Hydrocarbon Separations in Metal−Organic Frameworks

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S *Supporting Information*

ABSTRACT: New materials capable of separating mixtures of saturated, unsaturated, and aromatic hydrocarbons can enable more efficient industrial processes and cleaner energy. Outstanding challenges in hydrocarbon separations stem from the similar structures, properties, and reactivities of the molecules comprising many of these mixtures. With high surface areas, tunable pore geometries, and adjustable surface functionality, metal−organic frameworks hold tremendous promise for effecting previously difficult or impossible separations. In this review, we provide a comprehensive account of the metal−organic frameworks that have been investigated for hydrocarbon separations within the context of their potential relevance for separating various industrial alkane-, alkene-, and aromatic-containing mixtures.

KEYWORDS: *metal−organic frameworks, hydrocarbons, gas separations*
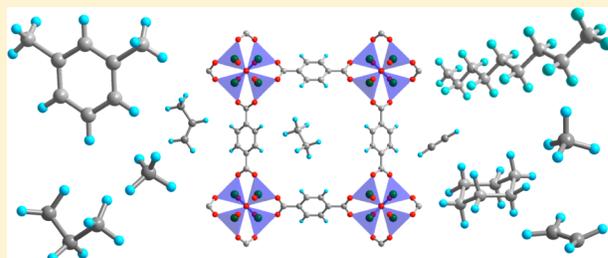
■ INTRODUCTION

Hydrocarbon mixtures are separated into various component fractions on enormous scales for the production of fuels and chemical feedstocks. Owing to the high energy costs associated with many of these critical separation processes, the development of metal−organic frameworks that could enable efficient adsorptive separations represents an exciting new direction of study. In this review, our goal is to be inclusive of all adsorbates composed of only carbon and hydrogen atoms, focusing exclusively on these adsorbates[1−12] and reporting on all types of hydrocarbon mixtures.[13−15] The use of metal−organic frameworks within membranes[16−18] or as components in capillary columns[19−21] is not treated.

Nearly all hydrocarbons are generated from petroleum or natural gas processing.[22] Natural gas, which is primarily methane, also contains ethane, propane, and butanes. Petroleum can be composed of hundreds of thousands of chemicals and varies in its composition between 50 and 97 wt % hydrocarbons. Petroleum is divided into fractions based upon boiling points: butanes and lighter, gasoline, naphtha, kerosene, gas oil, and residue. Compositions among these fractions vary widely.[22] The liquids and gases discussed in this review mostly fall into the light gas, gasoline, or naphtha fractions, although adsorption of some longer alkane kerosene components have been reported and are included.

Improvements in separation efficiency and investigations of separations that have not yet been reported provide a strong motivation for studying the behavior of hydrocarbon molecules within porous materials.[22] In particular, the extraordinary chemical tunability of the pore geometry and surface functionality within metal−organic frameworks can facilitate control over adsorption selectivity, while their high surface areas generally give rise to a large separation working capacity. As we will see, both the most fundamental separations such as

methane/ethane separations and more esoteric separations have already been investigated to a considerable extent within metal−organic frameworks. While estimating a priority order for industrial relevance is challenging, the separation of essentially all hydrocarbons generated within the same petroleum fraction can be considered both industrially relevant and a tool for better understanding the separation abilities of metal−organic frameworks.

Seven metal−organic frameworks are encountered repeatedly in the hydrocarbon separation studies performed to date, and a brief discussion of each is useful to inform the content of this review (Figure 1). The canonical MOF-5 is among the simpler structures, consisting of a cubic network built from $[Zn_4O]^{6+}$ tetrahedra connected via 1,4-benzenedicarboxylate $(bdc^{2−})$ linkers.[23] Lauded for its stability and structural similarity to zeolites, ZIF-8 contains Zn^{2+} cations linked by 2-methylimidazolate (MeIM).[24] The structure of ZIF-8 is somewhat flexible, and gate-opening effects can be seen for different adsorbates. The structure of $Cu_3(btc)_2$ (HKUST-1) consists of $Cu_2(O_2C)_4$ paddlewheel units connected via 1,3,5-benzenetricarboxylate $(btc^{3−})$ linkers. Upon activation, the Cu^{2+} centers each have an axial coordination site open and pointing into the pore, allowing rich reactivity at this Lewis acidic site.[25] The structure of the frameworks $M_2(dobdc)$ (M = Mg, Mn, Fe, Co, Ni, Zn; $dobdc^{4−}$ = 2,5-dioxido-1,4-benzenedicarboxylate) (Figure 1), sometimes referred to as M-MOF-74 or CPO-27-M, also contains coordinatively unsaturated divalent metal cations.
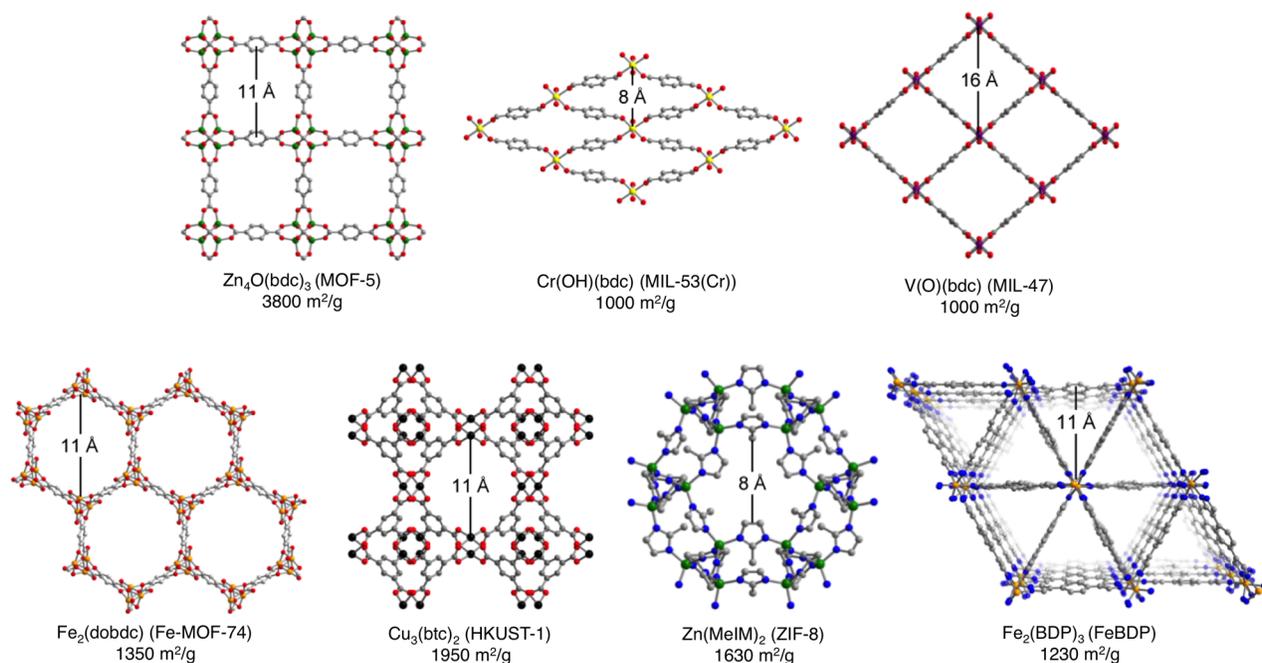
Figure 1. Crystallographic structure, molecular formula, common name, BET surface area, and centroid−centroid pore diameters or distances for the structure types regularly encountered in hydrocarbon separations. Surface areas are reported in references within this review with the exception of MIL-53,[28] MIL-47,[28] and $Cu_3(btc)_2$.[29] Green, red, gray, yellow, purple, orange, dark red, and blue correspond to Zn, O, C, Cr, V, Fe, Cu, and N, respectively. Variations of these structures can include functional groups bound to the organic ligand such as the "IRMOF" series of MOF-5 or amino-MIL-53, which includes an amino group bound to the central benzene ring of the linker. Metal cations can also differ within the $M_2(dobdc)$ and MIL-53 series, which in this figure contain Fe and Cr, respectively. MIL-53 is shown in the "narrow pore", or closed, form, although this material can also expand to a structure very similar to that of MIL-47.

Here, the metal centers are exposed with an exceptionally high surface density of ∼3 open metal sites per 100 Å^2, leading to particularly high separation capacities. The similar structures of MIL-47 and MIL-53 are both composed of bdc^{2-} struts, with MIL-47 containing V, while MIL-53 can be based upon Al, Sc, Cr, Fe, Ga, or In.[26] Although MIL-47 is relatively rigid, the MIL-53 materials are flexible frameworks that can open and close like an accordion in the presence or absence of different adsorbates.[27]

Here, we will focus on how the variations within such structures can lead to the facile separation of various important hydrocarbon mixtures. Concepts related to adsorptive separations, such as distinctions among isotherm types,[30] calculating enthalpy of adsorption,[31] and ideal adsorbed solution theory (IAST)[31] are explained in detail elsewhere. In addition, it should be noted that the physical properties of most of the adsorbates found in this review have been tabulated.[4] The strength of adsorption of all of the references in this review are tabulated in Table S1, including the material(s), the adsorbates, and the experiments or theory performed to generate these values. Throughout the body of the text, all results are experimental unless otherwise specified.

■ SATURATED HYDROCARBON MIXTURES

Normal alkanes can be found in petroleum from trace levels to up to 50 wt % of the hydrocarbon content. Methane through *n*-decane are relevant as gasoline components, while alkanes up to C20 are present in kerosene.[32] Ethane is a feedstock for ethylene plants, while propane and butanes are feedstocks for chemicals or petroleum refining processes. Longer alkanes are further reacted either in catalytic reforming or isomerization

because their low octane numbers make them of little value other than as niche feedstocks.[22,33]

To explain the results presented for linear alkane separations within metal−organic frameworks, some broad theories are under development and investigation. In MOF-5 and PCN-6′, a "clustering" phenomenon has theoretically been shown to occur below the critical temperature of an adsorbate, which strongly affects the selectivity of linear alkanes, especially when the temperature of separation is above the critical temperature of one adsorbate and below that of another.[34] Further, a general trend is seen in which stronger adsorption is usually coupled to an entropic cost as it leads to a loss in degrees of freedom.[35]

Short Normal Alkanes. Given its high surface area and thermal stability, MOF-5 (Figure 1) serves as an excellent platform for the adsorption of short chain hydrocarbons.[34,36−40] A theoretical study demonstrated that the van der Waals interactions with the pore surfaces enforce a trend of both the enthalpy and entropy of adsorption becoming more negative with increasing chain length.[41] An adsorption step in the isotherms is seen at increasing pressures for smaller alkanes, and these adsorbates boast a higher capacity as well. In a mixture, the more strongly adsorbing, longer alkanes are preferred until the selectivity reaches a maximum, when the entropic cost of ordering the long adsorbates overcomes the enthalpic benefit to adsorption (Figure 2). Similar results are seen experimentally.[35]

The separation of methane from *n*-butane was also investigated computationally for five materials isostructural to MOF-5, wherein the bdc^{2-} linker was replaced with multiring dicarboxylate ligands.[42] Up to 40 bar, methane exhibits a typical Type I isotherm that does not saturate, while *n*-butane isotherms all show a pronounced capillary condensation step
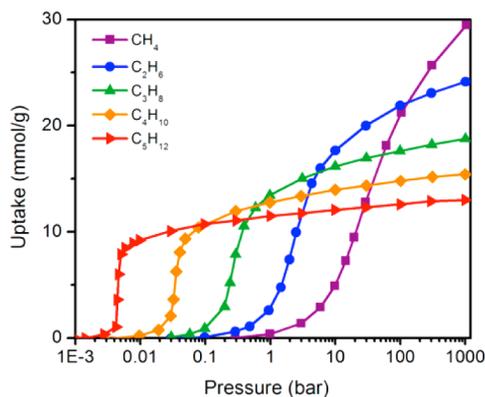
Figure 2. Theoretically determined adsorption isotherms of linear alkanes in MOF-5 at 300 K. Reprinted with permission from ref 41. Copyright 2006 American Chemical Society.

that occurs at different pressures depending on the linker length. Generally, increasing the length of the linker leads to decreased selectivity. However, the framework containing 9,10-anthracene dicarboxylate, which has the same length as bdc^{2-} but more aromatic surfaces lining the pores, was found to exhibit selectivities an order of magnitude higher than that of MOF-5.

The strength of adsorption is more than double for *n*-butane than for methane in both MOF-5 (−23.6 and −10.6 and kJ/mol, respectively) and Cu$_3$(btc)$_2$ (−29.6 and −12.0 kJ/mol, respectively).[43] Many theoretical alkane separation processes have also shown similar results in Cu$_3$(btc)$_2$ (Figure 1).[20,44−47]

Adsorption strengths for methane, ethane, propane, and butane in MIL-47 (Figure 1) increase with chain length, and pairing theory with experiment suggests that no preferential binding sites exist within the pores at low loadings.[48,49] At high loadings, methane and ethane prefer the μ_2-O groups while *n*-butane prefers the aromatic linkers. Propane and ethane were shown to rotate freely and have no preferred orientation, while *n*-butane is more confined.

Differences in adsorption behavior among linear alkanes is also seen in MIL-53(Cr) (Figure 1), where at 303 K a step is observed in the adsorption of *n*-propane through *n*-nonane, but not for methane or ethane.[50] Powder diffraction data suggest that this step is associated with framework swelling.[51] Structural transitions occur as a result of the relative affinities of any guest for the open or closed forms of the structure.[52] Generally, alkane adsorption in the MIL-53 series, including amino-MIL-53,[53,54] is highly temperature dependent due to the thermodynamics of the framework breathing. Interestingly, despite their isostructural nature the same steps seen in MIL-53(Cr) arise in MIL-53(Al) at different pressures.[50]

Adsorption isotherms for C1−C4 gases in MIL-53(Fe) are much more complex than in the MIL-47 or MIL-53(Al, Cr) cases.[55] At 303 K, MIL-53(Fe) has two intermediate phases in addition to the completely open or completely closed structures. This difference leads to stepwise adsorption of all short alkanes as opposed to only those with three carbons and higher.

