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Prospects for principles of size and shape selective separations using zeolites

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Abstract

Despite extensive investigation of zeolites beds and membranes, many aspects of separation using zeolites are not yet well understood. There is a pressing need to state general principles of size and shape selective separations. This work collates important experimental, theoretical and simulation contributions to size and shape selectivity. We review aspects that are well understood, highlight conflicting ideas that have been proposed, and identify aspects that have yet to be addressed adequately.

Keywords: Zeolites; Size and shape selective separations; Simulation

1. Introduction

1.1. Prospects for size and shape separation

The regular nanoporous networks of zeolites and other crystalline molecular sieves have been put to extensive and increasing use for separations. Among the most exciting applications are size and shape selective separation. There is an increasing interest in zeolite membranes for efficient, inexpensive separations to replace current expensive processes particularly when the components are very similar in boiling point (e.g., xylenes) or are too fragile to expose to high temperature (e.g., many pharmaceuticals).

General principles for design and optimization of size and shape selective separations are elusive, largely because the thermodynamics of confined fluids is still under investigation. The fluid molecules in a pore of molecular dimension experience a potential energy that varies strongly with position. As a result, the adsorbed phase is highly inhomogeneous. The pair correlation function and density depend strongly on the position inside the pore. Even if the wall can be considered nearly atomistically smooth, the adsorbed fluid will be strongly heterogeneous across the radius of the pore. Langmuir and related models of adsorption can be inadequate if they do not take into account details of adsorbate–adsorbate interactions or the spatial heterogeneity of the energetics within the nanopore.

Several distinct regimes of size selective separation can be delineated (as schematically described in Fig. 1). The simplest regime, molecular sieving, has received a great deal of attention and will not be treated in this review. Instead, we will focus on regimes of size and shape selective separations wherein all components of the mixture can enter the pore. In the size selective regime, the zeolite differentiates between molecules of different size based on how they interact within the pore. Whereas in molecular sieving it is always the smaller molecule that is selectively adsorbed, in size selective separations, either the smaller or the larger component may be selectively adsorbed [1,2]. In our review of this regime, then, we will focus mainly on simulation work that allows us to summarize general guidelines for size-selective separations.

The third regime concerns the situation where there is little difference between the average size of the molecules to be separated. Instead, the chief difference is in their shape. In principle, shape selective separations should be described by the same physics as size selective separations since we are simply considering more subtle characteristic dimensions – e.g., the placement of substituents in isomers. However, theoretical and simulation investigations of shape selective adsorption in zeolites have not been as focused or extensive as those of simpler size selective separations for spherical molecules. For the most part, only single component studies are available; we will aim to review what insights into shape selective adsorption can be gleaned from them. We will

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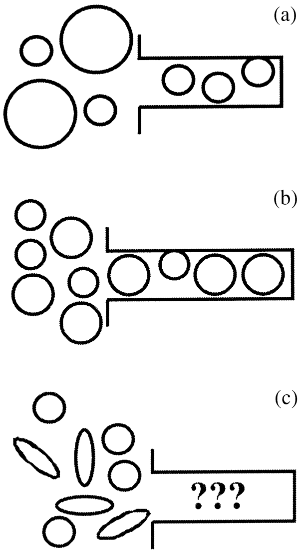

Fig. 1. A schematic of the mechanisms for separation using zeolite membranes: (a) Molecular sieving is based on a gross separation of sizes; the larger molecule stays out. (b) Size based separation differentiates between the interactions of the mixture components (of different sizes) within the pore space when both components can access the pore space. One might find cases where it is the larger molecule that preferentially adsorbs. (c) Shape based separation differentiates between the interactions of the mixture components of different shapes. Very little is known about the behavior of such systems.

review with some care the extensive experimental and simulation work on separating C_8 aromatic isomers using ZSM-5 zeolites.

1.2. Scope of this review

We will summarize available principles of shape based separation and current prospects for practical implementation. The scope and utility of an effective shape separation protocol based on such principles are profound; e.g., for separation of isomers in the food, pharmaceutical, and specialty chemical industries. We will also suggest studies that need to be done and issues that need to be resolved.

Though the main focus of this paper is size and shape selectivity at equilibrium, at the end of this treatment we will also comment on diffusion. Predicting and controlling selectivity is complicated by the role that diffusion might play in separations. The literature on the effect of adsorbate size on single-component diffusion is substantial, but that on binary (or multicomponent) diffusion and on the effect of sorbate shape is only just developing.

1.3. Introduction and caution regarding simulation methods

The interpretation of experiment and the formulation of principles can be aided immeasurably by theory and simulation. Simulation in particular provides a way to artificially isolate and study postulated mechanisms. Theory, sometimes with analytical solutions may be available for very simple approximations of adsorption systems; these are extremely valuable for their insight and predictive ability. For the most part, though, in this review we will focus on problems for which no general, easily solved theory is yet available.

The simplest type of analysis performed is the calculation of energy potential function for an isolated sorbate at various positions inside the pore. A number of approximations have been developed to efficiently reduce computational time. The system typically contains hundreds of molecules and to rigorously account for the degrees of freedom involved with translational, rotational and vibrational modes is a daunting task. Very often, vibration modes of freedom are neglected and so is the rotation of a functional group about a bond. These approximations are justifiable when simulating relatively large time scale processes. One may attempt to assign partial charges, and in other case one may neglect these. There are so many options available that, in general, we recommend that sensitivities of the results to these choices be assessed.

In extreme cases, entire molecules may be assumed to be Lennard-Jones spheres (e.g., methane). Since such an extreme approximation would result in the loss of shape of more complex molecules; somewhat more detailed but still approximate combinations of Lennard-Jones atoms may be used to represent the adsorbate molecules. However, one must be aware of the approximations made. For a non-spherical molecule, its orientation within the pore space will have to be specified by the Euler angles – the angles that three unique orthonormal planes make with the axes of the frame of reference. During a simulation event, rotation of the molecule will have to be accounted for along with translation.

With few exceptions, molecular simulations in zeolites neglect the fact that the adsorption of molecules into pore spaces can change the zeolite framework. Indeed, we will see cases of crystal transformations [3–7] upon the adsorption of *p*-xylene; it is not yet known to what degree this plays a role in shape selective separations from mixtures. In a rigorous simulation, the atomic bonds in the zeolite crystal should be allowed to relax owing to adsorbate–pore interactions. However, this increases the complexity of the problem enormously. A large portion of the computation is then devoted to calculating new positions of the atoms of the zeolites after every move. It is not a trivial calculation to appropriately model zeolite flexibility since various modes of vibration would have to be considered. Various approximations have ranged from allowing some vibrational modes of freedom to assuming a rigid lattice structure [8–12]. Keffer et al. [12] found that rigid zeolite approximation compared well with simulations accounting for the flexibility of the zeolite at low adsorbate loading.

These approximations increase the efficiency of computation enormously and in most cases do not sacrifice the physics of the problem. One must be careful to ensure that the approximation does not distort the physics of the problem in a way that affects the phenomena that one intends to study – for example while applying the rigid lattice approximation to the case of adsorption of *p*-xylene in silicalite. Perhaps the best approach is to consider different possible crystal structures as guided by experiment [9].

