Metal-Organic Frameworks

High Propene/Propane Selectivity in Isostructural Metal–Organic Frameworks with High Densities of Open Metal Sites**

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Crystalline metal–organic frameworks (MOFs)[1] have attracted great attention in the past decade due to their modular, tailorable structures, as well as their potential in applications such as gas storage[2] and separations.[3] Open metal sites in some MOFs provide special adsorption sites, which are favorable for H_2 storage,[4] CO_2 capture,[5] and CO_2 separations.[6]

Propene is an important commercial petrochemical, produced on a large scale. Its production requires separation from propane/propene mixtures, but this is intrinsically difficult due to the similar physical and chemical properties of these molecules. Energy-intensive, costly cryogenic distillation has been used for over 70 years for this separation.[7] In general, adsorptive separation is an energy- and cost-effective alternative to distillation,[7] and a few MOFs have shown potential for propene/propane separations through either an equilibrium-based,[8] a kinetic-based[9] or a gate-opening mechanism.[10] Notably, open metal sites have been shown to play important roles in the two existing reports on the equilibrium separation of propene/propane mixtures.[8] From a combined experimental and simulation study, Lamia et al. reported that open Cu^{2+} sites in HKUST-1 interact preferentially with propene, due to specific interactions between the electron-rich π-bonding orbital in propene and the vacant s-orbital of the open metal sites.[8a] Yoon et al. experimentally demonstrated that the existence of unsaturated Fe^{2+} and Fe^{3+} sites in MIL-100(Fe) substantially increases the strength of interaction with unsaturated propene molecules (the heat of

adsorption was up to 70 kJ mol^{-1} at low coverage), which leads to high selectivity for propene over propane (ca. 29).[8b] However, this high selectivity was observed at very low pressure (0.0025 bar), and it decreased markedly with increasing pressure presumably due to satuaration of the open metal sites.[8b]

Herein, we report the adsorption selectivities of propene over propane for a series of isostructural frameworks M-MOF-74 (M = Co, Mn, and Mg) with high concentrations of open metal sites. Adsorption experiments, ideal adsorbed solution theory (IAST) predictions, breakthrough experiments, first-principles calculations, and grand canonical Monte Carlo (GCMC) simulations reveal that Co-MOF-74 exhibits the highest thermodynamic propene/propane selectivity (ca. 46) ever reported for MOFs, due to strong π-complexation between the open Co^{2+} sites and the propene molecules. Remarkably, these high selectivities occur at ambient pressure and temperature, conditions favorable for industrial adsorptive separations. An unusual increase of the C_3H_6/C_3H_8 selectivity with increasing pressure is observed due to emergent behavior of the system that arises from the appropriate pore size relative to the size of the propene molecules.

The series of M-MOF-74 materials[11] is also denoted CPO-27-M[5b] or M/DOBDC[5a] (DOBDC^{4-} = 2,5-dioxido-1,4-benzene-dicarboxylate) in the literature. These materials have 1D hexagonal channels of 11–12 Å diameter with high densities of open metal sites (Figure 1) that can potentially interact with propene. Here, single-component adsorption isotherms for propene and propane were measured exper-

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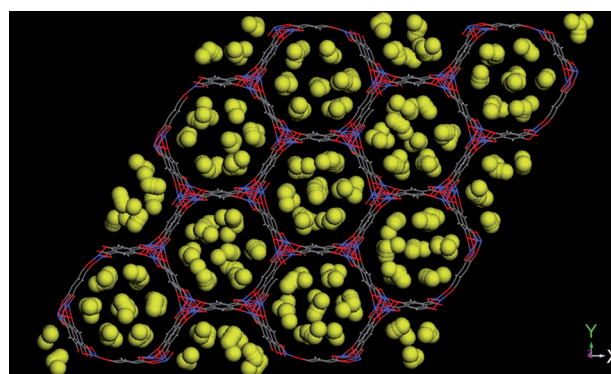[+] These authors contributed equally to this work.

