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# Low concentration CO<sub>2</sub> capture using physical adsorbents: Are Metal-Organic Frameworks becoming the new benchmark materials?

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## Keywords

**CO<sub>2</sub> capture, traces CO<sub>2</sub> removal, air capture, physical adsorbents, MOFs**

## Abstract

The capture and separation of traces and concentrated CO<sub>2</sub> from important commodities such as CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, is becoming important in many areas related to energy security and environmental sustainability. While trace CO<sub>2</sub> concentration removal applications have been modestly studied for decades, the spike in interest in the capture of concentrated CO<sub>2</sub> was motivated by the need for new energy vectors to replace highly concentrated carbon fuels and the necessity to reduce emissions from fossil fuel-fired power plants. CO<sub>2</sub> capture from various gas streams, at different concentrations, using physical adsorbents, such as activated carbon, zeolites, and metal-organic frameworks (MOFs), is attractive. However, the adsorbents must be designed with consideration of many parameters including CO<sub>2</sub> affinity, kinetics, energetics, stability, capture mechanism, in addition to cost. Here, we perform a systematic analysis regarding the key technical parameters that are required for the best CO<sub>2</sub> capture performance using physical adsorbents. We also experimentally demonstrate a suitable

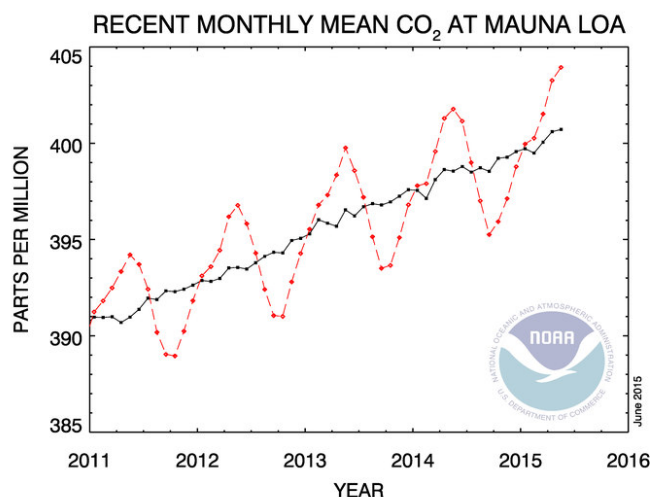
material model of Metal Organic Framework as advanced adsorbents with unprecedented properties for CO<sub>2</sub> capture in a wide range of CO<sub>2</sub> concentration. These recently developed class of MOF adsorbents represent a breakthrough finding in the removal of traces CO<sub>2</sub> using physical adsorption. This platform shows colossal tuning potential for more efficient separation agents.

## Introduction

Meeting energy demands while addressing climate change may lead to cleaner and affordable oil/gas supplies for future generations. CO<sub>2</sub> has been found to be the main anthropogenic contributor to the greenhouse gas effect, responsible for 60% of the atmospheric temperature increase, commonly referred to as “global warming”.<sup>1, 2</sup> Among the various sources of CO<sub>2</sub>, approximately 30% is generated by fossil fuel power plants and 25% from transportation sector, making them one of the major contributors to global warming.<sup>3</sup> Despite their impact on the environment, fossil fuels are expected to remain the leading source of energy for the coming years for both power generation and transportation.

Data recorded at the Mauna Loa Observatory in Hawaii revealed that an exponential increase in CO<sub>2</sub> emissions occurred in the last decades (Figure 1). For the first time in human history, the CO<sub>2</sub> concentration reached 400 parts per million (ppm) in 2013, an unseen concentration since the atmospheric concentration has been monitored.<sup>4</sup>

It is widely recognized that development and implementation of novel and affordable technological solutions to reduce greenhouse gas (GHG) emissions, particularly CO<sub>2</sub>, is a vital step toward fossil fuel-based sustainable energy.<sup>5</sup> One such solution is the use of physical adsorbents, such as activated carbon, zeolites, and metal-organic frameworks (MOFs). In this paper, we review the key parameters that are required for the best CO<sub>2</sub> capture performance using physical adsorbents. We also demonstrate that MOFs could be a promising physical adsorbents for CO<sub>2</sub> with huge potential to replace existing benchmark materials for CO<sub>2</sub> capture at low concentration and moderate temperatures.



**Figure 1.** Monitoring of CO<sub>2</sub> emission at Mauna Loa in Hawaii showing that the CO<sub>2</sub> concentration surpassed 400 ppm in May 09 2013.<sup>4</sup>

## Discussion

Gas separation using adsorption has gained considerable attention as a viable technology for the CO<sub>2</sub> removal of from different gas streams.<sup>5</sup> This attention was motivated by the ability of solid adsorbents to reduce the required energy for activation/regeneration as compared to liquid amine scrubbing.<sup>6</sup> The design of adsorbents for CO<sub>2</sub> capture must take into account the following parameters:

(i) **High CO<sub>2</sub> adsorption capacity:** Knowledge about the shape/steepness of equilibrium adsorption isotherms is essential for the evaluation of potential adsorbents. Suitable materials should exhibit high CO<sub>2</sub> uptake particularly at low pressure. From the steepness of the adsorption isotherm at low pressure, it is possible to establish a preliminary, highly qualitative assessment of the CO<sub>2</sub> affinity for a given adsorbent in comparison with benchmark CO<sub>2</sub> adsorbents.<sup>5, 7, 8</sup> Porosity and energetics are the key factors influencing the CO<sub>2</sub> adsorption capacity.

(ii) **Fast adsorption kinetics:** Adsorption kinetics affects the working adsorption capacity in dynamic processes such as adsorption in a fixed bed column. A suitable CO<sub>2</sub> adsorbent will have a high rate of adsorption for CO<sub>2</sub> but not necessarily for the less absorbable gases (such as CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>, etc.),

resulting in a working adsorption capacity close to equilibrium capacity over a wide range of operating conditions.<sup>9</sup>

(iii) **High CO<sub>2</sub> selectivity:** The selectivity of the adsorbent for CO<sub>2</sub> has a direct impact on the degree of purity of the product during operation in the adsorption column. This in turn affects the economics of the process. CO<sub>2</sub> selectivity is a product of a complex interplay between the porosity (pore size), kinetics and the charge density of the adsorbent.<sup>10</sup> The charge density is directly related to CO<sub>2</sub> interactions with the adsorbent framework.<sup>11, 12</sup>

(iv) **Mild conditions for regeneration:** The ability to regenerate the adsorbents is a key parameter in the selection of materials for CO<sub>2</sub> separation. Optimal interactions should be neither too weak nor too strong. Too weak bonding results in low CO<sub>2</sub> adsorption capacity at low pressure, but easy regeneration. Conversely, strong bonding induces high adsorption capacity but desorption will be difficult and costly.<sup>6</sup> We focus our analysis and discussion on examples of materials (mainly physical adsorbents) that show the best compromise in terms of the intensity of CO<sub>2</sub> energetics<sup>13</sup> as well as the uniformity of interactions.<sup>10</sup>

(v) **High stability:** The adsorbents lifetime, which determines the frequency of their replacement, has a direct impact on the economics of any commercial-scale operation. The stability of the material is a key property that should be considered from the early stage of synthesis and evaluation. This vital parameter is generally overlooked during small-scale synthesis. Only a few works have considered the recyclability and degradation in terms of the stability of CO<sub>2</sub> adsorbents.<sup>6, 13-16</sup>

(vi) **Tolerance to impurities:** The degree of tolerance and the affinity of the adsorbent to impurities such as moisture and acid gases may significantly affect their use. When materials are affected by such impurities, additional purification steps are required.

(vi) **Cost:** As far as novel adsorbents are concerned, information on the cost and other economic considerations is rather scarce in the open literature, particularly with regard to MOFs. Cost-related

factors will therefore not be discussed in this work, even though the cost of a MOF will undoubtedly decrease when industrial-scale synthetic methods are developed.

The debate among scientists and engineers regarding the aptness of zeolites, activated carbon and MOFs for CO<sub>2</sub> capture, has favoured the first two because of their availability on the large scale, their low cost and their demonstrated stability. The synthesis of MOFs at industrial scale is in its infancy and mainly carried out at the large pilot scale, while activated carbons and zeolites have been synthesized on the industrial large scale for decades.<sup>17</sup> The development of zeolites from discovery to commercialization took three to four decades.<sup>18</sup> It is then to be expected that large scale implementation of MOFs will take at least the same time frame. The huge choice of inorganic clusters and organic linkers for MOFs fabrication suggest that they can be easily tuned unlike activated carbon and zeolites, although it is often very difficult to predict the structures of MOFs<sup>19,20</sup> and the effects of their functionalization before synthesis. Overall, work on the rational design, development and synthesis of MOFs that target particular applications remains scarce.<sup>20-24</sup>

To evaluate the performance of various adsorbents, we selected a series of materials from each family to compare their adsorption properties in terms of porosity, gravimetric/volumetric uptake (at low CO<sub>2</sub> concentrations up to 50 % and a total pressure of 1 bar, in balance with N<sub>2</sub> and CH<sub>4</sub> and H<sub>2</sub>), energetics, selectivity, stability and tolerance to water vapor. We also describe the physical separation mechanisms involved in the most promising CO<sub>2</sub> adsorbents.

Several types of MOFs have been proposed for CO<sub>2</sub> capture, including (i) MOFs with open metal sites,<sup>25-37</sup> (ii) MOFs without open metals sites,<sup>38-55</sup> (iii) MOFs with narrow pore size via interpenetration<sup>10,56,57</sup> or shortening the size of the ligands,<sup>10,41</sup> and (iv) MOFs decorated with specific functional groups, including (NH<sub>2</sub>, OH, etc.).<sup>23,51,58-64</sup> Functionalization of these types of MOFs may be carried out by post-synthetic modification (PSM) on the open metal sites,<sup>47,65-69</sup> by post-synthetic metal exchange,<sup>70</sup> or direct use of functionalized ligands.<sup>23,51,58-60</sup> The amines (or sulfonates) PSM of porous organic polymers (POPs, COFs, etc.), another subfamily of porous material, has also been



proposed.<sup>71-74</sup> From these types of materials, we discuss selected ones that offer the best compromise between selectivity, uptake, kinetics and the energy input for desorption in CO<sub>2</sub> capture.