Parameters used in the potential functions are frequently obtained by matching to experiment. For instance, the parameters for Lennard-Jones methane might be made to match the apparent collision diameter of methane and the adsorption energy. More fundamentally, though, the parameters of interaction between adsorbate molecules or with the zeolite lattice may also be estimated from ab initio calculations [13–15] or from extensive correlations with spectroscopy and diffraction.

It is worthwhile to preface the review with a few general comments about simulations. Various versions of Monte Carlo (MC) simulations and molecular dynamics (MD) have been used to simulate related phenomena. Allen and Tildesley [16] provide an excellent text on the details of simulation of condensed phases which are most relevant to confined fluids in pores. The results of a simulation are only as accurate as the model and algorithm used allow. There are two extreme approaches among researchers using simulation. One has it that the simulation should be as realistic as possible and should quantitatively report observables such as the heat of adsorption. Another extreme has it that simulation (and even more so, theory) can be used to better understand phenomena and trends, even if the numbers are inaccurate. Both points of view have merit. We will try in this review to point out the tension between these two goals.

The Monte Carlo method is simply a statistical technique used to numerically evaluate integrals. MC methods are powerful and useful in molecular modeling simply because they provide a method to evaluate stochastically the configurational integrals in statistical mechanics expressions for thermodynamic variables of a system. For an in-depth study of statistical mechanics, texts by McQuarrie [17] or Hill [18] are excellent examples.

Molecular dynamics is just the opposite. Each step in a molecular dynamics simulation is expected to conform to Newton's laws; it is not stochastic, but deterministic. (Still, one generally hopes to start with a number of different initial states and to evaluate averages). Haile writes [19] "The essence of molecular dynamics is simply stated: numerically solve the *N*-body problems of classical mechanics." MD techniques numerically integrate Newton's laws of motion through time for a *N*-body system, given the initial specification of particle velocities and positions, a description of particle–particle interactions as well as any external potential. Both MC and MD techniques have been skilfully used to efficiently simulate adsorption and diffusion in pore spaces.[1]

2. Single component adsorption

2.1. Introduction

A thorough study of the fundamentals of separation using zeolites requires us to understand in depth single component adsorption. In this section we aim to review literature investigating single component adsorption characteristics in nanopores. Single component studies are particularly useful in identifying adsorption sites, energy barriers to intersite hops, ordering and orientation of the adsorbates within the pore space.

2.2. Effect of size in smooth model pores

First, we are interested in the effect of size and shape of the pore on adsorption of spherical molecules. Simulations have been used to study spherical molecules adsorbed in smooth walled (i.e., no atomistic detail) slit [20–27], cylindrical [28–40], and spherical pores [41–43]. At low loading, the heat of adsorption becomes more exothermic as a better fit between pore and adsorbate is achieved [35]. In a broad study seeking to quantify adsorbate–pore interaction and their consequence on adsorption, Keffer et al. [44] outlined the effect of the nanopore shape, and of confinement on density profiles, energy and entropy of the adsorbate fluid. These dependencies are used to quantify sorption. At low chemical potentials, adsorption in smooth pores is largely influenced by the *energetics* of the system; adsorption increases with increasing adsorbate–pore interaction which is the result of greater pore curvature and with better fit in size between pore and adsorbate.

However, at high loading, the density distribution begins to show more localization of the sorbates, suggesting packing of the adsorbate. The density now decreases with the degree of confinement – i.e., with decrease in pore curvature and increase in pore size. Adsorbate–adsorbate interactions begin to dominate the total energy. Adsorption is strongly influenced by the *entropy*, i.e. by the ability to fit in the confined space. There may be sudden changes in the adsorbate density in the pore corresponding to changes in order-

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[1] Variations of MC and MD techniques have been used for efficient calculations. Forester and Smith [11] have used molecular dynamics in the constrained reaction coordinate dynamics ensemble (what they call 'Bluemoon' simulations) as an alternative to transition state theory to predict free energies and diffusion coefficients of benzene in silicalite. The transition state theory assumes that an intermediate complex is formed during the hop and the rate of the hop is completely defined by the rate of formation of that complex. Constrained coordinate reaction dynamics, on the other hand, defines the path (or paths) of maximum ease for a molecule to move from one site to another. The adsorbate is assumed to take this path, MC simulations being used to follow its trajectory.

ing of the adsorbate with increase in size of the confining pores. These trends will be important to us later as we consider mixtures; we will review instances where the accessible volume, and hence the configurational entropy, helps to dictate selectivity at high loading for whichever component can best arrange itself in the pore space.

2.3. Effect of size in atomistic pores

Smooth pores are poor approximations of real nanopores. The atomistic structure will introduce significant spatial variation of the potential function on size scales comparable to the adsorbate size. As a result, adsorbate molecules usually find it most favorable to reside in certain discrete sites rather than in continuous volumes (e.g., layers in a slit pore, annular rings in a cylinder). By studying the adsorbate–pore interactions of a single adsorbate molecule at different positions in the pore space (potential energy maps), it is possible to locate and classify the adsorption sites that will be occupied at low loading. For instance, Keffer et al. [12] identified the adsorption sites at low loadings for a number of zeolites. At low to moderate loading, they and Jameson et al. [45,46] found a high correlation between these sites and the maxima in density distributions. However, as Li and Talu [10] show, both *energetic and entropic* considerations influence which sites get occupied preferentially.

At high loading, though, most of the available sites are occupied. If the separation between the sites is comparable to or smaller than the adsorbate size, crowding will occur. If neighboring sites are occupied, the volume available to the adsorbates may become highly constricted. In some cases this interference can even force new sites to be created.

Van Tassel et al. [47] studied Xe, Ar, CH_4 (modeled as a sphere) adsorption in NaA and further clarified the role of entropy at high coverage. The size of the adsorbate and the separation between low coverage sites could be used together to determine the depression of the configurational entropy because of crowding. In this way, they were able to construct a simplified lattice model for adsorption that correctly predicted the full isotherm.

2.4. Effect of shape in smooth model pores

Shaped molecules bring added complications. The issue is not only where the molecule adsorbs but also how is it oriented. At high loading, especially, packing is strongly affected by the orientation of the adsorbate molecules. A study of shaped molecules in smooth pores would help identify the importance of orientation on adsorbate energy and packing abilities without added influence of atomistic features and discrete sites. This would further provide guidelines in selection of zeolites for separation based on a very gross parameter – the size of the pores. Unfortunately, we have not found such studies in the literature.

2.5. Effect of shape in atomistic pores – the case of xylenes and benzene in silicalite

At present, we wish only to review what has been done with single-component adsorption. We will focus our attention on the most extensive work – that on *p*-xylene and benzene in ZSM-5. Unfortunately, the other isomers of xylene have received little attention. The isomers of xylene provide an ideal example of molecules with shape differences. We will analyze these examples elaborately in an attempt to elucidate what can be learnt from single component adsorption studies vis-à-vis selectivity. These cases will also exemplify the complexity of such studies.

For the problem at hand, it is impossible to appreciate the contribution of simulations without reviewing the experimental evidence. The review is not meant to be exhaustive; rather, it is meant to introduce the reader to the issues that simulation helped to clarify.

