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Advances in Porous Adsorbents for CO₂ Capture and Storage

Arindam Modak and Subhra Jana

Additional information is available at the end of the chapter

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Abstract

The steady increase of anthropogenic CO₂ in ambient air, owing to the fossil fuel, power plants, chemical processing and deforestation caused by the usage of land, is a key challenge in the on-going effort to diminish the effect of greenhouse gases on global climate change by developing efficient techniques for CO₂ capture. Global warming as a consequence of high CO₂ level in the atmosphere is considered as one of the major long lasting problems in the twenty-first century. Concern over these major issues with regard to severe climate change and ocean acidification motivated us to develop the technologies that capture the evolved CO₂ from entering into the carbon cycle. Therefore, CO₂ capture and storage technology is attracting increasing interest in order to reduce carbon level in the atmosphere which in turn mitigates global climate issues. In this regard, highly efficient adsorbents e.g.; zeolites, alkali metal oxides, activated carbon, porous silica show considerable progress in post combustion CO₂ capture. Recently, metal-organic frameworks (MOFs), porous organic polymers (POPs), porous clays, N-doped carbon etc. are explored as versatile and quite elegant way for next-generation CO₂ capture. In this chapter, we will discuss the broad prospect of MOFs, POPs, nanoporous clays and porous carbon for CO₂ storage and sequestration through utilization of their nanospace chemistry.

Keywords: CO₂ capture and sequestration, metal-organic frameworks (MOFs), porous organic polymers (POPs), nanoporous clays, porous carbon

1. Introduction

In the late nineteenth century, Goddard Institute for Space Studies (GISS) found that global temperature is increasing on account of global warming at least 0.8°C in every year since 1951, which is continuing to increase still twenty-first century because of the release of greenhouse gases [1]. Based on such criteria “*The Intergovernmental Panel on Climate Change*” (IPCC)

declares that this excessive CO₂ emission is markedly related to global climate change and hence could adversely affect global temperature [2]. Furthermore, studies reveal that compared to the CO₂ level of 280 ppm during pre-industrial era, CO₂ concentration increases to 401 ppm in 2015, mainly because of human activity and anthropogenic industrial revolution that needs an ultimatum to check the atmospheric CO₂ level [3]. Thus, in order to diminish carbon level, CO₂ capture and storage/sequestration (CCS) as well as CO₂ capture and utilization (CCU) should have been implemented for considering a ultra-low carbon content environment. Regarding CCS processes, physical adsorption, absorption and membrane separation technologies are being involved to store CO₂ in adsorbents which later buried in deep underground. As for instances, liquid amines like monoethanolamine and diethanolamine are traditionally being utilized to store CO₂ through CCS processes [4], however, despite the wide use of such methods, it suffers from major drawbacks like corrosive nature and volatility of amines, decomposition of the generated salts as well as expensive regeneration cost [5]. Therefore, the requirement of new supports e.g.; porous organic polymers (POPs) [6], metal organic frameworks (MOFs) [7], zeolites [8], zeolitic imidazolate frameworks (ZIF) [9], microporous carbon [10], perovskites, hydrotalcites, clathrate hydrates [11], etc. are mandatory to overcome such drawbacks. It is worth mentioning, porous materials with suitably decorated narrow micropores/ultra narrow micropores are significant in adsorbing large quantity of CO₂ through utilization of hollow nanospace, hence, these materials could be promising in frontier research in order to check the adverse effect of CO₂ that is continuously releasing as tens of billions of tons in each year. Again, MOFs, POPs etc. having wide diversity in structure engineering, can stabilize various organometallic complexes through utilization of their surface functional sites, which in turn enhances their CO₂ adsorption efficacy. Although CCS has wide applications, but only storage in nanopores could partially solve the carbon emission problems because underground leaking cannot be completely ruled out. This circumstance justifies the implementation of suitable process that could simultaneously convert the captured CO₂ to value-added products [12]. Nevertheless, being cheap and easy availability, CO₂ is enriched as C1 feedstock and has broad scope of serving as C1 chemistry to produce important products e.g. fuels, commodity chemicals, agrochemicals, valuable materials and so on [13].

In this chapter, we describe the fabrication of several important solid materials for controlling environmental remediation of CO₂ through CCS techniques and also highlight their potential utility for CO₂ adsorption purposes. However, our major aim is to focus the profound application and usage of several solid-phase adsorbents like, MOFs, POPs, nanoporous carbon, porous clays for CO₂ capture and sequestration study.

2. Promising materials for CO₂ capture

2.1. Metal-organic frameworks (MOF)

MOFs constitute of a new class of materials which could serve as an ideal platform for the development of next-generation CO₂ capture materials because of their large capacity for adsorption of gases and easy tailorability of their structures [14]. MOFs are also called

coordination polymers because of their propensity to build up by metal atoms (ions) linked together by multifunctional organic ligands. Therefore, MOFs synthesis is a consequence of the linkage between the inorganic and organic chemistry, and it has been considered that MOFs are pioneered by Hagerman et al. [15], Batten and Robson [16], Zhou and Kitagawa [17] and Yaghi et al. [18].

