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Electronic Supplementary Information

Accurate quantum chemical energies for the interaction of hydrocarbons with oxide surfaces: $CH_4/MgO(001)$

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- 1. MP2 results
- 2. Calculation of C_6 parameters for ${\rm Mg}^{2 \text{+}}$ and ${\rm O}^{2 \text{-}}$
- 3. DFT+D results
- 4. Hybrid MP2:DFT+D results

1. Supplementary MP2 results

Figure S1 shows the CH_4 - Mg_9O_9 interaction energy as a function of the distance R for CH_4 in the monopod, dipod and tripod configurations, i.e. pointing with one, two or three CH bonds, respectively, to the surface. The aug'-cc-pVQZ basis set has been used and on Mg the 1s and 2s cores are frozen. The results confirm that the dipod configuration is the most favorable. For the dipod configuration, the minimum energy distance is R = 334 pm.



Figure S1. BSSE corrected MP2/aug'-cc-pVQZ interaction energy as function of the C-Mg distance for CH_4 on Mg_9O_9 (C1x1/2 cluster) in three different configurations shown on top: monopod (left), dipod (middle) and tripod (right).

Table S1 Hartree Fock (HE) and correlativ	on energy (corr)	of the Ma stom	and Ma ²⁺ ion in Hartree
Table ST. Hallee-FUCK (nr) and correlatio	Jii energy (con)	or the wy atom	

Basis	Freezing	E _{HF} (Mg)	E _{corr} (Mg)	E _{HF} (Mg ²⁺)	E _{corr} (Mg ²⁺)
cc-pVQZ	1s, 2s, 2p	-199.614233	-0.024319	-198.830381	a
cc-pVQZ	1s	-199.614233	-0.054358	-198.830381	-0.022807
cc-pCVQZ	1s	-199.614233	-0.325360	-198.830404	-0.287009

^a it is impossible to calculate the correlation if no active occupied cores are available

X=	ΔE_{HF}	$\Delta {\sf E}_{\sf HF}{}^{\sf C}$	ΔE_{corr}	ΔE_{corr}^{C}	ΔE_{MP2}	$\Delta E_{MP2}{}^{C}$	ΔE_{MP2}^{CBS}	(X,Y) ^c
D	0.251	0.826	-3.112	-2.001	-2.861	-1.175		
Т	0.761	0.818	-2.568	-2.209	-1.807	-1.391	-1.482	(D,T)
Q	0.790	0.817	-2.398	-2.260	-1.608	-1.442	-1.480	(T,Q)
5	0.815	0.817	-2.345	-2.275	-1.530	-1.458	-1.474	(Q,5)
cbs (Q,5) ^b	0.841	0.818	-2.290	-2.291	-1.449	-1.474		

Table S2. MP2/aug-cc-pVXZ interaction energy for the CH₄ dimer at the ROT configuration.^{a,b}

^a BSSE corrected results are indicated by a superscript C
^b Note that the energies in Table 3 are given per molecule, i.e. are obtained from the CBS(Q,5) result of this Table by dividing by 2.
^c X-zeta and Y-zeta results used to get the CBS estimate

2. Calculation of C_6 parameters for Mg^{2+} and O^{2-}

Following Grimme¹ the C₆ constants,

 $C_6^{i}=0.05\cdot N\cdot I_i\cdot \alpha_i$

are calculated from the ionization potential, I, the polarizability, α^i , and the number N, which is 2, 10, 18, 36, and 54 for atoms from rows 1–5 of the periodic table, see Table S3. The environment of the ions in solid MgO has been represented by 6 point charges of magnitude -1/3 at the positions of first neighbor ions in case of Mg²⁺, and by full ion effective core potentials with an effective charge set to +1/3 to avoid overpolarisation in the case of O²⁻. The ionization potential calculated for O²⁻/(epc-10,+1/3)6 was still unrealistically small (0.042 Hartree) compared to the valence band edge of MgO which is formed by O 2p orbitals. Therefore, we have used the neutral Mg₉O₉ cluster to calculate the ionization potential.

Both the polarizability and the ionization potential for Mg^{2+} in MgO are vastly different from the values calculated for an atom with the result that the C₆ parameter for Mg^{2+} in MgO is one order of magnitude smaller than the value suggested for Mg atoms (interpolated between Ne and Al), and very close to that of the isoelectronic Ne atom.

In contrast, the C_6 parameter for O^{2-} in MgO differs by less than 5% from that obtained for O atoms. This is due to compensation between an increased polarizability and a decreased ionization potential (by about a factor of 2).

