Supporting Information

Cu–Pd Single-Atom Alloy Catalyst for Efficient NO reduction

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Table S1. Summary of EXAFS curve fitting for Pd-based catalysts.

<table>
<thead>
<tr>
<th>sample</th>
<th>shell</th>
<th>N</th>
<th>R(Å)</th>
<th>ΔE (eV)</th>
<th>σ²(Å²)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd black</td>
<td>Pd–Pd</td>
<td>12 (fix)</td>
<td>2.74 ± 0.00</td>
<td>6.1 ± 0.3</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>Pd–Pd</td>
<td>8.1 ± 0.7</td>
<td>2.73 ± 0.00</td>
<td>4.7 ± 0.6</td>
<td>0.009</td>
<td>0.010</td>
</tr>
<tr>
<td>CuPd/Al₂O₃</td>
<td>Pd–Cu</td>
<td>4.6 ± 0.6</td>
<td>2.60 ± 0.02</td>
<td>4.7 ± 2.5</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Pd–Pd</td>
<td>6.0 ± 0.5</td>
<td>2.65 ± 0.01</td>
<td>3.9 ± 0.8</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>Cu₅Pd/Al₂O₃</td>
<td>Pd–Cu</td>
<td>8.4 ± 0.9</td>
<td>2.57 ± 0.01</td>
<td>2.1 ± 1.3</td>
<td>0.007</td>
<td>0.010</td>
</tr>
</tbody>
</table>
Figure S1. XRD patterns of Cu/Al₂O₃, Pd/Al₂O₃, and Cu–Pd/Al₂O₃. The Cu–Pd solid-solution alloy phases with bimetallic composition close to that of the fed ratio were formed: Cu/Pd = 1, Cu₀.₅Pd₀.₅; Cu/Pd = 3, Cu₀.₇₅Pd₀.₂₅; Cu/Pd = 5, Cu₀.₈₃Pd₀.₁₇. The diffraction peak intensity changes depending on the metal loadings as summarized Table 1.

Figure S2. HAADF-STEM images of (a) Cu₅Pd/Al₂O₃ and (b) Cu/Al₂O₃.
Figure S3. Pd K-edge XANES spectra of Pd-based catalysts.

Figure S4. Pd K-edge $k^3$-weighted EXAFS oscillations of Pd-based catalysts.
Figure S5. Fourier-filtered EXAFS oscillations (solid curve) and the curve fit (dashed line) for (a) Pd/Al$_2$O$_3$, (b) CuPd/Al$_2$O$_3$, and (c) Cu$_5$Pd/Al$_2$O$_3$. 

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Figure S6. (a) NO conversion and (b) N\textsubscript{2} selectivity in NO+CO reaction over Pd/Al\textsubscript{2}O\textsubscript{3}, Cu/Al\textsubscript{2}O\textsubscript{3}, and Cu\textsubscript{5}Pd/Al\textsubscript{2}O\textsubscript{3} catalysts.

Figure S7. \( C_{\text{N}_2} \) and \( C_{\text{N}_2\text{O}} \) in NO+CO+O\textsubscript{2} and NO+CO+O\textsubscript{2}+C\textsubscript{3}H\textsubscript{6} reactions over Cu\textsubscript{5}Pd/Al\textsubscript{2}O\textsubscript{3}, Cu/Al\textsubscript{2}O\textsubscript{3}, and Pd/Al\textsubscript{2}O\textsubscript{3} catalysts.
Figure S8 Dependence of reaction rate on NO and CO partial pressures ($P_{\text{NO}}$ and $P_{\text{CO}}$, respectively) in NO reduction by CO over Cu/Al$_2$O$_3$ and Cu$_5$Pd/Al$_2$O$_3$.
Figure S9. Optimized structures of adsorbates and the corresponding transition states during $(\text{NO})_2$ dimer formation and its subsequent decomposition to $\text{N}_2\text{O}$ and $\text{O}$ over (a) Cu(211) and (b) Pd - substituted Cu(211). For clarity, metal atoms in the sub-surface region are shown as small dots.
Figure S10. Energy diagrams of CO oxidation over Cu(111) and Pd-substituted Cu(111) surfaces. Total energy of the slab plus free CO$_2$ was set zero. TS search was performed with the intermediate structure (CO·O) as a tentative final state.

