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Molecular Simulation of Propane−Propylene Binary Adsorption Equilibrium in Zeolite 4A

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The configurational-bias Monte Carlo (CBMC) technique in the grand-canonical (μVT) ensemble has been used to calculate the pure and binary adsorption equilibrium isotherms of propane and propylene in zeolite 4A (zeolite Na-LTA) at 298.15, 373, 423, and 473 K in the 0−500 kPa pressure range. The influence of sodium cations on the adsorption properties of zeolite 4A was investigated using the united atom (UA) force field in order to establish effective Lennard−Jones (LJ) parameters for interactions between the cations and the sp^2-hybridized bond of propylene as well as the other cation−carbon interactions present in this system. A cation-free zeolite Linde type A (LTA) framework and the inclusion of sodium cations into the zeolite framework have been studied in this work. The quality of the parameters describing the carbon−sodium interactions was investigated by comparing with published experimental results for the cation-free LTA and by using other published LJ interaction parameters. Surprisingly, it was found that the sodium force field developed by Calero et al. [*J. Am. Chem. Soc.* **2004**, *126*, 11377] which is suitable for studying adsorption in other Na-contained zeolite frameworks, namely, FAU and MFI, does not work well for the Na-LTA system. It turns out that this is due to the interaction with sodium, as the simulations without cations agree very well with adsorption experiments on cation-free LTA. Our force field for zeolite 4A is in good agreement with recent experiments which show that the adsorbed amount of propane is much higher than reported previously. Good agreement of simulations with experiments was also obtained for adsorption of propane/propylene mixtures in zeolite 4A.

1. Introduction

Propane/propylene separation is among the most energy-intensive separations in the petrochemical industry. Adsorption in zeolite 4A appears as a promising alternative in terms of energy and operating costs. Molecular simulations can provide reliable predictions of adsorption properties and thus become very interesting to replace long, time-consuming experiments.

Molecular simulations became a powerful tool to predict physical and chemical properties of a wide range of materials in recent years. As a consequence of rapid increase in computer power, more accurate results can be obtained and it is possible to simulate more complex systems within a reasonable period of time.

Microscopic and macroscopic properties of guest molecules in zeolitic hosts are among the processes in which molecular simulations play an important role. Sorption and diffusion in zeolites have been studied by molecular dynamics (MD) and Monte Carlo (MC) simulation techniques.[2]

The behavior of simple molecules, such as linear and branched alkanes in siliceous zeolites as silicalite, has been widely studied by molecular simulation techniques, which can generate ensemble average properties of the host−guest system. Experimental and MC simulated propane adsorption equilibrium isotherms in silicalite were reported.[3−5] The heat of adsorption of propane, propene, and other alkanes and alkenes was measured using ferrierite, mordenite, silicalite, and amorphous silica, based on Fourier transform infrared spectroscopy.[6] Propane and *n*-butane were found to adsorb onto silanol groups on the external surface of ferrierite indicating the presence of free energy barriers preventing the alkanes from entering the micropores. The 8-ring, pure silica zeolite ITQ-12 has a unique, temperature dependent adsorption selectivity and high potential for the separation of propylene from propylene/propane mixtures.[7] Configurational-bias grand-canonical Monte Carlo (CB-GCMC) simulations with identity-swap moves for the adsorption of liquid mixtures of *n*-alkanes in silicalite from C_5 to C_{12} together with batch adsorption measurements for the same systems were reported.[8] Additional improvements of the force field, concerning reproduction of experimental isotherms, particularly the inflection points, Henry coefficients, heats of adsorption, pre-exponential factors, entropies of adsorption, and maximum loadings were developed.[1,9,10] Ab initio geometries and interaction energies have been used to optimize empirical force field parameters, which were determined by reproducing experimental heats of vaporization and molecular volumes for pure solvents. Application of this approach was performed on methane, ethane, and propane.[11]

There are numerous experimental studies on the adsorption of alkane/alkene mixtures in zeolite 4A,[12−16] although published works on simulation techniques, applied to the evaluation of the adsorption properties of alkane/alkene in zeolite 4A are scarce.[17] The configurational-bias Monte Carlo (CBMC) technique was applied to calculate adsorption isotherms of various alkenes and their mixtures in siliceous zeolites.[18]

The objective of this work is to describe adsorption properties of propane and propylene on zeolite 4A through molecular simulations using theCBMC simulation technique applied to the grand-canonical ensemble and to compare simulation results with experimental[12,13,15] and other simulation data.[17] Experi-

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ments on zeolite 4A show different adsorption behavior for alkanes/alkenes and are of potential interest for industry, as the search for an effective adsorbent remains as a primary research interest. The experiments also show that equilibration time is important, since large differences among diverse experimental studies have been found.[12−14] CBMC techniques allow overcoming equilibration problems in molecular simulations; they are helpful to understand these differences.

