# Supporting Information

# Unlocking the Catalytic Activity of an Eight-atom Gold Cluster with a Pd Atom

Jiayu Xu,[1] Shun Xu,[1] Mingyang Chen,[2,3]* and Yan Zhu[1,]*

[1]School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[2]Center for Green Innovation, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

[3]Beijing Computational Science Research Center, Beijing 100193, China

## Supporting Figures and Tables

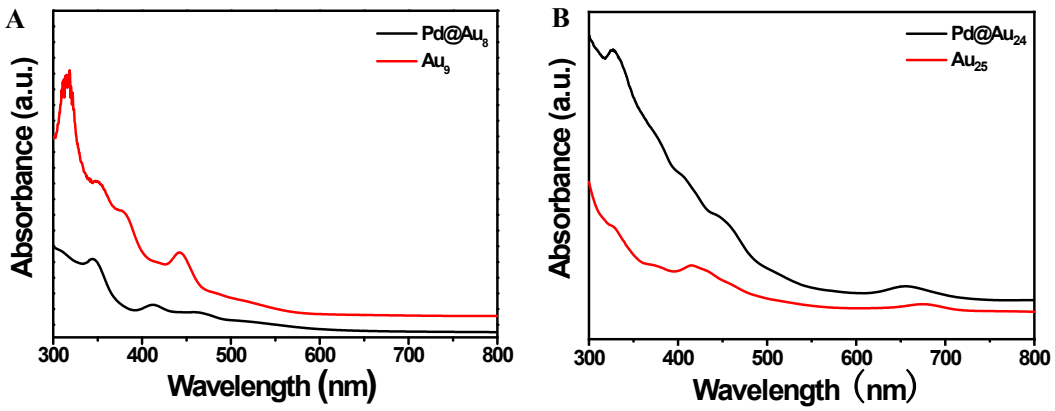



**Figure S1.** UV-vis spectra of (A) fresh $Au_8Pd$ and $Au_9$; (B) fresh $Au_{24}Pd$ and $Au_{25}$ clusters.

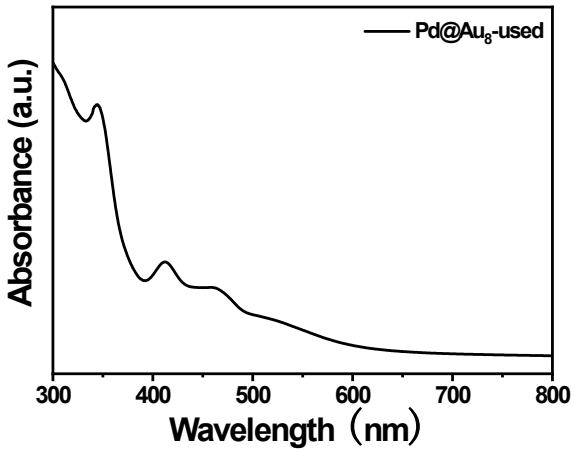



**Figure S2.** UV-vis spectrum of the spent $Au_8Pd$ solved in $CH_2Cl_2$.

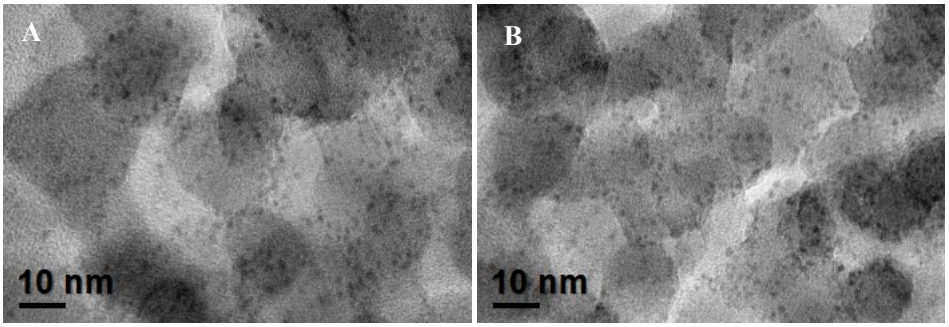



