This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
NOTTS-400 exhibits CO$_2$ separation from CH$_4$ when the material was exposed to a binary (CO$_2$/CH$_4$) equimolar gas-mixture and this was confirmed by in-situ FTIR spectroscopy.
Separation of CO$_2$ from CH$_4$ and CO$_2$ capture in the presence of water vapour in NOTT-400

Maximiliano R. Gonzalez,$^{a}$ Juan H. González-Estefan,$^{b}$ Hugo A. Lara-García,$^{b}$ Pedro Sánchez-Camacho,$^{b}$ Elena I. Basaldella,$^{a,c}$ Heriberto Pfeiffer$^{b}$ and Ilich A. Ibarra$^{a,b}$

From a binary equimolar gas-mixture of CO$_2$ and CH$_4$, NOTT-400 shows CO$_2$ separation from CH$_4$. By kinetic uptake experiments, this material confirms a maximum of 4.3 wt% CO$_2$ capture at 30 °C and a significant 2-fold increase (~9.3 wt%) in CO$_2$ capture under 40% relative humidity of water vapour.

Air pollution and global warming are two of the foremost threats to our civilisation.$^{1-6}$ Of particular significance are the rapidly increasing levels of carbon dioxide (CO$_2$) emissions, due to burning of fossil fuels. Fossil fuels are non-renewable$^7$ and cannot continue as a principal energy source in the far future$^8$ due to the limited reserves. Natural gas (CH$_4$) is a very desirable fuel because it burns cleaner than any other fossil fuel (e.g. petrol or coal).$^9$ However, the quality of natural gas, coming from land fields and biogas plants, is considerably low with impurities like CO$_2$ (20 to 35%), N$_2$, H$_2$O and H$_2$S.$^{10}$ Then, pre-combustion CO$_2$ capture from natural gas is essential to maximise its energy content. Additionally, post-combustion CO$_2$ capture from plant flue gas is also crucial in order to control greenhouse emissions.$^{11}$

CO$_2$ separation and sequestration have extremely motivated many governments to invest in the development of new methods for efficiently and effectively capturing CO$_2$.$^{12}$ Conventional absorption in aqueous alkanolamine solutions has been extensively used and studied, but it has many major limitations as an adsorbent for industrial CO$_2$ capture due to its heat instability and corrosion towards vessels and pipelines.$^{13}$ Thus, the use of porous solids for the adsorption of CO$_2$ is a timely research area and the search for materials with a high adsorption capacity, structural stability, fast sorption kinetics and mild regeneration properties, remains a major challenge.

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are amongst the most promising 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.$^{14,15}$ Despite the high CO$_2$ capacity and selectivity that PCPs show, many gas separation processes involve the exposure to water vapour. However, few PCPs have shown good stability to water, and water is most often unfavourable to gas separations.$^{16}$ Among those few examples, Hong et al.$^{17}$ reported a water-stable PCP based on a binuclear [In$_2$(µ-OH)] building block (see Scheme S1, ESI†), InOF-1, constructed from a flexible BPTC$^{*}$ ligand (H$_2$BPTC= biphenyl-3,3’,5,5’-tetracarboxylic acid) which also showed a high CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivities (by using the experimental single-component gas adsorption isotherms). Interestingly, the effect of water on the CO$_2$ capture has only recently been investigated on PCPs.$^{18,19}$

Llewellyn and co-workers$^{20}$ investigated the CO$_2$ adsorption in some PCPs under different relative humidities of water vapour. Indeed, HKUST-1, was shown to degrade in the presence of humidity, and UiO-66 did not show any enhanced CO$_2$ uptake.$^{20}$ In the case of MIL-100(Fe), a remarkable 5-fold increase in CO$_2$ uptake was observed with increasing relative humidity (RH), 105 mg g$^{-1}$ at 40% RH. Additionally, Yaghi et al.$^{21}$ showed that the presence of hydroxyl functional groups increase the affinity of the framework for water. Thus, in the present work we have chosen a material entitled NOTT-400$^{22}$ based on a binuclear [Sc$_2$(µ-OH)] building block (see Scheme S1, ESI†) which is isostructural to the water-stable InOF-1$^{17}$ and possesses hydroxo functional groups (µ-OH) to study the separation of a binary gas mixture (not a single-component gas) of CO$_2$ and CH$_4$ and we have successfully performed CO$_2$ capture in the presence of water vapour.

