

Communication

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Partitioning MOF-5 into confined and hydrophobic compartments for carbon capture under humid conditions

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Supporting Information Placeholder

ABSTRACT: Metal-organic frameworks (MOFs), by virtue of their remarkable uptake capability, selectivity and ease of regeneration, hold great promise for carbon capture from fossil fuel combustion. However, their stability towards moisture together with the competitive adsorption of water molecule against CO₂ drastically dampens their capacity and selectivity under real humid flue gas conditions. In this work, an effective strategy was developed to tackle the above obstacles by partitioning the channels of MOFs into confined and hydrophobic compartments by in-situ polymerization of aromatic acetylenes. Specifically, polynaphthylene was formed via radical reaction inside the channels of MOF-5 and served as partitions without altering the underlying structure of the framework. Compared with pristine MOF-5, the resultant material (PN@MOF-5) exhibits a doubled CO2 capacity (78 vs. 38 cm³/g at 273 K and 1 bar), 23-times higher CO_2/N_2 selectivity (212 vs. 9), and significantly improved moisture stability. The dynamic CO₂ adsorption capacity can be largely maintained (> 90%) under humid condition during cycles. This strategy can be applied into other MOF materials and may shed light on designing new MOFpolymer materials with tunable pore sizes and environment to promote their practical applications.

Fossil fuel combustion from stationary sources makes up the majority of the total anthropogenic CO_2 contributions, raising huge environmental challenges facing our planet.^[1] Although aqueous alkanolamine solutions are the state-ofthe-art capture absorbents that broadly implemented in power plants for CO_2 capture, the regeneration of them from carbamates inevitably leads to a huge energy penalty.^[2] Metal-organic frameworks (MOFs), constructed from organic links and metal ions or clusters, represent one of the most promising materials for CO_2 capture and storage.^[2c,3] Owing to their high porosity, structural diversity, tunable pore environment, and atomically well-defined skeleton, MOFs have been extensively explored in various applications, such as gas storage and separation, catalysis, and chemo-sensing.^[4]

Increasing MOF surface area and pore size is one of the most efficient approaches to maximize CO₂ uptake and can dramatically enhance the storage capacity under high pressure (> 3-5 MPa).^[5] But such high adsorption is often not viable when used in a post-combustion power plant where the pressure of the flue gas from smoke stacks usually maintains below 0.3 MPa.^[6] Indeed, pore surface functionalization of MOFs is the most widely used method for the efficient and selective carbon capture. Generally, functional groups with high polarity, such as pyridine, -OH, -NO₂, -CN, -SH, etc., and/or open metal sites decorating the walls of MOFs pores are favorable, since CO2 molecule processes a large quadrupole moment and these functional sites are able to induce polarization and enhance affinity. [3a,3b,7] Another effective way to improve the CO₂ capacity and selectivity is to anchor basic amine groups onto the skeleton of MOFs to mimic the chemisorption in the liquid absorbents.^[8] Nevertheless, aside from ~75% N₂ and ~15% CO₂, a typical postcombustion flue gas also contains 5%~7% water, which must be thoroughly took into consideration for real applications.^[2c,3a,3b,9] During the separation process, water molecules with higher polarity and binding energy will strongly compete against CO₂, and therefore, the active adsorptive sites in MOFs are easily poisoned by only small amount of water. Consequently, the capacity and selectivity will be dramatically dampened under real humid flue gas conditions.^[10]

Needless to say that many MOF structures are vulnerable under moisture conditions, and the collapse of the framework by slow hydrolysis can significantly lower the separaperformance and impede tion their practical application.^[10c,11] Alternatively, trapping CO₂ in a confined space offers opportunities to separate gas molecules based on size. Due to the difficulties in the design and synthesis of MOFs with pore openings that exactly match for CO₂ molecule in kinetic diameter, only few pioneering works have been reported.^[12] Therefore, the demand of a facile method to prepare moisture-stable MOF materials that can selectively adsorb CO2 over other gas components and water molecules from flue gas is ever urgent yet largely unmet.

Recently, Cohen et al. reported polymer-metal-organic frameworks that can selective adsorption of CO2 against N2 and exhibited high water stability.^[13] Kitagawa *et al.* are pioneered in in-situ polymerization of vinyl monomers inside the channels of MOFs.^[14] Inspired by their works, herein, we report a strategy that can divide the open channels of MOFs into confined and hydrophobic compartments by in-situ polymerization of aromatic acetylenes inside MOF pores. Thus-obtained MOF material can capture and trap CO2 molecules and effectively retard the diffusion and repel water molecules. We intentionally selected MOF-5, a famous and highly porous MOF structure that can also be produced in industrial scale (> 1 ton per 30 mins)^[15], to serve as the prototype host material. 1,2-diethynylbenzene (DEB) as monomer were adsorbed and encapsulated in MOF-5 and further heated at elevated temperature to afford polynaphthylene (PN) inside the channels via Bergman cyclization and subsequent radical polymerization (Scheme 1), and this composite is denoted as PN@MOF-5. Due to its hydrophobic and linear nature, PNs in MOF-5 can act as partitions to segregate the micropores with ~1.2 nm in width into ultra micropores (≤ 0.7 nm) and simultaneously improve the stability of PN@MOF-5 towards moisture.