Atom/Ion	Ν	α (Bohr ⁻³)	I ^ª (Hartree)	C ₆ (J·nm ⁶ /mol)	C ₆ (Ref. ¹)
Al	18	31.54	0.389 ^f	11.05	10.79
Mg	18	74.89	0.277	18.68	5.71 ^b
Ne	10	1.60	0.876	0.70	0.63
$Mg^{2+}/(-1/3)_{6}^{c}$	10	0.48	2.573	0.62	
0	10	3.32	0.445	0.74	0.70
O ²⁻ /(+1/3) ₆ ^c	10	7.62	0.234	0.89	
O ²⁻ /(epc-10,+1/3) ₆ ^d	10	6.12	0.253 ^e	0.77	

Table S3. Polarizabilities, α , and ionization potentials,^a I, (in atomic units) calculated with U-PBE0/QZVP and C₆ coefficients (in Jnm⁶/mol), calculated starting from different electronic states.

^a I=E(X^+) –E(X)

^b obtained as average of Ne (0.63) and Al (10.79)

^c First shell counter ions are represented by six point charges of -1/3

^d First shell counter ions are represented by full ion effective core potentials with the effective charge set to +1/3

e ionization potential of the C1x1/2(Mg₉O₉) cluster

 $f AI^{+}$ ion is considered in the high spin state

Reference

S. Grimme, J. Comput. Chem. 27, 1787 (2006).

3. Supplementary DFT+D results



Figure S2. DFT/TZVP+D interaction energies for CH_4/Mg_9O_9 as function of the C-Mg distance R for the monopod (top) and tripod (bottom) configurations compared to the MP2/aug'-cc-pVQZ results.

	PB	E	B3LYP		
Basis set (def2)	ΔE	ΔE^{C}	ΔE	ΔE ^C	
SVP	-6.36	+2.06	+1.27	+9.31	
TZVP	-0.63	+1.52	+7.05	+9.28	
TZVPP	-0.93	+1.30	+6.71	+9.03	
QZVP	+0.74	+1.11	+8.37	+8.69	

Table S4. DFT interaction energies for different basis sets for CH_4/Mg_9O_9 at R=300 pm. The dispersion contribution is -8.53 kJ/mol for PBE and -11.94 kJ/mol for B3LYP.

Table S5. Contribution of CH_4 - surface modes to the zero-point vibrational energy. PBE+D results for the ROT model.

Mode	Wavenumbers (cm ⁻¹)	E _{ZPV}
Translation, parallel	37.8, 37.8, 37.9, 38.2, 38.3, 38.6, 39.8, 41.1	1.85
Translation, parallel	45.7, 47.0, 48.5, 48.5, 48.8, 50.0, 50.9, 51.5	2.34
Trans., perpendicular	91.4, 96.1, 96.2, 96.6, 96.7, 99.7, 99.8, 100.5	4.65
Rotation, parallel	121.6, 121.9, 122.6, 123.0, 123.3, 123.6, 123.9, 124.6	5.89
Rotation, perpendicular	145.6, 145.7, 146.3, 146.6, 146.8, 147.1, 147.8, 148.0	7.02
Rotation, parallel	244.9, 245.1, 268.9, 269.2, 271.6, 271.9, 280.8, 282.1	12.77

4. Supplementary hybrid MP2:DFT+D results

		PAR, Θ=1			ROT, Θ=	1	ISO, Θ=1/4
		S2x2/3			S2x2/3		S2x2/5
	ΔE^{*C}	ΔE_{L}^{C}	ΔE^{C}	$\Delta {E^{*}}^{C}$	ΔE_L^C	ΔE^{C}	ΔE ^C
MP2/cbs(C1x1/2;P+D)	-5.26 ^c	-1.94	-7.20	-5.26 ^c	-3.36	-8.62	-5.26 ^c
PBE+D*/TZVP	-8.17	-4.31	-12.48	-8.24	-5.01	-13.25	-9.77
$\Delta_{\text{HL}}{}^{d}$	+1.74	+2.52	+4.26	+1.74	+1.80	+3.54	+1.74
Δ_{LL}^{e}	-1.17	+0.15	-1.02	-1.24	+0.15	-1.09	-2.77
MP2:PBE+D	-6.43	-1.79	-8.22	-6.50	-3.21	-9.71	-8.03
B3LYP+D*	-6.29	-2.75	-9.04	-6.45	-3.33	-9.79	-6.56
D*//B3LYP+D*	-14.72	-5.59	-20.31	-14.72	-5.07	-19.79	-14.94
$\Delta_{\text{HL}}{}^{\text{d}}$	-2.60	+0.72	-1.88	-2.60	-0.16	-2.76	-2.60
Δ_{LL}^{e}	-3.63	-0.09	-3.72	-3.79	-0.13	-3.92	-3.90
MP2:B3LYP+D	-8.89	-2.03	-10.92	-9.05	-3.49	-12.54	-9.16

Table S6. Hybrid MP2:DFT adsorption energies for S2x2/3 slab models at R=300 pm (kJ/mol per molecule).

 c CBS(Q,5) extrapolation for the aug'-cc-pCVnZ series d defined as $E_{MP2}\text{-}\,E_{DFT\text{+}D}$, see eq. 4 e see eq. 2