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Article

Boosting Acetylene Packing Density within an Isoreticular Metal−Organic Framework for Efficient C_2H_2/CO_2 Separation

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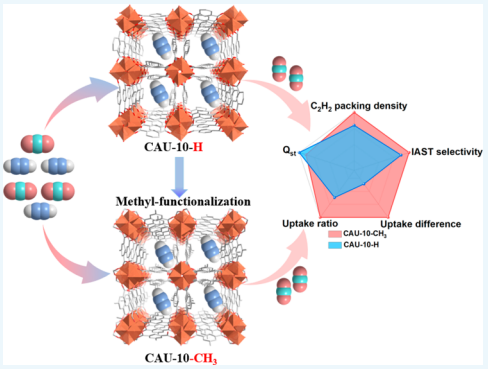
ABSTRACT: Porous solid adsorbents for C_2H_2/CO_2 separation are generally confronted with poor stability, high cost, or high regeneration energy, which largely inhibit their industrial implementation. A desired adsorbent material for practical implementation should exhibit a good balance between low cost, high stability, scale-up production feasibility, and good separation performance. An effective strategy is herein explored based on reticular chemistry through embedding methyl groups in a prototype microporous metal−organic framework (MOF) featuring low cost and high stability to effectively separate an C_2H_2/CO_2 mixture. The anchored methyl groups on the pore surfaces could strongly boost the C_2H_2 packing density and specifically enhance the C_2H_2/CO_2 separation performance, as distinctly established by single-component gas sorption isotherms. The CAU-10-CH_3 material exhibits an excellent C_2H_2 packing density of 486 g L^{-1} and high adsorption differences between C_2H_2 and CO_2 uptake (147%), outperforming the prototype benchmark material CAU-10-H (392 g L^{-1} and 53%). The highly selective adsorption of C_2H_2 over CO_2 was achieved by a lower C_2H_2 adsorption enthalpy (25.18 kJ mol^{-1}) compared to that with unfunctionalized CAU-10-H. In addition, dynamic column breakthrough experiments further confirm CAU-10-CH_3's efficient separation performance for the C_2H_2/CO_2 mixture. CAU-10-CH_3 accomplishes the benchmark balance between cost, stability, scale-up, and separation performance for C_2H_2/CO_2 separation, establishing its promise for industrial implementation. This approach could further facilitate the development of advanced MOF adsorbents to address challenging separation processes. Thus, this study paves the route for the practical implementations of MOF materials in the gas adsorption and separation field.



KEYWORDS: *Metal−organic framework, methyl functionalization, C_2H_2 packing density, C_2H_2/CO_2 separation, practical implementation*

INTRODUCTION

Acetylene (C_2H_2), one of the most essential building blocks for industrial chemicals, is widely used to produce commercial chemicals and electric materials such as vinyl acetate, acrylonitrile, and polyester plastics.[1] C_2H_2 is commonly manufactured by the thermal cracking of hydrocarbons or the partial combustion of methane, wherein a small amount of carbon dioxide (CO_2) impurity inevitably coexists and decreases the subsequent utilization efficiency.[2−4] Therefore, it is essential to eliminate the CO_2 impurity from the C_2H_2/CO_2 mixture to produce pure C_2H_2 gas to better meet the implementation demands of the different domains. However, the close boiling points (189.3 K for C_2H_2 and 194.7 K for CO_2) and highly similar molecular sizes (3.3 × 3.3 × 5.7 $Å^3$ for C_2H_2 and 3.2 × 3.3 × 5.4 $Å^3$ for CO_2), along with the same kinetic diameters (both are 3.3 Å) of the linear-shaped CO_2 and C_2H_2 molecules,[5−7] make C_2H_2/CO_2 separation a challenging task. Currently, cryogenic distillation and solvent extraction are the two primary methods to achieve highly effective separation of C_2H_2/CO_2 mixtures, but these processes often come with potential security risks and are more energy-intensive.[8−10] In this context, the development of novel adsorptive separation technology employing porous solid adsorbents based on a physical adsorption mechanism is strongly driven by the significant reduction in the energy footprint.

