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Review

Recent Progress Towards Light Hydrocarbon Separations Using Metal–Organic Frameworks

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Industrial hydrocarbon separations are performed on an immense scale, accounting for a significant fraction of global energy consumption. Supplanting thermally driven separation processes (e.g., distillation) with adsorbent-based technologies could greatly reduce energy expenditures and production costs associated with these commodity chemicals. Significant effort has been expended towards the development of metal–organic frameworks (MOFs) as adsorbents for this purpose, owing to their high surface areas and crystallinity, as well as their structural and chemical tunability. This review presents some of the recent progress made in MOF material design to accomplish separations of $C_{2–3}$ hydrocarbons, which are crucial to the production of high-grade ethylene and propylene.

Separations of $C_{2–3}$ Hydrocarbons

Annual global production of ethylene and propylene exceeds that of all other commodity organic compounds [1]. The majority of this output is diverted to the synthesis of polyethylene and polypropylene, respectively – processes that require very high monomer purities. Like other olefins, ethylene and propylene are generally not present in petroleum or natural gas reserves, but are instead produced primarily via thermal or catalytic cracking [2]. Crude ethylene- and propylene-rich fractions isolated from cracking units contain substantial quantities of the corresponding paraffins (approximately 10–40 wt% for C_2 and 3–10 wt% for C_3), as well as low levels of alkynes (approximately 1–2 wt% for C_2 and 1–5 wt% for C_3) [2]. The latter can poison polymerization catalysts and are either removed via solvent extraction or selectively hydrogenated using noble-metal catalysts [3]. Separation of the olefin/paraffin mixtures is more challenging and relies almost exclusively on high-pressure cryogenic distillation, utilizing columns with as many as 160 trays [2,4]. This process is particularly energy intensive and represents a large portion of the cost for ethylene and propylene production [5]. Astoundingly, the purification of ethylene and propylene alone accounts for 0.3% of global energy consumption [1], providing substantial incentive to realize scalable separations of $C_{2–3}$ olefins using more efficient, non-thermally driven processes.

MOFs are highly versatile, porous crystalline solids that have garnered much interest as adsorbents for challenging hydrocarbon separations [5–10]. Comprising inorganic nodes connected by organic linkers in two or three dimensions, these materials exhibit an impressive degree of structural and chemical diversity and a highly ordered nature that facilitates the elucidation of structure/function relationships and attainment of large separation **working capacities** (see Glossary). Many studies have examined the adsorptive separation of light hydrocarbon mixtures using MOFs, leading to significant improvements in key properties such

Highlights

Adsorptive hydrocarbon separations can be accomplished using rigid metal–organic frameworks (MOFs) under equilibrium or kinetic conditions, or flexible frameworks containing gated pores that selectively expand in the presence of a given component.

MOFs featuring open metal sites can strongly bind and adsorb large quantities of unsaturated hydrocarbons, a motif that has been advantageous for olefin/paraffin separations. This approach is of limited utility for the separation of alkynes/olefins, which both feature polarizable π-electron clouds.

A number of frameworks, including those featuring metal-bound peroxo ligands, have been shown to be selective for paraffins over olefins, and their further investigation may inform the design of materials ideal for obtaining high-purity ethylene or propylene.

The most promising MOFs for alkyne/olefin separations feature small pores lined with polar groups and aromatic rings, which selectively adsorb alkynes via both hydrogen bonding and π–π interactions.

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as capacity and selectivity. In this review, we outline recent advances in the design of MOFs for the separation of C_{2-3} olefin/paraffin or alkyne/olefin mixtures, with discussion focused on distinct structural features and corresponding adsorption mechanisms that can engender selectivity. Rather than an exhaustive summary of recent progress, we focus on the most promising and innovative achievements from the past several years while emphasizing the benefits and challenges of each approach. We do not discuss the separation of methane from C_{2+} organics and instead refer the interested reader to several recent reviews [5,7,11]. Detailed information on IUPAC isotherm types [12] and **ideal adsorbed solution theory (IAST)** [13,14] are found elsewhere.

Separations of Ethylene/Ethane and Propylene/Propane Mixtures

If the ratio of adsorbed and gas-phase species reaches equilibrium for all mixture components, an adsorptive separation can be described as taking place under thermodynamic equilibrium conditions. Conversely, adsorbents with small pore apertures that inhibit rapid adsorption of one or more components can effect selectivity through kinetic means. Below, we discuss olefin/paraffin separations that fall under each category. Following, we discuss two special classes of adsorbents: those that leverage gate-opening phenomena and those that selectively adsorb paraffins over the corresponding olefins.

Separations Under Thermodynamic Equilibrium

As a result of their relatively diffuse π-orbitals, olefins generally engage in stronger interactions with polarizing surfaces relative to their saturated counterparts. As such, frameworks containing pore walls lined with coordinatively unsaturated metal sites feature prominently in studies of olefin/paraffin separations. The first studies of MOFs bearing open metal sites for ethylene/ethane separations examined HKUST-1 [$Cu_3(btc)_2$; btc^{3-} = benzene-1,3,5-tricarboxylate] [15–17]. Computational investigations revealed that both hydrocarbons preferentially adsorb near the unsaturated Cu^{2+} sites in this material, with low to moderate binding energies differing by less than 2 kJ/mol [16]. The enthalpy of C_2H_4 adsorption (computed as -32 kJ/mol at low coverage) [17] is low in magnitude compared to other frameworks with open metal sites, resulting in a very modest selectivity for ethylene. In contrast, the M_2(dobdc) frameworks [also MOF-74, CPO-27, or M_2(dhtp); M = Mg, Mn, Fe, Co, Ni, Zn; $dobdc^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate] perform well in the separation of light olefin/paraffin pairs [18–21]. These materials feature 1D hexagonal channels lined with a high density of exposed M^{2+} metal sites, which preferentially adsorb unsaturated hydrocarbons with high capacities, while their large pore size (11 Å) facilitates rapid adsorption and desorption kinetics. The adsorption enthalpy magnitudes for ethylene and propylene (38–48 and 47–53 kJ/mol, respectively) are much larger than for the corresponding paraffins (25–29 and 33–37 kJ/mol for ethane and propane, respectively) [21]. The Fe_2(dobdc) material has a high ethylene capacity of 6.0 mmol/g at 1 bar and 318 K and a moderate ethylene/ethane IAST selectivity of 13 and can fractionate an equimolar mixture to yield 99% pure ethylene [20]. For a 1:1 propylene/propane mixture, Mn_2(dobdc) and Fe_2(dobdc) both show selectivities in excess of 14. Strong yet reversible olefin adsorption in these congeners arises due to their ability to engage in a limited degree of **π-backbonding**, despite their high-spin electron configurations [22].

