Coal is an abundant resource that is heavily relied upon for global energy, and therefore emission-free coal-fired power plants are a necessary near-term component of a clean energy future.1 Integrated gasification and combined cycle (IGCC) systems equipped with precombustion CO2 capture, wherein CO2 is separated from H2 and sequestered, are promising in this regard.2 The technology for separating H2 and CO2 is already well-developed due to the tremendous scale of H2 production (50 million tons per year worldwide) and is primarily accomplished using pressure-swing adsorption (PSA).3 Here, porous zeolites or activated carbons selectively and reversibly adsorb impurities in the presence of H2 at high pressures. Methods for altering the current PSA specifications to meet the needs of precombustion CO2 capture in an IGCC system are being explored,4 although vast improvements in CO2/H2 separations must be made to render this strategy economically viable.5 Regardless, optimizing the efficiency of adsorptive H2 purification in industry is also of crucial importance to minimizing energy usage;5 since, at current production rates, which are steadily rising, a 10% increase in the efficiency of the process could save the energy output of approximately 18 average US coal-fired power plants.6

Much of the energy input for a PSA system is used in mass transport of the gas and regeneration of the adsorbents, and as a result improving adsorbent selectivity and the capacity for CO2 would increase efficiency.7 Extensive experimental7 and theoretical8 investigations suggest that further optimization of zeolites and activated carbons will yield only modest improvements in CO2/H2 separation performance. Thus, there is a need for new types of adsorbents with the potential for displaying significantly improved CO2 capacity and selectivity.

Microporous metal—organic frameworks offer significant promise in this regard but have yet to be experimentally investigated for the separation of CO2 from H2. These materials exhibit record internal surface areas and, as a result, a tremendous CO2 storage capacity5 at the pressures relevant for a CO2/H2 separation (ca. 5–40 bar).3a,b,6a Further, the high adsorbent surface area could enhance the selectivity for adsorption of CO2 over H2, since H2 packs more efficiently than CO2 due to its smaller size.10 Moreover, the ability to adjust the nature of the surfaces within these materials could potentially be exploited to increase the strength of the interaction with CO211 and has already spurred investigations into their uses in other industrially relevant gas separations, such as CO2/N2,12a,13 CO2/CH4,12a,13 and O2/N2 separations.14

Despite the recent interest in high-pressure, fixed-bed separation applications using metal—organic frameworks as the adsorbent,12b their study for CO2/H2 separations has thus far been limited to theoretical investigations, which have predicted excellent selectivities.10,15 Herein, we report the first experimental study of the utility of metal—organic frameworks for high-pressure CO2/H2 separation by PSA16 We consider single-component CO2 and H2 adsorption isotherms as an initial indicator of efficiencies and further adopt a complementary theoretical model for the prediction of the performance of each material under realistic mixed gas conditions.

The compounds Zn4O(BTB)2 (MOF-177, BTB3 = 1,3,5-benzenetribenzoato)17 and Be12(OH)12(BTB)4 (Be-BTB)18 were chosen as representative of metal—organic frameworks exhibiting a high surface area and a rigid framework structure. As a flexible framework, Co(BDP) (BDP2− = 1,4-benzenedipyrazolate) was selected owing to its high surface area relative to most compounds of this type.19 Finally, H4[(CuCl)3(BTTri)6] (Cu-BTTri, BTTri3− = 1,3,5-benzenetris(triazolate)), and Mg2(dobdc) (dobdc4− = 1,4-dioxido-2,5-benzenedicarboxylate) were chosen as prototypical of the broad class of metal—organic frameworks that possess surfaces.
Figure 1. Absolute adsorption isotherms for CO₂ (green triangles) and H₂ (blue circles) in MOF-177, Co(BDP), Cu-BTTri, and Mg₃(dobdc) at 313 K. The BET surface area (SA) obtained for each framework is given.

Figure 2. IAST CO₂/H₂ selectivities for a 80:20 H₂/CO₂ mixture at 313 K, as calculated from gas sorption isotherms collected for the metal–organic frameworks MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg₃(dobdc), activated carbon JX101,25 and zeolite 13X.26

selectivities, presumably owing to the greater polarizability of CO₂ versus H₂. At saturation, Mg₃(dobdc) adsorbs 1.8 CO₂ molecules per Mg and Cu-BTTri adsorbs 4.5 CO₂ molecules per Cu (see Figures S9 and S10). These values, and particularly the steep rise in the lower pressure data for the former case, suggest that the observed selectivity can preliminarily be ascribed to interactions with the open metal cation sites. Indeed, the enhanced interaction of guest gas molecules, and specifically CO₂, in porous materials with coordinatively unsaturated metal sites is well-established.11a,13d,23

With a greater concentration of cationic sites exposed on its surfaces, Mg₃(dobdc) shows the best performance, exhibiting a selectivity that gradually decreases from 859 at 5 bar to 305 at 40 bar. We note that this material has also previously been shown to exhibit a high CO₂/N₂ and CO₂/CH₄ selectivity.11a,12d

For comparison, CO₂ and H₂ isotherm data for common PSA adsorbents,6b,6c zeolite SA24 and two activated carbons,24,25 were taken from the literature and treated similarly using IAST. Due to the variability in activated carbons, both JX10125 and BPL24 were considered in an effort to broaden the scope of the comparison. Data for zeolite 13X26 were also included, since this material has recently been shown to outperform zeolite SA in terms of CO₂ capacity25 and breakthrough measurements.28 Zeolite 13X selectivity values are depicted in Figure 2 at 313 K (determined from interpolating adsorption data at 303 and 323 K), and Mg₃(dobdc) outperforms zeolite 13X at all pressures. Selectivities for zeolite SA at 303 K (which can be assumed to decrease at 313 K) are similar to those of Mg₃(dobdc), but with higher values at low pressures and slightly lower values at high pressures (see Figure S14). Thus, in terms of selectivity, Mg₃(dobdc) can be expected to perform the separation of CO₂ from H₂ at least as well as any known adsorbent under the conditions assessed. The selectivity values for a 60:40 H₂/CO₂ mixture relevant to precombustion CO₂ capture27 are shown in Figure S15 and follow approximately the same hierarchy.