Various force fields are available to study adsorption in zeolites as well as many different parameters for cation−carbon interactions.[1,9,17] Two different force fields for the simulation of adsorption loadings of propane/propylene in zeolite 4A at several pressures and temperatures are applied in this work, in order to show the influence of nonframework sodium cations on the results. First, a recently developed force field by Calero et al. was used for our study, as it was successfully applied in the description of the adsorption properties of linear alkanes in the sodium form of FAU-type zeolites[1] and later its applicability to Na-MFI[19] and Na-MOR[20] zeolites was confirmed. On the basis of this force field, we developed Lennard−Jones (LJ) parameters for the interactions between the sodium cations and the adsorbates (propane/propylene). The set of LJ parameters was adjusted to the experimental adsorption data of zeolite 4A and validated to other hydrocarbons (methane and ethane). The reference experimental studies on propane−propylene adsorption in zeolite 4A are from Grande, Gigola, and Rodrigues,[12] Da Silva and Rodrigues,[13] and Järvelin and Fair.[15] Available simulation data from Zhang, Furukawa, and Nitta[17] have been also taken into consideration. The quality of the sodium interactions was tested by comparing with experimental results for the cation-free Linde type A (LTA) framework of Corma et al.[21]

2. Configurational-Bias Monte Carlo

In the grand-canonical (or μ, V, T) ensemble the temperature, volume, and chemical potential are fixed. In MC simulations, the zeolite crystals are allowed to exchange molecules with a reservoir of molecules at a fixed chemical potential.[22,23] The alkane/alkene molecules are described with the united atom (UA) model, in which each CH_n group is treated as single interaction center. In the CBMC algorithm, the chain is built from a first united atom, placed at a random position. The second atom is added to the first one and a harmonic potential is used for the bond length. The chain is grown segment by segment. Trial moves to insert and delete molecules have to be added. The nonframework cations are also described as single interaction centers, but these are charged, unlike the united atoms of the hydrocarbons.[1] The zeolite framework is assumed to be rigid and the cations move freely in the zeolite and adjust their positions according their interactions with the other atoms present in the system. The influence of zeolite framework flexibility is small in adsorption.[24] For more details, see refs 9 and 25.

3. Force Fields

In the present work, an LTA framework model was used to represent zeolite 4A structure. For hydrocarbon−hydrocarbon interactions, a united atom (UA) force field was used.[9,26] All nonbonded interactions are described with the Lennard−Jones (LJ) 12−6 potential,[27]

$$u(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{1}$$

where r_{ij} is the bead−bead separation, ϵ_{ij}, the LJ well depth, and σ_{ij}, the LJ diameter, for beads i and j. The well-known Lennard−Jones parameters are developed by reproducing model pure solvent properties, such as heats of vaporization and molecular volumes. Parametrization of force fields can be made either by ab initio studies[28] or empirical methods. Parameters are then fitted to the experimental data of liquid properties at atmospheric pressure and vapor−liquid phase equilibria of several fluids.[29] The Lennard−Jones potential does not represent the actual intermolecular interactions for any particular substance, and other types of potentials are suitable to describe interactions terms between polar species or charged atoms. Computational simplicity and availability of a large number of results for its properties make the Lennard−Jones potential a very efficient tool in molecular simulations.[1,3,23,30] To determine the interactions of different pseudo-atoms, the Lorentz−Berthelot mixing rules have been used.

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}), \quad \epsilon_{ij} = (\epsilon_{ii}.\epsilon_{jj})^{1/2} \tag{2}$$

All bond lengths are fixed (see Table 1).

Table 1. Parameters for the United Atom (UA) Force Field[1,18]

bond energy constant		$k_l/k_B = 96\,500$ K/Å^2
reference bond length	CH_i−CH_j	$l_0 = 1.53$ Å
	CH_i= CH_j	$l_0 = 1.33$ Å
bend energy constant	propane	$k_\theta/k_B = 62\,500$ K/rad^2
	propylene	$k_\theta/k_B = 70\,400$ K/rad^2
reference bend angle	propane	$\theta_0 = 114°$
	propylene	$\theta_0 = 119.7°$

Table 2. Number of Monte Carlo Cycles Used in the Calculation of Propane Loadings in Zeolite 4A at 473 K

pressure (kPa)	loadings (molecules/unit cell)[a]	10^4 MC cycles	10^6 MC cycles	10^6 MC cycles
27.75	2.11	2.10	2.14	2.14
75		5.17	5.17	5.17
89.5	5.63	5.94	5.86	5.85
126.37	7.93	7.63	7.69	7.64
150		8.59	8.60	8.60
220.77	10.73	10.97	10.97	10.90
300		12.68	12.71	12.69

[a] Grande, Gigola, and Rodrigues.[12]

3.1. Coulombic Interactions. Ewald summation or an equivalent technique can be used for calculating electrostatic interactions in a periodic (or pseudoperiodic) system. The Ewald technique is widely described elsewhere.[22,29] In practice, the convergence of the Ewald sum is controlled by three variables: the real space cutoff, r_{cut}; the convergence parameter, α; and the largest reciprocal space vector, k_{max}, used in the reciprocal space sum. In this work, the Ewald summation parameters $\alpha = 0.3$ and $k_{max} = 9$ were used.

