

Electronic Supplementary Information

Highly active Rh₁/CeO₂ single-atom catalyst for low-temperature CO Oxidation

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Experimental details:

1. Reagents

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (99.99%) and $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. Cerium nitrate hexahydrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%)], $\text{PdCl}_2(\text{NH}_3)_4$ and sodium carbonate [Na_2CO_3 (99.99%)] were purchased from Sigma-Aldrich. NaBH_4 was purchased from Damao Chemical Reagent factory. Polyvinyl alcohol (PVA) was purchased from Aladdin. Ultrapure water was homemade by a Millipore Autopure system. All reagents were used without further purification. Helium (99.999%), hydrogen (99.999%), nitrogen (99.999%), 5 vol% CO/He, 10 vol% O_2 /He, 0.02 vol% SO_2 /He and mixed gas of 1 vol% CO, 1 vol% O_2 balance with He were purchased from Dalian GuangMing Special Gas Products Co., Ltd.

2. Catalyst preparation

2.1 Preparation of CeO_2 support

CeO_2 support was prepared by a co-precipitation method. In detail, an aqueous solution of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 1 mol/L) was added dropwise to an aqueous solution of sodium carbonate (Na_2CO_3 , 1 mol/L) under stirring at 50 °C. After continuing stirring and aging for 2 h, respectively, the suspension was filtrated with multiple washing. The resulting precipitate was dried at 60 °C overnight and then calcined at 400 °C for 5 h.

2.2 CeO_2 supported catalysts

The Rh/ CeO_2 single atom catalyst (SAC) was prepared by a facile adsorption precipitation method. Typically, 400 mg pre-synthesized CeO_2 support was dispersed into 30 mL of ultrapure water with rigorous stirring. Then, 10 mL aqueous RhCl_3 solution with appropriate concentration was dropwise added (1 mL/min) to the suspension. After stirring for 3 h and aging for 1 h, the resulting precipitate was filtered and washed, then dried at 60 °C overnight and without any further heat treatment denoted as Rh_1/CeO_2 .

0.04 wt% Pd₁/CeO₂ synthesized by the same method, only replaced RhCl₃ solution with PdCl₂(NH₃)₄ solution. 0.04 wt% Pt₁/CeO₂ was prepared by incipient impregnation method. 400 mg CeO₂ was added to 0.4 mL H₂PtCl₆ solution with appropriate concentration, and dried at 80 °C overnight and without any further heat treatment. The actual metal loadings of all samples were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS).

For comparison, a CeO₂ supported Rh nanoparticles (NPs) catalyst with 0.04 wt% loading was prepared by depositing colloidal Rh NPs onto the support. Colloidal Rh NPs were prepared by NaBH₄ reduction under PVA protection. 200 mL RhCl₃ solution (0.5 mmol/L) was mixed with 40 mL PVA solution (1 mg/mL) 10 min with rigorous stirring. Then, 2 mL NaBH₄ solution (7.5 mg/mL) was added to the mixed solution at once with rigorous stirring. The solution turned to dark brown color. Appropriate amount of colloidal Rh nanoparticles solution was mixed with ultrapure water under stirring. Then, 500 mg CeO₂ was added with rigorous stirring at 90 °C until the water evaporated. The obtained sample was calcined at 350 °C for 4 hours in air to remove the protection agent and denoted as Rh_{NP}/CeO₂.

3. Catalytic performance test

The catalytic performances of the catalysts for CO oxidation were evaluated in a fixed-bed tubular quartz reactor with an inner diameter of 4 mm at atmospheric pressure. Typically, 50 mg of the catalyst was used for the reaction test except the stability test in which the space velocity was indicated. Before reaction, the catalysts (Rh_{NP}/CeO₂, Rh₁/CeO₂, Pt₁/CeO₂ and TWC) were pre-reduced in 10 vol% H₂/He at 200 °C for 0.5 h. Pd₁/CeO₂ were purging He for 10 min before reaction. Then, the feed gas containing 1 vol% CO, 1 vol% O₂ and balance He was allowed to pass through the reactor at a flow rate of 33.3 mL/min, corresponding to a WHSV (weight hourly space velocity) of 40 000 mL g_{cat}⁻¹ h⁻¹. The inlet and outlet gas compositions were on line analyzed by a gas chromatograph (6890) equipped with a TDX-01 column and a thermal conductivity detector using He as carrier gas. The CO

conversion rates were calculated based on the difference between inlet and outlet CO concentrations. In the stability test with presence of SO₂ and H₂O, before reaction, the catalysts Rh₁/CeO₂ were pre-reduced in 10 vol% H₂/N₂ at 200 °C for 0.5 h, then with N₂ purging for 15 min. The temperature was maintained as 140 °C. In the first 170 min, 0.5 vol% CO, 10 vol% O₂, He balance. From 170 to 1525 min, 0.5 vol% CO, 10 vol% O₂, 0.002 vol% SO₂, He balance. From 1525 to 1725 min, SO₂ was removed from the stream. From 1725 to 1860 min, 0.5 vol% CO, 10 vol% O₂, 2 vol% H₂O, He balance. After 1395 min, H₂O was removed from the stream. WHSV = 40 000 mL g_{cat}⁻¹ h⁻¹.