It is customary to say that the framework components of MOFs are required to precisely control for specific type of CO₂ capture e.g. post-combustion capture, pre-combustion capture, oxy fuel combustion and potentially even for the specific power plant in which the capture system is to be installed. In this regard, significant efforts have been made recently in improving the gas separation performances of MOFs and some studies are therefore being under consideration for evaluating the prospects of deploying these materials in real-world CO₂ capture [19]. This has been predominately invented by Noro et al. [20] and Yaghi et al. [18]. The wide diversity in its structure makes it possible to construct material with high surface area [21], tailor the material properties and thus its affinity towards specific gas molecules [22, 23]. Accordingly, it would be possible to develop MOF-based sorbents with large capacity and high selectivity for CO₂ storage purposes.

It can be stated that most of the MOFs are synthesized using non-renewable organic solvents like N,N-dimethylformamide, dioxane, etc., although few MOFs (CD-MOF) can also be made from green solvents like ethanol, water etc. [27]. During synthesis, high surface area MOFs are filled with solvent molecules. Since MOFs are being used for CO₂ storage, therefore, the solvent inside the pores are required to remove without any disturbance in its porous structure. However, special care must be taken to assure that the structure does not collapse. It is worthy to mention that the thermal stability of the MOF is expected to be lower than that of zeolites/zeolite analogues because MOFs have lower metal-linker binding energy than that of zeolites having stronger Si-O, Al-O linkages. In **Figure 1**, some representative MOF structures are shown.

The CO₂ storage capacity of MOFs is being measured at different temperature and pressure. There has also been established a positive connection between storage capacity and surface area at high pressure. Yaghi et al. [18] were first to explain the relationship between surface area and CO₂ uptake capacity. Among several MOFs, MOFs with square

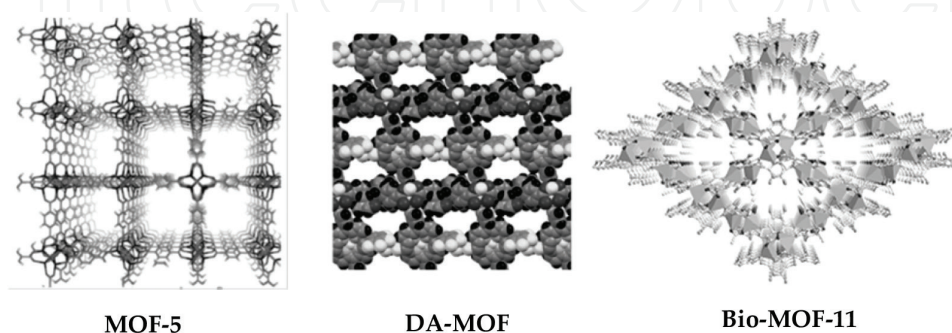


Figure 1. Crystal structure of several MOFs, e.g.; MOF-5 [24], DA-MOF [25], CO₂(adenine)₂-(CH₃CO₂)₂ (bio-MOF-11) [26], with permission from respective references.

channels (MOF-2) [28], pores with open metal sites (MOF-505, $\text{Cu}_3(\text{BTC})_2$) [29], interpenetrated (IRMOF-11) [29], CO_2 (adenine) $_2$ -(CH_3CO_2) $_2$ functionalized bio-MOF-11 are interesting [30]. It is important to mention that MOF-177 has the high surface area ($4500 \text{ m}^2 \text{ g}^{-1}$) and possesses high uptake of CO_2 (60 wt% at 35 bar) at high pressure. Very recently, ultrahigh porous MOFs are prepared by Furukawa et al. from $\text{Zn}_4\text{O}(\text{CO}_2)_6$ unit, containing one or two organic linkers and among them MOF-210 showed highest BET surface area ($6240 \text{ m}^2 \text{ g}^{-1}$) and high pore volume ($3.6 \text{ cm}^3 \text{ g}^{-1}$) reported till date [31]. The ultrahigh porosity of MOF-210 has been achieved mainly because of the expanding organic linkers. As for instance, by extending the size of the 1,3,5-benzenetricarboxate (BTC) in MOF-177 by replacing with larger 4,4',4''-(benzene-1,3,5-triyl-tris(benzene-4,1-iy)) tribenzoate (BBC), MOF-200 was obtained with even higher BET than that of MOF-177 [32]. Strikingly, MOF-210 and MOF-200 show ~71 wt% CO_2 uptake capacity at 298 K and 50 bar pressure, which are highest and considered as new record among all solid porous materials. For CO_2 capture at ambient condition as well as flue gas condition, CO_2 capture is not only influenced by surface area but is also dependent on adsorbent- CO_2 interaction. In this context, Mg-MOF-74 [$\text{Mg}_2(\text{DOT})$; DOT: 2,5-dioxidoterephthalate] consisting of an open framework with Mg^{2+} sites shows high CO_2 storage capacity of 35.2 wt% at 298 K and 1 bar [32]. It is pertinent to mention that open metal sites are mandatory in achieving high CO_2 storage capacity. In **Table 1**, we present some MOFs having significance in CO_2 capture at low and high pressure.

