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## CO<sub>2</sub> capture under humid conditions in NH<sub>2</sub>-MIL-53(Al): the influence of the amine functional group†

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The hydrostable MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) CO<sub>2</sub> capture properties were confirmed by kinetic uptake experiments, under different humidity conditions with maximum CO<sub>2</sub> captures of approximately 6.0 wt% and 4.6 wt%, respectively, at 5% RH at 30 °C. In the case of MIL-53(Al) this corresponds to a 1.7-fold increase (CO<sub>2</sub> capture) in comparison to anhydrous conditions. NH<sub>2</sub>-MIL-53(Al) exhibited a considerably stronger affinity to water than MIL-53(Al), and its ability to capture CO<sub>2</sub> under humid conditions, was significantly reduced. The *in situ* FTIR experiments show how the hydrophobicity of the pores within MIL-53(Al) enhanced and sustained the CO<sub>2</sub> adsorption capabilities of the material under more realistic CO<sub>2</sub> capture conditions.

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## Introduction

One of the main contributors to climate change (global warming) is carbon dioxide (CO<sub>2</sub>) emission from fossil fuel combustion.<sup>1a</sup> Indeed, fossil fuel combustion provides more than 85% of the energy required for industrial applications.<sup>1b</sup> The CO<sub>2</sub> levels have increased, from 1990 to date, up to 45% (ref. 2) as a result of human activities *e.g.* steel production and coal-fired power plants.<sup>1</sup> Thus, the rigorous reduction of these CO<sub>2</sub> emissions is fundamental in order to minimise the risk that global warming represents to our society. One strategy towards reducing CO<sub>2</sub> emissions is to capture and permanently sequester CO<sub>2</sub>. To achieve this goal, the development of new methodologies for efficient CO<sub>2</sub> capture has been addressed by many international initiatives.<sup>3</sup> Poliakoff<sup>4</sup> proposed 'the twelve principles of CO<sub>2</sub> chemistry' where CO<sub>2</sub> capture represents one of these principles (maximise integration) and thus, highly porous solid materials are very promising candidates for the solution of this worldwide task.

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have received significant attention as potentially valuable CO<sub>2</sub> capture media,<sup>5</sup> since these materials can be tailored as a function of the size, shape and chemical

composition of the pores.<sup>6</sup> One of the main limitations that PCPs show, when used as CO<sub>2</sub> capture materials, is their water instability.<sup>7,8</sup> For example H<sub>2</sub>O molecules could block the binding adsorption sites and as a result of it, these obstruct the adsorption of the desired target-molecules.<sup>8</sup> Additionally, water could reallocate the bound ligand, leading to the disintegration of the PCP structure.<sup>8</sup> Since moisture is always present in the environment, it must be considered for any adsorption and storage process. Therefore, water stability of PCPs is one key property for any CO<sub>2</sub> capture applications. As an example, industrial flue gas which results from the burning of fossil fuels, is typically saturated with 5–7% of H<sub>2</sub>O.<sup>9</sup>

Recently, there is a substantial amount of PCPs that have shown relatively good stability to water: NOTT-401,<sup>10</sup> MIL-100,<sup>11</sup> UiO-66,<sup>12</sup> InOF-1,<sup>13</sup> MIL-101,<sup>14</sup> MIL-53<sup>15</sup> and Cu(bc ppm)H<sub>2</sub>O.<sup>16</sup> Thus, some of these moisture-stable PCPs have been used in storage (H<sub>2</sub>O) technologies for arid environments,<sup>17</sup> proton conductivity<sup>18</sup> and heat-pumps chillers.<sup>19</sup>

The combined adsorption of CO<sub>2</sub> and water (CO<sub>2</sub> + H<sub>2</sub>O) in PCPs has recently been investigated.<sup>20</sup> Commonly, the adsorption of water diminishes the CO<sub>2</sub> capture (adsorption). However, Walton,<sup>21</sup> LeVan<sup>22</sup> and Matzger<sup>23</sup> showed that when water adsorption in PCPs is controlled, this can increase the CO<sub>2</sub> capture in PCPs. Llewellyn<sup>24</sup> studied the CO<sub>2</sub> capture (under different relative humidity conditions) in the mesoporous material entitled MIL-100(Fe), and an outstanding 5-fold enhance in the CO<sub>2</sub> uptake was achieved. In a comprehensive study about the effect of the functional group on the adsorption behaviour, Walton<sup>25</sup> exhibited how the amine functional group acts as a directing agent for the H<sub>2</sub>O molecules within the pores of the UiO-66 series, which provided more efficient packing. Moreover, Yaghi *et al.*<sup>17</sup> suggested that the existence of hydroxyl

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functional groups, inside the porous material, increases the affinity of PCPs for H<sub>2</sub>O.

