Electronic supplementary information

3DOM CeO_2-supported Ru_3M (M = Au, Pd, Pt) alloy nanoparticles with improved catalytic activity and chlorine-tolerance in trichloroethylene combustion

Xing Zhang,[a] Lingyun Dai,[b] Yuxi Liu,*[a] Jiguang Deng,[a] Lin Jing,[a] Xiaohui Yu,[a] Zhuo Han,[a] Kunfeng Zhang,[a] Hongxing Dai*[a]

[a] *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, 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.*

[b] *Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States. Fax: 412 419 4050; Tel: 412 419 4050.*

* Corresponding author.

E-mail addresses: yxliu@bjut.edu.cn (Dr. Y.X. Liu); hxdai@bjut.edu.cn (Prof. H.X. Dai)

Tel. No.: +8610-6739-6118; Fax: +8610-6739-1983.

Catalyst preparation procedures:

The 3DOM CeO_2 support was fabricated by adopting the Pluronic F127-assisted three-dimensionally aligned polymethyl methacrylate (PMMA) microsphere-templating method. The PMMA microspheres were synthesized by a modified emulsifier-free emulsion polymerization method. Under magnetic stirring and at room temperature (RT), 0.5 g of Pluronic F127, 1.0 g of citric acid, and 2.5 g of $Ce(NO_3)_3\cdot 6H_2O$ were dissolved in 6.0 g of ethanol aqueous solution (40 vol%) under stirring. After dissolution, 2.0 g of highly ordered PMMA colloidal crystal microspheres was soaked in the above mixed solution for 3 h. After the PMMA microspheres were thoroughly wetted, the excessive liquid was filtered via a Buchner funnel connected to vacuum (0.07 MPa). Finally, after being filtered and dried at RT for 24 h, the solid was transferred to a ceramic boat and thermally treated in a tubular furnace. After being filtered and dried at RT for 24 h, the obtained powders were calcined in a N_2 flow of 200 mL/min at a ramp of 1^oC/min from RT to 300 ^oC and kept at this temperature for 3 h, then cooled to 50 ^oC in the same atmosphere, and finally calcined in an air flow of 200 mL/min at a ramp of 1 ^oC /min from RT to 600 ^oC and maintained at 600 ^oC for 5 h, thus generating the 3DOM CeO_2 support.

The 3DOM CeO_2-supported Ru_yM alloy nanoparticles ($x$$Ru_yM$/3DOM CeO_2; x is the total loading (wt%) of Ru and M, y is the Ru/M molar ratio, and M = Au, Pd, Pt), xRu/3DOM CeO_2, and xPd/3DOM CeO_2 were prepared via a polyvinyl alcohol (PVA)-protected reduction route with PVA (MW = 10,000 g/mol) as protecting agent and $NaBH_4$ as reducing agent. The typical preparation process was as follows: A certain amount of PVA (noble metal/PVA mass ratio = 1.0 : 1.2) was added to a ruthenium (III) chloride hydrate and $HAuCl_4$, $PdCl_2$ or

$H_2PtCl_6 \cdot 6H_2O$ mixed aqueous solution (0.01 mol/L) in an ice bath using an N_2-bubbled $NaBH_4$ reduction method. After being mixed uniformly, a desired amount of 3DOM CeO_2 was added to the mixed solution (the theoretical noble metal loading (x) in xRu$_y$M was 1.00 wt%; and the theoretical Ru/M molar ratio (y) in each sample was 3.00), and the mixture was further vigorously stirred for 3 h. Then, a $NaBH_4$ aqueous solution (0.1 mol/L; noble metal/$NaBH_4$ molar ratio = 1.0 : 5.0) was dropwise added to form a dark brown suspension. The obtained suspension was stirred for 7 h to make the reaction homogenous. The wet precipitate was filtered, washed with 2.0 L of deionized water and 1.0 L of absolute ethanol, dried at 80 ^oC overnight, and calcined in air at 500 ^oC for 2 h (The filtering, washing, and calcination treatments could totally remove the adsorbed Cl^-, Na^+, and PVA), thus obtaining the xRu$_y$M/3DOM CeO_2 samples. The xRu/3DOM CeO_2 and xPd/3DOM CeO_2 (the theoretical Ru or Pd loading (x) = 1.0 wt%) samples were prepared according to the above method using the ruthenium (III) chloride hydrate and $PdCl_2$ as noble metal precursor, respectively. The inductively coupled plasma–atomic emission spectroscopic (ICP–AES) technique was used to measure the actual Ru$_y$M, Ru, and Pd loadings (x) in the xRu$_y$*M*/3DOM CeO_2, xRu/3DOM CeO_2, and xPd/3DOM CeO_2 samples, and the results are listed Table 1.

Catalyst characterization procedures:

The actual Ru$_y$M, Ru, and Pd contents in the xRu$_y$M/3DOM CeO_2, xRu/3DOM CeO_2, xPd/3DOM CeO_2 samples were measured using the ICP–AES technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. Each sample was dissolved in a mixture of concentrated HCl and HNO_3 aqueous solutions with a volumetric ratio of 3.0 : 1.0 prior to analysis.

