

Supplementary Information for:

**Understanding CO oxidation on the Pt(111) surface
based on reaction route network**

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S1. Effects of the number of layers and adsorption-induced surface relaxation

The energies for four kinds of adsorbates were computed by using different slab models, frozen two-layered slab (a), frozen three-layered slab (b), and a thawed layer over frozen two-layered slab model (c). Table S1 shows the relative electronic energies to the total energy of CO(g), O₂(g), and the “clean” slab. The effect of introduction of the third layer is small. The adsorption-induced surface relaxation was observed in our calculation around O atom adsorbed in the fcc hollow site, however, the relaxation of the first layer does not affect largely on energy except CO₂(g)+O (MIN0). Such stabilization of CO₂(g)+O (product) structures does not affect our kinetic analysis, so that we adopted the frozen two-layered slab model in this study.

Table S1. Electronic energies of the most stable structure of each adsorption state, CO+O₂ (MIN114), CO+2O (MIN83), OC-OO (MIN131), and CO₂(g)+O (MIN0), relative to that of CO(g)+O₂(g). (a) frozen two-layered slab model, (b) frozen three-layered slab model, (c) a thawed layer over frozen two-layered slab model.

	ΔE [kJ mol ⁻¹]		
	(a)	(b)	(c)
CO+O ₂ (MIN114)	-288.1	-275.7	-291.7
CO+2O (MIN83)	-389.1	-379.1	-378.2
OC-OO (MIN131)	-242.0	-240.7	-248.0
CO ₂ (g)+O (MIN0)	-426.9	-426.3	-445.7

S2. Adsorption energies and adsorption sites of CO, O₂, and O atom on the Pt(111) surface

The adsorption free energy (ΔG_{ads}) was calculated as the difference between the Gibbs energy of the molecule adsorbed on the Pt slab ($G_{\text{mol+slab}}$) and the sum of the Gibbs energies of the molecule in the gas phase (G_{mol}) and the “clean” slab (G_{slab}):

$$\Delta G_{\text{ads}} = G_{\text{mol+slab}} - (G_{\text{mol}} + G_{\text{slab}})$$

The Pt slab was kept frozen throughout this study, then G_{slab} is identical to the potential (electronic) energy (E_{slab}). Calculated adsorption energies at 300 K for CO, O₂, and O atom were listed in Table S2(a)–(c). For CO adsorption, the fcc hollow site gives the largest adsorption energy, but a number of experimental results suggest the atop site is the most favorable adsorption site for CO molecule.^{1–5} This problem is known as CO puzzle, and only meta-GGA or hybrid functional can reproduce the experimental trend.^{4,5} However, the all of CO(fcc)+O₂, CO(hcp)+O₂, and CO(atop)+O₂ adsorption states are contracted into the same superstate in our RCMC kinetic analyses (see Figures 2 and 4), because CO migration paths occur in a much shorter timescale than bond rearrangement processes between CO and O₂. Therefore, we do not distinguish the adsorption sites for our purpose in this study. In case of O₂ molecular adsorption, the top-bridge-top (t-b-t) configuration is most preferable which is consistent with previous studies,^{6,7} and the chemisorption makes superoxide state (O₂⁻) of oxygen. The fcc hollow site is most preferable in the case for O atomic adsorption. Our calculated adsorption energies might be comparable with the experimental values.⁸ The adsorption energy depends on the coverage of adsorbate, especially at the low coverage range. Our computational model corresponds to the coverage of 1/16 ML (0.0625 ML),⁹ and we listed the adsorption heats ($\Delta H_{\text{ads,exp}}$) from the experimental data in Ref. 8 in Table S2. It is known that O₂ molecule on the Pt(111) easily dissociate in the low coverage range (< 0.5 ML) even at low temperature,^{6,7,10–13} so that we added the adsorption heat for O₂ molecular adsorption,

which was determined in the high coverage limit at 100K,¹⁰ in Table S2.

Table S2. Adsorption free energies (ΔG_{ads}), enthalpies (ΔH_{ads}), and entropies (ΔS_{ads}) for CO, O₂, and O on the Pt(111) surface at 300 K, at 1/16 ML coverage.

(a) CO	atop	fcc	hcp
ΔG_{ads} [kJ mol ⁻¹]	-133.3	-158.6	-151.3
ΔH_{ads} [kJ mol ⁻¹]	-180.3	-206.2	-200.0
ΔS_{ads} [J mol ⁻¹ K ⁻¹]	-156.6	-158.6	-162.6
$\Delta H_{\text{ads,exp}}$ [kJ mol ⁻¹] ⁸		-175	
(b) O₂	t-b-t	t-f-b	t-h-b
ΔG_{ads} [kJ mol ⁻¹]	-23.0	-15.2	-10.8
ΔH_{ads} [kJ mol ⁻¹]	-71.3	-62.0	-57.5
ΔS_{ads} [J mol ⁻¹ K ⁻¹]	-161.0	-155.8	-156.0
$\Delta H_{\text{ads,exp}}$ [kJ mol ⁻¹] ¹⁰		(-38) [†]	
(c) O atom	atop	fcc	hcp
ΔG_{ads} [kJ mol ⁻¹]	-220.6	-317.6	-290.8
ΔH_{ads} [kJ mol ⁻¹]	-254.7	-355.5	-328.7
ΔS_{ads} [J mol ⁻¹ K ⁻¹]	-115.5	-128.1	-128.1
$\Delta H_{\text{ads,exp}}$ [kJ mol ⁻¹] ⁸		-250	

[†] Experimental data in the high coverage limit at 100K, and the heat of compression (RT term) added to the experimentally measured differential heat of adsorption from thermal desorption spectra (TDS).

References and Notes

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