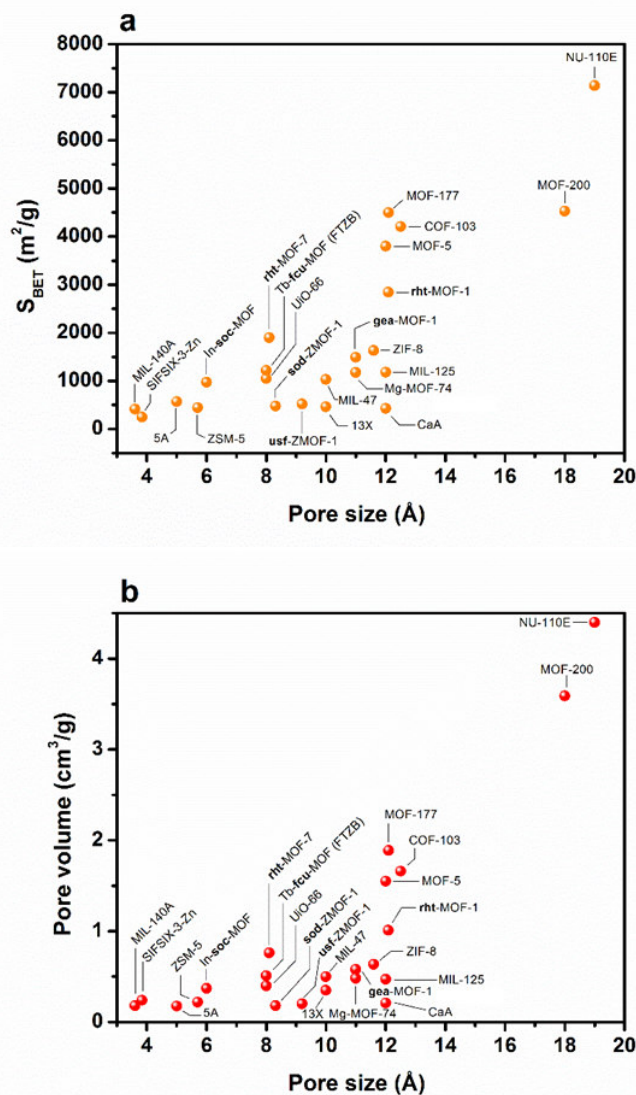
For a more comprehensive account on CO<sub>2</sub> adsorbents, we direct the reader to excellent reviews by Sumida *et al.* 2012,<sup>24</sup> Choi *et al.* 2009<sup>75</sup> and Sayari *et al.* 2011.<sup>5</sup> Reviews covering MOFs as gas separation and gas storage media are also highly recommended.<sup>76-84</sup>

### **Porosity: surface area, pore volume, pore size distribution and shape**

The porosity of adsorbents (also called solid separation agents) is one of the key features associated with the selective adsorption/diffusion of gases into the pores,<sup>24</sup> which in turn drives the separation of fluids. Without optimal permanent porosity, the solid adsorbent containing functional groups will be unproductive in adsorption technology. Since the discovery of zeolites, activated carbons and MOFs, a general tendency in the development of new separation agents for CO<sub>2</sub> removal was to design and synthesize porous materials with high surface areas in which the correlation between the porosity parameters (surface area, pore volume and pore size) was obviously recognized but rarely discussed. Zeolites and MOFs may contain ordered channels, cages, or a combination of both, while activated carbons possess heterogeneous slit-shaped pores.

High surface area materials often exhibit large pore volumes and relatively large pore sizes in the range of micropores (Figure 2a). Conversely, low surface area materials exhibit insignificant pore volumes and relatively reduced pore sizes (Figure 2b). The general tendency is that the enhancement of surface area and pore volume is achieved by increasing the pore size. Nevertheless, such correlations are applicable only to strictly homogeneous solid adsorbents particularly in case of MOFs containing uniform pore sizes. This behavior is verified for optimally activated<sup>85</sup> MOFs containing uniform channels but difficult to obtain for few examples of MOFs with exceptionally high cavity sizes and various window sizes, such as MIL-100<sup>86</sup> and MIL-101.<sup>87</sup> COF-1<sup>88</sup> and other staggered layered structures are also examples of the invalidity of this tendency.

Many reports in the literature described different approaches for tuning the porosity of different materials.<sup>24, 89</sup> In this regard, MOFs exhibited better possibility in terms of pore size tunability as compared to zeolites and activated carbons,<sup>5</sup> although contrary to what happened with zeolites eight decades ago, there has been no strong incentive so far for scientists and industrialists to put these unique and tunable materials into applications using rational synthesis and design.<sup>18</sup>



**Figure 2.** Correlation between pore size and (a) surface area, (b) pore volume for different materials.

The tunability of MOFs can be illustrated in the case when pores are deliberately functionalized for the purpose of increasing the affinity of one particular gas vs. another one or when the pore size is narrowed to exclude one molecule vs. another.<sup>90</sup> As an example a large number of publications in the last decades related to the use of zeolites, activated carbon and MOFs for gas separation and CO<sub>2</sub> capture in particular, implemented the strategy of tuning the specific surface area as the main approach to enhanced CO<sub>2</sub> separation. For this purpose, the design and synthesis of new MOFs has been conducted based on isoreticular strategy using extended (larger) rather than shorter ligands. In this regard, CO<sub>2</sub> uptake at atmospheric pressure and above was the main reference parameter to evaluate CO<sub>2</sub> adsorbents. This single parameter strategy was shown to be not effective in achieving highly effective CO<sub>2</sub> microporous adsorbents at very low pressure.<sup>10</sup>

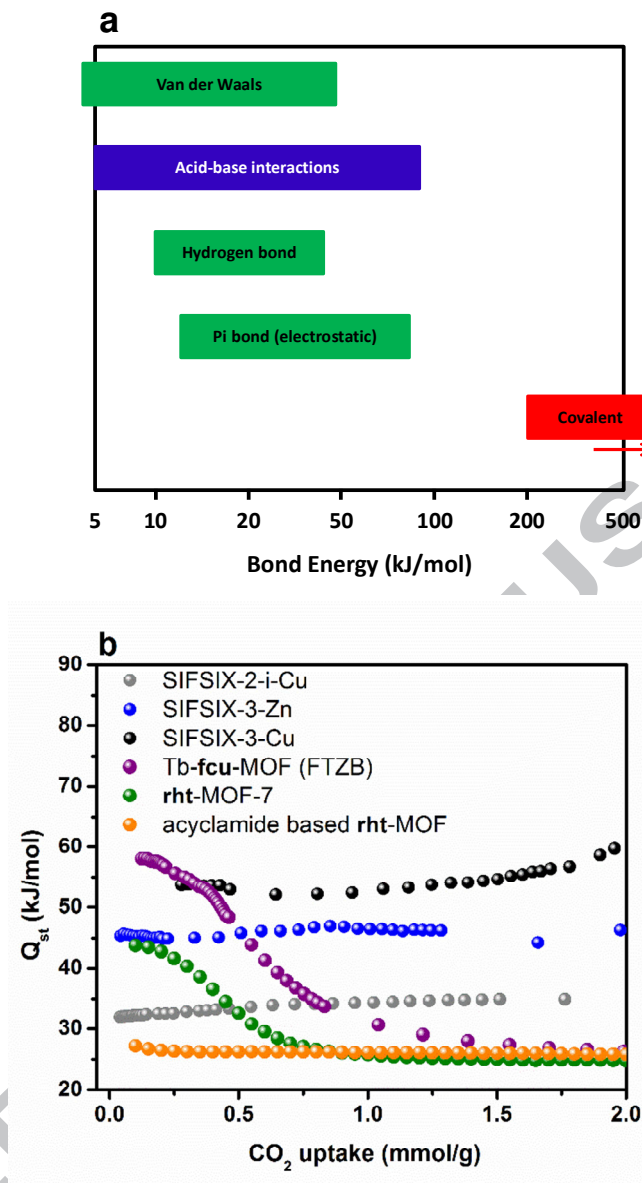
Microporous CO<sub>2</sub> adsorbents combining both high surface areas and large pore volumes with relatively large uniform micropore sizes (0.8-2 nm) exhibited high CO<sub>2</sub> uptake at medium and high pressures,<sup>24</sup> in addition to suitable (fast) kinetics<sup>9</sup> but very low selectivity toward CO<sub>2</sub>. Conversely, microporous adsorbents with small pore sizes (0.35-0.8 nm) had low surface areas, small pore volumes and comparatively very low CO<sub>2</sub> uptake at high pressure, but slightly higher CO<sub>2</sub> uptake and selectivity at very low pressure.<sup>22</sup> Thus the relative enhancement of CO<sub>2</sub> separation performance (uptake, selectivity) at low pressure (0.05-0.15 bar) upon the reduction of pore size was clearly established and showed that the pore opening was large enough to allow optimal gas diffusion and implementation of suitable charge density. Further reduction in pore size close to 0.33 nm may lead to further enhancement of CO<sub>2</sub> selectivity via a purely molecular sieving mechanism driven mainly by gas diffusion.<sup>90,91</sup> It is to note that such selectivity is generally very difficult to achieve.

With regard to adsorption equilibrium-based materials, the effect of pore shape (cylindrical channels or spherical cages) on the pore size uniformity of the and further on the CO<sub>2</sub> separation performance has not been reported. The presence of cages in the adsorbent structure, particularly in zeolites and MOFs, contributes in the local increase of the pore size, leading on one hand to broadening the pore size distribution and on the other hand to decreasing the CO<sub>2</sub> uptake and selectivity at low pressure.

The case of activated carbon is more difficult to predict and model as it does not contain homogeneous pore network. In all these cases, it is logical to assume that adsorbents with uniform channelled pores (of appropriate size) and high charge density will be more suitable for CO<sub>2</sub> separation. However, it is very hard to isolate the effect of pore size from CO<sub>2</sub>-adsorbent interactions. Thus, it is more appropriate to discuss the effect of uniformity in terms of energy distribution, which is more universal, rather than in terms of pore size distribution.

**CO<sub>2</sub> interaction energy, intensity and distribution.**

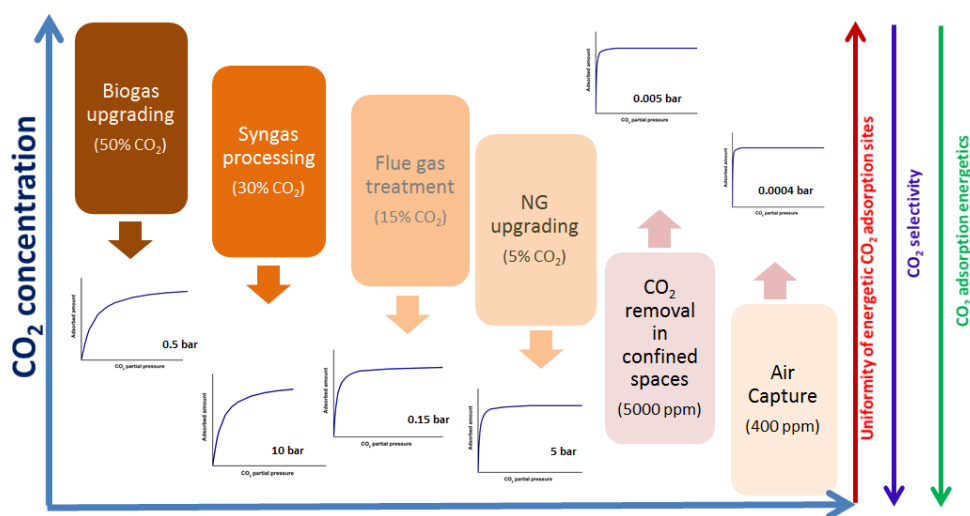
The CO<sub>2</sub> adsorbent interaction energy ( $Q_{st}$  of CO<sub>2</sub> adsorption or heat of adsorption) and its distribution over the pores is an intrinsic property that dictates the affinity of the pore surface to CO<sub>2</sub>, which in turn plays a major role in determining the adsorption selectivity and the necessary energy required to release CO<sub>2</sub> during the regeneration step. With regard to the CO<sub>2</sub> interaction intensity, an optimal  $Q_{st}$  for CO<sub>2</sub> capture should be in the range of 30-60 kJ/mol which is indicative of fully reversible physisorption of CO<sub>2</sub> as well as moderately strong CO<sub>2</sub>-sorbent interactions. In fact, this will allow mild regeneration conditions, which is a key property in the selection of materials for CO<sub>2</sub> separation. Obviously, this requirement is strongly dependant on the CO<sub>2</sub> concentration. The lower the CO<sub>2</sub> concentration in gas stream, the higher CO<sub>2</sub> interactions (or  $Q_{st}$ ) is needed for effective CO<sub>2</sub> removal.



**Figure 3.** a) limits of reversible-non reversible CO<sub>2</sub> interactions, b) examples of Q<sub>st</sub> of CO<sub>2</sub> adsorption vs loading for different adsorbents with (i) strong homogeneous interactions (black and blue), (ii) intermediate homogeneous interactions (grey) and weak homogeneous interactions (orange) and (iii) strong heterogeneous interactions (purple and green).