The M_2(*m*-dobdc) series of frameworks (M = Mg, Mn, Fe, Co, Ni, Zn; *m*-$dobdc^{4-}$ = 4,6-dioxido-1,3-benzenedicarboxylate) features a topology structurally analogous to the M_2(dobdc) family (Figure 1A,B). Importantly, the open metal sites in M_2(*m*-dobdc) exhibit higher charge densities than their M_2(dobdc) homologs, leading to more exothermic adsorption of both olefins and paraffins [23,24]. For M = Mn, Fe, Co, and Ni, the M_2(*m*-dobdc) frameworks are more olefin selective than the corresponding M_2(dobdc) frameworks

Glossary

π-Backbonding: the donation of electrons from a filled metal *d* orbital into an empty orbital localized on the metal-bound substrate. This interaction is π-symmetric with respect to the metal–substrate bond vector. Backbonding is often significant in transition metal–olefin complexes (as well as for many other metal–ligand combinations) and is synergistic with classical ligand-to-metal donation.

Ideal adsorbed solution theory (IAST): a theory developed by Prausnitz and Myers that facilitates the evaluation of adsorbent performance in multicomponent adsorption using only single-component isotherm data. Derived from solution thermodynamics, IAST holds good predictive power for a range of adsorbents and adsorbates.

Production capacity: also termed ‘productivity’; the quantity of a purified component that can be obtained from a given mixture before the adsorbent must be regenerated. This metric affords one of the best measures by which to judge the efficacy of an adsorbent for a given separation. While its value is difficult to estimate from single-component isotherms alone, the production capacity will in general positively correlate with both selectivity and capacity. Quantitative multicomponent breakthrough experiments allow direct measurement of production capacity.

Type I isotherm: the canonical Langmuir adsorption isotherm. It is monotonic and concave in shape with respect to the x-axis (pressure), with the isotherm slope continuously decreasing with increasing pressure and displaying saturation behavior.

Type IV isotherm: while the lowest-pressure region of this isotherm appears analogous to a Type I isotherm, a ‘step’ (i.e., a rapid rise in uptake) at some intermediate pressure is evident. At still-higher pressures, the isotherm displays saturation behavior. Type IV isotherms can arise due to capillary condensation of adsorbates or, more relevantly to this review, due to flexibility or a phase change of the adsorbent.

Working capacity: the quantity of adsorbate that can be recovered

(Figure 1C). Single-crystal X-ray diffraction analyses revealed shorter M–C_{olefin} distances in these M_2(*m*-dobdc) materials, which may allow for enhanced π-backbonding relative to M_2(dobdc) [24]. The most olefin-selective framework, Fe_2(*m*-dobdc), exhibits IAST selectivities of 25 and 56 for equimolar mixtures of ethane/ethylene and propane/propylene, respectively (298 K, 1 bar) [23]. In general, tuning the polarizing power of open metal sites through synthetic chemistry is an underexplored approach that may afford a wealth of opportunities to improve known adsorbent systems.

High selectivity for the adsorption of olefins over paraffins has also been observed for frameworks containing unsaturated Cu^+ or Ag^+ centers introduced via post-synthetic methods [25–30]. In contrast to divalent metals, these d^{10} coinage metals bind olefins through robust covalent interactions involving appreciable π-backbonding and have far less affinity for paraffins, given their low polarizing power. The resulting adsorption enthalpies for ethylene or propylene in these materials can approach or surpass −100 kJ/mol. Although large selectivities may arise from this strong interaction, regeneration of these frameworks can be quite difficult. Additionally, an inverse relationship was shown to exist between the monovalent

from an adsorption/desorption cycle within a specified range of pressures and temperatures. This value is most frequently calculated from single-component isotherms rather than experiments that survey simultaneous sorption of multiple mixture components. Accordingly, in isolation, the working capacity of an adsorbent is not indicative of utility for the separation of a given mixture. However, a large working capacity combined with high selectivity may portend favorable separation performance and can lead to a high production capacity.

