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HIGHLIGHT

# Novel porous solids for carbon dioxide capture

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The development of novel materials for  $CO_2$  capture has received much attention during the past decade. Herein, we focus on the latest advances in novel porous solids as highly effective adsorbents for  $CO_2$  capture. The advantages and existing barriers of each porous material and their future perspectives will be discussed.

Capture and storage of carbon dioxide  $(CO_2)$  from the fuel exhaust of power plants, currently a major source of CO2 emissions, has received much attention during the past decade due to the global warming issue. Great efforts have been orientated to developing versatile strategies for the capture and storage of CO2 in an environmentally benign and economical fashion. Among the conventional methods including cryogenic distillation, chemical solvent scrubbing, adsorption, and separation, separation processes based on solid sorbents are considered to be one of the most efficient approaches in terms of low cost and good cycle performance. Over the past few decades, a number of novel-structured porous solids based on metal-organic

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frameworks (MOFs), porous silica, zeolite and porous carbon have emerged and can be used as CO2 adsorbents. These materials generally show high CO<sub>2</sub> capture capacity and good selectivity, and are easy to handle and free of environmental issues (e.g. corrosion problems). It is expected such new adsorbents could be easily adapted for а conventional industrial adsorption process. Hence, in this highlight, we mainly focus on a discussion of the latest advances in novel porous solids as highly effective adsorbents for CO2 capture. The advantages and disadvantages of each porous material will be discussed. Finally, the remaining challenges and the future perspectives will be highlighted.

# 1. Metal-organic frameworks (MOFs) and related materials

Metal-organic frameworks (MOFs), generally built from metal ions connected

by organic linkers, are a new family of crystalline porous materials.1 MOF synthesis is in most cases carried out using a solvent, and the pores of the as-synthesized MOFs are filled with solvent molecules. Their unique structural properties such as robustness, super-high internal surface areas (up to 5000  $m^2g^{-1}$ ), high pore volumes (up to 5  $\text{cm}^3\text{g}^{-1}$ ) and low densities (up to 0.015 gcm<sup>-3</sup>) ensure their high adsorption capacity when used in gas adsorption and storage applications. Yaghi and co-workers first investigated the possibility of MOFs as CO2 adsorbents.<sup>2</sup> They found one of the MOFs (MOF-2) gave an unexpectedly high CO<sub>2</sub> adsorption capacity of 2 mmolg<sup>-1</sup> at 1 atm and -78 °C. This result triggered many subsequent investigation on various MOFs as CO<sub>2</sub> capture materials.<sup>3-11</sup> One of the common feature of MOFs is that they show remarkable CO<sub>2</sub> adsorption capacities under high pressures, e.g.



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MOF-177 exhibits the highest capacity, among the known porous materials, for  $CO_2$  of 33.5 mmolg<sup>-1</sup> at 41.4 atm.<sup>3</sup> The microporous character and rigid framework of these MOFs ensure that the release of the trapped CO<sub>2</sub> is difficult. In contrast to those MOFs with rigid frameworks, novel MOFs, such as MIL-53(Cr),<sup>4,5</sup> MIL-88<sup>6</sup> and SNU-M10,<sup>7</sup> surprisingly exhibiting a breathing framework with flexible and dynamic properties, and show extreme changes of shape when guest molecules are inserted or removed. Such properties greatly benefit the capture and release performance of gaseous molecules.

In addition to the adsorption capacity and good release behavior, the selectivity is a crucial factor relevant to CO<sub>2</sub> separation. Extensive research for new types of MOFs is being conducted with the aim of achieving better selectivity.8-12 The recently reported breathing framework CID-3, with suitable micropore size and structural flexibility, showed highly selective adsorption properties of CO<sub>2</sub> from a ternary O2, N2 and CO2 mixture.8 High selectivity for CO<sub>2</sub> adsorption was also observed for MOFs possessing a number of adsorption sites including open metal sites and functional groups.10,11 For example, the activated CPO-27-M (M = Ni, Mg) with coordinatively unsaturated metal sites showed the ability of CO<sub>2</sub> capture preferentially over N2 and CH4.9 An enhancement in the CO<sub>2</sub> uptake relative to CH<sub>4</sub> was also achieved for the flexible amino-MIL-53 (Al) compared with its parent MIL-53 (Al).<sup>10</sup> Similar enhancements have been reported in the amine-functionalized frameworks USO-2-Ni-A and USO-3-In-A.

relative to their non-functionalized analogs.<sup>11</sup> Clearly, the presence of amino groups and exposed metal sites enhance the selectivity of these frameworks for  $CO_2$  adsorption.

