A scalable robust microporous AI-MOF for post-combustion carbon capture

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Abstract

Adsorptive separation via scalable and inexpensive adsorbents is now considered among the credible alternative solutions for post-combustion carbon mitigation via selective physisorption of CO₂. As industrial gas streams contain many times water vapours, the use of sorbents showing limited detrimental effect of humidity on the working capacity in the operating conditions is considered as a major advantage contributing to lowering the operating costs and/or accelerating the capture process. Here we report on a robust microporous aluminum tetracarboxylate framework, MIL-120(AI)-AP, (MIL and AP refers to Materials from Institute Lavoisier and for Ambient Pressure synthesis, respectively), which possesses high CO_2 uptake (1.9 mmol g⁻¹ at 0.1 bar, 298 K) due to a favorable pore architecture combining high density of μ_2 -OH groups and stacked aromatic rings, close to the performances of the benchmark CO₂ physisorbent, CALF-20 (CALF stands for Calgary Frameworks). Advanced in situ synchrotron X-ray diffraction measurement together with GCMC simulations allowed to get deeper insights into the preferential sites that the structure of MIL-120(AI) offers for a favorable CO₂ capture, while revealing the importance of the μ_2 -OH and their accessibility to CO₂ for controlling the gas uptakes at low pressure. This supports further the great potential of MIL-120(AI)-AP towards post-combustion capture. Meanwhile, Q_{st} (CO₂) value of MIL-120(AI)-AP (44 kJ mol⁻¹) prone to relatively low energy penalty for full regeneration compared to amine-based solutions (90~140 kJ mol⁻¹) and to their stability limitations. Moreover, a phase transition from monoclinic to triclinic occurs due to partial removal of free water molecules, with ca. 40% water molecules still remaining trapped between AI oxo/hydroxo chains, enabling additional interactions with CO₂ molecules during adsorption step. Finally, an environmentally friendly ambient pressure green route, relying on the use of inexpensive raw materials, was optimized to prepare the MIL-120(AI)-AP at kg-scale with high yield and high quality. The MOF was further shaped as millimeter (mm)-sized beads with inorganic binders while first evidences of its efficient CO_2/N_2 separation ability were validated by breakthrough experiments, thus suggesting the high potential of this MOF in a view of integration into an industrial scale CO₂ capture process.

1.1 Introduction

Carbon capture and storage (CCS) is envisioned to significantly tackle increasing levels of atmospheric CO₂ achieving the prevention of global warming.¹ Among the current potential carbon capture technologies, post-combustion capture of flue gas emitted from power plants and carbon-intensive industries as steel or cement industries is considered as a feasible and economically viable process as it might be potentially retrofitted to the existing fleet of coal-fired power stations or industrial plants.² So far, aqueous amine solution through a combination of chemical and physical absorption affinity with CO₂ molecule, is the most applicable and mature technology for CO₂ capture.^{3,4} However, raising important environmentally issues as well as a high energy penalty, up to 60-80% of total thermal energy consumption for a coal-fired power plants, in the worst case.⁵ Physisorptive CO₂ capture as an efficient low-heat technology is thus expected to provide much lower energy consumption for regeneration due to the energy consumption of rich amine solutions regeneration (87 kJ mol⁻¹ for the most efficient current solvents).^{6,7}

Porous solid adsorbents, such as zeolites, are potential candidates due to their excellent working capacity and selectivity of CO₂ over other gases present in the industrial gas stream.^{8,9} However, despite their relatively low production cost and high thermal/chemical stability, the detrimental competitive adsorption of water molecules significantly decreases their CO₂ working capacity and selectivity as well as require very high temperature regeneration to desorb free water.9 Alternatively, aminefunctionalized porous materials or porous organic materials are suitable alternative candidates.¹⁰⁻¹² For instance, Long et al. have grafted tetraamine chains on the large pores $Mg_2(dobpdc)$ (dobpdc = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) through postsynthesis modification method, improving the efficiency in CO₂ capture under harsh conditions relevant to natural gas flue emissions.¹³ Most notably, the relatively higher thermal stability of the tetraamine-functionalized framework was exploited, enabling a regeneration through a direct steam contact with steam, resulting in a significant energy savings over the conventional methods. However, the relatively high energy penalty for the regeneration, long term stability issues, lack of sustainability and/or challenges in the up-scaling make these classes of solids questionable for real industrial separation processes.¹⁴ Robust metal-organic frameworks (MOFs), built either from high valence metal oxoclusters/chains and poly-carboxylates or phosphonates, or alternatively metal(II) poly-azolates, are also candidates for CO₂ capture. Their high customizability enabling a precise tuning and functionalization of the pore structure, has been intensively investigated for selective gas separation applications.¹⁵⁻¹⁷ Indeed, one can either for instance easily tune their hydrophobic character to mitigate the negative effect of water and/or modify them with exogenous chemical species for enhanced performances. Very recently, CALF-20, a microporous robust Zn₂(1,2,4-triazolate)₂(oxalate) material (CALF stands for Calgary Frameworks) has emerged as the new benchmark CO₂ sorbent with physisorptive mechanism for the CO₂ capture from cement flue gas.¹⁸. Thanks to its relatively moderate heat of adsorption (ca. 39 kJ mol⁻¹) (compared to chemisorption in amine based-solutions), excellent CO₂ capacity in post-combustion conditions (2.47 mmol g^{-1} at 0.1 bar and 298 K), and moderate hydrophilicity, it was exploited, once coated on a rotary bed, for the efficient capture of CO₂ in presence of moisture up to ca. 25-30% RH (while

