Electronic Supporting Information (ESI) for

Interplay between Spin-selection Rule and Frontier Orbital Theory in O₂ Activation and CO Oxidation by Single-Atom-Sized Catalysts on TiO₂(110)

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Supplemental Texts:

- S1: Geometries, adsorption energies, and kinetic properties of TM_n on rutile $TiO_2(110)$.
- S2: Magnetic properties of defective rutile $TiO_2(110)$ and $TM_n@TiO_2(110)$ complexes.
- S3: Orbital analysis for O₂ adsorption on Ni@TiO₂(110) and Ni₂@TiO₂(110).

S1: Geometries, adsorption energies, and kinetic properties of TM_n on rutile $TiO_2(110)$.

First, we confirm that in the experiment¹ the deposited Pd_n species are located in the oxygen defect sites (see Figure S1(A)) of the TiO₂(110) surface. It is noted that, on the defect-free rutile $TiO_2(110)$ surface, the Pd atom prefers to adsorb on the site (denoted as B_{Ti-O}) bridging a surface five-coordinated Ti atom and its nearest neighboring O_b atom, with an adsorption energy (E_{ads}) of 1.205 eV, see the initial state (IS) structure presented in Figure S2 (A). Using the nudged elastic band method, we obtain a very small energy barrier of ~0.16 eV for the diffusion of a single Pd atom between two neighboring B_{Ti-O} sites on the defect-free surface. However, the diffusion barrier on the defective $TiO_2(110)$ surface (see Figures S1(A) and S2(A)) increases to ~0.58 eV (see Figure S2(B)) from the O_b -vac site to the nearest B_{Ti-O} site. Furthermore, the Pd₂ dimer experiences a large diffusion barrier of 1.16 eV from the defect site to the neighboring hollow sites, see Figure S2(C). Therefore the preference of the surface oxygen defect sites for these Pd species is consistent with the observed low diffusion rate of the Pd catalyst particles deposited on $TiO_2(110)^1$. We also note that the calculated band gap of the defect-free $TiO_2(110)$ surface is 2.36 eV, while the presence of one Ob-vac within the (4×2) unit cell produces the defect states dominantly characterized by the Ti-3d orbitals, reducing the band gap to 1.57 eV. The latter result quantitatively agrees well with previous observations that the band gap was much reduced on the defective TiO₂(110) surface²⁻⁴.



Figure S1: (color online): (A) Ball and stick model of the $TiO_2(110)$ surface. Small (blue) spheres represent Ti ions, and large (red) spheres represent O ions. For distinction, O ions bonding to the five-fold-coordinated Ti ions are drawn with relatively smaller spheres. A bridging oxygen vacancy (O_b -vac) is indicated with yellow ellipse. In (B), (C), (D), and (E), the most stable structures of Pd, Ni, Pd₂, and Ni₂ (in green) deposited around the O_b -vac site are displayed, respectively.

In Figures S1(B)-S1(E), we show the optimized structures of the Pd_n and Ni_n catalysts (n=1, 2) on the defective TiO₂(110) surface. As shown in Figures S1(B) and S1(C), the optimized structures of Pd@TiO₂(110) and Ni@TiO₂(110) are very similar to each other, where the pinned Pd atom in the O_b-vac site lies 0.71 Å above its neighboring bridging O atom, slightly larger than that (0.59 Å) for the pinned Ni atom. However, for the cases of Pd₂@TiO₂(110) and Ni₂@TiO₂(110), the optimized structures show a distinct difference between each other: *i.e.*, the two Pd atoms position asymmetrically around the O_b-vac site along the line of O_b, whereas the two Ni atoms favor to be pinned almost symmetrically in the O_b-vac site (see Figures S1(D) and S1(E), respectively). This difference between Pd₂@TiO₂(110) and Ni₂@TiO₂(110) is likely due to the larger bond length of the Pd dimer (2.62 Å) than that (2.20 Å) of the Ni dimer.