**Figure S3.** TEM images of the $Au_8Pd/SiO_2$ catalysts (A) before reaction and (B) after reaction.

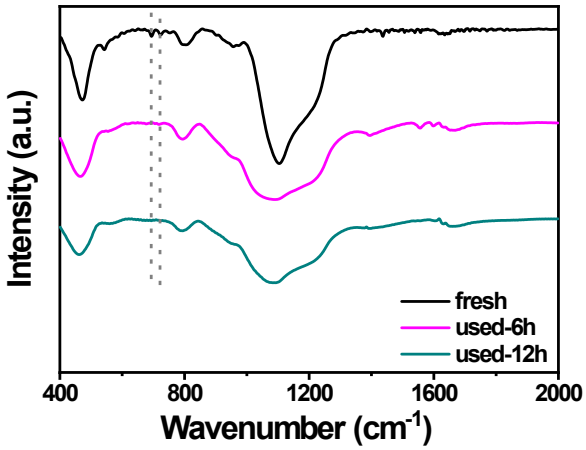



**Figure S4.** IR spectra of the $Au_8Pd$ catalyst before reaction and after reaction.

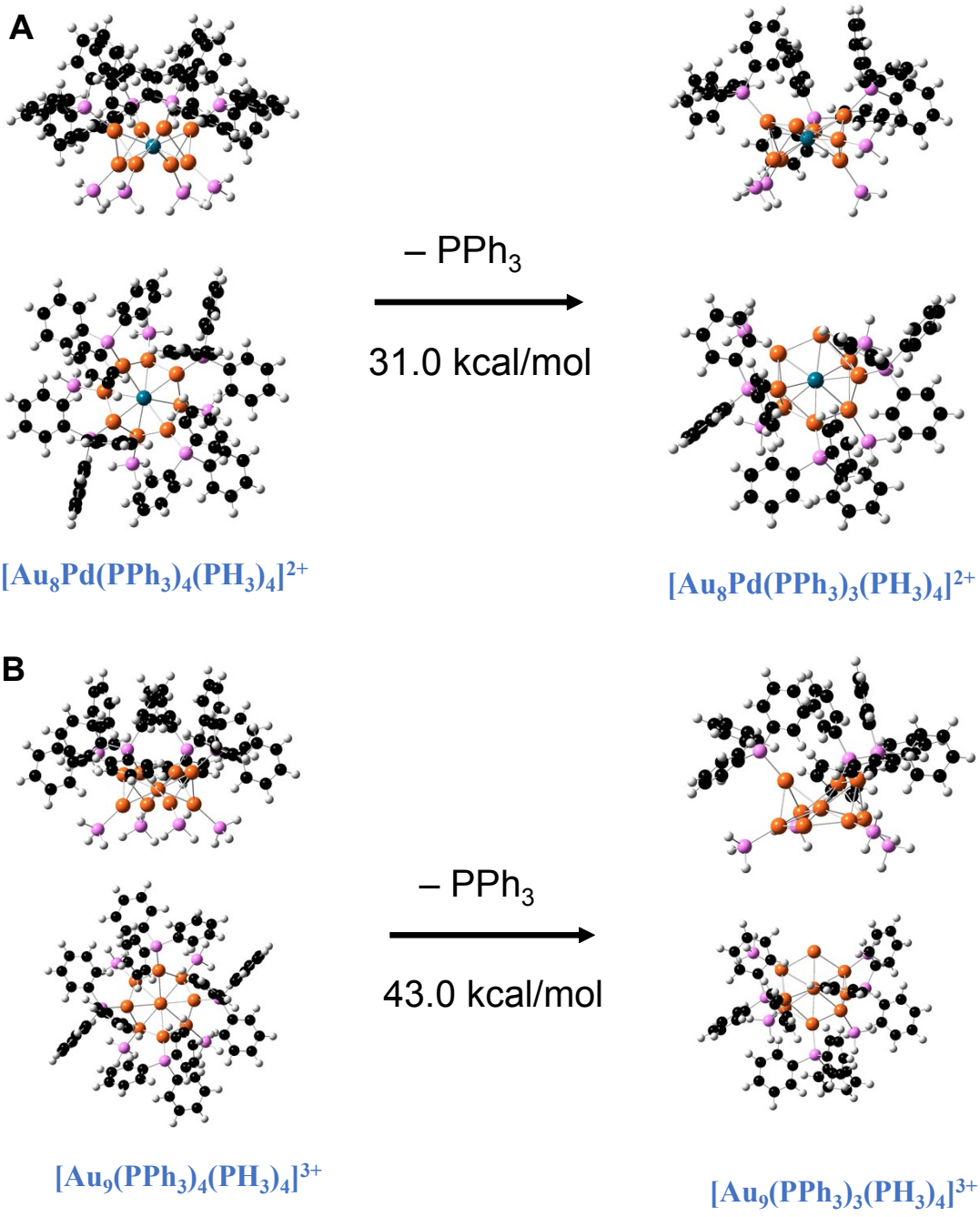
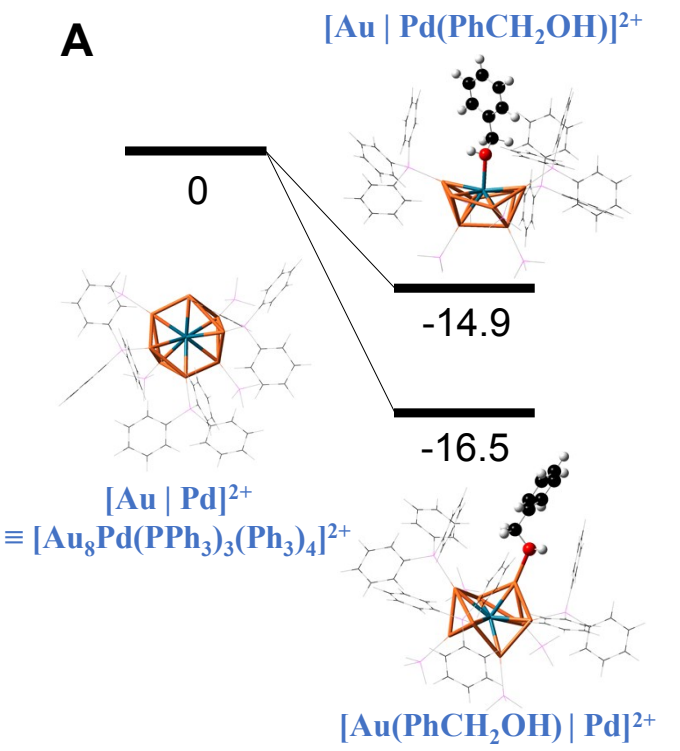
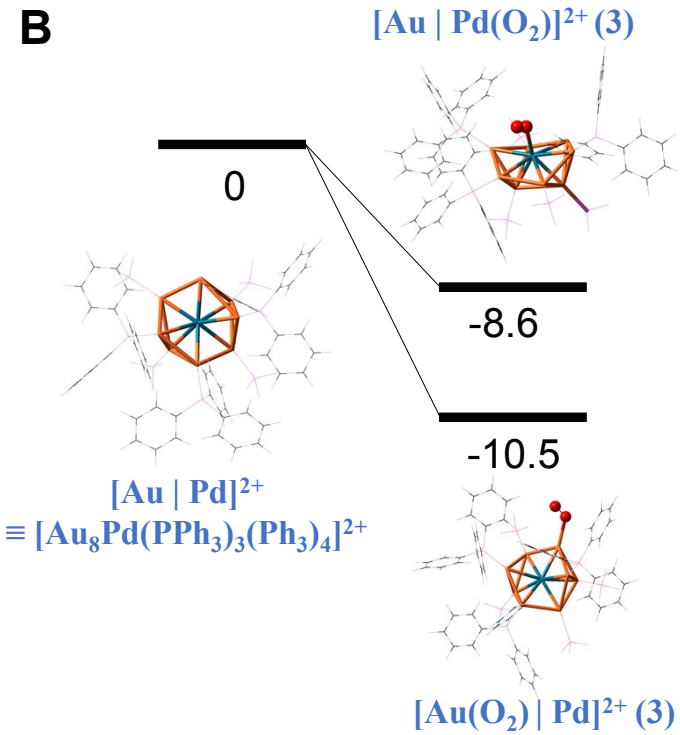



