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Carbon dioxide capture in the presence of water vapour in InOF-1[†]

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Kinetic uptake experiments on InOF-1 confirm a maximum of 5.42 wt% CO₂ capture at 30 °C and a significant 2-fold increase (~11 wt%) in CO₂ capture under 20% relative humidity of water vapour. InOF-1 captures CO₂ under humid conditions (10% and 20% RH) and at relatively high temperatures (40 and 50 °C) without any degradation of the crystalline structure which was corroborated by PXRD.

Introduction

Global warming is one of the biggest threats that our society has to solve since it causes extreme climate changes. The cumulative carbon dioxide (CO₂) emissions in the atmosphere are continuously increasing due to anthropogenic activities and these, unwittingly, generate the undesirable green gas effect.¹ The accelerating global energy demands and consumption of carbon-based fuels are the main triggers to the increasing CO₂ levels,² and these energy requirements are expanding promptly due to rapid world population growth, increases in the standard of living and the development of technologies, leading to a doubling in the energy demand over the last three decades.³ Therefore, CO₂ separation and capture have motivated many governments to invest in the development of new methods for efficiently and effectively capturing CO₂.⁴

Typical CO₂ absorption in aqueous alkanolamine solutions has been widely used and studied, but it has many major limitations as an adsorbent for industrial CO₂ capture due to its heat instability and corrosion on vessels and pipelines.⁵ Thus, the use of porous solids for the adsorption of CO₂ is a timely research area and the search for materials with a high adsorption capacity, structural stability, high tolerance against 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 among the most interesting candidates for gas separation, because their sorption selectivity towards

small molecule adsorbates is directly tunable as a function of the topology and chemical composition of the micropores.⁶ Porous metal-organic materials having high surface areas and high pore volumes normally show high CO₂ storage capacities at room temperature and at relatively high pressures.⁷ Although the PCPs show high CO₂ capacity and selectivity, many gas separation processes in industry involve the exposure to water vapour. However, water molecules can compete with any gas molecules for the active sites (within PCPs) or disrupt the ligand bonding between organic molecules and metals, resulting in the collapse of the structure.⁸ Capturing CO₂ from real flue gas (high humidity and high temperature) is indeed a great challenge.

Recently, there is a considerable number of PCPs that have shown relatively good stability to water,⁹ and some interesting examples are: UiO-66,¹⁰ HKUST-1,¹¹ MIL-100,¹² MIL-101,¹³ and MIL-53.¹⁴ Doonan *et al.*¹⁵ reported a water stable MOF (Cu(bcppm)H₂O, H₂bcppm = bis(4-(4-carboxyphenyl)-1H-pyrazolyl)-methane) that also showed exceptionally selective separation for CO₂ over N₂.

However, more than structural stability, the direct contact of PCPs to water can seriously reduce their gas storage capacity and water is most often unfavourable to gas separations.¹⁶ The effect of water on the CO₂ capture has only recently been investigated on PCPs.¹⁷ Matzger and co-workers^{17b} studied the effect of humidity on the performance of M/DOBDC (M = Zn^{II}, Ni^{II}, Co^{II} or Mg^{II}) by collecting N₂/CO₂/H₂O breakthrough curves at different relative humidities. LeVan *et al.*¹⁸ found that a small amount of water did not decrease and may in fact increase the CO₂ capacity of PCPs. Eddaoudi and co-workers¹⁹ demonstrated that a material entitled SIFSIX-3-Cu was a recyclable and moisture stable MOF that showed enhanced CO₂ uptake and selectivity in highly diluted gas streams.