structured with polysulfone-based binder). This MOF was also proven to be scalable at the ton-scale using an ambient pressure optimised protocol. Its production at the hundred tons scale is now ongoing in order to be integrated into larger scale industrial applications. Fluorinated MOFs, such as SIFSIX and TIFSIX based MOFs or NbOFFIVE-1-Ni, are also considered as potential candidates for the post combustion capture due to their outstanding capacity and CO₂/N₂ selectivity.¹⁹⁻²² However, their long-term hydrolytic stability is in most cases limited while their large-scale production is still hampered with strong safety issues, due to the potential formation of HF. From the material cost point of view, aluminium based MOFs (AI-MOFs), if relying on cheap commercial polycarboxylic acids, and inexpensive AI metal source, whenever they can endow comparable CO₂ adsorption performance with CALF-20, stand themselves as promising candidates for CO₂ capture. One could highlight additional potential robust MOFs candidates, such as A520 or Al fumarate,^{23,24} MIL-91(Ti),²⁵ MIL-160(AI),²⁶⁻²⁸ (MIL stand for Materials from Institute Lavoisier) which can be obtained easily in kilogram scale product via facile, green and one-pot synthesis procedure and simply manufactured as structured adsorbents, e.g., pellets, beads, monoliths, fibres. However, their CO₂ capacity is significantly lower compared to the benchmark CALF-20.

In this regard, we investigated the performance of other existing microporous Al-based We selected the robust microporous aluminum 1,2,4,5-benzene MOFs. tetracarboxylate framework MIL-120(Al), thanks of its excellent CO_2 capture efficiency at relatively low pressure (1.9 mmol g^{-1} at 0.1 bar at 298 K), comparable to the best amine-free benchmark CO_2 adsorbents as well as its cheap composition. Indeed, the high affinity of this MOF to CO₂ was initially briefly described by Loiseau et al. more than a decade ago.²⁹ Thus, due to its promising performances, we have further explored this MOF through an in-depth joint experimental/computational study to shed light on the key features driving its remarkable CO₂ adsorption performances. GCMC simulations showed that the high density of μ_2 -OH groups exposed to the channels plays a pivotal role on the CO₂ adsorption at very low pressure, with a relatively moderate (isosteric) heat of adsorption (Q_{st}) (44 kJ mol⁻¹) (comparable to benchmark CO_2 physisorbents). This MOF also possesses very high CO_2/N_2 selectivity of 95 and 122 for the corresponding binary mixture $15CO_2:85N_2$ and $5CO_2:95N_2$ respectively at 0.1 bar and 298 K, as estimated based on the ideal adsorbed solution theory (IAST). Indeed, all these features confer to MIL-120(AI) a high potential for the CO₂ capture from flue gases. Furthermore, as this material was initially made under hardly scalable hydrothermal conditions, we developed an alternative eco-friendly ambient-pressure (AP) synthesis procedure relying on cost-effective chemicals suitable leading to the scale-up of MIL-120(AI)-AP, with a crystallinity and porosity comparable to the hydrothermal sample, denoted MIL-120(AI)-HP (HP stands for High Pressure). An in situ synchrotron Powder X-Ray Diffraction (PXRD) experiments was carried out to better understand the structural behavior of these microporous frameworks and revealed that unlike MIL-120(AI)-HP, MIL-120(AI)-AP exhibits a phase transition, from monoclinic to triclinic, during the activation step and removal of the guest (water) molecules. It also indicated that a significant amount of free water molecules (ca. 35-40% crystallographic occupancy) remains trapped between AI hydroxo chains, resulting into additional interaction with CO₂ molecules during their adsorption. Finally, the environment friendly synthesis, high yield, easy processability to the kilogram scale was exploited to produce enough material for shaping prior to breakthrough separation tests that confirm the efficient adsorptive separation of CO₂/N₂ using MIL-120(AI)-AP.

