

Supporting Information

Including dispersion in density functional theory for adsorption on flat
oxide surfaces, in metal-organic frameworks and in acidic zeolites[†]

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1. CO, CO₂/Mg₂(dobdc)

There is no reliable heat of adsorption for CO in Mg₂(dobdc). Therefore, experimental Gibbs free energy of Bloch *et al.* (-2.0 kJ/mol) and the entropy term (Table 6 of Kundu *et al.*¹ anharmonicity included, -37.8 kJ/mol) are used to obtain an estimate of $\Delta H_{298} = -39.8 \pm 1.0$ kJ/mol. The uncertainty is calculated as difference between calculated and experimental Gibbs free energy. By considering corrections for thermal contributions, zero-point vibrational energy and RT term (2.54, 3.94 and -2.84 kJ/mol, Table 6 of Kundu *et al.*¹) a reference value of -43.8 ± 1.0 kJ/mol is obtained.

For CO₂ the experimental reference value of -49.0 kJ/mol is obtained by correction of the isosteric heat of adsorption of Queen *et al.*². (-43.5 kJ/mol at 298 K) by the calculated $\Delta H - \Delta E$ difference (2.7 kJ/mol, Table 2 and 1 of Sillar *et al.*³) and lateral interactions (-2.81 kJ/mol, Table 3 of Sillar *et al.*³). Additionally, the QM:QM value is obtained by adding the lateral interactions to the result reported in Table 1 of Sillar *et al.*³.

Table S1. Calculated electronic adsorption energy per molecule, ΔE (kJ/mol), for adsorption of six CO or CO₂ in Mg₂(dobdc) and the difference to the reference value, Δ (kJ/mol) at different level of theory.

		CO		CO ₂	
		ΔE	Δ	ΔE	Δ
ΔE_{ref}		-43.8 ^a		-49.0 ^b	
QM:QM		-43.3 ^c	0.5	-51.6 ^d	-2.6
B3LYP	D2(Ne)	-38.6	5.2	-47.3	1.7
	D2	-40.9	2.9	-50.8	-1.8
	D3	-41.3	2.5	-49.8	-0.8
	TS	-41.1	2.7	-50.9	-1.9
PBE	D2(Ne)	-41.3	2.5	-41.5	7.5
	D2	-42.8	1.0	-44.0	5.0
	D3	-42.4	1.4	-43.4	5.6
	TS	-45.2	-1.4	-47.6	1.4
	dDsC	-45.7	-1.9	-46.2	2.8
	MBD	-44.8	-1.0	-48.0	1.0
	MBD/HI	-41.9	1.9	-41.7	7.3
	MBD/FI	-44.3	-0.5	-45.7	3.3
revPBE	vdW	-42.8	1.0	-50.6	-1.6
optB86b	vdW	-51.9	-8.1	-57.0	-8.0

^a estimated uncertainty ± 1.0 kJ/mol and see comment above

^b see comment above

^c ref.¹, estimated uncertainty ± 1.0 kJ/mol

^d ref.³ and lateral interaction is considered (Table 3 of ref.³)

Table S2. Distances between the closest Mg^{2+} of $Mg_2(dobdc)$ and carbon of each adsorbate, R (pm), and bond angle, φ (degree). CO has a linear adsorption structure whereas CO_2 adsorption structure is tilted.

		CO		CO ₂	
		$R(C\cdots Mg^{2+})$	$\varphi(Mg^{2+}-C-O)$	$R(O\cdots Mg^{2+})$	$\varphi(Mg^{2+}-O-C)$
Obsd.		241 ^a	167 ^a		
B3LYP	D2(Ne)	247.8 - 248.1	175	228	138
	D2	247.8 - 248.1	175	228	138
	D3	247.5 - 247.8	175	229	138
	TS	245.7 - 246.0	175	228	138
PBE	D2(Ne)	245.6 - 245.9	174	230	137
	D2	246.2 - 246.6	174	229	137
	D3	246.5 - 246.9	175	233	139
	TS	246.5 - 246.9	174	234	138
	dDsC	243.8 - 244.2	174	229	138
	MBD	244.8 - 245.0	174	230	139
	MBD/HI	245.8 - 245.8	174	231	138
	MBD/FI	244.9 - 245.1	174	230	138
revPBE	vdW	255.0 - 255.7	174	239	137
optB86b	vdW	245.3 - 245.6	174	228	136

^a Neutron powder diffraction, ref.⁴

2. CO, CH₄, C₂H₆/MgO(001)

Table S3. Calculated electronic adsorption energy, ΔE (kJ/mol), for CO and monolayer of methane and ethane at MgO(001), the difference, Δ (kJ/mol), and the difference per carbon atom, Δ/n_c (kJ/mol), to the reference value.

