Study on the Adsorption Performance of a Direct Air Capture CO_2 Adsorbent

1. Background

Rising atmospheric CO_2 concentrations have intensified interest in carbon-capture technologies capable of achieving negative emissions. Among these, Direct Air Capture (DAC) removes CO_2 directly from ambient air, where the partial pressure of CO_2 is approximately 40 Pa, far lower than flue gas concentrations (~12 kPa). This low driving force imposes stringent requirements on adsorbent materials and limits the applicability of membrane separation or cryogenic methods. Solid sorbents, in contrast to liquid amine solutions, avoid issues associated with solvent volatility, corrosion, and high regeneration energy, making them well-suited for DAC systems.(1)

A wide range of solid sorbents has been explored, including alkali/alkaline-earth materials, metal–organic frameworks (MOFs), supported amines, and hybrid wet adsorbents.(2) Effective DAC sorbents must combine high CO_2 adsorption capacity, rapid kinetics, and strong CO_2/N_2 and CO_2/H_2O selectivity, while also maintaining stability across multiple adsorption–desorption cycles. Literature studies illustrate the challenges and potential approaches. For example, amine-grafted porous polymer networks (PPNs) demonstrate high selectivity at 400 ppm CO_2, and microporous MOFs modified with silica-rich additives exhibit substantial improvements in CO_2 uptake due to enhanced micropore volume.(3,4) Other works highlight the significant influence of humidity, as water molecules may compete with CO_2 for adsorption sites on hydrophilic surfaces, reducing CO_2 selectivity and breakthrough performance.(5)

In this study, we investigate the pore-structure characteristics and CO_2 adsorption performance of a MOF adsorbent using N_2 physisorption, CO_2 physisorption, TGA-based adsorption measurements, and CO_2 breakthrough experiments with the goal of understanding how surface area, pore structure, and ambient humidity influence DAC-relevant performance metrics. These measurements provide a foundation for evaluating the suitability of the material for DAC applications and for optimizing future sorbent designs.

2. Experiment

A MOF-based adsorbent was selected for characterization under DAC-relevant conditions, including N_2 physisorption, CO_2 adsorption isotherms, TGA adsorption capacity testing, and breakthrough curve analysis.

Nitrogen adsorption–desorption isotherms were measured at 77 K using a **Matrix 1000** specific surface area and pore size analyzer from **AMI**. The data was used to calculate the BET surface area, micropore volume, and pore size distribution.

CO_2 adsorption isotherms at 25 °C were also measured using the **Matrix 1000** analyzer from **AMI**.

The **TGA 1000** thermogravimetric analyzer from **AMI** was used to determine CO_2 uptake under two conditions:

- ✓ Pure CO_2, 50 mL/min, pretreatment at 80 °C followed by adsorption at 25 °C
- ✓ 400 ppm CO_2 / N_2 mixture, 50 mL/min carrier gas, with pretreatment and adsorption performed at 80 °C and 25 °C respectively.

Breakthrough tests were performed using a **BTsorb 100** penetration curve and mass-transfer analyzer from **AMI** at 400 ppm CO_2, 40% relative humidity, 10 mL/min flow, 298 K, and 1 bar. Breakthrough profiles were used to calculate dynamic adsorption capacity under humid DAC conditions.

3. Results

As shown in Figure 1a, the MOF material exhibits a Type I isotherm, characteristic of a microporous adsorbent. The BET surface area was measured as 1160 m²/g, with a micropore volume of 0.438 cm³/g and a maximum pore width of 0.390 nm, indicating an abundance of ultramicropores well-suited for CO_2 adsorption at low pressures.

