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# Scalable metal–organic frameworks for efficient low concentration CO<sub>2</sub> capture under humid flue gas conditions

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The global energy supply still largely relies on fossil fuels, whose combustion releases significant amounts of carbon dioxide (CO<sub>2</sub>), the primary anthropogenic greenhouse gas linked to climate change. Adsorption on solid porous materials offers a promising alternative to conventional amine-based systems for CO<sub>2</sub> capture from industrial flue gases. While various materials, including zeolites and metal–organic frameworks (MOFs), have been extensively studied for high-concentration CO<sub>2</sub> streams, post-combustion capture at low concentrations (below 5% CO<sub>2</sub>) under realistic conditions with water vapor remains poorly explored. Material selection requires balancing CO<sub>2</sub> adsorption capacity against water affinity, as strong hydrophilicity deteriorates regeneration efficiency. The challenge is to identify scalable, environmentally friendly materials that maintain high CO<sub>2</sub> selectivity under realistic flue gas conditions containing both low CO<sub>2</sub> concentrations and significant water vapor. Here, we show that CALF-20, a scalable MOF, exhibits superior CO<sub>2</sub> adsorption selectivity and regenerability compared to other tested materials, both in dry and humid conditions. Under dynamic breakthrough conditions using 2.5% CO<sub>2</sub> and 50% relative humidity, CALF-20 maintained a high CO<sub>2</sub> uptake (1.49 mmol g<sup>-1</sup>) consistent with static isotherm data, and demonstrated complete regenerability at 80 °C without loss of performance over multiple cycles. These results directly contrast with hydrophilic zeolites, which, despite high raw CO<sub>2</sub> capacities, are unsuitable under realistic, humid flue gas. Our results under industrially relevant post-combustion conditions demonstrate that low water affinity combined with moderate CO<sub>2</sub> capacity outperforms high-capacity hydrophilic materials. This approach represents an effective pathway for CO<sub>2</sub> capture under realistic conditions and provides valuable insights for the development of selective, robust, and scalable CO<sub>2</sub> adsorbents. Such developments are expected to contribute significantly to reducing atmospheric CO<sub>2</sub> emissions and addressing climate change mitigation targets in the coming years.

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## Introduction

The global energy supply still largely relies on fossil fuels such as petroleum, coal, and natural gas, which remain the backbone of modern industrial and transportation energy systems. However, the combustion and processing of these fuels release significant amounts of carbon dioxide (CO<sub>2</sub>), the primary anthropogenic greenhouse gas.<sup>1</sup> Every year, over 40 billion tons of CO<sub>2</sub> are emitted into the atmosphere from activities including power generation, cement production, and iron and steel manufacturing.<sup>2–4</sup> These emissions are directly associated with climate change phenomena, such as global warming, ocean acidification, and environmental issues, including

urban smog and acid rain. To mitigate atmospheric CO<sub>2</sub> emissions, the 27 countries of the European Union have adopted binding reduction targets to address climate change in the coming decades.<sup>5</sup> In response to this challenge, several strategies based on solvents, sorbents, and membranes have emerged as key approaches to reduce CO<sub>2</sub> emissions. Among these methods, adsorption on solid sorbents, commonly referred to as carbon capture and storage (CCS),<sup>6</sup> has attracted increasing attention as a promising alternative to conventional amine-based solvent systems.<sup>7</sup> This versatile approach allows for CO<sub>2</sub> capture across a wide range of concentrations. The CO<sub>2</sub> concentration varies significantly depending on the gas mixture. Direct air capture (DAC) enables the extraction of CO<sub>2</sub> directly from ambient air, where its concentration is low, around 430 ppm (0.043%).<sup>8</sup> In contrast, large-scale industrial and energy sectors, including petroleum, coal, and natural gas, emit CO<sub>2</sub>-rich streams with concentrations up to 50% in the gaseous mixture. For the latter, high-concentration capture

