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DVS & BTA Case Study 623

Co-adsorption of Carbon Dioxide and Water in a MOF for Post Combustion Capture

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Carbon capture is a critical development that is often hindered by the impact of humidity. This study evaluates the realistic performance of a leading point-source capture material provided by novoMOF for point-source capture using the Dynamic Vapor Sorption (DVS) Carbon and the Breakthrough Analyzer (BTA) Frontier instruments. Precise gravimetric adsorption by the DVS Carbon reveals this MOF to be a strong CO_2 sorbent stable to multiple CO_2 sorption cycles, and exposure to up to 50% Relative Humidity (RH). Using the BTA Frontier, precise competitive adsorption of CO_2 in the presence of humidity was measured, a necessary criterion for usage in humid post combustion gas flows. This note highlights the synergistic application of the DVS Carbon and BTA Frontier for analyzing novel porous materials for mixed gas separations allowing for accelerated development.

Introduction

Recent reports highlight the significantly diminishing carbon budget available to avert the 2.0 °C and 1.5 °C global temperature limits set by the 2015 Paris Agreement.[1] To meet these goals, new technologies must complement the ongoing replacement of fossil fuels. Carbon capture is a critical technology that encompasses the direct air capture (DAC) of CO_2 from the atmosphere, and point-source capture (PSC) that targets the removal of CO_2 from industrial effluent streams.[2] PSC offers the most readily deployable and cost-efficient means to implement carbon capture. However, notable drawbacks with current technology involving liquid amines, such as high energy requirements, have limited their use. Advancements in porous materials, in particular metal-organic frameworks (MOFs), have provided a more commercially viable pathway to carbon capture with the development of MOFs like CALF-20[3] that display high uptake and moderate selectivity of CO_2 over H_2O.[4]

In the context of MOFs and other carbon capture materials, water interaction properties are being extensively studied as humidity often competes for binding sites and compromises stability. Single-component H_2O or CO_2 isotherms of porous materials provide valuable initial insights but are poor indicators of uptake under competitive conditions, which typically requires challenging and time-consuming experimentation. Conventional manometric and gravimetric techniques are typically insufficient to measure co-adsorption due to their inability to differentiate the contribution from each component. Advanced gravimetric and chromatographic techniques, specifically Dynamic Vapor Sorption (DVS) and Breakthrough Analysis (BTA), are essential to address these challenges. The Dynamic Vapor Sorption Carbon instrument, designed for gravimetric adsorption analysis, provides precise measurements of total CO_2 and H_2O uptake under controlled conditions. Complementing this, the BTA Frontier instrument enables dynamic analysis of gas mixtures,

simulating real-world capture scenarios. Together, these instruments offer a robust solution for evaluating sorbent performance.

This application note showcases the advanced capabilities of the DVS Carbon and the BTA Frontier (Fig 1) through the evaluation of a potential next-generation carbon capture sorbent provided by novoMOF. By demonstrating the precise, realistic characterization afforded by these instruments, we highlight their ability to streamline development and optimization of advanced materials for carbon capture, addressing the urgent need for effective climate change mitigation strategies.

Method

Samples of the promising post combustion carbon capture material were supplied by novoMOF in a powdered or pelletized form.

Isothermal, time-resolved uptake and kinetics experiments were performed using approximately 15 mg of sample (in powder form) at target temperatures of 14, 25, or 40 °C on a DVS Carbon instrument equipped with a high-resolution low-mass UltraBalance (0.01 µg sensitivity). The combined uptake of CO_2 and H_2O was measured gravimetrically in a temperature-controlled incubator (±0.01 °C accuracy). Gas composition was adjusted by blending a saturated H_2O stream in N_2 and/or pure CO_2 with dry N_2, maintaining a total flow rate of 200 sccm, equally split between a sample and reference chamber, to achieve the desired concentrations. Relative humidity was monitored with a capacitive sensor, and CO_2 was measured using the patented Speed of Sound (SOS) technology.[5] Prior to each experiment, the sample was activated by flowing pure N_2 at the target temperature for 2 h. Each equilibration step was completed when the rate of mass change (dm/dt) was <0.002 wt%/min for 10 min. The sample was activated under N_2 flow at 150 °C before testing.

Breakthrough experiments were conducted on 252 mg (activated mass) of a pelletised version of the MOF, loaded into a 4 mm inner diameter tube, using a BTA Frontier instrument with a 50 sccm total flow rate. Outlet H_2O and CO_2 concentrations were measured with a capacitive RH sensor and an NDIR sensor, respectively. The sample was activated under N_2 flow at 150 °C before testing.

