

Supplementary Material

Enhanced performance of supported ternary metal catalysts for the oxidation of toluene in the presence of trichloroethylene

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Catalyst characterization procedures:

X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and a nickel filter ($\lambda = 0.15406$ nm). BET (Brunauer-Emmett-Teller) surface areas and pore-size distributions of the samples were determined via N_2 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 actual metal contents in the as-obtained samples were determined using the inductively coupled plasma–atomic emission spectroscopic (ICP–AES) technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. Each sample was dissolved in a mixture of concentrated HCl (37 wt%) and HNO_3 (75 wt%) aqueous solutions with a volumetric ratio of 3 : 1 prior to analysis.

Transmission electron microscopic (TEM) images of the as-obtained samples were recorded using a JEOL JEM-2010 instrument. The X-ray photoelectron spectroscopy (XPS) was used to determine the Pt 4f, W 4f, Ru 3p, O 1s, Cr 2p and Mn 2p binding energies (BEs) of the surface species with Mg $K\alpha$ ($h\nu = 1253.6$ eV) as the excitation source. The C 1s signal at 284.6 eV was taken as reference for BE calibration.

Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, ca. 0.05 g of the sample (40–60 mesh) was loaded to a fixed-bed U-shaped quartz microreactor (i.d. = 4 mm) and pretreated in an 20 vol% O_2/He flow of 30 mL/min at 300 °C for 1 h. After being cooled to room temperature (RT) at the same atmosphere, the sample was purged in a N_2 flow of 30 mL/min for 30 min. The pretreated sample was exposed to a flow (30 mL/min) of 10 vol% H_2/Ar mixture and heated from RT to 900 °C at a ramp of 10 °C/min.

The alteration in H₂ concentration of the effluent was monitored online by the chemical adsorption analyzer. Temperature-programmed desorption of oxygen (O₂-TPD) was carried out on the apparatus same as that used in the H₂-TPR experiments. The sample (0.05 g) was first treated at 300 °C for 1 h in a 20 vol% O₂/He flow of 30 mL/min and cooled to RT in the same atmosphere, and kept in the same flow for 1 h. Before the sample was heated from RT to 900 °C at a ramp of 10 °C/min, a He flow of 30 mL/min was employed to remove the O₂ left in the U-shaped quartz microreactor for 30 min, and the oxygen concentration in the effluent was continuously monitored by a thermal conductivity detector (TCD).

Temperature-programmed desorption of toluene and TCE (toluene+TCE-TPD) was carried out on the apparatus same as that used in the H₂-TPR experiments. Prior to the test, 0.05 g of the sample was pretreated in a 20 vol% O₂/He flow of 30 mL/min at 300 °C for 1 h with a ramp of 10 °C/min. After the sample was cooled to 50 °C at the same atmosphere, the mixed VOCs were purged into samples through gas cylinder until the sample reached an adsorption saturation of mixed VOCs, and then the sample was flushed with a He flow of 30 mL/min until the baseline was smooth. The system was heated up to 900 °C at a ramp of 10 °C/min in the He atmosphere. The products were detected by the mass spectrometer. Temperature-programmed surface reaction of the mixed VOCs (toluene+TCE-TPSR) was carried out with the pretreatments same as that used in the VOCs-TPD. The system was heated up to 900 °C at a ramp of 10 °C/min under the atmosphere of 20 vol% O₂ and toluene-TCE mixture. The products were detected by the mass spectrometer.

The metal dispersion was measured using chemisorption (AutoChem II 2920, Micromeritics). The sample was reduced in a H₂ flow (30 mL/min) at 200 °C for 2 h, purged

with a He flow (30 mL/min) for 1 h and cooled to 50 °C. Then, it was saturated with pulses of CO. The uptake of CO during the chemisorption was measured by a TCD.

