

Supplementary Materials: Catalytic Performance of Gold Supported on Mn, Fe and Ni Doped Ceria in the Preferential Oxidation of CO in H₂-Rich Stream

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The supplementary materials include the detailed procedures for the catalyst preparation and characterization and more characterization results.

1. Catalyst preparation

A series of CeM (M = Mn, Fe and Ni) mixed oxides, with an M/Ce molar ratio of 1/8, were synthesized by a modified hydrothermal method [1,2]. All chemical reagents were of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC, Beijing, China) and used as received without further purification. Typically, Ce(NO₃)₃·6H₂O (4.0 mmol) and corresponding dopants (C₄H₆MnO₄·4H₂O, Fe(NO₃)₃·9H₂O or Ni(NO₃)₂·6H₂O, 0.5 mmol) were dissolved in aqueous KOH solution (90 mL, 6 mol L⁻¹) in a Teflon beaker, which was stirred continuously for 30 min at room temperature and then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 110 °C for 24 h. After cooling down to room temperature, the obtained solid product was recovered by filtration and washed with deionized water. The final solid product was dried at 80 °C for 12 h and calcined at 400 °C in air for 4 h. For comparison, undoped CeO₂ was also prepared by the same procedure.

Gold catalysts were then prepared through the colloidal deposition method, as described previously [1–4]. Typically, polyvinyl alcohol (PVA) as protecting agent was added, with an Au/PVA weight ratio of 1.5, into the aqueous HAuCl₄ solution (100 mg L⁻¹) at room temperature under vigorous stirring. The obtained solution was then stirred further for 10 min. A given quantity of aqueous NaBH₄ solution (0.1 M; the molar ratio of NaBH₄/Au was 5) was then injected rapidly, forming the colloidal gold solution in dark orange-brown color. After that, the ceria support (CeM or CeO₂) was then added into the colloidal gold solution under stirring; the mixture was stirred until the solution was decolorized, which indicated a complete adsorption of Au on the support (a gold loading of 1 wt.% was designated). In these previous steps, all the containers were covered with aluminum foil to exclude possible light radiation. The resultant solid materials were collected by filtration and washed with deionized water. Finally, the supported Au catalysts (Au/CeM or Au/CeO₂) were obtained by drying at 80 °C for 4 h and calcining at 250 °C in air for 4 h.

2. Catalyst characterization

The textural properties were measured by nitrogen sorption at -195.8 °C with on TriStar 3000 Gas Absorption Analyzer (Micromeritics Instrument Co., Norcross, CA, USA). The solid samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement.

The actual composition of the catalyst samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo iCAP 6300, Thermo Scientific, Waltham, MA, USA). To prepare the solution for elemental analysis, 2 mL of concentrated nitric acid was used to dissolve 40 mg of catalyst sample, followed by adding 2 mL of 30 wt.% H₂O₂; the solution was then diluted to 1000 mL with de-ionized water.

X-ray powder diffraction (XRD) patterns of the catalyst samples were collected on an advanced X-ray diffractometer (Bruker AXS D8, Berlin, Germany) with monochromated Cu K α radiation (154.06 pm, 40 kV, and 40 mA). The measurements were made at room temperature in the 2 θ range of 5° to 85° with a scanning rate of 4 ° min⁻¹. The average crystallite size was estimated from the line broadening of the most intense XRD reflections with Scherrer formula and the cell parameter of cubic CeO₂ is obtained by the MDI Jade5 software.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the catalyst samples were obtained by using a JEM 2010 microscope (JEOL Ltd., Tokyo, Japan) operating at 200 kV and equipped with an energy-dispersive X-ray (EDX) instrument. To get an appropriate electron transparency, the catalyst was crushed into fine powder and then a holey carbon film copper grid was dipped into the crushed powder.

Raman spectra were recorded on a dispersive LabRam HR800 microscope (Horiba Jobin Yvon, Longjumeau, France) with a 20 mW green laser (514 nm) without filter, using an 1800 grooves/mm grating and a 100× objective with a confocal pinhole of 10 μm.

Temperature programmed reduction by hydrogen (H₂-TPR) was performed on a Micromeritics AutoChem II 2920 Chemisorption Analyzer (Micromeritics Instrument Corp., Norcross, GA, USA). Approximately 100 mg of the catalyst sample (40–60 mesh) was used in each measurement [1,5]. The catalyst sample was first pretreated in an argon flow containing 5 vol.% oxygen (30 mL min⁻¹) at 250 °C for 30 min, followed by purging with pure argon (30 mL min⁻¹) at the same temperature for 30 min and then cooling down to 0 °C for the supports (CeO₂ and CeM) and to -10 °C for the gold catalysts (Au/CeO₂ and Au/CeM). After that, a flow of 10% hydrogen in argon (30 mL min⁻¹) was switched into the system and the catalyst sample was heated up to 800 °C at a ramp of 10 °C min⁻¹. The amount of H₂ uptake during the heating for reduction was measured by a thermal conductivity detector (TCD), which was calibrated by quantitative reduction of a determined amount of CuO to metallic copper.

X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI-5800 spectrometer (Chanhassen, MN, USA) with Al K α radiation and a multichannel detector. Approximately 100 mg of the powder sample was compressed into a wafer for analysis. The survey spectra were measured in the binding energy (BE) range of 0–1100 eV; the detail spectra of the Au 4f and Ce 3d regions were measured in the ranges of 80–90 eV and 875–925 eV, respectively. The BE values were calibrated with the signal of contaminated carbon C 1s at 284.6 eV. The spectra were decomposed by using XPSPEAK software (Ver. 4.1) after applying a Shirley background subtraction and Gaussian (80%)–Lorentzian (20%) decomposition parameters. Atomic ratios were calculated from the peak areas that were calibrated by the sensitive factors provided by the equipment manufacturer.

