Electronic Supplementary Information

Nanoparticulate Pt on mesoporous SBA-15 doped with extremely low amount of W as highly selective catalyst for glycerol hydrogenolysis to 1,3-propanediol

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1. Preparation

The chemicals, unless specified, were commercially available from Sinopharm Chemical Reagent. The gases were commercially available from Shanghai Youjiali Liquid Helium. The mesoporous W-SBA-15 supports with the nominal W/Si atomic ratios of 1/1280, 1/960, 1/640, 1/320, 1/160, and 1/80 were synthesized by the sol-gel strategy modified from the protocol of Stucky and co-workers.¹ Namely, 5.0 g triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, $M_{\rm av}$ = 5800, Aldrich) as the template and 28.0 g distilled water were added to a vessel containing 150 ml HCl aqueous solution (2.0 M), and then stirred at 313 K for 4 h. To the solution, 10.0 g tetraethoxysilane (TEOS) was added and stirred for another 30 min. Then, a prescribed volume of Na₂WO₄·2H₂O aqueous solution (0.20 M) was added to attain the desired W/Si ratio. The sol was aged at 313 K under gentle stirring for 24 h and transferred into a 200 ml-capacity Teflon-lined stainless steel autoclave. After hydrothermal treatment at 368 K for 72 h, the resulting solids were filtered off, washed with distilled water, dried at 368 K for 24 h, and calcined at 773 K in air for 4 h to remove the template. The nomenclature of the as-synthesized supports used throughout, i.e., W-SBA-15(n), lists the nominal W/Si atomic ratio in the parentheses. Siliceous SBA-15 was synthesized in a similar manner but in the absence of Na₂WO₄·2H₂O.

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For the preparation of the Pt/SBA-15 and Pt/W–SBA-15 catalysts, 0.50 g of the assynthesized support was impregnated with 4.0 ml H₂PtCl₆·6H₂O aqueous solution (1.93 mM) under gentle stirring for 3 h at 333 K. It was dried overnight at 393 K and reduced in 5 vol% H₂/Ar flow (100 ml min⁻¹) at 573 K for 3 h with a heating rate of 2 K min⁻¹. The nominal Pt loading was 3.0 wt% for all the catalysts.

The method for the preparation of the Pt/M–SBA-15 (M = Cr, Mo, V, and Al) catalysts was similar to that for the Pt/W–SBA-15(1/640) catalyst except for changing Na₂WO₄·2H₂O to Na₂CrO₄·4H₂O, Na₂MoO₄·2H₂O, NaAlO₂, or Na₃VO₄·12H₂O as the precursors for Cr, Mo, Al, and V, respectively. The atomic ratio of M/Si was fixed at 640 in these catalysts.

2. Characterization

 N_2 physisorption was conducted on a Micromeritics Quadra apparatus at 77 K. The sample was loaded in a glass adsorption tube and pretreated at 523 K under flowing N_2 for 3 h. The bulk composition was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP–AES; Thermo Elemental IRIS Intrepid).

CO chemisorption was conducted on a Micromeritics 2750 chemisorption apparatus equipped with a thermal conductivity detector (TCD) to determine the active surface area (S_{Pt}) and dispersion (D) of Pt. The weighed sample (~50 mg) was reduced in 5 vol% H₂/Ar at 573 K for 3 h, purged by He at 473 K for 2 h, and then cooled down to 298 K. Pure CO pulses were injected until the eluted peak did not change in intensity.² The CO/Pt adsorption stoichiometry of 1/1 was used to calculate the S_{Pt} and D values.³

Small-angle X-ray scattering (SAXS) measurements were conducted on a Bruker Nanostar U SAXS system using Cu K α radiation ($\lambda = 0.15418$ nm). The tube voltage was 40 kV, and the current was 35 mA. The *d*-spacing was calculated by the formula $d = 2\pi/q$, and the unit cell parameter was calculated by the formula $a = 2d_{10}/\sqrt{3}$. The wide-angle powder X-ray diffraction (XRD) patterns were acquired on a Bruker AXS D8 Advance X-ray diffractometer using Ni-filtered Cu K α radiation equipped with a LynxEye 1-dimensional linear Si strip detector. The tube voltage was 40 kV, and the current was 40 mA. The 2θ angles were scanned from 5° to 80° at 5° min⁻¹ with a step size of 0.02°.

Transmission electron microscopic (TEM) imaging and high-angle annular dark field (HAADF) imaging were performed on a Tecnai G² S-Twin F20 field-emission (S)TEM microscope operated at 200 kV. The catalyst was ground in an agate mortar, dispersed in anhydrous ethanol, and dripped onto a carbon film-coated copper grid. Particle size distribution (PSD) histogram of the Pt NPs was constructed by randomly measuring at least 200 NPs.

