Supplementary Information

In situ observations of structural dynamics of platinum-cobalt-hydroxide nanocatalyst under CO oxidation

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Estimation of the Weisz–Prater criterion

From the Arrhenius-type plot of the kinetics measurement, the apparent activation energy \( (E_a) \) of the Pt2-Co/SiO\(_2\) catalyst is 14 kJ·mol\(^{-1}\) in the low temperature region \(<343 \text{ K}\). This is lower than the commonly accepted value \((20 \text{ kJ·mol}^{-1})\) where the reaction might be limited by the intraparticle diffusion, rather than by kinetic control. In order to check whether the catalytic results were influenced by intraparticulate mass transfer, we estimated the Weise-Prater criterion.\(^1\) The Weise-Prater criterion \( C_{W-P} \) could be calculated by:

\[
C_{W-P} = \frac{r_{obs} \rho C R_p^2}{D_{eff} C_S},
\]

where \( r_{obs} \) is the initial global reaction rate, \( \rho_C \) is the catalyst density, \( R_p \) is the catalyst particle radius, \( D_{eff} \) is the effective diffusivity of the reactants in the pores, and \( C_S \) is the substrate concentration on the catalyst surface. From the catalyst particle size of 100-120 mesh \((1.5 \times 10^{-4} \text{ m})\), the CO concentration of 1\%, and the reaction rate of \(3.8 \times 10^{-3} \text{ mol·kg}^{-1} \cdot \text{s}^{-1}\), from Eq. (1) we have

\[
C_{W-P} = \frac{(3.8 \times 10^{-3} \text{ mol·kg}^{-1} \cdot \text{s}^{-1}) \times (1.3 \times 10^3 \text{ kg} \cdot \text{m}^3) \times (1.5 \times 10^{-4} \text{ m})^2}{8.9 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1} \times 0.45 \text{ mol} \cdot \text{m}^3} = 2.8 \times 10^{-2} \ll 1.
\]

The obtained \( C_{W-P} = 2.8 \times 10^{-2} \ll 1 \) ensures that the internal diffusion effects could be neglected during the kinetic experiments.

Details of EXAFS curve-fittings

The least-squares curve-fittings of the EXAFS data of Pt2-Co/SiO\(_2\) were performed using the ARTEMIS module implanted in IFEFFIT.\(^2\) Fittings were done in the \( R \)-space within the \( R \)-range of 1.2–3.3 Å for the \( k^2 \chi(k) \) functions in the \( k \)-range of 2.5–12.0 Å\(^{-1}\). A Hanning window with window width of \( dk = 1.0 \text{ Å}^{-1} \) was used. The number of independent points are then \( N_{ipt} = 2 \Delta k \cdot \Delta R / \pi = 2 \times (12.0–2.5) \times (3.3–1.2)/\pi = 12. \)

Before fitting the data of Pt2-Co/SiO\(_2\), we fit the data of Pt foil by fixing the coordination number of nearest Pt–Pt bond and the amplitude reduction factor \( S_0^2 \) was allowed to vary. This yielded the best-fit value of \( S_0^2=0.84 \). Then the \( S_0^2 \) was fixed at this value when fitting the EXAFS data of catalyst samples. For fitting the EXAFS data of Pt2-Co/SiO\(_2\) collected at 300 K in the He and CO + O\(_2\) atmosphere, two coordination
pairs of Pt–Pt and Pt–Co were included, because no sign of surface oxidization could be observed from both XANES and EXAFS spectra. For each pair, the coordination number $N$, interatomic distance $R$, Debye-Waller factor $\sigma^2$, and edge-energy shift $\Delta E_0$ were treated as adjustable parameters. The number of adjustable parameters is $N_{\text{para}} = 4 + 4 = 8$, less than $N_{\text{ipt}} = 12$. Inspection of the obtained parameters in Table 1 shows that the $\Delta E_0$’s for the Pt–Pt ($\Delta E_0 = 5.7$ eV) and Pt–Co ($\Delta E_0 = 6.0$ eV) bonds are nearly unchanged in the He and CO + O$_2$ atmosphere. Therefore, for fitting the EXAFS data of Pt2-Co/SiO$_2$ at higher temperatures, the $\Delta E_0$’s for the same bonds were fixed in order to reduce the number of adjustable parameters and to break the strong correlation between $\Delta E_0$ and $R$.

For the data collected within temperature ranges of 343–423 K, an additional Pt–O pair was considered to account for the FT peak at 1.7 Å (Fig. 3c) and three coordination pairs of Pt–O, Pt–Pt and Pt–Co were included. For each pair, the coordination number $N$, interatomic distance $R$, and Debye-Waller factor $\sigma^2$ were treated as adjustable parameters. $\Delta E_0$ was also an adjustable parameter. Besides, for the data collected at 423 K, a common third cumulant $C_3$ for the Pt–Pt and Pt–Co bonds were included to account for the anharmonicity of the interatomic potential. The total number of adjustable parameters is $N_{\text{para}} = 4 + 3 + 3 + 1 = 11$, or $N_{\text{para}} = 4 + 3 + 3 = 10$, less than $N_{\text{ipt}} = 12$.

For the data collected at 473 K, the two-shell model including a Pt–O and a Pt–Pt pair is sufficient to give a satisfactory match. Therefore, the number of adjustable parameters is $N_{\text{para}} = 4 + 3 + 1 = 8 < N_{\text{ipt}}$.

