</tr>
<tr>
<td>Selectivity of sorptive gases</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
Table 3: Characteristics and usage of some common adsorption isotherm models

<table>
<thead>
<tr>
<th>Isotherms (*)</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
</table>
| Langmuir     | - Two parameter isotherm for noncompetitive, nondissociative adsorption  
+ Assumptions:  
  + The surface is homogeneous  
  + Each adsorption site holds only one molecule  
  + There are no interactions between adsorbate molecules | [42] |
| Freundlich   | - Two parameter model  
- No physical basis for equations (purely empirical and no theoretical basis)  
- Multilayer adsorption with different distribution of adsorption heat and force over the heterogeneous surface  
- It does not work well for adsorption on a highly ordered surfaces, only fits adsorption data taken over a small range of pressure and has little predictive value  
- Ignores interactions between adsorbate and adsorbate  
- Assumes that adsorbate randomly populates the available adsorption sites  
- It fails when the concentration of the adsorbate is very high | [42] [43] |
| Toth         | - Three parameter model  
- Empirical equation to describe heterogeneous adsorption systems  
- The most successful isotherm both at low and high pressure on heterogeneous surfaces  
- Ignore adsorbate/adsorbate interactions |  |
| Tempkin      | - Two parameter model  
- Accounts interactions between adsorbate and adsorbate  
- Does not consider how the adsorbate layer is arranged | [41] [44] |
| BET          | - Three parameter model, multilayer adsorption  
- Uniform heat of adsorption (heat of adsorption of the second and subsequent layers is equal to the heat of liquefaction of the solute)  
- Multiple gas molecules can be adsorbed to each site  
- Gases in the second and higher layers are assumed to be liquid like  
- Used for determining pore surface area of solid matrices for gas adsorption | [41] [45] |

(*) $q$ is amount adsorbed in equilibrium with the concentration of adsorbate in gas phase (mmol g$^{-1}$ and mg g$^{-1}$ for Tempkin isotherm). $q_m$ is maximum adsorption amount (mmol g$^{-1}$). $P$ is equilibrium pressure of the adsorbate in gas phase (kPa). $b$ is equilibrium constant of adsorption (kPa$^{-1}$). $K_F$ is Freundlich constant. $1/n$ is heterogeneity factor and an indicator for adsorption capacity. $t$ is Toth isotherm exponent related to surface heterogeneity (usually less than or equal to unity). $K_T$ is Temkin constant related to heat of sorption (J mole$^{-1}$). $A$ is Temkin isotherm constant (L g$^{-1}$). $R$ is gas constant (8.314 J mole$^{-1}$ K$^{-1}$). $T$ is absolute temperature (K). $C_e$ is amount of adsorbed adsorbate per unit mass of unabsorbed adsorbate concentration in solution at equilibrium (mg L$^{-1}$). $K_{BET}$ is the BET adsorption isotherm (L mg$^{-1}$). $C_s$ is adsorbate monolayer saturation concentration (mg L$^{-1}$). $q_i$ is theoretical isotherm saturation capacity (mg g$^{-1}$). $q_e$ is equilibrium adsorption capacity (mg g$^{-1}$).
Table 4: Classification of solid matrices used to entrap gases

<table>
<thead>
<tr>
<th>Classification basis</th>
<th>Molecular composition</th>
<th>Structure</th>
<th>Solid matrices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic</td>
<td>Ordered (crystalline)</td>
<td>Activated carbons (*)</td>
</tr>
<tr>
<td></td>
<td>Inorganic</td>
<td>Disordered (non-crystalline)</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Activated carbons</strong> (*)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

(*) These matrices can be classified as organic or inorganic
Table 5: The studies on gas adsorption using various forms of activated carbons