The aforementioned MOFs perform well at high pressures, accompanied with large CO<sub>2</sub> uptake capacity, but do not perform well at low pressures (e.g. MOF-177). Recently, Snurr et al. compared 14 MOFs for CO<sub>2</sub> capture at low pressures.<sup>13</sup> It was demonstrated that M\DOBDC (where M = Zn, Mg, Ni, or Co and DOBDC = dioxybenzenedicarboxylate)MOFs show the best performance among the 14 MOFs (including Pd(2-pymo)<sub>2</sub>, HKUST, UMCM, IRMOF, etc.) for CO<sub>2</sub> capture at low pressures (e.g. 0.1 bar, the anticipated partial pressure of CO<sub>2</sub> in flue gas) and room temperature. Particularly, Mg/DOBDC significantly outperforms all other MOFs in the low pressure range, by hosting  $\sim 12$  molecules of CO<sub>2</sub> per unit cell at 0.1 atm.14 In M\DOBDC MOFs, their CO<sub>2</sub> uptakes increase with decreasing M-O bond length and atomic weight of M in the framework. Below 1 bar, MOFs having a high density of open metal sites are expected to exhibiting high CO<sub>2</sub> capture capability.

At present, though MOFs show a variety of robust structures and excellent performance in  $CO_2$  capture capacity and selective adsorption, their powder form, poor chemical and thermal stability pose major obstacles to use in realistic industrial conditions. In addition, prior to  $CO_2$  adsorption, a high vacuum is always necessary for the activation of MOFs in order to empty the trapped guest molecules within the pores, and that often requires long evacuation times.



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2. Zeolites and related materials

Zeolites are important synthetic products with typical microporous features, a highly crystalline structure and excellent thermal stability. Zeolite 13X modified with monoethanolamine, ethylenediamine and isopropanol amine was intensively studied as a  $CO_2$  adsorbent using a pressure swing adsorption technique.<sup>15</sup> However, due to the limitations of surface area and pore volume, their adsorption capacities are always low. Moreover, surface chemistry of zeolites for binding  $CO_2$  is less developed.

Zeolitic imidazolate frameworks (ZIFs) are a newly emerging class of porous crystals with extended threedimensional structures constructed from tetrahedral metal ions (e.g. Zn, Co) bridged by imidazolate (Im).16 These materials combine the advantages of both traditional zeolites (good chemical and thermal stability) and modern MOFs (high uptake capacities for  $CO_2$ ), so they are considered as a new type of zeolite related material and are expected to have a good performance in the field of  $CO_2$ capture. Differing from many MOFs, ZIFs have a high affinity for CO<sub>2</sub> molecules at low pressures. For example, MOF-177 shows a maximum uptake of 0.17 mmolg<sup>-1</sup> CO<sub>2</sub> at 25 °C and 1 atm, while ZIF-6917 exhibits a capacity of 1.8 mmolg<sup>-1</sup>, ten times higher than MOF-177.3

Another benefit over MOFs is that ZIFs show a higher selectivity for  $CO_2$ from other relevant fuel gases such as CO. ZIFs can selectively separate CO<sub>2</sub> from industrially relevant gas mixtures which are required for practical separation processes, and meanwhile, maintain exceptional uptake capacities.16 For example, ZIF-100, which is thermally stable up to 500 °C, can trap 1.7 mmolg<sup>-1</sup> CO<sub>2</sub> at 0 °C, under dried conditions, and shows good selectivity in gas pairs such as  $CO_2/CH_4$ ,  $CO_2/CO$  and  $CO_2/N_2$ (50: 50 v/v), with the selectivity factors of up to  $5.9 \pm 0.4$ ,  $17.3 \pm 1.5$  and  $25.0 \pm 2.4$ , respectively.<sup>18</sup> Although some ZIFs exhibit good chemical and thermal stability in water and in a number of different organic solvents,19 superior to MOFs, CO<sub>2</sub> capture using ZIFs as adsorbents under steam or moisture conditions is rarely reported.