Though ZSM-5 is generally an aluminosilicate crystal, it can be prepared with exceedingly low Al content. Some authors refer to the purely siliceous form as silicalite – we will do this in the following sections just to make it clear that in all cases we are dealing with virtually purely siliceous crystals. The crystal structure is shown schematically in Fig. 2, with features approximately to scale. Both the straight channels and the cross-channels (also referred to by some authors as sinusoidal or zig-zag channels) are circumscribed by rings containing 10 silicon atoms. The first structural studies of ZSM-5 were done in 1978 [48,49]. Olson et al. [50] indicate that the empty zeolite has almost round straight and cross channels. Prospective sorption sites for *p*-xylene are:

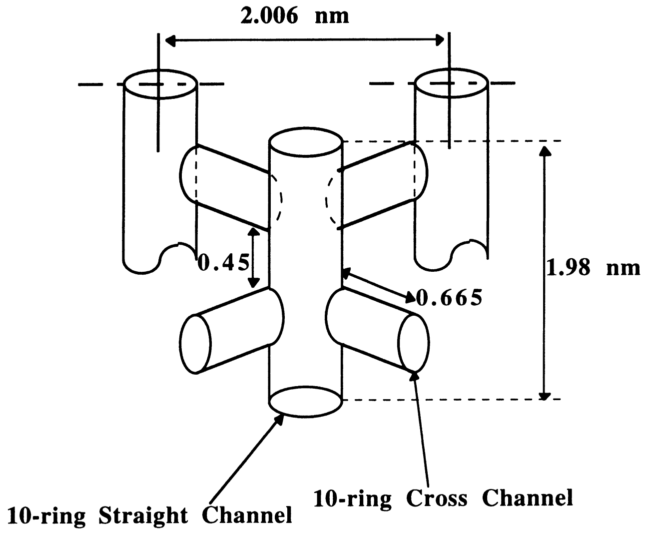

Fig. 2. The pore strucutre of a silicalite crystal (in its ORTHO phase) represented by the space group Pnma. The straight channels have cross-sectional dimensions of 0.54 nm×0.56 nm while the cross channels have dimensions of 0.51 nm×0.55 nm [53].

1. at the intersections of the straight and cross channels,
2. in the straight channels (between intersections),
3. in the cross channels.

2.5.1. Sorption and calorimetry

Pope [51,52] used a set of adsorption isochores to study the molar enthalpy, entropy and free energy of sorption of *p*-xylene (and other aromatics) in silicalite and ZSM-5. He explored a loading up to 8 molecules per unit cell and temperatures from 298 to 400 K. The enthalpy of adsorption of *p*-xylene gradually grows more exothermic with loading. The entropy of adsorption of *p*-xylene gradually grows more unfavorable. Thus in this early study it seemed that *p*-xylene adsorption is well-behaved, in the sense that there was no indication of rearrangement, phase changes, obvious multiple types of sites, etc. This was somewhat surprising, though, since benzene (discussed below) did seem to show complex behavior. Pope notes, though, that sorption of *p*-xylene was very slow at loadings greater than two and he reports highly non-linear vant Hoff plots (log pressure vs. inverse temperature); these problems may have obscured high loading features for *p*-xylene.

Thamm [53] measured adsorption calorimetry for *p*-xylene in silicalite. His results, however, show an abrupt increase in adsorption heat at a loading of about 4. He suggests the existence of two energetically distinct sets of adsorption sites. There is no mention, however, that the pore fluid or the zeolite lattice may be undergoing a phase change.

Richards and Rees [54] also measured adsorption isotherms and calorimetry of *p*-xylene in silicalite. They see hysteresis in the adsorption isotherm of *p*-xylene beginning (on the adsorption branch) at a loading of about 4, which they attribute to transition in the sorbed fluid. Like Thamm, they observe a sharp increase in heat of adsorption at about 4 molecules per unit cell. Richards and Rees also observe that the differential entropy of the system becomes sharply more unfavorable at about 4 molecules per unit cell. This suggests ordering of the adsorbate.

Talu et al. [55] also measured adsorption isotherms of *p*-xylene in silicalite; they examined temperature dependence more extensively. Their adsorption isotherms show a transition from type IV (i.e., with steps) to type I with increasing temperature. They infer a change in phase and even plot a binodal curve. It is not clear from the isotherms alone, though, whether the phase change is of the adsorbed fluid, of the zeolite, or a concerted phase change.

Garcia and Weisz [56] show that the adsorption of *o*-xylene into ZSM-5 was much slower than *p*-xylene. They also present the adsorption isotherm of *o*-xylene. The isosteric heats of adsorption of *m*-, *o*- and *p*-xylene are comparable [57]. Expectedly, on comparison of data from Garcia and Weisz and from Richards and Rees, we find that the amounts of the *o*- and *p*-xylene adsorbed at equilibrium under similar conditions are comparable.

Adsorption of benzene in silicalite has also been extensively studied. Pope [51,52] used a set of adsorption isochores to study the molar enthalpy, entropy and free energy of sorption of benzene in silicalite. The enthalpy of adsorption of benzene shows a maximum magnitude at 5–6 benzene per unit cell. The entropy of adsorption of benzene, though, shows an extremum, with the least favorable entropy at 5–6 benzene per unit cell. Pope argued that benzene must experience a rearrangement in packing at intermediate loading.

Thamm [58] also examined benzene adsorption calorimetry and showed that adsorption becomes more exothermic at a loading of 4. At the time, the authors suggested that this could be caused by the presence of two distinct adsorption sites, but the results also support the hypothesis of a phase change.

Guo et al. [59] use gravimetrically measured adsorption of benzene and postulated that there are two sites; specifically that cross channels are filled first, then the straight channel. But later, the same group (Li and Talu) [10] points out that the benzene should occupy the intersection rather than the straight channel because the intersection allows more available volume (and hence entropy). Guo et al. also postulate a phase change involving the benzene presumed to be in the cross channel.

2.5.2. Spectroscopy and diffraction

Changes in the silicalite phase has been observed by various investigators using a number of experimental techniques, such as Si-NMR and powder XRD (Fyfe et al. [3–5]), variable-temperature MAS carbon NMR (Reischmann et al. [6]) and single crystal X-ray crystallography (van Koningsveld et al. [7]). In this section we will not detail what each group found; rather we will summarize what is known on adsorption of *p*-xylene in silicalite and its effects on the pore structure. A sequence of transition of the crystal structure from monoclinic (at low loading, per Fyfe et al. [3,4]) to ORTHO (at a loading of 2, per Fyfe et al.) to PARA – schematically shown in Fig. 3 (at a loading of 4, per van Koningsveld [7], and confirmed in 1990 by Fyfe et al. [5]) has been observed. A similar transition is known to occur with a change in temperature as well. (van Koningsveld et al. say that as-synthesized ZSM-5, still holding the templating TPA, is also ORTHO). The principle difference caused by these phase changes seems to be a flattening of the cross channels as loading increases. They widen in one direction and narrow in another. In other words, the elliptical cross-section becomes more eccentric and is well described in the work of van Koningsveld et al. [7]. Consistent with Reischmann et al. [6], van Koningsveld et al. found that the *p*-xylene molecules lie in the intersections and in the cross channels. Moreover, the molecules in the intersection are nearly parallel to the straight channel with the phenyl ring in the mid-plane between the openings of the cross channel pores. In addition, molecules in the cross channel are more tightly constricted by the framework lattice. Schematics of

