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Alkaline-earth metal-oxide overlayers on TiO_2: Application toward CO_2 photoreduction

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Table S1 Lattice parameters for bulk alkaline-earth metal oxides and TiO_2 anatase.

	Experiment	DFT	DFT-D2
MgO	4.21[a]	4.24	4.19
CaO	4.81[a]	4.83	4.77
SrO	5.16[a]	5.21	5.13
BaO	5.52[a]	5.62	-
TiO_2 anatase	a= 3.79 c= 9.54[b]	a= 3.81 c= 9.73	a= 3.79 c= 9.73

[a]Experimental data is from reference [1].
[b]Experimental data is from reference [2].

Table S2 Calculated CO_2 adsorption energies (kJ/mol) on (100) surfaces of alkaline-earth metal oxides, MgO, CaO, SrO, and BaO with DFT and DFT-D2 methods.

	CO_2 Adsorption Energies (kJ/mol)							
	Type 1		Type 2		Type 3		Type 4	
	DFT	DFT-D2	DFT	DFT-D2	DFT	DFT-D2	DFT	DFT-D2
MgO	-28	-42	15	-25	-11	-34	-3	-14
CaO	-113	-129	-121	-137	14	-6	18	6
SrO	-159	-174	-174	-187	-17	-38	-8	-15
BaO	-210		-210		-13		-5	

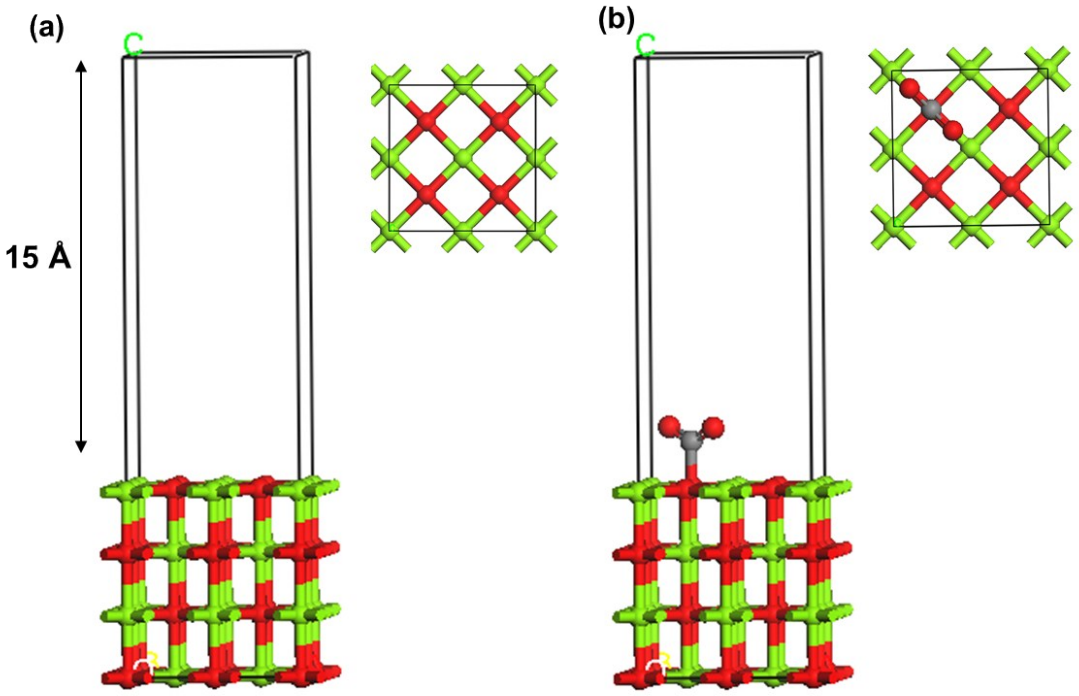

Figure S1 Alkaline earth metal oxide (100) 2x2 supercell (MgO as an example, 0.25 ML CO_2 in Type 1 geometry) used in this study for CO_2 adsorption. Red: O, Grey: Ti, Green: Mg, Dark Grey: C.

