Density Functional Theory (DFT) Studies of CO Oxidation Reaction on M_{13} and $Au_{18}M$ Clusters (M = Au, Ag, Cu, Pt and Pd): The Role of Co-adsorbed CO Molecule

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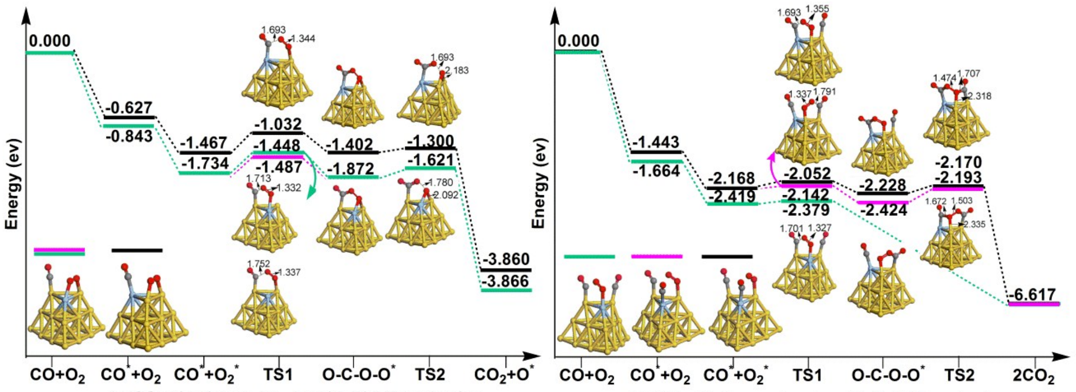
Figure S1. Energy diagrams of CO oxidation on $Au_{18}M$ (M=Ag, Cu, Pt, Pd) doped cluster under both bi-molecular LH and tri-molecular LH mechanism. The symbol '*' refers to the atom or molecule or the intermediate being adsorbed on the $Au_{18}M$-cluster (M=Ag, Cu, Pt, Pd). The energies (in eV) are computed at the PBE/DND level. The bond length is in unit of Å.

Figure S2. The PDOS of heteroatom M of $Au_{18}M$ cluster and $Au_{18}M$-CO model is displayed (M=Au, Ag, Cu, Pt, Pd).

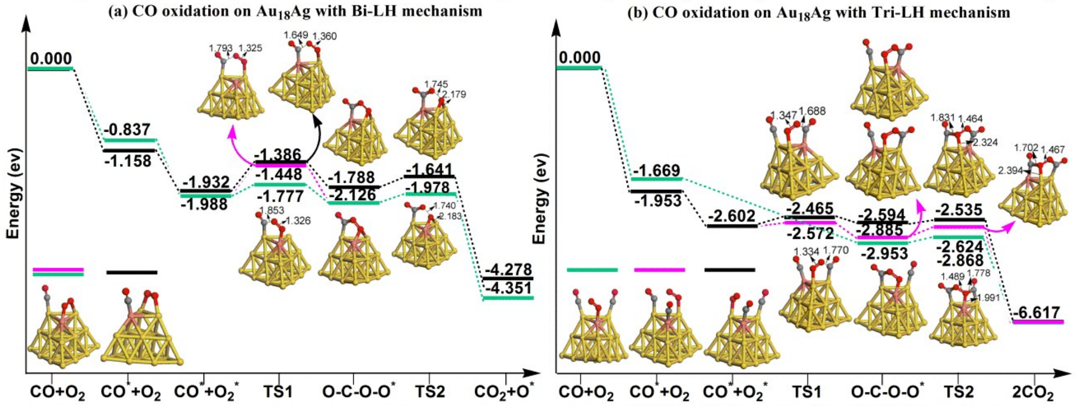
Part S1. Details of micro-kinetic analysis of the reaction rate for CO oxidation over M_{13} and $Au_{18}M$ (M=Au, Ag, Cu, Pt, Pd) clusters.

