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Entropic Separation of Styrene/Ethylbenzene Mixtures by Exploitation of Subtle Differences in Molecular Configurations in Ordered Crystalline Nanoporous Adsorbents

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S Supporting Information

ABSTRACT: The separation of styrene/ethylbenzene mixture is of great importance in the petrochemical industry. Current technology uses distillation; this separation is difficult because of the small, 9 K, difference in the boiling points. An alternative separation method uses selective adsorption in nanoporous materials such as zeolites and metal–organic frameworks. Here we present a simulation screening study for the separation of styrene/ethylbenzene mixture by adsorptive means in nanoporous materials near pore saturation conditions. Under these conditions, different entropic mechanisms can dictate the separation process. Commensurate stacking has the best trade-off between selectivity and saturation capacity and offers a geometrical solution to the separation problem. MIL-47 has the right channel size and topology for styrene to exhibit commensurate stacking offering high capacity and selectivity for styrene over ethylbenzene. Out of all the screened structures, MIL-47 was found to be the best candidate for the separation of styrene/ethylbenzene mixture.

INTRODUCTION

Styrene is an important feedstock in the petrochemical industry. The reactivity of its vinyl group makes styrene easy to polymerize and copolymerize, and therefore, it serves as raw material for the production of a great variety of materials, with the two most important being polystyrene and rubber.¹ Although styrene appears in small quantities in nature, the global consumption (of the order of millions of tons per year) requires its commercial production. There are two main methods to obtain styrene: dehydrogenation of ethylbenzene and coproduction of styrene and propylene oxide via hydroperoxidation of ethylbenzene. Direct dehydrogenation of ethylbenzene to styrene accounts for the majority of the production. The conventional method involves two steps: the alkylation of benzene with ethylene to produce ethylbenzene and the dehydrogenation of the ethylbenzene to produce styrene. Complete conversion is not achieved in the reactor, and therefore, the product stream contains a large fraction of ethylbenzene that has to be removed.

The preferred technology for the separation of ethylbenzene from styrene nowadays is extractive distillation² and vacuum distillation^{3,4} together with inhibitors like phenylene-diamines or dinitrophenols to avoid styrene from polymerizing. However, because of the similarity in the boiling point of styrene (418 K) and ethylbenzene (409 K), this process is energetically expensive and most of the energy needed for the production of styrene is used in the separation process. The process is even more complicated due of the presence of side products like toluene, *o*-xylene, and benzene.

An alternative energy-efficient separation strategy involves utilizing the molecular, chemical, and geometrical differences by means of adsorptive separation with nanoporous materials like metal–organic frameworks and zeolites. Ahmad et al.⁵ performed liquid chromatography separation using HKUST-1(Cu₃(BTC)₂) a metal–organic framework with open Cu(II) sites and BTC(1,3,5-benzenetricarboxylate) linkers. They found that styrene is preferentially adsorbed in the structure because of the coordinative interaction of styrene with the Cu(II) in a π -complexation mechanism. Maes et al.^{6,7} and Remy et al.⁸ reported results on MIL-47(V) and MIL-53(Al), showing both structures are capable of separation in the liquid phase. They found that in MIL-47(V) styrene selectivity is related to styrene capacity for packing, while for MIL-53(Al) styrene selectivity is related to adsorption enthalpy (interaction with the carboxylate). For competitive adsorption in static conditions, they reported separation factors of 3.6 and 4.1 for MIL-47(V) and MIL-53(Al), respectively, and for an equimolar mixture in dynamic conditions (breakthrough experiments using a column filled with crystallites in an HPLC apparatus) they found separation factors of 2.9 and 2.3. They also observed that if a more realistic mixture is taken into account (with toluene and *o*-xylene) in MIL-53, *o*-xylene and toluene are retained even longer, which makes the material good for impurity removal. Yang and Yan⁹ conducted experiments on stationary phase HPLC with MIL-101(Cr), a material built

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from a hybrid supertetrahedral building unit formed by terephthalate ligands and trimeric chromium octahedral clusters. Similar to the case of HKUST-1, they reported a higher affinity toward styrene due to the π - π interactions with the metal-organic framework walls and the unsaturated metal sites. They also reported the efficient separation of impurities like *o*-xylene and toluene.