Au L_{III}-edge X-ray absorption spectroscopy (XAS) were conducted at the beam line 1W1B of Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). Au L_{III}-edge XAS spectra were collected at room temperature in the fluorescence mode using a solid state detector. The XAS spectra were analyzed with the program WinXAS 3.2 [6]. Background subtraction and normalization were performed by fitting linear polynomials to the pre-edge and the post-edge region of the absorption spectra, respectively. E₀ value was determined by the maximum in the first derivative in the edge region.

3. Catalytic tests and analytical procedure

The catalytic test for CO PROX in a H₂-rich stream was carried out in a quartz tubular flow microreactor with an internal diameter of 6.0 mm at atmospheric pressure, as described previously [7]. The catalyst was evaluated in the fresh state without any pretreatment. For each test, about 200 mg of catalyst sample (40–60 mesh) was used. The reaction stream consisted of 1.0% CO, 1.0% O₂, 50.0% H₂ (by volume), and balanced N₂, with a space velocity of 30,000 ml g⁻¹ h⁻¹. CO and CO₂ in the effluent gas were periodically analyzed online with a gas chromatograph equipped with a column packed with carbon molecular sieve, a post-column methanator that converted CO and CO₂ into CH₄, and a flame ionization detector (FID). The consumption of oxygen was also periodically determined online with a gas chromatograph equipped with a column packed with 13X molecule sieve and a thermal conductivity detector (TCD). The CO and O₂ conversions (x_{CO} and x_{O_2}) were calculated with the CO and O₂ concentrations in the reactant and effluent streams. The selectivity of CO PROX or CO₂ selectivity (S_{CO_2}) was defined as the fraction of O₂ consumption for the CO oxidation to CO₂ over the total O₂ consumption.

$$\text{CO conversion } (x_{\text{CO}}) = [\text{CO}_2]_{\text{out}} / ([\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}}) \times 100\%$$

$$\text{O}_2 \text{ conversion } (x_{\text{O}_2}) = ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) / [\text{O}_2]_{\text{in}} \times 100\%$$

$$\text{CO}_2 \text{ selectivity } (S_{\text{CO}_2}) = x_{\text{CO}} / 2x_{\text{O}_2}$$

4. More characterization results

Figure S1 and Figure S2 show the XRD patterns and TEM images of the Au/CeFe and Au/CeNi catalysts after the long-term tests. Obviously, the XRD patterns of Au/CeFe and Au/CeNi catalysts remain almost unchanged in comparison with the fresh catalysts (Figure S1). In addition, the long-term tests also have little influence on the morphology of two catalysts, as seen from the TEM images (Figure S2). All these suggest that there are no structural changes for the doped Au/CeFe and Au/CeNi catalysts after the long-term tests, in comparison with the fresh ones.

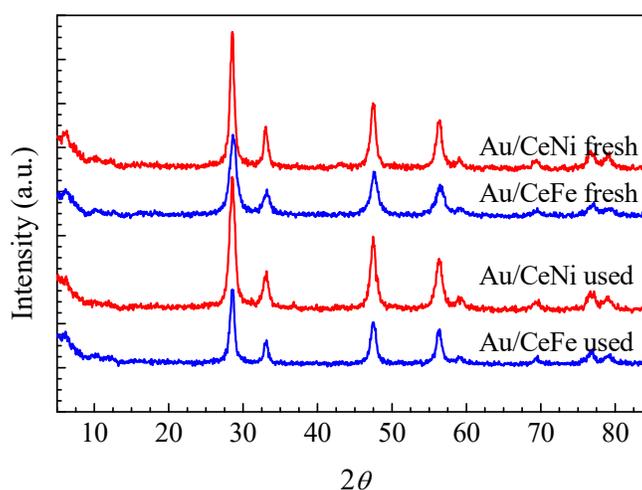


Figure S1. XRD patterns of the Au/CeFe and Au/CeNi catalysts before and after the long-term test for CO PROX in H₂-rich stream.

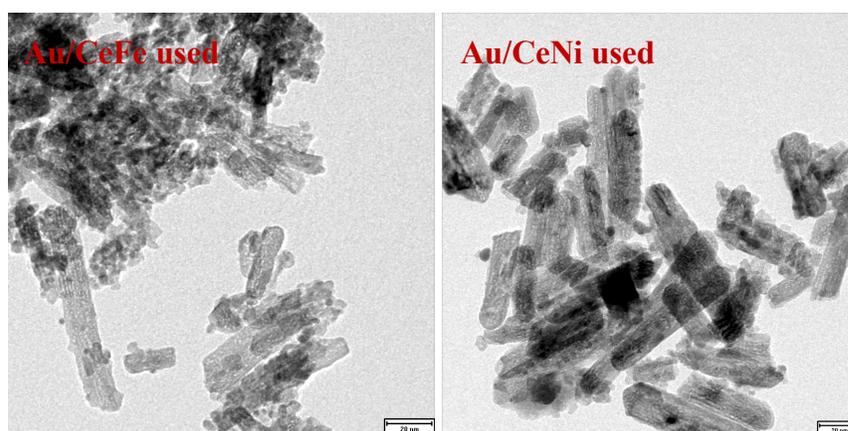


Figure S2. TEM images of the Au/CeFe and Au/CeNi catalysts after the long-term test for CO PROX in H₂-rich stream.

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