Fig 1. DVS Carbon (Left) and BTA Frontier (Right) instruments.

Results

Single component CO_2 isotherms were collected at 25 and 40 °C, showcasing a type-I isotherm with a saturation uptake of 18.71 wt% (4.25 mmol/g) and 15.74 wt% (3.58 mmol/g) achieved at 0.95 bar CO_2 (95 vol%) in the powder form (Fig 2a). At 15 vol% CO_2 conditions, relevant for many post combustion carbon capture applications, this resulted in an uptake of 9.28 wt% (2.11 mmol/g) and 4.78 wt% (1.09 mmol/g) at 25 and 40 °C , respectively, which compares favorably to known carbon capture sorbents with a similar use case such as CALF-20[3] , and MUF-16[6] with ~2.7 and ~1.2 mmol/g, respectively, at 293 K, 0.15 bar CO_2. The isosteric enthalpy of adsorption was calculated to be around 42.1 kJ/mol at low loading, dropping to 38.6 kJ/mol at 15.6 wt. % loading (Fig 2a, inset), in an optimal range for energy-efficient sorbent regeneration.[7]

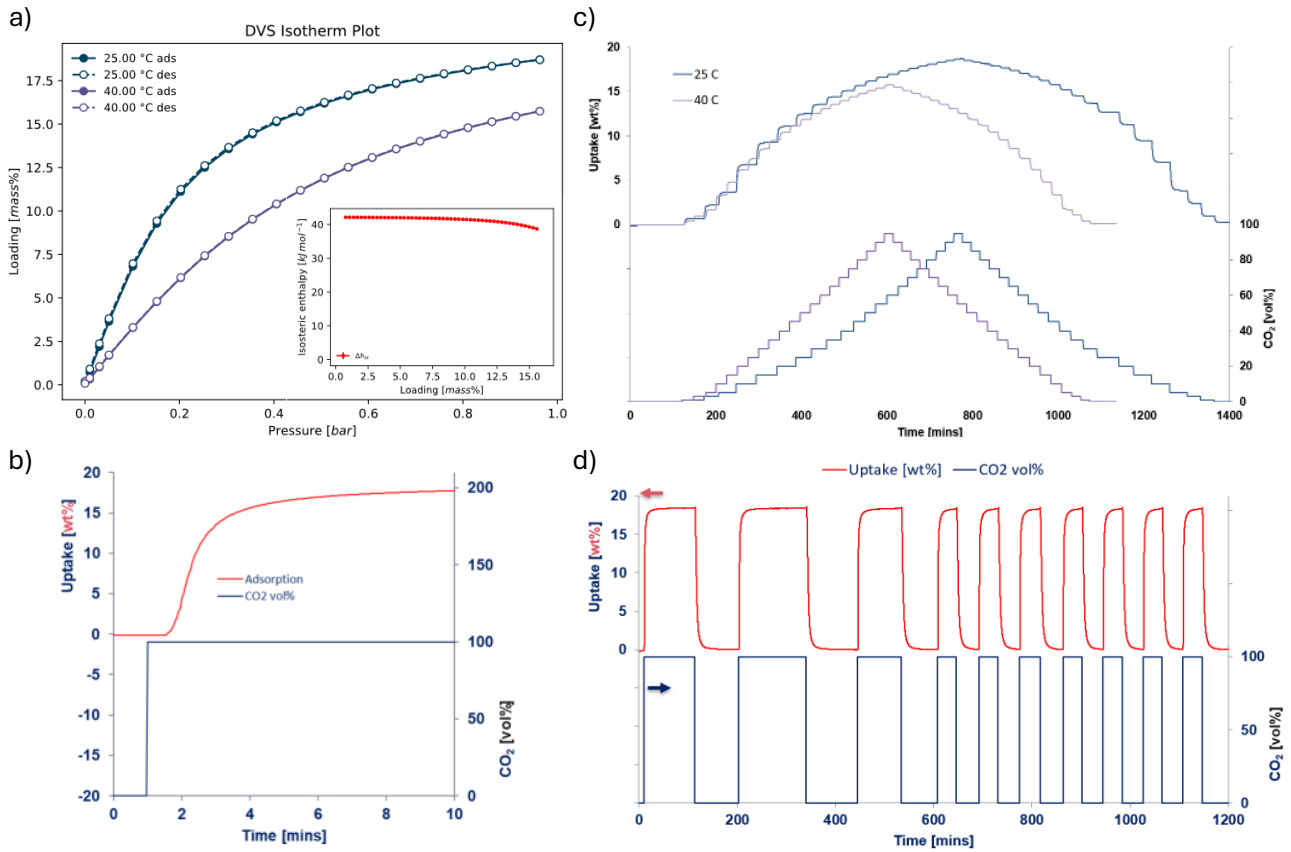

Fig 2. a) CO_2 adsorption isotherm in a nitrogen carrier and isosteric enthalpy as a function of CO_2 loading (inset graph); b) adsorption kinetics for CO_2 at 25 °C; c) CO_2 sorption kinetics in a nitrogen carrier; d) CO_2 cycling in a DVS.

A viable carbon capture sorbent must also exhibit fast kinetics, cycle stability, and sustained activity upon exposure to process-relevant relative humidity conditions. These properties were evaluated using the DVS Carbon by cycling between 0 and 100 vol% CO_2. The sorbent demonstrated rapid kinetics, achieving near-complete loading and unloading in less than 5 min (Fig 2b), with a full isotherm collection taking ~1400 min (Fig 2c). Given that the mass signal combines both mass and thermal transfer together, the short equilibration time attests to the speed of the adsorption and desorption processes. The MOF maintained stable uptake over 10 cycles (Fig 2d), confirming the consistent CO_2 sorption performance.