Part S2. Details of Kinetic Monte Carlo Simulations



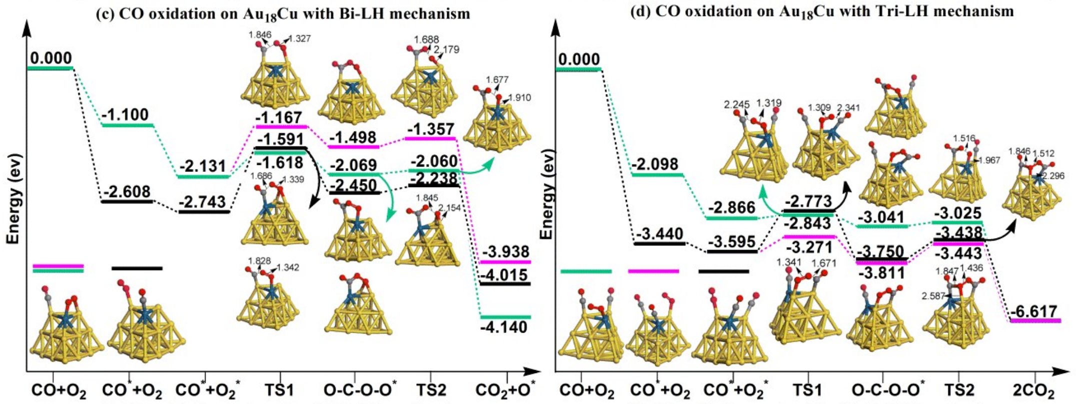
(a) CO oxidation on Au$_{18}$Ag with Bi-LH mechanism

(b) CO oxidation on Au$_{18}$Ag with Tri-LH mechanism



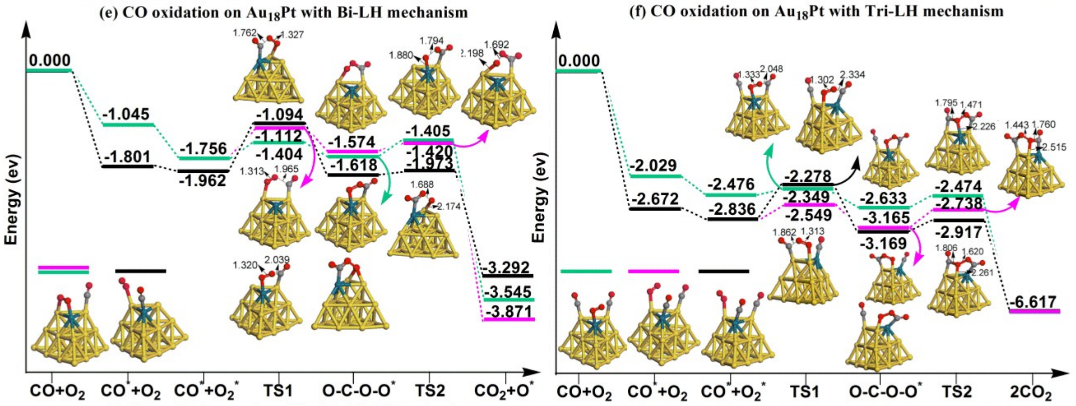
(c) CO oxidation on Au$_{18}$Cu with Bi-LH mechanism

(d) CO oxidation on Au$_{18}$Cu with Tri-LH mechanism



(e) CO oxidation on Au$_{18}$Pt with Bi-LH mechanism

(f) CO oxidation on Au$_{18}$Pt with Tri-LH mechanism



(g) CO oxidation on Au$_{18}$Pd with Bi-LH mechanism

(h) CO oxidation on Au$_{18}$Pd with Tri-LH mechanism

Figure S1. Energy diagrams of CO oxidation on Au$_{18}$M (M=Ag, Cu, Pt, Pd) doped cluster under both bi-molecular LH and tri-molecular LH mechanism. The symbol '*' refers to the atom or molecule or the intermediate being adsorbed on the Au$_{18}$M-cluster (M=Ag, Cu, Pt, Pd). The energies (in eV) are computed at the PBE/DND level. The bond length is in unit of Å.

TableS1. The energy parameters used in the reaction rate calculations for CO oxidation over icosahedra M_{13}. The Energy is in the unit eV.

