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Highlighting the Anti-Synergy between Adsorption and Diffusion in Cation-Exchanged Faujasite Zeolites

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ABSTRACT: Using configurational-bias Monte Carlo simulations of adsorption equilibrium and molecular dynamics simulations of guest diffusivities of CO$_2$, CH$_4$, N$_2$, and O$_2$ in FAU zeolites with varying amounts of extra-framework cations (Na$^+$ or Li$^+$), we demonstrate that adsorption and diffusion do not, in general, proceed hand-in-hand. Stronger adsorption often implies reduced mobility. The anti-synergy between adsorption and diffusion has consequences for the design and development of pressure-swing adsorption and membrane separation technologies for CO$_2$ capture and N$_2$/O$_2$ separations.

1. INTRODUCTION

Despite the burgeoning research and development activities on novel metal–organic frameworks (MOFs) in separation applications, cation-exchanged zeolites remain viable contenders for use as adsorbents in the industrial practice. For post-combustion CO$_2$ capture, Na$^+$ cation-exchanged FAU (faujasite) zeolite, NaX, also commonly known by its trade name 13X (with Si/Al $\approx$ 1.2), is considered to be the benchmark adsorbent, with the ability to meet government targets for CO$_2$ purity and recovery.\(^1\) NaX zeolites are also of potential use in natural gas purification,\(^2\) alkane/alkene separations,\(^4\)–\(^8\) and hydrogen purification processes.\(^9\)–\(^13\) Coulombic interactions of CO$_2$ and unsaturated alkenes with the extra-framework cations (e.g., Na$^+$, Ca$^{++}$, Li$^+$, and Ba$^{++}$) result in strong binding; the binding strength and selectivity can be tuned by the appropriate choice of the extra-framework cations and the adjustment of the Si/Al ratios.\(^9\)–\(^11,20,24\)–\(^26\)

Li$^+$ cation-exchanged FAU (faujasite) zeolite is commercially used for separation of N$_2$/O$_2$ mixtures.\(^23,27,28\) For supplying medical grade oxygen to prevent hypoxemia-related complications related to COVID-19, portable medical oxygen concentrators commonly use LiLSX (LS = low silica; Si/Al $\approx$ 1) to achieve high N$_2$/O$_2$ adsorption selectivities, ensuring enhanced rejection of purified O$_2$, the desired product.\(^29\)–\(^30\)

For separation applications using pressure-swing adsorption (PSA) technology, consisting of adsorption/desorption cycles, there is often a mismatch between the requirements of strong adsorption and ease of desorption.\(^31\) For example, NaX has a very strong affinity for CO$_2$, but the regeneration requires application of deep vacuum. For CO$_2$ capture from flue gases, Prats et al.\(^25,26\) have used molecular simulations of mixture adsorption in FAU to determine the optimum Si/Al ratio for PSA operations.

In the design and development of PSA technologies employing cation-exchanged zeolite adsorbents, we also require data on the intracrystalline diffusivities of guest molecules. Most commonly, diffusion limitations cause distended breakthrough characteristics and reduction in the purities of the desired products.\(^31–36\) Diffusivity data are also of vital importance in the development of zeolite membrane constructs for mixture separations in which cation-exchanged zeolites are used as thin layers or as fillers in mixed-matrix configurations.\(^37–43\)

The primary objective of this communication is to gain some fundamental thermodynamic insights into the adsorption and diffusion characteristics of a variety of guest molecules such as CO$_2$, CH$_4$, N$_2$, and O$_2$ in FAU zeolites with varying amounts of extra-framework cations: Na$^+$ and Li$^+$. The desired insights are obtained by performing configurational-bias Monte Carlo (CBMC) simulations of adsorption and molecular dynamics (MD) simulations of diffusion in Na- and Li-exchanged FAU zeolites with varying Si/Al ratios. The CBMC and MD simulation methodologies, along with details of the force field implementations, are detailed in the Supporting Information accompanying this publication. We aim to demonstrate the
anti-synergy between adsorption and diffusion; the stronger the binding of a guest molecule, the lower is its mobility. Such insights are of vital importance in determining the optimum Si/Al ratio of zeolite for use in PSA technologies or in membrane constructs.

