

Identifying the Morphology of Pt Nanoparticles for the Optimal Catalytic Activity towards CO Oxidation

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Theoretical Methods

MSR model. The MSR model was based on the Wulff theory,¹ adsorption isotherms and first-principles calculations to quantitatively predict the equilibrium geometries of metal NPs under reactive gas conditions.²

In CO oxidation reaction atmosphere, considering the adsorption of CO and O₂ (dissociative adsorption) on NP surface, the equilibrium shape of Pt NPs can be constructed using the modified interface tension:

$$\gamma_{hkl}^{int} = \gamma_{hkl} + [\theta_{CO}(E_{ads}^{CO} - z(w_{CO-CO}\theta_{CO} + w_{CO-O}\theta_O)) + \theta_O(E_{ads}^O - z(w_{CO-O}\theta_{CO} + w_{O-O}\theta_O))]/A_{at} \quad (1)$$

where γ_{hkl} is the surface tension under vacuum, E_{ads} is the adsorption energy of one gas molecule on the surface, z is the number of the nearest neighbors of an adsorption site, w is the lateral interactions between the first neighboring adsorbed molecules on the surface, and A_{at} is the surface area per surface atom site. θ is the coverage of the adsorbates on the surface, which can be derived based on the Fowler-Guggenheim (F-G) adsorption isotherm:³

$$\frac{\theta_{CO}}{1 - (\theta_{CO} + \theta_O)} = P_{CO} K_{CO} \exp\left(\frac{z(w_{CO-CO}\theta_{CO} + w_{CO-O}\theta_O)}{k_B T}\right) \quad (2)$$

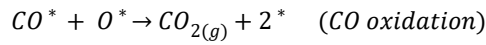
$$\frac{\theta_O}{1 - (\theta_{CO} + \theta_O)} = \sqrt{P_{O_2} K_{O_2}} \exp\left(\frac{z(w_{CO-O}\theta_{CO} + w_{O-O}\theta_O)}{k_B T}\right) \quad (3)$$

where P is the gas pressure, T is the temperature, k_B is the Boltzmann constant. K is the equilibrium constant which is defined as:

$$K = \exp\left(-\frac{E_{ads} - T(S_{ads} - S_{gas})}{k_B T}\right) \quad (4)$$

where S_{ads} is the entropy of adsorbed gas molecule, and S_{gas} is the entropy of gas-phase molecule obtained from the NIST-JANAF thermochemical tables.⁴

KMC Model. For the CO oxidation reaction over Pt NPs, seven reaction-related elementary steps are considered as follows:



where the * represents a surface site and the subscript i/j represent different surface site. The Gillespie algorithm was adopted in the KMC simulation.^{5,6} The time for the system changing from one state to another is given by:

$$\Delta t = -\frac{\ln(u)}{k_{tot}} \#(5)$$

where k_{tot} is the sum of the rate constants of all possible events, u is a random number on the interval (0,1].

The adsorption rate constants are calculated by the collision theory:

$$k_{ads} = \frac{s_0 A_{at} P}{\sqrt{2\pi M k_B T}} \#(6)$$

where s_0 is the sticking coefficient of adsorbate, and M is the mass of the gas molecule. The sticking coefficients of CO and O are estimated based on the experimental values.⁷⁻⁹

The desorption rate constants can be obtained by the adsorption equilibrium isotherm:

$$k_{des} = \frac{k_{ads}}{KP} \#(7)$$

The transition state theory (TST) is utilized to evaluate the diffusion and the reaction rate constants:¹⁰

$$k = \frac{k_B T}{h} \left(\frac{Z^{TS}}{Z^{IS}} \right) \exp\left(-\frac{E_a}{k_B T}\right) \quad (8)$$

where h is the Planck constant, Z^{TS} and Z^{IS} are the partition functions for the transition and initial state, respectively (in this work $\frac{Z^{TS}}{Z^{IS}} \approx 1$). E_a is the corresponding energy barrier.

