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Application Note 111

Realistically evaluating the capabilities of Zeolite 13X as a sorbent for Direct Air Capture in different scales

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In this study, the sorption capabilities of zeolite 13X were evaluated for the Direct Air Capture (DAC) of CO_2 under realistic ambient conditions using multiple sorption instruments. Experiments were conducted at 400 ppm CO_2, using the Dynamic Vapor Sorption (DVS) Carbon, DVS Vacuum, and Breakthrough Analyzer (BTA) Frontier systems. Zeolite 13X demonstrated efficient CO_2 capture highlighting the complex interactions between CO_2 and water vapor, emphasizing the competitive adsorption behavior under humid environments. True co-sorption data from BTA experiments revealed the significant impact of humidity on CO_2 capture, with water occupying adsorption sites and reducing CO_2 uptake at higher relative humidity levels. This comprehensive analysis focuses on the importance of evaluating sorbent materials under both dry and humid conditions to optimize DAC technologies.

Introduction

The concentration of carbon dioxide (CO_2) in the atmosphere has surpassed 400 parts per million (ppm), a level that significantly contributes to global warming and climate instability [1]. This increase in CO_2 levels is primarily driven by human activities such as fossil fuel combustion, deforestation, and industrial processes [1]. As a result, the need for effective and innovative methods to reduce atmospheric CO_2 has become increasingly important. **Direct Air Capture (DAC)** is a type of carbon capture technology designed to address the escalating challenge of climate change by removing CO_2 directly from the atmosphere. This differs from **Point Source Capture** (**PSC**), which focuses on emissions at their source. DAC operates independently of emission points, making it a versatile and scalable solution for mitigating the effects of greenhouse gases on a global scale.

At the atmospheric concentration of 421 ppm, corresponding to 0.04% by volume or 40 Pascal of partial pressure, capturing CO_2 poses specific technical challenges due to the diffuse nature of the gas in the atmosphere, varying conditions, and interference of other components, particularly humidity. However, successfully capturing and sequestering CO_2 at these levels would demonstrate DAC's potential to significantly reduce the atmospheric burden of this greenhouse gas, thereby helping to stabilize the climate, restore natural carbon balances, and achieve international climate goals [2].

One of the primary technologies currently used for DAC is based on solid sorbent materials – materials that have a high affinity for CO_2. These sorbents, usually as varied as amine-functionalized porous materials, alkali or alkali metal oxides and hydroxides, metal-organic frameworks (MOFs) and zeolites, bind CO_2 from the air. Once saturated with CO_2, the sorbents are regenerated by applying heat, vacuum or other methods to release the captured CO_2, which can then be stored or utilized [3]. Studies have demonstrated that these solid sorbents can achieve significant CO_2 uptakes and exhibit stable performance over multiple cycles, making them promising for scalable and efficient DAC applications.

Measuring the performance of solid sorbents for CO_2 capture at realistic DAC conditions is particularly important for assessing and scaling up promising materials [4]. DAC involves overcoming several significant challenges. The main issue is the low concentration of CO_2 in the ambient air, which means that over 1300 m^3 of air needs to be fully scrubbed to remove just 1 kg of CO_2. Changing atmospheric conditions such as temperature and pressure heavily influence sorbent performance, making it difficult to maintain consistent capture performance. Additionally, the kinetics of CO_2 capture at ultra-low concentrations are typically slow, requiring precise measurement techniques. The presence of humidity can also impact CO_2 adsorption in various ways, competing for adsorption sites, affecting chemical reactions or simply acting as a thermal sink. Evaluating the energy required for sorbent regeneration is important, as high regeneration energy can undermine the overall feasibility of DAC processes. Ensuring long-term stability and durability of sorbents over multiple cycles adds another layer of complexity, requiring extensive and time-consuming testing [5-7].