Férey<sup>26</sup> reported for the very first time the MIL-53 porous coordination polymer series. Particularly, the Al(III) based version of MIL-53, entitled MIL-53(Al), is water stable<sup>15</sup> and in a previous work,<sup>27</sup> we reported the enhanced CO<sub>2</sub> capture properties in the presence of water in MIL-53(Al). Thus, in here we selected the amine functionalised MIL-53(Al), NH<sub>2</sub>-MIL-53(Al), to study the CO<sub>2</sub> sequestration under humid conditions and we made a comparison with the non-functionalised material, MIL-53(Al). NH<sub>2</sub>-MIL-53(Al), first reported by Blom *et al.*,<sup>28</sup> is constructed by infinite trans chains of corner-sharing (*via* OH groups, μ<sub>2</sub>-OH) AlO<sub>4</sub>(OH)<sub>2</sub> octahedra interconnected by NH<sub>2</sub>-BDC<sup>2-</sup> ligands (NH<sub>2</sub>-BDCH<sub>2</sub> = 2-amino-terephthalic acid, Fig. 1). Thus, three dimensional microporous framework structure is formed with diamond-shaped one dimensional channels (Fig. 1). The material NH<sub>2</sub>-MIL-53(Al) has previously exhibited very interesting CO<sub>2</sub> adsorption properties<sup>28,29</sup> and it also has provided promising results in research fields such as heterogeneous catalysis,<sup>30</sup> nonlinear optics<sup>31</sup> and negative compressibility.<sup>32</sup>

## Experimental section

We previously reported a continuous flow methodology for the synthesis of PCPs in pure water.<sup>33</sup> Thus, MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) were synthesised using this approach and calcined (extraction of terephthalic and 2-amino-terephthalic acid from the pores) in an oven at 330 °C for 3 days. These samples were labelled as post-synthesised. Thermogravimetric analyses (see Fig. S1, ESI†) and bulk powder X-ray diffraction (PXRD) patterns (see Fig. S2, ESI†) of the post-synthesised MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) samples, corroborated that the framework structures of these materials were preserved upon the removal of terephthalic and 2-amino-terephthalic acid. It is worth to mention that, as previously reported,<sup>26b</sup> the post-synthesised samples of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) correspond to the lt form (room temperature in which water is located within the channels).<sup>26b</sup> N<sub>2</sub> adsorption isotherms for activated MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al), corresponding to the calcined form (ht)<sup>26b</sup> empty channels,<sup>26b</sup> (180 °C under vacuum for 12 h) at 77 K were employed to calculate the BET surface area (0.01 < P/P<sub>0</sub> < 0.04) of 1096 m<sup>2</sup> g<sup>-1</sup> and 780 m<sup>2</sup> g<sup>-1</sup>, respectively. In the case of MIL-53(Al), the BET surface area of 1096 m<sup>2</sup> g<sup>-1</sup> is consistent with previously reported values that range between 1270 m<sup>2</sup> g<sup>-1</sup> and

933 m<sup>2</sup> g<sup>-1</sup>.<sup>26,33</sup> For sample NH<sub>2</sub>-MIL-53(Al), the surface area (BET) calculated as 780 m<sup>2</sup> g<sup>-1</sup>, is lower to the value reported by Blom *et al.*<sup>28</sup> of 960 m<sup>2</sup> g<sup>-1</sup> and higher than the value reported by Gascon and co-workers<sup>30</sup> of 675 m<sup>2</sup> g<sup>-1</sup>. Guo *et al.*<sup>29f</sup> showed how the synthesis conditions (modifying the ratio of water in the DMF–water mixed solvent system) have a considerable impact on the crystal size and morphology of the material NH<sub>2</sub>-MIL-53(Al) which is directly observed on the BET surface area from values of 950 m<sup>2</sup> g<sup>-1</sup> to 1882 m<sup>2</sup> g<sup>-1</sup>.<sup>29f</sup> Thus, although our BET surface value (780 m<sup>2</sup> g<sup>-1</sup>) is in the lower end of the values reported in the literature, the rapid synthesis of NH<sub>2</sub>-MIL-53(Al) in only water<sup>33</sup> represents a greener methodology with an excellent potential for scale-up.