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#### 3. Mesoporous silica materials

Ordered mesoporous silica materials have attracted attention for CO<sub>2</sub> adsorption due to their high surface area and precise tuning of pore sizes.<sup>20,21</sup> However, pure silica surfaces do not offer strong adsorption sites for CO<sub>2</sub> molecules. Compared to the microporous feature of MOFs and ZIFs, the mesoporous characteristics of silica facilitates rapid gas diffusion. Moreover, abundant hydroxyl groups on the surface of silica offer an opportunity for grafting amine groups in terms of improving the affinity and interaction of silica surface to CO2. To date, mesoporous silica grafted with various amine functional groups was studied for CO2 capture.22,23 For example, polyethyleneimine (PEI)-modified mesoporous silica MCM-41 (MCM-41-PEI) shows up to a 112 mgg<sup>-1</sup> capacity at 75 °C, which is 13 times higher than that (8.6 mgg<sup>-1</sup>) of the parent MCM-41.<sup>24</sup> In addition, pore-expanded MCM-41 and its triamine-grafted aminopropyland counterparts were tested as CO<sub>2</sub> adsorbents.<sup>25</sup> They show high CO<sub>2</sub> uptake and good selectivity in both dry and humid conditions, and especially at very low CO<sub>2</sub> concentrations. The CO<sub>2</sub> adsorption capacity of aminopropyl-grafted poreexpanded MCM-41 reaches 3.67 mmolg<sup>-1</sup> at 0.05 atm and 25 °C and relative humidity (RH) of 74%.26 Even at 2% CO2 concentration at 25 °C, triamine-grafted pore-expanded MCM-41 gives a capacity of 1.75 mmolg<sup>-1</sup>.<sup>27</sup> Thus, the nature of the amine group significantly affects the CO<sub>2</sub> adsorption capacities of such modified MCM-41.

Very recently, Sayari and co-workers demonstrated that amine-containing MCM-41 CO<sub>2</sub> adsorbents show multicycle stability under appropriate moisture conditions. The effect of water vapor in an adsorption process was identified using <sup>13</sup>C NMR and *in situ* DRIFT techniques. Under humid conditions, surface amine groups interact with CO<sub>2</sub> to form bicarbonate with a stoichiometric ratio CO<sub>2</sub>/ N = 1. Interestingly, the deactivated adsorbent can be completely regenerated after a treatment at 200 °C under a flow of N<sub>2</sub> containing 0.15% relative humidity for 24 h.<sup>28</sup>

Besides MCM-41, large mesopore SBA-15 was also widely investigated for  $CO_2$  capture. It was shown that SBA-15

only shows enhanced CO<sub>2</sub> adsorption after surface amine-functionalization. For example, hyper-branched aminosilica material (SBA-HA) with abundant, covalently bonded amine groups show multicycle stability, and a high capacity of 3.1 mmolg<sup>-1</sup> at 25 °C and 1 atm, when used to treat a simulated flue gas consisting of 10% CO<sub>2</sub>/Ar saturated with water.23 Furthermore, PEI-impregnated SBA-15<sup>29</sup> and hierarchical porous silica monolith<sup>30</sup> both showed significantly higher CO<sub>2</sub> capture and a reversible and durable sorption performance. PEI-SBA-15 shows up to a 140  $mgg^{-1}$  capacity at 75 °C, which is 28 times higher than that of the parent SBA-15 (5.0 mgg<sup>-1</sup>).<sup>29</sup> PEI-monolith shows a capacity of 16.5 wt.% CO2 under 5% N2/CO2 humid mixture at 75 °C.30 For porous silica solids, the major problem is their structural degradation in the presence of steam, which can lead to the release of the grafted or impregnated amines, thus lowering their CO<sub>2</sub> adsorption capacity as well as causing corrosion problems.

### 4. Porous carbons and related materials

Porous carbons have played an important role in gas adsorption for many years due to their high specific area, large pore volume, variable pore structure, and high chemical and thermal stability. Commercial activated carbon, BPL, with specific area of 1141 m<sup>2</sup>g<sup>-1</sup> is able to adsorb 7 mmolg<sup>-1</sup> CO<sub>2</sub> under the conditions of 25 °C and 35 bar; while under the same conditions MAXSORB activated carbon with specific area of 3250 m<sup>2</sup>g<sup>-1</sup> can capture up to 25 mmolg<sup>-1.31</sup> These results are comparable to MOFs and ZIFs.