Reaction Mechanism	M_{13}	$E_{ad}(CO)$	$E_{ad}(O_2)$	$E_a(TS1)$	$E_a(TS2)$	$E_a(TS)$	$R(s^{-1})$
Bi-molecular	Au_{13}	-1.467	-0.582	0.374	0.311	0.374	6.499×10^{-8}
	Ag_{13}	-1.218	-0.706	0.177	0.560	0.560	2.273×10^{2}
	Cu_{13}	-1.792	-1.124	0.203	0.216	0.216	2.387×10^{-1}
	Pt_{13}	-2.449	-0.792	0.777	0.002	0.777	8.548×10^{-28}
	Pd_{13}	-1.953	-0.843	0.510	0.060	0.510	5.067×10^{-14}
Tri-molecular	Au_{13}	-2.871	-0.433	0.296	0.442	0.442	3.467×10^{-9}
	Ag_{13}	-2.112	-0.577	0.267	0.160	0.267	5.646×10^{-2}
	Cu_{13}	-3.472	-0.979	0.258	0.590	0.590	9.611×10^{-5}
	Pt_{13}	-4.908	-0.790	0.779	1.102	1.102	1.193×10^{-28}
	Pd_{13}	-3.755	-0.745	0.430	0.648	0.648	2.499×10^{-14}

Table S2. The energy parameters used in the reaction rate calculations for CO oxidation over $\mathrm{Au_{18}M}$ (M = Au, Ag, Cu, Pt and Pd). The Energy is in the unit eV. The reaction pathways **a-c** and **a'-c'** refer to Scheme 1.

CO Oxidation under Bimolecular LH Mechanism (Involving One CO and One O_2 Molecule)

Clusters	Reaction Pathways	$E_{ad}(CO)$	$E_{ad}(O_2)$	$E_a(TS1)$	$E_a(TS2)$	$E_a(TS)$	$R(s^{-1})$
$\mathrm{Au_{19}}$[d]		-0.640	-0.640	0.500	0.260	0.500	9.337×10^{2}
$\mathrm{Au_{18}Ag}$	**a**	-0.843	-0.891	0.286	0.251	0.286	6.477×10^{5}
	b	-0.843	-0.891	0.247	0.251	0.251	2.922×10^{6}
	c	-0.627	-0.839	0.435	0.102	0.435	3.377
$\mathrm{Au_{18}Cu}$	**a**	-0.837	-1.151	0.211	0.148	0.211	3.869×10^{2}
	b	-0.837	-1.151	0.540	0.149	0.540	1.049×10^{-3}
	c	-1.158	-0.774	0.546	0.147	0.546	2.396×10^{-2}
$\mathrm{Au_{18}Pt}$	**a**	-1.100	-1.031	0.513	0.009	0.513	3.141×10^{3}
	b	-1.100	-1.031	0.964	0.140	0.964	7.349×10^{-5}
	c	-2.608	-0.135	1.152	0.212	1.152	6.028×10^{-48}
$\mathrm{Au_{18}Pd}$	**a**	-1.045	-0.712	0.352	0.213	0.352	3.348×10^{2}
	b	-1.045	-0.712	0.645	0.154	0.645	3.692×10^{-3}
	c	-1.801	-0.161	0.868	0.010	0.868	4.784×10^{-29}

CO Oxidation under Trimolecular LH Mechanism (Involving Two CO and One O_2 Molecule)

Clusters	Reaction Pathways	$E_{ad}(CO)$	$E_{ad}(O_2)$	$E_a(TS1)$	$E_a(TS2)$	$E_a(TS)$	$R(s^{-1})$
$\mathrm{Au_{19}}$[d]		-1.220	-0.400	0.090	0.050	0.090	2.798×10^{8}
$\mathrm{Au_{18}Ag}$	**a'**	-1.664	-0.755	0.040	*	0.040	1.490×10^{11}
	b'	-1.443	-0.725	0.025	0.231	0.231	7.080×10^{-3}
	c'	-1.443	-0.725	0.116	0.058	0.116	1.007×10^{7}
$\mathrm{Au_{18}Cu}$	**a'**	-1.669	-0.795	*	0.085	0.085	1.255×10^{9}
	b'	-1.953	-0.651	0.030	0.261	0.261	1.045×10^{1}

