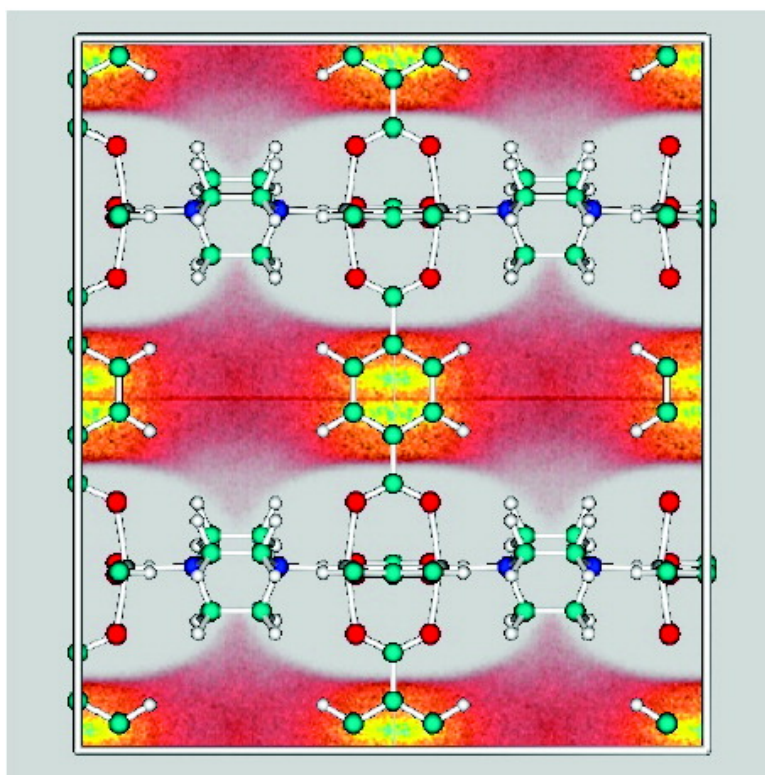


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Separation and Molecular-Level Segregation of Complex Alkane Mixtures in Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) are a new class of nanoporous materials that have good stability, high void volumes, and well-defined tailorable cavities of uniform size.¹ MOFs consist of metal oxide vertices interconnected by rigid or semirigid organic molecules having terminal functional groups that bind to the metal corners. The pores of MOFs can be systematically varied by a judicious choice of linker molecules and/or metal corners. Moreover, the higher void volumes in comparison to, for example, zeolites could potentially lead to very efficient separation processes. In this paper, we show that MOFs are highly selective for separating alkanes based on the degree of branching in complex, multicomponent mixtures. This is potentially useful for removing low research octane number (RON) alkanes from a mixed alkane stream. In addition, we report an unusual molecular-level segregation of molecules based on their degree of branching.

The separation of alkane mixtures using nanoporous materials is up to date usually achieved by selective adsorption within zeolitic materials. Calero et al.² and Krishna et al.³ showed using simulations that linear, monomethyl, and dimethyl alkanes in the 5–7 carbon atom range can be separated using silicalite-1 (MFI-topology) by exploiting configurational entropy effects. There are only a few papers on separation of alkanes in MOFs. Düren and Snurr simulated methane/*n*-butane mixtures in a family of related MOFs and found that selectivity for *n*-butane varied strongly with the MOF linker molecule.⁴ Several groups simulated mixtures of branched and linear alkanes in IRMOFs but did not observe significant selectivities for these structures.⁵ Experimentally, Chen et al. demonstrated that linear alkanes can enter the pores of MOF-508, but branched alkanes cannot.⁶ Interestingly, recently Barcia et al. found experimentally that hexane could be kinetically separated from 3-methylpentane and 2,2-dimethylbutane by fixed bed adsorption using a $Zn_2(1,4\text{-}bdc)_2(\text{dabco})$ MOF,⁷ where “*bdc*” denotes 1,4-benzenedicarboxylate and “*dabco*” denotes 1,4-diazabicyclo[2.2.2]-octane. In this work we refer to this structure, synthesized by Dybtsev et al.,⁸ as MOF-1. Figure 1 shows a cartoon of the structure. For the adsorbates in this study, the structure is essentially a one-dimensional channel system. MOF-1 is thermally stable and easily reactivated and reused.⁸

