

Computational Study of the CO Adsorption and Diffusion in Zeolites

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1. Methods and parameters in the simulations

Most of the published molecular simulation studying in zeolites at this time have used Kiselev model [1]. In this model zeolite atoms are fixed and interaction of guest atoms with silicon atoms takes into account by effective interaction only with the surrounding oxygen atoms. This model has showed a notable degree of success, both in using the molecular dynamics method to compute the diffusivities via the Einstein relation[2] and using the Monte Carlo method to calculate the sorption of hydrocarbons[3].

GCMC Simulation. Adsorption of carbon monoxide was investigated by Monte Carlo method in grand canonical (uvt) ensemble using the MCCCSTowhee[4] program for rigid framework models of MFI. This Monte Carlo molecular simulation tool allows to apply Configuration-bias Monte-Carlo (CBMC) technique. Simulations has been performed in 2 simulation boxes: adsorbent and adsorptive reservoir. The following probabilities were employed for GCMC moves involving CO particles: insertion/deletion (50%); translation (25%); intrabox reinsertion (25%). For each chemical potential, 10^7 steps were used to equilibrate the system, and a further were used for data collection. A cutoff radius of 9.5 Å multiple unit cells were used so that each cell parameter had minimum dimension of 19 Å. The Towhee code requires analyte chemical potentials rather than pressures as input. In this work, we use GCMC simulations (one simulation box only) in the isobaric-isothermal (npt) ensemble to determine CO pressure at a given chemical potential.

Perfect MFI crystal was modeled in its orthorhombic form (*Pnma* space group). The crystallographic parameters are $a=20.0511\text{Å}$, $b=19.8757\text{Å}$, $c=13.3682\text{Å}$, where a is main direction of zigzag, and b is direction of the straight channels. The

crystallographic axis of the zeolite will be used as a frame of reference for the simulation box, a for x , b for y , and c for z . Simulated box consist of 1 x 1 x 2 unit cells. For pure silica chabazite (CHA) the model crystal is rhombohedral (R3m space group) with $a=13.675\text{\AA}$, $b=13.675\text{\AA}$, $c=14.767\text{\AA}$, and the simulation cell comprises 3 x 3 x 2 unit cells. The all-silica DDR zeolite is also rhombohedral (R3m space group), and its lattice parameters are $a=13.795\text{\AA}$, $b=13.795\text{\AA}$, $c=40.750\text{\AA}$. In this instance, the simulation cell comprises 3 x 3 x 1 unit cells. Initial atomic positions were obtained from the Database of zeolite structures[5]. Charge assignments for the atoms in the zeolite framework taken from [6-7] has been 2.05e and -1.075e for Si and O atoms correspondently. The 'bond increment' method of charge assignment has been used for the framework. The polar model of carbon monoxide [8] consists of two different Lenard -Jones centers and two partial charges, each with a value of 0.0223e , negative at the oxygen atom and positive at the carbon has been used. These charge values produce a dipole of 0.12 D, which is very close to the experimental value. The bond length of the CO molecule was fixed at the experimental value, 1.128 Å (9). The Lennard–Jones parameters are $\sigma = 3.55\text{ \AA}$ and $\varepsilon / k_B = 37.15$, K for C atoms and $\sigma = 2.95\text{ \AA}$ and $\varepsilon / k_B = 61.57$, K for O atoms. The Lorentz–Berthelot rules [10] for mixing interaction lead to the following values for C–O $\sigma=3.25\text{ \AA}$ and $\varepsilon / k_B = 47.87$. This parameters were investigated in [11-12], where has been used to study the distribution of CO molecules in sl clathrate and for direct Gibbs-ensemble Monte Carlo simulation of phase equilibrium. Following [7] Lenard-Jones parameters for carbon and oxigen interaction with framework oxigen atoms has been set to $\sigma = 2.7815\text{ \AA}$, $\varepsilon / k_B = 50.2\text{ K}$ and $\sigma = 2.9195\text{ \AA}$, $\varepsilon / k_B = 84.93\text{ K}$ correspondently.

Cutoff distance $r_{\text{cut}}=9.5\text{\AA}$ (near one half of smallest unit cell size) has been applied in simulation for Coulomb and van der Waals interactions and analytical tail corrections were used to estimate interactions beyond this cutoff distance. The electrostatic interactions were computed using the Ewald summation method[13].

