Supplementary material

In situ DRIFT spectroscopy insights into the reaction mechanism of CO and toluene co-oxidation over Pt-based catalysts

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**Experimental section**

**Catalyst characterizations**

Characterization of the phase structure of each catalyst sample by the X-ray diffraction (XRD) patterns, and was recorded on a Panalytical X'Pert PRO system (Cu Kα: 1.5406Å; 40KV; 40Ma), the range of 2θ angles of the scan is 5 to 90°.

The Brunauer-Emmett-Teller (BET) surface areas of the catalysts were acquired from N$_2$ adsorption-desorption at −196 °C using the Micromeritics ASAP 2020 M. The catalyst samples were desorbed at 150 °C under vacuum for 4h before the analysis.

The Pt-based catalysts were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, iCap 6300).

Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2010F at an accelerating voltage of 200 kV.

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a multifunctional imaging electron spectrometer (VG, XLESCALAB 250Xi) equipped with monochromatic Al Kα (hν = 1486.6 eV) radiation. The binding energy was calibrated using the adventitious carbon (C 1s) at 284.6 eV.

Hydrogen temperature programmed reduction (H$_2$-TPR) were carried out using a Micromeritics Autochem 2920 with a TPx system and a thermal conductivity detector (TCD).

All of the operando diffuse reflectance infrared FT spectroscopy (DRIFTS) results were collected on an FTIR spectrometer (Nicolet IS50R FT-IR) equipped with a Harrick DRIFT cell and an MCT/A detector in the range of 650–8000 cm$^{-1}$ with 32 scans at a resolution of 4 cm$^{-1}$ using a KBr window. In a typical experiment, the powder samples were pre-treated in pure N$_2$.
(100 mL min\(^{-1}\)) at 300 °C for 1 h to remove the residuals. After cooled down to 50 °C, and a background spectrum was collected at 4 cm\(^{-1}\) resolution for 32 scans in N\(_2\) atmosphere. Then, the reactant gas (1.0 vol.% CO or 500 ppm toluene) was continuously introduced into the in situ reaction chamber. The DRIFTS spectra (4000–650 cm\(^{-1}\)) were collected and continuously recorded for 1h to realize the adsorption equilibrium.

**Catalytic oxidation of CO/toluene**

The catalytic activity was carried out in a fixed-bed quartz tubular micro-reactor (Φ = 10.0 mm) with 100 mg catalyst and 400 mg quartz sands (40–60 mesh). The volumetric composition of the reactant mixture was 1.0 vol.% CO/1000 ppm toluene containing synthetic air (20% O\(_2\) + balance N\(_2\)), and the total continuous flow was 100 mL min\(^{-1}\), corresponding to a weight hourly space velocity (WHSV) of 60,000 mL g\(^{-1}\) h\(^{-1}\). The range of temperature was 100 to 250 °C. The concentrations of the reactants and products were monitored online by gas chromatography (Shimadzu GC-2014) equipped with two flame ionization detector (FID). To study the effect of water vapor on the catalytic activity, the on-stream CO/toluene oxidation experiment was carried out in the presence and absence of different water vapor (1.0 vol.%, 5.0 vol.% and 10 vol.%) obtained by bubbling. The CO and toluene conversions (\(\eta_{\text{CO}}\), %, \(\eta_{\text{toluene}}\), %) were calculated according to the following equation:

\[
\eta_{\text{CO}}(\%) = \frac{(C_{\text{in}} - C_{\text{out}})}{C_{\text{in}}} \times 100\% \\
\eta_{\text{toluene}}(\%) = \frac{(C_{\text{in}} - C_{\text{out}})}{C_{\text{in}}} \times 100\%
\]

Where \(C_{\text{in}}\) and \(C_{\text{out}}\) are the CO or toluene concentration in the feed gas and in the product, respectively.
Catalytic activity can also be evaluated by comparing the apparent activation energy ($E_a$) values of catalysts, a sample with a lower $E_a$ value in a catalytic reaction will possess excellent catalytic activity. It has been reported that CO/VOCs combustion follows first-order kinetics at CO/VOCs concentration less than 20% under presence of excess oxygen with the equations:

$$
\gamma_{\text{toluene}} = \frac{N_{\text{toluene}} \times \eta_{\text{toluene}}}{W_{\text{cat}}}
$$

(3)

$$
\gamma_{\text{toluene}} = -\kappa = \left[-A \exp\left(-\frac{E_a}{RT}\right)\right]c
$$

(4)

Where $N_{\text{toluene}}$, $W_{\text{cat}}$, $\gamma$, $\kappa$, $A$, and $E_a$ correspond to the C$_{\text{toluene}}$ gas flow rate (mol s$^{-1}$), catalyst weight (g), reaction rate ($\mu$mol g$^{-1}$ s$^{-1}$), rate constant (s$^{-1}$), pre-exponential factor, and apparent activation energy (kJ mol$^{-1}$), respectively. The $\kappa$ values are calculated from the reaction rates and toluene conversions. $E_a$ value in the catalytic CO reaction is calculated by the same equations.
Fig. S1 XRD patterns of Pt-Al₂O₃, Pt-Co₃O₄ and Pt-CeO₂ samples.

Fig. S2 N₂ adsorption-desorption isotherms of Pt-Al₂O₃, Pt-Co₃O₄ and Pt-CeO₂ samples.
Fig. S3 H$_2$-TPR profiles of these as-synthesized CeO$_2$ and Co$_3$O$_4$ samples.

Fig. S4 C 1s XPS spectra of these as-synthesized Pt-based samples.
Fig. S5 CO and toluene conversions in simple and mixture conditions of (a) CeO$_2$ nanorod and (b) Co$_3$O$_4$ nanosheet. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at WHSV=60,000 mL g$^{-1}$ h$^{-1}$. 
Fig. S6 Arrhenius plots for (a) CO and (b) toluene oxidation over different Pt-based samples.
Fig. S7 (a) CO and (b) toluene conversions of fresh Pt-Al₂O₃ and fresh Pt-Al₂O₃ after reduction at different conditions. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at WHSV=60,000 mL g⁻¹ h⁻¹.
Fig. S8 CO conversion of Pt-CeO$_2$ catalysts in the absence of O$_2$ reaction condition: 1.0 vol.% CO and 5 vol.% H$_2$O balanced with N$_2$.

Fig. S9 (a, c) CO and (b, d) toluene conversions of Pt-CeO$_2$ catalysts at different CO/toluene concentration. All the reactions were kept at WHSV=60,000 mL g$^{-1}$ h$^{-1}$. 
Table S1. Catalytic activities of the Co$_3$O$_4$, CeO$_2$, Pt-Al$_2$O$_3$, Pt-Co$_3$O$_4$ and Pt-CeO$_2$ samples.

<table>
<thead>
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<th>Sample</th>
<th>Temperature (°C)</th>
<th>Simple conditions</th>
<th>Mixture conditions</th>
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<td></td>
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<td>T$_{10%}$</td>
<td>T$_{50%}$</td>
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<td>Toluene</td>
<td>148</td>
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