
Supplementary Material

PdPt_y/V₂O₅–TiO₂: Highly Active Catalysts with Good Moisture- and Sulfur Dioxide-Resistant Performance in Toluene Oxidation

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Content

Item	Page
Catalyst characterization procedures	3–6
Catalytic evaluation procedures	7
Figure S1	8
Figure S2	8
Figure S3	9
Figure S4	10
Figure S5	10
Figure S6	11
Figure S7	11
Table S1	12

Catalyst characterization procedures:

The crystal structures of the as-obtained samples were characterized by means of the X-ray diffraction (XRD) technique on a Bruker/AXS D8 Advance diffractometer (AXS, Bruker, Berlin, Germany), with Cu K α radiation and nickel filter ($\lambda = 0.15406$ nm).

The actual noble metal contents (x and y) of Pt and/or Pd in x Pt/V₂O₅-TiO₂, x Pd/V₂O₅-TiO₂, and x PdPt _{y} /V₂O₅-TiO₂ were determined by the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) technique using a Thermo Electron IRIS Intrepid ER/S spectrometer (Thermo Electron Corporation, Waltham, MA, USA). Each sample was dissolved in a mixture of concentrated HCl and HNO₃ aqueous solutions with a volumetric ratio of 3:1 prior to analysis.

To analyze 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-scanning transmission electron microscopic (HAADF-STEM, FEI G280-200/Chemi-STEM C, Potsdam, Germany) images and element mappings were acquired on the equipment FEI G2 80-200/Chemi-STEM Cs-corrected transmission electron TEM with probe corrector. For the preparation of the TEM (JEOL JEM-2010, Tokyo, Japan) specimen, we first added the solid powders to a certain volumetric amount of ethanol after ultrasonic dispersion, then dropped the mixture on the carbon foil, and finally obtained the TEM specimen after drying. In the present work, we used the ultra-thin

carbon foil (T11032, Beijing XXBR Technology, Beijing, China) for the preparation of the TEM specimen, and the ultra-thin carbon foil (01824, TED PELLA INC, Redding, CA, USA) for the preparation of the spherical aberration-corrected (Cs) STEM specimen. Particle-size distributions of the samples were estimated by measuring the diameters of 200 particles (according to the HADDF-STEM images) with the Origin data processing software.

BET (Brunauer–Emmett–Teller, Micromeritics ASAP 2020 analyzer, Norcross, GA, USA) surface areas and pore-size distributions 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 under vacuum for 2.5 h.

The thermogravimetric analysis (TGA) technique was used to measure weight losses of the samples. 10 mg of the 0.46PdPt_{2.10}/V₂O₅–TiO₂ or 0.47Pt/V₂O₅–TiO₂ sample was heated in a N₂ flow of 100 mL/min at a ramp of 10 °C/min from 25 to 800 °C using the Setaram Labsys evo instrument (Setaram, Lyon, France).

The X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Fisher Scientific, Waltham, MA, USA) was used to determine the Pt 4f, Pd 3d, Ti 2p, V 2p, O 1s, and C 1s binding energies (BEs) of the surface species with Mg K α ($h\nu$ = 1253.6 eV) as the excitation source. The C 1s signal at BE = 284.6 eV was taken as reference for BE calibration.

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) equipped with a custom-made thermal conductivity detector (TCD). In

each measurement, 50 mg of the sample was first pretreated in an O₂ flow of 30 mL/min at 250 °C for 1 h and then cooled to RT for the removal of the adsorbed CO₂ and H₂O. The sample was then subjected to a 10 vol% H₂/Ar (balance) flow of 30 mL/min and heated at a ramp of 10 °C/min from RT to 900 °C. The alteration in H₂ 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.

Oxygen temperature-programmed desorption (O₂-TPD) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) and a mass spectrometer (OmniStar GSD320). Prior to each test, 60 mg of the sample was preheated in an O₂ flow of 30 mL/min at 250 °C for 1 hr. After cooling to RT, a helium flow of 30 mL/min was switched on to purge the left O₂ in the system for 1 hr. After that, the samples were heated in a helium flow of 30 mL/min from RT to 900 °C at a rate of 10 °C/min, and the O₂-TPD profiles were recorded in the mean time.

