Intrinsic D<sub>2</sub>/H<sub>2</sub> Selectivity of NaX Zeolite: Interplay between Adsorption and Kinetic Factors

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ABSTRACT: We present the first calculations of intrinsic D<sub>2</sub> over H<sub>2</sub> (D<sub>2</sub>/H<sub>2</sub>) selectivity in well-defined crystalline nanoporous material, namely, NaX zeolite. Feynman path integrals with realistic force field (Kowalczyk, P.; Gauden, P. A.; Terzyk, A. P.; Pantatosaki, E.; Papadopoulos, G. K. J. Chem. Theory Comput. 2013, 9, 2922–2929) are used to calculate zero- and finite-pressure adsorption D<sub>2</sub>/H<sub>2</sub> selectivity on NaX at 77 K. The kinetic selectivity is computed by classical molecular dynamics with Feynman–Hibbs quantum effective potentials. We found that within Henry’s law region the intrinsic D<sub>2</sub>/H<sub>2</sub> selectivity of NaX is only \( \sim 1.22-1.31 \). On the contrary, the theoretical and experimental adsorption D<sub>2</sub>/H<sub>2</sub> selectivities on NaX are 1.49 and 1.6, respectively. A reduction of adsorption selectivity by approximately 13–19% is explained by faster self-diffusion of H<sub>2</sub> than D<sub>2</sub> molecules in NaX crystal (i.e., normal isotope kinetic effect on self-diffusion). Our results clearly demonstrate the interplay between adsorption and kinetic factors that may have important implications for separation of H<sub>2</sub>/D<sub>2</sub> mixtures using permselective nanoporous membranes.

1. INTRODUCTION

The separation of hydrogen isotope gas mixtures into their components can be achieved through a variety of techniques, including: thermal diffusion, cryogenic distillation, selective diffusion through alloy membranes, selective formation of hybrids, and self-developing gas chromatography. All these techniques are practiced in laboratories; however, low separation factor and high cost of these energy-intensive processes hampers their application in industry.

Since the theoretical work of Beenakker et al., the separation of hydrogen isotope gas mixtures using nanoporous materials has attracted a lot of attention in materials science and engineering. The process of separation of hydrogen isotopes using nanoporous material relies on one (or a combination of two) distinctive mechanisms: adsorption selectivity and kinetic selectivity.

In adsorption separations (equilibrium controlled), the quantum-mediated interactions of heavier D<sub>2</sub> with surface atoms are stronger as compared to lighter H<sub>2</sub>, allowing its enrichment in nanoporous material. Challa et al. predicted extremely high D<sub>2</sub> separation selectivity on the order of 100 for H<sub>2</sub>/D<sub>2</sub> gas mixtures adsorbed in single-walled carbon nanotubes below the critical point of H<sub>2</sub>. Tanaka et al. showed a quantum molecular sieving effect with single-walled carbon nanohorns using low-temperature adsorption measurements and semiclassical computer simulations. Applying numerically exact path integral simulations, Kowalczyk et al. showed that the size, topology, and atomistic composition of the nanoporous materials have a great impact on the D<sub>2</sub>/H<sub>2</sub> equilibrium selectivity. High equilibrium selectivity of D<sub>2</sub> over H<sub>2</sub> of \( \sim 6 \) at 77 K can be achieved in square-shaped carbon pores with size of 0.24 nm (note that the collision diameter of classical H<sub>2</sub> is 0.296 nm).