Highly flexible materials outside of the MIL series can exhibit behavior similar to that of the MIL-53 frameworks. In the flexible framework material Zn$_2$(bpdc)$_2$(bpee) (bpdc^{2-} = 4,4′-biphenyldicarboxylate; bpee = 1,2-bipyridylethylene), the gate opening pressure decreases with alkane size from *n*-butane to methane.[56]

In ZIF-8 (Figure 1), the capacity hierarchy for short alkanes is methane > ethane > propane > *n*-butane.[57] In ZIF-7, which is built from benzimidazole in contrast to the 2-methylimidazole linkers of ZIF-8, ethane, propane, and *n*-butane show gate-opening pressures of 0.12, 0.012, and 0.008 bar, respectively, at 298 K.[58] These results demonstrate that adsorption strength is inversely correlated with gate-opening pressure. The compound Ni$_8$(5-bbdc)$_6$(μ_3-OH)$_4$ (bbdc^{2-} = 5-*tert*-butyl-1,3-benzenedicarboxylate) can also discriminate methane/ethane or ethane/propane mixtures based on gate-opening phenomena, and, by carefully controlling the temperature, it is possible to separate methane and ethane from propane and butane, or separate methane from ethane, propane, and butane.[59]

To summarize, trends can be found among short normal alkane adsorption in metal−organic frameworks. Adsorption steps are often seen, either from a gate-opening step in the material or from capillary condensation within the pores. These steps occur at different pressures for different adsorbates. Additionally, the molar capacity is usually comparatively higher for shorter alkanes while the strength of adsorption is lower. The smaller size allows for more molecules to fit in the pores, but each adsorbate has less molecular surface area for van der Waals interactions. Due to the variety of adsorption step locations as well as the consistent thermodynamic behavior of adsorption, it can be assumed that metal−organic frameworks could be used to separate many more mixtures of linear alkanes than the ones reviewed here.

Long Normal Alkanes. The same trends and behaviors seen for shorter normal alkanes extend to longer normal alkanes, as does the conclusion that most separations are possible using metal−organic frameworks. The studies of longer alkanes reported here are all at temperatures between 294 and 313 K in metal−organic frameworks with rigid structures.

The strength of adsorption between longer alkanes and the surfaces of metal−organic frameworks is generally correlated with the potential for van der Waals interactions. Accordingly, the reported strengths of adsorption followed the order *n*-pentane > propane > butane in Zn$_2$(bdc)$_2$(dabco) (dabco =1,4-diazabicyclo[2.2.2]octane), which has a structure in which two-dimensional sheets of bdc^{2-}-linked zinc-paddlewheel units are pillared by dabco.[60] This trend can presumably explain the behavior of an analogous framework, Zn$_2$(bdc)$_2$(bpy) (bpy =4,4′-bipyridine), which can separate *n*-pentane from *n*-hexane.[61] Similarly, a porphyrin-linked covalent polymer, PCPF-1, demonstrates linearly increasing adsorption capacities for C5−C8 linear hydrocarbons.[62]

Comparisons among adsorbents rather than adsorbates also confirms the role of van der Waals forces in alkane separations. The adsorption of pentane, hexane, and heptane in MOF-5 is weaker than in MOF-5 isostructures with longer linkers owing to the fewer available van der Waals interactions with each individual linker.[36]

Mechanisms other than thermodynamic selectivities have also been shown to separate long alkanes. As alkanes increase in length, pore size can begin to dictate differences in adsorption. A metal−organic framework with cylindrical channels and small channel windows, Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ (H$_2$fipbb = 4,4′-(hexafluoroisopropylidine)bis(benzoic acid)), can selectively sieve linear hydrocarbons longer than butane, as modeling shows that the corrugations along the channels creates pockets which can accommodate short alkanes but not *n*-pentane or higher.[63]

While Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ has uniform pores, separate types of pores within the same material can also dictate separation. The differences in adsorption of C5−C9 linear alkanes were explored in MIL-100(Cr) and MIL-101(Cr).[64]

All adsorbates exhibit a small adsorption step only apparent at low pressures. In MIL-100, this was attributed to the filling of the smaller of the two types of pores in the material based upon the percentage each contributed to the total volume. In both materials, n-nonane was adsorbed significantly less than the smaller alkanes due to entropic effects.

MIL-47, MIL-53(Cr), and a series of flexible MIL-88(Fe) structures have been investigated for longer alkane adsorption and separation. Increasing the alkane chain length leads to a decrease in the molar uptake capacity for MIL-47 and MIL-53.[65−67] The MIL-53 isotherms show a distinct step that occurs at a lower pressure for n-nonane compared to n-hexane, and similar results were seen with the MIL-88(Fe) materials. Interestingly, simulations illustrate that shorter alkanes are more distorted from a traditional trans conformation in MIL-47.[68]

Changes in adsorption attributed to flexibility are not confined to the MIL-53 series. A flexible material TetZB constructed from zinc nodes, 4,4′-bipyridine, and tetrakis[4-(carboxyphenyl)oxamethyl]methane is an open pore structure when evacuated and closes upon initial alkane adsorption.[69] Comparing among normal alkanes, the adsorption step moves to higher pressures for longer hydrocarbons. This is in contrast to other stepwise adsorption behavior in metal−organic frameworks such as MOF-5,[36] and industrially this reversal could render TetZB an ideal material for a specific set of separation conditions.

Cyclic Alkanes. Cyclic alkanes, often referred to as naphthenes, such as cyclohexane, decalin, and terpenes, compose up to 60% of the hydrocarbon content in petroleum.[22] They are produced as part of the cracking process. Cyclohexane and cyclododecane are used industrially, while cyclopentane is not.

Generally, linear alkanes bind more strongly than their cyclic counterparts in metal−organic frameworks. Presumably, this is a result of linear alkanes maximizing van der Waals surface overlap, whereas cycloalkanes have geometric restrictions to adsorption. The strength of adsorption of n-hexane is significantly higher than that of cyclohexane in MIL-100(Fe) and MIL-100(Cr),[70] MIL-47,[65] M(bdc)(ted)$_{0.5}$ (M = Zn, Cu) (ted = triethylenediamine),[71] and amino-MIL-53.[53]

The large pore surfaces of MOF-5 only vaguely follow the above trend. Theoretically, MOF-5 adsorbs n-decane only approximately 10% more strongly than butylcyclohexane.[40] Cyclohexane and n-hexane bind with the same adsorption strength, while the larger dipole moment of methylcyclohexane leads to a 10% stronger interaction. In contrast, lower-surface-area isostructures of MOF-5 with more bulky and longer linkers show a strength of adsorption much higher for n-hexane than for cyclohexane.[35]

Capacities of linear and cyclic alkanes do not necessarily follow as predictable of a trend as adsorption strength: the capacity for cyclopentane and n-pentane are comparable in the porphyrin-linked covalent polymer PCPF-1, while the cyclohexane capacity is nearly 50% higher than the n-hexane capacity.[62]

Branched Alkanes. The separation of branched and linear alkanes is highly relevant to gasoline production. Octane number, which is proportional to economic value, is higher for branched isomers than for linear alkanes. For C5, C6, and C7 hydrocarbons, the mixture from the distillation unit is fed into an isomerization reactor, which transforms the mixture into equilibrium ratios of the isomers. The less valuable linear isomers are removed by sieving and fed back into the isomerization unit, while the rest of the isomers are added to gasoline.[72] n-Butane is used to generate isobutane, which is then used in alkylation reactions to generate higher-octane chains.[73]

Separation of linear alkanes from their branched counterparts has been reported in metal−organic frameworks. Binary C4 and C5 isomer mixtures were investigated computationally in MOF-5 and one of its isostructures with an amino group on the central benzene ring of the linker. The branched isomers exhibited higher uptake capacities than the linear isomers.[74] Small differences in adsorption enthalpy between linear and branched isomers are seen both experimentally and theoretically in Cu$_3$(btc)$_2$ and MOF-5,[41,43] and some other metal−organic frameworks can sieve linear alkanes from their branched isomers.[63,65]

The separation of linear from branched alkanes does not necessarily improve upon existing technology, as zeolites currently perform these separations with a sieving mechanism. Separation among the branched isomers, however, represents a new frontier in this (nondistillative) technology. Importantly, among nonlinear alkanes, more branching is associated with a higher octane number and value. This type of separation is illustrated in Figure 3b. Ideally, the separation will generate fractions according to branching, as seen in the schematic, but two fractions composed of the most valuable dibranched isomers and all of the lesser valuable isomers together is also an advance in this technology. The tunable pore surface
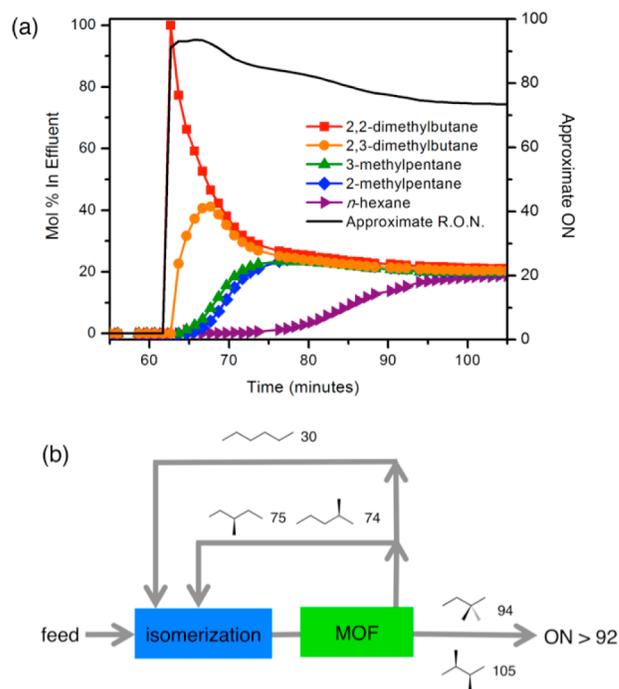
Figure 3. (a) Breakthrough results of hexane isomers on a column of Fe$_2$(BDP)$_3$. (b) Schematic demonstrating the separation process possible when the separation generates fractions according to the degree of branching (ON = octane number).[72]

geometries in metal−organic frameworks allow for shape selectivity and therefore advances in this separation.

Modeling studies demonstrate the promise of metal−organic frameworks for shape-selective isomer separations. Calculations show MOF-5 to be capable of separating all three pentane isomers at 300 K.[41] The linear isomers were found to adsorb near the vertices, while the branched ones were sterically hindered from doing so. Similarly, the isomers of butane and pentane were modeled in two pairs of comparable metal−organic frameworks.[75] An isostructure to MOF-5 with a pyrene-derived linker, IRMOF-14, and its catenated counterpart were one pair. The other pair was again catenated and noncatenated versions of the same material, here an isostructure to $Cu_3(btc)_2$ with a triazine−tribenzoate linker. In the 20 total isotherms (five adsorbates in four materials), all showed stepwise adsorption. Contrary to previous results,[44] the experiments showed that all materials were selective for the less branched isomer in any isomer pair and that the catenated frameworks adsorbed these more selectively.

Two-dimensional sheets composed of zinc paddlewheels pillared by nitrogen-donor ligands have been extensively studied for branched isomer separations. In a five-component breakthrough experiment in which a mixture of n-pentane, 2-methylbutane 2,2-dimethylbutane, 2-methylpentane, and n-hexane was passed through a column of $Zn_2(bdc)_2(bpy)$, only 2,2-dimethylbutane and 2-methylpentane showed any overlap.[61] A 13-component mixture of pentane, hexane, and heptane isomers was simulated in the pores of a similar material, $Zn_2(bdc)_2(dabco)$.[76] With the exception of 2,3-dimethylpentane, the adsorbates followed a general trend of higher octane numbers achieving lower uptake capacity. This was explained with the concept that more flexible alkanes were able to "adapt" to the pore environment and utilize the available surface area more effectively. Experimentally, $Zn_2(bdc)_2(dabco)$ has been shown to separate n-hexane, 3-methylpentane, and 2,2-dimethylbutane.[77]

In addition to canonical materials such as MOF-5, $Cu_3(btc)_2$, and the group of pillared frameworks covered above, other metal−organic frameworks have been studied in isolation. Amino-MIL-53(Al) was demonstrated to somewhat separate pentane, hexane, and heptane isomers through a shape selective mechanism.[53] This conclusion was arrived at by examining the nonlinearity of the relationship between vapor pressure and Henry's constants, which has previously been demonstrated to correlate with shape selectivity. Additionally, single-component isotherms in $Zn(Hbdc)(dmtrz)$ (dmtrz = 3,5-dimethyl-$1H$,1,2,4-triazole) suggest that the material is selective for n-hexane and 3-methylpentane over 2,2-dimethylbutane.[78] A variety of hexane binary breakthrough experiments were performed at 398 K on ZIF-76, ZIF-8, and IM-22, a material designed specifically for alkane isomer separations.[79] Among these materials, the best performance was seen in IM-22 which achieved a modest separation of 3-methylpentane from 2,2-dimethylbutane.

The above examples illustrate the preferred elution order for branched alkane separations, where more branched alkanes elute first. This is because isolating the least adsorbed species is more straightforward than isolating the most adsorbed isomer. This order is not always observed, as seen in UiO-66.[80] On the basis of the pore size, the order of elution in a breakthrough column is n-hexane, followed by 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane. The separation is not complete, however. Modifications to this material can be made which effect its performance; decorating the linker with functional groups changes the pore size and somewhat alters the order of elution.[81]

The above examples illustrate marked improvements in alkane isomer separations over zeolites; however, none offer a complete separation of the considerably more valuable highly branched isomers from the less branched. In contrast, it has been shown experimentally that the five hexane isomers can be separated into useful fractions on a column of $Fe_2(BDP)_3$ ($BDP^{2−}$ = 1,4-benzenedipyrazolate), a metal−organic framework with triangular channels (Figure 1).[72] The acute angles in the pores of this structure are able to maximize interactions with n-hexane and show increasingly weaker interactions and greater entropic costs for the more branched hexanes. Such regular sharp angles are generally not possible in zeolites, owing to the obtuse Si−O−Si and O−Si−O bond angles, and this separation serves as an example of the properties of metal−organic frameworks allowing for advances in separation technologies. Breakthrough experiments are able to separate an equimolar mixture of hexanes into three fractions: the dibranched, monobranched, and linear hexane (Figure 3a). This result allows for a potentially even greater improvement to the isomerization process, because n-hexane can be added to the reactor earlier than the methylpentanes, which would increase efficiency (Figure 3b). These properties are a result of the triangular shape of the channels and also the width of those channels: simulations showed that a slightly wider triangular channel would reduce the amount of surface area associated with the triangular corner features, while a narrower channel would not accommodate all of the hexanes. Importantly, these results were also shown computationally to extend to pentanes and heptanes, even enabling fractionation of a C5−C7 mixture by degree of branching.