In order to measure the specific reaction rate and turnover frequency (TOF) value, the catalytic CO oxidation reaction was conducted under a differential model where the CO conversion was controlled below 20 %. The average of CO conversions 20, 40, and 60 min was used to calculate the specific rate. TOF value was then calculated based on the specific rate and the dispersion of Rh₁/CeO₂, which is 100% for SACs.

The kinetic measurements were also performed under a differential model. For Rh₁/CeO₂ the reaction rates were measured at 140 °C and the concentrations of CO and O₂ were controlled in the ranges of 0.5 - 2.0 vol% and 0.8 - 3.0 vol%, respectively. For Rh_{NP}/CeO₂ the reaction rates were measured at 200 °C and the concentrations of CO and O₂ were also in the ranges of 0.5 - 2.0 vol% and 0.8 - 3.0 vol%, respectively.

4. Characterization Techniques.

The actual metal loadings of all samples were determined by ICP-OES on 7300DV instrument (PerkinElmer) and ICP-MS on NexION 300D instrument (PerkinElmer).

The powder X-ray diffraction (XRD) characterizations were conducted on a X'pert PRO X-ray diffractometer using Cu K α radiation ($\lambda = 0.15432$ nm), operating at 40 kV and 40 mA.

High-angle annular dark-field scanning transmission electron microscopy

(HAADF-STEM) images were obtained on a HITACHI HF5000 microscope and operated at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was performed to locate elemental distribution of Rh, O and Ce. The scanning transmission electron microscopy (STEM) studies were obtained on a JEOL JEM-2100F microscope operated at 200 kV. The samples were ultrasonically dispersed in ethanol, and then the resulting solution was dripped onto the carbon film supported by a copper grid.

In situ diffuse reflectance infrared Fourier transform spectra (DRIFTs) were acquired on a Bruker Equinox 55 spectrometer equipped with a mercury cadmium telluride (MCT) detector at a resolution of 4 cm^{-1} using 32 scans. The samples were put in a reaction cell, and before CO adsorption, the samples were reduced in situ at 200 °C with 10 vol% H₂/He for 0.5 h, cooled to room temperature in helium, and background spectrum was recorded. Then 5 vol% CO/He was introduced into the samples, the spectra were collected until the state steady. Then pure helium was introduced to remove the extra CO gas. Then increase the temperature to 50 °C, 80 °C, 110 °C and 150 °C and the spectra were collected.

In situ X-ray photoelectron spectra (XPS) were determined on a ESCALAB250xi equipment using Al K α radiation (1486.6 eV, 12.5 kV, 250 W) to obtain the binding energies and oxidation states of Rh, Ce and O elements. In-situ XPS experiments was performed with the following procedure. The catalyst was pressed to thin sheet and fixed on the sample holder. After recording the spectra of the fresh catalyst in the analyzer chamber, the sample was transferred into the preparation chamber to do the reduction. The sample was heated in 10% H₂-He flow to 200 °C and maintained for 0.5 h, then the sample was cooled to room temperature. The reduced sample was directly returned to the analyzer chamber without exposure to air. Then XPS data were recorded.

Table S1. The metal loading of various catalysts

Catalyst	Loading (wt%)
Rh ₁ /CeO ₂	0.023
Rh _{NP} /CeO ₂	0.044
Pt ₁ /CeO ₂	0.045
Pd ₁ /CeO ₂	0.026
TWC-Pt	0.17
TWC-Rh	0.05
TWC-Pd	0.66

