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p-Xylene-Selective Metal−Organic Frameworks: A Case of Topology-Directed Selectivity

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Supporting Information

ABSTRACT: Para-disubstituted alkylaromatics such as *p*-xylene are preferentially adsorbed from an isomer mixture on three isostructural metal−organic frameworks: MIL-125(Ti) ($[Ti_8O_8(OH)_4(BDC)_6]$), MIL-125(Ti)-NH_2 ($[Ti_8O_8(OH)_4(BDC\text{-}NH_2)_6]$), and CAU-1(Al)-$NH_2$ ($[Al_8(OH)_4(OCH_3)_8(BDC\text{-}NH_2)_6]$) (BDC = 1,4-benzenedicarboxylate). Their unique structure contains octahedral cages, which can separate molecules on the basis of differences in packing and interaction with the pore walls, as well as smaller tetrahedral cages, which are capable of separating molecules by molecular sieving. These experimental data are in line with predictions by molecular simulations. Additional adsorption and microcalorimetric experiments provide insight in the complementary role of the two cage types in providing the para selectivity.

The isolation of *p*-xylene (pX) from a mixture of xylenes is one of the most important liquid-phase separations in industry.[1] Regular distillation is not an option because the boiling points of the isomers are too close [e.g., 138.35 °C for pX; 139.10 °C for *m*-xylene (mX)]. Crystallization as well as azeotropic or extractive distillation[2] can be used to separate all three isomers, but the preferred technology is separation by adsorption, as in the commercial Parex process.[2] This process employs the simulated-moving-bed (SMB) concept using a zeolite adsorbent material. On the basis of the kinetic diameters (∅), one may separate the slimmer pX ($\varnothing_{pX}$ = 0.58 nm) from *o*-xylene (oX; $\varnothing_{oX}$ = 0.65 nm) and mX ($\varnothing_{mX}$ = 0.64 nm) by molecular sieving using medium-pore zeolites with the MFI topology (e.g., silicalite or ZSM-5).[3] However, the uptake capacity of such zeolites is relatively limited. Therefore, the currently used material is an FAU-type zeolite (e.g., zeolite KBaY), which shows a moderate selectivity for the para isomer based on xylene−cation interactions and favorable pX packing in the faujasite supercages.[3a]

More recently, several metal−organic frameworks (MOFs)[4] have been found suitable for performing liquid-phase purifications and separations,[5] including the difficult separation of pX and mX.[5a] However, no MOF material has been described that exhibits a clear para preference in the liquid phase, which is highly desired for an adsorbent to be used in an SMB process.[6] For instance, while the $V^{IV}{=}O$ terephthalate MIL-47 prefers pX over mX, it does not discriminate between pX and oX.[5a] For a MOF to be selective toward the para isomer, several properties may be exploited: one can look for a preferential interaction between the framework and the para isomer, or one may combine this with a molecular sieving effect. In view of the kinetic diameters, molecular sieving of xylenes can be achieved only with cages or windows in a range between ∼0.5 and 0.64 nm. Rather than the synthesis and experimental screening of a large variety of MOFs to find a para-selective material, a more efficient strategy would be to determine the pore size distributions computationally from the crystal structures and discard any structures with pore sizes outside the desired range. Next, the performance of the remaining structures could be tested using molecular simulations before a detailed experimental study is conducted. Here we reveal that MIL-125(Ti)[7a] and MIL-125(Ti)-NH_2[7b] are capable of selectively isolating pX from a mixture of xylenes. After the adsorption behavior was simulated, a detailed experimental study involving continuous and batch experiments as well as microcalorimetry was performed on MIL-125(Ti)-NH_2 to evaluate the adsorption mechanism that was suggested by the molecular simulation. Finally, these findings were extrapolated to a third material, CAU-1(Al)-NH_2,[7c] which has a similar framework structure, as well as to other higher alkylaromatic adsorbates.

An extended computational screening of more than 25 MOF structures was conducted; details are given in the Supporting

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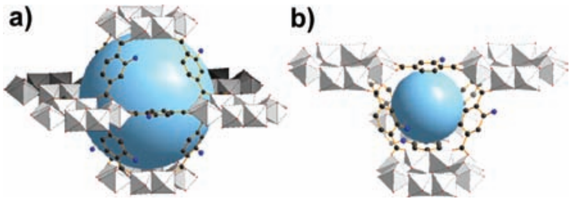

Figure 1. Representation of the (a) octahedral and (b) tetrahedral cages in MIL-125(Ti)-NH_2. The large blue spheres represent the effectively accessible volumes of the cages.