Depending on the structural and chemical properties of the adsorbent, cycling may be achieved via temperature, pressure (or vacuum), concentration swing adsorption or a combination thereof. In

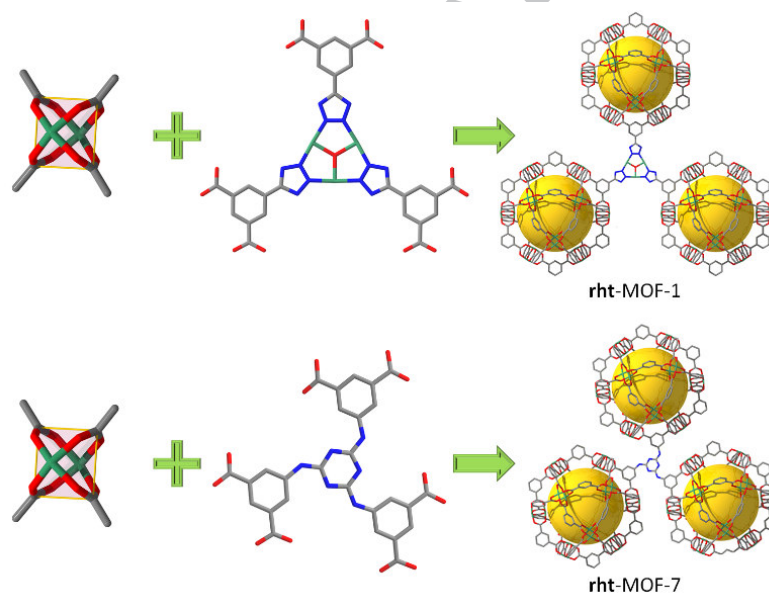
practice, incorporation of functional groups within pores (of different sizes) can be used to modify adsorbent-adsorbate interactions (e.g., van der Waals, electrostatic, hydrogen bonding or acid-base interactions (Figure 3a)) and affect CO<sub>2</sub> uptake and selectivity. Optimal interactions should be neither too weak nor too strong. Too weak bonding results in low CO<sub>2</sub> adsorption capacity at low pressure, but easy regeneration. Conversely, strong bonding induces high adsorption capacity but desorption is difficult and costly (Figure 3a). The relationship between the most important intrinsic properties for CO<sub>2</sub> capture at different concentration is shown in Figure 4. In fact, the general tendency is that application with lower CO<sub>2</sub> concentration will require much higher selectivity toward CO<sub>2</sub> which will induce much higher interactions with the adsorbent framework. Besides, application having increased CO<sub>2</sub> concentrations will require much uniform energy distribution of effective adsorption sites to sustain high selectivity.



**Figure 4.** The relationship between the CO<sub>2</sub> isotherm shapes, CO<sub>2</sub> adsorption selectivity and CO<sub>2</sub> adsorption energetics intensity and distribution for CO<sub>2</sub> capture applications at different CO<sub>2</sub> concentrations.

In this regard, our group and others developed various strategies to enhance and homogenize the CO<sub>2</sub> adsorption energetics in MOF structures.<sup>31, 76-81</sup> The examples of strategies mentioned here reflect

material synthesis strategies that generate desired CO<sub>2</sub> capture properties. One example of MOFs developed for the CO<sub>2</sub> capture purpose was based on modification of the **rht**-MOF platform developed initially by Eddaoudi and co-workers in 2008<sup>92</sup> based on the singular (3,24)-connected net (**rht**-MOF-1). This platform was successfully used to prepare a deliberately functionalized **rht**-MOF-7 (Figure 5) exhibiting high affinity to CO<sub>2</sub> at lower loading as a result of a unique combination of amine and triazine moieties decorating the available high surface area, windows and pores. As compared to the parent sample, **rht**-MOF-1, **rht**-MOF-7 exhibited steeper CO<sub>2</sub> isotherms at very low partial pressure and relatively higher isosteric heat of adsorption but only at low loading (first CO<sub>2</sub> molecules adsorbed). This finding suggested that the addition of triazine and amine functional groups enhanced the interaction of **rht**-MOF-7 with CO<sub>2</sub> (green dots in Figure 3b); in addition, the  $Q_{st}$  was low enough to allow complete reversible desorption using the vacuum swing regeneration mode.<sup>23</sup>

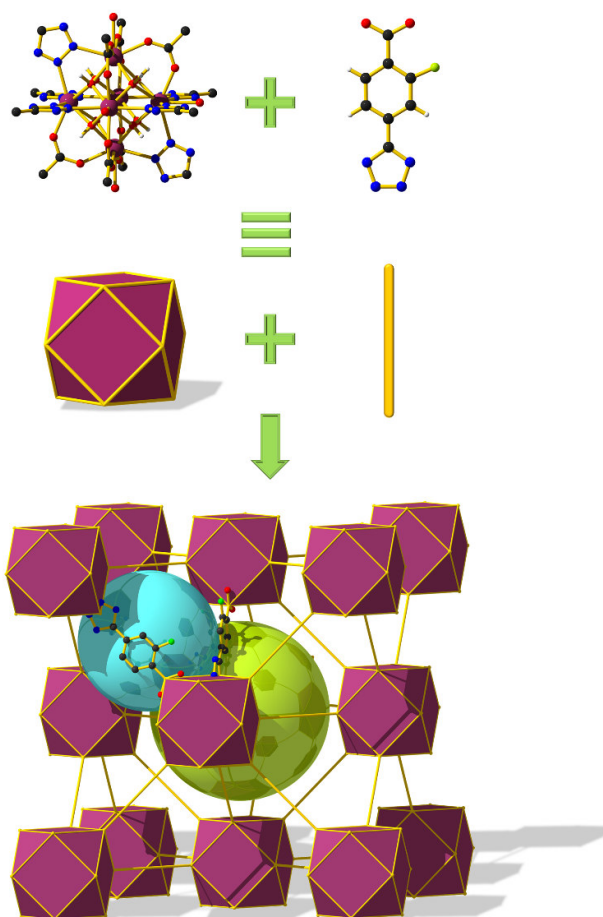


**Figure 5.** ***rht**-MOF-1 and **rht**-MOF-7 differ in the composition of the trigonal building block. The trigonal building block of **rht**-MOF-1(top), is a copper trimer connecting three 5-tetrazoleisophthalate ligands, whereas the trigonal building block in **rht**-MOF-7 (bottom) is a single hexacarboxylate ligand composed of three isophthalate moieties linked to a central triazine core through amine linkages.*

In another example, a series of **fcu**-MOFs (Figure 6) based on rare-earth metals and linear fluorinated/non-fluorinated, homo-/hetero-functional ligands was targeted and synthesized. This particular **fcu**-MOF platform was selected due to its unique structural characteristics combined with the ability to dictate and regulate its chemical properties (e.g., tuning of the electron-rich rare-earth metal ions and high localized charge density, a property arising from the proximal positioning of polarizing tetrazolate moieties and fluorine atoms that decorate the exposed inner surfaces of the confined conical cavities).<sup>31</sup> Other MOF based on rare-earth (**Y-pek**-MOF-1) having open metals sites but no tetrazolate and fluoro groups shows poor CO<sub>2</sub> capture ability at low pressure but exhibits one of the highest to date CO<sub>2</sub> volumetric uptakes of 25 bar.<sup>93</sup>

This unique combination of properties for **fcu**-MOF was found to have an unprecedented effect on increasing the CO<sub>2</sub> adsorption energetics to a high value of 58 kJ/mol (purple dots in Figure 3b), and the adsorption was fully reversible. As in the case of **rht**-MOF-7, the number of adsorption sites associated with the high  $Q_{st}$  (58 and 47 kJ/mol for Tb-**fcu**-MOF (FTZB) and **rht**-MOF-7, respectively) was very limited and these sites were quickly saturated, leading to a decrease in  $Q_{st}$  as the CO<sub>2</sub> uptake increased. It is important to mention that similar  $Q_{st}$  behavior was reported for MIL-100(Cr)<sup>25</sup> at the low coverage of 62 kJ/mol and other zeolites.<sup>11-12</sup> In light of the high affinity of **rht**-MOF-7 and Tb-**fcu**-MOF for CO<sub>2</sub>, it was reported that these materials may be used for highly selective CO<sub>2</sub> capture, but only for the removal of low CO<sub>2</sub> concentrations. Although these MOFs have very interesting properties, they may not be able to remove relatively high CO<sub>2</sub> concentrations, such as in the case of post-combustion capture (5-15% CO<sub>2</sub>).



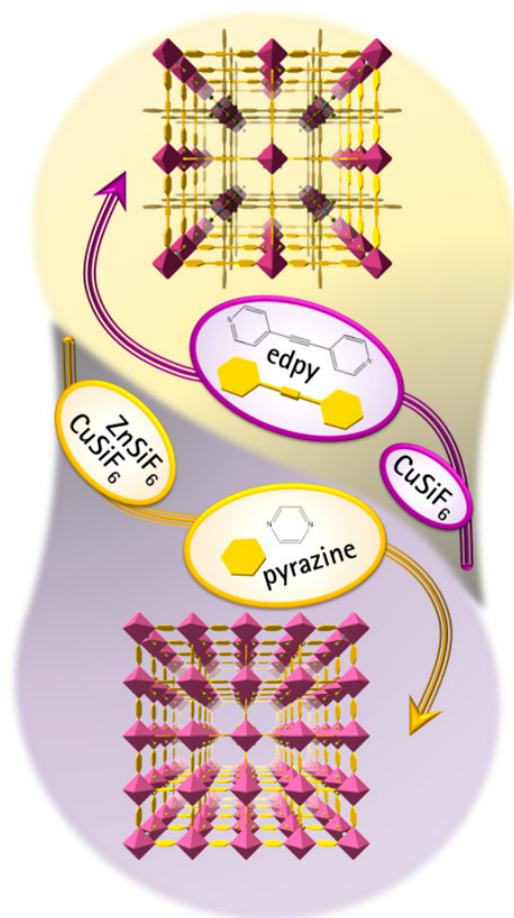


**Figure 6.** A ball-and-stick representation of a *fcu*-MOF-1 compound, constructed from the assembly of 12 connected carboxylate/tetrazolate-based molecular building blocks (MBBs) linked together via a linear and hetero-functional 2-fluoro-4-(tetrazol-5-yl)benzoate (FTZB) organic linker, to give a 3-periodic *fcu*-MOF with two types of polyhedral cages, i.e., tetrahedral (blue sphere) and octahedral (green sphere).

The strength of the interactions is not the only important factor that has to be considered, but their uniformity over the entire material framework is also of prime importance to ensure high CO<sub>2</sub> affinity (affecting in turn the CO<sub>2</sub> selectivity) over a wide range of CO<sub>2</sub> concentrations (Figure 3b and 4). This requires a homogenous distribution of these strong adsorption sites to allow CO<sub>2</sub> adsorption with identical interaction strengths. In line with this, a new class of MOFs with periodically arrayed hexafluorosilicate (SiF<sub>6</sub>) pillars<sup>10, 94</sup> (Figure 7) characterized by one-dimensional channels with

different sizes and exhibiting uniform and strong energy distribution with increased CO<sub>2</sub> uptake (grey, blue, and black dots, Figure 3b) were recently reported. Other noticeable results were obtained using different pillars such as MF<sub>6</sub> (M=Ti, Sn)<sup>38</sup> or MO<sub>4</sub><sup>2-</sup> (M=Cr, W, Mo)<sup>42, 95</sup> for the construction of MOFs.

These SiF<sub>6</sub> based MOFs, particularly the isostructural analogues constructed using (the shorter) pyrazine ligand (Figure 7), showed unprecedented selectivity for CO<sub>2</sub>. Uniform CO<sub>2</sub> interaction (energy) distribution is one of the essential requirements to ensure (in addition to narrow pore size) that high selectivity is maintained over a wide range of CO<sub>2</sub> adsorption loading.<sup>10, 94</sup> This key aspect has not been tackled and discussed in the literature so far, which explains the scarcity of materials that are able to fulfill the technical requirements for CO<sub>2</sub> capture.<sup>96</sup> It is important to mention that the higher is the CO<sub>2</sub> concentration in the stream, the steadier should be the adsorption energy (heat of adsorption). The synergetic relationship between the porosity (pore size) and the CO<sub>2</sub> adsorption interactions will be different from one application to another depending on the less absorbable (the more selective) molecule (N<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, etc.) and will be discussed in the next section.