Metal−organic frameworks (MOFs), also named porous coordination polymers (PCPs) and coordination polymers (CPs), have attracted tremendous attention as greatly

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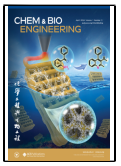

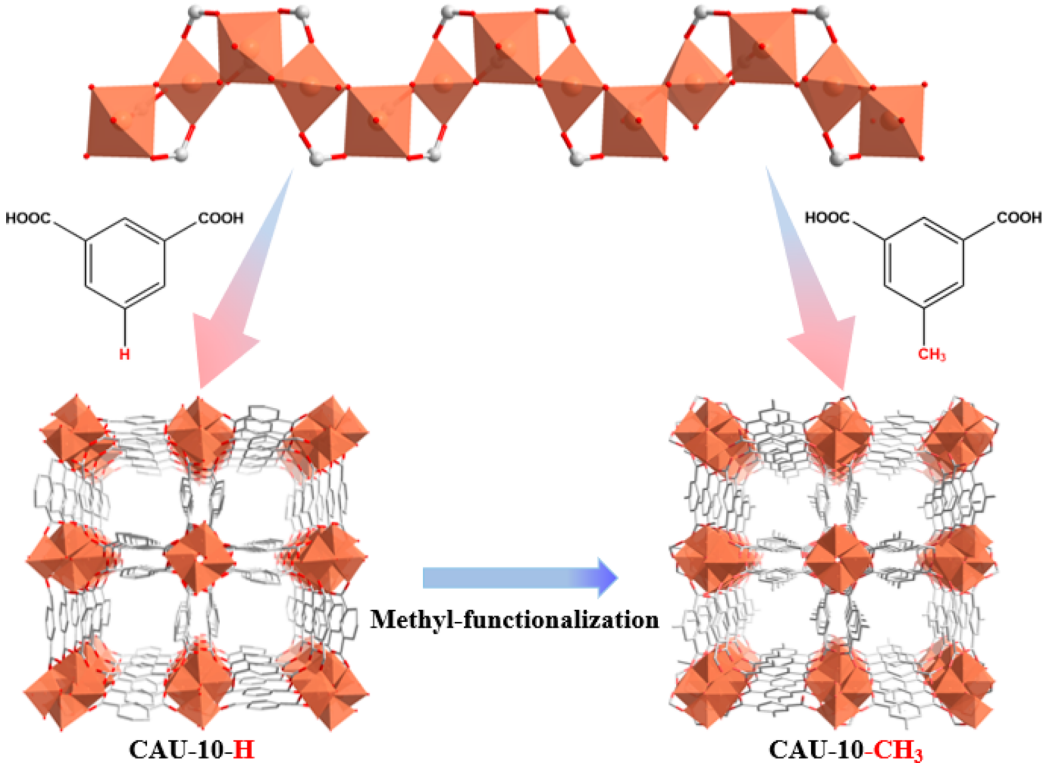

Figure 1. Isostructural frameworks of CAU-10-H and CAU-10-CH_3 assembled from helical chains of AlO_6-polyhedra and isophthalic acid/5-methylisophthalic acid linkers.

