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Low concentration CO₂ capture using physical adsorbents: Are Metal-Organic Frameworks becoming the new benchmark materials?

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Keywords

CO₂ capture, traces CO₂ removal, air capture, physical adsorbents, MOFs

Abstract

The capture and separation of traces and concentrated CO₂ from important commodities such as CH₄, H₂, O₂ and N₂, is becoming important in many areas related to energy security and environmental sustainability. While trace CO₂ concentration removal applications have been modestly studied for decades, the spike in interest in the capture of concentrated CO₂ 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. CO₂ 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 CO₂ 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 CO₂ capture performance using physical adsorbents. We also experimentally demonstrate a suitable

material model of Metal Organic Framework as advanced adsorbents with unprecedented properties for CO₂ capture in a wide range of CO₂ concentration. These recently developed class of MOF adsorbents represent a breakthrough finding in the removal of traces CO₂ 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. CO₂ 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”.^{1, 2} Among the various sources of CO₂, approximately 30% is generated by fossil fuel power plants and 25% from transportation sector, making them one of the major contributors to global warming.³ 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 CO₂ emissions occurred in the last decades (Figure 1). For the first time in human history, the CO₂ concentration reached 400 parts per million (ppm) in 2013, an unseen concentration since the atmospheric concentration has been monitored.⁴

It is widely recognized that development and implementation of novel and affordable technological solutions to reduce greenhouse gas (GHG) emissions, particularly CO₂, is a vital step toward fossil fuel-based sustainable energy.⁵ 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 CO₂ capture performance using physical adsorbents. We also demonstrate that MOFs could be a promising physical adsorbents for CO₂ with huge potential to replace existing benchmark materials for CO₂ capture at low concentration and moderate temperatures.

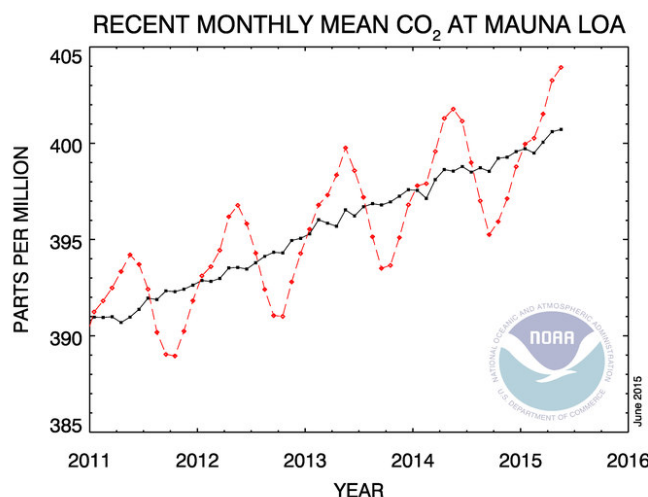


Figure 1. Monitoring of CO₂ emission at Mauna Loa in Hawaii showing that the CO₂ concentration surpassed 400 ppm in May 09 2013.⁴

Discussion

Gas separation using adsorption has gained considerable attention as a viable technology for the CO₂ removal of from different gas streams.⁵ This attention was motivated by the ability of solid adsorbents to reduce the required energy for activation/regeneration as compared to liquid amine scrubbing.⁶ The design of adsorbents for CO₂ capture must take into account the following parameters:

(i) **High CO₂ adsorption capacity:** Knowledge about the shape/steepness of equilibrium adsorption isotherms is essential for the evaluation of potential adsorbents. Suitable materials should exhibit high CO₂ 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 CO₂ affinity for a given adsorbent in comparison with benchmark CO₂ adsorbents.^{5, 7, 8} Porosity and energetics are the key factors influencing the CO₂ 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 CO₂ adsorbent will have a high rate of adsorption for CO₂ but not necessarily for the less absorbable gases (such as CH₄, H₂, N₂, etc.),

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

(iii) **High CO₂ selectivity:** The selectivity of the adsorbent for CO₂ 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. CO₂ selectivity is a product of a complex interplay between the porosity (pore size), kinetics and the charge density of the adsorbent.¹⁰ The charge density is directly related to CO₂ interactions with the adsorbent framework.^{11, 12}

(iv) **Mild conditions for regeneration:** The ability to regenerate the adsorbents is a key parameter in the selection of materials for CO₂ separation. Optimal interactions should be neither too weak nor too strong. Too weak bonding results in low CO₂ adsorption capacity at low pressure, but easy regeneration. Conversely, strong bonding induces high adsorption capacity but desorption will be difficult and costly.⁶ We focus our analysis and discussion on examples of materials (mainly physical adsorbents) that show the best compromise in terms of the intensity of CO₂ energetics¹³ as well as the uniformity of interactions.¹⁰

(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 CO₂ adsorbents.^{6, 13-16}

(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 CO₂ 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.¹⁷ The development of zeolites from discovery to commercialization took three to four decades.¹⁸ 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^{19,20} 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.²⁰⁻²⁴

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 CO₂ concentrations up to 50 % and a total pressure of 1 bar, in balance with N₂ and CH₄ and H₂), energetics, selectivity, stability and tolerance to water vapor. We also describe the physical separation mechanisms involved in the most promising CO₂ adsorbents.

