Supporting Information

Adsorption in Zeolites Using Mechanically Embedded ONIOM Clusters

Ryan E. Patet[1,2], Stavros Caratzoulas[1,2], Dionisios G. Vlachos[1,2]

[1]Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

[2] Catalysis Center for Energy Innovation (CCEI), www.efrc.udel.edu

S1. Quasi-Rotor Harmonic Oscillator Approximation (qRRHO)

It is well known that treating the translational or rotational degrees of freedom of a guest molecule in a host molecule (e.g., zeolite) as low-frequency harmonic oscillations results in inaccurate thermal corrections. In the limit of zero frequency, the vibrational energy of the harmonic oscillator approaches *kT* instead of *kT/2*, which is the correct contribution of a translational or rotational degree of freedom. In the same limit, the entropy of a harmonic oscillator diverges to infinity.

Following Head-Gordon,[1] we use Equations (1)-(3) to compute the vibrational thermal energy and replace frequencies below a cut-off frequency of 100 cm^{-1} with *kT/2* by means of a switching function $\omega(\nu_i)$:

$$U_{qRRHO} = \sum_i \left[\omega(\nu_i) U_{RRHO} + \left(1 - \omega(\nu_i)\right)\frac{1}{2}kT\right] \tag{1}$$

$$U_{RRHO} = \frac{1}{2}N_A h\nu_i + kT\left(\frac{h\nu_i}{kT}\right)\frac{e^{-h\nu_i/kT}}{\left(1 - e^{-h\nu_i/kT}\right)} \tag{2}$$

$$\omega(\nu_i) = \frac{1}{1 + \left(\nu_0/\nu_i\right)^4} \tag{3}$$

where ν_i is the vibrational frequency, ν_0 is the cut-off frequency (chosen to be 100 cm^{-1}), N_A is Avogadro's number, h is Planck's constant, k is Boltzmann's constant, and T is temperature.

In the qRRHO approximation to the entropy proposed by Grimme,[2] the low-frequency contributions to the vibrational entropy of the harmonic oscillator are replaced by a corresponding rotational entropy:

$$S_{qRRHO} = \sum_i \left[\omega(\nu_i) S_{HO} + \left(1 - \omega(\nu_i)\right) S_{RR}\right] \tag{4}$$

$$S_{RR} = k\left[\frac{1}{2} + \ln\left\{\left(\frac{8\pi^3 \mu' kT}{h^2}\right)^{1/2}\right\}\right] \tag{5}$$

$$\mu' = \frac{\left(h/8\pi^2\nu_i\right)B_{av}}{\left(h/8\pi^2\nu_i\right) + B_{av}} \tag{6}$$

$$S_{HO} = R\left[\frac{h\nu_i}{k\left(e^{h\nu_i/kT} - 1\right)} - \ln\left(1 - e^{-h\nu_i/kT}\right)\right] \tag{7}$$

where B_{av} is an average molecular moment of inertia chosen to be 10^{-44} kg m^2.

S2. Calculated Entropies of Adsorption

In Table S1, we present the calculated entropies of adsorption within the qRRHO approximation for adsorption of *n*-C1 to *n*-C8 alkanes in H-MFI and compare with experimental values reported by De Moor et al.[3] For the guest molecule, we have assumed 2-dimensional free translations on a molecular surface area of 200 pm × 600 pm.[3]

Table S1. Adsorption entropies within the qRRHO approximation.

Temp. (°C)	Exp.[3]	25	50	75	100	125	150	200
Methane	—	-59.3	-58.1	-57.0	-56.0	-55.1	-54.2	-53.3
Ethane	—	-76.7	-76.0	-75.3	-74.7	-74.1	-73.5	-72.9
Propane	-94	-101.9	-101.4	-101.0	-100.5	-100.1	-99.7	-99.3
n-Butane	-104	-112.5	-112.0	-111.6	-111.2	-110.9	-110.5	-110.1
n-Pentane	-118	-120.5	-120.1	-119.8	-119.5	-119.2	-118.9	-118.6
n-Hexane	-121	-126.2	-125.9	-125.7	-125.4	-125.2	-125.0	-124.7
n-Heptane	—	-148.8	-148.8	-148.8	-148.8	-148.8	-148.7	-148.7
n-Octane	—	-159.4	-159.7	-160.0	-160.2	-160.4	-160.6	-160.8

REFERENCES

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