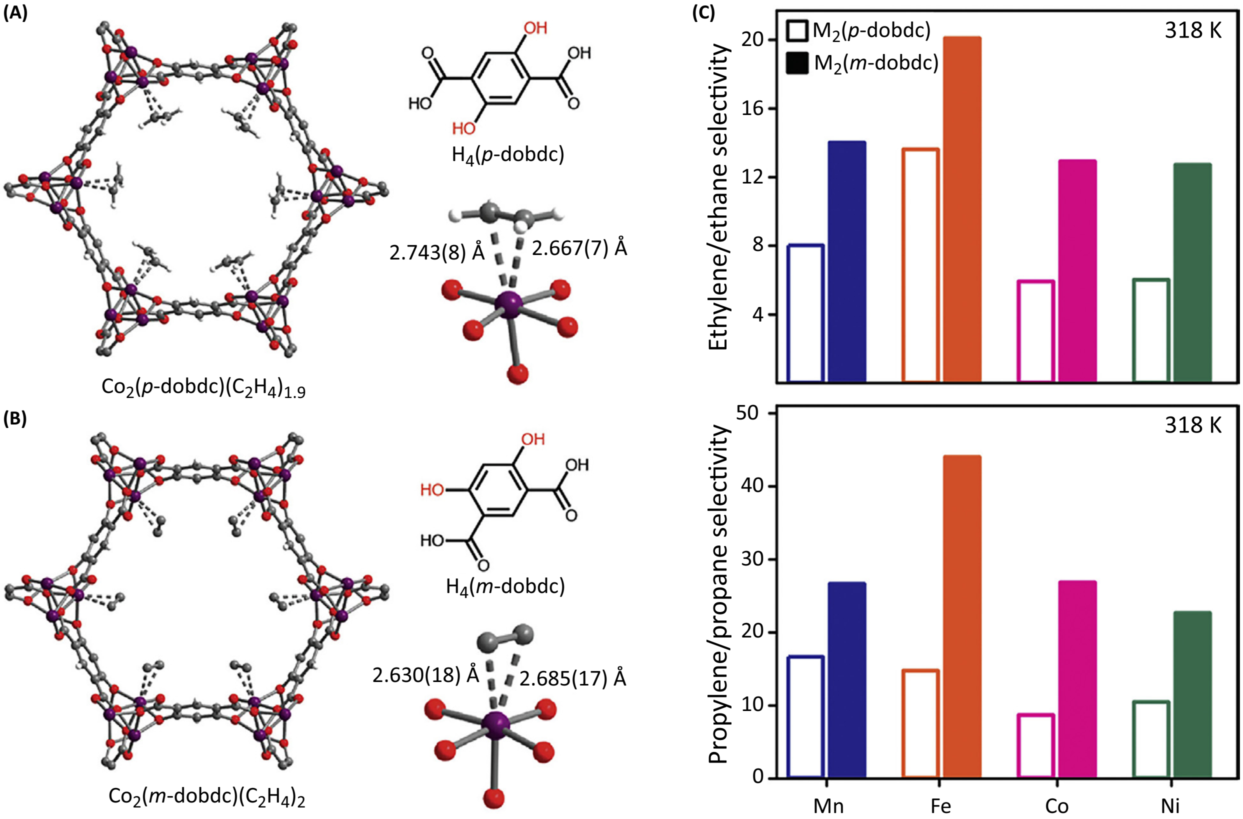

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Figure 1. Olefin/Paraffin Separations Using M_2(m-dobdc). Comparison of the ligands, framework structures, and ethylene binding geometries for Co_2(dobdc) (A) and Co_2(*m*-dobdc) (B), as obtained via single-crystal X-ray diffraction studies. Purple, red, gray, and white spheres represent Co, O, C, and H atoms, respectively. (C) Comparison of M_2(dobdc) and M_2(*m*-dobdc) selectivity values from ideal adsorbed solution theory (IAST) for separations involving equimolar feeds of ethylene/ethane (top) and propylene/propane (bottom) at 318 K. Adapted, with permission, from [23].

cation loading and framework surface area, which can result in a tradeoff between selectivity and separation working capacity [30].

While most frameworks lacking open metal sites do not exhibit a marked thermodynamic preference for olefin adsorption, a notable exception is NOTT-300 [$Al_2(OH)_2$(bptc); bptc^{4-} = biphenyl-3,3′,5,5′-tetracarboxylate], which has been studied for C_2 hydrocarbon separations [31]. This material features pores lined with corner-sharing $AlO_4(OH)_2$ octahedra that are linked via Brønsted acidic *cis*-μ_2-OH moieties. The primary ethylene binding site is above these bridging groups, and in its lowest energy conformation the ethylene π-cloud is oriented directly towards the hydroxide groups. While this interaction does not engender particularly exothermic adsorption of ethylene ($\Delta h_{ads} = -16$ kJ/mol at low coverage), ethane binding is substantially weaker, leading to a high IAST selectivity of 48.7 for a 1:1 mixture at 1 bar. The reliance on acidic hydroxides to selectively bind ethylene may render NOTT-300 less susceptible to poisoning by Lewis-basic contaminants (e.g., H_2S, H_2O) than frameworks that exploit open metal sites. In addition, the relatively weak binding enthalpies suggest that adsorbent regeneration should be facile and require minimal energy.

Separations Under Kinetic Conditions

While the majority of frameworks studied for adsorptive olefin/paraffin separations operate under thermodynamic equilibrium, certain materials separate light hydrocarbon mixtures based on kinetic selectivity. In such cases, the size and shape of the framework channels dictate the rate of hydrocarbon adsorption. Candidate materials must feature pores that inhibit the passage of a given paraffin while allowing access to the more compact olefin [32]. Recent reports have focused largely on propylene/propane separations, and several frameworks containing pore apertures in the 4–5-Å range have been shown to exhibit enhanced uptake rates of propylene compared with propane despite similar equilibrium capacities [33–35].

Perhaps the most well-studied framework for the kinetic separation of light olefin/paraffin mixtures is ZIF-8 [Zn(MeIm)$_2$; MeIm$^-$ = 2-methylimidazolate] [36] (Figure 2). The 12-Å-wide internal cavities of the activated material are accessible via apertures of only 3.4 Å, but the 2-methylimidazole linkers can rotate to widen this window and enable the entry of larger guest