Separation based on adsorption relies on either adsorption or diffusion characteristics. At low loadings (i.e., the Henry regime), the selectivity is mainly driven by enthalpic effects, and favors the molecule with the strongest interaction with the framework. Selectivity is therefore strongly related to adsorbent and adsorbate properties such as dipole moment, polarizability, quadrupole moment, and magnetic susceptibility. At saturation conditions (industrial setup), the selectivity is driven by either enthalpic effects and/or entropic effects, like (i) “commensurate freezing”,¹⁰ which favors molecules for which size is commensurate with the channel; (ii) “size entropy”,^{11,12} which favors the smallest molecules; (iii) “length entropy”,^{11,13–15} which favors the molecules with the shortest effective length (footprint) in one-dimensional (1D) channels; (iv) “commensurate stacking”,¹⁶ which favors molecules with stacking arrangements that are commensurate with the dimensions of one-dimensional channels; (v) “face-to-face stacking”,¹⁷ which favors molecules that, when reoriented, significantly reduce their footprint in one-dimensional channels.

The various separation strategies for exploitation of molecular packing effects have been reviewed recently.¹⁸

Styrene and ethylbenzene are very similar molecules, with the main difference being that styrene is a flat molecule whereas ethylbenzene is not. Finding structures with selective adsorption for styrene is not easy. In this work, we present a screening study for the separation of styrene and ethylbenzene at liquid conditions. We propose to separate on the basis of a difference in saturation loading because it is more cost-efficient and utilizes the pore volume most efficiently.

METHODOLOGY SECTION

Methodology. The systems were modeled using classical force fields. The adsorbates were modeled with OPLS-AA force field for organic liquids.¹⁹ In previous work¹⁶ we have shown that the use of these force fields is in good agreement with experiments. Because we were interested in the selectivity of planar/nonplanar molecules and not in their conformational changes, adsorbates were described as multisite rigid molecules with properties and configurations shown in Figure 1. The parameters for the interaction of the adsorbates (Lennard-Jones and electrostatic interactions) together with a schematic representation of the molecules showing the atom types are presented in Table 1. Cross-interactions with other molecules and the framework were computed using Lorentz-Berthelot mixing rules.

The frameworks were modeled as rigid with atom positions taken from crystallographic experimental data. Most MOFs were further optimized using VASP^{23,24} with the cell fixed to the experimentally determined unit cell size and shape (PBE^{25,26} exchange-correlation functional with dispersion corrections²⁷ was used and the PAW method was applied to describe the core atoms; convergence criteria of the ionic forces was set to 1×10^3 eV/Å). The metal-organic frameworks were modeled using the DREIDING force field,²⁸ and van der Waals parameters not found in DREIDING were taken from the universal force field (UFF).²⁹ DREIDING and UFF force fields were designed to be very generic, so that broad coverage of the periodic table, including inorganic compounds, metals, and transition metals, could be achieved. UFF was tailored for simulating molecules containing any combination of elements in the periodic table. For

Figure 1. Styrene (top) and ethylbenzene (bottom) configurations. The figure shows the typical properties of the modeled adsorbates. Distances are “molecular shadow lengths”²⁰ from Materials Studio.²¹ Besides small differences in the charges, the main difference between these molecules is their height (planarity).

Table 1. OPLS-AA Force Field Parameters for Styrene and Ethylbenzene^{19a}

atom/group	q [e ⁻]	σ [Å]	ϵ [kcal mol ⁻¹]
C	-0.115	3.55	0.070
C1	-0.115	3.55	0.076
C2	-0.005	3.50	0.066
C3	-0.180	3.50	0.066
C4	-0.000	3.55	0.076
C5	-0.115	3.55	0.076
C6	-0.148*	3.55	0.076
H	0.115	2.42	0.030
H1	0.060	2.42	0.030
H2	0.074*	2.42	0.030

^aThe vinyl group charges (*) were taken from Siu et al.²²

the zeolites, the TraPPE³⁰ force field was used. This force field was specifically developed for zeolites.

The charge-charge interactions were computed using the Ewald summation (relative precision 10^{-6}). Charges for the frameworks were computed by minimizing the difference of the classical electrostatic potential and a quantum mechanics electrostatic potential over many grid points using the REPEAT method.^{31,32}

Adsorption Isotherms. To compute the adsorption isotherms, we performed Monte Carlo simulation in the grand-canonical ensemble (or μ, V, T ensemble). In this ensemble, the number of adsorbates fluctuates until equilibrium conditions are reached: the temperature and chemical potential of the gas inside and outside the adsorbent are equal. Because in confined systems the fraction of successful insertions and deletions is very low, reaching equilibrium with conventional Monte Carlo methods can be very time-consuming. In this study, we used the Configurational Bias Continuous Fractional Monte Carlo (CB/CFCMC)³³ method to enhance the success rate of insertions and deletions. The method is a combination of the Configurational Bias Monte Carlo (CBMC),^{34–36} where molecular growth is biased toward favorable configurations, and Continuous Fractional Component Monte Carlo (CFCMC),³⁷ in which molecules are gradually inserted or deleted by scaling their interactions with the surroundings. We have shown in previous work³³ that the results obtained with this method do not differ from CBMC calculations but the efficiency is higher. More details can be found in the Supporting Information.