promising solid adsorbents, as they integrate the merits of functional pore surface and tunable pore sizes/shapes for different kinds of gas separations, ranging from relatively simple—those including CO_2/N_2, CH_4/N_2, etc.[11−18]—to more intricate and challenging—including olefin/paraffin and alkyne/alkene separations.[19−25] Among the various kinds of gas separations, C_2H_2/CO_2 separation has been considered one of the most complex and challenging due to their highly similar physiochemical properties. Since the pioneering study of the first MOF adsorbent for C_2H_2/CO_2 separation was reported in 2005,[1] a large number of MOF adsorbents have been developed to realize C_2H_2/CO_2 separation via the effective strategies of pore functionalization and pore tuning based on reticular chemistry.[26−32] Another plausible strategy is to embed strong functional sites, such as open metal sites, into ultramicroporous MOF materials to enhance C_2H_2 binding affinity and improve C_2H_2/CO_2 selectivity. However, these strong interactions with C_2H_2 generally may cause high regeneration energy and concurrently compact pore space, resulting in relatively low adsorption capacities, as exemplified by NKMOF-1-Ni and Cu^I@UiO-66-$(COOH)_2$.[33,34] Isoreticular chemistry could allow for the construction and synthesis of MOF materials with optimal pore size/shape and functions for selective binding of C_2H_2 over CO_2 in C_2H_2/CO_2 separation. For example, amine-functionalized MOFs could strengthen the C_2H_2-selective behavior and C_2H_2/CO_2 separation performance,[4,27] and a vertex strategy within layered MOFs could improve C_2H_2/CO_2 separation performance.[10] In short, isoreticular chemistry could serve as an effective strategy to construct MOF materials to achieve challenging gas mixture separation. Since the terminal aim of the development of porous solid adsorbents is industrial implementation, in addition to separation performance, some key factors such as stability, cost, and scale-up production must be considered. On one hand, the practical implementation conditions may contain a small number of acidic gases or water, which requires the adsorbents to possess high chemical stability. On the other hand, low-cost precursors may be better for practical implementation, which is related to scalability. The ideal adsorbent materials should offer a good balance between stability, cost, and separation performance for practical industrial implementation for C_2H_2/CO_2 separation; such a MOF material is yet scarce.

In this context, we chose stable and economically feasible CAU-10-H as the prototype for surface functionalization by linker methylation to afford CAU-10-CH_3. The insertion of methyl may be a one-stone-two-birds strategy. On one hand, the methyl group is considered a hydrophobic group and the methylation may enhance the water stability; on the other hand, the methyl functionalization within the prototype surface may improve gas sorption performance. As expected, compared with prototype CAU-10-H, CAU-10-CH_3 adsorbent exhibits a higher C_2H_2 packing density (486 g L^{-1}) and larger C_2H_2/CO_2 uptake difference (defined as $n(C_2H_2) - n(CO_2)/n(CO_2)$) (147%), as exhibited by single-component gas sorption tests. Such C_2H_2 density is ultrahigh within reported MOFs, and CAU-10-CH_3 exhibits a low C_2H_2 heat of adsorption (25.18 kJ mol^{-1}). In addition. CAU-10-CH_3 exhibits a good C_2H_2/CO_2 mixture separation performance, as demonstrated by breakthrough experiments. Modeling studies disclose the preferential adsorption sites for C_2H_2 and CO_2 at the molecular level. Combined with its high stability, low cost, scale-up feasibility, and good separation performance, CAU-10-CH_3 may be promising for practical industrial implementation.

