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

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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. 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 distillation and vacuum distillation, 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 to 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. performed liquid chromatography separation using HKUST-1(Cu(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. and Remy et al. 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 Yan conducted experiments on stationary phase HPLC with MIL-101(Cr), a material built...
from a hybrid supercubic building unit formed by terphenylate 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 α-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 fixed to the experimentally determined unit cell size and shape (PBE35,36 exchange-correlation functional with dispersion corrections19 was used and the PAW method was applied to describe the core atoms; convergence criteria of the ionic forces was set to 1 × 10−6 eV/Å). The metal–organic frameworks were modeled using the DREIDING force field,21,22 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 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 10−5). 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 μVT 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 Fractional Monte Carlo (CB/CFCMC)35 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 work37 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 1. Styrene (top) and ethylbenzene (bottom) configurations. The figure shows the typical properties of the modeled adsorbates.](image)

**Table 1. OPLS-AA Force Field Parameters for Styrene and Ethylbenzene**

<table>
<thead>
<tr>
<th>atom/group</th>
<th>q [e−]</th>
<th>σ [Å]</th>
<th>ε [kcal mol−1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-0.115</td>
<td>3.55</td>
<td>0.070</td>
</tr>
<tr>
<td>C1</td>
<td>-0.115</td>
<td>3.55</td>
<td>0.076</td>
</tr>
<tr>
<td>C2</td>
<td>-0.005</td>
<td>3.50</td>
<td>0.066</td>
</tr>
<tr>
<td>C3</td>
<td>-0.180</td>
<td>3.50</td>
<td>0.066</td>
</tr>
<tr>
<td>C4</td>
<td>-0.000</td>
<td>3.55</td>
<td>0.076</td>
</tr>
<tr>
<td>C5</td>
<td>-0.115</td>
<td>3.55</td>
<td>0.076</td>
</tr>
<tr>
<td>C6</td>
<td>-0.148*</td>
<td>3.55</td>
<td>0.076</td>
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<tr>
<td>H</td>
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<td>2.42</td>
<td>0.030</td>
</tr>
<tr>
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<td>2.42</td>
<td>0.030</td>
</tr>
<tr>
<td>H2</td>
<td>0.074*</td>
<td>2.42</td>
<td>0.030</td>
</tr>
</tbody>
</table>

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

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 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, molecules are forced to adsorb parallel to the channels. The observed 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. 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 $5.3 \times 5.6$ Å and the zigzag channels have a diameter of $5.1 \times 5.5$ 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 arises 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 differences 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 MAZ and AFI 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 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.
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, 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 $1 \times 10^6$ 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-47 and MAF-X8. 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 $1 \times 10^6$ Pa and $1 \times 10^9$ Pa. At $1 \times 10^9$ 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 ethylbenzene. Interestingly, commensurate stacking occurs at lower loading for styrene than for ethylbenzene. We can see in Figure 5 that at $1 \times 10^6$ 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. 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
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. 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 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

\[ S_{ads} = \frac{q_1}{q_2} \frac{f_2}{f_1} \]

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

\[ \text{capacity} = q_1 \]

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...
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 $1 \times 10^6$ 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.

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

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