X-ray diffraction (XRD) patterns of the samples were measured using a Rigaku D/Max RA diffractometer with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA, and crystal phases of the samples were identified using the JCPDS database. Scanning electron microscopic (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus (operating at 10 kV). To analyze porous structures and noble metal particle sizes of the samples, their high-resolution transmission electron microscopic (HRTEM) images were obtained using the JEOL-2010 equipment (operating at 200 kV). High angle annular dark field and scanning transmission electron microscopic (HAADF−STEM) images and element mappings were acquired on the equipment FEI G2 80−200/Chemi−STEM Cs-corrected transmission electron TEM with probe corrector. BET surface areas and pore sizes of the samples were determined on a Micromeritics ASAP 2020 instrument via N_2 adsorption at −196 ^{o}C with the sample being degassed under vacuum at 300 ^{o}C for 2 h before measurement, and calculated using the Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) methods, respectively.

Laser Raman spectra were obtained on a LabRam-HR800 with a 325 nm He–Gd laser source. The spectral resolution was 4 cm^{-1}, with a scanning range of 150–2000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) was used to measure the Ce 3d, O 1s, Ru 3p, Au 4f, Pd 3d, Pt 4f, and C 1s binding energies (BEs) of surface species using Mg Kα ($h\nu$ = 1253.6 eV) as excitation source. In order to remove the adsorbed water and carbonate species on the surface, the samples were treated in an O_2 flow of 20 mL/min at 400 ^{o}C for 1 h and then cooled to RT, followed by transferring the pretreated samples into the spectrometer in a transparent Glove Bag filled with helium. The pretreated samples were outgassed in the preparation chamber (10^{-5} Torr) for 0.5 h and then introduced into the analysis chamber (3×10^{-9} Torr) for XPS spectrum recording. All of the peaks were referenced to the BE (284.6 eV) of C 1s for calibration.

Hydrogen temperature-programmed reduction (H_2-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics) equipped with a custom-made thermal conductivity detector (TCD). In each measurement, 50 mg of the sample was first pretreated in an O_2 flow of 30 mL/min at 400 ^{o}C for 1 h and then cooled to 50 ^{o}C for the removal of the adsorbed CO_2 and H_2O. The sample was then subjected to a 10 vol% H_2–90 vol% Ar flow of 30 mL/min and heated at a ramp of 10 ^{o}C/min from 50 to 900 ^{o}C. The alteration in H_2 concentration of the effluent was monitored online by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard powered CuO (Aldrich, 99.995%) sample.

NH_3 temperature-programmed desorption (NH_3-TPD) was performed in a quartz fixed-bed microreactor on a chemical adsorption analyzer (Autochem II 2920-MS). 50 mg of the sample was pretreated in a N_2 flow of 20 mL/min at 300 ^{o}C for 1 h. After being cooled to 50 ^{o}C, the sample was exposed to a NH_3 flow of 30 mL/min for 1 h, and then switched to a N_2 flow of 30 mL/min for 1 h for the removal of the physically adsorbed NH_3. Finally, NH_3 desorption took place at a ramp of 10 ^{o}C/min from 50 to 900 ^{o}C. The reactant, such as NH_3 (m/z = 17), was analyzed online by mass spectrometer (OmniStar GSD320).

H_2O-temperature programmed desorption (H_2O-TPD) was performed in a quartz tube reactor system equipped with a Autochem II 2920-MS. Prior to the TPD analysis, 100 mg of the sample was first pre-heated at 400 °C in 20 vol. % O_2/Ar flow (30 ml/min) for 1 h, cooled to 100 °C, and swept by He for another 1 h. 5 vol % H_2O /Ar (30 ml/ min) was introduced into the catalyst bed for 40 min. A He flow (30 ml/min) was then purged through the catalysts for 1 h to remove physiosorbed H_2O. After that, the sample was heated to 900 °C at a ramp of 10 °C/min and H_2O was continuously monitored.

Oxygen temperature-programmed desorption (O_2-TPD) was carried out on the apparatus same as that in the H_2-TPR experiments. Prior to each test, 50 mg of the sample was treated in an O_2 flow of 30 mL/min at 400 ^{o}C for 1 h to remove the adsorbed CO_2 and H_2O, and was then slowly cooled to 50 ^{o}C. Thereafter, it was swept with a He flow of 30 mL/min for 1 h and then heated from 50 to 900 ^{o}C. The oxygen concentration in the effluent was continuously monitored by a thermal conductivity detector. There were several tiny peaks assignable to the background noises. By integrating the oxygen signal with time, we obtained the peak area corresponding to 1 mL of pure oxygen.