Zeolites have been suggested as sorbent materials for DAC processes due to several key properties. Firstly, they possess a highly porous structure with a large surface area, and generally contain strongly interacting cages or counterions, that ensure a high uptake of CO_2. One common zeolite already in use in various industrial processes is zeolite 13X – an aluminosilicate zeolite with a faujasite crystal structure and exchanged with sodium counterions. It is a cheap, widely available material, commonly used for oxygen generation, desulfurization and gas drying. 13X is highly stable and has shown affinity for CO_2 [8]. Moreover, it can be regenerated and reused in multiple cycles without significant loss of efficiency, making it economically promising for large-scale DAC operations [9]. Nevertheless, it also has a strong affinity for water and has shown degradation at high temperature in a humid environment which may interfere with its performance towards CO_2. For this reason, they are not prime sorbent candidates for DAC however they are a popular choice as CO_2 sorbents due to being cost-effective and have well-defined pore structures that can selectively capture CO_2 under controlled conditions, such as in industrial gas separation or post-combustion capture, where moisture is less of a concern.

In this study, we look at how to evaluate zeolite 13X for DAC at the lab scale, using several powerful instruments DVS Carbon, DVS Vacuum and BTA Frontier, to understand its effectiveness as a carbon capture sorbent material under real-world conditions of low pressures of 400 ppm and influenced by humidity.

Methods

Zeolite 13X was sourced from Zeochem as binderless pellets of 1.2-1.4 mm diameter. Around 20 mg of zeolite 13X were used for DVS and 230 mg for BTA experiments.

The **DVS Vacuum** was used to provide detailed insights under low partial pressure of CO_2. The Vacuum is a gravimetric instrument that accurately controls the inlet and outlet flowrates around the sample, maintaining a target pressure. The sample was activated at 300 °C under high vacuum of $5x10^{-6}$ Torr for 240 minutes.

To measure CO_2 sorption performance under realistic conditions, the **DVS Carbon Advanced** was used. Prior to sorption, the sample was activated *in situ* at 300 °C under a flow of pure N_2. Adsorption and desorption were measured from 0 to 5000 ppm using and advanced mixing system connected to cylinders of either 400 ppm CO_2 in N_2, 1% CO_2 in N_2 and or pure N_2. CO_2 concentrations are achieved by mixing variations of connected gases at a total flow rate of 200 sccm. Mixed concentrations are verified using the NDIR probe dedicated to ppm-level CO_2 detection. A key difference between the two instruments is that the DVS Carbon uses a carrier gas to dilute the incoming CO_2 stream, allowing the user to observe the impact of carrier gases, like nitrogen.

Breakthrough experiments were carried out in the **BTA Frontier**, a self-contained breakthrough instrument which can accurately control concentrations of water and CO_2 over a packed bed. A silanized glass column of 4 mm inner diameter was packed with crushed zeolite 13x pellets, held in place with quartz wool. Pressure drop was verified to be negligible over the column. Sample was activated *in situ* at 300 °C under a flow of pure N_2.

Results

In the first instance, to assess the potential of the material, single component isotherms of CO_2 are commonly performed. First, the sample was pre-treated at high temperature to ensure the removal of pre-adsorbed species. Afterwards, the sample was cooled to 25 °C. Figure 1 compares the CO_2 isotherms from 0% to 100% by volume concentration using both DVS Carbon and DVS Vacuum systems.

The sample shows a Langmuirian type 1 isotherm consistent with high uptake below 20 % CO_2 that plateaus as saturation is approached. The desorption curves closely match the sorption curves over the high concentration range, suggesting good reversibility and minimal hysteresis.

