Supporting Information

Decoding Atomic-Level Structures of the Interface between Pt Subnanocrystals and Nanostructured Carbon

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1. Kinetic analysis of CO Oxidation

The well accepted reaction mechanism for CO oxidation ($CO(g)+\frac{1}{2}O_2(g) \rightleftarrows CO_2(g)$) is given below:

$$CO(g)+* \underset{-k_1}{\overset{k_1}{\rightleftarrows}} CO* \quad (1)$$

$$\frac{1}{2}O_2(g)+* \underset{-k_2}{\overset{k_2}{\rightleftarrows}} O* \quad (2)$$

$$CO*+O* \underset{-k_3}{\overset{k_3}{\rightleftarrows}} CO_2*+* \quad (3)$$

$$CO_2* \underset{-k_4}{\overset{k_4}{\rightleftarrows}} CO_2(g)+* \quad (4)$$

According to the site balance, we have $\theta_{CO}+\theta_O+\theta_{CO_2}+\theta_*=1$.

If we assume step (3) is the rate-determining step (RDS), then the forward reaction of the other three elementary steps are in pseudo-equilibrium with the reverse on and we have

$$K_1 \cdot P_{CO(g)} \cdot \theta_* = \theta_{CO*}$$

$$K_2 \cdot P_{O_2(g)}{}^{0.5} \cdot \theta_* = \theta_{O*}$$

$$K_4 \cdot \theta_{CO_2*} = P_{CO_2(g)} \cdot \theta_*$$

Thus, the free site coverage can be obtained

$$\theta_* = \frac{1}{1+K_1 \cdot P_{CO} \cdot + K_2 \cdot P_{O_2}{}^{0.5} + K_4{}^{-1} \cdot P_{CO_2}}$$

Since the overall reaction rate can be expressed as

$$r_{CO} = k_3 \cdot \theta_{CO*} \cdot \theta_{O*}$$

we have

$$r_{CO} = k_3 \cdot \left(K_1 \cdot P_{CO(g)} \cdot \theta_*\right) \cdot \left(K_2 \cdot P_{O_2(g)}{}^{0.5} \cdot \theta_*\right)$$

At very low reactant pressures, we can assume to a first approximation that $\theta_* \approx 1$, and, consequently,

$$r_{CO} = k_3 \cdot K_1 \cdot K_2 \cdot P_{CO} \cdot P_{O_2}{}^{0.5}$$

That is,

$$r_{\mathrm{CO}} = k_{3,0}\exp\left(\frac{-E_3}{RT}\right)\cdot K_{1,0}\exp\left(\frac{-\Delta H_1}{RT}\right)\cdot K_{2,0}\exp\left(\frac{-\Delta H_2}{RT}\right)\cdot P_{\mathrm{CO}}\cdot P_{\mathrm{O_2}}^{0.5}$$

$$= k_{3,0}\cdot K_{1,0}\cdot K_{2,0}\exp\left(\frac{-E_3-\Delta H_1-\Delta H_2}{RT}\right)\cdot P_{\mathrm{CO}}\cdot P_{\mathrm{O_2}}^{0.5}$$

Thus, the apparent activation energy and pre-exponential factor are

$$E_{app} = \frac{\partial \ln r_{CO}}{\partial T}\cdot RT^2 = E_3 + \Delta H_1 + \Delta H_2$$

and

$$A = k_{3,0}\cdot K_{1,0}\cdot K_{2,0}$$

respectively, where $k_{3,0} = \frac{k_{\mathrm{B}}T}{h}\exp\left(\frac{\Delta S_3^{\ddagger}}{R}\right)$, $K_{1,0} = \exp\left(\frac{\Delta S_1}{R}\right)$, and $K_{2,0} = \exp\left(\frac{\Delta S_2}{R}\right)$.

It follows that the apparent entropy of activation is the entropy change from the gaseous reactants of CO and O_2 to the rate-determining transition state:

$$\Delta S_{app} = \Delta S_1 + \Delta S_2 + \Delta S_3^{\ddagger}$$

2. Experimentally derived apparent activation energy, pre-exponential factor, and apparent entropy of activation

In Figure 8, the least squares fitted lines for the Pt/p-CNF and Pt/f-CNF are

$$\ln TOF = -5938.4\frac{1}{T} + 14.691$$

and

$$\ln TOF = -2873.6\frac{1}{T} + 4.590$$

respectively. The slope of fitted line is $\frac{-E_{app}}{R}$ and the intercept is $\ln\left(\frac{A\cdot P_{CO}\cdot P_{O_2}^{0.5}\cdot M}{D}\right)$, where E_{app} is the apparent activation energy, A pre-exponential factor, P_{CO} and P_{O2} the partial pressures of CO and O_2, M the atomic weight of Pt, and D the dispersion of Pt catalyst, respectively. Then, the apparent activation energies (E_{app}) are calculated from the slopes of fitted lines, and the pre-exponential factors (A) are calculated from the intercepts, as given in

Table S1. The apparent entropy of activation (ΔS_{app}) is calculated from the pre-exponential factor (A), where $A = \frac{k_B T}{h} \cdot \exp\left(\frac{\Delta S_{app}}{R}\right)$.

Table S1. Apparent activation energy (E_{app}), pre-exponential factor (A), and apparent entropy of activation (ΔS_{app}) for CO preferential oxidation on the Pt/p-CNF and Pt/f-CNF

	A	ΔS_{app} (J/mol·K)	E_{app} (kJ/mol)
Pt/p-CNF	8.74×10^8	-75.0	49.4
Pt/f-CNF	4.34×10^4	-154.6	23.9