

Electronic Supplementary Information for

Water-Gas-Shift Reaction on Reduced Gold-Substituted $\text{Ce}_{1-x}\text{O}_2(111)$ Surfaces: the Role of Au Charges

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Table S1. Comparison between the results obtained by the PW91 and HSE06 exchange-correlation functionals for the reaction of $\text{H}_2\text{O}^{\text{V}} + \text{Au} \rightarrow \text{OH}^{\text{V}} + \text{H}^{\text{Au}}$ on various reduced $\text{Au}@V_{\text{Ce}}$ surfaces with a $p(3 \times 3)$ supercell.

Oxygen vacancies	$\Delta E_{\text{rxn}} / \text{eV}$	
	PW91	^a HSE06
(V ₀₁)-	1.63	1.50
(V ₀₁ , V ₀₂)-	0.66	0.69
(V ₀₁ , V ₀₂ , V ₀₃)-	0.53	0.58
(V ₀₁ , V ₀₂ , V ₀₄)-	-0.51	-0.62

^a. Single point calculations were carried using a (1×1×1) k-point mesh on the geometries predicted by the PW91 functional.

Table S2. Comparison of various results obtained by (2×2×1) and (4×4×1) k-point meshes. The calculations were carried out by the PW91 functional on various reduced Au@V_{Ce} surfaces with a p(3×3) supercell without the zero-point energy correction. q[Au]: the Bader charge on Au; E_f^V : the formation energy of oxygen vacancies; $E_{ads}(H_2O)$: the adsorption energy of a water molecule.

Oxygen vacancies	q[Au] / e		E_f^V /eV		$E_{ads}(H_2O)$ /eV	
	2×2×1	4×4×1	2×2×1	4×4×1	2×2×1	4×4×1
(V _{O1})-	1.12	1.19	-0.03	-0.03	-0.81	-0.79
(V _{O1} , V _{O2})-	0.40	0.41	1.21	1.21	-0.94	-0.94
(V _{O1} , V _{O2} , V _{O3})-	0.33	0.33	2.10	2.12	-0.83	-0.85
(V _{O1} , V _{O2} , V _{O4})-	-0.59	-0.59	3.64	3.64	-0.93	-0.93

Table S3. The imaginary Frequency (IMF) of the transition state for each step of the proposed WGS reaction mechanism on the Au@V_{Ce} surfaces with various oxygen vacancy configurations

Elementary Step	Oxygen Vacancies	IMF /cm ⁻¹
$\text{H}_2\text{O}^{\text{V}} \rightarrow \text{OH}^{\text{V}} + \text{H}^{\text{Au}}$	(V _{O1})-	242 <i>i</i>
	(V _{O1} , V _{O2})-	269 <i>i</i>
	(V _{O1} , V _{O2} , V _{O3})-	578 <i>i</i>
	(V _{O1} , V _{O2} , V _{O4})-	479 <i>i</i>
$\text{CO}_{(\text{g})} + \text{OH}^{\text{V}} \rightarrow \text{cis-OCOH}^*$	(V _{O1} , V _{O2})-	288 <i>i</i>
	(V _{O1} , V _{O2} , V _{O3})-	145 <i>i</i>
	(V _{O1} , V _{O2} , V _{O4})-	132 <i>i</i>
$\text{cis-OCOH}^* + \text{H}^{\text{Au}} \rightarrow \text{CO}_2^* + \text{H}_2^*$	(V _{O1} , V _{O2})-	693 <i>i</i>
	(V _{O1} , V _{O2} , V _{O3})-	753 <i>i</i>
	(V _{O1} , V _{O2} , V _{O4})-	425 <i>i</i>

CO oxidation (oxygen vacancy creation)

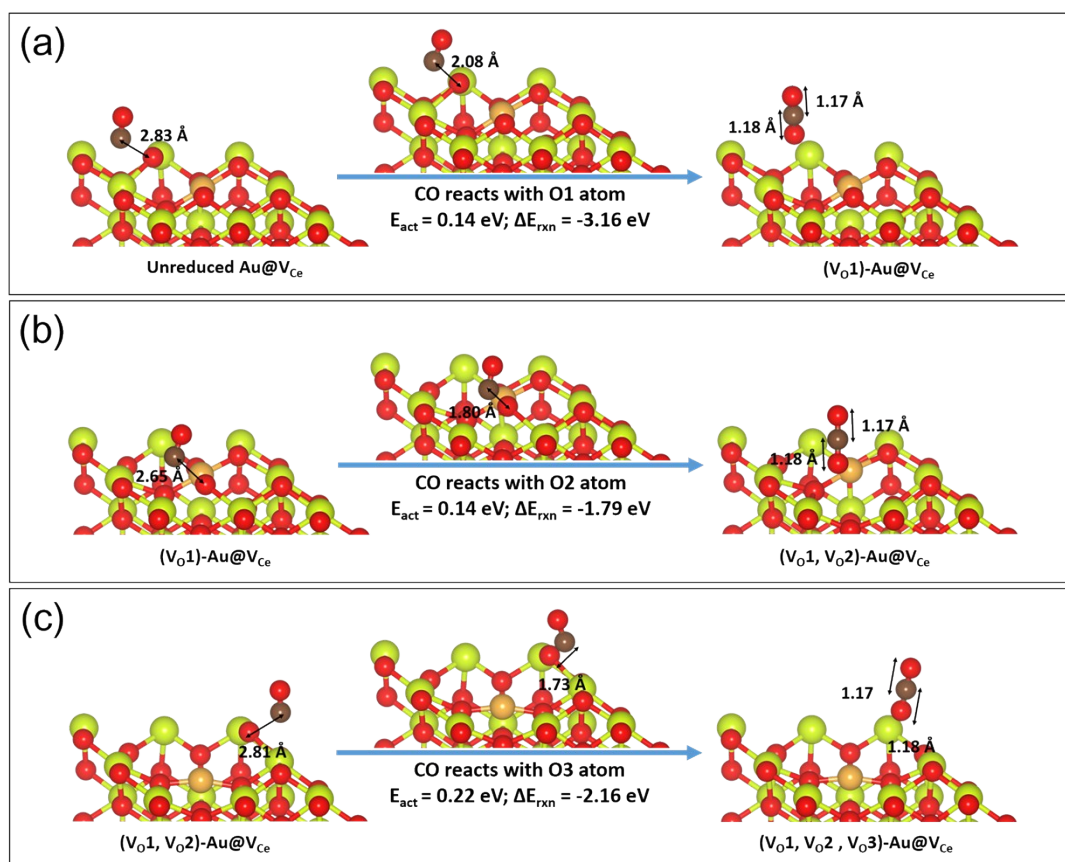


Figure S1. Structures and energies without the zero-point energy correction for CO molecules reacting with surface oxygens on (a) the unreduced-, (b) the (V_{O1})- and (c) the (V_{O1}, V_{O2})-Au@V_{Ce} surfaces. Ce, O, Au, and C atoms are shown by green, red, orange and brown spheres, respectively. The (V_{O1}, V_{O2}, V_{O4})-Au@V_{Ce} surface is created by migration of the O₄ oxygen atom of the (V_{O1}, V_{O2}, V_{O3})-Au@V_{Ce} surface to the V_{O3} vacancy with surface relaxation. The migration reaction is 1.54 eV.