Fourier transfer infrared (Py-FTIR) spectra of pyridine adsorption on the samples were measured on a Nicolet 6700 spectrometer equipped with an MCT detector in diffuse reflection mode. The sample was first purged with 20 vol% O_2/Ar (30 mL/min) at 400 °C for 1 h, and background measurements were collected at 150, 250, and 350 °C, respectively. The pyridine vapor was then admitted to the IR cell for 15 min at 150 °C. After sweeping with Ar (30 ml/min) for 30 min, the spectra of adsorbed pyridine were collected at the desired desorption temperature (150, 300 or 450 °C).

Ammonia-adsorption FTIR (NH_3-FTIR) measurements were performed with ZnSe windows coupled to Bruker Tensor II spectrometer with a liquid nitrogen-cooling MCT detector. In the FTIR cell, catalysts were pretreated at 400 °C under N_2 for 1 h, and then cooled to 100 °C. The background spectrum was recorded with flowing He and subtracted from the catalyst spectrum. After that, a mixture flow (20 mL/min) of 5 vol% NH_3 + N_2 (balance) was passed through the IR cell for 0.5 h. A N_2 flow (30 mL/min) was passed through the IR cell, and FTIR spectra of the samples were recorded in the N_2 flow at 100 °C, with an accumulation of 32 scans and a spectrum resolution of 4 cm^{-1} and the background spectrum was recorded. After that, the mixture flow was switched to the N_2 flow (30 mL/min) and the FTIR spectra were recorded after N_2 purging for 10 min.

Temperature-programmed surface reaction (TPSR) was carried out under the conditions same as those in catalytic activity test in order to detect the reactants and products in effluence. First, the (20 vol% O_2 + 80 vol% N_2) gas mixture containing 1000 ppm TCE of 30 mL/min passed through the catalyst bed at 50 °C for 1 h. After adsorption-desorption of TCE reached an equilibrium, the sample was purged with a N_2 flow of 30 mL/min for 1 h. Then, the catalyst bed was heated at a ramp of 10 °C/min from 50 to 900 °C. The reactant and products, such as TCE ($m/z = 95$), CO_2 ($m/z = 44$), CO ($m/z = 28$), Cl_2 ($m/z = 70$), HCl ($m/z = 36$), and PCE ($m/z = 166$), were analyzed online by mass spectrometer (OmniStar GSD320).

In situ diffuse reflectance Fourier transform infrared spectroscopic (in situ DRIFTS) experiments were carried on a Bruker Tensor II spectrometer with a liquid nitrogen-cooling MCT detector. Before the in situ DRIFTS experiment, 50 mg of the sample was loaded onto a high-temperature IR cell with ZnSe windows, and preheated in an O_2 flow of 30 mL/min at

300 ^{o}C for 1 h. Subsequently, the sample was cooled to RT and purged with a N_2 flow of 30 mL/min for 1 h, and then the background spectrum was recorded at different temperatures. Finally, the sample was kept in a reactant mixture flow (10 mL/min) of 1000 ppm TCE + 20 vol% O_2 + 80.0 vol% N_2 (or + 5 vol% water vapor), and DRIFTS spectra of the samples in the temperature range of 150–400 ^{o}C were recorded by accumulating 32 scans at a spectrum resolution of 4 cm^{-1}.

Catalytic performance evaluation procedures:

Catalytic activities of the samples were carried out in a continuous flow fixed-bed quartz microreactor (i.d. = 6 mm). 50 mg of the sample (40−60 mesh) was mixed with 0.25 g of quartz sand (40−60 mesh) for minimization of hot spots. Before measurement, the sample was treated in O_2 (20 mL/min) at 300 ^{o}C for 1 h. After being cooled to RT, the reactant gas mixture (1000 ppm TCE + 20 vol% O_2 + N_2 (balance)) with a total flow of 16.7 mL/min was passed through the catalyst bed, giving a SV of ca. 20,000 mL/(g h). The pipe was heated to 100 ^{o}C using the heating belt to minimize the possible adsorption of the TCE on the inner pipe surface. After the reaction was stabilized at a certain temperature for 30 min, the reactants and products were online analyzed by a gas chromatograph (GC−7890B, Agilent) equipped with a flame ionization detector (FID) and a TCD, using the Agilent 19091J−413 HP−5 (30 m in length), G3591−81141 and G3591−81142 (silica gel), and G3591−81022 (molsieve 5A, 2.44 m in length of each packing column). The TCD was used to analyze the CO_2 and CO concentrations, whereas the FID was used to analyze the concentrations of the organic compounds, and the conversion of TCE was calculated based on the peak area after running for 20 min (sampling 3 times) at the given temperature and the error was controlled within 0.2 %. TCE conversion = ($c_{\mathrm{inlet}} - c_{\mathrm{outlet}}$)/$c_{\mathrm{inlet}}$ × 100 %, where the c_{inlet} and c_{outlet} are the inlet and outlet TCE concentrations in the feed stream. The by-products were online analyzed by a gas GC-MS (GC-7890B, MS-5977A, Agilent).