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methods include pre-combustion capture and oxy-fuel combustion capture with CO<sub>2</sub> concentration between 15–50% (150 000–500 000 ppm).<sup>6</sup> Post-combustion capture, on the other hand, deals with lower CO<sub>2</sub> concentrations, usually between 2 and 15%.<sup>9,10</sup> Numerous studies have investigated CO<sub>2</sub> adsorption in DAC and pre-combustion processes. However, fewer have focused on post-combustion adsorption, particularly at CO<sub>2</sub> concentrations below 5%, for which only limited literature is available. Low-CO<sub>2</sub> flue gas, typically containing 1–5% CO<sub>2</sub>, originated from natural-gas-fired or high-air-flow combustion systems, and is significantly more challenging and energy-intensive to treat than higher-concentration industrial exhaust.<sup>11</sup>

Over the past decade, extensive research efforts have focused on testing and optimizing various porous materials for CO<sub>2</sub> capture,<sup>1,12–14</sup> including active carbons (ACs),<sup>15,16</sup> zeolites,<sup>17,18</sup> porous-organic polymers (POPs),<sup>19,20</sup> and metal-organic frameworks (MOFs).<sup>21,22</sup> From these studies, several criteria have emerged as essential prerequisites for efficient CO<sub>2</sub> adsorbents: (i) high CO<sub>2</sub> adsorption capacity, (ii) low regeneration temperature, (iii) high selectivity towards CO<sub>2</sub>, (iv) chemical and thermal stability, and (v) scalability and cost-effectiveness.<sup>23</sup> Each class of material exhibits distinct advantages, yet none fully satisfies all these requirements simultaneously.<sup>24</sup> Siegelman *et al.* provided a qualitative assessment of the key performance metrics for these materials.<sup>25</sup> AC offer high stability and low cost but exhibit limited CO<sub>2</sub> selectivity and tunability. In contrast, POPs are highly tunable but challenging to regenerate and not yet commercially available. Zeolites combine high stability and large-scale production, but present only limited structural tunability. Furthermore, their hydrophilic nature leads to moderate selectivity towards CO<sub>2</sub>. MOFs distinguish themselves by exhibiting both high selectivity for CO<sub>2</sub> and low regeneration temperatures. These materials, composed of organic linkers and metal nodes, offer exceptional tunability. Extensive research efforts have focused on reducing the synthesis costs and enabling large-scale production. Emphasis has been placed on employing non-toxic metals such as aluminium and zinc, and benign ligands like carboxylates and oxalates, alongside the use of water as a solvent. Eliminating filtration and washing steps further reduces energy consumption and waste generation by preventing the formation of undesired by-products.<sup>26–28</sup> Several MOFs are now synthesized at scale, including copper trimesate HKUST-1,<sup>29</sup> zirconium terephthalate UiO-66,<sup>30</sup> and zinc oxalate triazolate CALF-20.<sup>31</sup> Recently, our laboratory developed a single-step spray-drying synthesis of aluminium fumarate (Al-Fum), which removes the need for filtration and washing.<sup>32</sup> This method has also been extended to other aluminium-based MOFs such as MIL-120 and MIL-160.<sup>33</sup>

In this study, we evaluate the CO<sub>2</sub> adsorption capacity of porous materials under realistic flue gas conditions. Only scalable and non-toxic materials are tested through static and dynamic adsorption experiments. The initial step employs a volumetric apparatus to select materials with low affinity for water, a critical factor often overlooked in previous studies. The subsequent dynamic adsorption tests, conducted both in

the absence and presence of water co-adsorption, enable identification of a material suitable for post-combustion capture at a low CO<sub>2</sub> concentration of 2.5%, a condition rarely investigated. Successive adsorption-desorption cycles confirm the robustness of the selected materials. This work provides valuable insights for developing selective, robust, and scalable CO<sub>2</sub> adsorbents capable of efficient operation under realistic post-combustion conditions.

## Experimental

### Materials

NaX, NaY, and NaMOR zeolites are obtained from Saint-Gobain. CALF-20 is provided by SINTEF. Al-Fum is synthesized by spray-drying according to the previously reported method,<sup>32</sup> and MIL-120 as well as MIL-160 are synthesized similarly using the spray-drying technique.<sup>33</sup> Deionized water is used in all static and dynamic adsorption experiments. For static CO<sub>2</sub> sorption experiments, pure CO<sub>2</sub> (>99.95%, Messer) is used. For dynamic adsorption experiments, a gas mixture of 5% CO<sub>2</sub> in N<sub>2</sub> (>4.97%, Air Liquide) is used.

