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Supplementary Information

Doped h-BN monolayer as efficient noble metal-free catalysts for CO oxidation: role of dopant and water in activity and catalytic de-poisoning

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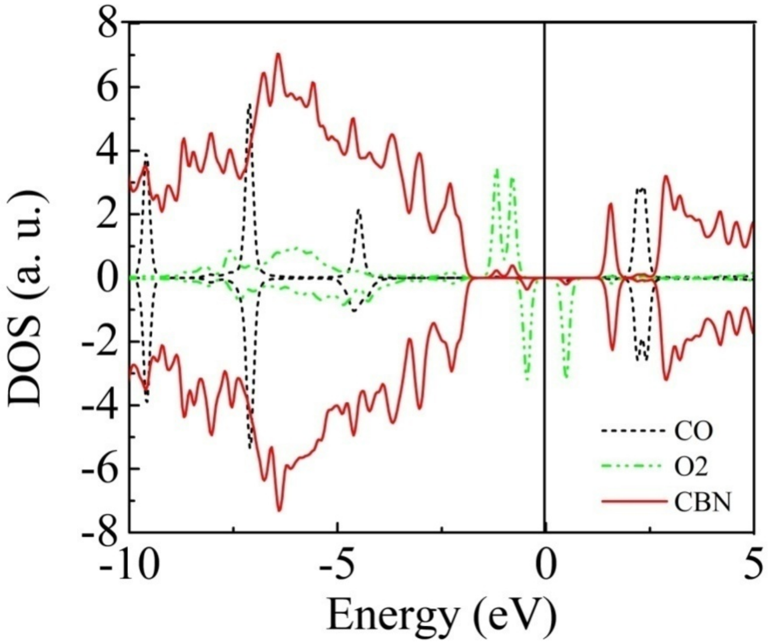

Fig. S1 Partial density of states of a CO molecule adsorbing on CBN surface pre-adsorbed with O_2. Strong hybridization between O_2 valence states and the CBN surface indicate strong bonding to the surface. The O_2 molecule acquires electrons while the donor levels of CBN become empty. From the PDOS of the CO molecule, we find that the states of CO are almost unaffected, implying that CO does not interact with the surface.

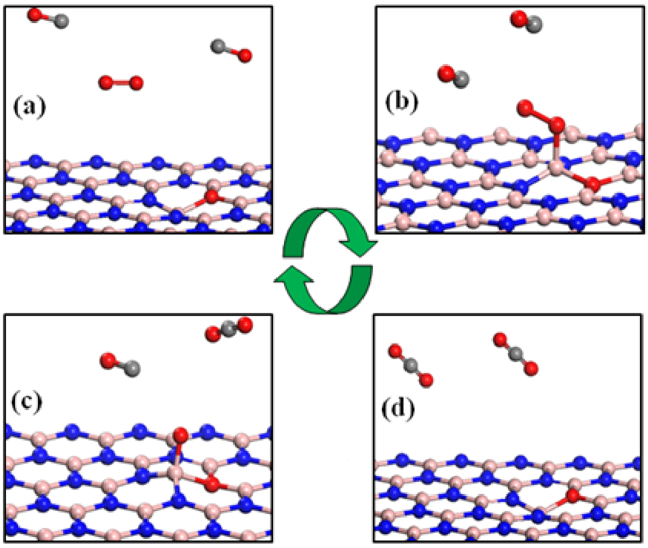

Fig. S2 Schematic of the reaction pathway of the ER mechanism in OBN surface. (a) The initial state is taken to be the case when the reactants and the surface are non interacting (b) The adsorption of O2, which is exothermic (c) the reaction of the first CO with the adsorbed oxygen, resulting in an atomic O adsorbed to the surface (d) the reaction of the second CO with the atomic oxygen to form two CO_2 molecules, that easily desorb from the surface.

The charge density difference has been calculated with respect to the fragments as

$$\Delta\rho = \rho_{O2\ldots\,CO@OBN} - (\rho_{O2\ldots\,CO} + \rho_{OBN})$$

where $\rho_{O2\ldots\,CO@OBN}$ is the electron density of the total $O_2\ldots$ CO + OBN system, and $\rho_{O2\ldots\,CO}$ and ρ_{OBN} are the unperturbed electron densities of the sorbate and substrate, respectively.

Electron accumulation on the B-C bond indicates strong chemisorptions of the intermediate with the surface.

