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DVS Application Note 117

Water and CO_2 co-sorption landscape in CALF-20, a prototypical MOF, for post combustion capture

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The development of efficient carbon capture technologies is critical for mitigating anthropogenic CO_2 emissions and achieving climate neutrality targets. Metal-organic frameworks (MOFs), particularly mildly hydrophobic variants such as CALF-20, have emerged as promising physisorbents for industrial-scale CO_2 capture from humid gas streams. This application note presents a comprehensive gravimetric investigation of single-component and multicomponent CO_2 and H_2O sorption on CALF-20 using the DVS Carbon Advanced platform. This specialized instrument enables independent control of CO_2 concentration (from ppm levels to 100 vol%) and relative humidity (0–98% RH) across a wide temperature range (5–450°C), providing unprecedented capability for systematic co-sorption studies under realistic operating conditions. Single-component isotherms were acquired at multiple temperatures to characterize the temperature dependence of CO_2 and water uptake. Co-sorption experiments with constant background concentrations of one component while scanning the other revealed competitive sorption behavior and enabled construction of complete three-dimensional sorption surfaces. The results provide quantitative data essential for process design and optimization of carbon capture systems utilizing this benchmark MOF material.

Introduction

Carbon capture and storage (CCS) technologies, including point-source capture from industrial flue gas and direct air capture (DAC), represent critical components of the portfolio of solutions required to achieve climate goals [1, 2]. The development of efficient, durable, and cost-effective sorbent materials capable of selective CO_2 capture from complex gas mixtures under realistic operating conditions remains a central challenge in this field.

Metal-Organic Frameworks (MOFs) have attracted considerable attention as next-generation CO_2 capture materials [3], winning the Nobel Prize in 2025. While many MOFs exhibit exceptional CO_2 uptake capacity under idealized dry conditions, the majority suffer from poor hydrothermal stability or substantial performance degradation in the presence of water vapor, a ubiquitous component of industrial flue gases and ambient air. This critical limitation has hindered the transition of MOF-based capture systems from laboratory demonstrations to industrial implementation. Calgary Framework 20 (CALF-20) represents a significant breakthrough in addressing the stability and performance challenges associated with MOF-based CO_2 capture [4]. This zinc-triazole-oxalate framework exhibits a unique combination of properties that position it as a benchmark material for industrial applications. CALF-20 demonstrates high CO_2 capacity and selectivity over N_2 despite a physisorptive mechanism with moderate enthalpy of sorption (approximately 30–35 kJ/mol), enabling energy-efficient regeneration cycles. The framework's slight hydrophobic character allows CO_2 capture from wet gas streams, while its exceptional chemical and mechanical stability enable operation under harsh conditions including steam regeneration and direct flue gas contact [4].

Comprehensive characterization of sorbent performance under realistic operating conditions requires precise control over multiple environmental variables including temperature, CO_2 concentration, and humidity. Traditional sorption measurement approaches typically examine single-component isotherms or employ simplified binary gas mixtures, providing incomplete information about competitive sorption phenomena and synergistic effects that govern performance in multicomponent systems. The DVS Carbon platform addresses this critical measurement gap by enabling independent, simultaneous control of both CO_2 and H_2O concentrations while monitoring mass changes with sub-microgram resolution using an ultrasensitive microbalance.

This application note presents a comprehensive gravimetric investigation of single-component and multicomponent CO_2 and H_2O sorption on CALF-20 using the DVS Carbon Advanced platform.

Methods

All measurements were conducted using the SMS DVS Carbon Advanced gravimetric sorption analyzer. The instrument combines a high-resolution UltraBalance with a temperature controlled enclosure and independent CO_2 and H_2O generation systems, allowing systematic variation of gas composition and temperature while recording mass changes with high sensitivity.

The DVS Carbon platform enables control of CO_2 concentration from low ppm levels up to 100 vol% at atmospheric pressure, together with humidity control from dry to near-saturated conditions across a wide temperature range. Concentrations can be programmed separately in either stepwise or ramped profiles, enabling complex co-sorption, cycling, and regeneration protocols. Temperature control from 5°C to 450°C is achieved through a combination of a thermostatted sample enclosure and high-temperature local heater.