Atom 1	Atom 2	$\epsilon/\text{kB (K)}$	$\sigma (\text{\AA})$	Charge (e)
Adsorbed Molecules				
C(CO)	C(CO)	37.15	3.55	0.0223
O(CO)	O(CO)	61.57	2.95	-0.0223
C(CO)	O(CO)	47.87	3.25	
Zeolite				
O(zeo)	O(zeo)	-	-	-1.025
Si(zeo)	Si(zeo)	-	-	2.05
Zeolite - Adsorbed Molecules				
C(CO)	O(zeo)	50.2	2.7815	-
O(CO)	O(zeo)	84.93	2.9195	-

Table S1 Force field parameter values for the atomic interactions.

2. Fitting for empirical adsorption models

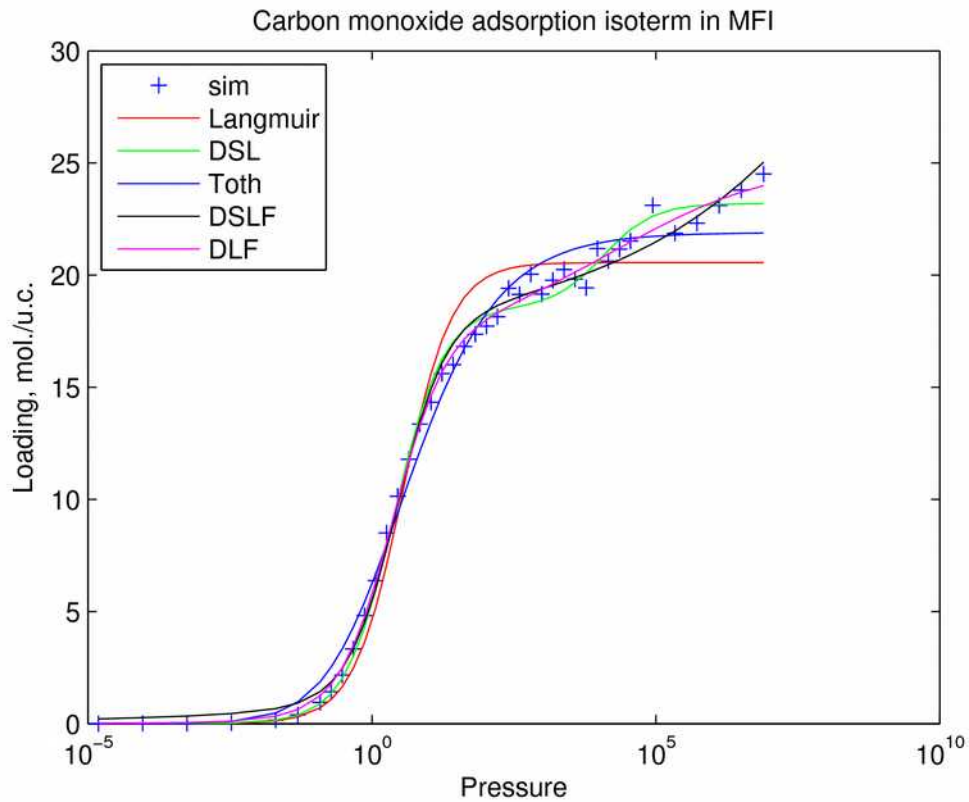


Figure S1. Adsorption isotherms fitted to different empirical adsorption models, loading in molecules per unit cell, pressure in atm.

Empirical adsorption model	Formula
Langmuir model	$N = N_m \frac{bP}{(1+bP)}$
Toth model	$N = N_m \frac{bP}{(1+(bP)^t)^{\frac{1}{t}}}$
Dual-site Langmuir model (DSL)	$N = N_{m_1} \frac{b_1 P}{(1+b_1 P)} + N_{m_2} \frac{b_2 P}{(1+b_2 P)}$
Dual Langmuir-Freundlich model(DSLF)	$N = N_m \frac{bP}{(1+bP)} + \alpha_F P^{C_F}$
Dual-site Langmuir-Freundlich model (DLF)[14]	$N = N_{m_1} \frac{b_1 P^{c_1}}{(1+b_1 P^{c_1})} + N_{m_2} \frac{b_2 P^{c_2}}{(1+b_2 P^{c_2})} \quad (1)$

Table S2 Different empirical adsorption models .