In situ DRIFTS spectra were recorded on a Nicolet 6700 (TENSOR II (BRUKER)) FT-IR spectrometer with a liquid-nitrogen-cooled MCT detector. In the *in situ* DRIFTS studies, 30 mg of the sample was loaded to a high-temperature IR cell with a SeZn window, a N₂ flow (30 mL/min) was passed through the IR cell at 30 °C for 20 min, and the background spectrum was recorded. Subsequently, the N₂ flow was switched to the mixture gas (1000 ppm toluene + 200 ppm TCE + 20 vol% O₂ + N₂ (balance)) flow of 16.67 mL/min at elevated temperatures from RT to 50, 110, 210, 310 and 400 °C, respectively, and the *in situ* DRIFTS spectra were recorded when the sample was kept at the given temperature for 30 min. The DRIFT spectra were recorded with an accumulation of 32 scans and a spectrum resolution of 4 cm⁻¹.

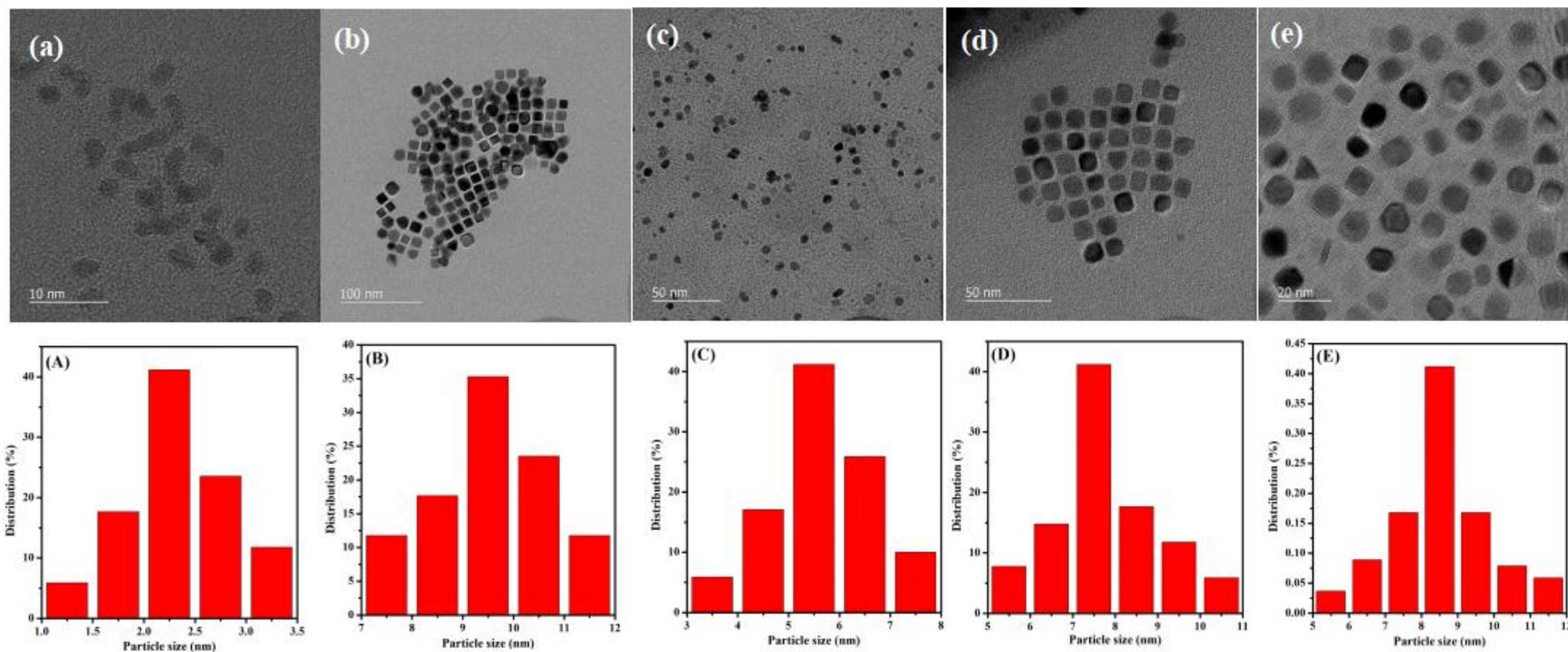


Figure S1. TEM images and particle-size distributions of (a, A) Pt, (b, B) PtW, (c, C) PtWRu, (d, D) PtWCr, and (e, E) PtWMn NPs.

