Adsorption 11: 361–366, 2005

Monte Carlo Investigations of the Water Adsorption Behavior in MFI Type Zeolites for different Si/Al Ratios with Regard to Heat Storage Applications

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Abstract. Adsorption processes are turning more and more important for heat transformation applications like thermally driven heat pumps and cooling cycles as well as heat storage. Standard adsorption materials have not been developed for these purposes. New materials are necessary in order to improve the adsorption characteristics for these applications. Molecular simulations are seen as a promising tool to investigate the influence of molecular structure on the adsorption characteristics and thus to provide means for future improvements of such materials for application in heat transformation.

Here, Molecular simulations of adsorption isotherms are performed using the Sorption module within Cerius^2 from Accelrys Inc. Existing Force-Fields are examined for their use in Grand Canonical Monte Carlo Simulation (GCMC) of water adsorption in zeolites. The augmented Consistent Valence Force-Field (CVFF-aug) is currently the best available force-field for use with non-polerizable water models like SPC in zeolite frameworks as reported by Hill and Sauer (1994a). Hence, this force field is used to compare simulated adsorption isotherms with experimental data obtained at Fraunhofer ISE for different types of zeolites.

The significance of the Al/Si ratio is investigated with regard to a material optimization for the use in heat transformation applications.

Furthermore the role of the extra-framework cations is evaluated as different ions are placed inside the zeolite structure. In the first instance the SPC (Berendsen et al., 1981) water model is used in the simulation.

Keywords: adsorption, monte carlo simulation, water, MFI

Introduction

The field of molecular simulation enfolds a broad range, from model systems of generally theoretical interest to real fluids or solids in material science up to applications in life science, e.g. drug design. This paper evaluates the usability of the Cerius^2-suite as a tool for adsorbent optimization, mainly microporous or nanoporous structures like zeolites, with regard to heat storage applications.

A GCMC program for simulation of water adsorption developed in our working group so far only includes a short-ranged water model (Mueller et al., 1996).

This is the first attempt to use Cerius^2 for the search for improved adsorbens. The Cerius^2 -suite form Accelrys Inc. (formerly Molecular Simulations Inc.) is presently the only available commercial simulation suite that complies with the requirements for this task, which are to simulate water adsorption in the grand canonicle ensemble within different structures. One of the strength of Cerius^2 is the availability of a large database of molecular zeolite structures, including the contents of the 'Atlas of zeolite framework types' (Baerlocher et al., 2001). Furtherone the force-field engine OFF (Open Force-Field) used in combination

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with the sorption module of the suite implements an efficient Ewald summation algorithm proposed by Karasawa and Goddard (1989).

Simulation Details

Force Field Implementation

To simulate water adsorption with the Cerius^2 suite several modules are necessary:

- Visualizer, the core product for all user interactions
- Crystal Builder, 3-D periodic crystal structure construction and display
- Cation Locator, placing charge balancing cations
- Sorption-module for the GCMC simulation of adsorption in microporous materials
- Open Force Field (OFF), the force field engine calculating all interactions

As the Sorption module is mandatory, we had to use the OFF-engine, which turned out as an unexpected handicap for the further simulations. Within OFF, several water models are implemented. The "Simple Point Charge" model SPC (Berendsen et al.,1981), the "transferable intermolecular potential" models TIP3P, TIP4P and TIPS2 (Jorgensen et al., 1983) and the Bernal-Fowler H2O_BF model (Bernal and Fowler, 1933).

There exist several special purpose force fields for OFF (as described in Molecular Simulations Inc., (1997a) and Molecular Simulations Inc. (1998)), for example Sorption Yashonath FF 1.01 for adsorption of saturated hydrocarbons in zeolites.

Unfortunately, none of the supplied force fields was suitable for simulation of water adsorption in zeolites. It was confirmed by Accelrys support staff that actually no force field for the OFF engine can be used to simulate water adsorption in zeolites with any water model. As published by Channon et al. (1998), the Catalysis Suite (using Discover force field engine, (see Molecular Simulations, Inc. (1997b)) from MSI was able to simulate exactly what we wanted to. It seems, that code from previous simulation suites was not fully integrated into Cerius^2 products, as the Discover engine cannot be used with the Sorption module within the Cerius^2 suite.