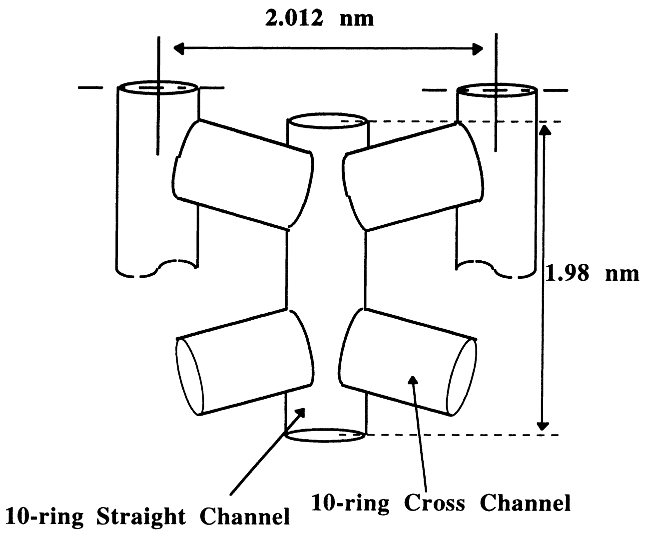

Fig. 3. The pore structure of a silicalite crystal (in its PARA phase) represented by the space group Pnma. The straight channels have cross-sectional dimensions of 0.61 nm×0.48 nm while the cross channels have dimensions of 0.62 nm×0.46 nm [7]. Notice that the cross channels are more skewed than in the ORTHO phase. van Koningsveld et al. [7] show the change in the cross channel structure with the changing phases.

adsorption of *p*-xylene in ORTHO and PARA phase are presented in Fig. 4.

Similar studies have been to identify adsorption sites of benzene. By neutron diffraction Taylor [60] indicates that at high loadings (>4),benzene is adsorbed at the intersections and in the straight channels up to the maximum loading of observed, about 8. He suggests that there may be two benzenes per intersection, but this is confusing since this would allow a maximum loading of 12. He does not think benzene will be found in the cross channel. Deuterium NMR work by Portsmouth and Gladden [61] also shows that there is a change in the adsorption sites with increased loading. The authors, without apparent basis, have interpreted these results as showing that benzene fills the straight channels before the intersections, and think that benzene would not be found in the cross. They suggest that there is so much room in the straight channel for benzene to pack that there is much less need for it to go into the crowded cross channels. (We will see striking disagreement with simulation work of Snurr [9] and Talu [10]). In case of benzene adsorbing in silicalite, we have come across no evidence of phase change in the crystal structure. The contrast in behavior of benzene with *p*-xylene might be attributed mainly to the smaller size of benzene.

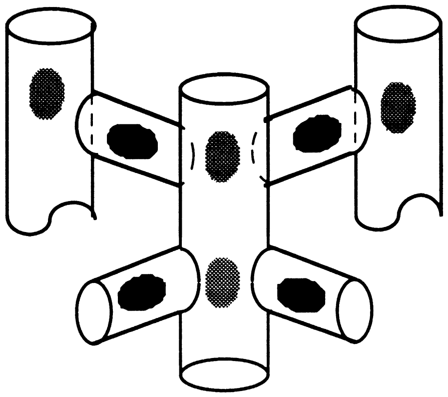

Fig. 4. A schematic of the adsorption sites of *p*-xylene in silicalite. The light shaded ellipses represent the *p*-xylene molecules that adsorb at the intersection sites at low loadings (<4 molecules per unit cell) while the dark ellipses represent the adsorption at the cross channel sites at higher loadings (>4 molecules per unit cell).

2.5.3. Simulations

Li and Talu [10] calculate the potential energy field for a single *p*-xylene in the ORTHO phase of silicalite. They model *p*-xylene as a collection of Lennard-Jones spheres with rigid bonds neglecting coulombic contributions to adsorbate–adsorbate or adsorbate–pore interactions; we will comment on whether this is important below. They show with limited Monte Carlo simulations that at low occupancies, *p*-xylene is most likely to reside in the channel intersections even though the site in the straight channel has the most attractive potential energy for adsorption. It is the intersection, with the higher accessible volume and hence the lower free energy that is preferentially occupied. Thus they point out the importance of the entropic effect on adsorption. This result is consistent with NMR studies [6] as well as X-ray crystallography [7]. It also provides evidence that at low pressures, the intersections are preferably occupied by *p*-xylene.

Snurr et al. [9] have performed MC simulations of adsorption of *p*-xylene in silicalite, accounting for van der Waals and coulombic interactions between adsorbate molecules as well as adsorbate–pore interactions. Electrostatic interactions are included to account for the quadrupole moments of the sorbate and to bring the heat of adsorption into agreement with experimental values. Partial charges are also placed on the atoms of the silicalite lattice. The electrostatic contribution to the long range interactions is significant. The inclusion of electrostatic interactions does affect the total potential field. However, it is unclear whether the electrostatic interactions only help make the model more accurate but do not alter the physics or whether they change the physics of adsorption as well.

Snurr et al. [9] attempt to account for the change in silicalite structure in the following way – they study adsorption in both ORTHO and PARA phases of silicalite. For *p*-xylene adsorbing onto silicalite, they find the following:

- ORTHO (which is thought to exist at low loadings): the authors suggest that the results concur with van Koningsveld, which we take to mean that the intersections are occupied. The maximum loading observed was 4 per unit cell, meaning that neither straight nor cross channels become occupied at reasonable pressures.

- PARA (which is thought to exist at high loadings): the authors again state that the results concur with van Koningsveld, which we take to mean that the intersections and cross channels sites are occupied, but not the straight channels. In this lattice structure the two sites are of comparable energy.

The monoclinic form was not considered. Snurr's results are consistent with the experimental work of Reischmann et al. [6], and van Koningsveld et al. [7]. Their predictions are roughly consistent with those of Talu et al. [10], and may suggest that electrostatic interactions do not drastically change the underlying physics of the adsorbate location (but no doubt predict the isotherm more accurately), which may further suggest that adsorption characteristics may then be dictated primarily by packing.

Nakazaki et al. [62] calculated the adsorption energies of single atoms of the xylene isomers along the main silicalite channel. Significantly, *p*-xylene manifests regions of attractive interactions corresponding to its adsorption sites. On the other hand, neither *m*- nor *o*-xylene show significant attractive interactions anywhere within the straight channel. This suggests that neither *m*- nor *o*-xylene will favorably adsorb in the straight channel. The cross channel being more constricted, we would guess the same to be true there as well.

Similar simulations have also been performed for adsorption of benzene. Vigne-Maeder and Jobic [63] have identified three adsorption sites of different energies for benzene in silicalite in the ORTHO phase. They use interaction energy calculations (accounting for electrostatic interactions between benzene and silicalite and atomic bond polarizability) to show that benzene preferably occupies the intersection rather than the cross channel sites at low loadings. They note that their calculations are in agreement with X-ray and neutron diffraction studies of Taylor [60]. Looking at the activation energies for motion between various sites within the pore space, they infer that at low loading, benzene will be constrained to move in the straight channel. The differential heat of adsorption, in their calculations, is constant up to a loading of 4 molecules and then sees a subsequent rise. This represents the shift in sites being occupied though the authors propose to specifically interpret it as occupation of intersections up to 4 molecules and then progressive filling of side channel sites. They further propose that filling of the straight channels sites forces some of the adsorbates at the intersections to move to the cross channels.