<table>
<thead>
<tr>
<th>Gases</th>
<th>Raw materials</th>
<th>Adsorption conditions</th>
<th>Adsorption amount of gas (g 100g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>ACs (1,036 m² g⁻¹)</td>
<td>P = 0.101 MPa T = 288.15-306.15 K</td>
<td>0.41-13.40</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>ACF-15 (1,585 m² g⁻¹)</td>
<td>P = 0.101 MPa T = 393.15 K</td>
<td>11.00</td>
<td>[99]</td>
</tr>
<tr>
<td></td>
<td>NH₃-ACF-15</td>
<td></td>
<td>58.00</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>Coconut shell (h)</td>
<td>P = 3.50 MPa T = 298.15 K</td>
<td>10.60-13.40</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>CFC-73</td>
<td>4.00 MPa &amp; 298 K</td>
<td>15.24</td>
<td>[53]</td>
</tr>
<tr>
<td>CO₂</td>
<td>AC1 (553 m² g⁻¹)</td>
<td></td>
<td>26.00</td>
<td></td>
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<tr>
<td></td>
<td>AC2 (809 m² g⁻¹)</td>
<td></td>
<td>14.70</td>
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<tr>
<td></td>
<td>Charcoal (135 m² g⁻¹)</td>
<td></td>
<td>12.00</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>Coal (100 m² g⁻¹)</td>
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<td>5.50</td>
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<tr>
<td>CH₃OH</td>
<td>ACs (1,342 m² g⁻¹) (e)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>8.50 MPa &amp; 284.3 K</td>
<td>23.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.80 MPa &amp; 287.5 K</td>
<td>35.00</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.59 MPa &amp; 283.9 K</td>
<td>42.00</td>
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<tr>
<td></td>
<td></td>
<td>0.15 MPa &amp; 282.2 K</td>
<td>44.00</td>
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<td></td>
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<td>3.36 MPa &amp; 273.3 K</td>
<td>80.90</td>
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<td></td>
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<td>3.06 MPa &amp; 282.2 K</td>
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<tr>
<td></td>
<td></td>
<td>2.03x10⁻² MPa &amp; 298.8 K</td>
<td>20.10</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1.93x10⁻² MPa &amp; 298.9 K</td>
<td>8.00</td>
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</tr>
<tr>
<td>CO₂</td>
<td>C (1,361 m² g⁻¹)</td>
<td>P = 0.101 MPa T = 298.15 K</td>
<td>7.00</td>
<td>[90]</td>
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<tr>
<td></td>
<td>CN800 (1,190 m² g⁻¹)</td>
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<td>8.40</td>
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<tr>
<td>Cl₂</td>
<td>ACs (1,000 m² g⁻¹) (f)</td>
<td>0.101 MPa &amp; 297.15 K</td>
<td>11.00</td>
<td>[25]</td>
</tr>
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<tr>
<td>Chlorpyrifos</td>
<td>BCA (985 m² g⁻¹) (b)</td>
<td>P = 0.101 MPa T = 283 K</td>
<td>0.18</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>CSA (1,001 m² g⁻¹)</td>
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<td>0.25</td>
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<tr>
<td>CO₂</td>
<td>Active carbon fiber</td>