In kinetic separations, gaseous H<sub>2</sub>/D<sub>2</sub> mixtures are separated because of their different diffusion rate within the pore network of the nanomaterial. Bhatia et al. studied self-diffusion of pure H<sub>2</sub> and D<sub>2</sub> in zeolite rho and Takeda 3 Å carbon molecular sieves. They noticed weak inverse isotopic effects showing the heavier D<sub>2</sub> diffuse faster than H<sub>2</sub> at 77 K. Recently, Contescu et al. used quasielastic neutron scattering to study the self-diffusion of pure H<sub>2</sub> and D<sub>2</sub> adsorbed in nanoporous carbon at 10–40 K. The measured self-diffusivity value for D<sub>2</sub> was 76 times higher than the one of H<sub>2</sub>, indicating different ordering of hydrogen isotopes in carbon nanopores. Pantatosaki et al. showed high equilibrium D<sub>2</sub>/H<sub>2</sub> selectivity on the order of 100 for H<sub>2</sub>/D<sub>2</sub> gas mixtures adsorbed in single-walled carbon nanotubes below the critical point of H<sub>2</sub>. Tanaka et al. showed a quantum molecular sieving effect with single-walled carbon nanohorns using low-temperature adsorption measurements and semiclassical computer simulations. Applying numerically exact path integral simulations, Kowalczyk et al. showed that the size, topology, and atomistic composition of the nanoporous materials have a great impact on the D<sub>2</sub>/H<sub>2</sub> equilibrium selectivity. High equilibrium selectivity of D<sub>2</sub> over H<sub>2</sub> of \( \sim 6 \) at 77 K can be achieved in square-shaped carbon pores with size of 0.24 nm (note that the collision diameter of classical H<sub>2</sub> is 0.296 nm).

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combined semiclassical atomistic simulations and quasielastic neutron scattering experiments to study the H\textsubscript{2} and D\textsubscript{2} self-diffusivities in NaX. The computed values for H\textsubscript{2} were greater than those corresponding to D\textsubscript{2} for various loadings, in agreement with the kinetic theory of gases. Moreover, self-diffusion coefficients for both isotopes exhibited a very large increase with loading. In a recent work, Kaneko and co-workers\textsuperscript{16} studied separations of H\textsubscript{2}/D\textsubscript{2} gaseous mixtures in representative nanoporous materials (activated carbon fibers, carbon molecular sieves, synthetic zeolites, and single-walled carbon nanotubes) using a homemade flow-measurement apparatus. Different flow rates of D\textsubscript{2} and H\textsubscript{2} through packed bed columns filled with the aforementioned materials were achieved at 77 K. However, the dynamics separation factor showed strong dependence on the type of nanomaterial used, yielding a maximum selectivity of 3.05 for D\textsubscript{2} over H\textsubscript{2} for the synthetic zeolite MS13X.\textsuperscript{16}

To the best of our knowledge, no experimental and theoretical estimations of intrinsic D\textsubscript{2}/H\textsubscript{2} selectivity on nanoporous materials are published. Filling this research gap is an important problem because high D\textsubscript{2}/H\textsubscript{2} adsorption selectivity can compensate high H\textsubscript{2}/D\textsubscript{2} kinetic selectivity and vice versa. Strongly adsorbed molecules, preferentially heavier D\textsubscript{2}, may diffuse slower than the lighter H\textsubscript{2} showing similar overall flow through permselective nanoporous membranes. Furthermore, speculations about the H\textsubscript{2}/D\textsubscript{2} gas mixture adsorption/diffusion derived from the experimental (or theoretical) results corresponding to pure gas adsorption/diffusion data should be taken with caution.\textsuperscript{14} This is because in narrow nanopores the cooperative effects between adsorbed hydrogen isotopes are significant. Therefore, fundamental studies on H\textsubscript{2}/D\textsubscript{2} gas mixture separation in representative and well-defined nanoporous materials are necessary to further advance our understanding of hydrogen isotope separation using permselective nanoporous materials.

NaX is a cage-like zeolite used in industry for recovering of O\textsubscript{2} from N\textsubscript{2} via pressure swing adsorption processes.\textsuperscript{17} The separations of the hydrogen isotope mixtures using permselective nanoporous membranes are performed under flow conditions. Thus, the key questions that we would like to address in the current study are what is the value of intrinsic D\textsubscript{2}/H\textsubscript{2} selectivity on NaX at 77 K? What kinetic and adsorption contributions to intrinsic selectivity are? The flow measurements are typically performed for dilute H\textsubscript{2}/D\textsubscript{2} mixtures at 77 K,\textsuperscript{16} thus, we focus merely on Henry’s law region (i.e., ideal state of the adsorbed mixture). In section 2, we briefly remind of the thermodynamics and kinetics relations used for the calculation of the intrinsic selectivity. Simulation details with descriptions of force fields and molecular models are given in section 3. In section 4, we present our results with published experimental data. Final conclusions are given in section 5.