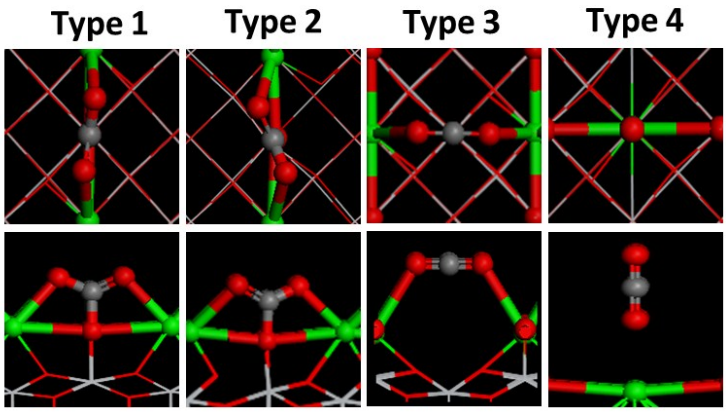

Figure S2 Four different geometries of CO_2 adsorption on 0.5 ML SrO/TiO_2. The coverage of CO_2 is 0.5 ML. Red: O, Grey: Ti, Green: Sr, Dark Grey: C.

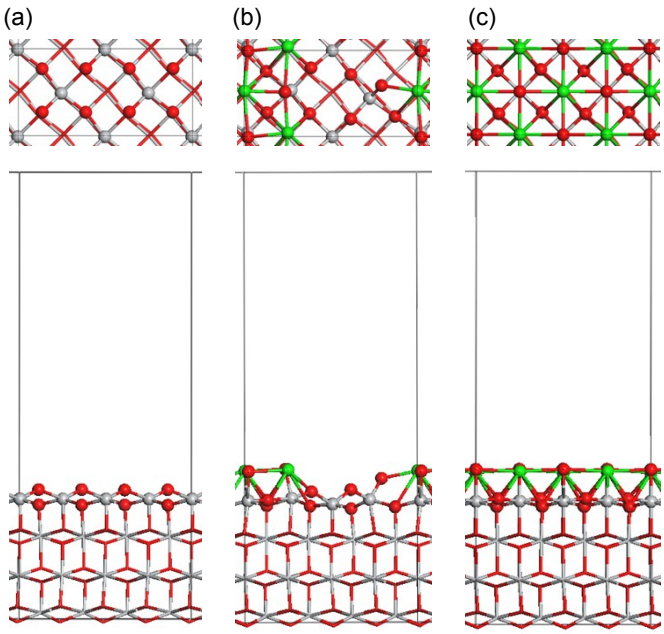

Figure S3 Top and side views for 2√2x√2 (a) TiO_2, (b) 0.5 ML SrO/TiO_2, and (c) 1 ML SrO/TiO_2 models used in this study for studying CO_2 reduction pathway. Red: O, Grey: Ti, Green: Sr.

Table S3. Entropic and zero-point energy (ZPE) corrections for molecules.

	TS (kJ/mol)	ZPE (kJ/mol)
H_2 (g)	39	26
H_2O (g)	56	55
CO (g)	59	13
CO_2 (g)	64	30

Table S4. Zero-point energy (ZPE) corrections (kJ/mol) for adsorbed species on the (2√2x√2) slabs.

	TiO_2		0.5 ML SrO/TiO_2		1 ML SrO/TiO_2	
	No 2 H_{ED}	With 2 H_{ED}	No 2 H_{ED}	With 2 H_{ED}	No 2 H_{ED}	With 2 H_{ED}
*CO_2	29	29	26	26	26	26
*COOH	56	56	55	55	55	51
*CO	13	12	13	12	9	9

References

[1] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Thomson Learning, 1976.
[2] A. Selloni, A. Vittadini, M. Grätzel, Surf. Sci. 402-404 (1998) 219.