Several types of MOFs have been proposed for CO₂ capture, including (i) MOFs with open metal sites,²⁵⁻³⁷ (ii) MOFs without open metals sites,³⁸⁻⁵⁵ (iii) MOFs with narrow pore size via interpenetration^{10,56,57} or shortening the size of the ligands,^{10,41} and (iv) MOFs decorated with specific functional groups, including (NH₂, OH, etc.).^{23,51,58-64} Functionalization of these types of MOFs may be carried out by post-synthetic modification (PSM) on the open metal sites,^{47,65-69} by post-synthetic metal exchange,⁷⁰ or direct use of functionalized ligands.^{23,51,58-60} The amines (or sulfonates) PSM of porous organic polymers (POPs, COFs, etc.), another subfamily of porous material, has also been

proposed.⁷¹⁻⁷⁴ 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 CO₂ capture.

For a more comprehensive account on CO₂ adsorbents, we direct the reader to excellent reviews by Sumida *et al.* 2012,²⁴ Choi *et al.* 2009⁷⁵ and Sayari *et al.* 2011.⁵ Reviews covering MOFs as gas separation and gas storage media are also highly recommended.⁷⁶⁻⁸⁴

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,²⁴ 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 CO₂ 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 activated⁸⁵ 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-100⁸⁶ and MIL-101.⁸⁷ COF-1⁸⁸ 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.^{24, 89} In this regard, MOFs exhibited better possibility in terms of pore size tunability as compared to zeolites and activated carbons,⁵ 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.¹⁸

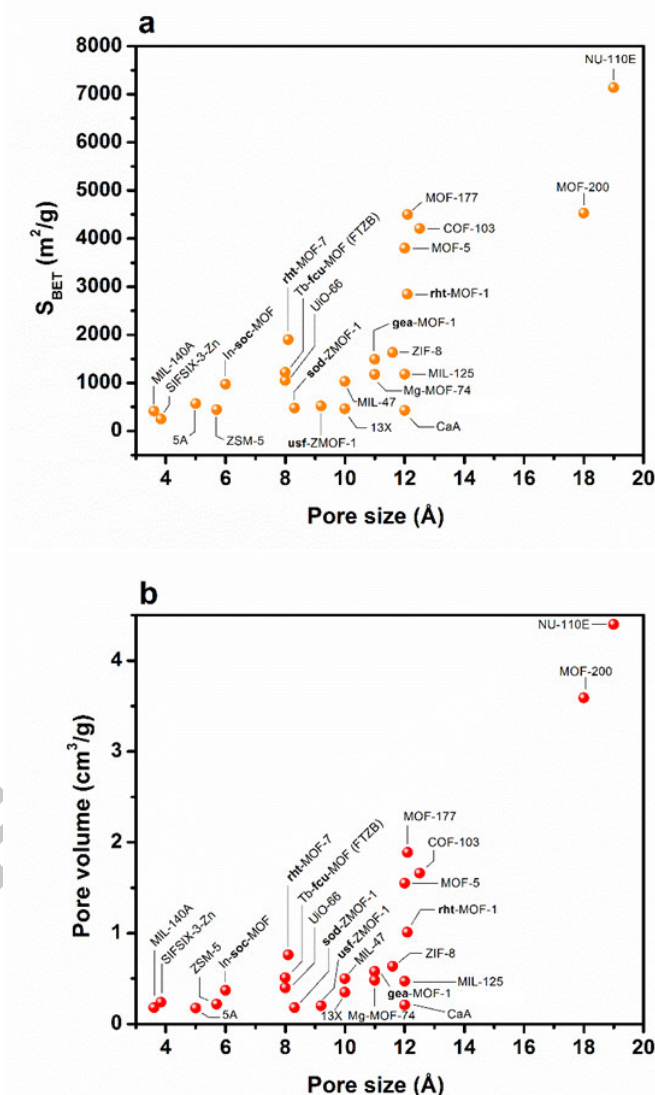


Figure 2. Correlation between pore size and (a) surface area, (b) pore volume for different materials.

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.⁹⁰ 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 CO₂ capture in particular, implemented the strategy of tuning the specific surface area as the main approach to enhanced CO₂ separation. For this purpose, the design and synthesis of new MOFs has been conducted based on isorecticular strategy using extended (larger) rather than shorter ligands. In this regard, CO₂ uptake at atmospheric pressure and above was the main reference parameter to evaluate CO₂ adsorbents. This single parameter strategy was shown to be not effective in achieving highly effective CO₂ microporous adsorbents at very low pressure.¹⁰

Microporous CO₂ adsorbents combining both high surface areas and large pore volumes with relatively large uniform micropore sizes (0.8-2 nm) exhibited high CO₂ uptake at medium and high pressures,²⁴ in addition to suitable (fast) kinetics⁹ but very low selectivity toward CO₂. Conversely, microporous adsorbents with small pore sizes (0.35-0.8 nm) had low surface areas, small pore volumes and comparatively very low CO₂ uptake at high pressure, but slightly higher CO₂ uptake and selectivity at very low pressure.²² Thus the relative enhancement of CO₂ 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 CO₂ selectivity via a purely molecular sieving mechanism driven mainly by gas diffusion.^{90,91} 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 CO₂ 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 CO₂ 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 CO₂ separation. However, it is very hard to isolate the effect of pore size from CO₂-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.

