Supplemental information

Tuning the structure of bifunctional Pt/SmMn$_2$O$_5$ interface for promoted low-temperature CO oxidation activity

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Supplementary details of microkinetic analysis

The full catalytic cycle includes the following equations:

\[
2\text{CO}(g) + \text{Pr/Mn-X} \xrightleftharpoons[k_{-1}\text{a}]{k_{1}\text{a}} \text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^* \quad (\text{step i to ii})
\]

\[
\text{O}_2(g) + \text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^* \xrightleftharpoons[k_{-2}\text{a}]{k_{2}\text{a}} \text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^*\sim\text{O}^* \quad (\text{step ii to iii})
\]

\[
\text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^* \xrightleftharpoons[k_{-3}\text{a}]{k_{3}\text{a}} \text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^*\sim\text{O}^* \quad (\text{step iii to iv})
\]

\[
\text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^* \xrightleftharpoons[k_{-4}\text{a}]{k_{4}\text{a}} \text{CO}_{\text{Pt}}\sim\text{CO}_{\text{Pt}} \sim \text{O}^*\sim\text{CO}_2^* \quad (\text{step iv to v})
\]

\[
\text{CO}_{\text{Pt}}\sim\text{O}^* \sim\text{CO}_2^* \xrightleftharpoons[k_{-5}\text{a}]{k_{5}\text{a}} \text{CO}_{\text{Pt}}\sim\text{O}^*+\text{CO}_2(g) \quad (\text{step v to vi})
\]

\[
\text{CO}_n\sim\text{O}^* \xrightleftharpoons[k_{-6}\text{a}]{k_{6}\text{a}} \text{CO}_2^* \quad (\text{step vi to vii})
\]

\[
\text{CO}_2^* \xrightleftharpoons[k_{-7}\text{a}]{k_{7}\text{a}} \text{Pr/Mn-X} + \text{CO}_2(g) \quad (\text{step vii to i})
\]

The corresponding reaction rates \((r_i)\) for each step in the full catalytic cycle are calculated as:

\[
r_1 = k_{\text{ads1}} \cdot p(\text{CO})^2 \cdot \theta_{\text{pt-Mn-X}} - k_{-1} \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*} = k_{\text{ads1}} \cdot p(\text{CO})^2 \cdot \theta_{\text{pt-Mn-X}} (1-x_1) \quad (1)
\]

\[
r_2 = k_{\text{ads2}} \cdot p(\text{O}_2) \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*} - k_{-2} \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*} = k_{\text{ads2}} \cdot p(\text{O}_2) \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*} (1-x_2) \quad (2)
\]

\[
r_3 = k_3 \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*\sim\text{O}^*} = k_3 \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*} (1-x_3) \quad (3)
\]

\[
r_4 = k_4 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} - k_{-4} \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} = k_4 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} (1-x_4) \quad (4)
\]

\[
r_5 = k_5 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} - k_{-5} \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} = k_5 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} (1-x_5) \quad (5)
\]

\[
r_6 = k_6 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} - k_{-6} \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} = k_6 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} (1-x_6) \quad (6)
\]

\[
r_7 = k_7 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} - k_{-7} \cdot \theta_{\text{pt-Mn-X}} \cdot p(\text{CO}_2) = k_7 \cdot \theta_{\text{CO}_n\sim\text{O}^*\sim\text{CO}_2^*} (1-x_7) \quad (7)
\]

where \(x_1\sim x_7\) are defined as:

\[
x_1 = \frac{k_{-1} \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*}}{k_{\text{ads1}} \cdot p(\text{CO})^2 \cdot \theta_{\text{pt-Mn-X}}} \quad (8)
\]

\[
x_2 = \frac{k_{-2} \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*}}{k_{\text{ads2}} \cdot p(\text{O}_2) \cdot \theta_{\text{pt-Mn-X}}} \quad (9)
\]

\[
x_3 = \frac{k_{-3} \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*\sim\text{O}^*}}{k_3 \cdot \theta_{\text{CO}_n\sim\text{CO}_n\sim\text{O}^*\sim\text{O}^*}} \quad (10)
\]
\[ x_4 = \frac{k_{-4} \theta_{\text{CO}_2,\text{O}^*-\text{CO}_2^*}}{k_4 \theta_{\text{CO}^n,\text{O}^*-\text{CO}_2^*}} \] (11)

