

Supporting Information

Coupled Palladium–Tungsten Bimetallic Nanosheets/TiO₂ Hybrids with Enhanced Catalytic Activity and Stability for the Oxidative Removal of Benzene

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Chemicals:

Palladium(II) 2,4-pentanedionate ($\text{Pd}(\text{acac})_2$, Pd 34.7 %), tri-*n*-octylphosphine (TOP, 90 %), 1-octadecene (90 %), hexacarbonyltungsten ($\text{W}(\text{CO})_6$, 97 %), and benzyl ether (BE, 98 %) are obtained from the Alfa Aesar Company. Oleylamine (OAm, 80–90 %) is obtained from the Acros Organics Company. Titanium oxide (40 nm in particle size) is purchased from the Aladdin Company. Ethanol, toluene, and cyclohexane are purchased from the Sinopharm Chemical Reagent Co. Ltd. *L*-ascorbic acid is purchased from the Tianjin Fuchen Chemical Reagents Factory.

Catalyst Preparation:

Synthesis of PdW-S3 Nanosheets (NSs). The synthesis conditions of PdW-S3 NSs are similar to those of PdW-S1 NSs, except that the amount of $\text{W}(\text{CO})_6$ is reduced to 0.05 mmol.

Synthesis of Pd Nanocrystals (NCs). 0.15 mmol of $\text{Pd}(\text{acac})_2$ is mixed in benzyl ether (10 mL) and OAm (1.084 mL) in a three-necked flask. After dissolving at room temperature (RT), the flask is purged with argon, and tri-*n*-octylphosphine (0.73 mL) was added. Then, the solution is degassed for 1 h to remove water and other impurities after heating to 100 °C. Subsequently, the mixture is heated to 290 °C under the protection of argon and kept for 30 min. After being cooled to RT, the products are isolated by centrifugation and washed with an ethanol–cyclohexane mixture several times. The as-obtained nanoparticles (NPs) are re-dispersed in a nonpolar organic solvent.

The Pd/WO_x/TiO₂ catalyst is prepared by a two-step wet impregnation method. An appropriate amount of tungstic acid (H₂WO₄) is dissolved in about 5 mL of deionized water at 80 °C under continuous stirring, followed by adding an appropriate amount of TiO₂ (theoretical tungsten loading is 1.0 wt%), stirring continuously at 80 °C to evaporate water, and drying in an oven at 110 °C for 24 h. The resulting solid is calcined in a muffle furnace at 500 °C for 4 h. Then, an appropriate amount of Pd NPs is loaded on the surface of the above solid in 10 mL of cyclohexane under stirring at RT for 12 h. After centrifugation, the as-obtained wet powders are dried in a vacuum drying chamber. Finally, the dried powders are transferred to a muffle furnace for calcination at 350 °C for 2 h.

The PdW/TiO₂ catalyst is prepared using the wet impregnation method. An appropriate amount of palladium chloride (PdCl₂) is dissolved in about 5 mL of deionized water at 80 °C under continuous stirring, followed by adding an appropriate amount of tungstic acid (H₂WO₄), then a certain amount of TiO₂ is added into the solution (theoretical palladium loading is 0.65 wt%, theoretical tungsten loading is 0.93 wt%), followed by stirring continuously at 80 °C to evaporate water and drying in an oven at 110 °C for 24 h. The resulting solid is reduced in a tubular furnace in a 10 vol% H₂ (Ar as balance gas) flow of 100 mL min⁻¹ at 700 °C for 2 h, and the obtained sample is denoted as PdW/TiO₂.

Catalyst characterization procedures:

Crystal structures of the as-obtained catalysts are characterized by means of the

X-ray diffraction (XRD) technique on a Bruker/AXS D8 Advance diffractometer, with Cu K α radiation and nickel filter ($\lambda = 0.15406$ nm). Laser Raman spectra of the catalysts are measured on a Bruker RFS/100 Raman spectrometer equipped with a Nd:YAG laser (1064 nm) and an InGaAs detector. The actual metal contents in the as-obtained catalysts are determined using the inductively coupled plasma–atomic emission spectroscopic (ICP–AES) technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. Each catalyst is dissolved in a mixture of concentrated HCl (37 wt%) and HNO₃ (75 wt%) aqueous solutions with a volumetric ratio of 3 : 1 prior to analysis.

