Trace CO₂ capture by an ultramicroporous physisorbsent with low water affinity

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CO₂ accumulation in confined spaces represents an increasing environmental and health problem. Trace CO₂ capture remains an unmet challenge because human health risks can occur at 1000 parts per million (ppm), a level that challenges current generations of chemisorbents (high energy footprint and slow kinetics) and physisorbents (poor selectivity for CO₂, especially versus water vapor, and/or poor hydrolytic stability). Here, dynamic breakthrough gas experiments conducted upon the ultramicroporous material SIFSIX-18-Ni-β reveal trace (1000 to 10,000 ppm) CO₂ removal from humid air. We attribute the performance of SIFSIX-18-Ni-β to two factors that are usually mutually exclusive: a new type of strong CO₂ binding site and hydrophobic similarity to ZIF-8. SIFSIX-18-Ni-β also offers fast sorption kinetics to enable selective capture of CO₂ over both N₂ (S_Cu) and H₂O (S_CW), making it prototypal for a previously unknown class of physisorbents that exhibit effective trace CO₂ capture under both dry and humid conditions.

INTRODUCTION

Ever-increasing carbon dioxide (CO₂) levels in the atmosphere represent a global challenge for mankind (1, 2). CO₂ contributes to climate change (3), but atmospheric CO₂ is not only relevant to climate change but also a major health issue in confined spaces such as meeting rooms, aircraft, submarines, and spaceships, which can also suffer from elevated CO₂ concentrations. Whereas the specific concentrations of CO₂ that cause impairment of higher-order decision-making or long-term health risks remain uncertain (4), CO₂ capture (C-capture) devices are routinely deployed in spacecraft and submarines to control CO₂ concentration (5). Further, very recently, it was suggested that chronic exposure to levels as low as 1000 parts per million (ppm) can be harmful (6).

Generally, C-capture devices are the most expensive aspect of a C-capture, transport, and sequestration system because they exhibit high regeneration energy, require large equipment size, and result in equipment corrosion (7). While traditional C-capture technologies are suitable for large anthropogenic point sources where CO₂ levels are high, different approaches are required for mobile sources (8). C-capture using solid sorbents offers an energy-efficient alternative to traditional processes (9), but the challenge of C-capture is exacerbated for trace CO₂ removal from air (~400 ppm for direct air capture (DAC) and 1000 to 10,000 ppm for confined spaces) under variable conditions (gas composition, humidity level, and temperature). The sorbents currently used in indoor air quality (IAQ) control involve the use of activated carbon impregnated with MgO and/or CaO; C-capture occurs via chemical fixation of CO₂ as metal oxides transform to metal carbonates (10). A downside of this process lies with declined performance over repeated cycles (11). Further, the fact that CO₂ binding must be highly selective over atmospheric N₂ (S_CN ≥ 2500) and H₂O (S_CW ≥ 100) disqualifies all known physisorbt materials from consideration (12, 13). Chemisorbents, on the other hand, are limited by poor sorption kinetics, energy-intensive regeneration, and chemical/thermal degradation on cycling (14).

The demand for energy-efficient solutions to trace gas separations has spurred research into porous metal-organic materials (MOMs) (15), also known as porous coordination polymers (16), or metal-organic frameworks (MOFs) (17). Unlike traditional classes of porous sorbents, these materials can be designed from first principles to afford control over pore size and chemistry. Unfortunately, MOFs, such as zeolites, typically lack the high selectivity and fast kinetics required for the removal of trace CO₂, in general, and from humid air, in particular (13). Many MOFs and zeolites are negatively affected by moisture (18, 19). Hybrid ultramicroporous materials (HUMs) (20), the current benchmarks for trace gas capture including C-capture (21) and acetylene capture (22), are also affected by humidity (18). The fact that the introduction of alkyl groups into pores can reduce the water affinity of MOMs (23) prompted us to study whether such an approach in HUMs might address the need for a porous material that combines (i) high affinity for CO₂ and (ii) low affinity for H₂O. Here, we report the first example of such a material.