Therefore it was necessary to implement a new force field into Cerius^2 that could be used with these water models for the simulation of adsorption in zeolites and OFF as engine. Upon making inquiries in literature (Channon et al., 1998; Hill and Sauer, 1994a, 1995, 1994b; Hill et al., 2000a, 2000) and with help from Accelrys support staff, the augmented Consistent Valence Force Field (CVFF-aug) was selected as the most suitable candidate. We therefore extracted and converted parameter from a BIOSYM-version of the CVFF-aug force field which includes additional atom types and parameters for silicates, aluminsilicates, clays and aluminophosphates. The parameters used to simulate water adsorption in zeolites are listed in Table 1.

Nonbond Interactions

The energy of interactions between nonbond atoms is accounted for by van der Waals and electrostatic terms. Van der Waals interactions are described by a Lennard-Jones potential, whereas the long-range coulombic interactions are calculated using the Ewald sum method. Hydrogen bonds are a natural consequence of the standard van der Waals and electrostatic parameters of the SPC-Water model. Hence no special hydrogen bond function is used.

Preparing Zeolite Model

Within Cerius^2, most of the molecular zeolite structures types listed in the "Atlas of zeolite framework types" are available. As for the example of the zeolite

Table 1. LJ-parameters used for simulation of water adsorption in zeolites.

Atom type	Used for	Mass	r_0 (Å)	ε (kcal/mol)	Charge (e)
HSP	Hydrogen in water molecule for SPC-model	1.00797	Ignored	Ignored	0.41
OSP	Oxygen in water molecule for SPC-model	15.999400	3.55318	0.155416	−0.82
Sz	Silicon atom in zeolites	28.08600	4.549	0.04	0.0
Oz	Oxygen atom in zeolites	15.999400	3.21	0.228	0.0
Az	Tetrahedral Aluminum atom in zeolites	26.98154	0.831049	2565.28	−1.0
$NH4^+$	United atom type for ammonium ion	14.00674	3.84362	0.368674	1.0

framework type MFI, a pure silicalite, the "disorder"-option within the "Build"-module is used to create zeolite-models with specific silicon/aluminium ratios from 6 up to 27. Silicon atoms are substituted randomly, taking Loewenstein's rule into account, by aluminium atoms to obtain the desired target Si/Al ratio. (As reported by Nachtigallova et al. (1999), there is no experimental information about prefered T-sites for substitution. Calculations show that the energy difference between the most and the least favorable sites is not larger than 5 kcal/mol).

The next step is placing the charge-balancing cations at energetically favored positions inside the generated zeolite model via the "Cation Locator"-module.

Excluded Volume Calculation

Finally, the volume accessible to water molecules is calculated, as grand canonical Monte Carlo simulations cannot distinguish between accessible pores and pores which are occupiable but not accessible (see Fig. 1 and Table 2). The volume of the zeolite skeleton is consequentially marked as not accessible, which speeds up the simulation.

Influence of Si/Al Ratio

To examine the significance of the Si/Al ratio, experimental measurements and simulations have been carried out on zeolite ZSM-5, which belongs to the MFI-framework type and are available with a broad range of Si/Al ratios. Although this zeolite type is not very applicable to heat storage or heat pumping, it is a good choice for studying the influence of the different parameters on the water adsorption equilibria. The reason for the use of this zeolite type is due to restrictions of the simulation with Cerius[2] (see below and Fig. 2).

The pure silicalite is hydrophobic, but becomes more and more hydrophilic with increasing number of

Table 2. Cavity-Grid calculation output for test probe with different diameter. Calculations for MFI-Type zeolite with Si/Al ratio of 22.

Test probe radius (nm)	0.20	0.26	0.28	0.316
Vol. occupied by test probe (Å^3/ u.c.)	4.19	9.20	11.49	16.52
Total volume (Å^3/ u.c.)	21328.10	21328.10	21328.10	21328.10
Available volume (Å^3/ u.c.)	8552.47	8429.29	8398.50	8318.68
Occupiable volume (Å^3/ u.c.)	3735.77	2743.76	2479.84	2092.06
Accessible volume (Å^3/ u.c.)	3717.20	2743.21	2478.50	2090.40
Occup. but inaccessible (Å^3/ u.c.)	18.57	0.56	1.33	1.67
Total surface area (Å^2 /u.c)	3702.40	2957.37	2702.72	2262.30