Information (SI). From this screening round, MIL-125(Ti)-NH_2[7b] emerged as a candidate structure with potential para selectivity. The quasi-cubic tetragonal structure of MIL-125(Ti)-NH_2 is built from cyclic octamers of edge- and corner-sharing $TiO_5(OH)$ octahedra that are connected by 2-aminoterephthalate linkers. Each octamer is surrounded by 12 secondary building unit (SBU) neighbors: four linkers are in the plane of the octameric wheel while four are above and four are below, resulting in a 3D structure that contains two types of cages (Figure 1). The large octahedral cages have been described as having a 1.25 nm accessible diameter;[7a] for the smaller tetrahedral cages, an approximate diameter of 0.61 nm has been proposed. The two types of cages are connected through triangular cage windows, with an aperture size in the range 0.5−0.7 nm. It should be noted that such aperture and cage sizes are to be interpreted less strictly in MOFs than in zeolites because of the potential for conformational changes in the pore wall. The tetrahedral cages have a rather complex shape with a cruciform cross-section, which allows pX molecules to be accommodated easily, while oX and particularly mX do not seem to fit inside (Figure S1 in the SI). All three isomers should have easy access to the octahedral cages. Similar structures have been reported for MIL-125(Ti)[7a] and CAU-1(Al)-NH_2.[7c]

Molecular simulations of vapor-phase adsorption of pX, mX, and oX suggest that the preference of MIL-125(Ti)-NH_2 for pX originates in both types of cages (Figure 2 and Figure S2). In general, the adsorption of xylenes in the tetrahedral cage seems to be energetically less favorable than the adsorption in the octahedral cages. At low vapor pressures, mX and oX can be localized only in the large octahedral cages of the structure. In these cages, both oX and mX are adsorbed in a rather disordered way in the center of the cages. pX is also adsorbed toward the center of the octahedral cages, but because of its shape, it manages to pack more efficiently and maximize adsorbate−adsorbate as well as adsorbate−framework interactions in comparison with oX and mX (Table S2 in the SI).

Accommodating xylenes inside the tetrahedral cages entails an energy penalty that is smaller for pX than for oX and even considerably smaller than for mX (Table S1). Because of their small kinetic diameter, additional pX molecules can be adsorbed, enhancing the preference of the overall material even further toward pX (Table S3). The selectivities predicted from molecular simulations of equimolar mixtures are 3.4 for a mixture of pX and mX and 2.8 for a mixture of pX and oX at 1 kPa. In summary, the simulations suggest that next to the para-selective octahedral cages, the narrow tetrahedral cages are able to accommodate pX molecules as well.

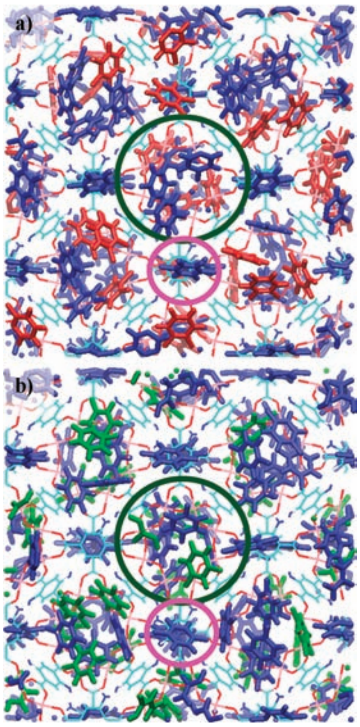

Figure 2. Molecular simulation snapshots of equimolar mixtures of (a) pX (blue) and oX (red) and (b) pX (blue) and mX (green) in MIL-125(Ti)-NH_2 at 1 kPa and 300 K. The large octahedral and small tetrahedral pores are highlighted in dark-green and pink, respectively.

To verify empirically the predicted adsorption selectivities, experimental separations were performed in a breakthrough setup by pumping binary solutions of xylenes in heptane over a column filled with MIL-125(Ti)-NH_2 crystallites. Initially, no xylenes eluted, indicating that they were completely adsorbed from the alkane background. In all of the experiments, the bulkier mX and oX molecules eluted first, followed by the slimmer pX molecules (Figure 3). In both breakthrough experiments, a clear so-called roll-up effect[8] was observed (Figure 3): initially both compounds are adsorbed, but as the structure gets saturated, the more preferred pX starts to displace the other isomers out of the cages, resulting in a temporary increase in the outlet concentration of the less preferred compound. This displacement implies that pX and either mX or oX compete for the same space in the cages of the host and confirms the results of the simulations, which suggested that pX is preferred in the octahedral cages over mX or oX. Furthermore, pX is likely to be accommodated in the tetrahedral cages, further enhancing the para selectivity. Average separation factors of 2.2 for pX versus oX and 3 for the important couple pX versus mX were obtained; these values correspond well to the separation factors obtained from the molecular simulations (Table 1).

