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Ethane/Ethene Separation Turned on Its Head: Selective Ethane Adsorption on the Metal−Organic Framework ZIF-7 through a Gate-Opening Mechanism

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Abstract: Ethane is selectively adsorbed over ethylene in their mixtures on the zeolite imidazolate framework ZIF-7. In packed columns, this results in the direct production of pure ethylene. This gas-phase separation is attributed to a *gate-opening* effect in which specific threshold pressures control the uptake and release of individual molecules. These threshold pressures differ for the different molecules, leaving a window of selective uptake operation. This phenomenon makes ZIF-7 a perfect candidate for the separation of olefins from paraffins, since in contrast to most microporous materials, the paraffin is selectively adsorbed. Mixture adsorption, as studied by breakthrough experiments, demonstrates that gate-opening effects can be effectively used to separate molecules of very similar size.

Distillation is still the primary process used to separate most of the naphtha products. The columns for separating the olefins from the paraffins of the C2, C3, and C4 components are among the most energy-intensive distillation applications in oil refining.[1] The olefin/paraffin separation makes up almost 7% of the total distillation energy demand of the United States.[2] The smaller the molecules to be separated, the larger the energy demand of the process: for example, ethane/ethylene separation takes place in a cryogenic distillation tower consisting of over 150 trays.[2] The energy demand of this distillation represents up to 85% of the total cost of the entire process.[3]

Adsorption appears to be the most attractive alternative because of the maturity of the basic technology.[4] However, since most of the existing adsorbents display a stronger affinity for the unsaturated hydrocarbon,[5−8] this technology is not yet economically favorable: the high purity of the paraffin required for polymerization processes and the desirable high recovery rates oblige pressure-, vacuum-, and temperature-swing adsorption (PSA, VSA, and TSA) processes to operate in at least a four-bed, five-step fashion that results in a high energy demand and a large capital investment.[9] In this sense, the discovery of adsorbents that show a higher selectivity for the paraffin would be the Holy Grail: the whole separation scheme would become much simpler.[4] Although a few materials show higher olefin uptakes during single-component adsorption, to the best of our knowledge, no separation report confirming this behavior has been reported to date.[10−12]

Zeolite imidazolate frameworks (ZIFs) are a subfamily of metal−organic frameworks (MOFs) that display exceptional thermal stability. They are named after the resemblance of the metal−imidazolate−metal bond angles to the Si−O−Si angles in zeolites.[13] Because of their high stability, wide topological variety, and intrinsic hydrophobic properties, ZIFs are very attractive for many separation applications. Indeed, recent reports point out high selectivities for the separation of carbon dioxide from methane.[13] In the case of olefin/paraffin separation, very little is known about the performance of MOFs: CuBTC and ZIF-8 have been applied for the adsorptive separation of propane/propylene[14,15] and isobutane/isobutene[16] mixtures, showing a fair selectivity toward the unsaturated hydrocarbon, while MIL-96 is capable of separating all three C5 diolefin isomers from C5 monoolefins and paraffins.[17]

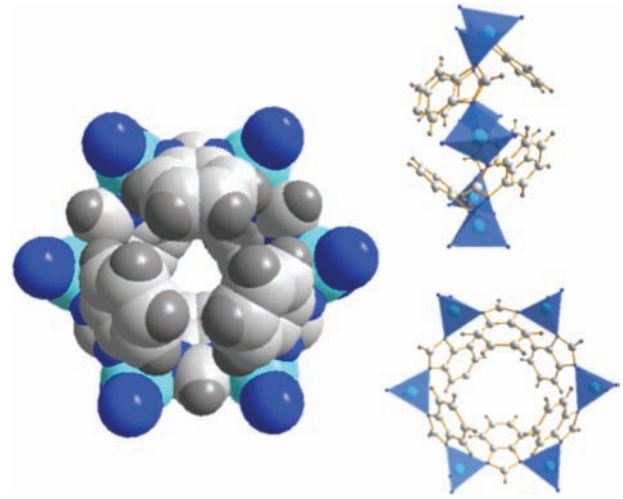

Figure 1. (left) Main cavity of ZIF-7. (right) Lateral (top) and front (bottom) views of the six-membered-ring (6MR) pore opening. Zn clusters are represented as polyhedra.

