Density Functional Theory Study of the Interaction of H_2O, CO_2 and CO with the ZrO_2 (111), Ni/ZrO_2 (111), YSZ (111) and Ni/YSZ (111) Surfaces

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This document contains the binding energies at the non-equivalent adsorption sites for H_2O, CO_2 and CO molecules on ZrO_2(111) (**Figure S1** and **Table S1**), Ni/ZrO_2(111) (**Figure S2** and **Table S2**), YSZ(111) (**Figure S3** and **Table S3**) and Ni/YSZ(111) (**Figure S4** and **Table S4**). We have not reported here the zero point energy. This document also contains the $Zr_xO_yH_z$ clusters studied in Ref. 40 and discussed in our manuscript (**Figure S5**).

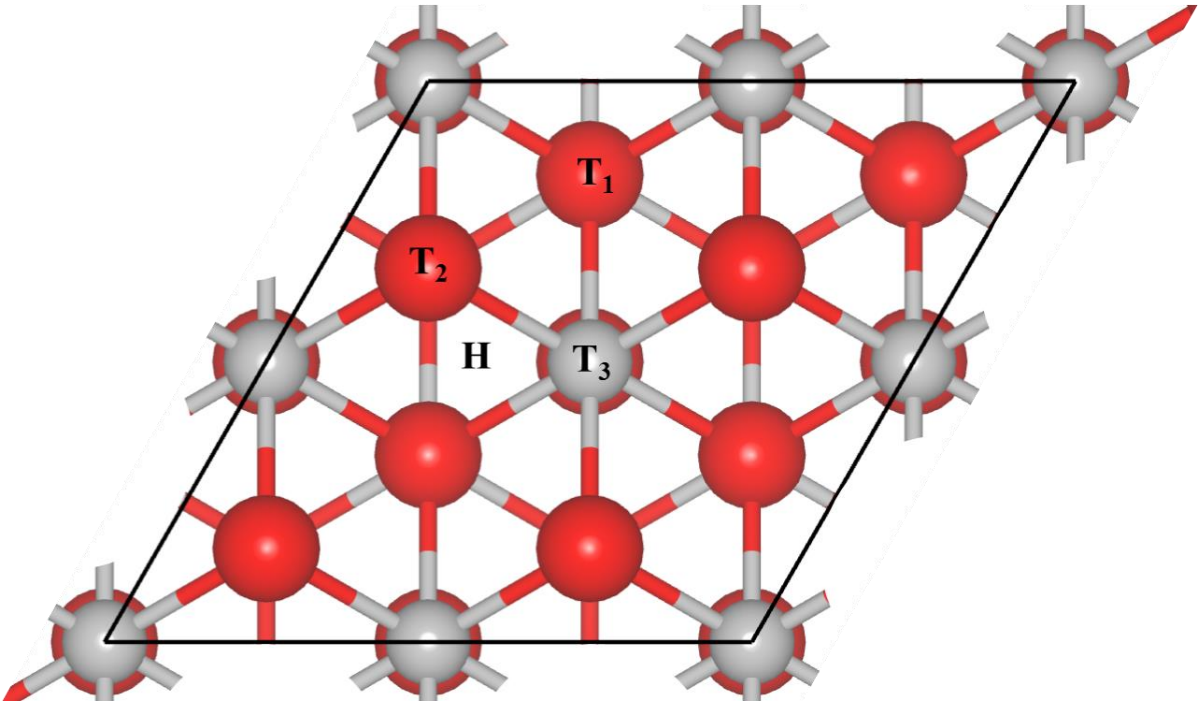

Figure S1 4 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on ZrO_2 (111) (top view). Colour key: red and grey spheres correspond to oxygen and Zr, respectively.

Table S1. Binding energies 9in eV) of the 4 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on ZrO_2 (111).