The adsorption energies were obtained by fitting a scaling relationship with the generalized coordination numbers (GCN), which has been described in detail in the previous work of Calle-Vallejo et al.¹¹ The energy barriers for CO oxidation reaction were evaluated by the Brønsted-Evans-Polanyi (BEP) relations with the fitted adsorption energies of CO and O.¹² In our simulation, the interaction effect between adsorbed molecules is included by considering the repulsion energy between the nearest neighbor adsorbates (w_{CO-CO} , w_{CO-O} , w_{O-O}). The effective adsorption energy of CO (O) at sites with n_{CO} nearest neighbors adsorbed CO and n_O nearest neighbors adsorbed O are calculated by:

$$E_{ads}^{eff}(CO) = E_{ads}^{CO} - (n_{CO}w_{CO-CO} + n_Ow_{CO-O}) \quad (9)$$

$$E_{ads}^{eff}(O) = E_{ads}^O - (n_Ow_{O-O} + n_{CO}w_{CO-O}) \quad (10)$$

The repulsion energies between adsorbed molecules were estimated by averaging the corresponding values on (100), (110), and (111) surfaces of Pt. For diffusion barrier on the terrace, the values of 0.58 eV and 0.05 eV were obtained for O and CO diffusion on Pt (111) surface by DFT calculation. In order to speed up the simulations, the diffusion barrier of CO is increased to 0.68 eV. This method has been proven reliable and applied in previous studies.^{9, 13-15} For diffusion across the step sites, the barriers are calculated by adding 0.68 (0.58) to the difference in adsorption energy of CO (O) at different sites.

DFT Calculations. All calculations in this work were performed with the spin-polarized density functional theory (DFT) within the Vienna Ab Initio Simulation Package (VASP).¹⁶⁻¹⁹ The projector augmented wave (PAW) approach²⁰ with a plane-wave energy cutoff of 400 eV was used. The electronic self-consistent energy and the forces on all atoms are converged within 10^{-5} eV and 0.05 eV/Å, respectively.

The Perdew, Burke, and Ernzerhof formulation of the generalized-gradient approximation (GGA-PBE)^{21,22} was used to obtain the surface tensions of three low-index facets (100), (110) and (111) of Pt by optimizing (1×1) supercells with different atomic layers. The revised-PBE (RPBE) exchange-correlation functional was used to get the adsorption energies and the lateral interactions of CO and O on Pt surfaces. The reason of using the RPBE functional only in the adsorption calculations is because it was reported to give more precise gas-metal interaction but less accurate metal surface energy.²³⁻²⁵ The (4×4), (2×2) and (1×1) slab models were constructed to calculate E_{ads}^{CO}/E_{ads}^O , W_{CO-O} and W_{CO-CO}/W_{O-O} , respectively. The energy barriers of diffusion and reaction were obtained by the climbing-image nudged elastic band (CI-NEB) method from VTST tools.²⁶

²⁷ All slab models were separated with a 15 Å vacuum space along the Z axis. Each model contained 6 atomic layers, and the bottom 2 layers were fixed. The K points were set to be (3 × 3 × 1), (4 × 4 × 1), and (8 × 8 × 1) for the (4 × 4), (2 × 2), and (1 × 1) supercells, respectively. All related parameters required for MSR model and KMC simulation are listed in Table S1 and Table S2.

Table S1. Data required for MSR model: surface tension under vacuum γ_{hkl} (eV/Å²), adsorption energies E_{ads} (eV) and lateral interactions w (eV).

	γ_{hkl}	E_{ads}		w		
		CO	O	w_{CO-CO}	w_{O-O}	w_{CO-O}
Pt (100)	0.112	-1.703	-1.026	-0.172	-0.129	-0.137
Pt (110)	0.113	-1.865	-1.153	-0.192	-0.224	-0.216
Pt (111)	0.087	-1.494	-0.982	-0.198	-0.176	-0.129

Table S2. Equations and fitting parameters required for KMC simulation.

Adsorption energy (eV)	CO	$E_{ads}^{CO} = -2.90 + 0.18 \times GCN$
	O	$E_{ads}^O = -2.49 + 0.22 \times GCN$
Energy barrier (eV)	CO oxidation reaction	$E_a^{rea} = 1.41 + 0.24 \times (E_{ads}^{CO} + E_{ads}^O)$
	CO diffusion	0.68
	O diffusion	0.58
Repulsive energy (eV)	CO-CO	-0.187
	O-O	-0.176
	CO-O	-0.160
Sticking coefficient	CO	1.0 (edges & corners), 0.9 (facets)
	O	1.0 (edges & corners), 0.1 (facets)