Selectivities to HCl and Cl_2 were measured by bubbling the outlet gas mixture in a NaOH aqueous solution (12.5 mmol/L) for 0.5 h each time. The Cl_2 concentration in the bubbled solution was determined by the chemical titration method using the ferrous ammonium sulfate aqueous solution with *N*,*N*-diethyl-*p*-phenylenediamine as indicator, and the Cl^- concentration was measured using an ion selective electrode. The selectivities of HCl and Cl_2 were calculated as follows: $S_{HCl} = [HCl]/([HCl] + 2[Cl_2]) \times 100$ %, and $S_{Cl2} = 2[Cl_2]/([HCl] + 2[Cl_2]) \times 100$ %, where $[Cl_2]$ and [HCl] are the outlet concentrations of Cl_2 and HCl, respectively.

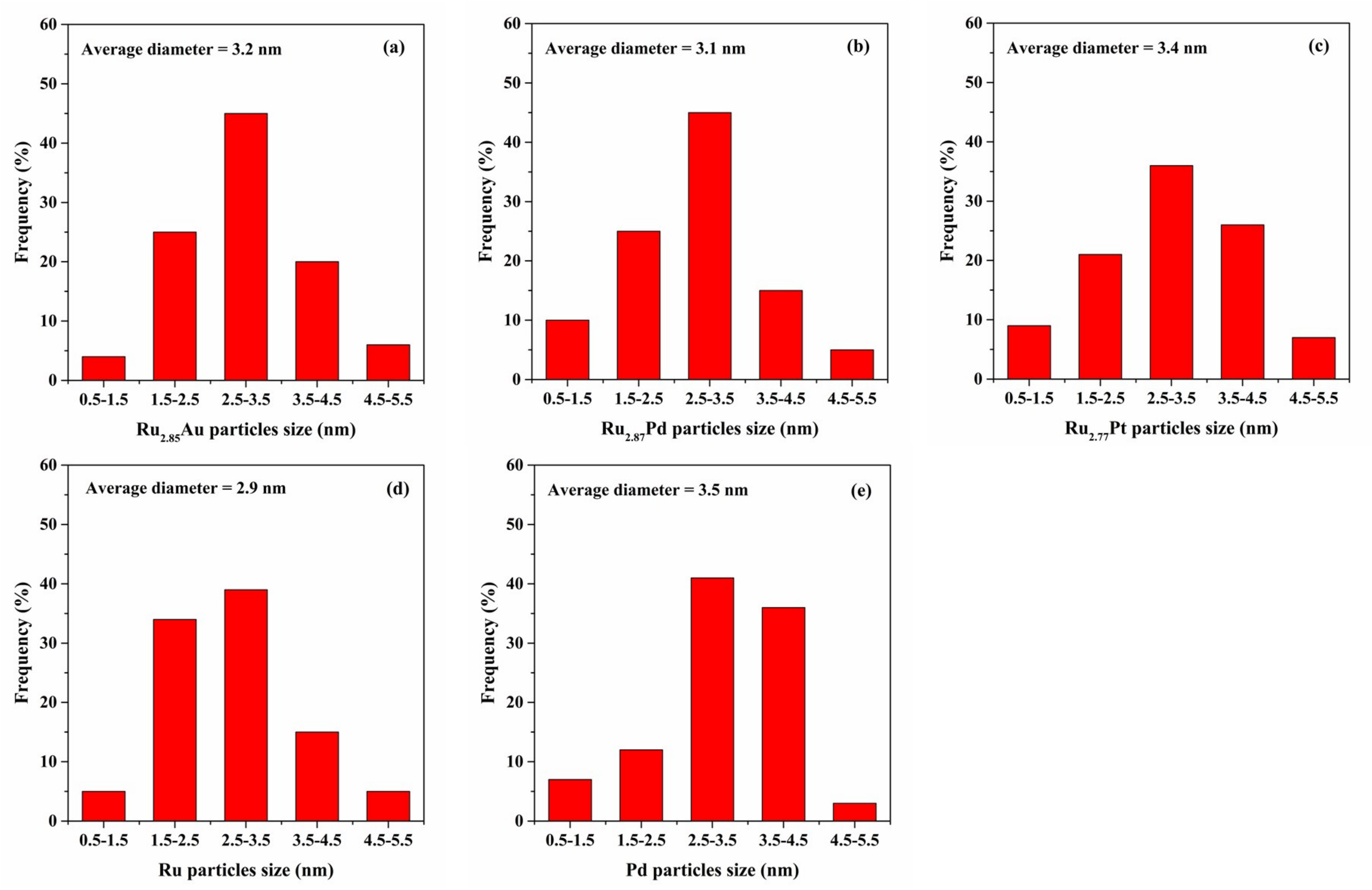

Fig. S1. Noble metal particle size distributions of (a) 0.91Ru$_{2.85}$Au/3DOM CeO$_2$, (b) 0.93Ru$_{2.87}$Pd/3DOM CeO$_2$, (c) 0.90Ru$_{2.77}$Pt/3DOM CeO$_2$, (d) 0.85Ru/3DOM CeO$_2$, and (e) 0.88Pd/3DOM CeO$_2$.

