Supplementary material

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

Qi Zhang[a,1], Shengpeng Mo[a,1], Jiaqi Li[a], Yuhai Sun[a], Mingyuan Zhang[a], Peirong Chen[a], Mingli Fu[a,b,c], Junliang Wu[a,b,c], Limin Chen[a,b,c] and Daiqi Ye[a,b,c] *

[a] *School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China*

E-mail address: cedqye@scut.edu.cn (D. Ye);

[b] *National Engineering Laboratory for VOCs Pollution Control Technology and Equipment, Guangzhou Higher Education Mega Centre, Guangzhou 510006, PR China*

[c] *Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control (SCUT), Guangzhou Higher Education Mega Centre, Guangzhou 510006, PR China*

[1] *Qi Zhang and Shengpeng Mo are co-first authors.*

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 K_{α}: 1.5406A; 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 (η_{CO}, %, $\eta_{toluene}$, %) were calculated according to the following equation:

$$\eta_{CO}(\%) = \frac{(C_{in} - C_{out})}{C_{in}} \times 100\% \tag{1}$$

$$\eta_{toluene}(\%) = \frac{(C_{in} - C_{out})}{C_{in}} \times 100\% \tag{2}$$

Where C_{in} and C_{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:

$$\gamma_{\text{toluene}} = \frac{N_{\text{toluene}} \times \eta_{\text{toluene}}}{W_{cat}} \tag{3}$$

$$\gamma_{toluene} = -\kappa c = \left[-A \exp\left(-\frac{E_a}{RT} \right) \right] c \tag{4}$$

Where N_{toluene}, W_{cat}, γ, κ, A, and E_a correspond to the C_{toluene} gas flow rate (mol s^{-1}), catalyst weight (g), reaction rate (μmol g^{-1} s^{-1})), rate constant (s^{-1}), pre-exponential factor, and apparent activation energy (kJ mol^{-1}), respectively. The κ values are calculated from the reaction rates and toluene conversions. E_a value in the catalytic CO reaction is calculated by the same equations.

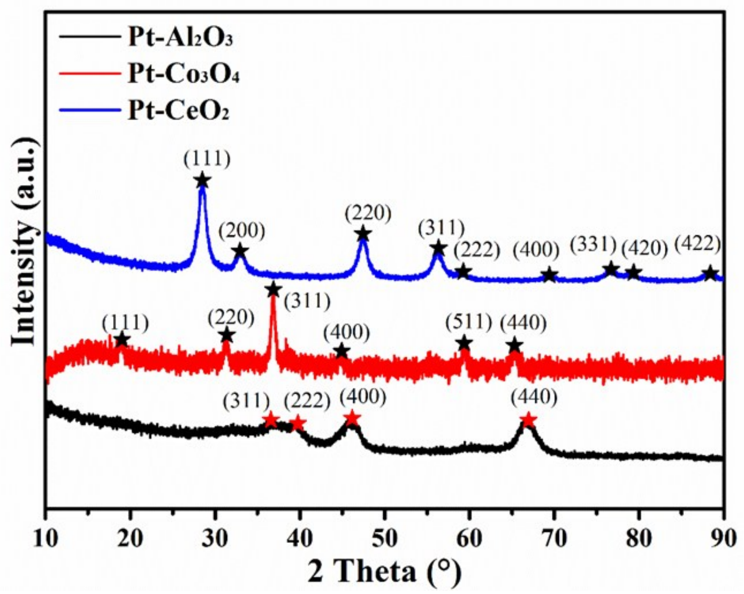


Fig. S1 XRD patterns of Pt-Al_2O_3, Pt-Co_3O_4 and Pt-CeO_2 samples.