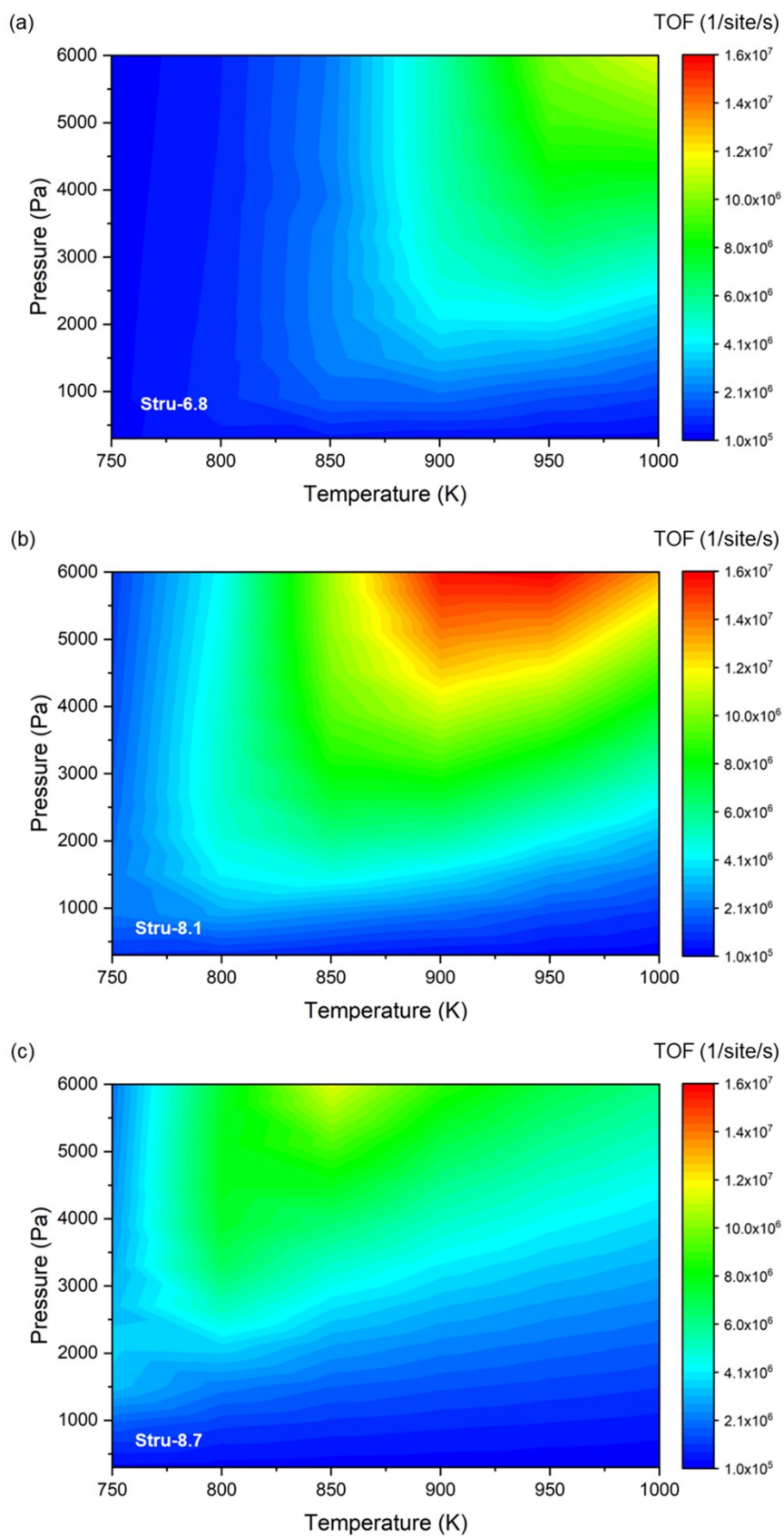
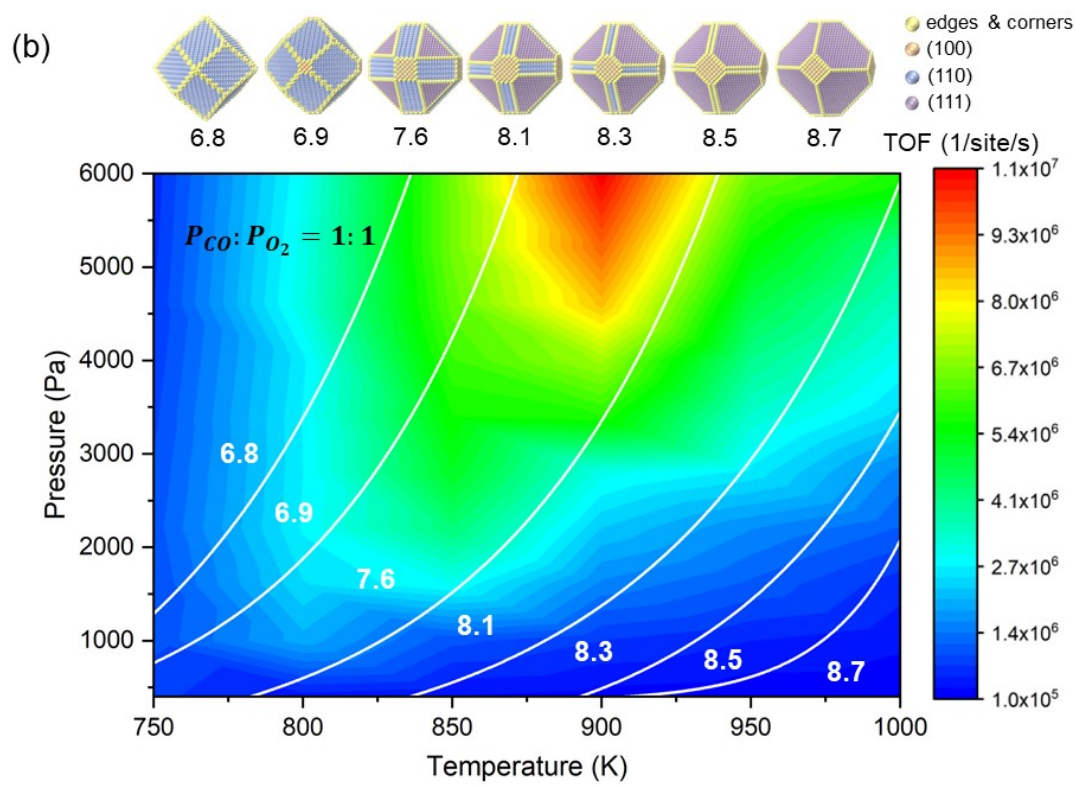
