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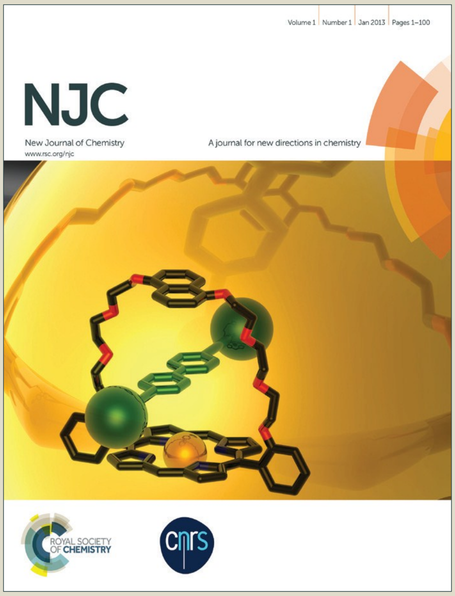

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LETTER

CO_2 capture in the presence of water vapour in MIL-53(Al)

Cite this: DOI: 10.1039/c3nj00000x

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Received 00th XXXXX 2013,
Accepted 00th XXXXX 2013

DOI: 10.1039/c3nj00000x

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MIL-53(Al) shows a CO_2 capture of 3.5 wt% by kinetic uptake experiments, under anhydrous conditions at 30 °C. When this material is exposed to water vapour (20% RH and 30 °C), there is a considerable 1.5-fold increase in the CO_2 capture up to 5.2 wt%.

Global warming and the resulting climate change is one of the biggest threats that our society has to solve. The cumulative carbon dioxide (CO_2) emissions in the atmosphere are continuously rising due to anthropogenic activities and these, inadvertently, generate the undesirable greenhouse gas effect.[1] The accelerating global energy demands and consumption of carbon-based fuels are the main causes to the increasing CO_2 levels.[2] To address these problems many countries have been motivated to invest in capturing and permanently sequestering CO_2, requiring the development of new methods for efficient CO_2 capture.[3]

The absorption of CO_2 by aqueous solutions of amines, which take advantage of the Lewis acidity of CO_2, have been widely studied. However they also have many major limitations as an absorbent for industrial CO_2 capture due to thermal instability, and corrosion on vessels and pipelines.[4] Therefore, the use of porous solids as an alternative medium for the adsorption of CO_2 is a timely research area. The search for materials with a high adsorption capacity, structural stability, high tolerance to humidity, fast sorption kinetics and mild regeneration properties, remains a major challenge for practical applications.

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are amongst the most promising candidates for gas separation; due to the ability to selectively adsorb small molecules. This selectivity can be tuned as a function of the topology and chemical composition of the micropores. [5,6] Although PCPs can exhibit high CO_2 capacity and selectivity in the absence of water, many gas separation processes involve the exposure to water vapour. Water molecules can compete with gas molecules for the active sites (within PCPs) or disrupt the bonding between the organic ligand and metal, resulting in the collapse of the structure.[7] Therefore capturing CO_2 from real flue gas (high humidity and high temperature) is indeed a great challenge. Recently, a considerable number of PCPs have been reported with relatively good stability to water, for example: UIO-66,[8] NOTT-401,[9] MIL-100,[10] MIL-101,[11] MIL-53[12] and InOF-1.[13] A water stable MOF ($Cu(bcppm)H_2O$, H_2bcppm= bis(4-(4-carboxyphenyl)-1*H*-pyrazolyl)methane) that also showed exceptionally selective separations for CO_2 over N_2 was reported by Doonan *et al.*[14]

In addition to causing structural instability, direct contact between water and PCPs can seriously reduce their gas storage capacity; with exposure to water often unfavourable to gas separations.[15] The effect of water on CO_2 capture in PCPs has only recently been investigated.[16-19] Llewellyn and co-workers[20] investigated the CO_2 adsorption in some PCPs under different relative humidities. Yaghi *et al.*[21] showed that the presence of hydroxyl functional groups increase the affinity of the framework for water.