Computationally, over 100 metal−organic frameworks have been examined for hexane and heptane isomer separation at 433 K.[82] By examining both the uptake capacity and the selectivity for branched over linear isomers—metrics that are explained to be equally important to the engineering separation process—the authors were able to discover that ZIF-77, a rarely discussed metal−organic framework, is particularly well suited for separating dibranched from monobranched from linear isomers. Potentially, these results could be verified experimentally and compared to those of $Fe_2(BDP)_3$.

The above examples all pertained to gasoline. Similarly, in diesel fuel longer alkanes such as cetanes (16 carbon chains) have variable worth in the final product.[83] n-Hexadecane is much more valuable than its isomer 2,2,4,4,6,8,8-heptamethyl-nonane (isocetane),[84] and these isomers can be separated by sieving in $Zn_2(adc)_2(dabco)$ ($adc^{2−}$ = 9,10-anthracenedicarboxylate).[85]

■ UNSATURATED HYDROCARBONS

Although alkenes are generally not present in petroleum[22] they can be found in distilled fractions as a result of the cracking that occurs during distillation. They are also synthesized from a variety of reagents and used as extremely important industrial precursors, mostly for making polymers. For example, nearly 25 trillion tons of ethylene are generated per year, and the vast majority of the cost of production is in separation from other hydrocarbons.[86]

Here, the treatment of metal−organic frameworks for separations involving unsaturated hydrocarbons is subdivided into four categories. Some examinations do not fall neatly into

one of these categories, such as the adsorption of propylene, isobutene, and propane in Cu$_3$(btc)$_2$[87−89] and MIL-100(Fe),[90] the adsorption of methane, acetylene, ethylene, and propane in a novel covalent-organic framework,[91] and acetylene/ethylene separation in an enantiopure metal−organic framework.[92]

Of metal−organic frameworks that boast impressive alkane/alkene separation abilities, two main strategies can be seen: sieving and adsorption on unsaturated metal centers. Sieving materials such as ZIF-8 selectively adsorb the alkane, while unsaturated metal centers preferentially interact with the alkene or alkyne through interaction with the π-system.[93,94] These unsaturated metal centers are found in the M$_2$(dobdc) series; however, other materials such as MIL-100(Fe)[95] and Cu$_2$L-(H$_2$O)$_2$ (L$^{4−}$ = biphenyl-3,3′,5,5′-tetra(phenyl-4-carboxylate)[96] can also interact strongly with double bonds in a side-on fashion to generate strong selectivities. The identity of the metal center can alter the separation ability, and generally softer metals interact more strongly with double bonds.

In each of the sections below considering C1, C2, and C3 alkene/alkane separations, the remarkable separation results of Fe$_2$(dobdc) are presented.[97] Neutron diffraction studies of methane, acetylene, ethane, ethylene, propane, and propylene not only show verifiably the side-on binding of the double bond to the metal center, but also the short distances between the hydrogen atoms and the Fe^{2+} cations for the unsaturated adsorbates (Figure 4). Computational modeling has confirmed these results.[98]

Methane/Acetylene. Acetylene is typically viewed as less industrially relevant than ethylene[99] and can be obtained as a byproduct of petroleum and natural gas processing.[33] Additionally, a number of industrial processes exist for the oxidative and nonoxidative coupling of methane into ethane, ethylene, and acetylene, although many of these processes realize incomplete methane conversion. Thus, there is a clear benefit to recovering unreacted methane from these processes. Given the large differences in the physical properties of methane and C2 hydrocarbons, both size selective effects and metal−hydrocarbon interactions can be tuned to achieve a high selectivity within a metal−organic framework.

There have been a number of recent reports investigating methane/acetylene separations with metal−organic frameworks.[100−113] The earliest was in Cu$_2$(EBTC) (EBTC$^{4−}$ = 1,1′-ethynebenzene-3,3′,5,5′-tetracarboxylate).[100] This framework boasts a high surface area and open Cu^{2+} sites similar to those found in Cu$_3$(btc)$_2$ (Figure 1), and an acetylene uptake capacity (7.14 mmol/g) nearly 10 times higher than that of methane at 295 K. The strength of acetylene adsorption in this material is substantially higher than in Cu$_3$(btc)$_2$ (as well as another material with open Cu^{2+} binding sites, MOF-505). This is likely a combined result of Cu^{2+}−acetylene interactions, pore size, geometry, and a weak interaction between the carbon−carbon triple bond of acetylene and EBTC$^{4−}$.

A majority of the subsequent studies of methane/acetylene separations have involved low-surface-area frameworks (<700 m^2/g BET), often exhibiting interpenetration.[103,104,108,114−118] These materials typically suffer from capacity limitations. For example, Zn$_5$(bta)$_6$(tda)$_2$ (bta$^−$ = 1,2,3-benzenetriazolate, tda$^−$ = thiophene-2,5-dicarboxylate) displays a selectivity of 15.5 for an equimolar acetylene/methane mixture at 295 K, but an acetylene capacity of just 1.96 mmol/g at 1 bar.[103]

In contrast, compounds of the type M$_2$(dobdc) couple selectivity for adsorption with high surface area and a high density of open metal sites.[97] For example, Fe$_2$(dobdc) displays
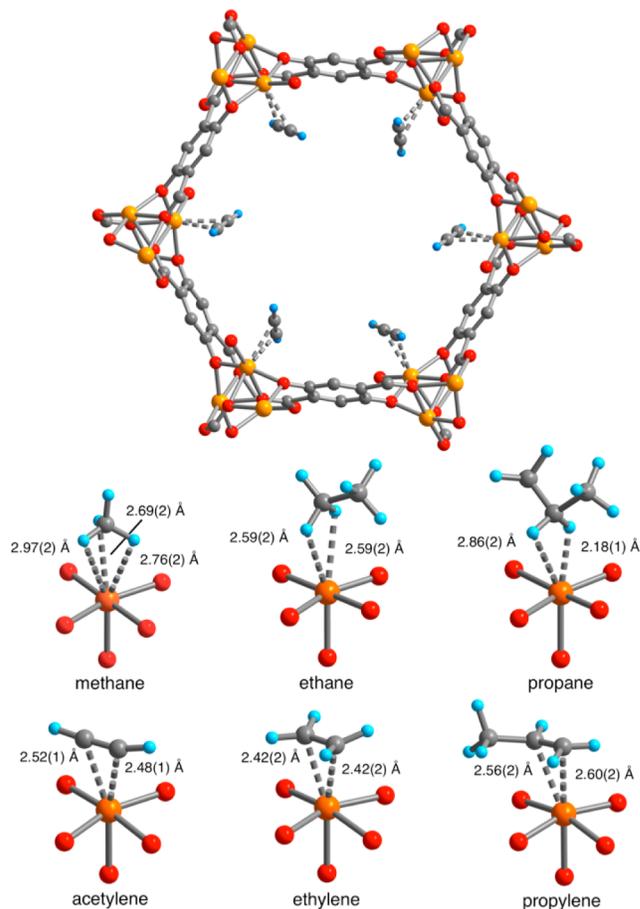
Figure 4. (Top) Structure of acetylene bound to the open Fe^{2+} sites in Fe$_2$(dobdc), where orange, red, gray, and blue spheres represent Fe, O, C, and D atoms, respectively, and (bottom) the first coordination spheres for the iron centers in the solid-state structures obtained upon dosing methane,[136] ethane, propane, acetylene, ethylene, and propylene.[97]

an acetylene capacity of 6.89 mmol/g and an acetylene/methane adsorption selectivity of approximately 700 at 1 bar and 318 K (from an equimolar mixture of methane, ethane, ethylene, and acetylene). This is a direct result of the large difference in the isosteric heat of adsorption between the two molecules (−47 kJ/mol vs −20 kJ/mol). Additionally, both Mg$_2$(dobdc) and Co$_2$(dobdc) are well-suited for the separation of acetylene and methane. Both frameworks bind acetylene with more than twice the adsorption strength of methane. Calculations indicate that these frameworks will perform well in the separation of methane from an equimolar methane, ethane, ethylene, and acetylene mixture at 296 K and 1 bar of total pressure.[119] On a volumetric basis, they outperform 19 other frameworks investigated, as well as materials with open Cu^{2+} sites such as MOF-505, Cu$_3$(btc)$_2$, and PCN-16.

Ethane/Ethylene. Ethylene is generated primarily by refining crude oil, and over 10^8 tons of it were produced in 2005. After the cracking process, the series of separations to isolate ethylene from the dozens of other hydrocarbons present are incredibly complex. Ethane is an important feedstock for ethylene production, and as a result the separation of ethylene from ethane is of great industrial relevance.[120]

Sieving in metal−organic frameworks can enable the discrimination of ethane and ethylene. The compounds ZIF-7 and ZIF-8 illustrate this concept. The adsorption isotherms for

ethane and ethylene in ZIF-7 at 298 K are Type IV, with negligible uptake until a "gate-opening" event, after which uptake rapidly increases and quickly saturates at approximately 1.75 mmol/g.[58,121] The three regions of the adsorption isotherm are explained as adsorption to the external surface of the particles, gate opening and adsorption in the cavities of the material, and, finally, filling of the cavities with adsorbate. The pore apertures in ZIF-7 of ~3 Å are too small to allow adsorption of either molecule and significant structural flexing must take place for adsorption to occur. It has been postulated that the threefold symmetry of the methyl groups of ethane allows the molecule to interact favorably with the triangular pore windows of the framework. This allows ethane to adsorb at lower pressures than ethylene. Accordingly, ZIF-7 performed well in an actual separation process, producing pure ethylene from an equimolar mixture in a breakthrough experiment. Similarly, ZIF-8 selectively adsorbs ethane over ethylene.[17,122,123]

Thermodynamic separations of ethane and ethylene can also be achieved in metal−organic frameworks. Ethane and ethylene are equally polarizable, lack a dipole moment, and have small quadrupole moments,[4] and therefore metal−organic frameworks with exposed cation sites are one of the few attractive options for their efficient separation. Frameworks without this feature adsorb ethane and ethylene with nearly identical adsorption enthalpies, including MOF-5[40] and amino-MIL-53,[53] and an entire series of zinc carboxylate frameworks that have been extensively studied for this application.[110,111,114−118]

The first investigation into metal−organic frameworks with open metal sites for ethane/ethylene separations was performed with $Cu_3(btc)_2$[44] and has been followed up computationally.[124,125] The noticeable difference in the shapes of the isotherms indicate ethylene selectivity. Subsequent calculations showed that ethylene binds stronger than ethane based on both hydrogen bonding interactions between the −CH₂ protons and the electronegative oxygen atoms in the $Cu_2(O_2C)_4$ paddlewheel units, as well as some degree of π-backbonding from the copper cations to the alkene. Given its very limited backbonding capability, this framework displays a theoretical IAST selectivity of only approximately 2 for an equimolar ethylene/ethane mixture at 1 bar and 298 K.[126]

The $M_2(dobdc)$ frameworks perform exceptionally well for the separation of ethane/ethylene mixtures. The first reports were of ethane and ethylene isotherms in $Mg_2(dobdc)$ at various temperatures.[127] Although this framework displays similar saturation capacities for these two gases at a given temperature, the isosteric heat of adsorption of ethylene is much higher than that of ethane (−43 vs −27 kJ/mol). Although the isosteric heat of ethane adsorption increases with increasing loading, likely a result of adsorbate−adsorbate interactions, the ethylene adsorption enthalpy remains higher over the entire loading range investigated. As expected, GCMC calculations indicate that the primary adsorption site is the coordinatively unsaturated Mg^{2+} cation.

With soft, high-spin Fe^{2+} cation sites exposed on its surface, $Fe_2(dobdc)$ performs even better for the separation of these molecules.[97] Increased π-backbonding as compared to Mg^{2+} results in an increased selectivity for ethylene over ethane, which increases from 7 in $Mg_2(dobdc)$ to 18 in $Fe_2(dobdc)$. In a breakthrough experiment, $Fe_2(dobdc)$ is capable of separating an equimolar ethane/ethylene mixture at 1 bar and 318 K into 99% and 99.5% pure components, respectively. Neutron powder diffraction experiments confirm that indeed the

unsaturated metal cation is the strongest adsorption site, and ethylene adsorbs via the anticipated side-on binding mode (Figure 4). Other members of the $M_2(dobdc)$ family both theoretically and experimentally display high ethylene/ethane selectivity based on preferential coordination of the alkene to the metal cations in these frameworks.[119,128] The selectivity follows the trend $Fe^{2+} > Mn^{2+} > Ni^{2+} \approx Co^{2+} > Mg^{2+} > Zn^{2+}$, which is likely associated with the relative softness of the (high-spin) metal center, together with its ability to engage in π-backbonding.