CO₂ interaction energy, intensity and distribution.

The CO₂ adsorbent interaction energy (Q_{st} of CO₂ adsorption or heat of adsorption) and its distribution over the pores is an intrinsic property that dictates the affinity of the pore surface to CO₂, which in turn plays a major role in determining the adsorption selectivity and the necessary energy required to release CO₂ during the regeneration step. With regard to the CO₂ interaction intensity, an optimal Q_{st} for CO₂ capture should be in the range of 30-60 kJ/mol which is indicative of fully reversible physisorption of CO₂ as well as moderately strong CO₂-sorbent interactions. In fact, this will allow mild regeneration conditions, which is a key property in the selection of materials for CO₂ separation. Obviously, this requirement is strongly dependant on the CO₂ concentration. The lower the CO₂ concentration in gas stream, the higher CO₂ interactions (or Q_{st}) is needed for effective CO₂ removal.

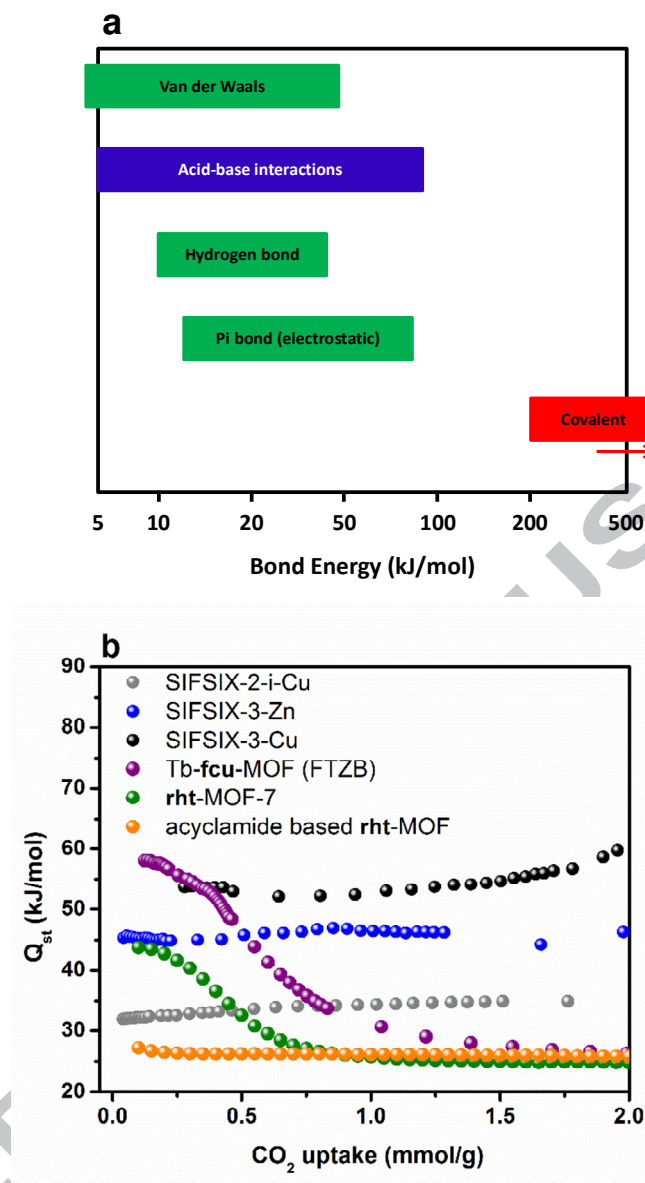


Figure 3. a) limits of reversible-non reversible CO_2 interactions, b) examples of Q_{st} of CO_2 adsorption vs loading for different adsorbents with (i) strong homogeneous interactions (black and blue), (ii) intermediate homogeneous interactions (grey) and weak homogeneous interactions (orange) and (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 CO₂ uptake and selectivity. Optimal interactions should be neither too weak nor too strong. Too weak bonding results in low CO₂ 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 CO₂ capture at different concentration is shown in Figure 4. In fact, the general tendency is that application with lower CO₂ concentration will require much higher selectivity toward CO₂ which will induce much higher interactions with the adsorbent framework. Besides, application having increased CO₂ concentrations will require much uniform energy distribution of effective adsorption sites to sustain high selectivity.