Kinetic uptake experiments were performed using a thermobalance (Q500 HR, from TA) at room temperature (30 °C) with a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>). Post-synthesised samples of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) were placed inside the thermobalance and activated by heating from room temperature to 180 °C for 1 h and under a flow of N<sub>2</sub> gas (calcined form, ht).<sup>26b</sup> After the activated sample was cooled down, the temperature was set to 30 °C and a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was carried out. With a humidity-controlled thermobalance (Q5000 SA, from TA) kinetic uptake experiments at 30 °C with a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) were performed on activated samples (180 °C for 1 h and under a flow of N<sub>2</sub> gas) of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al).

Ambient conditions (20 °C and 50% RH) Fourier transform Infrared (FTIR) spectroscopy spectra were obtained on a Bruker Alpha spectrometer equipped with an attenuated total reflectance (ATR) accessory at room temperature in the range 500–4000 cm<sup>-1</sup>. For these experiments activated samples of MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al), (calcined form, ht)<sup>26b</sup> were placed on the spectrometer and their behaviour under ambient conditions was monitored by consecutive FTIR measurements (every five minutes) until no change was observed.

## Results and discussion

First, dynamic and isothermal (30 °C) CO<sub>2</sub> experiments were performed on MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) (see Experimental). Fig. 2 shows the kinetic uptake experiments at 30 °C, where weight gain, represents the amount of CO<sub>2</sub> captured in both materials. Then, the maximum CO<sub>2</sub> uptake for MIL-53(Al) and

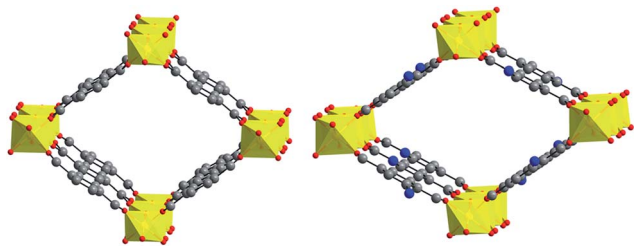


Fig. 1 Crystal structures of ht MIL-53(Al) and ht NH<sub>2</sub>-MIL-53(Al). Aluminium: yellow; oxygen: red; carbon: grey; nitrogen: blue. Hydrogen atoms omitted for clarity.

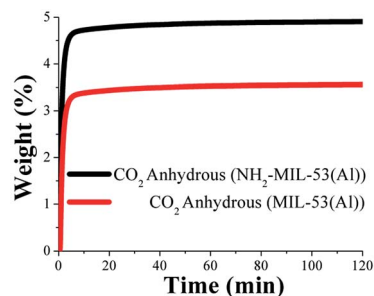


Fig. 2 Kinetic uptake experiments performed at 30 °C with a CO<sub>2</sub> flow of 60 mL min<sup>-1</sup>.

NH<sub>2</sub>-MIL-53(Al) were found to be 3.5 wt% and 4.9 wt%, respectively, which were reached after only 10 min and remained constant until 120 min, when the experiment was finished. The amine functionalised NH<sub>2</sub>-MIL-53(Al) has previously shown to enhance the CO<sub>2</sub> uptake over the non-functionalised material.<sup>28</sup> Interestingly, Gascon and co-workers<sup>34</sup> demonstrated that this CO<sub>2</sub> enhancement is not due to the direct interaction of the amine functional (-NH<sub>2</sub>) group with adsorbed CO<sub>2</sub>; instead, the presence of the amine modulates the 'breathing' behaviour of NH<sub>2</sub>-MIL-53(Al), which is, the flexibility of the framework. Thus, the amine favours the narrow-pore structure conformation in which, the interactions of the specific adsorbates (*e.g.* CO<sub>2</sub>) with the pore walls are higher than for the parent MIL-53(Al), affording higher CO<sub>2</sub> uptake.