2. THEORY: INTRINSIC SELECTIVITY

Following the solution-diffusion model, the intrinsic D\textsubscript{2}/H\textsubscript{2} selectivity (also known as ideal) is defined as follows\textsuperscript{18–20}

\[
S = \frac{K_{D_2}/K_{H_2}}{K_{D_2}/K_{H_1}}
\]

where \(K_{D_2}/K_{H_2}\) is the ratio of Henry’s constants (i.e., adsorption selectivity) reflecting the relative solubility of the two mixture components (here H\textsubscript{2} and D\textsubscript{2}) in NaX, and \(D_{D_2}/D_{H_2}\) denotes the ratio of their self-diffusivities (i.e., kinetic selectivity). Equation 1 is exact under ideal conditions within Henry’s law region because cooperative effects between adsorbed mixture components can be neglected.

The adsorption D\textsubscript{2}/H\textsubscript{2} selectivity at the zero-pressure limit can be computed from\textsuperscript{6,9,11,21}

\[
\frac{K_{D_2}}{K_{H_2}} = \frac{\int d\Gamma \int d\omega \int dr \exp[-U_{D_2}(\Gamma, \omega, r)/k_BT]}{\int d\Gamma \int d\omega \int dr \exp[-U_{H_2}(\Gamma, \omega, r)/k_BT]}
\]

where \(U\) denotes the solid–fluid interaction energy; \(r\) is the position of the path center of mass that quantized the hydrogen isotope molecule; and \(\Gamma\) and \(\omega\) are the path’s internal conformation and orientation in porous material under study, respectively. In the current paper, we computed equilibrium selectivity from eq 2 using the Monte Carlo integration algorithm.

At finite pressures, the adsorption D\textsubscript{2}/H\textsubscript{2} selectivity is given by the following expression\textsuperscript{21–23}

\[
S_{\text{equl}} = \frac{\rho_{D_2}^p/\rho_{H_2}^p}{\rho_{D_2}/\rho_{H_2}}
\]

where \(\rho^p\) and \(\rho^b\) are the equilibrium densities of D\textsubscript{2} and H\textsubscript{2} in NaX and the coexisting bulk mixture, respectively. Note that at low mixture concentrations (in the linear region of the isotherm) eq 3 must converge to eq 2 because all cooperative effects between adsorbed molecules can be neglected. Therefore, the comparison of theoretical results obtained from eq 2 and eq 3 at very low pressures is an important test of the methodology.

The self-diffusion (known as tracer diffusion) of H\textsubscript{2} and D\textsubscript{2} adsorbed in NaX can be computed via the Einstein equation\textsuperscript{18,24,25}

\[
D_i = \frac{1}{6N} \lim_{t \rightarrow 0} \frac{d}{dt} \langle [r(t) - r(0)]^2 \rangle
\]

where \(r\) is the center of mass position vector, and \(\langle \ldots \rangle\) is the ensemble average. Note that a calculation of self-diffusion coefficient in the zero-pressure limit is a channeling problem due to the finite size of the simulation systems. To check the accuracy of our self-diffusion calculations, we propose to compute the collective diffusion coefficient (known as mutual) of H\textsubscript{2} and D\textsubscript{2} adsorbed in NaX using the following expression\textsuperscript{18,24}

\[
D_b = \frac{1}{6N} \lim_{t \rightarrow 0} \frac{d}{dt} \langle [R(t) - R(0)]^2 \rangle
\]

where \(R\) is the center of mass position of the swarm of N-molecules. In the linear part of the adsorption isotherm (Henry’s law region)\textsuperscript{24}

\[
\lim_{\rho \rightarrow 0} D_b = \lim_{\rho \rightarrow 0} D_i
\]

Plotting a variation of pure H\textsubscript{2} and D\textsubscript{2} self- and collective-diffusion coefficients with NaX loading allows us to precisely define the region where the cooperative effects between adsorbed hydrogen isotopes can be neglected.