To investigate the use of MOF-1 as an adsorbent for alkane separations relevant to industrial processes, we simulated a multicomponent mixture in the C₅–C₇ range using grand canonical Monte Carlo (GCMC). Details are given in the Supporting Information. We note that the simulations are performed using a rigid framework, although flexibility for MOFs might be more important than in zeolites. However, for alkanes we expect the differences to be small. Figure 2 shows the absolute adsorption

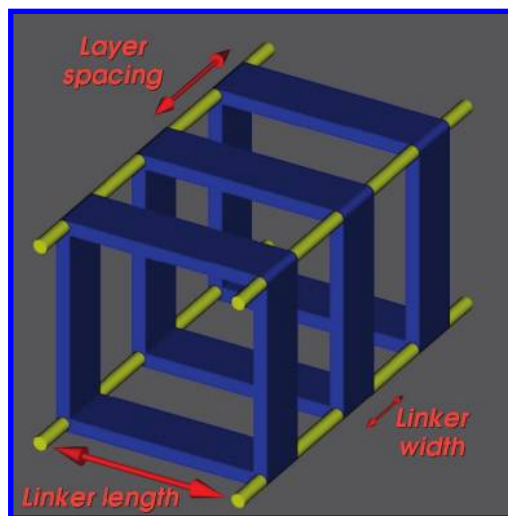


Figure 1. Schematic of the building blocks of MOF-1. The *bdc* linkers form a series of “boxes” that are pillared by *dabco* molecules to form one-dimensional channels.

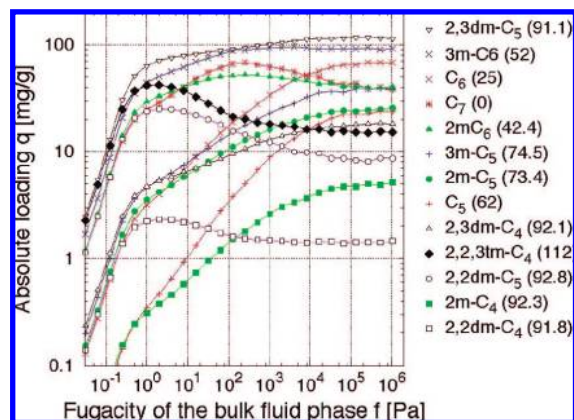


Figure 2. Multicomponent isotherms at 298 K: an equimolar 13-component mixture of *n*-pentane, *n*-hexane, *n*-heptane, 2-methylbutane, 2-methylpentane, 2-methylhexane, 3-methylpentane, 3-methylhexane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2,2-dimethylpentane, 2,3-dimethylpentane, and 2,2,3-trimethylbutane in MOF-1. Numbers in brackets denote the Research Octane Number. The order in the legend corresponds to the adsorption order at high loading. The statistical uncertainty of the computed loadings is smaller than the symbol size.

isotherms predicted for a 13-component alkane mixture in MOF-1. The numbers at the right side of the figure are the research octane numbers. The figure shows a striking result: with the exception of 2,3-dimethylpentane, species with a lower RON are adsorbed strongly over the full pressure range, while species with a higher