Transmission electron microscopic (TEM) images of the catalysts are recorded using a JEOL JEM-2010 instrument. The HAADF–STEM and element mapping images are also taken on the Cs-corrected cold field-emission JEM-ARM200F operated at accelerating voltage 200 kV. BET (Brunauer–Emmett–Teller) surface areas of the catalysts are measured via N₂ adsorption at –196 °C on a Micromeritics ASAP 2020 analyzer, with the catalysts being outgassed at 300 °C under vacuum for 2 h before measurement. The X-ray photoelectron spectroscopy (XPS) is used to determine the Pd 3d, W 4f, 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 284.6 eV is taken as reference for BE calibration.

Hydrogen temperature-programmed reduction (H₂-TPR) experiments are carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, ca. 0.05 g of the sample (40–60 mesh) is loaded to a

quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pretreated in an 20 vol% O₂/He flow of 30 mL min⁻¹ at 300 °C for 1 h. After being cooled to RT at the same atmosphere, the sample is purged in a He flow of 30 mL min⁻¹ for 15 min. The pretreated sample is exposed to a flow (50 mL min⁻¹) of 5 vol% H₂/Ar (v/v) mixture and heated from RT to 900 °C at a ramp of 10 °C min⁻¹. The alteration in H₂ concentration of the effluent is monitored online by the chemical adsorption analyzer. The reduction peak is calibrated against that of the complete reduction of a known standard powdered CuO (Aldrich, 99.995%). NH₃ temperature-programmed desorption (NH₃-TPD) is conducted on an AutoChem II 2920 equipment (Micromeritics). Prior to the test, 0.2 g of the sample is pretreated in 30 mL min⁻¹ pure He at 350 °C for 1 h with a ramp of 10 °C min⁻¹. After cooled to 50 °C at the same atmosphere, the sample is exposed to a flow (30 mL min⁻¹) of 5 vol% NH₃/He (v/v) mixture until saturation, and then the sample is flushed with helium until the baseline is smooth. The NH₃ desorption curves are recorded from 100 to 600 °C at a heating rate of 10 °C min⁻¹ in the He atmosphere. The metal dispersion is measured using chemisorption (AutoChem II 2920, Micromeritics). The sample is reduced in a H₂ flow (30 mL min⁻¹) at 150 °C for 2 h, purged with a He flow (30 mL min⁻¹) for 1 h and cooled to 50 °C. Then, it is saturated with pulses of carbon monoxide. The amount of CO uptake during the chemisorption is measured by a thermal conductivity detector (TCD).

In situ DRIFTS are carried on a Nicolet 6700 FT-IR spectrometer with a liquid-nitrogen-cooled MCT detector. In the in situ DRIFTS studies, 30 mg of the

sample is loaded to a high-temperature IR cell with a KBr window, a N₂ flow (20 mL min⁻¹) is passed through the IR cell at 25 °C for 20 min, and the background spectrum is recorded. Subsequently, a mixture (1000 ppm benzene + 20 vol% O₂ + N₂ (balance)) flow of 16.67 mL min⁻¹ is passed through the IR cell at 25 °C for 30 min. After that, the mixture flow is switched to the N₂ flow (30 mL min⁻¹) and the in situ DRIFTS spectra are recorded after N₂ purging for 1, 2, 8, 15, and 30 min, respectively. After that, the N₂ flow is switched to the mixture (1000 ppm benzene + 20 vol% O₂ + N₂ (balance)) flow of 16.67 mL min⁻¹ at elevated temperatures from RT to 100, 130, 160, 180, 200, 220 and 240 °C, respectively, and the in situ DRIFTS spectra are recorded when the sample is kept at the given temperature for 20 min. The DRIFT spectra are recorded with an accumulation of 32 scans and a spectrum resolution of 4 cm⁻¹.

In order to investigate the accumulation of hydroxyls on the catalyst surface, we conduct *in-situ* DRIFT experiments in the presence or absence of water over TiO₂/PdW-S1 and Pd/TiO₂ sample. Prior to the *in-situ* DRIFT experiment, the samples are first pretreated in 20 vol% O₂ at 250 °C for 1 h, cooled to 200 °C, and purged in a mixture of O₂ and N₂ for 1 h. The background spectra are collected. Then, 1000 ppm benzene is introduced to the chamber, the *in-situ* DRIFT spectrum is recorded after benzene adsorption for 1 h; after introducing 5 vol% H₂O for 1 h, the *in-situ* DRIFT spectrum is recorded; when H₂O is cut off and the sample is purged in a mixture of 1000 ppm benzene + O₂ + N₂ for 1 h, the *in-situ* DRIFT spectrum is recorded again.