### Characterization of the adsorbents

X-ray diffraction (XRD) patterns are recorded using a Bruker (Siemens) D5000 diffractometer. Diffractograms are collected over a  $2\theta$  range of 5° to 50°, with a step size of 0.02° and a counting time of 1 second per step, employing CuK $\alpha$  radiation ( $\lambda = 1.54059 \text{ \AA}$ ). N<sub>2</sub> physisorption measurements are performed on a Microtrac Belsorp Mini X instrument at 77 K. Prior to measurements, approximately 50 mg of each sample is out-gassed overnight at 140 °C (Al-Fum, CALF-20, MIL-120, MIL-160) or 300 °C (NaMOR, NaX, NaY). Adsorption experiments are conducted within a relative pressure ( $P/P_0$ ) range from 0 to 1. Equilibrium is defined by a pressure variation of less than 0.3% over 300 seconds at each data point. Characterization of the adsorbents is presented in the SI (Fig. S1 and Table S1).

### Static sorption experiments

Volumetric static adsorption/desorption experiments of water and CO<sub>2</sub> are performed using a commercially available Microtrac Belsorp Max II. Before the experiment, materials are activated under vacuum at 140 °C or 300 °C, depending on the material, using a BelPrep Vac. Isotherms are then obtained by applying incremental pressures of water or CO<sub>2</sub> within the cell. Thermodynamic equilibrium is considered achieved when the total pressure variation within the cell falls below 0.3% over 300 seconds. Isotherms are performed at different temperatures (0, 10, and 20 °C) to apply Polanyi's adsorption potential theory and to validate the establishment of thermodynamic equilibrium (SI).<sup>34</sup>

### Dynamic sorption experiments

Dynamic breakthrough adsorption experiments are conducted using a custom-built apparatus described in the SI



(Scheme S1), and consists of an adaptation of the setup described elsewhere.<sup>35</sup> The column consists of a glass tube with an internal diameter of 4 mm, packed with approximately 250 mg of nanoporous material to a height of 4 cm, depending on the powder density. Before the adsorption, the materials are activated under N<sub>2</sub> flow at 140 °C (the maximum temperature allowed by the setup) to remove any adsorbed molecules. The CO<sub>2</sub> concentration in the inlet stream ( $C_0$ ) is verified before each breakthrough experiment by bypassing the column and measuring with a CO<sub>2</sub> detector (Vaisala Carbocap with CO<sub>2</sub> probe GMP251). Adsorption experiments are performed at atmospheric pressure ( $\approx 100$  kPa) and at a constant temperature of 20 °C. For dry adsorption experiments, a mixture containing 2.5% CO<sub>2</sub> (100 mL min<sup>-1</sup> total flow) is generated by mixing a 50 mL min<sup>-1</sup> flow of 5% CO<sub>2</sub> in N<sub>2</sub> with 50 mL min<sup>-1</sup> pure N<sub>2</sub> (resulting contact time  $\tau = 0.3$  s). CO<sub>2</sub> concentrations in the outlet flow ( $C$ ) are continuously monitored by the detector. For wet adsorption experiments, the pure N<sub>2</sub> dilution flow is replaced with a 50 mL min<sup>-1</sup> N<sub>2</sub> flow at 99% relative humidity (RH) generated using a Flexi Wet 200 apparatus (Setaram), yielding an overall flow of 100 mL min<sup>-1</sup> with 2.5% CO<sub>2</sub> and 50% RH ( $p_{\text{H}_2\text{O}} = 1.15$  kPa). Water vapor concentration is measured by a calibrated hygrometer. Following adsorption, regeneration is carried out by flowing a pure N<sub>2</sub> flow of 100 mL min<sup>-1</sup> while heating the column to the target temperature with a controlled ramp rate. Multiple adsorption/regeneration cycles are performed either under dry or humid conditions to assess material stability. To compare the different water adsorption capacities, every breakthrough graph is presented for 1 gram of dried adsorbent (min g<sup>-1</sup>). A symbol “ $\approx$ ” is added before the numeric value, which points to the error evaluated at 5%. The MOF/zeolite particles (300–600  $\mu\text{m}$ ) are sufficiently small to minimize intraparticle diffusion resistance, and external mass transfer is adequate at the low total flow rate of 100 mL min<sup>-1</sup> through a 4 mm diameter column. Under our conditions, the superficial velocity is low ( $\sim 0.083$  m s<sup>-1</sup>), resulting in a Sherwood number indicating efficient gas–solid mass transfer. The bed height (4–8 cm) promotes near plug-flow behavior, and the modest pressure drop (1.05 bar) confirms the absence of flow constraints. Heat generated during adsorption is minimal due to the low CO<sub>2</sub> loading and moderate adsorption enthalpy of MOF/zeolite materials, yielding an estimated temperature rise of  $<0.5$  K. Therefore, under these conditions, breakthrough behavior is governed by adsorption equilibrium, with no significant mass- or thermal-transfer limitations.