Toluene temperature-programmed desorption (toluene-TPD) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) and a mass spectrometer (OmniStar GSD320). Prior to each test, 60 mg of the sample was preheated in an O₂ flow of 30 mL/min at 250 °C for 1 hr. After cooling to RT, a (1000 ppm toluene + N₂ (balance)) mixture flow was passed through the sample. After that, a N₂ flow of 30 mL/min was used to purge the toluene in the system for 30 min. After the purge process was finished, we heated the sample

in a N₂ flow of 30 mL/min from RT to 900 °C, and used a mass spectrometer to monitor the concentration changes of toluene ($m/z = 91$), H₂O ($m/z = 18$), and CO₂ ($m/z = 44$).

(C₇H₈ + SO₂) temperature-programmed desorption ((C₇H₈ + SO₂)-TPD) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) and a mass spectrometer (OmniStar GSD320). Prior to each test, 60 mg of the sample was preheated in an O₂ flow of 30 mL/min at 250 °C for 1 h. After cooling to RT, a (1000 ppm methane + N₂ (balance)) mixture flow was passed through the sample. After cooling to RT, a (50 ppm SO₂ + N₂ (balance)) mixture flow was passed through the sample. After that, a N₂ flow of 30 mL/min was used to purge the (C₇H₈ + SO₂) in the system for 30 min. After the purge process was finished, we heated the sample in a N₂ flow of 30 mL/min from RT to 900 °C, and used a mass spectrometer to monitor the concentration changes of toluene ($m/z = 91$), H₂O ($m/z = 18$), CO₂ ($m/z = 44$), and SO₂ ($m/z = 64$).

SO₂ adsorption on the samples were measured by the Fourier transform infrared spectroscopy (ATR-FTIR, TENSOR II, Bruker, Berlin, Germany). The FTIR spectra of the 0.47Pt/V₂O₅-TiO₂ and 0.46PdPt_{2.10}/V₂O₅-TiO₂ samples after toluene oxidation for 8 h in the presence of 50 ppm SO₂ and the fresh 0.47Pt/V₂O₅-TiO₂ and 0.46PdPt_{2.10}/V₂O₅-TiO₂ samples.

In situ diffuse reflectance infrared Fourier transform spectroscopic (in situ DRIFTS) experiments of the samples were carried on a Bruker Tensor II spectrometer with a liquid nitrogen-cooling MCT detector (Bruker, Berlin, Germany). Before the in situ

DRIFTS experiment, 30 mg of the sample was loaded on a high-temperature IR cell with ZnSe windows, and preheated in an O₂ flow of 30 mL/min at 250 °C for 1 h. Subsequently, the sample was cooled to RT and purged with a N₂ 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 ((1000 ppm toluene + 20 vol% O₂ + 80 vol% N₂(balance)) or (1000 ppm toluene + 50 ppm SO₂ + 20 vol% O₂ + 80 vol% N₂(balance)) flow of 10 mL/min, and in situ DRIFTS spectra of the samples in the temperature range of 140–270 °C were recorded by accumulating 32 scans at a spectrum resolution of 4 cm⁻¹.

Catalytic evaluation procedures:

Catalytic activities of the samples were evaluated in a continuous-flow fixed-bed quartz tubular microreactor (i.d. = 6.0 mm). 25 mg of the sample (40–60 mesh) was diluted with 250 mg of quartz sand (40–60 mesh) for minimizing the effect of possible hot spots. The reactant feed stream was composed of (1000 ppm toluene + 20 vol% O₂ + N₂(balance)) with a total flow of 16.7 mL/min, giving a toluene/O₂ molar ratio of 1/200 and a space velocity (SV) of ca. 40,000 mL/(g h). Before the test, the sample was treated in O₂ (20 mL/min) at 250 °C for 1 h. In the case of SO₂ introduction, 50 ppm SO₂ from a SO₂ cylinder (balanced with N₂) was introduced to the reaction system through a mass flow controller. In the case of water vapor introduction, 5.0 vol% H₂O were introduced by passing the feed stream through a

water saturator at 46.5 °C. In the case of CO₂ addition, 5.0 vol% CO₂ from a CO₂ cylinder (balanced with N₂) was introduced to the reaction system via a mass flow controller. Reactants and products were analyzed online by gas chromatography (GC-2014C, Shimadzu) equipped with a flame ionization detector (FID), using a stabilwax®-DA column (30 m in length) for toluene separation. All of the measurements were carried out under the steady-state reaction conditions.