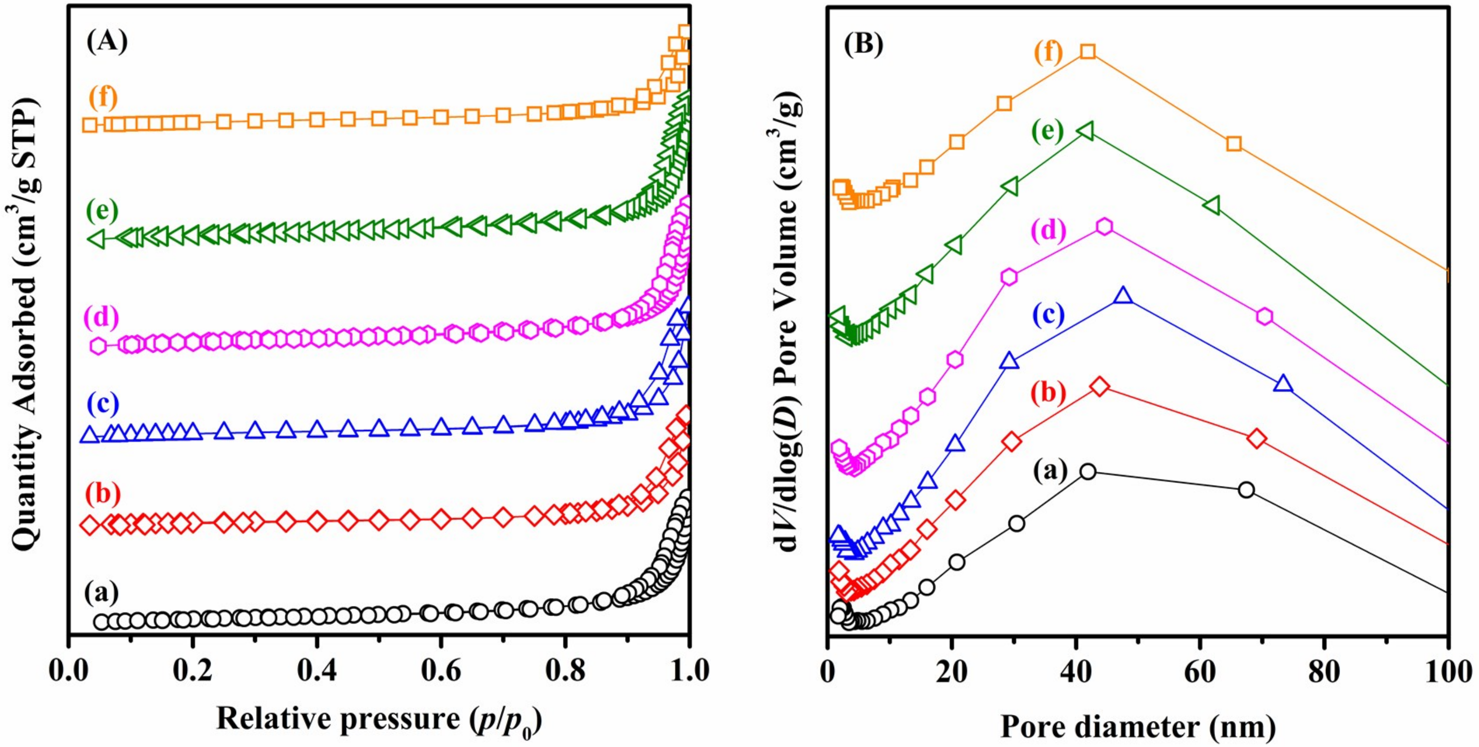

Fig. S2. (A) N_2 adsorption−desorption isotherms and (B) pore-size distributions of (a) 3DOM CeO_2, (b) $0.91Ru_{2.85}Au$/3DOM CeO_2, (c) $0.93Ru_{2.87}Pd$/3DOM CeO_2, (d) $0.90Ru_{2.77}Pt$/3DOM CeO_2, (e) 0.85Ru/3DOM CeO_2, and (f) 0.88Pd/3DOM CeO_2.