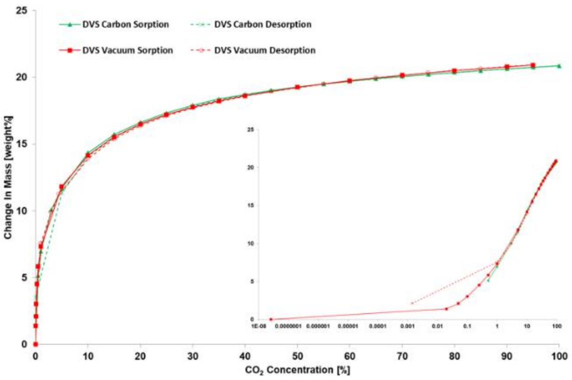

Figure 1. Sorption and desorption isotherms of CO_2 on zeolite 13X using the DVS Carbon and DVS Vacuum. In the bottom right of the figure is the sorption plotted on a log scale.

However, experiments at high concentrations do not show the full picture. To evaluate the uptake of CO_2 at atmospheric concentrations, a single point sorption experiment on zeolite 13X was recorded, providing data on its adsorption capacity and rate of uptake at these concentrations. In the DVS Carbon the sample was exposed to a concentration of CO_2 of 400 ppm flow of 200 sccm dry nitrogen as seen in Figure 2. The sample demonstrated a 1.57% increase in mass from CO_2 adsorption, corresponding to an uptake of 0.36 mmol of CO_2 per gram of zeolite. A similar experiment is shown in the same figure that uses a pure atmosphere of CO_2 at a partial pressure of 40 Pa, equivalent to 400 ppm concentration. The overall sorption kinetics are seen to be faster than in the carrier gas. The difference is likely to be due to a change of mass transport mechanisms and molecular diffusion through the carrier gas. Thermal effects cannot be ruled out but are unlikely at this sample size and guest concentration. After an initial fast kinetic regime, the uptake rate decreases significantly. This comparison highlights the importance of evaluating sorption kinetics experiments at realistic conditions.

This targeted analysis helps in understanding the material's capacity and kinetics towards CO_2 at DAC conditions. In contrast, analyzing CO_2 sorption at concentrations up to 5000 ppm covers a wider spectrum of CO_2 encompassing both atmospheric and indoor. Figure 3Figure 3a shows the COFigure 3and Figure 3b shows the resulting isotherm. At 400 ppm (40 Pa) the uptake is consistent with the results obtained in Figure 1, while it reaches a maximum uptake of over 5 wt% at 5000 ppm (505 Pa). The overall sorption/transport kinetics are slower at low concentrations, and it is clear that an equilibrium has not been reached below 1000 ppm (101 Pa). Desorption is more gradual and interestingly, there is evidence of pronounced hysteresis, as under an inert gas flow more than