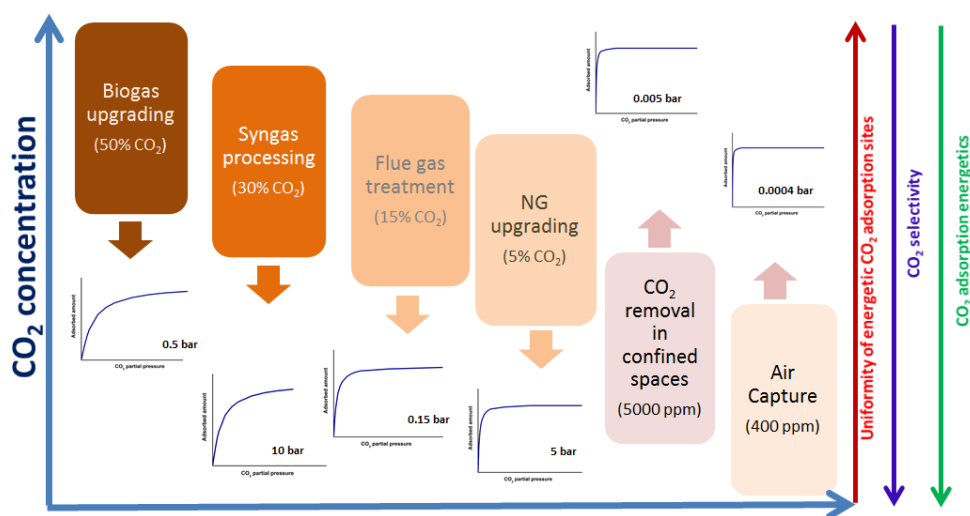


Figure 4. The relationship between the CO₂ isotherm shapes, CO₂ adsorption selectivity and CO₂ adsorption energetics intensity and distribution for CO₂ capture applications at different CO₂ concentrations.

In this regard, our group and others developed various strategies to enhance and homogenize the CO₂ adsorption energetics in MOF structures.^{31, 76-81} The examples of strategies mentioned here reflect

material synthesis strategies that generate desired CO₂ capture properties. One example of MOFs developed for the CO₂ capture purpose was based on modification of the **rht**-MOF platform developed initially by Eddaoudi and co-workers in 2008⁹² 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 CO₂ 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 CO₂ isotherms at very low partial pressure and relatively higher isosteric heat of adsorption but only at low loading (first CO₂ molecules adsorbed). This finding suggested that the addition of triazine and amine functional groups enhanced the interaction of **rht**-MOF-7 with CO₂ (green dots in Figure 3b); in addition, the Q_{st} was low enough to allow complete reversible desorption using the vacuum swing regeneration mode.²³

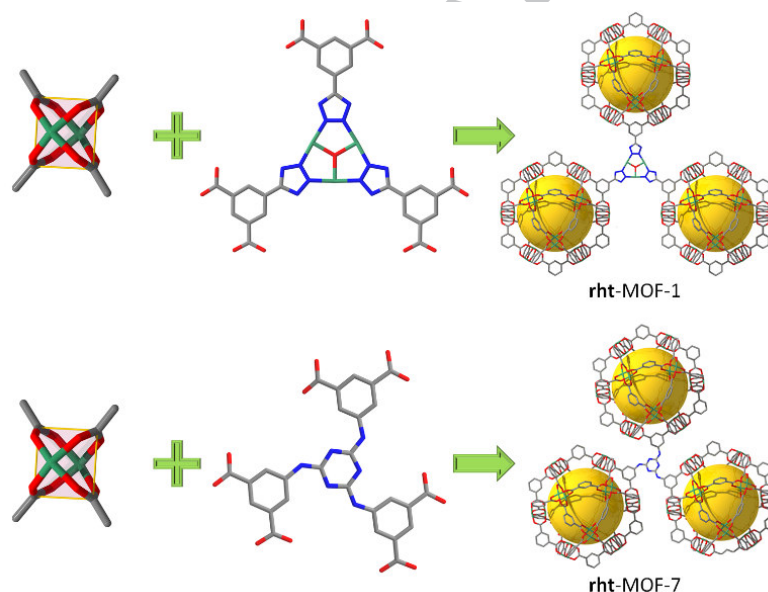


Figure 5. ***rht**-MOF-1 and **rht**-MOF-7 differ in the composition of the trigonal building block. The trigonal building block of **rht**-MOF-1(top), is a copper trimer connecting three 5-tetrazoleisophthalate ligands, whereas the trigonal building block in **rht**-MOF-7 (bottom) is a single hexacarboxylate 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).³¹ Other MOF based on rare-earth (**Y-pek**-MOF-1) having open metals sites but no tetrazolate and fluoro groups shows poor CO₂ capture ability at low pressure but exhibits one of the highest to date CO₂ volumetric uptakes of 25 bar.⁹³

This unique combination of properties for **fcu**-MOF was found to have an unprecedented effect on increasing the CO₂ 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 CO₂ uptake increased. It is important to mention that similar Q_{st} behavior was reported for MIL-100(Cr)²⁵ at the low coverage of 62 kJ/mol and other zeolites.¹¹⁻¹² In light of the high affinity of **rht**-MOF-7 and Tb-**fcu**-MOF for CO₂, it was reported that these materials may be used for highly selective CO₂ capture, but only for the removal of low CO₂ concentrations. Although these MOFs have very interesting properties, they may not be able to remove relatively high CO₂ concentrations, such as in the case of post-combustion capture (5-15% CO₂).