3. SIMULATION DETAILS

3.1. Particle Interactions: Path Integral Calculations.

We computed the total potential energy from the discrete path
integral expression for the density matrix in the primitive approximation:\textsuperscript{26–30}

\[ U = U^{\text{int}} + U^{\text{ext}} \]  
\[ U^{\text{int}} = \frac{mP}{2(\beta h)^2} \sum_{i=1}^{P} \sum_{k=1}^{N} |r_i - r_{i+k}|^2 \]  
\[ U^{\text{ext}} = \frac{1}{P} \sum_{i<j}^{P} \phi_{\text{ff}}(r_{ij}) + \frac{1}{P} \sum_{i=1}^{P} \sum_{k=1}^{N} \phi_{\text{ext}}(r_k) \]

(7)

(8)

where \( r_{ij} = |r_i - r_j|; r_k = |r_i - r_j|; N \) is the number of quantum particles in the simulation box; \( P \) is the number of classical “beads” in ring polymers; \( \beta = 1/(k_B T) \) is the inverse of thermal energy; \( m \) denotes the mass of particle; and \( h = h/2\pi \) is the reduced Planck constant, \( h \). Owning to the cyclic condition of the ring polymers, if \( k = P \), then \( k + 1 = 1 \).

As shown previously,\textsuperscript{31} we employed the spherically symmetric Silsber–Goldman potential for calculation of fluid–fluid interactions, \( \phi_{\text{ff}} \).\textsuperscript{32} The solid–fluid interactions, \( \phi_{\text{ff}} \), were computed from our force-field parametrized for hydrogen adsorption in NaX (see the description of the experimental H\textsubscript{2} isotherm at 77 K in ref 31). We used \( P = 16 \) beads per ring polymer for both H\textsubscript{2} and D\textsubscript{2} at 77 K. To check the accuracy of our theoretical results, we performed additional path integral simulations with a different number of beads per polymer chain for H\textsubscript{2} and D\textsubscript{2}. For lighter H\textsubscript{2} we used \( P = 32 \), whereas for heavier D\textsubscript{2} we used \( P = 16 \). PI-GCMC thermodynamic averages computed for \( P = 32 \) and \( P = 16 \) are indistinguishable (see Figure 1S in the Supporting Information).

3.2. Adsorption Selectivity at the Zero-Pressure Limit.

We computed the adsorption selectivity of D\textsubscript{2} over H\textsubscript{2} at zero pressure from eq 2 using the homemade path integral Monte Carlo integration (MCI) algorithm (see Wang et al.\textsuperscript{33}). First, we simulated 100 conformations of ideal gas H\textsubscript{2} (and independently D\textsubscript{2}) ring polymers at 77 K using the staging path integral Monte Carlo simulation in the canonical (NVT) ensemble.\textsuperscript{25,29} The internal configurations of these ring polymers were stored in two databases (e.g., one for H\textsubscript{2} and a second for D\textsubscript{2}). Next, the NaX crystal framework (i.e., a unit cell Na\textsubscript{86}Al\textsubscript{86}Si\textsubscript{106}O\textsubscript{384} digitally reconstructed on the basis of X-ray and neutron diffraction data)\textsuperscript{15} was placed inside the cubic simulation box with side length 50.198 Å. We adopted a previous set up for the MCI, i.e., cubic simulation box with periodic boundary condition and minimum image convention for computing molecular interactions in \( x \), \( y \), and \( z \) directions.\textsuperscript{31} Our MCI scheme consists of three steps. In the first step, we selected the ideal gas ring configuration of H\textsubscript{2} (or D\textsubscript{2}) for computation of the Henry’s constant of the heavier isotope) from the respective database using uniform random distribution. Next, the selected gas ring polymer was inserted into the simulation box with a random position and orientation. Finally, we computed the solid–fluid potential and corresponding Boltzmann weight for inserted gas ring polymer (see eq 2). Our MCI run utilized \( 5 \times 10^5 \) configurations. To calculate statistical error bars, we ran 15 independent MCI calculations for both H\textsubscript{2} and D\textsubscript{2}. Error bars were computed assuming a normal (Gaussian) distribution for the computed values of Henry’s constants.