2. THE GIBBSIAN CONCEPT OF SPREADING PRESSURE

The spreading pressure, $\pi$, is related to the molar chemical potential, $\mu_i$, by the Gibbs adsorption equation:  

$$ A_d\pi = \sum_{i=1}^{n} q_i d\mu_i $$

where $A$ represents the surface area per kg of framework, and $q_i$ is the component molar loading in the adsorbed phase mixture. At thermodynamic equilibrium, the $\mu_i$ are related to the partial fugacities in the bulk fluid mixture  

$$ d\mu_i = RT\ln f_i $$

In developing the ideal adsorbed solution theory (IAST), Myers and Prausnitz write the following expression relating the partial pressures to the mole fractions, $x_i$, in the adsorbed phase mixture  

$$ f_i = P_i^{0}x_i; \quad i = 1, 2, ..., n $$

In eq 5, $P_i^{0}$ is the pressure for sorption of every component $i$, which yields the same spreading pressure, $\pi$, for each of the pure components as that for the $n$-component mixture:

$$ \frac{\pi A}{RT} = \int_{0}^{\rho_i^f} \frac{q_i^0(f)}{f} df = \int_{0}^{\rho_i^f} \frac{\phi_q^0(f)}{f} df = \int_{0}^{\rho_i^f} \frac{q_i^0(f)}{f} df $$

In eq 5, $q_i^0(f)$ is the pure component adsorption isotherm. Since the surface area $A$ is not directly accessible from experimental data, the surface potential $\pi A/RT \equiv \Phi$, with the units mol kg$^{-1}$, serves as a convenient and practical proxy for the spreading pressure $\pi$. As derived in detail in the Supporting Information, the fractional pore occupancy, $\theta_i$, is related to the surface potential by  

$$ \theta = 1 - \exp \left( -\frac{\Phi}{q_{sat, mix}} \right) $$

where $q_{sat, mix}$ is the saturation capacity for mixture adsorption. Equation 6 implies that $\Phi$ may also be interpreted as a proxy for the pore occupancy; it is the fundamentally correct yardstick to compare the adsorption and diffusion characteristics of different host materials.

In view of eq 3, we may express the adsorption selectivity for the $i-j$ pair as follows  

$$ S_{ads} = \frac{q_i / q_j}{f_i / f_j} = \frac{x_i / x_j}{f_i / f_j} = \frac{P_i^{0}}{P_j^{0}} $$

Applying the restriction specified by eq 5, it follows that $S_{ads}$ is uniquely determined by the surface potential $\Phi$, irrespective of the mixture composition and total fugacity, $f_i$.

3. RESULTS AND DISCUSSION

3.1. CO$_2$ Capture Using Na-Exchanged FAU. Figure 1a plots the CBMC data on isosteric heats of adsorption, $Q_{st}$, a measure of the binding energies, of CO$_2$ and CH$_4$ in FAU (0 Al, all-silica), NaY (54 Al uc$^{-1}$), and NaX (86 Al uc$^{-1}$) zeolites, determined at 300 K, plotted as a function of the surface potential $\Phi$. (b) MD simulations of the self-diffusivities, $D_{diff}$ of CO$_2$ and CH$_4$ in FAU, NaY, and NaX zeolites, determined at 300 K, plotted as a function of the surface potential $\Phi$. All simulation details and input data are provided in the Supporting Information accompanying this publication.

![Figure 1](https://doi.org/10.1021/acsomega.2c00427)
the unary self-diffusivities, $D_{i, \text{self}}$, of CO$_2$ and CH$_4$ in FAU (0 Al), NaY, and NaX zeolites. Compared at the same surface potential $\Phi$, the hierarchy of self-diffusivities is precisely reverse of the hierarchy of $Q_{\text{ads}}$. Noteworthily, CH$_4$, the guest with the larger kinetic diameter of 3.8 Å, has a higher mobility than CO$_2$, which has a smaller kinetic diameter of 3.3 Å. The fallacy of using kinetic diameters to anticipate hierarchies in the diffusivity values has been underscored in published works.\textsuperscript{15,21}

CBMC simulations were carried out for equimolar ($f_1 = f_2$) CO$_2$(1)/CH$_4$(2) mixtures in FAU (0 Al), NaY, and NaX zeolites. The values of the adsorption selectivities, $S_{\text{ads}}$, are plotted in Figure 2a as a function of $\Phi$. The hierarchy of $S_{\text{ads}}$ face, the component permeabilities may be estimated from the following expression\textsuperscript{41}

$$\Pi_i = \frac{\rho D_{i, \text{self}} q_i^f}{f_i}$$ (8)

For FAU (0 Al), NaY, and NaX zeolites, Figure 3a,b compares the values of the CO$_2$ permeabilities, $\Pi_i$, and the permeation selectivity

$$S_{\text{perm}} = \frac{\Pi_1}{\Pi_2} = S_{\text{ads}} \times S_{\text{perm}}$$ (9)