<td>P (b) = 0.05 MPa T = 325.15 K</td>
<td>4.74</td>
<td>[42]</td>
</tr>
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<tr>
<td>SO₂</td>
<td>Cl-VOCs (g)</td>
<td>Commercial ACs (856 - 927 m² g⁻¹)</td>
<td>4.80</td>
<td>[6]</td>
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<tr>
<td></td>
<td></td>
<td>(856 - 927 m² g⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>P = 0.152 MPa T = 308.15 K</td>
<td>20.08</td>
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</tr>
<tr>
<td>CO₂</td>
<td>AC (730-2,930 m² g⁻¹)</td>
<td>P = 0.100 MPa T = 273 K &amp; 300 K</td>
<td>273 K = 35.42</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300 K = 20.02</td>
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</tr>
<tr>
<td>CH₄</td>
<td>BPL (1,000 m² g⁻¹)</td>
<td>P = 3.8 MPa T = 300 K</td>
<td>19.80</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td>AX-21 (3,000 m² g⁻¹)</td>
<td></td>
<td>52.80</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>AC (897 m² g⁻¹)</td>
<td>2.068 MPa &amp; 300 K</td>
<td>37.40</td>
<td>[55]</td>
</tr>
<tr>
<td>CO₂</td>
<td>CACM-32 (1,150-1,330 m² g⁻¹)</td>
<td>P = 0.101 MPa T = 273 K</td>
<td>16.40</td>
<td>[103]</td>
</tr>
<tr>
<td></td>
<td>PACM-28 (820-1,640 m² g⁻¹)</td>
<td></td>
<td>16.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C3SN400 (1,323 m² g⁻¹)</td>
<td>0.103 MPa &amp; 309.15 K</td>
<td>7.60</td>
<td>[94]</td>
</tr>
<tr>
<td>CF₄</td>
<td>AC (Carboactive G)</td>
<td>0.10 MPa &amp; 300 K</td>
<td>14.96</td>
<td>[5]</td>
</tr>
<tr>
<td>CO₂</td>
<td>BPL (1,150 m² g⁻¹)</td>
<td>2.7 MPa &amp; 273 K</td>
<td></td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>A10 (1,200 m² g⁻¹)</td>
<td>2.8 MPa &amp; 273 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>Maxsorb (3,250 m² g⁻¹)</td>
<td>3.3 MPa &amp; 273 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Norit R1 (1,450 m² g⁻¹)</td>
<td>2.9 MPa &amp; 273 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC-A (1,207 m² g⁻¹)</td>
<td>2.3 MPa &amp; 273 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) NH₃-ACF-15 is treated with ammonia at 1,073 K for 60 min; SO₂ adsorption is carried out with presence of O₂ and H₂O which induces the conversion of SO₂ to H₂SO₄, resulting in very high SO₂ adsorption capacity. (b) Combining chemical activation of coconut shell with H₃PO₄ or ZnCl₂ followed by physical activation with CO₂. (c) Coal-based, extruded carbon (2 mm diameter pellets), courtesy of Sutcliffe Speakman Carbons Ltd. (UK). (d) Terbutyl mercaptan (TBM) and tetrahydrothiophene (THT) odorants. (e) These are the partial pressures of TBM (6.74 ppmv) and THT (6.95 ppmv) in a mixture with helium at 3.5 MPa pressure. (f) C is a wood-based granular carbon manufactured by a phosphoric acid activation process; CN800 is activated carbon modified with ammonia at temperature 1,073 K. (g) Pellet diameter (4 mm), density (409 kg m⁻³), and 2-3% moisture content. (h) BCA is bone charcoal activated carbon. (i) Partial pressure. (j) Chlorinated volatile organic compounds (dichloromethane).
Table 6: Summary of some research on gas encapsulation by using carbon nanotubes (CNs)