Figure S11. Energy diagrams of N$_2$O bending (IS→MS) and its subsequent decomposition to N$_2$ and O (MS→FS) over (a) Cu(111) and (b) Cu(211) surfaces. For Cu(211), conversion from IS to MS was barrier-less. Total energy of slab and free N$_2$O was set to zero.
Figure S12. Optimized structures of adsorbates (IS, MS, and FS) and the corresponding transition states (TS1 and TS2) during N$_2$O bending and its subsequent decomposition to N$_2$ and O over (a) Cu(111) and (b) Cu(211) surfaces. For clarity, metal atoms in the sub-surface region are shown as small dots.
Kinetic Analysis

A Langmuir-Hinshelwood type mechanism with an (NO)$_2$ dimer formation and decomposition was considered for NO–CO reaction over Cu-based catalysts as follows:

1. NO adsorption
   
   \[ NO + \sigma \rightleftharpoons NO \cdot \sigma \]

2. CO adsorption
   
   \[ CO + \sigma \rightleftharpoons CO \cdot \sigma \]

3. NO dimerization
   
   \[ 2NO \cdot \sigma \rightleftharpoons (NO \cdot \sigma)_2 \]

4. N–O scission
   
   \[ (NO \cdot \sigma)_2 \rightleftharpoons N_2O \cdot \sigma + O \cdot \sigma \]

5. N$_2$O decomposition
   
   \[ N_2O \cdot \sigma \rightleftharpoons N_2 + O \cdot \sigma \]

6. CO oxidation
   
   \[ CO \cdot \sigma + O \cdot \sigma \rightleftharpoons CO_2 + 2\sigma \]

7. N$_2$O desorption
   
   \[ N_2O \cdot \sigma \rightleftharpoons N_2O + \sigma \]

where, $\sigma$ indicates an adsorption site. Each step can be regarded to be in equilibrium except when it is the rate-determining step. Therefore, the equilibrium constants are generally defined as follows:

\[
K_1 = \frac{\theta_{NO}}{P_{NO}}(1 - \theta) \\
K_2 = \frac{\theta_{CO}}{P_{CO}}(1 - \theta) \\
K_3 = \frac{\theta_{(NO)_2}^2}{\theta_{NO}^2} \\
K_4 = \frac{\theta_{N_2O}^2}{\theta_{(NO)_2}^2} \\
K_5 = \frac{P_{N_2} \theta_O}{\theta_{N_2O}} \\
K_6 = \frac{P_{CO_2}(1 - \theta)^2}{\theta_{CO} \theta_O} \\
K_7 = \frac{P_{N_2O}(1 - \theta)}{\theta_{N_2O}}
\]

where, $P_X$, $\theta_X$, and $1 - \theta$ are the partial pressure of $X$, coverage of $X$, and percentage of vacant site:

\[
1 - (\theta_{NO} + \theta_{CO} + \theta_{(NO)_2} + \theta_{N_2O} + \theta_O)
\]

respectively.
Assuming that NO adsorption (1) is the rate determining step, the overall reaction rate can be expressed using a rate constant \( k \) as follows:

\[
r = kP_{NO}(1 - \theta)
\]

here, \( 1 - \theta \) is expressed using the equilibrium constants and \( P_X \) as follows:

\[
1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

where, \( a, b, \) and \( c \) are expressed as follows:

\[
a = K_3^{0.5}K_4^{-1.5}K_5^{1.5}K_7^{2}P_{N_2}^{0.5}P_{N_2O}^{2}, \quad c = -1
\]

\[
b = K_7^{-1}P_{N_2O}(K_3^{-0.5}K_4^{-1}K_5^{0.5}P_{N_2}^{-0.5} + K_5^{-1}K_6^{-1}K_7^{2}P_{CO_2}^{2}P_{N_2}P_{N_2O}^{2} - 1 + 1) + 1
\]

Based on these, the reaction orders for \( P_{NO} (x) \) and \( P_{CO} (y) \) on the overall reaction rate should be described as follows: \( x = 1, y = 0 \).

This indicates the first- and zero-order dependences of \( r \) on \( P_{NO} \) and \( P_{CO} \), respectively. This does not agree with the experimental results.

Assuming that CO adsorption (2) is the rate determining step, the overall reaction rate can be expressed using a rate constant \( k \) as follows:

\[
r = kP_{CO}(1 - \theta)
\]

here, \( 1 - \theta \) is expressed using the equilibrium constants and \( P_X \) as follows:

\[
1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

where, \( a, b, \) and \( c \) are expressed those shown in the solution for (1).

Based on these, the reaction orders for \( P_{NO} (x) \) and \( P_{CO} (y) \) on the overall reaction rate should be described as follows: \( x = 0, y = 1 \).
This indicates the zero- and first-order dependences of \( r \) on \( P_{NO} \) and \( P_{CO} \), respectively, which is inconsistent with the experimental results.

Next, we assume that NO dimerization (3) is the rate determining step: the overall reaction rate can be expressed using a rate constant \( k \) as follows:

\[
r = kK_1P_{NO}^2(1 - \theta)^2
\]

here, \( 1 - \theta \) is expressed using the equilibrium constants and \( P_X \) as follows:

\[
1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

where, a, b, and c are expressed as follows:

\[
a = K_1^{-1}K_3^{-2}P_{NO}^{-1}P_{NO}^2
\]

\[
b = K_1P_{NO} + K_2P_{CO} + K_7^{-1}P_{N_2}^{-1}(K_5P_{N_2}^{-1} + 1) + 1
\]

\[
c = -1
\]

Based on these, the ranges of the reaction orders for \( P_{NO} (x) \) and \( P_{CO} (y) \) on the overall reaction rate should be as follows: \( 2 < x < 4 \), \( 0 < y < 2 \). This does not agree with the experimental results with negative \( x \).