\[ x_5 = \frac{k_{-5} \theta_{\text{CO}^n,\text{O}^*-\text{O}} * p(\text{CO}_2)}{k_5 \theta_{\text{CO}^n,\text{O}^*-\text{O}}^*} \] (12)

\[ x_6 = \frac{k_{-6} \theta_{\text{CO}_2^*}}{k_6 \theta_{\text{CO}^n,\text{O}^*-\text{O}}^*} \] (13)

\[ x_7 = \frac{k_{-7} \theta_{\text{CO}_2^*} * p(\text{CO}_2)}{k_7 \theta_{\text{CO}_2^*}^*} \] (14)

\( r_1 \) are solved based on the mean-field steady-state condition \( \frac{\partial \theta}{\partial t} = 0 \). The set of master equations is listed as (15)~(22).

\[ \frac{\partial \theta_{\text{r}_{\text{Mn}}}^*}{\partial t} = 0 \Rightarrow r_1 - r_1 = 0 \] (15)

\[ \frac{\partial \theta_{\text{CO}^n,\text{O}^*-\text{O}}}{\partial t} = 0 \Rightarrow r_1 - r_2 = 0 \] (16)

\[ \frac{\partial \theta_{\text{CO}^n,\text{O}^*-\text{O}_2^*}}{\partial t} = 0 \Rightarrow r_2 - r_3 = 0 \] (17)

\[ \frac{\partial \theta_{\text{CO}^n,\text{O}^*-\text{O}_{\text{O}_2}^*}}{\partial t} = 0 \Rightarrow r_3 - r_4 = 0 \] (18)

\[ \frac{\partial \theta_{\text{CO}^n,\text{O}^*-\text{CO}_2^*}}{\partial t} = 0 \Rightarrow r_4 - r_5 = 0 \] (19)

\[ \frac{\partial \theta_{\text{CO}^n,\text{O}^*-\text{O}_2}^*}{\partial t} = 0 \Rightarrow r_5 - r_6 = 0 \] (20)

\[ \frac{\partial \theta_{\text{CO}_2^*}}{\partial t} = 0 \Rightarrow r_6 - r_7 = 0 \] (21)

\[ x_7 x_6 x_5 x_4 x_3 x_2 x_1 = \frac{k_{-7} k_{-6} k_{-5} k_{-4} k_{-3} k_{-2} * p(\text{CO}_2)^2}{k_{\text{ads}} k_{\text{ads}} k_{\text{ads}} k_{\text{ads}} k_{\text{ads}} k_{\text{ads}} * p(\text{CO})^2 * p(\text{O}_2)} \] (22)

Since the sequential steps after \( \text{O}_2 \) dissociation are strongly exothermic with much low barrier energies, we have assumed the adsorption of \( \text{CO} \) and \( \text{O}_2 \) in equilibrium and the rate of \( \text{CO}_2 \) formation \( (r) \) is equal to the rate of \( \text{O}_2 \) dissociation.
Therefore, the equilibrium constants ($K_1$ and $K_2$) can be written as:

$$K_1 = \frac{k_{ads1}}{k_{-1}} = \frac{\theta_{CO_n-CO_n-*}}{p(CO)^2 \theta_{\text{Me-x}}^{CO_n}}$$  \hspace{1cm} (23)

$$K_2 = \frac{k_{ads2}}{k_{-2}} = \frac{\theta_{CO_n-CO_n-O_2*}}{p(O_2)^* \theta_{\text{Me-x}}^{CO_n}}$$  \hspace{1cm} (24)

The site balance at the interface leads to the following equation of the coverages of species.

$$\theta_{\text{Me-x}} + \theta_{CO_n-CO_n-*} + \theta_{CO_n-CO_n-O_2*} = 1$$  \hspace{1cm} (25)

