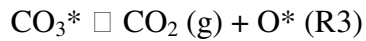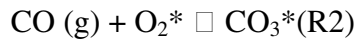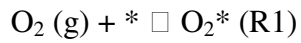# Supporting Information

Microkinetic model for CO oxidation by a CMM

Based on a CMM for CO oxidation, the microkinetic model for small nanoparticles is simply as follows:

O_2 (g) + * ⯀ O_2* (R1)

CO (g) + O_2* ⯀ CO_3*(R2)

CO_3* ⯀ CO_2 (g) + O* (R3)

O* + CO (g) ⯀ CO_2 (g) + * (R4)

Here, the rate of CO_2 formation is equal to the maximum of the rate of the reaction R3. Effect of the reaction R4 is negligible because it is fast and barrierless. Assuming that the first two reactions are in equilibrium, therefore the rate of R1 and R2 is as following:

$$\text{rate(R1)} = k_1^+ p(O_2)\theta_* - k_1^- \theta_{O_2} \rightarrow \theta_{O_2} = K_1 p(O_2)\theta_*$$

$$\text{rate(R2)} = k_2^+ p(CO)\theta_{O_2} - k_2^- \theta_{CO_3} \rightarrow \theta_{CO_3} = K_2 p(CO) K_1 p(O_2)\theta_*$$

Finally, the rate of CO_2 formation, $\text{rate(R3)}^{\text{max}}$, is as follows:

$$\text{rate(R3)}^{\text{max}} = k_3^+ \theta_{CO_3} = k_3^+ K_1 K_2 p(CO) p(O_2)\theta_*$$

where K_1 and K_2 are the equilibrium constants for R1 and R2, $p(CO)$ and $p(O_2)$ are the partial pressures of CO and O_2. k_i^+ and k_i^- represents the forward and the backward reaction constant for Ri, respectively.

Because the sum of the coverage of adsorbed O_2, CO_3 and free adsorption sites should be equal to 1, we can numerically derive θ_* from θ_{O_2} and θ_{CO_3}:

$$\theta_{O_2} + \theta_{CO_3} + \theta_* = 1 \rightarrow \theta_* = \frac{1}{\left(K_1 p(O_2) + K_1 p(O_2) K_2 p(CO) + 1\right)}$$

where θ_{O_2}, θ_{CO_3}, and θ_* are the coverage of adsorbed O_2, CO_3 on nanoparticles, and free sites of the surface.

Note that the reaction R1 and R2 concerns the adsorption of O_2 and CO, respectively.

Therefore, the rate constants K_1 and K_2 are,

$$K_1 = \exp\left(\frac{-\Delta G1}{kT}\right) = \exp\left(\frac{-(\Delta E1 - T\Delta S1)}{kT}\right)$$

$\Delta E1 = $ Energy of O_2 adsorption

$\Delta S1 = $ Entropy change involved in O_2 adsorption

and

$$K_2 = \exp\left(\frac{-\Delta G2}{kT}\right) = \exp\left(\frac{-(\Delta E2 - T\Delta S2)}{kT}\right)$$

$\Delta E2 = $ Energy of CO adsorption (CLI formation)

$\Delta S2 = $ Entropy change involved in O_2 adsorption

For R3, the maximum rate can be obtained as follows:

$$\text{rate}(R3)^{\max} = k_3^+ \theta_{CO_3} = k_3^+ K_1 K_2 p(CO) p(O_2) \theta_*$$

where,

$$k_3^+ = \frac{kT}{h} \exp\left(\frac{-\Delta G3^+}{kT}\right) = \frac{kT}{h} \exp\left(\frac{-\left(E_{de} - T\Delta S3^+\right)}{kT}\right)$$

E_{de} = Energy of desorption of CO_2 molecule

$\Delta S3^+ = 0$

Sabatier activity (SA) of nanoparticles mentioned in this study was calculated with the

rate(R3)^{max} as follows:

$$SA = kTln\left(\frac{rate(R3)^{max}}{h/kT}\right)$$

at T=273 K, p(CO)=0.01 bar, and p(O_2)=0.21 bar.