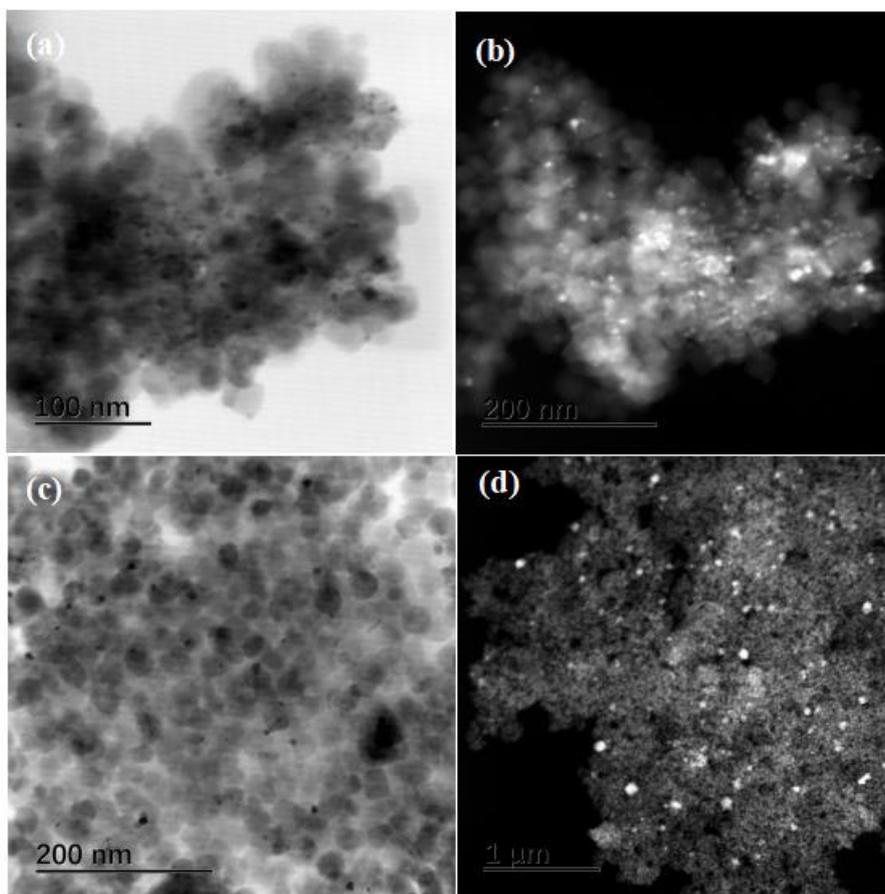


Figure S2. (a) TEM and (b) HAADF-STEM images of Pt/TiO₂, (c) TEM and (d) HAADF-STEM images of PtW/TiO₂.