	c'	-1.953	-0.651	0.137	0.059	0.137	1.642×10^{3}
$Au_{18}Pt$	**a'**	-2.098	-0.767	0.023	0.016	0.023	1.185×10^{8}
	b'	-3.440	-0.155	0.324	0.367	0.367	4.810×10^{-50}
	c'	-3.440	-0.155	0.822	0.312	0.822	5.037×10^{-42}
$Au_{18}Pd$	**a'**	-2.029	-0.447	0.127	0.159	0.159	1.827×10^{2}
	b'	-2.672	-0.164	0.288	0.427	0.427	4.373×10^{-26}
	c'	-2.672	-0.164	0.558	0.252	0.558	9.457×10^{-24}

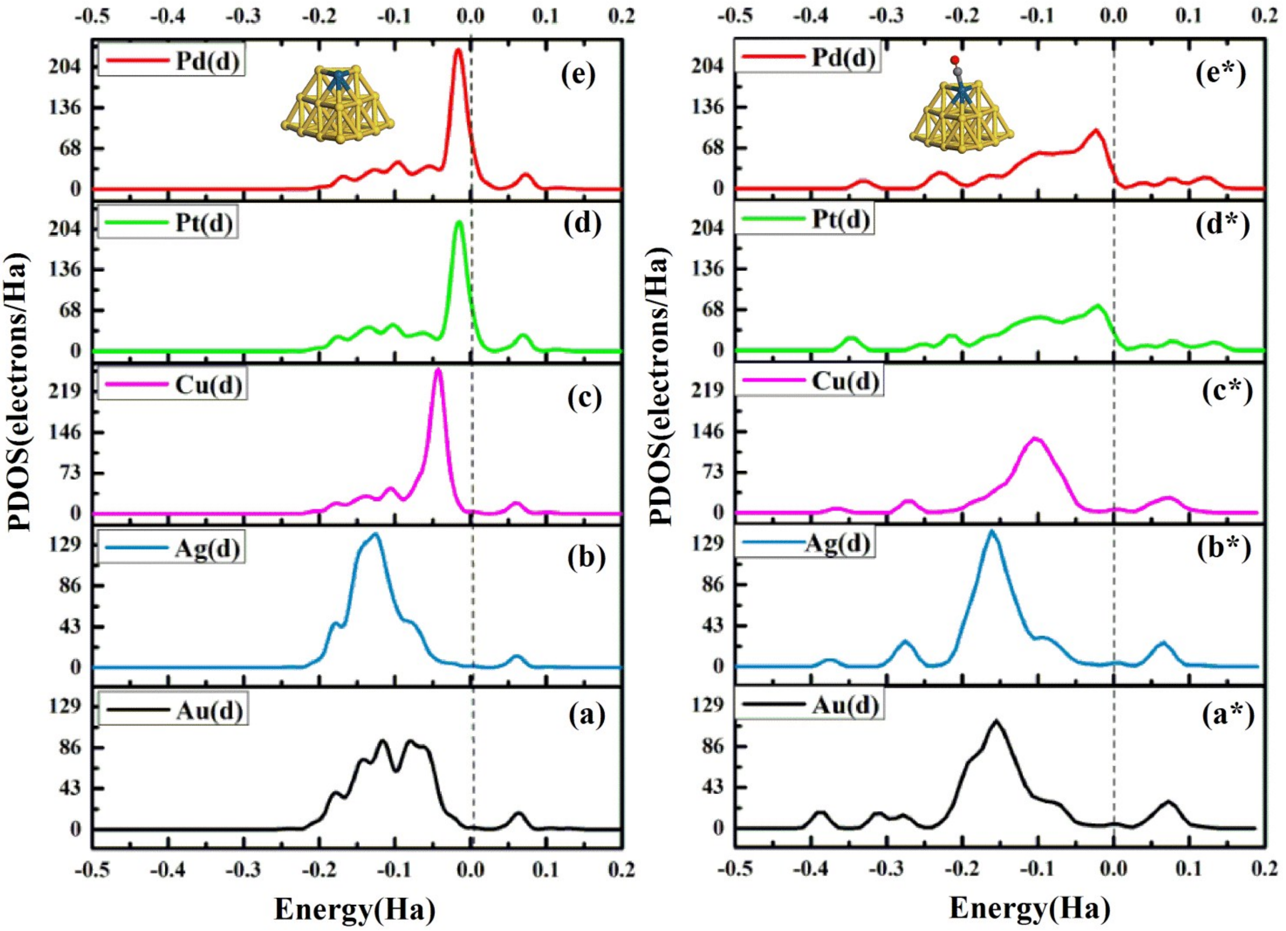


Figure S2. The PDOS of d-orbitals of heteroatom M on (a-e) $Au_{18}M$ cluster and (a*-e*) $Au_{18}M$-CO model is displayed (M=Au, Ag, Cu, Pt, Pd).

Part S1. Details of micro-kinetic analysis of the reaction rate for bare M_{13} and $Au_{18}M$ (M=Au, Ag, Cu, Pt, Pd) clusters.

The micro-kinetic model for CO oxidation on bare metallic nanoclusters is simplified as follows for bi-molecular and tri-molecular mechanisms. The energy parameters used in computed reaction rates for various reaction mechanisms are given in Table S1-S2.

1. Micro-kinetic analysis for the bi-molecular process:

$$CO(g) + * \to CO^* \qquad k1 \tag{1}$$

$$O_2(g) + * \to O_2^* \qquad k2 \tag{2}$$

$$CO^* + O_2^* \to OCOO^* + * \qquad k3 \tag{3}$$

$$OCOO^* \to CO_2 + O^* \qquad k4 \tag{4}$$

Here the k1, k2, k3, and k4 are rate constants for four reaction steps.

Assuming the adsorption of O_2 and CO are in equilibrium, the reaction rate of reaction steps (1) and (2) are zero, we obtained $r_1 = 0$ and $r_2 = 0$:

$$k_1^+ p(CO)\theta^* = k_1^- \theta_{CO}$$

$$\theta_{CO} = \frac{k_1^+}{k_1^-} p(CO)\theta^* = K_1 p(CO)\theta^*$$

$$K_1 = exp\left(\frac{-\Delta G1}{k_B T}\right)$$

$$k_2^+ p(O_2)\theta^* = k_2^- \theta_{O_2}$$

$$\theta_{O_2} = \frac{k_2^+}{k_2^-} p(O_2)\theta^* = K_2 p(O_2)\theta^*$$

$$K_2 = exp\left(\frac{-\Delta G2}{k_B T}\right)$$

where K_1 and K_2 are the equilibrium constant of reaction steps (1) and (2), ΔG1 and ΔG2 are the Gibbs free energies. Here we do not consider the entropy change during all reaction steps, the ΔG1 and ΔG2 are the adsorption energies of CO and O_2. The θ^* is the coverage of unoccupied reaction sites on catalyst surface and p(CO) and p(O_2) are the partial pressure of CO and O_2.

Using the 'steady-state' approximation and neglect the reverse reaction, we can obtain the coverage of θ_{OCOO}:

$$r_3 = r_4$$

$$k_3^+ \theta_{CO}\theta_{O_2} = k_4^+ \theta_{OCOO}$$

$$k_3^+ = \frac{k_BT}{h} exp\left(\frac{-\Delta G3}{k_BT}\right)$$

$$k_4^+ = \frac{k_BT}{h} exp\left(\frac{-\Delta G4}{k_BT}\right)$$

$$\theta_{OCOO} = \frac{k_3^+ \theta_{CO}\theta_{O_2}}{k_4^+}$$

Because the sum of the coverage of adsorbed molecules and intermediate should equal to 1, we can numerically derive θ^* from θ_{CO} and θ_{O_2}:

$$\theta_{CO} + \theta_{O_2} + \theta_{OCOO} + \theta^* = 1$$

$$K_1p(CO)\theta^* + K_2p(O_2)\theta^* + \frac{k_3^+ K_1K_2p(CO)p(O_2)(\theta^*)^2}{k_4^+} + \theta^* = 1$$