RESULTS

[Ni(L)₂(SiF₆)]ₙ, L = 3,3′,5,5′-tetramethyl-1H,1′H-4,4′-bipyrazole, was prepared by hydrothermal reaction of L with NiSiF₆·6H₂O to afford a light blue powder, SIFSIX-18-Ni-α (Fig. 1A), an analog of SIFSIX-18-Cd (24). Heating SIFSIX-18-Ni-α to 85°C under vacuum induced a phase transition to SIFSIX-18-Ni-β (Fig. 1, B and C) and a 13.4% reduction in unit cell volume (see the Supplementary Materials for full details). Both forms of SIFSIX-18-Ni are primitive cubic (pcu) nets composed of two-dimensional layers of Ni(II) nodes cross-linked by organic linkers that are pillared by inorganic anions (SiF₆²⁻). The resulting square channels are lined with inorganic anions, weakly basic nitrogen atoms, and methyl groups (Fig. 1B). After confirming bulk phase purity and crystallinity (Fig. 1C), particle size distribution analysis revealed a relatively uniform mean diameter of ca. 14 μm (Fig. 1D and fig. S6). Scanning electron microscopy revealed block-shaped morphology (Fig. 1D, inset).
The sorption properties of SIFSIX-18-Ni-β were first examined using single-component isotherms (Fig. 2A and figs. S8 to S11). For comparative purposes, six additional physisorbent materials representing three classes of sorbents with strong potential for IAQ control were also evaluated: two MOFs [Mg-MOF-74, the benchmark MOF for C-capture (25), and ZIF-8, a hydrophobic MOF (26)], a zeolite that is known both as a desiccant and as a C-capture sorbent [Zeolite 13X (27)], and three HUMs that are known for their high CO₂ selectivity versus both N₂ and CH₄ [NbOFFIVE-1-Ni (28), TIFSIX-3-Ni (29), and SIFSIX-3-Ni (18, 19)] (Fig. 2, A and B, and figs. S13 to S18). The pure gas isotherms at CO₂ partial pressures relevant to DAC (ca. 500 ppm) and IAQ control (CO₂, 0.005 to 0.01 bar) reveal that only the HUMs exhibit strong C-capture performance. At 1000 ppm, CO₂ uptakes were as follows: NbOFFIVE-1-Ni and TIFSIX-3-Ni, 1.8 and 1.7 mmol g⁻¹, respectively; SIFSIX-18-Ni-β, SIFSIX-3-Ni, and Zeolite 13X, ca. 0.8 mmol g⁻¹; Mg-MOF-74 and ZIF-8, negligible. The HUMs were found to exhibit similar CO₂ sorption performance between 0.005 and 0.01 bar with near-full loading at 0.01 bar. Mg-MOF-74 and Zeolite 13X exhibited CO₂ uptakes of 0.9 (~13% loading) and 1.7 mmol g⁻¹ (~28% loading) at 0.005 bar CO₂ and 298 K, respectively. No sorbent was observed to exhibit substantial N₂ uptake at 1.0 bar and 298 K (Table 1 and figs. S10 and S13 to S18).

With respect to H₂O sorption, Zeolite 13X (18.8 mmol g⁻¹), TIFSIX-3-Ni (7.5 mmol g⁻¹), NbOFFIVE-1-Ni (10.1 mmol g⁻¹) and SIFSIX-3-Ni (8.8 mmol g⁻¹) were found to exhibit high uptake at 95% relative humidity (RH). Conversely, ZIF-8 (2.6 mmol g⁻¹) and SIFSIX-18-Ni-β (1.6 mmol g⁻¹) exhibited low H₂O uptake consistent with surface sorption. Under ambient pressure, SIFSIX-18-Ni-β adsorbed 0.96 mmol g⁻¹ at 95% RH (Fig. 2E) accompanied by a phase transition to SIFSIX-18-Ni-α [in situ powder x-ray diffraction (PXRD); fig. S5], however regenerable by temperature swing. Mg-MOF-74 was not studied due to its hydrolytic instability (18, 30).