In MC simulations accounting for electrostatic and van der Waals interactions, (actually published before Vigne-Maeder), Grauert and Fiedler [64] (we also presume, in the ORTHO phase) suggested a somewhat different arrangement, though. Their results are based on MC simulations and account for electrostatic interactions. They find that at low loadings, (<4 molecules per unit cell) it is the intersections that get occupied. However, they predict that at higher loadings (up to about 8 benzene molecules), it is the straight channels that get occupied and the molecules at the intersections shift to the cross channel sites. Thus at a maximum loading of about 8, they think the intersections will be unoccupied. Since they did not include coulombic interactions, though, it would be interesting to know if this is the reason their prediction is different from what follows.

Snurr et al. [9] also simulated adsorption of benzene. They suggest (in Figs. 2 and 6 of [9]) that experimental observations can be explained and qualitatively predicted by simulations only when a change in crystal structure with adsorption is accounted for. The maximum coverage can also be predicted correctly only if this shift in crystal structure is assumed. With this assumption, they show that for benzene adsorbing in silicalite:

- ORTHO (exists at low loadings): intersections fill up preferentially, then straight channel and cross almost simultaneously (>4) with the intersections still occupied.
- PARA (exists at high loadings): intersection and cross channel fills up almost simultaneously with almost no occupancy in the straight channels.

Snurr's results concur with the calculations of Jobic. It is instructive how much difference that a small change in the lattice structure makes on the sites being occupied. However, the simulations disagree with the interpretation of experiments offered by Gladden, who believed the cross channels to be empty. They also disagree with the interpretation of experiments offered by Taylor, who believed that there could be two benzenes in the intersection. Finally, they disagree with the interpretation of simulations offered initially by Guo, who (tentatively) suggested that the straight channel rather than the intersection would be occupied. It is noteworthy, though, that later Talu pointed out that *p*-xylene prefers the intersection because of higher accessible volume, and it is reasonable to suppose that the argument would hold for benzene as well.

We have seen several suggestions of phase changes. Lee et al. [65] demonstrate that it is conceivable that a fluid phase transition could explain hysteresis in the isotherms. However, there are inconsistencies in their results as pointed out by Snurr et al. [66] who then go on to develop a predictive approach based on a lattice simulation that satisfactorily models the adsorption behavior of benzene in silicalite.

It is has been observed by Richards and Rees that *p*-xylene shows a hysteresis loop at a coverage greater than 4 molecules in silicalite. However, hysteresis was not observed with other adsorbates such as ethane or propane. Clearly this is not simply a case of capillary condensation. Richards and Rees interpret this behavior as evidence of phase transition at adsorbate loading of >4 molecules per unit cell. Talu et al. [55] have experimentally studied adsorption of benzene and *p*-xylene in silicalite and have looked at the effect of temperature. They speculate on the possibility of a fluid phase change with adsorption. Thamm [53,58] found a sharp change in differential adsorption energy for benzene in silicalite at loading 4 molecules per unit cell and partially attributed this behavior to the energetic difference in the adsorption sites for adsorption of molecules whose kinetic diameters are very close to the pore diameters. The adsorbate–adsorbate interactions begin 'abruptly at moderate adsorbed amount' and account for the abrupt change in differential molar heat of adsorption from a constant value. This further indicates the formation of molecular associates – suggesting a possibility of a change in phase. Thus, for benzene and *p*-xylene adsorption in silicalite, adsorbate–pore interaction is important at low coverage, while adsorbate–adsorbate interaction also affects the physics of adsorption at high coverage.

It must be noted that the literature presents two forms of change of phase – that of the crystal structure is established; that of the pore fluid is suggested based on experimental observations. Interestingly, both these transformations occur at a loading of about 4 molecules per unit cell. This brings up a question regarding the basis of the suggestions regarding the phase transition of the pore fluid. It is not clear whether there is a real transition of the pore fluid itself, whether it is the result of the rearrangement of the adsorbate owing to the phase transition of the crystal structure or whether it is a concerted phase change of the crystal–pore fluid system. The present body of work does not address this issue satisfactorily. Further, the reversibility of the phase transition has not been elucidated satisfactorily either.

2.6. Summary

In smooth pores only, energetic effects influence adsorption at low chemical potentials while entropic effects also contribute to adsorption at high chemical potentials. With atomistic pores, adsorption occurs at specific sites and these can be identified by analyzing the interaction energy of a single adsorbate molecule with the zeolite lattice. However, even at low chemical potentials, entropic as well as energetic influences affect the order of the sites getting occupied.

Examples of xylenes in silicalite, then, confirm the basic tenets mentioned above – that entropic as well as energetic effects determine the order in which the sites adsorb. Further, we see that ordering of the sorbates within the pore space affects adsorption energies and we expect that it will affect selectivity as well. With *p*-xylene especially, we notice that inclusion of complexities such as coulombic interactions and partial charges seems not to affect the physics of the process which seems to imply that adsorption characteristics may be determined primarily by packing. In the case of benzene, the results of various investigators contradict each other. This is probably because measurements and simulations were performed without proper care or knowledge regarding the phase of the host lattice structure and the transitions with loading.

We think that the differences between the adsorption behavior of *p*-xylene and benzene are primarily owing to the differences in sizes. Further, comparison of adsorption isotherms of *p*- and *o*-xylene show that *p*-xylene would adsorb more easily in silicalite and seem to suggest that *p*-xylene will be selectively adsorbed from a mixture of *p*-/*o*-xylene owing to differences in the kinetics of adsorption (i.e., on the basis of *p*-xylene adsorbing more quickly). We will verify whether this is true in a later section.

This case study exemplified the complexity of even single component adsorption. We see phase transformation of the lattice structure with loading – a phenomena whose inclusion in the model makes a significant difference to the results. It is instructive to realize that a little change in the lattice structure can cause a significant change in the adsorption. Whatever its cause, the appearance of a phase change strengthens our opinion that both energetic and entropic considerations are important in modeling adsorption.

3. Binary adsorption

3.1. Introduction

It might seem obvious to infer from single component behavior that the component which adsorbs more strongly would be selectively adsorbed from a binary mixture. For example, it would seem intuitive to hypothesize that the more exothermally adsorbing molecule would be preferably adsorbed but Monson [2], Somers et al. [26], Dunne and Myers [43], Cracknell and Nicholson [67], and others have shown cases where the less energetically favorable molecule is selectively adsorbed. Such apparent oddities invite a study of the effects of pore shapes and sizes on adsorption and diffusion of adsorbates. It has been suggested that binary adsorption of aromatics in silicalite may offer counter-intuitive trends as well. For example, on its own, very little *m*-xylene is adsorbed in silicalite. However, it has been claimed [68] that after an adsorption/desorption cycle of *p*-xylene, one can see some adsorption of *m*-xylene. We can gauge the possibility of selectivity during adsorption by comparing the free energies of the single components, but without a clue to how they interact between themselves, quantifying separation is not easy. Luckily, a large body of experimental and theoretical work exists for size selectivity.