Figure 1. A snapshot from a GCMC simulation for C_3H_6 adsorption in Co-MOF-74 at 1 bar and 298 K, looking down the 1-D hexagonal channels. Under this condition, each metal site is occupied by one propene molecule (1.08 C_3H_6 per Co^{2+}). C: gray; H: white; O: red; Co: blue. Yellow spheres indicate the carbon atoms in propene.

imentally in a series of M-MOF-74 (M = Co, Mn, and Mg) materials for pressures up to 1 bar at 298 K. As shown in Figure 2a and Figure S4 (Supporting Information), all of the
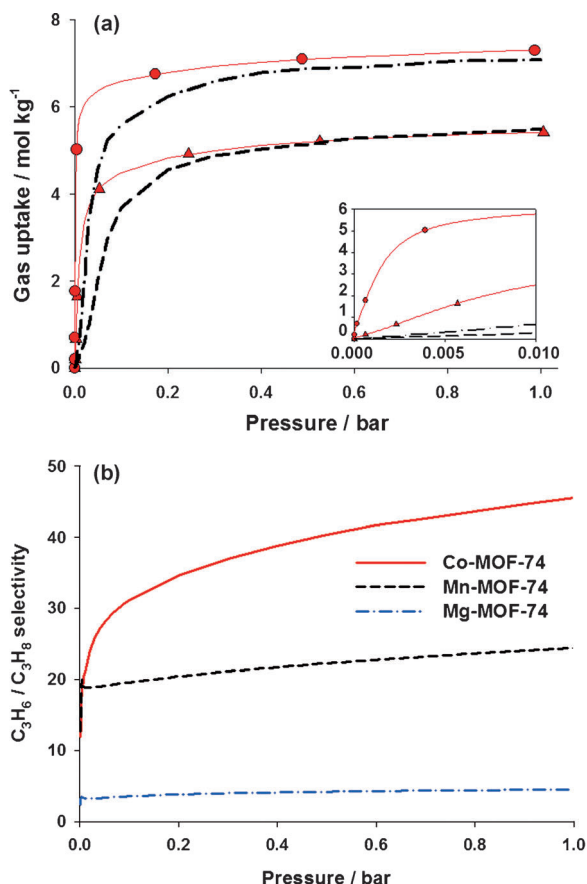

Figure 2. a) Adsorption isotherms for C_3H_6 (circles) and C_3H_8 (triangles) in Co-MOF-74 at 298 K. The inset shows the low-pressure isotherms. Solid lines through the experimental data are fits of the dual-site Langmuir–Freundlich model.[12] The dashed-dot and dashed lines are the simulated C_3H_6 and C_3H_8 isotherms, respectively. b) The IAST-predicted C_3H_6/C_3H_8 selectivities for equimolar mixture adsorption in a series of M-MOF-74 materials at 298 K as a function of pressure. These were calculated using the experimental isotherms.

isotherms display saturation around 0.2 bar. At higher pressures, none of these materials show significant differences between propene and propane uptake, although propene shows slightly higher uptake than propane, which may be attributed to more efficient packing of propene molecules due to the smaller molecular size and/or stronger interactions with the metal sites. The adsorbed amount of propene reaches 7.29 mol kg^{-1} at 298 K and 1 bar in Co-MOF-74, which corresponds to 1.14 C_3H_6 molecules per Co^{2+} site (Figure S6). This indicates that the channels of Co-MOF-74 are mostly saturated with propene molecules after each open Co^{2+} site is occupied by one propene molecule. From this, we can reason that open metal sites play an important role even at higher pressures. At low pressures, selective adsorption of propene over propane is clearly demonstrated for all three MOFs, especially for Co-MOF-74 and Mn-MOF-74. The selectivity is

connected to strong specific interactions of propene molecules with the open metal sites in the M-MOF-74 frameworks, as demonstrated below using first-principles calculations.

We also performed GCMC simulations to calculate the propene and propane isotherms in Co-MOF-74. As shown in Figure 2a, the simulated propene and propane isotherms on Co-MOF-74 match reasonably well with the experimental ones, although they underestimate adsorption at very low pressures, especially for propene. The underestimation at low pressures may come from strong interactions between gas molecules and open metal sites, which are hard to model using simple force fields.

