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Simulating Adsorptive Expansion of Zeolites: Application to Biomass-Derived Solutions in Contact with Silicalite

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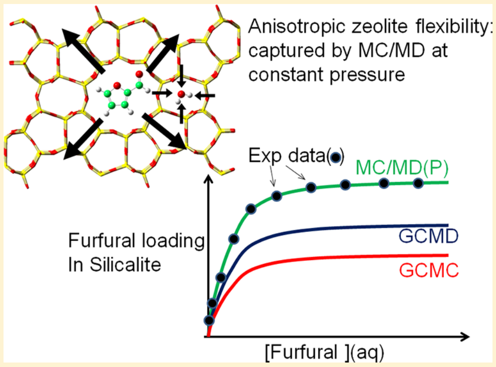
Supporting Information

ABSTRACT: We have constructed and applied an algorithm to simulate the behavior of zeolite frameworks during liquid adsorption. We applied this approach to compute the adsorption isotherms of furfural−water and hydroxymethyl furfural (HMF)−water mixtures adsorbing in silicalite zeolite at 300 K for comparison with experimental data. We modeled these adsorption processes under two different statistical mechanical ensembles: the grand canonical ($V-N_z-\mu_g-T$ or GC) ensemble keeping volume fixed, and the $P-N_z-\mu_g-T$ (osmotic) ensemble allowing volume to fluctuate. To optimize accuracy and efficiency, we compared pure Monte Carlo (MC) sampling to hybrid MC−molecular dynamics (MD) simulations. For the external furfural−water and HMF−water phases, we assumed the ideal solution approximation and employed a combination of tabulated data and extended ensemble simulations for computing solvation free energies. We found that MC sampling in the $V-N_z-\mu_g-T$ ensemble (i.e., standard GCMC) does a poor job of reproducing both the Henry's law regime and the saturation loadings of these systems. Hybrid MC−MD sampling of the $V-N_z-\mu_g-T$ ensemble, which includes framework vibrations at fixed total volume, provides better results in the Henry's law region, but this approach still does not reproduce experimental saturation loadings. Pure MC sampling of the osmotic ensemble was found to approach experimental saturation loadings more closely, whereas hybrid MC−MD sampling of the osmotic ensemble quantitatively reproduces such loadings because the MC−MD approach naturally allows for locally anisotropic volume changes wherein some pores expand whereas others contract.



1. INTRODUCTION

The increasing global demand for energy and the current dependence on fossil fuels have prompted a flurry of investigations into the refinement of biomass as a renewable resource for generating liquid transportation fuels and other products.[1] Current research efforts are aimed at moving away from specialized crops such as sugar and corn, instead producing biofuels from more general lignocellulosic sources, hence decoupling food and fuel markets.[2] Research on generating these new second-generation biofuels requires the study of catalytic and separation processes for transforming plant material composed mainly of cellulose, hemicelluloses, and lignin into more useful platform chemicals.[3,4] Zeolites have recently been found to show significant promise for aqueous-phase processing of sugars[5,6] because of their shape-selective properties in reactions and separations.[7] However, because most zeolite catalytic processing occurs in the vapor phase,[8] molecular-level understanding of how biomass-derived species compete with liquid water for zeolite pore space remains limited.[9] In the present article, we address this issue by constructing and applying new molecular simulations for modeling mixture adsorption in zeolites with flexible, expanding frameworks.

Zeolites are nanoporous, crystalline aluminosilicates with a rich variety of pore structures[7] as well as applications in selective adsorption.[10,11] For example, Tsapatsis and co-workers recently reported experimental adsorption isotherms[9] of furfural−water and hydroxymethyl furfural (HMF)−water solutions in all-silica zeolites with structure types FAU, MFI, FER, and BEA.[12] Such experiments raise the following fundamental questions: How do biomass-derived species and solvent compete for zeolite pore space? How do zeolite pore shape and size respond to such adsorption processes? And finally, how should such behavior be modeled by molecular simulation methods? Adsorption into zeolite materials has been simulated extensively, generally using the Grand Canonical Monte Carlo scheme[10,11] with applications varying from adsorption of long chain hydrocarbons[13] to bulky aromatic molecules.[14] However, despite substantial progress in sampling methodologies,[15,16] most GCMC simulations enforce the constant-volume constraint of the Grand Canonical ensemble

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by keeping all zeolite framework atoms fixed in space. This is the main limitation addressed in the present work.

Snurr et al.[17] presented a simple yet elegant approach for modeling liquid-phase adsorption. In their approach, the external liquid phase is assumed to be in equilibrium with a vapor phase, which in turn is in equilibrium with an adsorbed phase inside the zeolite framework. Equilibrium between the external liquid and vapor phases is represented using thermodynamic equations of state. This poses one of the main limitations of this method, as vapor pressures of biomass-derived feeds are typically quite low, precluding accurate knowledge of vapor−liquid equations of state. Below, we utilize an extended ensemble approach recently reported by Xiong et al. for modeling alcohol adsorption in silicalite from aqueous solutions[18] to the present problem of modeling aqueous furfural and HMF adsorption in silicalite.

As mentioned above, a fundamental problem with standard GCMC is the constraint of constant volume during adsorption. Many experimental data support the notion of zeolite flexibility,[19−21] for example, the evidence that *n*-hexane adsorption into MFI films causes macroscopic strain and film curvature.[21] To model such flexibility, we pursue below the study of a constant-pressure ensemble (the $P{-}N_z{-}\mu_g{-}T$ or osmotic ensemble[22−25]) to allow for unit-cell expansion (and contraction) upon adsorption of water and biomass-derived species. We investigate sampling this ensemble with pure MC and also with hybrid MC−MD sampling. Hybrid Monte Carlo has been studied formally by Duane et al.[26] and Mehlig et al.[27] This general approach has been used by Faller and de Pablo to model structural changes in polymers[28] and by Ghoufi and Marin[29] and Coudert et al.[30] to model flexibility of metal−organic frameworks. We find below that, whereas pure MC sampling of the osmotic ensemble equilibrates guest loading in less CPU time, hybrid MC−MD is required to quantitatively reproduce experimental saturation loadings because of anisotropic pore expansion in these host−guest systems.

The remainder of this article is organized as follows: section 2 discusses the models and methods for simulating liquid mixture adsorption; section 3 describes the simulation results in comparison with experimental data; and section 4 offers a summary, concluding remarks, and suggestions for future work.

2. MATERIALS AND METHODS

This section discusses the approaches used to model the adsorption of biomass-derived solutions into silicalite zeolite including the distortions suffered by the silicalite lattice during this process. We considered the furfural−water and HMF−water solutions as the foci of our study due to their increasing importance in biomass processing and the availability of experimental adsorption data for these systems.[9] For convenience, we refer to either furfural or HMF as solute and water as solvent unless referred to by their actual names. We chose to study the all-silica MFI framework (silicalite) because of the close fit of solute molecules inside silicalite's pores and the fact that the acid form of silicalite (H-ZSM-5) has shown promising shape-selectivity in direct catalytic-fast-pyrolysis of biomass to biofuels.[31] In what follows, we describe the various models, thermodynamic ensembles, potential energy functions, and sampling techniques used to perform our simulations.

A. Zeolite System. Silicalite is an MFI-type zeolite ideally containing only Si and O atoms. In this work we, have considered the orthorhombic phase of silicalite. Although phase transitions of silicalite to nonorthorhombic phases from adsorption of, for example, *p*-xylene, have been observed[32] and debated[33] for several decades, no such transition is known from adsorption of furfural or HMF in silicalite. We thus focus, for simplicity, on the orthorhombic phase of silicalite reported by Olson et al.[34] This framework has a unit cell with lattice parameters a = 20.07 Å, b = 19.92 Å, and c = 13.42 Å and all three angles equal to 90°. To ensure a sufficiently large simulation box, we included two unit cells in the c direction resulting in a simulation cell with 192 Si atoms and 384 O atoms. The pore structure of silicalite comprises two distinct channels: straight channels that run along the b direction of the unit cell with an average pore size between 5.1−5.5 Å and zigzag channels located along the ac plane with a pore size range of 5.3−5.6 Å.[12] This pore structure gives channels with sizes similar to the kinetic radii of furfural and HMF, 5.5 and 6.2 Å, respectively.[35]

B. Overall Forcefield Model. The approximate potential energy has the following overall form:

$$V = V_Z + V_W + V_S + V_{ZW} + V_{ZS} + V_{WW} + V_{SS} + V_{WS}$$

where V_Z, V_W, and V_S are the intramolecular distortion potential energies of the zeolite framework, water molecules, and solute molecules (furfural or HMF), respectively. In addition, V_{ZW} and V_{ZS} are the zeolite−water and zeolite−solute host−guest interactions; whereas V_{WW}, V_{SS}, and V_{WS} are the water−water, solute−solute, and water−solute intermolecular interactions. The zeolite−water−solute phase requires all these interactions, whereas the external water−solute solution only requires V_W, V_S, V_{WW}, V_{SS}, and V_{WS}. In general, each term (except for V_W and V_S) includes long-range Coulombic interactions evaluated with atomic point charges and the Ewald summation method.[36] Here, we discuss our choice(s) for each term.