Scheme 1. (a) Illustration of competitive adsorption of CO_2 against H_2O at the surface and edge of PN. (b) Polymerization of DEB in MOFs.



In contrast to MOF-5, which is water-sensitive, PN@MOF-5 can retain its crystallinity and porosity upon exposure to humid air (> 40 h, RH = 40%). More importantly, the ultra micropores and exposed large amount of aromatic edges and surfaces in PN@MOF-5 allow its efficient capture of CO₂ (Scheme 1). Compared with pristine MOF-5, the thermodynamic adsorption capacity of CO₂ is doubled and selectivity of CO₂/N₂ (14/86, 1 bar, 273 K) is 23-times increased for PN@MOF-5. Furthermore, in breakthrough experiments, PN@MOF-5 largely maintained its dynamic

 CO_2 capacity under humid conditions (> 90% retention rate under RH = 65%).

The details for the polymerization of DEB in MOF-5 were described in Supporting Information. A significant color change from white to brown was observed after heating (Figures S3 and S4), indicative of the formation of highly conjugated polymers. The powder X-ray diffraction pattern (PXRD) of PN@MOF-5 is consistent with that of MOF-5 (Figure S5), revealing the crystalline structure is retained during inclusion and polymerization of DEB. ¹³C solid state NMR spectra of PN@MOF-5 as well as the PN polymer isolated from PN@MOF-5 (Figure S7) display the signals of aromatic carbons belonging to the polynaphthylene at ~128 ppm. The disappearance of C≡C-H stretching vibration at 3300 cm⁻¹ and C=C-H bending vibration at ~700 cm⁻¹ in the fourier transform infrared attenuated total reflection (FTIR-ATR) spectrum of PN@MOF-5 (Figure S8) reflects the high polymerization degree of acetylene. As determined by elemental analysis, the loading amount of PN in the hostpolymer inclusion is 15.0 wt% (Table S1). The PN loading can be adjusted by carefully altering the amount of solvent used for washing before polymerization, and accordingly, another three inclusion samples with a 3.2, 34 and 40 wt% PN loading (denoted as PN_x@MOF-5, x means loading amount%) were obtained. Scanning electron microscopy (SEM) and optical microscopy images (Figures S9 and S10) of the two PN@MOF-5 samples display their preserved crystal morphologies. To address whether the PN polymers are homogeneously existed in large domains (greater than a nanometer scale), each crystal was dissected into two segments. The color is almost evenly distributed in each crystal, and the higher the loading amount, the deeper the color.



Figure 1. (a) Pore size distributions of PN@MOF-5, PN_{3.2}@MOF-5 and MOF-5 based on quenched solid-state density functional theory. (b) CO_2 sorption isotherms of PN@MOF-5 and MOF-5 at 273, 283 and 298 K.

Nitrogen sorption isotherm tests at 77 K were conducted to access their porosities. Analyses of the sorption curves of MOF-5, $PN_{3,2}@MOF-5$ and PN@MOF-5 (Figure S11) by the Brunauer-Emmett-Teller (BET) method give specific surface areas of 3200, 2600 and 1200 m² g⁻¹, respectively (Figures S12-S14). Quenched solid-state density functional theory (QSDFT) was utilized to deduce the pore size distributions (Figure 1a). Interestingly, along with the increasing of PN loadings, the pores with 1.2 nm (MOF-5 pores) in 1

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59 60 width are gradually diminished whereas the pores with 0.6 nm (partitioned pores) in width are emerged and boosted significantly. These results demonstrate that the PN polymers can act as partitions to segregate the channels of the crystals into confined compartments. Although these analyses do not preclude the presence of PN polymers wrapped the surface of crystals, we believe that the overall consideration of the pore size distribution analysis, PXRD measurements and microscopy images strongly support that most PN polymers are distributed inside the crystal channels and serve as partitions.



Figure 2. (a) Contact angle measurements. (b) Nitrogen sorption profiles of PN@MOF-5 and MOF-5 for exposure to humidity for different times.