From the experimental isotherms, the selectivities for propene/propane mixtures were calculated using the ideal adsorbed solution theory (IAST),[13] which has been shown to accurately describe gas-mixture adsorption in representative zeolites[14] and MOFs.[12, 14a, 15] Figure 2b presents the IAST-derived selectivities for equimolar C_3H_6/C_3H_8 mixtures in the three isostructural MOFs. As expected from the low-pressure single-component adsorption data, Co-MOF-74 (ca. 46) and Mn-MOF-74 (ca. 24) exhibit substantially higher selectivities than does Mg-MOF-74 (ca. 4.5). The most remarkable finding is that Co-MOF-74 shows excellent selectivity (46) even at 1 bar. As mentioned above, to the best of our knowledge, MIL-100(Fe) with mixed valence Fe^{2+}/Fe^{3+} metal sites exhibits the highest previously reported thermodynamic selectivity (ca. 29) among MOFs for propene/propane separations, but the high selectivity is achievable only at very low pressure (0.0025 bar).[8b]

To confirm the selective adsorption of propene over propane under mixture conditions, we performed break-through experiments for Co-MOF-74 as a representative case. The activated adsorbent was initially saturated with C_3H_8 as commonly performed in pressure swing adsorption processes and breakthrough measurements.[16] The breakthrough curve of an equimolar mixture of C_3H_6 and C_3H_8 in Figure 3 shows that C_3H_6 is completely separated from C_3H_8 with a considerable C_3H_6 separation capacity (6.8 mol kg^{-1})—a value close to the saturated uptake of C_3H_6 (7.3 mol kg^{-1}) from the single-component isotherm. The breakthrough experiment indicates
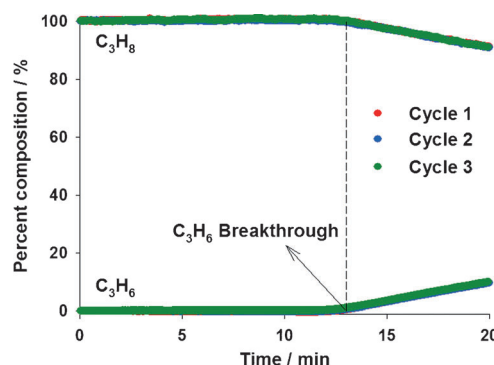

Figure 3. Breakthrough curves of equimolar mixtures of propene and propane (total flow rates = 30 mL min^{-1}) in a packed column of Co-MOF-74 that is initially saturated with C_3H_8. These curves were obtained for three consecutive cycles after the column had been regenerated by flowing pure propane.

that under mixture flow, Co-MOF-74 primarily adsorbs propene, consistent with the IAST results. Moreover, essentially identical breakthrough curves were obtained after the propene-saturated adsorbent was regenerated simply by flowing pure propane, a very mild protocol for regeneration.

To investigate the nature of the interaction between propene or propane and the open metal sites, we turned to first-principles calculations. The calculated binding energies (E_b) and the distance between the metal and the adsorbate

Table 1: Summary of propene and propane binding energy calculations using MP2 level of theory.

M	E_b (D(M—C))[a,b]	
	propene	propane
Co	49.0 (2.60)	24.4 (3.37)
Mn	45.1 (2.73)	24.5 (2.93)
Mg	44.8 (2.86)	23.6 (3.24)

[a] E_b is the calculated binding energy (kJ mol^{-1}). [b] D(M—C) is the calculated metal–carbon distance (Å). For propene, it is the average for the two C=C carbon atoms; for propane, it is the average for the two carbon atoms closest to the metal.

carbon atoms (D(M—C)) are summarized in Table 1. The results show that propene binding to Co^{2+} is the strongest among the metals studied, which accounts qualitatively for the superior C_3H_6/C_3H_8 selectivity of Co-MOF-74. Moreover, the overall trends of the calculated E_b and D(M—C) agree well with the experimental gas adsorption results in Figure 2. In addition, the first-principle calculations (also from different levels of theory) consistently show that Co-MOF-74 gives the largest difference in binding energies between propene and propane (Table S3). This agrees well with the experimental observation that Co-MOF-74 shows the highest C_3H_6/C_3H_8 selectivity. The trends are also consistent with the result of a recent study on acetylene storage in a series of M-MOF-74 materials (M = Co, Mn, Mg, and Zn) in which Co-MOF-74 showed the strongest interaction with acetylene molecules.[17]