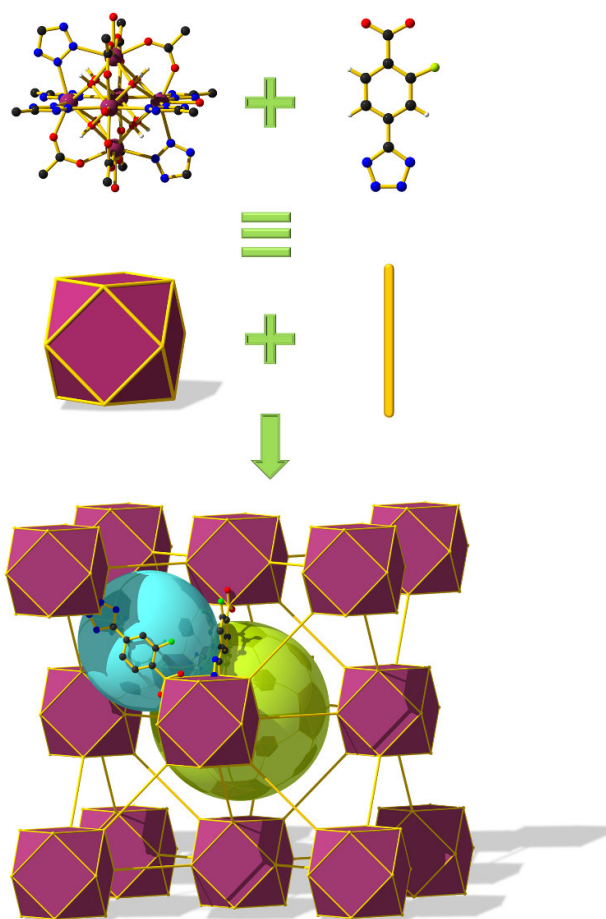


Figure 6. A ball-and-stick representation of a **fcu-MOF-1** compound, constructed from the assembly of 12 connected carboxylate/tetrazolate-based molecular building blocks (MBBs) linked together via a linear and hetero-functional 2-fluoro-4-(tetrazol-5-yl)benzoate (FTZB) organic linker, to give a 3-periodic **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 CO₂ affinity (affecting in turn the CO₂ selectivity) over a wide range of CO₂ concentrations (Figure 3b and 4). This requires a homogenous distribution of these strong adsorption sites to allow CO₂ adsorption with identical interaction strengths. In line with this, a new class of MOFs with periodically arrayed hexafluorosilicate (SiF₆) pillars^{10, 94} (Figure 7) characterized by one-dimensional channels with

different sizes and exhibiting uniform and strong energy distribution with increased CO₂ uptake (grey, blue, and black dots, Figure 3b) were recently reported. Other noticeable results were obtained using different pillars such as MF₆ (M=Ti, Sn)³⁸ or MO₄²⁻ (M=Cr, W, Mo)^{42, 95} for the construction of MOFs.

These SiF₆ based MOFs, particularly the isostructural analogues constructed using (the shorter) pyrazine ligand (Figure 7), showed unprecedented selectivity for CO₂. Uniform CO₂ 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 CO₂ adsorption loading.^{10, 94} 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 CO₂ capture.⁹⁶ It is important to mention that the higher is the CO₂ concentration in the stream, the steadier should be the adsorption energy (heat of adsorption). The synergetic relationship between the porosity (pore size) and the CO₂ adsorption interactions will be different from one application to another depending on the less absorbable (the more selective) molecule (N₂, CH₄, O₂, etc.) and will be discussed in the next section.

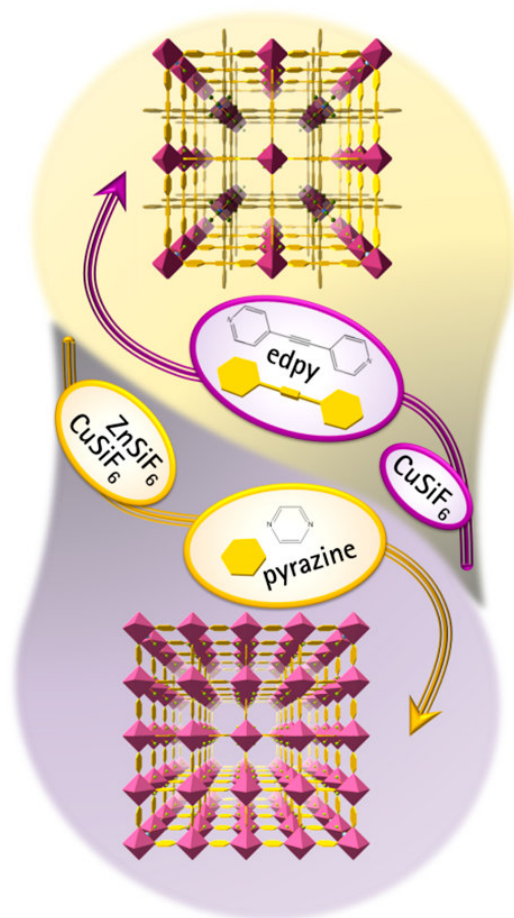


Figure 7. Pore size tuning in the channel structures of *SIFSIX-2-Cu-i*, *SIFSIX-3-Zn* and *SIFSIX-3-Cu*. (Up), *SIFSIX-2-Cu-i*; pores size 5.15 Å, BET apparent surface area (N_2 adsorption) 735 m^2/g . (Down), *SIFSIX-3-Zn*; pores size 3.84 Å, apparent BET surface area (determined from CO_2 adsorption 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 CO₂ capture,⁹⁷⁻¹⁰⁰ however few of them established a direct relationship between the cost of CO₂ capture and 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 CO₂ from flue gas using PSA should exhibit CO₂ selectivity above 500, combined with a working capacity in the range of 2 to 4 mmol/g for a CO₂/N₂ 10/90 mixture (Figure 8).¹⁰¹ 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 CO₂ versus other probe molecules (relatively larger and smaller than CO₂) is dictated mainly by the strength (regardless of the uniformity) of CO₂ interactions driving the separation process of CO₂ from less absorbable commodities such as CH₄, N₂, O₂ and H₂. Examples of adsorbents that use the equilibrium-based mechanism are activated carbon Maxsorb,¹⁰² zeolite Y,¹⁰³ Mg-MOF-74¹⁰⁴ (Figure 8), **rht**-MOF-7²³ and **fcu**-MOFs³¹ discussed earlier, as well as almost all MOFs reported for CO₂ capture.²⁴ These materials exhibit generally large average pore size (0.4 nm and higher).