Chemical formulae	BET ($\text{m}^2 \text{ g}^{-1}$)	CO_2 storage (wt%)	Temp. (K)	Pressure (bar)	References
MOF-177	4500	60	298	50	[31]
MOF-210	6240	71	298	50	[31]
Mg-MOF-74	1640	35.2	298	1	[32]
$\text{Cu}_2(\text{abtc})_3$	—	38.5	273	1	[36]
Dy(BTC)	655	27.2	273	1	[37]
$\text{Al}_4(\text{OH})_2(\text{OCH}_3)_4(\text{BDC-NH}_2)_3$	1268	24.1	273	1	[38]
$\text{Zn}_2(\text{BTetB})$	1370	19.7	273	1	[39]
$[\text{In}_3\text{O}(\text{diazDBC})1.5(\text{H}_2\text{O})_3](\text{NO}_3)_3$	892	17.9	273	1	[40]
$\text{Co}_4(\text{OH})_2(\text{p-CDC})_3$	1080	16.4	273	1	[41]
$\text{Cu}(\text{bpy})_2(\text{BF}_4)_2$	—	13.8	273	1	[42]
$\text{Cu}_2(\text{bptb})$	1217	12.6	273	1	[43]
$\text{Zn}_2(\text{BTetB})(\text{DMF})_2$	800	12.1	273	1	[30]
$\text{Zn}_2(\text{BDoborDC})_4$	800	12.1	273	1	[44]
$\text{Ni}(\text{bpy})_2(\text{BF}_4)_2$	—	11.9	273	1	[34]
$\text{Ni}_2(\text{bpy})_3(\text{NO}_3)_4$	—	10.6	273	1	[45]
$\text{Cd}(\text{mim})_2$	2420	5.6	273	1	[46]

Table 1. CO_2 adsorption capacity of metal-organic frameworks at low and high pressure.

On the other hand, thermal degradation of MOFs generally happens on account of metal-ligand bond breaking. As a consequence, thermal stability of MOFs is predominately dependent on both the metal-linker bond strength and the number of linkers connected to metal sites. Indeed, MOFs can be stable up to 300°C without degradation of the framework structure [17, 18], which is crucial for post-combustion CO₂ capture from flue gas under moist conditions.

Since open metal sites in MOFs show considerably good CO₂ uptake property, one common question that may rise among readers is the effect of water on CO₂ uptake because water can easily coordinate to open metal sites. It has been found that in some cases small amount of water can accelerate CO₂ adsorption in some MOFs. Yazaydin et al. have observed that water molecules coordinated to open metal sites of Cu-BTC (HKUST-1) and thus significantly increase CO₂ adsorption of this framework [33]. However, in other cases; water could only destroy the MOF structure and shows a detrimental effect on CO₂ adsorption. Kizzie et al. showed the effect of humidity on the CO₂ capture performance of M/DOBDC series of MOFs (M = Zn, Ni, Co and Mg; DOBC = 2,5-dioxidobenzene-1,4-dicarboxylate), demonstrating a significant decrease in the CO₂ uptake capacities for Mg/DOBC and Zn/DOBC [34]. Recently, Liu et al. also described water stability of various MOFs after their pretreatment, further suggesting their stability in aqueous condition [35].

2.2. Porous organic polymers (POP)

POPs are recently developed as an important class of porous materials, constructed from light-weight elements (C, H, O, N) and linked by strong covalent bonds, which show huge potential in a variety of applications, e.g.; gas storage and separation, catalysis, sensing, energy storage, optoelectronics and to mention a few [8, 47–49]. A series of vibrant characteristics of POPs, such as high-specific surface area, good physicochemical stability, tunable pore dimensions, topologies and chemical functionalities, make them suitable adsorbents for CO₂ capture.

POPs are widely used and have been classified according to their synthesis conditions, which includes polymers of intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), covalent organic polymers, hypercrosslinked polymers (HCPs), crystalline triazine-based frameworks (CTFs), porous organic frameworks (POFs), porous aromatic frameworks (PAFs), polymeric organic networks (PONs) and so on. In each networks, the state-of-the art development in the design, synthesis, characterization and the CO₂ adsorption performances has been reviewed [50, 51]. Additionally, CO₂ uptake capacity and adsorption enthalpy can also be controlled through manipulation of POP surface area, pore size and/or its functionality at the surfaces. Understanding all these aspects could lead to the development of new possibilities of novel POP frameworks to target CO₂ capture, where the amorphous characteristics, high cross-linked ultra-microporous structures could be crucial in determining CO₂ adsorption performances. Herein, we describe the critical factors that directly influence the CO₂ uptake property for POPs.

There is a direct correlation between POP surface area and its porous structures. It is said that CO₂ uptake capacity is dependent on the high specific surface area. It has also been suggested that CO₂ uptake of an adsorbent increases with increasing CO₂ pressure, which demonstrates that controlling of surface property might be advantageous in tailoring CO₂ uptake

phenomenon. Significant development in the synthesis of high surface area POP materials has been done by several researchers, among which the synthesis of porous aromatic framework (PAF-1) developed by Qiu et al. via Yamamoto homocoupling of tetrahedral monomers (tetrakis(4-bromophenyl)methane) is significant [52]. Owing to the in-built generation of diamondoid framework topology by the cross-linking of tetrahedral monomers, it creates open and interconnected pores which give rise to high surface area (BET: $5600 \text{ m}^2 \text{ g}^{-1}$) and good CO_2 storage capacity (29.5 mmol g^{-1} , 298 K, 40 bar). Later significant contribution has been developed by modifying with other quadricovalent building centers [53], which forms PPN-3 (with adamantane-system), PPN-4 (replaced tetrahedral carbon by silicon) and PPN-5 (replaced tetrahedral carbon by Germanium), as shown in **Figure 2**. Importantly, all these POPs possess exceptionally high surface area. It should be noted that PPN-4 having BET surface area of $6461 \text{ m}^2 \text{ g}^{-1}$ considers as highest surface area among all reported POPs till date. The exceptionally high surface area enables PPN-4 to have excellent CO_2 storage capacity (48.2 mmol g^{-1}) at 50 bar and 295 K.