Separately, the water sorption characteristics of the material were investigated by DVS. A series of sorption isotherms recorded (Fig 3) showed a low uptake of water, with signs of deliquescence above 75% RH at 5 and 25 °C, while a mass loss is observed at 55% RH at 40 °C indicating a greater sensitivity to humidity when combined with higher temperature. Up to 6 wt%, the isosteric enthalpy was calculated the be in the range of ~39 kJ/mol (Fig 3, inset).

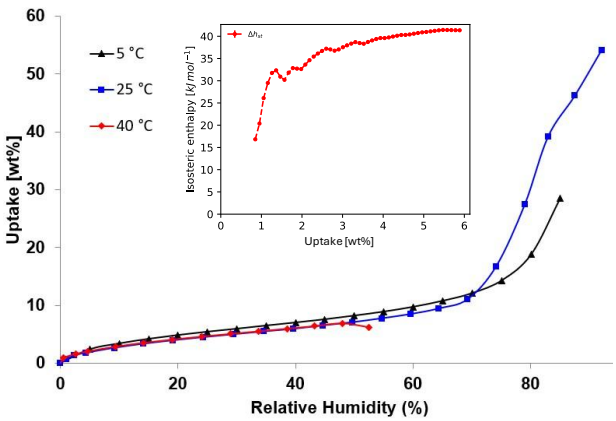

Fig 3. Water sorption isotherm at 5, 25, and 40 °C. The 40 °C isotherm was terminated at 55% RH due to mass loss.

To further explore the influence of high levels of humidity exposure on the CO_2 capacity, CO_2 sorption cycles were conducted before and after exposure to progressively increasing flows of humid gas (25, 50, and 75 % RH in nitrogen) (Fig 4). The MOF displayed a stable uptake after three CO_2 cycles after exposure to 25 and 50% RH nitrogen streams. However, some loss of CO_2 uptake capacity became apparent after exposure to 75% RH as subsequent CO_2 exposure results in *ca.* 35% reduced uptake, The combination of such testing conditions enabled by the DVS Carbon allows for a ready evaluation of the stability limits for this material allowing for relevant process parameters and suitable handling procedures to be developed.

Post-combustion effluent streams will invariably contain, in addition to CO_2, significant amounts of

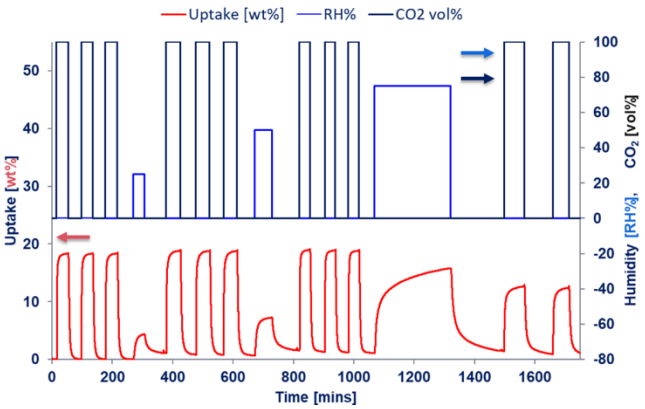

Fig 4. CO_2 and H_2O cycling of the MOF in a DVS Carbon.

