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## **Supporting Information for**

### A Novel Single Atom Catalyst for CO Oxidation at Humid Environmental Conditions:

#### Ni-Embedded Divacancy Graphene

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#### Supplementary Results

**Fig. S1** The most stable structure of defective graphene with carbon divacancy, where the letters indicate the possible adsorption positions of hollow site, top site and bridge site for Ni atom.



**Fig. S2** The atomic structures of defective graphene with Ni atoms adsorbed at  $B_1$  (a),  $Hol_1$  (b),  $Hol_3$  (c) and  $Hol_4$  (d) are shown in the up panel. The Ni atom on T1 site simultaneously diffused to B1 site, while the Ni atom on T<sub>2</sub>, T<sub>2</sub>, T<sub>2</sub>, B<sub>2</sub>, B<sub>3</sub>, B<sub>4</sub>, B<sub>5</sub>, and  $Hol_2$  sites simultaneously diffused to  $Hol_1$  site after Geometry Optimization. The pathways for the diffusion of the adsorbed Ni atom from B<sub>1</sub> to  $Hol_1$  (e), from  $Hol_3$  to  $Hol_1$  (f), and from  $Hol_1$  to  $Hol_4$  (g) are shown in the down panel.

#### Theoretical Details of Micro-kinetic Analysis

The most favorable reaction pathway (TER path) includes the two chemical adsorbed CO molecules and one physical adsorbed  $O_2$  molecule. After adsorption of the first CO molecule on the bare Ni site, the second CO also possibly adsorbs on the

Ni site. In addition, the Ni site after adsorption of the first and the second CO are both possible occupied by  $O_2$  molecule and thus deactivate the Ni site. Here, the labels "\*" and "‡" represent the bare Ni site and Ni site with the first adsorbed CO molecule. The competing adsorption of  $O_2$  on these two kinds of sites is displayed as Equation (5) and (6):

$$CO(g) + * \xrightarrow{K_{co}^*} OC^*$$

$$K^{\dagger}$$
(1)

$$CO(g) + \stackrel{*}{\stackrel{}{\to}} \stackrel{K_{co}}{OC^{\dagger}}$$

$$(2)$$

$$O_{2}^{\dagger}(g) + OC^{*} + OC^{\dagger} \xrightarrow{\kappa_{1}} OC^{*} OOCO^{\dagger}$$
(3)

$$OC^* OOCO^{\dagger} \xrightarrow{\kappa_2} 2CO_2(g)^{\dagger} + *$$
 (4)

$$O_2(g) + * \to O_2^*$$
 (5)

$$O_2(g) + \stackrel{K_{O_2}^{\dagger}}{\to} O_2^{\dagger}$$
(6)

The adsorption of CO and O<sub>2</sub> can be assumed in kinetic equilibrium, and the coverage of CO ( $\theta_{co}^*$  and  $\theta_{co}^{\dagger}$ ) and O<sub>2</sub> ( $\theta_{02}^*$  and  $\theta_{02}^{\dagger}$ ) at different sites with the partial pressures of  $P_{co}$  and  $P_{02}$  are obtained by the following equations:

$$\theta_{co}^* = K_{co}^* P_{CO} \theta_* \tag{7}$$

$$\theta_{co}^{\dagger} = K_{co}^{\dagger} P_{CO} \theta_{\dagger} \tag{8}$$

$$\theta_{O_2}^* = K_{O_2}^* P_{O_2} \theta_* \tag{9}$$

$$\theta_{O_2}^{\,\dagger} = K_{O_2}^{\,\dagger} P_{O_2} \theta_{\,\dagger} \tag{10}$$

The equilibrium constants are obtained by the following equations:

$$K_{co}^{*} = \exp\left[\frac{-\left(\Delta E_{CO}^{*} - T\Delta S_{CO}\right)}{k_{B}T}\right]$$
(11)

$$K_{co}^{\dagger} = \exp\left[\frac{-\left(\Delta E_{CO}^{\dagger} - T\Delta S_{CO}\right)}{k_B T}\right]$$
(12)

$$K_{o_{2}}^{*} = \exp\left[\frac{-\left(\Delta E_{o_{2}}^{*} - T\Delta S_{o_{2}}\right)}{k_{B}T}\right]$$
(13)

$$K_{o_{2}}^{\dagger} = \exp\left[\frac{-\left(\Delta E_{o_{2}}^{\dagger} - T\Delta S_{o_{2}}\right)}{k_{B}T}\right]$$
(14)

where  $\Delta E_{CO}^{*}$ ,  $\Delta E_{CO}^{\dagger}$ ,  $\Delta E_{O_{2}}^{*}$  and  $\Delta E_{O_{2}}^{\dagger}$  are the adsorption energies of CO and O<sub>2</sub> on site \* and site  $\ddagger$ , and  $\Delta S_{CO}$  and  $\Delta S_{O2}$  represent the entropy change upon CO and O<sub>2</sub> adsorption, respectively.

