



Supporting Information

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Supporting information for:

Trends in the Catalytic CO Oxidation Activity of Nanoparticles

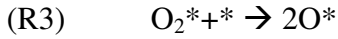
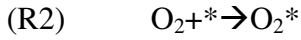
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Methods

The results are based on density functional theory (DFT) calculations. The publicly available program DACAPO^[1] was employed. The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies up to 408eV (30 Ry). The density cutoff is 816 eV. The core electrons are treated with Vanderbilt non-local ultrasoft pseudopotentials.^[2] The exchange-correlation potential and energy are described employing the RPBE generalized gradient correction self-consistently.^[1] Monkhorst-Pack meshes^[3] with $1\times 1\times 1$ or $6\times 6\times 1$ \mathbf{k} -grid sampling in the Brillouin zone are used for the clusters and 111-surfaces, respectively. The (111)-surface is modeled by a 2×2 unit cell with a slab thickness of 4 layers where the two lower layers are fixed and the two upper layers are fully relaxed. The clusters are calculated in a box of $15\times 15\times 15$ Å³ with periodic boundary conditions. All the atoms in the cluster are kept fixed with a lattice constant corresponding to the bulk value. Oxygen adsorption energies are calculated relative to H₂O and H₂ in the gas phase and then referred to O₂ in the gas phase using the reaction energy of H₂O formation from O₂ and H₂ from experiment.^[4] This avoids the problems associated with a DFT treatment of the triplet state of the gas phase O₂.^[5] For CO adsorption energies, we have included a recently proposed correction scheme to avoid the well known problem of over-binding and wrong site assignment for CO when using DFT (For CO on the cluster the correction for the same type of site on the (111)-surface is used.).^[6,7]

Steady state kinetics

For the 12-atom metal cluster an analytical solution to the micro-kinetic model can be found as follows:



The rate of forming CO_2 is $r(\text{CO}_2) = r_4 + r_5$

Assume that the two first reactions are in equilibrium and write θ_{O_2} and θ_{CO} as functions of θ_{O} and θ_* :

$$r_1 = k_1^+ p(\text{CO})\theta_* - k_1^- \theta_{\text{CO}} \Rightarrow \theta_{\text{CO}} = \left(\frac{k_1^+}{k_1^-} \right) p(\text{CO})\theta_* = K_1 p(\text{CO})\theta_*$$

$$r_2 = k_2^+ p(\text{O}_2)\theta_* - k_2^- \theta_{\text{O}_2} \Rightarrow \theta_{\text{O}_2} = \left(\frac{k_2^+}{k_2^-} \right) p(\text{O}_2)\theta_* = K_2 p(\text{O}_2)\theta_*$$

The rate expressions for the last 3 elementary reactions can be written as:

$$r_3 = k_3^+ \theta_{\text{O}_2} \theta_* - k_3^- \theta_{\text{O}}^2 = k_3^+ K_2 p(\text{O}_2) \theta_* \theta_* - k_3^- \theta_{\text{O}}^2 = x_3 \theta_*^2 - y_3 \theta_{\text{O}}^2$$

$$r_4 = k_4^+ \theta_{\text{CO}} \theta_{\text{O}} - k_4^- p(\text{CO}_2) \theta_*^2 = k_4^+ K_1 p(\text{CO}) \theta_* \theta_{\text{O}} - k_4^- p(\text{CO}_2) \theta_*^2 = x_4 \theta_* \theta_{\text{O}} - y_4 \theta_*^2$$

$$r_5 = k_5^+ \theta_{\text{O}_2} \theta_{\text{CO}} - k_5^- p(\text{CO}_2) \theta_{\text{O}} \theta_* = k_5^+ K_1 K_2 p(\text{O}_2) p(\text{CO}) \theta_* \theta_* - k_5^- p(\text{CO}_2) \theta_{\text{O}} \theta_* = x_5 \theta_*^2 - y_5 \theta_{\text{O}} \theta_*$$

To simplify, the constants x_i and y_i , $i=3,4,5$ have been defined.

Looking at the total rate of forming O^* , it is seen that for each R3 reaction 2 O^* are formed, for each R4 reaction 1 O^* is consumed, and for each R5 1 O^* is formed. We now assume that the formation of O^* is in steady state and thus that:

$$R(O^*) = 2r_3 - r_4 + r_5 = 0$$

This gives:

$$2(x_3\theta_*^2 - y_3\theta_o^2) - (x_4\theta_*\theta_o - y_4\theta_*^2) + (x_5\theta_*^2 - y_5\theta_o\theta_*) = 0$$

Viewing this as a second order equation in θ_o one gets:

$$D = B^2 - 4AC = (x_4 + y_5)^2 \theta_*^2 + 8y_3(2x_3 + y_4 + x_5) \theta_*^2$$

Since all the constants x_i and y_i are positive, D is positive:

$$\theta_o = \frac{-B \pm \sqrt{D}}{2A} = \theta_* \left(\frac{x_4 + y_5}{4y_3} \left(-1 \pm \sqrt{1 + \frac{8y_3(2x_3 + y_4 + x_5)}{(x_4 + y_5)^2}} \right) \right)$$