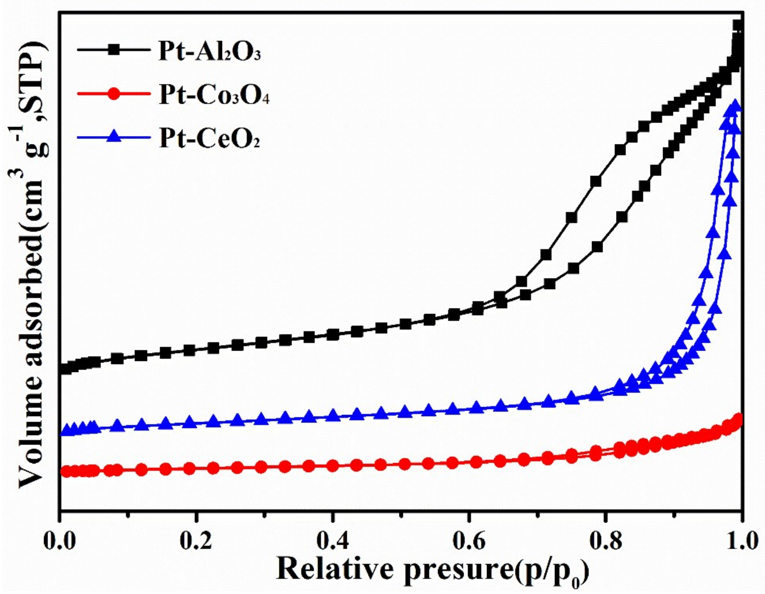


Fig. S2 N_2 adsorption-desorption isotherms of Pt-Al_2O_3, Pt-Co_3O_4 and Pt-CeO_2 samples.

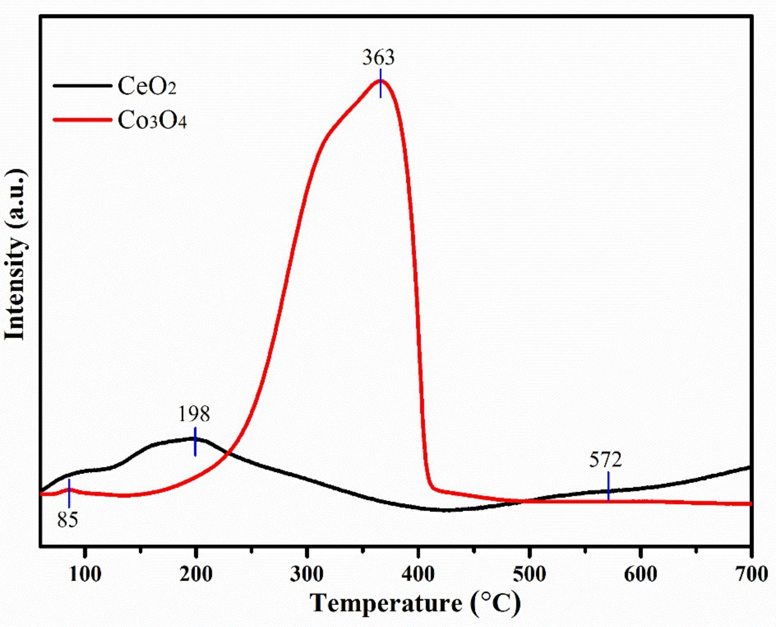


Fig. S3 H_2-TPR profiles of these as-synthesized CeO_2 and Co_3O_4 samples.

