Supporting Information

Theoretical Study of Ripening Mechanisms of Pd Clusters on Ceria

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1. Gas-phase Pd_n clusters

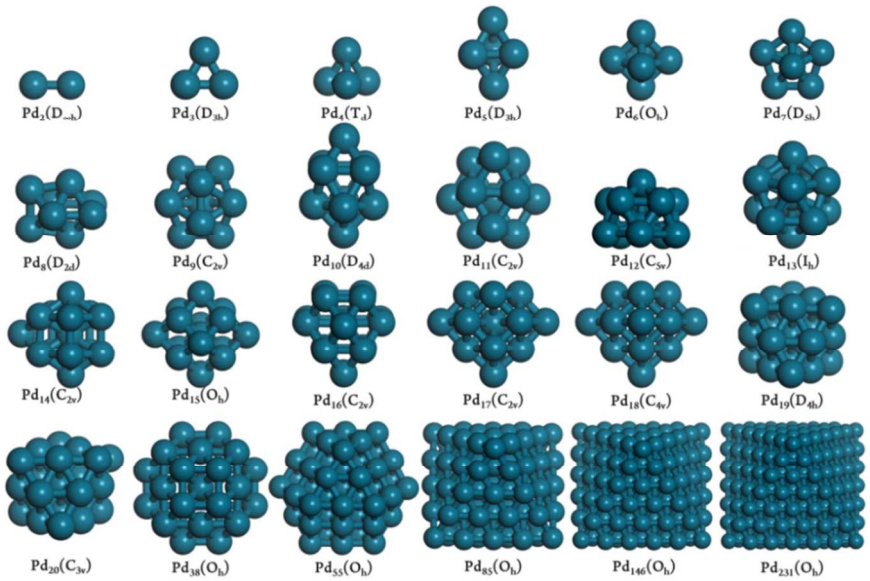

Figure S1a. Lowest-energy structures of Pd_n clusters with n = 2-20, 38, 55, 85, 146 and 231.

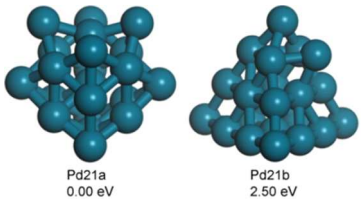

Figure S1b. Determined configurations of most stable Pd_{21} cluster and the supported Pd_{21} cluster in gas phase. The supported Pd_{21} cluster is unstable in gas phase, and the ceria support can change the stability and morphology of clusters due to the interplay between cluster and ceria support.

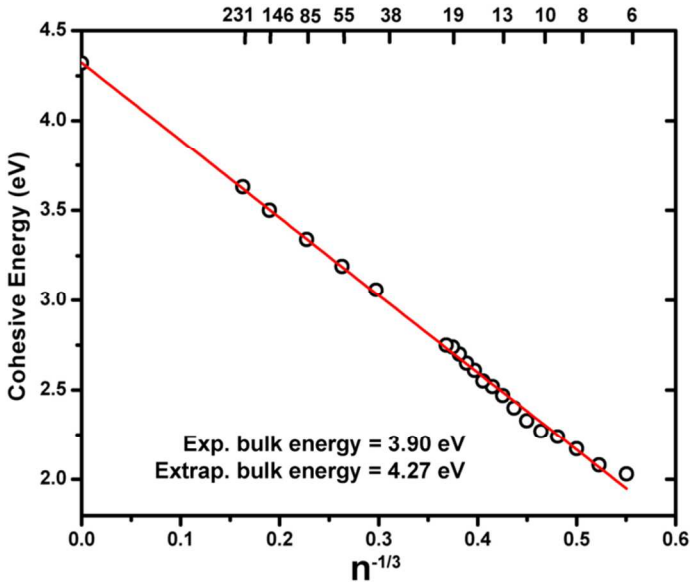

Figure S2. Cohesive energy of Pd_n clusters, with n = 2-20, 38, 55, 85, 146 and 231 as a function of $n^{-1/3}$.