After the first gas separation experiment was carried out (see Experimental), the most characteristic FTIR bands for the CO$_2$ (2349 cm$^{-1}$) and CH$_4$ (3016 cm$^{-1}$) molecules, were analysed. In Fig. 1 it is possible to observe a continuous
increase in the characteristic band intensities (Fig. 1), for CO\textsubscript{2} and CH\textsubscript{4} in time. In other words, from spectrum 1 to spectrum 10 the intensity of the characteristic FTIR band is increasing while the transmittance is decreasing.

Thus, the normalised intensities for CO\textsubscript{2} and CH\textsubscript{4} at each scan (from 1 to 10) are practically the same (Fig. 2, right) suggesting that when the resulting flow of each pure-gas component (not a mixture of gases) is analysed separately by FTIR spectroscopy, the molecules of CO\textsubscript{2} and CH\textsubscript{4} arrive at the same time to the FTIR detector. These results confirm that NOTT-400 is more selective to CO\textsubscript{2} than CH\textsubscript{4} when a binary equimolar (0.13 mmol min\textsuperscript{-1}) gas-mixture of CO\textsubscript{2} and CH\textsubscript{4} flows through an activated sample. We interpreted this selectivity as the time delay of the CO\textsubscript{2} molecules in reaching the FTIR detector. By polynomial regressions of the normalised intensities on Fig. 2 (left), we estimated this delay to be ~28 s (see Fig. S7 and S8 ESI†). Finally a third experiment was carried out: in order to confirm that this delay was caused by the adsorption selectivity shown by NOTT-400 (a microporous PCP) rather than other phenomena, a non-porous material was mounted in the BEL-REA system. PCM-14\textsuperscript{23} is a dense coordination polymer that has shown to be a non-porous material when it is activated between 25-150 °C. Thus, a sample of PCM-14 (40 mg) was activated at 150 °C for 2h under a flow of N\textsubscript{2} gas and then directly exposed to binary equimolar (0.13 mmol min\textsuperscript{-1}) CO\textsubscript{2} and CH\textsubscript{4} gas mixture. Thus, the resulting flow gas was analysed by FTIR spectroscopy and just 6 scans were recorded, until the detector was saturated. By normalisation of the characteristic FTIR intensities, we plotted the normalised intensities of each CO\textsubscript{2} and CH\textsubscript{4} scans (see Fig. S9, ESI†). Interestingly, the normalised intensities for CO\textsubscript{2} and CH\textsubscript{4} at each scan (from 1 to 6) are practically the same (see Fig. S9, ESI†) confirming that the time delay is due to the microporosity of NOTT-400.

Dynamic and isothermal CO\textsubscript{2} experiments were carried out on NOTT-400 (see Experimental Termobalance, ESI†) Fig. 3, left, shows the kinetic uptake experiments from 30 °C to 100 °C. At 30 °C the material exhibited the maximum weight % gain, which represents the maximum amount of CO\textsubscript{2} captured.

This amount corresponds to 4.3 wt% and it was rapidly reached after just ~300 s (5 min) and it kept constant until the end of the experiment (3600 s or 60 min). At 40 °C the uptake was estimated to be 3.5 wt% and it was also reached after around 300 s (Fig. 3, left). Clearly, while the temperature is increased (from 30 to 100 °C), the CO\textsubscript{2} weight (%) decreases gradually (Fig. 3, left) to 0.5 wt% (at 100 °C). In order to confirm that this decrease is not due to sample degradation, we have run PXRD experiments performed at different temperatures (30, 40, 50, 60, 70, 80, 90 y 100 °C) with a CO\textsubscript{2} flow of 60 mL/min. Each curve shows the experimental data and the symbols were used to differentiate them; (right) PXRD patterns of each NOTT-400 samples after the kinetic CO\textsubscript{2} isotherms were carried out at different temperatures.