Llewellyn and co-workers²⁰ investigated the CO₂ adsorption in some PCPs under different relative humidities of water vapour. Certainly, HKUST-1, was shown to degrade in the presence of water vapour, and UiO-66 did not show any enhanced

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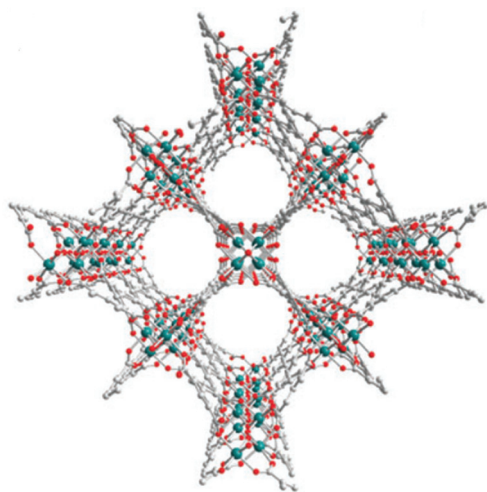


Fig. 1 View of the crystal structure of InOF-1 along the *c*-axis (indium: green; oxygen: red; carbon: grey; hydrogen omitted for clarity).²²

CO₂ uptake.²⁰ In the case of MIL-100(Fe), a remarkable 5-fold increase in CO₂ uptake was observed with increasing relative humidity (RH), 105 mg g⁻¹ at 40% RH. In addition, Yaghi *et al.*²¹ showed that the presence of hydroxyl functional groups increases the affinity of the framework for water. Thus, in the present work we have chosen a material entitled InOF-1²² (Fig. 1), a water-stable PCP based on a binuclear [In₂(μ₂-OH)] building block (Fig. S1, ESI†), constructed from a flexible BPTC⁴⁻ ligand (H₄BPTC = biphenyl-3,3',5,5'-tetracarboxylic acid) and possessing hydroxo functional groups (μ₂-OH), to study the CO₂ capture in the presence of water vapour.

Experimental

Indium nitrate, In(NO₃)₃ (156 mg, 0.40 mmol) and biphenyl-3,3',5,5'-tetracarboxylic acid, H₄BPTC (33 mg, 0.10 mmol) were dispersed in CH₃CN (5 ml), DMF (5 ml) and HNO₃ (65%, 0.2 ml) and sealed in a pressure tube. The clear solution was heated at 85 °C in an oil bath for 72 h. The tube was cooled to room temperature over a period of 12 h and the colourless crystalline product was separated by filtration, washed with DMF (5 ml) and dried in air. Yield: 72% (based on ligand).

The uncoordinated solvent molecules in the pores of the as-synthesized InOF-1 were exchanged for acetone and this promotes accessibility to the desolvated framework after activation by heating. Thus, thermogravimetric analysis (see Fig. S2, ESI†) and bulk powder X-ray diffraction patterns (see Fig. S3, ESI†) of the as-synthesised and desolvated InOF-1 confirmed that the material consistently retains its structural integrity upon solvent removal. N₂ adsorption isotherms for activated InOF-1 at 77 K were used to calculate the BET surface area (0.01 < *p/p*₀ < 0.04) of 1060 m² g⁻¹.

Kinetic uptake experiments were performed by using a thermobalance (Q500 HR, from TA) at different temperatures with

a constant CO₂ flow (60 mL min⁻¹). Then, acetone-exchanged samples of InOF-1 were placed into the thermobalance and activated by heating from room temperature to 180 °C for 1 h and under a flow of N₂ gas. After the activated sample was cooled down, the desired temperature and a constant CO₂ flow (60 mL min⁻¹) were set. With a humidity-controlled thermobalance (Q5000 SA, from TA), kinetic uptake experiments at 30, 40 and 50 °C with a constant CO₂ flow (60 mL min⁻¹) were carried out on activated samples (180 °C for 1 h and under a flow of N₂ gas) of InOF-1.

Results and discussion

Dynamic and isothermal CO₂ experiments were carried out on InOF-1. Fig. 1, left, shows the kinetic uptake experiments from 30 °C to 50 °C. At 30 °C the material exhibited the maximum weight% gain, which represents the maximum amount of CO₂ captured. This amount corresponds to 5.24 wt%, which was rapidly reached after just 5 min and it was constant until the end of the experiment (60 min). At 40 °C the uptake was estimated to be 3.77 wt%, which was also reached after approximately 5 min (Fig. 2, top). Finally, at 50 °C the maximum uptake was 2.88 wt%.