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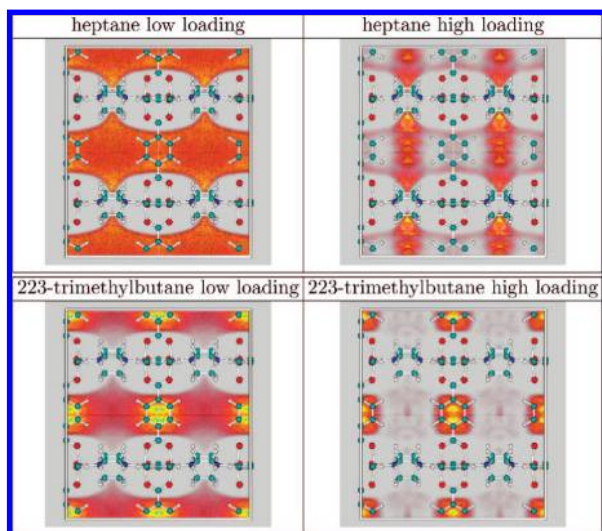


Figure 3. Average positions of all the beads of a linear alkane (top) and a triply branched alkane (bottom) in a 13-component mixture at low (left) and high loading (right) in the metal–organic framework MOF-1. The channels are running from left to right. Brighter colors indicate a higher atom density. At high density, molecules segregate according to their degree of branching. Mono- and dibranched alkanes show a gradual transition between the two extremes shown here.

RON are only weakly adsorbed. This high selectivity for low RON molecules could be exploited for octane boosting via adsorption. A mixed stream of alkanes could be passed through a column of the MOF; alkanes with a low RON will adsorb into the material and be removed from the stream exiting the column. These predominantly linear and monobranched alkanes can be recycled to an isomerization reactor and isomerized to the more desired branched molecules.

Some interesting competitive adsorption effects are observed in Figure 2. At medium and higher pressures the bulky shorter 2,2-dimethylbutane, 2,2-dimethylpentane, and 2,2,3-trimethylbutane are driven out of the framework and replaced by other molecules (their adsorption isotherms decrease after about 1 Pa in Figure 2). Figure 3 shows how the structure of the MOF leads to highly ordered arrangements of molecules within the pores and to molecular-level segregation of the molecules. This provides some insight into the selectivity observed in Figure 2. At low loading, *n*-heptane is adsorbed uniformly along the channels, whereas 2,2,3-trimethylbutane adsorbs preferentially near the “boxes” defined by the *bdc* linkers (Figure 1). At high loading, 2,2,3-trimethylbutane again adsorbs within the boxes, and in contrast to its low-loading behavior, *n*-heptane adsorbs almost completely in the regions between the boxes. Siting locations for other molecules are given in the Supporting Information. The mono- and dibranched molecules show a gradual transition between the behavior of the linear and tribranched molecules shown in Figure 3. The bulky and highly branched molecules have fewer low energy sorption sites, but the more flexible linear molecules can adapt to fill more regions of the MOF. We note the adsorption hierarchy itself is similar to that for MFI, where MFI might be better for certain alkane mixtures and

MOF-1 better for others. However, the physics and reasons for the separation are very different.

The siting and segregation results suggest exciting new possibilities for the design and creation of highly selective adsorption sites in MOFs. The use of multiple linkers to form “boxes” creates sites where molecules are surrounded on four sides by organic walls that can be tailored to attract or repel particular species in a mixture. This stands in contrast to the well-studied IRMOFs, where molecules fill up the corners first^{4,9} and then tend to adsorb along walls defined by a single linker¹⁰ because of the alternating tilt of the linkers. Using the general pore structure shown in Figure 1, one can tune the “width” and “length” of the linker, as well as the distance between the boxes. The latter could be used to control whether the structure is effectively a one-dimensional channel or a three-dimensional intersecting channel system for a certain guest molecule. This opens up the possibility of “molecular traffic control”,^{11,12} where species in a mixture diffuse preferentially along different channel directions based on size or chemical nature. Because the positions of guest molecules are easily obtained from molecular simulation, simulation can play an important role in understanding siting in MOFs, how this affects adsorption properties, and ultimately how MOFs can be designed for particular applications.

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Supporting Information Available: Framework positions, simulation methods and algorithms, averaged snapshots from simulation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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