2. Isomers of each Pd_n clusters (n = 1-21, 41) on CeO_2(111) surface

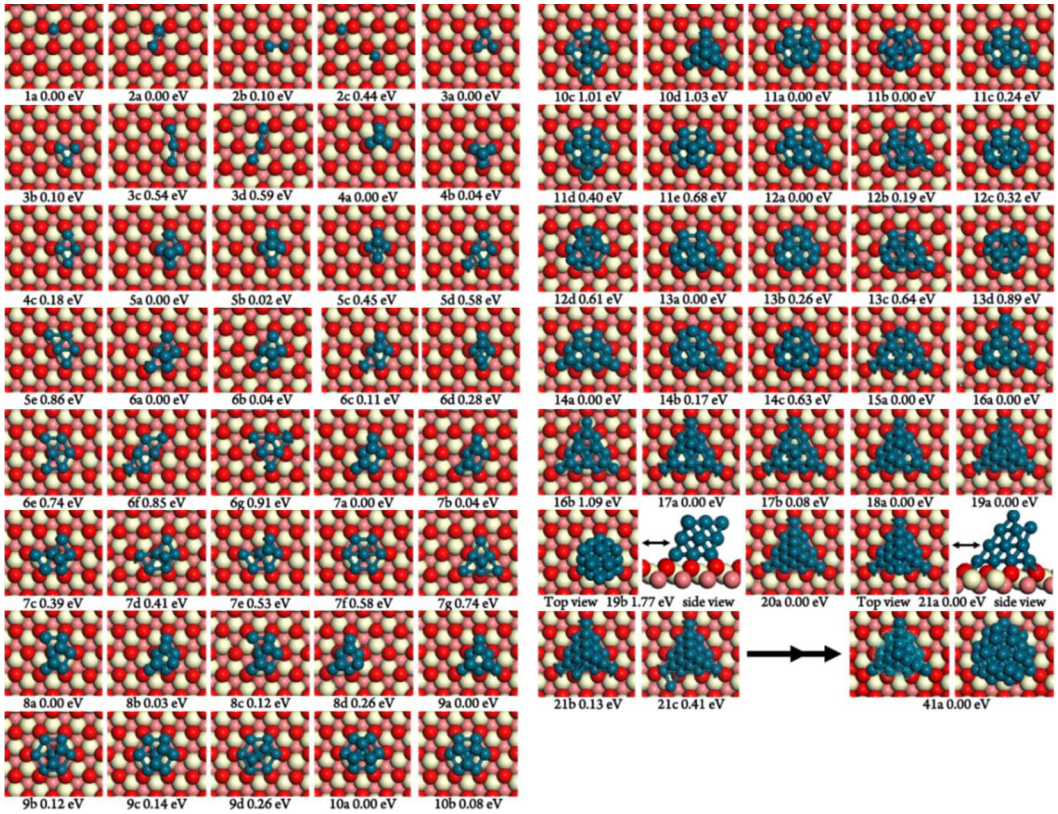

Figure S3a. Various isomers and relative energies of Pd_n clusters on CeO_2(111) surface. Color code: dark-cyan, Pd; red, surface O; light-coral, subsurface O; light-yellow: Ce.