Molecules	Initial Adsorption site	Initial Orientation	Binding energy (eV)
H_2O	T_1	Parallel	-1.14
		Perpendicular	-1.14
	T_2	Parallel	-1.14
		Perpendicular	-1.14
	T_3	Parallel	-1.14
		Perpendicular	-1.14
	H	Parallel	-1.14
		Perpendicular	-1.14
CO_2	T_1	Parallel	-0.25
		Perpendicular	-0.25
	T_2	Parallel	-0.24
		Perpendicular	-0.24
	T_3	Parallel	-0.25
		Perpendicular	-0.25
	H	Parallel	-0.25
		Perpendicular	-0.25
CO	T_1	Parallel	-0.40
		Perpendicular	-0.10
	T_2	Parallel	-0.40
		Perpendicular	-0.40
	T_3	Parallel	-0.12
		Perpendicular	-0.40
	H	Parallel	-0.12
		Perpendicular	-0.40

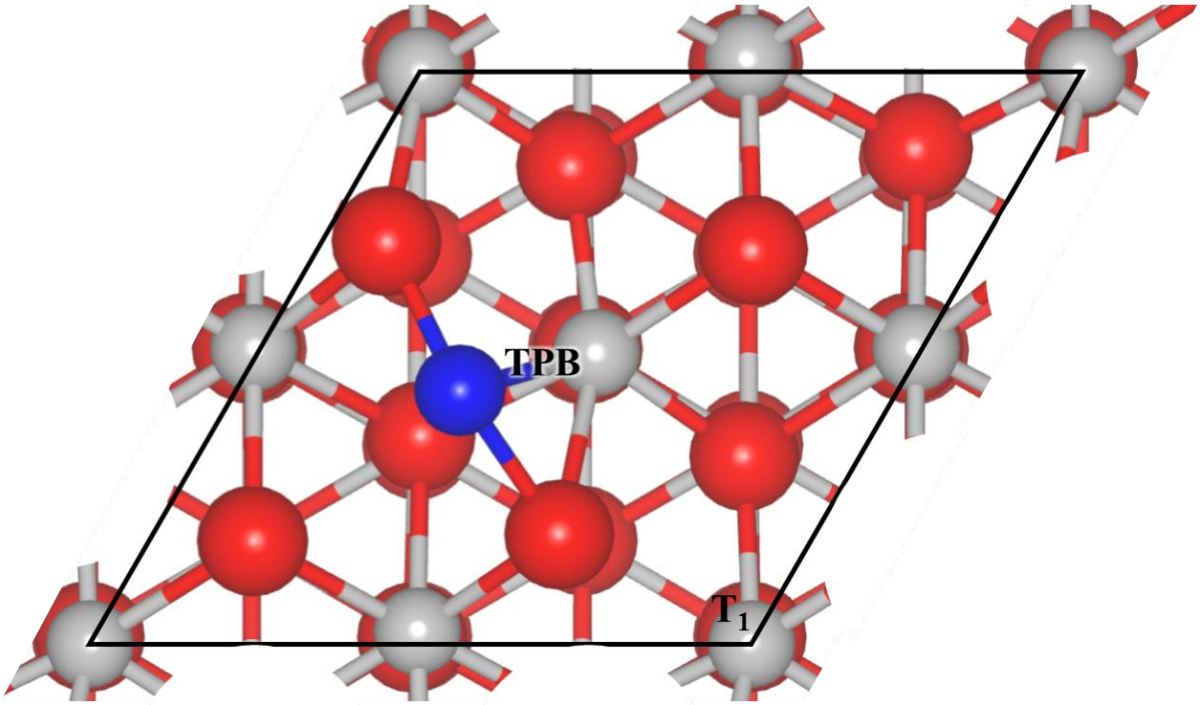

Figure S2. 2 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on Ni/ZrO_2 (111) (top view): at the triple phase boundary (TPB) and on top of the Zr (T1) which is the most favourable adsorption sites for the three molecules on the clean ZrO_2(111) surface. Colour key: red, grey and blue spheres correspond to oxygen, Zr and Ni respectively.

Table S2. Binding energies (in eV) of the 2 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on Ni/ZrO_2 (111).