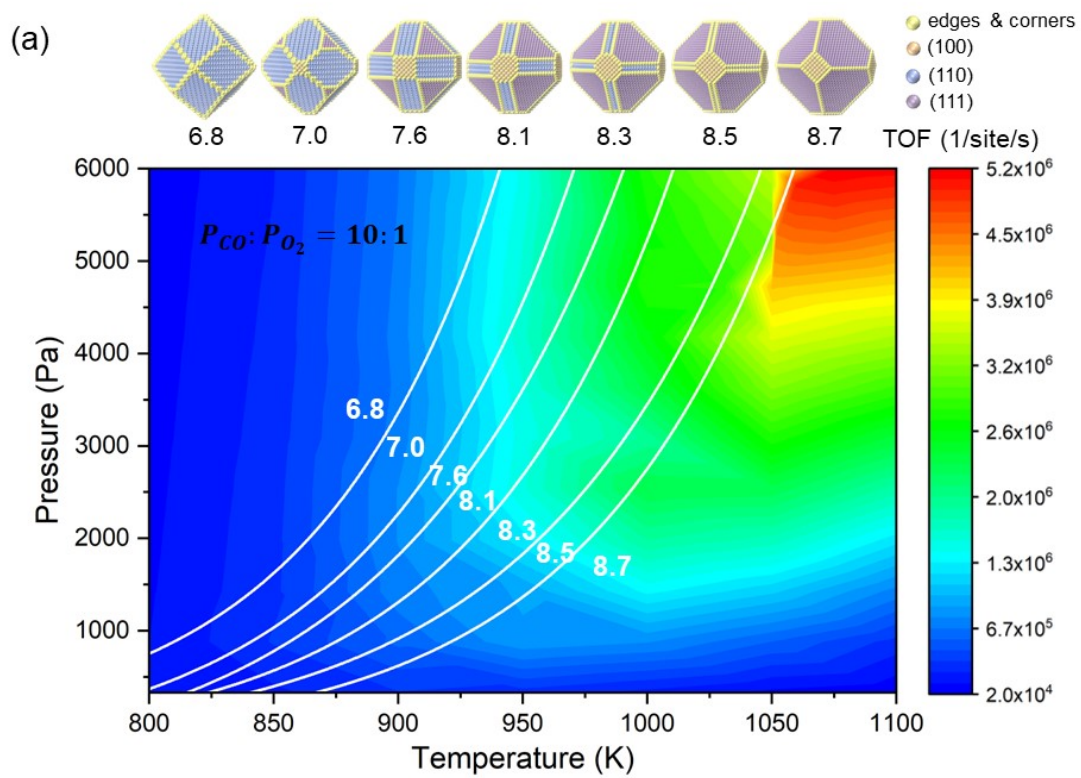