## Results and discussion

### Static adsorption experiments

Static CO<sub>2</sub> adsorption isotherms are performed at three different temperatures using three sodium-exchanged zeolites and four scalable MOFs. To verify thermodynamic equilibrium, Polanyi's adsorption potential theory is applied. Polanyi's adsorption potential theory describes adsorption as

the filling of a potential field near a solid surface, rather than as the simple layer-by-layer attachment of molecules.<sup>36</sup> In microporous materials in particular, adsorption is therefore interpreted as the volume filling of pores. For a given adsorbent–adsorbate system, when the amount adsorbed is plotted as a function of the adsorption potential, isotherms measured at different temperatures collapse onto a single curve, commonly referred to as the master curve. The characteristic curves are obtained for almost all adsorbate/adsorbent pairs, confirming the reach of thermodynamic equilibrium (Fig. S2). Only MIL-120 differs from other materials and a deviation is observed. Thermodynamic equilibrium is not reached for this material, highlighting diffusional constraints during CO<sub>2</sub> adsorption. From the isotherms performed at 20 °C, no plateau is observed for any of the materials (Fig. 1a). This suggests that the adsorption is not complete, as the saturated vapor pressure of CO<sub>2</sub> at 20 °C ( $P_{\text{v,sat}} = 3485.1$  kPa) is not reached at the maximum operating pressure of 100 kPa. The highest adsorption capacities are recorded for NaY and NaX, with 6.14 and 5.85 mmol g<sup>-1</sup>, respectively, followed by CALF-20 (3.88 mmol g<sup>-1</sup>) and MIL-160 (3.64 mmol g<sup>-1</sup>). NaMOR adsorbs 3.24 mmol g<sup>-1</sup>. The lowest capacities are observed for Al-Fum and MIL-120, with adsorption capacities of 2.60 and 1.84 mmol g<sup>-1</sup>, respectively. Using the CO<sub>2</sub> concentration in the application case of low flue gas conditions (2.5%), the adsorption order changes: NaX maintains a high capacity of 3.15 mmol g<sup>-1</sup> (54% maintained), whereas the capacity of NaY

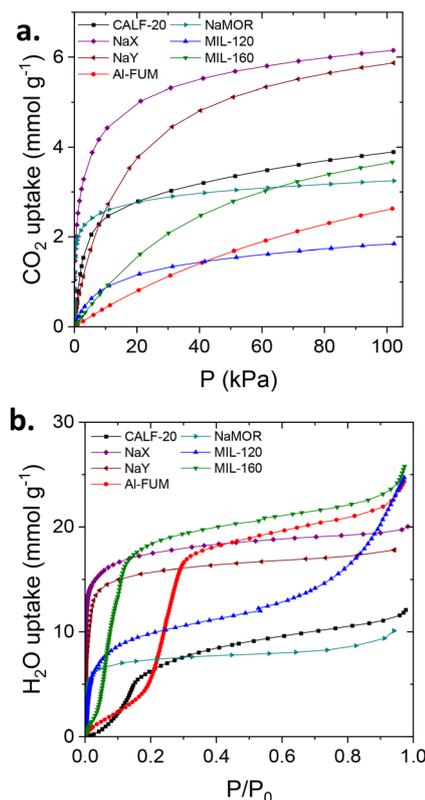


Fig. 1 CO<sub>2</sub> (a) and H<sub>2</sub>O (b) adsorption isotherms at 20 °C.