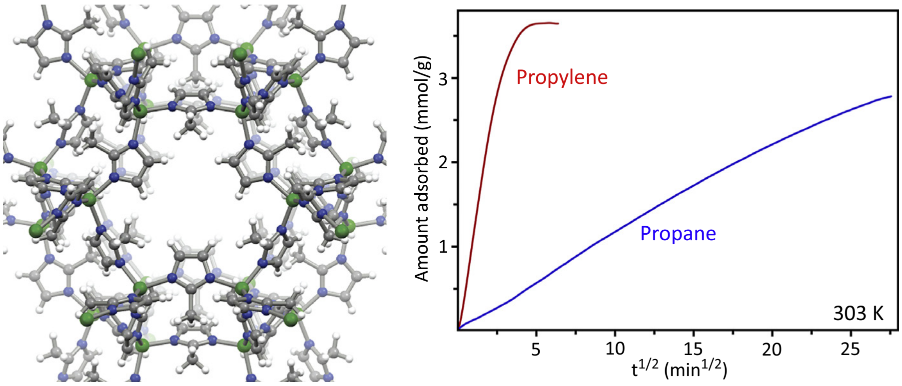

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Figure 2. Kinetic Separation of Propylene from Propane Using ZIF-8. Left: Crystal structure of a portion of activated ZIF-8, as reported in [37], showing the constricted six-membered ring windows that provide access to the internal pores. Green, blue, gray, and white spheres represent Zn, N, C, and H atoms, respectively. Right: Single-component kinetic analysis of propylene and propane uptake by ZIF-8 at 303 K and 0.8 bar, as reported in [36].

molecules [37]. Although the framework exhibits nearly identical equilibrium capacities for propane and propylene at 1 bar [38], the activation energy for propane diffusion is much greater than for propylene, leading to large differences in their uptake rates [36,39]. Polycrystalline membranes comprising ZIF-8 [40–45] or its cobalt(II) analog ZIF-67 [Co(MeIm)$_2$] [42,46] have also received attention for propylene/propane separations. Owing to the smaller sizes of ethylene and ethane, only modest differences are observed in their ZIF-8 membrane diffusivities [47,48].

The total sieving of the slightly larger alkane from the corresponding olefin can be viewed as the extreme limit of kinetic selectivity, and two notable works have achieved this feat for $C_{2–3}$ olefin/paraffin pairs. Essentially complete exclusion of propane was reported for NbOFFIVE-1-Ni [Ni(NbOF$_5$)(pz)$_2$; pz = pyrazine; KAUST-7] [49]. In this material, canting of the pyrazine linkers fosters favorable contacts with the pillaring $NbOF_5^{2-}$ anions but severely constricts the pore aperture, rendering it impenetrable to propane at ambient temperatures. Despite sluggish kinetics, NbOFFIVE-1-Ni does adsorb propylene, and the 298-K isotherm for this material displays Type I behavior with a low saturation capacity of <1.5 mmol/g at 1 bar. Breakthrough experiments confirmed that near-perfect selectivity is indeed feasible. Analogously, a recent report demonstrated the size exclusion of ethane by UTSA-280 [Ca(C_4O_4)(H_2O); $C_4O_4^{2-}$ = squarate] [50], which features a rigid pore structure that permits ethylene adsorption with surprisingly fast kinetics. The material exhibits an ethylene capacity of 2.5 mmol/g at 298 K and 1 bar while the ethane uptake under these conditions is only 0.1 mmol/g, leading to an approximated selectivity on the order of 10^4. The ability of NbOFFIVE-1-Ni and UTSA-280 to discriminate between similarly sized components renders them standard-bearers in the development of sieving materials for olefin/paraffin mixtures. However, materials capable of size sieving are also characterized by generally low surface areas that limit their capacities. Accordingly, the design of a framework featuring both high surface area and small pore apertures that exclude paraffins would represent a significant leap forward in materials design for kinetic olefin/paraffin separations.

Separations Using Flexible MOFs

Several frameworks have been reported to achieve the separation of light olefin/paraffin pairs via selective gate-opening processes. This mechanism is exemplified by flexible ZIF-7 [Zn(bim)$_2$, bim$^-$ = benzimidazolate], which exhibits a **Type IV adsorption isotherm** at ambient temperatures for both ethylene and ethane [51,52]. Interestingly, the gate-opening pressure is lower for ethane than for ethylene, rendering ZIF-7 a rare example of an ethane-selective framework (see below). The utility of ZIF-7 for the separation of ethylene and ethane has been demonstrated via breakthrough experiments [53]. Ethane adsorption was determined to be more exothermic than ethylene adsorption at all measured pressures, helping to rationalize why gate opening occurs more readily for the alkane. From a structural standpoint, it has also been speculated that ethane maximizes van der Waals contacts due to its threefold rotational symmetry approximately coinciding with that of the ZIF-7 pores [51]. The framework CPL-1 [Cu$_2$(pzdc)$_2$(pz); pzdc^{2-} = 2,3-pyrazinedicarboxylate] exhibits a sharp step in its ethylene adsorption isotherm at 273 K and ~2 bar, while no step is seen for ethane at this temperature and pressures as high as 10 bar [54]. Breakthrough experiments at 8 bar and 273 K demonstrated successful separation of equimolar ethylene/ethane mixtures. The CPL-1 material also selectively adsorbs propylene over propane due to gate opening and is able to separate mixtures of these hydrocarbons at 273 K [55].

Another report demonstrated an intriguing allosteric pore-opening mechanism that is quite unique in the realm of hydrocarbon separations [56]. The evacuated form of Co(vttf)

{vttf^{2-} = 2,2′-[1,2-bis(4-benzoate)-1,2-ethanediylidene]bis-1,3-benzodithiole} is nonporous and features crosslinking via the coordination of tetrathiafulavalene sulfur atoms to the axial sites of the $Co_2(COO)_4$ paddlewheels. While the framework is unresponsive to ethane, ethylene coordinates to cobalt and induces a cooperative transition, displacing the tetrathiafulvalene linkers and yielding an open structure. Once open, however, the framework adsorbs both ethylene and ethane, resulting in only modest selectivities. Such coadsorption of multiple components represents one significant challenge facing the use of flexible frameworks for gas separations – especially when high product purity is required (Box 1).

Paraffin-Selective MOFs

For the purification of feeds containing paraffins as a minor component, an ideal adsorbent would selectively capture the saturated hydrocarbon, allowing high-purity olefin to elute without the need for a subsequent desorption cycle. The design of a paraffin-selective adsorbent is a challenging task, however, as few chemical handles are available to bias a material towards preferential binding of a saturated hydrocarbon. When paraffin selectivity has been observed, it is typically found to arise from the predominance of van der Waals contacts between the framework walls and the paraffin, relative to the comparatively compact and planar olefin. The chemical topology of paraffin-selective frameworks varies widely and these materials may feature pores that are hydrophobic or lined with polar groups. While the absence of overarching design principles for marshaling selective paraffin binding has perhaps hindered their discovery, these materials have grown in number over the past several years.