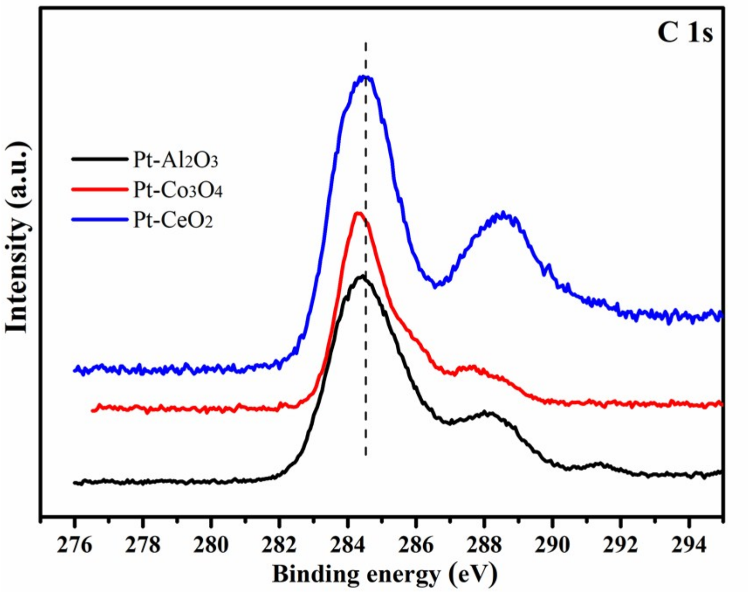
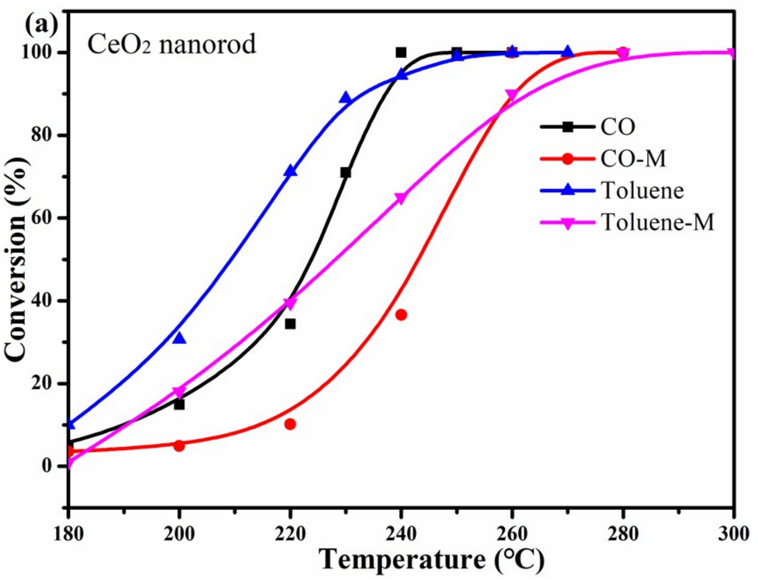


Fig. S4 C 1s XPS spectra of these as-synthesized Pt-based samples.



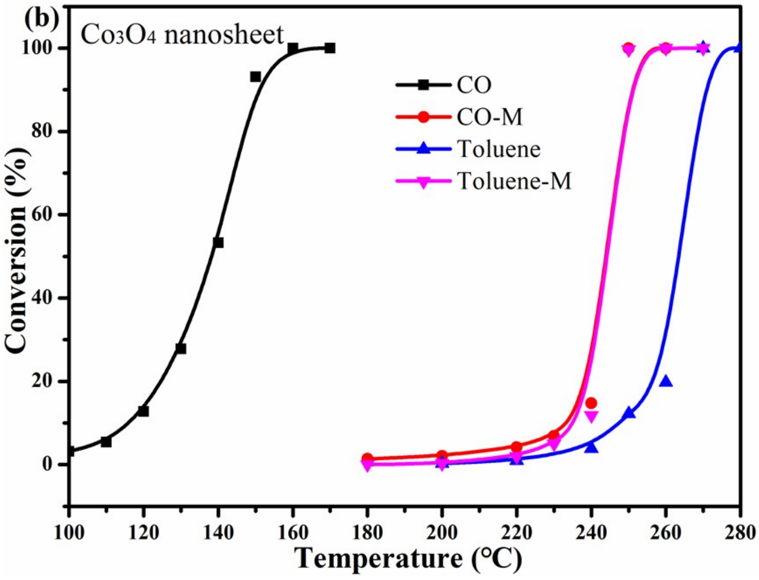


Fig. S5 CO and toluene conversions in simple and mixture conditions of (a) CeO_2 nanorod and (b) Co_3O_4 nanosheet. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at WHSV=60, 000 mL g^{-1} h^{-1}.