MIL-53 frameworks, first reported by Serre *et al.*,[22] are a very interesting and well-studied series of PCPs. In the present work we have chosen an Al(III) based, water-stable[12] material entitled MIL-53(Al), to study the CO_2 capture in the presence of water vapour. This material is built up of infinite *trans* chains of corner-sharing (via OH groups) $AlO_4(OH)_2$ octahedra interconnected by BDC^{2-} ligands (H_2BDC= 1,4-benzenedicarboxylic acid).

We recently reported the synthesis of MIL-53(Al) *via* a continuous flow process, using solely water as the reaction medium and requiring a residence time of only 5-6 min.[23] Through this approach we obtained large amounts of MIL-53(Al) which was calcined (extraction of terephthalic acid from within the pores) by heating in the oven at 330 °C for 3 days. Thermogravimetric analysis (calcined MIL-53(Al)) (see Fig. S1, ESI †) and bulk powder X-ray diffraction patterns (see Fig. S2, ESI †) of the calcined MIL-53(Al) confirmed that the material retains its structural integrity upon terephthalic acid removal. N_2 adsorption isotherms for activated MIL-53(Al) at 77 K were used to calculate the BET surface area ($0.01<p/p_o<0.04$) of 1096 m^2 g^{-1}.

Dynamic and isothermal CO_2 experiments were carried out on MIL-53(Al) (see Experimental). Fig. 1 (left) shows the kinetic uptake experiments at 30 ^oC and 50 ^oC. These two capture temperatures were chosen because they are of great interest in post-combustion CO_2 capture processes.[3b] The weight gain, which represents the amount of CO_2 captured, was higher at 30 °C than at 50 °C. At 30 ^oC the maximum uptake of 3.5 wt% was reached after 10 min and remained constant until the end of the experiment (120 min). At 50 ^oC the uptake was measured to be 2.1 wt% which was also reached after around 10 min (Fig. 1, left). As the temperature is increased (from 30 to 50 ^oC), the weight of CO_2 adsorbed decreased.

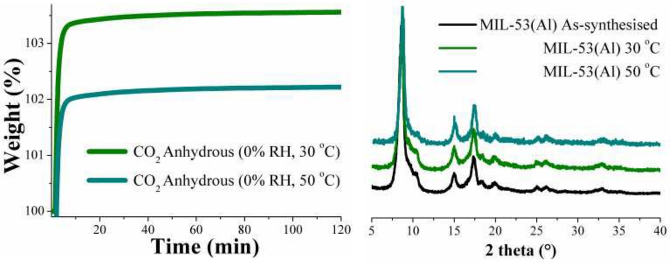

Fig. 1 (left) Kinetic uptake experiments performed at different temperatures (30 and 50 ^oC) with a CO_2 flow of 60 mL/min; (right) PXRD patterns of MIL-53(Al) samples before and after the kinetic CO_2 isotherms.

In order to confirm the decrease in CO_2 capture with temperature was not due to sample degradation, PXRD measurements were carried out on both samples after CO_2 capture experiments. Fig. 1 (right) shows that the crystallinity of the samples was retained after each CO_2 capture experiment.

For comparison, dynamic and isothermal CO_2 experiments were run on an inorganic mesoporous molecular sieve entitled MCM-41. MCM-41 is a very well-known porous material that has been used in a range of fields including; ion exchange, catalysis, sensing, drug delivery and gas adsorption.[24] The chemical environment and pore dimensions of MCM-41 (a mesoporous inorganic material), are very different to those of MIL-53(Al) (a microporous inorganic-organic material). Therefore, a comparison of the CO_2 uptake properties of both materials can provide a better understanding of the main characteristics required for an ideal CO_2 capturing material.