Competitive adsorption experiments of pX versus mX in batch mode confirmed the para preference. pX was adsorbed up to 12 wt % (Figure 4), which is close to its maximal loading in single-compound experiments (Figure 5). However, mX was adsorbed only up to 4 wt %, which is far less than what is obtained in the single-compound adsorption isotherm. The separation factor (α), after an initial decrease at low concentrations, tended to remain more or less constant at ∼3 for higher loadings. This is indicative of (partial) coadsorption rather than complete competitive displacement. The value of α is similar to

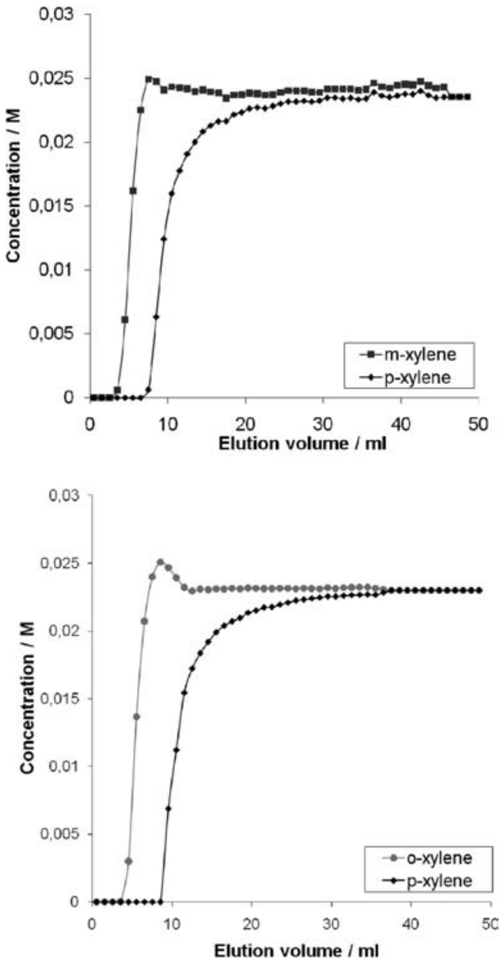

Figure 3. Breakthrough profiles for binary equimolar solutions of (top) mX and pX and (bottom) oX and pX in heptane (inlet concentrations 0.024 M) on a column filled with MIL-125(Ti)-NH_2 crystallites at 298 K: effluent concentrations of xylenes are shown as functions of the eluted volume. The curves have been corrected for dead volume.

Table 1. Average Separation Factors α_{ij} Calculated from the Breakthrough Experiments with Equimolar Binary Solutions of Xylene Isomers in Heptane (Inlet Concentrations 0.024 M)

	pX/mX	pX/oX	mX/oX
α_{ij}	3	2.2	0.97

those found for classical adsorbents (see the SI) and is also similar to the one obtained in the breakthrough experiments.

The order of preference was also confirmed in single-compound adsorption isotherms (Figure 5). pX was adsorbed most, reaching a saturation level of 14.5 wt %, while oX and mX were adsorbed only up to 10 wt %.

Microcalorimetric experiments confirmed the preferential interaction of the material with pX. The adsorption enthalpy for pX is significantly more negative than those for oX and mX at both low and high loadings (Figure S3). This can be explained by the better intermolecular packing arrangement of the pX molecules and the more favorable interaction between the pX molecules and the framework, as suggested by the molecular simulations.

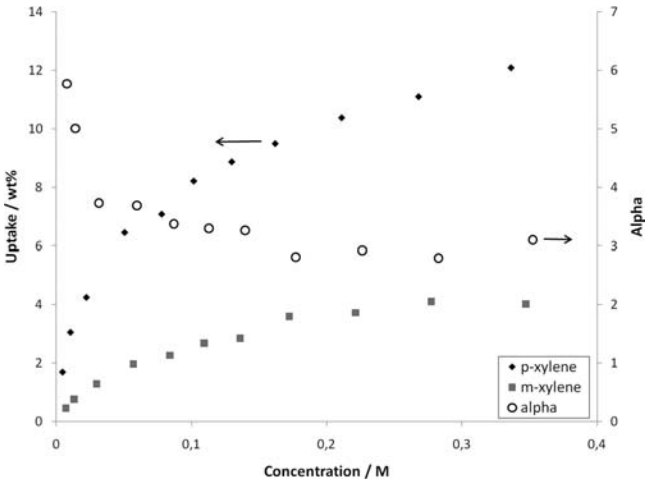

Figure 4. Competitive batch adsorption experiments on MIL-125(Ti)-NH_2: the uptake (wt %) from an equimolar mixture of mX and pX in heptane as a function of the equilibrium bulk-phase concentration of each compound is shown on the left axis. Separation factors α are given on the right axis.