Using the dual-site Langmuir-Freundlich fits of the pure component isotherms, breakthrough calculations were carried out by solving a set of partial differential equations for each of the species in the gas mixture.^{38,39} The molar loadings of the species at any position along the packed bed and at any time were determined from Ideal

Figure 2. (a) Simulated single component isotherms of styrene and ethylbenzene in MFI-para at 433 K. (b) Snapshot of ethylbenzene (top) and styrene (bottom) at 1×10^9 Pa and 433 K.

Adsorbed Solution Theory calculations. Video animations of the breakthrough behavior as a function of time of selected structures are available in the Supporting Information.

RESULTS

We perform a screening study of several zeolites and metal–organic frameworks for the separation of styrene/ethylbenzene mixture focusing on saturation conditions. Under these conditions, differences in the saturation capacity of the mixture components strongly dictate the separation.

In systems with small pores, like MRE and MTW zeolites, molecules are forced to adsorb parallel to the channels. The saturation capacity is determined by the effective length per molecule in the channel (*footprint*). Because of the similarity in the length of styrene and ethylbenzene, the difference in saturation capacities is almost negligible, making systems with small pores unsuitable candidates for the separation.

In structures with cavities or channels much larger than styrene and ethylbenzene molecular dimensions, like IRMOF-1 and Zn-DOBDC, molecules do not present any particular packing. The observed difference in the saturation capacities is a consequence of the natural packing of the molecules in liquid phase ($\rho_{\text{Eb}} = 0.8665$ g/mL, $\rho_{\text{St}} = 0.909$ g/mL). This makes these materials also unsuitable for the separation process.

We have identified a few materials where styrene has a higher saturation capacity than ethylbenzene. In the following we describe how this difference arises from the previously mentioned entropic mechanisms and we highlight their applicability for the separation process.

Size Exclusion. is observed in MFI-para.⁴⁰ MFI-para is a ZSM-5 zeolite which structure is a combination of interconnected straight and zigzag channels. The straight channels have a diameter of 5.3×5.6 Å and the zigzag channels have a diameter of 5.1×5.5 Å. In Figure 2 the simulated single component isotherms of styrene and ethylbenzene in MFI-para at 433 K and snapshots of styrene and ethylbenzene at 1×10^9 Pa and 433 K are presented. At low loadings molecules preferentially adsorb in the straight channels, the difference in loadings arise from a stronger interaction of styrene with MFI-para. At saturation conditions, styrene can obtain almost twice the loading of ethylbenzene because of a size exclusion effect in the zigzag channels in which ethylbenzene does not fit due to its height. When an equimolar styrene/ethylbenzene mixture is considered, the difference in loadings at saturation conditions is even larger (Supporting

Information Figure S2b). Breakthrough simulations confirm the strong styrene selectivity of MFI-para (Figures S3).

Face-to-Face Stacking. Face to-face stacking occurs in MAZ⁴¹ and AFI⁴² zeolites. MAZ and AFI are 1D-channel zeolites with dimensions that allow a molecular reorientation of ethylbenzene and styrene.

In Figure 3, we present the simulation results for the single component isotherms of ethylbenzene and styrene in AFI

Figure 3. Single component isotherms of styrene and ethylbenzene in AFI at 433 K. Inset: Snapshots of styrene (top) and ethylbenzene (bottom) at 1×10^3 and 1×10^9 Pa. At low loadings, both molecules are adsorbed with the phenyl group parallel to the channel axis. At higher pressures, styrene can arrange in a tilted face-to-face stacking configuration, which reduces its footprint and allows for a higher saturation capacity. The difference in saturation capacities ensures the selectivity of AFI toward styrene at saturation conditions in the mixture.

zeolite at 433 K. At low loadings, molecules are mostly adsorbed flat on the walls (parallel to the channels axis), and adsorption is dictated by enthalpy effects, which favors ethylbenzene. As the loading increases, the molecules undergo a molecular reorientation from a configuration parallel to the channel axis to a “pile” configuration with the phenyl groups facing each other. This new configuration (face-to-face stacking) reduces styrene’s footprint more than ethylbenzene’s footprint (Figure 4a) because of the nonplanarity of ethylbenzene, allowing styrene to obtain higher saturation loadings.