decreases noticeably to  $1.02 \text{ mmol g}^{-1}$  (17% maintained), nearly six times lower than at pure  $\text{CO}_2$  concentration. NaMOR and CALF-20 show the second and third highest adsorption capacities, with 2.19 and  $1.44 \text{ mmol g}^{-1}$ , respectively. MIL-120 adsorbs  $0.37 \text{ mmol g}^{-1}$ . Finally, the lowest capacities under these conditions are observed for MIL-160 and Al-Fum, adsorbing 0.23 and  $0.11 \text{ mmol g}^{-1}$ , respectively.

The study of water adsorption is essential to mimic realistic flue gas conditions, which typically contain water vapor around a relative humidity of 50%. The objective is to identify a nanoporous sorbent that minimizes water adsorption, allowing maximized  $\text{CO}_2$  uptake, and can be easily regenerated at low temperature. Materials exhibiting Type I isotherms characterize strong water affinity, resulting in temperature and energy-demanding regeneration. Conversely, materials displaying Type V isotherms tend to interact less with water molecules, facilitating regeneration under mild conditions (typically  $80 \text{ }^\circ\text{C}$ ).

Water adsorption experiments are performed at  $20 \text{ }^\circ\text{C}$  for all materials (Fig. 1b). Type-I isotherms are obtained for the three zeolites, whereas the four MOFs exhibit Type-V isotherms. To access the strength of interaction between water molecules and the adsorbent, and thereby predict the regeneration behavior, Henry's constants ( $K_H$ ) are derived from the low-pressure region of each isotherm (Fig. 2). As expected, based on the isotherm type, the three zeolites display high  $K_H$  values, indicative of strong adsorbate-adsorbent interactions. The highest  $K_H$  value is obtained for NaY ( $673.2 \text{ mmol g}^{-1} \text{ kPa}^{-1}$ ). In contrast, the MOFs show significantly lower  $K_H$  values ( $<40 \text{ mmol g}^{-1} \text{ kPa}^{-1}$ ), with CALF-20 exhibiting the weakest affinity ( $4.6 \text{ mmol g}^{-1} \text{ kPa}^{-1}$ ). The  $\alpha$  parameter (defined as the relative pressure  $P/P_0$  at which half of the total water uptake is reached<sup>37</sup>) supports the same trend, confirming the pronounced hydrophilicity of the zeolites and the moderate hydrophilicity of the MOFs.

For a relative humidity of 50%, MIL-160 adsorbs approximately  $20.5 \text{ mmol g}^{-1}$  of water while Al-Fum and NaX adsorb

$18.9$  and  $18.6 \text{ mmol g}^{-1}$ , respectively. Conversely, CALF-20 and NaMOR exhibit the lowest water adsorption capacities, with values of  $9.0$  and  $7.8 \text{ mmol g}^{-1}$ , respectively.

Although zeolites, particularly NaX and NaMOR, exhibit high  $\text{CO}_2$  adsorption capacities, their strong hydrophilicity limits their applicability for low  $\text{CO}_2$  concentrations. In addition, the regeneration temperature required to fully desorb water molecules is significantly higher than that of MOFs, reaching up to  $300 \text{ }^\circ\text{C}$ .<sup>38,39</sup>

### Dynamic adsorption experiments

Dynamic adsorption experiments are conducted to evaluate the effect of  $\text{N}_2$  in flue gas on  $\text{CO}_2$  adsorption, and to assess the selectivity between water and  $\text{CO}_2$ . Zeolites exhibiting strong hydrophilicity and high regeneration temperatures as evaluated using static adsorption experiments, only MOFs are selected for breakthrough adsorption experiments.