In order to probe the performance of the materials, ideal adsorbed solution theory (IAST) was employed to estimate mixed-gas adsorption behavior.21 The accuracy of IAST for estimating component loadings for adsorption of a wide variety of binary mixtures in zeolites has been established with the aid of Configurational-Bias Monte Carlo (CBMC) simulations.22 Specifically, it has previously been applied to the separation of CO₂ from H₂ within metal–organic frameworks15a–d and other porous solids.23 Further, CBMC simulations data provide evidence of the validity of its use for estimation of CO₂/H₂ equilibria in metal–organic frameworks and are presented in the Supporting Information.

Figure 2 shows the selectivities for CO₂ over H₂ under an 80:20 H₂/CO₂ gas mixture relevant to H₂ purification22 calculated for the metal–organic frameworks using the single-component gas sorption isotherms. Significantly, the two frameworks with exposed metal cation sites, Cu-BTTri and Mg₃(dobdc), display by far the highest

coated with exposed metal cations. All five compounds were synthesized and activated as previously reported, and their BET surface areas (see Figure 1) were determined from N₂ adsorption isotherms collected at 77 K (see Table S7 for Langmuir surface areas and pore volumes).

Figure 1 shows the single-component CO₂ and H₂ adsorption isotherms recorded at 313 K for MOF-177, Co(BDP), Cu-BTTri, and Mg₃(dobdc). Data for Be-BTB, which are similar to the results obtained for MOF-177, are presented in Figure S8. As might be expected, the CO₂ adsorption capacity scales roughly with surface area and is much higher than the corresponding adsorption capacity for H₂ due to the higher polarizability and quadrupole moment of the CO₂ molecule. The CO₂ adsorption capacity also scales qualitatively expected, the CO₂ adsorption capacity scales roughly with surface area due to the additional polarizing influence of the open metal cation sites. Indeed, the enhanced interaction of guest gas molecules, and specifically CO₂, in porous materials with coordinatively unsaturated metal sites is well-established.11a,13d,23

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Due to the nature of PSA purification, the working capacity—the difference between the capacity at the high intake pressure and at the lower purge pressure—is a critical metric for evaluating adsorbents.30 The CO2 working capacities for the metal—organic frameworks under an 80:20 H2/CO2 mixture and assuming a purge pressure of 1 bar were calculated using IAST and compared to the values obtained for the zeolites and activated carbons (see Figure 3). While gravimetric capacities (moles of CO2 adsorbed per kg of adsorbent) are normally reported when evaluating materials for a CO2/H2 separation, the volumetric working capacities (moles of CO2 adsorbed per L of adsorbent) were also calculated, since both factors are critical in designing a PSA separation process.60 Here, the true advantage of utilizing metal—organic frameworks comes to the fore. Owing to its greater specific surface area and larger pore sizes, Mg2(dobdc) outperforms the zeolites by a considerable margin, with CO2 working capacities for an 80:20 H2/CO2 mixture at 313 K for the metal—organic frameworks MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg2(dobdc), the activated Carbon JX10123 and zeolite 13X.24 This conclusion could also potentially apply to other separations within metal—organic frameworks. Industrially, adsorbents for this separation are tailored and optimized for each specific PSA system,3a and therefore the equilibrium adsorption data presented here provide an initial step toward improving the efficiency of the process. In order to validate the efficacy of metal—organic frameworks, however, additional experiments are still needed, such as investigating CO2 desorption by purge.30 This regeneration is not expected to stand in the way of their use, however, since the isosteric heats of CO2 adsorption in Mg2(dobdc) (47 kJ/mol)11a and Cu-BTTri (21 kJ/mol)12c are quite similar to those of the currently employed zeolite 5A (40 kJ/mol) and activated carbon (23 kJ/mol)30 (see Figure S20). Ultimately, the successful implementation of such new adsorbents could both reduce the substantial energy cost of hydrogen purification and eliminate CO2 emissions in the generation of electricity from coal. Along these lines, future work will probe whether metal—organic frameworks with good thermal and hydrolytic stability might even be suitable for the in situ separation of CO2 from H2 during sorption-enhanced water-gas shift reactions.31

**Figure 3.** IAST-calculated gravimetric (top) and volumetric (bottom) CO2 working capacities for an 80:20 H2/CO2 mixture at 313 K for the metal—organic frameworks MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg2(dobdc), the activated Carbon JX10123 and zeolite 13X.24

**REFERENCES**

While high-pressure CO₂ and H₂ adsorption isotherms have been reported previously for various metal–organic frameworks, including some of the ones studied here, to our knowledge they have never been investigated in relation to a realistic H₂ purification separation. See for example: (a) Miller, S. R.; Wright, P. A.; Devic, T.; Serre, C.; Férey, G.; Llewellyn, P. L.; Denoyel, R.; Gaberova, L.; Filinchuk, Y. Langmuir 2009, 25, 3618. (b) Guo, H.; Zhu, G.; Hewitt, I. J.; Qui, S. J. Am. Chem. Soc. 2009, 131, 1646.