The CO$_2$ permeabilities, $\Pi_i$, decrease with increasing values of $\Phi$. The $S_{\text{perm}}$ is a product of the adsorption selectivity and diffusion selectivity (cf. Figure 2a,b). While the $S_{\text{diff}}$ increases with $\Phi$ for all three hosts, the $S_{\text{ads}}$ increases with $\Phi$ until a maximum is reached for NaX and NaY and decreases on a further increase in $\Phi$. Consequently, the $S_{\text{perm}}$ also shows a maximum value for NaX and NaY. For the specific choice of upstream operating conditions, $f_1 = f_2 = 10^5$ Pa, Figure 3c shows the Robeson\textsuperscript{53} plot of $S_{\text{perm}}$ vs $\Pi_1$ for the three host structures. We note that the performances of both NaY and NaX lie above the line representing the Robeson upper bound.\textsuperscript{53} Since both $S_{\text{perm}}$ and $\Pi_1$ are important metrics governing the choice of the appropriate membrane material, there is room for optimization of the Si/Al ratio depending on the relative weightage to be assigned to permeation selectivity and permeability. CBMC/MD data that are analogous to those presented in Figures 2 and 3 are obtained for CO$_2$/N$_2$, CO$_2$/H$_2$, CO$_2$/H$_2$, CH$_4$/C$_2$H$_6$, and CH$_4$/C$_3$H$_8$ mixtures in FAU (0 Al), NaY, and NaX (see Figures S60–S64 of the Supporting Information).

### 3.2. N$_2$/O$_2$ Separations Using Li-FAU and Na-FAU

Figure 4a presents MD simulations of the unary self-diffusivities, $D_{i, \text{self}}$, for N$_2$ at 300 K in Li-exchanged FAU zeolites, with different Al contents per unit cell: 0, 48, 54, 86, and 96, plotted as functions of the surface potential $\Phi$; the contents of Li$^+$ are equal to that of Al. The magnitudes of $D_{i, \text{self}}$ decrease with increasing values of $\Phi$, which also serves as a proxy for the pore occupancy. At any specified value of $\Phi$, the values of the self-diffusivity, $D_{i, \text{self}}$, show the following trend: FAU (0 Al) $>$ FAU (48 Al) $\approx$ FAU (54 Al) $>$ FAU (86 Al) $\approx$ FAU (96 Al). This hierarchy of $D_{i, \text{self}}$ values correlates, inversely, with the corresponding values of the isosteric heats of adsorption of N$_2$ (cf. Figure 4b). N$_2$ has a significant quadrupole moment, and the electrostatic interaction potentials increase with increasing Al content, leading to increasing binding energies. The data in Figure 4a,b confirm that the diffusional mobility of N$_2$ is reduced with increased binding energy.

On the other hand, we note from Figure 4b that the isosteric heats of adsorption of O$_2$ are practically uninfluenced by the addition of extra-framework cations due to the significantly lower quadrupole moment of O$_2$. Therefore, we should anticipate that the mobility of O$_2$ should be practically independent of the degree of Li exchange; this expectation is fulfilled by the MD simulations of the self-diffusivities of O$_2$ in Li-FAU (see Figure 4c).

For 80/20 N$_2$/O$_2$ mixture adsorption, Figure 5a plots the adsorption selectivities, $S_{\text{ads}}$, of Li-exchanged FAU zeolites, with different Al contents. We note that the $S_{\text{ads}}$ decreases with increasing Al content. MD simulations of the N$_2$/O$_2$ diffusion selectivities, $S_{\text{diff}}$, plotted in Figure 5b, demonstrate the anti-synergy between adsorption and diffusion; the higher the

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**Figure 2.** Comparison of CBMC/MD simulations of (a) adsorption selectivities, $S_{\text{ads}}$, and (b) diffusion selectivities, $S_{\text{diff}}$, of CO$_2$/CH$_4$ mixtures in FAU (0 Al), NaY, and NaX zeolites at 300 K. The selectivities are plotted as a function of the surface potential $\Phi$. All simulation details and input data are provided in the Supporting Information accompanying this publication.
adsorption selectivity, the lower is the corresponding diffusion selectivity. Analogous CBMC and MD simulations with Na-exchanged FAU zeolites were also carried out; the results are provided in Figures S73–S81 of the Supporting Information.