		CO		CH ₄		C ₂ H ₆		
		ΔE	Δ	ΔE	Δ	ΔE	Δ	Δ/n_c
ΔE_{ref}		-20.6 ^a		-15.0 ^c		-24.4 ^c		
QM:QM		-21.2 ^b	-0.6	-14.0 ^d	1.0	-23.3 ^c	1.1	0.5
B3LYP	D2(Ne)	-16.9	3.7	-12.0	3.0	-22.6	1.8	0.9
	D2	-21.1	-0.5	-22.5	-7.5	-37.6	-13.2	-6.6
	D3	-26.9	-6.3	-30.1	-15.1	-48.1	-23.7	-11.8
	TS	-34.2	-13.6	-30.0	-15.0	-53.5	-29.1	-14.5
PBE	D2(Ne)	-22.1	-1.5	-14.7	0.3	-23.7	0.7	0.3
	D2	-26.8	-6.2	-24.3	-9.3	-37.5	-13.1	-6.5
	D3	-29.7	-9.1	-27.8	-12.8	-41.2	-16.8	-8.4
	TS	-39.4	-18.8	-34.1	-19.1	-54.8	-30.4	-15.2
	dDsC	-28.5	-7.9	-24.3	-9.3	-41.4	-17.0	-8.5
	MBD/HI	-24.7	-4.1	-17.1	-2.1	-28.2	-3.8	-1.9
	MBD/FI	-31.4	-10.8	-17.2	-2.2	-30.1	-5.7	-2.8
revPBE	vdW	-21.5	-0.9	-21.0	-6.0	-29.9	-5.5	-2.7
optB86b	vdW	-30.7	-10.1	-24.2	-9.2	-37.8	-13.4	-6.7

^a ref.⁵, estimated uncertainty ± 2.4 kJ/mol

^b ref.⁶, estimated uncertainty ± 0.5 kJ/mol

^c ref.⁶, estimated uncertainty ± 0.6 kJ/mol

^d ref.⁶, estimated uncertainty ± 1.0 kJ/mol

Table S4. Distances (pm) between the closest surface Mg^{2+} of $\text{MgO}(001)$ and the carbon of each adsorbate for different dispersion correction methods as difference to the QM:QM reference value. For methane monolayer equidistance is found but ethane monolayer is separated by two different distances (R_1 and R_2 as defined in ref.⁶).

		CO	CH ₄	C ₂ H ₆	
		$R(\text{C}\cdots\text{Mg}^{2+})$	$R(\text{C}\cdots\text{Mg}^{2+})$	R_1	R_2
QM:QM		250.8 ^a	312 ^b	314 ^c	
B3LYP	D2(Ne)	-3.8	-2	1	3
	D2	0.2	1	3	5
	D3	-4.8	1	5	6
	TS	-4.8	5	7	9
PBE	D2(Ne)	-10.8	-4	-1	1
	D2	-11.8	-13	-14	-14
	D3	-12.8	-2	-2	-1
	TS	-11.8	-8	-6	-5
	dDsC	-11.8	-4	-3	-1
	MBD/HI	-10.8	10	8	9
	MBD/FI	-12.8	1	-5	-4
revPBE	vdW	1.2	36	36	35
optB86b	vdW	-10.8	-1	1	3

^a ref.⁶, estimated uncertainty ± 1.4 pm

^b ref.⁶

^c distance between plane of the surface Mg atoms and the average plane of both carbon atoms, see Ref.⁶ for more details

3. Alkanes/H-chabazite

Table S5. Calculated electronic adsorption energy at different level of theories, ΔE (kJ/mol), for methane, ethane and propane via primary carbon in H-chabazite, deviation, Δ (kJ/mol), and deviation per number of carbon atom, Δ/n_c (kJ/mol), to the reference value.

		CH ₄		C ₂ H ₆			C ₃ H ₈ C(1°)		
		ΔE	Δ	ΔE	Δ	Δ/n_c	ΔE	Δ	Δ/n_c
ΔE_{ref}^a		-27.2		-33.5			-43.8		
QM:QM ^a		-25.3	1.9	-36.2	-2.7	-1.4	-46.7	-2.9	-1.0
B3LYP	D2	-36.6	-9.4	-51.5	-18.0	-9.0	-65.5	-21.7	-7.2
	D3	-38.1	-10.9	-53.7	-20.2	-10.1	-70.2	-26.4	-8.8
	TS	-34.0	-6.8	-50.9	-17.4	-8.7	-67.6	-23.8	-7.9
PBE	D2	-35.6	-8.4	-46.8	-13.3	-6.7	-58.7	-14.9	-5.0
	D3	-34.5	-7.3	-48.4	-14.9	-7.5	-61.9	-18.1	-6.0
	TS	-39.2	-12.0	-56.6	-23.1	-11.6	-73.0	-29.2	-9.7
	dDsC	-36.5	-9.3	-52.5	-19.0	-9.5	-68.1	-24.3	-8.1
	MBD	-35.2	-8.0	-49.1	-15.6	-7.8	-63.2	-19.4	-6.5
	MBD/HI	-30.2	-3.0	-43.3	-9.8	-4.9	-56.4	-12.6	-4.2
	MBD/FI	-30.0	-2.8	-41.7	-8.2	-4.1	-53.6	-9.8	-3.3
revPBE	vdW	-37.0	-9.8	-55.2	-21.7	-10.9	-75.7	-31.9	-10.6
optB86b	vdW	-40.6	-13.4	-54.1	-20.6	-10.3	-72.3	-28.5	-9.5