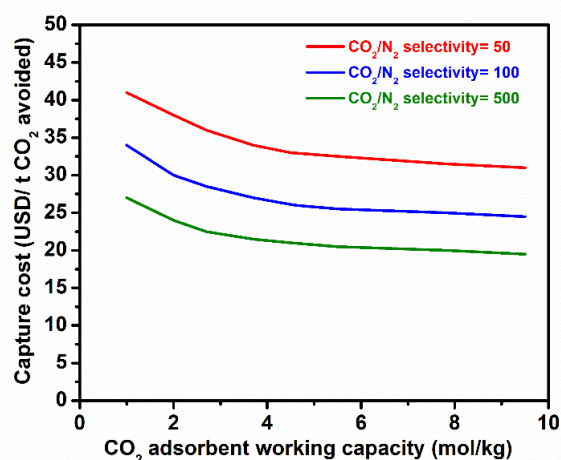


Figure 8. Relationship between the CO_2 capture cost, CO_2 selectivity, and working CO_2 capacity for solid sorbents.¹⁰¹

(ii) kinetics-driven sieving. When the pore size of the material is narrow enough (close to the molecular size of CO_2) kinetics driven molecular sieving is the most probable mechanism allowing the exclusion or slow diffusion of other larger probe molecules, such as CH_4 , N_2 and O_2 ,^{105, 106} thus providing materials with high kinetic selectivity, but not necessarily high productivity due to the possible small CO_2 uptake. Synthesis of materials with such narrow pore sizes is generally difficult to attain.^{24, 76-80}

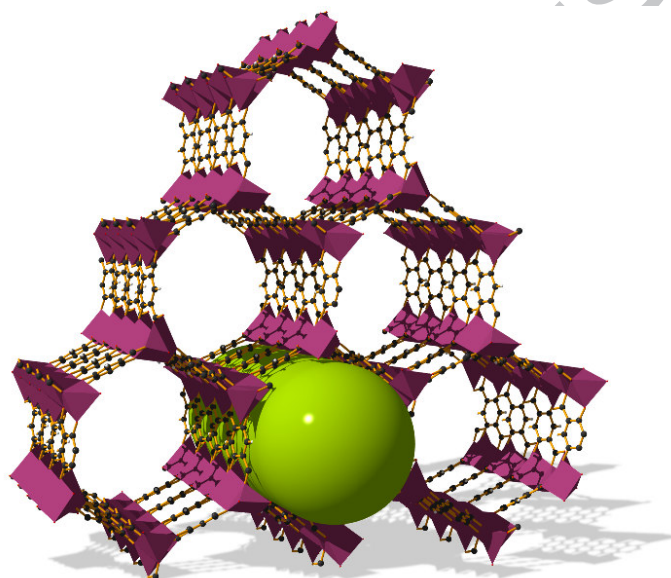


Figure 9. Structure of Mg-MOF-74 (Mg are purple polyhedra; C, black; O, red; H, light grey). One mono-dimensional honeycomb channel is highlighted by a green rod.

In case of MOFs adsorbents, it is evident from all reported approaches aiming to enhance the affinity for CO_2 that there is no single adsorption site approach that offers desired performances in terms of 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-1,¹⁰⁷ **tbo**-MOF-2,¹⁰⁸ and **rht**-MOF-1,⁹² the single site effect is not strong enough to promote the affinity (selectivity) to the required performances regardless the CO_2 concentration. Nevertheless, combining at least the effect of two adsorption sites

leads to obvious enhancement in CO₂ 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 CO₂ uptakes of various CO₂ adsorbents at 0.1 bar pressure as a function of porosity, energetics and selectivity. The synergetic effect and correlations involving porosity-charge density and CO₂ uptake are discussed in more detail in the next section.

In real-life applications, the volumetric CO₂ uptake is the parameter to consider rather than the gravimetric CO₂ 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 CO₂ 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 CO₂ at low pressure for the most promising materials. As shown in the figure, the SiF₆ compounds with narrow pore sizes and high charge densities were found to display very high volumetric uptake at very low pressures (up to 10% CO₂) compared with Maxsorb,^{8, 102} zeolite 13X,⁸ Mg-MOF-74¹⁰⁴ and UTSA-20¹⁰⁹. The SiF₆-based compounds exhibit higher CO₂ 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.^{10, 94} The mechanism that leads to these outstanding results is discussed in the next section.

Zeolites, activated carbon and MOFs generally exhibit very fast CO₂ 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 CO₂ (rapidly diffusing molecules) from other commodities, such as CH₄ and N₂ (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 CO₂ 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 CO₂ adsorption at low pressure and room temperature, CO₂ Q_{st} and CO₂ uptake at 0.1 bar pressure and CO₂ selectivity of the most promising/studied materials.