H_2O that may not be removed prior to contact with the sorbent without incurring additional cost. As such, co-adsorption of CO_2 and H_2O is an essential, yet experimentally challenging, parameter to study during material selection. Using the DVS Carbon, co-adsorption experiments were conducted by introducing 10 vol% CO_2, after a pre-saturation with water at 40% RH at 14, and 25 °C (Fig 5). In this way, the DVS Carbon allows for rapid, experimentally facile screening of small-scale material samples with simplified method development under co-adsorption conditions. To note, as this method does not distinguish the mass increase attributable to either H_2O or CO_2, it does not provide a quantitative measure of the uptake of each component. Nevertheless, this method can indicate whether the adsorption mechanism is cooperative (presence of both components enhances total uptake as observed in amine-functionalised polymers), competitive (water and CO_2 adsorb on the same sites, with one taking preference over the other) or non-interacting, where water and CO_2 have completely different sorption mechanisms and sites. Comparison to the single-component mass uptake under 10 vol% CO_2 or 40% RH at 25, and 14 °C (Fig 6a and 6b) does appear to show a relatively non-interactive uptake of both sorbates indicating a substantial CO_2 uptake even when the sample has been pre-saturated in the presence of humidity. For example, at 25 °C, 10 vol% CO_2 or 40% RH results in an uptake of 6.82 and 6.15 wt%, respectively, while under co-adsorption conditions (10 vol% CO_2 and 40% RH) a mass gain of 11.25 wt% is observed.

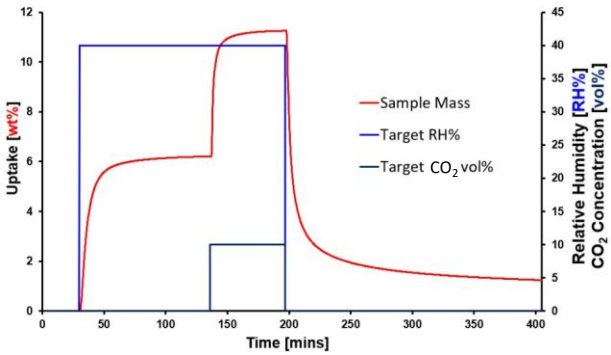

Fig 5. Co-adsorption of 40 % RH and 10 vol% CO_2 in a DVS Carbon at 25 °C.

Direct measurement of co-adsorption however requires determination of the composition of H_2O and CO_2 within the MOF at equilibrium, which requires the use of the breakthrough technique, as in the BTA Frontier instrument. A breakthrough analysis was performed using the pelletized MOF loaded into a column using 10 vol% CO_2 and 40% RH at 25 °C (Fig 7a). After equilibration, the adsorbed contents of the MOF were desorbed under nitrogen flow and heat (Fig 7b).

The BTA was conducted in the adsorption phase whereby 50 sccm of 10 vol% CO_2 and 40% RH was passed over the pelletized sample, followed by a desorption at elevated temperature under 15 sccm pure N_2. During adsorption, for the first ~1.5 min,

neither signal was observed indicating that both components were being adsorbed into the MOF sample. This is then followed by a 'breakthrough' of CO_2 as all available binding sites are saturated while H_2O, present in a lower concentration (~1.2 vol%), continues to be absorbed. Noticeable in this period is the lack of a substantial 'roll-up' of the CO_2, wherein incoming molecules of H_2O replace adsorbed CO_2 molecules which would result in an outlet CO_2 level in excess of the inlet (~10 vol%) value, further reinforcing the observed non-interaction between H_2O and CO_2 within the MOF. This is followed by an extended period of H_2O breakthrough, indicative of slow sorption kinetics or mass transfer resistance. When taking into account the flow rates and gas composition, this information allows for the adsorption uptake up to equilibrium to be calculated. The desorption phase begins with a sharp decrease in CO_2 and humidity as the carrier gas is switched to pure N_2, followed by a spike in CO_2 up to ~5.5 vol% and humidity up to 84% as a result of desorption of both components from the sorbent.

The collated uptake results from DVS and BTA are presented in Fig 6a. At 25 °C, the BTA demonstrated single component uptake of 5.69 and 4.46 wt% of to H_2O and CO_2, respectively, which closely align with the value obtained by the combined uptake measured in the DVS Carbon using a powder sample of MOF of 11.25 wt%. More interestingly, when exploring lower temperatures of 14 °C, the uptake for CO_2 when dry and in the presence of water is 34% higher. It is also worth noting that adsorbed water does not necessarily have to be desorbed from the sorbent to achieve a substantial CO_2 uptake, as can be seen in the cycling DVS experiment with background humidity seen in Fig 6c.