3.3. Path Integral Grand Canonical Monte Carlo: Binary Mixtures. We performed simulations of equimolar H\textsubscript{2}/D\textsubscript{2} mixture adsorption on NaX at 77 K and total mixture pressures up to 3 bar using the homemade path integral grand canonical Monte Carlo (PI-GCMC) code.\textsuperscript{30,31} We computed the absolute values of H\textsubscript{2} and D\textsubscript{2} mixture adsorption from

\[ \Gamma_k = \frac{N_k}{L^3} \]  
\[ q_{\alpha} = \frac{5}{2\beta} \frac{⟨E(N)⟩ - ⟨E(N)⟩}{⟨N^2⟩ - ⟨N⟩^2} \]  
\[ E = \frac{3NP}{2\beta} - U^{\text{int}} + U^{\text{ext}} \]

(10)

(11)

(12)

where \( U^{\text{int}} \) and \( U^{\text{ext}} \) are given by eqs 8 and 9, respectively.

Additionally, we used the Barker estimator to compute the total kinetic energy of the H\textsubscript{2}/D\textsubscript{2} mixture adsorbed in NaX:\textsuperscript{31–33}

\[ K_B = \frac{3P}{2\beta} - \frac{mP}{2N(\beta h)^2} \sum_{i=1}^{P} \sum_{k=1}^{N} |r_{ij} - r_{ij+k}|^2 \]  
\[ U_{\text{ij}}(r) = U_{\text{ij}}(r) + \frac{\beta h^2}{24m_i} \frac{d^2U_{\text{ij}}(r)}{dr^2} + \frac{2}{r} \frac{dU_{\text{ij}}(r)}{dr} \]  
\[ U_{\text{ij}}(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \]

(13)

(14)

(15)

In the classical limit (i.e., for the infinite dilution of the adsorbed H\textsubscript{2}/D\textsubscript{2} mixture), eq 13 must converge to the classical value of the kinetic energy, \( K_B = (3/2)k_BT \).

To trace the equimolar H\textsubscript{2}/D\textsubscript{2} mixture adsorption isotherm, we mimic experimental procedures by starting with an empty NaX crystal.\textsuperscript{25,31} Simulation runs were performed at gradually increasing chemical potentials of the equimolar bulk H\textsubscript{2}/D\textsubscript{2} mixture. The grand canonical ensemble simulations utilized 2 \times 10\textsuperscript{6} configurations, of which the first 1 \times 10\textsuperscript{8} was discarded to guarantee equilibration. For each simulated adsorption point, we calculated statistical error bars from 15 independent PI-GCMC runs.

3.4. Feynman–Hibbs Molecular Dynamics: Pure Components and Binary Mixtures. In the current work, all NaX framework atoms were kept fixed in their crystallographic positions, except for the off-framework Na cations, which were allowed to participate in the dynamics of the system. We treated hydrogen isotopes as spherical particles and computed the fluid–fluid and solid–fluid interactions by means of the quadratic form of the temperature-dependent effective potential of Feynman and Hibbs (FH-MD):\textsuperscript{26}

The (12,6) LJ fluid–fluid and solid–fluid parameters were previously validated against the quasielastic neutron scattering data and sorption experimental measurements.\textsuperscript{15} For interactions between hydrogen isotopes we used: \( \epsilon_{X-X}/k_B = 36.5 \) K and \( \sigma_{X-X} = 2.82 \) Å (here, a subscript X denotes H\textsubscript{2} and D\textsubscript{2} molecules).\textsuperscript{15} For hydrogen isotope NaX we used the following
cross-interaction LJ parameters: $\varepsilon_{X-O}/k_B = 56$ K, $\sigma_{X-O} = 2.8$ Å, $\varepsilon_{X-Na}/k_B = 265$ K, and $\sigma_{X-Na} = 2.8$ Å (here, a subscript O and Na denotes oxygen and Na cations in the NaX framework, respectively). For calculations of single-component diffusivity, configurations obtained from GCMC runs at the desired density were used as initial configurations in our FH-MD simulations (see ref 15 for more details). Configurations obtained from PI-GMC simulations of H$_2$/D$_2$ mixture adsorption were used as initial configurations for evaluation of single-component self-diffusion coefficients in adsorbed mixtures. FH-MD runs were conducted up to a time of 20 ns, utilizing the leapfrog Verlet scheme for integration of the equation of motion. We used an integration step of 1 fs in order to eliminate the energy drift. The self- and collective-diffusion coefficients were computed from eqs 4 and 5, respectively. Error bars were computed assuming a normal (Gaussian) distribution for the computed values of transport coefficients.