C. Zeolite Forcefield (V_Z). We employed the same zeolite framework forcefield presented in our previous work on microwave-driven zeolites.[37,38] This forcefield comprises Coulombic interactions with Si/O partial charges reported in ref 39, short-range Buckingham (exp-6) terms using parameters reported in ref 40, and three-body O−Si−O terms using a functional form and parameters reported by Catlow et al.[41] As shown by Combariza et al., this forcefield has shown good agreement with zeolite thermal expansion properties obtained from experimental results.[42]

D. Furfural and HMF Solute Forcefields (V_S, V_{SS}, V_{WS}, V_{ZS}). The intramolecular vibrations of both solutes − furfural and HMF − were described by the valence-bond forcefield reported by Oie et al.[43] This forcefield comprises harmonic terms for bond-stretching and angle-bending energies, whereras torsion energies are calculated by a Fourier series truncated after the second term. Short-range intermolecular energies for the solutes were modeled as a Lennard−Jones (12−6) fluid. Lennard−Jones parameters and atomic charges for HMF were taken from the OPLS-AA force field developed by Jorgensen and Maxwell.[44] Further development of this force field has shown extremely good agreement with experimental results for the behavior of furanic heterocycles in water.[45] Furfural parameters were taken from the cis−trans average configuration values given by Rivelino et al.;[46,47] this approach was shown to give a reasonable description of aqueous solvation around furfural. Solute−zeolite short-range parameters were constructed using the standard Lorentz−Berthelot combination rules: arithmetic averages for Lennard−Jones diameters and geometrical averages for Lennard−Jones well-depths.

E. Water Forcefields (V_W, V_{WW}, V_{ZW}). Water was modeled using two different sets of forcefield parameters: the TIP4P forcefield for water in the external liquid phase[48] and the model presented by Puibasset et al. for water molecules inside all-silica zeolites.[49,50] For molecular modeling of liquid water, many different force fields have been studied; good reviews and analyses of the different capabilities of these forcefields have been reported.[48,51] The SPC/E model appears to give excellent agreement for simulating properties of pure water. However, other studies have shown that substantial retuning is necessary when using SPC/E for modeling aqueous solutions.[52,53] In contrast, the TIP4P force field has shown good results for various furanic molecules in water[44,45,47] warranting its use in the present study. Because TIP4P is a rigid water model, there is no need to specify the intramolecular V_W term.

In the case of water adsorption inside hydrophobic (all-silica) zeolites, previous studies have shown that both the TIP4P and SPC/E forcefields may overestimate water loadings at relatively low water vapor pressures,[54] with both forcefields predicting loadings close to 45 molecules per unit cell inside silicalite, whereas experimental values are closer to 17 molecules per unit cell for pressures on the order of 1−2 kPa.[55,56] We note that Fuchs and co-workers have shown with both experiments and simulations that under *much higher* pressures, on the order of 50−100 MPa, saturation water loadings in silicalite *can* reach 45−50 molecules per unit cell.[57−60] This was interpreted as a first-order phase transition of water occurring in zeolite pores, a general phenomenon predicted by previous lattice model simulations,[61−63] analogous to bulk liquid condensation from vapor. Although saturation loadings of ∼45 molecules per silicalite unit cell are thus possible at very high pressures, they are not relevant at the much lower pressures considered in the present study. We thus require water−zeolite interaction parameters that reproduce water loadings measured at lower pressures.[55,56]

Puibasset et al. reported modifications to the SPC/E forcefield to account for this overestimation of water adsorption in silicalite.[49,50] These results are consistent with ab initio molecular dynamics simulations by Coudert et al.,[64] who found that the dipole moments of water inside all-silica zeolites are about 10% less than the bulk liquid water counterpart. By changing the atomic charges in water, Puibasset et al. found that water adsorption in zeolites could be fitted down to experimental values. Table 1 provides a summary of the forcefields used in this study with source references. A full listing of all forcefield parameters is provided in the Supporting Information.

Table 1. Summary of Forcefields Used in the Present Simulations

substance	type of interaction	refs
silicalite	all	Catlow,[41] Auerbach[40]
HMF	intramolecular vibrations	Oie[43]
	atomic charges	Jorgensen[44]
	L−J parameters	Jorgensen[44]
furfural	intramolecular vibrations	Oie[43]
	atomic charges	Rivelino[46]
	L−J parameters	Rivelino[46]
liquid water	all	TIP4P Jorgensen[48]
adsorbed water	all	Puibasset[50]

F. External Liquid Phase: Ensembles and Sampling. In principle, a proper treatment of the external solution phase in equilibrium with a zeolite-adsorbed phase is provided by the Gibbs ensemble approach of Panagiotopoulos.[65] This involves a simultaneous simulation of both solution and zeolite phases under separate periodic boundary conditions with total (solvent/solute + zeolite/solvent/solute) numbers of molecules, total volume, and temperature held fixed. The experimental furfural and HMF concentrations in the aqueous solutions studied by Ranjan et al.,[9] which we are directly modeling in the present work, involve relatively low concentrations of furfural and HMF. In the Gibbs ensemble calculations, such low concentrations would require large simulation cells and concomitantly long simulation times to model the external solution. As noted by Xiong et al.,[18] low solute concentrations allow the use of the *ideal solution* equation of state for the solute, which we discuss in more detail below. Regarding the solvent, Pearce and Gerster[66] found that, at low concentration of furfural in the liquid phase, the equilibrium vapor pressure is very similar to that of pure liquid water. Following the approach of Snurr and co-workers,[14,17] we use this vapor pressure (3559.7 Pa at 300 K) to compute the chemical potential of water assuming that the water vapor acts ideal under these conditions. This water chemical potential is then used in the simulation algorithms discussed below.

For the furfural and HMF solutes, the ideal solution equation of state gives the following relationship between the solute chemical potential in solution and its concentration:

$$\mu_i(C_i) = \Delta_{\text{solv}}\mu_i(C_0) + RT \times \log(C_i/C_o)$$

where μ_i is the chemical potential of the ith species in solution, C_i is the concentration, C_o is a reference concentration, R is the gas constant, T is absolute temperature, and $\Delta_{\text{solv}}\mu_i(C_0)$ is the molar Gibbs free energy of solvation from gas to solution phase at the reference concentration and temperature T.[67] We utilize the expanded ensemble (EE) approach recently applied by Xiong et al.[18] to compute the solvation Gibbs free energy; here we briefly review this approach.

The EE method provides an efficient way to collect statistics for the random insertion of a solute into a dense liquid.[18] The EE approach is similar in spirit to thermodynamic integration, in which a new interaction (e.g., solute−solvent) is introduced gradually through a coupling (or charging) parameter λ, which takes values from zero (no solute−solvent interaction) to unity (full solute−solvent interaction). In the EE approach, a grid of λ values (λ_i) is established, each value defining a sub-ensemble of equilibrium fluctuations associated with a the balancing factor η_i. The probability of occurrence of the ith subensemble is given by:

$$p(\lambda_i) \propto \exp(\eta_i)Q(N, P, T, \lambda_i)$$

where Q is the partition function for N solvent molecules at temperature T and pressure P in the ith subensemble. In a typical EE simulation,[18] molecular dynamics (MD) may be used to sample within a given subensemble, and Metropolis Monte Carlo (MC) can be used to attempt transitions between subensembles. In practice, one accumulates statistics for visiting the various subensembles. Assuming end points $\lambda_0 = 0$ and $\lambda_M = 1$, the solvation Gibbs free energy per mole (excess chemical potential) is given by the formula:

$$\Delta_{\text{solv}}\mu_i(C_0)/RT = -\ln[Q(N, P, T, \lambda_M = 1) /Q(N, P, T, \lambda_0 = 0)] = \ln[p(\lambda_0 = 0)/p(\lambda_M = 1)] + (\eta_M - \eta_0)$$

We have followed Xiong et al. in their use of an adaptive grid of balancing factors (η_i) to ensure efficient sampling of (i.e., swapping between) subensembles. For the bulk liquid simulations, we performed hybrid MC−MD simulations in the NPT ensemble attempting volume changes using the MC methodology presented below (vide infra) and using MC to attempt transitions between subensembles.

Details and parameters for these EE simulations are provided in the Supporting Information. The results below in Table 2 represent an average over two independent simulations. These simulations were found to be very computationally demanding, each running for a about 150 CPU hours on 3.2 GHz processors. The advantage of the ideal solution/expanded ensemble approach over the Gibbs ensemble calculation is that one only has to perform this excess chemical potential computation once per solute per temperature studied.

Table 2. Solvation Chemical Potentials of Furfural−Water and HMF−Water Solutions at STP

solute molecule	calculated free energy of solvation (kJ/mol)
furfural	−8.3
HMF	−7.9

G. Zeolite Adsorption Equilibrium: Ensembles and Sampling. We model adsorption equilibrium using both constant-volume and constant-pressure ensembles to investigate the effect of zeolite pore fluctuations on adsorption. We sample these ensembles in two ways: using pure Monte Carlo (MC), and using hybrid MC−MD simulations as described below.