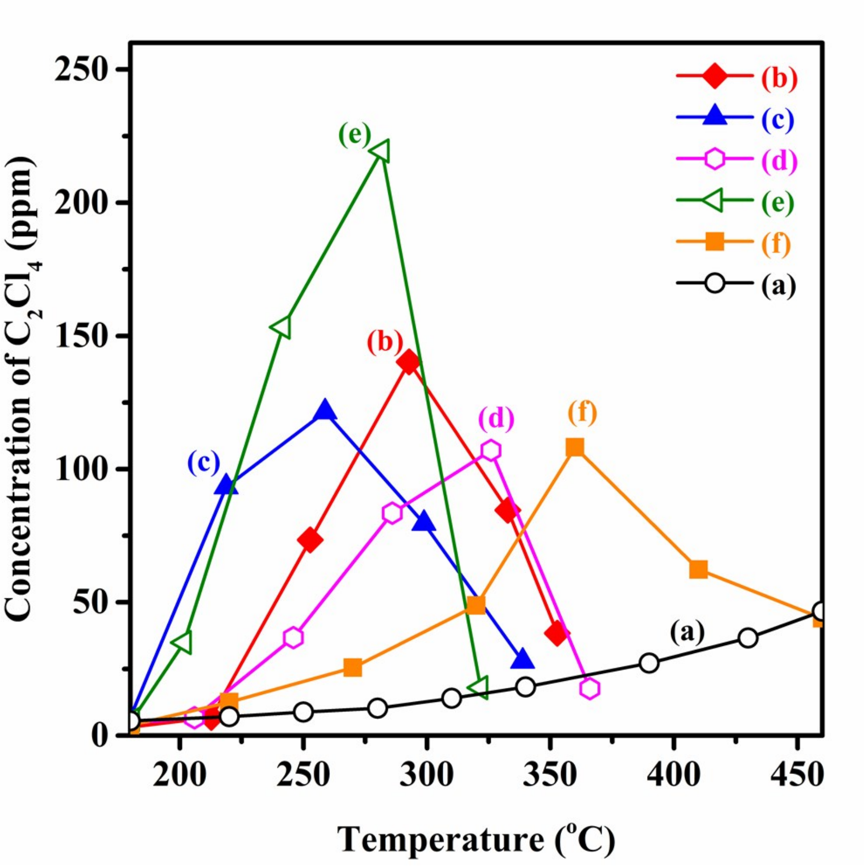

Fig. S3. Concentrations of the C_2Cl_4 by-product formed over (a) 3DOM CeO_2, (b) $0.91Ru_{2.85}Au$/3DOM CeO_2, (c) $0.93Ru_{2.87}Pd$/3DOM CeO_2, (d) $0.90Ru_{2.77}Pt$/3DOM CeO_2, (e) 0.85Ru/3DOM CeO_2, and (f) 0.88Pd/3DOM CeO_2 at SV = 20,000 mL/(g h).