![Fig. 1 FTIR spectra of the resulting exit exhaust of the binary equimolar (0.13 mmol min\textsuperscript{-1}) gas-mixture of CO\textsubscript{2} and CH\textsubscript{4} of: (left); the characteristic CO\textsubscript{2} band and (right); the characteristic CH\textsubscript{4} band.](Image 13x11 to 312x407)

![Fig. 2 Normalised characteristic FTIR intensities of CO\textsubscript{2} and CH\textsubscript{4} as a function of the number of scans. (Left) FTIR intensities from a resulting exit exhaust of the binary equimolar (0.13 mmol min\textsuperscript{-1}) gas-mixture of CO\textsubscript{2} and CH\textsubscript{4} (right) FTIR intensities from individual flows of CO\textsubscript{2} and CH\textsubscript{4}.](Image 316x224 to 423x305)

![Fig. 3 (left) Kinetic uptake experiments performed at different temperatures (30, 40, 50, 60, 70, 80, 90 y 100 °C) with a CO\textsubscript{2} flow of 60 mL/min. Each curve shows the experimental data and the symbols were used to differentiate them; (right) PXRD patterns of each NOTT-400 samples after the kinetic CO\textsubscript{2} isotherms were carried out at different temperatures.](Image 448x225 to 544x305)
measurements on each sample after these CO₂ capture experiments. Fig. 3 (right) shows that the crystallinity of the samples after each CO₂ capture experiments was retained. Indeed, we increased the temperature progressively up to 650 °C (see Fig. S10, ESI†) and there is a constant weight lost, suggesting that samples of activated NOTT-400 are not capturing CO₂ after 150 °C and what we observe is a gradual structural decomposition which was confirmed by PXRD (see Fig. S10, ESI†).

Motivated by the very promising results that Hong et al. reported,17 by showing an isostructural framework to NOTT-400 (InOF-1), which is water stable and exhibited high CO₂/N₂ and CO₂/CH₄ selectivities, we explored the water stability of NOTT-400. Then, acetone-exchanged samples of NOTT-400 were exposed to air and soaked in distilled water. PXRD patterns of these experiments (see Fig. S11, ESI†) then confirmed structural stability of NOTT-400 in water. This water-stability can be attributed to the presence of the hydroxo functional groups (within the pores of NOTT-400) which has been previously shown21 and these functional groups, enhance the affinity of the material for water. Thus, after establishing the best CO₂ capture temperature (30 °C, Fig.3, left), a kinetic isotherm experiment at 30 °C, with a constant CO₂ flow, and a relative humidity (RH) of 40% was carried out. It was decided to run this experiment with a 40% RH based on the remarkable results that Llewellyn et al.20 previously reported (5-fold increase in CO₂ uptake for MIL-100(Fe)).

An activated NOTT-400 sample (150 °C for 2h and under a flow of N₂ gas) was placed into a humidity-controlled thermobalance. After activation of the material, the equipment was stabilised at 40% RH (30 °C) and a constant CO₂ flow (60 mL min⁻¹) was started. Later, we repeated this experimental procedure on a different activated NOTT-400 sample and set a constant N₂ flow (60 mL min⁻¹). Fig. 4 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 progressing in time, see Fig. 4). This increase in weight is due the contribution of water and CO₂ or water and N₂, respectively.

![Fig. 4 Kinetic uptake experiments carried out at 30 °C and 40% RH with CO₂ (green spheres) and N₂ (blue spheres) flows of 60 mL/min, respectively.](image)

