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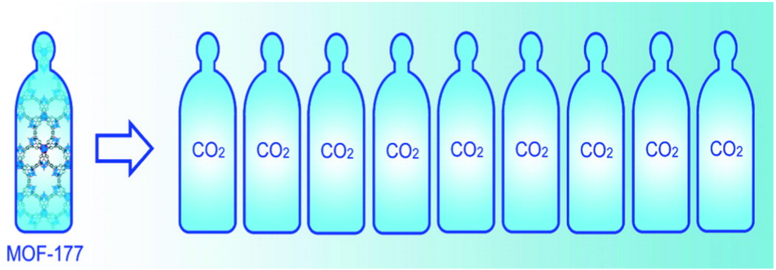

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Metal−Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature

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Removal of CO_2 from the flue exhaust of power plants, currently a major source of emissions, is commonly accomplished by chilling and pressurizing the exhaust or by passing the fumes through a fluidized bed of aqueous amine solution, both of which are costly and inefficient.[1a] Other methods based on chemisorption of CO_2 on oxide surfaces or adsorption within porous silicates, carbons, and membranes have been pursued as means for CO_2 uptake.[1b] However, in order for an effective adsorption medium to have long-term viability in CO_2 removal, it should combine two features: (i) a periodic structure for which CO_2 uptake and release is fully reversible and (ii) a flexibility with which chemical functionalization and molecular-level fine-tuning can be achieved for optimized uptake capacities.

Metal−organic frameworks (MOFs) represent a class of porous materials that offer these advantages for CO_2 storage: ordered structures, high thermal stability,[2a] adjustable chemical functionality,[2b] extra-high porosity,[2c] and the availability of hundreds of crystalline, well-characterized porous structures yet to be tested.[2d−k] Accordingly, we embarked on a program to assess the viability of MOFs in CO_2 storage. Nine compounds were selected in order to examine a range of structural and porous attributes (Figure 1). The list represents a cross-section of framework characteristics such as square channels (MOF-2),[3a] pores decorated with open metal sites (MOF-505 and $Cu_3(BTC)_2$),[3b,c] hexagonally packed cylindrical channels (MOF-74),[3d] interpenetration (IRMOF-11),[2b] amino- and alkyl-functionalized pores (IRMOFs-3 and -6),[2b] and the extra-high porosity frameworks IRMOF-1 and MOF-177. [2a,c]

Pure samples of these materials[4] were synthesized, characterized by powder X-ray diffraction and thermogravimetric analysis, activated to measure N_2 surface area, and then handled under an inert atmosphere. An activated carbon sample (Norit RB2) was also tested as a reference material.[5] The gravimetric uptake capacity of CO_2 for each MOF was determined by exposing an evacuated sample of the MOF adsorbent to increasing pressure increments of CO_2 gas at ambient temperature. The sample and gas were allowed to come to equilibrium for each of the increments, at which point the corresponding weight change was recorded, corrected for buoyancy, and plotted versus pressure.

The room-temperature CO_2 adsorption isotherms (Figure 2) of MOF-2, Norit RB2, MOF-505, MOF-74, and $Cu_3(BTC)_2$ samples all have typical monotonic isotherms (Type I) in which the more intense gas adsorption at low pressure forms a "knee" in the isotherm. We found this same shape for the low-temperature (195 K) MOF-2 isotherm when CO_2 sorption was first reported in MOFs.[3a] Similarly, in the room-temperature isotherms the pores begin to saturate at higher pressure, where the uptakes reach plateau capacities that qualitatively scale with surface area. On the other hand, the $Zn_4O(O_2C)_6$-type frameworks of IRMOFs-11, -3, -6, and -1 show substantially greater capacities for CO_2 than the other MOFs. Significantly, the isotherms of these four materials gradually

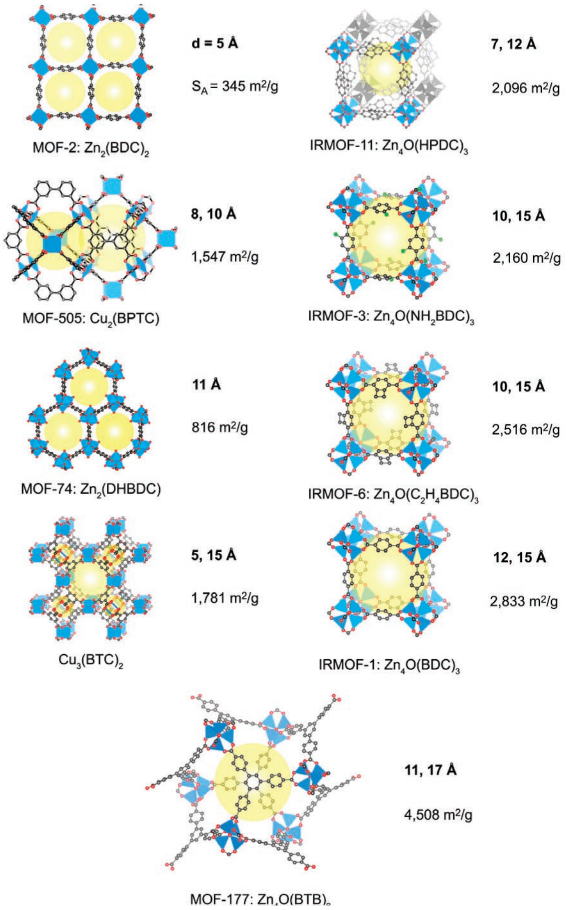

Figure 1. Crystal structures of MOFs examined for CO_2 storage capacity at room temperature. For each MOF, the framework formula, pore size, and surface area are given.