1.2 Results and discussion

1.2.1 Structure, synthesis optimization and adsorption performances

The single crystal structure of MIL-120(AI) or Al₄(OH)₈(C₁₀O₈H₂) xH₂O (x=4.8~5) was reported more than a decade ago by Loiseau et al., the MOF being prepared through a hydrothermal route.³⁰ Its inorganic sub-unit is composed of Al(OH)₄O₂ octahedra, with oxygen atoms from 4 hydroxyl groups and 2 different carboxylate groups belonging 2 neighboring organic ligands (pyromellitate or 1,2,4,5-benzenetetracarboxylate, abbreviated BTeC⁴⁻). This results in infinite AI hydroxo-chains, very uncommon in AI-MOFs, built of *trans-cis* edge sharing AI(OH)₄O₂ octahedra linked via double μ_2 -OH bridges. These chains are linked together through the carboxylates of the BTeC⁴⁻ (hereafter BTeC), thereby generating a three-dimensional framework that delimits one dimensional (1D) channels running along [001] direction with a section dimension of about 5.4 Å x 4.7 Å (Fig. 1A). Therefore, MIL-120(AI) provides two-fold denser hydroxyl polar groups than other corner-sharing modes commonly present in most Al-MOFs (Fig. 1B), which could be beneficial for enhanced CO_2 interactions with the framework. Another feature that has motivated us to explore the capabilities of this MOF for the CO₂ capture is the parallel arrangement of the aromatic groups of the BTeC with a distance ranging between 6.5 -7.0 Å (out of Van Der Waals radii) (Fig. 1C), recently predicted by Smit et al. as ideal adsorbaphore for CO₂.³¹

Interestingly, the AI/L (here, L = BTeC) ratio in the structure of MIL-120(AI) is as high as 4, much higher compared to other Al-MOFs, prone to enhanced chemical and thermal stabilities as well as to relatively lower costs, since it is estimated that for MOFs, the production cost is intimately correlated to that of the usually expensive organic ligand.³² Although the high-pressure CO₂ adsorption isotherm reported in 2009 showed already promising performances in terms of CO₂ uptake, there were neither clear evidence of the CO₂ capacity at low pressure (i.e., 0.2 bar and < 1 bar), CO₂/N₂ selectivity nor any in-depth investigation to understand the steep uptake at relatively low pressures. During the course of our study, a first study dealing with the CO₂ postcombustion properties of this MOF has been reported by Stylianou et al.^{33,34} Noted that in these two previous reports, the studied MOF samples were obtained by hydrothermal synthesis (i.e., 483 K), limiting the chances of synthesis scalability. In this work, we first prepared MIL-120(AI) following the reported hydrothermal synthesis, MIL-120(AI)-HP, and collected the CO₂ adsorption data at 298 K. Indeed, the obtained isotherm confirmed, as expected, the promising CO_2 capacity at low pressure (Fig. 1C). Motivated by these attractive adsorption performances, it was of a crucial importance to obtain this MOF following a simpler, safer, scalable and cost-effective synthesis protocol in view of the large-scale production and further exploitation in real separation processes. Therefore, we have carried out a thorough study to set up an optimized green synthesis at ambient pressure. It is important to note that reacting H₄BteC with Al(III) precursors can lead to different MOFs other than MIL-120(Al), namely MIL-118(AI) and MIL-121(AI).35



Figure 1. Crystal structure of MIL-120(AI). (A) General view along the *c* axis highlighting the MOF channels (water molecules were omitted for clarity). (B) Constitutive AI hydroxo-chains built of *trans-cis* edge sharing AI(OH)₄O₂ octahedra. (C) Representation of one channel emphasizing with its highly confined environment (represented by the yellow tube) due to dense network of μ_2 -OH and staked phenyl rings of BTeC. Color code: AI(OH)₄O₂, grey polyhedra; C, grey; O, light red; H, white. In (C), one of the chains is highlighted using purple polyhedra.

While both are based on more common infinite chains of trans-connected cornershared aluminum-centered octahedra, similar to that of MIL-53(AI)'s, in the case of MIL-121(AI), the ligand only involves 2 carboxylate groups to bridge the chains, leaving the remaining two others free, pointing towards the center of the channels. If the ratio AI/H₄BTeC/H₂O has a direct influence on the crystallization of the different phases, the initial pH of the reaction mixture was shown to be of major importance. Indeed, it was demonstrated, in the previously studied hydrothermal conditions, that the occurrence of MIL-120(AI), showcasing the highest density of μ_2 -OH and up to 4-fold higher Al/BTeC ratio, is driven by a basic pH > 10 (ca. 12 versus ca. 2 and 1.4 for MIL-118(Al) and MIL-121(AI), respectively). These observations were capital for the tailoring of the new synthetic conditions for the optimized synthesis under ambient pressure conditions. Thus, we selected less acidic Al-precursors to promote the formation of edge-sharing Al-chains and MIL-120(Al) phase, while we varied the Al/H₄BTeC ratio, the concentration and additives to control the pH/solubility). More details are provided in Table S1. The use of AI(OH)₃ systematically led to the formation of the MIL-121(AI) phase. Despite the basic nature of this precursor, its lack of solubility in water promoted acidic pHs due to the (faster) gradual dissolution of the H₄BteC. To reach higher solubility of AI precursor, we first explored the AI(OH)(OAc)₂ (OAc stands for acetate) which has weakly basic character and a relatively good solubility in water, while the released acetate groups can also contribute to control the crystallization process (as modulators). Interestingly, all the trials with different Al/H₄BteC ratios (ranging from 2 to 8) yielded MIL-120(AI) phase as a sole, pure and well crystallized structure, whereas the pH at the end of the reaction was neutral. It should be, however, noted that monitoring the starting pH can be misleading because of the higher solubility of the

H₄BTeC compared to the Al(OH)(OAc)₂ at room temperature. These first optimizations were carried out in 15-30 mL of water leading to ca. 1 g product. We then opted to reproducing similar synthetic conditions reacting stoichiometric precursors amounts (4Al/1BTeC: 80 mmol/20 mmol) in 300 mL in water to yield ca. 10 g of MIL-120(Al)-AP, which was further thoroughly washed in warm water before being analyzed and proven of high purity by a large set of complementary characterizations including PXRD, Fourier-Transform Infrared (FT-IR) spectroscopy, Thermal-Gravimetric Analysis (TGA), N₂ adsorption at 77 K, CO₂, and water adsorption at 298 K (see supplementary information for details, Fig. S1).