Catalytic evaluation procedures:

Activities of the catalysts are measured in a continuous-flow fixed-bed quartz tubular microreactor (i.d. = 6.0 mm). Before the test, all of the samples are pretreated in an O₂ flow of 20 mL min⁻¹ at 250 °C for 1 h. 50 mg of the catalyst (40–60 mesh) is diluted with 0.25 g of quartz sand (40–60 mesh) to minimize the effect of hot spots. The reactant mixture is composed of 1000 ppm benzene + 20% O₂ + N₂ (balance). The 1000-ppm benzene is generated by passing a N₂ flow through a pure benzene-containing bottle that is chilled in an isothermal bath at 8 °C. The total flow is 33.4 mL min⁻¹, giving a space velocity (SV) of 40 000 mL g⁻¹ h⁻¹. In the case of water vapor introduction, 1.0 and 5.0 vol% H₂O is introduced by passing the feed stream through a water saturator at different temperatures, respectively. In the case of CO₂ addition, 5 vol% CO₂ is introduced from a CO₂ cylinder with N₂ as balance gas. Reactants and products are analyzed online by gas chromatography (GC-14C, Shimadzu) with a flame ionization detector (FID), using a stabilwax-DA column (30 m in length) and a Carboxen 1000 column (3 m in length). The balance of carbon throughout the catalytic system is estimated to be 98.5 ± 1.5 %. Benzene conversion is defined as $(C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}} \times 100 \%$, where the C_{inlet} and C_{outlet} are the inlet and outlet benzene concentrations in the feed stream, respectively. The errors of benzene conversions over the as-obtained samples are ± 0.5 %. The errors of activation energies over the as-obtained samples are ± 7 kJ mol⁻¹. The reaction rates are calculated at benzene conversions below 20 %. The heat transfer effects can be avoided at low benzene conversions and low benzene concentrations in benzene

oxidation.