Molecules	Initial Adsorption site	Initial Orientation	Binding energy (eV)
H_2O	TPB	Parallel	-1.46
		Perpendicular	-1.40
	T_1	Parallel	-0.78
CO_2	TPB	Parallel	-1.37
		Perpendicular	-0.23
	T_1	Parallel	-0.27
CO	TPB	Parallel	-0.28
		Perpendicular	-0.28
	T_1	Perpendicular	-0.47

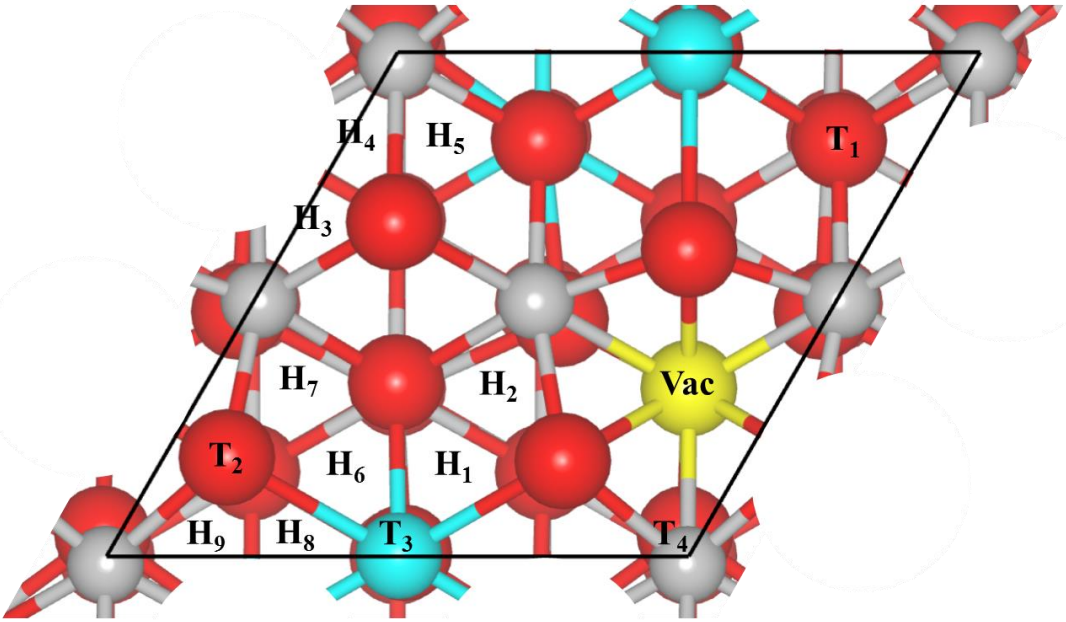

Figure S3. 5 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on YSZ (111) (top view). Colour key: red, grey and cyan spheres correspond to oxygen, Zr, and Y respectively. The oxygen vacancy is represented by the yellow sphere.

Table S3. Binding energies (in eV) of the 5 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on YSZ (111).

Molecules	Initial Adsorption site	Initial Orientation	Binding energy (eV)	Initial Adsorption site	Initial Orientation	Binding energy (eV)
H_2O	T_1	Parallel	-0.85	H_1	Parallel	-0.83
		Perpendicular	-0.85	H_2	Parallel	-0.39
	T_2	Parallel	-0.60	H_3	Parallel	-0.50
		Perpendicular	-0.86	H_4	Parallel	-0.54
	T_3	Parallel	-0.88	H_5	Parallel	-0.55
		Perpendicular	-0.87	H_6	Parallel	-0.86
	T_4	Parallel	-0.57	H_7	Parallel	-0.85
		Perpendicular	-0.57	H_8	Parallel	-0.85
	Vac	Parallel	-0.60	H_9	Parallel	-0.59
		Perpendicular	-0.29			
CO_2	T_1	Parallel	-0.36	H_1	Parallel	-0.31
		Perpendicular	-0.36	H_2	Parallel	-0.35
	T_2	Parallel	-0.27	H_3	Parallel	-0.17
		Perpendicular	-0.23	H_4	Parallel	-0.18
	T_3	Parallel	-0.37	H_5	Parallel	-0.18
		Perpendicular	-0.36	H_6	Parallel	-0.36
	T_4	Parallel	-0.36	H_7	Parallel	-0.36
		Perpendicular	-0.36	H_8	Parallel	-0.35
	Vac	Parallel	-0.28	H_9	Parallel	-0.35
		Perpendicular	-0.28			
CO	T_1	Parallel	-0.19	H_1	Perpendicular	-0.36
		Perpendicular	-0.38	H_2	Perpendicular	-0.25
	T_2	Parallel	-0.27	H_3	Perpendicular	-0.10
		Perpendicular	-0.27	H_4	Perpendicular	-0.17
	T_3	Parallel	-0.38	H_5	Perpendicular	-0.11
		Perpendicular	-0.38	H_6	Perpendicular	-0.37
	T_4	Parallel	-0.27	H_7	Perpendicular	-0.36
		Perpendicular	-0.27	H_8	Perpendicular	-0.36
	Vac	Parallel	-0.27	H_9	Perpendicular	-0.24
		Perpendicular	-0.23			