3. Comparison with experimental data

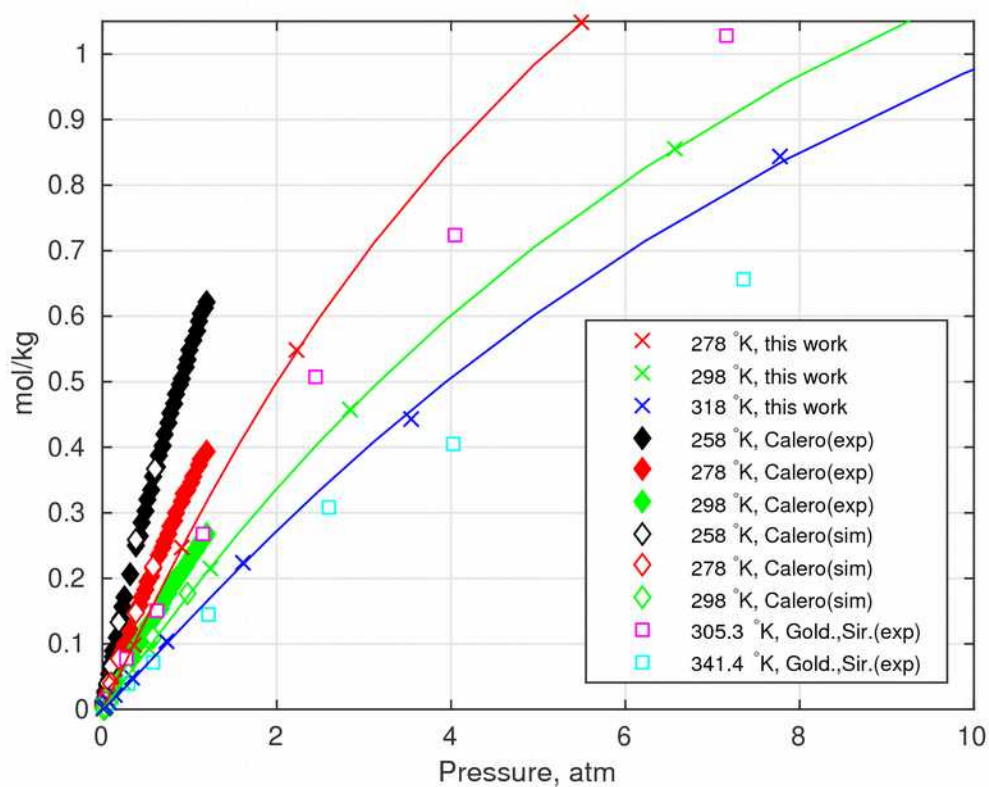


Figure S2. Computed adsorption isotherms of CO in MFI-type zeolite (solid line) at 278 K (red), 298 K (green) and 318 K (blue) fitted using the Langmuir-Freundlich (2) model and its comparison with experimental data(Golden, Sircar[19])

4. Dual-site Langmuir-Freundlich model parameters for of carbon monoxide adsoption in DDR, CHA and MFI zeolites in the pressure range 10^2 - 10^{12} Pa.

		N_{m_1} (mol/kg)	b_1	c_1	N_{m_2} (mol/kg)	b_2	c_2	residual
MFI	278°K	2.5272	2.617E-6	0.933	0.965	1.000E-3	0.310	0.041
	298°K	2.4725	1.657E-6	0.936	0.830	0.345E-3	0.388	0.032
	318°K	2.3214	0.752E-6	0.982	1.075	0.292E-3	0.405	0.043
DDR	278°K	3.3277	15.11E-6	0.795	0.855	0.413E-3	0.320	0.041
	298°K	3.2180	10.46E-6	0.796	0.873	1.144E-3	0.303	0.057
	318°K	3.1633	5.353E-6	0.832	0.917	0.221E-3	0.392	0.058
CHA	278°K	5.4766	0.896E-6	0.975	1.606	0.510E-3	0.357	0.077
	298°K	5.7940	1.721E-6	0.901	1.211	0.037E-3	0.446	0.134
	318°K	5.1546	0.785E-6	0.939	1.651	0.087E-3	0.487	0.060

Table S3. Dual-site Langmuir-Freunlich constant of carbon monoxide adsoption in DDR, CHA and MFI zeolites

