Supplementary Material

Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ nanorods supported gold and palladium alloy nanoparticles: High-performance catalysts for toluene oxidation

Wei Tan, Jiguang Deng*, Shaohua Xie, Huanggen Yang, Yang Jiang, Guangsheng Guo*, Hongxing Dai*

Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Key Laboratory of Advanced Functional Materials, Education Ministry of China, and Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

* To whom correspondence should be addressed:

Dr. Jiguang Deng Tel. No.: +86-10-6739-6118; Fax: +86-10-6739-1983 E-mail address: jgdeng@bjut.edu.cn

Prof. Guangsheng Guo Tel. No.: +86-10-6739-6118; Fax: +86-10-6739-1983 E-mail address: guogs@bjut.edu.cn

Prof. Hongxing Dai Tel. No.: +86-10-6739-6118; Fax: +86-10-6739-1983 E-mail address: hxdai@bjut.edu.cn

Content

Item	Page
Catalyst characterization procedures	3
Fig. S1	5
Fig. S2	6
Table S1	7
Fig. S3	8
Fig. S4	9
Fig. S5	10
Fig. S6	11

Catalyst characterization procedures:

The real noble metal (Au and/or Pd) contents in the Au/CZY, Pd/CZY, and Au_xPd_y/CZY samples were measured using the ICP-AES technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. The samples were dissolved in a mixture of concentrated HCl and HNO₃ with volumetric ratio of 3/1 prior to the analysis. X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Ka radiation and nickel filter ($\lambda = 0.15406$ nm). The ultraviolet-visible diffuse reflectance spectra (UV–Vis DRS) of the samples in the range of 350-750 nm were measured on a Shimadzu UV-2450 spectrophotometer using BaSO₄ as the standard. BET (Brunauer-Emmett-Teller) surface areas of the samples were determined via N₂ adsorption at -196 °C on a Micromeritics ASAP 2020 analyzer with the samples being outgassed at 300 °C for 2.5 h under vacuum before measurement. Scanning electron microscopic (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus (operating at 10 kV). Transmission electron microscopic (TEM) images and selected-area electron diffraction (SAED) patterns of the samples were obtained using the JEOL-2010 equipment (operating at 200 kV). X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was used to determine the Ce 3d, Zr 3d, Y 3d, O 1s, Au 4f, Pd 3d, and C 1s binding energies (BEs) of surface species using Mg K α (hv = 1253.6 eV) as excitation source. In order to remove the adsorbed water and carbonate species on the surface, the samples were pre-treated in O_2 (flow rate = 20 mL/min) at 450 °C for 1 h and then cooled to RT, followed by transferring the pre-treated samples into the spectrometer in a transparent Glove Bag (Instruments for Research and Industry, USA) filled with helium. The pre-treated samples were outgassed in the preparation chamber (10^{-5} Torr) for 0.5 h and then introduced into the analysis chamber (3 \times 10⁻⁹ Torr) for XPS spectrum recording. The C 1s signal at 284.6 eV was taken as a reference for BE calibration.

Hydrogen temperature-programmed reduction (H2-TPR) experiments were carried out on a

chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, *ca.* 0.02 g of catalyst (40–60 mesh) was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pretreated in an O₂ flow of 30 mL/min at 300 °C for 1 h. After being cooled at the same atmosphere to RT, the pretreated sample was exposed to a flow (50 mL/min) of 5% H₂–95% Ar (v/v) mixture and heated from RT to 750 °C at a ramp of 10 °C/min. The alteration in H₂ concentration of the effluent was monitored on-line by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard of powdered CuO (Aldrich, 99.995%).



Fig. S1. Particle size distributions of (a) Au NPs in 0.90Au/CZY, (b) Pd NPs in 0.80Pd/CZY, (c) Au–Pd alloy NPs in 0.93Au₁Pd₁/CZY, (d) Au–Pd alloy NPs in 0.90Au₁Pd₂/CZY, and (e) Au–Pd alloy NPs in 0.91Au₂Pd₁/CZY.



Fig. S2. Kubelka–Munk function (F(R)) versus wavelength of (a) 0.90Au/CZY, (b) 0.93Au₁Pd₂/CZY, (c) 0.90Au₁Pd₁/CZY, (d) 0.91Au₂Pd₁/CZY, and (e) 0.80Pd/CZY, which were converted from their UV–Vis DRS spectra.

Catalyst	Temperatur e (°C)	Reaction rate (mmol/(g _{Au} s))	Ref.
0.90Au1Pd2/CZY	250	4.8×10^{-3}	The present work
4.7Au/CZY	250	4.0×10^{-3}	82
2.1 wt% Au/Fe ₂ O ₃	250	5.3×10^{-5}	83
4.3 wt% Au/CeO ₂	250	7.6×10^{-4}	84
$1.5 \text{ wt\% Au/Al}_2O_3$	250	3.3×10^{-4}	71
$0.96 \text{ wt\% Au/TiO}_2$	250	1.4×10^{-3}	85
3.4 wt% Au/3DOM La _{0.6} Sr _{0.4} MnO ₃	250	$8.7 imes 10^{-3}$	86

Table S1. Reaction rates over various catalysts for toluene oxidation reported in the literature.



Fig. S3. Effects of (A) SV at toluene concentration = 1000 ppm and (B) toluene concentration on the catalytic activity of $0.90Au_1Pd_2/CZY$ at SV = 20,000 mL/(g h).



Fig. S4. Catalytic activity as a function of on-stream reaction time over the $0.90Au_1Pd_2/CZY$ sample for toluene oxidation under the conditions of toluene concentration = 1000 ppm, toluene/O₂ molar ratio = 1/400, SV = 20,000 mL/(g h), and reaction temperature = 220 °C.



Fig. S5. XRD patterns of (a) the fresh $0.90Au_1Pd_2/CZY$ sample and (b) the used $0.90Au_1Pd_2/CZY$ sample after 50 h of on-stream reaction under the conditions of toluene concentration = 1000 ppm, toluene/O₂ molar ratio = 1/400, SV = 20,000 mL/(g h), and reaction temperature = 220 °C.



Fig. S6. HRTEM images and SAED patterns (insets) of (a) the fresh $0.90Au_1Pd_2/CZY$ sample and (b) the used $0.90Au_1Pd_2/CZY$ sample after 50 h of on-stream reaction under the conditions of toluene concentration = 1000 ppm, toluene/O₂ molar ratio = 1/400, SV = 20,000 mL/(g h), and reaction temperature = 220 °C.