3.2. Blocking of Sodalite Cages. LTA has two interconnecting, 3-dimensional channel systems: one consisting of connected α-cages, 11.4 Å in diameter, separated by 4.2 Å circular openings and the other consisting of β-cages, 6.6 Å in diameter, alternating with the α-cages and separated by 2.2 Å apertures.[31] A propane molecule does fit in the β-cages dimension (6.6 Å), but it is not accessible from the main α-cages through the small 2.2 Å apertures. However, in CBMC, attempts are made to insert a molecule at a random position so molecules could actually enter these cages. To prevent this, the β-cages are artificially blocked according to the procedure outlined in ref 32. The absence of this blocking could lead to false higher loadings, especially at low temperatures and/or high pressures, which are the most favorable conditions to a high adsorption loading.

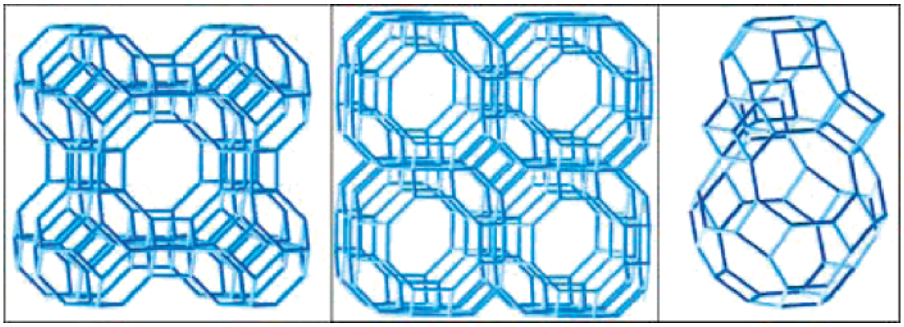

Figure 1. Three-dimensional framework of small-pore zeolite A.

Table 3. Lennard–Jones Force Field Parameters for Na^+ LTA[a]

	O_{Al}	O_{Si}	Na	CH_4	CH_3	CH_2-sp^3	CH_2-sp^2	CH-sp^2
CH_4	115.00	115.00	285.20[b]	158.50	130.84	94.21	116.07	86.31
	3.47	3.47	2.72	3.72	3.74	3.84	3.70	3.73
CH_3	93.00	93.00	197.20[b]	130.84	108.00	77.70	95.81	71.25
	3.48	3.48	2.65	3.74	3.76	3.86	3.72	3.75
CH_2-sp^3	60.50	60.50	137.78[b]	94.21	77.70	56.00	68.99	51.30
	3.58	3.58	2.95	3.84	3.86	3.96	3.82	3.85
CH_2-sp^2	77.30	77.30	398.40[b]	116.07	95.81	68.99	85.00	63.21
	3.50	3.50	3.14	3.70	3.72	3.82	3.68	3.70
CH-sp^2	62.50	62.50	289.02[b]	86.31	71.25	51.30	63.21	47.00
	3.46	3.46	3.17	3.73	3.75	3.85	3.70	3.73
Na	23.00	23.00	124.40	285.20[b]	197.20[b]	137.78[b]	398.40[b]	289.02[b]
	3.40	3.40	2.16	2.72	2.65	2.95	3.14	3.17

charge	O_{Al}	O_{Si}	Na	Si	Al
q (e)	−1.20	−1.025	+1.00	+2.05	+1.75

[a] The top entry is ϵ/k_B (K), and the σ (Å) value is the bottom entry of each field. The partial charges (e) of the framework and the sodium cations are given at the bottom of the table. O_{Al} are oxygens bridging one silicon and one aluminum atom, and O_{Si} are oxygens bridging two silicon atoms. Most of the parameters are taken from Calero et al.,[1] except the parameters of Na interactions which have been changed. Details are given in the text. The parameters of sp^2-bonded atoms are taken from the work of Jakobtorweihen, Hansen, and Keil.[18] [b] The LJ parameters for cation-carbon interactions obtained by adjusting the force field through fitting a full isotherm. The methodology is described in ref 1.

3.3. Duration of Simulations. The literature reports at least 5×10^5 cycles to compute adsorption equilibrium isotherms for molecules smaller than pentane. In each cycle, the number of trial moves equals the number of hydrocarbon molecules in the system with a minimum of 20. For longer chains and *NVT* simulations, 10^6 cycles are commonly used.[9] Other authors state that simulations of approximately 10^4–10^5 Monte Carlo cycles are normally sufficient for determining thermodynamic properties of a fluid interacting with a Lennard–Jones potential. Longer simulation runs are required for systems with strong or long-range interactions, such as ionic, associating or long-chain systems, or systems close to a critical point.[33] Comparison of results for simulations performed with 10^4, 10^5, and 10^6 Monte Carlo cycles is shown in Table 2. The number of 10^5 Monte Carlo cycles is enough to compute the adsorption isotherms of propane/propylene in zeolite 4A.