To confirm the adsorption capacities obtained from static experiments and the selectivity towards  $\text{N}_2$ , dynamic adsorption experiments with a  $\text{CO}_2$  concentration of 2.5% under dry conditions (Fig. 3) are first performed. All materials show characteristic symmetric S-shaped breakthrough profiles, indicative of plug-flow-like behavior. Integration of breakthrough curves shows that Al-Fum, the least effective MOF in this series, exhibits  $\text{CO}_2$  breakthrough after approximately one minute per gram and adsorbs only  $\approx 0.10 \text{ mmol g}^{-1}$  of  $\text{CO}_2$ . This value is consistent with static isotherm data, and confirms negligible  $\text{N}_2$  adsorption and unperturbed  $\text{CO}_2$  capture. Similarly, MIL-160 and MIL-120 show excellent agreement between dynamic and static adsorption, with capacities of  $\approx 0.27$  and  $\approx 0.39 \text{ mmol g}^{-1}$ , versus  $0.23$  and  $0.37 \text{ mmol g}^{-1}$ , respectively, from static adsorption experiments. Notably, CALF-20 completely adsorbs  $\text{CO}_2$  without any effluent detection for more than 10 minutes per gram. CALF-20 demonstrates the highest  $\text{CO}_2$  capacity with  $\approx 1.43 \text{ mmol g}^{-1}$ , in close agreement with its isotherm value of  $1.44 \text{ mmol g}^{-1}$ . These results highlight the selective  $\text{CO}_2$  adsorption of CALF-20 with

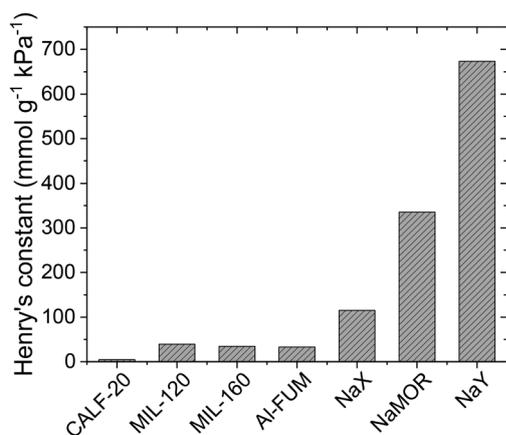


Fig. 2 Henry's constant obtained from  $\text{H}_2\text{O}$  isotherms performed at  $20 \text{ }^\circ\text{C}$ .

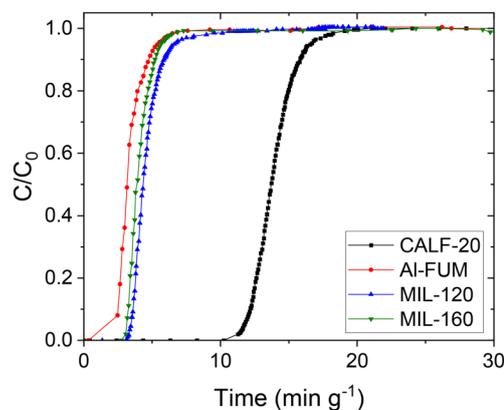


Fig. 3 Breakthrough adsorption experiments with a dry 2.5%  $\text{CO}_2$  concentration flow at  $20 \text{ }^\circ\text{C}$ .



no competition from  $N_2$  and confirm its superior performance, achieving almost four times the capacity of MIL-120, the second-best material.

In order to evaluate the regeneration performance of these materials, and thus the working capacity of the different MOFs, three adsorption cycles at 20 °C followed by regeneration at 80 °C under  $N_2$  are carried out. As expected, CALF-20 exhibits full desorption of previously adsorbed  $CO_2$ , allowing complete regeneration. The second and third cycles show consistent adsorption capacities of  $\approx 1.61 \text{ mmol g}^{-1}$  and  $\approx 1.50 \text{ mmol g}^{-1}$ , respectively (Fig. 4). MIL-160 and MIL-120 display similar behavior, achieving full  $CO_2$  regeneration, with a lower cycled working capacity (Fig. S3a and b). Breakthrough experiment performed on MIL-120 confirms the diffusional constraint of  $CO_2$  within the porous system, as already observed using static adsorption experiments. Indeed, during the regeneration step, while the outlet flow reaches 0  $\text{mmol g}^{-1}$  of  $CO_2$  after 11 minutes per gram under  $N_2$ , more than 30 min per gram are necessary to fully desorb  $CO_2$  (Fig. S4).

