Supporting information for:

Monte Carlo simulation of water adsorption in hydrophobic MFI zeolites with hydrophilic sites

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Appendix A: Water and Zeolite Potential models

Appendix B: Silicalite structures containing silanol nests

Appendix A: Water and Water-Zeolite Potential models

A.1) Water and water-zeolite interaction models proposed by Demontis, Suffritti and co-workers.

- Water model [1]:

$$V_{OO} = \frac{1}{4\pi\epsilon_0} \frac{q_O q_O}{r} + \frac{A}{r^{12}} - \frac{B}{r^6} + \frac{C}{r^4} - D \exp[-E r - F^2] \quad (1)$$

$$V_{OH} = \frac{1}{4\pi\epsilon_0} \frac{q_O q_H}{r} + A \exp(-Br) - \frac{C}{r^4} - D \exp[-E r - F^2] \quad (2)$$

$$V_{HH} = \frac{1}{4\pi\epsilon_0} \frac{q_H q_H}{r} + A \exp(-Br) - C \exp[-D r - E^2] \quad (3)$$

TABLE A.1. Parameters for the water model [Eqs. (1)-(3)].

Parameters	A	B	C	D	E	F
V_{OO} (kJ/mol)	3500000	3100	15.0	2.093	1.5	4.5
V_{OH} (kJ/mol)	19098.33	4.06	223.796			
V_{HH} (kJ/mol)	2134.86	2.76	4.186	1.5	3.15	
Charges						
q_O (e)	-0.65966					
q_H (e)	0.32983					

- Water-zeolite interaction model [2]:

$$V_{OOz} = \frac{1}{4\pi\epsilon_0} \frac{q_O q_{Oz}}{r} + \frac{A}{r^{12}} - \frac{B}{r^6} + \frac{C}{r^4} \quad (4)$$

$$V_{HOz} = \frac{1}{4\pi\epsilon_0} \frac{q_H q_{Oz}}{r} + \frac{A}{r^7} - \frac{C}{r^4} \quad (5)$$

TABLE A.2. Parameters for the water-zeolite interaction model [Eqs. (4)-(5)].

Parameters	A	B	C
V_{OOz} (kJ/mol)	8.36×10^5	3100	209
V_{HOz} (kJ/mol)	2090	179.9	
Charges			
q_O (e)	-1		
q_{Si} (e)	2		

A.2) Water model proposed by Errington and Panagiotopoulos [3]

$$V = \frac{\epsilon}{1 - \frac{6}{\alpha}} \frac{6}{\alpha} \exp \left[\alpha \frac{1 - r}{r_m} - \frac{r_m}{r} \right]^6 \quad (6)$$

where r_m is the value of r at which $V(r) = 0$, ϵ is the well depth (energy), α is the "steepness" of the repulsive energy. This expression can be rewritten in the form of familiar Buckingham potential:

$$V = A \exp -Br - \frac{C}{r^6} \quad (7)$$

with

$$A = \frac{6\epsilon}{\alpha - 6} \exp(\alpha)$$

$$B = \frac{\alpha}{r_m}$$

$$C = \frac{\alpha\epsilon}{\alpha - 6} r_m^6$$

A.3) PCFF potential parameters for intra-framework interactions in silicalite [4]

(Distances in Å, and energies in kcal/mol)

Van der Waals:

$$V_{VW} = \epsilon \left[2 \frac{r_m}{r}^9 - 3 \frac{r_m}{r}^6 \right] \quad (8)$$

$$O_Z - O_Z: \quad r_m = 3.4506, \epsilon = 0.16220$$

Bond Stretch:

$$V_{Bond} = k_2 (b - b_0)^2 + k_3 (b - b_0)^3 + k_4 (b - b_0)^4$$

$$O_Z - Si_Z: \quad k_2 = 325.443, k_3 = -943.3640, k_4 = 1454.67, b_0 = 1.6155.$$

Angle Bending:

$$V_{Bend} = k_2 \theta - \theta_0^2 + k_3 \theta - \theta_0^3 + k_4 \theta - \theta_0^4 \quad (9)$$

	θ_0	k_2	k_3	k_4
O _Z -Si _Z -O _Z :	176.2650	18.8146	37.9749	42.8222
Si _Z -O _Z -Si _Z :	110.6120	154.1860	-68.6595	23.6292

Torsion

$$V_{Torsion} = k_1 [1 + \cos(\varphi - \varphi_0)] + k_2 [1 + \cos(2\varphi - \varphi_0)] + k_3 [1 + \cos(3\varphi - \varphi_0)] \quad (10)$$

Si_Z-O_Z-Si_Z-O_Z: $k_2 = -0.3417$, $k_3 = 0.0961$, $k_4 = 0.1683$, $\varphi_0 = 0.0$.

Bond-Bond

$$V_{Bond-bond} = k [b - b_0] [b' - b'_0] \quad (11)$$

$$k = 178.8840$$

Bond-Angle

$$V_{Bond-Angle} = k [b - b_0] [\theta - \theta_0] \quad (12)$$

$$\text{Si}_Z\text{-O}_Z\text{-Si}_Z: k = 13.4905$$

$$\text{O}_Z\text{-Si}_Z\text{-O}_Z: k = 87.3528$$

Angle-Angle

$$V_{Angle} = k [\theta - \theta_0] [\theta' - \theta'_0] \quad (13)$$

$$\text{Si}_Z\text{-O}_Z\text{-Si}_Z\text{-O}_Z: k = 5.7889$$

Appendix B: Silicalite structures containing silanol nests

Figure B1. Silicalite structures containing (a) 0.5, (b) 1, (c) 2, (d) 4 silanol nests per unit cell.

References:

1. Cui P., Demontis P., Spanu S., Suffritti G.B., Tilocca A., *J. Phys. Chem. B.* **2003**, *107*, 4426-4436.
2. Demontis P., Stara G., and Suffritti G.B., *J. Phys. Chem. B.* **2003**, *107*, 4426-4436.
3. Errington J.R., Panagiotopoulos A.Z., *J. Phys. Chem. B.* **1998**, *102*, 7470.
4. Hill, J.-R.; Sauer, J.; *J. Phys. Chem.* **1994**, *98*, 1238.