For steps 3 and 4, the maximum rate is obtained as follows:

$$r_3 = k_3^+ \theta_{CO}\theta_{O_2} = k_3^+ K_1K_2p(CO)p(O_2)(\theta^*)^2$$

2. Micro-kinetic analysis for the tri-molecular process:

For the tri-molecular reaction mechanism, we have considered the two CO molecules adsorbed on the catalysts separately:

$$CO_{(1)}(g) + * \rightarrow CO_{(1)}^* \qquad k1 \qquad (1)$$

$$CO_{(2)}(g) + * \rightarrow CO_{(2)}^* \qquad k2 \qquad (2)$$

$$O_2(g) + {*} \rightarrow O_2^* \qquad k3 \qquad (3)$$

$$CO_{(1)}^* + O_2^* \rightarrow OCOO^* + {*} \qquad k4 \qquad (4)$$

$$OCOO^* + CO_{(2)}^* \rightarrow 2CO_2 + 2{*} \qquad k5 \qquad (5)$$

The reaction rate for five reaction steps are expressed as:

$$r_1 = k_1^+ p(CO)\theta^* - k_1^- \theta_{CO(1)}$$

$$r_2 = k_2^+ p(CO)\theta^* - k_2^- \theta_{CO(2)}$$

$$r_3 = k_3^+ p(O_2)\theta^* - k_3^- \theta_{O_2}$$

$$r_4 = k_4^+ \theta_{CO(1)}\theta_{O_2} - k_4^- \theta_{OCOO}\theta^*$$

$$r_5 = k_5^+ \theta_{OCOO}\theta_{CO(2)} - k_5^- p^2(CO_2)\,\theta^{*2}$$

Assuming the adsorption of O_2 and CO are in equilibrium, the reaction rate of reaction steps (1), (2), and (3) are zero, we obtained $r_1 = 0$, $r_2 = 0$, and $r_3 = 0$:

$$k_1^+ p(CO)\theta^* = k_1^- \theta_{CO(1)}$$

$$\theta_{CO(1)} = \frac{k_1^+}{k_1^-} p(CO)\theta^* = K_1 p(CO)\theta^*$$

$$K_1 = exp\left(\frac{-\Delta G1}{k_B T}\right)$$

$$k_2^+ p(CO)\theta^* = k_2^- \theta_{CO(2)}$$

$$\theta_{CO(2)} = \frac{k_2^+}{k_2^-} p(CO)\theta^* = K_2 p(CO)\theta^*$$

$$K_2 = exp\left(\frac{-\Delta G2}{k_B T}\right)$$

$$k_3^+ p(O_2)\theta^* = k_3^- \theta_{O_2}$$

$$\theta_{O_2} = \frac{k_3^+}{k_3^-} p(O_2)\theta^* = K_3 p(O_2)\theta^*$$

$$K_3 = exp\left(\frac{-\Delta G3}{k_B T}\right)$$

Using the ‘steady-state’ approximation and neglect the reverse reaction, we can obtain the coverage of θ_{OCOO}:

$$r_4 = r_5$$

$$k_4^+ \theta_{CO(1)} \theta_{O_2} = k_5^+ \theta_{OCOO} \theta_{co_{(2)}}$$

$$k_4^+ = \frac{k_B T}{h} exp\left(\frac{-\Delta G4}{k_B T}\right)$$

$$k_5^+ = \frac{k_B T}{h} exp\left(\frac{-\Delta G5}{k_B T}\right)$$

$$\theta_{OCOO} = \frac{k_4^+ \theta_{CO(1)} \theta_{O_2}}{k_5^+ \theta_{co_{(2)}}}$$

Because the sum of the coverage of adsorbed molecules and intermediate should equal to 1, we can numerically derive θ^* from θ_{CO} and θ_{O_2}:

$$\theta_{co_{(1)}} + \theta_{co_{(2)}} + \theta_{O_2} + \theta_{OCOO} + \theta^* = 1$$

$$K_1 p(CO) \theta^* + K_2 p(CO) \theta^* + K_3 p(O_2) \theta^* + \theta_{OCOO} = \frac{k_4^+ \theta_{CO(1)} \theta_{O_2}}{k_5^+ \theta_{co_{(2)}}} + \theta^* = 1$$

