Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Accurate Adsorption Energies for Small Molecules on Oxide Surfaces: CO/MgO(001)

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1. DFT calculations on periodic models

Table S1 Effect of k-point mesh and kinetic energy cut-off/pseudopotential: Desorption energies, E_d, lateral interaction energies, E_L, and relaxation energies, E_{relax}, all in kJ/mol, as well as Mg-C and Mg-O distances (in pm), obtained with PBE+D.

k-mesh	Γ	Γ	Γ	3x3x1	2x2x1	Γ
Slab[a,b]	4x4x6 [b]	4x4x7 [b]	4x4x4[b]	4x4x4[b]	6x6x4[c]	6x6x5 [c]
E_d	22.39	22.38	22.38	21.85	21.94	21.81
E_L	-0.02	0.00	-0.00	-0.00	0.00	-0.01
E_{relax}	1.08	1.13	1.15	1.14	1.22	1.26
C-O	114.3	114.3	114.4	114.4	114.3	114.3
Mg-C	240.6	240.4	240.6	240.6	241.3	241.4

[a] The Mg-O distance is fixed at 211.93 pm (optimized by PBE+D for the bulk), resulting in cell parameters of 847.75 pm (4x4) and 1271.23 pm (6x6). [b] Θ = 1/8. [c] Θ = 1/18. [d] hard PAW core potentials for the 1st-row elements with a cutoff of 1000 eV.

2. PBE+D and Hybrid MP2:DFT+D structure optimization

For PBE+D, the bulk Mg-O distance of 211.9 pm increases to 214.2 pm for the oxygen ion below the surface, and to 213.1 pm for the oxygen ion on the surface (Fig. S1). If there is no CO on the surface, the Mg-O distance decreases to 210.2 pm for the oxygen ion below the surface. The distance from the oxygen ions on the surface to the magnesium ions below the surface is 214.6 pm. Considering also the changes occurring in the second layer, all oxygen ions move 3.3 pm up, whereas the magnesium ions move 1.7 pm down.

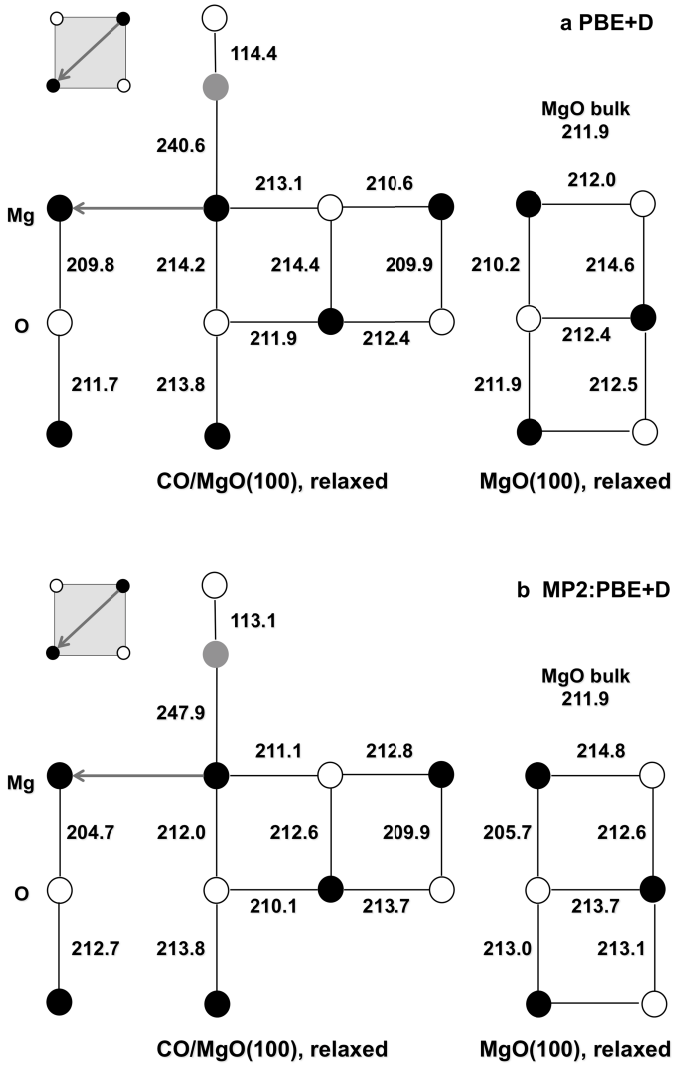
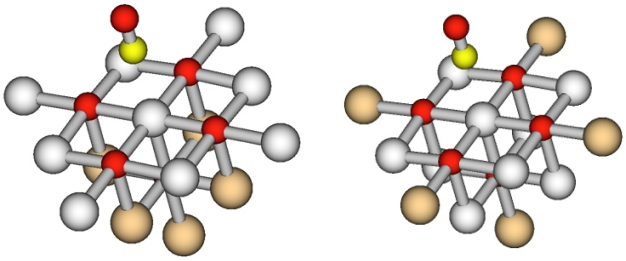


Figure S1 The PBE+D (a, top) and hybrid MP2:PBE+D (b, bottom) structures of CO/MgO(001) compared to MgO(001).

3. CCSD(T) calculations on cluster models

Additional CCSD(T) calculations with the augmented triple-zeta basis set have been done for the following embedded cluster models:

Mg_9O_5-up **Mg_9O_5-down**



Mg_9O_5-up has nine magnesium ions and four oxygen ions in the surface layer, but only one oxygen ion in the second layer, whereas the Mg_9O_5-down model has five magnesium ions in the surface layer and four in the second layer. Table S2 shows the results, which confirm the conclusions drawn in the main article.

Table S2 MP2, CCSD and CCSD(T) desorption energies (E_d* values in kJ/mol)[a] calculated for embedded cluster models and for different a'-cc-pC'VXZ basis sets and cbs(X-1,X) basis set extrapolation.

[Model] $_{pc\text{-}ecp}$	X=	MP2	CCSD	ΔCCSD	CCSD(T)	Δ(T)	ΔCCSD(T)
Mg_9O_5-down	D,T	21.02	17.80	-3.22	21.30	3.50	0.28
Mg_9O_5-down	D	13.96	10.84	-3.12	13.16	2.32	-0.80
Δ(Model)	D	-0.72	-0.71	0.01	-0.69	0.02	0.03
□□□□□ Mg_9O_5-down		22.23 ± 1.21	18.91 ± 1.12	-3.31 ± 0.09	22.20 ± 0.90	3.29 ± 0.22	-0.03 ± 0.31
Mg_9O_5-up	D,T	21.80	18.53	-3.27	22.04	3.51	0.24
Mg_9O_5-up	D	14.51	11.30	-3.21	13.66	2.36	-0.95
Δ(Model)	D	-1.27	-1.17	0.10	-1.19	-0.02	0.08
□□□□□ Mg_9O_5-up		22.73 ± 0.93	19.42 ± 0.89	-3.32 ± 0.05	22.69 ± 0.65	3.27 ± 0.24	-0.03 ±0.27

[a] $E_d^* = E^{pbc}(S//A{\cdot}S) + E^{pbc}(A//A{\cdot}S) - E^{pbc}(A{\cdot}S)$