Propane/Propylene. Like in ethane/ethylene separations, $Cu_3(btc)_2$ was among the first metal−organic frameworks to be studied for propane/propylene separations[87−89] and since then has been investigated extensively.[129−135] Analogous to its performance in methane/acetylene and ethane/ethylene separations, this material preferentially binds propylene over propane (−41.8 vs −28.5 kJ/mol at zero coverage) over a wide pressure range.[87] GCMC simulations suggest that propane is adsorbed most strongly in the small octahedral pockets present in the framework and that the strongest propylene binding sites in the framework are the Cu^{2+} sites. UV−vis spectroscopy confirms this as the primary propylene adsorption site because the d−d band associated with the Cu^{2+} cations centered at 540 nm shifts to a lower energy upon propylene coordination.[130] Propane has little to no effect on the UV−vis spectrum, supporting the notion that the primary adsorption sites are likely the octahedral cages in the framework. The promising results of $Cu_3(btc)_2$ propane/propylene separations have sparked interest in the mechanical stability and performance of the material, and one of the first steps in using industrial adsorbents is to shape them into pellets. Research has shown that spheres of $Cu_3(btc)_2$ maintain the highest propylene capacity upon shaping,[134] followed by tablets[89] and extrudates.[88]

ZIFs also show selective propane/propylene adsorption behavior through a sieving mechanism, as evidenced by size exclusion studies in ZIF-8.[123,137] Similarly to ethane, ZIF-7 displays inverse selectivity at 373 K, preferentially adsorbing propane over propylene.[58,121] This is thought to be a result of a gate opening effect in which propylene has a more favorable adsorption on the external surfaces of ZIF-7, delaying the pressure at which the framework opens.

Although other metal−organic frameworks display moderate propylene/propane selectivity based on gate opening and kinetic effects,[56,138] shape selectivity,[53] and pore size constraints,[111,114] the most selective materials are typically those containing a higher density of coordinatively unsaturated metal cation sites than in $Cu_3(btw)_2$. Every $M_2(dobdc)$ isostructure, with the exception of the newly synthesized copper analogue, has been investigated for propane/propylene separation.[93,97,119,127,128,139] In all cases $M_2(dobdc)$ binds propylene over propane with selectivities between 3 and 20, assuming an equimolar mixture. All six materials show increasing selectivity with increasing pressure as adsorbate−adsorbate interactions become more important. At 318 K and 1 bar of total pressure, $Fe_2(dobdc)$ is capable of separating an equimolar propane/propylene mixture into greater than 99% pure components. Another iron-based metal−organic framework, MIL-100(Fe), is capable of separating propane/propylene mixtures upon reduction of a portion of its Fe^{3+} centers.[95,140,141] The presence of open Fe^{2+} sites leads to an increase in the isosteric heat of propylene adsorption from −30 to −70 kJ/mol.

Long Alkanes and Alkenes. Alkanes are the primary starting materials for alkene synthesis, and the products of these reactions are mixtures of alkenes and unreacted alkanes which require separation for purification of various industrial feedstocks.[22,33] While some alkenes such as cyclohexene are not industrially relevant,[33] they are nonetheless informative from a fundamental perspective.

Separating longer alkenes from alkanes is more complex than shorter chains because of the distinct hydrophobic interactions of the long chains and interactions with the π cloud of the double bond. Sieving has been shown to be possible, as in the example of isobutane separation from C2 and C3 alkanes and alkenes due to rational design of pore sizes in Zn−carboxylate metal organic frameworks.[59,142] Additionally, hints of separation ability were reported in ZIF-7, where the saturation capacity of *trans*-2-butene is markedly lower than that of *n*-butane, *cis*-2-butene, and 1-butene.[58]

As a result of greater molecular surface area and geometric flexibility in long alkanes, their adsorption is generally stronger than that of their corresponding alkenes. This trend is seen for *n*-octane and 1-octene in a suite of metal−organic frameworks without unsaturated metal centers.[143] In a separate study, isostructures of MOF-5 were shown to bind *n*-hexane more strongly than 1-hexene. The strength of interaction was highest for MOF-5 and decreased with increasing carbon atoms per linker.[35] Modeling shows *n*-pentane adsorption to be slightly stronger than that of 1-pentene in MOF-5.[40]

As in shorter alkane/alkene separations, the most successful mechanisms rely on open metal sites, and these sites are selective for the alkene. This was shown by comparing metal−organic frameworks with and without these sites.[143] Additionally, the open metal sites in $Cu_3(btc)_2$ have been studied in depth. The material shows an expected preference for 1-pentene over *n*-pentane.[144] Isobutane and isobutene were also separated in this material, and the isosteric heats of adsorption were determined to be −42 and −46 kJ/mol, respectively.[145] A breakthrough experiment at 303 K revealed excellent separation characteristics.

MIL-53 and MIL-125 examples serve to illustrate that selective adsorption of longer alkenes and alkanes is complex and does not always depend on the presence of open metal centers. Despite a lack of these sites, strengths of adsorption within amino-MIL-53(Al) are higher for the alkene in pairs of C2, C3, and C5 normal alkanes and 1-alkenes.[53] *n*-Hexane and 1-hexene did not adhere to this pattern, and the binding was stronger to the alkane. *n*-Butane also bound more strongly than 1-butene; however, the experimental details were reported to be nonideal. This unexpected behavior is not limited to the MIL-53-type MIL materials, as isoprene was selectively adsorbed over 2-methylbutane in liquid-phase batch experiments in MIL-125 and amino-MIL-125.[146]

Alkene Mixtures. Alkene/alkene separations primarily consist of cis/trans isomer separations. The four butene isomers are generated during the cracking process, and their large-scale commercial use has been hampered by the lack of separation technologies to isolate individual isomers. Distillative separations of all four isomers are not feasible due to their close boiling points.[73] Therefore, over 70% of butene mixtures are used directly in either gasoline or alkylation reactions to form high-octane components of gasoline; however, about 10% are able to be used for specialty chemical manufacture.[147] The *cis* and *trans* isomers have varying reactivity and utility, and so improved separation technologies are an ongoing challenge.[148]

The adsorption of butenes has been reported in many materials. The compound $Cu(hfipbb)(H_2hfipbb)_{0.5}$ adsorbs 40% more of the *trans* isomer at 303 K,[63] as it is more volatile. In ZIF-7,[58] *cis*-2-butene fits into the pores better than the *trans* isomer. Interestingly, neither butene isomer was appreciably adsorbed in MIL-53(Al) or MIL-47, although the pore apertures are large enough to accommodate them as guests.[149]

In an *n*-hexane solution, $Cu_3(btc)_2$ selectively adsorbs *cis*-butene over the *trans* isomer, with a modest separation factor of 1.9:1.[149] The *cis* isomer is often favored in zeolites due to π-complexation with extraframework cations, and the open Cu^{2+} sites in $Cu_3(btc)_2$ result in the same behavior. As four Cu^{2+} centers point into one pore, after the adsorption of one butene per four Cu^{2+} centers, the selectivity drops. These results represent a vast improvement over the current near-inability to separate these isomers industrially. This separation extends to longer hydrocarbon *cis/trans* isomer pairs, as high as methyl-9-octadecenoate. An aluminum-based framework with benzene-tricarboxylate linkers, MIL-96, adsorbs more than double the amount of the slim *trans*-piperyline compared to *cis*-piperyline or isoprene.[144] This is also reflected in the enthalpies of adsorption of −54.6, −53.0, and −52.1 kJ/mol, respectively. A breakthrough column separated these alkenes as well.

In addition to *cis/trans* isomer separations, many other alkene mixture separations have been reported. In catalytic dehydrogenation processes, the location of double bonds in alkenes is random, and different alkene position isomers are feedstocks for specialty chemicals.[33] In $Cu_3(btc)_2$, the preferential adsorption of butane position isomers follows *cis*-2-butene > 1-pentene > *trans*-2-pentene.[149] In ZIF-7, the saturation capacity of 1-butene is nearly 25% lower than either 2-butene isomer at 338 K, although the capacity for *trans*-2-butene drops below the other butenes at 373 K.[58]

Alkenes with the double bond at the 1-position have the most industrial utility. They are synthesized in a variety of ways, but when produced from *n*-alkanes they are generated as a mixture of chain lengths.[33] The separation of 1-alkenes, ranging from ethene to hexene, was investigated in amino-MIL-53(Al). Adsorption enthalpy increased in magnitude approximately linearly with carbon number.[53]

In a more esoteric type of alkene separation, a homochiral Cd^{2+}-based framework theoretically achieved partial separation of enantiomers of 1,3-dimethyl-1,2-propadiene, 1,2-dimethylcyclobutane, and 1,2-dimethylcyclopropane.[151]

■ AROMATICS

Aromatics are present in all petroleum, and benzene is generally among the least represented molecules compared to others like substituted benzenes.[32] As polymer precursors, 24.6 million tons of styrene are produced per year. Vinyl toluenes[152] and cumene[153] are also important precursor molecules that require separation. Xylenes and other substituted benzenes are almost exclusively generated as mixtures and are important additives in gasoline. *p*-Xylene is used for industrial chemical processes of much more value than other C8 alkylaromatics, leading to the necessity of separation. The close boiling points lead to highly difficult and inefficient distillative separation processes. Ideal separation materials preferentially bind *p*-xylene. Approximately 60% of *p*-xylene is currently separated using adsorptive strategies; however, there is reported need for improvement in this technology. Once *p*-xylene is removed,[154] the remaining products also have disparate industrial worth. Subsequently, materials are valuable that selectively adsorb *m*-xylene, the next

(a)   (b)   (c)   (d)
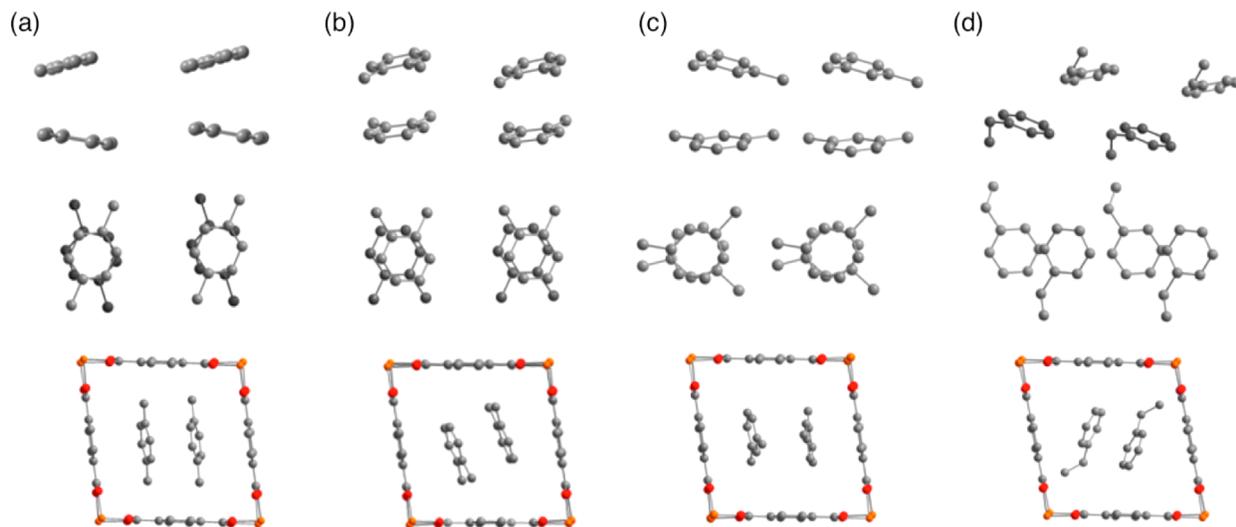
Figure 5. Structures of (a) *p*-xylene, (b) *o*-xylene, (c) *m*-xylene, and (d) ethylbenzene in MIL-47, where gray, red, and pink represent C, O, and V atoms, respectively. Reprinted with permission from ref 150. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

most valuable isomer, from mixtures which include other aromatics except *p*-xylene.[155]

C8 alkylaromatics, benzene, toluene, and polycyclic aromatic hydrocarbons dominate the body of work covering adsorptive separations of aromatic compounds in metal−organic frameworks. Some more esoteric separations have also been reported, such as separating fullerenes[156,157] or industrially relevant[158] substituted naphthalenes.[149,159]

Isosteric heats of adsorption for the most common aromatics studied in metal−organic frameworks—benzene, toluene, ethylbenzene, and xylenes—are available in Supporting Information Table S2. Among the many materials that have been studied, only MIL-47 and MIL-53 have shown substantial separation among the most industrially relevant mixtures. Specifically, MIL-47 demonstrated varying degrees of xylene separation ability among the many papers probing this adsorbent/adsorbate combination, including one detailing the excellent separation of *p*-xylene from *m*- and *o*-xylene. Additionally, MIL-53 can separate *p*-xylene from other xylenes and aromatics; however, this is through the nonideal process of selectively adsorbing the *para* isomer. MIL-101(Cr) was shown theoretically to separate xylene isomers in the elution order *p*-xylene > *m*-xylene > *o*-xylene,[160] and follow-up experimental studies could substantiate the promise of this material.[161] Due to the large body of work surrounding these materials and their exciting separation performance, they are treated in a separate section from the other materials.

Early work on metal−organic frameworks hinted at their ability to separate alkylaromatics,[162] and over time interesting behavior has been observed between metal−organic frameworks and aromatics. For example, one material forms in the presence of certain xylene isomers but not others.[163] Some materials have been reported to show almost no selectivity,[164,165] but the examples below illustrate the promise of metal−organic frameworks for aromatic separations.