Constant-Volume Monte Carlo. Equilibrium for a given species (e.g., furfural) between the liquid-solution phase and the zeolite-adsorbed phase is established by equality of the two chemical potentials assuming thermal equilibrium at constant temperature. A standard and simple way to enforce equality of chemical potentials is provided by the grand canonical (GC) ensemble, which fixes zeolite volume (V), guest chemical potentials for a multicomponent adsorbed phase (μ_g), and temperature (T).[36,68] We note, that although the GC ensemble is often called the $V-\mu_g-T$ ensemble, in the context of modeling adsorption in zeolites a more complete name is the $V-N_z-\mu_g-T$ ensemble taking into account the fixed number of zeolite atoms (N_z). The usual way to keep simulation volume constant is to fix the locations of all N_z zeolite atoms during GC additions and deletions of guest molecules.[68] This of course is a model assumption considering the great multiplicity of zeolite framework configurations consistent with a given volume; the very high bulk moduli of zeolite crystals[69,70] typically warrant this fixed-framework approximation especially for modeling adsorption of unbranched alkanes.

We report standard GCMC adsorption isotherms below using the forcefields described above. These typically involved 10^6 equilibration steps and another 10^6 steps for accumulating statistics on water and solute (furfural or HMF) loading in silicalite at 300 K. The four processes of addition/deletion of solute/solvent were attempted with equal probability. Following Snurr et al.,[16] we applied a bias when determining the center-of-mass for inserting molecules into silicalite. We mapped the pore-space potential energy landscape using a Lennard−Jones probe particle with the following properties (σ = 0.3 Å, ε = 0.096 kJ/mol). The insertion bias was removed in the Metropolis acceptance/rejection step following the approach of Snurr et al.[16] Molecular orientations for insertion were chosen at random. Guest intramolecular shapes were chosen at random from a library of equilibrium fluctuations following our earlier work[38] generated in the present case from the solution-phase MD described above in part F of section 2 for computing the aqueous solvation free energy.

Constant-Volume Monte Carlo−Molecular Dynamics. For tight-fitting guest species in zeolites, even small framework distortions can significantly change adsorption capacities and diffusion properties.[71] We investigate this possibility using three different approaches. The first involves hybrid MC−MD sampling of the GC ensemble inspired by our previous work on modeling microwave-activated desorption in zeolites,[38] in which MD was used to apply the microwave field, whereas GCMC was used to sample adsorption/desorption processes. In the present application of GCMC−MD, the MD allows for zeolite channel size and shape fluctuations at fixed total simulation cell volume. Intervals of 1000 steps of microcanonical ($V-N_z-N_g-E$) MD were interspersed between segments of 2000 GCMC steps. Each segment of 1000 MD steps was accepted with unit probability because of numerical energy conservation. The GCMC guest additions/deletions were attempted as described above in the pure MC simulations except in MC−MD sampling we used the last zeolite framework structure from the most recent MD segment. In this way, we treat the effect of framework fluctuations on guest adsorption by running GCMC for various MD-generated snapshots of the zeolite framework albeit at constant total volume. This resulted in faster equilibration than in the pure MC approach reaching adsorption equilibrium in 5 × 10^5 GCMC steps. When guest molecule insertions are accepted during the GCMC segments, initial velocities are also generated for use in the next MD segment propagated using the velocity Verlet algorithm with a 1 fs time step.

Constant-Pressure Monte Carlo. Although hybrid MC−MD sampling of the GC ensemble is expected to be more complete than fixed-framework sampling, the possibility remains that volume fluctuations of the simulation cell are required to reproduce experimental data. To investigate this, we applied the constant-pressure $P-N_z-\mu_g-T$ (osmotic) ensemble to investigate how volume changes influence adsorption capacities at P = 1 atm and T = 300 K. The thermodynamic potential for this ensemble is proportional to system size as controlled by the number of zeolite atoms, N_z.[23−25] We sampled this ensemble using both pure MC and hybrid MC−MD simulations. In the case of pure MC sampling, we followed the isothermal−isobaric approach given by McDonald.[72] Because of changes to the zeolite framework structure in the osmotic ensemble, we updated the biased-insertion potential energy map every 10^5 MC steps. Although in principle this may violate detailed balance, the effect is expected to be minimal. Volume changes, guest additions, and guest deletions were attempted with equal probabilities. Volume changes were made with the Parrinello−Rahman approach[73] with scaling factors in the 0.1−5.0% range. Although the orthorhombic simulation cell was conserved, the a, b, and c parameters were allowed to fluctuate independently in our approach. These osmotic MC simulations required 10^6 guest addition/deletion steps to reach loading equilibrium.

Constant-Pressure Monte Carlo−Molecular Dynamics. Although osmotic MC simulations allow for volume changes, they do not allow for local channel distortions wherein one region of the zeolite may expand and another region contract. To investigate this effect, we sampled the osmotic ensemble using hybrid MC−MD mostly as described above for the constant-volume MC−MD simulations. In this case, the ratio of MC volume changes to MC loading changes was kept at 1:2 (as above in pure osmotic MC), and the ratio of microcanonical MD to MC loading changes was set to 1:1 because more MD steps were required to equilibrate the system to volume changes made during MC. The MD time step was kept at 1 fs; volume changes larger than 5% were found to produce instabilities in the MD simulations. Reaching adsorption equilibrium in osmotic MC−MD required 7.5×10^5 MC addition/deletion steps. These were the most computationally demanding simulations reported in this article. Converging one point on an isotherm typically required 72 CPU hrs on a 3.2 GHz processor.

Figure 1 shows a general schematic of the algorithm used for the $P-N_z-\mu_g-T$ simulations sampled with both MC and MC−MD sampling techniques.

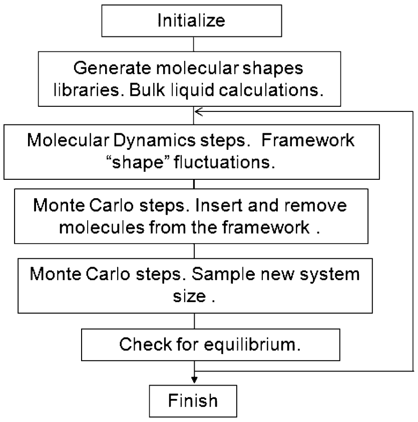

Figure 1. Schematic representation of simulations performed in the $P-N_z-\mu_g-T$ ensemble sampled using a combination of MC plus molecular dynamics techniques.

3. RESULTS AND DISCUSSION

Here, we report our results from the series of simulations performed to represent the behavior of furfural−water and HMF−water solutions in equilibrium with adsorbed phases inside the silicalite framework.

Figure 2 shows calculated isotherms of furfural−water solutions in contact with silicalite (only furfural loadings shown) using the $V-N_z-\mu_g-T$ ensemble sampled with pure MC and with hybrid MC−MD alongside experimental data from Ranjan et al.[9] Figure 2 shows the loadings in experimental units on the left of grams solute (furfural) per grams zeolite and also on the right in molecules per unit cell. We observe that neither MC nor MC−MD sampling techniques at constant volume reproduces the experimental saturation loadings. We also find in the initial linear (Henry's law) region of the isotherm that MC−MD underestimates the experimental slope by 10%, whereas pure MC underestimates the experimental slope by nearly twice as much (18%) indicating that even under low-solute-loading conditions the added channel flexibility afforded by hybrid MC−MD produces a noticeable effect. As the concentration of furfural in solution increases and the isotherm approaches saturation, Figure 2 shows growing discrepancies between constant-volume simulations and experiment indicating the need to relax the constant-volume constraint. The same pattern of error is seen for HMF solutions in Figure 3 with even larger saturation discrepancies presumably because of HMF's larger molecular size.

Our simulations suggest that furfural and HMF molecules fill the silicalite intersections at relatively low loadings and then fill the channels at higher loadings. Regarding the multicomponent nature of adsorption in these constant-volume simulations, we found that adsorption of oxygenates into a given pore space is contingent on water desorption from that same pore space. At negligible oxygenate loadings, water loadings in silicalite were found to be ∼35 waters per simulation cell (i.e., two unit cells), whereas at full oxygenate saturation water loadings are around 3−4 waters per unit cell, where in this latter case these waters share pore spaces with oxygenates. Below, we report a qualitatively different multicomponent behavior when relaxing the constraint of constant volume.

Figures 2 and 3 show that a constant-volume ensemble does not capture the saturation loading properties of either furfural or HMF in silicalite. We thus investigate the use of the $P-N_z-\mu_g-T$ ensemble to compute these isotherms using both pure MC and hybrid MC−MD for both furfural−water and HMF−water solutions exposed to silicalite (Figures 4 and 5, respectively). As discussed above, the pure MC sampling allows overall unit cell volume to fluctuate, whereas the hybrid MC−MD allows unit cell volume to change as well as fluctuations of local pores and channels. Figures 4 and 5 show, for furfural and HMF respectively, that pure MC sampling of the $P-N_z-\mu_g-T$ ensemble gets very close to saturation loadings of the oxygenates, whereas hybrid MC−MD sampling provides *quantitative agreement with experiment in all regions* of the isotherms.