4. RESULTS AND DISCUSSION

4.1. Adsorption Selectivity. Figure 1a shows the total H$_2$ and D$_2$ mixture component absolute adsorption isotherms in NaX at 77 K. As expected, heavier D$_2$ is preferentially adsorbed over H$_2$ from the equimolar H$_2$/D$_2$ bulk mixture at finite pressures. Variation of the adsorption D$_2$/H$_2$ selectivity with mixture loading shows more features of competitive adsorption (see Figure 1b). We notice that maximum adsorption selectivity of 1.46 ± 0.2 computed at very low pressures decreases rapidly with NaX filling up to ~2–3 molecules per unit cell. The adsorption selectivity computed at zero pressure of 1.49 in favor of D$_2$ is in good agreement with PI-GCMC results (see Table 1). Furthermore, the reported experimental adsorption D$_2$/H$_2$ selectivity of 1.63–3.0 is in good agreement with our theoretical calculations considering the intrinsic heterogeneities of NaX zeolite at the atomistic scale (e.g., variation of Si:Al ratio and long-range-ordering, Na cation occupancy of the crystallographic positions, defects, presence of impurities, and others). The kinetic energy of adsorbed hydrogen isotopes converges to its classical value for low pore concentrations, as is expected from theory (see Figure 1c). Furthermore, on approaching the dilution region, the isosteric enthalpy of D$_2$/H$_2$ mixture adsorption is maximal, and it is dominated by solid–fluid interactions, $q_{vdw}$, as shown in Figure 1d. Thus, we conclude that the adsorbed phase is enriched in the D$_2$ component and can be treated as an ideal up to ~2–3 molecules per unit cell. At higher NaX loadings, cooperative effects between adsorbed hydrogen isotopes cannot be neglected. The microscopic PI-GCMC snapshots clearly show preferential adsorption of D$_2$ in narrow windows interconnecting the NaX cages (see Figure 2a,b). It is not surprising because these cylindrical windows are the most attractive adsorption sites (i.e., those presenting the deepest minima in the Na−X/D$_2$ potential energy field). A decrease in D$_2$/H$_2$ adsorption selectivity with