Since the coverages are always positive numbers, only the solution with the 'plus' is physical. We define the constant W as:

$$\theta_o = \theta_* W$$

We can now calculate θ_* using the sum-rule

$$\theta_* + \theta_o + \theta_{CO} + \theta_{O_2} = 1 \Rightarrow$$

$$\theta_* + W\theta_* + K_1 p(CO)\theta_* + K_2 p(O_2)\theta_* = 1 \Rightarrow$$

$$\theta_* = \frac{1}{1 + W + K_1 p(CO) + K_2 p(O_2)}$$

The relations between the rate constants and the activation energies are found as follows:

For the elementary reactions in equilibrium i.e. (R1) and (R2), the rate constants are:

$$K_1 = \exp\left(\frac{-\Delta G_1}{kT}\right) = \exp\left(\frac{-(\Delta E_1 - T\Delta S_1)}{kT}\right)$$

$$\Delta E_1 = E_{final} - E_{initial} = E_{chem}(CO) - E_{gas}(CO)$$

$$\Delta S_1 = S_{final} - S_{initial} - S_{gas}(CO)$$

and

$$K_2 = \exp\left(\frac{-\Delta G_2}{kT}\right) = \exp\left(\frac{-(\Delta E_2 - T\Delta S_2)}{kT}\right)$$

$$\Delta E_2 = E_{final} - E_{initial} = E_{chem}(O_2) - E_{gas}(O_2)$$

$$\Delta S_2 = S_{final} - S_{initial} = -S_{gas}(O_2)$$

We assume that the entropy of all surface bound species is zero.

For the non-equilibrium reactions the activation energy of each direction is used:

$$E_a = E_{TS} - E_{IS}$$

$$E_a(k^+) = E_a$$

$$E_a(k^-) = E_{TS} - E_{FS} = E_a + E_{IS} - E_{FS}$$

For reaction (3), the O_2 dissociation, $O_2^{*+*} \rightarrow 2O^*$ one gets:

$$K_3 = \exp\left(\frac{-\Delta G_3}{kT}\right) = \exp\left(\frac{-(\Delta E_3 - T\Delta S_3)}{kT}\right)$$

$$\Delta E_3 = E_{final} - E_{initial} = 2E_{chem}(O) - E_{chem}(O_2)$$

$$\Delta S_3 = 0$$

$$\Delta S_3^+ = 0$$

$$E_a(k_3^+) = E_{TS}(3) - E_{chem}(O_2)$$

$$k_3^+ = \frac{kT}{h} \exp\left(\frac{-\Delta G_3^+}{kT}\right) = \frac{kT}{h} \exp\left(\frac{\Delta S_3^+}{k}\right) \exp\left(\frac{-E_a(k_3^+)}{kT}\right) = \frac{kT}{h} \exp\left(\frac{-(E_{TS}(3) - E_{chem}(O_2))}{kT}\right)$$

The change in entropy is zero for the O_2 dissociation and the activation energy can be calculated using the BEP relation and the scaling relation.

$$\Delta S_3^- = 0$$

$$E_a(k_3^-) = E_{TS}(3) - 2E_{chem}(O)$$

$$\begin{aligned} k_3^- &= \frac{kT}{h} \exp\left(\frac{-\Delta G_3^-}{kT}\right) = \frac{kT}{h} \exp\left(\frac{\Delta S_3^-}{k}\right) \exp\left(\frac{-E_a(k_3^-)}{kT}\right) \\ &= \frac{kT}{h} \exp\left(\frac{-(E_{TS}(3) - 2E_{chem}(O))}{kT}\right) \end{aligned}$$

For reaction (4), $O^* + CO^* \rightarrow CO_2 + 2^*$, one gets:

$$K_4 = \exp\left(\frac{-\Delta G_4}{kT}\right) = \exp\left(\frac{-(\Delta E_4 - T\Delta S_4)}{kT}\right)$$

$$\Delta E_4 = E_{final} - E_{initial} = E_{gas}(CO_2) - E_{chem}(O) - E_{chem}(CO)$$

$$\Delta S_4 = S(CO_2)$$

$$\Delta S_4^+ = 0$$

$$E_a(k_4^+) = E_{TS}(4) - E_{IS}(k_4^+) = E_{TS}(4) - E_{chem}(CO) - E_{chem}(O)$$

$$\begin{aligned} k_4^+ &= \frac{kT}{h} \exp\left(\frac{-\Delta G_4^+}{kT}\right) = \frac{kT}{h} \exp\left(\frac{\Delta S_4^+}{k}\right) \exp\left(\frac{-E_a(k_4^+)}{kT}\right) \\ &= \frac{kT}{h} \exp\left(\frac{-(E_{TS}(4) - E_{chem}(CO) - E_{chem}(O))}{kT}\right) \end{aligned}$$

