

Supporting Information

Size and Stoichiometry Effect of FePt Bimetal Nanoparticle

Catalyst for CO Oxidation: A DFT Study

Lu Li ^{1,2}, Yan-Zhou Wang ², Xiao-Xu Wang ², Ke-Ke Song ², Xiao-Dong Jian ³, Ping

Qian ^{1,2*}, Yang Bai ^{1,4}, Yan-Jing Su ^{1,4*}

¹ Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, Beijing, China

² Department of Physics, University of Science and Technology Beijing, Beijing, China

³ National Supercomputer Center in Tianjin, Tianjin, China

⁴ Corrosion and Protection Center, University of Science and Technology Beijing, Beijing, China

Correspondence and requests for materials should be addressed to Y-J.S. (email: yjsu@ustb.edu.cn) or P.Q. (email: qianping@ustb.edu.cn).

The micro-kinetic model for CO oxidation reaction on Pt nanoparticles.

The micro-kinetic model of CO oxidation by co-adsorbed CO and O₂ on the Pt cluster is presented:



The reaction rate constants of the above elementary reactions is represented by K₁ - K₅. According to the Langmuir adsorption model ¹, the reaction kinetic process is as follows:

1. The adsorption process of CO accounts for the reaction equilibrium.

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

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

$$K_1 = \exp\left(\frac{-\Delta G_{CO}}{k_B T}\right) = \exp\left(\frac{-(E_{ads}^{CO} - T \cdot \Delta S_{CO})}{k_B T}\right)$$

$$R_1 = \frac{d\theta_{CO}}{dt} = k_1^+ p(CO)\theta^* - k_1^- \theta_{CO}$$

2. The adsorption process of O₂ account for the reaction equilibrium.

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

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

$$K_2 = \exp\left(\frac{-\Delta G_{O_2}}{k_B T}\right) = \exp\left(\frac{-(E_{ads}^{O_2} - T \cdot \Delta S_{O_2})}{k_B T}\right)$$

$$R_2 = \frac{d\theta_{O_2}}{dt} = k_2^+ p(O_2)\theta^* - k_2^- \theta_{O_2}$$

$E_{ads}^{O_2}$ is O_2 adsorption energy with the value of -1.63 eV

E_{ads}^{CO} is CO adsorption energy with the value of -1.87 eV

ΔS_{O_2} is the entropy change of O_2 adsorption with the value of 197.7 J/mol•K

ΔS_{CO} is the entropy change of CO adsorption with the value of 205.1 J/mol•K

In the elementary reaction (S-4), the maximum reaction rate of CO_2 is equal to the rate of CO_2 formation in the whole reaction process.

- The process of intermediate product $O=C-O-O$ accounts for the reaction equilibrium and the max rate of intermediate product is directly related to the final product CO_2 .

$$R_3^{\max} = R_4^{\max}$$

$$R_3^{\max} = k_3^+ \theta_{CO} \cdot \theta_{O_2}$$

$$R_4^{\max} = k_4^+ \theta_{OCO}$$

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

$$k_3^+ = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_3}{k_B T}\right) = \frac{k_B T}{h} \exp\left(\frac{-(-E_{act} - T\Delta S)}{k_B T}\right)$$

$$\Delta S = 0$$

$$R_3 = k_3^+ \theta_{O_2} \theta_{CO} - k_3^- \theta_{OCO} \theta^*$$

$$R_4^{\max} = \frac{d\theta_{OCO}}{dt} = R_3^{\max} = k_3^+ \theta_{CO} \cdot \theta = k_3^+ K_1 K_2 p(CO) p(O_2) (\theta^*)^2$$

In the overall reaction process, the total coverage should be equal to one.

Considering the different adsorption and activation energy of edge-atom and face-atom, one can get the following relationships:

Reactions on edge atoms:

$$\theta_{CO} + \theta_{O_2} + \theta_{OCO} + \theta^* = \frac{N_{edge}}{N_{edge} + N_{face}}$$

Reactions on face atoms:

$$\theta_{CO} + \theta_{O_2} + \theta_{OCO} + \theta^* = \frac{N_{face}}{N_{edge} + N_{face}}$$

The reaction rates are calculated at $T=300$ K, $p(\text{CO})=0.01$ bar, $p(\text{O}_2)=0.21$ bar. The results are listed in Table 4.

Partition function q :

Partition function q can be divided into five parts in thermodynamics statistics: partition function of translation q_t , partition function of rotation q_r , partition function of vibration q_v , partition function of electronic movement q_e , partition function of nuclear movement q_n . For O_2 : $q_e = 3, q_n = 1$.

$$q = q_t q_r q_v q_e q_n$$

$$q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

$$q_r = \frac{T}{\sigma \Theta_r}$$

$$q_v = \prod_i \frac{1}{1 - \exp\left(\frac{h\omega_i}{2\pi k_B T}\right)}$$

Where Θ_r is the characteristic temperature of rotation, V is the volume of the particle movement space, ω_i is the inherent frequency, σ is the symmetry number of the molecule, $\sigma_{CO} = 1, \sigma_{O_2} = 2$.