Figure S2: (color online): Ball and stick model for kinetic processes of the Pd monomer diffusion on $TiO_2(110)$ surface: (A) between two neighboring preferred hollow sites, different U values (in eV) only take minor role in the diffusion barriers (E_{bar} in eV); (B) from the oxygen defect site to its nearest neighboring hollow site; (C) Pd₂ dimer diffusion from the oxygen defect site to the neighboring hollow site.

S2: Magnetic properties of defective rutile TiO₂(110) and TM_n@TiO₂(110) complexes.

We note that bulk Pd (Ni) is nonmagnetic (ferromagnetic), but the spin state of Pd(Ni) at the atomic regime can be different from that of the bulk. Hence, these two elements are good benchmark examples to clarify whether the spin-selection rule determines their catalytic capabilities for O₂ activation. Therefore, we first focus on the magnetic properties of the TM_n@TiO₂(110) complexes (TM=Pd, Ni; *n*=1, 2). As presented in Figure S3(A), in the present spin-polarized calculations, the TiO₂(110) surface with an oxygen vacancy is paramagnetic with a magnetic moment of 2 μ_B ⁵, equivalent to the spin quantum number *S*=1. For the gas phases of Pd, Pd₂, Ni, and Ni₂ species, we obtain S=0, 1, 1, and 1, respectively, in agreement with available

experimental observations⁶. As also shown in Figures 1(a) and 1(c) in the main text, we also find that both Pd@TiO₂(110) and Pd₂@TiO₂(110) complexes have an identical spin-triplet state with S=1. It is interesting to note that both complexes exhibit almost equally localized magnetic moment of 1 μ_B at each of two surface Ti atoms⁵, as presented in Figures S3(B) and S3(C). On the other hand, Ni@TiO₂(110) has a spin singlet state with S=0 (as indicated by the LDOS in Figure 2(C)), indicating that the magnetic moment of Ni is totally quenched upon an interaction with the unpaired electron of the oxygen vacancy via an anti-ferromagnetic (AFM) coupling. However, when the spin-triplet Ni dimer is deposited on the vacancy site, both the local magnetic moments of the Ni dimer and TiO₂(110) are well maintained, giving rise to *S*=2 for the Ni₂@TiO₂(110) complex (see Figure S1(E) and Figure S3(D)).



Figure S3: Spin densities of (A) O_{b-vac} -Ti $O_2(110)$, (B) $Pd@TiO_2(110)$, (C) $Pd_2@TiO_2(110)$, and (D) $Ni_2@TiO_2(110)$ are displayed in dark color with an isosurface of 0.005 e/A^3 . The O_b -vac sites are circled.

S3: Orbital analysis for O₂ adsorption on Ni@TiO₂(110) and Ni₂@TiO₂(110).

According to the spin-selection rule, a spin-singlet substrate is generally inert to incoming spin-triplet O_2 molecule. However, as compared to the case of Pd@TiO₂(110), a significantly reduced HOMO(Ni)-LUMO(O₂) gap of 0.49 eV in O₂-Ni@TiO₂(110) renders the deposited Ni single atom fairly active to O₂ adsorption via the hybridization of HOMO(Ni) and LUMO(O₂). This hybridization results in a broadening of the Ni 3*d* states (see Figure 3(C) in the main text) and a charge transfer of 0.46 *e* from Ni@TiO₂(110) to adsorbed O₂, obtained by Bader charge analysis. Similarly, for the O₂-Ni₂@TiO₂(110) system, a small HOMO(Ni₂)-LUMO(O₂) gap of 0.70 eV with the high magnitude of LDOS originating from Ni₂ accounts for the enhanced O₂ activation via the strong orbital hybridization of HOMO(Ni₂) and LUMO(O₂), as shown in Figure 3(D). Here, we obtain a significant charge transfer of ~0.8 *e* from Ni₂@TiO₂(110) to the adsorbed O₂, leading to a nearly spin-singlet excited state, as implied by the LDOS in the middle panel of Figure 3(D) and the spin density in Figure 2(D). Thus, we conclude that the small HOMO(TM)-LUMO(O₂) gap as well as the high LDOS for the deposited Ni₂ catalyst can induce significantly both charge and spin transfers between Ni₂ and O₂ through their orbital hybridizations.

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