The adsorption of  $CO_2$  under model flue gas conditions requires evaluating the competitive adsorption behavior of  $CO_2$  and  $H_2O$ . Breakthrough experiments (inlet flow of 2.5%  $CO_2$  and 50% RH) are conducted using CALF-20, the material with the highest  $CO_2$  adsorption capacity. Adsorption of  $CO_2$  and  $H_2O$  occurs in three steps (Fig. 5, zoom in Fig. S5). During the first stage, both  $CO_2$  and  $H_2O$  are co-adsorbed during the initial 10 minutes per gram, resulting in the uptake of  $\approx 1.49 \text{ mmol g}^{-1}$  of  $CO_2$ . This value agrees closely with that obtained under dry conditions ( $\approx 1.43 \text{ mmol g}^{-1}$ ) and with the adsorption isotherm, thereby confirming the robustness of CALF-20 for  $CO_2$  capture under realistic flue gas conditions. In the second stage, a  $CO_2$  roll-up is observed, leading to the complete desorption of  $CO_2$  ( $\approx 1.45 \text{ mmol g}^{-1}$ ) even as water continues to adsorb. Water begins to break after approximately one hour per gram, with its outlet concentration gradually increasing before a sharp rise after 3.5 hours per gram. In the third and final stage, equilibrium is reached after 4 hours per gram, at which point the outlet composition matches that of

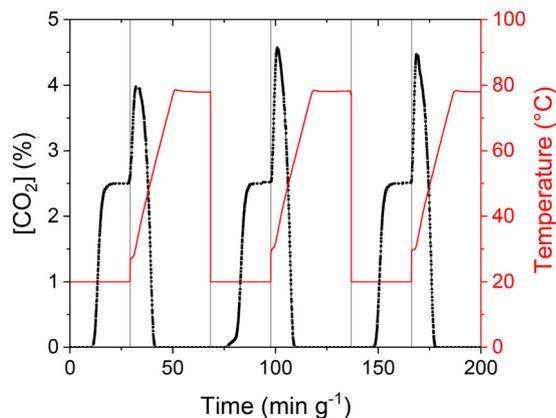


Fig. 4 Cycles of adsorption/regeneration with a dry 2.5%  $CO_2$  concentration flow on CALF-20 at 20 °C.

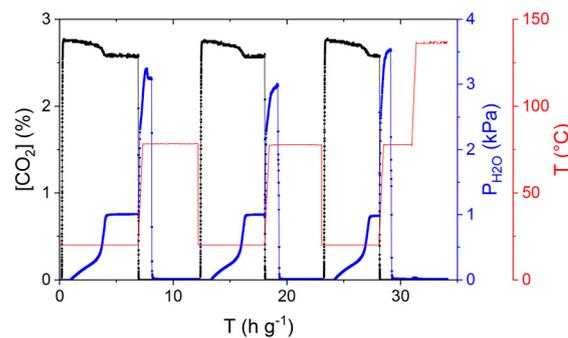


Fig. 5 Cycles of adsorption/regeneration with a 2.5%  $CO_2$  concentration flow and relative humidity of 50% on CALF-20 at 20 °C.

the inlet gas for both  $CO_2$  and  $H_2O$ . Integration of the breakthrough curve for  $H_2O$  yields a total uptake of  $\approx 8.70 \text{ mmol g}^{-1}$ , which is in good agreement with static adsorption measurements on CALF-20 at 50% RH ( $9.0 \text{ mmol g}^{-1}$ ). Regeneration of the material is achieved by switching the gas feed to pure  $N_2$  while increasing the temperature gradually to 80 °C ( $5 \text{ °C min}^{-1}$ ). During this heating step, no  $CO_2$  could be detected in the outlet flow as it is already fully desorbed during the later step, while  $\approx 8.90 \text{ mmol g}^{-1}$  of water is desorbed. This value is consistent with the amount adsorbed during the uptake step, confirming the complete regeneration of CALF-20.