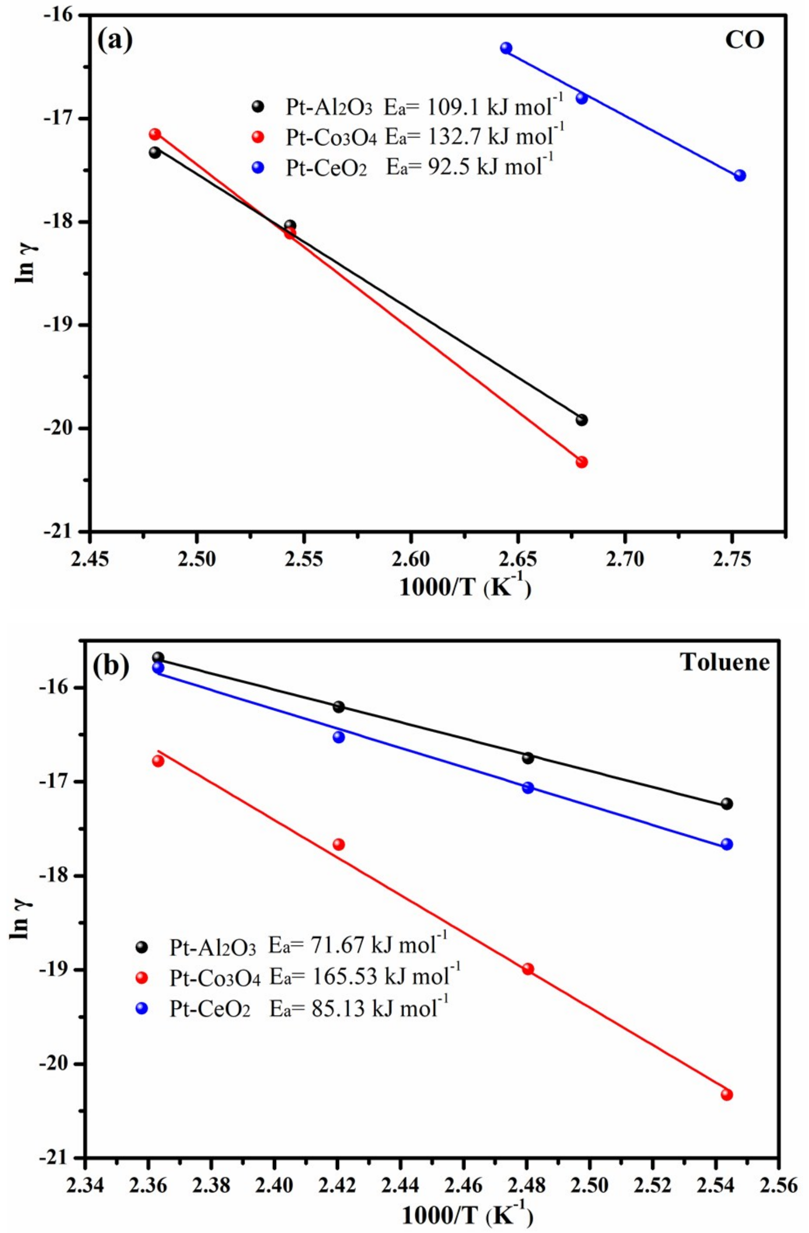


Fig. S6 Arrhenius plots for (a) CO and (b) toluene oxidation over different Pt-based samples.