Fig. S1 The contour plot of the TOF under different temperatures and total pressures ($P_{CO}/P_{O_2} = 2:1$) for Stru-6.8 (a) and Stru-8.7 (b).



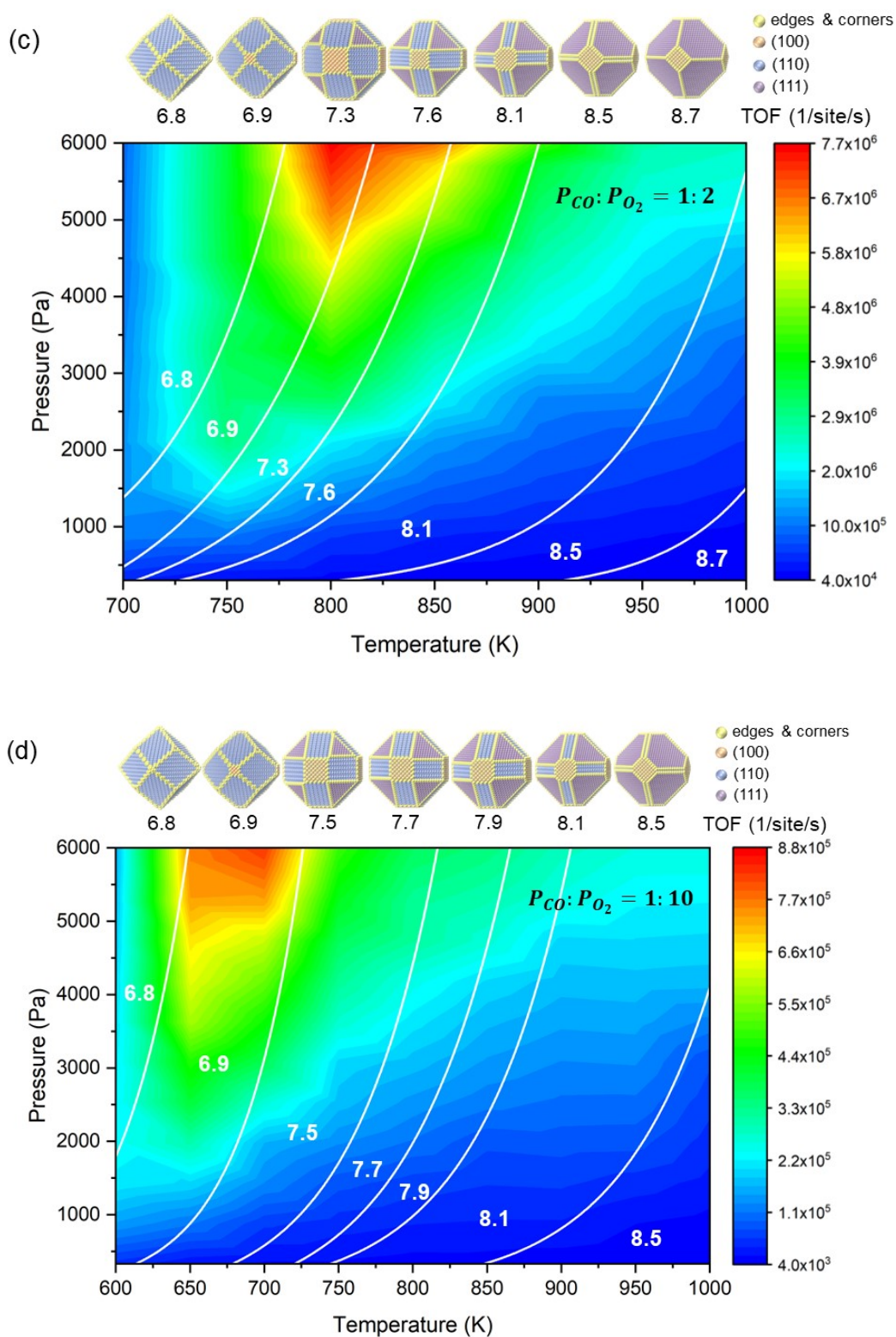


Fig. S2 The contour plot of the TOF under different temperatures and total pressures with P_{CO}/P_{O_2} of 10:1 (a), 1:1 (b), 1:2 (c), 1:10 (d) for RCD structures. Typical structures with different CN are shown at the top of each figure.

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