Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Gold Clusters on Nb-doped $SrTiO_3$: Effects of Metal-Insulator-Transition on Heterogeneous An Nanocatalysis

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O_2 Adsorption on Au_8@$SrTiO_3$ (001) Surface with SrO Termination

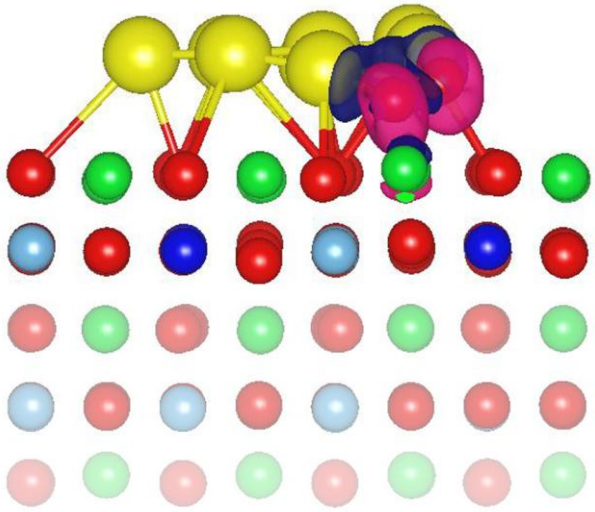

Figure S1 Relaxed structures for O_2 molecule adsorbed on Au_8@$SrTiO_3$ (001) surface with SrO termination doped by Nb (2.08%). Superimposed are the isosurfaces of differential charge density (isovalue=0.02 e/Å^3). The differential charge is calculated by $\Delta\rho=\rho(O_2+Au_8@SrTiO_3(001)) - (\rho O_2 + \rho Au_8@SrTiO_3(001))$. Blue (red) color indicates the electron depletion (accumulation). It is found that compared to undoped case, the metal-insulator-transition induced charge transfer increases the adsorption energy of the O_2 molecule from 0.82 to 1.36 eV, and the O-O bond length from 1.38 to 1.52 Å.

ER Type of CO Oxidation Catalyzed by Au8@SrTiO3 (001) Surface with TiO2 Termination: The First Step

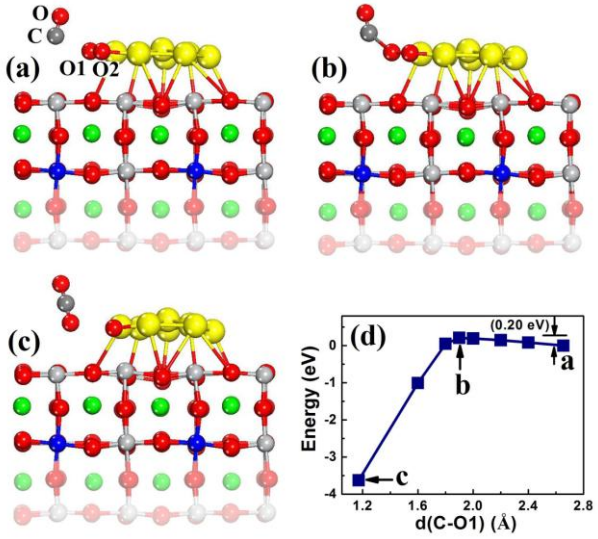

Figure S2. ER type of CO oxidation catalyzed by Au_8@SrTiO3 (001) surface with TiO_2 termination doped by Nb (1.92%). (a) Initial state: d(O1-O2)=1.43 Å, d(C-O2)=2.65 Å. (b) Transistion state: d(O1-O2)=1.50 Å, d(C-O2)=1.9 Å. (c) Final state: the formation of CO_2. (d) Energy profile along the reaction coordinate.

The Second Step of Reaction: CO+O→CO2 for TiO2 Terminated Surface

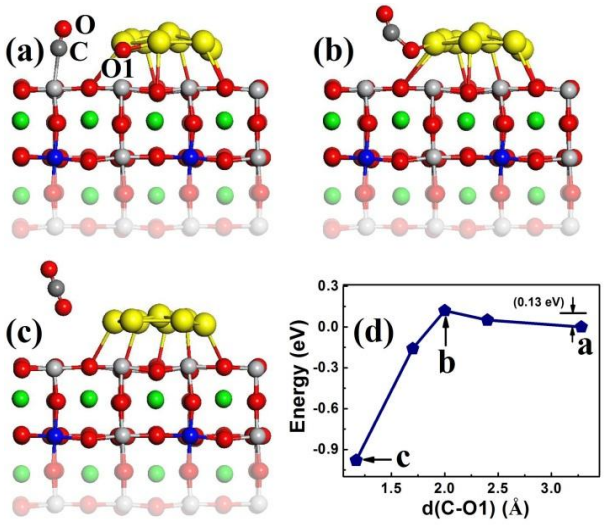

Figure S5. The LH mechanism of the second step CO oxidation catalyzed by Au_8@SrTiO3 (001) surface with TiO_2 termination doped by Nb (1.92%). (a) Initial state: d(C-O1)=3.28 Å,. (b) Transistion state: d(C-O1)=2.0 Å. (c) Final state: the formation of CO_2. (d) Energy profile along the reaction coordinate.