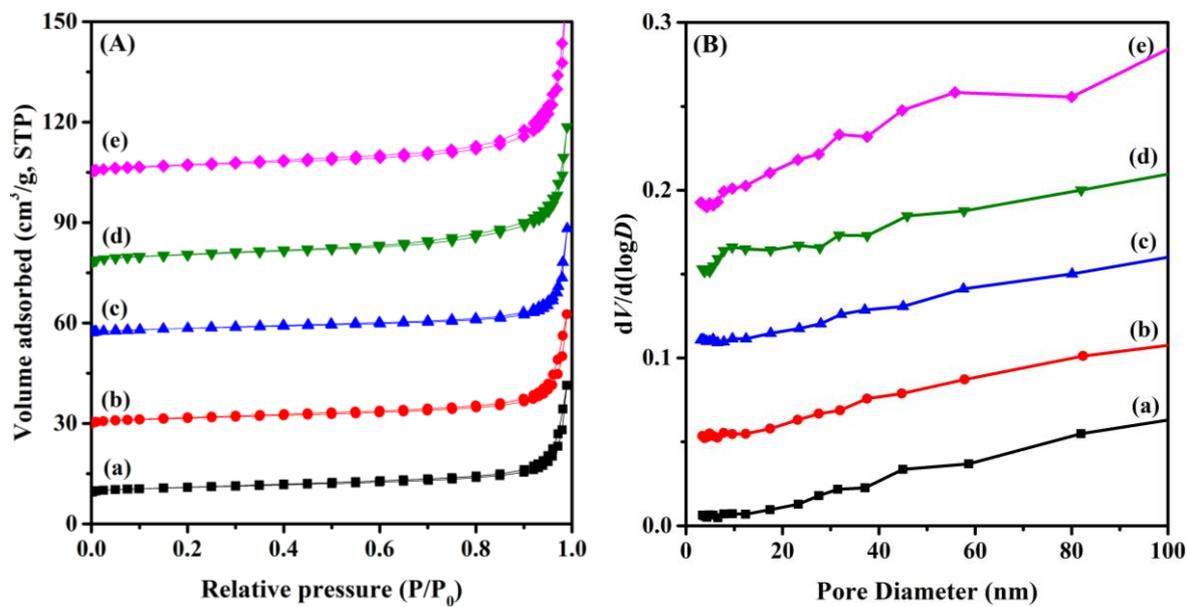


Figure S3. (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distributions of (a) Pt/TiO₂, (b) PtW/TiO₂, (c) PtWRu/TiO₂, (d) PtWCr/TiO₂, and (e) PtWMn/TiO₂.

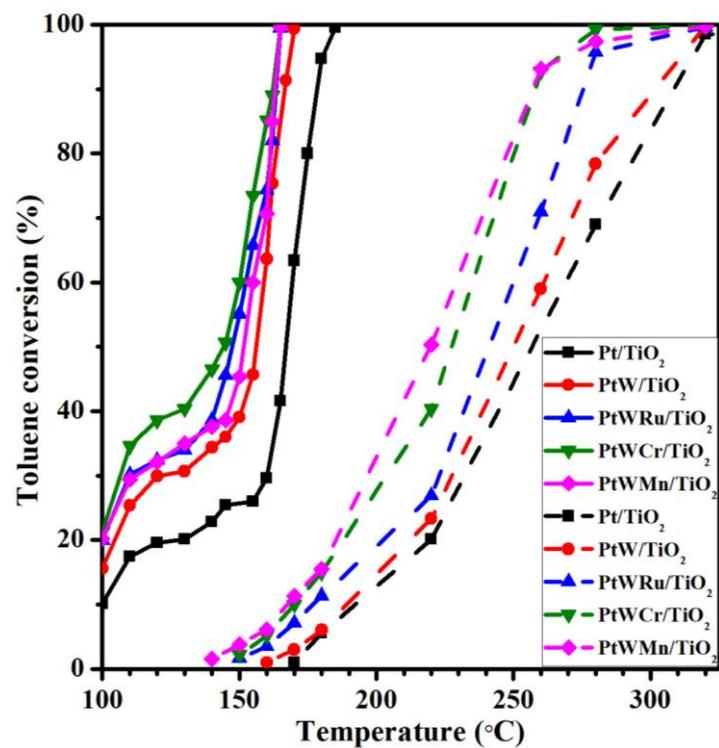


Figure S4. Toluene conversion as a function of temperature over the samples (solid curves: in the absence of TCE; dotted curves: in the presence of 200 ppm TCE).