Here we report the unique, unrivaled performance of ZIF-7, an adsorbent displaying a strong preferential adsorption of paraffin over olefin. ZIF-7 is formed by connecting Zn metal clusters through benzimidazole (BIM) linkers. It has a sodalite topology with a crystallographic six-membered-ring (6MR) pore opening (Figure 1). The position of the benzene rings in the optimized structure in vacuum narrows the pore entrance to ∼0.3 nm.[13,18−20] However, as has been reported for many other MOFs,[21] the linkers have some freedom to rotate over a certain angle, allowing molecules larger than 0.3 nm to enter the main cavities.

Figure 2 shows the adsorption isotherms of several light hydrocarbons on the ZIF-7 framework at 25 °C. Three regions can be distinguished: a step region where the adsorbed amount strongly increases with pressure flanked by two regions where the uptake increases much more weakly with pressure. At low pressures, the uptake is very low, while in the step region it rapidly increases in a small pressure range to a loading of ∼1.5 mol kg^{-1} (∼3 molecules per cavity), after which the hydrocarbon uptake develops more slowly with pressure. We attribute these three regions to adsorption at the external surface, adsorption inside the cavities, and further filling of the cavities, respectively. Since the crystallographic pore opening of ZIF-7 is 0.3 nm, the observed type-IV isotherms can only be understood in terms of a change in the conformation of

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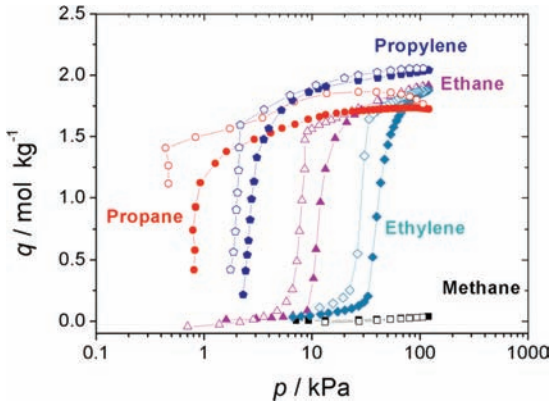

Figure 2. Adsorption (closed symbols)−desorption (open symbols) isotherms of several hydrocarbons on ZIF-7 powder at 25 °C.

the benzimidazole linker. The interaction between the adsorbate and the BIM linker strongly affects the adsorption process, resulting in a *gate-opening* effect.[22−25] Specific threshold pressures control the uptake and release of individual molecules, unlocking the openings to the ZIF-7 cavities. It is speculated that because of the threefold symmetry of the methyl groups, they fit best in the largest opening of the ZIF-7 cage, a three-lobe structure formed by three benzene rings (Figure 1); hence, ethane can penetrate at lower pressures than ethylene. This creates a pressure window in which ethane adsorbs while ethylene does not. Apparently, the ease of uptake increases with molecular mass and becomes effective for molecules larger than methane, which showed virtually no adsorption over the pressure range considered.

Although gate-opening effects have been reported for several metal organic frameworks,[22−26] very little has been published on mixture selectivity for these kinds of systems. Apart from the exciting scientific curiosity that gate opening represents, it remained to be demonstrated that this effect is selective in the presence of several adsorbates. Therefore, we assessed the performance of ZIF-7 for the separation of olefin/paraffin mixtures: binary adsorption was studied in terms of breakthrough experiments. Figure 3 shows the separation performance for a 40:40:20 ethane/ethylene/hydrogen mixture over a 60 mm, $^1/_4$ in. column filled with 500 mg of ZIF-7 pellets (particle size 500−710 μm). H_2 was used as a nonadsorbing diluent to determine the residence time in the setup and accurately calculate the separation selectivity. Practically from the beginning of the experiment, ethylene free of ethane was obtained until 2.5 mL of ethane (0.25 mol kg^{-1}) had been adsorbed. After that point the paraffin kept adsorbing, but some breakthrough was observed. It is noted that even though the partial pressure of ethylene used was enough to *open* the structure, the ZIF-7 adsorbent showed remarkable ethane selectivity.