For steps 4 and 5, the maximum rate is obtained as follows:

$$r_4 = k_4^+ \theta_{CO(1)} \theta_{O_2} = k_4^+ K_1 K_3 p(CO) p(O_2) (\theta^*)^2$$

In present calculations, we use the reaction condition T = 298 K, p(CO) = 0.01 bar, $p(O_2)$ = 0.21 bar for all reaction rate calculations. Table 1-2 summarizes reaction rates for all bare metallic clusters at different reaction sites and via different kinds of mechanisms

Part S2. Details of Kinetic Monte Carlo Simulations

The KMC algorithm enables a system to evolve in real time with dynamically varied system configurations. From a current configuration, KMC tells how to obtain the next system configuration and also how to calculate the time interval Δt between the two configurations. In this work we used the Bortz–Kalos–Lebowitz (BKL) KMC algorithm [1], which is briefly introduced as follows. First, one should count all the possible events at the current configuration and calculate the rate of each event as $r(i)$ ($i = 1, 2, \ldots, n$, n is the total number of events). The total rate is obtained by $R = \sum_{i=1}^{n} r(i)$. Second, in the BKL algorithm, one can choose a random number $rand_1$ with a uniform distribution in the range [0, 1), which is used to locate the kth event that satisfies the condition

$$\sum_{i=1}^{k} r(i) > R \times rand_1 > \sum_{i=1}^{k-1} r(i)$$

Finally, the event k will be selected to occur that leads to the next system configuration. The time interval between the two successive events (waiting time) is calculated as

$$\Delta t = -\frac{1}{R}\ln(rand_2)$$

where $rand_2$ is another random number in the range [0, 1).

In present KMC simulations, the reaction rate r of an elementary event on a per site basis is calculated based on transition state theory (TST) and statistical mechanics, as given by Eq. 1:

$$r(T) = \frac{k_B T}{\mathrm{h}} f^{TST}(T) exp\left(- \frac{E_a}{k_B T} \right) = A exp\left(- \frac{E_a}{k_B T} \right) \tag{1}$$

$$f^{TST}(T) = \frac{q^{TS}}{q^{IS}} \tag{2}$$

where k_B is the Boltzmann constant, h is Planck's constant, f is the ratio of partition function q at the TS and that at the initial state (IS), A is the pre-exponential factor, and E_a is the reaction barrier, which are obtained from the DFT calculations.

The equations for calculating the rate of adsorption/desorption and surface reactions are obtained as follows. For the typical surface elementary reaction $IS \longrightarrow [TS]^{\neq} \longrightarrow FS$ involving only a high-vibrational-frequency bond breaking/formation ($hv > \mathrm{k_B T}$), the rate can be simplified as Eq. 3 where the zero point energy correction is taken into account in reaction barrier E_a.

$$r(T) = \frac{k_B T}{h} \exp\left(-\frac{E_a}{k_B T}\right) \tag{3}$$

For the adsorption and desorption rate calculations, the adsorption rate can be described by Eq. 4 by measuring the collision rate of particles with mass m_i impinging onto a plane with an area of A at temperature T and pressure p_i:

$$r_i^{ad}(T, p_i) = S_i(T) \frac{p_i A}{\sqrt{2\pi k_B m_i T}} \tag{4}$$

where S_i is the sticking coefficient, accounting for a reduction in the sticking probability since not every collision will lead to a successful adsorption. It was shown that the Eq. 4 is identical to the Eq. 5 by considering the ideal gas laws[2]:

$$k_{ad} = \frac{k_B T}{\mathrm{h}} \exp\left(- \frac{\Delta G_i^{ad}}{k_B T} \right) \tag{5}$$

[1] A.B. Bortz, M.H. Kalos, J.L. Lebowitz, *J. Comput. Phys.* **1975**, 17, 10.

[2] Tang, Q.; Hong, Q-J; Liu, Z-P. *J. Catal.* **2009**, *263*, 114.