4. Zeolite A Structure and Characterization

Zeolite A exhibits the LTA (Linde Type A) structure, shown in Figure 1. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure. The unit cell is cubic (a = 24.61 Å) with $Pm\bar{3}m$ symmetry. Zeolite A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. It thermally decomposes at 700 °C.[34]

Zeolite LTA framework and synthesis were reported 50 years ago.[35,36] The refined unit cell structure of zeolite 4A (the LTA-synthesized Na variety) has 12 Na atoms, placed as follows: eight near the center of 6-rings, three in the plane of 8-rings, and one in the large cavity opposite a 4-ring. All 12 Na atoms were found in unusual coordinations, as in many dehydrated zeolites, but the distances to the nearest neighbors were reasonable (2.32 ± 0.01 to 2.59 ± 0.15 Å) when compared to other Na-bearing silicates.[37] A graphical representation of the LTA framework in Figure 1 shows connectivity among framework tetrahedral atoms. Detailed crystallographic description can be found elsewhere.[34–37]

Refinement of the crystal structure of dehydrated zeolite 4A confirmed that Al and Si atoms alternate throughout the framework to give the 24.61 Å true unit cell.[37] The composition of $Na_{96}A1_{96}Si_{96}0_{384}$ for this full supercell, which represents a supercage containing the nonframework sodium cations, was used in our simulations. Replacement of aluminum by silicon generates a simulation box with a cation-free unit cell.

5. Simulations Results

5.1. Propane Adsorption in Cation-Free Zeolite A. Synthesis of Al-free and pure silica zeolites with the LTA structure is described by Corma et al.[21] as well as adsorption capacities of ITQ-29, the cation-free form of LTA measured for several adsorbates, including propane. Simulation results for propane agree with experimental results on ITQ-29 at a pressure of 100 kPa and temperatures of 298, 313, and 333 K, which are shown in Table 4. These simulated results are 10% higher than experimental propane loadings in ITQ-29. When no cations are present, the LJ parameters of the force field according to Calero et al.[1] and the force field developed in this work for the interactions between the adsorbate and the LTA framework are able to reproduce experimental results, as expected.

5.2. Force Field Validation for the Sodium Cations. In order to validate the force field employed in this work, the

Table 4. Propane Loadings in Cation-Free LTA Compared with Experimental Adsorption Capacities of Zeolite ITQ-29[21] [a]

	experimental	force field	
Temp	ITQ-29 (molec/uc)	this work (molec/uc)	Calero et al.[1] (molec/uc)
298 K	25	28	28
313 K	23	25	25
333 K	20	20	21

[a] Pressure = 100 kPa. Experimental results are for propane as adsorbate.

Table 5. Comparison of Simulation Results Obtained by Using Different Cation−Carbon Interaction Parameters[a]

	force field		experimental	
adsorbate[a]	Calero et al.[1] (molec/uc)	this work (molec/uc)	(molec/uc)	ref
methane	53	31	32	Mohr et al.[38]
ethane	46	39	42	Eagan and Anderson[39]
propane	32	20	18	Grande, Gigola, and Rodrigues[12]

[a] Results correspond to the maximum adsorption loadings of pure adsorbate in zeolite 4A. The conditions under which simulations were performed are the same as those experimentally reported: (methane) $T = 273$ K, $p = 350$ kPa; (ethane) $T = 283$ K, $p = 40$ kPa; (propane) $T = 423$ K, $p = 366.39$ kPa.

Table 6. Physical Properties of Zeolite 4A[14]

adsorbent density (g cm^{-3})	1.21
adsorbent porosity (dimensionless)	0.315
zeolite average crystal radius (cm)	1.9×10^{-4}
average extrudate diameter (cm)	0.055

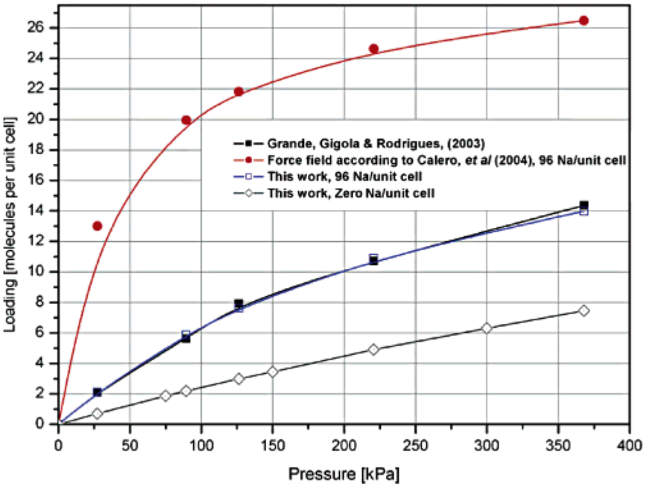

Figure 2. Adsorption equilibrium isotherms of propane in Na-LTA (zeolite 4A) at $T = 473$ K. The standard cation number is 96 sodium cations per unit cell.