It is interesting to investigate why pure MC sampling in the $P-N_z-\mu_g-T$ ensemble still does not quantitatively reproduce experimental saturation loadings, whereas hybrid MC−MD does so. The results in Table 3 begin to shed light on this; Table 3 shows silicalite unit cell volumes from $P-N_z-\mu_g-T$ MC and $P-N_z-\mu_g-T$ MC−MD simulations of furfural−water adsorption alongside average channel diameters from these simulations for straight and zigzag channels. These channel diameters were computed from oxygen-atom locations on opposite sides of channels and hence reveal trends in available channel spaces. Here, we observe that, whereas the overall unit cell volume for hybrid MC−MD sampling is smaller than that obtained by pure MC sampling, the mean channel diameters obtained from MC−MD exceed those from pure MD. This suggests that, whereas the overall unit cell volume increases upon adsorption (Table 3), some regions of the zeolite pore space expand more (e.g., channels), whereas other regions expand less or may even contract upon adsorption. In our pure-water $P-N_z-\mu_g-T$ simulations, the silicalite unit cell volume was found to shrink from 5390 Å^3 (bare silicalite) to 5266 Å^3 (water-filled silicalite).

Inspired by this notion, we investigated structural aspects of the silicalite−furfural−water system near saturation. Equilibrium snapshots (e.g., Figure 6) corroborate the picture described above, wherein adsorption of furfural molecules in channel segments causes slight channel expansion, whereas some of the remaining water molecules are pushed into regions of the silicalite structure that are generally inaccessible to the

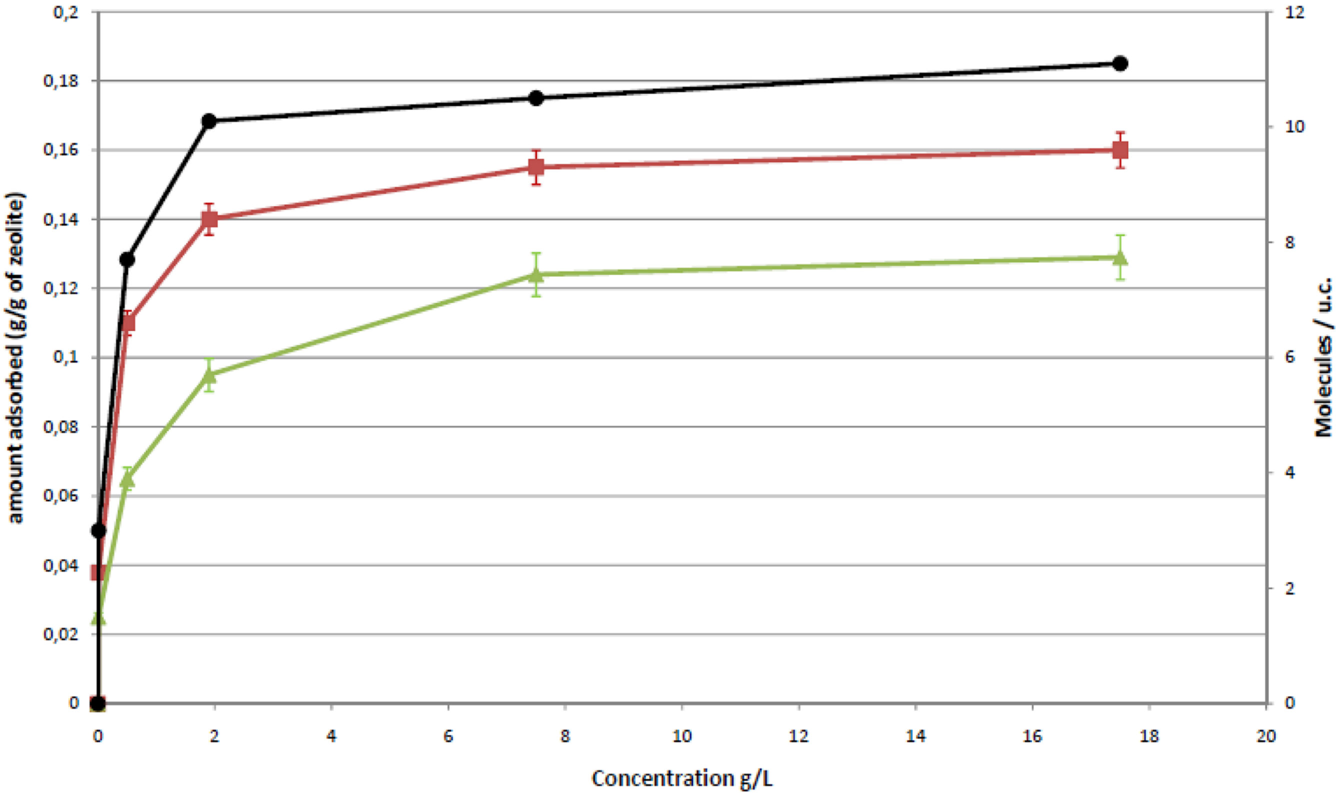

Figure 2. Furfural−water adsorption isotherms in silicalite at 300 K assuming constant-volume ensemble. (●) experimental data from ref 9, (■) MD + MC sampling, (▲) standard GCMC simulations with a fixed framework geometry.

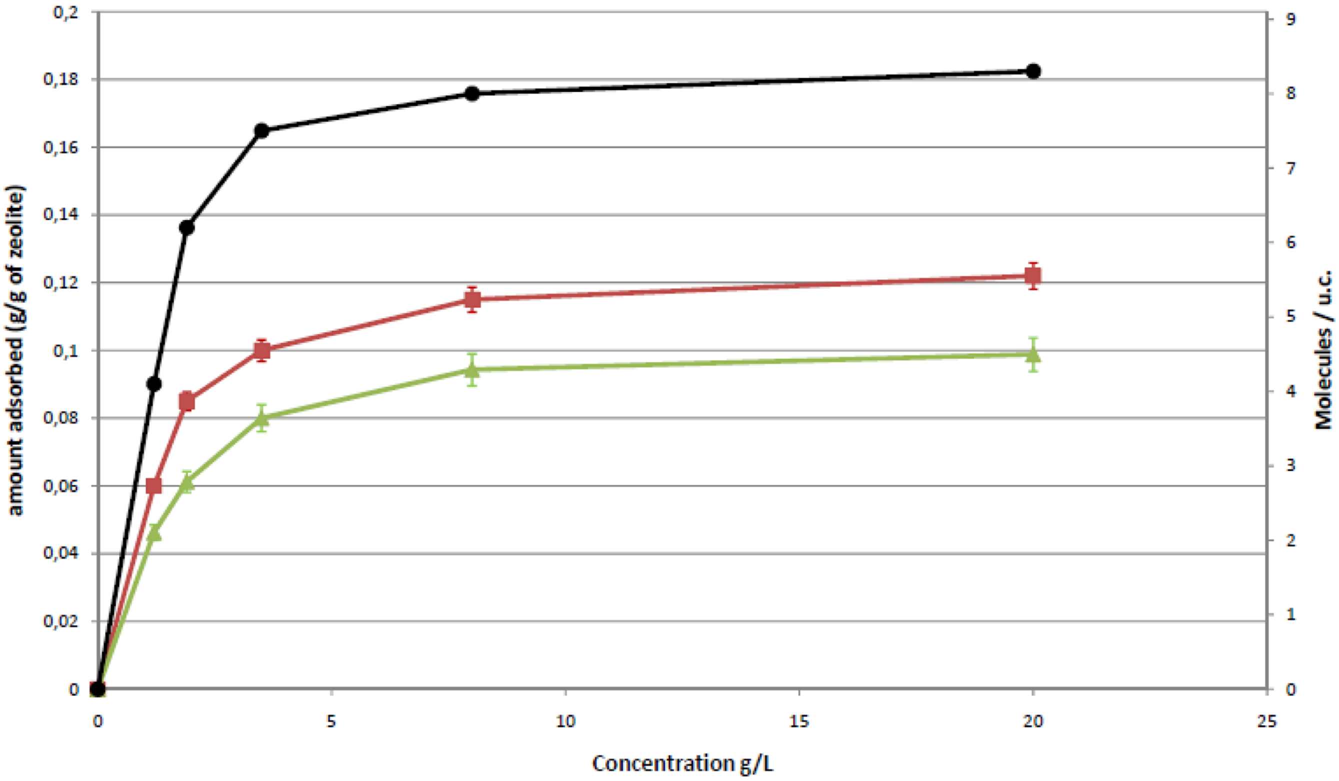

Figure 3. HMF−water adsorption isotherms in silicalite at 300 K assuming constant-volume ensemble. (●) experimental data from ref 9, (■) MD + MC sampling, (▲) standard GCMC simulations with a fixed framework geometry.

organic oxygenates, such as in the small pore spaces in the silicalite structure bounded by 4-, 5-, and 6-ring windows. Water molecules likely access these spaces through 6-ring windows as they do in, for example, sodalite. The HMF−water