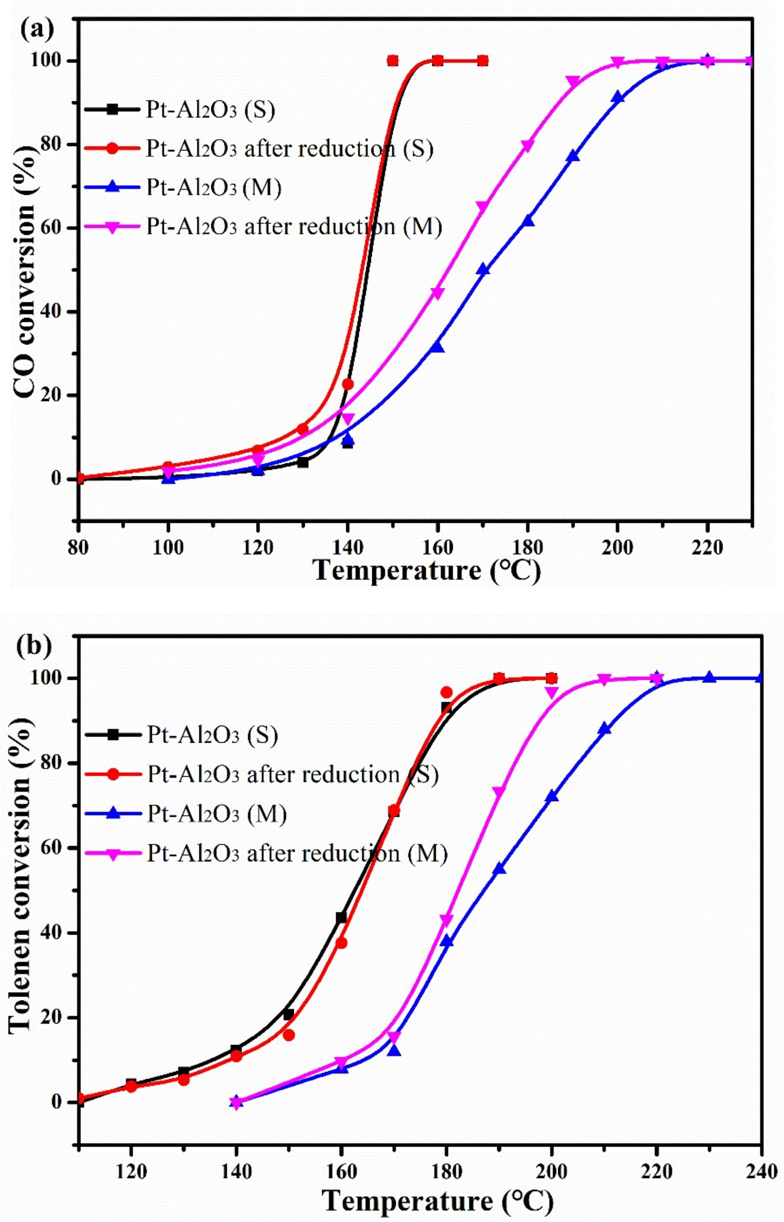


Fig. S7 (a) CO and (b) toluene conversions of fresh Pt-Al_2O_3 and fresh Pt-Al_2O_3 after reduction at different conditions. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at WHSV=60, 000 mL g^{-1} h^{-1}.

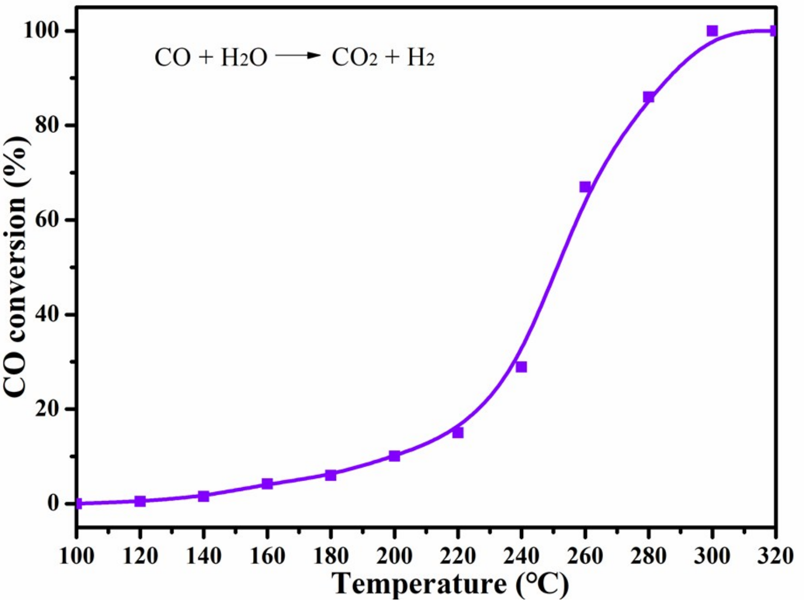


Fig. S8 CO conversion of Pt-CeO$_2$ catalysts in in the absence of O$_{2.}$ reaction condition: 1.0 vol.% CO and 5 vol.% H_2O balanced with N_2.