Reports of frameworks that are selective for propane over propylene have been limited primarily to materials from the ZIF family. The aforementioned ZIF-7 and ZIF-8 materials exhibit mild thermodynamic preferences for propane adsorption in certain temperature and pressure regimes [38,52] and ZIF-4 [$Zn(im)_2$] is selective for propane below 0.4 bar at 293 K, although the selectivity inverts at higher pressures [57]. All of these materials are also only marginally selective for the adsorption of ethane over ethylene.

A handful of frameworks that show generally favorable capacities of C_2H_6 (>3 mmol/g at 1 bar and 298 K) exhibit modest ethane selectivities (~2 at 1 bar) [58–61]. Interestingly, the material MAF-49 [Zn(batz); batz^{2-} = bis(5-amino-1,2,4-triazol-3-yl)methane] exhibits a large ethane adsorption enthalpy of −60 kJ/mol at low coverage [62]. Despite a low ethane capacity of 1.7 mmol/g at 316 K and 1 bar, this material also exhibits a moderate IAST selectivity of 9 under the same conditions for an equimolar C_2H_4/C_2H_6 mixture (the value reduces to 2.7 at 298 K [63]). Notably, MAF-49 was shown to be capable of producing 99.98%-pure ethylene from a 1:1 mixture using a single breakthrough column. Molecular simulations indicate that ethane makes many contacts with free amino and triazolate nitrogen atoms in the primary binding site. The framework $Cu(qc)_2$ (qc$^-$ = quinolone-5-carboxylate) alternatively features hydrophobic

Box 1. Assessing Selectivity in Flexible or Pore-Gated Frameworks

Evaluating the potential of pore-gated or flexible MOFs for a given separation presents some unique challenges. By far the most common evaluation method for any adsorbent involves measuring single-component isotherms and comparing these for different adsorbates to derive selectivities. This method holds good predictive value for many framework and adsorbate combinations, and selectivity values calculated using IAST are typically in reasonable agreement with those directly measured from breakthrough experiments. However, the central assumptions made in deriving the equations that underlie IAST do not hold true for frameworks that undergo structural transitions upon guest adsorption. In addition, the ‘opened’ form of a framework can exhibit similar affinities for multiple components in a mixture, which can result in drastic overestimations of selectivity when relying on single-component isotherm data alone. Only multicomponent equilibrium adsorption data provide a valid assessment of thermodynamic selectivity in such frameworks for a given mixture. Unfortunately, these experiments are difficult to perform and require instrumentation that is not available to many researchers. In lieu of such measurements, it is highly preferable to perform multicomponent breakthrough measurements to evaluate the performance of the framework in the presence of all relevant species.

channels lined with aromatic rings that serve as adsorption sites for both C_2H_4 and C_2H_6 [63]. However, the larger ethane molecules engage in more C−H···π contacts–as revealed from neutron diffraction studies–leading to a selectivity for ethane over ethylene that reaches 3.4 at 298 K and 1 bar for a 1:1 mixture.

The material $Fe_2(O_2)$(dobdc) was recently shown to bind ethane with a surprisingly large adsorption enthalpy of −67 kJ/mol [64], leading to a C_2H_6/C_2H_4 selectivity of 4.4 for a 1:1 mixture at 298 K and 1 bar. Remarkably, breakthrough experiments using a 1:1 mixture and a single column of the framework also yielded ethylene in 99.99% purity. Prepared via the addition of O_2 to Fe_2(dobdc), $Fe_2(O_2)$(dobdc) features η^2-bound peroxo species at 50% of the iron sites [65], and an analysis of powder neutron diffraction data indicated that these ligands engage in close contacts with one $-CH_3$ group of adsorbed ethane (Figure 3). The origin of such strong and selective ethane binding in this framework remains unknown and certainly merits further investigation.

Separation of Alkyne/Olefin Mixtures

MOFs that have been studied for C_{2-3} alkyne/olefin separations are generally selective for alkyne adsorption. Alkynes typically constitute only 1–5 mol% of crude ethylene and propylene feedstocks. Therefore, an alkyne-selective adsorbent that exhibits minimal olefin uptake is an excellent candidate for efficiently performing this separation. The reduction of alkyne concentrations to low ppm levels is necessary for an olefin to be certified as ‘polymer grade’, representing a decrease in alkyne concentration of roughly four orders of magnitude. Accordingly, very high alkyne selectivities and capacities are required to enable the production of high-grade olefins in desirable quantities.