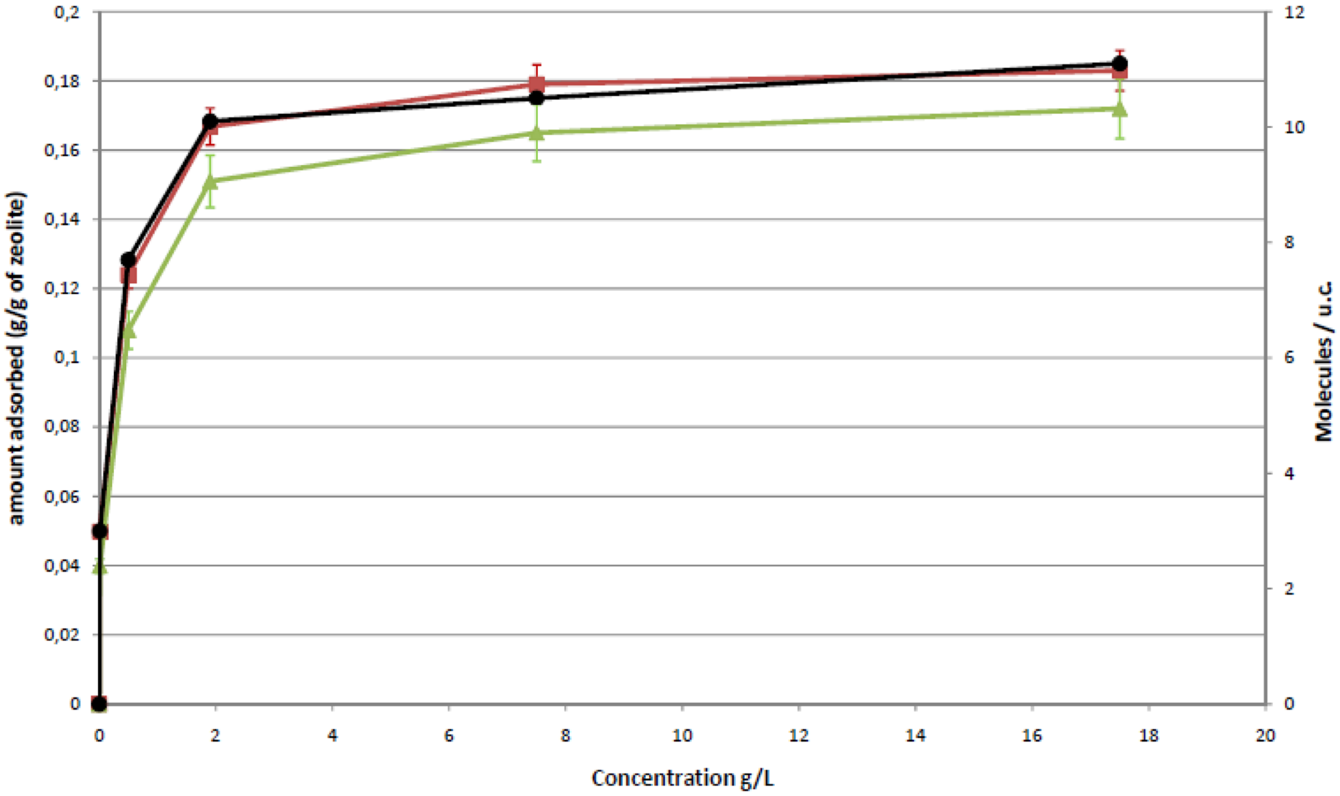

Figure 4. Furfural−water adsorption isotherms in silicalite at 300 K and constant pressure (1 atm). (●) experimental data from ref 9, (■) MD + MC sampling of system loading and topology, (▲) simulations with only MC sampling.

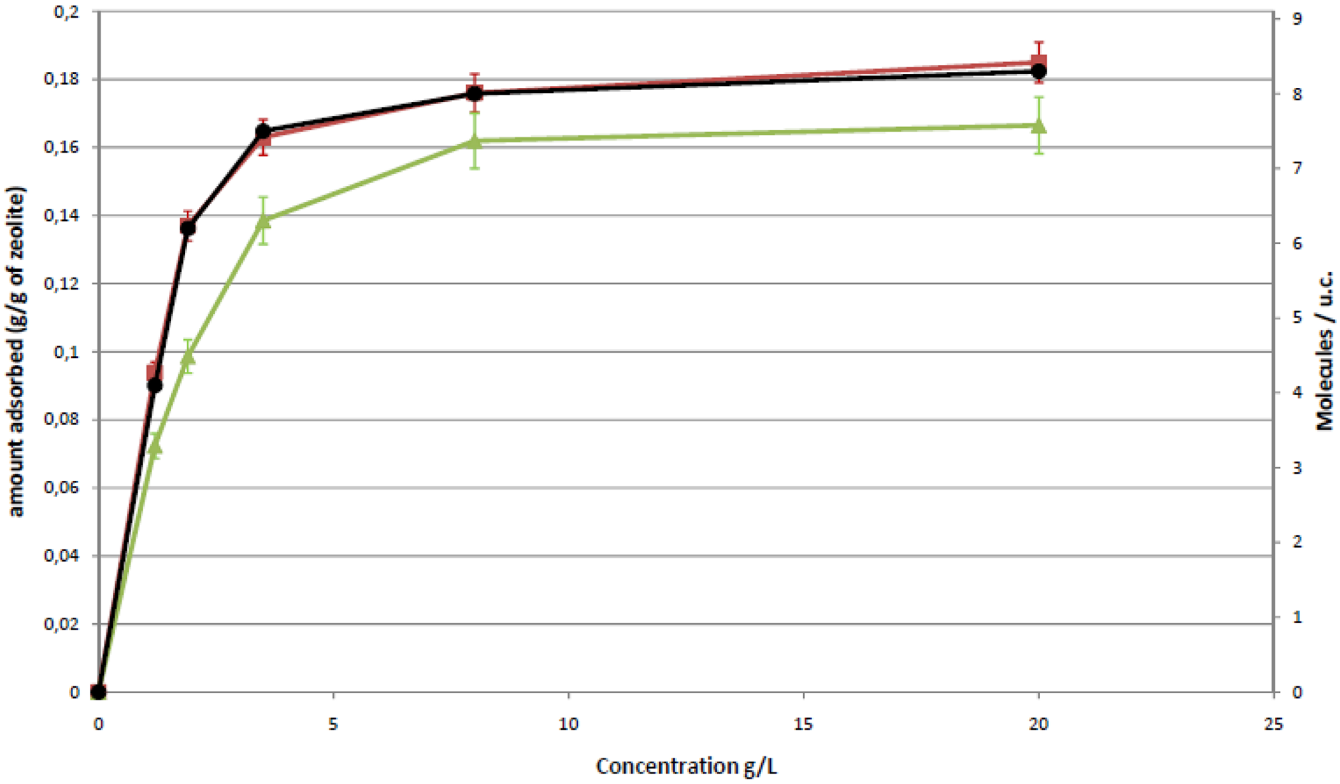

Figure 5. HMF−water adsorption isotherms in silicalite at 300 K and constant pressure (1 atm). (●) experimental data from ref 9, (■) MD + MC sampling of system loading and topology, (▲) simulations with only MC sampling.

systems behave qualitatively the same way (data not shown). The contraction of these smaller pore spaces and concomitant expansion of channels during the MD segments of the hybrid MC−MD was found to produce energetically favorable

Table 3. Zeolite Mean Unit Cell Volumes and Mean Channel Diameters upon Furfural Saturation from Aqueous Solution at 300 K

simulation scheme	silicalite unit cell mean volume (Å^3)	straight channel long axis mean diameter (Å)	zigzag channel long axis mean diameter (Å)
bare zeolite exp[12]	5333	5.60	5.50
bare zeolite $P-N_z-\mu_g-T$	5390	5.35	5.47
$P-N_z-\mu_g-T$ MC	5501	5.43	5.52
$P-N_z-\mu_g-T$ MC + MD	5482	5.44	5.55

adsorption environments for smaller clusters of water molecules. Such water clustering in zeolites has been observed experimentally by Bussai et al.[74] and Turov et al.,[75] where they attribute certain chemical shifts to the formation of water−water hydrogen bonds.

The simulated behavior of water at constant pressure and oxygenate saturation found herein from hybrid MC−MD sampling − that is, retention of small water clusters in otherwise inaccessible regions of the zeolite − is quite different from that observed in pure MC sampling of the $P-N_z-\mu_g-T$ ensemble. Indeed, water molecules mostly desorb upon furfural or HMF saturation in pure MC because of the difficulty in producing collective framework MC moves that swell channels and shrink small pockets of the silicalite framework as occurs during MD segments. Such *locally anisotropic* framework fluctuations go beyond the unit cell anisotropy treated by the Parrinello−Rahman sampling method.[73]

To test the importance of constant-pressure MC−MD sampling of *multicomponent* adsorption, we performed simulations of a hypothetical furfural gas phase in contact with silicalite. This is very difficult to achieve experimentally because of furfural's negligible vapor pressure and low thermal stability. Nonetheless, such single-component adsorption simulations provide apples-to-apples comparisons with the multicomponent systems discussed above. Adsorption isotherms of gas-phase furfural in silicalite at 300 K and 1 atm are shown in Figure 7 comparing pure osmotic MC and hybrid osmotic MC−MD approaches. Figure 7 shows nearly perfect agreement between the two sampling approaches, especially in the saturation region, indicating that under single-component conditions the kind of locally anisotropic framework fluctuations discussed above are unimportant because of the lack of water in the system. Qualitatively identical results were obtained for gas-phase HMF in silicalite (data not shown). We thus surmise that, in general, hybrid MC−MD sampling of the $P-N_z-\mu_g-T$