Assuming that N–O bond scission of \((NO)_2\) dimer (4) is the rate determining step, the overall reaction rate can be expressed using a rate constant \( k \) as follows:

\[
r = kK_1^2K_3P_{NO}^2(1 - \theta)^2
\]

here, \( 1 - \theta \) is expressed using the equilibrium constants and \( P_X \) as follows:

\[
1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

where, a, b, and c are expressed as follows:

\[
a = K_1^2K_3P_{NO}^2
\]

\[
b = K_1P_{NO} + K_2P_{CO} + K_7^{-1}P_{N_2}^{-1}(K_5P_{N_2}^{-1} + 1) + 1
\]

\[
c = -1
\]
Based on these, the ranges of the reaction orders for \( P_{NO} (x) \) and \( P_{CO} (y) \) on the overall reaction rate should be as follows: \(-2 < x < 0\), \( 0 < y < 2\), which is well consistent with the experimental orders for both Cu/Al_2O_3 and Cu_5Pd/Al_2O_3.

Then, we assume that N_2O decomposition (5) is the rate determining step, affording the overall reaction rate expressed as follows:

\[
r = kK_7^{-1}P_{N_2O}(1 - \theta)
\]

here, \( 1 - \theta \) is expressed using the equilibrium constants and \( P_X \) as follows:

\[
1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

where, \( a, b, \) and \( c \) are expressed as follows:

\[
a = K_2^{-1}K_4^{-1}K_6^{-1}K_7^{-1}P_{N_2O}P_{CO}P_{CO}^{-1}
\]

\[
b = K_1P_{NO} + K_2P_{CO} + K_7^{-1}P_{N_2O}(K_5P_{N_2}^{-1} + 1) + 1
\]

\[
c = -1
\]

Based on these, the ranges of the reaction orders for \( P_{NO} (x) \) and \( P_{CO} (y) \) on the overall reaction rate should be as follows: \( 0 < x < 1\), \( 0 < y < 2\), which is inconsistent with the experimental results with negative \( x \).

When CO oxidation (6) is assumed as the rate determining step, the overall reaction rate is expressed as follows:

\[
r = kK_2K_5K_7^{-1}P_{N_2}^{-1}P_{N_2O}P_{CO}(1 - \theta)^2
\]

here, \( 1 - \theta \) is expressed using the equilibrium constants and \( P_X \) as follows:

\[
1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

where, \( a, b, \) and \( c \) are expressed those shown in the solution for (3).
Based on these, the ranges of the reaction orders for $P_{NO} (x)$ and $P_{CO} (y)$ on the overall reaction rate should be as follows: $0 < x < 2, 1 < y < 3$. This does not agree with the experimental results.

When $N_2O$ desorption (7) is assumed as the rate determining step, the overall reaction rate is expressed as follows:

$$r = kK_2^{-1}K_5^{-1}K_6^{-1}P_{N_2}P_{CO_2}P_{CO}^{-1}(1 - \theta)$$

Here, $1 - \theta$ is expressed using the equilibrium constants and $P_X$ as follows:

$$1 - \theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where, $a$, $b$, and $c$ are expressed as follows:

$$a = K_2^{-1}K_4^{-1}K_5^{-1}K_6^{-1}P_{N_2}P_{CO_2}^{-2}P_{CO}^{-2}$$

$$b = K_1P_{NO} + K_2P_{CO} + K_2^{-1}K_6^{-1}P_{CO_2}(K_5^{-1}P_{N_2} + 1)P_{CO}^{-1} + 1$$

$$c = -1$$

Based on these, the ranges of the reaction orders for $P_{NO} (x)$ and $P_{CO} (y)$ on the overall reaction rate should be as follows: $0 < x < 1, 1 < y < 3$. This does not agree with the experimental results.

Thus, assuming N–O bond scission of $(NO)_2$ dimer (4) as the rate-determining step exclusively gave the reaction order ranges consistent with the experiment. On the basis of these results, we concluded that the rate-determining step of NO–CO reaction over Cu-based catalysts is N–O bond scission of $(NO)_2$ dimer.

**Appendix Table 1. Summary of reaction orders**

<table>
<thead>
<tr>
<th>RDS in NO–CO</th>
<th>$r = kP_{NO}^xP_{CO}^y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$x = 1$</td>
</tr>
<tr>
<td>(2)</td>
<td>$x = 0$</td>
</tr>
<tr>
<td>(3)</td>
<td>$2 &lt; x &lt; 4$</td>
</tr>
<tr>
<td>(4)</td>
<td>$-2 &lt; x &lt; 0$</td>
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</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>0 &lt; x &lt; 1</th>
<th>0 &lt; y &lt; 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1 &lt; y &lt; 3</td>
</tr>
<tr>
<td>7</td>
<td>0 &lt; x &lt; 1</td>
<td>1 &lt; y &lt; 3</td>
</tr>
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