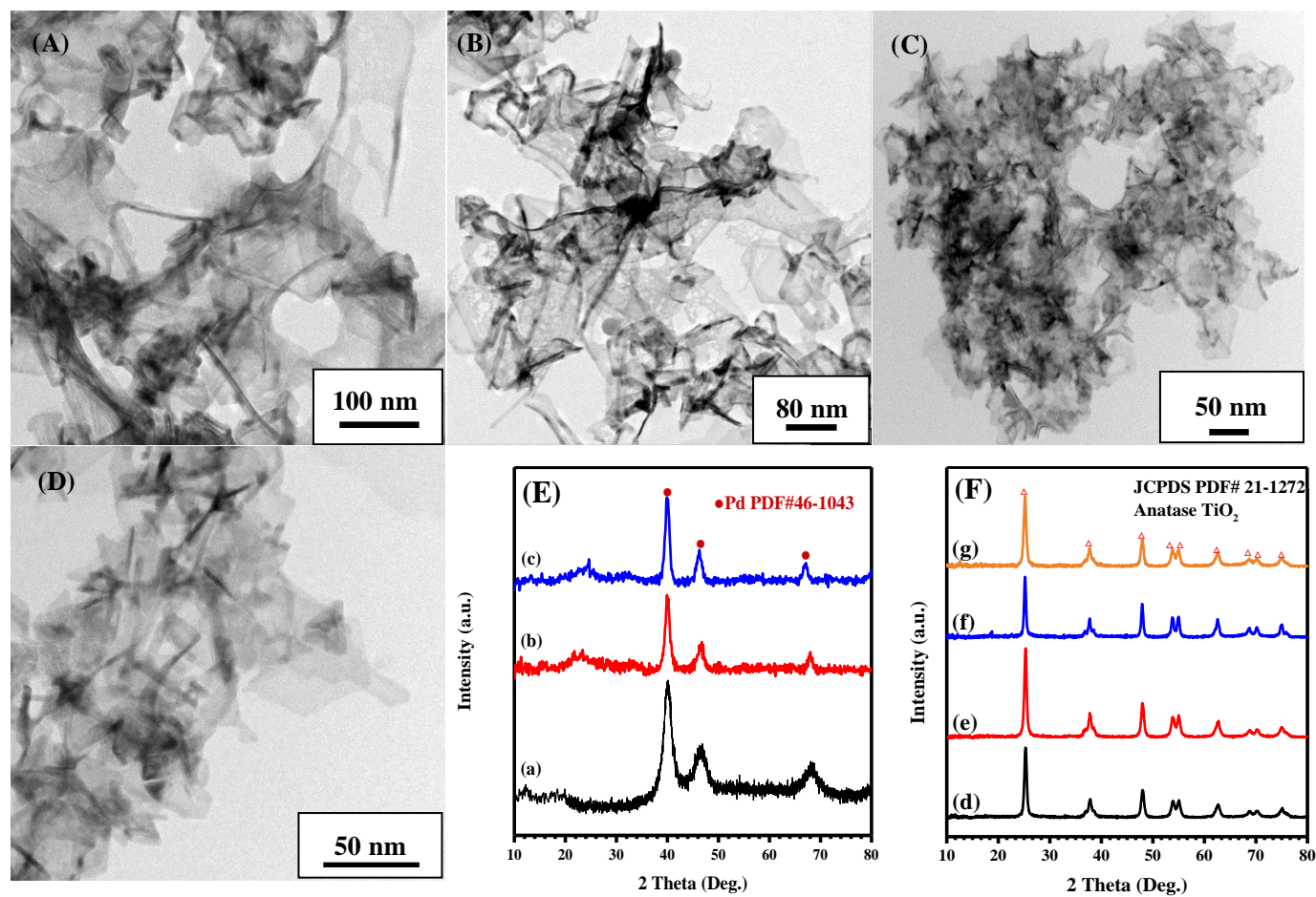


Figure S1. TEM images of (A, B) PdW-S1 NSs and (C, D) PdW-S2 NSs; (E, F) XRD patterns of (a) Pd NCs, (b) PdW-S2 NSs, (c) PdW-S1 NSs, (d) Pd/TiO₂, (e) TiO₂/PdW-S2, (f) TiO₂/PdW-S1, and (g) Pd/WO_x/TiO₂.

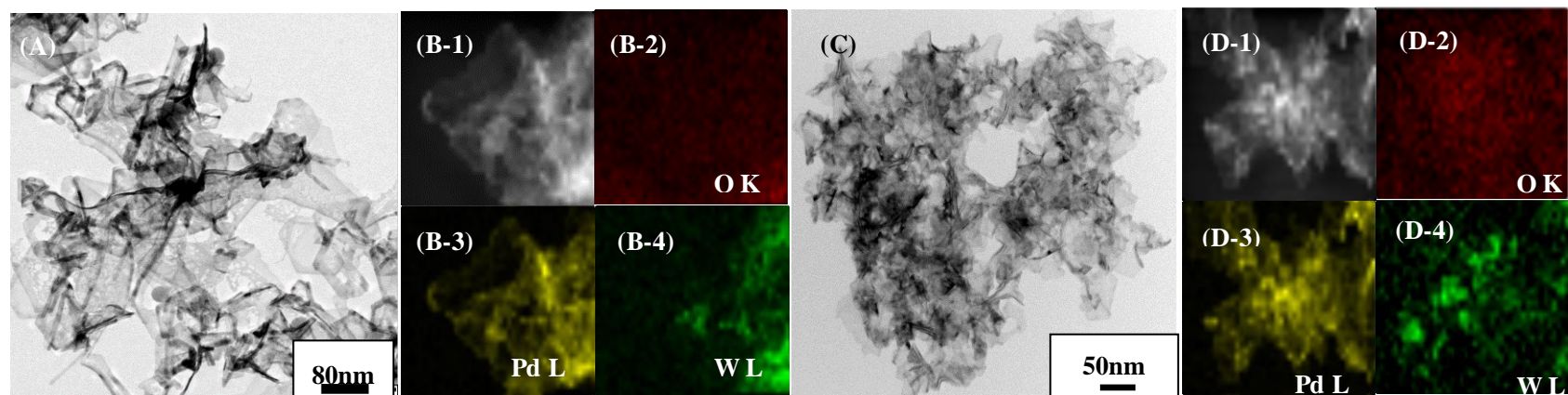


Figure S2. (A, C) TEM images and (B-1–4, D-1–4) corresponding EDS elemental mapping images of (A, B-1–4) PdW-S1 NSs and (C, D-1–4) PdW-S2 NSs.

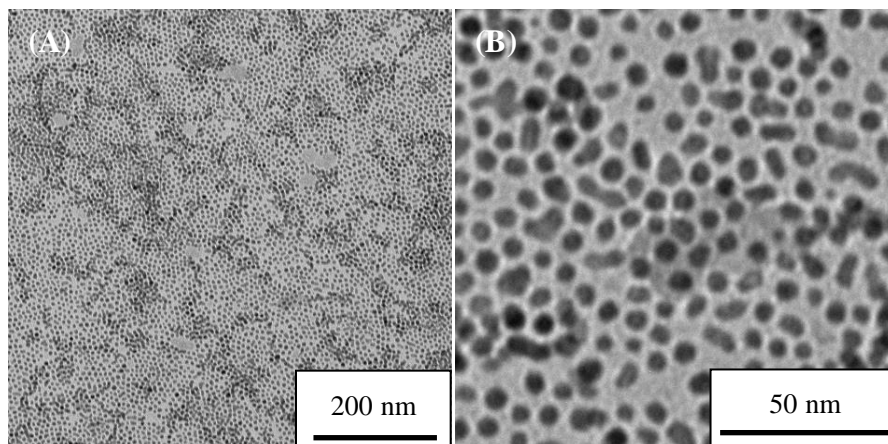


Figure S3. (A, B) TEM images of the as-obtained Pd NPs.

