Electronic Supplementary Information:

Facile Synthesis of Highly-dispersed Pt/CeO$_2$ by Spontaneous Surface Redox Chemical Reaction for CO Oxidation

Fangxian Cao, a Sai Zhang, a Wei Gao, a Tian Cao b and Yongquan Qu a*

a Center for Applied Chemical Research, Frontier Institute of Science and Technology, and Shaanxi Key Laboratory of Energy Chemical Process Intensification, School of Chemical Engineering and Technology, Xi’an Jiaotong University, Xi’an, 710049, China. E-mail: yongquan@mail.xjtu.edu.cn.

b Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China.

Experimental Section

All chemicals were of analytical grade without further purification before utilization. Deionized water used in experiments was purified with a resistivity of 18.2 MΩ cm.

Method

Synthesis of non-porous CeO$_2$/Ce(OH)$_3$ nanorod precursors

Ce(NO$_3$)$_3$·6H$_2$O (1.736g) and NaOH (19.2g) were dissolved in 5mL and 75mL deionized water, respectively. The two solutions were thoroughly mixed in Pyrex bottle and the mixture was aged under continuous stirring for 30 min. Subsequently, the Pyrex bottle was transferred into a temperature-controlled electric oven and kept at 100 °C for 24 h. After cooling to room temperature, the solid products were washed by deionized water and ethanol alternatively for three times and dried at 60 °C.

Synthesis of porous nanorods of CeO$_2$ (PN-CeO$_2$)

PN-CeO$_2$ were synthesized by the second hydrothermal treatment of non-porous CeO$_2$/Ce(OH)$_3$ nanorod precursors at 175 °C for 12 h. The solid products were collected by centrifugation, washed with deionized water and dried at 60 °C.

Synthesis of Pt/CeO$_2$-HT catalysts
Pt/CeO$_2$-HT catalysts were synthesized by a hydrothermal process, in which the spontaneous surface redox chemical reaction between Ce$^{3+}$ species and [PtCl$_6$]$^{2-}$ happened. Typically, 140 mg of as-synthesized non-porous CeO$_2$/Ce(OH)$_3$ nanorods were dispersed in 70mL deionized water by sonication. After the addition of the desired amount of H$_2$PtCl$_6$ solution into the above-mentioned non-porous CeO$_2$/Ce(OH)$_3$ nanorods suspension, the mixture was transferred into 100mL Teflon-lined autoclave and kept at 175 °C for 12 h. Theoretical Pt loading was controlled at 1 wt%. After cooling to room temperature, the solid products were washed by deionized water for three times and dried at 60 °C.

**Synthesis of Pt/CeO$_2$ catalysts by impregnation method**

As a comparison, Pt/CeO$_2$ catalysts (Pt/CeO$_2$-IM) with the same Pt weight loading were also synthesized by the impregnation method. Briefly, 1.0 g of PN-CeO$_2$ was dispersed in 5 mL of deionized water and then the desired amount of H$_2$PtCl$_6$ solution was added with a continuous stirring for 3 h at room temperature. Then, the mixture was evaporated completely at 60 °C. Finally, the powders were collected for future use.

**Characterization**

Transmission electron microscopy (TEM) measurements were performed on Hitachi HT-7700 with the accelerating voltage of 120 kV and Tecnai G2 F20 S-TWIN microscope with the accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were collected from a Rigaku Powder X-ray diffractometer with the Cu Kα radiation. Nitrogen adsorption and desorption measurements were performed on an ASAP 2020 HD88 (Micromeritics). Before measurements, the catalysts were degassed at 50 °C under vacuum for 24 h to ensure a clean surface. The specific area was calculated by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was measured from the desorption branch of isotherms using the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectra (XPS) were obtained on a Thermo Electron Model K-Alpha with Al Kα as the excitation source.

**Pt nanoparticles dispersion:** The dispersion of Pt was obtained from CO chemisorption by using CO pulses at room temperature (ChemBET TPR/TPD chemisorption analyzer). Typically, the sample (100mg) was reduced at 200 °C for 1 h under a flow of H$_2$ (20 sccm), and then cooled down to room temperature following by purging with He (30 sccm) for 30 min. A given amount of CO (87 μL) was injected in a pulse every 5 min until the intensity of peak reached a constant value.

**In-situ Fourier transform infrared spectroscopy measurements:** In-situ Fourier transform infrared spectroscopy measurements of CO chemisorptions measurements were preformed on a Nicolet iS 10 spectrometer equipped with a MCT detector. Before measurements, the sample was treated by a mixture gas of 10 vol. % H$_2$/Ar (50 sccm). A background spectrum was collected after Ar purge for 15 min. Subsequently, the sample was exposed to 2 % CO in Ar at a flow rate of 25
sccm for 30 min until saturation. Next, the sample was purged with Ar at a flow rate of 25 sccm for 30 min to remove the gas phase CO and then the in-situ FT-IR spectrum was collected with 32 scans at a resolution of 4 cm⁻¹.

**Catalytic CO oxidation**

CO oxidation is used as a model reaction to evaluate the catalytic performance of Pt/CeO₂ catalysts prepared via different methods. Before performing the evaluation, all catalysts were reduced under a 50 sccm flowing mixture gas of H₂/Ar with the volumetric ratio of 1:9 at 200°C for 60 min. Specifically, the catalytic activity was evaluated on the home-made fixed bed quartz reactor. The mixture gas of 0.5 sccm of CO, 0.5 sccm of O₂ and 49 sccm of Ar was delivered into the reactor loaded with 125 mg of Pt/CeO₂ catalysts (60 ~ 100 mesh). The temperature of ramping rate was controlled at 5 °C/min. The effluent of CO and CO₂ were recorded by an in-line gas chromatograph equipped with a flame ionization detector (FID).

The CO conversion was calculated according to:

\[ X(\%) = \frac{(CO_{\text{inlet}} - CO_{\text{outlet}})}{CO_{\text{inlet}}} \times 100 \]

Where \( X \) is the CO conversion, \( CO_{\text{inlet}} \) presents the initial CO concentration in the inlet, and \( CO_{\text{outlet}} \) presents the CO concentration in the outlet.
Figure S1 (a) XRD patterns of PN-CeO$_2$ and Ce(OH)$_3$/CeO$_2$ precursor (b) XRD patterns of Pt/CeO$_2$-HT and Pt/CeO$_2$-IM

Figure S2 N$_2$ adsorption-desorption isotherms of PN-CeO$_2$, Pt/CeO$_2$-HT and Pt/CeO$_2$-IM.

Figure S3 (a) XPS spectra of Ce 3d of PN-CeO$_2$, Pt/CeO$_2$-HT and Pt/CeO$_2$-IM (b) XPS spectra of Cl 2p of Pt/CeO$_2$-HT and Pt/CeO$_2$-IM
Figure S4 Comparison of $T_{10}$, $T_{50}$, $T_{90}$, $T_{99}$ of Pt/CeO$_2$-HT and Pt/CeO$_2$-IM for CO oxidation.