A sample of MCM-41[25] was placed in a thermobalance (see Experimental) and at 30 ^oC exhibited a maximum CO_2 uptake of 1.0 wt% (see Fig. S3, ESI †). This uptake was reached after 40 min and remained constant until 120 min (end of the experiment). At 50 ^oC the CO_2 uptake was 0.6 wt% and was also reached after around 40 min (see Fig. S3, ESI †). PXRD experiments demonstrated the retention of the sample crystallinity after each CO_2 capture experiments (see Fig. S4, ESI †).

Motivated by the very interesting results previously reported by Llewellyn *et al,*[20] (5-fold increase in CO_2 uptake for MIL-100(Fe) in the presence of water); kinetic isotherm experiments were carried out at different temperatures and relative humidities. A sample of MIL-53(Al) was placed into a humidity-controlled thermobalance and after activation of the material, the equipment was allowed to stabilise at 20% RH and 30 ^oC. A constant CO_2 flow (60 mL min^{-1}) was started and the change in weight of the sample was measured for 120 minutes. To measure the water uptake in the absence of CO_2, this experimental procedure was repeated on a different sample of MIL-53(Al), without the constant CO_2 flow. Fig. 2 (left) shows the kinetic uptake experiments at 30 ^oC for CO_2+H_2O (20% RH) and only H_2O (20% RH). In both isotherms, the material shows an increase in weight with time, due the contributions of CO_2+H_2O or only H_2O, respectively.

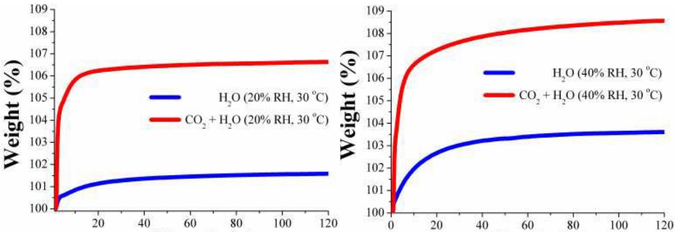

Fig. 2 (left) Kinetic uptake experiments carried out at 30 ^oC using MIL-53(Al) and 20% RH with CO_2+H_2O (red line) and only H_2O (blue line); (right) kinetic uptake experiments carried out at 30 ^oC and 40% RH with CO_2+H_2O (red line) and only H_2O (blue line).

In order to find the maximum CO_2 capture at 20% RH and 30 °C, we need to remove the contribution of water from the total weight increase. The CO_2 capture at 20% RH is simply the difference between the two isotherms (CO_2+H_2O and H_2O). In Fig. 2 (left) the gradual weight increase (for CO_2+H_2O and H_2O) starts at 0 min and stabilises at ~ 20 min. interestingly, under anhydrous conditions the CO_2 uptake reached stability faster, at approximately 10 min (see Fig. 1, left). This equilibrium discrepancy is due to the nature of the water vapour adsorption process that in general takes considerably more time to reach equilibrium than the gas adsorption process in microporous materials.[26] From 10 min to 120 min (end of the experiment), the maximum amounts of CO_2+H_2O and only H_2O captured were 106.7 wt% and 101.5 wt%, respectively and by taking the difference of these two values the CO_2 capture in the material was ~ 5.2 wt%. Therefore, there was a 1.5 fold increase in the CO_2 capture from 3.5 wt% under anhydrous conditions to 5.2 wt% with 20% RH. This enhancement in CO_2 uptake in the presence of water can be explained by CO_2 confinements effects induced by bulky molecules (H_2O).[27] Indeed, Walton and co-workers[28] proposed that functional groups (such as OH) act as directing agents for water in the pores, which allows for more efficient packing.