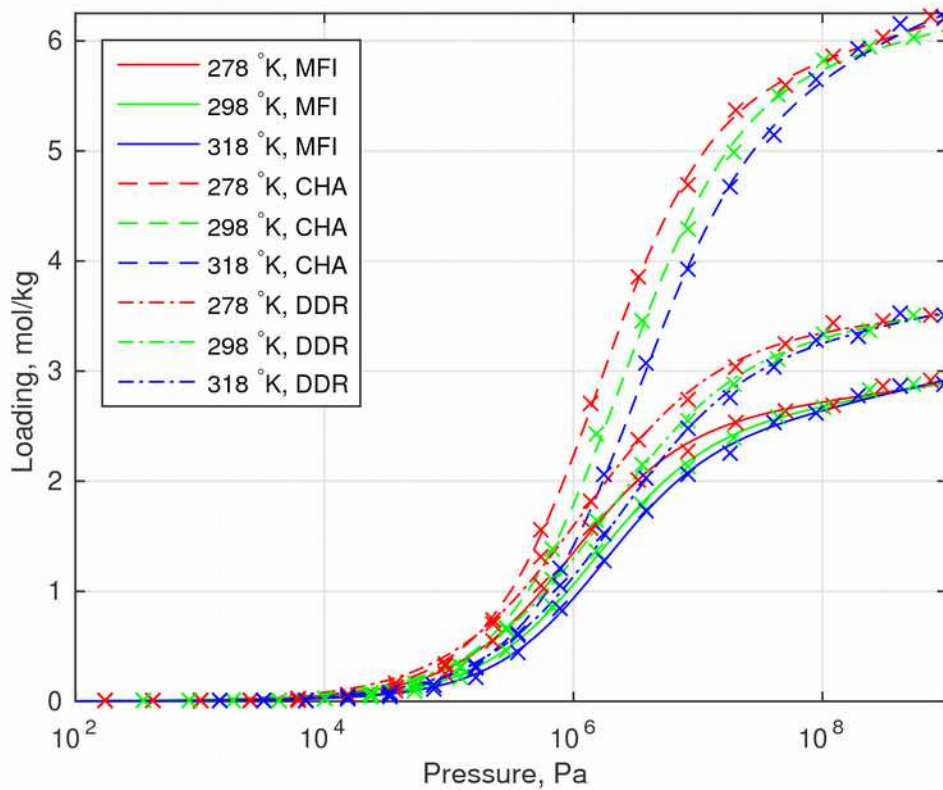


Figure S3. Computed adsorption isotherms of CO in MFI (solid line), CHA (dash-dotted line) and DDR (dashed line) at 278 K (red), 298 K (green) and 318 K (blue), fitted using the dual-site Langmuir-Freundlich model (1).

5. Langmuir-Freunlich and Toth model parameters for of carbon monoxyde adsoption in DDR, CHA and MFI zeolites in the pressure range 10^2 - 10^6 Pa.

Adsorption in the interval of pressures 10^2 - 10^6 Pa is more common used and coincide many applications. Fitting adsorption isotherm in Henry law region gives parameters for Langmuir-Freundlich(2) and Toth(3) models shown in Table S4. Despite combining features of both Langmuir and Freundlich models, the Langmuir-Freundlich isotherm still does not follow the expected linear behavior at low pressures. The Toth isotherm, on the other hand, does satisfy both low and high pressure limits.

$$N = N_m \frac{b P^c}{(1 + b P^c)} \quad (2)$$

$$N = N_m \frac{b P}{(1 + (b P)^t)^{\frac{1}{t}}} \quad (3)$$

		Langmuir-Freundlich				Toth constants			
		N_m (mol/kg)	b	c	residual	N_m (mol/kg)	b Pa ⁻¹	t	residual
MFI	278°K	2.5068	0.6505E-6	1.0520	10.57E-6	1.9794	1.3926E-6	1.3976	16.05E-6
	298°K	2.2344	0.4555E-6	1.0535	23.69E-6	1.5870	1.1097E-6	1.5466	14.34E-6
	318°K	2.1535	0.2497E-6	1.0860	335.4E-6	1.7855	0.7685E-6	1.5209	123.6E-6
DDR	278°K	3.8558	2.6150E-6	0.9222	164.2E-6	6.7981	0.7577E-6	0.6016	124.6E-6
	298°K	2.6820	1.6676E-6	0.9660	172.8E-6	2.8279	1.1212E-6	0.8855	159.3E-6
	318°K	2.3818	0.6064E-6	1.0361	333.9E-6	2.2057	0.9479E-6	1.1845	218.3E-6
CHA	278°K	5.6670	0.4577E-6	1.0296	0.861E-6	3.9435	0.8863E-6	1.3968	1.774E-6
	298°K	6.7254	0.2998E-6	1.0195	8.672E-6	4.8028	0.5151E-6	1.2906	12.37E-6
	318°K	5.3868	0.2850E-6	1.0194	9.896E-6	3.6106	0.5185E-6	1.3558	4.878E-6