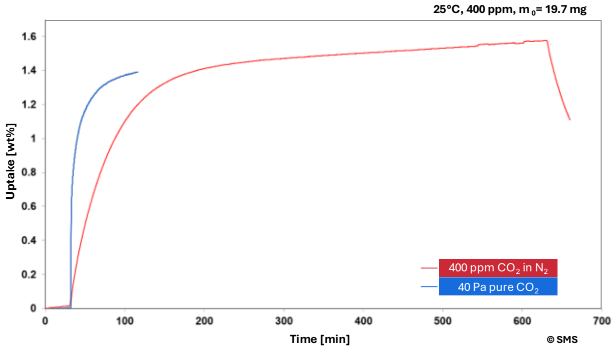

Figure 2: Single step adsorption of Zeolite 13X at 400 ppm CO_2 and 25°C

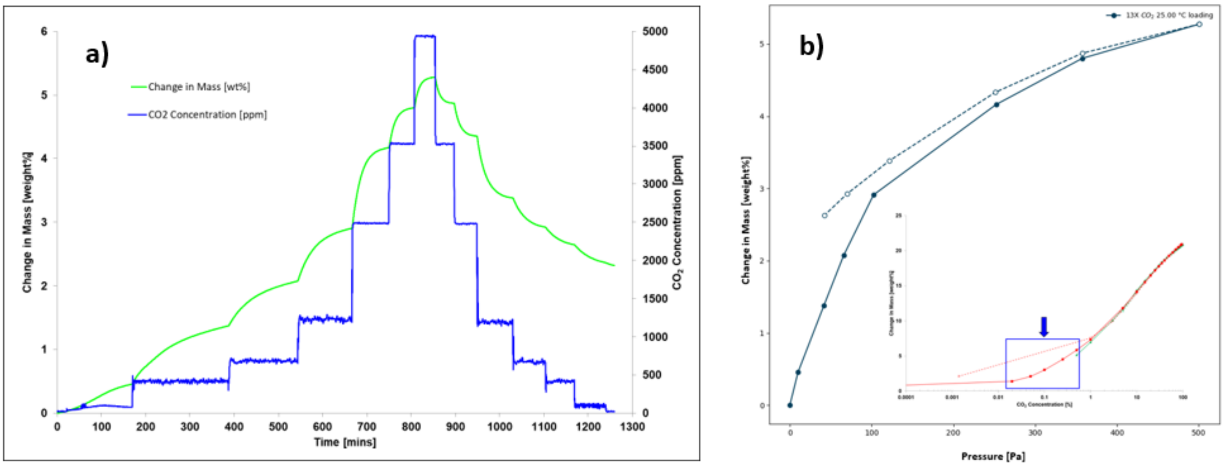

Figure 3. Sorption profiles of Zeolite 13X using the DVS Carbon showing a) a stepwise experiment changing CO_2 concentration from 0-5000 ppm showing both sorption and desorption profiles and b) the resulting isotherm focusing on the uptake of CO_2 at 400 ppm in the inset.

40% of the total uptake is retained. This indicates the presence of small amounts of strong CO_2 binding sites.

The single component results suggest that zeolite 13X is fairly effective in capturing CO_2 at DAC levels. An average capacity of 0.34 mmol/g is counterbalanced by strong sites suggesting good selectivity towards CO_2 compared to N_2 and O_2. Sorption kinetics are also promising, although require further investigation to deconvolute the contributions of various diffusional barriers and transport mechanisms.

The most common contaminant in DAC processes is water, in the form of atmospheric humidity. Relative humidity (RH) can vary from below 20% to 100%. The presence of water is likely to interfere with the sorption of CO_2 of the solid sorbent. Figure 4 compares the isotherms of single component water uptake on 13X at two different temperatures, 25°C and 40°C, across the full range relative humidity. The uptake at 40 °C is very slightly lower than at 25 °C, indicating that higher temperatures slightly reduce the water adsorption capacity of zeolite 13X. Nevertheless, 13X takes up a high amount of water, and more importantly around 80% of this capacity is reached at the lowest RH measured, below 1%.

This observation is important in predicting the competition between water and CO_2 for adsorption sites on zeolite 13X. Its hydrophobicity implies water competes more effectively for the available sites on the zeolite, potentially inhibiting CO_2 uptake.

While the results so far predict an important effect of water on CO_2 uptake, it is very difficult to predict co-sorption performance from single-component isotherms, as they do not account for the complex interactions between water and CO_2. To accurately determine co-sorption capacities, true co-sorption data, such as that obtained from packed bed breakthrough in the BTA Frontier, is essential. This data provides a more reliable measure of how competing gases behave in realistic capture conditions.

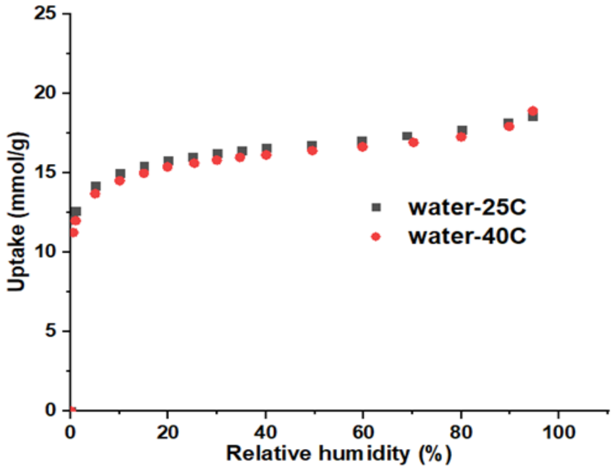

Figure 4. Isotherms of water uptake on zeolite 13X at 25 °C and 40 °C across varying relative humidity, illustrating the competitive impact of temperature on water adsorption