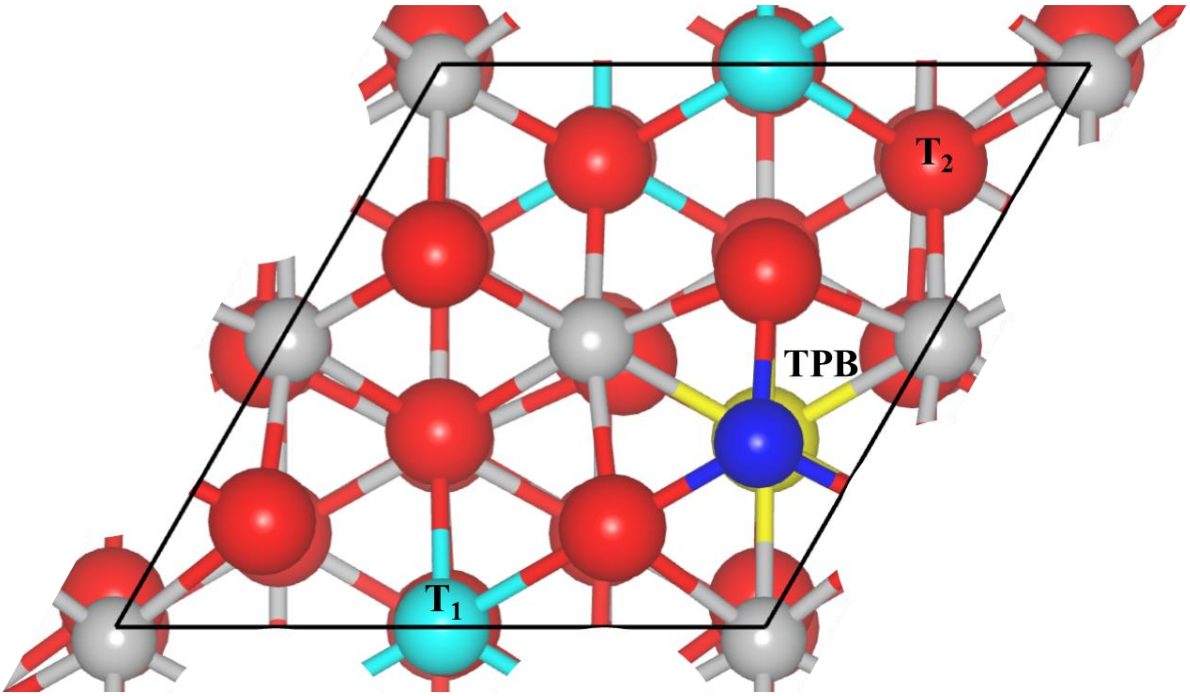

Figure S4. 2 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on Ni/YSZ (111) (top view): at the triple phase boundary (TPB) and on top of the Zr (T_1) and oxygen (T_2) which are the most favourable adsorption sites for H_2O and CO_2, and CO molecules on the clean YSZ (111) surface, respectively. Colour key: red, grey, cyan and blue spheres correspond to oxygen, Zr, Y and Ni respectively. The oxygen vacancy is represented by the yellow sphere.

Table S4. Binding energies (in eV) of the 2 non-equivalent initial adsorption sites for H_2O, CO_2 and CO molecules on Ni/YSZ (111).