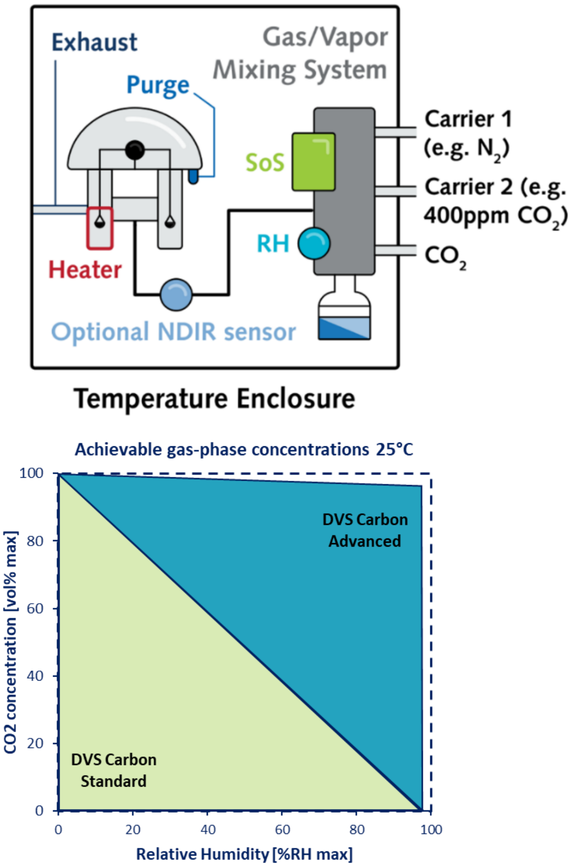

Figure 1: (Top) A schematic of the DVS Carbon Advanced. (Bottom) The possible CO_2 and H_2O co-sorption phase space for the DVS Carbon family.

This unique combination of capabilities allows systematic exploration of the complete sorption behavior across the multidimensional parameter space relevant to carbon capture applications including flue gas treatment, biogas upgrading, and direct air capture.

CALF-20 was used as received for all measurements. Prior to analysis, samples were activated by heating at 180 °C for at least 180 minutes under a dry gas purge to remove residual solvent and sorbed species. Sample masses of approximately 10–50 mg were employed to provide adequate signal-to-noise ratio while maintaining rapid equilibration kinetics and minimizing thermal gradients within the sample bed.

Results

Single component isotherms

Single component CO_2 and H_2O sorption isotherms were measured at multiple temperatures covering the range from cold conditions 5°C to hot gas 105°C at a total pressure of 1 bar. The CO_2 concentration and RH were increased in a stepwise manner with equilibrium criteria based on mass change rate (<0.002%/min over 10 minutes) ensuring accurate determination of equilibrium uptake at each point. Desorption branches were measured by decreasing concentration in reverse sequence to assess hysteresis behavior. An isobar (temperature steps at constant concentration) at 20 vol% CO_2 and an isohume (temperature steps at constant relative humidity) at 20 RH% were also recorded from 5 to 150°C, in 10°C increments.

Fig 2a presents the CO_2 dataset for CALF-20. The isotherms exhibit Type I character according to the IUPAC classification, consistent with micropore filling. The material shows substantial capacity at 15-50% CO_2, common concentration ranges for post combustion capture, above 3 mmol/g at 25°C. At higher temperatures, the uptake decreases significantly, reflecting the exothermic nature of the physisorption process. This behavior is quantitatively described by the Clausius-Clapeyron relationship and enables estimation of the isosteric enthalpy of sorption across the loading range, as depicted in Fig 2c. A useful measurement to quickly evaluate temperature dependence of sorption at a constant concentration is the isobar – which can be seen in the grey squares in Fig 2a. The dataset allows for a full 3D sorption surface to be built, as depicted in Fig 2b.

Minimal hysteresis between sorption and desorption branches confirms the reversible, physisorptive nature of CO_2 binding in CALF-20, consistent with the framework's lack of open metal sites or strongly interacting functional groups. This reversibility is critical for cyclic capture-release processes and contributes to the material's demonstrated long-term stability over hundreds of thousands of cycles [4].