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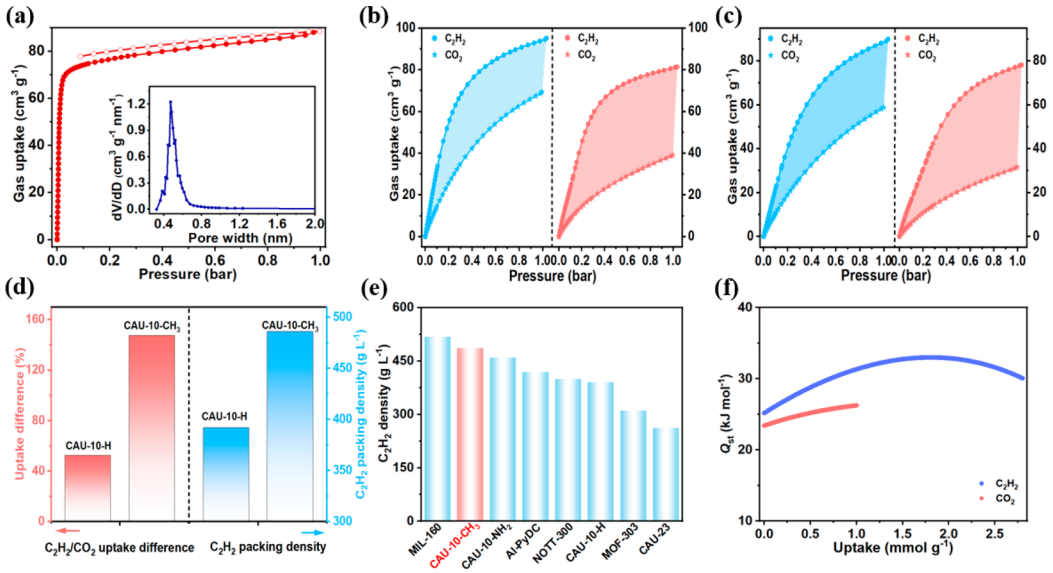

Figure 2. (a) CO_2 sorption isotherms of CAU-10-CH_3 at 195 K. Inset shows the pore size distribution for CAU-10-CH_3. Gas adsorption isotherms of CAU-10-H (left) and CAU-10-CH_3 (right) for C_2H_2 and CO_2 at (b) 288 and (c) 298 K. (d) C_2H_2/CO_2 uptake difference and C_2H_2 density comparison of CAU-10-H and CAU-10-CH_3. (e) Comparison of C_2H_2 density at 100 kPa and room temperature for CAU-10-CH_3 and other well-known Al-based MOF materials. (f) Isosteric heat of adsorption of C_2H_2 and CO_2 for CAU-10-CH_3.

RESULTS AND DISCUSSION

The pair of isoreticular ultramicroporous MOFs, CAU-10-H and CAU-10-CH_3, were synthesized according to previously reported methods with some modifications (Figure 1).[35,36] The powder X-ray diffraction (PXRD) patterns of the as-synthesized samples agreed well with the simulated ones derived from the crystallographic data, suggesting that this pair of ultramicroporous MOFs were successfully prepared with high purity and good crystallinity (Figures S1 and S2). In both ultramicroporous MOFs, each Al^{3+} ion adopts a six-coordinated configuration with an octahedral geometry and is coordinated with six oxygen atoms from two bridging −OH ions and four different carboxylate groups. The AlO_6 chains are further linked to V-shaped organic ligands (isophthalate and 5-methylisophthalate) and extended into the three-dimensional frameworks of CAU-10-H and CAU-10-CH_3, respectively (Figure 1). There are no open metal sites in the structures of CAU-10-H and CAU-10-CH_3 owing to the full coordination of the Al^{3+} ion. In particular, compared to CAU-10-H, CAU-10-CH_3 possesses free methyl groups within the pore channels, which reduces the pore sizes to 5.8 × 5.8 $Å^2$ from 6.8 × 7.5 $Å^2$. Thermogravimetric analysis (TGA) suggested that the CAU-10-CH_3 was stable until approximately 770 K (Figure S4), and the result of the in situ-variable temperature PXRD was well consistent with the TG curve (Figure S5). According to the PXRD pattern characterization, no structural damage or loss of crystallinity was observed in MOF CAU-10-CH_3 after different treatments, including immersion in different organic solvents or different pH value (pH = 1−12) aqueous solutions for 1 week (Figures S6 and S7). These characterizations reveal that the MOF CAU-10-CH_3 possesses good thermal and chemical stability, which are beneficial for its use in practical implementations.