Therefore, it can be arguably said that the design followed by the synthesis of high surface area POPs from tetrahedral building block is a promising approach for CO_2 storage at high pressure. Apart from BET surface area, porous structure also triggers CO_2 uptake phenomenon, as controlling the pore size similar to the kinetic diameter of CO_2 molecule (Size: 3.3 \AA) can significantly enhance the storage capacity. So far many researches have been made significant effort to make POPs from tetrahedral building units as CO_2 adsorbents and among them hypercrosslinked (HCPs) amorphous polymers are important. HCPs exhibit unique property in gas storage capacity due to its highly cross-linked network which prevents the interconnected porous frameworks from being collapsed [54]. In **Figure 3**, the formation of cross-linked HCP is presented.

The unique advantage for the synthesis of HCPs, possesses huge prospect in materials chemistry research because it requires cheap, readily available precursors and FeCl_3 as non-toxic catalyst. Therefore, utilizing this procedure, several aromatic polymers can be easily prepared as described by Cooper et al. [55] In presence of 1,1'-binaphthol the resulting HCP shows $1015 \text{ m}^2 \text{ g}^{-1}$ BET surface area with high CO_2 uptake capacity (3.96 mmol g^{-1} , 1 bar). The high CO_2 capture capacity is hardly affected by aqueous environment owing to strong hydrophobicity of HCPs. Another interesting research has been done by Puthiaraj

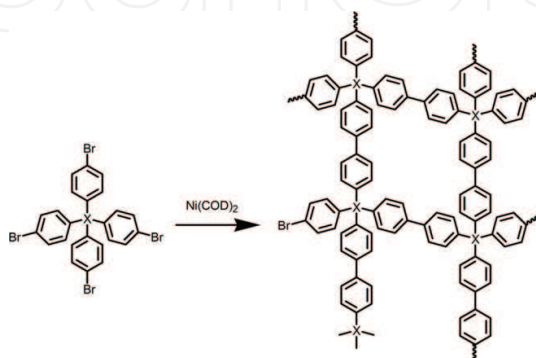


Figure 2. Synthetic routes for high surface area PPN-4 (X: Si), PPN-5 (X: Ge), PAF-1 (X: C) from tetrahedral building blocks.

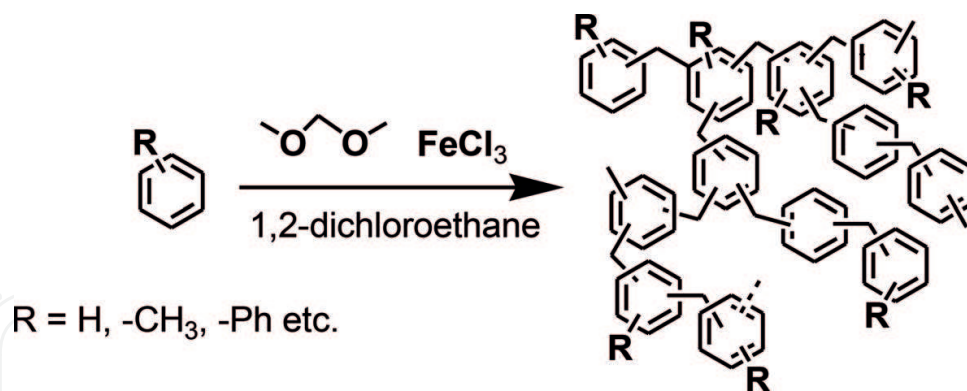


Figure 3. Schematic representation of the formation of hypercrosslinked porous polymers.

et al., where the knitting polymerization has been utilized for binding tetraphenyl aromatic moieties (**Figure 4**) [56]. Unlike the conventional Suzuki/Sonogashira coupling reactions, HCP polymerization promotes the cross-linking between tetrahedral aromatic moieties in a facile way. In continuation with this research, silicon (Si) and germanium (Ge) containing nanoscale hyper-cross-linked aromatic polymers (PHAPs) were reported by FeCl₃ mediated Friedel – Crafts alkylation between tetraphenylsilane or tetraphenylgermanium as a building block and formaldehyde dimethyl acetal as a cross-linker, which yields high surface area (1137–1059 m² g⁻¹) stable polymers having high CO₂ adsorption capacity (104.3–114.4 mg g⁻¹) with an isosteric heat of adsorption in the range of 26.5–27.3 kJ mol⁻¹ (**Figure 4**). It is worthy to mention that controlled synthesis of silicon and germanium-based nanoscale POPs is very difficult and shows intense research activities because Si and Ge are crucial in influencing physical properties of these POPs.

Although high BET surface area is necessary for influencing CO₂ adsorption behavior, however, it is not the prime reason, indeed adsorbate-adsorbent interaction might be quite effective for adsorption at low CO₂ pressure and for selective adsorption of CO₂ in presence of other gases. In this regard, N, P, O, S etc. atoms when incorporated into POPs, show dramatic change in adsorption capacity as well as in the selectivity; because heteroatoms can improve

