Supporting Information

The influences of reducing agents on the structure-activity relationships between oxygen vacancy and Au sites for CO preferential oxidation

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1. Characterization techniques

X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance diffractometer (manufactured in Germany), which was equipped with a Ni-filtered Cu Kα radiation source, operating at 40 kV and 40 mA. The Bragg's angles were scanned at a step of 0.02° within a 2θ range spanning from 10° to 80°.

Transmission electron microscope (TEM) and high-resolution TEM (HR-TEM) images were captured on a FEI Tecnai F30 microscope furnished with an energy dispersive spectroscopy (EDS).

The N_2 adsorption-desorption measurements were executed on a NOVA 1000e device from Quantachrome. All samples were degassed at 200 °C under vacuum conditions for 2 hours before the experiments. The specific surface area and pore size distribution were computed by applying the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) formula.

Raman spectra were detected by a Witec Alpha300R Raman imaging instrument, with a 633 nm laser excitation and operating at a power of 5 mV.

Ultraviolet-visible (UV-vis) absorption spectra were obtained by using a YOKE PY2600 spectrometer within the wavelength range from 200 to 800 nm.

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific^{TM} K-Alpha^{TM+} spectrometer, with the C 1s peak at 284.8 eV adopted as the reference for calibrating the binding energy.

Electrochemical impedance spectroscopy (EIS) was investigated in a three-electrode electrochemical system. The setup included a saturated calomel electrode (reference electrode), a carbon rod (counter electrode), and a glassy carbon electrode (GCE, working electrode). The sample was fabricated into a slurry and dropped onto the GCE surface. For slurry preparation, 5 mg of the sample and 5 mg of Ketjenblack were ultrasonically dispersed in a mixed solvent system containing 950 μL of ethanol and 50 μL of naphthol. During the test, the frequency range was set from 100 kHz to 0.1 Hz through an electrochemical workstation (CHI 660E), and the voltage was set at −0.55 V *vs.* reversible hydrogen electrode (RHE).

Electron paramagnetic resonance (EPR) was performed at 100 K on a Bruker EMXplus-6/1 spectrometer using a 9.4 GHz of resonant frequency at a microwave power of 6.3 mW.

H_2 temperature-programmed reduction (H_2-TPR) experiments were conducted on a chemical adsorption apparatus equipped with a thermal conductivity detector (TCD). For each experiment, 50 mg of the sample was loaded into a quartz tube and pretreated at 200 °C in N_2 for 30 minutes to eliminate any physisorbed molecules. After cooling to 50 °C, the atmosphere was switched to 5% H_2/N_2 (30 mL min^{-1}) and the sample was heated up to 900 °C at a rate of 10 °C min^{-1}. O_2-pulse experiments were operated to measure the oxygen activation capacity of samples, and the samples were pre-reduced with 5% H_2/N_2 at 200 °C for 0.5 hours before the testing. The dosage of sample was 50 mg, and the pulse temperature was set as 40 °C with He as the carrier gas. In the O_2-pulse experiment, a 1 mL quantitative loop was filled and a 5% O_2/He gas mixture was injected via a six-port valve for pulse introduction. When the pulse peak intensity reached steady-state equilibrium, the corresponding peak area represented the 1 mL volume of 5% O_2/He gas. Under non-steady-state conditions, the difference in peak areas between other peaks and the stabilized peak quantitatively corresponded to the O_2 consumed by the samples.

2. Measurements of catalytic activity

The catalytic activity of CO-PROX was evaluated on a continuous-flow fixed-bed reactor. A specified amount of catalyst (50 mg) was loaded into a quartz tube. The reaction gas mixture consisted of 1 vol% CO, 1 vol% O_2, 50 vol% H_2, and 48 vol% N_2, with the flow rates of each gas controlled by mass flow controllers, and the total flow rate set to 30 mL min^{-1}. A K-type thermocouple attached to the outer side of the quartz tube measured the temperature near the catalyst bed. The reaction temperature range for the activity test was between 30 and 180 °C, with samples taken every 10 °C. A stabilization period of 20 minutes was required before each sampling.

The gas composition before and after the reaction was analyzed online using a gas chromatograph. The chromatograph was equipped with an HQ pre-column and a TDX-01 packed column for separation of different components. H_2 and O_2 were detected by TCD, while CO and CO_2 were first passed through a nickel reformer and then detected by the flame ionization detector (FID). The catalytic activity was evaluated by CO conversion and the O_2 to CO_2 selectivity.

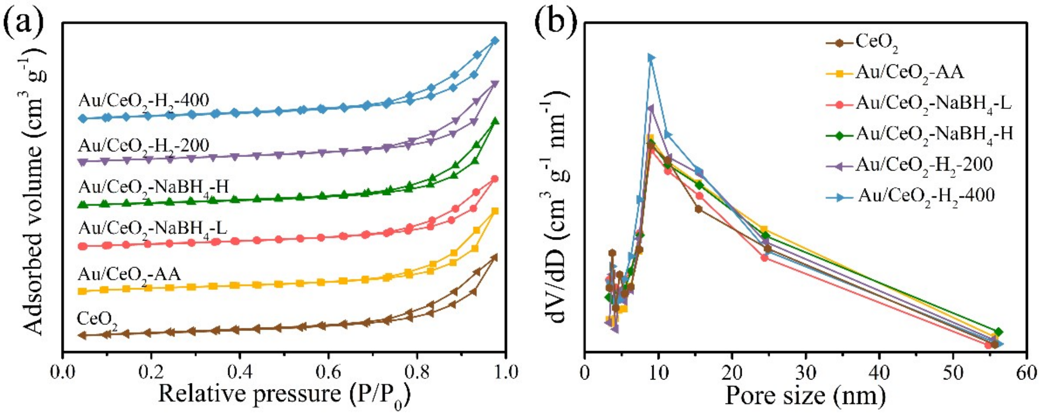

Fig. S1 (a) N_2 adsorption-desorption isotherm and (b) pore size distribution of catalysts.

Table S1 Pore textural properties of the prepared catalysts.

Sample	**S_{BET} (m^2/g)**	**V_{total} (cm^3/g)**	**D_p (nm)**
CeO_2	72	0.27	15
Au/CeO_2-AA	68	0.30	16
Au/CeO_2-$NaBH_4$-L	71	0.28	15
Au/CeO_2-$NaBH_4$-H	72	0.32	18
Au/CeO_2-H_2-200	70	0.30	17
Au/CeO_2-H_2-400	76	0.32	16

Table S2 The valence state composition of Ce, Au and O elements by XPS analysis

Sample	Au/at%			Ce/at%		O/at%		
	Au^0	Au^+	Au^{3+}	Ce^{3+}	Ce^{4+}	O_I	O_{II}	O_{III}
Au/CeO_2-AA	31.6	48.2	20.2	29.0	71.0	63.3	31.2	5.5
Au/CeO_2-$NaBH_4$-L	49.0	25.8	25.2	26.7	73.3	65.8	25.2	9.0
Au/CeO_2-$NaBH_4$-H	68.6	20.6	10.8	30.7	69.3	59.5	35.8	4.7
Au/CeO_2-H_2-200	70.0	30.0	-	25.4	74.6	72.4	22.5	5.1
Au/CeO_2-H_2-400	47.5	52.5	-	27.0	73.0	63.8	30.2	6.0
Au/CeO_2-H_2-400-used	69.1	30.9	-	28.8	71.2	64.4	31.9	3.7