To obtain the guest-free framework, the as-synthesized CAU-10-CH_3 was solvent exchanged with methanol for 3 days. The permanent porosity of activated CAU-10-CH_3 was confirmed by CO_2 sorption isotherms at 195 K. As shown in Figure 2a, CAU-10-CH_3 exhibits a typical type I isotherm profile with CO_2 uptake up to 88.47 $cm^3\ g^{-1}$ at 195 K, indicating its microporous nature. The Brunauer−Emmett−Teller (BET) surface area and pore volume of CAU-10-CH_3 were estimated to be 312 $m^2\ g^{-1}$ and 0.187 $cm^3\ g^{-1}$, respectively, smaller than those of prototype CAU-10-H (627 $m^2\ g^{-1}$ and 0.28 $cm^3\ g^{-1}$), owing to the decreasing pore space resulting from embedding methyl sites in CAU-10-CH_3. Additionally, the pore size distribution (PSD) of CAU-10-CH_3 was estimated to be 4.7 Å based on the non-local density functional theory (NLDFT) method (Figure 2a). The ultramicroporous pore space is conducive to the separation of small gas molecules and packing of gas molecules in a dense pore space.

The stable framework and microporous pore feature provide us with infinite motivation to explore the adsorption performance of CAU-10-CH_3 toward C_2H_2 and CO_2. Thus, the single-component gas adsorption isotherms of C_2H_2 and CO_2 were measured at 288 and 298 K (Figure 2b,c). As shown in Figure 2c, the C_2H_2 uptake capacity values at 298 K and 100 kPa are 89.88 and 78.28 $cm^3\ g^{-1}$ for CAU-10-H and CAU-10-CH_3, respectively. The C_2H_2 uptake on CAU-10-CH_3 is slightly lower than that on CAU-10-H, which is mainly attributed to the small pore volume. Interestingly, compared to CAU-10-H, the CO_2 adsorption capacity on CAU-10-CH_3 significantly decreases to 31.64 $cm^3\ g^{-1}$ from 58.75 $cm^3\ g^{-1}$, indicating that the pore volume instead of number of methyl sites makes a larger contribution to the CO_2 adsorption. The markedly decreased CO_2 uptake on CAU-10-CH_3 leads to a great C_2H_2/CO_2 uptake difference of 147% compared to that on CAU-10-H (53%). In addition, the C_2H_2/CO_2 uptake ratio is improved from 153% for CAU-10-H to 247% for CAU-10-CH_3, and these results suggest its promising potential for C_2H_2/CO_2 separation. We note that the pore volume decreased significantly and the C_2H_2 uptake capacity decreased only slightly, so we speculate that the C_2H_2 packing density may be improved. According to the C_2H_2 adsorption capacity in CAU-10-CH_3 and the corresponding pore volume, the C_2H_2 packing density is estimated to be 486 g L^{-1} at 298 K and 100

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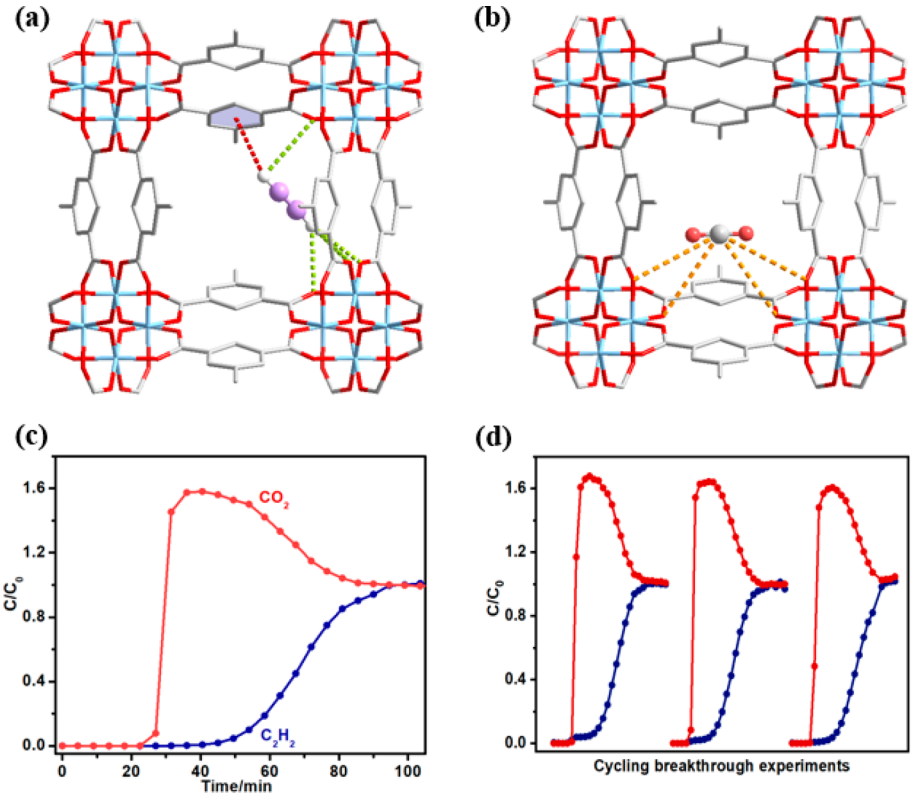