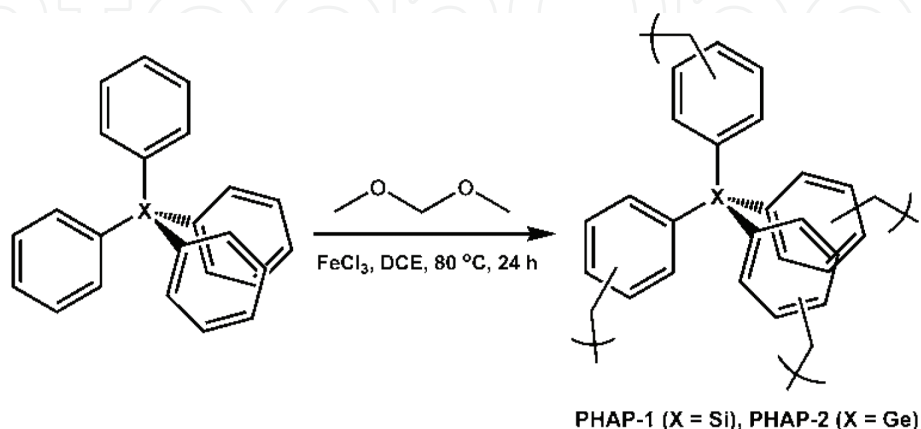


Figure 4. Synthesis of porous hypercrosslinked aromatic polymers (PHAP) containing central hetero atoms Si, Ge other than carbon. CO₂ uptake capacity is given at the right; reproduced with permission from Ref. [56].

isosteric heat of adsorption between sorbent and sorbate. To address this issues POPs with different functional sites e.g. pyridine (PON-2) or thiophene (PON-3) have been prepared, which exhibit favorable interaction with CO_2 despite of having low surface areas [PON-2 ($189 \text{ m}^2 \text{ g}^{-1}$) and PON-3 ($44 \text{ m}^2 \text{ g}^{-1}$)] than only phenyl-based PON (BET $1447 \text{ m}^2 \text{ g}^{-1}$), clearly explaining the effect of hetero-atom in POP structure [57]. Based on this proposal, a variety of N-containing POPs with several functional sites e.g. carbazole, triazine, porphyrin, benzimidazole, azo, etc. have been reported by several researchers as discussed in the subsequent section.

Microporous polycarbazole (CPOP-1) through polymerization of carbazole has been prepared by Chen et al. by oxidative polymerization of carbazole with FeCl_3 as cheap and non-toxic catalyst [58]. CPOP-1 shows high BET surface area ($2220 \text{ m}^2 \text{ g}^{-1}$), narrow pore size (0.62 nm) together with the presence of electron-rich carbazole units and high charge density at N-sites, which facilitate uptake of polarizable CO_2 molecule through local dipole-quadrupole interactions. The CO_2 uptake of CPOP-1 is as high as 4.8 mmol g^{-1} at 273 K and 1 bar, along with its high selectivity for CO_2/CH_4 (33) and CO_2/N_2 (25) separation is also noticeable on account of the framework composition. Consequently, they have also prepared CPOP-(2-7) through this reaction and among them CPOP-7 exhibits the best uptake capacity for CO_2 (3 mmol g^{-1} at 273 K and 1 bar) [59]. Among other N-containing polymeric adsorbents, covalent triazine frameworks (CTFs) are interesting. CTFs are efficiently applied to CO_2 capture purposes and are generally synthesized at high temperature ($>400^\circ\text{C}$) by molten ZnCl_2 which usually acts as Lewis acid catalyst as well as solvents. CTFs possess moderate BET surface area ($1235 \text{ m}^2 \text{ g}^{-1}$), while showing excellent CO_2 uptake capacity (4.2 mmol g^{-1} , 1 atm, 273 K) [60]. Again, several PCTFs were synthesized through the modifications of CTFs using branched arms precursors. Importantly, PCTF-1 with biphenyl, PCTF-2 with terphenyl and PCTF-3 with quaterphenyl rings have been developed, which show BET surface area as 853, 811 and $395 \text{ m}^2 \text{ g}^{-1}$ respectively [61]. When the middle benzene ring of CTF has been replaced by the strong polar group, such as benzothiadiazole, forming PCTF-4 which shows highest CO_2 uptake of 4.7 mmol g^{-1} at 273 K and 1 bar. Later, Zou and others prepared a nitrogen-rich polysulfone/polymer (PSF/SNW-1) membrane by introducing nano-sized SNW-1 particles through intrinsically small micropores into PSF matrix via spin-coating [62]. Gas sorption measurements demonstrated that SNW-1 exhibits high adsorption capacity and good affinity towards CO_2 because of its high microporosity and the presence of functional amino groups. For CO_2 separation, it demonstrates an excellent separation performance including high separation factor (34 and 40 for CO_2/CH_4 and CO_2/N_2) and high CO_2 permeability (22.4 barrer). Furthermore, long thermal stability is also noticeable and further satisfies that SNW-1/PSF membrane is stable and robust; exhibiting its potentiality in the practical application of CO_2 capture.

Based on the above discussion, it is evident that the effect of N-substituted POPs markedly influence CO_2 adsorption and separation processes. Regarding this, porphyrin containing microporous POP shows potential application in this area. Porphyrin-based POPs are generally synthesized from expensive Pd and Ni catalysts by a tedious way [63]. However, Modak and Bhaumik introduced a new method with FeCl_3 for the formation of porphyrin polymers through a one pot bottom up chemistry involving the condensation between pyrrole and several aromatic dialdehydes [64, 65]. In this report, authors reported the formation of Fe-POP-1/2/3 having $750\text{--}875 \text{ m}^2 \text{ g}^{-1}$ BET surface area, narrow microporosity (0.75–1.1 nm)

and excellent adsorbent for CO₂ (19 wt%, 273 K, 1 atm; by Fe-POP-1), shown in **Figure 5**. This research has further been extended by changing aromatic dialdehydes to aromatic trialdehyde using 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(oxy)tribenzaldehyde as tripodal precursor. The advantage of using this organic precursor is enormous, because it introduces both triazine and porphyrin networks in a single TPOP-1 material, which stores high amount of CO₂ (6.2 mmol g⁻¹ or 27.3 wt% at 3 bar, 273 K).