LH and ER Type of CO Oxidation Catalyzed by Au8@SrTiO3 (001) Surface with SrO Termination: The First Step

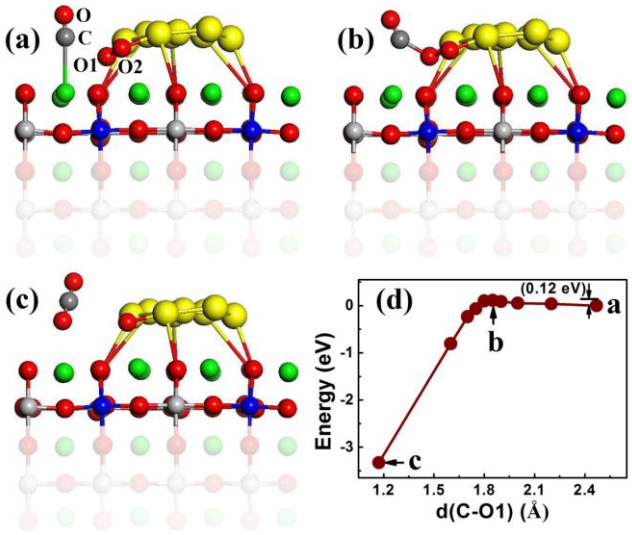

Figure S3. LH type of CO oxidation catalyzed by Au_8@SrTiO3 (001) surface with SrO termination doped by Nb (2.08%). (a) Initial state: d(O1-O2)=1.52 Å, d(C-O2)=2.46 Å. (b) Transistion state: d(O1-O2)=1.56 Å, d(C-O2)=1.75 Å. (c) Final state: the formation of CO_2. (d) Energy profile along the reaction coordinate.

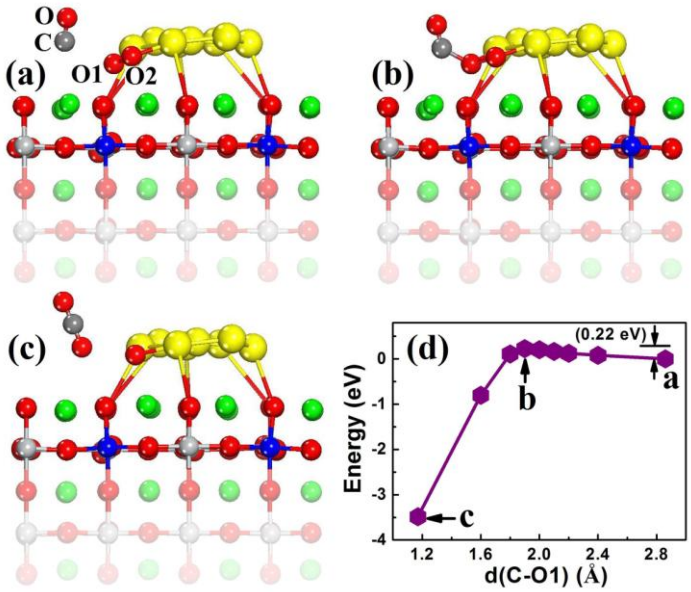

Figure S4. ER type of CO oxidation catalyzed by Au_8@SrTiO3 (001) surface with SrO termination doped by Nb (2.08%). (a) Initial state: d(O1-O2)=1.52 Å, d(C-O2)=2.86 Å. (b) Transistion state: d(O1-O2)=1.53 Å d(C-O2)=1.9 Å. (c) Final state: the formation of CO_2. (d) Energy profile along the reaction coordinate.

The Second Step of Reaction: CO+O→CO2 for SrO Terminated Surfaces

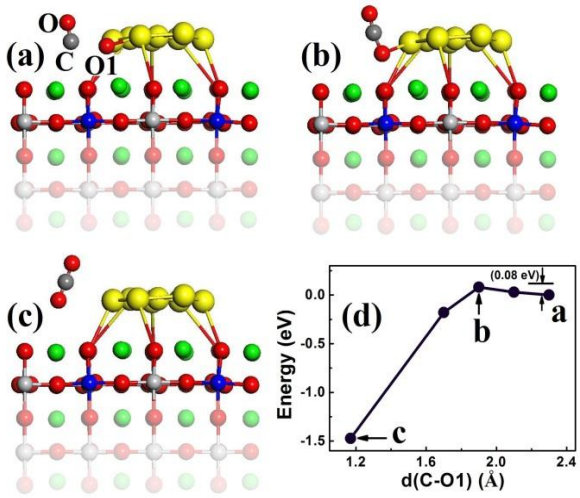

Figure S6. ER mechanism of CO oxidation with the remaining O atom catalyzed by Au_8@SrTiO3 (001) surface with SrO termination doped by Nb (2.08%). (a) Initial state: d(C-O1)=2.21 Å,. (b) Transistion state: d(C-O1)=1.9 Å. (c) Final state: the formation of CO_2. (d) Energy profile along the reaction coordinate.