In MOF-5, the theoretical order of adsorption strength increases in the order *m*-xylene > ethylbenzene > toluene > benzene.[40] MOF-5 can experimentally separate any xylene isomer from ethylbenzene in a breakthrough column, and in a quaternary mixture the three xylenes elute essentially together at 523 K.[166] Similarly, Zn$_2$(bdc)$_2$(dabco) binds alkylaromatics

preferentially, with the Henry's constants following the order *o*-xylene > *m*-xylene > ethylbenzene > *p*-xylene; however, quaternary breakthrough experiments show little to no separation.[167] The theoretical Zn$_2$(bdc)$_2$(dabco) selectivity for *o*-xylene over the other C8 aromatics lies between 1.3 and 1.9 at temperatures as high as 448 K.[168]

Breakthrough separations of *o*- and *p*-xylene in ZIF-8, ZIF-76, Cu$_3$(btc)$_2$, Ni$_2$(dobdc), and RHO-ZMOF, a zeolitic imidazolate framework with extraframework In^{3+} cations, showed selectivity for the *ortho* isomer with the exception of ZIF-8.[143] The reason for the selectivity in ZIF-8 was the required "saloon door"-style opening of the pore aperture, leading to sieving selectivity. Sieving is also seen in MIL-96, wherein tri-isopropylbenzene can be separated from *p*-xylene, *m*-xylene, and 1,3,5-trimethylbenzene.[169]

Nonsieving chromatographic separations have also been achieved. Benzene, toluene, ethylbenzene, and naphthalene were separated on a packed column of MIL-100(Fe) at 298 K using methanol and water as the mobile phase.[170] The framework Cd(4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole)$_2$ adsorbs only toluene and benzene in the presence of xylenes. When only xylenes are present, *o*- and *m*-xylene adsorb in equal amounts, while *p*-xylene is not adsorbed measurably.[171] In MIL-101, the molecular cross-sectional area is nearly linearly related to uptake capacity for alkylaromatic compounds,[172] although a packed column of MIL-101(Cr) was not found to separate the corresponding liquid mixture.[160]

Open-metal sites in Cu$_3$(btc)$_2$ and Ni$_2$(dobdc) have been theoretically shown to be inaccessible for binding the π-system in alkylaromatics.[155] Selectivity can still be seen in these frameworks, as Cu$_3$(btc)$_2$ can separate xylenes, benzene, toluene, and ethylbenzene chromatographically[20] and preferentially adsorbs a mixture of aromatics in the order decalin, tetralin, 1,2,4-trimethylbenzene, *o*-xylene, *p*-xylene, *m*-xylene, ethylbenzene, toluene, and finally benzene.[173] Modest adsorption selectivity has been observed in fibers coated with Cu$_3$(btc)$_2$, which adsorb more *p*-xylene than ethylbenzene, toluene, styrene, trimethylbenzene, or benzene.[174] Despite similar single-component isotherms and only modest separation in a breakthrough,[175] styrene and ethylbenzene were separated by a factor of 6 in batch experiments in Cu$_3$(btc)$_2$.[176]

Perhaps the most promising material outside of the MIL family for aromatic separations is UiO-66. This material separates ethylbenzene and all three xylenes in a breakthrough scenario, although the crucial separation between the *para* and *meta* isomers is only modest.[80,177]

MIL-47 and MIL-53. MIL-47 and MIL-53 have been studied extensively for aromatic hydrocarbon separations, both in tandem and individually. In these studies, theoretical models are highly useful, as C8 alkylaromatics in MIL-47 and MIL-53(Al) can be modeled with near-experimental accuracy.[178] When comparing the xylene selectivities in these frameworks, those in MIL-47 are much higher.[150] The strengths of adsorption of C8 alkylaromatics in MIL-47 are not substantially different, and coupling that observation with incongruent uptake capacities leads to the conclusion that entropic differences dominate the selectivities in this material, although enthalpic differences do enhance the separations. Rietveld refinement of powder diffraction data for MIL-47 crystallites loaded with the four C8 alkylaromatics confirmed this hypothesis, as shown in Figure 5. Styrene and ethylbenzene vapor separation in MIL-47 and MIL-53(Al) were also shown to be enthalpic for MIL-53(Al) and entropic for MIL-47, although the selectivity for styrene is higher in MIL-53(Al).[179] Density functional theory calculations support the hypothesis that xylene isomer separation is primarily entropically driven in MIL-47.[180]

Despite different separation mechanisms and performance, similar strategies can be used to modify sorption within the pores of MIL-47 and MIL-53. When the bdc^{2-} linker of MIL-47 or MIL-53(Al) is partially fluorinated, both *o*- and *p*-xylene are still adsorbed significantly, whereas water sorption is significantly less and the MIL-53(Al) fluorinated analogue is extremely water resistant.[181] This property is favorable because hydrolytic stability is crucial for industrial applications.

Due to its superior separation abilities, the mechanism of alkylaromatic adsorption in MIL-47 has been of great interest. Clear conclusions were extracted about the bonding of xylenes in MIL-47 using previous results and calorimetrically derived adsorption enthalpies.[153] The ethylbenzene heat of adsorption is derived primarily from the alkyl group interaction with the framework walls, while *p*-xylene can overlap with another *p*-xylene molecule and the walls of the framework ideally and *m*-xylene requires some tilt to fit into the pores that decreases the strength of adsorption. Both entropy and enthalpy factors result in chromatographic separation of ethylbenzene, while enthalpic factors are primarily responsible for the *para/meta* separation. These observations held true at high and low loadings. Most other alkylaromatics fall along a linear trend of increasing adsorption enthalpy with molecular polarizability.[182] Size exclusion generates small deviations from this trend, with mesitylene and *o*- and *m*-xylene being examples of lower enthalpy than expected based on their polarizability.

Breakthrough results vary drastically among different reports. This is often a byproduct of different experimental temperatures and total pressures; however, in a quaternary mixture at 338 K three separate fractions were observable: ethylbenzene eluted first, followed by a close combination of *p*- and *m*-xylene, and finally *o*-xylene (Figure 6).[183] In a separate study, MIL-47 showed selectivity for *p*- over *m*-xylene and almost complete separation of all three xylene isomers in a chromatographic column. This same sample could not separate ethyltoluene isomers.[184] Activation conditions were shown to alter its selectivity only slightly.
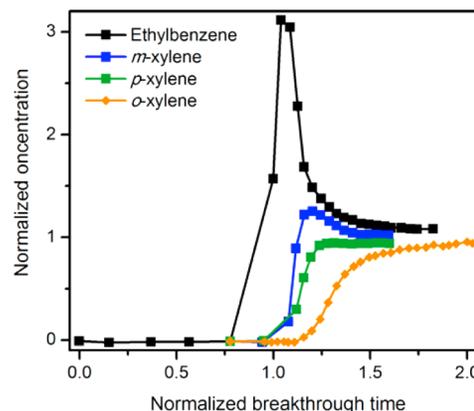
Figure 6. Results of a four-component breakthrough experiment on MIL-47 at 383 K and 0.5 bar total hydrocarbon pressure. Reprinted with permission from ref 183. Copyright 2008 American Chemical Society.

Other alkylaromatics can also be separated in MIL-47. Longer alkyl chains have been shown to bind more strongly, as seen by comparing cumene vs. *n*-propylbenzene. The same trend is seen for the series spanning from ethylbenzene to *n*-octylbenzene.[153]

The adsorption of alkylaromatics in MIL-53 compounds has also been studied extensively. Single-component isotherms of xylenes and ethylbenzene in MIL-53(Al) show that an adsorption step present in all of these isotherms moves to higher pressures at higher temperatures.[185] These single-component adsorption differences are reflected in the adsorption strengths of these different adsorbates, which follow the order ethylbenzene > *o*-xylene > *m*-xylene > *p*-xylene, and further increases with increasing coverage, ranging between −10 and −20 kJ/mol. The structures of MIL-53(Al) loaded with xylenes reflect the adsorption and breakthrough data. Both methyl groups of *o*-xylene can interact with the framework carboxylate groups, while only one *m*- and *p*-xylene each can have this interaction. The framework is most distorted upon adsorption of *o*-xylene and least for the *para* isomer. The entropy of adsorption is significantly less negative for *o*-xylene than for the other two isomers, which explains the discrepancy between the relative enthalpies and breakthrough elution order.[185,186] The flexibility of MIL-53(Al) creates a separation environment that is highly dependent on total pressure, as at 383 K the separation is poor at 0.0009 bar but improves at 0.056 bar.[187]

Liquid and gas-phase separation of C8−C10 alkylaromatics have also been reported for MIL-53(Al).[188] In batch experiments, the selectivity order is *o*-xylene > ethylbenzene> *p*-xylene ≈ *m*-xylene. Similarly, *p*- and *m*-ethyltoluene were not separated from each other but were baseline separated from *o*-ethyltoluene and *o*-cymene. Similar behavior was seen for pelletized MIL-53(Al).[189]

A study focusing on the structural transitions of MIL-53(Al) showed that all C8 alkylaromatics cause a distortion in the flexible framework structure;[153] however, the distortion caused by the interaction of the xylene methyl groups with the carboxylates of the framework is less disfavored than that caused by ethylbenzene. Both methyl groups in *o*-xylene can interact favorably with the framework, leading to the high strength of adsorption. This study reported that *p*-xylene has more possible adsorption sites and, therefore, is entropically

favored. These competing factors result in the difficulty of separation of xylene isomers in MIL-53(Al). In liquid chromatography separations, MIL-53(Al) outperformed a conventional LCMS column for toluene and ethylbenzene separation at 298 K,[190] although different eluents have produced different results.[191]

Excellent alkylaromatic separation in MIL-53 is not limited to the aluminum isostructure. In a variety of experiments, xylene isomers have been found to behave differently in the pores of MIL-53(Fe).[192] The isotherm of o-xylene is essentially of Type I, while that of m-xylene shows one step and that of p-xylene shows two: one at the same pressure as m-xylene and one at a lower pressure. The o-xylene isomer is adsorbed with substantially higher uptake capacity than the other isomers, although m-xylene has the highest strength of adsorption. Crystal structures of MIL-53(Fe) loaded with xylenes show similar behavior between o- and m-xylenes, with $\pi-\pi$ interactions between the xylene and the bdc^{2-} linker. This interaction is not found in p-xylene. Binary breakthrough experiments with the three xylene isomers show separation of *para/ortho* and *para/meta* mixtures. In addition to MIL-53(Fe), a Mn-based MIL-53 analogue with pyridine N-oxides as μ_2-O substitutes shows better π overlap with benzene than toluene.[193]

Polycyclic Aromatic Hydrocarbons. Polycyclic aromatic hydrocarbons, or PAHs, are carcinogenic byproducts of incomplete combustion of organic matter such as fossil fuels.[194] The emissions of PAHs totaled approximately 550 000 tons in 2004.[195] The major source of PAHs in air, water, soil, and food are anthropogenic—either vehicular emissions or stationary sources such as petroleum cracking or residential heating.[196,197] Their vapor pressures span a range of $\sim10^7$, and they can be present in the gas phase (e.g., naphthalene) or as adsorbed solids (organics with five rings and higher).[198] Their separation is critical to obtaining an environmental profile of these pollutants.[199] The current CGMS separation techniques for separation are far from optimized, as the uncertainties of quantitation are quite high. Metal−organic frameworks could serve as a new frontier in PAH separation for analysis. Additionally, preconcentration of these pollutants from air samples is under investigation, and adsorbents such as metal−organic frameworks could serve a dual purpose of preconcentration and analytical separation. This preconcentration inquiry is relatively new in metal−organic frameworks, but promising results have shown promise for extracting PAHs from water.[200−202]

The wide range of sizes of PAHs allows for size-exclusion separations. To this end, both Cu$_3$(btc)$_2$ and MOF-5 can sieve pyrene from phenanthrene, anthracene, naphthalene, and benzene, as well as benzene from a more complex mixture of PAH's.[175]

The strength of adsorption of polycyclic aromatic hydrocarbons at low loadings in metal−organic frameworks is relatively strong, and therefore they can often be discriminated based on adsorption strength. These differences in adsorption strength were seen theoretically in Cu$_3$(btc)$_2$, MOF-5 isostructures, and MIL-53(Cr).[207] Experimentally, PAHs were separated on a reverse-phase liquid chromatography column packed with MIL-53(Al).[190]

Strengths of adsorption were also used to separate PAHs using a less conventional strategy: When exposed to an activated sample of Ni$_2$(μ_2−OH$_2$)(1,3-bdc)$_2$(tpcb), (tpcb = tetrakis(4-pyridyl)cyclobutane), naphthalene sublimes and is adsorbed selectively from a mixture of naphthalene and anthracene. The ability of naphthalene to align favorably within the pores was cited as the reason for this selectivity.[203]

The separation of PAHs is generally for identifying components of mixtures, and therefore the separation is not necessary if identification can be achieved without it, and different PAHs can be detected, albeit not separated, using creative techniques in metal−organic frameworks. For example, the magnetic susceptibility of the spin-crossover compound [Fe(dpe)][Pt(CN)$_4$] (dpe = *trans*-(1,2-di(4-pyridyl)-ethylene) changes drastically among guests phenazine, anthracene, and naphthalene.[204]

Aromatics and Aliphatics. The separation of aromatics from aliphatics is applicable to petroleum refining.[33] These molecules all fractionate together and ultimately need to be separated for a variety of uses. Separation generally involves inefficient distillation or extraction, while sometimes π-complexation adsorbents are used.[205] Some papers report single isotherms of hydrocarbons of interest, but without thermodynamic or separation data, little information about their separation ability can be deduced.[206] Other studies report a lack of separation ability, as in the nearly identical strength of adsorption of benzene and cyclohexane in M(bdc)(ted)$_{0.5}$ (M = Zn, Cu).[71]

Generally, metal−organic frameworks can interact more strongly with alkylaromatics than small molecules or aliphatic hydrocarbons, as seen theoretically in Cu$_3$(btc)$_2$, MOF-5 isostructures, and MIL-53(Cr).[207] Similarly, a series of metal−azolate frameworks[208] can selectively adsorb specific aromatics in nonaromatic solvents.

Comparing aromatic rings with hydrocarbons of similar sizes, some metal−organic frameworks bind aliphatics more strongly than their aromatic counterparts. Decalin theoretically binds MOF-5 slightly more strongly than tetralin, an adsorbate with the same number of carbons but three unsaturated bonds.[40] Benzene binds less strongly than n-hexane or 1-hexene in amino-MIL-53.[53] Benzene is less strongly adsorbed than cyclohexane or n-hexane in MIL-47, which shows distinctive structural deformations upon adsorption of benzene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, cyclohexene, and cyclohexane.[209]

The majority of aromatic/aliphatic separation studies show preference for the aromatic adsorbate, presumably due to favorable interactions with the aromatic linkers. The strength of adsorption of toluene is much higher than that of n-hexane in MIL-101(Cr).[210] Some novel materials separate benzene from cyclohexane very effectively. When exposed to a 1:1 mixture of benzene and cyclohexane, a disproportionate amount of benzene is adsorbed in the pores of NH$_4$[Cu$_3$(μ_3-OH)(μ_3-4-carboxypyrazolato)$_3$].[101] Similarly, a pillared zinc carboxylate framework adsorbs essentially entirely benzene when exposed to a 1:1 benzene:cyclohexane mixture.[211] Here, pore size was posited to be the source of the selectivity.