3.2. Size selective adsorption from mixtures

Separation on the basis of the differences in adsorbate sizes (when both components can enter the pore) is termed size selectivity (as distinct from molecular sieving). Size selective separation is due to differences in interaction of the components within the pore space where the differences in interaction are attributes of the differences in adsorbate sizes. We will see, though, that the selectivity can be a non-monotonic function of the bulk composition, the pore architecture, etc.

A number of investigators have studied model systems such as hard spheres or LJ spheres in slits, cylindrical pores and spherical cages in order to identify the principles of selectivity based on sizes. Somers et al. [26], using Monte Carlo and molecular dynamics simulations of a binary mixture of cyclohexane and octamethylcyclotetra-siloxane (OMCTS) in slit micropores at 1 atm and 303 K, found that the composition of the pore fluid oscillated with pore size reflecting the ability of the species to pack into layers. In some pores large enough to admit both species, they observed a strong preference for the larger molecule (super-selectivity) at some pore sizes and for the smaller molecule at other pore sizes. This could not be predicted on the basis of energetic interactions alone. Cracknell and Nicholson [67] also observed super selectivity for ethane while studying a mixture of LJ approximated methane–ethane system in slit pores. Dunne and Myers [43] simulated a mixture of CCl_2F_2 and CO_2 in spherical pores decorated to represent zeolite 13X and found that the selectivity for CCl_2F_2 – the larger molecule – could be as high as 50–1.

Tan and Gubbins [22] studied methane–ethane mixtures in slit pores and the effect of the Lennard-Jones parameters, showing that the greater the difference between these parameters, the greater would be the selectivity. Formation of distinct layers of mixture was observed at temperatures well below critical and at high pressures. The composition of the layers varied, becoming methane-rich with increasing distance from the wall. Curry and Cushman [69] studying binary mixtures in structured slit micropores demonstrated three mechanisms of selectivity – molecular layering, liquid-like layering parallel to the walls and solid-like epitaxial ordering due to the atomic structure of the pore wall.

In a model zeolite-A, Van Tassel et al. [47] have simulated Xe/Ar and Xe/CH_4 mixtures. They found a preference of Xe at low loadings and a preference for the smaller molecule at higher loadings. This might have been the first time in zeolite simulations that such a reversal in selectivity was observed, reflecting a change in the mechanism governing selectivity. The increased selectivity of the smaller molecule was partially attributed to its ability to pack better within the micropore.[2]

At this juncture, this body of work needed some general principles based on physics of adsorbate and zeolite interactions to put these results into perspective. Such a broad theory was provided by the work of Monson [2] and subsequently by Keffer et al. [1]. Monson [2] studied selective adsorption of mixtures (adsorbate interactions approximated as square wells) in one dimension, where he found that molecular size effects and strength of adsorbate–pore interactions are the dominant influences on the ordering of the fluid within the pore. The selectivity depended strongly on attractive adsorbate interaction. Molecular size differences promoted the adsorption of the smaller molecule but when adsorbate–pore interactions were similar, the component with strong adsorbate–adsorbate interaction adsorbed selectively.

Keffer et al. [1] looked at size separation and its dependency on adsorbate characteristics, size and curvature defining the confinement within the zeolite pore space as well as external conditions such as the chemical potential. At low coverage, adsorbate size (with the larger ones favorably adsorbed) and the energy parameter of the adsorbate were the important parameters; size being more important. A more attractive energy parameter enhanced adsorption through both adsorbate–adsorbate and adsorbate–pore interactions. Since all of these affect the adsorbate–pore energy, they follow from the single component study which says that at low chemical potentials, adsorption is largely influenced by the energetics of the system.

At higher coverage, though, the adsorbate size is by far the most important parameter; usually the smaller molecules adsorb favorably. From single component adsorption it is known that extensive entropic contribution to adsorption is greatest at high loadings. Thus the ability to pack more becomes crucial to minimizing the free energy. There is also a slight favorability for molecules with lower energy parameters since a molecule with a steep energy potential will be less favored when the adsorbate begin to pack tightly. At low chemical potentials, the demand to put in more adsorbate molecules is low and thus the focus is on the most favorable energy. A larger molecule that ‘fits’ better into the pore space is able to offer the best energy state. At high chemical potential, the demand is on being able to pack in as many molecules as possible. Thus the particles that can pack more easily begin to dominate the pore space.

These tenets explain why a high curvature (more confining pore) can be favorable at low potentials while low curvature (less confining pore) would be favorable at high potentials. They also explain why a pore system can allow larger molecules in while keeping the smaller ones out. There is a shift in the dominant mechanisms influencing adsorption as one changes the chemical potential. One can thus visualize how there can be a shift in the size of molecule preferentially adsorbed with change in chemical potential.

Keffer et al. [1], tested these broad principles on binary systems, namely, Xe/Ar and Xe/tetramethyl-silane (TMS). In the Xe/Ar mixture (bulk composition of 30% Xe), Xe has a larger size indicating that Xe should adsorb favorably at low chemical potentials while Ar should adsorb favorably at high chemical potentials. The energetic parameter (e_{wXe}/e_{wAr}=2.259) also favors Xe at low loadings and Ar at high. The results echo expectations at low chemical potentials. However, at high chemical potentials, results are not very straight forward. When the pore size is very small, only Ar is

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[2] Subsequently, Jameson et al. [70] have studied the competitive adsorption of Xe–Kr in NaA by NMR as well as by MC simulations, focusing on the formation and composition of adsorbate clusters in the zeolite cages.

adsorbed due to molecular sieving. Once the pore size is increased to be able to admit Xe, the adsorbed fluid is over 99% Xe. This opposes the expectation that the smaller adsorbate is always favored at high chemical potentials. Xe is preferentially adsorbed since its size relative to the pore allows most favorable packing. Although there are slight energetic and mass advantages for Xe, neither can explain this overwhelming selectivity. As the pore size is increased, the mole fraction of Xe drops down and on further increase oscillations in selectivity are observed as Xe and Ar compete to pack. Thus it is the ability to packing and not just the adsorbate size that matters. Layers of adsorbate are observed within the pore space. The selectivity is higher for spherical cages and drops with decreasing confinement (curvature). It has been shown in single component adsorption that the smaller molecule will be favored due to better packing (the entropy effect). Thus Xe must be able to overcome this barrier in order to displace Ar and is only able to do so when the pore size allows it to balance the entropic advantage for Ar (more Ar can enter the pore) against its own combined energetic and entropic contributions. They also note that selectivities can be established for non-attracting hard spheres showing that the entropic contribution is dominant. However, the energetic contribution should not be discarded.