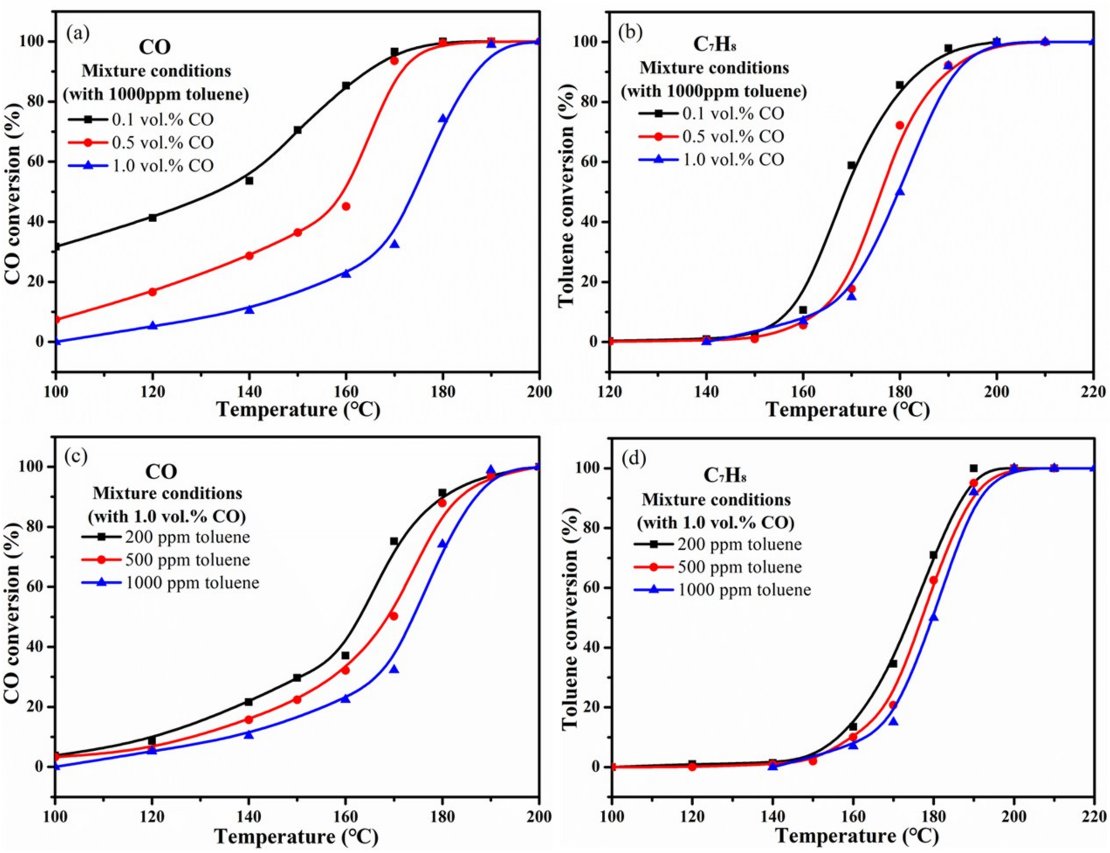


Fig. S9 (a, c) CO and (b, d) toluene conversions of Pt-CeO$_2$ catalysts at different CO/toluene concentration. All the reactions were kept at WHSV=60, 000 mL g^{-1} h^{-1}.

Table S1. Catalytic activities of the Co_3O_4, CeO_2, Pt-Al_2O_3, Pt-Co_3O_4 and Pt-CeO_2 samples.

Sample	Temperature (°C)	Simple conditions			Mixture conditions		
		T_{10}/°C	T_{50}/°C	T_{99}/°C	T_{10}/°C	T_{50}/°C	T_{99}/°C
Co_3O_4	CO	115	136	160	235	245	250
	Toluene	245	265	270	236	245	250
CeO_2	CO	200	225	240	224	245	260
	Toluene	180	210	250	190	230	270
Pt-Al_2O_3	CO	141	145	150	141	170	210
	Toluene	133	162	190	150	187	220
Pt-Co_3O_4	CO	140	145	150	160	192	210
	Toluene	153	176	190	170	198	210
Pt-CeO_2	CO	101	111	125	140	174	190
	Toluene	148	164	180	170	180	195