Catalytic activities of the samples were evaluated using the temperatures ($T_{50\%}$ and $T_{90\%}$) required for achieving toluene conversions of 50 and 90 %, respectively. The balance of carbon in the catalytic system was 99.5 ± 1.5 %. The toluene conversion was calculated using the following equation: Toluene conversion (%) = $100 \times ([\text{Toluene}]_{\text{inlet}} - [\text{Toluene}]_{\text{outlet}})/[\text{Toluene}]_{\text{inlet}}$, where the $[\text{Toluene}]_{\text{inlet}}$ and $[\text{Toluene}]_{\text{outlet}}$ are the inlet and outlet toluene concentrations in the feed stream, respectively.

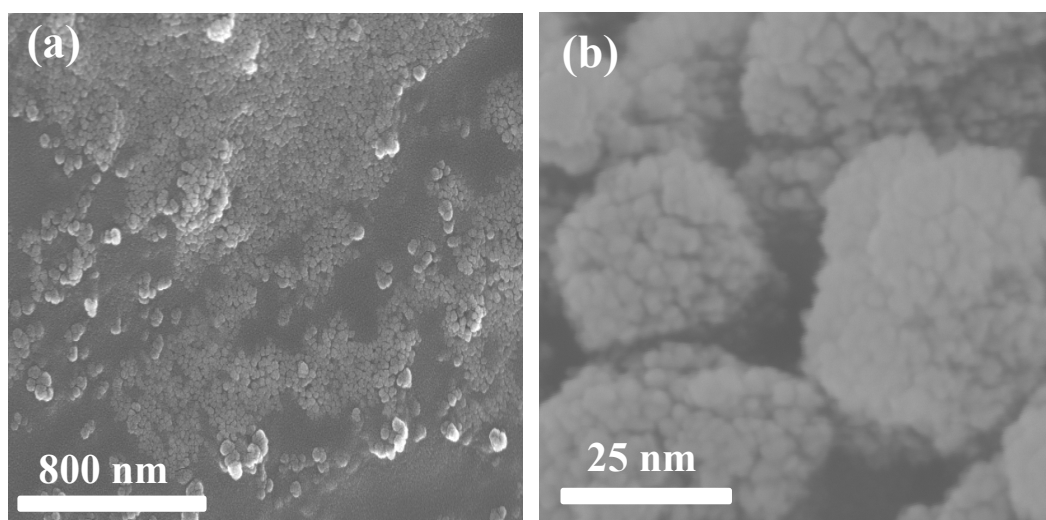


Figure S1. (a, b) SEM images of the V₂O₅-TiO₂ support.