**Figure 7.** Pore size tuning in the channel structures of *SIFSIX-2-Cu-i*, *SIFSIX-3-Zn* and *SIFSIX-3-Cu*. (Up), *SIFSIX-2-Cu-i*; pores size 5.15 Å, BET apparent surface area ( $N_2$  adsorption) 735  $m^2/g$ . (Down), *SIFSIX-3-Zn*; pores size 3.84 Å, apparent BET surface area (determined from  $CO_2$  adsorption isotherm) 250  $m^2/g$ ; *SIFSIX-3-Cu*; pores size 3.5 Å, apparent BET surface area (determined from  $CO_2$  adsorption isotherm) 300  $m^2/g$ .

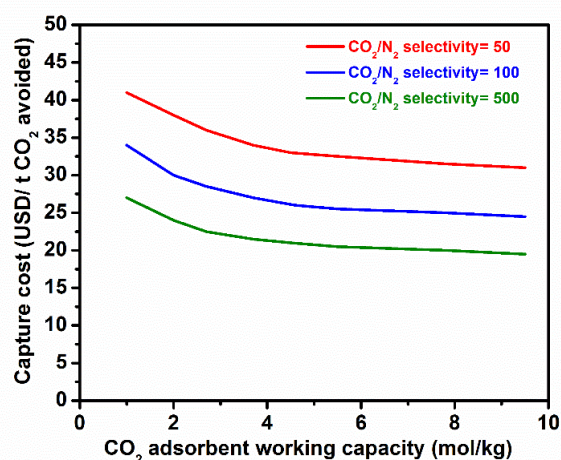
#### **$CO_2$ selectivity, uptake and kinetics**

The  $CO_2$  adsorption capacity and kinetics collectively dictate the efficiency of the  $CO_2$  capture process (amount of treated gas per time period), whereas the phase purity of the separated commodities from  $CO_2$  or the purity of the captured  $CO_2$  is primarily correlated with the  $CO_2$  adsorption selectivity over other gases. The last is the most influential parameter in adsorption-based separation processes.

To the best of our knowledge, there have been a sizeable amount of published reports on the economic feasibility of CO<sub>2</sub> capture,<sup>97-100</sup> however few of them established a direct relationship between the cost of CO<sub>2</sub> capture and the the intrinsic properties of the adsorbents. Nevertheless, a recent study projected that the ideal solid sorbent for cost-effective post-combustion capture and separation of CO<sub>2</sub> from flue gas using PSA should exhibit CO<sub>2</sub> selectivity above 500, combined with a working capacity in the range of 2 to 4 mmol/g for a CO<sub>2</sub>/N<sub>2</sub> 10/90 mixture (Figure 8).<sup>101</sup> Given this baseline, various adsorbents can be evaluated for their suitability to replace costly liquid amine scrubbing or cryogenic distillation.

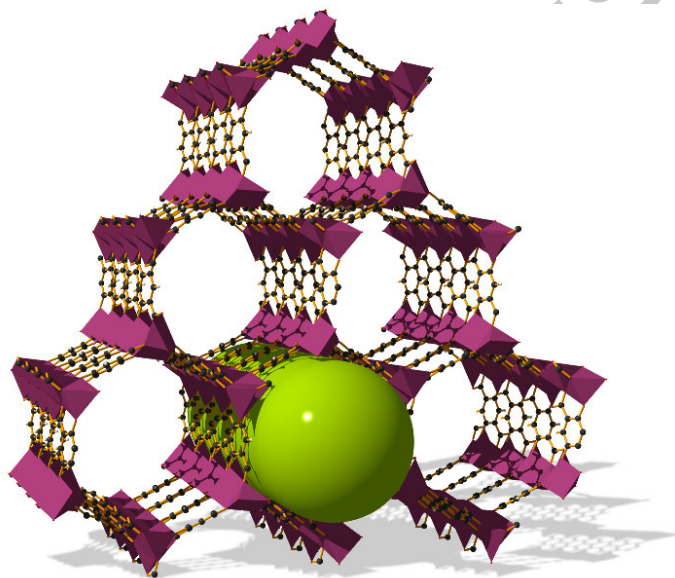
In adsorption science, two main separation mechanisms are largely documented:

(i) the equilibrium-based mechanism, where the selectivity of a given adsorbent toward CO<sub>2</sub> versus other probe molecules (relatively larger and smaller than CO<sub>2</sub>) is dictated mainly by the strength (regardless of the uniformity) of CO<sub>2</sub> interactions driving the separation process of CO<sub>2</sub> from less absorbable commodities such as CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>. Examples of adsorbents that use the equilibrium-based mechanism are activated carbon Maxsorb,<sup>102</sup> zeolite Y,<sup>103</sup> Mg-MOF-74<sup>104</sup> (Figure 8), **rht**-MOF-7<sup>23</sup> and **fcu**-MOFs<sup>31</sup> discussed earlier, as well as almost all MOFs reported for CO<sub>2</sub> capture.<sup>24</sup> These materials exhibit generally large average pore size (0.4 nm and higher).



**Figure 8.** Relationship between the  $\text{CO}_2$  capture cost,  $\text{CO}_2$  selectivity, and working  $\text{CO}_2$  capacity for solid sorbents.<sup>101</sup>

(ii) kinetics-driven sieving. When the pore size of the material is narrow enough (close to the molecular size of  $\text{CO}_2$ ) kinetics driven molecular sieving is the most probable mechanism allowing the exclusion or slow diffusion of other larger probe molecules, such as  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{O}_2$ ,<sup>105, 106</sup> thus providing materials with high kinetic selectivity, but not necessarily high productivity due to the possible small  $\text{CO}_2$  uptake. Synthesis of materials with such narrow pore sizes is generally difficult to attain.<sup>24, 76-80</sup>



**Figure 9.** Structure of Mg-MOF-74 (Mg are purple polyhedra; C, black; O, red; H, light grey). One mono-dimensional honeycomb channel is highlighted by a green rod.

In case of MOFs adsorbents, it is evident from all reported approaches aiming to enhance the affinity for  $\text{CO}_2$  that there is no single adsorption site approach that offers desired performances in terms of  $\text{CO}_2$  uptake and selectivity. For example, in MOFs with open metal sites but without high charge densities and/or suitable pore sizes, such as HKUST-1,<sup>107</sup> **tbo**-MOF-2,<sup>108</sup> and **rht**-MOF-1,<sup>92</sup> the single site effect is not strong enough to promote the affinity (selectivity) to the required performances regardless the  $\text{CO}_2$  concentration. Nevertheless, combining at least the effect of two adsorption sites

leads to obvious enhancement in CO<sub>2</sub> separation properties as in the example of Mg-MOF-74/CPO-27 (open-metal sites and hydroxyl group, Figure 9) at low pressure and the above-cited examples (**rht**-MOF-7 and **fcu**-MOFs) at very low pressure. Table 1 presents the CO<sub>2</sub> uptakes of various CO<sub>2</sub> adsorbents at 0.1 bar pressure as a function of porosity, energetics and selectivity. The synergetic effect and correlations involving porosity-charge density and CO<sub>2</sub> uptake are discussed in more detail in the next section.

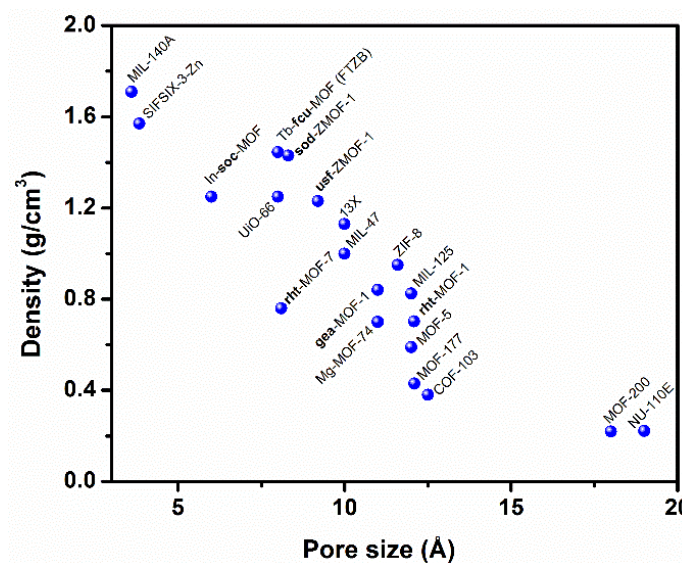
In real-life applications, the volumetric CO<sub>2</sub> uptake is the parameter to consider rather than the gravimetric CO<sub>2</sub> uptake. Therefore another important parameter to take into account is the density of the separation agent. Figure 10 shows the relationship between the densities of different CO<sub>2</sub> adsorbents as a function of pore size. Noticeably, the material density increases with the diminution of the pore size. Figure 11 shows the volumetric uptake of CO<sub>2</sub> at low pressure for the most promising materials. As shown in the figure, the SiF<sub>6</sub> compounds with narrow pore sizes and high charge densities were found to display very high volumetric uptake at very low pressures (up to 10% CO<sub>2</sub>) compared with Maxsorb,<sup>8, 102</sup> zeolite 13X,<sup>8</sup> Mg-MOF-74<sup>104</sup> and UTSA-20<sup>109</sup>. The SiF<sub>6</sub>-based compounds exhibit higher CO<sub>2</sub> adsorption selectivity than the previously mentioned materials. Interestingly, these materials have highly uniform pore size and energy distributions as shown in Figure 3b and elsewhere.<sup>10, 94</sup> The mechanism that leads to these outstanding results is discussed in the next section.

Zeolites, activated carbon and MOFs generally exhibit very fast CO<sub>2</sub> adsorption kinetics. This parameter may be exploited for kinetic-selective separation using materials with narrow pore sizes. In fact, a pore smaller than 4 Å will have the potential to sieve CO<sub>2</sub> (rapidly diffusing molecules) from other commodities, such as CH<sub>4</sub> and N<sub>2</sub> (slowly diffusing gases) using kinetics as the main driving force, as discussed earlier. Implementing this methodology is challenging, but should be possible to achieve for MOFs. Coordination chemistry may lead to the design, discovery and development of new MOFs with finely tuned porosities and chemical compositions targeting kinetic CO<sub>2</sub> separation. Coordination chemistry may offer a great tool to develop adsorption kinetics-based materials.

**Table 1.** Specific surface area, pore volume and pore size of selected best solid-state materials for CO<sub>2</sub> adsorption at low pressure and room temperature, CO<sub>2</sub> Q<sub>st</sub> and CO<sub>2</sub> uptake at 0.1 bar pressure and CO<sub>2</sub> selectivity of the most promising/studied materials.