In order to obtain additional evidence that the increase in uptake is an increase in the CO_2 capture and not an increase in the amount of water adsorbed, we carried out an additional kinetic isotherm experiment. Thus, an activated MIL-53(Al) sample (*vide supra*) was placed into a humidity-controlled thermobalance (at 30 ^oC) and the equipment was stabilised at

20% RH. After the equilibrium was reached, we open a constant CO_2 flow (60 mL min^{-1}), Fig. 3. In Fig. 3 the gradual weight increase (only H_2O) starts at 0 min and stabilises at around 20 min. From 20 min to 95 min the H_2O uptake was constant (plateau) and at 95 min the CO_2 flow was opened and a sharp weight gain, which reached stability at approximately 110 min, was observed (see Fig. 3). From 110 min to 180 min (end of the experiment), the maximum amount of CO_2 captured corresponds to ~ 5.2 wt%.

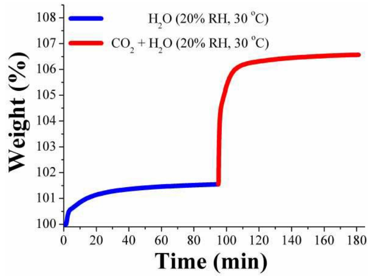

Fig. 3 Kinetic uptake experiment carried out at 30 °C and 20% RH with H_2O (blue line) and CO_2 (red line).

Later, kinetic uptake experiments were performed on an activated sample of MIL-53(Al) at 30 °C and 40% RH. Fig. 2 (right) shows a gradual weight increase (for CO_2+H_2O and H_2O) which starts at 0 min and stabilises at around 40 min. Thus, when the relative humidity (RH) was increased from 20 to 40% the stabilisation time was also considerably increased. At 40% RH the maximum quantities of CO_2+H_2O and H_2O captured were 108.5 wt% and 103.7 wt%, respectively and by taking the difference of these two values the CO_2 capture was approximately 4.8 wt%.

This value represents an increase in CO_2 capture relative to the anhydrous value of 3.5 wt% but a decrease from the value of 5.2 wt% under 20% RH. We rationalised that at higher water loadings (*e.g.*40% RH) the directing effect of the OH groups is reduced due to an increase in the water disorder (within the pore) caused by thermal agitation and therefore, diminishing the CO_2 capture.

To explore the effect of temperature on the capture of CO_2 under humid conditions, kinetic uptake experiments were performed on activated samples of MIL-53(Al) at 20% RH and 50 °C. This humidity was chosen as a higher CO_2 capture and shorter stabilisation time were obtained at 20% RH than 40% RH for the same material at 30 °C. Fig. 4 shows the gradual weight increase for CO_2+H_2O and H_2O under these conditions. The total CO_2 capture value was 3.1 wt% with a stabilisation time of ~ 20 min. Thus, the CO_2 capture at 50 °C was approximately 1.5 fold increased: from 2.1 wt% under anhydrous conditions to 3.1 wt% with 20% RH.

To confirm that there was no sample degradation, PXRD measurements and N_2 adsorption isotherms (BET surface area) were carried out on all the samples after CO_2 capture experiments (see Fig. S5, ESI †), which demonstrated that the crystallinity and the surface area of the samples were retained. These results are very promising for the application of PCPs in a more realistic CO_2 capture scenario: humidity conditions and relatively high temperature (50 °C).

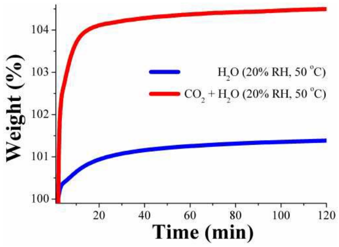

Fig. 4 Kinetic uptake experiments carried out at 50 °C and 20% RH with CO_2+H_2O (red line) and only H_2O (blue line)

Kinetic isotherm experiments were also carried out on activated samples of MCM-41 at 30 °C with 20% RH and 40% RH (see Figs. S6 and S7, ESI †). The total CO_2 capture values were 1.1 and 1.2 wt% respectively and in both cases the stabilisation times were around 50 min. These values represent a small CO_2 capture improvement, (from anhydrous conditions to 20 and 40% RH), from 1.0 to 1.1 wt% at 20% RH and 1.2 wt% at 40% RH. PXRD measurements confirmed the retention of the crystallinity after each CO_2 experiment (see Fig. S8, ESI †).