Indeed, the PXRD pattern of the synthesized sample is an excellent agreement with the theoretical one calculated from the crystallographic structure, with a slightly broader profile compared to that of MIL-120(AI)-HP, mainly due to the difference of particle sizes (i.e., few microns versus submicron, for the HP and AP syntheses, respectively). FT-IR spectra and TGA analyses (Fig. S1B-C) also showed very good agreement for the samples obtained from hydrothermal and ambient pressure methods, although the steps of the TGA curves were slightly less well defined in the case of MIL-120(AI)-AP and a total decomposition occurring ca. 50°C lower compared to MIL-120(AI)-HP. Unexpectedly, the N2 isotherms measured at 77 K (Fig. S1D) showed a significant difference in uptakes (almost 2-fold higher) in favor of MIL-120(AI)-AP, with a calculated BET surface area for the latter of about 590 m²·g⁻¹. A possible explanation could be associated to a slightly less good purification (i.e., free ligand removal and/or discrepancies in structural behavior at very low temperature due to differences in particles sizes. The high density of μ_2 -OH groups in this structure confers to MIL-120(AI) a hydrophilic character, consistent with the experimental water adsorption isotherms of MIL-120(AI)-HP and MIL-120(AI)-AP at 298 K (Fig. S1E). Furthermore, single-component adsorption isotherms of CO₂ and N₂ were carried out at 298 K. As shown in Fig. 2A, the CO₂ uptake in MIL-120(AI)-AP was 1.90 mmol g^{-1} $(73.1 \text{ cm}^3 \text{ cm}^{-3})$, based on the crystallographic density, 1.57 cm³ g⁻¹, as calculated for the reported CIF obtained for single crystal XRD, without taking into account any guest molecule) and 3.87 mmol g⁻¹ (148.8 cm³ cm⁻³, STP) at 0.1 and 1 bar, respectively, which is comparable although slightly higher, to that of the hydrothermally synthesized sample and the very recent reported results.³³ Noteworthy, the occurrence of a small step at 0.35 bar of CO₂ occurs only in the case of MIL-120(AI)-HP. Additionally, under the same measurement conditions, MIL-120(AI)-AP adsorbed a much lower amount of N_2 (0.04 and 0.33 mmol g⁻¹ at 0.1 and 1 bar, respectively). Estimation of the CO₂/N₂ selectivity was performed by applying the ideal adsorbed solution theory (IAST) model (Tables S2-3) and revealed for MIL-120(AI)-AP and the corresponding binary mixture, $15CO_2$:85N₂ and $5CO_2$:95N₂, a CO_2/N_2 selectivity as high as 95 and 122 at 0.1 bar and 298 K, respectively (Fig. 2B). This confirms the high potential of MIL-120(AI)-AP for the separation of CO₂ from flue gases (5-15% CO₂) such as those emitted from industrial plants or other sources. Meanwhile, coverage-dependence of the isosteric enthalpy of adsorption (Q_{st}) was determined for CO₂ in MIL-120(AI)-AP by applying the Clausius-Clapeyron equation to single component adsorption isotherms collected at 288 K, 298 K, and 308 K (Fig. S2). The experimental Q_{st} of CO₂ at near-zero coverage was found to be 44 kJ mol⁻¹ (Fig. 2C), which is slightly higher than that reported previously for benchmark CO₂ adsorbent CALF-20 (39 kJ mol⁻¹). The Q_{st} gradually decreases with the increase of CO_2 loading then reaches a mean-value of 38 kJ mol⁻¹. The overall results strongly suggest the good CO₂ capture performance of this MOF due to its high CO₂ working capacity, high CO₂/N₂ selectivity, while still exhibiting a low energy consumption for regeneration. As highlighted in Fig. 2D and Fig. S3, it is noteworthy to mention that at 0.1 bar and 1 bar at 298 K, the CO₂ uptake of MIL-120(AI)-AP is comparable to those of benchmark CO₂ adsorbents (if not higher in some cases), such as MOF-based adsorbents (CALF-20,¹⁸ Mg-MOF-74,³⁶ UTSA-16,³⁷ ALF (AI-Formate MOF),³⁸ SIFSIX-3-Cu,³⁹ mmen-Mg₂(dobpdc),¹³ SIFSIX-3-Zn,²¹ Ni-MOF-74⁴⁰) as well as several cationic zeolites (NaX,⁴¹ ETS-4/10,⁴² ETS stands for Engelhard Titanium Silicates).



