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Flexible (Breathing) Interpenetrated Metal−Organic Frameworks for CO_2 Separation Applications

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Carbon dioxide capture and separation is a major road block for the safe storage of carbon into deep geological formations.[1] The major source of CO_2 emissions are from coal fired power plants where only 30% of CO_2 is captured, resulting in increased CO_2 emissions in the atmosphere. Conventional methods such as alkyl amine solutions are used to scrub the CO_2 from exhaust gas streams, which is costly and inefficient. The major drawbacks of the existing technology include low CO_2 wt%, degradation of the solvent, and the high temperature required to regenerate the adsorbed gas.[2]

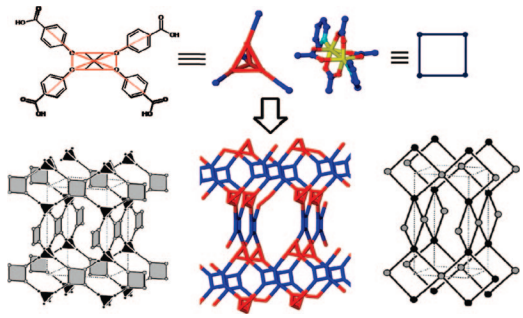

Figure 1. Representation of PtS network from **1** and Zn_2 paddlewheel connected by bipyridine molecules.

Therefore alternative concepts based on chemical adsorption of CO_2 onto metal oxides and physical adsorption on activated carbons, silicas, zeolites, and nonporous calixarenes[3,4] were proposed, but microporous metal−organic frameworks (MOFs) have received considerable attention during the past couple of years. This may be due to the high mass flux, thermal stability, adjustable chemical functionalities, extra high porosity, and availability of hundreds of well characterized materials reminiscent to zeolites.[5] Several research groups, including Yaghi,[6] Kitagawa,[7] Ferey,[8] Rosseinsky,[9] Zaworotko,[10] Hupp, and others, have developed a number of MOFs for gas storage and separation applications.[11−16] For example, Yaghi and co-workers have shown that MOF-177 exhibits a CO_2 sorption capacity of 1.4 g of CO_2 per gram of sorbent material.[17] This is a significant improvement over commercially available zeolites sorbents. However, most MOFs have been deliberately designed with very large pore sizes or channels to achieve maximum loadings. While effective, the penalty is again lack of selectivity, which is required for gas separation applications. To approach this problem, we have designed and developed coordination solids based on a tetrahedral organic linker, tetrakis[4-(carboxyphenyl)oxamethyl]methane, **1** as a building block to generate MOFs with metal salts and organic pillars.

Self-assembly of **1** with zinc nitrate hexahydrate and bipyridine in dimethyl formamide resulted in complex **3** (Supporting Information, Scheme S1). Crystallographic measurments on complex **3** confirm the tetrahedral ligand was connected to two zinc atoms in a paddle-wheel fashion. The paddle wheels are further pillared by 4,4′-bipyridine molecules occupying the axial sites of the Zn_2 paddle wheels to form a three-dimensional (3D) structure (Figure 1). The overall structure of **3** is a pair of identical PtS nets of **3**, which are mutually interpenetrated with each other to form doubly interpenetrated frameworks (Scheme S1). The pores in **3** are partially filled with 4,4′-bipyridine molecules that are connected to paddle-wheel SBUs of the framework while the remaining channels are filled with solvent DMF and water molecules (SI, Figures S2−S4). Thermogravimetric analysis of the complex **3** shows 25 to 30% of weight loss between room temperature and 250 °C, which corresponds to the loss of DMF and water molecules (Figure S5). Prior to the sorption studies, the surface area of the activated sample was calculated using the N_2 adsorption at 77 K, which exhibits a typical type I isotherm with 1150 $m^2\ g^{-1}$ of surface area (Figure S6−S7). The surface area and the solvent accessible void space in this sample are significantly reduced when compared to other open metal−organic frameworks due to the interpenetration of the 3D framework in the solid state.