The BTA Frontier is an important tool for evaluating solid sorbents for DAC as it simulates real-world conditions of flow through a packed column (or ‘bed’ of the sorbent) at a controlled temperature. The data provides critical information on the total capacity, usable capacity (the time before significant breakthrough occurs) and the kinetics of the sorption process, all of which are essential for evaluating the performance of sorbent materials in gas separation and carbon capture applications. More importantly, it provides true multicomponent data under dynamic flow conditions in both dry and humid regimes and allows evaluation of the regeneration process. This analysis is crucial for understanding the real influence of water on DAC performance in zeolite 13X.

Figure 5a shows a typical breakthrough curve obtained from the BTA Frontier at 400 ppm CO_2 concentration and a temperature of 25 °C and a flowrate of 50 sccm. The concentration of CO_2 is monitored at the column outlet (C) when a flow of a constant concentration (C_0) is put through the inlet. Initially, as the gas flows through the sorbent, the material captures the CO_2, and nothing is seen at the outlet (C/C_0 close to 0). Over time, the sorbent material becomes increasingly saturated, leading to the "breakthrough" point, where the concentration of gas passing through the material begins to rise. The curve then steepens, reflecting the mass transfer zone closely related to the sharpness of the front through the column, itself largely a function of sorption kinetics. The equilibrium time marks the point where the sorbent is fully saturated, and the gas concentration at the outlet matches the inlet concentration (C/C_0 close to 1). A mass balance is then performed to calculate the total CO_2 uptake. A blank experiment is typically performed to account for the dead volume of the column and is subtracted to obtain accurate uptakes. While the BTA Frontier measures both inlet and outlet flowrates, flow change effects are minimal at these low concentrations and are herein ignored.

Figure 5b and c show the same 400 ppm CO_2 breakthrough when the inlet flow is at an RH of 30%, and 60%. The experiment at 30% RH shows a different breakthrough curve. CO_2 breaks through at a similar time as before around the 100-minute mark. This shows that the CO_2 front has passed through the column and after saturating it. However, soon after the CO_2 concentration at the outlet rises to above 400 ppm – nearly double the inlet value. This can be explained by the slower front of water that passes through the column, preferentially adsorbing and displacing the previously adsorbed CO_2. When the water front breaks through after 200 minutes, both concentrations equilibrate to their inlet values. This phenomenon is sometimes referred to as the ‘roll-up.’ Figure 5c of breakthrough at 60% RH, shows a more pronounced roll-up, with both fronts breaking through earlier due to the higher quantity of water in the inlet stream.

Figure 6 shows the integration of the BTA data to obtain the equilibrium uptake of CO_2 and H_2O. When there’s no humidity present, CO_2 uptake is in good agreement with the previous single