Ultraviolet–visible diffuse reflectance spectrum (UV–vis DRS) was collected on a Perkin–Elmer Lambda 650s spectrometer from 200 to 600 nm with a step size of 1 nm. BaSO₄ was used as a standard reflector. Fourier-transform infrared spectroscopy (FTIR) was conducted on a Nicolet Nexus 470 IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The sample was finely ground, evenly mixed with KBr with a weight ratio of 1/20, and pelletized. The spectral resolution was 4 cm⁻¹, and 32 scans were recorded for each spectrum.

Temperature-programmed desorption of NH₃ (NH₃-TPD) was performed on the apparatus for CO chemisorption. About 100 mg of the catalyst was pretreated at 473 K for 1 h under He and cooled down to 373 K. After saturation adsorption in flowing 10 vol% NH₃/He (25 ml min⁻¹) for 1 h,⁴ the sample was purged with He to remove the physisorbed NH₃, followed by heating from 373 to 973 K at a ramping rate of 10 K min⁻¹. The area of the desorption peak was integrated and employed to quantify the amount of the acid sites by referring to that calibrated by a 100 μ L-capacity loop using the same adsorbate.

For qualitative acid site measurements using pyridine as the probe molecule (Py-IR), about 20 mg of the catalyst diluted with KBr was pressed into a self-supporting wafer of 2 cm in diameter. The wafer was placed in the IR cell with CaF₂ windows, evacuated at 573 K for 1 h, and then exposed to pyridine vapor after being cooled down to 303 K. The Py-IR spectrum was recorded at 373 K after evacuation for 30 min.

X-ray photoelectron spectroscopy (XPS) was conducted on a Perkin-Elmer PHI

5000C spectrometer with Al K α radiation (hv = 1486.6 eV) as the excitation source. The catalyst was evacuated in the pretreatment chamber at 298 K overnight, and then transferred to the analyzing chamber with background pressure lower than 2 × 10⁻⁹ Torr. All binding energy (BE) values were referenced to the Si 2p BE of the support at 103.3 eV with an uncertainty of ± 0.2 eV.

X-ray absorption spectrum at the Pt L₂-edge was acquired on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF) in the fluorescence mode. The typical electron beam energy was 3.5 GeV, and the current was 300 mA. The catalyst was pasted on the scotch tape, fixed on the Al window, and inserted in the sample stage. Extended X-ray absorption fine structure (EXAFS) data were analyzed by the IFEFFIT package following the standard procedures.⁵ The background was subtracted by extrapolating the pre-edge region onto the EXAFS region. The $\chi(E)$ data were normalized with respect to the edge jump step using the Athena program of the IFEFFIT package.⁶ The normalized $\chi(E)$ data was transformed from the energy space to the k-space with $\chi(k)$ multiplied by k^3 to compensate for the oscillations in the highk region. The k³-weighted $\chi(k)$ data in the k-space ranging from 3.5 to 11.9 Å⁻¹ were Fourier transformed to the *R*-space. The processed $\chi(k)$ data were fitted in the *R*-space ranging from 1.5 to 3.3 Å using the Artemis program of the IFEFFIT package. Theoretical backscattering amplitudes and phase shifts for the Pt-Pt and Pt-O pairs were calculated using the FEFF6 code with face centered cubic (fcc) Pt and PtO as the references, respectively.⁷ From these analyses, microstructural parameters, such as the coordination number (CN), coordination distance (R), Debye–Waller factor ($\Delta\sigma^2$), and inner potential correction (ΔE_0), were obtained.

3. Catalytic Studies

The hydrogenolysis of glycerol was carried out in a 10 ml Teflon-lined stainless steel autoclave, in which 200 mg of catalyst and 2.0 g of 30 wt% glycerol aqueous solution were charged. The concentration of glycerol mimics that of crude glycerol.⁸ The autoclave was sealed and purged with H₂ six times to expel air. If not specified, the reaction temperature was 423 K, the H₂ pressure was 4.0 MPa, and the stirring rate

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was 500 rpm. After reaction, the liquid phase was analyzed on a GC-9560 gas chromatograph fitted with an HP-INNO Wax capillary column (30 m × 0.32 mm × 0.50 μ m) and a flame ionization detector (FID). The liquid products were also qualified by gas chromatography-mass spectrometry (GC–MS, Finnigan Voyager) using identical HP-INNO Wax capillary column. The gas phase was analyzed on a GC-9560 gas chromatograph fitted with a 2 m-long TDX-01 packed column connected to a TCD and on a GC-9160 gas chromatograph fitted with a PONA capillary column (50 m × 0.25 mm × 0.50 μ m) connected to an FID. Propane was identified as the sole carbon-containing gaseous product.