The isosteric heat of adsorption (Qₜ) values for CO₂ are generally flat across the range of loading and decrease in line with the low pressure uptakes reported above: NbOFFIVE-1-Ni (54 kJ mol⁻¹) > SIFSIX-18-Ni-β (52 kJ mol⁻¹) > TIFSIX-3-Ni (50 kJ mol⁻¹) > SIFSIX-3-Ni (45 kJ mol⁻¹) > Mg-MOF-74 (42 kJ mol⁻¹) > Zeolite 13X (39 kJ mol⁻¹) > ZIF-8 (26.7 kJ mol⁻¹) (Fig. 2C, Table 1, figs. S19 and S20, and tables S2 and S3) (29). Gravimetric CO₂ adsorption at 1 bar/303 K revealed that whereas SIFSIX-18-Ni-β, NbOFFIVE-1-Ni, TIFSIX-3-Ni, and SIFSIX-3-Ni exhibit lower CO₂ uptake than Mg-MOF-74 and Zeolite 13X, they offer superior kinetics, reaching 90% of their equilibrium loading within ca. 1 min of exposure versus 20 to 40 min (Fig. 2D). Under dry/wet trace CO₂/N₂ mixtures, the C-capture kinetics of SIFSIX-18-Ni-β even outperforms the benchmark silica chemisorbent TEPA-SBA-15 (figs. S53 and S54) (31). Selectivity determined via ideal adsorbed solution theory (IAST) (32) revealed that, at 298 K, SIFSIX-18-Ni-β in effect serves as a partial sieve for S⁻ (figs. S9 and S45). The IAST selectivity for S⁻ data, which was calculated at 74% RH and 500 ppm CO₂, is 16.2, with higher S⁻ values of 54.0 and 173.1 at 0.005 and 0.01 bar CO₂, respectively (table S1).
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Fig. 2. Single-component sorption, kinetic studies, and “sweet spot” for CO₂ binding. (A and B) Low-pressure CO₂ isotherms at 298 K. (C) Isosteric heat of adsorption profiles for CO₂. (D) Gravimetric CO₂ uptake (1.0 bar) versus time at 303 K. (E) Dynamic vapor sorption (DVS) isotherms for H₂O at 298 K. (F) CO₂ binding sites in SIFSIX-18-Ni-β determined by ab initio periodic computation. Dashed lines indicate CO₂–HUM internuclear distances from 2.81 to 2.99 Å. Color code: C, gray; H, white; O, red; N, sapphire; Si, yellow; F, cyan; Ni, light blue.

Table 1. Isosteric heat of adsorption, gas sorption, and selectivity data.

| Material          | CO₂ Qst (kJ mol⁻¹)* | CO₂ uptake (298 K) (mmol g⁻¹) | N₂ (298 K, 1 bar) (mmol g⁻¹) | H₂O (298 K, 95% RH) (mmol g⁻¹) | IAST selectivity† |
|-------------------|---------------------|--------------------------------|-----------------------------|--------------------------------|--------------------|
| Mg-MOF-74         | 42                  | 0.05                           | 0.9                         | 1.6                            | ~33.33†            |
| Zeolite 13X       | 39                  | 0.4                            | 1.4                         | 1.8                            | 18.76              |
| SIFSIX-18-Ni-β    | 52                  | 0.4                            | 1.8                         | 2.2                            | 1.64/0.96†         |
| SIFSIX-3-Ni       | 45                  | 0.4                            | 1.2                         | 1.8                            | 8.80               |
| NbOFFIVE-1-Ni     | 54                  | 1.3                            | 2.0                         | 2.3                            | 10.09              |
| TIFSIX-3-Ni       | 49                  | 1.2                            | 1.9                         | 2.0                            | 7.46               |
| ZIF-8             | 27                  | ~0.0006                        | <0.005                      | 0.01                           | 1.44†              |

*Virial fitting of CO₂ sorption data collected between 0 and 10 mbar. †Data collected on surface measurement systems vacuum DVS unless otherwise stated. ‡Selectivity for sorbents was determined by interpolation of raw isotherm data points (see the Supplementary Materials for further details). §Selectivity based upon 500 ppm CO₂ concentration. ||Selectivity based upon 500 ppm CO₂ concentration/74% RH. ¶Water uptake for Mg-MOF-74 was acquired from (30). #Water uptake based upon surface measurement systems intrinsic DVS data. ‡‡IAST selectivity suggests partial sieving (see the Supplementary Materials). ††IAST cannot be calculated due to negative adsorption observed as a result of phase change in the presence of water. #Calculated at 74% RH and 500 ppm.

and figs. S25 and S26). These SCW values are not corrected for surface sorption and are likely to be even higher. In summary, SIFSIX-18-Ni-β is, to our knowledge, the first physisorbent that combines strong C-capture performance and low water uptake.