Molecules	Initial Adsorption site	Initial Orientation	Binding energy (eV)
H_2O	TPB	Parallel	-0.34
		Perpendicular	-0.27
	T_1	Parallel	-0.73
CO_2	TPB	Parallel	-0.32
		Perpendicular	-0.32
	T_1	Parallel	-0.31
CO	TPB	Parallel	-2.37
		Perpendicular	-1.83
	T_2	Perpendicular	-0.36

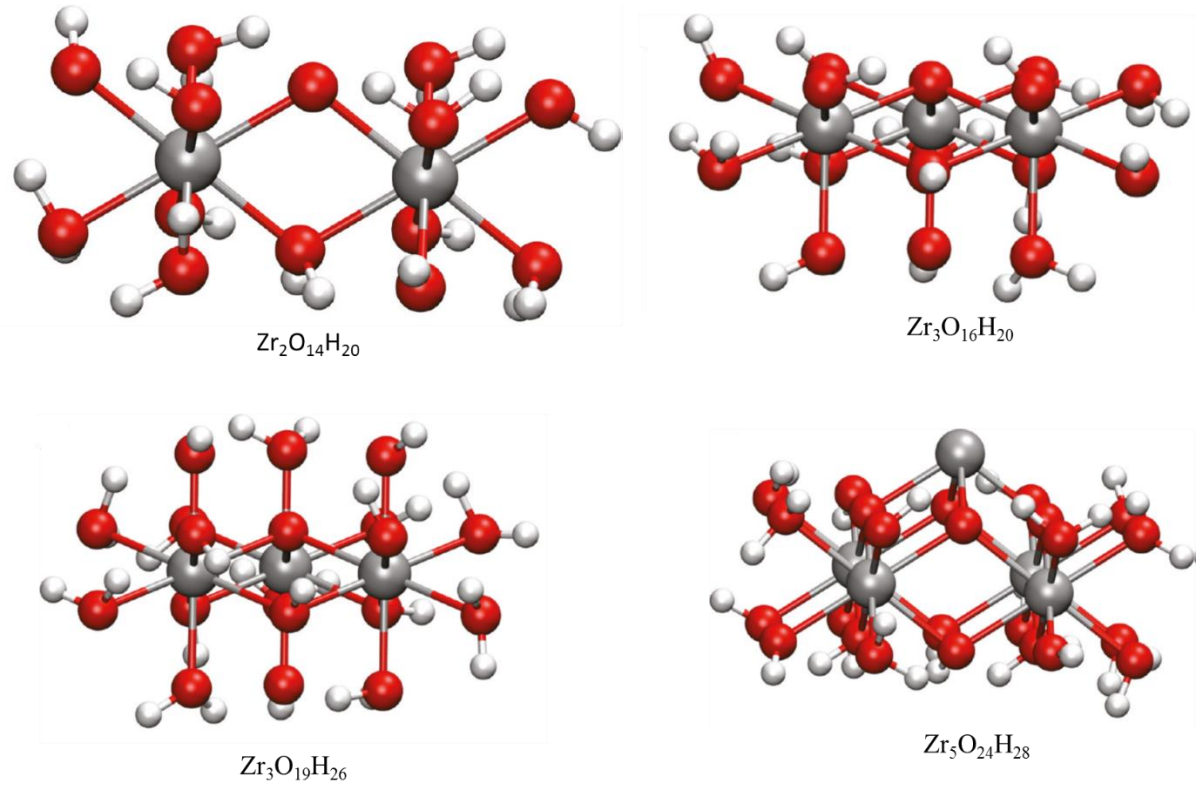

Figure S5 Representation of the $Zr_xO_yH_z$ clusters studied in Ref. 40 and discussed in our manuscript. Adapted with permission from V. Hornebecq, C. Kn, P. Boulet, B. Kuchta, P.L. Llewellyn, Adsorption of Carbon Dioxide on Mesoporous Zirconia: Microcalorimetric Measurements, Adsorption Isotherm Modeling, and Density Functional Theory Calculations, J. Phys. Chem. C. 115 (2011) 10097–10103. Copyright (2011) American Chemical Society.