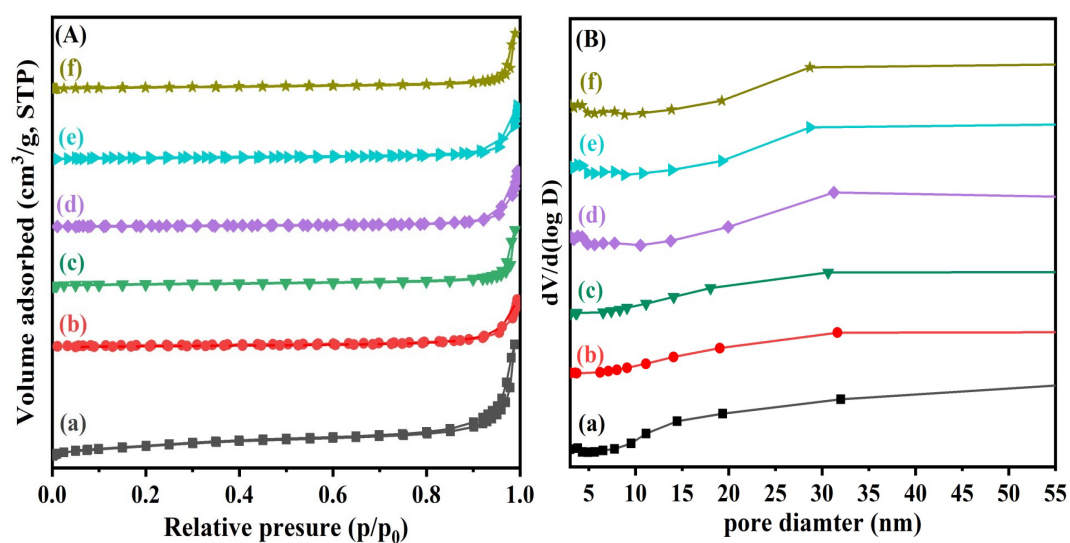


Figure S2. (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distributions of (a) $\text{V}_2\text{O}_5\text{--TiO}_2$, (b) $0.39\text{Pd}/\text{V}_2\text{O}_5\text{--TiO}_2$, (c) $0.47\text{Pt}/\text{V}_2\text{O}_5\text{--TiO}_2$, (d) $0.49\text{PdPt}_{0.44}/\text{V}_2\text{O}_5\text{--TiO}_2$, (e) $0.41\text{PtPt}_{0.85}/\text{V}_2\text{O}_5\text{--TiO}_2$, and (f) $0.46\text{PdPt}_{2.10}/\text{V}_2\text{O}_5\text{--TiO}_2$.