To confirm the total regeneration of CALF-20 at 80 °C, three consecutive adsorption cycles under realistic flue gas conditions followed by regeneration at 80 °C are performed (Fig. 5). The breakthrough profiles for both  $CO_2$  and  $H_2O$  are consistent across cycles, with similar adsorption capacities observed. These results demonstrate the full regeneration and excellent working capacities at equilibrium of CALF-20 after multiple adsorption/regeneration cycles for  $CO_2$  capture under low concentration  $CO_2$  conditions.

Compared with Al-Fumarate and MIL-series MOFs, which often present open metal sites or polar functional groups that strongly interact with water, CALF-20's pore environment is dominated by hydrophobic triazolate linkers and no open metal sites, reducing initial water binding and maintaining  $CO_2$  uptake under moderate humidity.<sup>40</sup> Binary adsorption studies highlight that CALF-20's  $CO_2$  adsorption is retained over a broader humidity range, whereas water uptake in other materials is less affected by  $CO_2$ .<sup>41</sup> The mechanism behind CALF-20's performances was already discussed by Ho and Paesani.<sup>42</sup>  $CO_2$  binding is thermodynamically more favorable under dilute conditions and humidity, and the relatively hydrophobic nature of the framework suppresses  $H_2O$  uptake at low to moderate humidity. The presence of  $CO_2$  slows  $H_2O$  reorientation dynamics and lowers water entropy, indicating reduced  $H_2O$  mobility, while  $H_2O$  enhances  $CO_2$  reorientation and can increase its adsorption. These competitive yet interdependent thermodynamic and dynamic effects likely underpin the experimentally observed  $CO_2$  "roll-up" behavior under humid conditions.



## Conclusions

In this study, various scalable and environmentally friendly microporous materials are evaluated for CO<sub>2</sub> capture under realistic post-combustion flue gas conditions. Static adsorption results showed that zeolites exhibit high CO<sub>2</sub> adsorption capacities and low total water uptake. However, their pronounced hydrophilicity, confirmed by pure Type-I isotherms and high Henry's constant, indicates a strong affinity for water. This affinity inevitably leads to competitive adsorption between water and CO<sub>2</sub> under realistic conditions. Conversely, although MOFs such as MIL-160, MIL-120, and Al-Fum adsorb moderate amounts of CO<sub>2</sub> alongside significant water uptake, their Type-V water adsorption isotherms and significantly lower Henry's constants relative to zeolites suggest a reduced affinity for water. Among these materials, CALF-20 stands out by demonstrating low water adsorption coupled with high CO<sub>2</sub> uptake. This performance is validated in dynamic adsorption experiments using CO<sub>2</sub> under post-combustion conditions with a concentration of 2.5%, aligning well with the results of static experiments for equivalent concentrations. No competitive adsorption between N<sub>2</sub> and CO<sub>2</sub> is observed, confirming the excellent selectivity of CALF-20 towards CO<sub>2</sub>. Moreover, successive adsorption–regeneration cycles demonstrated the good stability of the material in dry conditions. Dynamic adsorption experiments under realistic flue gas conditions demonstrate that CALF-20 maintains its high CO<sub>2</sub> adsorption capacity and cycle reproducibility even in the presence of water vapor. Despite these positive results, long-term stability over several years must be established to confirm its suitability for practical applications.

This study represents an effective pathway for CO<sub>2</sub> capture under realistic conditions. Future work should focus on porous materials with reduced water affinity and enhanced CO<sub>2</sub> capacity to advance this technology. Such developments are expected to contribute significantly to reducing atmospheric CO<sub>2</sub> emissions and addressing climate change mitigation targets in the coming years.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. T. A.: data curation, formal analysis, investigation, visualization, writing – original draft, writing – review & editing. M. B.: formal analysis, investigation, writing – review & editing. C. C.: data curation, formal analysis. C. D.: data curation, methodology. D. F.: funding acquisition, supervising, writing – review & editing.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

All data from this study are available within the article and its supplementary information (SI). Supplementary information: additional experimental data, including physisorption isotherms, characterization data, and breakthrough experiment details. See DOI: <https://doi.org/10.1039/d6dt00282j>.

All single gas isotherms are also available in AIF format. Any further data are available from the corresponding author upon request.

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