Interestingly, for each MOF, the C_3H_6/C_3H_8 selectivity increases with increasing pressure (Figure 2b). The highest selectivities were obtained at 1 bar (the highest pressure examined). These results were unexpected from the single-component isotherms, which show only minor differences for propene versus propane uptake at pressures of 0.1 bar or higher. The increase of C_3H_6/C_3H_8 selectivity with increasing pressure can be explained as follows. At low pressures, both propene and propane molecules are independently adsorbed on the MOF surface, which creates a certain degree of selectivity due to the different interactions of propene and propane with the MOF. As the pressure increases, more and more of the open metal sites are occupied by gas molecules, which induces competitive adsorption between propene and propane. Because each open metal site prefers C_3H_6, the C_3H_6 molecules occupy most of the metal sites with the increasing pressure. Since only a small amount of pore volume is left after all the metal sites are occupied by propene molecules (Figure 1), the adsorption of propane is strongly suppressed. This results in a significant increase of the C_3H_6/C_3H_8 selectivity with increasing pressure, a characteristic that is

favorable for applications of these materials to industrial adsorptive separation processes. The increasing C_3H_6/C_3H_8 selectivity with increasing pressure was also confirmed by GCMC simulations for equimolar mixtures of propene and propane (Figure S11a).

Our explanation of the unusual selectivity behavior observed for C_3H_6/C_3H_8 in MOF-74 relies on the proper match between the pore size and the size of the molecules such that the pore volume is filled when each metal site is occupied by one propene molecule. If this is true, then increasing selectivity with increasing pressure should be not observed for smaller molecules, such as C_2H_4/C_2H_6 mixtures. To confirm this, single-component adsorption isotherms for ethene and ethane were measured experimentally in Co-MOF-74. As shown in Figure S5, there is selective adsorption of ethene over ethane, especially at low pressures. However, as we expected, the IAST-predicted selectivity for equimolar
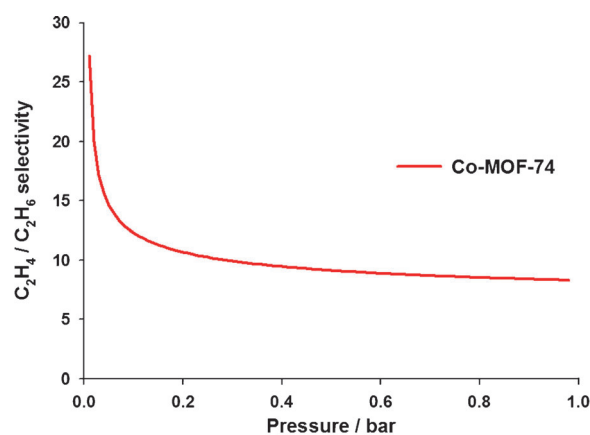

Figure 4. The IAST-predicted C_2H_4/C_2H_6 selectivities for equimolar mixture adsorption in Co-MOF-74 at 298 K as a function of pressure. These were calculated using the experimental isotherms in Figure S5.

C_2H_4/C_2H_6 mixture (Figure 4) shows drastically different behavior compared to the C_3H_6/C_3H_8 selectivity. The C_2H_4/C_2H_6 selectivities in Co-MOF-74 are high (ca. 27) at low pressures and then rapidly decrease with increasing pressure. This decreasing tendency of C_2H_4/C_2H_6 selectivity with increasing pressure was confirmed by GCMC simulations for equimolar mixtures of ethene and ethane (Figure S11b). In addition, unlike propene adsorption, a considerable amount of pore volume is left after all the metal sites are occupied by ethene molecules (Figure S10). These results support the idea that the special selectivity behavior observed in C_3H_6/C_3H_8 separation is an emergent property that arises from the appropriate size of propene molecules relative to the pore sizes.

In summary, a series of isostructural M-MOF-74 materials (M = Co, Mn, and Mg) with high densities of open metal sites have been examined for the selective adsorption of propene over propane. Co-MOF-74 exhibits the highest thermodynamic C_3H_6/C_3H_8 selectivity reported for any MOF to date at ambient temperature and pressure, making this material promising for adsorptive propene/propane separation pro-

cesses. The trend of selectivities for the series of M-MOF-74 materials is explained well by the binding strengths from first-principles calculations. For all M-MOF-74 materials, the selectivity increases with increasing pressure due to the special structural properties of these MOFs: high densities of metal sites as well as optimal pore widths and volumes. Creating high densities of open metal sites in pores of limited volume may be a powerful general strategy for generating new adsorbents for olefin/paraffin and other separations.

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