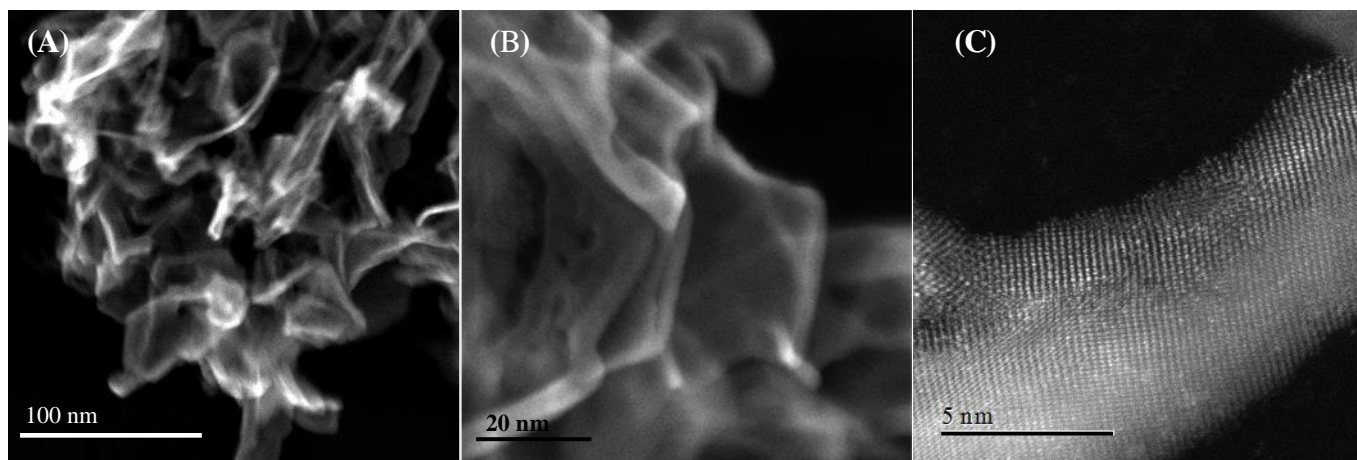


Figure S4. (A–C) Additional aberration-corrected HAADF–STEM images of PdW-S1 NSs.

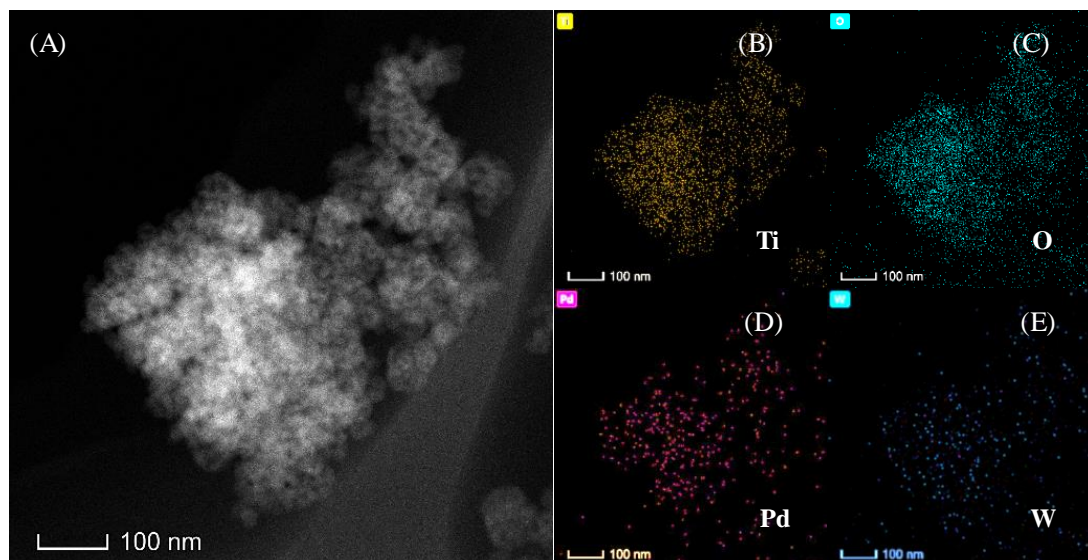


Figure S5. (A) Aberration-corrected HAADF-STEM images and (B–E) corresponding EDS elemental mappings of $\text{TiO}_2/\text{PdW-S1}$.