Kinetic isotherm experiments at 30 °C and different relative humidities (5, 10 and 30% RH) were carried out. We chose these RH values based upon the investigation of water confined in the isostructural material MIL-53(Cr), proposed by Paesani.<sup>35a</sup> Through computational infrared spectroscopy, they showed<sup>35a</sup> that H<sub>2</sub>O molecules (at low water loadings) interact strongly with the pore walls of this material, MIL-53(Cr), *via* hydrogen bonding between the μ<sub>2</sub>-OH functional group and H<sub>2</sub>O, whereas intermolecular interactions between H<sub>2</sub>O molecules become considerably stronger at higher loading. Haigis<sup>35b</sup> postulated by molecular dynamics (MD) that water molecules can form hydrogen bonds with the bridging hydroxo functional groups (μ<sub>2</sub>-OH) depending on the water loading in the material MIL-53(Cr). In addition, Maurin *et al.*<sup>36</sup> demonstrated by GCMC simulations, in the same material MIL-53(Cr), that at low H<sub>2</sub>O loadings, the water molecules are homogeneously distributed inside all the pores of the material. Our hypothesis is that at low water loadings, the channels within the materials MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) supply a template (with μ<sub>2</sub>-OH and μ<sub>2</sub>-OH + -NH<sub>2</sub> functional groups, respectively) for a more efficiently packing of H<sub>2</sub>O molecules and thus, these H<sub>2</sub>O molecules can then hydrogen-bond to the CO<sub>2</sub> molecules enhancing the total CO<sub>2</sub> capture.

Then, an activated MIL-53(Al) sample, ht form,<sup>26b</sup> (180 °C for 1 h and under a flow of N<sub>2</sub> gas) was stabilised at 30 °C and 5% RH. After the equilibrium was reached a constant CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was carried out (see Fig. 3, left). The continuous weight gain (only H<sub>2</sub>O) starts at 0 min and stabilised at around 25 min. Differently, under anhydrous conditions the CO<sub>2</sub> uptake quickly reached stability (10 min, see Fig. 3). Since the diffusion

coefficient of water is smaller than CO<sub>2</sub>, the vapour adsorption (water) process takes considerably more time to reach stability than the gas adsorption process in microporous materials.<sup>37</sup> Then, from 25 min to 165 min the H<sub>2</sub>O uptake (0.5 wt%), which is in good agreement with water adsorption isotherms,<sup>38</sup> was invariable (plateau). Next, at 165 min the CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was opened and a quick weight increase was observed and reached stability at approximately 200 min (see Fig. 3, left). As we previously observed,<sup>39</sup> the adsorbed amount of H<sub>2</sub>O is unchanged after the dosing of H<sub>2</sub>O + CO<sub>2</sub> vapour-gas mixture. Then, from 200 min to the end of the experiment (350 min), the maximum amount of CO<sub>2</sub> captured (taking into consideration the water uptake of 0.5 wt%) corresponded to 6.0 wt%. Thus, the CO<sub>2</sub> capture was approximately 1.7-fold increased when applying 5% RH (from 3.5 wt% to 6.0 wt%) in comparison to anhydrous conditions. This CO<sub>2</sub> capture enhancement, in the presence of RH, can be attributed to CO<sub>2</sub> confinement effects induced by H<sub>2</sub>O molecules.<sup>40</sup>

On an activated sample (ht form)<sup>26b</sup> of NH<sub>2</sub>-MIL-53(Al), *vide infra*, kinetic CO<sub>2</sub> uptake experiments were carried out at 30 °C and 5% RH. In Fig. 3 (right) the kinetic uptake experiment is shown for NH<sub>2</sub>-MIL-53(Al) where the constant water weight increase begins at 0 min and stabilises at approximately 50 min. From 50 to 165 min the water uptake was constant and equal to 1.6 wt% (in good agreement with the water adsorption isotherms<sup>38</sup>). Next, the CO<sub>2</sub> flow (60 mL min<sup>-1</sup>) was started and a sharp weight uptake was observed (see Fig. 3 right). The stabilisation was achieved at around 200 min with a total CO<sub>2</sub> capture of 4.6 wt%. This capture, under relative humidity conditions, was certainly lower than under anhydrous conditions (4.9 wt%) representing a 0.3 wt% decrease.