Compared to commercial activated carbon, polymer-based synthetic porous carbons have well-controlled pore structure and high purity. The surface chemistry of such carbons can be adjusted either during or after preparation by choosing different carbon precursors and polymerization catalyst or by post-treatment. Pevida and coworkers prepared highly porous nitrogen-enriched carbons from melamine-formaldehyde resins using fumed silicas with porogen sizes of 7 nm and 14 nm. The obtained carbons can adsorb 2.25 mmol g<sup>-1</sup> of CO<sub>2</sub> at 25 °C and 1 atm under pure CO<sub>2</sub> flow. Even in 15%  $CO_2$  balanced with  $N_2$ , the adsorption

capacity was 1.41 mmol  $g^{-1}$  of CO<sub>2</sub> under similar conditions.<sup>32</sup>

Titirici and coworkers reported that amine-rich carbonaceous materials derived from glucose showed a very high  $CO_2$  uptake up to 4.1 mmolg<sup>-1</sup> at 25 °C and 1 atm.<sup>33</sup> Due to the fact that these carbon materials have low specific surface areas (~10 m<sup>2</sup>g<sup>-1</sup>) and no microporosity, the high  $CO_2$  uptake is thus attributed to the large amount of grafted oligoamine moieties. After 14 months storage, the same samples exhibit a 10–15% reduction of the  $CO_2$  uptake capacities of the initial ones.

Very recently, a new type of nitrogendoped porous carbon monolith was designed and synthesized for CO<sub>2</sub> capture using resorcinol-formaldehyde as carbon precursor and the amino acid L-lysine as the catalyst in a very effective and rapid way. Such carbons possess a hierarchical pore structure, wherein highly interconnected macropores provide low-resistant pathways for the diffusion of CO<sub>2</sub> molecules, while the abundant micropores ensure the effective trapping of  $CO_2$ . Significantly, the use of lysine as catalyst is capable of generating covalently bonded nitrogen-containing groups on the surface of carbon, which enhanced the  $CO_2$  adsorption capacity. A capacity of up to 3.13 mmolg<sup>-1</sup> can be achieved at 25 °C and 1 atm under a pure CO<sub>2</sub> flow.<sup>34</sup>

The aforementioned examples open the door for the design and preparation of highly effective carbonaceous  $CO_2$  adsorbents with controlled pore features and tailored surface chemistry. These porous carbons should combine the merits of designed synthesis (controlled pore structure and task-specific surface chemistry) and the intrinsic properties of porous carbon such as excellent chemical and thermal stability, fully developed porosity and abundant microporosity, and accordingly meet the complex requirements of efficient adsorbents for  $CO_2$  capture.

### 5. Summary and perspectives

The  $CO_2$  capture capabilities of various novel porous solids including MOFs, zeolites, ZIFs, silicas and carbons have been highlighted. For clarity, a detailed summary of the textural properties and  $CO_2$  capacities of these materials is compiled in Table 1 cataloged by the class

