Atomic Under-coordination Induced Catalytic and Magnetic Fascinations of Pt and Rh nanoclusters

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Supplementary Information

Figure S2. Rh 3d_{5/2} energy shifts positively with the decrease of its coverage for Rh deposited on the (a) well-ordered, (b) slightly Ar⁺-pretreated, (c) strongly Ar⁺-pretreated TiO2(110)−(1×1) surfaces.\(^5\) (Reprinted with permission from Berkó et al., “Encapsulation of Rh Nanoparticles Supported on TiO2(110)-(1 × 1) Surface: XPS and STM Studies”, J. Phys. Chem. B 1998, 102, 3379-3386. Copyright (2014) by ACS), (d) TiO2 (110) surface at 300K. The spectra correspond to equivalent Rh coverage of about 0.1, 0.2, 0.3, 0.45, 0.6, 0.75 and 1.5 monolayers (ML).\(^6\) (Reprinted with permission from Sadeghi and Henrich, “Rh on TiO2: model catalyst studies of the strong metal-support interaction”. Applications of Surface Science 1984, 19, 330-340. Copyright (2014) by Elsevier), (e) TiO2 (110) surface at 300 K and (f) TiO2 (110) surface at 160 K.\(^7\) (Reprinted with permission from Óvári and Kiss, J., “Growth of Rh nanoclusters on TiO2: XPS and LEIS studies”. Appl. Surf. Sci. 2006, 252, 8624-8629. Copyright (2014) by Elsevier).

Figure S3. Lattice constant contracts with reducing the nanoparticle size for Pt deposited on (a) NiAl(110) substrate,\(^8\) (Reprinted with permission from Klimenkov et al., “The structure of Pt-aggregates on a supported thin
Figure S4. The spin-polarized DOS of (a-d) 5d-Pt singlet state, and (e-h) 5d-Pt triplet state, and (i-l) 4d-Rh quartet state. Inset is the difference between spin-up and spin-down states in DOS. The spin-up and spin-down configurations are indicated by the up and down arrows, respectively. The Fermi level is set at 0 eV. Same as CO$_{147}$ and MD$_{15}$ of Pt and Rh NPs shown in Figure 6 of the main text, the DOS distributions of spin-up and spin down states split for triplet state of Pt and quartet state of Rh whereas no split for the singlet state of Pt for various cluster sizes and structures, indicating the magnetic property is related to the under-coordinated atoms in the skin regardless of the size and structures of Pt and Rh NPs.
Figure S5. The spin-polarized PDOS of (a-d) 5d-Pt singlet state, (e-h) 5d-Pt triplet state, and (i-l) 4d-Rh quartet state. Inset is the difference between spin-up and spin-down states in DOS. The spin-up and spin-down configurations are indicated by the up and down arrows, respectively. The Fermi level is set at 0 eV. Same as CO_{147} and MD_{75} of Pt and Rh NPs shown in Figure 6 of the main text, the PDOS distributions of spin-up and spin down states split for triplet state of Pt and quartet state of Rh whereas no split for the singlet state of Pt for various cluster sizes and structures, indicating the magnetic property is related to the under-coordinated atoms in the skin regardless of the size and structures of Pt and Rh NPs.
Table S1. The effective CN ($z_i$), bond length ($d_i$), bond contraction coefficient ($C_i$), shell index ($i$), magnetic moment ($\mu$), and “charge transfer” of atoms at different positions of Pt$_{13}$ and Rh$_{13}$ nanoclusters. The results obtained by double numerical (DN) basic set in Dmol$^3$.21

<table>
<thead>
<tr>
<th>Structure</th>
<th>Position</th>
<th>atom</th>
<th>$z_i$</th>
<th>$d_i$ (Å)</th>
<th>$C_i$-1 (%)</th>
<th>Shell</th>
<th>Magnetic moment ($\mu$)</th>
<th>“Charge Transfer” (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt Singlet</td>
<td>Pt Triplet</td>
<td>Rh</td>
<td>Pt Singlet</td>
<td>Pt Triplet</td>
<td>Rh</td>
<td>Pt Triplet</td>
<td>Rh</td>
<td>Pt Singlet</td>
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<tr>
<td>CO$_{13}$</td>
<td>1-2</td>
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<td>2.652</td>
<td>-2.14</td>
<td>-2.12</td>
<td>-1.39</td>
<td>1</td>
</tr>
<tr>
<td>MD$_{13}$</td>
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<td>2.696</td>
<td>2.625</td>
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<td>-2.84</td>
<td>-2.42</td>
<td>-</td>
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<tr>
<td>1-3</td>
<td>2.43</td>
<td>2.793</td>
<td>2.715</td>
<td>-28.83</td>
<td>-28.83</td>
<td>-28.64</td>
<td>1</td>
<td>1.894</td>
</tr>
</tbody>
</table>

Figure S6. The spin-polarized DOS of Pt with singlet and triplet states for (a-b) CO$_{13}$ and (c-d) MD$_{13}$ structures calculated by DN basic set in Dmol$^3$. Inset is the difference between spin-up and spin-down states in DOS. The spin-up and spin-down configurations are indicated by the up and down arrows, respectively. The Fermi level is set at 0 eV.
Figure S7. The spin-polarized PDOS of Pt with singlet and triplet states (a-b) CO$_{13}$ and (c-d) MD$_{13}$ structures calculated by DN basic set in Dmol$^3$. Inset is the difference between spin-up and spin-down states in PDOS. The spin-up and spin-down configurations are indicated by the up and down arrows, respectively. The Fermi level is set at 0 eV.

Figure S8. The spin-polarized DOS of Rh with quartet state (a) CO$_{13}$ and (b) MD$_{13}$ structures calculated by DN basic set in Dmol$^3$. Inset is the difference between spin-up and spin-down states in DOS. The spin-up and spin-down
configurations are indicated by the up and down arrows, respectively. The Fermi level is set at 0 eV.

![Figure S9](image.png)

**Figure S9.** The spin-polarized PDOS of Rh with quartet state (a) CO$_{13}$ and (b) MD$_{13}$ structures calculated by DN basic set in Dmol$.^1$ Inset is the difference between spin-up and spin-down states in PDOS. The spin-up and spin-down configurations are indicated by the up and down arrows, respectively. The Fermi level is set at 0 eV.

REFERENCES