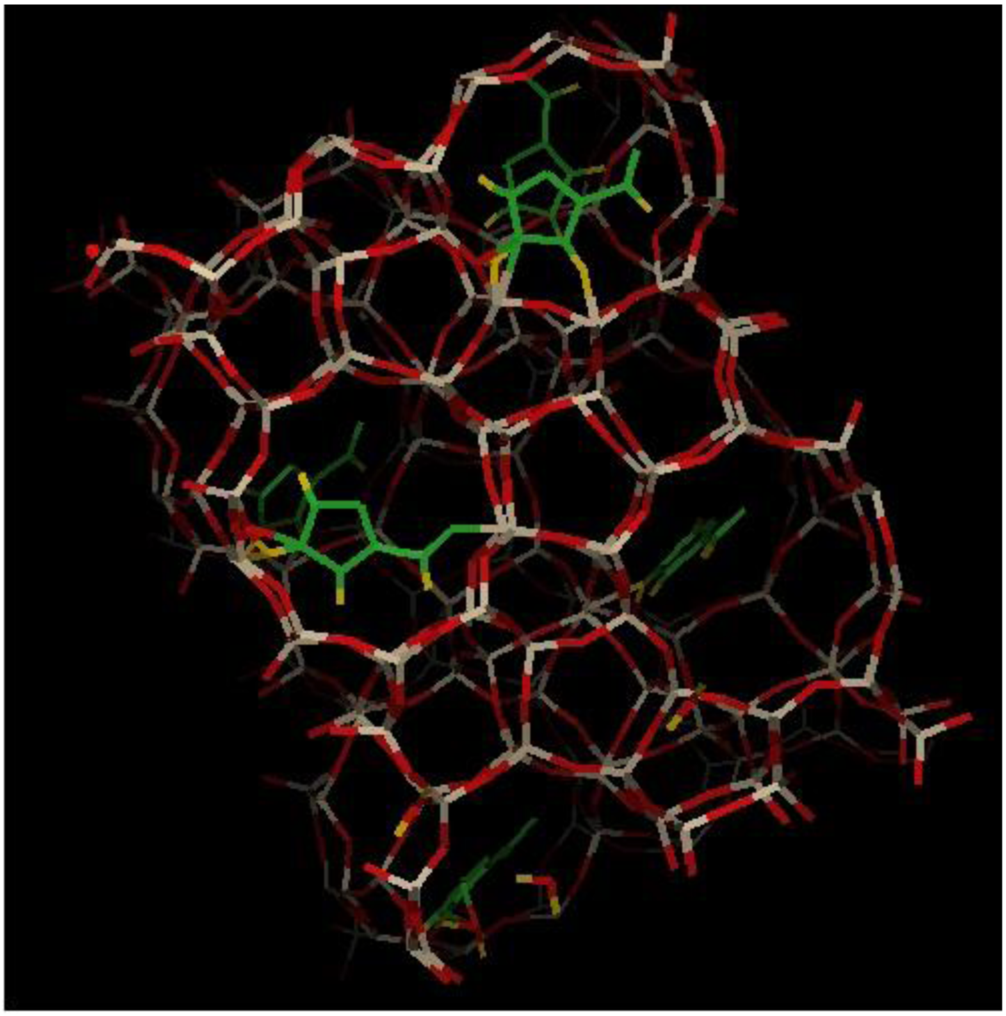

Figure 6. Equilibrium snapshot of water and furfural in silicalite at 300 K showing water (hydrogen in yellow) located in very small pores that are inaccessible to furfural.

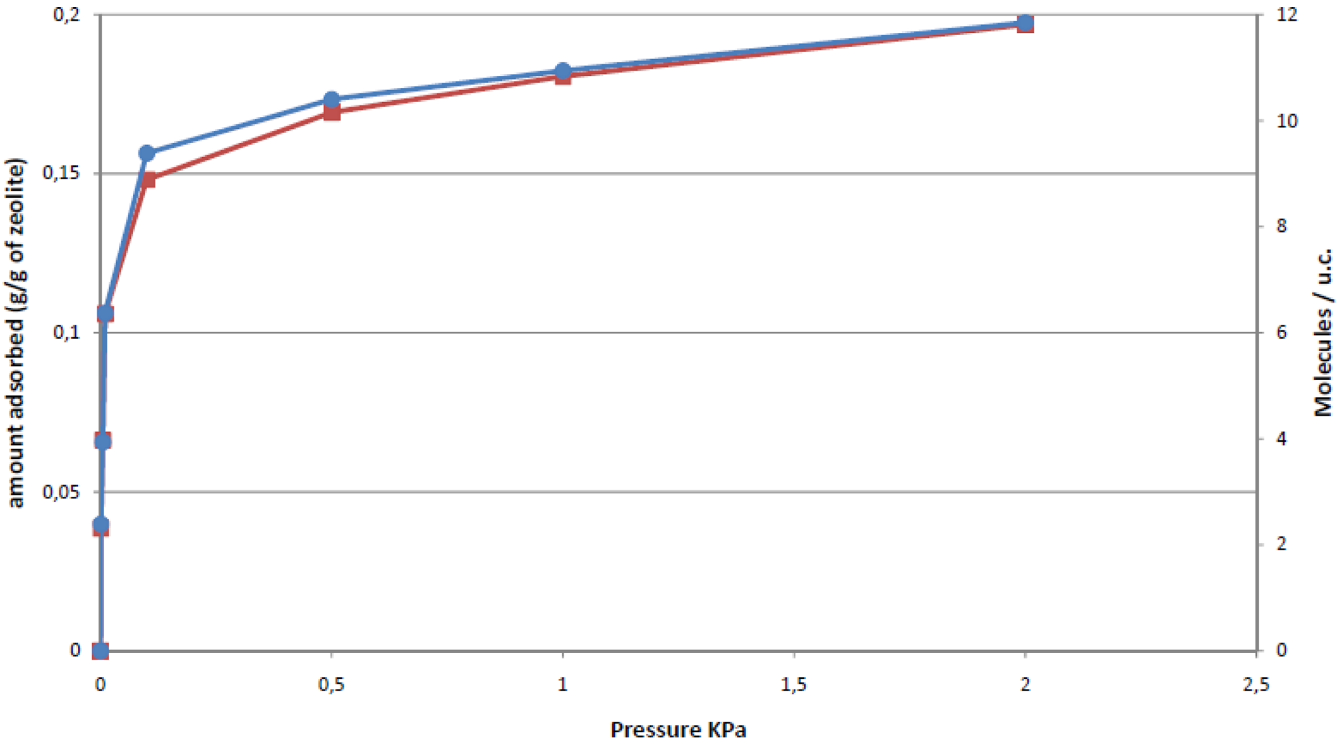

Figure 7. Simulation of gas-phase furfural adsorbed in silicalite at 300 K showing quantitative agreement at constant pressure (1 atm) between pure MC and hybrid MC−MD under such single-component conditions. (●) MD + MC sampling, (■) pure MC sampling.

ensemble is crucial for simulating multicomponent adsorption systems where adsorption of one component swells the zeolite, whereas adsorption of the other tends to shrink the pores.

There remains the possibility that deficiencies in the forcefield − for example, too large furfural and/or HMF Lennard−Jones diameters − necessitate framework flexibility as a compensatory but erroneous effect to reproduce saturation loadings. To test this, we have computed single-component furfural isotherms at *constant volume* (rigid zeolite) with a focus on saturation loadings at 300 K using both pure MC and hybrid MC−MD simulation methods. We have found that constant-volume GCMC saturates at 11.3 ± 0.5 furfural molecules per simulation cell (2 silicalite unit cells), constant-volume GCMD saturates at 11.4 ± 0.4 furfurals per simulation cell, and constant-pressure pure MC and MC−MD both saturate at 11.7 ± 0.2 furfurals per cell (Figure 7). Although there appears to be a weak trend, these results are within the statistical uncertainties and thus cannot be distinguished. This agreement would not be possible if, for example, atomic diameters were set to too-large values, only to be compensated by framework flexibility. The agreement among these constant-volume and constant-pressure saturation loadings supports our conclusion above that the need for framework flexibility in general, and anisotropic flexibility in particular is an effect of *multicomponent* adsorption.

4. SUMMARY AND CONCLUDING REMARKS

We have simulated multicomponent furfural−water or HMF−water adsorption from solution phases into silicalite zeolite at 300 K for comparison with experimental data of Ranjan et al.[9] We used two different established forcefields for bulk and adsorbed water to account for the different water dipoles in bulk and adsorbed phases. The simulations were performed in constant-volume ($V{-}N_z{-}\mu_g{-}T$) and constant-pressure ($P{-}N_z{-}\mu_g{-}T$ or osmotic) ensembles, both sampled with either pure Monte Carlo (MC) or with hybrid MC−MD methods. The external solutions were treated as ideal with excess chemical potentials computed with extended ensemble methods.