With the strategies, the curve-fitting results for Pt2-Co/SiO$_2$ under various conditions are shown in Figure S5 and the parameters are listed in Table 1. All the yielded $R$-factors are not larger than 0.01, indicating the good fitting qualities.
Supplementary Figures

**Figure S1.** Aberration-corrected HAADF-STEM images of Pt2-Co/SiO$_2$ sample.

**Figure S2.** (a) Co $K$-edge XANES spectra of Pt2-Co/SiO$_2$ catalysts and Co(OH)$_2$ bulk. (b) Their corresponding FT spectra of the $k^3\chi(k)$ functions within the $k$-range of 2.4-12.5 Å$^{-1}$. 

[Image of Supplementary Figures]

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**Figure S3.** XRD pattern of the as-synthesized Pt2-Co/SiO2 catalyst.

**Figure S4.** (a) Temporal evolutions of DRIFTS spectra for CO adsorbed on Pt/SiO2 after O2 injection at 300 K. (b) Percentages of integrated area of CO adsorbed on different surface sites against the oxidation time of O2.
Figure S5. The curve-fitting results of the Pt2-Co/SiO2 sample showing the magnitude (red) and the imaginary part (blue) of the FT curves under various conditions: (a) He@300 K; (b) CO + O2@300 K; (c) CO + O2@343 K; (d) CO + O2@383 K; (e) CO + O2@423 K; (f) CO + O2@473 K.
Figure S6. Comparison of the Co K-edge in-situ data of Pt2-Co/SiO2 collected at 300 and 423 K under the reaction atmosphere: (a) XANES, (b) the FT curves of EXAFS.

Figure S7. In-situ Pt L3-edge XAFS spectra of pre-reduced Pt1-Co/SiO2 in the first cycle of changing conditions: in He at 300 K, and in the CO + O2 reaction atmosphere at various temperatures. (a) XANES spectra; (b) the k^2-weighted EXAFS oscillatory χ(k) functions, and (c) non-phase-shift-corrected R-space FT curves of the k^2χ(k)functions. For comparison, the data of Pt foil and PtO2 bulk are also displayed.
Figure S8. The curve-fitting results of the Pt1-Co/SiO₂ sample showing the magnitude (red) and the imaginary part (blue) of the FT curves under various conditions: (a) He@300 K; (b) CO + O₂ @300 K; (c) CO + O₂ @343 K; (d) CO + O₂ @383 K; (e) CO + O₂ @423 K.
Figure S9. Arrhenius plot of the kinetics measurement at temperatures above 343 K for Pt2-Co/SiO2, yielding the apparent activation energy $E_a = 53$ kJ·mol$^{-1}$.

Table S1. Structure parameters of Pt1-Co/SiO2 under various conditions extracted from quantitative curve-fittings of the Pt $L_3$-edge EXAFS data.

<table>
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<tr>
<th>Condition</th>
<th>Pair</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E_0$ (eV)</th>
<th>$C_3 (10^4 $Å$^3$)</th>
<th>$\eta^*$</th>
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<tr>
<td>Pt foil</td>
<td>Pt-Pt</td>
<td>12</td>
<td>2.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>He @300 K</td>
<td>Pt-Co</td>
<td>1.5±0.5</td>
<td>2.65±0.02</td>
<td>0.008±0.001</td>
<td>10.0±1.7</td>
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<td>14%</td>
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<td>Pt-Pt</td>
<td>9.0±0.4</td>
<td>2.72±0.02</td>
<td>0.009±0.001</td>
<td>7.2±0.5</td>
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<td>CO+O$_2$ @300 K</td>
<td>Pt-Co</td>
<td>1.3±0.3</td>
<td>2.70±0.02</td>
<td>0.011±0.002</td>
<td>10</td>
<td>-</td>
<td>13%</td>
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<tr>
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<td>Pt-Pt</td>
<td>9.0±0.4</td>
<td>2.73±0.02</td>
<td>0.009±0.001</td>
<td>7.2</td>
<td>-</td>
<td></td>
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<td>CO+O$_2$ @343 K</td>
<td>Pt-O</td>
<td>0.3±0.2</td>
<td>2.02±0.03</td>
<td>0.005±0.004</td>
<td>8.3±2.0</td>
<td>-</td>
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<td>Pt-Co</td>
<td>1.1±0.3</td>
<td>2.71±0.03</td>
<td>0.015±0.004</td>
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<td>Pt-Pt</td>
<td>8.8±0.3</td>
<td>2.73±0.02</td>
<td>0.009±0.001</td>
<td>7.2</td>
<td>-</td>
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<td>CO+O$_2$ @383 K</td>
<td>Pt-O</td>
<td>0.4±0.1</td>
<td>2.05±0.02</td>
<td>0.005±0.003</td>
<td>6.6±1.5</td>
<td>-</td>
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<tr>
<td></td>
<td>Pt-Co</td>
<td>0.7±0.1</td>
<td>2.69±0.03</td>
<td>0.009±0.004</td>
<td>10</td>
<td>-</td>
<td>7%</td>
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<td>Pt-Pt</td>
<td>8.8±0.3</td>
<td>2.74±0.02</td>
<td>0.011±0.001</td>
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<tr>
<td>CO+O$_2$ @423 K</td>
<td>Pt-O</td>
<td>0.7±0.2</td>
<td>2.03±0.02</td>
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<td>Pt-Co</td>
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<td>10</td>
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<td>Pt-Pt</td>
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*$\eta$ is the extent of Pt-Co alloying, calculated by $\eta = N_{Pt-Co}/(N_{Pt-Co}+N_{Pt-Pt})$.

References