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

*Size of window; ^a determined from CO₂ adsorption; ^b determined from breakthrough measurements; ^c determined from gravimetric-densimetric gas analysis; NA: not available.

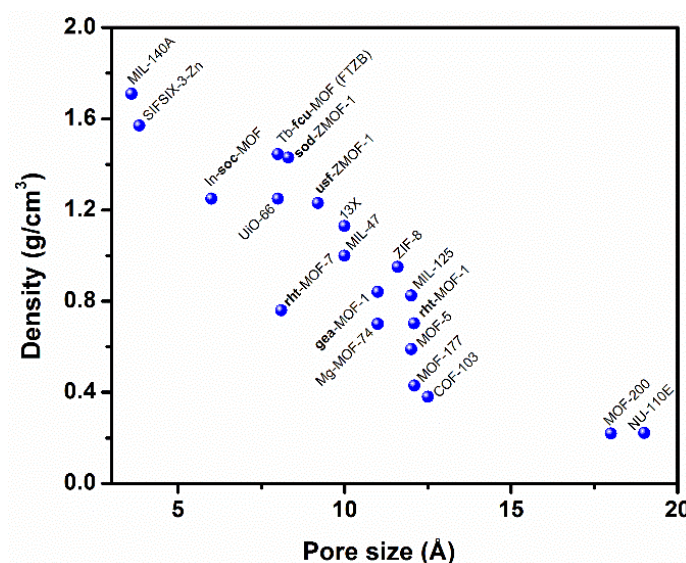


Figure 10. Correlation between the adsorbents pore size of and their corresponding crystal density.

Synergetic effects in MOFs with optimal pore size and charge density

Recently, a combined mechanism involving optimal thermodynamics (energetics) and kinetics for CO₂ capture at intermediate, low¹⁰ and trace CO₂ concentrations⁹⁴ was reported. This unique combination of high charge density and optimal pore size allowed the boundaries of CO₂ 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 CO₂, 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 CO₂ adsorption in the pores and exclusion of both larger (O₂, N₂, CH₄) and smaller (H₂) probe molecules, resulting in an extremely high selectivity toward CO₂, comparable to reactive amine bearing materials.⁵

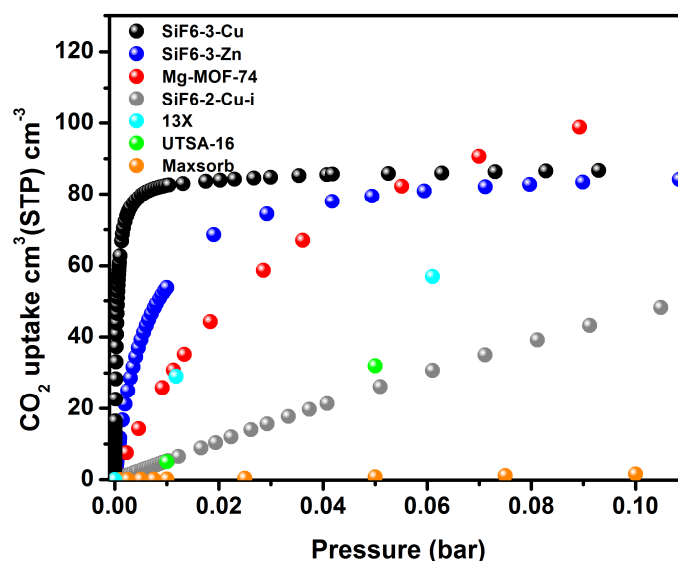


Figure 11. Volumetric uptake at low pressure of the most promising adsorbents

From a structural and chemical point of view, this finding showed clearly that for this particular case, the SiF₆-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 SiF₆, favourable to CO₂ attraction. These structural and chemical features afforded the construction of physical adsorbents with high selectivity toward CO₂ and suitable CO₂ uptake and energetics. A material with such attributes in addition to suitable kinetics, permitting a short cycling time (easy regeneration), could lower the CO₂ capture cost to as little as 20 USD/ton of CO₂ 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 CO₂ capture in particular. For the particular case of SiF₆-based MOFs, upon the increase of the channel size from 3.84 to 5.15 Å in SiF₆-Cu-bipyridine, constructed using a bipyridine linker, the charge density decreased leading to a drastic decrease in CO₂ selectivity.¹⁰ 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_{st}* of 53 KJ/mol. Accordingly, the CO₂ uptake was dramatically increased, particularly at trace concentrations and low CO₂ partial pressure.⁹⁴ This finding was reported to be the first ever high CO₂ uptake (1.24 mmol/g) at

trace CO₂ concentration (400 pm) 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)^{67, 116} at 298 K (for example TRI-PE-MCM-41(1 mmol/g)).⁸ 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.^{29, 104, 117} In fact, the combination of open magnesium sites together with the hydroxyl groups (in 10 Å channel size) led to significantly high CO₂ uptake but not as high CO₂ selectivity as in the case of **SIFSIX**. The relatively lower CO₂ selectivity for Mg-MOF-74 compared to SiF₆-based MOFs can be logically explained by the relatively high channel size (10 Å vs. 4.9 Å and 3.84 Å for SiF₆-Cu-bipyridine and **SIFSIX**-3-Zn) and the declining Q_{st} as a function of CO₂ loading.