MOF-5 also binds aromatics more strongly than aliphatics. In an early study, MOF-5 was shown to adsorb cyclohexane slightly more strongly and with a modestly higher capacity than benzene.[212] However, a later, more rigorous investigation showed contrasting results.[35] Adsorption isotherms were reported for benzene, toluene, cyclohexane, methylcyclohexane, 1-hexene, and n-pentane through n-octane in MOF-5 and two isostructures. When comparing the same number of carbons, the aromatics bound more strongly than the cyclic aliphatics.

Open metal sites can allow for even more selective binding to aromatics. Through a comparison with MIL-53(Al), the open Cu^{2+} sites in $Cu_3(btc)_2$ were shown to adsorb *m*-xylene in the presence of an alkane solvent. As the length of the alkane solvent decreased, less was adsorbed for each material. The capacity of *m*-xylene decreased to almost zero for MIL-53(Al) and plateaued near 4 wt % for $Cu_3(btc)_2$.[149] The selectivity of $Cu_3(btc)_2$ for benzene or toluene over cyclohexane is preserved and potentially enhanced when polyoxometalates are present in the pores.[213]

CONCLUSIONS AND OUTLOOK

Since the outset of hydrocarbon separation experiments in metal−organic frameworks approximately a decade ago, the ability to separate mixtures more efficiently—or even access previously impossible separations—has demonstrated the utility of these materials. The variety of normal alkanes studied has shown that, for a given system, a metal−organic framework seemingly exists for separating any mixture of saturated adsorbates. The pore shapes of metal−organic frameworks offer a novel platform for separating branched alkanes based on shape, as zeolites or other porous materials are constructed in ways that preclude features such as acute angles. As a result, valuable highly branched isomers that could only be isolated by distillation can now be separated by adsorption. Additionally, coordinatively unsaturated metal centers have been shown to be an excellent strategy for separating alkenes from alkanes. Finally, the separation of xylenes (and other aromatics) has been demonstrated in the MIL series of metal−organic frameworks, a separation which was also previously inaccessible.

This review has attempted to be comprehensive, and yet the number of metal−organic frameworks is limited to only a fraction of the materials reported to date. New structure types or properties could improve upon the results seen here. Using the current canon of literature results to direct efforts toward new or overlooked metal−organic frameworks, specifically those that are stable to heat and impurities like water, could result in new discoveries. Petroleum technology, from which most hydrocarbons are derived, is highly mature, and therefore investigations of other porous materials like zeolites have been exhaustive, making metal−organic frameworks with novel properties particularly exciting. Experimentally, future directions could focus strongly on breakthrough data. These results are particularly useful in evaluating the practical ability of a material to separate hydrocarbons, either with new frameworks or materials that have been evaluated using adsorption or computer modeling. Advances in computational modeling have also begun to allow for screening of large databases of real and predicted metal−organic framework structures, and this strategy could continue to be used in partnership with experimental work.[214] Modeling studies can also investigate dozens of adsorbates on a single promising material, potentially identifying materials that could be scaled up for use in a variety of processes.[215]

ASSOCIATED CONTENT

S Supporting Information

Tabulated strengths of adsorption of selected adsorbates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Fletcher, A. J.; Thomas, K. M.; Rosseinsky, M. J. *J. Solid State Chem.* **2005**, *178*, 2491.

(2) Férey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380.

(3) Keskin, S.; Liu, J.; Rankin, R. B.; Johnson, J. K.; Sholl, D. S. *Ind. Eng. Chem. Res.* **2009**, *48*, 2355.

(4) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477.

(5) Cychosz, K. A.; Ahmad, R.; Matzger, A. J. *Chem. Sci.* **2010**, *1*, 293.

(6) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115.

(7) Chmelik, C.; Kärger, J. *Chem. Soc. Rev.* **2010**, *39*, 4864.

(8) Zou, R.; Abdel-Fattah, A. I.; Xu, H.; Zhao, Y.; Hickmott, D. D. *CrystEngComm* **2010**, *12*, 1337.

(9) Das, M. C.; Xiang, S.; Zhang, Z.; Chen, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 10510.

(10) Krishna, R.; van Baten, J. M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 10593.

(11) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869.

(12) Jhung, S. H.; Khan, N. A.; Hasan, Z. *CrystEngComm* **2012**, *14*, 7099.

(13) Zhang, Z.; Xiang, S.; Chen, B. *CrystEngComm* **2011**, *13*, 5983.

(14) He, Y.; Zhou, W.; Krishna, R.; Chen, B. *Chem. Commun.* **2012**, *48*, 11813.

(15) Wu, H.; Gong, Q.; Olson, D. H.; Li, J. *Chem. Rev.* **2012**, *112*, 836.

(16) Stallmach, F.; Gröger, S.; Künzel, V.; Kärger, J.; Yaghi, O. M.; Hesse, M.; Müller, U. *Angew. Chem., Int. Ed.* **2006**, *45*, 2123.

(17) Bux, H.; Chmelik, C.; Krishna, R.; Caro, J. *J. Membr. Sci.* **2011**, *369*, 284.

(18) Shah, M.; McCarthy, M. C.; Sachdeva, S.; Lee, A. K.; Jeong, H.-K. *Ind. Eng. Chem. Res.* **2012**, *51*, 2179.

(19) Chang, N.; Gu, Z.-Y.; Yan, X.-P. *J. Am. Chem. Soc.* **2010**, *132*, 13645.

(20) Münch, A. S.; Mertens, F. O. R. L. *J. Mater. Chem.* **2012**, *22*, 10228.

(21) Gu, Z.-Y.; Yang, C.-X.; Chang, N.; Yan, X.-P. *Acc. Chem. Res.* **2012**, *45*, 734.

(22) Leffler, W. L. *Petroleum Refining in Nontechnical Language*, 4th ed.; Penwell: Tulsa, 2008.

(23) Li, H.; Eddaoudi, M.; O'Keefe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

(24) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keefe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186.

(25) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.

(26) Mowat, J. P. S.; Seymour, V. R.; Griffin, J. M.; Fairen-Jimenez, D.; Düren, T.; Ashbrook, S. E.; Wright, P. A. *Dalton Trans.* **2012**, *41*, 3937.

(27) Trung, T. K.; Déroche, I.; Rivera, A.; Yang, Q.; Yot, P.; Ramsahye, N.; Vinot, S. D.; Devic, T.; Horcajada, P.; Serre, C.; Maurin, G.; Trens, P. *Microporous Mesoporous Mater.* **2011**, *140*, 114.

(28) Hamon, L.; Serre, C.; Devic, T.; Loiseau, T.; Millange, F.; Férey, G.; De Weireld, G. *J. Am. Chem. Soc.* **2009**, *131*, 8775.

(29) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494.

(30) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.

(31) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724.

(32) Speight, J. G. *The Chemistry and Technology of Petroleum*, 4th ed.; CRC Press: Laramie, 2006.

(33) Griesbaum, K.; Behr, A.; Biedenkapp, D.; Voges, H.-W.; Garbe, D.; Paetz, C.; Collin, G.; Mayer, D.; Höke, H. Hydrocarbons. *Ullman's Encyclopedia of Industrial Chemistry*; Electronic Release; Wiley-VCH: Weinheim, 2012.

(34) Krishna, R.; van Baten, J. M. *Langmuir* **2010**, *26*, 8450.

(35) Gutierrez, I.; Diaz, E.; Vega, A.; Ordonez, S. *J. Chromatogr., A* **2013**, *1274*, 173.

(36) Sarkisov, L.; Düren, T.; Snurr, R. Q. *Mol. Phys.* **2004**, *102*, 211.

(37) Dubbeldam, D.; Frost, H.; Walton, K. S.; Snurr, R. Q. *Fluid Phase Equilib.* **2007**, *261*, 152.

(38) Martín-Calvo, A.; García-Pérez, E.; Castillo, J. M.; Calero, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7085.

(39) Fairen-Jimenez, D.; Seaton, N. A.; Düren, T. *Langmuir* **2010**, *26*, 14694.

(40) Luebbers, M. T.; Wu, T.; Shen, L.; Masel, R. I. *Langmuir* **2010**, *26*, 11319.

(41) Jiang, J.; Sandler, S. I. *Langmuir* **2006**, *22*, 5702.

(42) Düren, T.; Snurr, R. Q. *J. Phys. Chem. B* **2004**, *108*, 15703.

(43) Farrusseng, D.; Daniel, C.; Gaudillere, C.; Ravon, U.; Schuurman, Y.; Mirodatos, C.; Dubbeldam, D.; Frost, H.; Snurr, R. Q. *Langmuir* **2009**, *25*, 7383.

(44) Wang, Q. M.; Shen, D. M.; Bülow, M.; Lau, M. L.; Deng, S. G.; Fitch, F. R.; Lemcoff, N. O.; Semanscin, J. *Microporous Mesoporous Mater.* **2002**, *55*, 217.

(45) Yang, Q.; Zhong, C. *ChemPhysChem* **2006**, *7*, 1417.

(46) Martín-Calvo, A.; García-Perez, E.; Manuel Castillo, J.; Calero, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7085.

(47) Chmelik, C.; Kärger, J.; Wiebcke, M.; Caro, J.; van Baten, J. M.; Krishna, R. *Microporous Mesoporous Mater.* **2009**, *117*, 22.

(48) Rosenbach, N. J.; Ghoufi, A.; Déroche, I.; Llewellyn, P. L.; Devic, T.; Bourrelly, S.; Serre, C.; Férey, G.; Maurin, G. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6428.

(49) Jobic, H.; Rosenbach, N. J.; Ghoufi, A.; Kolokolov, D. I.; Yot, P. G.; Devic, T.; Serre, C.; Férey, G.; Maurin, G. *Chem.—Eur. J.* **2010**, *16*, 10337.

(50) Trung, T. K.; Trens, P.; Tanchoux, N.; Bourrelly, S.; Llewellyn, P. L.; Loera-Serna, S.; Serre, C.; Loiseau, T.; Fajula, F.; Férey, G. *J. Am. Chem. Soc.* **2008**, *130*, 16926.

(51) Llewellyn, P. L.; Maurin, G.; Devic, T.; Loera-Serna, S.; Rosenbach, N.; Serre, C.; Bourrelly, S.; Horcajada, P.; Filinchuk, Y.; Férey, G. *J. Am. Chem. Soc.* **2008**, *130*, 12808.

(52) Coudert, F.-X.; Mellot-Draznieks, C.; Fuchs, A. H.; Boutin, A. *J. Am. Chem. Soc.* **2009**, *131*, 3442.

(53) Couck, S.; Rémy, T.; Baron, G. V.; Gascon, J.; Kapteijn, F.; Denayer, J. F. M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9413.

(54) Couck, S.; Gobechiya, E.; Kirschhock, C. E. A.; Serra-Crespo, P.; Juan-Alcañiz, J.; Joaristi, A. M.; Stavitski, E.; Gascon, J.; Kapteijn, F.; Baron, G. V.; Denayer, J. F. M. *ChemSusChem* **2012**, *5*, 740.

(55) Llewellyn, P. L.; Horcajada, P.; Maurin, G.; Devic, T.; Rosenbach, N.; Bourrelly, S.; Serre, C.; Vincent, D.; Loera-Serna, S.; Filinchuk, Y.; Férey, G. *J. Am. Chem. Soc.* **2009**, *131*, 13002.

(56) Nijem, N.; Wu, H.; Canepa, P.; Marti, A.; Balkus, J. K. J.; Thonhauser, T.; Li, J.; Chabal, Y. J. *J. Am. Chem. Soc.* **2012**, *134*, 15201.

(57) Fairen-Jimenez, D.; Galvelis, R.; Torrisi, A.; Gellan, A. D.; Wharmby, M. T.; Wright, P. A.; Mellot-Draznieks, C.; Düren, T. *Dalton Trans.* **2012**, *41*, 10752.

(58) van den Bergh, J.; Gücüyener, C.; Pidko, E. A.; Hensen, E. J. M.; Gascon, J.; Kapteijn, F. *Chem.—Eur. J.* **2011**, *17*, 8832.

(59) Ma, S.; Sun, D.; Wang, X.-S.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 2458.

(60) Mishra, P.; Uppara, H. P.; Mandal, B.; Gumma, S. *J. Chem. Eng. Data* **2012**, *57*, 2610.

(61) Chen, B. L.; Liang, C. D.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1390.

(62) Wang, X.-S.; Liu, J.; Bonefont, J. M.; Yuan, D.-Q.; Thallapally, P. K.; Ma, S. *Chem. Commun.* **2013**, *49*, 1533.

(63) Pan, L.; Olson, D. H.; Ciemnolonski, L. R.; Heddy, R.; Li, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 616.

(64) Trung, T. K.; Ramsahye, N. A.; Trens, P.; Tanchoux, N.; Serre, C.; Fajula, F.; Férey, G. *Microporous Mesoporous Mater.* **2010**, *134*, 131.

(65) Finsy, V.; Calero, S.; García-Perez, E.; Merkling, P. J.; Vedts, G.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3515.

(66) Trung, T. K.; Ramsahye, N. A.; Trens, P.; Tanchoux, N.; Serre, C.; Fajula, F.; Férey, G. *Microporous Mesoporous Mater.* **2010**, *134*, 134.

(67) Ramsahye, N. A.; Trung, T. K.; Scott, L.; Nouar, F.; Devic, T.; Horcajada, P.; Magnier, E.; David, O.; Serre, C.; Trens, P. *Chem. Mater.* **2013**, *25*, 479.

(68) Déroche, I.; Rives, S.; Trung, T.; Yang, Q.; Ghoufi, A.; Ramsahye, N. A.; Trens, P.; Fajula, F.; Devic, T.; Serre, C.; Férey, G.; Jobic, H.; Maurin, G. *J. Phys. Chem. C* **2011**, *115*, 13868.