MOFsMOF-2, [Zn(BDC)-(DMF)] MIL-53, Cr(OH)(O <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> -CO) flexible frameworkMIL-53, Cr(OH)(O <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> -CO) flexible frameworkSNU-MI0, [(Ni <sub>2</sub> L <sup>3</sup> )(bptc)]SNU-MI0, [(Ni <sub>2</sub> L <sup>3</sup> )(bptc)]CID-3, {[Zn(ndc)(bpy)]}, flexible frameworkNi <sub>2</sub> (dhtp) unsaturated metal sitesNi <sub>2</sub> (dhtp) unsaturated metal sitesNi <sub>2</sub> (dhtp) unsaturated metal sitesCID-3, SizeNi <sub>2</sub> (dhtp) unsaturated metal sitesNi <sub>2</sub> (dhtp) unsaturated metal sitesSizeAmino-MIL-53(A1) flexible frameworkAmino-MIL-53(A1) flexible frameworkSizeSizeAmino-MIL-53(A1) flexible frameworkSizeAmino-MIL-53(A1) flexible frameworkSizeSizeAmino-MIL-53(A1) flexible frameworkZeolite & ZIFsNoncethanolamine modified 13X SizeSilicaZiF-69SilicaAziridine modified SBA-15 Triamine modified SBA-15 Aminopropyl-grafted MCM-41 Polyethyleneinnine MCM-41 Polyethyleneinnine SBA-15Aminopropyl-grafted MCM-41	MOF-2, [Zn(BDC) · (DMF)] MOF-177, [Zn <sub>4</sub> O(BTB) <sub>2</sub> (DEF) <sub>15</sub> ] MIL-53, Cr(OH)(O <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> -CO <sub>2</sub> ) flexible framework SNU-M10, [(Ni <sub>2</sub> L <sup>2</sup> )(bptc)] SNU-M10, [(Ni <sub>2</sub> L <sup>2</sup> )(bptc)] CID-3, {[Zn(ndc)(bpy)]}, flexible framework framework Ni <sub>2</sub> (dhtp) unsaturated metal sites	270 4500 505		Test conditions	611.122	Ref.
e & ZIFs	ii <sub>2</sub> L²)(bptc)] dc)(bpy)]},, flexible turrated metal sites	505	3.18 33.5 5-8 ° 5	1 atm, -78 °C 41.4 atm, 25 °C 4.9 atm, 31 °C 4.9-9.9 atm, 31 °C		0 m v
e & ZIFs	dc)(bpy)]},, flexible turated metal sites		0.0 2.1 2.1	19.7 aturt, 51 0.6 atm, 25 °C 1 atm, 25 °C	15% CO <sub>2</sub> /N <sub>2</sub> , 25 °C: 24 : 1 (v/v) at 0.61 atm; 98 : 1 (v/v) at 1.0 atm	٢
e & ZIFs	tturated metal sites		3.4 3.5 2.5 (O <sub>2</sub> ) 1.6 (N <sub>2</sub> ) 0.20; 0.44 (O <sub>2</sub> ); 0.60 (N <sub>2</sub> )	$\begin{array}{c} 10 \text{ atm. } 25 ^{\circ}\text{C} \\ 45 \text{ atm. } 25 ^{\circ}\text{C} \\ 74 \text{ atm. } 25 ^{\circ}\text{C} \\ 96 \text{ atm. } 25 ^{\circ}\text{C} \\ 80 \text{ atm. } 25 ^{\circ}\text{C} \\ 80 \text{ atm. } 25 ^{\circ}\text{C} \\ 102 \text{ c} \\ 102 \text$	$CO_2: O_2: N_2 = 1:21:78, 30 \text{ atm}, 25$ °C: separation factor S = 39	×
e & ZIFs		1218	11.6 7.4 (CH4)	1:21:78 21.7 atm, 25 °C 49 atm, 25 °C, CH4	40% CO <sub>2</sub> /60% CH4, 50 °C: 65% CO <sub>2</sub> adsorbed, 35% CH4	6
e & ZIFs	3(AI) flexible		2.3 0 (CH4) 6.7 2.4 (CH )	2 atm, 30 °C 2 atm, 30 °C, CH <sub>4</sub> 11.8 atm, 30 °C 20.6 atm, 30 °C	adsorbed 50% CO <sub>2</sub> /50% CH <sub>4</sub> , 30 °C: 100% CO <sub>2</sub> adsorbed, 100% CH <sub>4</sub> pass through	10
e & ZIFs	USO-2-Ni-A $(Ni_2(1.4-bdc)_2(dabco)$	1530	2.4 (СП4) 3.2	29.0 atm, 30 ℃, ℃114 1 atm, 31 °C		11
	(amme)) 13X Monoethanolamine modified 13X Isonronanol amine modified 13X	385 15	0.36 0.45 0.52	1 atm, 75 °C, 15% CO <sub>2</sub> /85% He	I	15
		950	1.8	1 atm, 0 °C	50% CO <sub>2</sub> /50% CO, 25 °C, semaration factor S = 20.0	16,17
		1730	2.5		Separation factor $S = 20.9$ 50% CO <sub>2</sub> /50% CO, 25 °C, senaration factor $S = 37$ 8	
Triamine modifi Polyethyleneimir Polyethyleneimir Aminopropyl-gr KIT-6 monolith	ified SBA-15	169	3.1	1 atm, 25 °C, 10% CO <sub>2</sub> /88.4% Ar/	20% CO <sub>2</sub> /88.4% Ar/1.6% H <sub>2</sub> O	23
Polyethyleneimir Polyethyleneimir Aminopropyl-gr KIT-6 monolith	ified MCM-41	367	2.05	dry 5% CO <sub>2</sub> /N <sub>2</sub>	5% CO <sub>2</sub> /95% N <sub>2</sub>	25,27
Aminopropyl-gr KIT-6 monolith	nine MCM-41 nine SBA-15	80	2.5 3.18	21/0 KMJ, 5/0 CO2/N2 1 atm, 75 °C 5% CO2/N2 1 atm, 75 °C, 14.9% CO2/A3% O2 in	5% CO <sub>2</sub> /95% N <sub>2</sub>	24 29
KIT-6 monolith	Aminopropyl-grafted MCM-41		2.05 3.67	N2 0.05 atm, 25 °C, Dry 5% CO <sub>2</sub> in N2, 0.05 atm, 25 °C, RH 74%, 5% CO <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub> , O <sub>2</sub> /N <sub>2</sub> /O <sub>2</sub> , CO <sub>2</sub> /CH <sub>4</sub> , CO <sub>2</sub> / H <sub>2</sub>	26
	ch (65 wt% PEI)	16	4.8 5.9	m N2, 1 atm, 75 °C, dry CO2 1 atm, 75 °C, humid CO2	$CO_2/N_2$	30
Carbon Activated carbon MAXSORB Activated carbon BPL MFB-600 Hierarchical nores	on MAXSORB on BPL archical nores	3250 1150 261	3.8 25 2.25	1 atm, 75 °C, dry 5% CO <sub>2</sub> /N <sub>2</sub> 34.5 atm, 25 °C 34.5 atm, 25 °C 1 atm, 25 °C		31
Carbon monolith Hierarchical pores	ith Hierarchical	~500	0.86 1.41 0.43 3.1	1 atm, 75 °C 1 atm, 25 °C, 15% CO <sub>2</sub> /N <sub>2</sub> 1 atm, 75 °C, 15% CO <sub>2</sub> /N <sub>2</sub> 1 atm, 25 °C		34