Figure 2. CO₂ adsorption performances of MIL-120(AI)-HP and MIL-120(AI)-AP at 298 K. (A) CO₂ (in red and blue, respectively) and N₂ (in grey) adsorption isotherms at 298 K. Zoom on the step region is given in the inset. (B) IAST selectivity at different compositions for MIL-120(AI)-AP. (C) Isosteric heat of sorption *versus* CO₂ uptake for MIL-120(AI)-AP. (D) Comparison of volumetric and gravimetric CO₂ uptakes at 0.1, 1 bar, at 298 K between MIL-120(AI)-AP and benchmark adsorbents including MOFs and zeolites. The volumetric uptake was calculated using the crystallographic density.

As mentioned earlier, MIL-120(AI)-AP possesses a high ratio of metal to ligand (4:1), which is (by far) higher than the other MOFs. Since the ligand is the main limiting component in MOFs production cost,³² this shall be highly advantageous for a large-scale industrial synthesis. In fact, if the performances are crucial features for a given application, other aspects including material's cost, sustainability (including stability), processability, are also important criteria to take into account, in particular when it potentially implies a very large-scale application such as the CO₂ capture requiring a huge amount of adsorbents, i.e. more than a few hundred tons per plant.^{43,44} TGA

coupled with variable-temperature PXRD analysis (Fig. S4), confirmed that MIL-120(AI) exhibits an excellent thermal stability (up to 400°C), although some small variations in diffracted Bragg peaks could be observed starting from 100°C, very likely due to a slight structural flexibility induced by guest removal and/or some bond rearrangement (e.g., OH groups, etc.). Moreover, MIL-120(AI)-AP also showed an exceptional hydrolytic stability, withstanding to boiling water for (at least) 10 days as confirmed by the well-preserved crystallinity and CO₂ capacity, as per the provided PXRD and high-pressure CO₂ isotherms data, respectively (Fig. S5). This is, to our knowledge, the most hydrothermally stable AI-carboxylate based MOF reported to date. Consequently, this encouraged us to further characterize deeply the CO₂ adsorption behavior of MIL-120(AI)-AP.

1.2.2 In situ synchrotron PXRD studies

In comparison with MIL-120(AI)-HP, the CO₂ adsorption isotherms of MIL-120(AI)-AP did not exhibit any step behavior during CO₂ adsorption, and this regardless of the purification quality and the activation temperature. In an attempt to better understand this intriguing behavior and to shed light on the preferential interaction sites between the CO₂ and the porous framework, *in situ* synchrotron PXRD experiments (at the European Synchrotron Radiation Facility (ESRF), France) for both samples were carried out, by monitoring the PXRD patterns starting from the activation processes (heating up to 373 K under dynamic secondary vacuum) and during all over the CO₂ loading up to 4000 mbar. Variable temperature PXRD data collected directly during activation steps are depicted in Fig 2.

The analysis of the PXRD patterns evolution during the heating process revealed in the case of MIL-120(AI)-HP, the related crystal systems and space groups remained unchanged, monoclinic (*C2/m* ($n^{\circ}15$)), despite some variations in cell parameters, particularly an increase of the β angle and *c* parameter of ca. 2.2 deg and 0.15 Å, respectively (Fig. 3A and S6). Unexpectedly, MIL-120(AI)-AP displayed a different behavior associated to a phase transition at around 350 K from monoclinic (*C2/m*) to triclinic (*P*-1 ($n^{\circ}2$)) phase (Fig. 3B and Fig S10). The differences in particles sizes (micrometrics *versus* submicronic for HP and AP phases, respectively) could explain the difference in behavior.^{45,46} Interestingly, the structures solved from PXRD data, after being heated up to 373 K and cooled to 298 K, showed in both cases, that, in the measurement conditions, water molecules interacting with the AI-chains through the μ_2 -OH groups are tightly bounded and around 1/3 can still remain attached (water molecule occupancy of ca. 0.33 and 0.39, for the HP, and AP phases, respectively, Fig. S8, S11).



Figure 3. Variable temperature synchrotron PXRD data. Measurements performed under dynamic vacuum (activation step) for (A) MIL-120(AI)-HP, showing no phase transition, while remaining monoclinic; and (B) MIL-120(AI)-AP revealing phase transition, at ca. 357 K, from monoclinic to triclinic. Heating rate is equal to 6 K/min, up to 373 K in (A) and 420 K in (B).