![Figure 1.](image-url)
NaX filling can be explained by the sequential saturation of the most energetic adsorption centers inside narrow windows. It is interesting to note that at around $\sim 25$–$30$ molecules per unit cell the adsorption selectivity slightly rises up to 1.31, and further it decreases as adsorption progresses. At the maximum, the kinetic energy reaches 126 K (note that the classical value of kinetic energy is 115.5 K) indicating positional localization of adsorbed hydrogen isotope molecules. Microscopic PI-GCMC snapshots shown in Figure 3a clearly show that adsorbed hydrogen isotopes are not filling the entire spherical NaX cages uniformly. They are first preferentially adsorbed close to NaX entrance windows, where the most probable crystallographic positions of Na cations are located (see clusters of hydrogen isotopes around windows displayed in Figure 3a). Fluid–fluid interactions with hydrogen isotope molecules that are already adsorbed in windows contribute to attractive potential fields around Na cations (see fluid–fluid contribution to the isosteric enthalpy of H$_2$/D$_2$ mixture adsorption shown in Figure 1d). As adsorption proceeds further, the large spherical cages are progressively filled by hydrogen isotope molecules with a small selectivity toward heavier D$_2$ (see Figure 3b). The enthalpy of H$_2$/D$_2$ mixture adsorption is decreasing up to $\sim 5$ kJ/mol, which clearly shows that NaX cages have low adsorption energy, and therefore, they are weakly selective toward heavier D$_2$. Conversely, the highest adsorption selectivity of NaX for D$_2$
First, the normal isotope effect on self-diffusion is predicted for all densities of adsorbed phases. In agreement with kinetic theory of gases, lighter H\textsubscript{2} self-diffuses faster in NaX than heavier D\textsubscript{2}. This theoretical prediction is consistent with a recent quasi-elastic neutron scattering experiment (QENS).\textsuperscript{15} Second, we found that self-diffusion coefficients are initially increasing up to ~60 molecules per NaX unit cell, as shown in Figure 4a. Note that the NaX is an energetically heterogeneous crystal. The most attractive adsorption centers are occupied first. The H\textsubscript{2}/D\textsubscript{2} mixture adsorption at infinite dilution is thus accompanied by high enthalpy (see Figure 1d). As adsorption progresses, the adsorption energy centers with lower energies are successively occupied by hydrogen isotopes. Those molecules are loosely bonded, thus the self-diffusivity is increasing with loadings. On the contrary, the enthalpy of mixture adsorption is decreasing as adsorption centers with lower energies are occupied (see Figure 1d). At higher pore densities, the motion of hydrogen isotopes is hindered by frequent intermolecular collisions. Stronger interactions between adsorbed hydrogen isotopes are reflected by an increase of fluid–fluid contribution to the adsorption enthalpy. Therefore, the mobility of both H\textsubscript{2} and D\textsubscript{2} is decreasing at higher pore concentrations. The maximum kinetic selectivity of D\textsubscript{2} over H\textsubscript{2} of ~0.82 is reached at low pore concentrations of hydrogen isotopes (see Figure 4b). At finite pore loadings the kinetic selectivity is strongly nonlinear because of the impact of cooperative effects between adsorbed hydrogen isotopes. Collective diffusivities coincide with self-diffusivities at low loadings for either H\textsubscript{2} or D\textsubscript{2}, but at moderate and higher concentrations they diverge (see Figure 2S in Supporting Information). With the exception of the region of high densities (around ~80 or more molecules per unit cell), the collective diffusion coefficients are higher than their self-diffusion counterparts. As shown by Maginn et al.,\textsuperscript{37} higher collective diffusivity can be explained by smoother flux autocorrelation function (FCF) compared to velocity autocorrelation function (VACF). The magnitude of the negative “backscattering” region is less for the FCF than for the VACF.\textsuperscript{37}

The normal isotope effect on single-component self-diffusion of hydrogen isotopes in adsorbed mixtures is theoretically predicted (see Figure 4c). The maximum kinetic selectivity of D\textsubscript{2} over H\textsubscript{2} of ~0.65 is reached at 0.3 mole fraction of H\textsubscript{2} and is further increasing with H\textsubscript{2} mole fraction (see Figure 4d). At high pore loadings (i.e., ~0.46 H\textsubscript{2} mole fraction), the H\textsubscript{2} and D\textsubscript{2} self-diffusion coefficients are very similar due to frequent intermolecular collisions. Therefore, we conclude that kinetic effects are negligible in dense adsorbed phases.

Let us now focus on the region of low NaX loading, where intrinsic D\textsubscript{2}/H\textsubscript{2} selectivity is defined by eq 1. The self- and collective diffusivities do indeed have similar values for less than ~2 molecules per NaX unit cell (see Figure 1S in Supporting Information). The computed kinetic selectivity of 0.82–0.88 (see Table 1) in favor of H\textsubscript{2} shows that single particle mobility of lighter H\textsubscript{2} is higher than heavier D\textsubscript{2}. It is not surprising because there are no kinetic restrictions for hydrogen isotope self-diffusion in NaX crystal. Moreover, D\textsubscript{2} molecules are bounded more strongly than H\textsubscript{2} because higher quantum...
fluctuations of lighter $\text{H}_2$ decrease solid–fluid interactions.\(^{31}\) Thus, overall, the adsorption selectivity in favor of $\text{D}_2$ is reduced by faster kinetics of $\text{H}_2$.