For reaction (3) and (4), the backward reactions are negligible due to the much higher reaction barriers than those of the corresponding forward reactions. The rate constant k for reaction (3) and (4) can be calculated based on transition state theory:

$$k = \frac{k_B T}{h} \times \frac{Q_{TS}}{Q_A Q_B} \times exp^{[i0]} \left[ -\left(\frac{\Delta E_{bar}}{k_B T}\right) \right]$$
(15)

where  $Q_{TS}$  is the transition state partition function,  $Q_{A}$  and  $Q_{B}$  are the partition functions. The  $\Delta E_{bar}$  represents the reaction barrier for the corresponding step. Finally, we can obtain the rate constant  $k_1 = 1.13 \times 10^7$ /s and  $k_2 = 7.90 \times 10^7$ /s.

Campbell's degree of rate control (DRC) analysis<sup>1</sup> was used to identify the elementary step that controls the overall CO oxidation rate. The degree of rate control coefficient  $\chi_{RC,i}$  for a specific elementary step (*i*) is calculated as following:

$$\chi_{RC,i} = \left(\frac{\partial lnr}{\partial lnk_i}\right)_{k_j \neq i'^{K_i}}$$
(16)

where *r* is the overall reaction rate,  $k_i$  is the forward rate constant and  $K_i$  is the equilibrium constant for step *i*.

The coverage of MS ( $\theta_{MS}$ ) can be calculated by applying the 'steady-state' approximation:

$$\frac{d\theta_{MS}}{dt} = k_1 P_{0_2} \theta_{co}^* \theta_{co}^\dagger - k_2 \theta_{MS} = 0$$
(17)

$$\theta_{MS} = \frac{k_1}{k_2} P_{O_2} \theta_{co}^* \theta_{co}^* \tag{18}$$

The sum of coverage of adsorbents (CO, O<sub>2</sub> and MS) and free active sites should be 1 for both site \* and  $\ddagger$  site, respectively. Then, we can calculate  $\theta_*$  and  $\theta_{\ddagger}$  as follows:

$$\theta_* + \theta_{co}^* + \theta_{O_2}^* + \theta_{MS} = 1 \tag{19}$$

$$\theta_{\ddagger} + \theta_{co}^{\dagger} + \theta_{0}^{\dagger}_{2} = 1 \tag{20}$$

$$\theta_{\dagger} = \frac{1}{1 + K_{C0}^{\dagger} P_{C0} + K_{0_2}^{\dagger} P_{0_2}}$$
(21)

$$\theta_{*} = \frac{1}{1 + K_{C0}^{*}P_{C0} + K_{02}^{*}P_{02} + \frac{k_{1}}{k_{2}} \frac{K_{C0}^{*}K_{C0}^{*}P_{02}(P_{C0})^{2}}{k_{2}1 + K_{C0}^{*}P_{C0} + K_{02}^{*}P_{02}}$$
(22)

Based on the thermodynamic condition of T = 298 K,  $P_{CO} = 0.01$  bar,  $P_{O2} = 0.21$  bar as applied in the reference,<sup>2</sup> the maximum formation rate for CO<sub>2</sub> can be calculated as following:

$$r_{CO_2} = 2k_2\theta_{MS} = 2k_1K_{CO}^*K_{CO}^*K_{CO}^*P_{O_2}(P_{CO})^2\theta_*\theta_{\dagger} = 1.06 \times 10^7/s$$

Where step R3 (the formation of OCOOCO intermediate) is the rate determining step according to Campbell's degree of rate control analysis.

# The elementary steps considered for CO oxidation following ER mechanism (Figure 6) are summarized as following:

$$\mathcal{CO}(g) + * \xrightarrow{K_{co}^*} \mathcal{OC}^*$$
(23)

$$O_2(g) + * \xrightarrow{K_{O_2}} O_2^*$$
 (24)

$$O_{2}^{*} + CO^{\dagger}(g) \xrightarrow{k_{1}} CO_{2}^{\dagger}(g) + O^{*}$$
(25)

$$0^* + C0^{\dagger}(g) \xrightarrow{\kappa_2} C0^{\dagger}_2(g) + *$$
 (26)

The coverage of the intermediate species, i.e. O<sup>\*</sup> is obtained by applying steadystate approximation. The sum of coverage of adsorbents (CO, O<sub>2</sub> and O<sup>\*</sup>) and free active sites should be 1 for site \*. Hence,  $\theta_*$  is calculated as following for ER mechanism

$$\theta_{*} + \theta_{co}^{*} + \theta_{0_{2}}^{*} + \theta_{o}^{*} = 1$$
(27)

$$\theta_{*} = \frac{1}{1 + K_{C0}^{*} P_{C0} + K_{0_{2}}^{*} P_{0_{2}} + \frac{k_{1}}{k_{2}} K_{0_{2}}^{*} P_{0_{2}}}$$
(28)

The maximum rate for  $CO_2$  formation following ER mechanism can be obtained as following:

$$r_{CO_2} = 2k_1\theta_{O_2}^*P_{CO} = 9.6 \times 10^{-60}/s$$

Here, step R3, i.e. formation of  $O^*$  and physisorbed  $CO_2$ , is the rate determining step according to Campbell's degree of rate control theory.

#### Reference:

- (1) C. Stegeimann, A. Andreasen and C. T. Campbell, J. Am. Chem. Soc., 2009, 131, 8077-8082.
- (2) H. Y. Kim, H. M. Lee and G. Henkelman, J. Am. Chem. Soc., 2012, 134, 1560-1570.