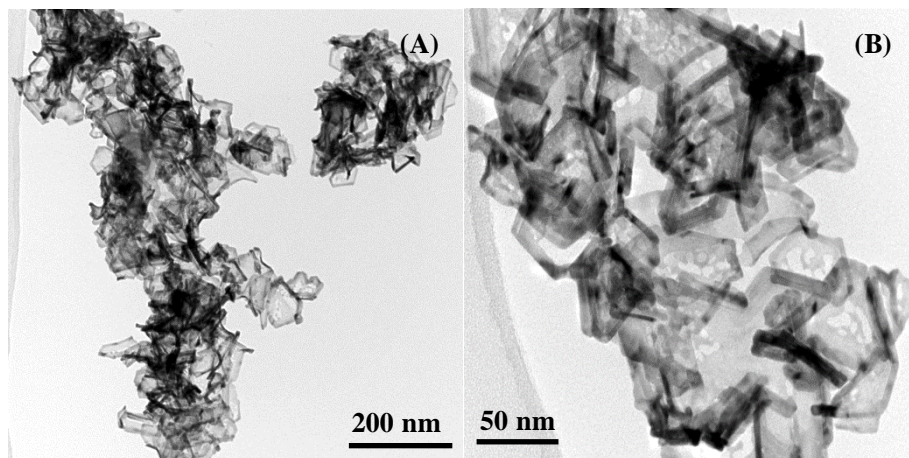


Figure S6. TEM images of PdW-S3 NSs.

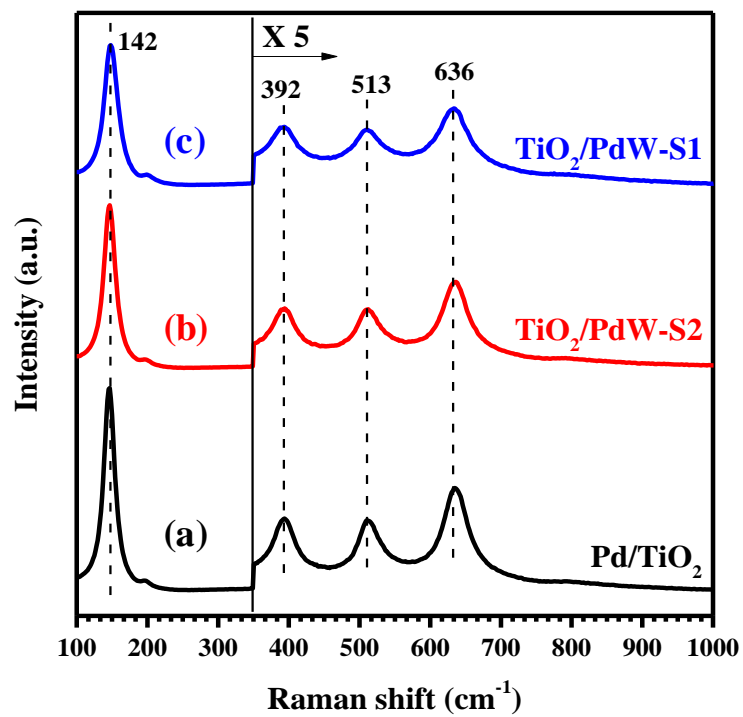


Figure S7. Raman spectra of (a) Pd/TiO₂, (b) TiO₂/PdW-S2, and (c) TiO₂/PdW-S1.