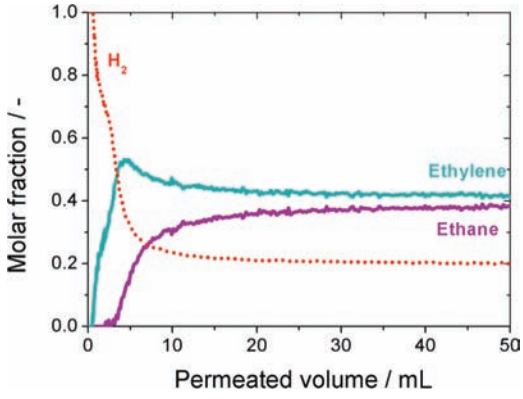

Figure 3. Breakthrough profile (molar fraction at the exit of the column vs permeated volume) obtained for an equimolar mixture of C_2H_4 and C_2H_6 on a column packed with ZIF-7 pellets at 25 °C and 1 bar. H_2, contributing the 20% of the mixture flow, was added to monitor the dead volume of the breakthrough setup [flow rates: $F_{C_2H_6} = F_{C_2H_4} = 4$ mL(STP)/min].

These results confirm ZIF-7 as an excellent adsorbent for the selective separation of ethane from ethylene and demonstrate that gate-opening effects can be effectively used to discriminate between molecules with very similar properties. At the end of the breakthrough experiment, almost 4 times more ethane than ethylene had adsorbed on the MOF. This paraffin/olefin selectivity is the same in magnitude as the inverse olefin/paraffin selectivity found for zeolite 13X,[6,7,9,27,28] a state-of-the-art adsorbent for this separation. Since in the case of ZIF-7 this *inverse selectivity* yields 100% pure ethylene during the adsorption cycle in a breakthrough experiment, simpler and cheaper processes based on this new adsorbent can be designed.

In order to fully appreciate the potential of ZIF-7 for this type of separation, desorption from a saturated column was also studied. For practical purposes, regeneration of the adsorbent is an important aspect, as it determines a large part of the operational cost of the adsorptive separation process.[4] Figure 4 shows the desorption profile measured at the outlet of the breakthrough column presaturated with a mixture of C_2H_4 and C_2H_6. The column was flushed with He [55 mL(STP)/min] and kept at a constant temperature of 30 °C. The concentration of the very weakly adsorbed C_2H_4 declined faster than the larger amount of C_2H_6, but both were desorbed in less than 6 min, which is about the same as the time required for the uptake process of Figure 3 (∼7 min). The remarkable *hump* observed at the end of ethane desorption deserves special attention: it seems that gate opening also plays an important role in this step, accelerating the kinetics of desorption. In accordance with the steep isotherm steps, a decrease in the adsorbate partial pressure efficiently drives the desorption process, resulting in a time scale similar to that for the uptake process. This is rather uncommon, as many adsorption processes exhibit a so-called favorable adsorption isotherm, resulting in a much more difficult (i.e., slower) desorption process. This result emphasizes the high potential of ZIF-7.

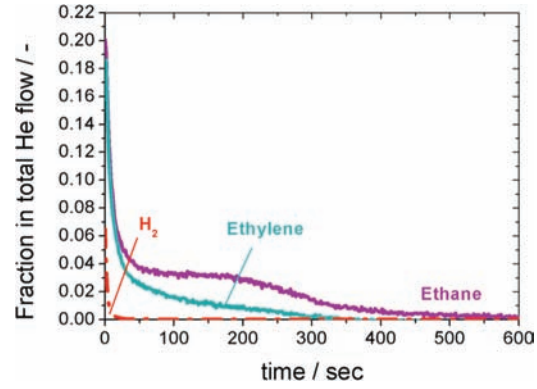

Figure 4. Desorption profiles of ethylene and ethane from a ZIF-7 column at 25 °C and 1 bar total pressure under continuous He flow [55 mL(STP)/min].

In summary, we have shown the first example of a microporous material displaying selective adsorption of paraffins over olefins. The interaction between the adsorbates and the benzene rings in the narrow ZIF-7 windows appears to dominate the adsorption process, inducing a *gate-opening* effect and selectively discriminating between molecules with very similar sizes but different shapes. This gate-opening effect can be utilized in the separation

of mixtures, resulting in an *inverse adsorption selectivity* for the paraffin. In addition, desorption of the adsorbed species proceeds quickly, even at low temperatures. These findings might finally open the door to simpler and more efficient separation processes. Moreover, ZIF-7 membranes are already available,[18] and they might display in a similar fashion the selective permeation of paraffins. Finally, because of the almost infinite chemical diversity of MOFs, we forecast[29] further improvements in the separation efficiency through, for example, functionalization[30] of the BIM linker.

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Supporting Information Available: Full experimental details (synthesis, characterization, XRD data, and experimental methodology). This material is available free of charge via the Internet at http://pubs.acs.org.

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