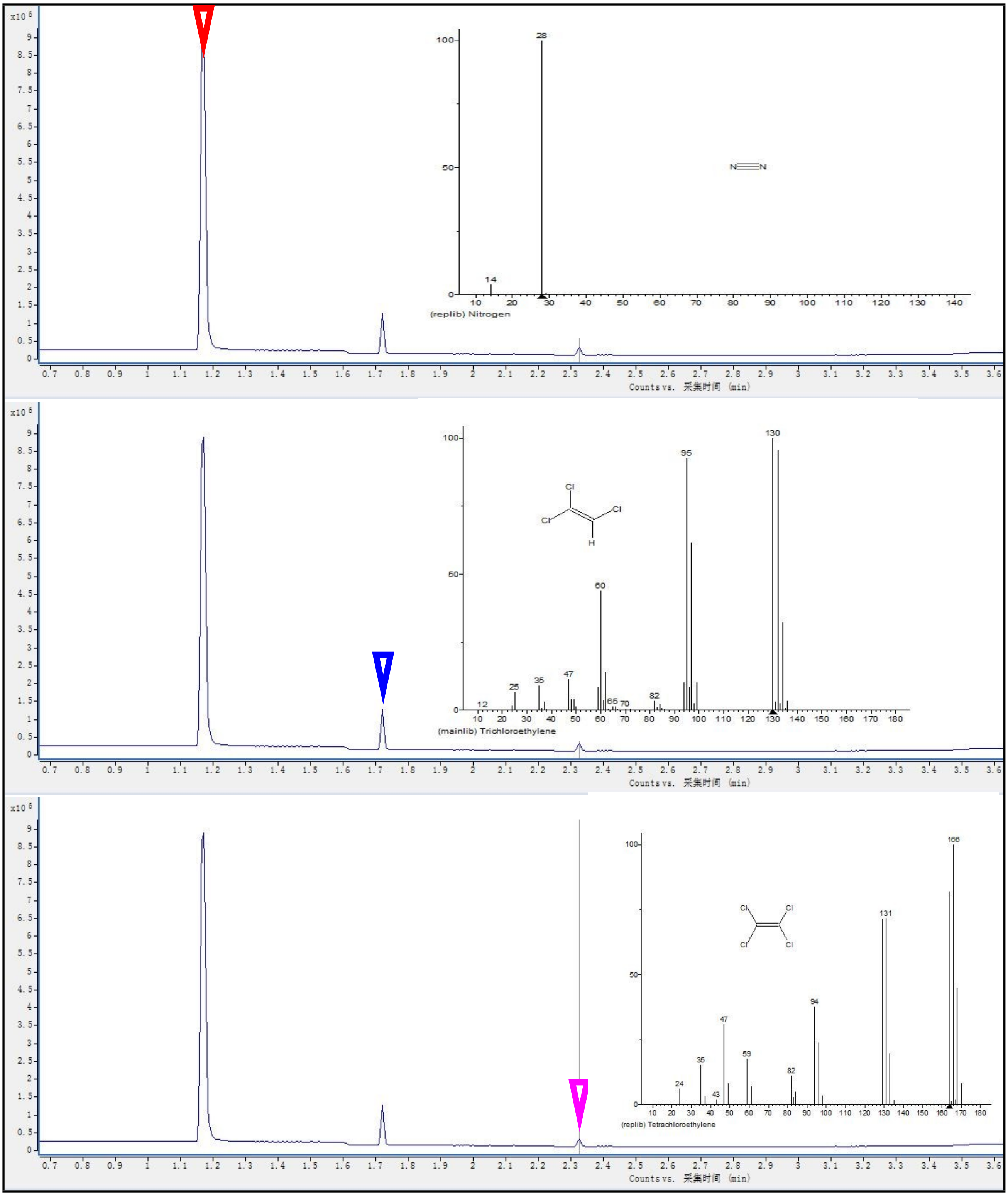

Fig. S4. Reaction intermediate products detected by the GC-MS during 1000-ppm TCE oxidation process over 0.93Ru$_{2.87}$Pd/3DOM CeO$_2$ at 220 ^{o}C.

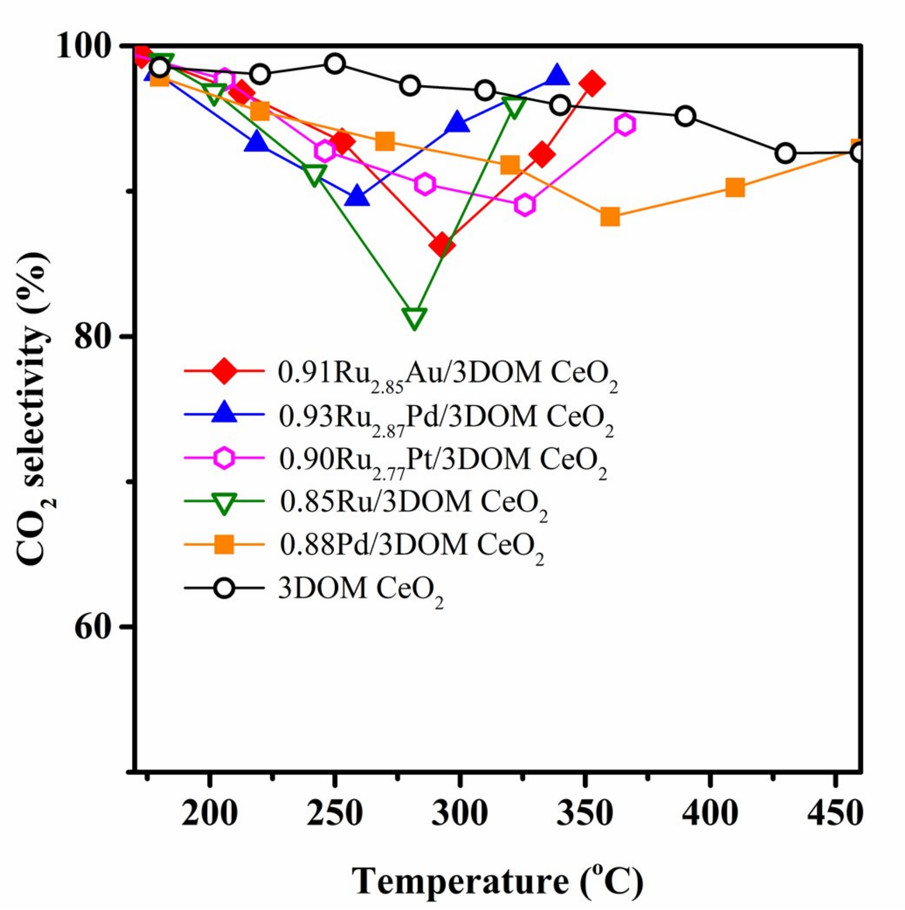

Fig. S5. Selectivity of CO_2 formed over the samples at SV = 20,000 mL/(g h).