Figure 3. Preferential binding sites for (a) the C_2H_2 molecule and (b) the CO_2 molecule in the pore of CAU-10-CH_3 determined by grand canonical Monte Carlo simulation. (c) Experimental column breakthrough curves for an equimolar C_2H_2/CO_2 mixture with a total flow of 1.5 mL min^{-1} in an absorber bed packed with CAU-10-CH_3 at ambient conditions. (d) Cycling tests of the equimolar C_2H_2/CO_2 mixture on CAU-10-CH_3 at ambient conditions.

kPa. This C_2H_2 packing density value is markedly higher than that of prototype MOF CAU-10-H (392 g L^{-1}) (Figure 2d), and is also about 413 times the gaseous C_2H_2 density (1.1772 g L^{-1}, at 273 K and 101.3 kPa), which demonstrates that the C_2H_2 molecules could be effectively packed in the pore space of CAU-10-CH_3. Notably, this packing density value is comparable to or higher than those of many well-known Al-based MOF materials, such as CAU-10-NH_2 (460 g L^{-1}),[27] NOTT-300 (~400 g L^{-1}),[37] CAU-23 (262 g L^{-1}),[38] and MOF-303 (310.7 g L^{-1}) (Figure 2e).[39] A promising adsorbent material should have good repeatability and cycling stability for the practical implementation of C_2H_2 storage. Therefore, cyclic C_2H_2 sorption measurements were conducted. As expected, the adsorption capacity of C_2H_2 in CAU-10-CH_3 showed no loss after five consecutive tests at 298 K (Figure S9), suggesting that CAU-10-CH_3 is a promising adsorbent candidate in C_2H_2 storage and C_2H_2/CO_2 separation.

To further evaluate the separation performance of CAU-10-CH_3 toward the C_2H_2/CO_2 mixture, the adsorption selectivity was calculated through the extensively studied ideal adsorbed solution theory (IAST). As shown in Figure S11, the IAST selectivity of CAU-10-CH_3 for an equimolar C_2H_2/CO_2 mixture is estimated to be 4.6 at 298 K and 100 kPa, which is slightly higher than that of the prototype CAU-10-H (4.0). In addition, this IAST selectivity value is comparable to those of many promising materials, including JNU-1 (3.6),[40] MUF-17 (6.0),[41] IPM-101 (5.4),[42] NUM-20 (5.4),[43] JXNU-11(Fe_2Ni) (2.7),[44] FJU-90a (4.3),[45] SIFSIX-Cu-TPA (5.3),[46] CAU-23 (3.8),[38] UPC-200(Al)-F-BIM (3.15),[47] PCP-31 (7.0),[48] etc. The high uptake difference and C_2H_2 packing density and good IAST selectivity indicated the potential of CAU-10-CH_3 for efficient C_2H_2/CO_2 separation.