To understand its unexpectedly strong C-capture properties, we modeled the CO₂ binding site in SIFSIX-18-Ni-β by ab initio and empirical simulations. The empirically modeled structure of a 2 × 2 × 2 box of unit cells of SIFSIX-18-Ni-β (fig. S57) revealed a series of CH–O interactions supplementing the expected C–F binding between the electropositive carbon atoms of CO₂ and fluorine moieties of SIFSIX (Fig. 2F). The initial binding site for CO₂ from ab initio periodic computation resembles that in other SIFSIX systems in that there is an interaction with a SIFSIX moiety (C_CO₂ – F_SIFSIX = 2.94 Å; Fig. 2F). However, the binding site is otherwise distinct in that there...
are also electrostatic attractions between the partially negative O atoms of CO₂ and partially positive methyl hydrogen atoms of SIFSIX-18-Ni-β. In addition, empirical simulations revealed a C₈CO₂ – FSIFSIX distance of as low as 2.54 Å at 298 K. Concurrent O₈CO₂ – H₈HUM interactions of 2.81, 2.89, 2.91, 2.92, 2.93, 2.96, 2.99, and 3.09 Å were also found in the optimized structure (see the Supplementary Materials for full details). This binding site more resembles the type of binding site typically found in enzymes than that of other HUMs.

Real-time trace C-capture performance for each physisorbent was examined via fixed-bed column breakthrough experiments (Fig. 3, A to F; figs. S27 to S40; and table S4) using binary CO₂/N₂ mixtures that mimic indoor CO₂ concentrations: 1000/3000 ppm, 298 K, dry/74% RH (4). The dry 1000 ppm CO₂ saturation uptake of SIFSIX-18-Ni-β was observed to be 0.7 mmol g⁻¹ with a breakthrough retention time of 715 min g⁻¹ (Fig. 3A and fig. S27). TIFSIX-3-Ni offered the best dry 1000 ppm CO₂ saturation uptake and breakthrough retention time of the sorbents studied (1.6 mmol g⁻¹ and 1670 min g⁻¹, respectively) (Fig. 3A). However, at 74% RH, SIFSIX-18-Ni-β was found to be the top performing material with CO₂ saturation uptake of 0.3 mmol g⁻¹ and a breakthrough time of ca. 260 min g⁻¹; the performance of the other sorbents studied was degraded by >80% humidity (Fig. 3B). For the dry 3000 ppm CO₂/N₂ experiments, the CO₂ sorption performances of TIFSIX-3-Ni and Zeolite 13X are comparable with saturation uptakes and breakthrough retention times of ca. 2.1 mmol g⁻¹ and 700 min g⁻¹, respectively (Fig. 3C and table S4). Under the same conditions, CO₂ saturation uptakes for SIFSIX-18-Ni-β (ca. 1.5 mmol g⁻¹), NbOFFIVE-1-Ni (ca. 1.9 mmol g⁻¹), SIFSIX-3-Ni (ca. 1.6 mmol g⁻¹), and ZIF-8 (ca. 0.002 mmol g⁻¹) (retention times for the first three: ca. 520, 425, and 322 min g⁻¹, respectively) were observed. However, at 74% RH, the performance of both NbOFFIVE-1-Ni and Zeolite 13X deteriorated with CO₂ saturation uptakes of only 0.5 and 0.1 mmol g⁻¹, respectively (retention times: ca. 128 and 20 min g⁻¹, respectively) (Fig. 3D). Under the same conditions, SIFSIX-18-Ni-β, TIFSIX-3-Ni, and SIFSIX-3-Ni stand out from Zeolite 13X and NbOFFIVE-1-Ni with CO₂ saturation uptakes of 0.8, 0.8, and 0.9 mmol g⁻¹, respectively. Notably, the CO₂ retention time for SIFSIX-18-Ni-β (ca. 316 min g⁻¹) was greater than those of SIFSIX-3-Ni and TIFSIX-3-Ni (ca. 187 and 283 min g⁻¹, respectively).