The CO₂ loading under different pressures at 298 K was further investigated. Furthermore, for deeper understanding on the positions of guest molecules (loaded CO_2 and remaining water) and their interactions with the framework, the CO_2 loading under different pressures at 298 K was further investigated and the structure of MIL-120(AI)-HP loaded with 1000 mbar of CO₂ was successfully solved. To minimize the motion effects, the sample was cooled down to 200 K after the CO₂ loading. The obtained structure (triclinic P-1) revealed as expected, CO₂ molecules laying within the channels. In fact, each channel accommodates 2 arrays of CO_2 aligned along the c axis (Fig. 4A). More precisely, each array is composed of alternated CO₂ and H₂O molecules with occupancies of ca. 0.83 and ca. 0.33, respectively (Fig. 4B). As depicted in Fig. 4C, a closer look on the interaction of these molecules with the frameworks showed (i) that water molecules are mainly interacting with the μ_2 -OH $(d(O \cdots O))$ ranging from ca. 2.97 Å to 3.58 Å) groups from 2 different Al-chains, while (ii) CO_2 interacts from one side with μ_2 -OH through relatively weaker interactions than those with water $(d(O \cdots O) \approx 3.29 \text{ Å} \text{ and } 3.52 \text{ Å})$; and from another side with the aromatic phenyl rings that belong to 2 stacked BTeC (delimiting the channels) via dispersion and electrostatic interactions (very likely between the carbon of the aromatic ring and the central carbon atom of CO₂ in addition to further interactions between one electropositive aromatic H atom (not localized in this structure) and one electronegative O atom of CO_2).⁴⁷ More details about the phase transition analysis are included into the supporting information (Fig. S6-12 and Table S4). It is noteworthy to mention that MIL-120(AI)-HP exhibited a phase change from monoclinic to triclinic spotted in the pressure range between 300 mbar and 400 mbar, which is in line with the step observed within the same pressure range on the CO_2 isotherm measured at 298 K.



Figure 4. Crystal structure of MIL-120(AI)-HP loaded with 1000 mbar of CO₂ at 298 K and cooled down to 200 K. (A) General view along the *c* axis. (B) Top view of a part of one channel, and (C) a cut through a channel showing the arrays of alternated CO₂ and H₂O molecules and their interactions with the frameworks throughout μ_2 -OH and phenyl groups of the BTeC (represented as green and yellow dashed lines, respectively). Color code: Al(OH)₄O₂, grey polyhedra; C, grey; O, light red. H-atoms were not localized.

1.2.3 Molecular Simulation

Prior localizing the preferential adsorption sites for the guest molecules, and identifying the resulting host/guest interactions, there is a critical need to build an accurate structure model of the MOF sorbent in line with the crystallographic data, a key pre-requisite to further enable a fair comparison between the simulated and the experimental adsorption data. In this respect, it is worthy to note that we experimentally observed a slight decrease in the CO₂ uptake of MIL-120(AI)-AP when the sample was activated at higher temperatures (i.e., 423 K) under dynamic vacuum, compared with

303 K (Fig. S1F). This suggests that the presence of residual water molecules after the uncomplete evacuation at 303 K could establish additional interactions with CO₂ and more importantly with at least part of the hydrophilic μ_2 -OH groups that might induce different orientation of these adsorption sites towards the pore and hence their overall interactions with CO₂.

Following the conventional approach, the crystal structure of MIL-120(AI) was fully geometry optimized (both atomic positions and cell parameters allowed to relax) in its empty form at the Density Functional Theory (DFT) level. The structural and textural features of this DFT-optimized structure are in line with the experimental data collected for the sample (see Table S5). We further considered the DFT-optimization of the MIL-120(AI) structure loaded by different CO₂ loading and Table S6 summarizes the simulated CO₂ interaction energies which are rather high (44.6 ~ 51.0 kJ mol⁻¹) consistent with the experimental trend observed for the Q_{st}. This is associated with the specific arrangement of CO₂ in the channel forming strong interactions between the hydrogen atom of μ_2 -OH group and the oxygen atom of CO₂ molecule, as illustrated in Fig. 5A We further calculated the CO₂ adsorption isotherm at 298 K by grand Canonical Monte Carlo (GCMC) simulations using the DFT-optimized guest-free structure model. Fig. 5B, shows that the resulting CO₂ adsorption isotherm displays significantly higher and steeper uptakes at low pressures, compared to the experimental data, although the total uptakes at 1 bar are comparable. This indicates that when all μ_2 -OH groups of the MOF framework are available to freely interact with the CO₂ molecules in the channel, we would expect a very steep adsorption isotherm at the very low pressure. We further hypothesized that a reorientation of the μ_2 -OH groups could be induced by the presence of remaining adsorbed water molecules. This reorientation may lead for instance to intra-molecular OH...OH interactions leading to adsorption sites less accessible to CO₂ molecules, thus, decreasing the expected ideal uptake at low pressure. To explore this hypothesis, alternative structure models of MIL-120(AI) were built. A first one labeled as μ -OH sim model (Fig. S13) considers a reorientation of the OH groups to mimic possible OH...OH interactions. Fig. 5B reveals that the resulting simulated adsorption isotherm reproduces much better the experimental data, at least up to 0.2-0.25 bar, in line with a simulated adsorption enthalpy at low coverage of 38 kJ mol⁻¹ that matches also better the experimental Q_{st} value. Besides this, we created two additional structure models by incorporating one and two water molecules per unit cell followed by a DFT-optimization. These models named as μ_2 -OH 1water model and μ_2 -OH_2water model respectively, shown in Fig. S14 confirm that the water molecules preferentially adsorb around the μ_2 -OH groups. Fig. 5B further shows that their resulting GCMC-simulated adsorption isotherms also overestimate the sorption uptake at low pressure resulting from a relatively strong interaction between H_2O and CO₂ as illustrated in Fig. S15 and confirmed by the simulated adsorption enthalpy of 45.1 kJ mol⁻¹ and 44.9 kJ mol⁻¹. The slightly lower CO₂ uptake simulated for μ_2 -OH 2 water model at 1 bar can be explained by a substantial decrease of the accessible MOF porosity when 2 H₂O molecules are present in the unit cell. These overall simulation results demonstrate that the orientation and the accessibility of the μ_2 -OH groups plays a major role in the adsorption process taking place in this MOF.