For MAZ zeolite, a similar behavior is observed; however, because MAZ zeolite has smaller channels than AFI does, the angle at which molecules can reorient has a smaller effect on the reduction of the molecule’s footprint in the channels

Figure 4. Schematic representation of different entropic effects occurring in the separation of styrene and ethylbenzene in nanoporous materials. (a) The reduction of the molecule's footprint in the channels because of a reorientation into a face-to-face stacking configuration. (b) Effect of the channel size on the reorientation and therefore molecule's footprint reduction. (c) Comparison of the channel length needed for two molecules of styrene to have commensurate stacking vs two molecules of ethylbenzene to have face-to-face stacking.

(Figure 4b). When an equimolar mixture is considered, both AFI and MAZ zeolites are styrene selective at saturation conditions as shown in Figures S5b and S8b where the simulated mixture component isotherms at 433 K are presented.

Face-to-face stacking is also observed in DON zeolite. DON⁴³ is a structure with 1D-channels slightly larger than those of AFI and MAZ zeolites. This increase in dimensions favors ethylbenzene to undergo a molecular reorientation into a face-to-face stacking configuration but also, because the diameter of the channels are larger than the length of styrene, it induces styrene to adopt a “commensurate stacking” configuration where the stacking of two molecules with their phenyl groups facing each other is commensurate with the channel dimensions (Figure S10). This is also observed in MIL-53,⁴⁴ a metal–organic framework with lozenge-shaped rhombohedral channels of approximately 0.85 nm, as shown in Figure S13 where snapshots of styrene and ethylbenzene at 1×10^9 Pa and 433 K are presented. Because of styrene and ethylbenzene dimensions, styrene with commensurate stacking can obtain higher saturation capacities than ethylbenzene with face-to-face stacking as shown schematically in Figure 4c. This is also seen in DON and MIL-53 single component isotherms (Figures S11a and S14a). Mixture isotherms (Figures S11b and S14b) and breakthrough curves (Figures S12 and S15) further confirm that DON and MIL-53 are styrene selective structures.

Commensurate Stacking. Commensurate stacking for both styrene and ethylbenzene is observed in MIL-47⁴⁵ and MAF-X8.⁴⁶ MIL-47 is a metal–organic framework with lozenge-shaped rhombohedral channels which size (slightly larger than MIL-53) allows for ethylbenzene to also have commensurate stacking. In Figure 5 we present the simulated single component adsorption isotherms of ethylbenzene and styrene in MIL-47 at 433 K and snapshots of styrene and ethylbenzene at 1×10^6 Pa and 1×10^9 Pa. At 1×10^9 Pa both molecules have commensurate stacking, but in order for ethylbenzene to have commensurate stacking the phenyl groups have to be slightly shifted due to the nonplanar ethyl group. This shift affects the amount of ethylbenzene molecules that can be adsorbed (as compared to styrene) and therefore causes a difference in the saturation capacity of styrene and

Figure 5. Single component adsorption isotherms for styrene and ethylbenzene at 433 K in MIL-47. Inset: Styrene (top) and ethylbenzene (bottom) snapshots at 1×10^6 and 1×10^9 Pa. Styrene has commensurate stacking at lower pressures than ethylbenzene. Because of the out of plane ethyl group, ethylbenzene molecules have to be slightly shifted in order to have commensurate stacking and therefore less ethylbenzene molecules can be adsorbed in MIL-47 channels at saturation conditions.

ethylbenzene. Interestingly, commensurate stacking occurs at lower loading for styrene than for ethylbenzene. We can see in Figure 5 that at 1×10^6 Pa styrene already presents commensurate stacking while ethylbenzene seems to have more of a face-to-face stacking. In a mixture, this will favor styrene adsorption even more. In Figure 6, simulated mixture adsorption isotherms for an equimolar mixture in MIL-47 at 433 K are presented. MIL-47 is a styrene selective structure. Our results are in good qualitative agreement with Maes et al.⁶ Breakthrough simulations further confirm that MIL-47 is a styrene selective structure at saturation conditions.

