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Supplementary Information

CO Oxidation by MoS_2-Supported Au Nanoparticles: Effects of Vacancy Formation and Tensile Strain

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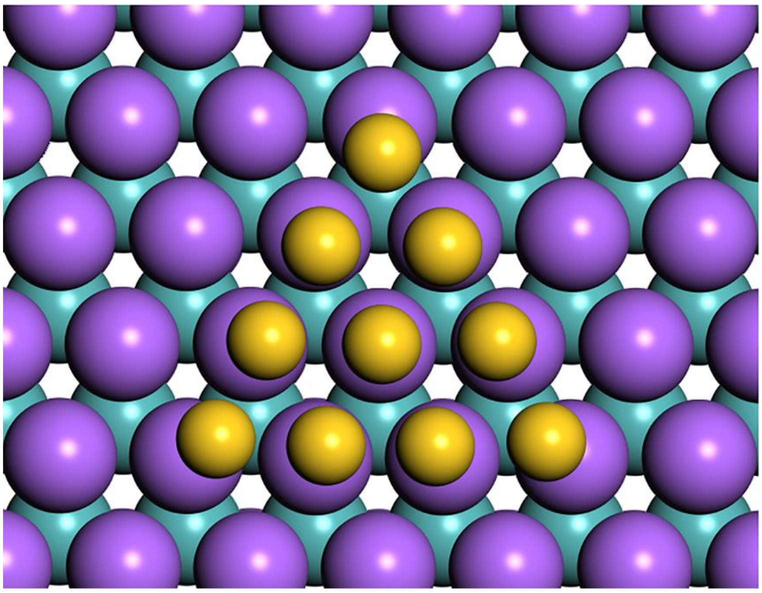
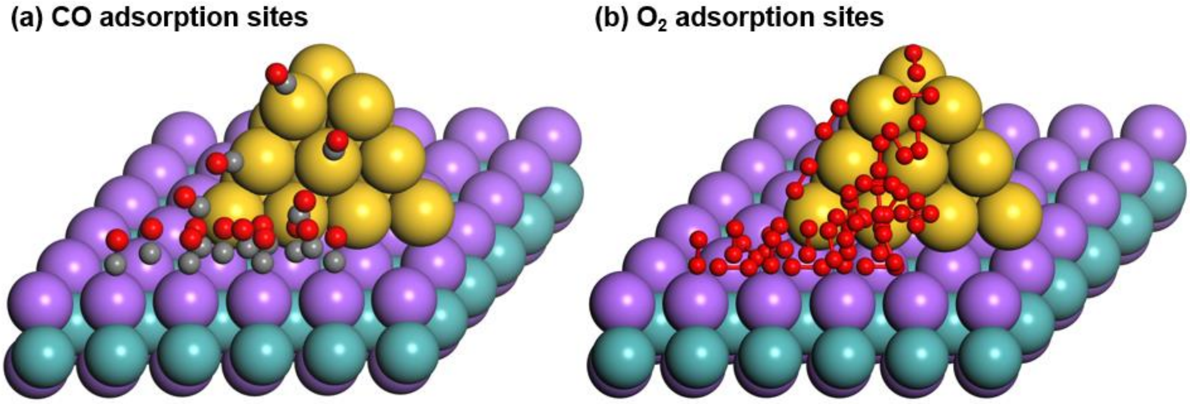


Fig. S1 The geometric configuration of the bottom layer of the Au_{19} clusters and the MoS_2 support. Each gold atom is well matched with the sulfur atom of the MoS_2 that is immediately beneath it. Three-fold symmetry is also clearly shown.


(a) CO adsorption sites

(b) O_2 adsorption sites

Fig. S2 CO and O_2 adsorption on Au_{19}/MoS_2. (a) and (b) show where the CO and O_2 adsorption was tested, respectively.