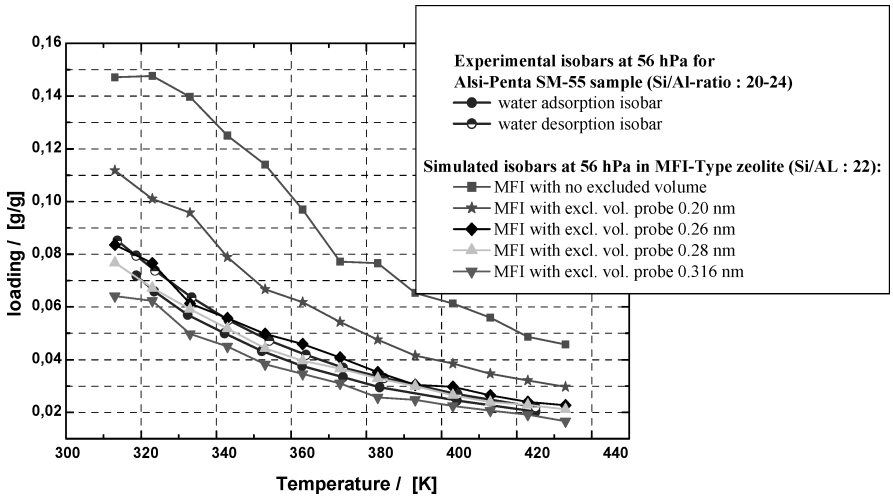

Figure 1. Analysis on the influence of different fractions of inaccessible pore volume (Cavity-Grid) and comparision with experimental isobars. Varied between the different simulated isobars is the probe diameter for the "cavity-grid" calculation. Using no cavity grid leads to an overestimation of loading. At a probe diameter of 0.26 nm, which can be stated as the "kinectic diameter"[1] of water, the agreement is good. Hence, this parameter was used in the following simulations. Simulation and mesaurement errors are smaller than symbol size, the lines are a guide to the eye.

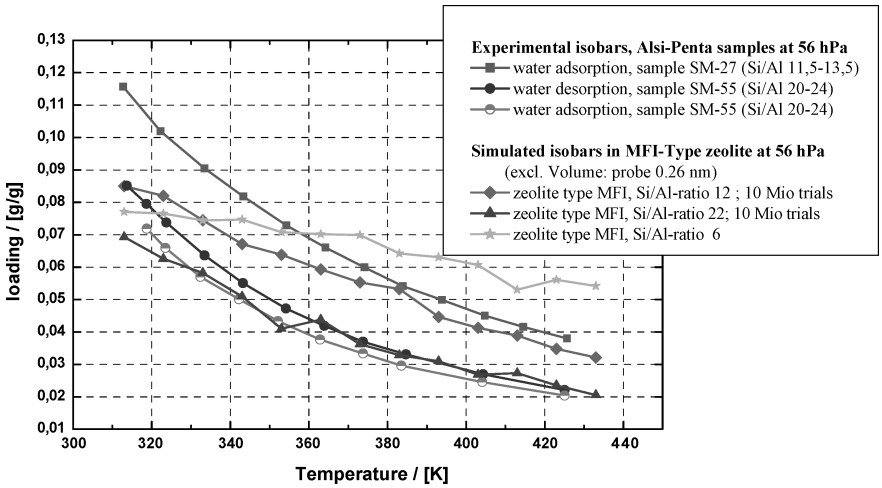

Figure 2. Influence of different Si/Al ratios on the water adsorption equilibria. Figure shows a comparision between simulated and experimental water adsorption isobars on zeolite samples with different Al/Si ratios at 56 hPa vapour pressure. Agreement for Si/Al ratio of 22 is good, for decreasing ratios getting worser due to simulation restrictions. Simulation and measurement errors are smaller than symbol size, the lines are a guide to the eye.

aluminium atoms and respectively increasing number of counterions. As shown in Fig. 2, the highest water loading of the Alsi-Penta sample SM-55 (Si/AL ratio: 22 ± 2) was about 0.085 ± 0.001 at 313 K, whereas the sample SM-27 (ratio: $12,5 \pm 1$) shows a maximum loading of 0.115 ± 0.001 at 313 K.

The simulated isobar for the Si/Al ratio of 22 is in good agreement with the experimental data. As for decreasing ratios (increasing number of aluminium and counterions) the simulations in the "high-loading"-area are getting worse, because of the immobility of the cations inside the zeolite framework during the water adsorption run (unfavorable positions of counterions prevents building of a "hydrate-shell") and a low creation/destruction ratio. At lower loadings, the simulated isobar is again in good agreement, because of the reduced importance of the counter-ion position.