<table>
<thead>
<tr>
<th>Gases</th>
<th>CNs types</th>
<th>Conditions</th>
<th>Gas absorption amount (g 100g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(*) CH₄</td>
<td>(a) SWNT</td>
<td>P = 35.62 MPa, T = 273 K</td>
<td>4.00</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td>(b) MWNT</td>
<td>P = 3.00 MPa, T = 303.15-323.15 K</td>
<td>2.17-3.03</td>
<td>[61]</td>
</tr>
<tr>
<td>O₂</td>
<td>SWNT</td>
<td>P = 1.3x10⁻¹⁰ MPa, T = 298.15 K</td>
<td>No oxygen uptake</td>
<td>[134]</td>
</tr>
<tr>
<td>(*) SF₆</td>
<td>SWNT</td>
<td>P = 2.07 MPa, T = 298 K</td>
<td>119.77</td>
<td>[129]</td>
</tr>
<tr>
<td>CO₂</td>
<td>MWNT</td>
<td>P = 0.101 MPa, T = 293.15 K, Cn = 15-50% (d)</td>
<td>4.33-11.40</td>
<td>[131]</td>
</tr>
<tr>
<td>(a) H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MWNT (**)</td>
<td>P = 20 MPa, T = 77.15 K; 150 K &amp; 293 K</td>
<td>293 K = 1.60, 150 K = 3.70, 298 K = 5.20</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>SWNT</td>
<td>P = 10 MPa, T = 298.15 K</td>
<td>4.20</td>
<td>[136]</td>
</tr>
<tr>
<td></td>
<td>Li-doped MWNT</td>
<td>P = 0.101 MPa, T = 473.15-673.15 K</td>
<td>2.50</td>
<td>[137]</td>
</tr>
<tr>
<td></td>
<td>SWNT</td>
<td>P = 11 MPa, T = 80 K</td>
<td>8.00</td>
<td>[138]</td>
</tr>
<tr>
<td></td>
<td>SWNT (v)</td>
<td>P = 10.132 MPa, T = 77 &amp; 298 K</td>
<td>77 K = 4.50, 298 K = 0.90</td>
<td>[139]</td>
</tr>
<tr>
<td></td>
<td>SWNT (**)</td>
<td>P = 7 MPa, T = 77 K</td>
<td>33.00</td>
<td>[140]</td>
</tr>
<tr>
<td></td>
<td>K-doped CNT (f)</td>
<td>P = 0.101 MPa, T = 313 K</td>
<td>14.00</td>
<td>[141]</td>
</tr>
<tr>
<td></td>
<td>Li-doped CNT</td>
<td>P = 0.101 MPa, T = 473-673 K</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td>CF₄</td>
<td>SWNT</td>
<td>P = 0.10 MPa, T = 300 K</td>
<td>21.12</td>
<td>[5]</td>
</tr>
<tr>
<td>CO₂</td>
<td>SWNT (c)</td>
<td>P = 0.107 MPa, T = 308.15 K</td>
<td>19.01</td>
<td>[142]</td>
</tr>
<tr>
<td>CCl₄</td>
<td>SWNT</td>
<td>P = 1.8x10⁻⁷ MPa, T = 224 K</td>
<td>47.68</td>
<td>[57]</td>
</tr>
<tr>
<td>Kr</td>
<td>SWNT</td>
<td>P = 1.2x10⁻⁴ MPa, T = 77 K</td>
<td>33.94</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>SWNT</td>
<td>P = 1.3x10⁻⁴ MPa, T = 110 K</td>
<td>55.14</td>
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</tr>
<tr>
<td>CH₄</td>
<td>SWNT</td>
<td>P = 1.72x10⁻⁵ MPa, T = 78.7 K</td>
<td>7.62</td>
<td>[128]</td>
</tr>
<tr>
<td>Kr</td>
<td>SWNT</td>
<td>P = 2.73x10⁻⁵ MPa, T = 77.3 K</td>
<td>34.36</td>
<td></td>
</tr>
</tbody>
</table>