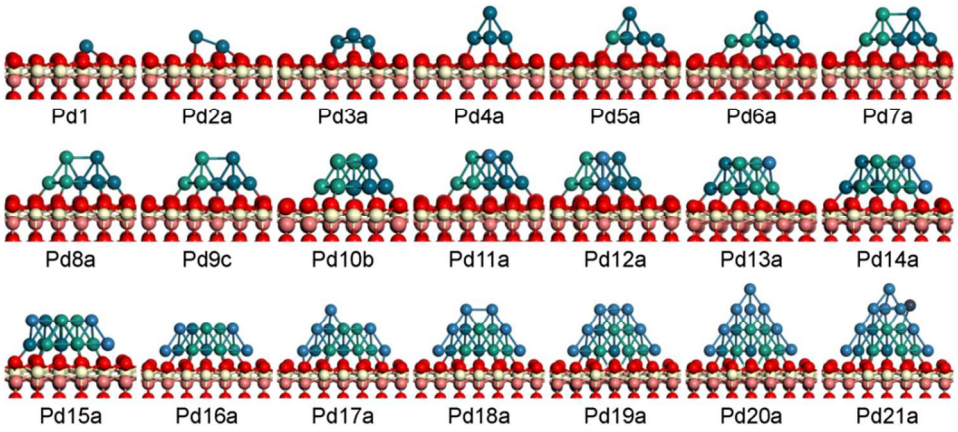

Figure S3b. The side-views of Stable Pd_n clusters (n = 1-21) on the $CeO_2(111)$ surface (Color code: red, surface O; light-yellow, Ce; coral, subsurface O; dark-cyan, 1st – 4th Pd; green, 5th – 10th Pd; blue, 11th – 20th Pd; black, 21st Pd). These structures correspond to ones in Figure 1, respectively.

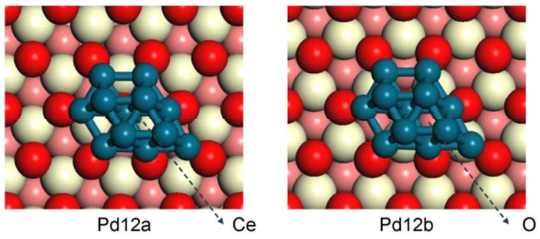

Figure S3c. Enlarged view on the structures of Pd12a and Pd12b. For 12a, the top three atoms correspond to the lattice O atoms in subsurface and the hollow site corresponds to Ce atom; while for 12b, the top three atoms correspond to the surface Ce atoms and the hollow site corresponds to subsurface O atom.

3. Diffusion of single Pd atoms on $CeO_2(111)$ surface

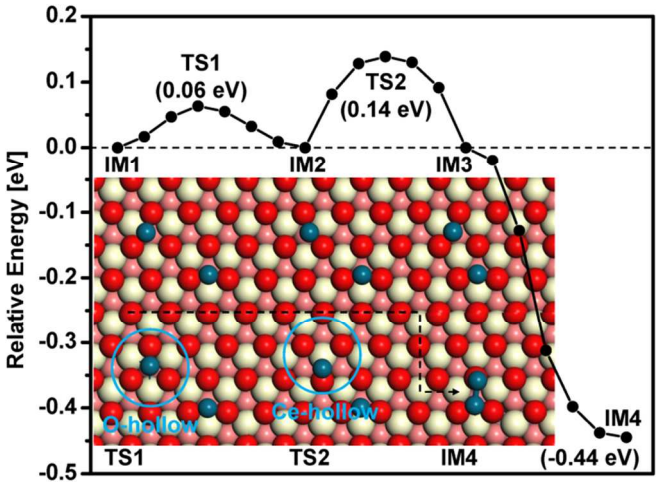

Figure S4. Diffusion Pathway of single Pd atoms on $CeO_2(111)$ surface.

4. Diffusion of Pd_n clusters (n = 2, 3, 7 and 10) on CeO_2(111) surface

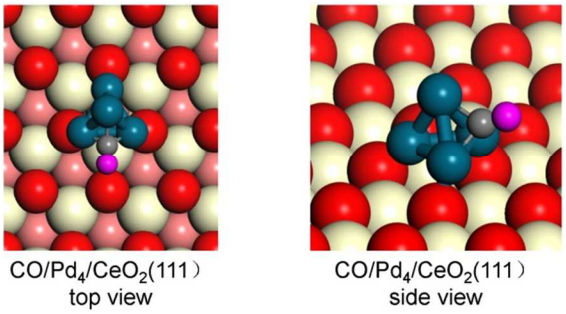

Figure S5. CO adsorption on the hollow site of supported Pd_4 cluster.