^a ref.⁷

Table S6. Adsorption structures of methane, ethane and propane in H-chabazite obtained with different methods. Reported is the distance (pm) between the proton of the OH group of the Brønsted site and the closest C atom relative to the QM:QM reference value. The energy difference between propane adsorption via the secondary or the primary carbon atom, $\Delta E(2^\circ - 1^\circ)$ is also reported (kJ/mol).

		CH ₄	C ₂ H ₆	C ₃ H ₈		
				C(1°)	C(2°)	$\Delta E(2^\circ - 1^\circ)$
QM:QM ^a		228	221	219	219	2.6
B3LYP	D2	-8	-2	1	12	1.3
	D3	0	3	2	12	1.3
	TS	0	1	0	7	1.9
PBE	D2	-14	-8	-8	0	0.7
	D3	-5	-2	-2	6	4.5
	TS	-8	-2	1	12	2.2
	dDsC	-12	-7	-4	0	2.0
	MBD	-11	-8	-8	2	1.1
	MBD/HI	-7	-2	-4	10	1.6
	MBD/FI	-9	-5	-7	4	1.4
revPBE	vdW	32	33	33	45	5.8
optB86b	vdW	-5	-1	1	4	11.8

^a ref.⁷

4. Performance with Δ/n_c

Table S7. Mean Unsigned Error, MUE (kJ/mol), Mean Signed Error, MSE (kJ/mol), and Absolute Maximum Deviation with corresponding system, |MAX| (kJ/mol), for adsorption energies calculated with different dispersion correction methods applied to various systems. For systems containing ethane or propane, errors per number of carbon atom (see Tables S3 and S5) were used.

		MUE	MSE	MAX	system
B3LYP	D2(Ne)	5.0	-1.4	9.4	CH ₄ /H-CHA
	D2	5.6	-4.9	9.4	CH ₄ /H-CHA
	D3	8.3	-7.7	15.1	CH ₄ /MgO(001)
	TS	8.9	-8.2	15.0	CH ₄ /MgO(001)
PBE	D2(Ne)	4.0	-1.4	8.4	CH ₄ /H-CHA
	D2	6.0	-4.5	9.3	CH ₄ /MgO(001)
	D3	7.3	-5.5	12.8	CH ₄ /MgO(001)
	TS	11.1	-10.8	19.1	CH ₄ /MgO(001)
	dDsC	7.2	-6.5	9.5	C ₂ H ₆ /H-CHA
	MBD/HI	3.7	-1.4	4.9	C ₂ H ₆ /H-CHA
	MBD/FI	3.7	-2.9	4.1	C ₂ H ₆ /H-CHA
revPBE	vdW	5.4	-5.2	10.8	C ₂ H ₆ /H-CHA
optB86b	vdW	9.4	-9.4	13.4	CH ₄ /H-CHA

5. Hybrid QM:QM results as reference

Table S8. Mean Unsigned Error, MUE (kJ/mol), Mean Signed Error, MSE (kJ/mol), Absolute Maximum Deviation, |MAX| (kJ/mol) and the system with the maximum absolute deviation for different dispersion corrected DFT approaches using hybrid QM:QM results as reference.

		MUE	MSE	MAX	system
B3LYP	D2(Ne)	7.7	-3.7	18.8	C ₃ H ₈ /H-CHA
	D2	8.9	-8.1	18.8	C ₃ H ₈ /H-CHA
	D3	13.0	-12.1	24.8	C ₂ H ₆ /MgO(001)
	TS	13.3	-12.6	30.2	C ₂ H ₆ /MgO(001)
PBE	D2(Ne)	5.9	-2.9	12.0	C ₃ H ₈ /H-CHA
	D2	8.9	-6.9	14.2	C ₂ H ₆ /MgO(001)
	D3	10.7	-8.5	17.9	C ₂ H ₆ /MgO(001)
	TS	17.0	-16.0	31.5	C ₂ H ₆ /MgO(001)
	dDsC	11.1	-10.2	21.4	C ₃ H ₈ /H-CHA
	MBD/HI	5.6	-2.7	9.9	CO ₂ /Mg ₂ (dobdc)
	MBD/FI	5.5	-4.1	10.2	CO/MgO(001)
revPBE	vdW	9.4	-9.0	29.0	C ₃ H ₈ /H-CHA
optB86b	vdW	13.4	-13.4	25.6	C ₃ H ₈ /H-CHA

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