A recent review article\(^7\) summarizes that the adsorptive separation of hydrogen isotopes should not be based on equilibrium but on kinetic quantifying. However, recent experimental/theoretical results published by Hirscher and coworkers\(^{38}\) clearly demonstrate the feasibility of achieving “equilibrium-based quantum separation” for industrial hydrogen isotope separation. The experimental value of $\text{D}_2/\text{H}_2$ equilibrium selectivity of 11.8 was reported for equimolar $\text{H}_2/\text{D}_2$ binary mixture adsorption in CPO-27 metal–organic framework at 30 mbar and 60 K.\(^{38}\) Our theoretical calculation of adsorption, kinetic, and intrinsic selectivity of $\text{D}_2$ over $\text{H}_2$ shows that separation of dilute $\text{H}_2/\text{D}_2$ mixtures on NaX at 77 K is equilibrium-controlled permeation (see Table 1). Note, however, that the kinetic factor reduces the adsorption selectivity by approximately $\sim$13−19%. Strong binding of $\text{D}_2$ molecules to metal sites in the CPO-27 framework (or any other nanoporous materials) may facilitate faster diffusion of $\text{H}_2$. As a result, at low concentrations of hydrogen isotopes in the CPO-27 framework, the kinetic factor may compensate high equilibrium selectivity measured by Hirscher et al.\(^{38}\)

Intrinsically, selectivity of nanoporous material is a convolution of adsorption and kinetic selectivity measured at ideal gas mixture conditions. Therefore, knowledge of both adsorption and kinetic data is necessary for understanding the microscopic mechanism of $\text{H}_2/\text{D}_2$ mixture permeance across the nanoporous membrane. Theoretical perme selectivity of 1.22−1.31 in favor of $\text{D}_2$ is quite low. This implies that separation of $\text{H}_2/\text{D}_2$ mixtures using NaX permselective membranes at 77 K is not economically feasible. The search for a synthetic zeolite candidate with optimized perme selectivity of $\text{D}_2$ over $\text{H}_2$ at 77 K will be the subject of our future work.

5. CONCLUSIONS

In this work, we studied the microscopic mechanism of $\text{D}_2$ permselective separation from $\text{D}_2/\text{H}_2$ mixtures in NaX at 77 K. The adsorption $\text{D}_2/\text{H}_2$ selectivity of 1.49 ± 0.01 computed at zero coverage is in good agreement with finite-precision path integral Monte Carlo simulations of equimolar $\text{H}_2/\text{D}_2$ mixture adsorption in NaX (1.46 ± 0.2) and the reported experimental value of 1.6.\(^{34−36}\) Higher solubility of $\text{D}_2$ results from lower quantum fluctuations (i.e., higher solid–fluid interactions) of a heavier isotope in NaX. The maximum of adsorption selectivity is predicted at infinite dilution of adsorbed mixtures, where the most attractive adsorption centers (narrow windows interconnecting the NaX cages) are preferentially occupied.

In agreement with recent QENS experiment,\(^{15}\) a weak normal kinetic isotope effect on self-diffusion of hydrogen isotopes in NaX is theoretically predicted at 77 K. We found that $\text{H}_2$ molecules self-diffuse faster than heavier $\text{D}_2$ for all NaX loadings. The kinetic selectivity of $\sim$0.86−0.88 in favor of $\text{H}_2$ is theoretically predicted at infinite dilution of the adsorbed phase (i.e., up to 2 molecules per unit cell). The intrinsic $\text{D}_2/\text{H}_2$ selectivity of NaX of $\sim$1.22−1.31 in favor of $\text{D}_2$ is driven by adsorption selectivity (i.e., by thermodynamic equilibrium).

Thus, we concluded that neglecting the kinetic factor in optimization of $\text{D}_2$ recovery from $\text{H}_2/\text{D}_2$ using permselective nanoporous membranes may result in overprediction of their performance at finite temperatures.