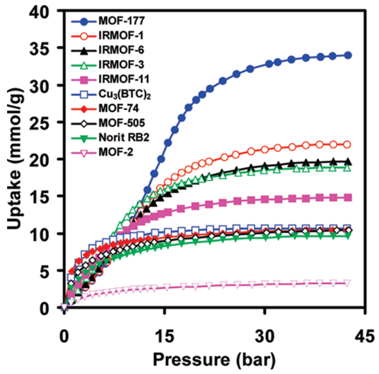

Figure 2. Comparison of gravimetric CO_2 capacities for several MOFs (and an activated carbon as a reference) determined at ambient temperature and pressures up to 42 bar.

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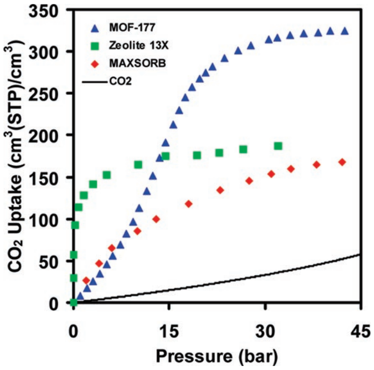

Figure 3. Comparison of the volumetric CO_2 capacity of crystalline MOF-177 relative to zeolite 13X pellets, MAXSORB carbon powder, and pressurized CO_2.

take on a sigmoidal shape (step) with increasing uptake. The appearance of the step in this pressure regime is due to larger effective pore sizes, which lead to a behavior that more closely resembles that of the bulk fluid.[6] The voluminous space enclosed by MOF-177 results in a CO_2 capacity of 33.5 mmol/g, which is far greater than that of any other porous material reported.

The fact that MOF-177 takes up more CO_2 at 35 bar does not preclude the use of other MOFs for CO_2 storage at lower pressures. This is revealed by a plot of the derivatives of the isotherms with respect to pressure.[4] The maxima in these plots are the inflection points of the original isotherm steps and are related to the optimal pressure for the most efficient CO_2 adsorption in each MOF. There is a clear progression from the higher-pressure step of MOF-177 (stemming from the 11- × 17-Å pores) down to the smaller-pore MOFs. This range of inflection points allows for the tailoring of MOFs to have maximal capacities at intermediate pressures, a valuable characteristic in the prospect of separations.

Consideration of IRMOF-3 and -6 accentuates the potential of tailoring the pores with different chemical groups. Given their isoreticular frameworks and similar pore shapes and sizes, one might expect the amino- and cyclobutyl-functionalized pores to have concurrent isotherm steps and similar capacities. The latter is true, yet the isotherm steps occur at distinctly different pressures. Sterically, the $-NH_2$ group and ortho $-H$ on the phenylene rings of IRMOF-3 occupy less space in the pore than the $-C_2H_4$ moiety of IRMOF-6. Consequently, the pore size of IRMOF-6 should be just smaller than IRMOF-3, which is contrary to the relative locations of their isotherm steps. Thus, steric forces alone cannot account for the difference in isotherm step pressures. It follows that the amino group is not innocent in its physisorptive influence on CO_2. That is, CO_2 is more attracted to the nitrogen either through hydrogen bonding or via interaction with the lone electron pair, reminiscent of the chemisorptive alkylamine solutions commonly used in acid gas removal.

Silica- and carbon-based physisorptive materials such as zeolites and activated carbons are often referenced as benchmark materials. Zeolites have enjoyed high utility in industrial applications based on their well-defined pore shapes and narrow pore-size distributions, but the highest reported gravimetric CO_2 capacity for these materials at ambient temperature is 7.4 mmol/g (at 32 bar) for zeolite 13X.[7] On the other hand, several carbons have been reported to have quite high capacities despite their amorphous nature, with a sample of MAXSORB showing an uptake of 25 mmol/g (at 35 bar).[8] We have shown here that the 33.5 mmol/g gravimetric CO_2 capacity of MOF-177 at ambient temperature exceeds these standard materials, having 150% of their capacity.

Comparison of the volumetric capacity of MOF-177 to those of current benchmark materials zeolite 13X and MAXSORB is shown in Figure 3, where the CO_2 isotherms are plotted along with that of an empty pressurized container. Remarkably, at 35 bar, a container filled with MOF-177 can capture 9 times the amount of CO_2 in a container without adsorbent, and about 2 times the amount when filled with benchmark materials. These results show that MOFs represent a new direction for preventing CO_2 in exhaust gases from reaching the atmosphere.

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Supporting Information Available: Syntheses, PXRD and TGA characterization, adsorption methods, and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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