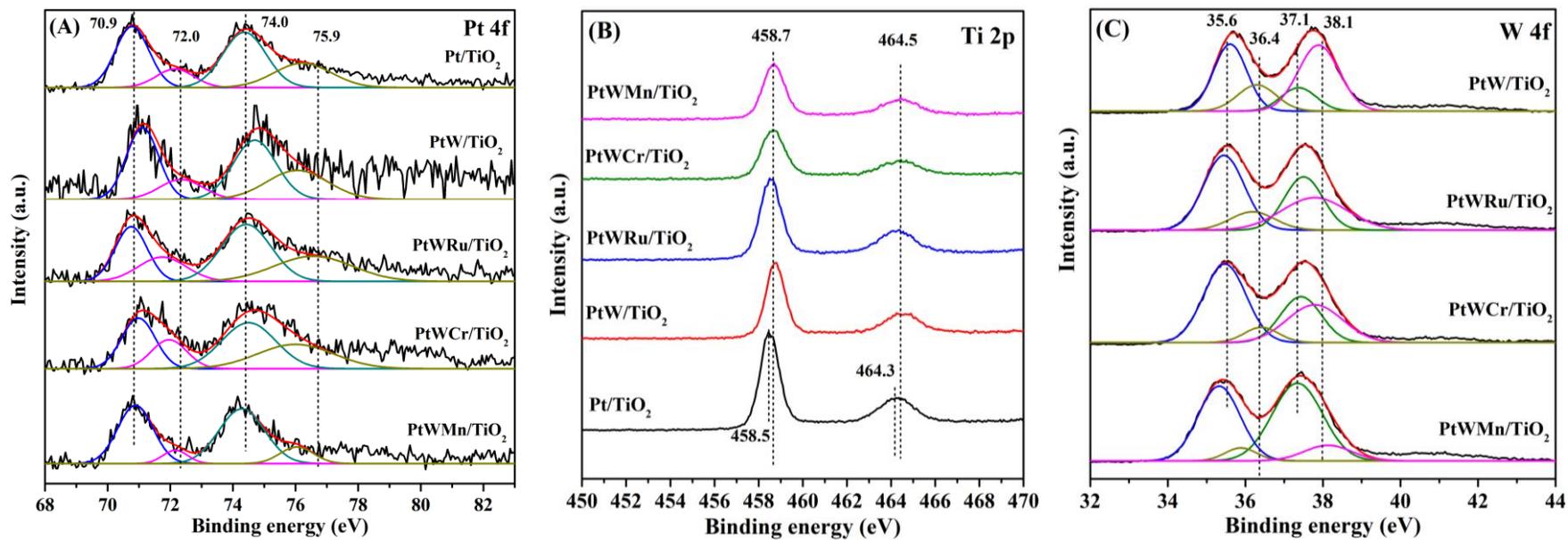


Figure S5. XPS spectra of (A) Pt 4f, (B) Ti 2p and (C) W 4f in each samples.

Table S1. $T_{50\%}$ and $T_{90\%}$ for toluene and TCE oxidation over the as-obtained samples.

Sample	Toluene conversion (alone)		Toluene conversion (in mixture of toluene&TCE)		TCE conversion (in mixture of toluene&TCE)	
	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)
Pt/TiO ₂	164	178	260	310	340	>500
PtW/TiO ₂	158	162	250	296	300	378
PtWRu/TiO ₂	148	160	240	275	272	305
PtWCr/TiO ₂	144	160	225	258	276	300
PtWMn/TiO ₂	150	159	216	255	272	318

Table S2. Assignments of the DRIFTS bands of the samples.

Wavenumber (cm ⁻¹)	Assignment	Ref.
3853	the vibration of OH	[39]
2930	Carbon–hydrogen stretching vibration bands of the aromatic rings (toluene)	[37]
1614	Water	[46]
1602	benzene ring vibration peak of the toluene	[41,42]
1365	Tertiary alcohol characteristic	[43]
1098	Primary alcohol characteristic	[44]
1655–1708	Symmetric stretching vibration of C=C	[45]