(a) SWNT is single-walled carbon nanotubes. (*) The values are the results of molecular dynamics simulation. (b) MWNT is multi-walled carbon nanotubes. (c) Measurements are performed in an ultrahigh vacuum chamber. (d) Influent CO₂ concentration. (e) For hydrogen adsorption on carbon nanotubes is well reviewed by Darkrima et al. (2002) [119]. (f) CNT is carbon nanotube. (g) SWNT is purified by a high pressure CO disproportionation (HiPCo) process. (*)(*) The values are the results of molecular dynamics simulation with triangular arrays of open and closed SWCNT of various diameters in a wide range of configurations.
### Table 7: Summary of research on gas entrapment into zeolites

<table>
<thead>
<tr>
<th>Gases</th>
<th>Zeolite types</th>
<th>Adsorption conditions</th>
<th>Adsorbed amount (g 100g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3A</td>
<td>5.52 MPa &amp; 623.15 K</td>
<td>15.29</td>
<td>[68]</td>
</tr>
<tr>
<td>N₂</td>
<td>3A (a)</td>
<td>12.41 MPa &amp; 623.15 K</td>
<td>5.63</td>
<td></td>
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<tr>
<td>Ar</td>
<td>3A</td>
<td>12.06 MPa &amp; 623.15 K</td>
<td>8.19</td>
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</tr>
<tr>
<td>CH₄</td>
<td>3A</td>
<td>P = 414 MPa; T = 623.15 K</td>
<td>6.90</td>
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</tr>
<tr>
<td></td>
<td>HSZ-320</td>
<td>P = 2.60 MPa; T = 303.15-323.15 K</td>
<td>1.52-1.98</td>
<td>[61]</td>
</tr>
<tr>
<td>DAY</td>
<td>P = 300 K (O₂) &amp; 600 K (N₂)</td>
<td>2.32-2.85</td>
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<td></td>
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<tr>
<td>N₂</td>
<td>KNaA (a)</td>
<td>P = 80 MPa; T = 500 K</td>
<td>9.00</td>
<td>[158]</td>
</tr>
<tr>
<td>O₂</td>
<td>(K₁₀(CO₂,Na) - A)</td>
<td>P = 3.7 MPa; T = 573.15 K</td>
<td>7.26</td>
<td>[159]</td>
</tr>
<tr>
<td></td>
<td>(K₁₀,Na₂,Na₂) - A</td>
<td>P = 101.3 MPa; T = 723.15-923.15 K</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3A</td>
<td>P = 0.027 MPa (CO₂) &amp; 0.067 MPa (N₂); T = 283.15 K</td>
<td>0.89</td>
<td>[160]</td>
</tr>
<tr>
<td>CH₄</td>
<td>ZSM-5</td>
<td>P = 0.81 MPa; T = 303.45 K</td>
<td>BaX = 5.27 &amp; NaX = 4.17</td>
<td>[161]</td>
</tr>
<tr>
<td></td>
<td>BaX</td>
<td>P = 268.5 MPa &amp; 623 K</td>
<td>BaX = 11.80 &amp; NaX = 10.60</td>
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<tr>
<td></td>
<td>3A</td>
<td>P = 13.07 MPa; T = 623 K</td>
<td>0.17</td>
<td>[37]</td>
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<td>Na₄₂⁺A</td>
<td>P = 15.2 MPa; T = 623 K</td>
<td>0.04</td>
<td>[162]</td>
</tr>
<tr>
<td>CH₄</td>
<td>Na-A (a)</td>
<td>268.5 MPa &amp; 623 K</td>
<td>5.26</td>
<td>[93]</td>
</tr>
<tr>
<td></td>
<td>4A</td>
<td>84.1 MPa &amp; 523 K</td>
<td>4.44</td>
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<tr>
<td>Ar</td>
<td>4A</td>
<td>268.5 MPa &amp; 623 K</td>
<td>15.91</td>
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</tr>
<tr>
<td>Kr</td>
<td>4A</td>
<td>435.7 MPa &amp; 623 K</td>
<td>33.85</td>
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<td>13X</td>
<td>P = 60.80 MPa; T = 673.15 K</td>
<td>8.90</td>
<td>[163]</td>
</tr>
<tr>
<td>Ar</td>
<td>Cs₂NaH⁻A</td>
<td>P = 64.34 MPa; T = 673.15 K</td>
<td>20.80</td>
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<tr>
<td>Kr</td>
<td>Cs₃NaH⁻A</td>
<td>P = 5.0 MPa; T = 298 K</td>
<td>9.17</td>
<td>[165]</td>
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<tr>
<td></td>
<td>13X</td>
<td>P = 2.5-500 MPa; T = 298.15 K</td>
<td>32.44</td>
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<tr>
<td>Ne</td>
<td>5A</td>
<td>3.61</td>
<td>11.81</td>
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</tr>
<tr>
<td>Ar</td>
<td>5A</td>
<td>4.06</td>
<td>0.53</td>
<td>[166]</td>
</tr>
<tr>
<td></td>
<td>10A</td>
<td>2.40</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12A</td>
<td>0.101 MPa &amp; 273 K</td>
<td>3.61 - 3.91</td>
<td>[14]</td>
</tr>
<tr>
<td>H₂</td>
<td>13X</td>
<td>P = 0.106 MPa; T = 77 K &amp; 87 K</td>
<td>77 K = 0.92</td>
<td>[167]</td>
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<td>ZIF-20</td>
<td>P = 0.106 MPa; T = 273 K</td>
<td>1.22</td>
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</tr>
<tr>
<td>CO₂</td>
<td>4A</td>
<td>P = 0.133 MPa; T = 273 K</td>
<td>0.53</td>
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<tr>
<td></td>
<td>K-CHA (a)</td>
<td>P = 0.013 MPa; T = 273 K</td>
<td>1.06</td>
<td></td>
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<tr>
<td></td>
<td>Ar</td>
<td>2.40</td>
<td>2.85</td>
<td></td>
</tr>
</tbody>
</table>

(a) Synthesized zeolite A containing 68% K⁺ and 32% Na⁺. (b) Hydrogen encapsulated in various types of zeolites is summarized in report of Vitillo et al. (2005) [168]. (c) 40% potassium-modified zeolite A. (d) Reported values are the highest adsorbed amount of gas from adsorption isotherm at different pressure ranges. (e) Chabazite with Si/Al of 2.4 ratios was synthesized and exchanged with cations K⁺.
Table 8: Gas adsorption by using metal-organic framework solid matrices