In the Xe/TMS system, TMS with a larger size was seen to be favored at low chemical potentials while Xe dominated the pore fluid composition at high chemical potentials. The ratio of energetic parameters ($e_{\mathrm{wTMS}}/e_{\mathrm{wXe}}$=1.258) also favored TMS at low loading and Xe at high loading. The mass ratio, though, favors Xe. Again at low chemical potentials, the results were as expected with TMS overwhelmingly dominating the pore fluid composition and the selectivity returning to bulk compositions at large pore sizes. At high loading, the mechanisms that caused oscillations in Xe/Ar system operate and corresponding results were observed. However, the oscillations were damped owing to the energetic ratio being smaller and the mass ratio favoring Xe. Thus Xe dominates the pore fluid composition except in a narrow range where TMS is able to overcome the barrier and balance the entropic effect.

In the same work, they isolated the effects of the various energy interactions. The adsorbate–pore interaction induces greater variations in selectivity than the adsorbate–adsorbate interactions. The adsorbate–adsorbate interactions cause an increase in pore-fluid density but does not induce any structure in the pore fluid – that being the effect of the adsorbate–pore interactions. Strong adsorbate–adsorbate interactions reduce oscillations in selectivity, consistently preferring the energetically favorable molecule.

3.3. *Shape selective adsorption from mixtures – the case of isomers of xylene*

Over the last 25 years, the separation of the isomers of xylene by zeolites has been studied, the motivation being economics of separation in the petrochemical industry. This is an ideal candidate for shape selective adsorption. No polar groups are involved, so the sorbates can be fairly modeled as collections of Lennard-Jones atoms (perhaps with small partial charges). Little work has been done in expostulating the principles of separation of molecules using the difference in their shapes (Cracknell and Nicholson showed the effect of differently shaped models for ethane [68,71]). In this section, we will carefully review investigations related to separation of mixtures of xylene isomers in an attempt to collate trends and principles of shape selective separation.

Earlier approaches used adsorption/desorption rate differences to find a basis for separation of xylenes. Parex [72] and Asahi [73] are among processes developed by the industry for the purpose. It was pointed out by Seko et al. [73] that separation of xylenes that have large molecular diameters, need large pore-size crystals; for example, natural faujasite, zeolite X or zeolite Y. Milewski and Berak [74] have studied the effect of preparation procedures on the selectivity for xylene isomer using potassium–barium-exchanged natural faujasite. For these systems, the influence of the potassium cation on selectivity occurred over large range of operational parameters while temperature had the least effect on selectivity. Higher selectivities were obtained at low content of Ba^{2+} cations. Santacesaria et al. [75] performed an extensive study of xylenes in zeolite Y and found that potassium-exchanged Y is a good material for separation of *p*- and *m*-xylenes. Comparing experimental data with simple Langmuir isotherms, they observed *p*-selectivity (the ratio of *p*-xylene adsorbed to *p*-xylene in bulk divided by ratio of other components adsorbed to the other components in bulk) depended on the coverage and was in the range of 5 at high coverage (close to maximum) and higher at low coverage. Temperature affected the equilibrium constants by influencing the entropy rather than the heat of adsorption. Thus, they concluded that selectivity must depend on the arrangement of the molecules in the intracrystalline cavities of the zeolite. There has been progress in the industry to improve natural faujasite and zeolite Y through modification of preparational procedures.

More recently though, investigators have concentrated on medium pore zeolites. Choudhary and Akolekar [76] propose that sorption of similar sized sorbate molecules in tight pores is strongly governed by the orientations and conformations accessible to the adsorbate in the confined space. Yan [77] points out that Venuto and Cattanach of Mobil [78], in a private communication in 1971, claim to have discovered that *p*-xylene can be separated from mixtures of *p*-, *m*- and *o*-xylenes using ZSM-5 zeolites as a selective adsorbent. From data in Namba et al. [79,80] work, we find that Dessau [81] saw that the ZSM-5 zeolite selectively adsorbs *p*-xylene from a mixture of *o*- and *p*-xylenes with a *p*- to *o*- selectivity of about 5–1. Namba et al. [79,80] have observed selectivities of *p*-xylene at about 66% in mordenite and as high as 99–1 in silicalite.

Namba et al. [79] noted that in the case of isomers of xylene or diisopropylbenzene, H-Mordenite exhibited some selectivity, but the somewhat smaller-pored H-ZSM-5 exhibited extremely high *p*-selectivity. In the case of cresol, H-ZSM-5 exhibited poor *p*-selectivity but pore constriction with Mg, P, B, Li, K or Na improved *p*-selectivity. In another work, Namba et al. [80] experimentally studied shape selective adsorption on H-ZSM-5 at various temperatures. They found that *p*-selectivity decreases with an increase in temperature and they attribute this trend to relaxation and decrease in rigidity of the lattice with increasing temperature. Further, they observe no 'kinetic diffusional effect' i.e., they see that when a fresh zeolite is exposed to a mixture of xylene isomers, the ratio of the amounts adsorbed with time is close to the selectivity at equilibrium.

Hudek et al. [82] also observed that *p*-xylene adsorbs onto H-ZSM-5 with greater ease than the ortho-isomer and that substitution into the zeolite lattice affects the selectivity owing to the change in the pore structure. Le Van Mao et al. [83] have studied shape selectivity in ZSM zeolites. They have attempted to correlate the crystalline characteristics of ZSM samples with their catalytic activity for *m*-xylene isomerization. In particular, large ZSM-5 crystalline particles were found to be more selective to *p*-xylene, suggesting that diffusion plays a role.

Karsli et al. [68] have concluded from experiments that sorption of *p*-xylene in silicalite proceeds in two regimes (in concordance with the observations of others [3–7,9,55,59–65]). Further, they observe that *o*- and *m*- adsorb extremely slowly in fresh silicalite but there is a significant increase when the zeolite has been exposed to a adsorption/desorption cycle of *p*-xylene. This seems to indicate that the adsorbate–pore interaction of *o*- or *m*-xylene is not very favorable. But when there is some *p*-xylene present, we think that adsorbate–adsorbate interaction between *p*- and *o*-/*m*-xylene is able to make the environment more favorable and help *o*-/*m*-xylene adsorption.[3] This suggests the increased influence of adsorbate–adsorbate interactions on selectivity. It also shows how mixture components interact to affect a change in the adsorption behavior. Finally, it raises the intriguing possibility that phase changes observed in *p*-xylene adsorption may cause drastic changes in separation selectivity.

The lion's share of work in shape selectivity has been restricted to C_8 isomers. However, the results may interest such fields as the food industry, the pharmaceutical industry, or the petrochemical industry among others. The separation reported in experiments may be due to energetic differences (which we have learned are typically more important at low loading) or due to packing differences [73]. At this stage, the contribution of energetic and entropic effects to selectivity is not well studied.

In this section we have been constrained by a paucity of data and so have only presented some sketchy ideas based on investigations presented in the literature. Absence of any simulations of selective adsorption in smooth pores has restricted the development of any broad principles. The present studies on binary mixture adsorption bring out instances of shape selectivity and the importance of certain mechanisms (adsorbate–adsorbate interactions and confinement). However, they are neither detailed nor systematic enough to develop general principles of shape selectivity. There are a number of questions that need to be answered. For instance,

- is confinement enough to achieve selectivity or is the presence of atomistic detail necessary (similar to the mechanisms of selectivity in reactions with bioenzymes)?
- thermodynamics and kinetics of separation are affected differently by changes in pore size. What is the optimal pore size to maximize the effect of thermodynamics and kinetics on selectivity?
- what is the relative importance of adsorbate–pore and adsorbate–adsorbate interactions and what roles do they play?
- how important is the entropic effect?
- how does the dimensionality of the pore affect adsorption and diffusion and thus how will it affect separation?