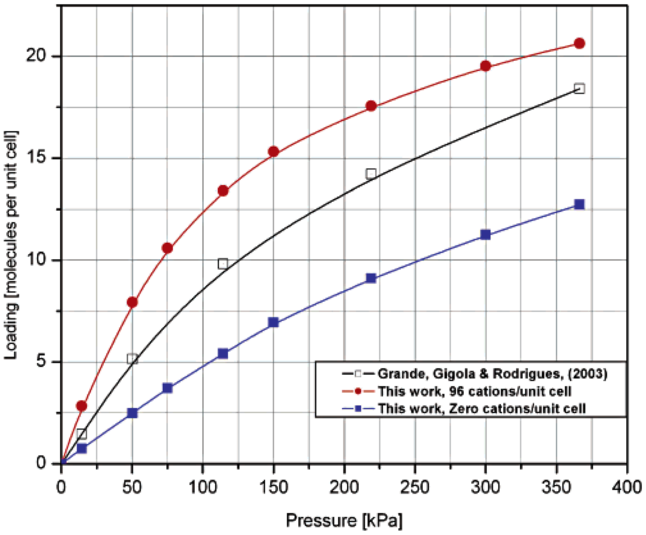

Figure 3. Comparison of adsorption equilibrium isotherms of propane in cation-free LTA and Na-LTA at $T = 423$ K. The standard cation number is 96 sodium cations per unit cell.

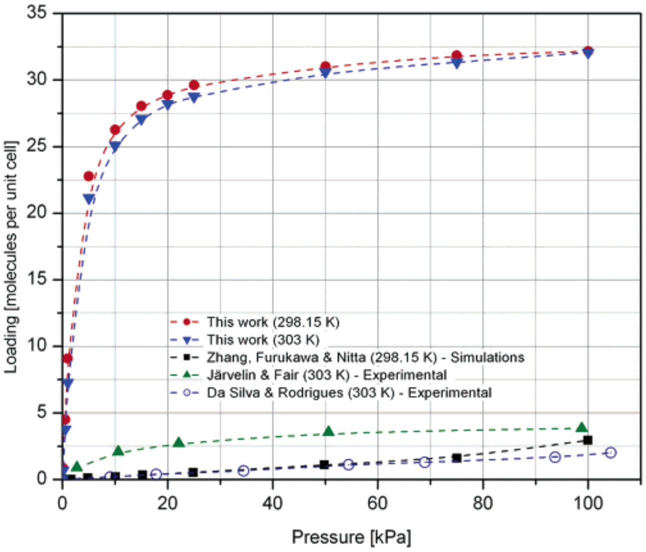

Figure 4. Adsorption equilibrium isotherms of propane in Na-LTA, comparison with other experimental and simulation results. The lines are guides to the eye.

maximum loadings of methane and ethane in zeolite 4A were calculated. The experimental loading of methane in zeolite 4A reported by Mohr et al.[38] has a value of 32 molecules per unit cell, and the simulated capacity was found to be 31 molecules of methane per unit cell.

Adsorption isotherms of ethane in zeolite 4A crystals at three temperatures were reported by Eagan and Anderson; the maximum experimental adsorption capacity of ethane at 273 K and 40 kPa was reported to be 42 molecules per unit cell.[39] CBMC simulations employing the force field parameters used in this work have been carried out under the same conditions, and a loading of 39 molecules per unit cell was found. Both methane and ethane simulation results are in good agreement with experimental data and provide a validation for the interaction parameters listed in Table 3.

As these interaction parameters substantially differ from those reported by Calero et al.[1] for faujasites, sets of simulations were also performed using parameters from Calero and co-workers.[1] Results for methane, ethane, and propane maximum loadings in zeolite 4A are shown in Table 5. It can be seen that the simulations results, using the force field according to Calero et al.,[1] considerably differ from the experimental data and this justifies a change in the cation interaction parameters of the force field for LTA.

5.3. Propane Adsorption in Na-LTA (Zeolite 4A). Simulations were carried out using our previously described force field. Experimental data were taken from the work of Grande, Gigola, and Rodrigues.[12] Propane adsorption isotherms were simulated at temperatures of 423 and 473 K and pressure ranges of 10^{-3} to 400 kPa. The experiments have demonstrated that propane takes three days at 423 K and two days at 473 K to reach equilibrium,[12] although it has been previously reported as a weakly adsorbed gas in zeolite 4A with no clear temperature