In MAF-x8, a metal–organic framework with square channels of approximately 1 nm, it is easier for ethylbenzene to have commensurate stacking than in MIL-47. The single component isotherms of both molecules behave in a very similar manner. The topology of the structure seems to induce a shift between parallel styrene molecules and allows for the ethyl group of ethylbenzene to stick in the channel “pockets” (Figure S19). This might be the reason for the smaller

Figure 6. Styrene/ethylbenzene separation using MIL-47 at 433 K. (a) Equimolar mixture isotherms and Ideal Adsorption Solution Theory (IAST) prediction based on pure component isotherms. (b) Simulated step breakthrough at 1×10^6 Pa total fugacity. The IAST prediction is in excellent agreement with the mixture simulations. The mixture and breakthrough simulations show a high styrene selectivity and loading in the mixture.

difference in saturation capacities of styrene and ethylbenzene compared to MIL-47.

Combination/Competition of Mechanisms. Combination/competition of mechanisms is observed in structures with a more complex topology. An example of this is MOF-CJ3 metal–organic framework.⁴⁷ The wide segment of the channels are big enough to allow for both styrene and ethylbenzene to form two parallel rows (commensurate stacking); however, the shape of the channels forces ethylbenzene molecules to adopt a configuration where the ethyl group is pointing to the channel “pockets”. Styrene has more freedom and molecules can arrange in a way that an extra styrene can be adsorb in the protracted segments in a configuration perpendicular to the channel (face-to-face stacking) (Figure 7). The interplay

Figure 7. Snapshots of styrene (top) and ethylbenzene (bottom) at 1×10^9 Pa and 433 K in MOF-CJ3.

between different mechanisms rarely makes the separation better. Even when all the mechanisms favor a specific molecule, the competition between them can induce enough disorder to destroy the selectivity one could achieve with a “pure”-mechanism.

DISCUSSION

There are two important factors to consider when using adsorption for separation processes at industrial conditions, namely, selectivity and capacity. A high selectivity ensures that less cycles are needed to achieve a high degree of purity in the separation, but a high capacity implies that the regeneration time is longer. For a binary mixture, the adsorption selectivity is defined as

$$S_{\text{ads}} = \frac{q_1/q_2}{f_1/f_2} \quad (1)$$

and the capacity is defined as the styrene loading in the adsorbed phase of a binary mixture.

$$\text{capacity} = q_1 \quad (2)$$

In Figure 8, the relationship between these two properties for different structures is presented. Structures with the same separation mechanism are plotted with the same color. An ideal structure for the separation would be located at the right top corner.

In structures where the separation is driven by size-exclusion (MFI-para), the selectivity is high because there is an

Figure 8. Selectivity as a function of styrene loading (capacity) in a binary mixture at 433 K and 1×10^6 Pa total fugacity. The structures are divided in different colors depending on the selectivity mechanism observed. Color code: Size exclusion (red), face-to-face stacking (purple), commensurate stacking (blue), commensurate-stacking/face-to-face stacking (green), and mixed (orange). The dotted red line corresponds to the ratio styrene/ethylbenzene at liquid conditions. There is a natural trade-off between selectivity and loading, and finding structures in the top right corner is not feasible. The black dashed line (guide to the eye) denotes the inverse relationship between selectivity and capacity. MIL-47 is a styrene selective material with a high capacity and therefore a good candidate for the styrene/ethylbenzene separation.

adsorption site available only for styrene (zigzag channels), but the capacity is rather low since for size-exclusion to occur among similar molecules, there has to be a very tight fit between the molecules and the adsorbent, usually associated with small pore systems.

In structures where the separation is driven by face-to-face stacking, the selectivity relies on the increase of the molecule's footprint difference, consequence of a reorientation, and piling. Ideally, only one of the mixture components should be able to reorient, but in the case of styrene and ethylbenzene the similarity in their length and width makes no significant difference in the pore size needed for the reorientation. The selectivity relies thus on how favorable the reorientation and piling are.

In MAZ and AFI, both molecules can reorient but the reorientation is restricted by the pore size, forcing a tilting in the face-to-face stacking configuration that is unfavorable for ethylbenzene to form a pile but it is favorable for styrene. This allows styrene to obtain higher saturation loadings and ensures MAZ and AFI styrene selectivity at saturation conditions.

However, face-to-face stacking only occurs at high loadings. In Figure 8, the selectivity is presented at 1×10^6 Pa; at this fugacity, MAZ is not yet styrene selective and AFI selectivity is almost negligible. The effect of face-to-face stacking in styrene selectivity can only be observed at higher loadings as shown in Figure S30, where the selectivity as a function of styrene loading for higher fugacities is presented. Face-to-face stacking can only occur when the reoriented molecules are commensurate with the channel diameter. This has an important restriction in the pore size and therefore in the capacity.