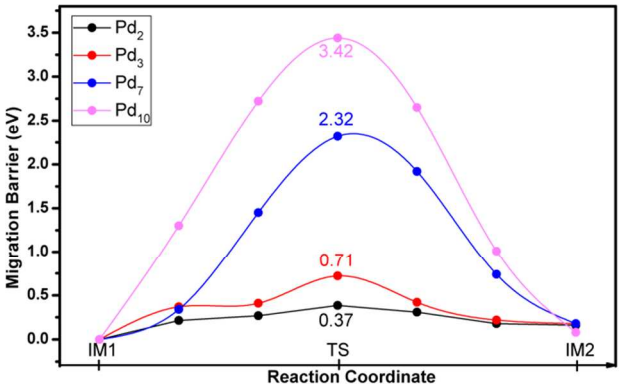

Figure S6. Potential energy profiles of Pd_n clusters (n=2, 3, 7, 10) migration on CeO_2(111) surface via two-step mechanism involving cluster rotation.

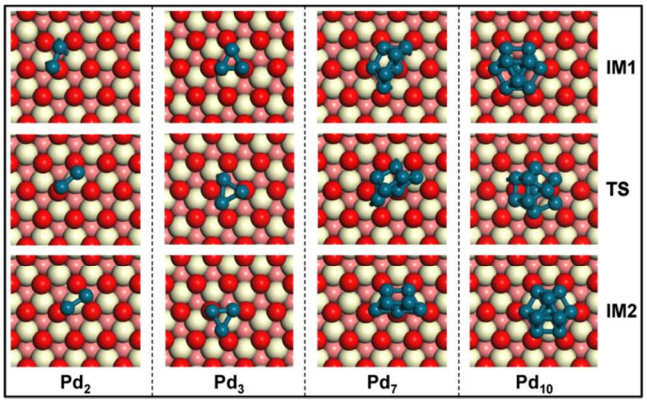

Figure S7. Relevant configurations of Pd_n clusters (n=2, 3, 7, 10) diffusion involving rotation on CeO_2(111) surface.

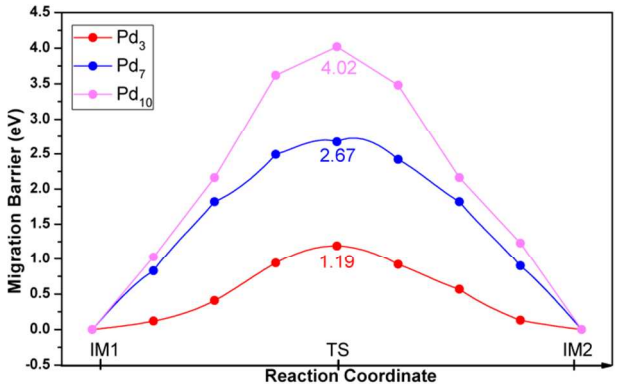

Figure S8. Potential energy profiles of Pd_n clusters (n= 3, 7, 10) migration on CeO_2(111) surface via direct mechanism.

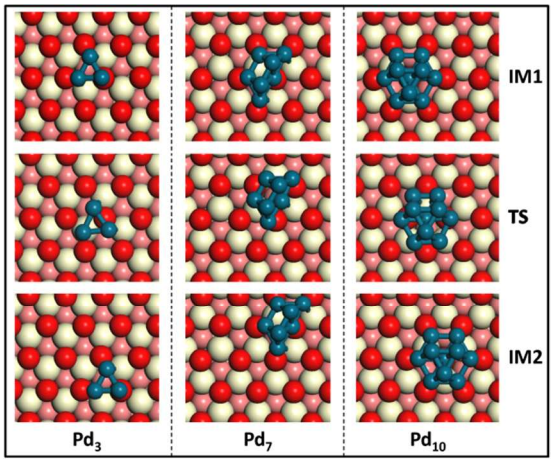

Figure S9. Relevant configurations of Pd_n clusters (n= 3, 7, 10) diffusion directly on CeO_2(111) surface.