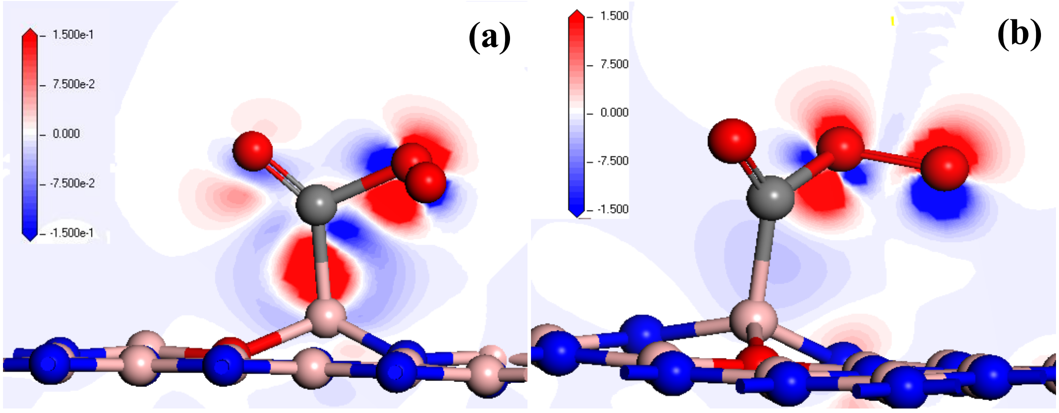

Fig. S3 Charge density difference plots of the intermediate $O_2\ldots$ CO on the OBN surface, shown along planes perpendicular to (a) CO (b) O_2. Red and blue regions indicate the electron accumulation and loss.

Microkinetic Modelling for Sabatier Activity:

The Sabatier activity was calculated using the microkinetic model for the LH mechanism as follows:

The reaction proceeds as:

$$CO + * \rightarrow CO^* \qquad (R1)$$

$$O_2 + * \rightarrow O_2^* \qquad (R2)$$

$$O_2^* + CO^* \leftrightarrow (O_2 \cdots CO)^* \rightarrow CO_2 + O^* \qquad (R3)$$

$$CO + O^* \rightarrow CO_2 + * \qquad (R4)$$

R1 and R2 denote the adsorption of CO and O_2 respectively while in R3, the simultaneous adsorption of the two reactants results in a stable intermediate that reacts to form CO_2.

Reactions R1 and R2 are assumed to be in equilibrium so that the forward and reverse rates are equal:

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

$$\theta_{co} = K_1 p(CO)\theta_*$$

and

$$k_2^+ p(O_2)\theta_* = k_1^- \theta_{o_2}$$

$$\theta_{o_2} = K_2 p(O_2)\theta_*$$

The rate determining step is R3 and hence the rate of CO_2 formation can be taken as the maximum of the rate of the reaction R3. Sabatier activity is the upper bound of the reaction rate R3, considering its forward rate alone:

$$(R3)max = k_3^+ \theta_{co}\theta_{o_2} = k_3^+ K_1 p(CO)\theta_* K_2 p(O_2)\theta_*$$

Here,

$$k_3^+ = \frac{kT}{\text{h}} e^{\frac{-E_a}{kT}}$$

E_a is the activation energy for CO_2 formation.

K_i is the equilibrium constant of reaction i,

p(CO) and $p(O_2)$ are the partial pressures of CO and O_2 : *p(CO)* = 0.01 bar and $p(O_2)$ = 0.21 bar at room temperature,

k_i^+ and k_i^- are the forward and backward rate constants for Ri respectively.

In order to calculate the coverages of CO and O_2 in terms of the free sites (θ_*) we employ the rule,

$$\theta_{o_2} + \theta_{co} + \theta_* = 1$$

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

With the rate constants given by

$$K_1 = e^{\frac{-\Delta G_1}{kT}}$$

where $\Delta G_1 = \Delta E_1 - T\Delta S_1$ is the change in Gibb's free energy of R1

ΔE_1 is the adsorption energy of CO

ΔS_1 is the change in entropy during CO adsorption

k is the Boltzmann constant

T is the temperature.

$$K_2 = e^{\frac{-\Delta G_2}{kT}}$$

where $\Delta G_2 = \Delta E_2 - T\Delta S_2$ is the change in Gibb's free energy of R2