Therefore, $r$ can be calculated as:

$$r = k_3 \theta_{CO_n-CO_n-O_2*} = \frac{k_3 k_1 K_2 p(CO)^2 p(O_2)}{1 + K_1 p(CO)^2 + K_2 p(CO)^2 p(O_2)}$$  \hspace{1cm} (26)
The detailed configurations of initial magnetic moment for each Mn atom under ferromagnetic (FM) and antiferromagnetic (AFM) states. The listed results in Table S1 showed that the AFM1 state is the ground state with the total energy of -531.09 eV and the optimized lattice constants of 2a = 1.464 nm, b = 0.859 nm, c = 0.568 nm.
Fig. S2

The optimized structures of Pt$_n$/SMO (n = 2, 4, 6 and 8). The clustering energies have been labeled, which are relative to the most stable configurations. The heights between bottom and top Pt atoms ($h_{Pt-Pt}$) have been labeled, which shows that the smaller $h_{Pt-Pt}$s can lead to more stable configurations for Pt$_2$ and Pt$_4$. On the contrary, the larger $h_{Pt-Pt}$s for Pt$_6$ and Pt$_8$ can result to more stable configurations.
Fig. S3  The total energies of Pt$_n$/SMO (n = 2, 4, 6 and 8) as a function of simulation time during the first-principle molecular dynamic simulations at 973 K. The inserted figures are the snapshots of Pt$_n$/SMO with the local minimum total energies.
Fig. S4  Top view and side view of the most stable configurations of (a) Pt$_3$ and (b) Pt$_5$ clusters on SMO surface. Atomic structures of SMO supported (c) Pt$_3$ and (d) Pt$_5$ clusters with an adsorbed CO molecule.
Fig. S5 The Bader charges of Pt atoms for Pt$_n$/SMO (n = 2, 4, 6 and 8) with the most stable structure.
Fig. S6  

(a)(b) The atomic structures of two types of rod-like Pt$_{20}$ clusters along $<110>$ direction. The optimized atomic structures of (c) Pt$_{20}$-1 and (d) Pt$_{20}$-2 bound on SMO (010) facet are presented with the clustering energies labeled at the bottom.
Fig. S7  (a) The Bader charges for the overlapped Pt atoms in [001] direction of Pt$_{20}$/SMO. (b) The LDOS and partial DOS for Pt 5$d$, O 2$p$ and Mn 3$d$ of the Pt/Mn$_2$ trimer interface of Pt$_{20}$/SMO.
The atomic structures of CO adsorption on Mn$_2$ dimer site of Pt$_n$/SMO (n = 1, 2, 4, 6, 8 and 20). The calculated adsorption energy ranges from -0.18 eV to -0.36 eV, which indicates the weakly physical adsorption of CO on the Mn$_2$ dimer site.
Fig. S9

The atomic structures of CO adsorption on isolated Pt clusters with the corresponding adsorption energies labeled at the bottom.
Fig. S10  Simulation snapshots for the evolution of CO adsorbed Pt\textsubscript{n}/SMO (n = 1, 2, 4, 6, 8 and 20) at 473 K.
The atomic structures of the initial states (IS), the transition states (TS) and the final states (FS) of $\text{O}_2$ dissociation on the Mn$_2$ dimer sites of bare SMO (010) facet and Pt$_n$/SMO. The distances between O atoms are labeled.
The contours of the differential charge density in the plane crossing the adsorbed O$_2$ molecule and Mn$_2$ dimer for (a) Pt$_1$/SMO, (b) Pt$_2$/SMO, (c) Pt$_4$/SMO, (d) Pt$_6$/SMO and (e) Pt$_8$/SMO. The distances (Å) between two neighbor atoms have been labeled.
Fig. S13  TOF calculated by the set of master equations of microkinetic model (black curve) and equation (6) in the text (red curve) as a function of reaction temperature.
Fig. S14 TOF as a functional of reaction temperature for Pt<sub>n</sub>/SMO (n = 1, 2, 4, 6, 8 and 20).
Fig. S15  The atomic structures of the initial states (IS), the transition states (TS) and the final states (FS) of O₂ dissociation on the Mn-Fe, Mn-Co and Mn-Ni hetero-dimer sites of Pt₃₀/SMO. Note that the pre-adsorbed CO molecules on the interfacial Pt sites have been considered due to their effects on the adsorption energy of O₂ on Mn dimer as discussed in the text. The distances between O atoms are labeled.
Fig. S16  The contours of the differential charge density in the plane crossing the adsorbed O$_2$ molecule and (a) Mn-Fe, (b) Mn-Co, (c) Mn-Ni hetero-dimers for Pt$_{20}$/SMO. The distances (Å) between two neighbor atoms have been labeled.
Fig. S17  TOF as a function of reaction temperature for Pt/Mn-Ni trimer interface.