<table>
<thead>
<tr>
<th>Gases</th>
<th>MOF types</th>
<th>Adsorption conditions</th>
<th>Adsorption amount (g 100 g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>MIL-53</td>
<td>P = 0.109 MPa &amp; T = 77 K</td>
<td>MIL-53 = 1.52, BNH₄@MIL-53 = 1.94, BNH₄@MIL-53 = 2.15</td>
<td>[190]</td>
</tr>
<tr>
<td></td>
<td>BNH₄@MIL-53 (a)</td>
<td>P = 0.104 MPa &amp; T = 273 K</td>
<td>MIL-53 = 1.58, BNH₄@MIL-53 = 18.90, BNH₄@MIL-53 = 20.70</td>
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</tr>
<tr>
<td>CO₂</td>
<td>Zn₂(bdc)(ted)₃ (bpee)</td>
<td>P = 4.10 MPa &amp; T = 300 K</td>
<td>Zn₂(bdc)(ted)₃ = 0.33, Ni(bdc)(ted)₃ = 0.26, Zn₂(bdc)(bpee) = 0.092</td>
<td>[201]</td>
</tr>
<tr>
<td>H₂</td>
<td>CPO-27-M (M = Ni, Co &amp; Mg)</td>
<td>P = 0.10 MPa &amp; T = 77 K</td>
<td>CPO-27-Mg = 2.56%, CPO-27-Co or Ni = 2.25</td>
<td>[202]</td>
</tr>
<tr>
<td>NO</td>
<td>Co-MOF (c)</td>
<td>P = 0.10 MPa &amp; T = 298.15 K</td>
<td>Co-MOF = 19.60</td>
<td>[13]</td>
</tr>
<tr>
<td>H₂</td>
<td>HKUST-1 (d)</td>
<td>P = 0.1 &amp; 1 MPa &amp; T = 77 K</td>
<td>0.1 MPa = 2.27, 1.0 MPa = 3.63</td>
<td>[173]</td>
</tr>
<tr>
<td>NO</td>
<td>Mg₂-MOF-74 (e)</td>
<td>P = 0.102 MPa &amp; T = 298 K</td>
<td>9.72</td>
<td>[195]</td>
</tr>
<tr>
<td></td>
<td>Zn₂At₂(ox) (f)</td>
<td>P = 0.12 MPa &amp; T = 273 K</td>
<td>18.90</td>
<td>[203]</td>
</tr>
<tr>
<td>CO₂</td>
<td>MIL-101 (g)</td>
<td>P = 0.015 MPa &amp; T = 303, 313 &amp; 353 K</td>
<td>353 K = 12.40, 313 K = 25.00, 303 K = 29.90</td>
<td>[194]</td>
</tr>
<tr>
<td></td>
<td>PEI-MIL-101-50</td>
<td>P = 0.100 MPa &amp; T = 298.15 K</td>
<td>P1: T1 = 1.45 &amp; T2 = 0.88, P2: T1 = 7.04 &amp; T2 = 4.40</td>
<td></td>
</tr>
<tr>
<td>H₂ &amp; N₂</td>
<td>PEI-MIL-101-75</td>
<td>P = 0.104 MPa &amp; T = 77 K</td>
<td>H₂ = 5.61, N₂ = 0.53</td>
<td>[206]</td>
</tr>
<tr>
<td></td>
<td>PEI-MIL-101-100</td>
<td>P = 0.101 MPa &amp; T = 298 K</td>
<td>H₂ = 1.52</td>
<td>[207]</td>
</tr>
<tr>
<td>CH₄</td>
<td>CH₄</td>
<td>P = 3.648 MPa &amp; T = 298 K</td>
<td>17.10</td>
<td>[204]</td>
</tr>
<tr>
<td>CH₄</td>
<td>CD-MOF-2 (i)</td>
<td>P = 0.102 MPa &amp; T = 298 K</td>
<td>0.50</td>
<td>[205]</td>
</tr>
<tr>
<td>CO₂</td>
<td>P = 0.107 MPa &amp; T = 273–298 K</td>
<td>11.80 - 15.10</td>
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</tr>
<tr>
<td>H₂ &amp; N₂</td>
<td>Mef-MOF (m)</td>
<td>P = 0.104 MPa &amp; T = 77 K</td>
<td>H₂ = 5.61, N₂ = 0.53</td>
<td>[206]</td>
</tr>
<tr>
<td>O₂ &amp; N₂</td>
<td>MOF-177 (n)</td>
<td>P = 0.101 MPa &amp; T = 298 K</td>
<td>N₂ = 0.30 &amp; O₂ = 0.60</td>
<td>[207]</td>
</tr>
<tr>
<td>H₂</td>
<td>MOF-177</td>
<td>P = 7.0 MPa &amp; T = 77 K</td>
<td>7.50</td>
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</tr>
<tr>
<td></td>
<td>IRMOF-1</td>
<td>P = 5.0 MPa &amp; T = 77 K</td>
<td>5.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IRMOF-6</td>
<td>P = 5.0 MPa &amp; T = 77 K</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IRMOF-11</td>
<td>P = 3.4 MPa &amp; T = 77 K</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IRMOF-20</td>
<td>P = 8.0 MPa &amp; T = 77 K</td>
<td>6.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HKUST-1</td>
<td>P = 8.0 MPa &amp; T = 77 K</td>
<td>3.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MOF-74</td>
<td>P = 2.6 MPa &amp; T = 77 K</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>CO₂ &amp; CH₄</td>
<td>Zn-MOF</td>
<td>P = 0.10 MPa &amp; T = 273–300 K</td>
<td>CO₂ = 10.40 [273 K] &amp; 8.20 [300 K]</td>
<td>[209]</td>
</tr>
<tr>
<td>H₂S</td>
<td>MIL-47(V)</td>
<td>P = 1.60 MPa &amp; T = 303.10 K</td>
<td>MIL-47(V) = 47.70</td>
<td>[210]</td>
</tr>
<tr>
<td></td>
<td>MIL-100(Cr)</td>
<td>P = 0.101 MPa &amp; T = 298.15 K</td>
<td>MIL-100(Cr) = 57.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MIL-101(Cr)</td>
<td>P = 0.101 MPa &amp; T = 298.15 K</td>
<td>MIL-101(Cr) = 129.50</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>HKUST-1</td>
<td>P = 0.101 MPa &amp; T = 298.15 K</td>
<td>11.50-17.20</td>
<td>[212]</td>
</tr>
</tbody>
</table>