For MIL-53(Al) the capture of CO_2 in the presence of water is considerably higher than that of MCM-41 and the stabilisation time is also shorter. Since MIL-53(Al) is a microporous material, the confinement effects[27] can play a greater role than in the mesoporous material MCM-41 as we previously observed in Sc(III)-based water stable microporous materials.[29]

In addition, we decided to run a CO_2 uptake experiment (60 mL min^{-1}) at 20% RH and 30 °C on a non-porous sample to provide a direct CO_2 capture comparison to MIL-53(Al), a microporous material. PCM-14[30] was chosen and a sample was activated at 150 °C for 1h, under a flow of N_2 gas, (since PCM-14 is a non-porous material, when activated between 25-150 °C). Under anhydrous conditions, from 0 to 120 min the maximum CO_2 uptake was 0.3 wt% (see Fig. S9, ESI†). From 0 min to 120 min the maximum CO_2 uptake (under 20% RH) was 0.7 wt% (see Fig. S10, ESI†). This result corroborated that there is no increase in CO_2 sequestration in a non-porous material when the relative humidity is 20% at 30 °C.

Finally, we run CO_2 sorption studies under static mode on MIL-53 (see Fig. S11, ESI†). The CO_2 capture was 9.6 wt% which is considerably higher than under dynamic conditions (3.5 wt%). However, the main objective of the present work is to demonstrate, in a more realistic scenario, how MIL-53(Al) performs when it is exposed to a constant CO_2 flow gas (60 mL/min) and under humidity conditions. Additionally, we carried out a water uptake, static, experiment at 30 °C (see Fig. S12, ESI†) which showed a good correlation with the dynamic experiment (at 20 RH% P/P_0, the water uptake was 1.5 wt%).

In summary, the Al(III) coordination polymer MIL-53(Al) shows, by kinetic isotherm experiments, a total CO_2 uptake of 3.5 wt% at 30 °C, which was rapidly reached after only approximately

10 min. CO_2 uptakes were measured using MIL-53(Al) under different relative humidity conditions (20 and 40% RH) and temperatures (30 and 50 °C), displaying a maximum CO_2 capture of approximately 5.2 wt% (20% RH and 30 °C). Significantly, this CO_2 capture under humid conditions represents a 1.5-fold increase in comparison to anhydrous conditions. Both MCM-41 and PCM-14 exhibit lower CO_2 capture in the presence of water, suggesting that the microporosity provided by MIL-53(Al) is fundamental for this capture process. The CO_2 confinement effects induced by H_2O[27] can occur within the micropores of MIL-53(Al) which combined with the directing effect of the hydroxo functional groups allow CO_2 to be accommodated more efficiently.[28] MIL-53(Al) is an ideal candidate for use in more realistic post-combustion CO_2 capture scenarios as it can be produced in a very short time, *via* continuous flow reactions,[23] and can capture CO_2 at relatively high temperatures (50 °C) in the presence of water.

Notes and references

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Acknowledgements

The authors thank Dr. A. Tejeda-Cruz (X-ray; IIM-UNAM). I.A.I thanks CONACyT (212318) and PAPIIT UNAM (IN100415), Mexico for financial support. E.G-Z. thanks CONACyT (156801) and CONACyT (236879), Mexico for financial support. Thanks to U. Winnberg (ITAM and ITESM) for scientific discussions. We gratefully acknowledge the receipt of a University of Nottingham 2012 EPSRC Doctoral Prize to P.A.B. We thank Prof. M. Schröder for his encouragement and Prof. M. Poliakoff and R. A. Howie for prompting us to carry out the experiment shown in Figure 3. We also thank RAH for advice on preparing the manuscript.

Electronic Supplementary Information (ESI) available: TGA data, PXRDP data and Kinetic Uptake Experiments. See DOI: 10.1039/b000000x/. See DOI: 10.1039/c000000x/

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