The vibrational contribution to the partition function $q_v = \prod_i \frac{1}{1 - \exp\left(\frac{h\omega_i}{2\pi k_B T}\right)}$

can be assumed to be frozen out when $\frac{h\omega_i}{2\pi k_B T}$ is high enough. In this case the

partition function q for $\frac{q_{TS}}{q_{CO}q_{O_2}}$ can be assumed to be close to one.

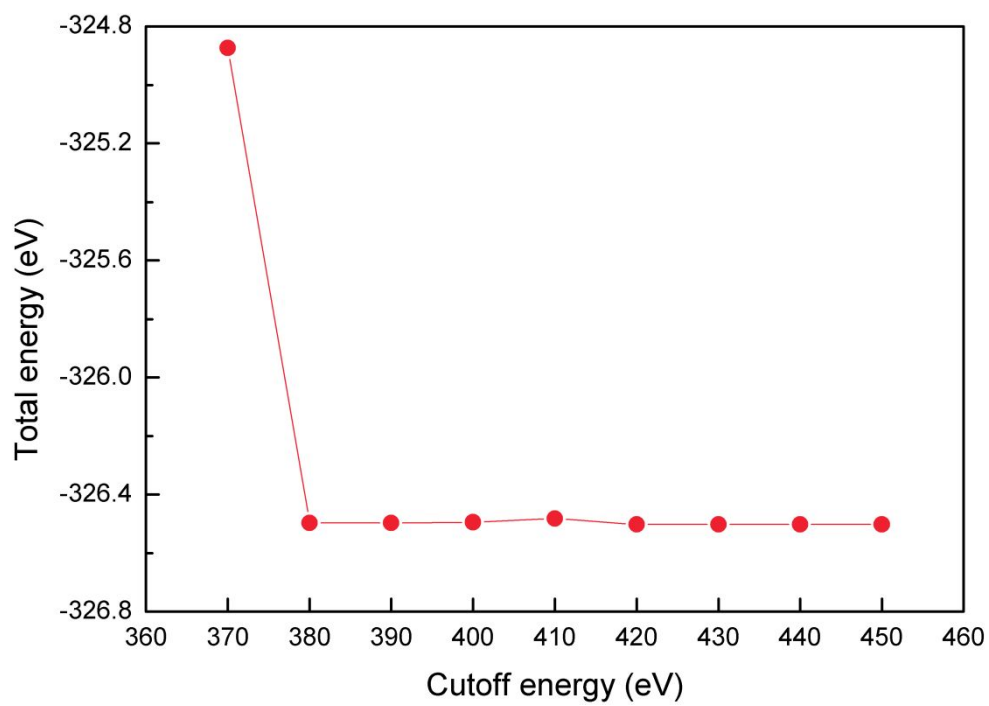


Figure S1. The cutoff energy test of FePt cluster.