CO <sub>2</sub> adsorbents	BET Surface area/ m <sup>2</sup> /g	Pore volume cm <sup>3</sup> /g	Pore size / Å	Q <sub>st</sub> / kJ/mol	Gravimetric CO <sub>2</sub> uptake mmol/g at 0.1 bar	CO <sub>2</sub> selectivity at 1 bar/ (CO <sub>2</sub> /N <sub>2</sub> ) composition	Reference
13X	570	0.17	10	44-54	2.41	≈500/ (10/90)	<sup>10</sup>
Maxsorb Activated carbon	2250	1.15	10	16.2	> 0.2	> 10/ (10/90)	<sup>102, 110</sup>
Mg-MOF-74	1640	0.57	10.8	47-52	5.00	182/ (15/85)	<sup>109, 111</sup>
rht-MOF-7	1900	0.76	6.4*	45/25	0.3	25/ (10/90)	<sup>23</sup>
rht-amide	3160	1.27	7.0*	26.3	0.63	22/ (50/50)	<sup>59</sup>
In-sod-ZMOF	475	0.18	4.1	30	0.36	NA	<sup>112, 113</sup>
sod-ZIF-8	1630	0.64	3.4	18	0.2	NA	<sup>55, 114</sup>
fcu-UIO-66	1020	0.45	6.5	35/26.5	NA	NA	<sup>46, 47</sup>
Tb-fcu-MOF-1	1220	0.51	5-6*	58.1/25.0	0.4	15/ (10/90)	<sup>31</sup>
UTSA-16	628	0.31	9.5x4.3	34.6	1.37	314/ (15/85)	<sup>109, 115</sup>
SiFSIX-2-Cu-i-	734	0.26	5.15	31.90	1.73	72 <sup>b</sup> / (10/90)	<sup>10</sup>
SiFSIX-3-Zn	250 <sup>a</sup>	NA	3.84	45.00	2.39	1700 <sup>c</sup> / (10/90)	<sup>10</sup>
SiFSIX-3-Cu	300 <sup>a</sup>	NA	3.5	54	2.4	< 2000 <sup>b</sup> / (10/90)	<sup>94</sup>

\*Size of window; <sup>a</sup> determined from CO<sub>2</sub> adsorption; <sup>b</sup> determined from breakthrough measurements; <sup>c</sup> determined from gravimetric-densimetric gas analysis; NA: not available.

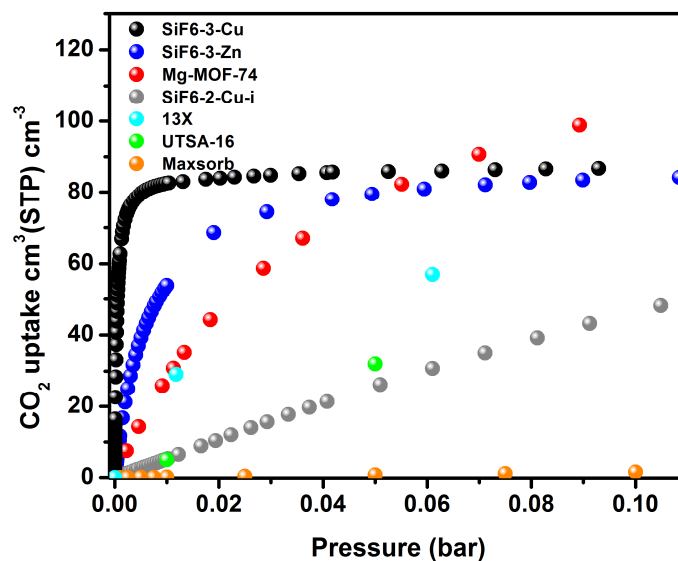


**Figure 10.** Correlation between the adsorbents pore size of and their corresponding crystal density.

### Synergetic effects in MOFs with optimal pore size and charge density

Recently, a combined mechanism involving optimal thermodynamics (energetics) and kinetics for CO<sub>2</sub> capture at intermediate, low<sup>10</sup> and trace CO<sub>2</sub> concentrations<sup>94</sup> was reported. This unique combination of high charge density and optimal pore size allowed the boundaries of CO<sub>2</sub> energetics to be pushed (with uniform distribution due to the high, homogeneous charge density) to the upper limit of physical reversible adsorption (45-52 kJ/mol) combined with highly favourable kinetics to CO<sub>2</sub>, owing to the small pore size in both SIFSIX-3-Zn (3.84 Å) and SIFSIX-3-Cu (3.5 Å) compounds. The synergetic effect led to a combined fast and strong CO<sub>2</sub> adsorption in the pores and exclusion of both larger (O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>) and smaller (H<sub>2</sub>) probe molecules, resulting in an extremely high selectivity toward CO<sub>2</sub>, comparable to reactive amine bearing materials.<sup>5</sup>





**Figure 11.** Volumetric uptake at low pressure of the most promising adsorbents

From a structural and chemical point of view, this finding showed clearly that for this particular case, the SiF<sub>6</sub>-M-pyrazine compounds exhibit moderate surface area and pore volume and comprise (i) only channels (no cages) with strictly uniform narrow pore size, (ii) combined high density and uniform positioning of SiF<sub>6</sub>, favourable to CO<sub>2</sub> attraction. These structural and chemical features afforded the construction of physical adsorbents with high selectivity toward CO<sub>2</sub> and suitable CO<sub>2</sub> uptake and energetics. A material with such attributes in addition to suitable kinetics, permitting a short cycling time (easy regeneration), could lower the CO<sub>2</sub> capture cost to as little as 20 USD/ton of CO<sub>2</sub> as shown in Figure 8. Because of the key structural and energetic uniformity requirements, we anticipate that MOFs exhibiting channels rather than cages will be more suitable for use in the combined equilibrium/kinetics gas separation in general and in CO<sub>2</sub> capture in particular. For the particular case of SiF<sub>6</sub>-based MOFs, upon the increase of the channel size from 3.84 to 5.15 Å in SiF<sub>6</sub>-Cu-bipyridine, constructed using a bipyridine linker, the charge density decreased leading to a drastic decrease in CO<sub>2</sub> selectivity.<sup>10</sup> Nevertheless, decreasing the channel size from 3.84 to 3.5 Å, by substitution of zinc for copper, pushed the boundaries of the reversible interaction to the upper limits of *Q<sub>st</sub>* of 53 KJ/mol. Accordingly, the CO<sub>2</sub> uptake was dramatically increased, particularly at trace concentrations and low CO<sub>2</sub> partial pressure.<sup>94</sup> This finding was reported to be the first ever high CO<sub>2</sub> uptake (1.24 mmol/g) at

trace CO<sub>2</sub> concentration (400 ppm) on a plain (without post-functionalization) MOF, driven only by physical adsorption. Interestingly, the gravimetric uptake of **SIFSIX**-3-Cu (pyrazine) at 400 ppm and 298 K (1.24 mmol/g) was 10 and 15.5 times higher than the corresponding uptakes for the zinc analogue **SIFSIX**-3-Zn (0.13 mmol/g) and Mg-MOF-74 (0.08 mmol/g), respectively, and even higher than the uptake of most of amine-supported mesoporous silica materials (with the optimal compromise of amine loading and kinetics)<sup>67, 116</sup> at 298 K (for example TRI-PE-MCM-41(1 mmol/g)).<sup>8</sup> The synergetic effect was also observed in Mg-MOF-74 (Figure 9), which is interestingly a MOF comprising mainly channels with uniform size (10 Å) but with a slightly non-uniform energy distribution.<sup>29, 104, 117</sup> In fact, the combination of open magnesium sites together with the hydroxyl groups (in 10 Å channel size) led to significantly high CO<sub>2</sub> uptake but not as high CO<sub>2</sub> selectivity as in the case of **SIFSIX**. The relatively lower CO<sub>2</sub> selectivity for Mg-MOF-74 compared to SiF<sub>6</sub>-based MOFs can be logically explained by the relatively high channel size (10 Å vs. 4.9 Å and 3.84 Å for SiF<sub>6</sub>-Cu-bipyridine and **SIFSIX**-3-Zn) and the declining  $Q_{st}$  as a function of CO<sub>2</sub> loading.

In an attempt to understand the relationships between the key properties of the materials (CO<sub>2</sub> uptake, energetics selectivity and structural properties) desirable for CO<sub>2</sub> capture on one hand and the degree of synergy between the intrinsic properties of the materials on the other hand, we propose to introduce a new parameter representing the intrinsic property of the materials called the CO<sub>2</sub> synergy indicator (SI), where

$$SI = \frac{Q_{sti} * \frac{Di}{di}}{Q_{st13X} * \frac{Di13X}{d13X}}$$

This parameter is based on equilibrium data of known reference CO<sub>2</sub> adsorbent, such as zeolite 13X.

The SI for 13X is therefore equal to 1, where  $Q_{sti}$  : is the isosteric heat of adsorption at very low loading for material 'i' that takes into account the interactions of CO<sub>2</sub> with the framework. This value should not be higher than 60 kJ/mol (the upper limit of physical adsorption that is of interest to us) and is assumed to be uniform over the CO<sub>2</sub> adsorption loading as in the case of the **SIFSIX**

compounds. In cases when the  $Q_{st}$  is not steady as a function of CO<sub>2</sub> uptake, the  $Q_{st}$  value should be the average value at different loadings.

$D_i$ : is the density of the evacuated framework. This parameter is combined with  $Q_{st}$  to reflect the materials charge density. The density used here is the one calculated theoretically for MOFs and the one reported in the open literature for zeolites and activated carbons.

$d_i$ : The pore diameter, which captures the effect of porosity (Figure 2) as the pore size has established correlations with the surface area and pore volume. In cases of materials containing cages, the pore size is considered to be the diameter of the biggest cage.

The larger is the SI indicator, the higher the impact of synergetic effect will be, which has direct effect on the CO<sub>2</sub> affinity and selectivity. This parameter considers only the equilibrium intrinsic properties of adsorption in relation to CO<sub>2</sub> and not the other less absorbable gases (O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>).

**Table 2.** Correlation between the synergy indicator as a function of selectivity for different CO<sub>2</sub> adsorbents

CO <sub>2</sub> adsorbent	Average $Q_{st}$ kJ/mol	CO <sub>2</sub> /N <sub>2</sub> selectivity	SI
13X	35	500	1
Mg-MOF-74	35	182	0.72
SiFSIX-2-Cu-i	35	140	2.06
SiFSIX-3-Zn	45	1700	4.65
SiFSIX-3-Cu	52	< 2000	6.2

As seen in Table 2, this parameter has a clear correlation with the selectivity towards CO<sub>2</sub> and reflects the occurrence of the synergetic effect, which has a direct impact on increasing the affinity toward CO<sub>2</sub>. This parameter is broad in definition and does not take into consideration the CO<sub>2</sub> diffusivities and the less absorbable molecules such as O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> in the particular case of CO<sub>2</sub> capture.

We suggest that the combination of the correct structural and chemical composition parameters is a major requirement in the design of MOFs for CO<sub>2</sub> capture. This finding should drive the work on materials chemistry for general gas separation applications and CO<sub>2</sub> capture in particular in the next years.

### **Effect of water vapor on these parameters at low CO<sub>2</sub> partial pressure**

The tolerance of CO<sub>2</sub> adsorbents to water vapor is one of the requirements for optimal operation of CO<sub>2</sub> capture processes using adsorption technologies.<sup>118-120</sup> It implies that CO<sub>2</sub> separation should not be affected by the presence of moisture. Depending on the class of adsorption sites, the effect of moisture on the adsorption properties can be different. Based on the information available so far in the literature, the effect of moisture on hydrophilic materials, such as zeolites<sup>5</sup> (for example, Faujasites X and Y, zeolite A, etc.) and MOFs with open metal sites,<sup>24</sup> will be some time a limiting factor. In this case, the preliminary removal of moisture from the stream is necessary to ensure the efficient use of the material properties. In contrast and in another particular case, it was reported that the CO<sub>2</sub> uptake by MIL-100(Fe) (with open metal sites) was improved in the presence of 40% relative humidity.<sup>32</sup> Conversely, the effect of moisture on hydrophobic materials such as activated carbons<sup>5</sup> and MOFs without open metal sites<sup>10</sup> will be minimal or insignificant. Another case where the presence of moisture induced enhanced CO<sub>2</sub> adsorption properties were amine bearing materials,<sup>5</sup> such as mesoporous silica<sup>9, 14</sup> and MOFs.<sup>24</sup> The observed enhancement in these systems was due to the occurrence of chemical adsorption via the formation of bicarbonate.<sup>5</sup> However, the contribution of this enhancement to the real process efficiency is not evident because of the slow adsorption rate during bicarbonate formation. Finally, it is important to mention that in the case of SiF<sub>6</sub>-based MOFs,<sup>10</sup> both the hydrophobicity and the high and uniform interaction with CO<sub>2</sub> are the main driving forces for their high tolerance to moisture when SiF<sub>6</sub>-pyrazine- based MOFs are exposed CO<sub>2</sub>.