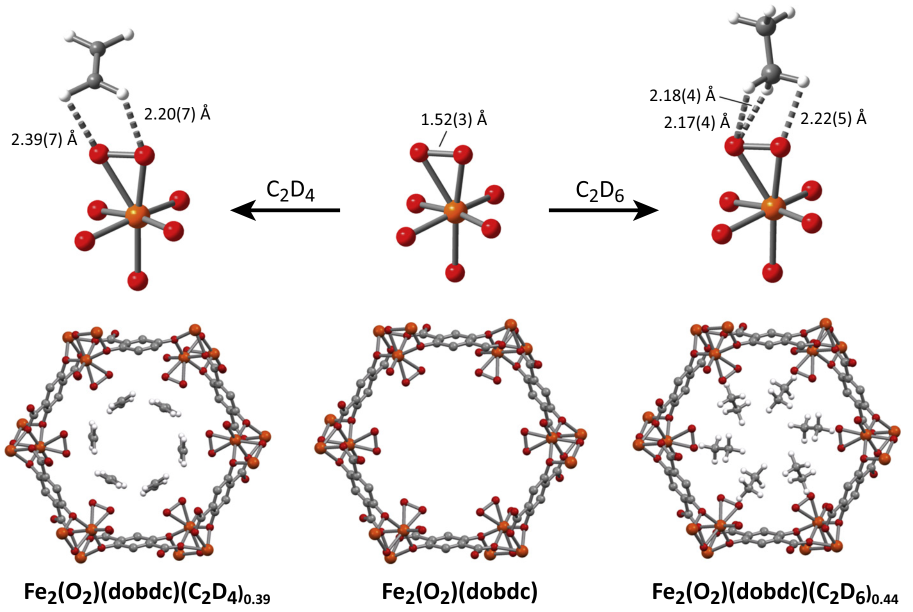

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Figure 3. Selective Adsorption of Ethane Over Ethylene by $Fe_2(O_2)$(dobdc). Comparison of the structures with C_2D_4 (left) and C_2D_6 (right) adsorbed in $Fe_2(O_2)$(dobdc), as determined from powder neutron diffraction data reported in [64]. Orange, red, gray, and white spheres represent Fe, O, C, and deuterium atoms, respectively.

Acetylene/Ethylene

Relatively few frameworks featuring open metal sites have proved useful for alkyne/olefin separations. These sites can exhibit a strong, although often indiscriminate, affinity for unsaturated hydrocarbons that may lead to high capacities but low selectivities. Breakthrough simulations for M_2(dobdc) (M = Mg, Fe, Co) have suggested that it may be possible to employ these materials in the production of polymer-grade C_2H_4 from a mixture containing 1% C_2H_2, although this result has not been demonstrated experimentally [19,20]. Given the small IAST selectivities determined for this mixture (<3 for all frameworks), the calculated **production capacities** for purified C_2H_4 were considerably less than those achievable from binary ethylene/ethane mixtures. A more promising result was obtained for UTSA-60 [Cu_2(btaa); btaa^{4-} = benzene-1,2,4,5-tetraacrytate], which features $Cu_2(COO)_4$ paddlewheel motifs [66]. While UTSA-60 adsorbs considerably less C_2H_2 than the M_2(dobdc) family due to a lower density of open metal sites, its higher acetylene selectivity of ~6 at 1 bar and 296 K (1:99C_2H_2/C_2H_4 mixtures) leads to a marked improvement in C_2H_4 production capacity as estimated from transient breakthrough simulations.

Given the smaller kinetic diameter of acetylene compared with ethylene (3.3 Å and 4.2 Å, respectively) [6], these two components may be separated by frameworks with pore windows sized appropriately to exclude ethylene. Several rigid frameworks have been shown to significantly hinder the adsorption of C_2H_4 while readily accommodating the more compact C_2H_2 molecule [67–72]. Certain frameworks featuring very narrow pores can also undergo selective gate opening in the presence of C_2H_2, leading to extraordinary differences in single-component C_2H_2 and C_2H_4 capacities [73–75]. Perhaps the most intriguing of these materials is UTSA-300 [Zn(SiF_6)(dps)$_2$; dps = 4,4′-dipyridylsulfide], a member of the SIFSIX family of frameworks (see below) [74]. In the activated framework, contacts between pyridyl H atoms *ortho* to nitrogen and the SiF_6^{2-} anions enforce a tilting of the pyridyl rings that obstructs the pores (Figure 4, left). However, cooperative gate opening occurs upon dosing with C_2H_2 pressures above ~0.2 bar (at 298 K), and in this 'open' phase C_2H_2 molecules bridge two SiF_6^{2-} units via hydrogen-bonding interactions (Figure 4, right). In contrast, no step associated with gate opening is seen in the low-pressure C_2H_4 isotherms. An experimental breakthrough study utilizing a packed

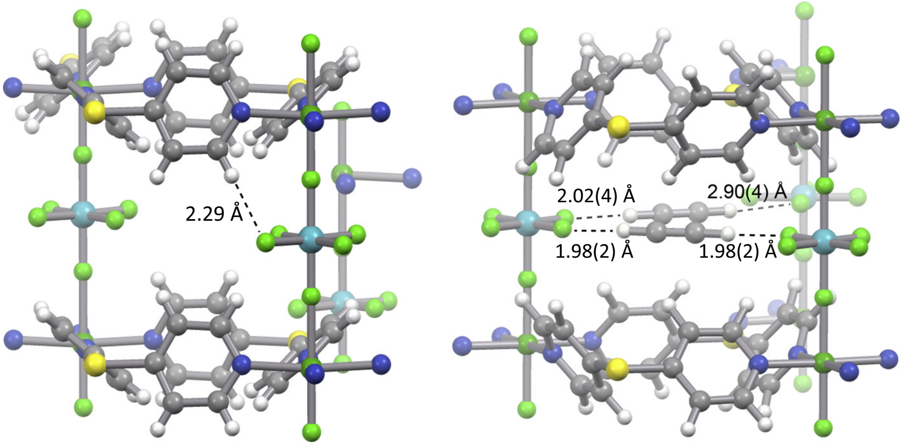

Figure 4. Selective Binding of Acetylene Over Ethylene by the Flexible Framework UTSA-300. Comparison of a portion of the crystal structures for activated, 'closed' (left) and C_2D_2-loaded (right) forms of the framework UTSA-300 [Zn (SiF_6)(dps)$_2$], as determined from neutron powder diffraction data reported in [74]. Dark-green, light-green, dark-blue, aqua, yellow, gray, and white spheres represent Zn, F, N, Si, S, C, and H/D atoms, respectively.

column of UTSA-300 and an equimolar mixture of ethylene and acetylene yielded ethylene with purity in excess of 99.9%.