From these kinetic uptake experiments (at 5% RH) on samples MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) it is clear that the material with the amine functional group (NH<sub>2</sub>-MIL-53(Al)) adsorbs more water than the non-functionalised (MIL-53(Al)), 1.6 and 0.5 wt%, respectively, suggesting that the affinity for water of the material NH<sub>2</sub>-MIL-53(Al) is considerably higher than for MIL-53(Al). In order to confirm this experimental evidence, we decided to run more kinetic CO<sub>2</sub> uptake isotherm experiments on MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al). First, at 30 °C and 10% RH, MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al), Fig. 4, showed water uptakes (plateau zone of the isotherm) of 1.0 wt% and 3.3 wt%, respectively and in good agreement with water adsorption isotherms,<sup>38</sup> with stabilisation

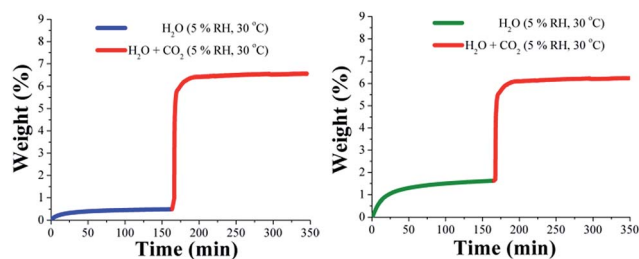


Fig. 3 Kinetic uptake experiments carried out at 30 °C and 5% RH for (left) MIL-53(Al), with H<sub>2</sub>O (blue line) and H<sub>2</sub>O + CO<sub>2</sub> (red line); (right) NH<sub>2</sub>-MIL-53(Al), with H<sub>2</sub>O (green line) and H<sub>2</sub>O + CO<sub>2</sub> (red line).

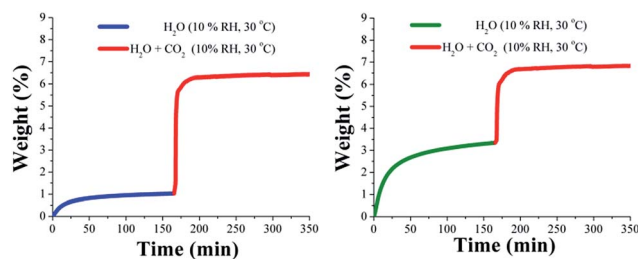


Fig. 4 Kinetic uptake experiments carried out at 30 °C and 10% RH for (left) MIL-53(Al), with H<sub>2</sub>O (blue line) and H<sub>2</sub>O + CO<sub>2</sub> (red line); (right) NH<sub>2</sub>-MIL-53(Al), with H<sub>2</sub>O (green line) and H<sub>2</sub>O + CO<sub>2</sub> (red line).

times of 50 min and 100 min, respectively (see Fig. 4). After the CO<sub>2</sub> flow was switched on, total CO<sub>2</sub> uptakes were 5.4 wt% for MIL-53(Al) and 3.5 wt% for NH<sub>2</sub>-MIL-53(Al), with a stabilisation time of 200 min for both isotherms (Fig. 4).

Finally, kinetic CO<sub>2</sub> uptake isotherm experiments on MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) at 30 °C and 30% RH were performed (Fig. 5). Then, the water uptakes for MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) were found to be 2.1 wt% and 7.0 wt%, respectively, consistent with water adsorption isotherms.<sup>38</sup> In the case of sample MIL-53(Al) the stabilisation time is approximately 100 min (Fig. 5, left) and for sample NH<sub>2</sub>-MIL-53(Al) there is not a clear stabilisation time since the isotherm did not show a plateau (see Fig. 5, right). After the CO<sub>2</sub> was started, the total CO<sub>2</sub> uptakes were 4.6 wt% for MIL-53(Al) and 0.5 wt% for NH<sub>2</sub>-MIL-53(Al). The stabilisation times for MIL-53(Al) were 200 min and for NH<sub>2</sub>-MIL-53 of approximately 220 min.

While increasing the relative humidity on the kinetic uptake experiments, in both MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) materials, their ability to capture CO<sub>2</sub> was undoubtedly reduced. In the case of MIL-53(Al), as we previously reported,<sup>27</sup> the presence of water within the micropores of the material enhances the CO<sub>2</sub> capture, and in the present work, the optimal relative humidity was found to be 5% RH (6.0 wt% CO<sub>2</sub> captured). In contrast, the presence of water in NH<sub>2</sub>-MIL-53(Al) did not favour the CO<sub>2</sub> capture even at low amounts (5% RH). From the dynamic and isothermal experiments it is possible to conclude that the material NH<sub>2</sub>-MIL-53(Al) exhibits a considerable stronger affinity to water than the non-functionalised material (MIL-53(Al)) and as a consequence of it, at 30 RH% the material was practically saturated with water leaving no room to the CO<sub>2</sub> molecules, resulting in a very reduced ability to capture CO<sub>2</sub> (only 0.5 wt%) in contrast to anhydrous conditions (4.9 wt%). In addition, due to the preference for the contracted structure (narrow-pore) that the amine functional group (-NH<sub>2</sub>) enforces<sup>34</sup> to the material NH<sub>2</sub>-MIL-53(Al), the accessibility to the pores is lower than in the non-functionalised material (MIL-53(Al)) which results in lower H<sub>2</sub>O + CO<sub>2</sub> captures at different RH.