NbOFFIVE-1-Ni and SIFSIX-18-Ni-β, the top performing sorbents, were further subjected to 5000 ppm/99.5% and 10,000 ppm/99% CO₂/N₂ breakthrough experiments (figs. S39 and S40). For SIFSIX-18-Ni-β, CO₂ saturation uptakes (dry/wet) were found to be 1.7/1.2 mmol g⁻¹ at 5000 ppm (retention times, 735/532 min g⁻¹, respectively) and 2.0/1.7 mmol g⁻¹ at 10,000 ppm (retention times, 440/410 min g⁻¹, respectively). For NbOFFIVE-1-Ni, the CO₂ saturation uptakes were lower under dry conditions and much lower under wet conditions: 1.5/0.7 mmol g⁻¹ at 5000 ppm (retention times, ca. 650/333 min g⁻¹, respectively) and 1.8/1.1 mmol g⁻¹ at 10,000 ppm (retention times, ca. 340/255 min g⁻¹, respectively). The performance of NbOFFIVE-1-Ni at 0.01 bar (10,000 ppm) is consistent with a previous report (28). Table S4 tabulates the breakthrough results at all CO₂ levels and reveals that SIFSIX-18-Ni-β is much less affected by the presence of moisture than the other C-capture sorbents at all levels from 1000 to 10,000 ppm.

The stability of SIFSIX-18-Ni-β was evaluated using an accelerated stability protocol adopted by the pharmaceutical industry (storage at 40°C and 75% RH) (33). PXRD data revealed that SIFSIX-18-Ni-β reverted to the α polymorph after 14 days, but it is regenerable.

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Fig. 3. Dynamic gas breakthrough and recyclability tests. Dynamic gas breakthrough tests for SIFSIX-18-Ni-β (red), NbOFFIVE-1-Ni (green), Zeolite 13X (blue), SIFSIX-3-Ni (orange), TIFSIX-3-Ni (gray), and ZIF-8 (purple) using (A) dry 1000 ppm, (B) 74% RH 1000 ppm, (C) dry 3000 ppm, and (D) 74% RH 3000 ppm CO₂/N₂ [v/v = 0.1/99.9% for (A) and (B) and v/v = 0.3/99.7% for (C) and (D)] gas mixtures (298 K; 1 bar; flow rate, 20 cm³ min⁻¹). (E) Bar diagram exhibiting the relative decline in CO₂ saturation uptake (%) of SIFSIX-18-Ni-β versus other physisorbents (dry/74% RH, 1000/3000 ppm CO₂/N₂). (F) Bar diagram of CO₂ retention times (min g⁻¹) under dry/74% RH, 1000/3000 ppm CO₂/N₂. (G) Decrease in % CO₂ uptake over six consecutive adsorption-desorption cycles for SIFSIX-18-Ni-β (CO₂/N₂ dry/wet gas mixtures of the following composition: 1000, 3000, 5000, and 10,000 ppm CO₂, without/with 74% RH, saturated with N₂).
Mukherjee et al., Sci. Adv. 2019; 5 : eaax9171     29 November 2019

SCIENCE ADVANCES | RESEARCH ARTICLE

FIG. 3G and figs. S48 to S51) further validated the trace C-capture performance. The fact that effluent CO₂ levels <50 ppm across all trace C-capture conditions (table S4) qualifies SIFSIX-18-Ni-β as a sorbent suitable for IAQ needs.

DISCUSSION

Whereas the use of physisorbents for trace C-capture offers a potentially superior alternative to traditional processes (34), even the top performing physisorbents such as zeolites and MOFs lack the selectivity and/or kinetics needed for trace C-capture under dry conditions. Further, the performances of NbOFFIVE-1-Ni and Mg-MOF-74 are degraded by their strong affinity for H₂O. Conversely, hydrophobic MOFs such as ZIF-8 exhibit low H₂O uptake but suffer from very low CO₂ uptake and/or selectivity. In essence, a Catch-22 situation exists: Pore surfaces with the requisite thermodynamics and kinetics to address trace level C-capture tend to also have binding sites that enable high water uptake (e.g., NbOFFIVE-1-Ni; figs. S21, S22, S29, and S30) (29, 35); hydrophobic pore surfaces that offer low water uptake tend to also exhibit low CO₂ affinity (e.g., ZIF-8). In this context, SIFSIX-18-Ni-β represents a paradigm shift in terms of both properties and pore design. With respect to properties, SIFSIX-18-Ni-β combines unexpectedly strong affinity for CO₂ along with the hydrophobicity that we anticipated from its methyl-decorated pores (36). With respect to design, the CO₂ binding site presents two synergistic features: a relatively strong C···F interaction to a SIFSIX moiety and six weak C-H···O interactions that exhibit exceptional CO₂ selectivity from wet CO₂/N₂ gas mixtures. SIFSIX-18-Ni-β, with binding sites that exhibit exceptional CO₂ selectivity from wet CO₂/N₂ gas mixtures. SIFSIX-18-Ni-β thereby offers highly effective C-capture performance under conditions that mimic C-capture from air in confined spaces and presents an energy-efficient potential solution to IAQ control. The nature of the binding site in SIFSIX-18-Ni-β is key to its performance and provides insight into how to generally improve the performance of physisorbents with respect to C-capture when CO₂ is present at trace levels in humid gas mixtures.