For the reverse reaction one gets:

$$\Delta S_4^- = -S(CO_2)$$

$$E_a(k_4^-) = E_{TS}(4) - E_{IS}(k_4^-) = E_{TS}(4) - E_{gas}(CO_2)$$

$$\begin{aligned} k_4^- &= \frac{kT}{h} \exp\left(\frac{-\Delta G_4^-}{kT}\right) = \frac{kT}{h} \exp\left(\frac{\Delta S_4^-}{k}\right) \exp\left(\frac{-E_a(k_4^-)}{kT}\right) \\ &= \frac{kT}{h} \exp\left(\frac{-S(CO_2)}{k}\right) \exp\left(\frac{-(E_{TS}(4) - E_{gas}(CO_2))}{kT}\right) \end{aligned}$$

For reaction (5), $O_2^* + CO^* \rightarrow CO_2 + O^* + ^*$ one gets:

$$K_5 = \exp\left(\frac{-\Delta G_5}{kT}\right) = \exp\left(\frac{-(\Delta E_5 - T\Delta S_5)}{kT}\right)$$

$$\Delta E_5 = E_{final} - E_{initial} = E_{gas}(CO_2) + E_{chem}(O) - E_{chem}(O_2) - E_{chem}(CO)$$

$$\Delta S_5 = S(CO_2)$$

$$\begin{aligned}\Delta S_5^+ &= 0 \\ E_a(k_5^+) &= E_{TS}(5) - E_{IS}(k_5^+) = E_{TS}(5) - E_{chem}(O_2) - E_{chem}(CO) \\ k_5^+ &= \frac{kT}{h} \exp\left(\frac{-\Delta G_5^+}{kT}\right) = \frac{kT}{h} \exp\left(\frac{\Delta S_5^+}{k}\right) \exp\left(\frac{-E_a(k_5^+)}{kT}\right) \\ &= \frac{kT}{h} \exp\left(\frac{-(E_{TS}(5) - E_{chem}(O_2) - E_{chem}(CO))}{kT}\right)\end{aligned}$$

For the reverse reaction one gets:

$$\begin{aligned}\Delta S_5^- &= -S(CO_2) \\ E_a(k_5^-) &= E_{TS}(5) - E_{IS}(k_5^-) = E_{TS}(5) - E_{gas}(CO_2) - E_{chem}(O) \\ k_5^- &= \frac{kT}{h} \exp\left(\frac{-\Delta G_5^-}{kT}\right) = \frac{kT}{h} \exp\left(\frac{\Delta S_5^-}{k}\right) \exp\left(\frac{-E_a(k_5^-)}{kT}\right) \\ &= \frac{kT}{h} \exp\left(\frac{-S(CO_2)}{k}\right) \exp\left(\frac{-(E_{TS}(5) - E_{gas}(CO_2) - E_{chem}(O))}{kT}\right)\end{aligned}$$

In Fig. S1 we show the volcano for CO oxidation on the 12 atom clusters calculated using the full kinetics. It can be seen to be close to the Sabatier volcano in Fig. 4.

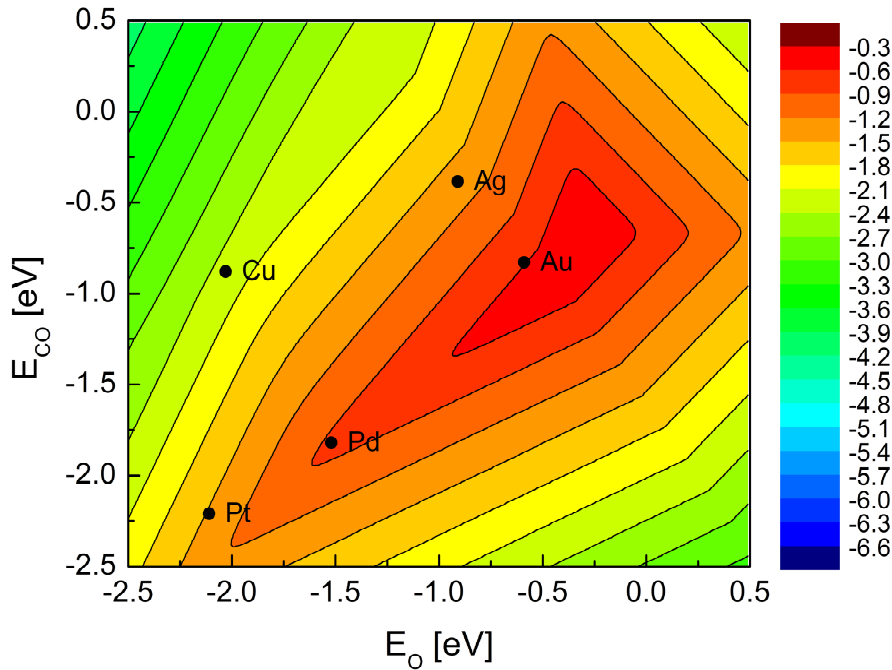


Figure S1. The analogue of Fig. 4(a) calculate using the full steady state kinetics.

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