We also need to identify features that might help separation and devise methods to tap them. Studying fictitious pores and hypothetical systems might help us answer these questions.

Simulation of adsorption (both single component as well as mixtures) in a real zeolite that is known to manifest shape selectivity – such as silicalite [79,80] – will be the test of our understanding of the physics of adsorption. It will also offer the opportunity to compare the simulation results with experimental data. Single component adsorption data is available for the isomers from various sources [51–59]. To account for differences in samples and laboratory conditions, it is recommended that a set of data from a single investigating group be available. Some experimental data on adsorption from mixtures of xylene isomers also exists [68,79,80]. The influence of adsorbate–adsorbate and adsorbate–pore interactions at different coverages and chemical potentials can be analyzed. The importance of the entropic effect can also be studied. Such a study should be able to bring out the differences between size and shape selectivity and whether the general principles hold in both cases. Having studied the behavior of shape differences in a real system, it would be instructive to isolate the various mechanisms. The first step in this direction might be to study the effect of confinement by looking at xylenes (as an example) in smooth slits or cylindrical pores. This would give us answers to such questions as whether it is atomistic

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[3] The other possibility is that it is the PARA phase that *o*- and *m*-xylene adsorb onto. However, we do not think that is so since literature suggests the phase transition is reversible in which case the silicalite crystal will revert to the ORTHO phase on desorption.

detail that causes selectivity or can simple confinement do the job. It would also give us an estimate of what the size of a pore should be to maximize the effect of confinement and mobility. By comparing the behavior of a mixture of shaped molecules approximated as hard molecules with those approximated as Lennard-Jones molecules, one can isolate the effect of adsorbate interactions. It would also tell us whether there is any contribution of molecular sieving effects on the selectivity.

It is our opinion that shape selectivity being in some ways an extension of size selectivity, the principles of selectivity should hold. Broadly, energetic effects should be important to shape selectivity at low loading while entropy should also contribute at higher loading. However, we believe that certain parameters, such as non-sphericity and orientation will strongly affect the ability to pack in the confined space and hence the entropy. How that will affect the inter-species interaction and the selectivity is not clear.

4. Possible role of diffusion

Up to this point, the simulations and experiments considered have assumed that adsorption is at equilibrium. In reality, though, selectivity will be influenced not only by which component is more stable in the pore, but also by how quickly it can move. Diffusion of the adsorbate through the pore space may affect separation selectivity. The effects of size on single component and binary diffusion have been well studied [84]. Here we will provide insight into single component diffusion and review the few studies of binary diffusion of shaped molecules. Again key examples are provided by studies of xylene in silicalite.

Typically, *p*-xylene is known to manifest more mobility in silicalite pore spaces than *o*-xylene which is more mobile than *m*-xylene. Nagy et al. [85] have used proton-decoupled ^{13}C NMR spectroscopy to show that *p*-xylene moves more rapidly in the ZSM-5 channel than *o*-xylene. (NMR techniques have been extensively used to study various facets of diffusion in pore space [85–88].) Using neutron scattering, Williams et al. [89] have seen that the mobility of *p*-xylene in silicalite is much less constrained than *o*- or *m*-xylene. Roque-Malherbe et al. [90] have compared the diffusion coefficients of *m*- and *o*-xylene (among other aromatics) in silicalite using FTIR spectroscopy to measure uptake. They have observed that diffusivities of *m*-xylene is smaller than *o*-xylene within these pore spaces.

Molecular motion within nanopores is affected mainly by the activation energy [91], the multiplicity of paths available for diffusion [92,93] and with coverage [94,95]. π-Electron clouds in the adsorbate [96,97] and non-localized cations in the pore structure [98–100] can affect the activation energy and thus diffusivity. At low coverage, diffusion has been described by activated hops on a lattice [92,101–103]. At high coverage, however, one needs to account for adsorbate–adsorbate interactions. Increasing coverage may block pores and cause a reduction in diffusivity [101]. In an extreme case of restrictive pores, Nivarthi et al. [86] and Gupta et al. [88] have shown that methane molecules can pass each other in the pores of AlPO$_4$-5 while ethane cannot and thus manifest single file motion.[4] This highlights the influence of relative size of the adsorbate and pore and thus the adsorbate–pore interactions on diffusivity.

There are very few studies of binary diffusion in nanopores. Differences in diffusivities are based on differences in activation energy, excluded pore volume, and diffusion pathways available besides inter-species adsorbate–adsorbate interaction. Comparing experimental work on the diffusivities of mixtures with pure components, several investigators [94,95,106] have concluded that encounters between unlike molecules within nanopores reduced the diffusivity of the more mobile component while the diffusivity of the less mobile component remained largely unaffected. With the isomers of xylene, Nakazaki et al. [62] have calculated a significant difference in the intersite jump barriers (activation energies) pointing to a more mobile *p*-xylene. Based on the energies of interaction, as well as from experimental measurements we know that diffusion is very slow in these zeolites – *p*-xylene having a diffusivity of $\sim 6\times 10^{-12}$ while *o*- and *m*- are $\sim 1\times 10^{-15}$ cm^2/s [82,107].

We have briefly reviewed diffusion in nanopores, pointing out some key experimental methods and highlighting trends in diffusion of mixtures that may potentially help separation. For more extensive review of diffusion in nanopores, the work of Karger and Pfeifer [108] on NMR studies of self-diffusion is recommended. Karger and Ruthven [84] also provide a reference to diffusion in zeolites. More recently Theodorou et al. [109] have reviewed experimental and simulation studies of diffusion in zeolites and they discuss MD techniques to study the process.

5. Conclusions

We have seen that the broad principles governing selectivity seem to be that at low loading, energetic contributions govern selectivity while entropic effects also become important at moderate to high loadings. These principles have been shown to explain a wide variety of scenarios involving size selective adsorption. Studies on shape selectivity have been sketchy at best and we have tried to give direction to this body of work. In conclusion, we believe that the general principles for selectivity should remain same for size or shape based selectivity though the importance of the adsor-

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[4] The channels may be constricting enough that the adsorbate may not be able to pass each other. This gives rise to correlated motion also referred to as single file diffusion. The dynamics of single file diffusion is postulated by Hahn and Karger [104] and conditions for its occurrence were studied by Keffer et al. [105]. Single file diffusion is different from Fickian diffusion and one might find here a basis for separation in 1D pores or in 2D pores where one component cannot access the side channels.

bate–pore or adsorbate–adsorbate interactions and the entropic effect might change. Based on experimental results, we think that adsorbate–adsorbate interactions are especially important in adsorption from mixtures. Since differences between the adsorbate–pore interactions of various components will be less distinct in shape based selectivity, entropic effects and the ability to pack will become a more critical factor. The ability of the adsorbate to pack and form ordered structures in the nanopores will influence the pore fluid composition. At this juncture it is not clear whether it is advantageous to use medium or large pore zeolites for separation. We have enunciated certain studies that need to be done to answer some of the questions and develop a broad set of postulates regarding shape selectivity.

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