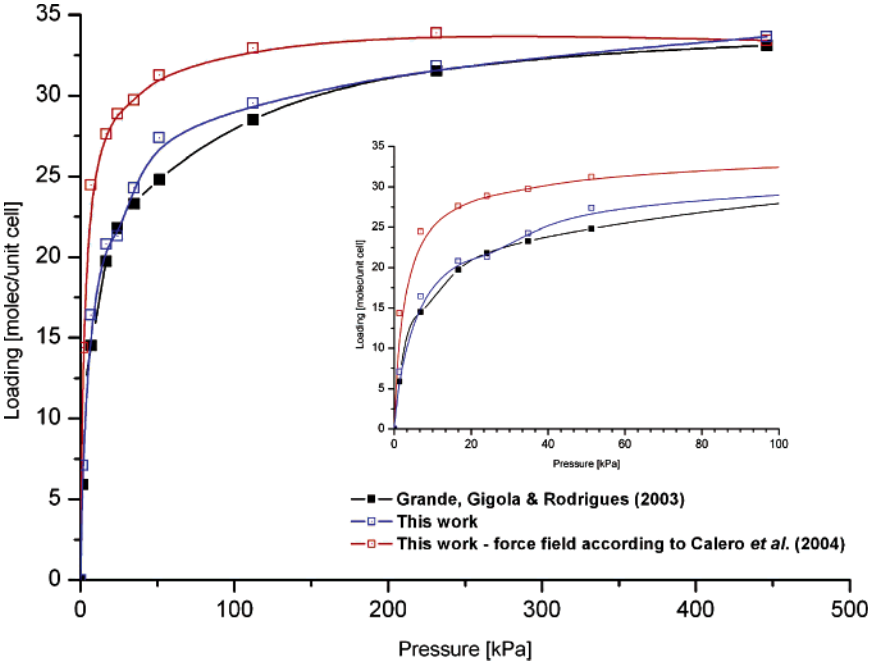

Figure 5. Adsorption equilibrium isotherms of propylene in zeolite 4A at $T = 373$ K. The smaller graph shows the pressure range from 0 to 100 kPa. The lines are guides to the eye.

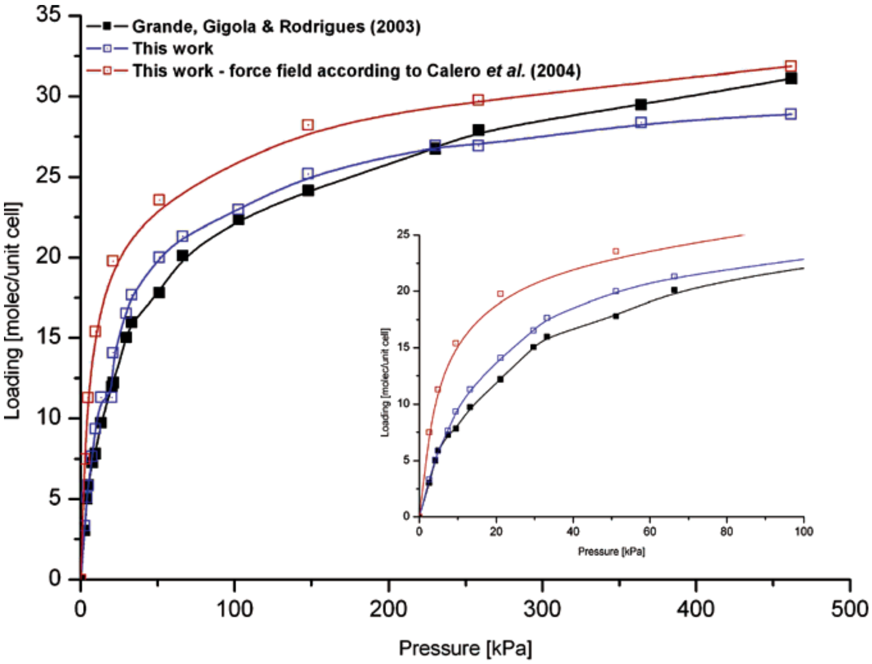

Figure 6. Adsorption equilibrium isotherms of propylene in zeolite 4A at $T = 423$ K. The smaller graph shows the pressure range from 0 to 100 kPa. The standard cation number is 96 sodium cations per unit cell. The lines are guides to the eye.

dependence, related to the molecular diameter of propane (4.3 Å) which is larger than the zeolite pore size (closer to 4.0 Å at 300 K).[13]

The adsorption capacity of zeolite 4A was found to be very sensitive to the conditions employed in dehydration or pelletization of industrial adsorbents.[40] The physical properties of zeolite 4A extrudates used in the work of Grande, Gigola, Rodrigues[12] are listed in Table 6. Details on analyses and characterization of this material are found in the work of Grande.[14]

Interactions between sodium cations, the zeolite framework, and alkanes have been recently reported for Na-FAU,[1] Na-MFI,[19] and Na-MOR[20] families of materials. The Lennard–Jones force field parameters explicitly distinguish silicon and aluminum atoms through the different types of oxygen framework atoms and take into account the interactions of nonframework cations with the adsorbates. However, the interactions with the cations from the work of Calero et al.,[1] were found to overestimate the adsorption capacities of methane, ethane, and propane when applied in simulations for Na-LTA (zeolite 4A) framework (see Table 5). Thus, on the basis of the parameters of Calero et al.,[1] the cation–adsorbate interactions for Na-LTA were determined. The set of parameters used for simulations of propane adsorption on zeolite 4A is listed in Tables 1 and 3.