In order to find the maximum CO₂ capture under 40% RH conditions, we need to differentiate the contribution of water to the weight increase. By simply taking the difference of 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. Therefore, by performing a kinetic uptake experiment on an activated NOTT-400 sample at 30 °C without any presence of water vapour (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 previous reports where the capacity of N₂ capture in PCPs at room temperatures is basically negligible.24 In Fig. 4, the gradual weight increase (for CO₂/H₂O and N₂/H₂O) starts at 0 s and stabilises at ~6000 s (100 min). Interestingly, under anhydrous conditions the CO₂ uptake rapidly reached stability (5 min, see Fig. 3, left). This equilibrium discrepancy is due to the nature of the vapour adsorption process that in general takes considerably more time to reach stability than the gas adsorption process in microporous materials.25 Then, from 600 s until approximately 11000 s (183.3 min) both isotherms seem to reach a plateau where both uptakes are practically constant. At 11000 s, the maximum amounts of CO₂/H₂O and N₂/H₂O captured are 51.1 wt% and 41.8 wt%, respectively and by taking the difference of these two values (since there is no N₂ uptake at 30 °C) the CO₂ capture in the materials is ~9.3 wt%. Finally, from 11000 s to 13000 s (Fig. 4, red rectangle) the flow of each gas and the relative humidity were stopped and the decrease in weight represents the gas and water vapour desorption. Therefore, the CO₂ capture was approximately 2-fold increased with a 40% RH. This enhance in CO₂ uptake in the presence of water can be explained by CO₂ conformations effects induced by bulky molecules (H₂O).26 Additionally, we decided to run a CO₂ experiment (60 mL min⁻¹) at 40% RH and 30 °C on an activated PCM-1425 sample (150 °C for 2h, under a flow of N₂ gas). Since PCM-14 is a non-porous material, when activated between 25-150 °C, it provided a direct CO₂ capture comparison to NOTT-400 (microporous material). Thus, from 0 s to 11000 s the maximum CO₂ uptake (under 40% RH) was 0.8 wt% (see Fig. S12, ESI†). This result corroborated that there is no CO₂ sequestration in a non-porous material when the relative humidity is 40% at 30 °C.

In summary, the Sc(III) coordination polymer NOTT-400 shows CO₂ separation from CH₄, in a more realistic scenario, when this material was exposed to a binary, CO₂/CH₄, equimolar gas-mixture. By kinetic isotherm experiments, NOTT-400 exhibits a total CO₂ amount of 4.3 wt% at 30 °C, which was rapidly reached after just approximately 300 s. Additionally, NOTT-400 exhibits high stability towards humidity, which was confirmed by PXRD. Due to this particularly high stability, NOTT-400 performs CO₂ uptake under relative humidity conditions (40% RH) and 30 °C, displaying a maximum CO₂ capture of approximately 9.3 wt%.

**Experimental**

**Gas Separation Experiments**

A catalytic reactor system (BEL-REA, BEL Japan; Fig. S3, ESI†) was employed, which allowed each sample of acetone-exchanged NOTT-400 (see Experimental, ESI†) to be activated (150 °C for 2h) under a flow of N₂ gas and then directly exposed to adsorbates (CO₂ and CH₄) *in situ*, and studied by FTIR spectroscopy over many cycles without physical manipulation or
exposure to air. In each study, an acetone-exchanged sample of NOTT-400 (40 mg) was placed into the holder sample in the BEL-REA system and activated as described above. Then, the system was allowed to cool down to 30 °C and the activated sample was exposed to a flow of the binary equimolar (0.13 mmol min⁻¹) gas mixture of CO₂ and CH₄. This mixture represents a more realistic composition for gas separation processes. Next, after stabilisation of the gas flow within the sample, the resulting exit exhaust gases (see Fig. S3, ESI†) was analysed by FTIR spectroscopy. Thus, each FTIR spectrum was recorded every 40 seconds (~0.66 min), until the detector was saturated, to make a total of 10 FTIR spectra (see Fig. S4, ESI†).

Notes and references

2. Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Del. Coyoacán, 04510, México D. F., Mexico. E-mail: argel@unam.mx
3. CIITEMA, Universidad Tecnológica Nacional, 60 y 124, (1900) La Plata, Argentina.

Acknowledgements

The authors thank Dr. A. Tejeda-Cruz (X-ray; IIM-UNAM) and CONACyT Mexico (212318) for financial support. M.R. G. thanks CONICET and BECAR Argentina for scholarship funding. Thanks to U. Winnberg for scientific discussions.