In spite the large amount of studies on MOFs stability toward water vapor and its effect on CO<sub>2</sub> adsorption properties, it is still not recognised that these promising MOF materials, such as **SIFSIX**, for CO<sub>2</sub> capture to be recyclable under hundreds of cycles. The main reason is that certain SiF<sub>6</sub>

assembled with pyrazine ligand could undergo phase transition from 3D to 2D structures upon extensive exposure to water (without presence of CO<sub>2</sub>).<sup>121</sup> Nevertheless if a gas pre-drying step is implemented, these materials are still very powerful for traces and low CO<sub>2</sub> concentration removal. Further work will be necessary to overcome this phase change.

#### **Thermal stability and effect of other impurities (NO<sub>x</sub>, SO<sub>x</sub>, H<sub>2</sub>S, etc.)**

The preservation of a material's structural, chemical and adsorption properties upon cyclic testing is a key requirement for any separation agent to reach wide acceptance on the commercial scale. Because of the physical adsorption nature of CO<sub>2</sub> separation agents, materials for which desorption occurs at the same temperature (or under very mild conditions) are needed. Thermal stability is therefore not a concern.

The stability of CO<sub>2</sub> separation agents in the presence of impurities such as SO<sub>2</sub> or H<sub>2</sub>S is desirable feature. Because of the complex safety issues associated with testing materials for toxic or corrosive gas adsorption, there is no extensive work on this subject and generally the topic remains largely unexplored. Zeolites,<sup>122</sup> activated carbons<sup>123</sup> and few MOFs (Cr<sup>III</sup>, V<sup>IV</sup>, Al<sup>III</sup> and Ti<sup>IV</sup> based)<sup>61, 124, 125</sup> were shown to be stable in the presence of SO<sub>2</sub>, H<sub>2</sub>S and water vapor. However, some Zn<sup>II</sup>- and Fe<sup>III</sup>-based MOFs with open metals sites were shown to form zinc<sup>125</sup> or iron<sup>124</sup> sulphide when exposed to H<sub>2</sub>S.

Because of the scarcity of toxic gases adsorption data, developing CO<sub>2</sub> adsorbents in the presence of H<sub>2</sub>S and SO<sub>2</sub> remains challenging and unexplored. Further work is necessary to understand the nature of MOFs that capture CO<sub>2</sub> in the presence of these gases.

#### **Conclusions**

The ultimate objective of this work is to discuss realistic points, based on existing CO<sub>2</sub> adsorbents from the open literature, that drive the development of materials suitable for CO<sub>2</sub> capture mainly at very low concentration. The aim of this review was not to refer to abundant work in materials chemistry concerning the CO<sub>2</sub> separation but rather to analyse the most promising CO<sub>2</sub> adsorbents and

particularly to understand the key parameters contributing to their performance. We also aimed to present a broad picture on the progress of the development of CO<sub>2</sub> separation agents.

The above discussion showed that although large porosity (high surface area and pore volume) is a key factor in gas storage, it is not necessarily important for applications related to the CO<sub>2</sub> removal at low CO<sub>2</sub> partial pressure. The optimal strength of CO<sub>2</sub> interactions is a key parameter for designing materials for CO<sub>2</sub> capture. Not only the strength of these interactions is important, but also its steadiness over a wide range of CO<sub>2</sub> adsorption uptake, to ensure highly selective operations over a wide range of CO<sub>2</sub> concentrations. Because of the relatively high degree of structure and pore tunability vs other class of materials, MOFs have a tremendous advantages and potential. With this regard, we discussed in this review the importance of the proper synergy between (a) the thermodynamics (energetics) with strict requirements (related to the charge density of the materials), (b) the correct structural properties (pore size) and (c) the highly favourable kinetics for CO<sub>2</sub> to achieve the desired adsorption attributes capable of CO<sub>2</sub> capture efficiency. This new combined approach was shown to be possible to achieve experimentally and effective using MOFs namely, SiF<sub>6</sub>-pyrazine compounds which are considered as a model materials for low CO<sub>2</sub> concentration capture uniquely driven by physical adsorption. However, further work is necessary to find pathways to prevent the phase transition of this class of MOF materials upon extensive exposure to gas streams containing water vapor.

### **Acknowledgment**

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### **Literature cited**

- [1] R. Monastersky, A burden beyond bearing, *Nature*, 458 (2009) 1091-1094
- [2] A. Yamasaki, An overview of CO<sub>2</sub> mitigation options for global warming - emphasizing CO<sub>2</sub> sequestration options, *J. Chem. Eng. Jpn.* 36 (2003) 361-375

- [3] D. Aaron and C. Tsouris, Separation of CO<sub>2</sub> from flue gas: A review, *Sep. Sci. Technol.* 40 (2005) 321-348
- [4] <http://www.esrl.noaa.gov/gmd/ccgg/trends/weekly.html>, accessed: November 1<sup>st</sup>, 2015
- [5] A. Sayari, Y. Belmabkhout and R. Serna-Guerrero, Flue gas treatment via CO<sub>2</sub> adsorption, *Chem. Eng. J.* 171 (2011) 760-774
- [6] S. Sjostrom and H. Krutka, Evaluation of solid sorbents as a retrofit technology for CO<sub>2</sub> capture, *Fuel*, 89 (2010) 1298-1306
- [7] Y. Belmabkhout, R. Serna-Guerrero and A. Sayari, Adsorption of CO<sub>2</sub>-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: Application for CO<sub>2</sub> separation, *Adsorption*, 17 (2011) 395-401
- [8] Y. Belmabkhout, R. Serna-Guerrero and A. Sayari, Adsorption of CO<sub>2</sub>-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: Application for gas purification, *Ind. Eng. Chem. Res.* 49 (2010) 359-365
- [9] V. Krungleviciute, K. Lask, A. D. Migone, J. Y. Lee and J. Li, Kinetics and equilibrium of gas adsorption on RPM1-Co and Cu-btc metal-organic frameworks: Potential for gas separation applications, *AIChE J.* 54 (2008) 918-923
- [10] P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, Ł. Wojtas, M. Eddaoudi and M. J. Zaworotko, Porous materials with optimal adsorption thermodynamics and kinetics for CO<sub>2</sub> separation, *Nature*, 495 (2013) 80-84
- [11] L. Grajciar, J. Čejka, A. Zukal, C. Otero Areán, G. Turnes Palomino and P. Nachtigall, Controlling the adsorption enthalpy of CO<sub>2</sub> in zeolites by framework topology and composition, *ChemSusChem.* 5 (2012) 2011-2022
- [12] A. Zukal, A. Pulido, B. Gil, P. Nachtigall, O. Bludsky, M. Rubes and J. Čejka, Experimental and theoretical determination of adsorption heats of CO<sub>2</sub> over alkali metal exchanged ferrierites with different Si/Al ratio, *Phys. Chem. Chem. Phys.* 12 (2010) 6413-6422
- [13] Y. Belmabkhout and A. Sayari, Isothermal versus non-isothermal adsorption-desorption cycling of triamine-grafted pore-expanded MCM-41 mesoporous silica for CO<sub>2</sub> capture from flue gas, *Energ. Fuel*, 24 (2010) 5273-5280
- [14] A. Sayari and Y. Belmabkhout, Stabilization of amine-containing CO<sub>2</sub> adsorbents: Dramatic effect of water vapor, *J. Am. Chem. Soc.* 132 (2010) 6312-6313
- [15] A. Sayari, Y. Belmabkhout and E. Da'na, CO<sub>2</sub> deactivation of supported amines: Does the nature of amine matter?, *Langmuir*, 28 (2012) 4241-4247
- [16] P. Bollini, S. Choi, J. H. Drese and C. W. Jones, Oxidative degradation of aminosilica adsorbents relevant to postcombustion CO<sub>2</sub> capture, *Energ. Fuel*, 25 (2011) 2416-2425
- [17] T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown and J. R. Long, Evaluation of cation-exchanged zeolite adsorbents for post-combustion carbon dioxide capture, *Energy Environ. Sci.* 6 (2013) 128-138
- [18] E. M. Flanigen, Chapter 2 zeolites and molecular sieves: An historical perspective, in *Studies in surface science and catalysis*, H. van Bekkum, E. M. Flanigen, P. A. Jacobs and J. C. Jansen (Eds.), Elsevier, (2001), 11-35

- [19] V. Guillerm, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah and M. Eddaoudi, A supermolecular building approach for the design and construction of metal-organic frameworks, *Chem. Soc. Rev.*, 43 (2014) 6141-6172
- [20] V. Guillerm, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil and M. Eddaoudi, Discovery and introduction of a (3,18)-connected net as an ideal blueprint for the design of metal-organic frameworks, *Nature Chem.* 6 (2014) 673-680
- [21] M. Eddaoudi, D. F. Sava, J. F. Eubank, K. Adil and V. Guillerm, Zeolite-like metal-organic frameworks (ZMOFs): Design, synthesis, and properties, *Chem. Soc. Rev.* (2014)
- [22] Y. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. C. Kravtsov, R. Luebke and M. Eddaoudi, Assembly of metal-organic frameworks (MOFs) based on indium-trimer building blocks: A porous MOF with soc topology and high hydrogen storage, *Angew. Chem. Int. Ed.* 46 (2007) 3278-3283
- [23] R. Luebke, J. F. Eubank, A. J. Cairns, Y. Belmabkhout, Ł. Wojtas and M. Eddaoudi, The unique rht-MOF platform, ideal for pinpointing the functionalization and CO<sub>2</sub> adsorption relationship, *Chem. Commun.* 48 (2012) 1455-1457
- [24] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, Carbon dioxide capture in metal-organic frameworks, *Chem. Rev.* 112 (2012) 724-781
- [25] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jung and G. Férey, High uptakes of CO<sub>2</sub> and CH<sub>4</sub> in mesoporous metal-organic frameworks MIL-100 and MIL-101, *Langmuir*, 24 (2008) 7245-7250
- [26] L.-C. Lin, J. Kim, X. Kong, E. Scott, T. M. McDonald, J. R. Long, J. A. Reimer and B. Smit, Understanding CO<sub>2</sub> dynamics in metal-organic frameworks with open metal sites, *Angew. Chem. Int. Ed.* 52 (2013) 4410-4413
- [27] X. Kong, E. Scott, W. Ding, J. A. Mason, J. R. Long and J. A. Reimer, CO<sub>2</sub> dynamics in a metal-organic framework with open metal sites, *J. Am. Chem. Soc.* 134 (2012) 14341-14344
- [28] Z. R. Herm, R. Krishna and J. R. Long, CO<sub>2</sub>/CH<sub>4</sub>, CH<sub>4</sub>/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub> separations at high pressures using Mg<sub>2</sub>(dobdc), *Micropor. Mesopor. Mater.* 151 (2012) 481-487
- [29] J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption, *Energy Environ. Sci.* 4 (2011) 3030-3040
- [30] K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly and J. R. Long, Hydrogen storage and carbon dioxide capture in an iron-based sodalite-type metal-organic framework (Fe-btt) discovered via high-throughput methods, *Chem. Sci.* 1 (2010) 184-191
- [31] D.-X. Xue, A. J. Cairns, Y. Belmabkhout, Ł. Wojtas, Y. Liu, M. H. Alkordi and M. Eddaoudi, Tunable rare-earth fcu-MOFs: A platform for systematic enhancement of CO<sub>2</sub> adsorption energetics and uptake, *J. Am. Chem. Soc.* 135 (2013) 7660-7667
- [32] E. Soubeyrand-Lenoir, C. Vagner, J. W. Yoon, P. Bazin, F. Ragon, Y. K. Hwang, C. Serre, J.-S. Chang and P. L. Llewellyn, How water fosters a remarkable 5-fold increase in