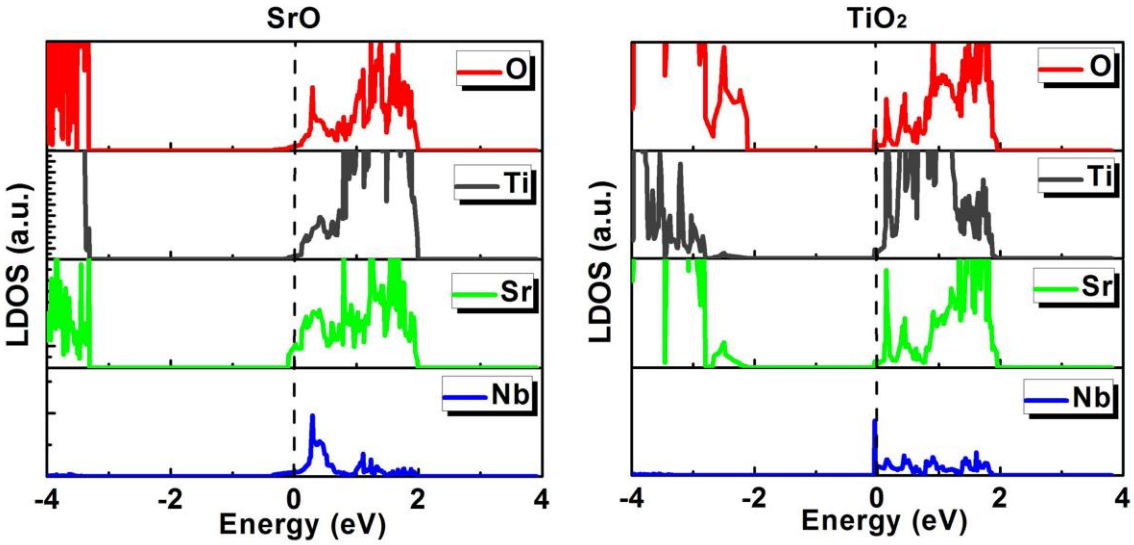

Fig. S7. Local density of states (LDOS) projected onto O, Ti, Sr and Nb atoms for Nb-doped $SrTiO_3$ (001) surfaces. Left panel shows the SrO-terminated surface with Nb dopant of 0.52%, and right panel shows the TiO_2-terminated surface with Nb dopant of 0.48%. Note that there are no gap states.

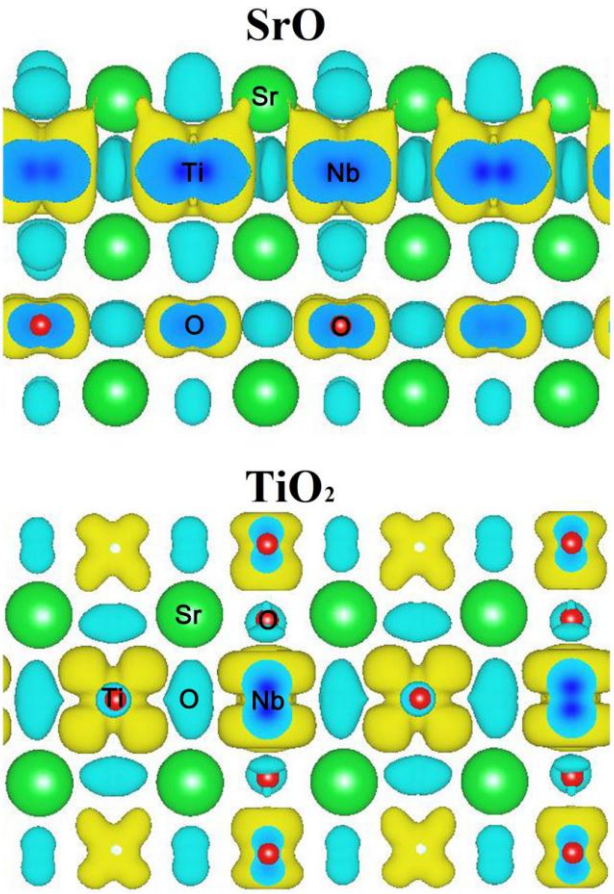

Fig. S8. Iso-surface of spin density for Nb-atom-doped $SrTiO_3$ (001) surface with SrO termination (Upper panel), and TiO_2 termination (lower panel). Note that there is one Nb atom in one supercell. It clearly shows the spin is delocalized over the whole supercell. It is also mentioning here that the magnetic properties of the system is a very complicated issue. Our calculations showed that the doping concentration has very significant effects on the magnetic moment. In many cases, the system is not magnetic.