In general, the constant-volume simulations underestimate oxygenate (furfural and HMF) saturation loadings regardless of whether pure MC or hybrid MC−MD sampling was used. Constant-pressure simulations come much closer to reproducing experimental oxygenate saturation loadings in silicalite and reach quantitative agreement using hybrid MC−MD sampling of the $P{-}N_z{-}\mu_g{-}T$ ensemble because only this approach allows for locally anisotropic zeolite framework fluctuations wherein some pores expand whereas others contract. This was found to be important for multicomponent furfural−water and HMF−water adsorption systems because the adsorbed oxygenate component tends to swell channels, whereas the adsorbed water phase tends to shrink smaller pockets of the silicalite framework upon oxygenate saturation. We predict that hybrid MC−MD sampling of the $P{-}N_z{-}\mu_g{-}T$ ensemble will generally be important for simulating multicomponent adsorption systems where adsorption of one component swells the zeolite, whereas adsorption of the other tends to shrink the pores.

Future research is needed to investigate whether solvents other than water produce such locally anisotropic zeolite framework fluctuations and whether simulation methods other than MD can sample such locally anisotropic framework fluctuations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the forcefield and also the parameters of the extended ensemble calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Parikka, M. Global Biomass Fuel Resources. *Biomass Bioenergy* **2004**, *27*, 613−620.

(2) Muller, S. A.; Anderson, J. E.; Wallington, T. J. Impact of Biofuel Production and Other Supply and Demand Factors on Food Price Increases In 2008. *Biomass Bioenergy* **2011**, *35*, 1623−1632.

(3) Huber, G. W.; Corma, A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.* **2006**, *106*, 4044−4098.

(4) Huber, G. W. *Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Next Generation Hydrocarbon Biorefineries*; National Science Foundation: Washington D.C., March, *2008*; p 180.

(5) Moliner, M.; Roman-Leshkov, Y.; Davis, M. E. Tin-Containing Zeolites Are Highly Active Catalysts For The Isomerization Of Glucose In Water. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 6164−6168.

(6) Taarning, E.; Osmundsen, C. M.; Yang, X. B.; Voss, B.; Andersen, S. I.; Christensen, C. H. Zeolite-Catalyzed Biomass Conversion To Fuels And Chemicals. *Energy Environ. Sci.* **2011**, *4*, 793−804.

(7) Auerbach, S. M.; Karrado, K. A.; Dutta, P. K. *Handbook of Zeolite Science and Technology*; Marcel Dekker: New York, 2003; p 1184.

(8) Carlson, T. R.; Tompsett, G. A.; Conner, W. C.; Huber, G. W. Aromatic Production From Catalytic Fast Pyrolysis Of Biomass-Derived Feedstocks. *Top. Catal.* **2009**, *52*, 241−252.

(9) Ranjan, R.; Thrust, S.; Gounaris, C. E.; Woo, M.; Floudas, C. A.; Vonkeitz, M.; Valentas, K. J.; Wei, J.; Tsapatsis, M. Adsorption of Fermentation Inhibitors from Lignocellulosic Biomass Hydrolyzates for Improved Methanol Yield and Value-Added Product Recovery. *Microporous And Mesoporous Materials* **2009**, *122*, 143−148.

(10) Fuchs, A. H.; Cheetham, A. K. Adsorption of Guest Molecules in Zeolitic Materials: Computational Aspects. *J. Phys. Chem. B* **2001**, *105* (31), 7375−7383.

(11) Smit, B.; Maesen, T. L. M. Molecular Simulations Of Zeolites: Adsorption, Diffusion, And Shape Selectivity. *Chem. Rev.* **2008**, *108*, 4215−4184.

(12) Baerlocher, C.; McCusker, L. B.; Olson, D. H. *Atlas of Zeolite Framework Types*, 6th ed.; Elsevier: Amsterdam, 2007.

(13) Maginn, E. J.; Bell, A. T.; Theodorou, D. N. Sorption Thermodynamics, Siting and Conformation of Long n-Alkanes in Silicalite as Predicted by Configurational-Bias Monte Carlo Integration. *J. Phys. Chem.* **1995**, *99*, 2057−2079.

(14) Chempath, S.; Low, J. J.; Snurr, R. Q. Molecular Modeling of Binary Liquid-Phase Adsorption of Aromatics in Silicalite. *AIChE J.* **2004**, *50*, 463−469.

(15) Mezei, M. A Cavity-Biased (T,V,μ) Monte-Carlo Method for the Computer-Simulation of Fluids. *Mol. Phys.* **1980**, *40*, 901−906.

(16) Snurr, R. Q.; Bell, A. T.; Theodorou, D. N. Prediction of Adsorption of Aromatic Hydrocarbons in Silicalite from Grand Canonical Monte Carlo Simulations with Biased Insertions. *J. Phys. Chem.* **1993**, *97*, 13742−13752.

(17) Chempath, S.; Denayer, J. F. M.; DeMeyer, K. M. A.; Baron, G. V.; Snurr, R. Q. Liquid-Phase Adsorption of Alkane Mixtures in Silicalite: Simulations and Experiment. *Langmuir* **2004**, *20*, 150−156.

(18) Xiong, R.; Sandler, S. I.; Vlachos, D. G. Alcohol Adsorption onto Silicalite from Aqueous Solution. *J. Phys. Chem. C* **2011**, *115*, 18659−18669.

(19) Sorenson, S. G.; Smyth, J. R.; Kocirik, M.; Zikanova, A.; Noble, R. D.; Falconer, J. L. Adsorbate-Induced Expansion of Silicalite-1 Crystals. *Ind. Eng. Chem. Res.* **2008**, *47*, 9611−9616.

(20) Guo, C. J.; Talu, O.; Hayhurst, D. T. Phase-Transition and Structural Heterogeneity - Benzene Adsorption on Silicalite. *AIChE J.* **1989**, *35*, 573−578.

(21) Krokidas, P. G.; Skouras, E. D.; Nikolakis, V. Lattice Dynamics Simulation of Thermal Contraction of Faujasites. *J. Phys. Chem. C* **2010**, *114*, 22441−22448.

(22) Theodorou, D. N. Molecular simulations of sorption and diffusion in amorphous polymers. In *Diffusion in Polymers*; Neogi, P., Ed.; Marcel Dekker: New York, 1996; pp 67−142.

(23) Escobedo, F. A. Novel Pseudoensembles for Simulation of Multicomponent Phase Equilibria. *J. Chem. Phys.* **1998**, *108* (21), 8761−8772.

(24) Banaszak, B. J.; Faller, R.; dePablo, J. Simulation of the Effects of Chain Architecture on the Sorption of Ethylene in Polyethylene. *J. Chem. Phys.* **2004**, *120* (23), 11304−11315.

(25) Zang, J.; Nair, S.; Sholl, D. S. Osmotic Ensemble Methods for Predicting Adsorption-Induced Structural Transitions in Nanoporous Materials Using Molecular Simulations. *J. Chem. Phys.* **2011**, *134*, 184103.

(26) Duane, S.; Kennedy, A. D.; Pendleton, B. J.; Roweth, D. Hybrid Monte-Carlo. *Phys. Lett. B* **1987**, *195*, 216−222.

(27) Mehlig, B.; Heermann, D. W.; Forrest, B. M. Hybrid Monte Carlo Method for Condensed-Matter Systems. *Phys. Rev. B* **1992**, *45*, 679−685.

(28) Faller, R.; dePablo, J. J. Constant Pressure Hybrid Molecular Dynamics-Monte Carlo Simulations. *J. Chem. Phys.* **2002**, *116*, 55−59.

(29) Ghoufi, A.; Maurin, G. Hybrid Monte Carlo Simulations Combined with a Phase Mixture Model to Predict the Structural Transitions of a Porous Metal-Organic Framework Material upon Adsorption of Guest Molecules. *J. Phys. Chem. C* **2010**, *114*, 6496−6502.

(30) Coudert, F. X.; Boutin, A.; Jeffroy, M.; Mellot-Draznieks, C.; Fuchs, A. H. Thermodynamic Methods and Models to Study Flexible Metal-Organic Frameworks. *ChemPhysChem* **2011**, *12*, 247−258.

(31) Carlson, T. R.; Jae, J.; Lin, Y. C.; Tompsett, G. A.; Huber, G. W. Catalytic Fast Pyrolysis of Glucose with ZSM-5: The Combined Homogeneous and Heterogeneous Reactions. *J. Catal.* **2010**, *270*, 110−124.

(32) Fyfe, C. A.; Kennedy, G. J.; DeSchutter, C. T.; Kokotailo, G. T. Sorbate-Induced Structural Changes in ZSM-5 (Silicalite). *J. Chem. Soc., Chem. Commun.* **1984**, *8*, 541−542.

(33) Mohanty, S.; Davis, H. T.; McCormick, A. V. Sorbate/Sorbent Phase Transition During Adsorption of p-Xylene in Silicalite. *AIChE J.* **2004**, *46* (8), 1662−1675.

(34) Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. Crystal-Structure and Structure-Related Propoerties of ZSM-5. *J. Phys. Chem.* **1981**, *85* (15), 2238−2243.

(35) Jae, J.; Tompsett, G. A.; Foster, A. J.; Hammond, K. D.; Auerbach, S. M.; Lobo, R. F.; Huber, G. W. Investigation into the Shape Selectivity of Zeolite Catalysts for Biomass Conversion. *J. Catal.* **2011**, *279*, 257−268.

(36) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Elsevier, Academic Press: San Diego, 2002.