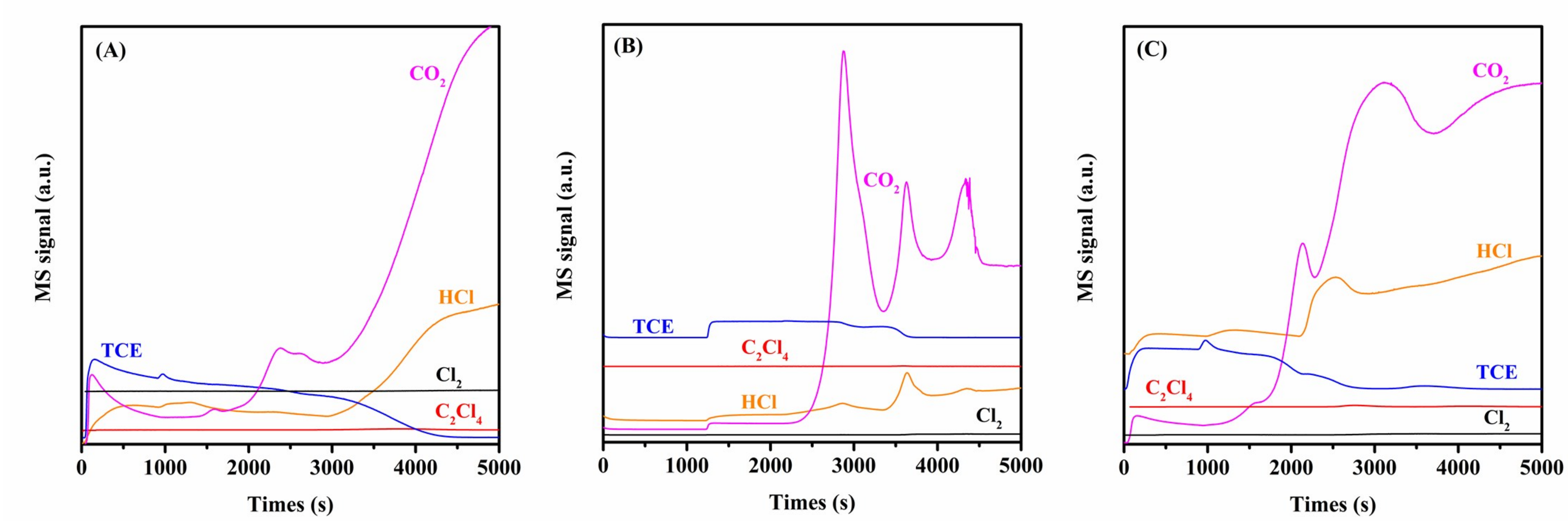

Fig. S6. TCE-TPSR profiles of (a) 3DOM CeO_2, (b) 0.85Ru/3DOM CeO_2, and (c) $0.93Ru_{2.87}Pd$/3DOM CeO_2 at SV = 20,000 mL/(g h).

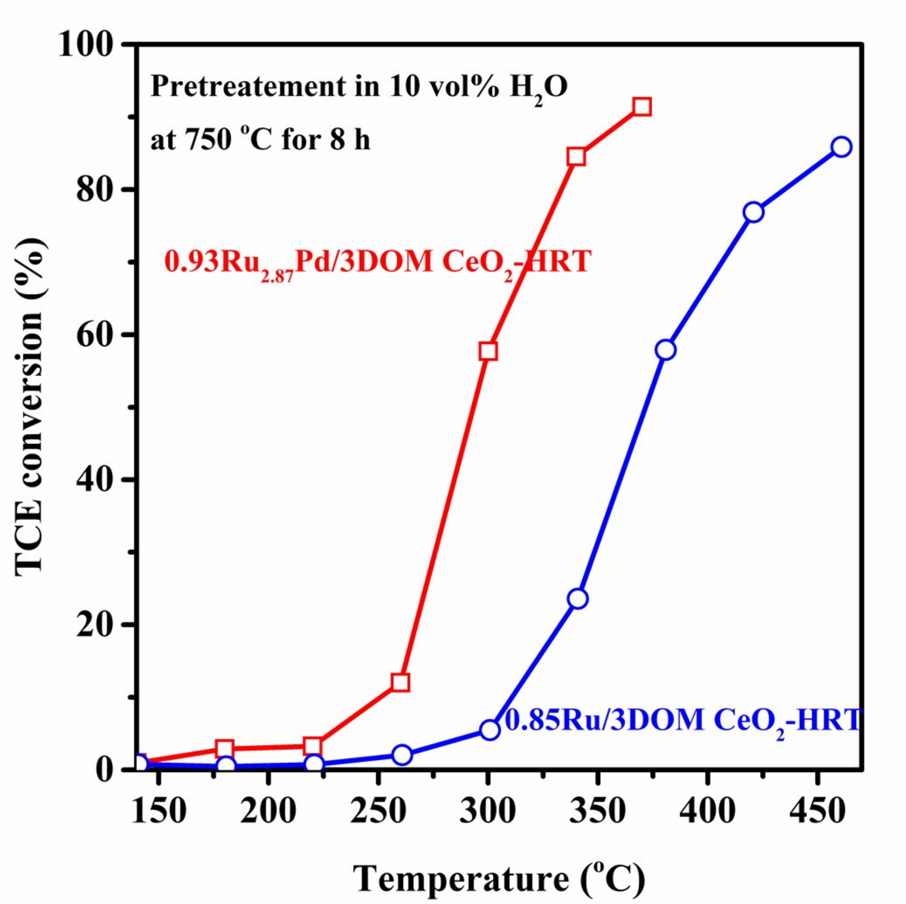

Fig. S7. Catalytic activities of the $0.93Ru_{2.87}Pd/3DOM\ CeO_2$-HRT and $0.85Ru/3DOM\ CeO_2$-HRT samples (which were pretreated in an air flow containing 10 vol% water vapor at 750 °C for 8 h) at SV = 20,000 mL (g h).