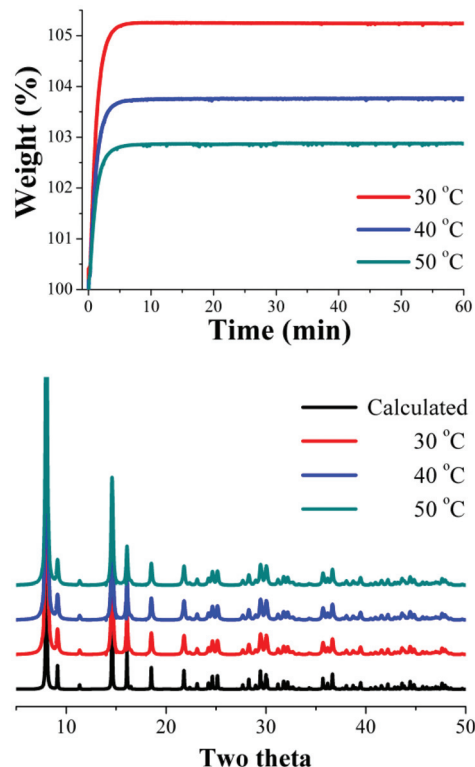


Fig. 2 (top) Kinetic uptake experiments performed at different temperatures (30, 40 and 50 °C) with a CO₂ flow rate of 60 mL min⁻¹; (bottom) calculated PXRD pattern of InOF-1 and PXRD patterns of each InOF-1 sample after the kinetic CO₂ isotherms were carried out at different temperatures.

Clearly, while the temperature is increased (from 30 to 50 °C), the CO₂ weight (%) gradually decreases (Fig. 2, top) from 5.24 to 2.88 wt%. In order to corroborate that this decrease is not due to sample degradation, we have carried out PXRD experiments on each sample after these CO₂ capture experiments. Fig. 2 (bottom) confirms that the crystallinity of the samples after each CO₂ capture experiment was retained.

Hong *et al.*²² showed, by PXRD experiments, that InOF-1 is a water stable PCP and this water-stability can be attributed to the presence of the hydroxo functional groups (inside the pores of InOF-1) as previously reported.¹⁷ Thus, kinetic isotherm experiments at 30, 40 and 50 °C, with a constant CO₂ flow, and a relative humidity (RH) of 40% were carried out. It was decided to perform these experiments with a 40% RH based on the extraordinary results that Llewellyn *et al.*²⁰ previously reported (a 5-fold increase in CO₂ uptake for MIL-100(Fe)).

First, an activated InOF-1 sample (180 °C for 1 h and under a flow of N₂ gas) was placed into a humidity-controlled thermo-balance. After activation of the material, the equipment was stabilized at 40% RH (30 °C) and a constant CO₂ flow (60 mL min⁻¹) was started. Afterwards, we repeated this experimental procedure on a new activated InOF-1 sample and set a constant N₂ flow (60 mL min⁻¹). Fig. 3 exhibits the kinetic uptake experiments at 30 °C and 40% RH for CO₂ and N₂. For both isotherms, it is clear to observe that the material shows a constant increase in weight (while the experiment is continuous in time, see Fig. 3). This increase in weight is due to the contribution of H₂O and CO₂ or H₂O and N₂, respectively.

In order to find the maximum CO₂ capture under 40% RH conditions, we need to differentiate the contribution of H₂O to the weight increase. By taking the difference between the two isotherms (CO₂ and N₂) we could obtain the CO₂ capture at 40% RH. This is valid if the material does not capture any N₂ at 30 °C. Consequently, by performing a kinetic uptake experiment on a newly activated InOF-1 sample at 30 °C without the presence of H₂O vapor (0% RH) with a constant N₂ flow (60 mL min⁻¹) we obtained a N₂ capture of approximately 0.01 wt%. This result is consistent with the previous reports where the capture capacity of N₂ capture in PCPs at room

temperatures is basically negligible.²³ In Fig. 3, the gradual weight increase for N₂/H₂O starts at 0 min and stabilises at ~55 min. In the case of CO₂/H₂O the weight increase starts at 0 min and stabilises after approximately 110 min.