Figures 2 and 3 show the experimental isotherms for propane adsorption[12] at 473 and 423 K and simulation results. Experi-

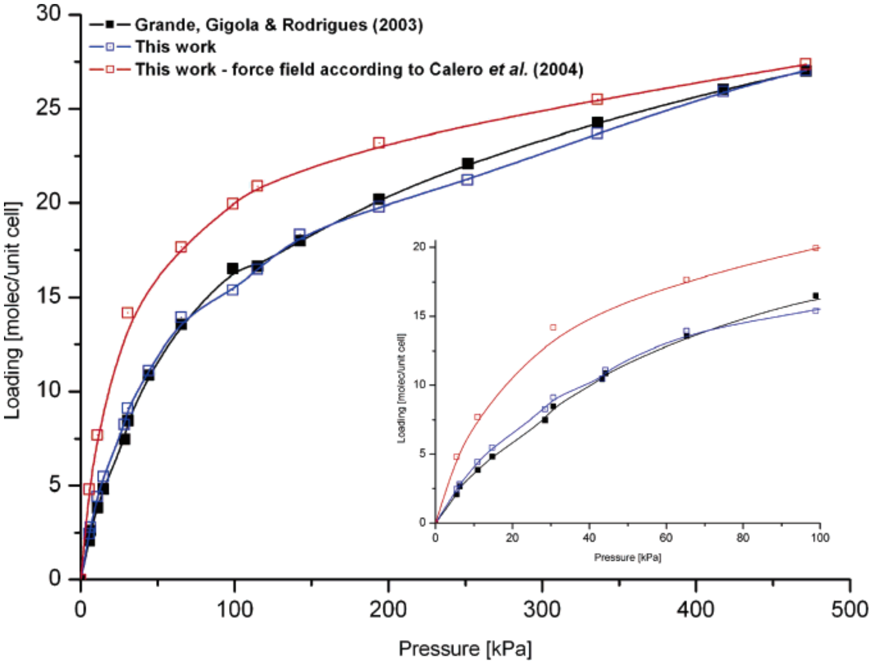

Figure 7. Adsorption equilibrium isotherms of propylene in zeolite 4A at $T = 473$ K. The smaller graph shows the pressure range from 0 to 100 kPa. The lines are guides to the eye.

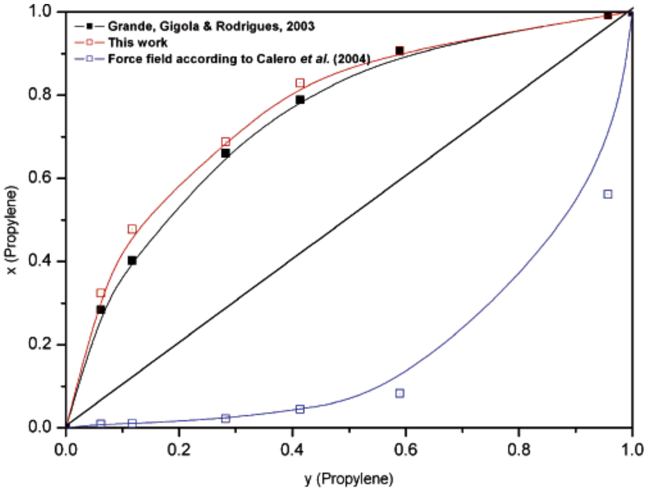

Figure 8. Propane/propylene equilibrium $x-y$ diagrams at 473 K.

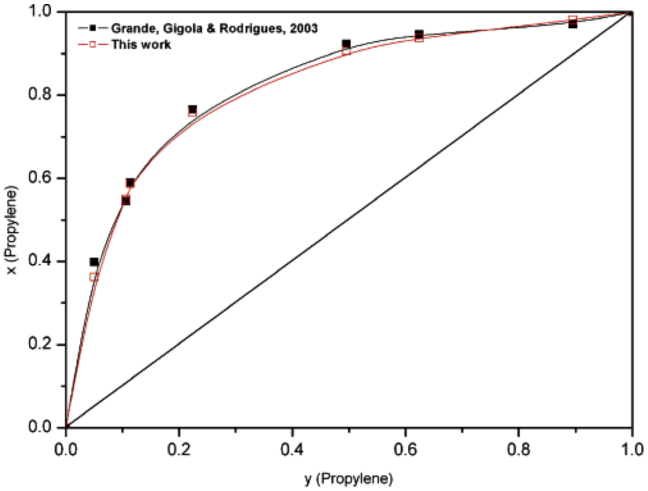

Figure 9. Propane/propylene equilibrium $x-y$ diagrams at 423 K.

mental values have been converted by considering that extrudates contain 80% of zeolite 4A crystals. The plots present simulations performed cation-free and with 96 cations per unit cell.

Simulation results for the propane adsorption equilibrium isotherm shown in Figure 2, at 473 K, are in excellent agreement with experimental data. Figure 2 also shows simulation results obtained by applying the force field according to Calero et al.[1] with 96 cations per unit cell, which are much higher than the experimental results. In Figure 3, at 423 K, our force field reproduces very well the shape of the adsorption equilibrium isotherm although the simulation results for zeolite 4A with 96 Na cations per unit cell show higher loadings than the experimental data. The deviations at 423 K suggest that propane could take a longer time to equilibrate.