The calculated TOF at 363 K are labelled.
Table S1  The optimized lattice constants, total energies and total magnetic moment of SMO bulk calculated with different initial magnetic states. The corresponding data in previous experimental study have also been listed for comparison.

<table>
<thead>
<tr>
<th></th>
<th>FM</th>
<th>AFM1</th>
<th>AFM2</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>b (Å)</td>
<td>8.574</td>
<td>8.590</td>
<td>8.578</td>
<td>8.596</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.722</td>
<td>5.676</td>
<td>5.697</td>
<td>5.672</td>
</tr>
<tr>
<td>E (eV)</td>
<td>-530.09</td>
<td>-531.09</td>
<td>-530.76</td>
<td>/</td>
</tr>
<tr>
<td>mag (μB)</td>
<td>55.95</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>


Table S2.  Adsorption energies ($E_{ads}$) of O$_2$ on Mn$_2$ dimer, the adsorption energy changes ($\Delta E_{ads}$) compared to pure SMO slab, and the distance changes between Mn ions ($\Delta d_{Mn-Mn}$) of Mn$_2$ dimer after binding with Pt clusters.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ads}$ of O$_2$ (eV)</th>
<th>$\Delta E_{ads}$ of O$_2$ (eV)</th>
<th>$\Delta d_{Mn-Mn}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMO</td>
<td>-0.68</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Pt$_1$/SMO</td>
<td>-0.60</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Pt$_2$/SMO</td>
<td>-0.25</td>
<td>0.43</td>
<td>0.09</td>
</tr>
<tr>
<td>Pt$_4$/SMO</td>
<td>-0.25</td>
<td>0.43</td>
<td>0.08</td>
</tr>
<tr>
<td>Pt$_6$/SMO</td>
<td>-0.50</td>
<td>0.18</td>
<td>0.04</td>
</tr>
<tr>
<td>Pt$_8$/SMO</td>
<td>-0.60</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Pt$_{20}$/SMO</td>
<td>-0.56</td>
<td>0.12</td>
<td>0.01</td>
</tr>
</tbody>
</table>
### Table S3. Formation energies ($E_{\text{form}}$) of Fe, Co and Ni dopants on SMO slab.

<table>
<thead>
<tr>
<th></th>
<th>Fe dopant</th>
<th>Co dopant</th>
<th>Ni dopant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{form}}$ (eV)$^a$</td>
<td>-0.60</td>
<td>-0.10</td>
<td>-1.28</td>
</tr>
</tbody>
</table>

$^a$ $E_{\text{form}}$ is defined as:

$$E_{\text{form}} = E_{\text{slab-X}} - E_{\text{slab}} - a \times E_{\text{XO}_b} + a \times E_{\text{MnO}_2} - a \times (2 - b) \times E_{\text{O}_2} / 2$$  \hspace{1cm} (27)

where $E_{\text{slab-X}}$ and $E_{\text{slab}}$ are the total energies of X doped and pure slabs ($X = \text{Fe, Co, Ni}$), respectively. $E_{\text{MnO}_2}$ and $E_{\text{XO}_b}$ are total energies of the stable oxides of Mn and X elements (MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$ and NiO). $E_{\text{O}_2}$ is the energy of an O$_2$ molecule.

### Table S4. $E_{\text{clu}}$ of Pt$_{20}$ clusters on pure and doped SMO slabs.

<table>
<thead>
<tr>
<th></th>
<th>Pure</th>
<th>Fe dopant</th>
<th>Co dopant</th>
<th>Ni dopant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{clu}}$ (eV)</td>
<td>-5.20</td>
<td>-5.21</td>
<td>-5.22</td>
<td>-5.22</td>
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