In contrast, under anhydrous conditions the CO₂ uptake rapidly reached stability (5 min, see Fig. 2, top). This equilibrium discrepancy is due to the nature of the vapour adsorption process that in general takes considerably more time to stabilise than the gas adsorption process in microporous materials.²⁴ Then, from 110 min until approximately 175 min both isotherms seem to reach a plateau where both uptake capacities are practically constant (Fig. 3). At 175 min, the maximum amounts of CO₂/H₂O and N₂/H₂O captured are 132 wt% and 131 wt%, respectively and by taking the difference between these two values (since there is no N₂ uptake at 30 °C) the CO₂ capture in the material is ~1 wt%.

Therefore, the CO₂ capture at 40% RH and 30 °C was considerably reduced in comparison with anhydrous conditions (from 5.24 to 1.00 wt%). At 40% RH and 40 °C (see Fig. S4, ESI†), as well as 40% RH and 50 °C (see Fig. S5, ESI†) the CO₂ capture was approximately the same (~1 wt%). This CO₂ capture reduction is not due to the degradation of the material after each experiment, since the PXRD experiments carried out on the samples after the N₂ and CO₂ capture experiments (see Fig. 4) showed that the retention of the crystallinity was maintained (see Fig. 4).

Then, in closer inspection of the porosity of InOF-1, this corresponds to the microporosity regime with a pore diameter of 7.6 Å.²² Interestingly, the remarkable result of a 5-fold increase in CO₂ uptake was obtained in a mesoporous material at 40% RH and 30 °C (MIL-100(Fe))²⁰ which comprises two types of mesoporous cages of free apertures of *ca.* 25 and 29 Å.²⁰ We then rationalised that at 40% RH the saturation of the micropores in InOF-1, with H₂O molecules, was completed and therefore, the inclusion of CO₂ molecules, into the micropores, was unfeasible. In order to confirm this hypothesis, we

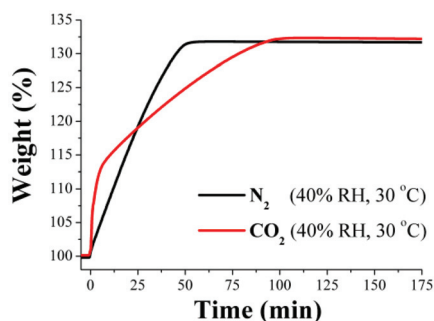


Fig. 3 Kinetic uptake experiments carried out at 30 °C and 40% RH with CO₂ (red line) and N₂ (black line) flow rates of 60 mL min⁻¹, respectively.

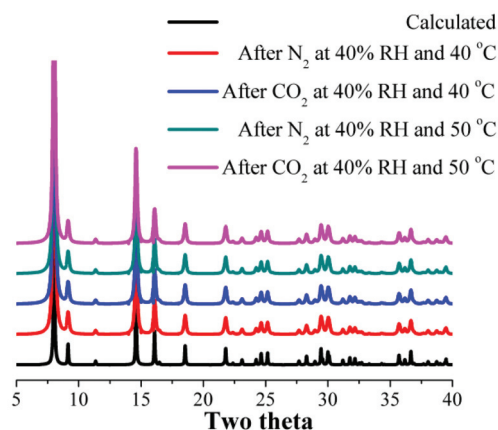


Fig. 4 Calculated PXRD pattern of InOF-1 and PXRD patterns of each InOF-1 sample after the kinetic N₂ and CO₂ isotherms at different temperatures.

reduced the relative humidity to half (20% RH) and more CO₂ capture experiments were carried out. Then, an activated InOF-1 sample was stabilised, in a humidity-controlled thermo-balance, at 20% RH (30 °C) and a constant CO₂ flow (60 mL min⁻¹) was started. Later, we replicated this experimental procedure on a new activated InOF-1 sample and set a constant N₂ flow (60 mL min⁻¹).