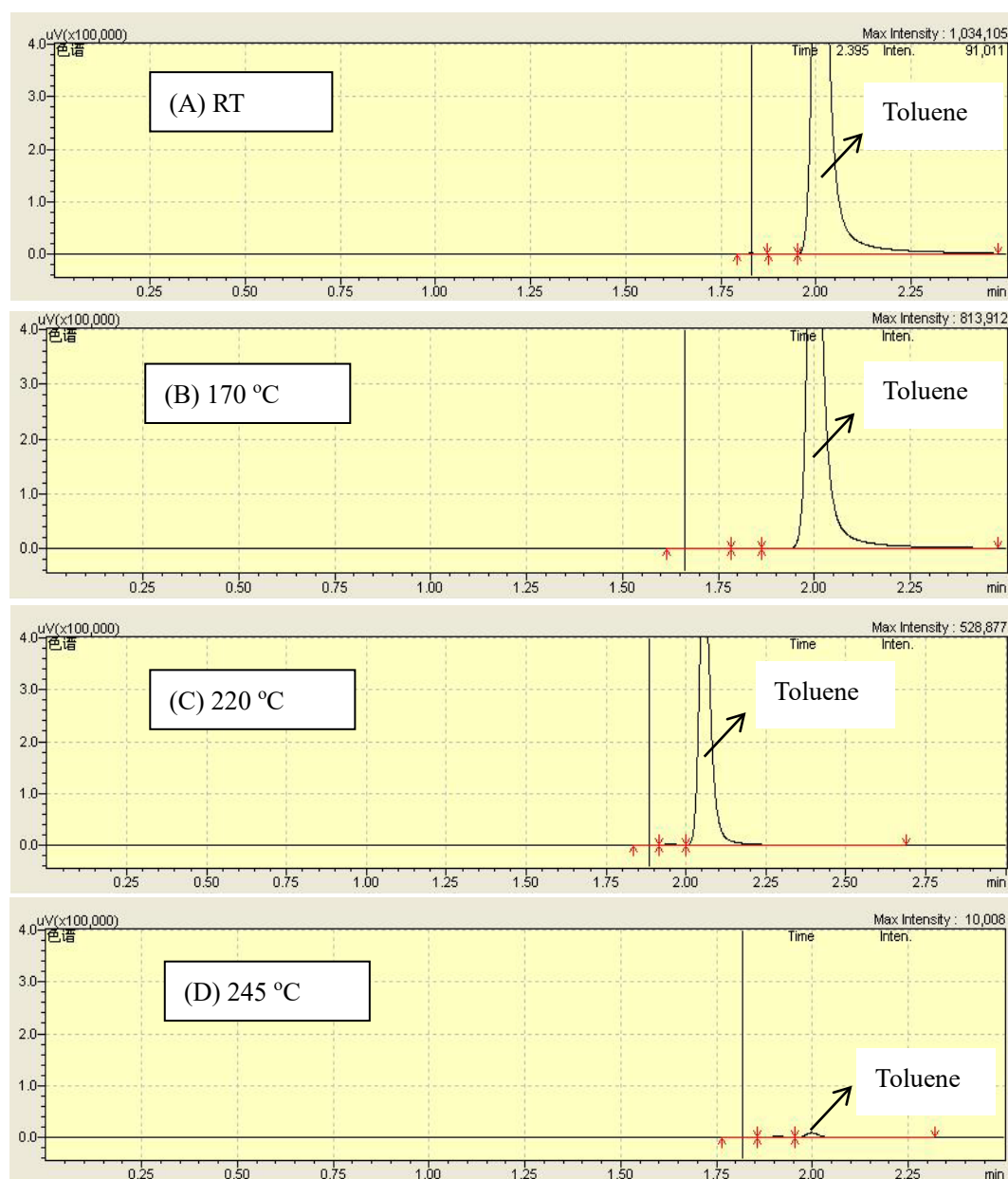


Figure S3. Gas chromatogram curves of toluene oxidation at (A) RT, (B) 170 °C, (C) 220 °C, and (D) 245 °C over the $0.46\text{PdPt}_{2.10}/\text{V}_2\text{O}_5\text{-TiO}_2$ sample at $\text{SV} = 40,000 \text{ mL}/(\text{g h})$.

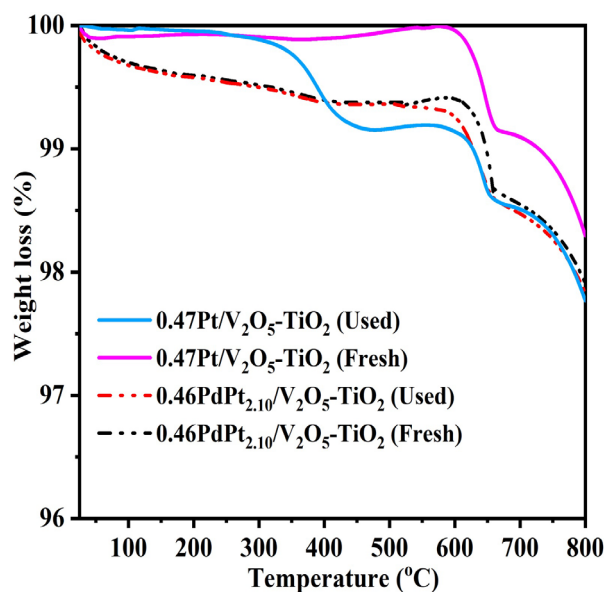


Figure S4. TGA curves of the fresh and used $0.46\text{PdPt}_{2.10}/\text{V}_2\text{O}_5\text{-TiO}_2$ and $0.47\text{Pt}/\text{V}_2\text{O}_5\text{-TiO}_2$ samples before and after 25 h of reaction in the presence of 50 ppm SO_2 at $\text{SV} = 40,000 \text{ mL}/(\text{g h})$.