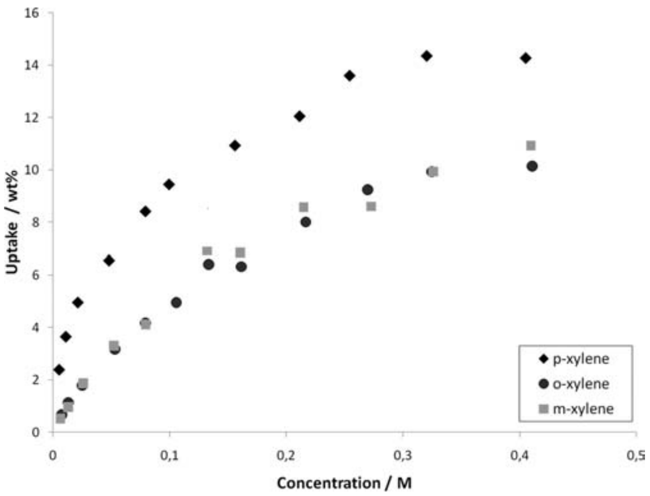

Figure 5. Single-compound adsorption isotherms on MIL-125(Ti)-NH_2 measured out of heptane in batch mode at 298 K: uptake (wt %) as a function of equilibrium phase concentration.

Table 2. Selectivities Calculated from the Uptakes from 0.028 M Equimolar Binary Solutions of pX and mX in Heptane by CAU-1(Al)-NH_2, MIL-125(Ti)-NH_2, and MIL-125(Ti)

	CAU-1(Al)-NH_2	MIL-125(Ti)-NH_2	MIL-125(Ti)
α_{p-m}	2.8	4.4	3.5

All of the experimental evidence for MIL-125(Ti)-NH_2 indicates that it is principally the structure, with its combination of narrow tetrahedral cages and larger octahedral cages, that is decisive for the para selectivity. This means that similar structures such as MIL-125(Ti) and CAU-1(Al)-NH_2 should also display para selectivity. As can be seen from the preliminary results in Table 2, all of these materials effectively adsorb pX over mX preferentially.

In addition to the fact that isotypic materials show a similar para-selective behavior for xylenes, it is also reasonable to assume that other alkylaromatic isomers with shapes and kinetic diameters similar to those of xylenes could be adsorbed with the same order of preference. This was confirmed for MIL-125(Ti)-NH_2 by pulse chromatographic results for the separation of xylenes, ethyltoluenes, and cymenes (Figure S4). Since the para compounds used have diameters similar to that of pX, this underpins the idea that MIL-125(Ti)-NH_2 has a preference toward para isomers because of its tetrahedral and octahedral cages. MIL-125(Ti)-NH_2 is the first MOF reported to be capable of separating *p*-cymene and *m*-cymene with a separation factor of >10.[9]

In an industrial context, not only the separation of the xylenes but also that of ethylbenzene (EB) and pX is relevant. Remarkably, MIL-125(Ti)-NH_2 also prefers pX over EB, with a separation factor of 1.6 calculated from a breakthrough experiment (Figure S5). As EB and pX have the same kinetic diameter, this proves that molecular sieving in the small tetrahedral cages is not the only mechanism determining the pX selectivity but that the shape of the molecules has a large influence as well on the preferential adsorption of pX in the octahedral cages.

In conclusion, we have shown that it is possible to select a MOF topology with a high pX preference through computational screening. On the basis of simulation data that were confirmed by experimental analysis, MIL-125(Ti)-NH_2, MIL-125(Ti) and CAU-1(Al)-NH_2 were found to be para-selective. The para selectivity originates from both types of cages, combining packing effects in the large cages with molecular sieving effects in the smaller cages to enhance the selectivity. This para selectivity is also present for the higher alkylaromatics, indicating the great potential of this topology for future separations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures; details on microcalorimetry, molecular simulations, and characterization of the materials; and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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