(a) BNH₄@MIL-53 & BNH₄@MIL-53 are MIL-53 incorporated 1.3 wt% & 1.7 wt% ammonia borane respectively. (b) bdc is 1,4-benzenedicarboxylate, ted is triethylenediamine, bocd is bicyclo[2.2.2]octane-1,4-dicarboxylate, bpee is 4,4′-biphenyldicarboxylate, bpee is 1,2-bipyrillene. (c) M₄(dhtp)(H₂O)₈H₂O with dhtp is 2,5-dihydroxyxypentaphthalic acid. (d) [M₄(C₆H₄O₈)(H₂O)₈]H₂O. (e) Copper benzene tricarboxylate MOFs. (f) Mg₂(DOT) with DOT is 2,5-dioxidoxypentaphthalate. (g) Atz is 3-amino-1, 2, 4-triazole & ox is oxalate. (h) Ni₃(dhtp)(H₂O)₈H₂O & dhtp is 2,5-dihydroxyxypentaphthalic acid. (i) MIL-101 loaded with 50, 75, 100 & 125% of polyethyleneimine (PEI). (j) CD-MOF-2 consisting of the renewable cyclic oligosaccharide γ-cyclohexetrin and RBOR. (k) [Mg₂(H₂O)₈][H₂O] and [H₂L] is 3,5-pyrazoledicarboxylic acid. (l) By adding a H₂ dissociating catalyst and using a bridge building technique to build carbon bridges for hydrogen spillover.