Gas sorption experiments using CO_2 were performed using an HPVA-100 volumetric device at room temperature. Sample **3** (∼80 mg) was placed in a sample chamber and activated at high temperature under vaccum for several hours. For low pressure experiments, 0.1 bar of CO_2 was dosed into the sample chamber every 10 min, and the volume adsorbed per gram of material was plotted against the pressure (Figure 2). At this pressure (1 bar) the calculated weight percentage was found to be close to 5 wt%, which is comparable to the other MOFs reported earlier. The absence of hysteresis during desorption of CO_2 is not surprising, and it has been found to be very common for materials with a pore size of 20 Å or less. The measurements were repeated several times by evacuating the sample and pressurizing with CO_2 again. The same weight percentage was obtained within ±5%. The CO_2 sorption plot at 1 bar suggests that sample **3** does not reach a saturation point; therefore high pressure experiments with CO_2 were conducted at ambient conditions. Figure 2 shows the absorption isotherm of CO_2 at high pressures that indicate a type I relationship with a step in the absorption at ∼10 bar. Such a step during the absorption of gases in organics and MOFs is not common though it has been observed in similar systems before.[18,19] A number of mechanisms

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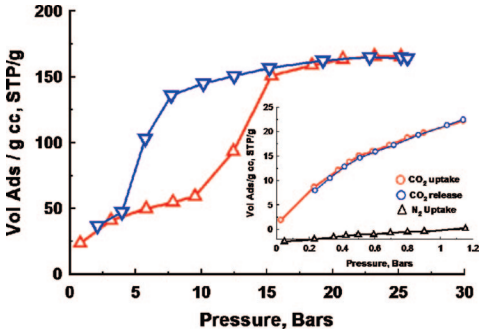

Figure 2. CO_2 kinetics at high pressure and 25 °C: △ and ▽ represent absorption and desorption. Selectivity of CO_2 over N_2 at 1 bar was shown (inset).

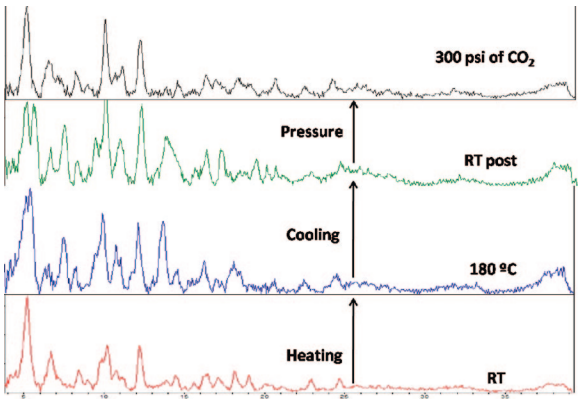

Figure 3. PXRD patterns of complex **3** at high temperature and pressure.

including molecular gate, breathing, and transformation from disorder phase to a more ordered phase were proposed, but the step adsorption in sample **3** was unclear. Several experiments using variable temperature and pressure powder X-ray were conducted to gain some insight into the mechanism of the step absorption. Powder XRD analysis of **3** at variable temperatures under vacuum indicate considerable change in the powder pattern. This could be due to the framework contraction upon solvent removal (Figure 3, SI Figures S8−S10). It is important to note that the original phase cannot be generated by simply returning to the original temperature; however when exposed to 200 psi of CO_2 at room temperature the sample was found to transform back to the original pattern suggesting the expansion of the framework due to the CO_2 inclusion (Figure 3, SI Figures S9−S10). These results suggest the breathing motion of **3** upon solvent loss and CO_2 inclusion. At this pressure (30 bar) the calculated CO_2 weight percentage in **3** was found to be 7.1 mmol/g, which is lower than the reported MOF-177 (35 mmol/g) and activated carbon (MAXSORB, 25 mmol/g) but comparable to that of zeolite 13X (7.4 mmol/g) at the same pressure.[17]

In this regard experiments using pure nitrogen and hydrogen were studied to know the selectivity of the material. Experiments with nitrogen at 1 bar were shown to sorb very little or no uptake of nitrogen. The selective sorption of CO_2 over N_2 in **3** is due to the small pore size and selective binding to the walls of the framwork.[20,21] Similar experiments on **3** at 20 bar of H_2 gas did not result in detectible absorption. This suggests that sample **3** can discriminate the gases (CO_2, 3.3 Å over N_2, 3.64 Å and H_2, 2.8 Å) based on the size/shape that can have significant industrial applications (Figure 2). The energetic nature of **3** during the absorption and desorption of CO_2 in **3** was found to be ∼20 kcal mol^{-1}, which is significantly lower than the well-known MEA and slightly higher than reported MOFs (Figure S11).

High selectivity for CO_2 over H_2 and N_2 is a requirement if these materials are to be used for CO_2 separations from synthesis gas and flue gas mixtures. Further studies on sample **3** and **1** with various metal salts and axial pillers for gas storage and separation applications and the selectivity of **3** toward other gases are under investigation.

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Supporting Information Available: Details of single-crystal X-ray structure analysis for **3**, surface area, thermogravimetric analysis, high temperature and pressure PXRD, heats of absorption, and complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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