In structures where styrene has commensurate stacking and ethylbenzene has face-to-face stacking (as observed in MIL-53 and DON), the difference in saturation capacities arises because the channel length needed to accommodate molecules of styrene in commensurate stacking is smaller than the channel length needed to accommodate molecules of ethylbenzene in face-to-face stacking. When an equimolar mixture is considered, styrene will be favored even more because it does not have to undergo any reorientation to achieve higher loadings. Structures with pore sizes that allow styrene to have commensurate stacking, but not ethylbenzene, are styrene selective and have a higher saturation capacity than structures that present face-to-face stacking or size exclusion.

In structures where both styrene and ethylbenzene can have commensurate stacking (MIL-47 and MAF-x8), the selectivity will depend on the efficiency in which the molecules can stack. In Figure 9, we present a schematic of commensurate stacking configurations of styrene and ethylbenzene. For ethylbenzene to have commensurate stacking, the "minimal length", the "packing length", or both have to be larger than that for styrene. At saturation conditions, this implies that more styrene molecules can be adsorbed than ethylbenzene ones, favoring the adsorption of styrene over ethylbenzene in a mixture. Commensurate stacking enhances the dimensional differences of styrene and ethylbenzene as "pairs" of molecules. Because commensurate stacking occurs in structures with larger pores, high capacity can be attained.

Commensurate stacking is the best mechanism for the separation of ethylbenzene and styrene. It offers a geometrical solution to the separation problem that ensures a high selectivity, and it occurs in open pore structures, ensuring a high capacity. The channel topology can facilitate or impede the selectivity.

Figure 9. Schematic differences of the channel dimensions needed for commensurate stacking. Because styrene is a planar molecule, commensurate stacking can occur in smaller channels. Commensurate stacking is a powerful separation mechanism for planar/nonplanar molecules.

In the case of MIL-47, the almost planar walls force ethylbenzene molecules to be shifted, increasing the difference in "length" per pair of molecules in the channel as compared to styrene. This makes MIL-47 a highly styrene selective material and the best candidate for the separation of styrene/ethylbenzene from the structures we screened.

CONCLUSION

Styrene and ethylbenzene are very similar molecules, and finding structures that can discriminate between them is not easy. At liquid conditions, the success in the separation process is strongly related to the difference in saturation capacities of the mixture components which in turn is strongly dictated by the underlying entropic mechanisms occurring in the nanoporous material. Commensurate stacking offers the best trade-off between saturation capacity and selectivity and is therefore a very efficient mechanism for the separation of styrene and ethylbenzene. Among the different structures we studied, MIL-47, a styrene selective structure, is the best candidate for the adsorptive separation of styrene/ethylbenzene mixture in nanoporous materials. Commensurate stacking offers a geometrical solution to the separation of planar/nonplanar molecules, and this enables a convenient approach to designing materials for the separation.

ASSOCIATED CONTENT

Supporting Information

Structural details of various materials investigated, pure component and mixture adsorption data, dual-Langmuir–Freundlich fits parameters for unary isotherms, and transient breakthrough simulation results for various materials. Video animations of the breakthroughs in various microporous adsorbents operating at a total pressure of 100 kPa and 433 K. 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.