Fig. 5 exhibits the kinetic uptake experiments at 30 °C and 20% RH for CO₂ and N₂. Again, for both isotherms, the material clearly shows a constant increase in weight. However, this time both isotherms exhibited a much faster weight increase for N₂/H₂O and CO₂/H₂O than at 40% RH, starting at 0 min and stabilising at ~15 min. Thus, from 15 min until approximately 175 min both isotherms reach a plateau where both uptake capacities are constant (Fig. 5). At 175 min, the maximum amounts of CO₂/H₂O and N₂/H₂O captured are 112 wt% and 101 wt%, respectively and by taking the difference between these two values (since there is no N₂ uptake at 30 °C) the CO₂ capture in the material is ~11 wt%.

Therefore, the CO₂ capture was approximately 2-fold increased with a 20% RH (from 5.24 wt% to 11 wt%) in comparison with anhydrous conditions. Clearly, when the relative humidity was reduced to 20%, the micropores of InOF-1 were partially saturated with H₂O molecules, allowing the CO₂ molecules to enter into the micropores of InOF-1. This enhancement in CO₂ uptake in the presence of water can be explained by CO₂ confinement effects induced by bulky molecules (H₂O).²⁵ Walton *et al.*²⁶ proposed that the functional groups (*e.g.* hydroxo functional groups inside the pores of InOF-1) act as a directing agent for water in the pores, which allows for more efficient packing. Additionally, we previously observed this enhanced-CO₂ uptake phenomenon in a couple of Sc(III) water stable PCPs.²⁷

The cycle stability of the material was investigated by running 11 kinetic uptake experiments on the same sample. Thus, an activated InOF-1 sample (180 °C for 1 h and under a flow of N₂ gas) was placed into a humidity-controlled thermo-balance and a constant CO₂ flow (60 mL min⁻¹) started at 20% RH. The experiment was stopped after 20 min (only to obtain

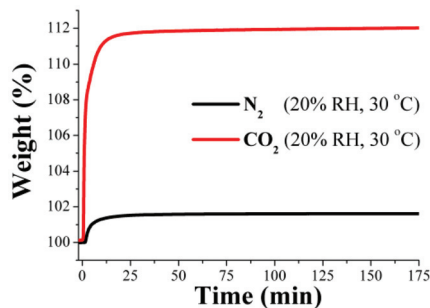


Fig. 5 Kinetic uptake experiments carried out at 30 °C and 20% RH with CO₂ (red line) and N₂ (black line) flow rates of 60 mL min⁻¹, respectively.

the maximum CO₂ uptake) and then, this protocol was repeated ten more times (with the same sample) to make a total of 10 cycles. The average CO₂ uptake of the cycles was 11.02 wt% (see Fig. S8, ESI†). In addition, the PXRD experiments confirmed the retention of the overall framework crystallinity after 10 cycles (see Fig. S9, ESI†).

We also performed kinetic uptake experiments at 30 °C and 10% RH finding a maximum CO₂ uptake of approximately 9 wt% (see Fig. S6, ESI†). Thus the highest amount of CO₂ capture was obtained under a relative humidity of 20%.

Additionally, we decided to perform a CO₂ experiment (60 mL min⁻¹) at 20% RH and 30 °C on an activated PCM-14²⁸ sample (150 °C for 2 h, under a flow of N₂ gas). Since PCM-14 is a non-porous coordination polymer, when activated between 25–150 °C, it offered a direct CO₂ capture in comparison with InOF-1 (a microporous material). Thus, from 0 min to ~180 min the maximum CO₂ uptake (under 20% RH) was 0.8 wt% (see Fig. S7, ESI†). This result corroborated that there is no CO₂ sequestration in a non-porous material when the relative humidity is 20% at 30 °C.