Figure 5. CO₂ adsorption at 298 K from GCMC simulations. (A) DFT-optimized structure of MIL-120(AI) (top) with one CO₂ loading (per unit cell). The dashed line represents the interaction between the CO₂ molecule and μ_2 -OH group of the framework. The bottom shows a snapshot of the structure loaded with 1 bar of CO₂. Color code: AI(OH)₄O₂, grey polyhedra; C, grey; O, light red; H, white. (B) Experimental and simulated single-component CO₂ adsorption isotherms. Different models (*cf. supporting information*) are investigated to capture the underlying dynamic behaviors of the μ_2 -OH group in the real adsorption process.

1.2.4 Green scalable synthesis and breakthrough tests

The reusability of MIL-120(AI)-AP solids was investigated upon six consecutive CO₂ adsorption/desorption cycles (Table S7), using different temperatures for the activation. The CO₂ uptake of MIL-120(AI)-AP solids after activating the sample at 25 °C under secondary vacuum during six hours in the first two measurements exhibited slightly higher values compared with the same sample after activation at 50 °C, as depicted in Fig. S16. This could be due to the residual traces of water after activation at 25 °C, resulting into slightly higher CO₂ uptakes. After a first activation at 50 °C, the CO₂ uptake did however not change much depending on the activation condition, strongly indicating that MIL-120(AI)-AP keeps a reproducible CO₂ uptake due to the dense μ_2 -OH groups in the channels.

Furthermore, to meet with a potential use for industrial separation processes where the sorbents need to be produced at very large scale, first attempts of kg scale synthesis of the MIL-120(AI)-AP solids were carried out (synthesis methods given in SI) based on the optimized AP synthesis method developed in this work. Considering the cost of aluminum precursors (Al₂(SO₄)₃ 18H₂O, Al(NO₃)₃ 9H₂O, AlCl₃ 6H₂O) and/or their low solubility, safety or corrosive issues, in addition their less acidic chemical nature (as discussed in the previous sections), two other precursors were also considered for the synthesis at larger scale (> 100 g), see Table S8. First, the optimized procedure using Al(OH)(CH₃COO)₂ was deployed, relying a 30 L glass line reactor equipped with a pressurized filtration system (Fig. S17), leading to a batch of MIL-120(AI)-AP up to 1-2 kg (per single synthesis). Later, a more cost-effective Al-precursor, namely NaAlO₂, among the less expensive Al source, was explored and served to demonstrate the feasibility of a multi-kg-scale cheaper synthesis with a higher Space-Time Yield (STY).⁴⁸ In both cases, high quality MIL-120(AI)-AP materials were easily synthesized with high yield (> 70%) at > 3 kg scales via green methods, as confirmed by PXRD patterns, FT-IR spectroscopy, TGA, CO₂ adsorption, and SEM/EDX results (Fig. 6A and Fig. S18-21). Noteworthy, the kg scale and the small-scale samples exhibited almost the same CO₂ uptake at 0.1 and 1 bar, at 298 K. When using AI(OH)(CH₃COO)₂ as an aluminum precursor, water was the only solvent in the synthesis procedure, and after washing with warm water, the STY reached a moderate value close to 30 kg m⁻³ day⁻¹. In the case of NaAlO₂, it was necessary to add acetic acid as a pH modulator to obtain MIL-120(AI)-AP because of the too high alkaline character of the starting NaAlO₂/H₂O solution. Remarkably, the STY value was higher, around 100 kg m⁻³ day⁻¹, due to a significantly higher concentration used for the reaction, which is comparable to the values obtained for zeolites (50 to 150 kg m⁻³ day⁻ ¹) or benchmark AI-MOFs such as MIL-160⁴⁹ or MOF-303.⁵⁰ Meanwhile, it is interesting to note the smaller particles sizes of MIL-120(AI)-AP obtained when NaAIO₂ is used instead of AI(OH)(CH₃COO)₂ as observed from SEM images (Fig. S20). This could be ascribed to a faster reaction/nucleation between Al(III) and BTeC in the case of former. Considering the requirements of the real application, MOFs powders need to be shaped not only to (i) avoid the tedious (and possibly risky) manipulation of powder, but also (ii) to minimize the pressure drop and thermal gradient across the adsorption column and ensure an optimal fluid and heat diffusion. Here, we have successfully shaped MIL-120(AI)-AP using inorganic binders, namely bentonite and silica, throughout an extrusion/spheronisation method. The CO₂ uptakes of the MIL-120(AI)-AP beads obtained with 10% of silica and 10% of bentonite were in good agreement with the uptake of the MOF in the powder form (Fig. 6B). Additionally, the MIL-120(AI)-AP beads exhibited a high and useful crushing strength particularly when using bentonite (~38 N for MIL-120(AI)-AP with 10% bentonite; ~9 N for MIL-120(AI)-AP with 10% silica) (Fig. S22-23) which is important for column filling robustness during CO₂ capture applications. The higher mechanical strength of beads obtained with the aluminum silicate bentonite might be due to the strong affinity between AI-OH groups that are likely to decorate the external surface of bentonite and MIL-120(AI)-AP. Finally, to evaluate the separation performance for CO₂/N₂ (15/85), first, dynamic