(69) Motkuri, R. K.; Thallapally, P. K.; Nune, S. K.; Fernandez, C. A.; McGrail, B. P.; Atwood, J. L. *Chem. Commun.* **2011**, *47*, 7077.

(70) Fan, L.; Yan, X.-P. *Talanta* **2012**, *99*, 944.

(71) Lee, J. Y.; Olson, D. H.; Pan, L.; Emge, T. J.; Li, J. *Adv. Funct. Mater.* **2007**, *17*, 1255.

(72) Herm, Z. R.; Wiers, B. W.; Mason, J. A.; van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. *Science* **2013**, *340*, 960.

(73) Obenhaus, F.; Droste, W.; Neumeister, J. Butenes. *Ullman's Encyclopedia of Industrial Chemistry*; Electronic Release; Wiley-VCH: Weinheim, 2012.

(74) Zhang, L.; Wang, Q.; Wu, T.; Liu, Y.-C. *Chem.—Eur. J.* **2007**, *13*, 6387.

(75) Babarao, R.; Tong, Y. H.; Jiang, J. *J. Phys. Chem. B* **2009**, *113*, 9129.

(76) Dubbeldam, D.; Galvin, C. J.; Walton, K. S.; Ellis, D. E.; Snurr, R. Q. *J. Am. Chem. Soc.* **2008**, *130*, 10884.

(77) Bárcia, P. S.; Zapata, F.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. *J. Phys. Chem. B* **2007**, *111*, 6101.

(78) Ling, Y.; Chen, Z.-X.; Zhai, F.-P.; Zhou, Y.-M.; Weng, L.-H.; Zhao, D.-Y. *Chem. Commun.* **2011**, *47*, 7197.

(79) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. *Ind. Eng. Chem. Res.* **2012**, *51*, 4692.

(80) Bárcia, P. S.; Guimaraes, D.; Mendes, P. A. P.; Silva, J. A. C.; Guillerm, V.; Chevreau, H.; Serre, C.; Rodrigues, A. E. *Microporous Mesoporous Mater.* **2011**, *139*, 67.

(81) Mendes, P. A. P.; Ragon, F.; Rodrigues, A. E.; Horcajada, P.; Serre, C.; Silva, J. A. C. *Microporous Mesoporous Mater.* **2013**, *170*, 251.

(82) Dubbeldam, D.; Krishna, R.; Calero, S.; Yazaydin, A. Ö. *Angew. Chem., Int. Ed.* **2012**, *51*, 11867.

(83) Knothe, G.; Matheaus, A. C.; Ryan, T. W., III. *Fuel* **2003**, *82*, 971.

(84) Creton, B.; Dartiguelongue, C.; de Bruin, T.; Toulhoat, H. *Energy Fuels* **2010**, *24*, 5396.

(85) Hirai, K.; Furukawa, S.; Kondo, M.; Uehara, H.; Sakata, O.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 8057.

(86) van Miltenburg, A.; Zhu, W.; Kapteijn, F.; Moulijn, J. A. *Chem. Eng. Res. Des.* **2006**, *84*, 350.

(87) Lamia, N.; Jorge, M.; Granato, M. A.; Almeida Paz, F. A.; Chevreau, H.; Rodrigues, A. E. *Chem. Eng. Sci.* **2009**, *64*, 3246.

(88) Ferreira, A. F. P.; Santos, J. C.; Plaza, M. G.; Lamia, N.; Loureiro, J. M.; Rodrigues, A. E. *Chem. Eng. J.* **2011**, *167*, 1.

(89) Plaza, M. G.; Ferreira, A. F. P.; Santos, J. C.; Ribeiro, A. M.; Müller, U.; Trukhan, N.; Loureiro, J. M.; Rodrigues, A. E. *Microporous Mesoporous Mater.* **2012**, *157*, 101.

(90) Plaza, M. G.; Ribeiro, A. M.; Ferreira, A.; Santos, J. C.; Hwang, Y. K.; Seo, Y.-K.; Lee, U.-H.; Chang, J.-S.; Loureiro, J. M.; Rodrigues, A. E. *Microporous Mesoporous Mater.* **2012**, *153*, 178.

(91) Ma, H.; Ren, H.; Meng, S.; Yan, Z.; Zhao, H.; Sun, F.; Zhu, G. *Chem. Commun.* **2013**, 9773.

(92) Xiang, S.-C.; Zhang, Z.; Zhao, C.-G.; Hong, K.; Zhao, X.; Ding, D.-R.; Xie, M-H.; Wu, C.-D.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. *Nat. Commun.* **2011**, *2*, 204.

(93) Böhme, U.; Barth, B.; Paula, C.; Kuhnt, A.; Schwieger, W.; Mundstock, A.; Caro, J.; Hartmann, M. *Langmuir* **2013**, *29*, 8592.

(94) Chavan, S. M.; Shearer, G. C.; Bloch, E.; Bordiga, S. *ChemPhysChem* **2012**, *13*, 445.

(95) Yoon, J.-W.; Seo, Y.-K.; Hwang, Y.-K.; Chang, J.-S.; Leclerc, H.; Wuttke, S.; Bazin, P.; Vimont, A.; Daturi, M.; Bloch, E.; Llewellyn, P. L.; Serre, C.; Horcajada, P.; Greneche, J.-M.; Rodrigues, A. E.; Férey, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 5949.

(96) Cai, J.; Yu, J.; Xu, H.; He, Y.; Duan, X.; Cui, Y.; Wu, C.; Chen, B.; Qian, G. *Cryst. Growth Des.* **2013**, *13*, 2094.

(97) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. *Science* **2012**, *335*, 1606.

(98) Verma, P.; Xu, X.; Truhlar, D. G. *J. Phys. Chem. C* **2013**, *117*, 12648.

(99) Passler, P.; Hefner, W.; Bucki, K.; Meinass, H.; Meiswinkel, A.; Wernicke, H.-J.; Ebersberg, G.; Müller, R.; Bässler, J.; Behringer, H.; Mayer, D. Acetylene. *Ullman's Encyclopedia of Industrial Chemistry*; Electronic Release; Wiley-VCH: Weinheim, 2012.

(100) Hu, Y.; Xiang, S.; Zhang, W.; Zhang, Z.; Wang, L.; Bai, J.; Chen, B. *Chem. Commun.* **2009**, 7551.

(101) Quartapelle Procopio, E.; Linares, F.; Montoro, C.; Colombo, V.; Maspero, A.; Barea, E.; Navarro, J. A. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 7308.

(102) Zhang, Z.; Xiang, S.; Rao, X.; Zheng, Q.; Fronczek, F. R.; Qian, G.; Chen, B. *Chem. Commun.* **2010**, *46*, 7205.

(103) Zhang, Z.; Xiang, S.; Chen, Y.-S.; Ma, S.; Lee, Y.; Phely-Bobin, T.; Chen, B. *Inorg. Chem.* **2010**, *49*, 8444.

(104) Chen, Z.; Xiang, S.; Arman, H. D.; Li, P.; Tidrow, S.; Zhao, D.; Chen, B. *Eur. J. Inorg. Chem.* **2010**, *24*, 3745.

(105) Guo, Z.; Xu, H.; Su, S.; Cai, J.; Dang, S.; Xiang, S.; Qian, G.; Zhang, H.; O'Keeffe, M.; Chen, B. *Chem. Commun.* **2011**, *47*, 5551.

(106) Chen, Z.; Xiang, S.; Arman, H. D.; Mondal, J. U.; Li, P.; Zhao, D.; Chen, B. *Inorg. Chem.* **2011**, *50*, 3442.

(107) Xue, Y.-S.; He, Y.; Ren, S.-B.; Yue, Y.; Zhou, L.; Li, Y.-Z.; Du, H.-B.; You, X.-Z.; Chen, B. *J. Mater. Chem.* **2012**, *22*, 10195.

(108) Zhang, Z.; Xiang, S.; Hong, K.; Das, M. C.; Arman, H. D.; García, M.; Mondal, J. U.; Thomas, K. M.; Chen, B. *Inorg. Chem.* **2012**, *51*, 4947.

(109) Colombo, V.; Montoro, C.; Maspero, A.; Palmisano, G.; Masciocchi, N.; Galli, S.; Barea, E.; Navarro, J. A. R. *J. Am. Chem. Soc.* **2012**, *134*, 12830.

(110) He, Y.; Zhang, Z.; Xiang, S.; Wu, H.; Fronczek, F. R.; Zhou, W.; Krishna, R.; O'Keeffe, M.; Chen, B. *Chem.—Eur. J.* **2012**, *18*, 1901.

(111) He, Y.; Xiang, S.; Zhang, Z.; Xiong, S.; Fronczek, F. R.; Krishna, R.; O'Keeffe, M.; Chen, B. *Chem. Commun.* **2012**, *48*, 10856.

(112) Xiong, S.; He, Y.; Krishna, R.; Chen, B.; Wang, Z. *Cryst. Growth Des.* **2013**, *13*, 2670.

(113) Xu, H.; He, Y.; Zhang, Z.; Xiang, S.; Cai, J.; Cui, Y.; Yang, Y.; Qian, G.; Chen, B. *J. Mater. Chem. A* **2013**, *1*, 77.

(114) Das, M. C.; Xu, H.; Xiang, S.; Zhang, Z.; Arman, H. D.; Qian, G.; Chen, B. *Chem.—Eur. J.* **2011**, *17*, 7817.

(115) Das, M. C.; Xu, H.; Wang, Z.; Srinivas, G.; Zhou, W.; Yue, Y.-F.; Nesterov, V. N.; Qian, G.; Chen, B. *Chem. Commun.* **2011**, *47*, 11715.

(116) He, Y.; Zhang, Z.; Xiang, S.; Fronczek, F. R.; Krishna, R.; Chen, B. *Chem. Commun.* **2012**, *48*, 6493.

(117) He, Y.; Zhang, Z.; Xiang, S.; Fronczek, F. R.; Krishna, R.; Chen, B. *Chem.—Eur. J.* **2012**, *18*, 613.

(118) Cai, J.; Yu, J.; Xu, H.; He, Y.; Duan, X.; Cui, Y.; Wu, C.-D.; Chen, B.; Qian, G. *Cryst. Growth Des.* **2013**, *13*, 2094.

(119) He, Y.; Krishna, R.; Chen, B. *Energy Environ. Sci.* **2012**, *5*, 9107.

(120) Zimmerman, H.; Walzi, R. Ethylene. *Ullman's Encyclopedia of Industrial Chemistry*; Electronic Release; Wiley-VCH: Weinheim, 2012.

(121) Gücüyener, C.; van, D. B. J.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2010**, *132*, 17704.

(122) Chmelik, C.; Freude, D.; Bux, H.; Haase, J. *Microporous Mesoporous Mater.* **2012**, *147*, 135.

(123) Zhang, C.; Lively, R. P.; Zhang, K.; Johnson, J. R.; Karvan, O.; Koros, W. J. *J. Phys. Chem. Lett.* **2012**, *3*, 2130.

(124) Nicholson, T. M.; Bhatia, S. K. *J. Phys. Chem. B* **2006**, *110*, 24834.

(125) Nicholson, T. M.; Bhatia, S. K. *Adsorpt. Sci. Technol.* **2007**, *25*, 607.

(126) Wang, S.; Yang, Q.; Zhong, C. *Sep. Purif. Technol* **2008**, *60*, 30.

(127) Bao, Z.; Alnemrat, S.; Yu, L.; Vasiliev, I.; Ren, Q.; Lu, X.; Deng, S. *Langmuir* **2011**, *27*, 13554.

(128) Geier, S. J.; Mason, J. A.; Bloch, E. D.; Queen, W. L; Hudson, M. R.; Brown, C. M.; Long, J. R. *Chem. Sci.* **2013**, *4*, 2054.

(129) Wagener, A.; Schindler, M.; Rudolphi, F.; Ernst, S. *Chem. Ing. Tech.* **2007**, *79*, 851.

(130) Yoon, J.-W.; Jang, I.-T.; Lee, K.-Y.; Hwang, Y.-K.; Chang, J.-S. *Bull. Korean Chem. Soc.* **2010**, *31*, 220.

(131) Jorge, M.; Lamia, N.; Rodrigues, A. E. *Colloids Surf., A* **2010**, *357*, 27.

(132) Fischer, M.; Gomes, J. R. B.; Fröba, M.; Jorge, M. *Langmuir* **2012**, *28*, 8537.

(133) Rubes, M.; Wiersum, A. D.; Llewellyn, P. L.; Grajciar, L.; Bludsky, O.; Nachtigall, P. *J. Phys. Chem. C* **2013**, *117*, 11159.

(134) Plaza, M. G.; Ribeiro, A. M.; Ferreira, A.; Santos, J. C.; Lee, U. H.; Chang, J.-S.; Loureiro, J. M.; Rodrigues, A. E. *Sep. Purif. Technol.* **2012**, *90*, 109.

(135) Gutiérrez-Sevillano, J. J.; Vicent-Luna, J. M.; Dubbeldam, D.; Calero, S. *J. Phys. Chem. C* **2013**, *117*, 11357.

(136) Lee, K.; Isley, W. C., III; Dzubak, A. L.; Verma, P.; Stoneburner, S. J.; Bloch, E. D.; Reed, D. A.; Hudson, M. R.; Lin, L.-C.; Kim, J.; Brown, C. M.; Long, J. R.; Neaton, J.; Smit, B.; Cramer, C. J.; Truhlar, D. G.; Gagliardi, L. *J. Am. Chem. Soc.* **2013**, submitted.

(137) Li, K.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H.; Zeng, H.; Li, J. *J. Am. Chem. Soc.* **2009**, *131*, 10368.

(138) Lee, C. Y.; Bae, Y.-S.; Jeong, N. C.; Farha, O. K.; Sarjeant, A. A.; Stern, C. L.; Nickias, P.; Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2011**, *133*, 5228.

(139) Bae, Y.-S.; Lee, C. Y.; Kim, K. C.; Farha, O. K.; Nickias, P.; Hupp, J. T.; Nguyen, S. T.; Snurr, R. Q. *Angew. Chem., Int. Ed.* **2012**, *51*, 1857.