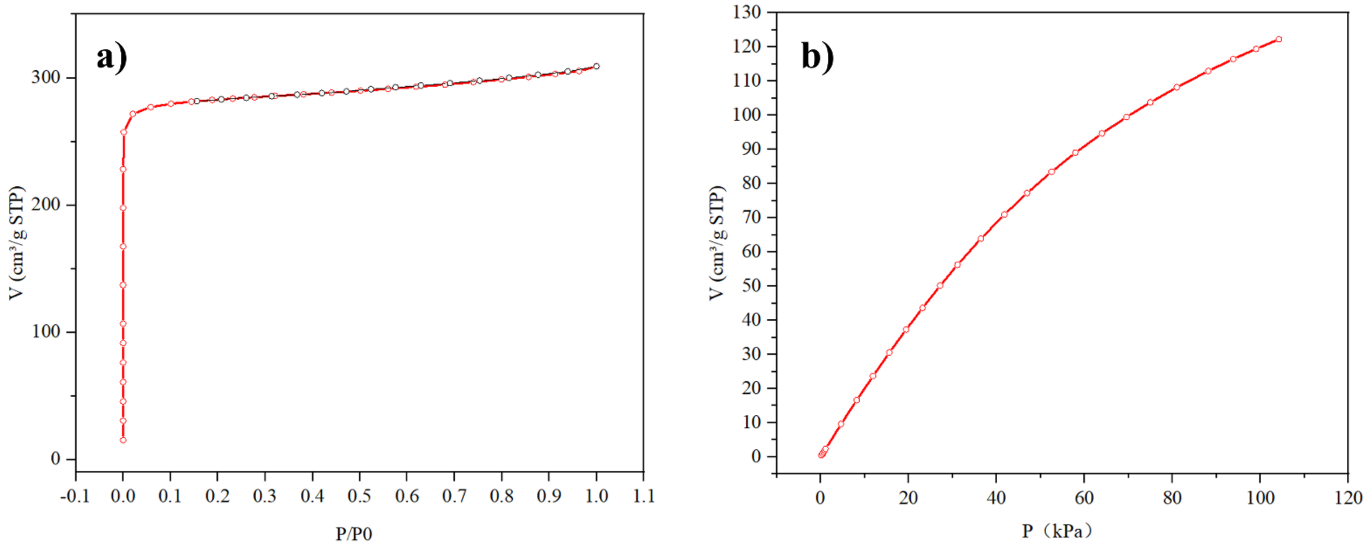

*Figure 1: a) N_2 adsorption and desorption isotherms at 77 K and b) CO_2 adsorption isotherms at 298 K obtained using the **Matrix 1000***

At 298 K and 1 bar, the CO_2 saturated adsorption capacity, shown in Figure 1b, reached 119 cm³/g (5.431 mmol/g), reflecting strong interaction between CO_2 molecules and the microporous network. This high capacity is consistent with the MOF material's large surface area and concentration of narrow micropores, which enhance adsorption potential energy in low-pressure regimes.

TGA measurements under pure CO_2 (Figure 2a) showed an uptake of 4.42 mmol/g, in agreement with the volumetric isotherm data. Under dilute CO_2 conditions (400 ppm), the measured capacity was 0.13 mmol/g (Figure 2b), substantially lower than the pure-gas capacity. This reduction is expected