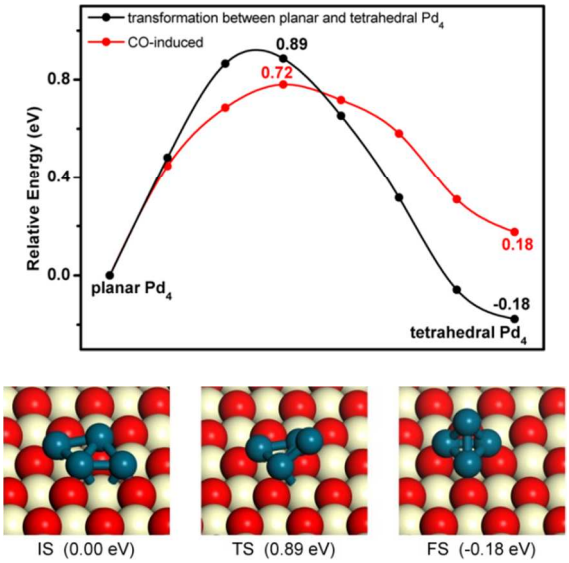

Figure S10. Transformation between planar and tetrahedral Pd_4 clusters (IS, TS and FS are initial, transition and final state).

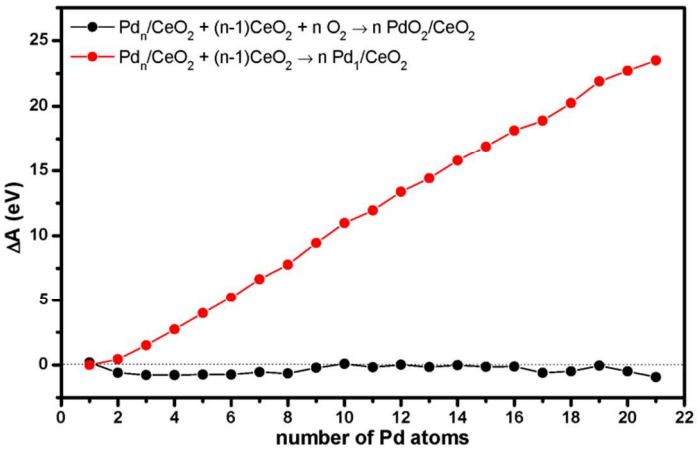

Figure S11. Thermodynamic analysis of (O_2-assisted) dispersion of Pd_n clusters (n = 2-21) on CeO_2(111) into Pd and PdO_2. The Showed are the Helmholtz free energies at 600 K.

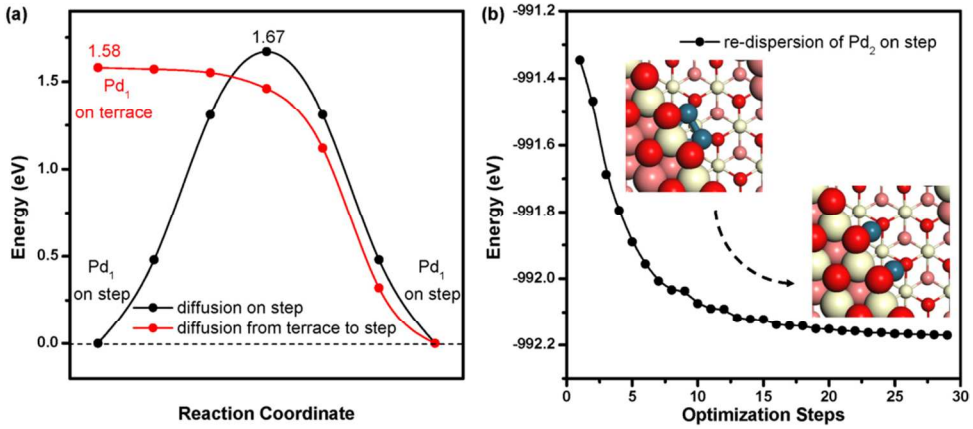

Figure S12. (a) Diffusion of single Pd atom on step (black line) and from terrace to step (red line) of CeO_2(111). (b) Optimization of Pd_2 cluster on step of CeO_2(111). (Color code: red, surface O of terrace; light-yellow, Ce; coral, subsurface O of terrace; dark-cyan, Pd).