**Figure S5.** Depassivation of (A) $[Au_8Pd(PPh_3)_4(PH_3)_4]^{2+}$ and (B) $[Au_8Pd(PPh_3)_4(PH_3)_4]^{2+}$ by the removal of one $PPh_3$. All of the species are ground state singlets. Color code: orange = Au, dark-cyan = Pd, red = O, black = C, pink = P, and grey = H.


A
[Au | Pd(PhCH2OH)]2+
0
-14.9
-16.5
[Au | Pd]2+
≡ [Au8Pd(PPh3)3(Ph3)4]2+
[Au(PhCH2OH) | Pd]2+


B
[Au | Pd(O2)]2+ (3)
0
-8.6
-10.5
[Au | Pd]2+
≡ [Au8Pd(PPh3)3(Ph3)4]2+
[Au(O2) | Pd]2+ (3)

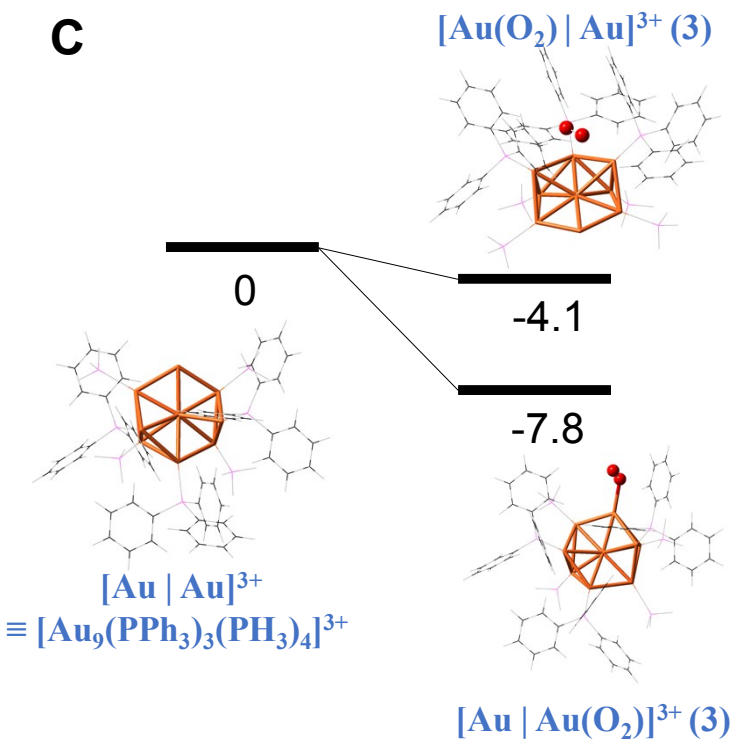



**Figure S6.** Adsorption of (A) benzyl alcohol over $[Au_8Pd(PPh_3)_3(PH_3)_4]^{2+}$, (B) $O_2$ over $[Au_8Pd(PPh_3)_3(PH_3)_4]^{2+}$, and (C) $O_2$ over $[Au_9(PPh_3)_3(PH_3)_4]^{3+}$. All of the species are ground state singlets unless otherwise indicated. Triplet ground states are indicated by '(3)'. Color code: orange = Au, dark-cyan = Pd, red = O, black = C, pink = P, and grey = H. Adsorption enthalpies are in kcal/mol.

**Table S1.** Predicted deprotonation energies for relevant species in the benzyl alcohol oxidation reactions with $O_2$ catalyzed by $Au_8Pd$ at the PBE/LANL2DZ level. All ground-state species are singlet unless otherwise noted ('(3)' for triplet).

| Reactant | Product | Deprotonation Energy kcal/mol |
|---|---|---|
| $PhCH_3$ | $PhCH_2^-$ | 383.3 |
| $PhCH_2OH$ | $PhCH_2O^-$ | 366.9 |
| $[Au(PhCH_2OH) \mid Pd(O_2)]^{2+}$ (3) | $[Au(PhCH_2O) \mid Pd(O_2)]^{+}$ (3) | 231.8 |
| $[Au(PhCH_2O) \mid Pd(OOH)]^{2+}$ | $[Au(PhCHO) \mid Pd(OOH)]^{+}$ | 209.4 |
| $[Au(PhCH_2OH) \mid PdO]^{2+}$ (3) | $[Au(PhCH_2O) \mid PdO]^{+}$ (3) | 234.3 |
| $[Au(PhCH_2O) \mid PdOH]^{2+}$ | $[Au(PhCHO) \mid PdOH]^{2+}$ | 205.9 |

**Table S2.** Predicted proton affinities for relevant species in the benzyl alcohol oxidation reactions catalyzed by $Au_8Pd$ at the PBE/LANL2DZ level. All ground-state species are singlet unless otherwise noted ('(3)' for triplet).

| Reactant | Product | Proton affinity kcal/mol |
|---|---|---|
| $O_2$ (3) | $O_2H^+$ (3) | 96.9 |
| $CO_3^{2-}$ | $HCO_3^-$ | 493.3 |
| $HCO_3^-$ | $H_2CO_3$ | 331.7 |
| $[Au(PhCH_2O) \mid Pd(O_2)]^+$ (3) | $[Au(PhCH_2O) \mid Pd(OOH)]^{2+}$ | 218.0 |
| $[Au(PhCHO) \mid Pd(OOH)]^+$ | $[Au(PhCHO) \mid PdO]^{2+}$ (3) + $H_2O$ | 232.4 |
| $[Au(PhCH_2O) \mid PdO]^+$ (3) | $[Au(PhCH_2O) \mid PdOH]^{2+}$ (3) | 247.2 |
| $[Au(PhCHO) \mid PdOH]^+$ | $[Au(PhCHO) \mid Pd]^{2+} + H_2O$ | 205.9 |