Recent examples of frameworks containing pores lined with Lewis-basic groups [67,72,74–85] or free anions [86,87] have demonstrated significant enhancements in the selective adsorption of C_2H_2. Among these are the SIFSIX family of frameworks, which generally comprise 2D M^{2+}–*N*-heterocycle nets pillared by hexafluorosilicate anions (Figure 5). The pores are lined with exposed SiF_6^{2-} groups and linker aryl rings, which can promote acetylene adsorption via the formation of hydrogen-bonding and multidimensional π-stacking interactions, respectively. A landmark study of these frameworks demonstrated highly selective adsorption of C_2H_2 over C_2H_4 and remarkable control of the C_2H_2 binding strength through modulation of the pore size [81]. One material, SIFSIX-1-Cu [$Cu(SiF_6)(bpy)_2$; bpy = 4,4′-bipyridine], was found to adsorb a substantial 8.5 mmol/g of C_2H_2 at 298 K and 1 bar, nearly twice the capacity of the larger-pore variant SIFSIX-2-Cu [$Cu(SiF_6)(py_2C_2)_2$; py_2C_2 = 4,4′-dipyridylacetylene]. However, both materials are only moderately selective for adsorption of C_2H_2 over C_2H_4 (IAST selectivities of 10.6 and 6.0 for 1:99 mixtures, respectively). In contrast, the two-fold interpenetrated framework SIFSIX-2-Cu-i binds C_2H_2 more strongly than any other rigid SIFSIX material ($\Delta h_{ads} = -41.9$ kJ/mol) as a result of hydrogen-bond formation between its H atoms and opposing SiF_6^{2-} anions across the square channels. Ethylene adsorption is significantly less exothermic ($\Delta h_{ads} = -30.7$ kJ/mol), resulting in a selectivity of 44.5 for a 1:99 C_2H_2/C_2H_4 mixture. Experimental breakthrough studies performed using SIFSIX-2-Cu-i yielded high-purity ethylene with C_2H_2 concentrations as low as 2 ppm.

Replacement of the 4,4′-dipyridylacetylene linker in SIFSIX-2-Cu-i with the slightly more compact 4,4′-azopyridine linker leads to isoreticular SIFSIX-14-Cu-i (UTSA-200), which achieves nearly complete exclusion of C_2H_4 [72]. While the 298 K single-component isotherm for C_2H_4 features a small step at intermediate pressures (~0.7 bar) due to linker rotation increasing the pore window size, ethylene uptake at 0.99 bar remains lower than that of C_2H_2 at 0.01 bar by a factor of 3.4. This remarkable preference for C_2H_2 adsorption leads to an astoundingly high IAST selectivity of 6000 at 1 bar (1:99 C_2H_2/C_2H_4) and a near doubling of the C_2H_4 production capacity compared with that measured for SIFSIX-2-Cu-i. Interestingly,

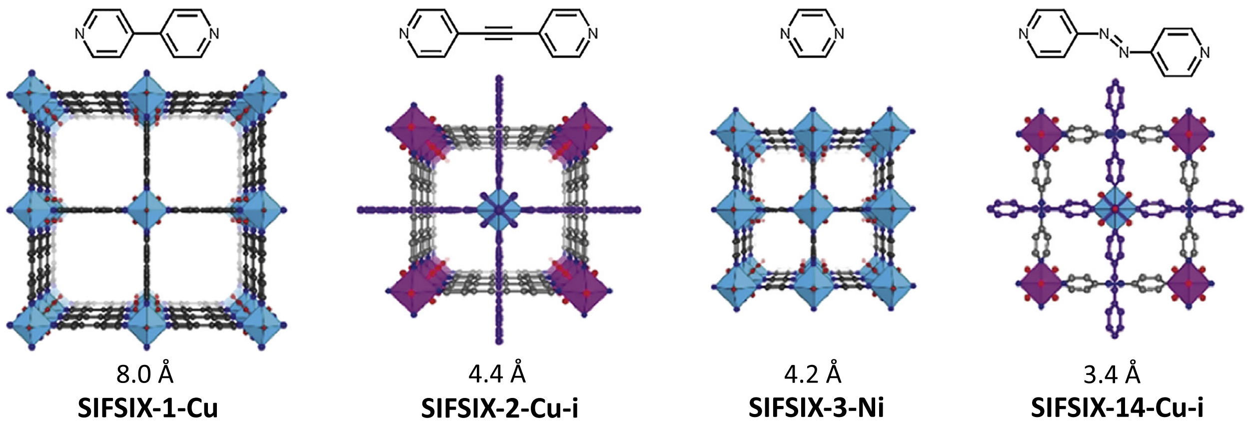

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Figure 5. Structures of Various SIFSIX Materials. Structures of portions of several SIFSIX frameworks discussed in the text along with corresponding linkers and pore aperture sizes. Gray, red, and blue spheres represent C, F, and N atoms, respectively. The skeletons of interpenetrated nets are depicted in dark purple. Adapted, with permission, from [93].

the degree of interpenetration in SIFSIX-14-Cu-i can be rationally modulated and was found to be positively correlated with C_2H_2/C_2H_4 separation performance [88]. Phases with decreasing degrees of interpenetration exhibited weakened C_2H_2 adsorption enthalpies and increasing C_2H_4 capacities, which respectively arise from a loss of strong C_2H_2 binding sites and an increase in the material surface area.

The material NKMOF-1-Ni {Cu[Ni(pdt)$_2$]; pdt^{2-} = pyrazine-2,3-dithiolate} also features square channels that were shown to be optimal for binding of C_2H_2 over C_2H_4 [80]. The framework exhibits a very high zero-coverage enthalpy of C_2H_2 adsorption of −60.3 kJ/mol. Here, the primary C_2H_2 binding site features hydrogen-bonding interactions with the thiolate sulfur atoms and π-stacking interactions with the four surrounding pyrazine rings. Although C_2H_4 also binds rather strongly in this material ($\Delta h_{\text{ads}} = -44.9$ kJ/mol at zero-coverage), the IAST selectivity for 1% C_2H_2 in C_2H_4 is quite high (approximately 50 at 298 K and 1 bar). Column breakthrough experiments yielded C_2H_4 containing sub-ppm levels of C_2H_2.