To confirm that there was no sample degradation, PXRD measurements and N<sub>2</sub> adsorption isotherms (BET surface area) were carried out on all the samples (MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al)) after CO<sub>2</sub> capture experiments (see Fig. S3 and S4, ESI†), which demonstrated that the crystallinity and the surface area of the samples were retained. The PXRD measurements were carried on samples at room temperature, meaning the It form.<sup>26b</sup>

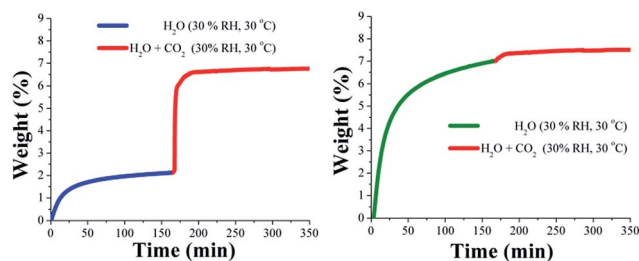


Fig. 5 Kinetic uptake experiments carried out at 30 °C and 30% RH for (left) MIL-53(Al), with H<sub>2</sub>O (blue line) and H<sub>2</sub>O + CO<sub>2</sub> (red line); (right) NH<sub>2</sub>-MIL-53(Al), with H<sub>2</sub>O (green line) and H<sub>2</sub>O + CO<sub>2</sub> (red line).

Since it is necessary to activate (see above) the samples for the BET surface area determination, the form was calcined or ht.<sup>26b</sup>

We then hypothesised that the different behaviour of these materials in the presence and absence of water can be explained in terms of the hydrophobicity of the pore surface in the PCPs and not in terms of the surface area, pore size or CO<sub>2</sub> adsorption under anhydrous conditions. Specifically, the polar NH<sub>2</sub> functionality in NH<sub>2</sub>-MIL-53(Al) makes the pore surfaces hydrophilic in nature, facilitating water diffusion across the pores of the material and providing additional binding sites for the incoming water, effectively blocking the pores and precluding CO<sub>2</sub> capture. On the other hand, the more hydrophobic nature of the pores and the scarcity of water binding-sites in the non-functionalised MIL-53(Al) hinder water diffusion therefore limiting water adsorption and leaving room for CO<sub>2</sub>.

To further investigate the kinetic behaviour of the adsorption process and prove our hypothesis we performed *in situ* Fourier transform infrared (FTIR) spectroscopy under ambient conditions (20 °C and 50% RH). The experiments were performed on activated samples (ht form)<sup>26b</sup> that were open to the atmosphere and immediately placed on the spectrometer to collect the first spectra ( $T = 0$ , Fig. 6). Then a spectrum was collected every five minutes until no further change was observed. Under these conditions, the samples were simultaneously exposed to ambient humidity, nitrogen, oxygen and small amounts of other gases, among which is CO<sub>2</sub> (approximately 400 ppm). The FTIR spectra of the non-functionalised MIL-53(Al) showed minor changes in the O-H region (3000–3600 cm<sup>-1</sup>), meaning that little to no water was adsorbed under these conditions. Conversely, there is an increase in the CO<sub>2</sub> stretching band (2358 cm<sup>-1</sup>), which clearly indicates that CO<sub>2</sub> is the preferred adsorbate over water and therefore, under these conditions, MIL-53(Al) does not immediately transition into its It (hydrated) form, and it instead adsorbs CO<sub>2</sub>. On the other hand, the FTIR spectra of NH<sub>2</sub>-MIL-53(Al) showed no evidence for CO<sub>2</sub> absorption, however there is a shift in the frameworks amino N-H and  $\mu_2$ -hydroxo O-H stretches along with a general broadening and signal increase of the overall 3000–3600 cm<sup>-1</sup> region. These changes can be attributed to the interaction of the NH<sub>2</sub> and OH groups in the pores with the