- low-pressure CO<sub>2</sub> uptake within mesoporous MIL-100(Fe), *J. Am. Chem. Soc.* 134 (2012) 10174-10181
- [33] L. Hamon, N. Heymans, P. L. Llewellyn, V. Guillerm, A. Ghoufi, S. Vaesen, G. Maurin, C. Serre, G. De Weireld and G. D. Pirngruber, Separation of CO<sub>2</sub>-CH<sub>4</sub> mixtures in the mesoporous MIL-100(Cr) MOF: Experimental and modelling approaches, *Dalton Trans.* 41 (2012) 4052-4059
- [34] N. A. Ramsahye, G. Maurin, S. Bourrelly, P. L. Llewellyn, T. Devic, C. Serre, T. Loiseau and G. Férey, Adsorption of CO<sub>2</sub> in metal organic frameworks of different metal centres: Grand canonical monte carlo simulations compared to experiments, *Adsorption*, 13 (2007) 461-467
- [35] J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P. B. Balbuena and H.-C. Zhou, Porous materials with pre-designed single-molecule traps for CO<sub>2</sub> selective adsorption, *Nature Commun.* 4 (2013)
- [36] S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang and M. Schroeder, Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host, *Nature Chem.* 4 (2012) 887-894
- [37] D. Britt, H. Furukawa, B. Wang, T. G. Glover and O. M. Yaghi, Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites, *P. Natl. Acad. Sci. USA*, 106 (2009) 20637-20640
- [38] P. Nugent, V. Rhodus, T. Pham, B. Tudor, K. Forrest, Ł. Wojtas, B. Space and M. Zaworotko, Enhancement of CO<sub>2</sub> selectivity in a pillared pcu MOM platform through pillar substitution, *Chem. Commun.* 49 (2013) 1606-1608
- [39] Y.-S. Bae, B. G. Hauser, O. K. Farha, J. T. Hupp and R. Q. Snurr, Enhancement of CO<sub>2</sub>/CH<sub>4</sub> selectivity in metal-organic frameworks containing lithium cations, *Micropor. Mesopor. Mater.* 141 (2011) 231-235
- [40] N. A. Ramsahye, G. Maurin, S. Bourrelly, P. L. Llewellyn, C. Serre, T. Loiseau, T. Devic and G. Férey, Probing the adsorption sites for CO<sub>2</sub> in metal organic frameworks materials MIL-53 (Al, Cr) and MIL-47 (V) by density functional theory, *J. Phys. Chem. C.* 112 (2008) 514-520
- [41] S. D. Burd, S. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, Ł. Wojtas and M. J. Zaworotko, Highly selective carbon dioxide uptake by Cu(bpy-n)<sub>2</sub>(SiF<sub>6</sub>) (bpy-1=4,4'-bipyridine; bpy-2=1,2-bis(4-pyridyl)ethene), *J. Am. Chem. Soc.* 134 (2012) 3663-3666
- [42] M. H. Mohamed, S. K. Elsaidi, Ł. Wojtas, T. Pham, K. A. Forrest, B. Tudor, B. Space and M. J. Zaworotko, Highly selective CO<sub>2</sub> uptake in uninodal 6-connected "mmo" nets based upon Mo<sub>4</sub><sup>2-</sup> (m = Cr, Mo) pillars, *J. Am. Chem. Soc.* 134 (2012) 19556-19559
- [43] S.-i. Noro, Y. Hijikata, M. Inukai, T. Fukushima, S. Horike, M. Higuchi, S. Kitagawa, T. Akutagawa and T. Nakamura, Highly selective CO<sub>2</sub> adsorption accompanied with low-energy regeneration in a two-dimensional Cu(II) porous coordination polymer with inorganic fluorinated PF<sub>6</sub><sup>-</sup> anions, *Inorg. Chem.* 52 (2013) 280-285

- [44] P. L. Llewellyn, S. Bourrelly, C. Vagner, N. Heymans, H. Leclerc, A. Ghoufi, P. Bazin, A. Vimont, M. Daturi, T. Devic, C. Serre, G. De Weireld and G. Maurin, Evaluation of MIL-47(V) for CO<sub>2</sub>-related applications, *J. Phys. Chem. C* 117 (2013) 962-970
- [45] A. D. Wiersum, J.-S. Chang, C. Serre and P. L. Llewellyn, An adsorbent performance indicator as a first step evaluation of novel sorbents for gas separations: Application to metal-organic frameworks, *Langmuir*, 29 (2013) 3301-3309
- [46] Q. Yang, V. Guillerm, F. Ragon, A. D. Wiersum, P. L. Llewellyn, C. Zhong, T. Devic, C. Serre and G. Maurin, CH<sub>4</sub> storage and CO<sub>2</sub> capture in highly porous zirconium oxide based metal-organic frameworks, *Chem. Commun.* 48 (2012) 9831-9833
- [47] A. D. Wiersum, E. Soubeyrand-Lenoir, Q. Yang, B. Moulin, V. Guillerm, M. Ben Yahia, S. Bourrelly, A. Vimont, S. Miller, C. Vagner, M. Daturi, G. Clet, C. Serre, G. Maurin and P. L. Llewellyn, An evaluation of UiO-66 for gas-based applications, *Chem. Asian. J.* 6 (2011) 3270-3280
- [48] G. D. Pirngruber, L. Hamon, S. Bourrelly, P. L. Llewellyn, E. Lenoir, V. Guillerm, C. Serre and T. Devic, A method for screening the potential of MOFs as CO<sub>2</sub> adsorbents in pressure swing adsorption processes, *ChemSusChem*. 5 (2012) 762-776
- [49] W. Yang, A. J. Davies, X. Lin, M. Suyetin, R. Matsuda, A. J. Blake, C. Wilson, W. Lewis, J. E. Parker, C. C. Tang, M. W. George, P. Hubberstey, S. Kitagawa, H. Sakamoto, E. Bichoutskaia, N. R. Champness, S. Yang and M. Schroeder, Selective CO<sub>2</sub> uptake and inverse CO<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> selectivity in a dynamic bifunctional metal-organic framework, *Chem. Sci.* 3 (2012) 2993-2999
- [50] C. Tan, S. Yang, N. R. Champness, X. Lin, A. J. Blake, W. Lewis and M. Schroeder, High capacity gas storage by a 4,8-connected metal-organic polyhedral framework, *Chem. Commun.* 47 (2011) 4487-4489
- [51] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks, *Acc. Chem. Res.* 43 (2010) 58-67
- [52] H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, Ultrahigh porosity in metal-organic frameworks, *Science*, 329 (2010) 424-428
- [53] W. Bo, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs, *Nature*, 453 (2008) 207-211
- [54] A. R. Millward and O. M. Yaghi, Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature, *J. Am. Chem. Soc.* 127 (2005) 17998-17999
- [55] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO<sub>2</sub> capture, *Science*, 319 (2008) 939-943
- [56] J. L. C. Rowsell and O. M. Yaghi, Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks, *J. Am. Chem. Soc.* 128 (2006) 1304-1315

- [57] B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath and W. Lin, Highly interpenetrated metal-organic frameworks for hydrogen storage, *Angew. Chem. Int. Ed.* 44 (2004) 72-75
- [58] T. Devic, F. Salles, S. Bourrelly, B. Moulin, G. Maurin, P. Horcajada, C. Serre, A. Vimont, J.-C. Lavalley, H. Leclerc, G. Clet, M. Daturi, P. L. Llewellyn, Y. Filinchuk and G. Férey, Effect of the organic functionalization of flexible MOFs on the adsorption of CO<sub>2</sub>, *J. Mater. Chem.* 22 (2012) 10266-10273
- [59] B. Zheng, J. Bai, J. Duan, Ł. Wojtas and M. J. Zaworotko, Enhanced CO<sub>2</sub> binding affinity of a high-uptake rht-type metal-organic framework decorated with acylamide groups, *J. Am. Chem. Soc.* 133 (2011) 748-751
- [60] P. Cui, Y.-G. Ma, H.-H. Li, B. Zhao, J.-R. Li, P. Cheng, P. B. Balbuena and H.-C. Zhou, Multipoint interactions enhanced CO<sub>2</sub> uptake: A zeolite-like zinc-tetrazole framework with 24-nuclear zinc cages, *J. Am. Chem. Soc.* 134 (2012) 18892-18895
- [61] S. Vaesen, V. Guillerme, Q. Yang, A. D. Wiersum, B. Marszalec, B. Gil, A. Vimont, M. Daturi, T. Devic, P. L. Llewellyn, C. Serre, G. Maurin and G. De Weireld, A robust amino-functionalized titanium (IV) based MOF for an improved separation of acid gases, *Chem. Commun.* (2013)
- [62] E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon and F. Kapteijn, Complexity behind CO<sub>2</sub> capture on NH<sub>2</sub>-MIL-53(Al), *Langmuir*, 27 (2011) 3970-3976
- [63] V. Benoit, R. S. Pillai, A. Orsi, P. Normand, H. Jobic, F. Nouar, P. Billefont, E. Bloch, S. Bourrelly, T. Devic, P. A. Wright, G. de Weireld, C. Serre, G. Maurin and P. L. Llewellyn, MIL-91(Ti), a small pore metal-organic framework which fulfils several criteria: An upscaled green synthesis, excellent water stability, high CO<sub>2</sub> selectivity and fast CO<sub>2</sub> transport, *J. Mater. Chem. A*, 4 (2016) 1383-1389
- [64] Q. Yang, S. Vaesen, F. Ragon, A. D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, P. L. Llewellyn, H. Jobic, C. Zhong, C. Serre, G. De Weireld and G. Maurin, A water stable metal-organic framework with optimal features for CO<sub>2</sub> capture, *Angew. Chem. Int. Ed.*, 52 (2013) 10316-10320
- [65] A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, Strong CO<sub>2</sub> binding in a water-stable, triazolate-bridged metal-organic framework functionalized with ethylenediamine, *J. Am. Chem. Soc.* 131 (2009) 8784-8785
- [66] T. M. McDonald, D. M. D'Alessandro, R. Krishna and J. R. Long, Enhanced carbon dioxide capture upon incorporation of N,N'-dimethylethylenediamine in the metal-organic framework Cubttri, *Chem. Sci.* 2 (2011) 2022-2028
- [67] T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong and J. R. Long, Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg<sub>2</sub>(dobpdc), *J. Am. Chem. Soc.* 134 (2012) 7056-7065
- [68] M. Anbia and V. Hoseini, Enhancement of CO<sub>2</sub> adsorption on nanoporous chromium terephthalate (MIL-101) by amine modification, *J. Nat. Gas. Chem.* 21 (2012) 339-343
- [69] Q. Yan, Y. Lin, C. Kong and L. Chen, Remarkable CO<sub>2</sub>/CH<sub>4</sub> selectivity and CO<sub>2</sub> adsorption capacity exhibited by polyamine-decorated metal-organic framework adsorbents, *Chem. Commun.* 49 (2013) 6873-6875