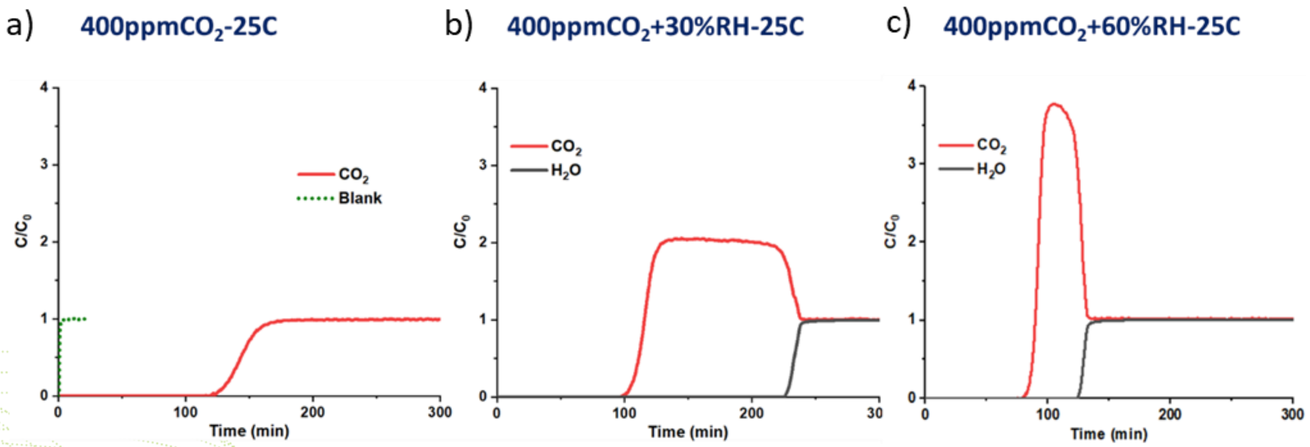

Figure 5 Breakthrough curves of zeolite 13X at 400 ppm and 25 °C at (a) 0% RH, (b) 30% RH and (c) 60% RH

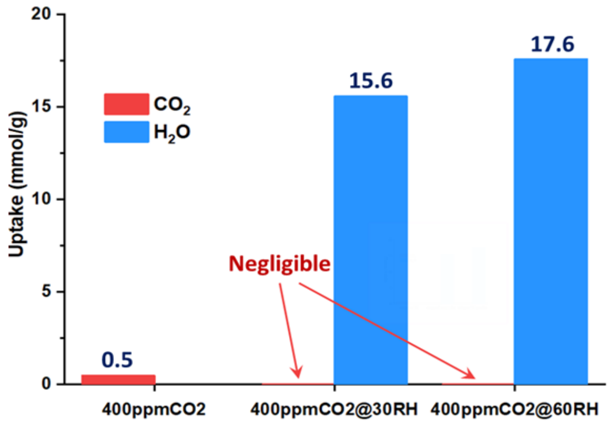

Figure 6: Uptake of CO_2 and H_2O by zeolite 13X at a concentration of 400 ppm CO_2 and a temperature of 25 °C, with varying relative humidity levels at 0%, 30%, and 60%.

component results from DVS. The data shows that as humidity increases to 30% and 60% RH, the uptake of CO_2 drops to negligible levels close to 0 and within the margin of error of the instrument. The uptake of H_2O at this humidity reaches values around 15 mmol/g and 17 mmol/g at 30% RH and 60% RH respectively, in close accordance with single component water uptake from DVS. This indicates strong competitive adsorption behavior, where water molecules preferentially occupy the adsorption sites on zeolite 13X, effectively fully inhibiting the adsorption of CO_2.

Overall, the breakthrough results indicate that increasing humidity levels reduce the CO_2 adsorption capacity of zeolite 13X, with water vapor increasingly occupying adsorption sites as humidity rises.

Conclusion

The investigation of zeolite 13X as a carbon capture sorbent material has demonstrated its potential for in Direct Air Capture applications. The findings indicate that zeolite 13X exhibits strong CO_2 adsorption capabilities, especially at low concentrations. However, the impact of humidity on CO_2 capture is significant, as water vapor competes for adsorption sites, thereby reducing the overall efficiency of zeolite 13X in real-world scenarios. The use of advanced techniques like the DVS Carbon, DVS Vacuum and the BTA Frontier has provided valuable insights into the kinetics, mass transport and diffusion capacity of zeolite 13X, highlighting the need for continued research to optimize its performance under varying environmental conditions. As climate change mitigation becomes increasingly critical, exploiting materials like zeolite 13X will play a pivotal role in developing effective strategies for reducing atmospheric CO_2 levels and achieving sustainability goals.

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