Table S4. Langmuir-Freunlich and Toth model constants of carbon monoxyde adsoption in DDR, CHA and MFI zeolites

6. Self and Maxwell-Stefan diffusivities of carbon monoxide in MFI.

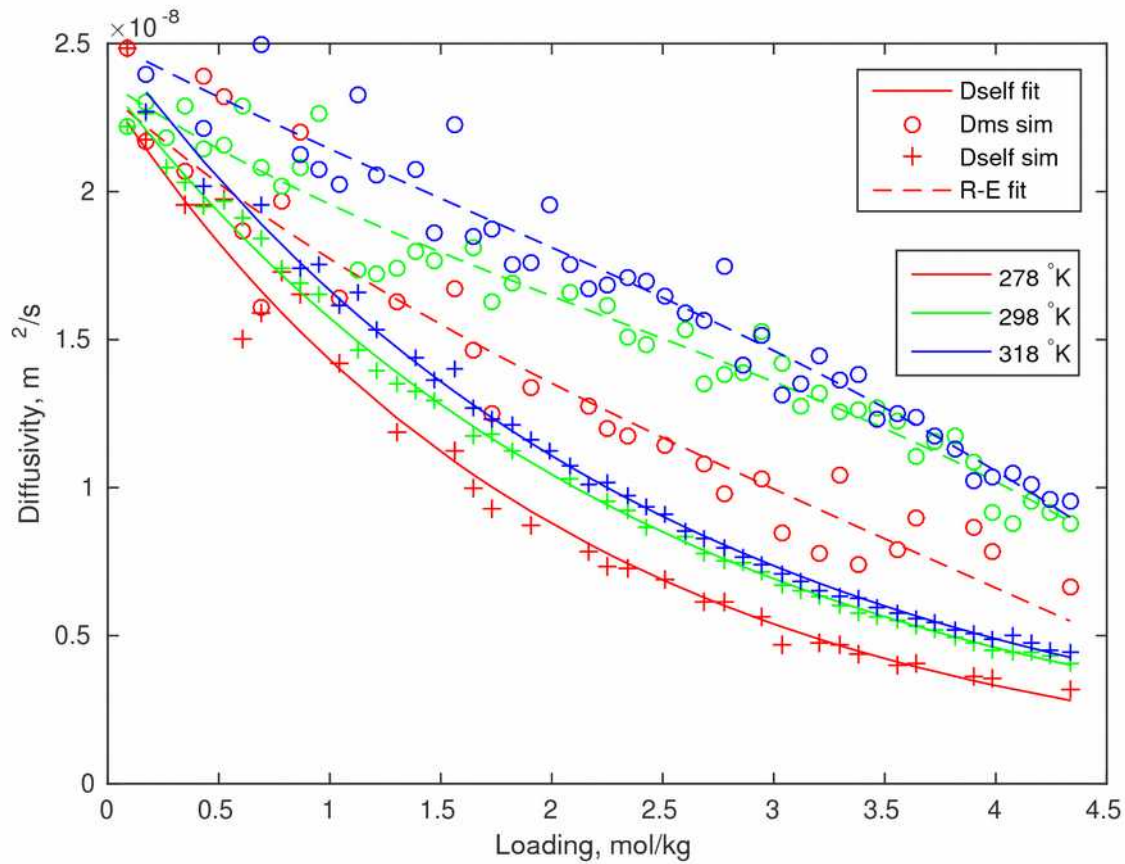


Figure S4. Carbon monoxide self- and Maxwell-Stefan diffusivities in MFI at 278 K (red), 298 K (green) and 318 K (blue). Lines shows simulation data fitted to exponential decay(4) for self-diffusivity and Reed-Ehrlich approximation for Maxwell-Stefan diffusivity.