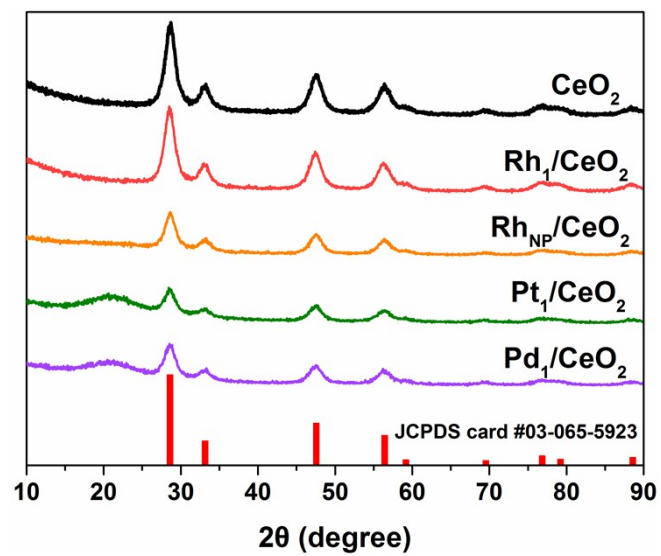


Fig. S1 XRD pattern of synthesized CeO_2 and as-prepared catalysts.

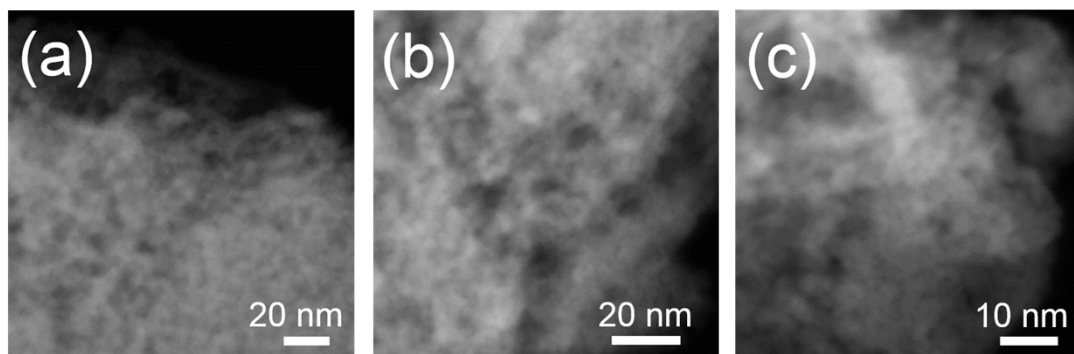


Fig S2. STEM images of Rh₁/CeO₂.

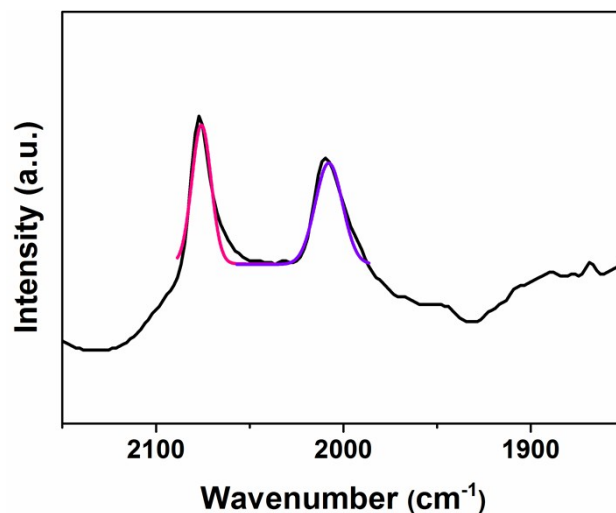


Fig. S3 Fittings of the DRIFT spectra of CO adsorption with Gaussian functions on Rh₁/CeO₂.

The high and low wavenumber component in the doublet feature of Rh(CO)₂ corresponds to the symmetric and anti-symmetric CO-stretching mode, respectively. The ratio of integrated absorbance ($A_{\text{asym}}/A_{\text{sym}}$) is related to the angle (2α) between carbonyl groups as follows:¹

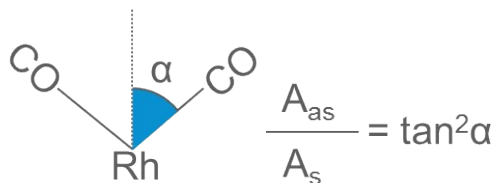


Table S2. IR bands of adsorbed CO on the Rh sites of Rh₁/CeO₂

IR band	Rh(CO) ₂	A_{sym}	Rh(CO) ₂	A_{asym}	$2\alpha(^{\circ})$
wavenumber (cm ⁻¹)	symmetric stretching		asymmetric stretching		
Rh ₁ /CeO ₂	2076	0.049	2009	0.057	94

Table S3. Activity comparison of Rh₁/CeO₂ SAC with the previously reported catalysts for CO oxidation