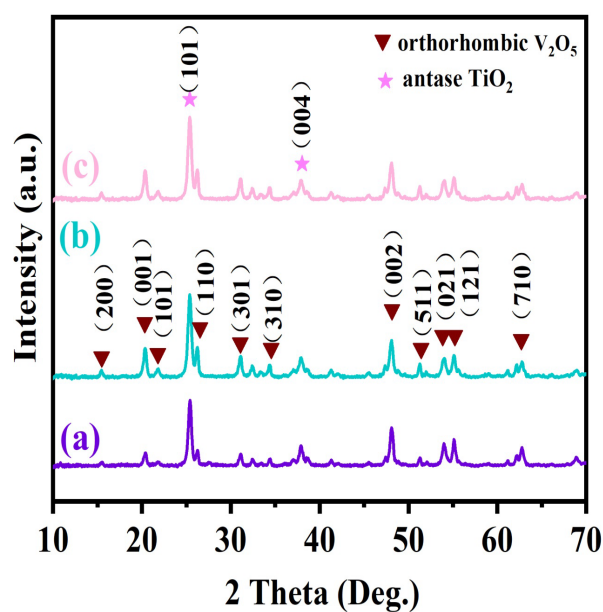


Figure S5. XRD patterns of (a) the fresh $0.46\text{PdPt}_{2.10}/\text{V}_2\text{O}_5\text{-TiO}_2$ sample, (b) the used $0.46\text{PdPt}_{2.10}/\text{V}_2\text{O}_5\text{-TiO}_2$ sample after 25 h of toluene oxidation in the absence of 50 ppm SO_2 , and (c) the used $0.46\text{PdPt}_{2.10}/\text{V}_2\text{O}_5\text{-TiO}_2$ sample after 25 h of toluene

oxidation in the presence of 50 ppm SO₂ at a SV of 40,000 mL/(g h).