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REFERENCES

- (1) Wunsch, J. *Polystyrene: Synthesis, Production and Applications*; Rapra Technology Ltd.: Telford, UK, 2000.
- (2) Gentry, J. C.; Kumar, S.; Wright-Wytcherley, R. Use Extractive Distillation to Simplify Petrochemical Processes. *Hydrocarbon Process.* **2004**, *93*, 62–66.
- (3) Randall, G. Method of Separating Ethylbenzene from Styrene by Low Pressure Drop Distillation. U.S. Patent 3.084.108, 1963; <http://www.google.com/patents/US3084108>.
- (4) van Tassell, H. Separation of Ethylbenzene and Styrene by Low Pressure. High Temperature Distillation. U.S. Patent 3.398.063, 1968; <http://www.google.com/patents/US3398063>.
- (5) Ahmad, R.; Wong-Foy, A. G.; Matzger, A. J. Microporous Coordination Polymers as Selective Sorbents for Liquid Chromatography. *Langmuir* **2009**, *25*, 11977–9.
- (6) Maes, M.; Alaerts, L.; Vermoortele, F.; Ameloot, R.; Couck, S.; Finsy, V.; Denayer, J. F. M.; De Vos, D. E. Separation of C5-hydrocarbons on Microporous Materials: Complementary Performance of MOFs and Zeolites. *J. Am. Chem. Soc.* **2010**, *132*, 2284–2292.
- (7) Maes, M.; Vermoortele, F.; Alaerts, L.; Couck, S.; Kirschhock, C. E. A.; Denayer, J. F. M.; De Vos, D. E. Separation of Styrene and Ethylbenzene on Metal-Organic Frameworks: Analogous Structures with Different Adsorption Mechanisms. *J. Am. Chem. Soc.* **2010**, *132*, 15277–15285.
- (8) Remy, T.; Ma, L.; Maes, M.; Vos, D. E. D.; Baron, G. V.; Denayer, J. F. M. Vapor-Phase Adsorption and Separation of Ethylbenzene and Styrene on the Metal-Organic Frameworks MIL-47 and MIL-53(Al). *Ind. Eng. Chem. Res.* **2012**, *5*, 14824–14833.
- (9) Yang, C.-X.; Yan, X.-P. Metal-Organic Framework MIL-101(Cr) for High-Performance Liquid Chromatographic Separation of Substituted Aromatics. *Anal. Chem.* **2011**, *71*, 7144–7150.
- (10) Smit, B.; Maesen, T. Commensurate “Freezing” of Alkanes in the Channels of a Zeolite. *Nature* **1994**, *374*, 42–44.
- (11) Talbot, J. Analysis of Adsorption Selectivity in a One-Dimensional Model System. *AIChE. J.* **1997**, *43*, 2471–2478.
- (12) Du, Z.; Manos, G.; Vlucht, T.; Smit, B. Molecular Simulation of Adsorption of Short Linear Alkanes and Their Mixtures in Silicalite. *AIChE. J.* **1998**, *44*, 1756–1764.
- (13) van Baten, J. M.; Krishna, R. Entropy Effects in Adsorption and Diffusion of Alkane Isomers in Mordenite: An Investigation using CBMC and MD simulations. *Microporous Mesoporous Mater.* **2005**, *84*, 179–191.
- (14) Krishna, R.; Smit, B.; Calero, S. Entropy Effects During Sorption of Alkanes in Zeolites. *Chem. Soc. Rev.* **2002**, *31*, 185–194.
- (15) Krishna, R.; van Baten, J. M. In Silico Screening of Metal-Organic Frameworks in Separation Applications. *Phys. Chem. Chem. Phys.* **2011**, *13*, 10593–10616.
- (16) Torres-Knoop, A.; Krishna, R.; Dubbeldam, D. Separating Xylene Isomers by Commensurate Stacking of p-Xylene within Channels of MAF-X8. *Angew. Chem. Int.* **2014**, *53*, 7774–7778.
- (17) Torres-Knoop, A.; Balestra, S. R. G.; Krishna, R.; Calero, S.; Dubbeldam, D. Entropic Separations of Mixtures of Aromatics by Selective Face-to-Face Molecular Stacking in One-Dimensional Channels of Metal-Organic Frameworks and Zeolites. *Chem. Phys. Chem.* **2015**, *16*, 532–535.
- (18) Krishna, R. Separating Mixtures by Exploiting Molecular Packing Effects in Microporous Materials. *Phys. Chem. Chem. Phys.* **2015**, *17*, 39–59.
- (19) Jorgensen, W.; Maxwell, D.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- (20) Rohrbaugh, R.; Jurs, P. Description of Molecular Shape Applied in Studies of Structure/Activity and Structure/Property Relationships. *Anal. Chim. Acta* **1987**, *199*, 99–109.
- (21) *Materials Studio*; Accelrys Software Inc.: San Diego, 2001–2007; <http://accelrys.com/products/materials-studio/index.html>.
- (22) Siu, S. W. I.; Pluhackova, K.; Bockmann, R. A. Optimization of the OPLS-AA Force Field for Long Hydrocarbons. *J. Chem. Theory Comput.* **2012**, *8*, 1459–1470.
- (23) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558.
- (24) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169.
- (25) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (26) Perdew, J. P.; Burke, K.; Ernzerhof, M. Erratum: Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (27) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (28) Mayo, S.; Olafson, B.; Goddard, W. DREIDING - A Generic Force-field for Molecular Simulations. *J. Phys. Chem.* **1990**, *94*, 8897–8909.
- (29) Rappé, A.; Casewit, C.; Colwell, K.; Goddard, W.; Skiff, W. UFF, A Full Periodic-table Force-Field for Molecular Mechanics and Molecular-Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
- (30) Bai, P.; Tsapatsis, M.; Siepmann, J. I. TraPPE-zeo: Transferable Potentials for Phase Equilibria Force Field for All-Silica Zeolites. *J. Phys. Chem. C* **2013**, *117*, 24375–24387.
- (31) Campana, C.; Mussard, B.; Woo, T. Electrostatic Potential Derived Atomic Charges for Periodic Systems Using a Modified Error Functional. *J. Chem. Theory Comput.* **2009**, *5*, 2866–2878.
- (32) Watanabe, T.; Manz, T.; Sholl, D. Accurate Treatment of Electrostatics during Molecular Adsorption in Nanoporous Crystals without Assigning Point Charges to Framework Atoms. *J. Phys. Chem. C* **2011**, *115*, 4824–4836.
- (33) Torres-Knoop, A.; Balaji, S. P.; Vlucht, T.; Dubbeldam, D. A Comparison of Advanced Monte Carlo Methods for Open Systems: CFMC vs CBMC. *J. Chem. Theory Comput.* **2014**, *10*, 942–952.
- (34) Siepmann, J. A. Method for the Direct Calculation of Chemical-Potentials for Dense Chain Systems. *Mol. Phys.* **1990**, *70*, 1145–1158.
- (35) Siepmann, J.; Frenkel, D. Configurational Bias Monte-Carlo - A New Sampling Scheme for Flexible Chains. *Mol. Phys.* **1992**, *75*, 59–70.
- (36) Frenkel, D.; Mooij, G.; Smit, B. Novel Scheme to Study Structural and Thermal-properties of Continuously Deformable Molecules. *J. Phys.: Condens. Matter* **1992**, *4*, 3053–3076.
- (37) Shi, W.; Maginn, E. Continuous Fractional Component Monte Carlo: An Adaptive Biasing Method for Open System Atomistic Simulations. *J. Chem. Theory Comput.* **2007**, *3*, 1451–1463.
- (38) Krishna, R. The Maxwell-Stefan Description of Mixture Diffusion in Nanoporous Crystalline Materials. *Microporous Mesoporous Mater.* **2014**, *185*, 30–50.
- (39) Krishna, R.; Long, J. Screening Metal-organic Frameworks by Analysis of Transient Breakthrough of Gas Mixtures in a Fixed Bed Adsorber. *J. Phys. Chem. C* **2011**, *115*, 12941–12950.
- (40) van Koningsveld, H.; F. Tuinstra, H. v. B.; Jansen, J. C. The Location of p-Xylene in a Single Crystal of Zeolite H-ZSM-5 with a New Sorbate-Induced, Orthorhombic Framework Symmetry. *Acta Crystallogr.* **1989**, *B45*, 423–431.
- (41) Galli, E. Crystal Structure Refinement of Mazzite. *Rend. Soc. Ital. Mineral. Petrol.* **1975**, *31*, 599–612.
- (42) Qiu, S.; Pang, W.; Kessler, H.; Guth, J. Synthesis and Structure of the $[\text{AlPO}_4]_{12}\text{Pr}_4\text{NF}$ Molecular Sieve with AFI Structure. *Zeolites* **1989**, *9*, 440–444.