Compartments with confined space together with abundant exposed surfaces and edges of aromatic rings in PN@MOF-5 are supposed to be favorable for CO₂ capture.^[16] Considering a balance between partitioning the MOF channels and partially blocking (Figure S15 and S16), we selected PN@MOF-5 to perform CO₂ sorption isotherm test at different temperatures and calculated its adsorption enthalpy. Remarkably, compared with MOF-5 (38 cm³ g⁻¹ at 273 K, 760 Torr), the doubled CO₂ capacity of PN@MOF-5 (Figure 1b) with just one third of the BET surface area of MOF-5 is achieved (78 cm³ g⁻¹ at 273 K, 760 Torr). It is worth noted that, derived from CO₂ adsorption isotherm at 273 K by using NLDFT method, the pore size distribution (Figure S17) displays a maximum at about 0.5-0.6 nm as well as partial pores at 0.37 and 0.81 nm. We further employed the Clausius-Clapeyron formula to determine the isosteric heats of adsorption (Q_{st}) from CO₂ adsorption isotherms at 273, 283 and 298 K (Figures 1b and S18). At zero loading the Q_{st} value $(-\Delta H)$ is 29 kJ/mol, and at higher loadings it decreases to ~24 kJ/mol, the value of which is still one third higher than that of MOF-5. The fact that twice amount of CO₂ are adsorbed in the comparatively low-surface-area material of PN@MOF-5 with larger Q_{st} can be attributed to the enhanced adsorbate-surface interactions to both sides or ends of the CO₂ molecules stemmed from confined pore size effect and the more exposed aromatic surfaces.

Ideal adsorption solution theory (IAST) was applied in order to predict the expected selectivity of CO_2 and N_2 for the materials (Figure 3a). Under simulated post-combustion flue gas composition (14% CO_2 , 86% N_2), the calculated CO_2/N_2 selectivity at 1 bar and 273 K for PN@MOF-5 (212) is almost 23 times higher than that of MOF-5 (9) (Table S2).

MOF-5 is very sensitive to moisture, as a result of the breakdown of the coordination bonds by the attack of water molecule.^[17] In contrast to the hydrophilic nature of MOF-5 with a water contact angle close to 0°, PN@MOF-5 is hydrophobic and exhibits a water contact angle of 135° (Figure 2a). MOF-5 completely loses its porosities within 6 h and transforms to MOF-69c^[18] within 40 h in a humid environment (RH = 40%), as evidenced by PXRD and N₂ sorption isotherm measurements (Figures 2b and S23). On the contrary, the BET surface area and crystallinity of PN@MOF-5 are preserved after 40-h moisture treatment (Figures 2b and S23), indicating that the inclusion of aromatic PN into the channels can effectively prevent the attack to the coordination bonds from water. Similar results are observed for PN_{3.2}@MOF-5 (Figures S24 and S25).



Figure 3. (a) Calculated IAST selectivity of CO_2 over N_2 at 273 K of a 14/86 gas mixture of CO_2/N_2 . (b) Capacities and (c) dynamic sorption curves of PN@MOF-5 and MOF-5 under dry conditions (blue) and in the presence of water (red).

Given the high humid stability, hydrophobicity and good CO2 uptake capacity, we carried out dynamic separation experiments to test the ability of PN@MOF-5 to separate CO₂ from N₂ with and without moisture (see details in Figure S26 in the SI). A mixed N_2/CO_2 gas with 16% CO₂ content was introduced to the bed, and the effluent was monitored by a mass spectrometer (Figure 3b and 3c). Under dry conditions, PN@MOF-5 adsorbent bed shows a dynamic CO_2 adsorption capacity of 34 cm³/g, which is one-and-ahalf times of MOF-5 (23 cm³/g) prepared under similar conditions. For humid condition test, a gas mixture $(V(N_2)/V(CO_2) = 84.16)$ with a RH value of 65% was introduced to the bed. The dynamic sorption capacity of PN@MOF-5 under moisture almost retains the value obtained under dry condition, while MOF-5 displays a 40% and 73% decrease in the first and second cycle (Figures 3b and 3c), respectively, in the presence of water. In addition, the topology of PN@MOF-5 remained intact after dynamic sorption, while the skeleton of MOF-5 was almost collapsed (Figure S29). For comparison, two representative MOFs, MOF-199 and NH₂-UiO-66 significantly lost their CO₂ capacity under humid conditions (Table S3).

In conclusion, we have reported a new strategy to divide MOF pores into confined compartments by *in-situ* polymerization of aromatic acetylene. For PN@MOF-5, a remarkable increase in CO₂ adsorption capacity from 38 to 78 cm^3/g and CO₂/N₂ selectivity from 9 to 212 at 273 K and 1 bar were obtained. Due to its hydrophobic nature, not only the stability of the framework toward moisture was significantly improved but also the competitive adsorption of water against CO₂ molecule was effectively inhibited. Consequently, the dynamic CO₂ capacity under humid conditions reached a 94% retention rate. The improved stability towards moisture and increased adsorption capacity of PN@UMCM-8 (Figure S32-S34) demonstrates the applicability of the present strategy. The abundant combinations of porous materials (i.e., MOFs, covalent organic frameworks,^[19] porous polymers, etc.) and conventional polymers will provide versatile material platforms for achieving multi-functions and practical applications.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental details and data (PDF).

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Notes

The authors declare no competing financial interests.

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