(140) Wuttke, S.; Baxin, O.; Vimont, A.; Serre, C.; Seo, Y.-K.; Hwang, Y. K.; Chang, J.-S.; Férey, G.; Daturi, M. *Chem.—Eur. J.* **2012**, *18*, 11959.

(141) Leclerc, H.; Vimont, A.; Lavalley, J.-C.; Daturi, M.; Wiersum, A. D.; Llwellyn, P. L.; Horcajada, P.; Férey, G.; Serre, C. *Phys. Chem. Chem. Phys.* **2011**, *13*, 11748.

(142) Ma, S.; Sun, D.; Yuan, D.; Wang, X.-S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 6445.

(143) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Chizallet, C.; Quoineaud, A.-A.; Pirngruber, G. D. *J. Am. Chem. Soc.* **2012**, *134*, 8115.

(144) Maes, M.; Alaerts, L.; Vermoortele, F.; Ameloot, R.; Couck, S.; Finsy, V.; Denayer, J. F. M.; De Vos, D. E. *J. Am. Chem. Soc.* **2010**, *132*, 2284.

(145) Hartmann, M.; Kunz, S.; Himsl, D.; Tangermann, O. *Langmuir* **2008**, *24*, 8634.

(146) Kim, S.-N.; Kim, J.; Kim, H.-Y.; Cho, H.-Y.; Ahn, W.-S. *Catal. Today* **2013**, *204*, 85.

(147) Obenaus, F.; Droste, W.; Neueister, J. Butenes. *Ullman's Encyclopedia of Industrial Chemistry*; Electronic Release; Wiley-VCH, Weinheim, 2012.

(148) Longo, P.; Grisi, F.; Guerra, G.; Cavallo, L. *Macromolecules* **2000**, *33i*, 4647−4659.

(149) Alaerts, L.; Maes, M.; van der Veen, M. A.; Jacobs, P. A.; De Vos, D. E. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2903.

(150) Alaerts, L.; Kirschhock, C. E. A.; Maes, M.; van der Veen, M. A.; Finsy, V.; Depla, A.; Martens, J. A.; Baron, G. V.; Jacobs, P. A.; Denayer, J. F. M.; De Vos, D. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 4293.

(151) Bao, X.; Broadbelt, L. J.; Snurr, R. Q. *Mol. Simul.* **2009**, *35*, 50.

(152) Maes, M.; Vermoortele, F.; Alaerts, L.; Denayer, J. F. M.; De Vos, D. E. *J. Phys. Chem. C* **2011**, *115*, 1051.

(153) Maes, M.; Vermoortele, F.; Boulhout, M.; Boudewijns, T.; Kirschhock, C.; Ameloot, R.; Beurroies, I.; Denoyel, R.; De Vos, D. E. *Microporous Mesoporous Mater* **2012**, *157*, 82.

(154) Minceva, M.; Rodrigues, A. E. *AIChE J.* **2007**, *53*, 138.

(155) Peralta, D.; Barthelet, K.; Pérez-Pellitero, J.; Chizallet, C.; Chaplais, G.; Simon-Masseron, A.; Pirngruber, G. D. *J. Phys. Chem. C* **2012**, *116*, 21844.

(156) Yang, C.-X.; Chen, Y.-J.; Wang, H.-F.; Yan, X.-P. *Chem.—Eur. J.* **2011**, *17*, 11734.

(157) Yang, C.-X.; Yan, X.-P. *J. Mater. Chem.* **2012**, *22*, 17833.

(158) Collin, G.; Höke, H.; Greim, H. Naphthalene and Hydronaphthalenes. *Ullman's Encyclopedia of Industrial Chemistry*; Electronic Release; Wiley-VCH: Weinheim, 2012.

(159) Maes, M.; Schouteden, S.; Hirai, K.; Furukawa, S.; Kitagawa, S.; De Vos, D. E. *Langmuir* **2011**, *27*, 9083.

(160) Yang, C.-X.; Yan, X.-P. *Anal. Chem.* **2011**, *83*, 7144.

(161) Hu, Z.; Chen, Y.; Jiang, J. *Langmuir* **2013**, *29*, 1650.

(162) Choi, E. Y.; Park, K.; Yang, C. M.; Kim, H.; Son, J. H.; Lee, S. W.; Lee, Y. H.; Min, D.; Kwon, Y. U. *Chem.—Eur. J.* **2004**, *10*, 5535.

(163) Devi, R. N.; Edgar, M.; Gonzalez, J.; Slawin, A.; Tunstall, D. P.; Grewal, P.; Cox, P. A.; Wright, P. A. *J. Phys. Chem. B* **2004**, *108*, 535.

(164) Moreira, M. A.; Santos, J. C.; Ferreira, A. F. P.; Loureiro, J. M.; Ragon, F.; Horcajada, P.; Yot, P. G.; Serre, C.; Rodrigues, A. E. *Langmuir* **2012**, *28*, 3494.

(165) Moreira, M. A.; Santos, J. C.; Ferreira, A. F. P.; Loureiro, J. M.; Ragon, F.; Horcajada, P.; Yot, P. G.; Serre, C.; Rodrigues, A. E. *Microporous Mesoporous Mater.* **2012**, *158*, 229.

(166) Gu, Z.-Y.; Jiang, D.-Q.; Wang, H.-F.; Cui, X.-Y.; Yan, X.-P. *J. Phys. Chem. C* **2010**, *114*, 311.

(167) Nicolau, M. P. M.; Bárcia, P. S.; Gallegos, J. M.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. *J. Phys. Chem. C* **2009**, *113*, 13173.

(168) Bárcia, P. S.; Nicolau, M. P. M.; Gallegos, J. M.; Chen, B.; Rodrigues, A. E.; Silva, J. A. C. *Microporous Mesoporous Mater.* **2012**, *155*, 220.

(169) Lee, J. S.; Jhung, S. H. *Microporous Mesoporous Mater.* **2010**, *129*, 274.

(170) Fu, Y.-Y.; Yang, C.-X.; Yan, X.-P. *J. Chromatogr. A* **2013**, *1274*, 137.

(171) Liu, Q.-K.; Ma, J.-P.; Dong, Y.-B. *Chem.—Eur. J.* **2009**, *15*, 10364.

(172) Yang, K.; Sun, Q.; Xue, F.; Lin, D. *J. Hazard. Mater.* **2011**, *195*, 124.

(173) Sarkisov, L. *Phys. Chem. Chem. Phys.* **2012**, *14*, 15438.

(174) Cui, X.-Y.; Gu, Z.-Y.; Jiang, D.-Q.; Li, Y.; Wang, H.-F.; Yan, X.-P. *Anal. Chem.* **2009**, *81*, 9771.

(175) Ahmad, R.; Wong-Foy, A. G.; Matzger, A. J. *Langmuir* **2009**, *25*, 11977.

(176) Maes, M.; Vermoortele, F.; Alaerts, L.; Denayer, J. F. M.; De Vos, D. E. *J. Phys. Chem. C* **2011**, *115*, 1051.

(177) Moreira, M. A.; Santos, J. C.; Ferreira, A. F. P.; Loureiro, J. M.; Ragon, F.; Horcajada, P.; Shim, K.-E.; Hwang, Y.-K.; Lee, U. H.; Chang, J.-S.; Serre, C.; Rodrigues, A. E. *Langmuir* **2012**, *28*, 5715.

(178) Rémy, T.; Baron, G. V.; Denayer, J. F. M. *Langmuir* **2011**, *27*, 13064.

(179) Rémy, T.; Ma, L.; Maes, M.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. *Ind. Eng. Chem. Res.* **2012**, *51*, 14824.

(180) Ghysels, A.; Vandichel, M.; Verstraelen, T.; van der Veen, M. A.; De Vos, D. E.; Waroquier, M.; Van Speybroeck, V. *Theor. Chem. Acc.* **2012**, *131*, 1234.

(181) Biswas, S.; Rémy, T.; Couck, S.; Denysenko, D.; Rampelberg, G.; Denayer, J. F. M.; Volkmer, D.; Detavernier, C.; Van Der Voort, P. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3552.

(182) Duerinck, T.; Couck, S.; Vermoortele, F.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. *Langmuir* **2012**, *28*, 13883.

(183) Finsy, V.; Verelst, H.; Alaerts, L.; de Vos, D.; Jacobs, P. A.; Baron, G. V.; Denayer, J. F. M. *J. Am. Chem. Soc.* **2008**, *130*, 7110.

(184) Alaerts, L.; Maes, M.; Jacobs, P. A.; Denayer, J. F. M.; De Vos, D. E. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2979.

(185) Duan, L.; Dong, X.; Wu, Y.; Li, H.; Wang, L.; Song, L. *J. Porous Mater.* **2013**, *20*, 431.

(186) Yang, C.-X.; Liu, S.-S.; Wang, H.-F.; Wang, S.-W.; Yan, X.-P. *Analyst* **2012**, *137*, 133.

(187) Finsy, V.; Kirschhock, C. E. A.; Vedts, G.; Maes, M.; Alaerts, L.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. *Chem.—Eur. J.* **2009**, *15*, 7724.

(188) Alaerts, L.; Maes, M.; Giebeler, L.; Jacobs, P. A.; Martens, J. A.; Denayer, J. F. M.; Kirschhock, C. E. A.; De Vos, D. E. *J. Am. Chem. Soc.* **2008**, *130*, 14170.

(189) Moreira, M. A.; Santos, J. C.; Ferreira, A. F. P.; Müller, U.; Trukhan, N.; Loureiro, J. M.; Rodrigues, A. E. *Sep. Sci. Technol.* **2011**, *46*, 1995.

(190) Liu, S.-S.; Yang, C.-X.; Wang, S.-W.; Yan, X.-P. *Analyst* **2012**, *137*, 816.

(191) Moreira, M. A.; Santos, J. C.; Ferreira, A. F. P.; Loureiro, J. M.; Rodrigues, A. E. *Ind. Eng. Chem. Res.* **2011**, *50*, 7688.

(192) El Osta, R.; Carlin-Sinclair, A.; Guillou, N.; Walton, R. I.; Vermoortele, F.; Maes, M.; de Vos, D.; Millange, F. *Chem. Mater.* **2012**, *24*, 2781.

(193) Xu, G.; Zhang, X.; Guo, P.; Pan, C.; Zhang, H.; Wang, C. *J. Am. Chem. Soc.* **2010**, *132*, 3656.

(194) Baek, S. O.; Field, R. A.; Goldstone, M. E.; Kirk, P. W.; Lester, J. N.; Perry, R. *Water Air Soil Pollut.* **1991**, *60*, 279.

(195) Zhang, Y.; Tao, S. *Atmos. Environ.* **2009**, *43*, 812.

(196) Menzie, C. A.; Potocki, B. P.; Santodonato, J. *Environ. Sci. Technol.* **1992**, *26*, 1278.

(197) Gan, S.; Lau, E. V.; Ng, H. K. *J. Hazard. Mater.* **2009**, *172*, 532.

(198) Zielinska, B.; Sagebiel, J.; Arnott, W. P.; Rogers, C. F.; Kelly, K. E.; Wagner, D. A.; Lightly, J. S.; Sarofim, A. F.; Palmer, G. *Environ. Sci. Technol.* **2004**, *38*, 2557.

(199) Pandey, S. K.; Kim, K.-H.; Brown, R. J. C. *TrAC, Trends Anal. Chem.* **2011**, *30*, 1716.

(200) Ge, D.; Lee, H. K. *J. Chromatogr., A* **2011**, *1218*, 8490.

(201) Chen, X.-F.; Zang, H.; Wang, X.; Cheng, J.-G.; Zhao, R.-S.; Cheng, C.-G.; Lu, X.-Q. *Analyst* **2012**, *137*, 5411.

(202) Huo, S.-H.; Yan, X.-P. *Analyst* **2012**, *137*, 3445.

(203) Liu, D.; Lang, J.-P.; Abrahams, B. F. *J. Am. Chem. Soc.* **2011**, *133*, 11042.

(204) Muñoz-Lara, F. J.; Gaspar, A. B.; Carmen Muñoz, M.; Arai, M.; Kitagawa, S.; Ohba, M.; Real, J. A. *Chem.—Eur. J.* **2012**, *18*, 8013.

(205) Takahashi, A.; Yang, F. H.; Yang, R. T. *Ind. Eng. Chem. Res.* **2000**, *39*, 3856.

(206) Zeng, M.-H.; Tan, Y.-X.; He, Y.-P.; Yin, Z.; Chen, Q.; Kurmoo, M. *Inorg. Chem.* **2013**, *52*, 2353.

(207) Greathouse, J. A.; Ockwig, N. W.; Criscenti, L. J.; Guilinger, T. R.; Pohl, P.; Allendorf, M. D. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12621.

(208) He, C.-T.; Tian, J.-Y.; Liu, S.-Y.; Ouyang, G.; Zhang, J.-P.; Chen, X.-M. *Chem. Sci.* **2013**, *4*, 351.

(209) Wang, X.; Eckert, J.; Liu, L.; Jacobson, A. J. *Inorg. Chem.* **2011**, *50*, 2028.

(210) Huang, C.-Y.; Song, M.; Gu, Z.-Y.; Wang, H.-F.; Yan, X.-P. *Environ. Sci. Technol.* **2011**, *45*, 4490.

(211) Hijikata, Y.; Horike, S.; Sugimoto, M.; Sato, H.; Matsuda, R.; Kitagawa, S. *Chem.—Eur. J.* **2011**, *17*, 5138.

(212) Eddaoudi, M.; Li, H. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391.

(213) Ma, F.-J.; Liu, S.-X.; Liang, D.-D.; Ren, G.-J.; Wei, F.; Chen, Y.-G.; Su, Z.-M. *J. Solid State Chem.* **2011**, *184*, 3034.

(214) First, E. L.; Gounaris, C. E.; Floudas, C. A. *Langmuir* **2013**, *29*, 5599.

(215) Duerinck, T.; Bueno-Perez, R.; Vermoortele, F.; De Vos, D. E.; Calero, S.; Baron, G. V.; Denayer, J. F. M. *J. Phys. Chem. C* **2013**, *117*, 12567.

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