CONCLUSIONS

A crystal engineering approach to pore size (ultramicroporosity) and pore chemistry (coupling of strong electrostatic interactions from inorganic anions and hydrophobicity from methyl groups) control has resulted in a HUM, SIFSIX-18-Ni-β, with binding sites that exhibit exceptional CO₂ selectivity from wet CO₂/N₂ gas mixtures. SIFSIX-18-Ni-β thereby offers highly effective C-capture performance under conditions that mimic C-capture from air in confined spaces and presents an energy-efficient potential solution to IAQ control. The nature of the binding site in SIFSIX-18-Ni-β is key to its performance and provides insight into how to generally improve the performance of physisorbents with respect to C-capture when CO₂ is present at trace levels in humid gas mixtures.

MATERIALS AND METHODS

Gas sorption measurements

Ultrahigh-purity gases, as received from BOC Gases [research-grade He (99.999%), CO₂ (99.995%), O₂ (99.999%), and N₂ (99.998%)], were used for gas sorption experiments. Adsorption experiments (up to 1 bar) for different pure gases were performed using a Micromeritics 3Flex 3500 surface area and pore size analyzer. Before sorption measurements, activation of SIFSIX-18-Ni was achieved by degassing the methanol-exchanged sample on a SmartVacPrep using dynamic vacuum and heating for 4 hours (sample was heated from room temperature to 348 K with a ramp rate of 5°C). Brunauer-Emmett-Teller (BET) surface areas were determined from the N₂ desorption isotherms at 77 K using the Micromeritics Microactive software except for NbOFFIVE-1-Ni and TIFSIX-3-Ni, whose BET surface areas were calculated from their 298 K CO₂ adsorption isotherms. About 200 mg of activated samples was used for the measurements. Very low pressure CO₂ measurements were performed using a Micromeritics 3Flex surface area and pore size analyzer at 273, 283, and 298 K. A Julabo temperature controller was used to maintain a constant temperature in the bath throughout the experiment. Bath temperatures of 273, 283, and 298 K were precisely controlled with a Julabo ME (v.2) recirculating control system containing a mixture of ethylene glycol and water. The low temperatures at 77 and 195 K were controlled using a 4-liter Dewar flask filled with liquid N₂ and dry ice/acetone, respectively. O₂ adsorption isotherm at 77 K was measured up to ~146 mmHg, because the saturation vapor pressure (P₀) of O₂ at 77 K is 147.8 mmHg.
Breakthrough experiments
In typical breakthrough experiments, ~0.3, 0.33, and 0.24 g of pre-activated SIFSIX-18-Ni-β, NbOFFIVE-1-Ni, and ZIF-8, respectively, and ~0.31 g of Zeolite 13X and TIFSIX-3-Ni were placed in quartz tubing (8 mm diameter) to form a fixed bed. First, the adsorbent bed was purged under a 25 cm³ min⁻¹ flow of He gas at 333 K for 30 min before breakthrough experiment. Upon cooling to room temperature, the gas flow was switched to the desired gas mixture at a particular flow rate (the respective flow rates are mentioned in the figure captions and in table S4). Here, trace CO₂/N₂ (~1000, 3000, 5000, and 10,000 ppm)/99.9, 99.7, 99.5, and 99%, respectively) breakthrough experiments were conducted at 298 K. The outlet composition was continuously monitored using a Hiden HPR-20 quartz infar capillary mass spectrometer until complete breakthrough was achieved. After each dry and wet breakthrough experiment, the packed column bed was regenerated at 403 K (SIFSIX-18-Ni-β, NbOFFIVE-1-Ni, ZIF-8, and TIFSIX-3-Ni) and 573 K (Zeolite 13X) with constant He flow (25 cm³ min⁻¹) for 120 min to ensure complete sample regeneration. Experiments in the presence of 74% RH were performed by passing the gas stream through a water vapor saturator at 298 K.
Behavioral Effects of Increased Carbon Dioxide Exposure in Humans 2016–2017

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