2.3. Porous clay materials

The key advantages of any porous materials involve flexible surface modification due to the availability of high surface area together with lower regeneration energy compared to the any conventional solvent methods. Among the several porous materials, clay minerals are one of the significant materials since they have unique physical properties because of their layered structure, small grain size and large surface to volume ratio. Apart from the mentioned advantages, clay possesses low cost, high mechanical and chemical stability that has been fascinated to the researchers and withdrawn specific research attention. A variety of clay minerals have been used for CO₂ capture, like halloysite, kaolinite, montmorillonite, nanosepiolite, bentonite, etc.

In a recent report, pristine halloysite nanotubes (HNTs) were pretreated with acid for selective removal of alumina and thus, produce mesoporous silica nanotubes (MSiNTs), which were then impregnated with polyethylenimine (PEI) to prepare an emerging nanocomposite MSiNTs/PEI (MP) for CO₂ adsorption [66]. Recently, Jana and coworkers demonstrate the development of several HNTs based solid adsorbents being grafted with diverse aminosilanes containing both primary and/or secondary amine sites over the surfaces of inexpensive

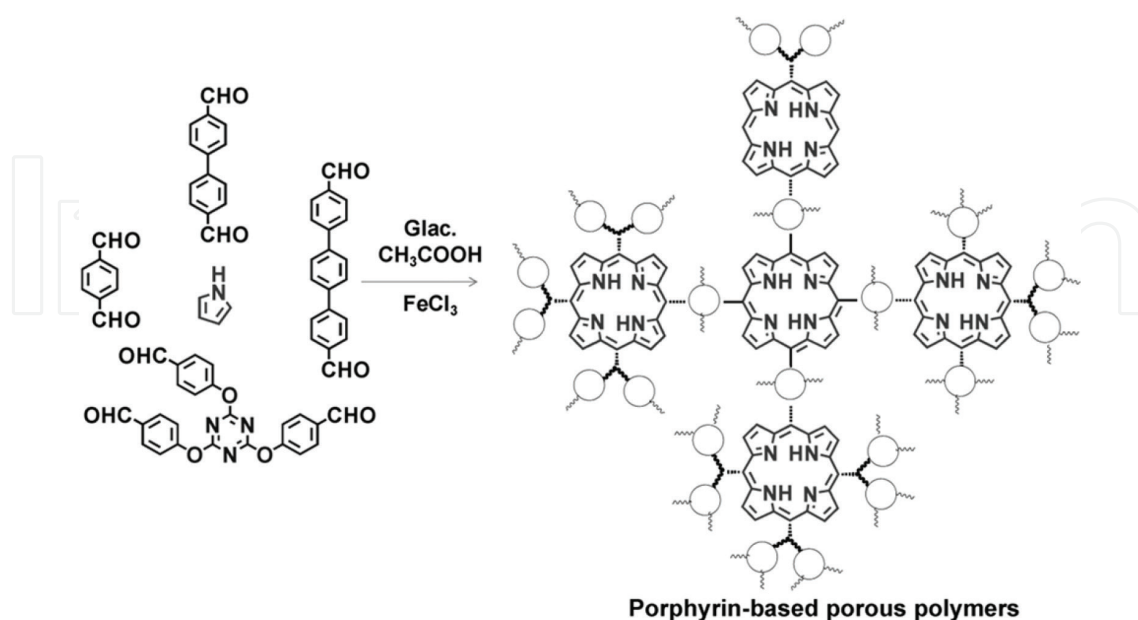


Figure 5. Schematic representation for the preparation of porphyrin-based porous polymers by electrophilic aromatic substitution of pyrrole with several aromatic dialdehydes and trialdehydes.

and easily available HNTs to capture CO_2 from the ambient air under room temperature and ambient pressure [67]. They have also explored the effect of relative humidity in terms of moisture on the adsorption kinetics of the adsorbents by carrying out the experiment on the seasonal ambient air [11], exhibiting that relative humidity basically regulates the atmospheric CO_2 adsorption and corresponding adsorption kinetics (**Figure 6**). Jana et al. also studied the kinetics of several stable isotopes of CO_2 present in the ambient air [68]. Schaefer et al. reported the adsorption of CO_2 onto kaolinite surfaces under geologic sequestration conditions and also verified through the density functional theory (DFT) [69]. Wang et al. developed montmorillonite supported PEI composite for CO_2 capture [70]; the CO_2 sorption efficacy was found to be 2.54 mmol g^{-1} under dry environmental condition and 3.23 mmol g^{-1} under moisture added condition. They also verified that the density of CO_2 in the clay pores is comparatively stable over a wide range of CO_2 pressures at a given temperature and at the excess sorption maximum. CO_2 sorption increases with decreasing temperature while the high pressure sorption properties demonstrate weak temperature dependence. Elliot A. Roth and coworkers synthesized amine-containing solid sorbent for CO_2 capture through the modification of the surface of montmorillonite nanoclay using aminopropyltrimethoxysilane and polyethylenimine [71]. They found that in pure CO_2 and 10% CO_2 in nitrogen gas streams the nanoclay loaded with only one of the amines exhibits ~6 wt% capture efficacy at 85°C and atmospheric pressure, whereas it is ~7.5 wt% CO_2 capture efficiency when the nanoclay immobilized with both the amines. Irani et al. utilized nanosepiolite as an inorganic-organic CO_2 sorbent by immobilizing tetraethylenepentamine (TEPA) onto acid-modified nanosepiolite, having capacity of 3 mmol g^{-1} for 1 vol% CO_2 in N_2 , along with