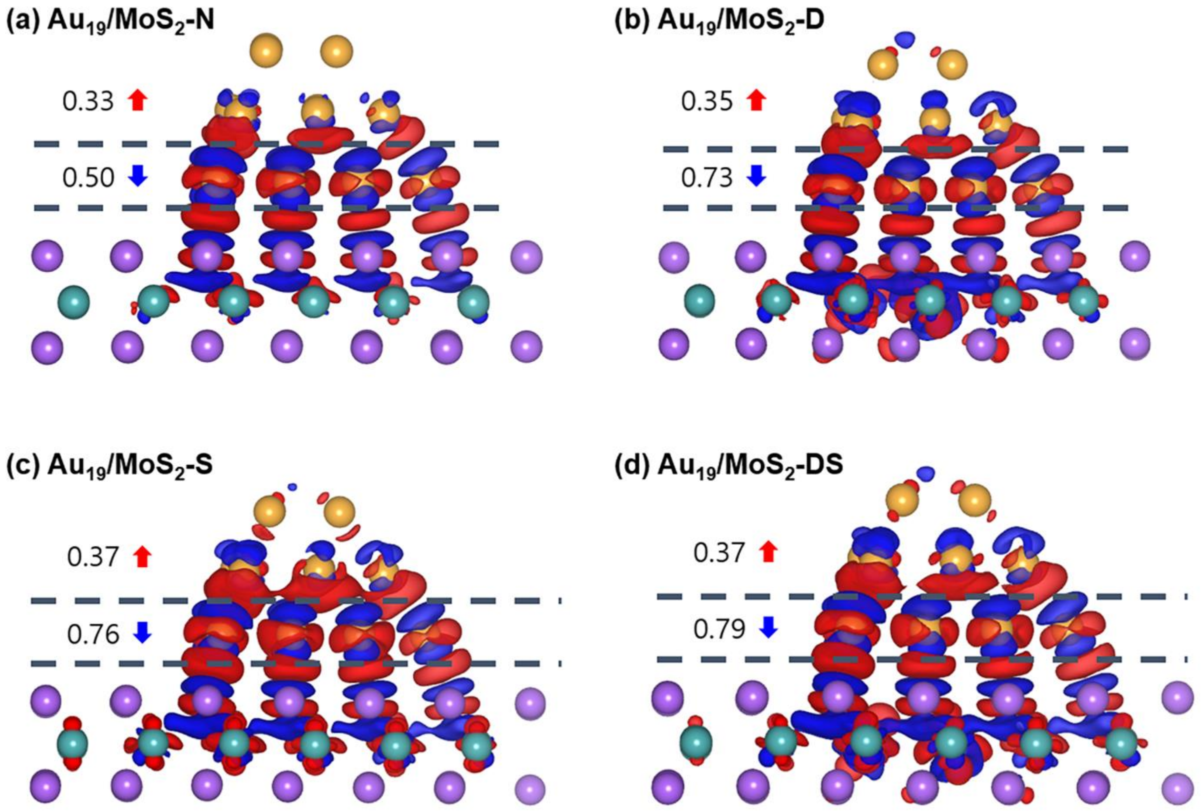


Fig. S3 The charge density difference (CDD) of the various Au_{19}-MoS_2 systems considered in this work. Electronic interaction between the cluster and the support seems to be enhanced by modification of the support compared to the bare system. Red isosurfaces represent electron accumulation and blue ones correspond to electron depletion. The isosurface value is 0.001 e/Bohr^3.