Catalyst	T (°C)	Reaction rate (mol _{CO} h ⁻¹ g _M ⁻¹)	TOF (s ⁻¹)	Note
Rh ₁ /CeO ₂	100	14.3	0.41 [a]	This work
Rh _{NP} /CeO ₂	160	3.1		This work
Rh/USY	110		0.04 [b]	Ref ²
Rh/TiO ₂	120		0.076 [b]	Ref ³
Rh/CeO ₂	110		0.056 [c]	Ref ⁴
Rh/SBA-15	100		0.0029 [d]	Ref ⁵
Rh ₁ /ZnO	180		0.63 [b]	Ref ⁶
Pt ₁ /CeO ₂	160		0.0087 [e]	Ref ⁷
Pt ₁ /CeO ₂	150		0.017 [b]	Ref ⁸
Pt-O-Pt/CeO ₂	100		0.43 [d]	Ref ⁸
Pt ₁ /CeO ₂	80		0.029 [b]	Ref ⁹
Pt ₁ /CeO ₂	225		0.12 [b]	Ref ¹⁰
Pd ₁ /CeO ₂	90		0.45 [b]	Ref ¹¹
Pd ₁ /CeO ₂	100		0.03 [e]	Ref ¹²

[a] TOFs were calculated based on the metal dispersion. For Rh₁/CeO₂, dispersion=100%; [b] Given by the author; [c] Calculated based on the TOFs read from figures; [d] Extrapolated based on the *E_a* and TOF given by the author; [e] Calculated based on flow rate, CO concentration, loading amount and light-off conversion read from figures.

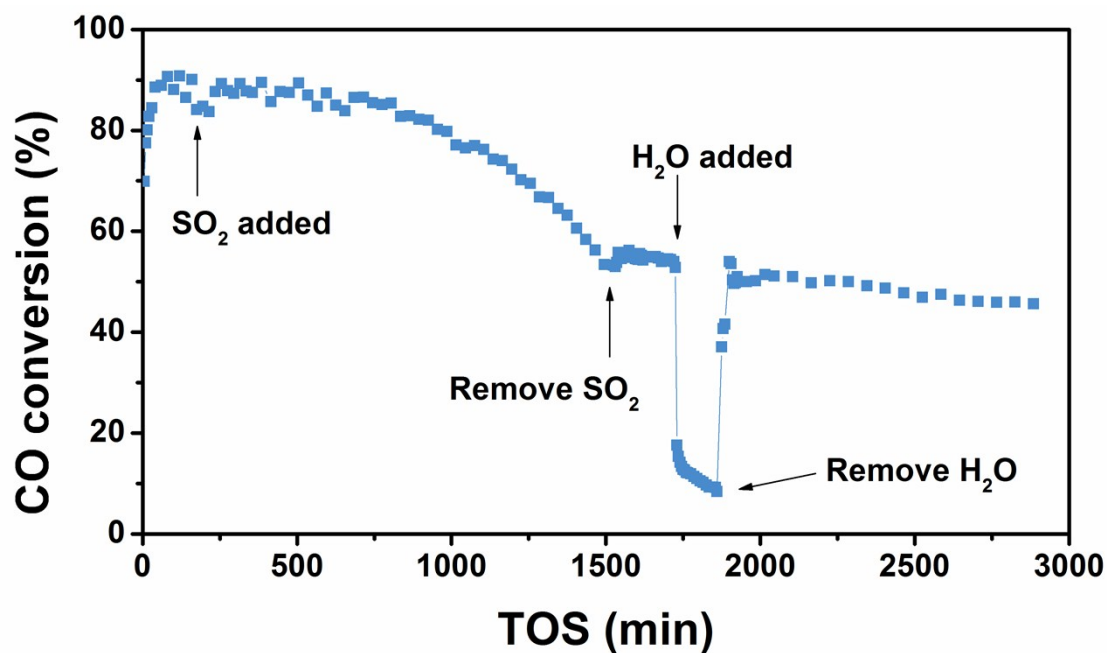


Fig. S4 CO conversion with time on stream (TOS) over Rh₁/CeO₂ catalyst at 140 °C in the presence of SO₂/H₂O. Reaction condition: In the first 170 min, 0.5 vol% CO, 10 vol% O₂, He balance. From 170 to 1525 min, 0.5 vol% CO, 10 vol% O₂, 20 ppm SO₂, He balance. From 1525 to 1725 min, SO₂ was removed from the stream. From 1725 to 1860 min, 0.5 vol% CO, 10 vol% O₂, 2 vol% H₂O, He balance. After 1395 min, H₂O was removed from the stream. Active metal weight hourly space velocity (WHSV_{Rh}) = 174 000 L h⁻¹ g_{Rh}⁻¹.

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