From the perspective of practical implementation of MOF materials as porous solid adsorbents, the heat of adsorption (Q_{st}) could also be a crucial factor, as adsorbents with low Q_{st} expend less energy for adsorbent regeneration and adsorbate recycling. In addition, the binding affinity between the guest molecule and the host framework could be assessed through the low-coverage heat of adsorption. Therefore, Q_{st} was calculated by fitting adsorption isotherms of C_2H_2 and CO_2 at different temperatures using the Virial model. As shown in Figure 2f, the Q_{st} values of C_2H_2 and CO_2 for CAU-10-CH_3 are determined as 25.18 and 23.40 kJ mol^{-1} at zero coverage, respectively, indicating that CAU-10-CH_3 exhibits a stronger binding affinity for C_2H_2 over CO_2. Compared with prototype CAU-10-H (~25 and 28 kJ mol^{-1} for CO_2 and C_2H_2, respectively), the introduction of a methyl group slightly decreases the initial Q_{st} for CAU-10-CH_3, which is consistent with the tendency of adsorption profiles, indicating less energy for adsorbent regeneration. However, the Q_{st} value of C_2H_2 for CAU-10-CH_3 is still very low compared with those of many benchmark MOFs, such as Cu^I@UiO-66-$(COOH)_2$ (74.5 kJ mol^{-1}),[34] ATC-Cu (79.1 kJ mol^{-1}),[49] NKMOF-1-Ni (60.3 kJ mol^{-1}),[33] ZJU-50a (40 kJ mol^{-1}),[50] TIFSIX-2-Ni-i (40 kJ mol^{-1}),[51] NTU-67 (44.1 kJ mol^{-1}),[52] and NUM-20 (38.83 kJ mol^{-1}).[43] The moderate Q_{st} value for CAU-10-CH_3 suggests that this MOF adsorbent could be regenerated under mild conditions, which shows promising potential for efficient C_2H_2/CO_2 separation.

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Chem Bio Eng. 2024, 1, 245−251

To further comprehensively understand the adsorption mechanism of CAU-10-CH_3, grand canonical Monte Carlo (GCMC) simulations were conducted to explore the binding sites of CO_2 and C_2H_2. As shown in Figure 3a,b, the preferential adsorption sites for C_2H_2 and CO_2 were located on one side of the inner pore, and the density distribution of C_2H_2 and CO_2 molecules indeed proved this result (Figure S18). It was observed that the C_2H_2 molecule interacted with the benzene ring of the organic ligand to form one C−H···π interaction (3.305 Å) and bound the oxygen atoms from carboxylate groups through multiple C−H···O interactions ranging from 2.812 to 3.492 Å (Figure 3a). In contrast, the CO_2 molecule only interacted with oxygen atoms from carboxylate groups, forming four (CO_2) $C^{\delta+}\cdots O^{\delta-}$ electrostatic interactions (4.510−4.545 Å) (Figure 3b). Comparing with the host−guest interactions within the prototype CAU-10-H, the C_2H_2−framework interaction was basically equivalent for CAU-10-CH_3 and CAU-10-H, yet the CO_2−framework interaction was obviously weaker for CAU-10-CH_3 than for CAU-10-H because it had longer distances (4.510−4.545 Å for CAU-10-CH_3 vs 3.692−3.729 Å for CAU-10-H). Such host−guest interaction differences agree well with the adsorption profile behavior. The static binding energies for C_2H_2 and CO_2 molecules in CAU-10-CH_3 were calculated from GCMC simulations to be 29.13 and 24.12 kJ mol^{-1}, respectively, which are well consistent with the tendency in the zero-coverage Q_{st} values (25.18 and 23.40 kJ mol^{-1} for C_2H_2 and CO_2, respectively). Overall, compared to CO_2−framework interactions, C_2H_2 displays typically more interactions with shorter distances with CAU-10-CH_3 at the preferential binding site, which explains the stronger binding affinity between C_2H_2 and the CAU-10-CH_3 framework.