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Table 9: The basic properties of α-, β-, and γ-cyclodextrin

<table>
<thead>
<tr>
<th>Properties</th>
<th>α-cyclodextrin</th>
<th>β-cyclodextrin</th>
<th>γ-cyclodextrin</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula (anhydrous)</td>
<td>C₃₆H₆₀O₃₀</td>
<td>C₄₂H₇₀O₃₅</td>
<td>C₄₈H₈₀O₄₀</td>
<td></td>
</tr>
<tr>
<td>Number of glucopyranose units</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Molecular weight (g mole⁻¹)</td>
<td>973</td>
<td>1135</td>
<td>1297</td>
<td></td>
</tr>
<tr>
<td>Solubility in water at 298.15 K (g 100mL⁻¹)</td>
<td>14.5</td>
<td>1.85</td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>Outer diameter (nm)</td>
<td>1.64</td>
<td>1.54</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>Cavity diameter (nm)</td>
<td>0.47-0.53</td>
<td>0.60-0.65</td>
<td>0.75-0.83</td>
<td></td>
</tr>
<tr>
<td>Height of torus (nm)</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>Cavity volume of 1 molecule (nm³)</td>
<td>0.174</td>
<td>0.262</td>
<td>0.427</td>
<td></td>
</tr>
<tr>
<td>Cavity volume of 1 molecule (mL)</td>
<td>104</td>
<td>157</td>
<td>256</td>
<td></td>
</tr>
<tr>
<td>Cavity volume of 1 gram (mL)</td>
<td>0.10</td>
<td>0.14</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

[216] [217] [218]
Table 10: Summary of some research on gas encapsulation by using cyclodextrins

<table>
<thead>
<tr>
<th>Gases</th>
<th>Cyclodextrin</th>
<th>Encapsulation conditions</th>
<th>Encapsulation amount (g 100g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄</td>
<td>α- cyclodextrin</td>
<td>P = 0.2-1.5 MPa, T = 298.15 K</td>
<td>2.74-2.88</td>
<td>[79]</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>P = 1-3 MPa, T = 298.15 K</td>
<td>4.20-4.66</td>
<td>[225]</td>
</tr>
<tr>
<td>CO₂</td>
<td>β-CD nanosponges (a)</td>
<td>P = 0.10 MPa, T = 293.15 K &amp; 393.15 K</td>
<td>293.15 K = 0.40, 393.15 K = 0.60</td>
<td>[226]</td>
</tr>
<tr>
<td>1-MCP</td>
<td></td>
<td>Directly bubbling in water suspension of nanosponges (0.101 MPa, 298.15K)</td>
<td>8.10-9.10</td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td></td>
<td></td>
<td>2.14</td>
<td></td>
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<tr>
<td>Kr</td>
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<td>2.84</td>
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<tr>
<td>Xe</td>
<td></td>
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<td>10.27</td>
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</tr>
<tr>
<td>O₂</td>
<td>α- cyclodextrin</td>
<td>P = 0.7-12 MPa, T = 293.15 K</td>
<td>1.04</td>
<td>[227]</td>
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<tr>
<td>CO₂</td>
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<td>5.87</td>
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<tr>
<td>C₂H₄</td>
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<td>1.81</td>
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</tr>
<tr>
<td>CH₄</td>
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<td>1.62</td>
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<tr>
<td>C₃H₈</td>
<td></td>
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<td>4.43</td>
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<tr>
<td>C₄H₁₀</td>
<td></td>
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<td>6.69</td>
<td></td>
</tr>
<tr>
<td>1-MCP</td>
<td>α- cyclodextrin</td>
<td>P = 0.101 MPa, T = 288.15 K</td>
<td>5.02</td>
<td>[225]</td>
</tr>
</tbody>
</table>

(a) Cross-linking of cyclodextrin with carbonilimidazole
**Table 11:** Potential application of gas encapsulated in various solid matrices

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Emission control</th>
<th>Clean energy production</th>
<th>Pharmacy</th>
<th>Removal of harmful gases</th>
<th>Nano-devices production</th>
<th>Food &amp; agricultural production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbons</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
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<tr>
<td>Carbon nanotubes</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
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<tr>
<td>Cyclodextrins</td>
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<tr>
<td>Zeolites</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<tr>
<td>Metal-organic frameworks</td>
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</tbody>
</table>
Highlights

- We present current status of gas encapsulation in various powder solid matrices.
- We describe molecular structure of solid matrices and gas adsorption mechanism.
- The gas storage capacity of various solid matrices is compared.
- Adsorption isotherm and release property of gases from matrices are described.
- We discuss potential applications of resultant complexes in various fields.