Finally, kinetic uptake experiments were performed on InOF-1 at 20% RH and 40 °C (see Fig. 6, top) and 20% RH and 50 °C (see Fig. 6, bottom). The total CO₂ capture values were 8 wt% and 6 wt% (Fig. 6), respectively. Thus, these values represent an approximately 2-fold CO₂ increase (from anhydrous conditions to 20% RH) from 3.77 wt% to 8 wt% at 40 °C and from 2.88 wt% to 6 wt% at 50 °C. These results are indeed very promising for the application of PCPs in a more realistic CO₂

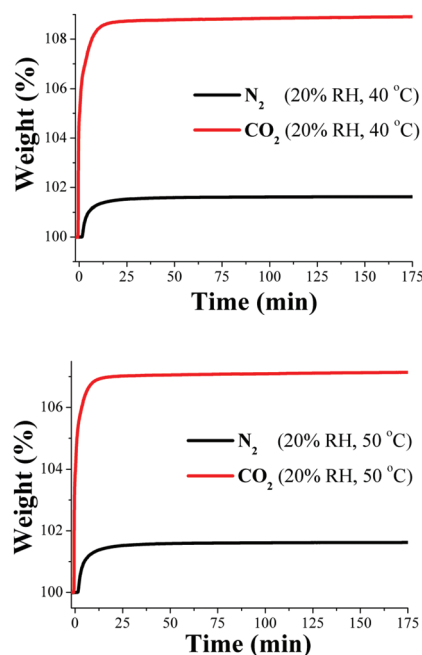


Fig. 6 (top) Kinetic uptake experiments carried out at 40 °C and 20% RH with CO₂ (red line) and N₂ (black line) flow rates of 60 mL min⁻¹, respectively; (bottom) kinetic experiments carried out at 50 °C and 20% RH with CO₂ (red line) and N₂ (black line) flow rates of 60 mL min⁻¹, respectively.

capture situation like flue gas (high humidity and high temperature).

Conclusions

In conclusion, InOF-1, a In(III) porous coordination polymer, exhibited a total CO₂ amount of 5.42 wt% at 30 °C shown by kinetic isotherm experiments, which was rapidly reached after approximately 5 min. While increasing the temperature of the kinetic isotherm experiments, the CO₂ capture capacity of InOF-1 decreased to 2.88 wt% at 50 °C. Remarkably, InOF-1 exhibits high stability towards humidity, which was confirmed by PXRD. We attributed this water stability, as previously reported,²¹ to the presence of hydroxo functional groups within the pores of InOF-1.

Due to this particularly high water stability, InOF-1 performs CO₂ uptake under relative humidity conditions. Finding the best partial saturation of H₂O molecules (percentage of relative humidity) into the micropores of InOF-1 is essential to increase the CO₂ uptake. Thus, after testing different relative humidity conditions (40%, 20% and 10% RH) and temperatures (30, 40 and 50 °C), we found that the maximum CO₂ capture was obtained at 20% RH and 30 °C with a total amount of ~11 wt%. Significantly, this CO₂ capture, under humid conditions, represents a 2-fold increase in comparison with anhydrous conditions.

It is also worth mentioning that this material captures CO₂ under humid conditions and at relatively high temperatures (40 and 50 °C) which are desirable in a more realistic CO₂ capturing scenario like flue gas. PCM-14 showed non-CO₂ capture under RH conditions, suggesting that the microporosity provided by InOF-1 is fundamental for this capture process. Since PCM-14 is a non-porous coordination polymer, when activated between 25–150 °C, the CO₂ confinement effects induced by H₂O²⁵ in porous materials cannot take place unlike in InOF-1, where these effects occur within the micropores as well as the directing effect of the hydroxo functional groups (inside the micropores of InOF-1) which can accommodate CO₂ more efficiently.²⁶

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