In an attempt to understand the relationships between the key properties of the materials (CO₂ uptake, energetics selectivity and structural properties) desirable for CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ adsorption loading as in the case of the **SIFSIX**

compounds. In cases when the Q_{st} is not steady as a function of CO_2 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_2 affinity and selectivity. This parameter considers only the equilibrium intrinsic properties of adsorption in relation to CO_2 and not the other less absorbable gases (O_2 , N_2 , CH_4 , H_2).

Table 2. Correlation between the synergy indicator as a function of selectivity for different CO_2 adsorbents

CO_2 adsorbent	Average Q_{st} kJ/mol	CO_2/N_2 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_2 and reflects the occurrence of the synergetic effect, which has a direct impact on increasing the affinity toward CO_2 . This parameter is broad in definition and does not take into consideration the CO_2 diffusivities and the less absorbable molecules such as O_2 , N_2 , CH_4 and H_2 in the particular case of CO_2 capture.

We suggest that the combination of the correct structural and chemical composition parameters is a major requirement in the design of MOFs for CO₂ capture. This finding should drive the work on materials chemistry for general gas separation applications and CO₂ capture in particular in the next years.

Effect of water vapor on these parameters at low CO₂ partial pressure

The tolerance of CO₂ adsorbents to water vapor is one of the requirements for optimal operation of CO₂ capture processes using adsorption technologies.¹¹⁸⁻¹²⁰ It implies that CO₂ 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 zeolites⁵ (for example, Faujasites X and Y, zeolite A, etc.) and MOFs with open metal sites,²⁴ 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 CO₂ uptake by MIL-100(Fe) (with open metal sites) was improved in the presence of 40% relative humidity.³² Conversely, the effect of moisture on hydrophobic materials such as activated carbons⁵ and MOFs without open metal sites¹⁰ will be minimal or insignificant. Another case where the presence of moisture induced enhanced CO₂ adsorption properties were amine bearing materials,⁵ such as mesoporous silica^{9, 14} and MOFs.²⁴ The observed enhancement in these systems was due to the occurrence of chemical adsorption via the formation of bicarbonate.⁵ 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 SiF₆-based MOFs,¹⁰ both the hydrophobicity and the high and uniform interaction with CO₂ are the main driving forces for their high tolerance to moisture when SiF₆-pyrazine- based MOFs are exposed CO₂.

In spite the large amount of studies on MOFs stability toward water vapor and its effect on CO₂ adsorption properties, it is still not recognised that these promising MOF materials, such as **SIFSIX**, for CO₂ capture to be recyclable under hundreds of cycles. The main reason is that certain SiF₆

assembled with pyrazine ligand could undergo phase transition from 3D to 2D structures upon extensive exposure to water (without presence of CO₂).¹²¹ Nevertheless if a gas pre-drying step is implemented, these materials are still very powerful for traces and low CO₂ concentration removal. Further work will be necessary to overcome this phase change.

Thermal stability and effect of other impurities (NO_x, SO_x, H₂S, 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 CO₂ 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 CO₂ separation agents in the presence of impurities such as SO₂ or H₂S 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,¹²² activated carbons¹²³ and few MOFs (Cr^{III}, V^{IV}, Al^{III} and Ti^{IV} based)^{61, 124, 125} were shown to be stable in the presence of SO₂, H₂S and water vapor. However, some Zn^{II}- and Fe^{III}-based MOFs with open metals sites were shown to form zinc¹²⁵ or iron¹²⁴ sulphide when exposed to H₂S.

Because of the scarcity of toxic gases adsorption data, developing CO₂ adsorbents in the presence of H₂S and SO₂ remains challenging and unexplored. Further work is necessary to understand the nature of MOFs that capture CO₂ in the presence of these gases.

Conclusions

The ultimate objective of this work is to discuss realistic points, based on existing CO₂ adsorbents from the open literature, that drive the development of materials suitable for CO₂ capture mainly at very low concentration. The aim of this review was not to refer to abundant work in materials chemistry concerning the CO₂ separation but rather to analyse the most promising CO₂ 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 CO₂ 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 CO₂ removal at low CO₂ partial pressure. The optimal strength of CO₂ interactions is a key parameter for designing materials for CO₂ capture. Not only the strength of these interactions is important, but also its steadiness over a wide range of CO₂ adsorption uptake, to ensure highly selective operations over a wide range of CO₂ 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 CO₂ to achieve the desired adsorption attributes capable of CO₂ capture efficiency. This new combined approach was shown to be possible to achieve experimentally and effective using MOFs namely, SiF₆-pyrazine compounds which are considered as a model materials for low CO₂ 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.

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Low concentration CO₂ capture using physical adsorbents: Are Metal-Organic Frameworks becoming the new benchmark materials?

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Highlights

- A deep analysis on low concentration CO₂ removal using physical adsorbent is proposed.
- In-depth understanding of what is crucial criteria for materials to be used in CO₂ capture.
- MOFs have an valuable assets vs. benchmark materials such as zeolites
- High porosity is not necessarily important for traces and low CO₂ concentration capture.
- The uniformity of energetic adsorption sites is not critical parameter for traces CO₂ capture