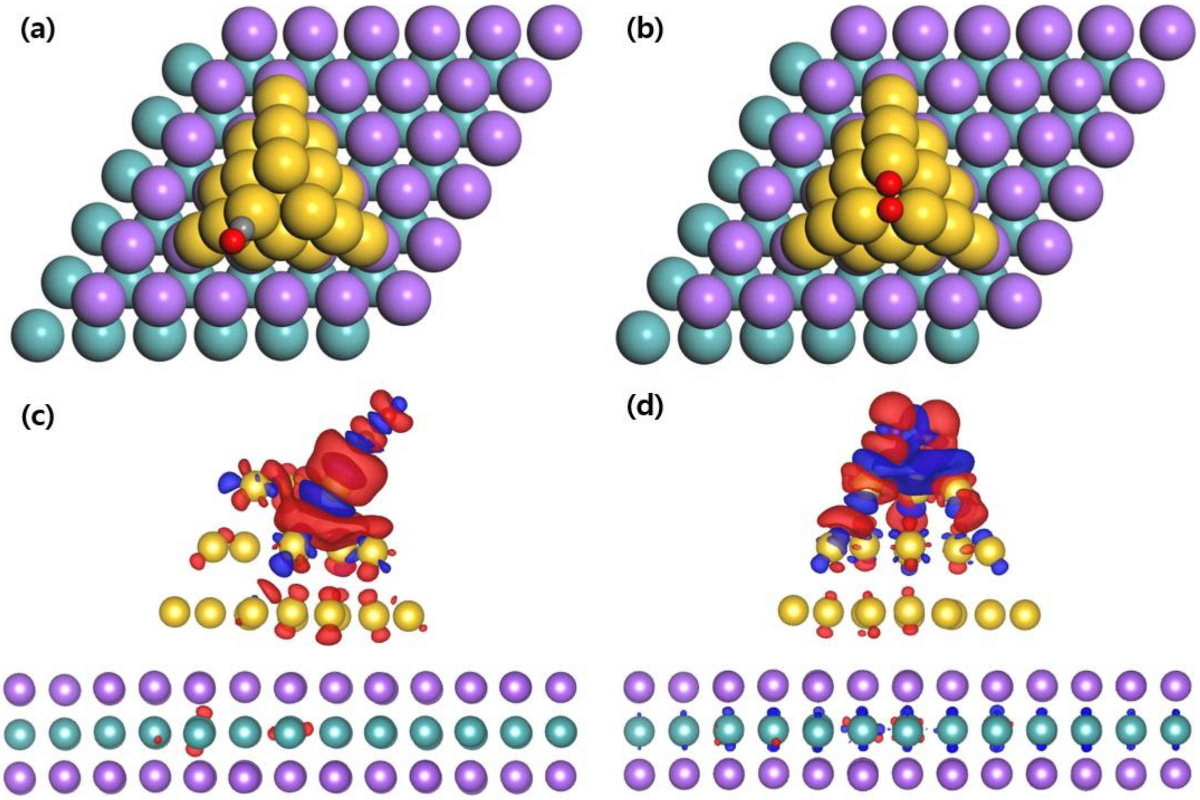


Fig. S4 Bonding of CO and O_2 to Au_3 active sites of an Au_{19} cluster supported by MoS_2. The black and red balls represent C and O atoms, respectively. The charge density differences of CO and O_2 adsorption are depicted in (c) and (d), respectively. Red isosurfaces represent electron accumulation, and blue isosurfaces correspond to electron depletion. The filling of the 2π* orbital of CO during CO adsorption is clearly observed. The CO molecular charge increased by a small amount, 0.05 e^-, and the O_2 molecule gained a large amount of charge, 0.56 e^-, on its 2π* orbital. The isosurface value is 0.001 e/$Bohr^3$.

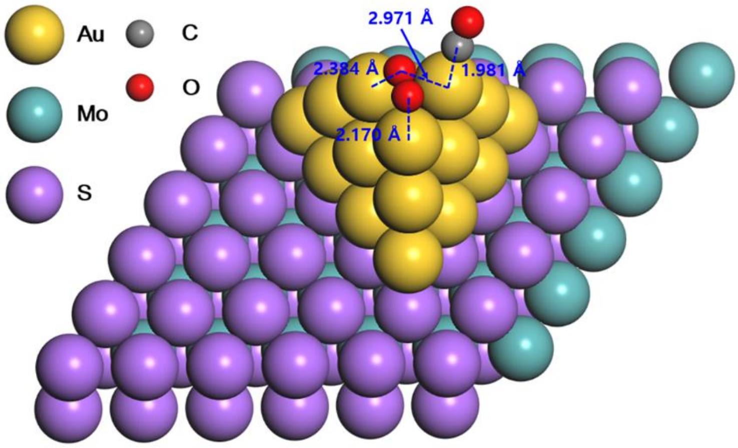


Fig. S5 A geometry-optimized configuration when CO and O_2 are coadsorbed on the Au_3 active site of the Au_{19} cluster.

Supplementary Video

The density functional molecular dynamics (DFT-MD) result for 6.5 ps at 300K is provided in ESI. Please see the attached video. This results supports that the pyramidal Au_{19} NP on the MoS_2 support does not exhibit any significant deformation during relaxation.

Theoretical Details of Micro-kinetic Analysis

The micro-kinetic model for CO oxidation via the bimolecular Langmuir-Hinshelwood mechanism on the Au_{19} cluster in Fig. 3 and Fig. 5 is described below.

Here, * represents the active sites of the Au_{19} cluster. CO and O_2 adsorb on the active sites, denoted as CO* and O_2*, respectively.

CO(g) + * ↔ CO* (R1: K_{CO}^{*})

O_2(g) + * ↔ O_2* (R2: $K_{O_2}^{*}$)

CO* + O_2* ↔ OCOO* (R3: k_3)

OCOO* ↔ CO_2(g) + O* + * (R4: k_4)