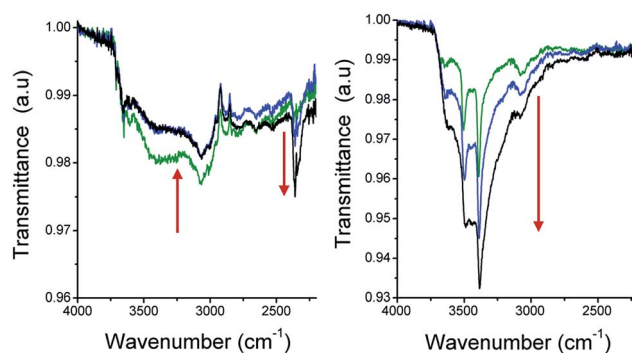


Fig. 6 FTIR spectra of activated samples of (left) MIL-53(Al), and (right) NH<sub>2</sub>-MIL-53(Al), under atmospheric conditions (20 °C and 50% RH). The green lines shows the  $T = 0$  spectra, blue is at  $T = 10$  min and the black one shows the spectra at  $T = 30$  min (saturated).



adsorbed water and are consistent with a rapid phase transition from the ht to lt form of NH<sub>2</sub>-MIL-53(Al).<sup>29d</sup> Therefore, and in good agreement with our kinetic uptake experiments, NH<sub>2</sub>-MIL-53(Al) rapidly adsorbs water effectively saturating the material and blocking its pores for CO<sub>2</sub> adsorption. Conversely, water adsorption by MIL-53(Al) is less favoured thus, allowing CO<sub>2</sub> to be adsorbed on the material. These results are in sharp contrast to the behaviour of these materials under anhydrous conditions, where NH<sub>2</sub>-MIL-53(Al) adsorbs more CO<sub>2</sub> than its non-functionalised counterpart MIL-53(Al).<sup>29</sup>

These results highlight how the hydrophobicity of the pores within a material can have dramatic effects on its overall CO<sub>2</sub> adsorption under humid conditions. Specifically, they show how an hydrophobic pore might help enhance and sustain CO<sub>2</sub> capture capabilities of a material under more realistic conditions.

## Conclusions

The hydrostable Al(III) coordination polymers MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al) exhibited, by kinetic isotherm CO<sub>2</sub> experiments, a total CO<sub>2</sub> uptake of 3.5 wt% and 4.9 wt%, respectively, at 30 °C. The CO<sub>2</sub> capture properties were evaluated on both materials, MIL-53(Al) and NH<sub>2</sub>-MIL-53(Al), under different relative humidity conditions (5, 10 and 30% RH) at 30 °C, showing maximum CO<sub>2</sub> captures of approximately 6.0 wt% and 4.6 wt%, respectively, at 5% RH. In the case of MIL-53(Al) this CO<sub>2</sub> capture under humid conditions corresponds to a 1.7-fold increase in comparison to anhydrous conditions. This CO<sub>2</sub> capture enhancement is attributed to CO<sub>2</sub> confinement effects induced by H<sub>2</sub>O<sup>40</sup> which occur within the micropores of MIL-53(Al) and in combination with the directing effect of the hydroxo functional groups (μ<sub>2</sub>-OH) permit CO<sub>2</sub> to be accommodated more efficiently.<sup>25</sup> Conversely, for sample NH<sub>2</sub>-MIL-53(Al) the capture of CO<sub>2</sub> under relative humidity conditions afforded a decrease of approximately 0.3 wt% when compared to anhydrous conditions. Since NH<sub>2</sub>-MIL-53(Al) showed a considerable stronger affinity to water than the non-functionalised material, its ability to capture CO<sub>2</sub> under humid conditions is significantly reduced and at 30 RH% the material was essentially saturated with water leaving no room to CO<sub>2</sub> molecules.

The kinetic uptake experiments in combination with *in situ* FTIR experiments show how the hydrophobicity of the pores within a material can have dramatic effects on its overall CO<sub>2</sub> adsorption under humid conditions, specifically, they show how an hydrophobic pore might help enhance and sustain CO<sub>2</sub> adsorption capabilities of a material under more realistic conditions.

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