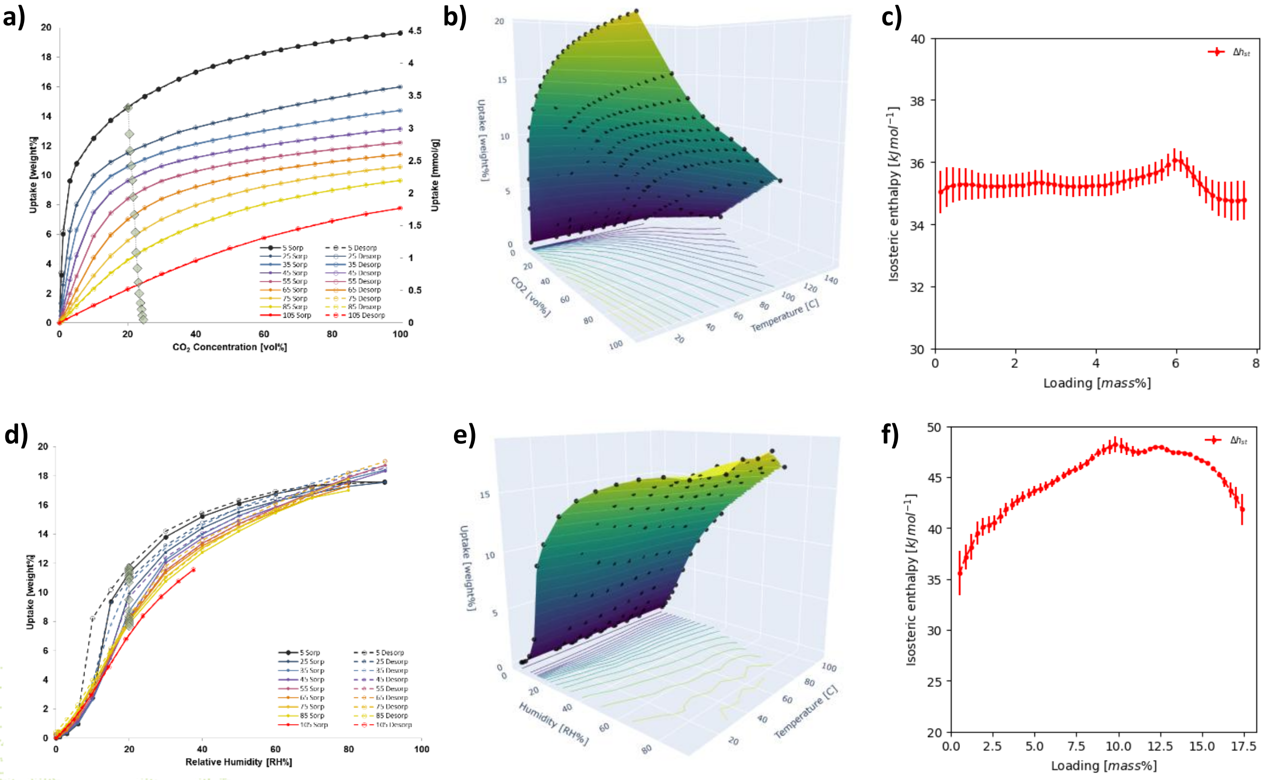

Figure 2: 2a) CO_2 Isotherms. 2b) CO_2 sorption surface. 2c) Isosteric enthalpy of sorption of CO_2 on CALF-20. 2d) H_2O Isotherms. 2e) H_2O sorption surface. 2f) Isosteric enthalpy of sorption of H_2O on CALF-20.

Water vapor sorption isotherms in Fig 2d reveal a partly hydrophobic character. At low relative humidity throughout the entire temperature range (<10 %RH), water uptake remains minimal, indicating weak water-framework interactions and negligible surface hydrophilicity. As humidity increases above 20 %RH, more water is adsorbed, signaling the onset of capillary condensation within the micropore network. The hydrophobic nature of the CALF-20 framework, comprising zinc metal centers fully coordinated by oxalate and triazolate linkers with aromatic character, delays water condensation to higher RH compared to hydrophilic analogues. This behavior is also evidenced by the resulting enthalpy of sorption as calculated in Fig 2f, where the initial adsorbed amount is found to have an enthalpy of below 44 kJ/mol, the vaporization enthalpy of water at 25°C.

The temperature dependence of water sorption provides insight into the thermodynamics of water clustering and condensation within the CALF-20 pore structure. As temperature increases the isotherm in the relative humidity space maintains a similar shape, with a slight shift towards a more linear rather than S-shaped isotherm.