Assuming that the R1 and R2 are in kinetic equilibrium, the rates of these reactions can be expressed as:

$$\mathrm{rate(R1)} = k_1^{+} P(CO)\theta^{*} - k_1^{-}\theta_{CO}^{*} = 0 \rightarrow \theta_{CO}^{*} = \left(\frac{k_1^{+}}{k_1^{-}}\right)\mathrm{P(CO)}\theta^{*} = K_{CO}^{*} P(CO)\theta^{*}$$

$$\mathrm{rate(R2)} = k_2^{+} P(O_2)\theta^{*} - k_2^{-}\theta_{O_2}^{*} = 0 \rightarrow \theta_{O_2}^{*} = \left(\frac{k_2^{+}}{k_2^{-}}\right)\mathrm{P}(O_2)\theta^{*} = K_{O_2}^{*} P(O_2)\theta^{*}$$

where

$$K_{CO}^{*} = \exp(\frac{-\Delta G_{CO}^{*}}{k_B T}) = \exp(\frac{-(E_{ads}^{CO} - T\Delta S_{CO}^{*})}{k_B T})$$

$$K_{O_2}^{*} = \exp(\frac{-\Delta G_{O_2}^{*}}{k_B T}) = \exp(\frac{-(E_{ads}^{O_2} - T\Delta S_{O_2}^{*})}{k_B T})$$

where ΔS_{CO}^{*} and $\Delta S_{O_2}^{*}$ represent the entropy change involved in CO adsorption and O_2 adsorption, respectively. k_i^{+} and k_i^{-} represent the forward and inverse reaction constants for Ri, respectively.

We assumed that the inverse reaction barrier of reaction 4 is large enough to neglect reaction 4. The OCOO coverage (θ_{OCOO}^{*}) can be calculated by applying the “steady-state” approximation:

$$\frac{d\theta_{OCOO}^{*}}{dt} = k_3^{+}\theta_{CO}^{*}\theta_{O_2}^{*} - k_3^{-}\theta_{OCOO}^{*} - k_4^{+}\theta_{OCOO}^{*} = 0$$

$$\theta_{OCOO}^{*} = \frac{k_3^{+}}{k_3^{-} + k_4^{+}}\theta_{CO}^{*}\theta_{O_2}^{*}$$

where

$$k_3^{+} = \frac{k_B T}{h}\exp\left(\frac{-E_3^{+}}{k_B T}\right)$$

$$k_3^{-} = \frac{k_B T}{h}\exp\left(\frac{-E_3^{-}}{k_B T}\right)$$

$$k_4^{+} = \frac{k_B T}{h}\exp\left(\frac{-E_4^{+}}{k_B T}\right)$$

E_3: Activation energy for reaction 3

E_4: Activation energy for reaction 4

Because the sum of CO*, O_2*, OCOO* and free adsorption sites should be equal to 1, we can numerically derive θ^{*} from θ_{CO}^{*}, $\theta_{O_2}^{*}$ and θ_{OCOO}^{*}:

$$\theta^{*}_{OCOO} + \theta^{*}_{CO} + \theta^{*}_{O_2} + \theta^{*} = 1$$

$$\frac{k_3^{+}}{k_3^{-} + k_4^{+}} K^{*}_{CO} P(CO) \theta^{*} K^{*}_{O_2} P(O_2) \theta^{*} + K^{*}_{CO} P(CO) \theta^{*} + K^{*}_{O_2} P(O_2) \theta^{*} + \theta^{*} - 1 = 0$$

$$\theta^{*} = \frac{-\left[K^{*}_{CO} P(CO) + K^{*}_{O_2} P(O_2)\right] + \sqrt{\left[K^{*}_{CO} P(CO) + K^{*}_{O_2} P(O_2)\right]^2 + 4\frac{k_3^{+}}{k_3^{-} + k_4^{+}} K^{*}_{CO} P(CO) K^{*}_{O_2} P(O_2)}}{2\frac{k_3^{+}}{k_3^{-} + k_4^{+}} K^{*}_{CO} P(CO) K^{*}_{O_2} P(O_2)}$$

The maximum rate of CO_2 formation, $\mathrm{Rate}(R4)^{max}$, can be obtained as:

$$\mathrm{Rate}(R4)^{max} = \theta^{*}_{OCOO} k_4^{+}$$

The reaction rate was calculated at T = 298 K, P(CO) = 0.01 bar, P(O_2) = 0.21 bar, ΔS_1 = 205.1 J/mol·K, and ΔS_2 = 197.7 J/mol·K [5].

We used the micro-kinetic model of reference [62] for CO oxidation via the trimolecular Langmuir-Hinshelwood mechanism on the Au_{19} cluster in Fig. 4.

References

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62. C. Liu, Y. Tan, S. Lin, H. Li, X. Wu, L. Li, Y. Pei and X. C. Zeng, *J. Am. Chem. Soc.*, 2013, **135**, 2583-2595