<sup>a</sup> Note: For clarity, the pressure units (e.g. kPa, MPa, bar, mmHg) and the temperature unit (K) used in the literature have been converted into units of atm and °C, respectively.

of material. Each material has advantages and disadvantages. To compete with liquid amines, porous solids must be costeffective and regenerative, less sensitive to steam and offer substantially greater capacities and selectivities for CO<sub>2</sub>. As a whole, MOFs with unique structures show high CO<sub>2</sub> adsorption capacity and good selectivity.35 However, the chemical and thermal stability of MOFs restricts them for application in high temperature or complex environments. Generally, the majority of MOFs will lose their structures at a temperature of 300 °C. Although MOFs have recently been reported whereby the framework was retained at 400 °C,36 the improvement of the chemical stability of MOFs is still a problematic issue to be addressed. ZIFs with similar structure to MOFs and good hydrothermal and chemical stability can selectively adsorb CO<sub>2</sub> at low pressure, which may be useful for the removal of trace amounts of CO<sub>2</sub> from mixtures. A key challenge for the industrial use of MOFs and ZIFs is to deliver them in shape suitable for applications; currently these known coordination polymers are mostly obtained as powders. Pure silica materials show a negligible CO2 uptake. However, amines supported or immobilized on porous silica exhibit a dramatic increase in CO2 uptake, with efficient mass transfer and a less corrosive nature compared to the corresponding liquid amines. When using amine-functionalized porous silicas as the adsorbent, it is preferable to avoid high temperature steam as this can cause the structural degradation of the porous silica. In terms of structural stability, recyclability and fabricability, porous carbons, especially synthetic polymer-based carbons are promising for a practical application to CO<sub>2</sub> capture in industry. In fact, porous carbons can be prepared with ultrahigh surface area (up to 3000 m<sup>2</sup>g<sup>-1</sup>) and a larger fraction of micropores, which are beneficial for CO<sub>2</sub> adsorption. In addition, porous carbons are usually more hydrophobic than zeolites and can be more resistant to steam. This would obviously be advantageous in the application of a steam-enriched  $CO_2$  gas flow. In our view, nitrogen-rich hierarchically structured carbon monolith is the ideal candidate for CO<sub>2</sub> capture due to its: easy handling, abundant basic sites (interacting with CO<sub>2</sub> molecules), size- and shape-selectivity and high surface area (micropores), easier mass-transfer to the adsorption sites (mesopores), and reduced pressure drop (macropores). In contrast to MOFs, ZIFs and silica, the synthesis of porous carbons with a welldefined pore structure is a less explored area. We believe that with a better understanding of the carbon chemistry, the design and synthesis of porous carbon with specific nanostructure and surface chemistry for CO<sub>2</sub> capture and storage can be realized in the near future. In addition to the creation of high performance CO<sub>2</sub> capture materials, one should bear in mind that the investigation of CO<sub>2</sub> release behavior of these materials is also important. Materials with properties such as high CO<sub>2</sub> capture capacity and low energy consumption for CO<sub>2</sub> release are more desirable for practical applications.

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