Recent studies have identified a fully reversible humidity transition in CALF-20 [7]. The large temperature space employed in this study is mostly outside the researched range for these transitions. Nevertheless, it is likely that many of the inflexion points are results of these structural transitions, potentially contributing to the observed sorption behavior. Similarly, as with CO_2, the full water sorption surface can be found in Fig 2e.

Co-sorption experiments

To obtain a full picture of CALF-20 uptake in the presence of both components, a systematic co-sorption study were performed using two complementary approaches. In the first approach, a constant background concentration of H_2O was maintained while scanning CO_2 concentration across the full range, enabling determination of CO_2 uptake as a function of CO_2 partial pressure at fixed water loadings, as exemplified in Fig 3c. In the second approach, a constant CO_2 background was maintained while varying humidity, shown in Fig 3a. Multiple background concentrations were employed for each component to build a comprehensive dataset over the full 0-100 vol% CO_2 and 0-98 RH% ranges. To note that the ability of the DVS Carbon Advanced allows for independent probing of the full co-sorption space from any direction.

The complete single-component and co-sorption datasets were integrated to construct a three-dimensional sorption surface representing total uptake as a function of both CO_2 and H_2O at fixed temperature, as can be seen in Fig 3b. This surface provides a comprehensive visualization of the multicomponent sorption landscape and serves as valuable tools for process modeling and optimization. The surfaces also reveal regions of the parameter space where synergistic effects may occur, warranting further multicomponent sorption investigations using complementary techniques such as in dynamic breakthrough analysis with devices such as the SMS BTA Frontier.

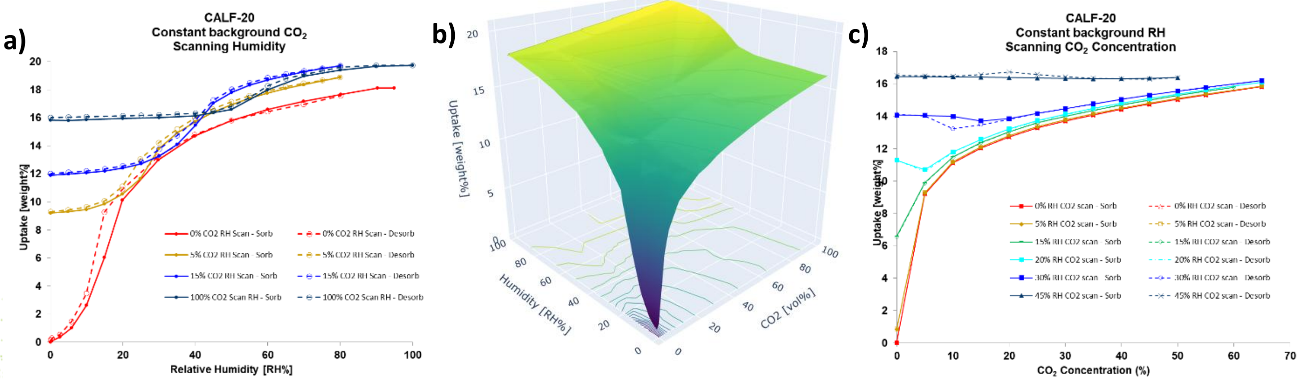

Figure 3: 2a) Constant CO_2 background maintained with a scanning RH. 2b) Co-sorption surface. 2c) Constant H_2O background maintained with a scanning CO_2 concentration.

Conclusions

This comprehensive gravimetric study demonstrates the power of the DVS Carbon platform to elucidate multicomponent CO_2 and H_2O co-sorption behavior on advanced sorbent materials under systematic variation of temperature, CO_2 concentration, and humidity. The independent control of CO_2 and H_2O partial pressures, a unique capability of the DVS Carbon, enables the acquisition of complete sorption datasets that fully characterize material performance across the multidimensional parameter space relevant to industrial carbon capture applications.

The experimental protocols and analysis approaches described herein are broadly applicable to evaluation of other carbon capture materials including functionalized MOFs, amine-grafted sorbents, zeolites, and porous carbons. The ability to replicate realistic operating conditions, including simultaneous presence of CO_2 and water at industrially relevant concentrations and temperatures, positions the DVS Carbon platform as an essential tool for accelerating the development and deployment of next-generation carbon capture technologies required to achieve global climate mitigation goals.

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