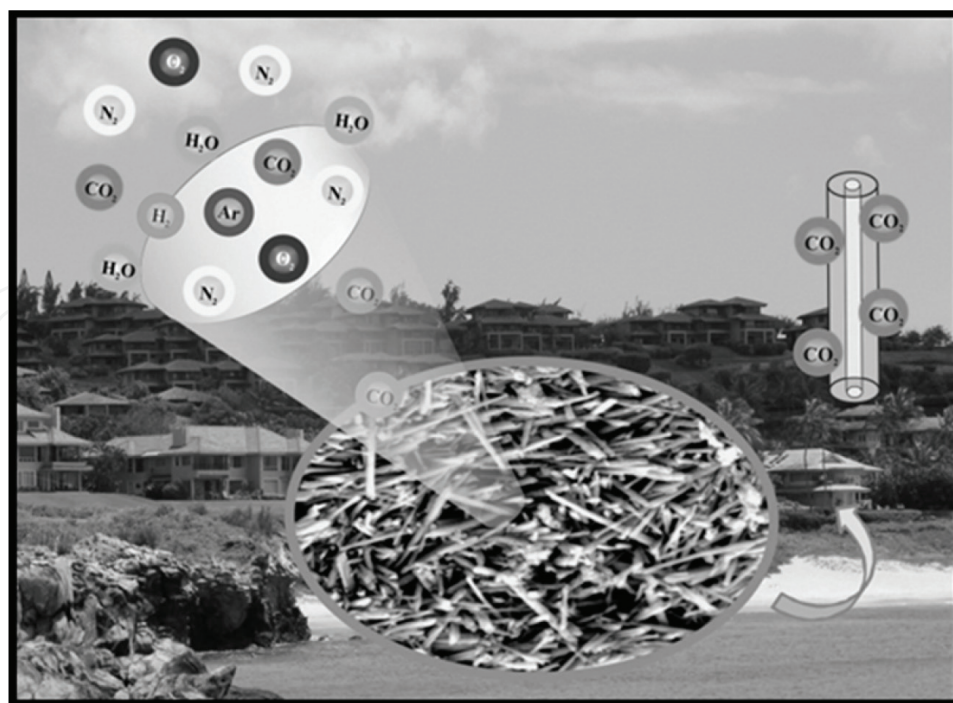


Figure 6. Schematic presentation of the trapping of CO_2 from the seasonal ambient air in clay based solid nanocomposites, adapted from Ref. [11] with permission from The Royal Society of Chemistry.

~1 vol% H₂O at 60°C [72]. Xiao and coworkers exploited an inexpensive and commercially available bentonite for CO₂ capture from flue gas after modified by sulfuric acid followed by immobilization of TEPA [73]. Hence, these low-cost clay based adsorbents introduce a new pathway in the frontier area of CO₂ capture and sequestration study and should make the procedure environmental friendly, robust, sustainable and thus a more attractive strategy.

2.4. Nanoporous carbon composite

Nanoporous carbon derived from various carbon precursors, such as polymer, biomass, coal, petroleum etc. shows enormous significance in small molecule adsorption due to high specific surface area, narrow pore size distribution, low preparation cost, easy-to-design, low energy requirements for regeneration, high stability in air and water and high flexibility in heteroatom doping/surface functionalization [74]. Porous carbons are prepared from physical/chemical activation of carbonaceous materials with CO₂, steam, ZnCl₂, KOH etc., which are generally employed as activating agents for the formation of microporous carbon [75]. In addition, templating method using zeolites, ZSM-5, several MOFs (MOF-5, ZIF-8, Al-PCP) acts as an effective carbon precursors in making amorphous carbon (**Figure 7**) [76].

Additionally, from the perspective of environmental friendliness and preparation cost, waste materials e.g. fly ash, coconut, carpet are quite popular to prepare high performance carbonaceous materials for CO₂ adsorption [77–79]. As for instance, porous carbons are prepared from hazelnut shells via carbonization and KOH activation. The obtained porous carbon exhibits a high specific surface area of ~1900 m² g⁻¹ and high pore volume (1–0.7) cm³ g⁻¹, which are approximately five times greater than those of carbon without activation [80]. Again, coffee residue has also been used as a sustainable source for the preparation of activated carbon with ZnCl₂ [81]. The textural properties of the samples thus prepared significantly depend on the ZnCl₂/C ratio. On the other hand, porous carbons are also prepared through a facile one step carbonization from porous polymers. Recently, Modak et al. have prepared microporous carbon (K-COP-M) having extremely high surface area of 2186 m² g⁻¹ and contains micropore