- [70] C. Hon Lau, R. Babarao and M. R. Hill, A route to drastic increase of CO<sub>2</sub> uptake in Zr metal organic framework UiO-66, *Chem. Commun.* 49 (2013) 3634-3636
- [71] W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna and H.-C. Zhou, Sulfonate-grafted porous polymer networks for preferential CO<sub>2</sub> adsorption at low pressure, *J. Am. Chem. Soc.* 133 (2011) 18126-18129
- [72] W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei and H.-C. Zhou, Polyamine-tethered porous polymer networks for carbon dioxide capture from flue gas, *Angew. Chem. Int. Ed.* 51 (2012) 7480-7484
- [73] W. Lu, J. P. Sculley, D. Yuan, R. Krishna and H.-C. Zhou, Carbon dioxide capture from air using amine-grafted porous polymer networks, *J. Phys. Chem. C* 117 (2013) 4057-4061
- [74] V. Guillerme, Ł. J. Weseliński, M. Alkordi, M. I. H. Mohideen, Y. Belmabkhout, A. J. Cairns and M. Eddaoudi, Porous organic polymers with anchored aldehydes: A new platform for post-synthetic amine functionalization en route for enhanced CO<sub>2</sub> adsorption properties, *Chem. Commun.* 50 (2014) 1937-1940
- [75] S. Choi, J. H. Drese and C. W. Jones, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, *ChemSusChem*. 2 (2009) 796-854
- [76] D. M. D'Alessandro, B. Smit and J. R. Long, Carbon dioxide capture: Prospects for new materials, *Angew. Chem. Int. Ed.* 49 (2010) 6058-6082
- [77] G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi and J.-S. Chang, Why hybrid porous solids capture greenhouse gases?, *Chem. Soc. Rev.* 40 (2011) 550-562
- [78] Y. Liu, Z. U. Wang and H.-C. Zhou, Recent advances in carbon dioxide capture with metal-organic frameworks, *Greenhouse Gas Sci. Technol.* 2 (2012) 239-259
- [79] J.-R. Li, J. Sculley and H.-C. Zhou, Metal-organic frameworks for separations, *Chem. Rev.* 112 (2012) 869-932
- [80] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena and H.-C. Zhou, Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks, *Coord. Chem. Rev.* 255 (2011) 1791-1823
- [81] X. Lin, N. R. Champness and M. Schroeder, Hydrogen, methane and carbon dioxide adsorption in metal-organic framework materials
- [82] Y. He, W. Zhou, G. Qian and B. Chen, Methane storage in metal-organic frameworks, *Chem. Soc. Rev.* 43 (2014) 5657-5678
- [83] E. Barea, C. Montoro and J. A. R. Navarro, Toxic gas removal - metal-organic frameworks for the capture and degradation of toxic gases and vapours, *Chem. Soc. Rev.* 43 (2014) 5419-5430
- [84] Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, Perspective of microporous metal-organic frameworks for CO<sub>2</sub> capture and separation, *Energy Environ. Sci.* 7 (2014) 2868-2899
- [85] O. K. Farha and J. T. Hupp, Rational design, synthesis, purification, and activation of metal-organic framework materials, *Acc. Chem. Res.* 43 (2010) 1166-1175
- [86] G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour and I. Margiolaki, A hybrid solid with giant pores prepared by a combination of targeted chemistry, simulation, and powder diffraction, *Angew. Chem. Int. Ed.* 43 (2004) 6296-6301

- [87] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, A chromium terephthalate-based solid with unusually large pore volumes and surface area, *Science*, 309 (2005) 2040-2042
- [88] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, Porous, crystalline, covalent organic frameworks, *Science*, 310 (2005) 1166-1170
- [89] A. Zupal, I. Dominguez, J. Mayerová and J. Čejka, Functionalization of delaminated zeolite itq-6 for the adsorption of carbon dioxide, *Langmuir*, 25 (2009) 10314-10321
- [90] D. M. Ruthven, *Principles of adsorption and adsorption processes*, (1984)
- [91] R. Yang, *Gas separation by adsorption processes*, World Scientific (Singapore and River Edge, NJ), (1997)
- [92] F. Nouar, J. F. Eubank, T. Bousquet, Ł. Wojtas, M. J. Zaworotko and M. Eddaoudi, Supermolecular building blocks (SBBs) for the design and synthesis of highly porous metal-organic frameworks, *J. Am. Chem. Soc.* 130 (2008) 1833-1834
- [93] D. Alezi, A. M. P. Peedikakkal, Ł. J. Weseliński, V. Guillerm, Y. Belmabkhout, A. J. Cairns, Z. Chen, Ł. Wojtas and M. Eddaoudi, Quest for highly connected metal-organic framework platforms: Rare-earth polynuclear clusters versatility meets net topology needs, *J. Am. Chem. Soc.* 137 (2015) 5421-5430
- [94] O. Shekhan, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil and M. Eddaoudi, Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture, *Nature Commun.* 5 (2014) 4228
- [95] M. H. Mohamed, S. K. Elsaidi, T. Pham, K. A. Forrest, B. Tudor, Ł. Wojtas, B. Space and M. J. Zaworotko, Pillar substitution modulates CO<sub>2</sub> affinity in "mmo" topology networks, *Chem. Commun.* 49 (2013) 9809-9811
- [96] J. Merel, M. Clausse and F. Meunier, Experimental investigation on CO<sub>2</sub> post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites, *Ind. Eng. Chem. Res.* 47 (2008) 209-215
- [97] E. S. Rubin, H. Mantripragada, A. Marks, P. Versteeg and J. Kitchin, The outlook for improved carbon capture technology, *Prog. Energy Combust. Sci.* 38 (2012) 630-671
- [98] S. Yeh and E. S. Rubin, A review of uncertainties in technology experience curves, *Energ. Econ.* 34 (2012) 762-771
- [99] E. S. Rubin, Understanding the pitfalls of CCS cost estimates, *Int. J. Greenh. Gas Control*, 10 (2012) 181-190
- [100] E. S. Rubin and H. Zhai, The cost of carbon capture and storage for natural gas combined cycle power plants, *Environ. Sci. Technol.* 46 (2012) 3076-3084
- [101] M. T. Ho, G. W. Allinson and D. E. Wiley, Reducing the cost of CO<sub>2</sub> capture from flue gases using pressure swing adsorption, *Ind. Eng. Chem. Res.* 47 (2008) 4883-4890
- [102] S. Himeno, T. Komatsu and S. Fujita, High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons, *J. Chem. Eng. Data*, 50 (2005) 369-376
- [103] G. D. Pirngruber, P. Raybaud, Y. Belmabkhout, J. Čejka and A. Zupal, The role of the extra-framework cations in the adsorption of CO<sub>2</sub> on faujasite Y, *Phys. Chem. Chem. Phys.* 12 (2010) 13534-13546

- [104] S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores, *J. Am. Chem. Soc.* 130 (2008) 10870-10871
- [105] C. G. Coe, Structural effects on the adsorptive properties of molecular sieves for air separation, in *Access in nanoporous materials*, T. J. Pinnavaia and M. F. Thorpe (Eds.), Springer US, (2002), 213-229
- [106] S. Hayashi, M. Kawai and T. Kaneko, Dynamics of high purity oxygen PSA, *Gas Sep. Purif.* 10 (1996) 19-23
- [107] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, A chemically functionalizable nanoporous material  $[\text{Cu}_3(\text{tma})_2(\text{H}_2\text{O})_3]_n$ , *Science*, 283 (1999) 1148-1150
- [108] J. F. Eubank, H. Mouttaki, A. J. Cairns, Y. Belmabkhout, Ł. Wojtas, R. Luebke, M. Alkordi and M. Eddaoudi, The quest for modular nanocages: tbo-MOF as an archetype for mutual substitution, functionalization, and expansion of quadrangular pillar building blocks, *J. Am. Chem. Soc.* 133 (2011) 14204-14207
- [109] S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions, *Nature Commun.* 3 (2012) 954
- [110] T. Otowa, R. Tanibata and M. Itoh, Production and adsorption characteristics of MAXSORB: High-surface-area active carbon, *Gas Sep. Purif.* 7 (1993) 241-245
- [111] Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, Metal-organic frameworks as adsorbents for hydrogen purification and precombustion carbon dioxide capture, *J. Am. Chem. Soc.* 133 (2011) 5664-5667
- [112] C. Chen, J. Kim, D. A. Yang and W. S. Ahn, Carbon dioxide adsorption over zeolite-like metal organic frameworks (ZMOFs) having a sod topology: Structure and ion-exchange effect, *Chem. Eng. J.* 168 (2011) 1134-1139
- [113] Y. L. Liu, V. C. Kravtsov, R. W. Larsen and M. Eddaoudi, Molecular building blocks approach to the assembly of zeolite-like metal-organic frameworks (ZMOFs) with extra-large cavities, *Chem. Commun.* (2006) 1488-1490
- [114] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, *P. Natl. Acad. Sci. USA*, 103 (2006) 10186-10191
- [115] Xiang, Wu, ZhangZhang, Fu, Hu and ZhangZhang, A 3D canted antiferromagnetic porous metal-organic framework with anatase topology through assembly of an analogue of polyoxometalate, *J. Am. Chem. Soc.* 127 (2005) 16352-16353
- [116] S. Choi, J. H. Drese, P. M. Eisenberger and C. W. Jones, Application of amine-tethered solid sorbents for direct  $\text{CO}_2$  capture from the ambient air, *Environ. Sci. Technol.* 45 (2011) 2420-2427
- [117] Z. Bao, L. Yu, Q. Ren, X. Lu and S. Deng, Adsorption of  $\text{CO}_2$  and  $\text{CH}_4$  on a magnesium-based metal organic framework, *J. Colloid Interf. Sci.* 353 (2011) 549-556
- [118] N. Al-Janabi, P. Hill, L. Torrente-Murciano, A. Garforth, P. Gorgojo, F. Siperstein and X. Fan, Mapping the Cu-btc metal-organic framework (HKUST-1) stability envelope in the

- presence of water vapour for CO<sub>2</sub> adsorption from flue gases, *Chem. Eng. J.* 281 (2015) 669-677
- [119] N. Al-Janabi, A. Alfutimie, F. R. Siperstein and X. Fan, Underlying mechanism of the hydrothermal instability of Cu<sub>3</sub>(btc)<sub>2</sub> metal-organic framework, *Front. Chem. Sci. Eng.* 10 (2016) 103-107
- [120] J. B. DeCoste, G. W. Peterson, B. J. Schindler, K. L. Killops, M. A. Browe and J. J. Mahle, The effect of water adsorption on the structure of the carboxylate containing metal-organic frameworks Cu-btc, Mg-MOF-74, and UiO-66, *J. Mater. Chem. A*, 1 (2013) 11922-11932
- [121] O. Shekhah, Y. Belmabkhout, K. Adil, P. M. Bhatt, A. J. Cairns and M. Eddaoudi, A facile solvent-free synthesis route for the assembly of a highly CO<sub>2</sub> selective and H<sub>2</sub>S tolerant nisifsix metal-organic framework, *Chem. Commun.* 51 (2015) 13595-13598
- [122] H. H. Yi, H. Deng, X. L. Tang, Q. F. Yu, X. Zhou and H. Y. Liu, Adsorption equilibrium and kinetics for SO<sub>2</sub>, NO, CO<sub>2</sub> on zeolites FAU and LTA, *J. Hazard. Mater.* 203 (2012) 111-117
- [123] J. P. Boudou, M. Chehimi, E. Broniek, T. Siemieniowska and J. Bimer, Adsorption of H<sub>2</sub>S or SO<sub>2</sub> on an activated carbon cloth modified by ammonia treatment, *Carbon*, 41 (2003) 1999-2007
- [124] L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. Férey and G. De Weireld, Comparative study of hydrogen sulfide adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) metal-organic frameworks at room temperature, *J. Am. Chem. Soc.* 131 (2009) 8775-8776
- [125] V. Guillerm, Synthesis, functionalization and sorption properties of new hybrid porous solids, PhD Thesis, University of Versailles - St-Quentin-en-Yvelines, France (2011)

# Low concentration CO<sub>2</sub> capture using physical adsorbents: Are Metal-Organic Frameworks becoming the new benchmark materials?

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## Highlights

- A deep analysis on low concentration CO<sub>2</sub> removal using physical adsorbent is proposed.
- In-depth understanding of what is crucial criteria for materials to be used in CO<sub>2</sub> capture.
- MOFs have an valuable assets vs. benchmark materials such as zeolites
- High porosity is not necessarily important for traces and low CO<sub>2</sub> concentration capture.
- The uniformity of energetic adsorption sites is not critical parameter for traces CO<sub>2</sub> capture