Propyne/Propylene

The successes achieved in the design of acetylene-selective frameworks have informed the pursuit of adsorbents that can selectively remove propyne from crude propylene feeds. For example, ELM-12 [Cu(OTf)$_2$(bpy)$_2$] contains triflate anions that are appropriately spaced to be bridged by two equivalents of C_3H_4 via hydrogen-bonding interactions [89]. A sizable IAST selectivity of 84 was calculated for a 1:99 mixture of C_3H_4/C_3H_6. Column breakthrough studies demonstrated the production of polymer-grade C_3H_6 from this mixture, with propyne concentration at the outlet being less than 2 ppm.

Other recent reports have focused on the SIFSIX materials and related frameworks containing pillaring inorganic anions [90–93]. The framework SIFSIX-3-Ni [Ni(SiF$_6$)(pz)$_2$] features channels appropriately sized for one propyne molecule and exhibits extraordinarily steep uptake of the gas in the ultralow pressure region of its 298 K isotherm, reaching nearly 90% of its saturation capacity (2.98 mmol/g) at 0.003 bar [91]. The material exhibits a high selectivity of 290 for a mixture of 0.1% propyne in propylene and outperforms a number of other frameworks in the removal of trace (0.1%) propyne from propylene as evaluated from column breakthrough experiments at 298 K and 1 bar.

Although the pores in activated SIFSIX-14-Cu-i (UTSA-200) appear to be too small to accommodate any C_3 hydrocarbon, dosing with C_3H_4 at 298 K yields a **Type I adsorption isotherm** that is very steep in the low-pressure region, and at 0.01 bar the material achieves more than 80% of its saturation capacity (3.58 mmol/g at 0.99 bar) [93]. Neutron powder diffraction experiments revealed significant structural distortions upon C_3H_4 dosing, which render the pores sufficiently spacious to accommodate the alkyne. Such plasticity is not evident upon introduction of C_3H_6, and despite a small step at ~0.5 bar in the 298 K propylene isotherm the uptake remains comparatively low (1.20 mmol/g at 0.99 bar), leading to a calculated C_3H_4 selectivity of over 20 000 for a 1:99 C_3H_4/C_3H_6 mixture. Column breakthrough experiments conducted at 298 K using a 1:99 mixture of C_3H_4/C_3H_6 revealed that SIFSIX-14-Cu-i outperforms all frameworks previously studied for this particular separation with respect to the reported production capacity for polymer-grade C_3H_6.

Concluding Remarks and Outlook

Access to varying pore sizes and functionalities in metal–organic frameworks has enabled researchers to realize many promising new adsorbents for light hydrocarbon separations. Control over the pore dimensions in particular allows for separations based on size and shape

Outstanding Questions

The excellent performance of Mn$_2$(*m*-dobdc) and Fe$_2$(*m*-dobdc) in olefin/paraffin separations suggests that soft open metal sites that retain weak π-basicity may represent an optimal balance between selective and reversible olefin binding. Will strengthening of olefin adsorption enthalpies or weakening of paraffin affinities be a more advantageous approach towards further increasing selectivity in materials of this type? What metals are the best candidates for such adsorbents?

What is the electronic origin of ethane selectivity in frameworks bearing exposed O_2^{n-} motifs? Can similar behavior be achieved using other hard, negatively charged groups?

What strategies can be used to increase the working capacities of rigid frameworks that operate by a size-sieving mechanism for olefin/paraffin separations? Can electronic motifs that contribute to strong olefin binding be installed to counter their low surface areas?

Beyond NOTT-300, can other frameworks that feature nonmetal electropositive groups (e.g., μ-OH) exhibit selective adsorption of olefins over paraffins?

How will MOFs featuring open metal sites perform in the separation of real-world hydrocarbon mixtures that potentially contain Lewis-basic contaminants capable of poisoning and/or outcompeting olefins for such sites?

Can any MOFs that exploit selective gate-opening mechanisms produce polymer-grade olefin from an industrially relevant mixture?

Given that alkyne removal usually precedes olefin/paraffin separation in real-world refining processes, how would the best-performing frameworks for alkyne capture perform in the separation of three-component alkyne/olefin/paraffin mixtures?

selectivity, and some of the highest selectivities have been achieved in frameworks with pore apertures that restrict adsorption to the smallest component in a mixture. Selectivity can also be achieved with materials featuring pores that maximize the number of framework–adsorbate interactions for a specific molecule, which can lead to preferential binding of components with better pore wall contact over those with inherently stronger interactions. In addition to pore dimensions, specific functional groups can be leveraged to impart selective binding. Sites with partial positive charge, such as coordinatively unsaturated metal sites and acidic hydroxide groups, can interact favorably with the electron density in olefin and alkyne π-bonds, while the partial negative charge in anionic moieties, such as SiF_6^{2-} and O_2^{2-}, can bind gases with electropositive C–H bonds.

As research on MOFs for these separations progresses and many more promising adsorbents are discovered, more rigorous methods and criteria need to be adopted to assess material performance accurately under industrially relevant conditions. For example, many frameworks have been evaluated only using single-component gas adsorption measurements, which fail to capture kinetic and non-ideal behavior that can significantly affect actual separation performance. Moreover, a comparison of materials based on selectivity or capacity alone may hinder analysis, because separation performance depends on both properties, and frameworks often exhibit a tradeoff between selectivity and capacity. Quantitative multicomponent breakthrough experiments enable both selectivity and capacity to be determined under conditions that more closely represent those of an actual separation process. In addition, such experiments allow for a more straightforward comparison of materials based on the amount of gas that can be purified per unit of adsorbent before the adsorbent bed must be regenerated (i.e., production capacity). The adsorption kinetics of these materials should also be assessed routinely in their evaluation for industrial applications. Future work would benefit from consideration of adsorbent stability and performance under multiple adsorption and regeneration cycles as well as in the presence of possible contaminants such as H_2, CO, CO_2, H_2S, and other olefins and alkynes (see Outstanding Questions).

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