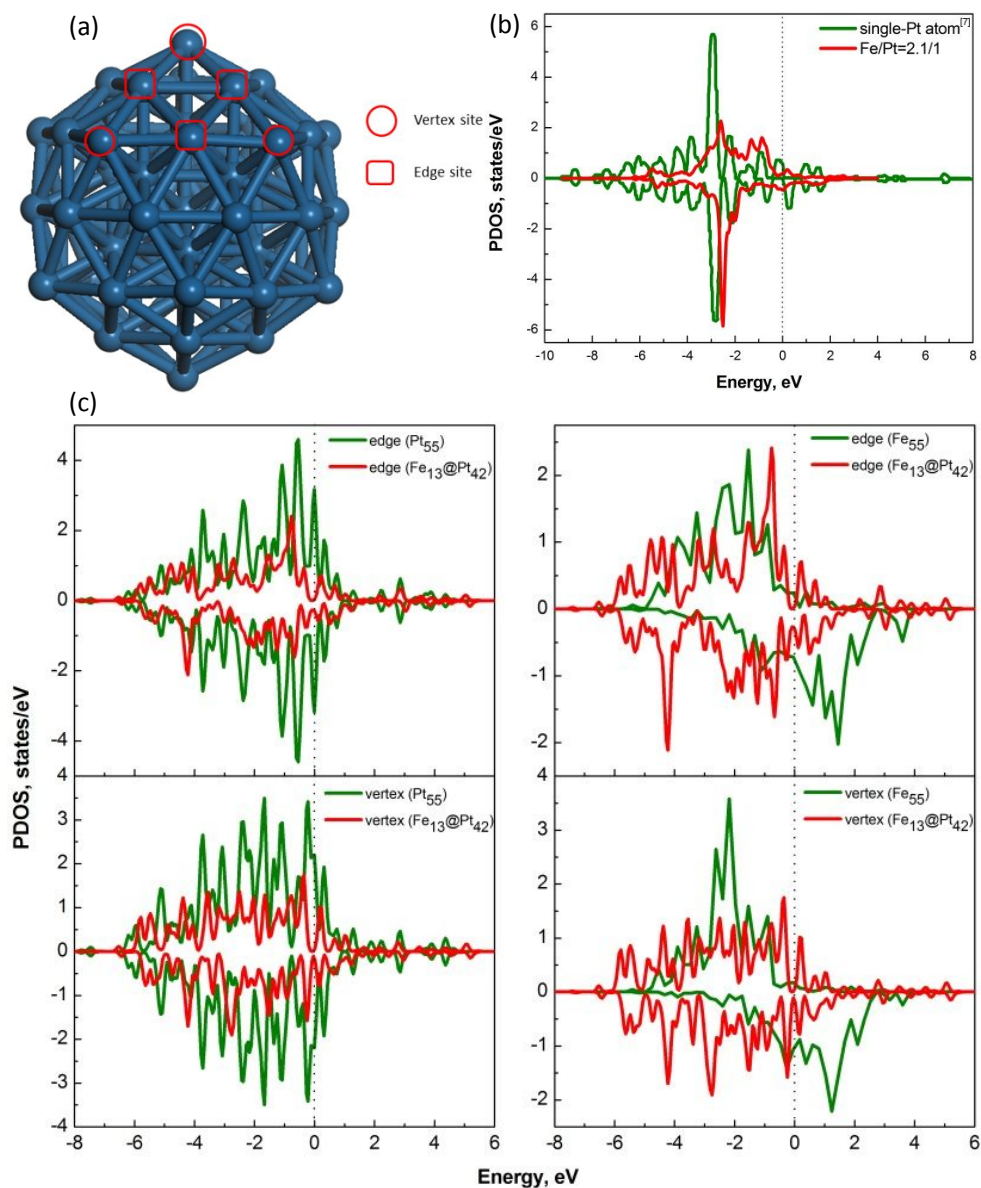


Figure S2. The specific electronic structures of different atomic ratio FePt clusters. (a) The model of Pt₅₅ nanoparticle and the specific sites. (b) The optimized structure of Pt₅₅ and the partial density of states (PDOS) of vertex site Pt atom of multi-spike-angular nanoparticle compared with single Pt atom of ALDPT/NGNs². (c) Fe₅₅ or Pt₅₅ nanoparticle compared with Fe₁₃@Pt₄₂ nanoparticle with vertex and edge sites. The Fermi level is shifted to zero and expressed with the vertical black dashed line. The PDOS shows the *d* orbital of vertex and edge Pt in four ratios FePt clusters.

Table S1. The sites of different geometry nanoparticles. (D is the diameter of different size nanoparticles, N_v is the number of vertex sites, N_e is the number of edge sites and N_f is the number of face sites).

Icosahedron

D	0.5 nm	1 nm	1.5 nm	2 nm	2.5 nm	3 nm	3.5 nm	4 nm	4.5 nm
N_v	12	12	12	12	12	12	12	12	12
N_e	30	120	270	480	750	1080	1470	1920	2430
N_f	-	-	-	20	80	180	320	500	720
D	5 nm	5.5 nm	6 nm	6.5 nm	7 nm	7.5 nm	8 nm	8.5 nm	9 nm
N_v	12	12	12	12	12	12	12	12	12
N_e	3000	3630	4320	5070	5880	6750	7680	8670	9720
N_f	980	1280	1620	2000	2420	2880	3380	3920	4500

Cubo-octahedron

D	0.5 nm	1 nm	1.5 nm	2 nm	2.5 nm	3 nm	3.5 nm	4 nm	4.5 nm
N_v	12	12	12	12	12	12	12	12	12
N_e	24	96	192	312	456	624	816	1032	1272
N_f	-	-	6	32	86	168	278	416	582
D	5 nm	5.5 nm	6 nm	6.5 nm	7 nm	7.5 nm	8 nm	8.5 nm	9 nm
N_e	12	12	12	12	12	12	12	12	12
N_v	1536	1824	2136	2472	2832	3216	3624	4056	4512
N_f	776	998	1248	1526	1832	2166	2528	2918	3336

Octahedron

D	0.8 nm	1.6 nm	2.4 nm	3.2 nm	4 nm	4.8 nm
N_v	6	6	6	6	6	6
N_e	48	192	432	768	1200	1728
N_f	-	8	72	200	392	648
D	5.6 nm	6.4 nm	7.2 nm	8 nm	8.8 nm	
N_v	6	6	6	6	6	
N_e	2352	3072	3888	4800	5808	
N_f	968	1352	1800	2312	2888	

Dispersed 1 nm FePt nanoparticle

Fe/Pt	10/1	2.7/1	2.1/1	1/1.2	1/3.2	1/10
N_v	5	12	12	12	12	12
N_e	-	5	2	96	120	120
N_f	-	-	-	15	-	-

References

1. Langmuir, I. The mechanism of the catalytic action of platinum in the reactions $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. *Faraday Soc* **1992**, *17*, 621-654.
2. Cheng, N.C.; Stambula, S.; Wang, D.; Banis, M. N.; Liu, J.; Riese, A.; Xiao, B. W.; Li, R. Y.; Sham, T. K.; Liu, L. M. et al. Platinum single-atom and cluster catalysis of the hydrogen evolution reaction. *Nat. Commun* **2016**, *7*, 13638.