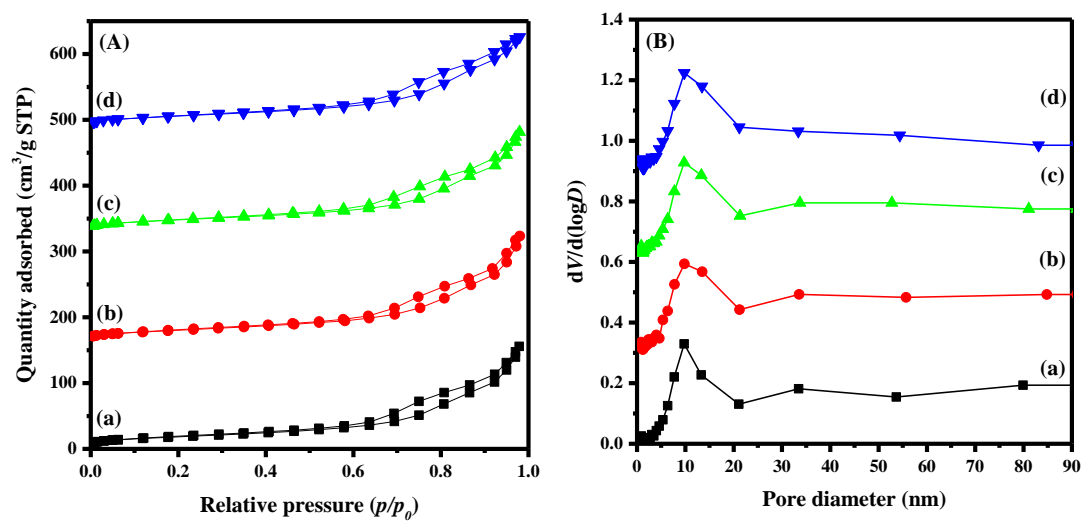


Figure S8. (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distributions of (a) Pd/TiO₂, (b) TiO₂/PdW-S2, (c) TiO₂/PdW-S1, and (d) Pd/WO_x/TiO₂.

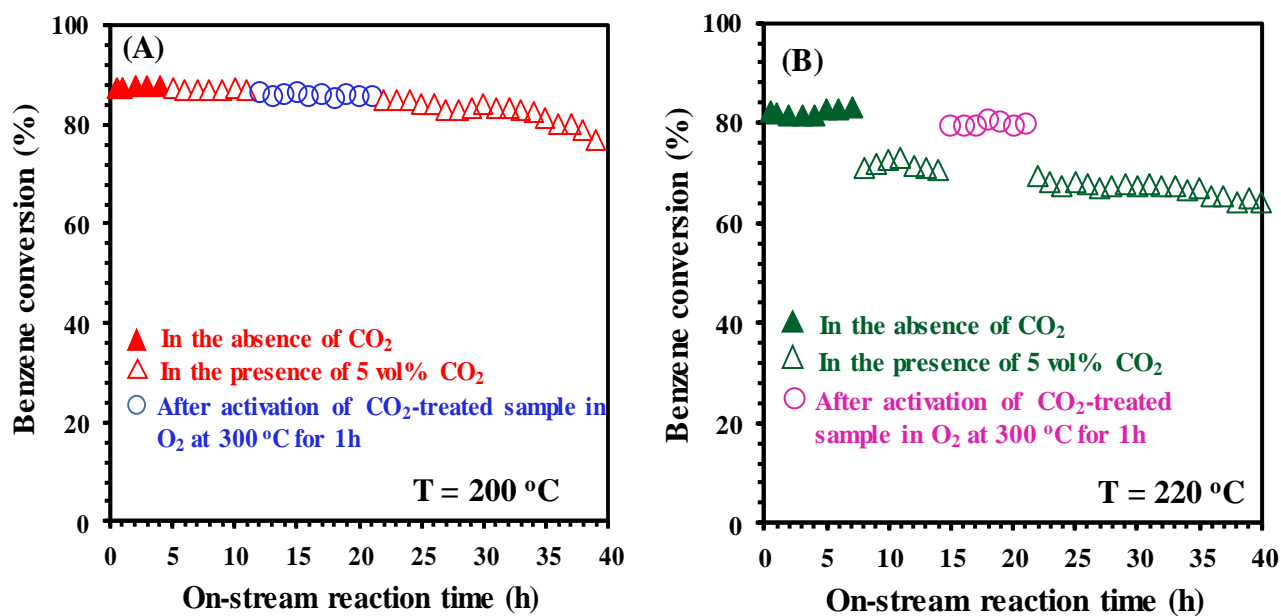


Figure S9. Effect of 5 vol% CO₂ on catalytic activity of (A) TiO₂/PdW-S1 and (B) Pd/TiO₂ and SV = 40 000 mL g⁻¹ h⁻¹.

