Electronic Supplementary Information

Initial reduction of CO_2 on perfect and O-defective CeO_2(111) surfaces: towards CO or COOH?

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In order to understand the spin polarized effect, we have tested the adsorption of CO_2 with spin unrestricted and spin polarized on perfect and O-defective CeO_2(111). The adsorption energies are shown in the following Table S1. As shown in Table S1, the adsorption energies of CO_2 on perfect and O-defective CeO_2(111) surfaces with spin unrestricted and spin polarized are almost equal. The largest difference value comes from adsorbed CO_2 in D-2 configuration, which is only 0.07 eV (-0.88 *vs.* -0.81 eV) and is far smaller than the DFT itself deviation.

Table S1 Adsorption energies (in eV) of adsorbed CO_2 on perfect and O-defective CeO_2(111) surfaces with spin unrestricted and spin polarized.

Configurations	E_{ads} (spin unrestricted)	E_{ads} (spin polarized)
P-1	-0.54	-0.54
P-2	-0.38	-0.37
P-3	-0.12	-0.12
D-1	-0.69	-0.63
D-2	-0.88	-0.81
D-3	-1.12	-1.10