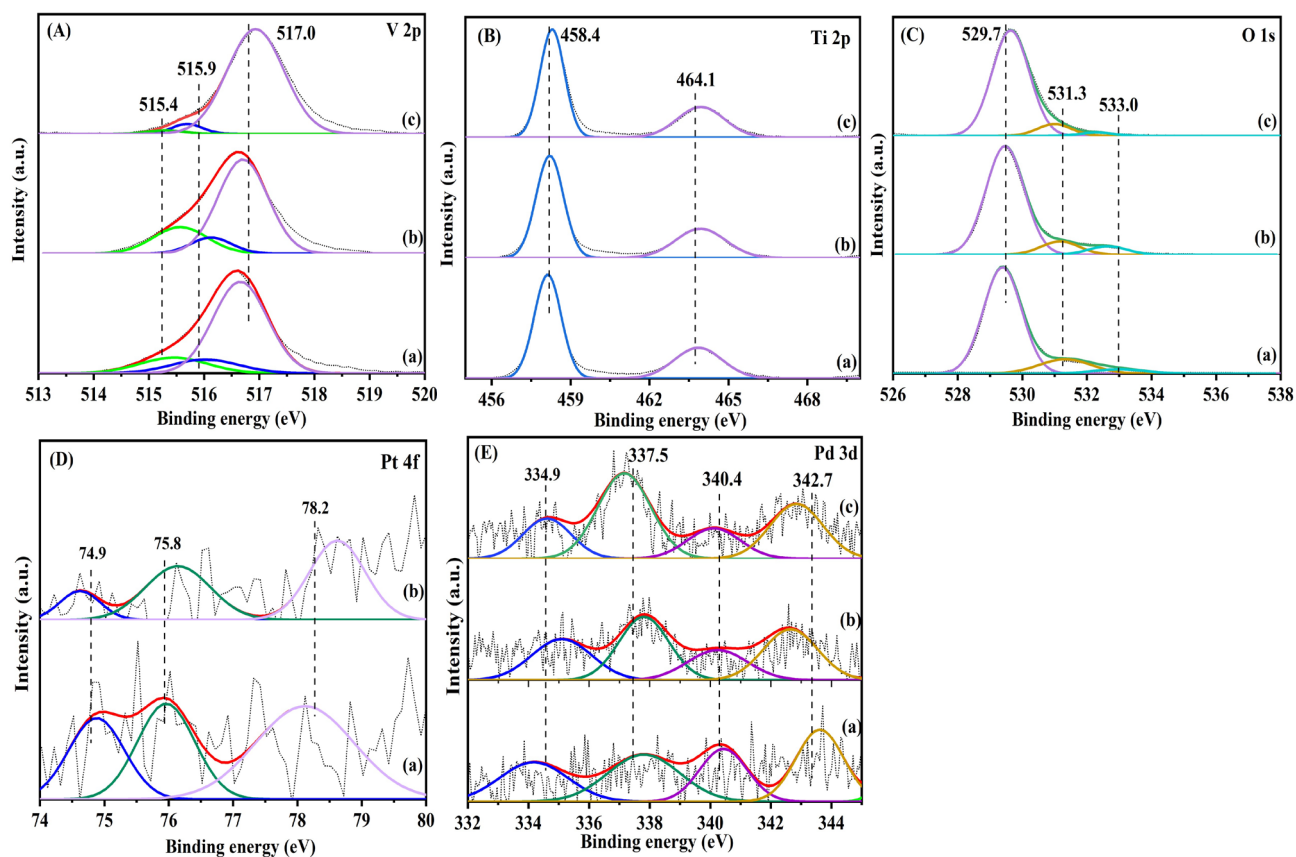


Figure S6. (A) V 2p, (B) Ti 2p, (C) O 1s, (D) Pt 4f, and (E) Pd 3d XPS spectra of (a) 0.41PdPt_{0.85}/V₂O₅-TiO₂, (b) 0.49PdPt_{0.44}/V₂O₅-TiO₂, and (c) 0.39Pd/V₂O₅-TiO₂.

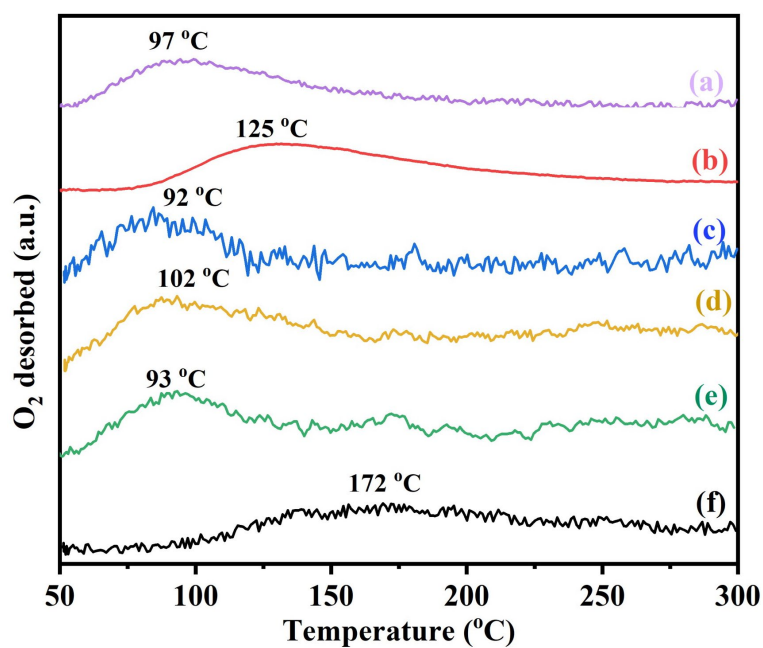


Figure S7. Partially enlarged O₂-TPD profiles of (a) 0.46PdPt_{2.10}/V₂O₅-TiO₂, (b) 0.41PdPt_{0.85}/V₂O₅-TiO₂, (c) 0.49PdPt_{0.44}/V₂O₅-TiO₂, (d) 0.47Pt/V₂O₅-TiO₂, (e) 0.39Pd/V₂O₅-TiO₂, and (f) V₂O₅-TiO₂.

Table S1. Comparison on catalytic activities for toluene oxidation of the 0.46PdPt_{2.10}/V₂O₅–TiO₂ sample obtained in the present work and the various catalysts reported in the literature.

Catalyst	Reaction condition (Toluene concentration & space velocity)	$T_{90\%}$ (°C)	Toluene oxidation activity	Ref.
			at 230 °C TOF _{Noble metal} ($\times 10^{-3} \text{ s}^{-1}$)	
0.46PdPt _{2.10} /V ₂ O ₅ –TiO ₂	1000 ppm & SV = 40,000 mL/(g h)	245	142.2	This work
0.5 wt% Pd/mesoporous ZrO ₂	1000 ppm & SV = 60,000 mL/(g h)	250	113.6	[27]
0.5 wt% Pt–WO ₃ /Ce _{0.65} Zr _{0.35} O ₂	1000 ppm & SV = 40,000 mL/(g h)	255	125.2	[28]
1.71 wt% Pd/InO _x @CoO _x	3000 ppm & SV = 30,000 mL/(g h)	253	131.1	[29]
1.0 wt% Pd/ZSM-5	1000 ppm & SV = 32,000 mL/(g h)	240	159.6	[30]
1.0 wt% Pd/Co ₃ AlO	1000 ppm & SV = 30,000 mL/(g h)	230	146.8	[31]

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