Figure S4 shows the self-diffusion coefficient and Maxwell-Stefan diffusivities calculated for CO from the slope of mean square displacement:

$$D_{self} = \frac{1}{6} \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \langle |\vec{r}(t + \Delta t) - \vec{r}(t)|^2 \rangle$$

and mean square displacement of the center of mass of the swarm of adsorbed molecules:

$$D_o = \frac{1}{2} \lim_{\Delta t \rightarrow \infty} \frac{1}{n} \frac{1}{\Delta t} \left\langle \left(\sum_{i=1}^n (\vec{r}_i(t + \Delta t) - \vec{r}_i(t)) \right)^2 \right\rangle$$

respectively. The self-diffusion coefficient depends on the occupancy, and can be described by

$$D_{self}(c) = D_{self}(c) \exp(-ac) \quad (4)$$

6. Reed-Ehrlich interaction energy of carbon monoxide in MFI, DDR and CHA.

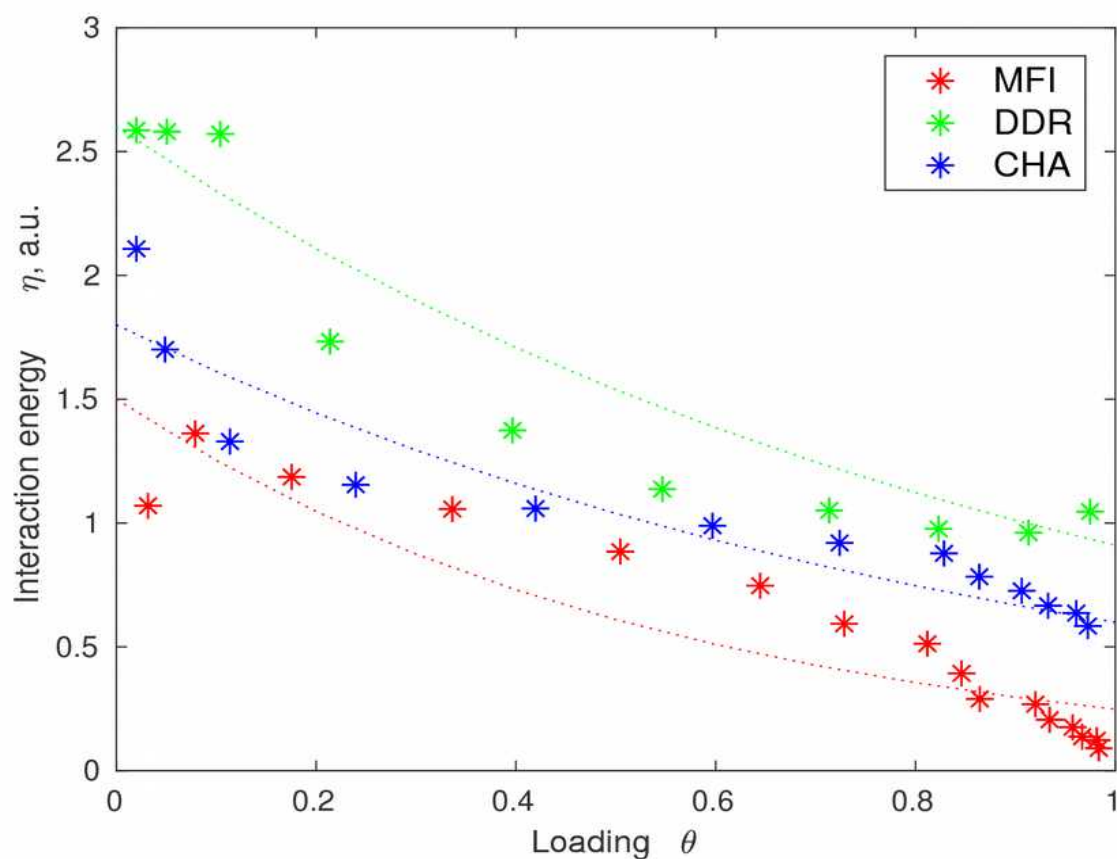


Figure S5. Reed-Ehrlich interaction energy versus loading of carbon monoxide in MFI, DDR and CHA. Dotted lines representing exponential dependences added to guide the eye only.

5. References.

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