Other sets of simulations have been performed and comparison with experimental[15] and simulation results[17] are shown in Figure 4. The low adsorption values for propane in zeolite 4A reported by Järvelin and Fair can be ascribed to the fact that, in experiments, the equilibration time was taken as 2 h;[15] in fact, the equilibration time for propane adsorption on zeolite 4A was found to be much longer:[12] three days at 423 K and two days at 473 K.

Regarding the differences in simulation results reported by Zhang, Furukawa, and Nitta[17] and our present work, they are not related to the type of force field used by those authors (the all-atom approach), but to the LJ interaction parameters of pseudo-atoms with the cations.

In the all-atom approach, the force field assigns the same values for partial charges of silicon and aluminum atoms, while the force field for Na-LTA simulations in the present work explicitly distinguishes the partial charges of silicon and aluminum atoms. However, the Lennard–Jones interactions with the cations have a major effect on the isotherms. The interactions by Zhang, Furukawa, and Nitta[17] are significantly weaker from those used in this work because they were adjusted to experimental results obtained after a too short equilibration time.

5.4. Propylene Adsorption in Na-LTA (Zeolite 4A). Adsorption properties of light alkenes in zeolite 4A determined by molecular simulation found in the literature are limited to the pioneer work of Zhang, Furukawa, and Nitta.[17] At that time, the available experimental data indicated a high selectivity in propane−propylene separation by adsorption in zeolite 4A, due to a very poor loading of propane and a high adsorption capacity for propylene in the zeolite 4A system.[13,15] However, further investigations have shown that the equilibration time for propane was much longer.[12]

5.4.1. Alkene−Sodium Interactions. The interactions of sp^2-bonded carbons with the sodium cations have been determined by adjustment of the simulation results to experimental data for the adsorption of propylene.[12] Simulations using our force field were carried out for a pressure range of 0−500 kPa and temperatures of 373, 423, and 473 K and are shown in Figures 5−7, in excellent agreement with the experiments. Also, simulations using the force field according to Calero et al.[1] were performed. The work of Calero et al.[1] deals only with adsorption of alkanes, so it was necessary to set LJ parameters to describe the sp^2-bonded carbons with the sodium cations. Such parameters have been taken from the work of Jakobtorweihen, Hansen, and Keil[18] and were added to the force field of Calero et al.[1] It should be noted that the differences between our force field and the force field of Calero et al.[1] are only in the interaction parameters of the sp^3-bonded carbons with the cations. Higher adsorption loadings are obtained for propylene adsorption in zeolite 4A when the force field according to Calero et al.[1] is used.

5.5. Propane−Propylene Binary Adsorption in Na-LTA (Zeolite 4A). Simulations of adsorption equilibrium for binary mixtures of propane/propylene have been performed at temperatures of 423 and 473 K and several molar fractions of propylene. The $x-y$ diagrams are shown in Figures 8 and 9. The simulations are in excellent agreement with the experimental results from the work of Grande, Gigola, and Rodrigues.[12] Figure 8 also shows results obtained using of the force field according to Calero and co-workers.[1] A completely different behavior of propane−propylene adsorption is clearly seen, as if propane would be more adsorbed than propylene. These results confirm once more that the carbon−cation interactions determined for other Na-zeolite frameworks are not suitable for that of Na-LTA.

6. Conclusions

Adsorption isotherms of propane, propylene, and propane/propylene mixtures in zeolite 4A have been computed by using a configurational-bias technique in the grand-canonical Monte Carlo ensemble. Comparison between the LTA sodium-free framework and taking the sodium cations and framework partial charges into account has been done. The Lennard−Jones parameters for carbon−cation interactions have been determined and validated through simulations of the adsorption loadings for other hydrocarbons in zeolite 4A. Simulation results have a very good agreement with recent experimental data at 473 K. The deviations at 423 K suggest that propane could take longer than three days to reach equilibrium of adsorption in zeolite 4A.

Previously reported simulation results shows very low adsorption loadings for propane in zeolite 4A, but this is due to the application of a different force field and to the fact of the reference experimental results were obtained after too short an equilibration time.

Also, CBMC simulations with cation-free zeolite LTA show good agreement with experimental loadings of propane in zeolite ITQ-29.

The binary adsorption equilibrium of propane/propylene mixtures was also studied by CBMC simulations with results in excellent agreement with recently published experimental data. The influence of different LJ parameters for carbon−cation interactions was also analyzed, and results clearly show that force field parameters developed to other framework types, namely, FAU, MFI, and MOR, overestimate the adsorption capacity of propane when applied to the LTA structure.

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Nomenclature

k_{max} = Ewald summation reciprocal space vector
$k_{1,2}$ = constants related to the bonded interactions: bond stretching and bond bending, respectively
l = bond length (Å)
r_{cut} = cutoff radius
P = absolute pressure
T = absolute temperature
U,u = potential energy, subscripts/superscripts are self-explanatory
V = volume

Greek Letters

α = Ewald summation convergence parameter (Å^{-1})
ϵ = characteristic energy in a pair potential
μ = chemical potential
θ = bending angle (rad)
σ = characteristic distance in a pair potential

Subscripts and Superscripts

i,j = pair of (pseudo) atoms

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