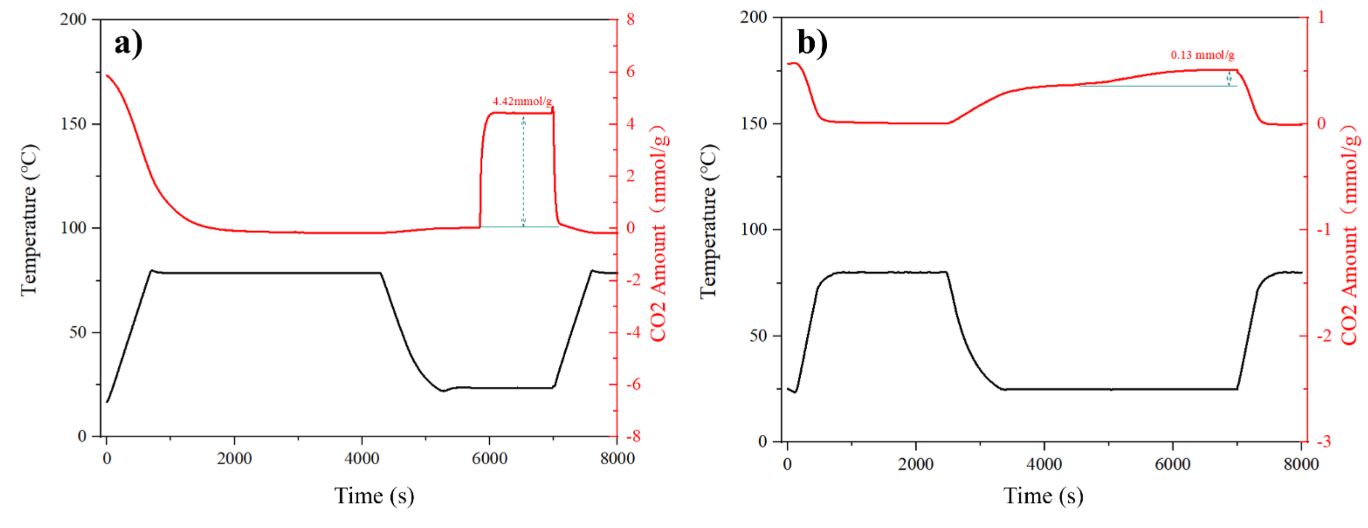

Figure 2: a) Pure CO_2 adsorption capacity and b) 400 ppm CO_2 adsorption capacity under dry conditions, determined by TGA experiments with the ***TGA 1000***

because low CO_2 partial pressure decreases the frequency of CO_2–surface collisions and reduces the probability of pore filling, especially in ultramicropores where adsorption is strongly pressure-dependent.

Breakthrough testing at 40% relative humidity (Figure 3) resulted in a dynamic CO_2 capacity of 0.004 mmol/g, significantly lower than under dry conditions. The presence of water vapor likely introduces competitive adsorption on hydrophilic sites, reducing CO_2 selectivity, particularly at low concentrations typical of DAC applications. This observation underscores the importance of hydrophobic surface modification or tailored pore environments for adsorbents intended for humid-air CO_2 capture.

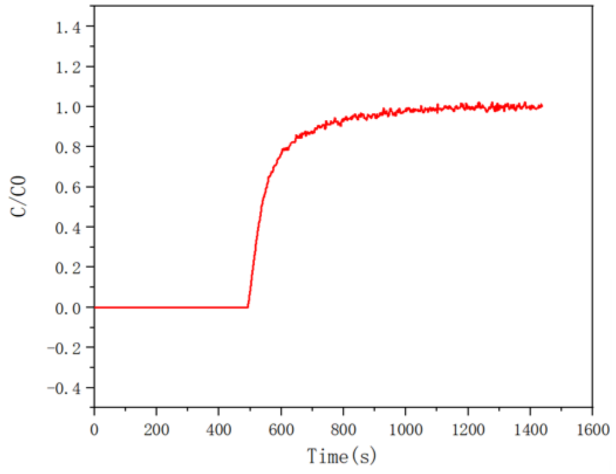

Figure 3: 400 ppm CO_2 penetration curve of a sample at 40% humidity, obtained with the ***BTsorb 100***

4. Conclusions

This study demonstrates that the MOF adsorbent possesses a high specific surface area and well-defined micropore structure, enabling substantial CO_2 adsorption under idealized, dry conditions. However, performance decreases sharply at low CO_2 partial pressures and in the presence of humidity, primarily due to competitive adsorption and reduced collision frequency. These findings highlight the need for surface hydrophobization, amine functionalization, or pore-environment tuning to improve DAC applicability.

From a measurement standpoint, the combined use of N_2 physisorption, volumetric CO_2 isotherms, and TGA adsorption analysis provides a comprehensive understanding of sorbent performance. The **Matrix 1000, TGA 1000, and BTsorb 100** all offer high sensitivity measurements for low-pressure adsorption, precise temperature control, and robust repeatability—critical for evaluating DAC sorbents where small differences in uptake are scientifically meaningful.

5. References

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