- (43) Wessels, T.; Baerlocher, C.; McCusker, L.; Creighton, E. An Ordered Form of the extra-large-pore zeolite UTD-1: Synthesis and Structure Analysis from Powder Diffraction Data. *J. Am. Chem. Soc.* **1999**, *121*, 6242–6247.
- (44) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Ferey, G. Very Large Breathing Effect in the First Nanoporous Chromium(III)-based Solids: MIL-53 or $\text{Cr}^{\text{III}}(\text{OH})\cdot\{\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\}\cdot\{\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}\}_x\cdot\text{H}_2\text{O}_y$. *J. Am. Chem. Soc.* **2002**, *124*, 13519–13526.
- (45) Barthelet, K.; Marrot, J.; Riou, D.; Ferey, G. A Breathing Hybrid Organic-Inorganic Solid with very Large Pores and High Magnetic Characteristics. *Ang. Chem., Int. Ed.* **2002**, *41*, 281–284.
- (46) He, C.-T.; Tian, J.-Y.; Liu, S.-Y.; Ouyang, G.; Zhang, J.-P.; Chen, X.-M. A Porous Coordination Framework for Highly Sensitive and Selective Solid-Phase Microextraction of Non-polar Volatile Organic Compounds. *Chem. Sci.* **2013**, *4*, 351–356.
- (47) Fang, Z.; Zheng, S.; Tan, J.; Cai, S.; Fan, J.; Yan, X.; Zhang, W. Tubular Metal-Organic Framework-based Capillary Gas Chromatography Column for Separation of Alkanes and Aromatic Positional Isomers. *J. Chromatogr. A* **2013**, 132–138.