(37) Blanco, C.; Auerbach, S. M. Nonequilibrium Molecular Dynamics of Microwave-Driven Zeolite-Guest Systems. *J. Phys. Chem. B* **2003**, *107*, 2409−2499.

(38) Santander, J. E.; Conner, W. C.; Jobic, H.; Auerbach, S. M. Simulating Microwave-Heated Open Systems: Tuning Competitive Sorption in Zeolites. *J. Phys. Chem. B* **2009**, *113*, 13776−13781.

(39) Jaramillo, E.; Auerbach, S. M. New Force Field for Na Cations in Faujasite-Type Zeolites. *J. Phys. Chem. B* **1999**, *103*, 9598−9594.

(40) Auerbach, S. M.; Henson, N. J.; Cheetham, A. K.; Metiu, H. I. Transport Theory for Cationic Zeolites: Diffusion of Benzene in Na-Y. *J. Phys. Chem.* **1995**, *99*, 10600−10608.

(41) Catlow, C. R. A.; Freeman, C. M. Molecular Dynamics Studies of Hydrocarbon Diffusion in Zeolites. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1947−1950.

(42) Combariza, A. F.; Sastre, G.; Corma, A. Propane/Propylene Diffusion in Zeolites: Framework Dynamics. *J. Phys. Chem. C* **2009**, *113*, 11246−11253.

(43) Oie, T.; Maggiora, G. M.; Christoffersen, R. E.; Duchamp, D. J. Development of a Flexible Intra- and Intermolecular Empirical Potential Function for Large Molecular Systems. *Int. J. Quantum Chem.* **1981**, *20*, 1−47.

(44) Jorgensen, W. L.; Maxwell, D. S.; Tiradores, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225−11236.

(45) McDonald, N. A.; Jorgensen, W. L. Development of an All-Atom Force Field for Heterocycles. Properties of Liquid Pyrrole, Furan, Diazoles, and Oxazoles. *J. Phys. Chem. B* **1998**, *102*, 8049−8059.

(46) Rivelino, R.; Coutinho, K.; Canuto, S. A Monte Carlo-Quantum Mechanics Study of the Solvent-Induced Spectral Shift and the Specific Role of Hydrogen Bonds in the Conformational Equilibrium of Furfural in Water. *J. Phys. Chem. B* **2002**, *106*, 12317−12322.

(47) Rivelino, R.; Canuto, S. Conformational Stability of Furfural in Aqueous Solution: The Role of Hydrogen Bonding. *Braz. J. Phys.* **2004**, *34*, 84−89.

(48) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D. Comparison Of Simple Potential Functions For Simulating Water. *J. Chem. Phys.* **1983**, *79*, 926−935.

(49) Puibasset, J.; Pellenq, R. J.-M. Grand Canonical Monte Carlo Simulation Study of Water Adsorption in Silicalite at 300 K. *J. Phys. Chem. C* **2008**, *112*, 6390−6397.

(50) Pellenq, R.-J.-M.; Roussel, T.; Puibasset, J. Molecular Simulations of Water in Hydrophobic Microporous Solids. *Adsorption* **2008**, *14* (4−5), 733−742.

(51) VanDerSpoel, D.; VanMaaren, P. J.; Berendsen, H. J. C. A Systematic Study of Water Models for Molecular Simulation: Derivation of Water Model Optimized for Use with a Reaction Field. *J. Chem. Phys.* **1998**, *108*, 10220−10300.

(52) vanBuuren, A. R.; Marrink, S. J.; Berendsen, H. J. C. A Molecular-Dynamics Study of the Decane Water Interface. *J. Phys. Chem.* **1993**, *97*, 9206−9212.

(53) Tieleman, D. P.; Berendsen, H. J. C. Molecular Dynamics Simulations of a Fully Hydrated Dipalmitoyl Phosphatidylcholine Bilayer with Different Macroscopic Boundary Conditions and Parameters. *J. Chem. Phys.* **1996**, *105*, 4871−4880.

(54) Ramachandran, C. E.; Chempath, S.; Broadbelt, L. J.; Snurr, R. Q. Water Adsorption in Hydrophobic Nanopores: Monte Carlo Simulations of Water in Silicalite. *Microporous Mesoporous Mater.* **2006**, *90*, 293−298.

(55) Olson, D. H.; Haag, W. O.; Borghard, W. S. Use of Water as a Probe of Zeolite Properties: Interaction of Water in ZSM-5. *Microporous Mesoporous Mater.* **2000**, *35−36*, 435−446.

(56) Eroshenko, V.; Regis, R. C.; Soulard, M.; Patarin, J. The Heterogeneous Systems "Water-Hydrophobic Zeolites": New Molecular Springs. *C. R. Physique* **2002**, *3*, 111−119.

(57) Desbiens, N.; Demachy, I.; Fuchs, A. H.; Kirsch-Rodeschini, H.; Soulard, M.; Patarin, J. Water condensation in hydrophobic nanopores. *Angew. Chem., Int. Ed.* **2005**, *44* (33), 5310−5313.

(58) Trzpit, M.; Soulard, M.; Patarin, J.; Desbiens, N.; Cailliez, F.; Boutin, A.; Demachy, I.; Fuchs, A. H. The effect of local defects on water adsorption in silicalite-1 zeolite: A joint experimental and molecular simulation study. *Langmuir* **2007**, *23* (20), 10131−10139.

(59) Cailliez, F.; Trzpit, M.; Soulard, M.; Demachy, I.; Boutin, A.; Patarin, J.; Fuchs, A. H. Thermodynamics of water intrusion in nanoporous hydrophobic solids. *Phys. Chem. Chem. Phys.* **2008**, *10* (32), 4817−4826.

(60) Cailliez, F.; Boutin, A.; Demachy, I.; Fuchs, A. H. Thermodynamic study of water confinement in hydrophobic zeolites by Monte Carlo simulations. *Mol. Simul.* **2009**, *35* (1−2), 24−30.

(61) Saravanan, C.; Auerbach, S. M. Simulations of high T_c vapor−liquid phase transitions in nanoporous materials. *J. Chem. Phys.* **1998**, *109* (20), 8755−8758.

(62) Saravanan, C.; Auerbach, S. M. Theory and simulation of cohesive diffusion in nanopores: Transport in subcritical and supercritical regimes. *J. Chem. Phys.* **1999**, *110* (22), 11000−11011.

(63) Dukovski, I.; Machta, J.; Saravanan, C.; Auerbach, S. M. Cluster Monte Carlo simulations of phase transitions and critical phenomena in zeolites. *J. Chem. Phys.* **2000**, *113* (9), 3697−3703.

(64) Coudert, F. X.; Vuilleumier, R.; Boutin, A. Dipole Moment, Hydrogen Bonding and IR Spectrum of Confined Water. *ChemPhysChem* **2006**, *7* (12), 2464−2467.

(65) Panagiotopoulos, A. Z. Direct Determination of Phase Coexistence Properties of Fluids by Monte Carlo Simulations in a New Ensemble. *Mol. Phys.* **1987**, *61*, 813−826.

(66) Pearce, E. J.; Gerster, J. A. Furfural-Water System: Experimental and Theoretical Vapor-Liquid Relationships. *Ind. Eng. Chem.* **1950**, *42*, 1418−1424.

(67) Atkins, P. W.; DePaula, J. *Physical Chemistry*, 9th ed.; Oxford University Press: Oxford, 2010.

(68) Norman, G. E.; Filinov, V. S. Investigation of Phase Transitions by a Monte Carlo Method. *High Temp. (USSR)* **1969**, *7*, 216−222.

(69) Astala, R.; Auerbach, S. M.; Monson, P. A. Density Functional Theory Study of Silica Zeolite Structures: Stabilities and Mechanical Properties of SOD, LTA, CHA, MOR and MFI. *J. Phys. Chem. B* **2004**, *108*, 9208−9215.

(70) Astala, R.; Auerbach, S. M.; Monson, P. A. Normal Mode Approach for Predicting the Mechanical Properties of Solids from First Principles: Application to Compressibility and Thermal Expansion of Zeolites. *Phys. Rev. B* **2005**, *71*, 014112.

(71) Turaga, S. C.; Auerbach, S. M. Calculating Free Energies for Diffusion in Tight-Fitting Zeolite-Guest Systems: Local Normal-Mode Monte Carlo. *J. Chem. Phys.* **2003**, *118*, 6512−6517.

(72) McDonald, I. R. NpT Ensemble Monte Carlo Calculations for Binary Liquid Mixtures. *Mol. Phys.* **1972**, *23*, 41−58.

(73) Parrinello, M.; Rahman, A. Strain Fluctuations and Elastic Constants. *J. Chem. Phys.* **1982**, *76*, 2662−2666.

(74) Bussai, C.; Fritzsche, S.; Haberlandt, R.; Hannongbua, S. Formation of Low-Density Water Clusters in the Silicate-Cage: A Molecular Dynamics Study. *J. Phys. Chem. B* **2003**, *107*, 12444−12450.

(75) Turov, V. V.; Brei, V. V.; Khomenko, K. N.; Leboda, R. ^{1}H NMR Studies of the Adsorption of Water in Silicalite. *Microporous Mesoporous Mater.* **1998**, *23*, 189−196.