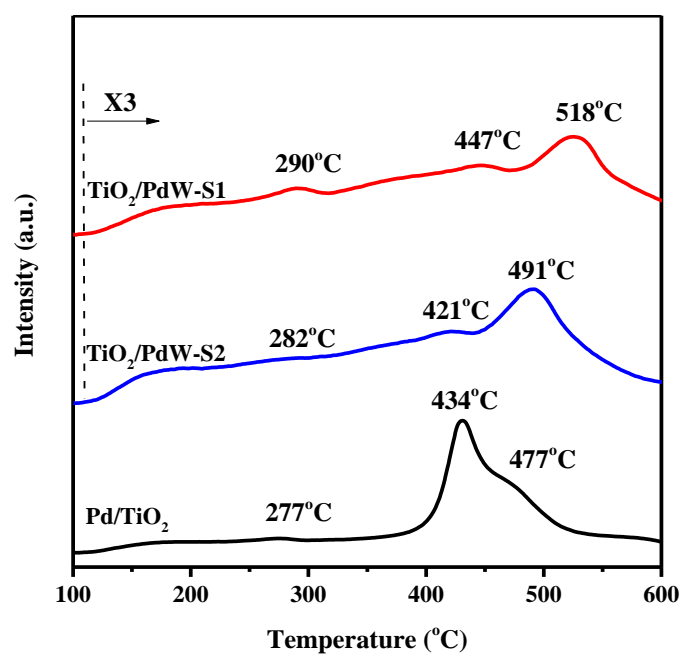


Figure S10. NH₃-TPD profiles of the as-obtained catalysts.

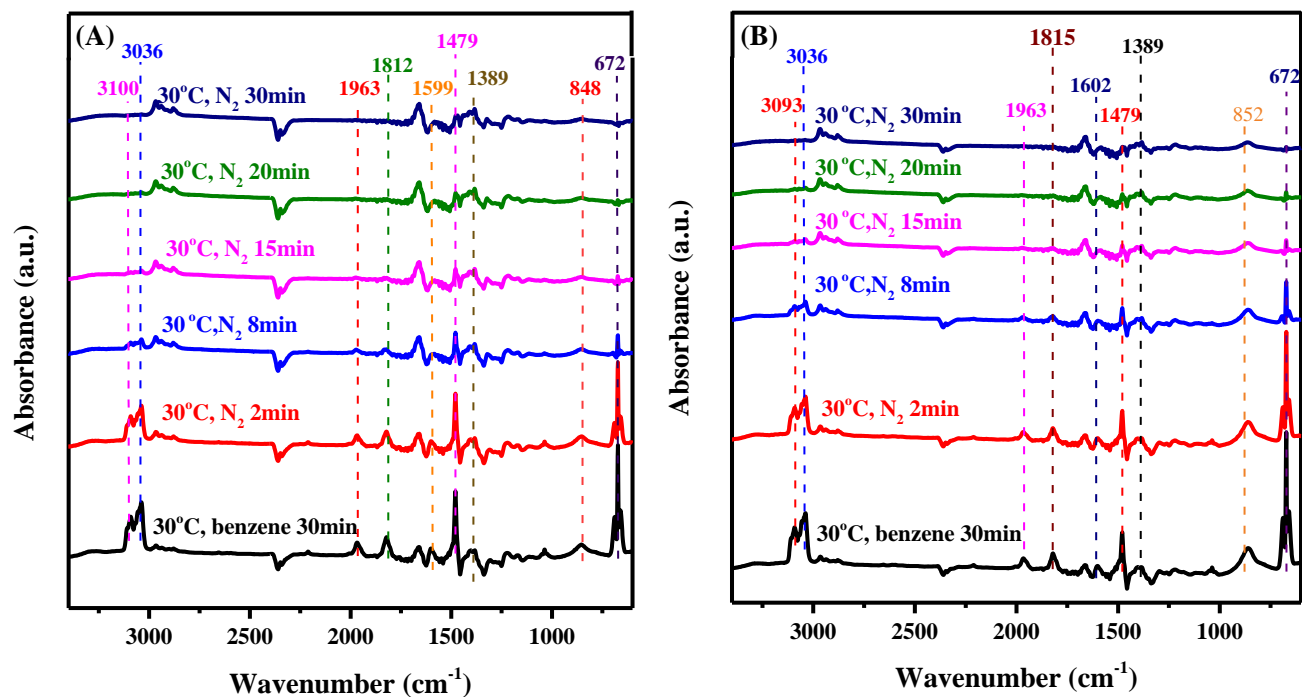


Figure S11. *In-situ* DRIFT spectra of benzene adsorption at 30 °C in a N₂ flow of 30 mL min⁻¹ on (A) Pd/TiO₂ and (B) TiO₂/PdW-S1, which are pretreated in a gas mixture (1000 ppm benzene + 20 vol% O₂ + N₂ (balance)) flow of 16.7 mL min⁻¹ at 30 °C.