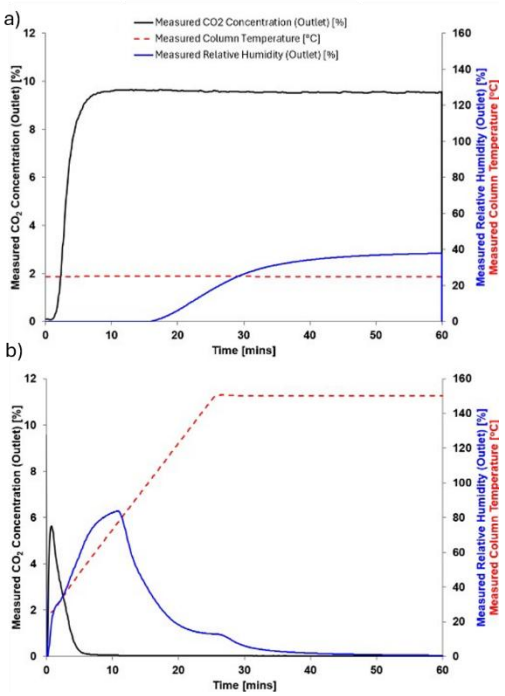

Fig 7. a) Adsorption and b) desorption breakthrough analysis of the MOF at 25 °C under 10 vol% CO_2 and 40 RH%.

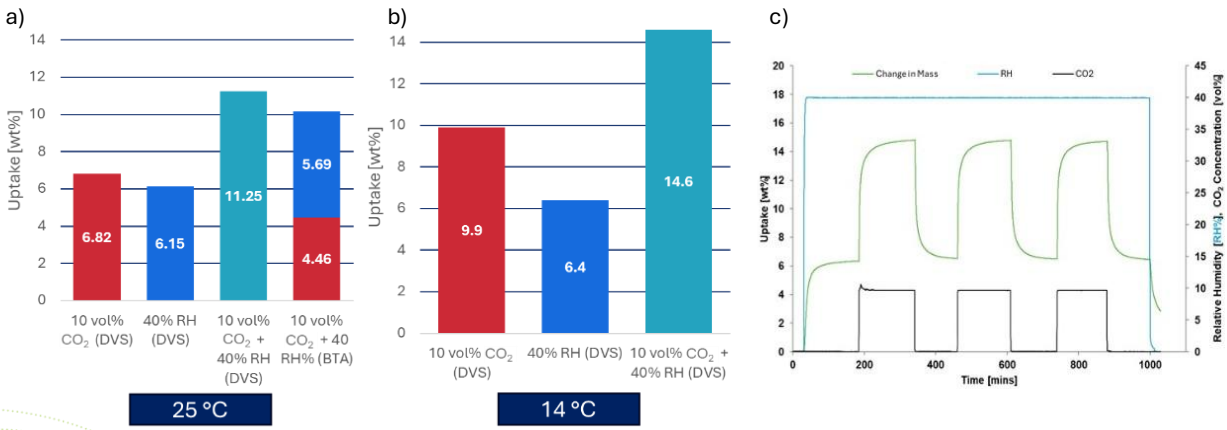

Fig 6a and b. Uptake of CO_2 (red) and H_2O (blue) into the MOF individually or through co-adsorption (cyan) in a DVS Carbon at different temperatures, as well as CO_2 and H_2O uptake at equilibrium measured on the BTA Frontier. Fig 6c. CO_2 cycling of the MOF under a constant flow of 40% RH.

Conclusion

Effective carbon capture requires sorbents that excel in CO_2 uptake despite the presence of humidity. Using the DVS Carbon's precise gravimetric analysis and the BTA Frontier's dynamic breakthrough testing, the MOF demonstrated robust CO_2 capacity at the 15 vol% conditions typical for post-combustion capture. The MOF showed a stable performance at 40% RH across multiple cycles. Co-adsorption measurements under breakthrough conditions confirmed the significant retention of CO_2 uptake under humid conditions, highlighting the novel MOF's potential to operate in gas streams with limited dehumidification. In combination, the integrated capabilities of the DVS Carbon and BTA Frontier allow for a comprehensive analysis of leading sorbent materials, advancing the development of sustainable carbon capture solutions.

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