Supporting Information for

Complex behavior of Pd₇ cluster supported on TiO₂(110) during CO oxidation : adsorbate-driven promoting effect

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S1 Computational details

All calculations were performed by using density-functional theory (DFT) as implemented in Vienna ab-initio simulation package (VASP).^{1,2} The interaction between ions and electrons is described using the projector augmented wave (PAW) method.^{3,4} The spin-polarized GGA-PW91 exchange-correlation functional⁵ is used with [Pd]- $5s^{1}4d^{9}$, [Ti]- $3s^{2}3p^{6}4s^{2}3d^{2}$, [O]- $2s^{2}2p^{4}$, and [C]-2s²2p² treated as valence electrons. The Kohn–Sham orbitals are expanded in a planewave basis set with a kinetic energy cutoff of 400 eV. The conjugate gradient algorithm was used in optimization and the convergence threshold was set to be 10⁻⁴ eV in total energy and 0.02 eV/Å in Hellmann-Feynman force on each atom. The previous DFT calculations using slab models for stoichiometric TiO2-supported metal clusters show that standard DFT-GGA and GGA+U result in the similar trends in stability of metal clusters, adsorption energy of an adsorbate, charge localization and electronic property.⁶⁻¹¹ We used a $p(4\times4)$ nine-layer (O-Ti-O) slab with a 15 Å vacuum between the slabs to model TiO_2 (110) surface. The Brillouin-zone was sampled by 4×4×1 k-points using the Monkhorst-Pack scheme.¹² In the calculations, all atoms were allowed to fully relax except those of the bottom six layers (O-Ti-O) in TiO₂ (110) slab, which were fixed at their optimized bulk positions. The reaction pathways of CO oxidation on Pd₇/TiO₂(110) were investigated by the climbing-image nudged elastic band method (CI-NEB).^{13,} ¹⁴ The adsorption energy is defined as $E_{ads} = E_{(ads/slab)} - E_{slab} - E_{(ads)}$, where $E_{(ads/slab)}$,

 $E_{slab,}$ and $E_{(ads)}$ are the total energy of ads/slab, clean surface, and gas-phase adsorbate molecule.



(b)



Figure S1. Potential energy profile for CO oxidation on Pd_7 -3D/TiO₂(110) via (a) O₂ dissociation on Pd sites and (b) O₂ dissociation at the interface, and (c) on CO-saturated Pd₇-2D/TiO₂(110) via O₂ dissociation on Pd sites.

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