For 80/20 N₂/O₂ mixture separations at a total fugacity of 100 kPa, Figure 6a compares the adsorption selectivities of Li-FAU and Na-FAU. For the same Al content, we note that the Sₘₐₜ values with Li-FAU are significantly higher than for Na-FAU. The interaction potential, engendered by the quadrupole moment, is inversely proportional to the cube of the center-to-center distance between nitrogen molecules and the extra-framework cation (see the detailed explanation provided in Chapter 2 of the Supporting Information). Due to the smaller ionic radius of Li⁺, compared to Na⁺, the N₂–Li⁺ distances are smaller than the N₂–Na⁺ distances; this is confirmed by radial
distribution functions for N₂–Li⁺ and N₂–Na⁺ pairs for 80/20
N₂/O₂ mixture adsorption in Li-FAU, with different Al
contents per unit cell: 0, 48, 54, 86, and 96. (b) MD simulations of
the N₂/O₂ diffusion selectivity, S_{diff}, at 300 K in Li-FAU zeolites. All
simulation details and input data are provided in the Supporting
Information accompanying this publication.

Figure 5. (a) CBMC simulations of the adsorption selectivity, S_{ads}, for
binary 80/20 N₂/O₂ mixture adsorption in Li-FAU, with different Al
contents per unit cell: 0, 48, 54, 86, and 96. (b) MD simulations of
the N₂/O₂ diffusion selectivity, S_{diff}, at 300 K in Li-FAU zeolites. All
simulation details and input data are provided in the Supporting
Information accompanying this publication.

The N₂/O₂ diffusion selectivities for Na-FAU are only
slightly higher than those of Li-FAU (see Figure 6b). The
CBMC/MD data rationalize the use of LiX, with Al ≈ 96 uc⁻¹,
in the industrial practice.^[29,30]

Figure 6 shows a Robeson plot of S_{perm} vs N₂ permeabilities
of N₂ for binary 80/20 N₂/O₂ mixture permeation across the
Li-FAU zeolite membrane at an upstream total pressure of 100
kPa. We note that the separation performance increases
monotonously with increasing degrees of Li⁺ exchange; the
permeabilities are significantly higher than the values reported
in the literature^[54] for polymeric and mixed-matrix membranes.

4. CONCLUSIONS
A combination of CBMC and MD simulations for adsorption
and diffusion of guest molecules CO₂, CH₄, N₂, and O₂ in FAU
zeolites with varying amounts of extra-framework cations (Na⁺
or Li⁺) was carried out to investigate the influence of varying
Si/Al ratios on mixture separations. Stronger adsorption, with
increasing amounts of extra-framework cations, results in
lowered diffusivities. For CO₂/CH₄ and N₂/O₂ mixture
separations, the adsorption selectivity, S_{ads}, and diffusion
selectivity, S_{diff}, do not proceed hand-in-hand. The anti-synergy
between adsorption and diffusion has important consequences
for the choice of the extra-framework cation, Na⁺ or Li⁺, and
the Si/Al ratio for use in PSA and membrane separation
technologies.
Figure 8. Robeson plot of $S_{\text{perm}}$ vs $N_2$ permeabilities for binary 80/20 $N_2/O_2$ mixture permeation across the Li-exchanged FAU zeolite membrane, with different Al contents per unit cell: 0, 48, 54, 86, and 96. All simulation details and input data are provided in the Supporting Information accompanying this publication.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00427.

CBMC and MD simulation methodologies; details of IAST calculations; Maxwell–Stefan formulation for mixture diffusion; CBMC data on unary isotherms and isotherm fits; CBMC and MD data on adsorption, diffusion, and permeation of mixtures in various cation-exchanged FAU zeolites (PDF)

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**NOMENCLATURE**

Latin Alphabet
- $A$: surface area per kg of framework, m$^2$ kg$^{-1}$
- $D_{\text{diff}}$: self-diffusivity of species $i$, m$^2$ s$^{-1}$
- $f_i$: partial fugacity of species $i$, Pa
- $f_{\text{eq}}$: total fugacity of bulk gas mixture, Pa
- $P_i$: sorption pressure, Pa
- $q_i$: component molar loading of species $i$, mol kg$^{-1}$
- $q_{\text{sat}}$: molar loading of species $i$ at saturation, mol kg$^{-1}$
- $Q_i$: isosteric heat of adsorption, J mol$^{-1}$
- $R$: gas constant, 8.314 J mol$^{-1}$ K$^{-1}$
- $S_{\text{diff}}$: diffusion selectivity, dimensionless
- $S_{\text{perm}}$: permeation selectivity, dimensionless
- $T$: absolute temperature, K
- $x_i$: mole fraction of species $i$ in the adsorbed phase

Greek Alphabet
- $\mu$: molar chemical potential of component $i$, J mol$^{-1}$
- $\pi$: spreading pressure, N m$^{-1}$
- $\theta$: fractional occupancy, dimensionless
- $\Pi$: membrane permeability of species $i$, mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$
- $\rho$: crystal framework density, kg m$^{-3}$
- $\Phi$: surface potential, mol kg$^{-1}$

**REFERENCES**