Attributed to the suitable pore environment and optimal pore size, CAU-10-CH_3 displayed a significant difference in adsorption between C_2H_2 and CO_2 and good IAST selectivity. The moderate heat of adsorption and high C_2H_2 packing density motivated us to explore the actual performance of CAU-10-CH_3 for the challenging C_2H_2/CO_2 mixture separation. The dynamic column breakthrough experiments were conducted at ambient conditions, and the activated sample was packed within a column with the equimolar C_2H_2/CO_2 mixture flowing at a total flow rate of 1.5 mL min^{-1}. As shown in Figure 3c, the C_2H_2/CO_2 mixture could be clearly separated by the MOF CAU-10-CH_3. When the C_2H_2/CO_2 mixture was passed over the fixed-bed column of CAU-10-CH_3, as predicted, the CO_2 substance was first eluted through the fixed-bed column at 22.5 min, and this process continued for 27 min, followed by C_2H_2 49.5 min later. The column breakthrough experiment was continued until the concentrations of the expelled gases were constant. In particular, a marked roll-up behavior of CO_2 was exhibited in the breakthrough experiments, suggesting that a large amount of previously adsorbed CO_2 could be replaced by the later inflow of C_2H_2, which indicates that C_2H_2 has a better competition capacity than that of CO_2 in the binding sites of CAU-10-CH_3. The dynamic captured amount of C_2H_2 was estimated to be 48.7 mL g^{-1}. In addition, the CAU-10-CH_3 adsorbent could maintain the same separation capacity after multiple cycles of dynamic column breakthrough measurements (Figure 3d), suggesting its good recycling separation capability. By virtue of the moderate adsorption heat of C_2H_2, CAU-10-CH_3 material could be easily regenerated by purging the fixed-bed column with inert gas under ambient conditions. Such results further show that the CAU-10-CH_3 adsorbent is a highly desirable adsorbent for C_2H_2/CO_2 separation. Combining with the low-cost precursors, stability framework, moderate heat of adsorption, and good C_2H_2/CO_2 separation performance, CAU-10-CH_3 could be a promising candidate adsorbent for addressing the challenging separation of C_2H_2/CO_2 mixture.

CONCLUSIONS

By virtue of isoreticular chemistry, we report a microporous MOF, CAU-10-CH_3, with high chemical stability and thermal stability featuring a suitable pore environment for effective C_2H_2/CO_2 separation, which could be synthesized by using low-cost precursors. CAU-10-CH_3 exhibits a high C_2H_2 storage density of 486 g L^{-1} and highly preferential adsorption of C_2H_2 over CO_2 at ambient conditions. In addition, this material displays a relatively low heat of adsorption for C_2H_2 (25.18 kJ mol^{-1}). Dynamic breakthrough experiments suggest a good C_2H_2/CO_2 separation performance, and the material could be easily regenerated through purging at ambient temperature. With the ultrahigh stability, low cost, feasibility of production, and good C_2H_2/CO_2 separation performance, CAU-10-CH_3 represents a good porous solid material with an outstanding balance among stability, separation performance, and cost, making it an excellent adsorbent for actual separation implementation. This study not only provides a promising strategy to achieve good C_2H_2/CO_2 separation behavior but also paves the route for constructing MOF materials with balanced stability, separation performance, and cost to facilitate their practical industrial implementation for important yet challenging gas separations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/cbe.3c00073.

Full experimental details, including materials syntheses, PXRD patterns, TGA curves, C_2H_2 sorption data, grand canonical Monte Carlo (GCMC) simulations, breakthrough experiments, and Figures S1−S18 (PDF)

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Notes

The authors declare no competing financial interest.

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Chem Bio Eng. 2024, 1, 245−251