Further increase in the framework aluminium content (Si/Al ratio of 6) leads to the expected effect of higher water loading within the temperature range of 370–440 K as shown in Fig. 2. Again, the simulation shows an unexpected low load, even an overlap with the simulated isobar for Si/Al = 12, in the lower temperature range, due to the simulation restrictions described above.

Conclusions

A new force field, including converted parameters from the original Biosym CVFF-aug force field, for the simulation of water adsorption in zeolites has been developed. In a first instance, parameter for aluminium, silicon, oxygen, ammonium and the SPC-water model have been integrated into the simulation with Cerius.[2]

The simulated isobars have been compared with experimental data to validate these parameters. In addition, the influence of the simulation parameters like excluded volume and the Si/Al ratio has been investigated. The variation of the excluded volume shows a good agreement with experimental data for a probe diameter of $d = 0.26$ nm which can be stated as the "kinetic diameter" of water.[1]

Due to the restriction of Cerius[2] it was not possible to move the cations during a sorption simulation. As result, the simulated isobars show a poor agreement with experimental data at higher loadings.This shows the importance of the cation position inside the zeolite framework. The cations are placed via the Cation Locator in an empty cell. Therefore the cations can occupy unfavorable positions during simulation which prevents building of a "hydrate shell".

In addition, as Cerius[2] doesn't use configurational bias monte carlo (Hensen et al., 2001) for creation/destruction, a successful creation or destruction at high loadings is very rare and consequently results with poor statistics are obtained (e.g. within a simulation run of 10 Mio steps, the Creation/Destruction rate in the last third is about 0.05%). Therefore it is very difficult to evaluate whether if the equilibrium

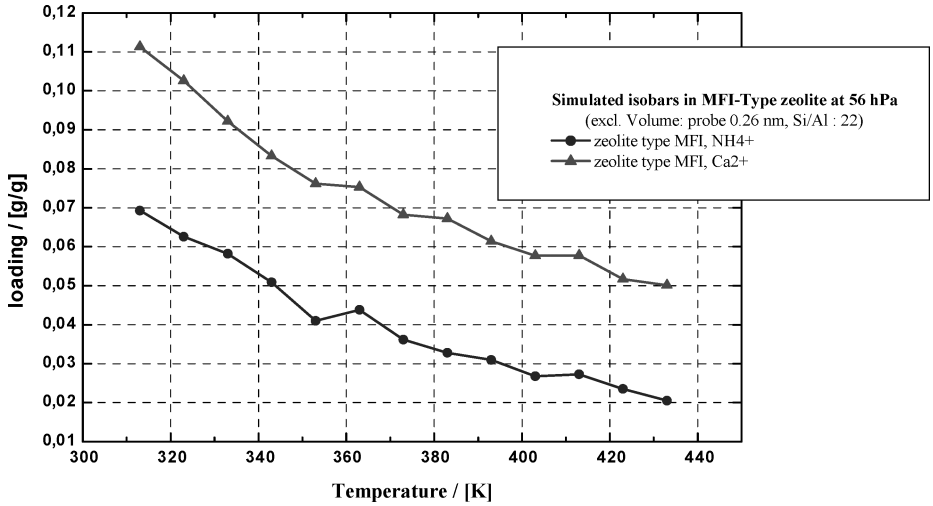

Figure 3. Influence of the used cations. Figure shows comparison between two simulated isobars on zeolite models with a Si/Al ratio of 22 and different charge balancing cations (Ammonium-ion vs. Ca^{2+}). The model with Ca^{2+} shows a significant higher loading, primarily caused by an increase of occupiable volume (+9.5%) due to the less number of required cations and stronger coulomb interactions (+40–54% av. energy/molecule) between the water molecules and the double charged cation.

is reached or not. Data analysis is performed through the "block transformation"-method of Flyvbjerg and Petersen (1989). The resulting simulation error is, due to the poor statistics, very small.

The influence of the charge balancing cations has been tested in two simulations of MFI-type zeolites with $NH4^{+}$ and Ca^{2+} (see Fig. 3). The zeolite model with Ca^{2+} shows a significant higher loading which depends primarily on the increase of occupiable volume (+9.5%) due to the less number of required cations and the stronger coulomb interactions between the water molecules and the dual charged cation (+40–54% av. energy/molecule).