ΔE_2 is the adsorption energy of O_2

ΔS_2 is the change in entropy during O_2 adsorption

Finally, the Sabatier activity is calculated as

$$Activity = kT\ ln\left(\frac{(R3)max}{h/kT}\right)$$

Microkinetic Modelling and Sabatier Analysis for ER mechanism:

The reaction proceeds as follows:

$O_2 + * \rightarrow O_2^*$ (R1)

$CO + O_2^* \rightarrow O^* + CO_2$ (R2)

$O^* + CO \rightarrow CO_2 + *$ (R3)

Assuming that reaction R1 is in equilibrium, we get

$$\theta_{o_2} = K_1 p(O_2)\theta_*$$

The formation of CO_2 (R2) is rate determining. The maximum of the rate R2 is calculated as the forward rate,

$$(\mathrm{R2})\mathrm{max} = k_2^{\,+}\, p(CO)\theta_{O2}$$

Where $$k_2^{\,+} = \frac{kT}{\mathrm{h}} e^{\frac{-E_a}{kT}}$$

Since the sum of coverages of the reactants and free sites has to be 1, we get

$$\theta_* + \theta_{o_2} = 1$$

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

Where K_1 is the equilibrium constant for R1 given by,

$$K_1 = e^{\frac{-\Delta G_1}{kT}}$$

where $\Delta G_1 = \Delta E_1 - T\Delta S_1$ is the change in Gibb’s free energy of R1