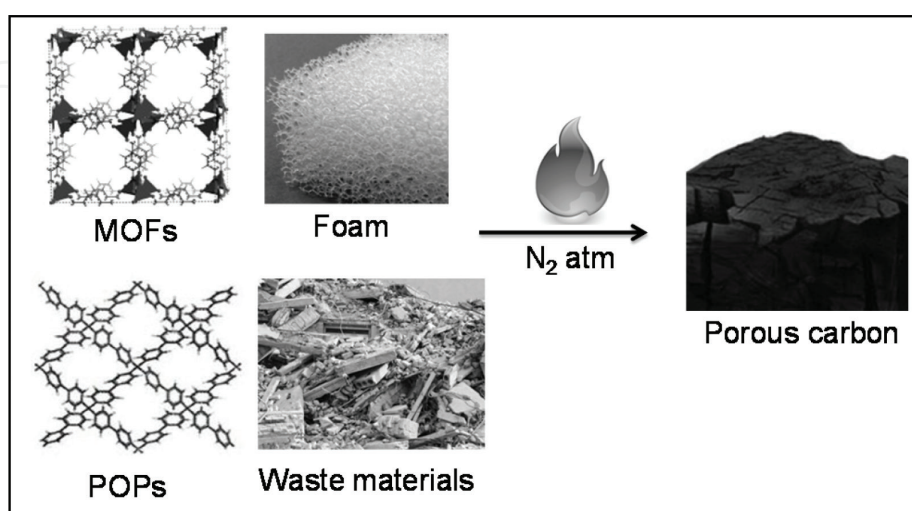


Figure 7. Schematic presentation of the formation of porous carbon from MOFs, POPs, foam and waste materials.

volume of $0.85 \text{ cm}^3 \text{ g}^{-1}$ [82]. K-COP-M has been produced by KOH activation of COP-M polymer in an inert condition and at very high temperature ($600\text{--}700^\circ\text{C}$). CO_2 adsorption potential of K-COP-M-600/700 have been evaluated, indicating that these frameworks adsorb $160\text{--}170 \text{ cm}^3 \text{ g}^{-1}$ ($7.6\text{--}7.1 \text{ mmol g}^{-1}$) CO_2 at 1 atm and 273 K, which is higher than that of non-activated carbon derived from COP-M (i.e. COP-M-600/700 stores $77\text{--}83 \text{ cm}^3 \text{ g}^{-1} \text{ CO}_2$). This signifies the utility of KOH in making effective adsorbents by creating ultra-small micropores in carbons. While heteroatom doping is significantly used in controlling the textural properties of porous carbon, carbonization of amine containing organic precursors substantially shows high N-doping and considers as an effective adsorbent of CO_2 with very good selectivity. There are several reports available in this respect [49, 83], among which N-doped composite developed by Kim et al. is interesting, where polyindole-reduced graphene oxide (PIG) hybrid was synthesized and later carbonized at $400\text{--}800^\circ\text{C}$ temperature and thus produces N-doped graphene sheets [84]. The N-doped graphene sheets are microporous having 0.6 nm pores with BET surface area of about $936 \text{ m}^2 \text{ g}^{-1}$ and show a maximum CO_2 uptake of 3.0 mmol g^{-1} at 25°C and 1 atm pressure. Nevertheless, high recycling stability of CO_2 uptake is noticed even after 10 recycling cycles; additionally this N-doped carbon shows CO_2/N_2 , CO_2/CH_4 separation ability of 23 and 4 respectively.

Alternatively, polyurethane foams (PUFs) are important thermosetting polymers and owing to its high nitrogen contents, it can be used as good precursor for N-doped carbon [85]. The global demand for polyurethanes was estimated to be 13.6 million tons in 2010, which leads to the generation of huge wastes. However, regeneration of spent polyurethane is not only high energy-consuming process, but also it produces toxic nitrogen oxides, carbon oxides etc. and causing severe environmental pollution. These wastes when carbonized at high temperature can produce nitrogen-doped carbon that can further reduce environmental pollution since these N-doped carbon shows CO_2 uptake capacities of 6.67 and 4.33 mmol g^{-1} at 0°C and 25°C under 1 bar, respectively. Finally, it can be said that like MOFs, POPs and porous clays, microporous carbon is also an alternative for CO_2 storage purposes.

3. Conclusion

In this chapter, we highlight important aspect of some promising materials, like MOFs, POPs, nanoporous carbon and porous clays as CO_2 adsorbents, which possess high BET surface area, tunable microporosity and facile surface engineering for enhancing interaction with CO_2 . All such features are however exempted from conventional zeolites, alkali metal oxides, activated carbon, porous silica, therefore, demonstrating the significance of new porous materials in developing carbon capture techniques. Considering the growth of rapid industrialization and abrupt emission of CO_2 in the atmosphere, an increasing concern to the social as well as marine lives, would be diminished through utilization of aforesaid functional materials to adsorb CO_2 . In the abovementioned sections, we have thus tried to summarize the recent advancement made in the synthesis and broad prospect of MOFs, POPs, nanoporous clays and porous carbon as potential adsorbents for CO_2 capture and storage. Nevertheless, in the near future, such promising materials would motivate to the

researchers to extend this work towards low pressure CO₂ adsorption, which may open a new route in the frontier area of carbon capture and sequestering study through the real world CO₂ capture under ultra-dilute condition.

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Author details

Arindam Modak¹ and Subhra Jana^{1,2*}

*Address all correspondence to: subhra.jana@bose.res.in

¹ Technical Research Centre, S. N. Bose National Centre for Basic Sciences, Salt Lake, Kolkata, India

² Department of Chemical, Biological & Macro-Molecular Sciences, S. N. Bose National Centre for Basic Sciences, Salt Lake, Kolkata, India

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