Further investigations and comparision with experimental data are necessary in order to improve the forcefield parameters for different cations. If the problem of the immobility of the counterions can be overcome, perhaps with our own simulation program, it should be possible to simulate isobars even with high Al-ratios more accurate. With regard to heat storage or transformation applications, simulation on these "high alumino" zeolites like FAU-type zeolites are promising new information on developping materials for these purposes.

Note

1. Breck gives a kinetic diameter of 0.265 nm for water.

References

Baerlocher, C., W. Meier, and D. Olson, *Atlas of Zeolite Framework Types*, 5 Edn., Elsevier, 2001. *(The atlas is available on the internet at http://www.iza-structure.org/databases)*

Berendsen, H.J.C., J.P.M. Postma, W.F. van Gunsteren, and J. Hermans, "Interaction Models for Water in Relation to Protein Hydration," in B. Pullmann (Ed.), *Intermolecular Forces*, pp. 331–342, Reidel, Dordrecht, 1981.

Bernal, J.D. and R.H. Fowler, "A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ion," *J. Chem. Phys. 1*, 515–548 (1933).

Breck, D.W., *Zeolite Molecular Sieves. Structure, Chemistry, and Use*, J. Wiley, New York, 1974.

Channon, Y.M., C.R.A. Catlow, A.M. Gorman, and R.A. Jackson, "Grand Canonical Monte Carlo Investigation, of Water Adsorption in Heulandite-Type Zeolites," *J. Phys. Chem. B*, **102**(21), 4045–4048 (1988).

Flyvbjerg, H. and H.G. Petersen, "Error Estimates on Averages of Correlated Data," *J. Chem. Phys.*, **91**, 461–466 (1989).

Hensen, E.J.M., T.J. Tambach, and B. Smit, "Adsorption Isotherms of Water in Li-, Na- and K-Montmorillonite by Molecular Simulation," *J. Chem. Phys.*, **115**, 3322–3329 (2001).

Hill, J. and J. Sauer, "Molecular Mechanics Potential for Silica and Zeolite Catalysts Based on ab Initio Calculations. 1. Dense and Microporous Silica," *J. Phys. Chem.*, (1994).

Hill, J. and J. Sauer, "Molecular Mechanics Potential for Silica and Zeolite Catalysts Based on ab-initio Calculations. 2. Aluminosilicates," *J. Phys. Chem.* (1995).

Hill, J.R., C.M. Freeman, and L. Subramanian, "Use of Force Fields in Materials Modeling," *Reviews in Computational Chemistry*, K.B.Lipkowitz and D.B. Boyd (Eds.), Vol. 16, pp. 141–216, Wiley-VCH, New York, 2000a.

Hill, J.R., A.R. Minihan, E. Wimmer, and C.J. Adams, "Framework Dynamics Including Computer Simulations of the Water Adsorption Isotherm of Zeolite Na-Map," *Physical Chemistry Chemical Physics*, **2**(18), 4255–4264 (2000).

Jorgensen, W.L., J. Chandrasekhar, J.D. Madura, R.W. Impey, and M.L. Klein, "Comparison of Simple Potential Functions for Simulating Liquid Water.," *Journal of Chemical Physics*, **79**(2), 926–935 (1983).

Karasawa, N. and W.A. Goddard, "Acceleration of Convergence for Lattice Sums.," *Journal of Physical Chemistry*, **93**, 7320–7327 (1989).

Molecular Simulations, Inc., *Cerius*^{2} *OFF*, Molecular Simulations Inc., San Diego,1997a.

Molecular Simulations, Inc., *MSI Forcefield Engines: CDiscover. CDiscover in Cerius2, Insight II, and standalone modes*., Molecular Simulations Inc., San Diego, 1997b.

Molecular Simulations, Inc., *Forcefield-Based Simulations*., Molecular Simulations Inc., San Diego, 1998.

Müller, Erich A., Luis F. Rull, Lourdes F. Vega and Keith E. Gubbins, "Adsorption of Water on Activated Carbons: A Molecular Simulation Study," *J. Phys. Chem*., **100**, 1189–1196 (1996).

Nachtigallova, D., P. Nachtigall, M. Sierka, and J. Sauer, "Coordination and Siting of cu+ Ions in zsm-5: A Combined Quantum Mechanics/Interatomic Potential Function Study," *Journal of Physical Chemistry and Chemical Physics*, **1**, 2019–2026 (1999).