ΔE_1 is the adsorption energy of O_2

ΔS_1 is the change in entropy during O_2 adsorption

The Sabatier Activity is defined as

$$Activity = kT\, ln\left(\frac{(R2)max}{\mathrm{h}/kT}\right)$$

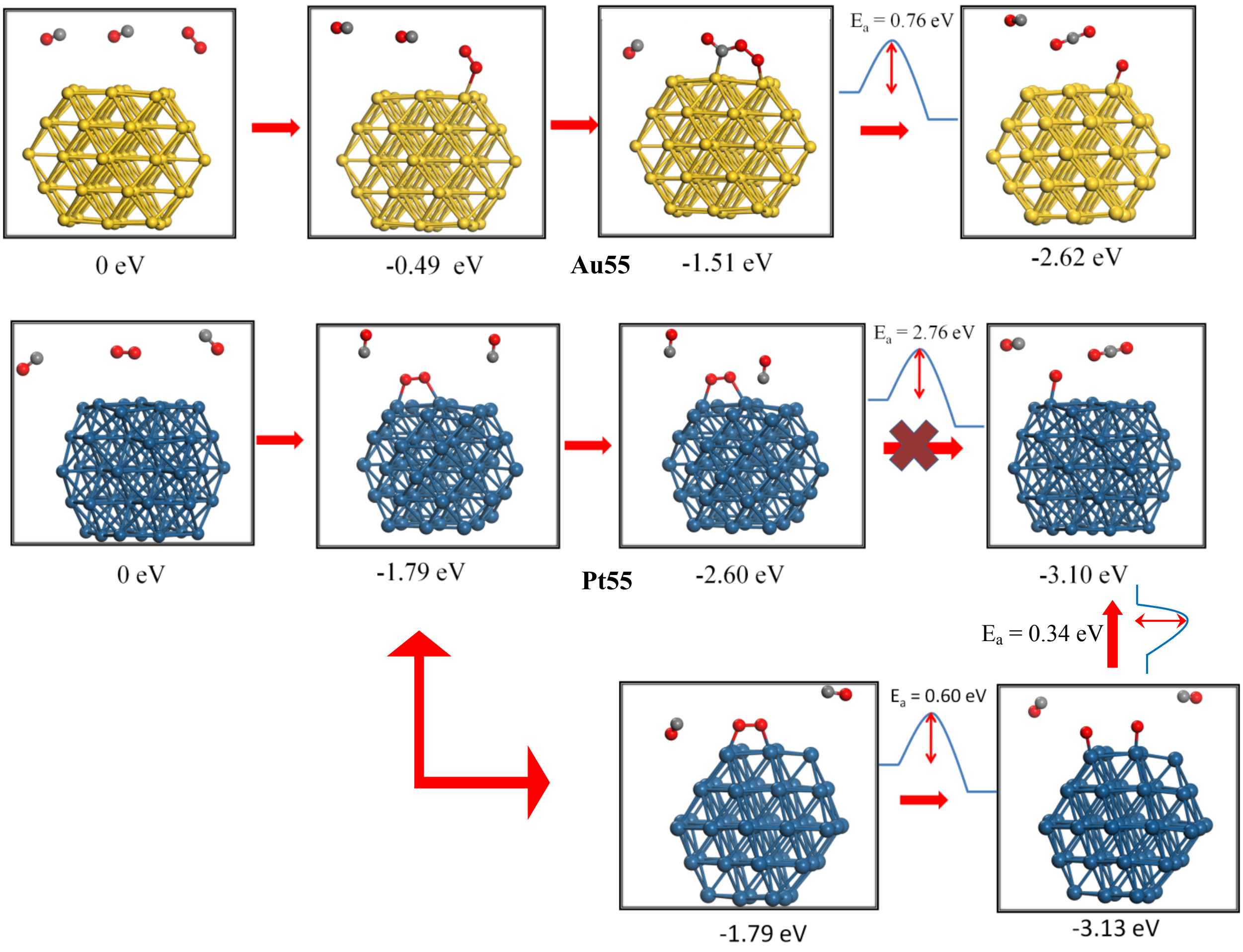

Fig. S4: Local configurations of the reactants on the Au55 and Pt55 clusters along the minimum-energy pathway for the formation of first CO_2. The reaction energies with reference to free (O_2 and two CO) molecule and surface (taken as 0 eV) are given beneath each Fig..

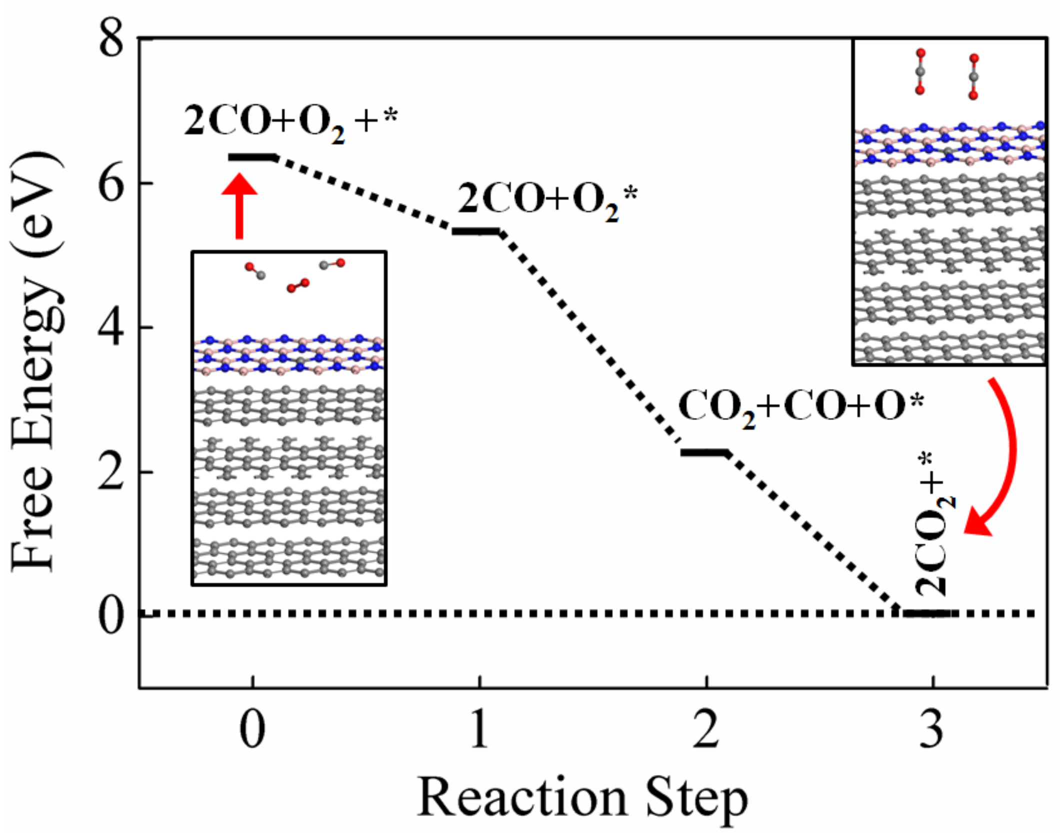

Fig. S5: Free energy pathways for CO oxidation via ER mechanism on C doped h-BN with graphitic substrate.