column breakthrough experiments were performed, in a packed column filled with activated MIL-120(AI)-AP with 10% silica and MIL-120(AI)-AP with 10% bentonite with a total flow of 1NI min⁻¹ (The experimental set-up is detailed in Fig. S24). As depicted in Fig. 6C-D, in both cases, highly efficient separation of CO_2 from the CO_2/N_2 mixture could be achieved: N₂ gas first eluted through the adsorption bed at the very beginning of the adsorption process while CO₂ appears at the outlet of the column from breakthrough time leading to a CO₂ pure productivity (0.67 mmol cm⁻³ for MIL-120(AI)-AP with 10% silica; 0.79 mmol cm⁻³ for MIL-120(AI)-AP with 10% bentonite). The breakthrough curves were used to experimentally determine the CO₂/N₂ selectivities 93 for MIL-120(AI)-AP with 10% silica and 98-108 for MIL-120(AI)-AP with 10% bentonite respectively. Additionally, both samples reactivated after measurement under humid conditions, performed the same breakthrough results, strongly indicating that this MOF can provide a good repeatability of CO₂ adsorption with full regeneration after exposure to humid atmosphere, although a slight modification of the breakthrough curves could be observed in the case of beads shaped with silica. Since the regeneration was achieved by heating, MIL-120(AI)-AP appears, so far, as a suitable adsorbent well adapted to TSA (thermal swing adsorption) carbon capture under real conditions.



Figure 6. CO₂ adsorption uptakes of MIL-120(AI)-AP. (A) CO₂ adsorption isotherms at 298 K on different scale batch preparations. (B) CO₂ adsorption isotherms comparison between pure and structured samples with 10% Bentonite or Silica. (C) Breakthrough curves for MIL-120(AI)-AP beads with 10% Si. (D) Breakthrough results of MIL-120(AI)-AP beads with 10% bentonite at 303 K. The activation condition for both samples was at 50°C for 12 hours under vacuum, run 1 refers to the measurement in dry conditions, run 2 refers to the measurement in dry conditions after exposure to humid conditions, while in between the sample was reactivated at 50°C under vacuum.

1.3 Conclusion

In this work, a highly robust and cheap aluminum-based microporous Al tetracarboxylate MOF, MIL-120(AI), was studied for post-combustion carbon capture. An environmentally friendly and economically viable ambient pressure synthesis route was developed leading to pure MIL-120(AI)-AP samples, as an alternative to the previously high temperature hydrothermal route. A combination of experimental and computational adsorption results first confirmed the high and selective CO₂ uptake of this MOF at low pressure owing to an adequate confined space combining high density of OH groups on the edge sharing AI chains of octahedra and packed phenyl group aligned along the inner walls of the channels. The moderate CO₂ enthalpy of adsorption of this MOF (comparable to benchmark MOF physisorbents) is an asset for its potential use for CO₂ capture application. *In situ* PXRD experiments evidenced an irreversible monoclinic to triclinic phase transition phenomenon for the MIL-120(AI)-AP. Besides, a kg-scale synthesis protocol for MIL-120(AI)-AP, could be obtained with high STY, using inexpensive commercially available precursors via a green and cheap

ambient pressure route. MIL-120(AI)-AP was also shaped with bentonite which provided good sorption performances while keeping a strong mechanic strength. Then, the efficient CO_2 adsorption performance of this MOF was further confirmed thanks to dynamic column breakthrough experiments. As the total production cost of this material is expected to be low and sustainable, this, in addition to its cheap friendly composition and high thermal/chemical stability, suggests that MIL-120(AI)-AP lies as one of the scarce MOFs to meet the necessary criteria towards its practical use in real postcombustion carbon capture processes.

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Author Contributions. The manuscript was written through the contributions of all authors. BC performed towards the synthesis and the basic characterization. D.F. and G.M. contributed towards the theoretical studies. I.D. performed the *in situ* synchrotron PXRD measurements and contributed towards the structures solutions. S.N. contributed to the gas and vapor sorption isotherms measurements and the analysis associated data. R.P. and DC contributed towards the scale-up and shaping studies with the help and the guidance of F.N.. N.H. and G.D.W. performed the dynamic breakthrough measurements and contributed towards identifying the potential in CO_2 capture process. G.M. and C.S. supervised the work and contributed towards the overall concept.

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