On the basis of the analysis results, the conversion of glycerol was calculated as: Conversion = (initial moles of glycerol – moles of glycerol after reaction)/(initial moles of glycerol) \times 100%.

The conversion of glycerol to liquid products (CTL) was calculated as: CTL = (total moles of C in liquid products)/(initial moles of C in glycerol × Conversion) × 100%.

The selectivity to a specific liquid product (Sel.) was calculated as: Sel. = (moles of C in a specific liquid product/moles of C in all liquid products) × 100%. The initial selectivity to 1,3-PDO was denoted as S_0 .

The yield of 1,3-PDO (Yield_{1,3-PDO}) was calculated as: Yield_{1,3-PDO} = (CTL × Sel. to 1,3-PDO) × 100%.

And the turnover frequency (TOF) of glycerol at conversion less than 10% was calculated as: $TOF = (moles of glycerol converted)/(moles of Pt on catalyst surface \times reaction time).$

Catalyst	Reaction conditions	CTL (%)	Sel. (%)	Yield (%)	Ref.
Pt/W-SBA-15(1/640)	423 K, 4.0 MPa, 30 h	86.8	70.8	61.5	This work
Pt/WO ₃ /ZrO ₂ ^a	443 K, 8 MPa, 18 h	85.8	24.2	20.8	9
Pt/WO ₃ /ZrO ₂	403 K, 4.0 MPa, 1 h	70.2	45.6	32.0	10
Pt/WO _x /AlOOH	453 K, 5.0 MPa, 12 h	100	66.0	66.0	11
2Pt-10WO _x /Al ₂ O ₃	433 K, 5.0 MPa, 1 h	64.2	66.1	42.4	12
Pt/WO ₃ /SBA-15	483 K, 0.1 MPa, 1 h	86.0	42.0	36.1	13
Pt/sulfated ZrO ₂ ^a	443 K, 7.3 MPa, 24 h	66.5	83.6	55.6	14
Ir–ReO _x /SiO ₂ ^b	393 K, 8 MPa, 24 h	62.8	59.0	37.1	15
Pt/HM	498 K, 0.1 MPa, 1 h	94.9	48.6	46.1	16
2Pt-5Cu/mordenite	483 K, 0.1 MPa, 1 h	90.0	58.5	52.7	17

Table S1 A comparison of the catalytic results of the Pt/W–SBA-15(1/640) catalyst with those of the literature catalysts showing high selectivity and yield of 1,3-PDO in glycerol hydrogenolysis

 $^{\it a}$ 1,3-Dimethyl-2-imidazolidinone as the solvent. $^{\it b}$ H_2SO_4 as the additive.

Catalyst	Conversion	CTL	Sel. (C% in liquid products)					Viald $(0/)$
Catalyst	(%)	(%)	1,3-PDO	1,2-PDO	1-PrOH	2-PrOH	Others	$1 \text{ leld}_{1,3-\text{PDO}} (\%)$
Pt/Cr-SBA-15(1/640)	7.7	7.6	0.4	trace	0.6	98.8	0.2	trace
Pt/Mo-SBA-15(1/640)	5.7	5.6	1.1	0.7	0.6	97.3	0.3	0.1
Pt/Al-SBA-15(1/640)	0.8	0.8	0.7	4.3	80.6	14.3	0.1	trace
Pt/V-SBA-15(1/640)	5.4	5.2	2.9	8.6	18.5	69.0	0.1	0.2
W-SBA-15(1/640)	3.0	2.6	6.5	8.9	63.5	12.8	8.3	0.2
$Pt/SBA-15 + W-SBA-15(1/640)^{b}$	85.0	84.9	36.8	trace	57.8	4.0	1.4	31.2

Table S2 The catalytic results of the control catalysts in glycerol hydrogenolysis^a

^{*a*} Reaction conditions: 200 mg of catalyst, 2.0 g of 30 wt% glycerol aqueous solution, temperature of 423 K, H₂ pressure of 4.0 MPa, stirring rate of 500 rpm, and 30 h. ^{*b*} The physically mixed Pt/SBA-15 + W–SBA-15(1/640) catalyst contains 200 mg of Pt/SBA-15 and 200 mg of W–SBA-15(1/640) to attain the same amounts of Pt and W as those in the Pt/W–SBA-15(1/640) catalyst.

Temperature Conversion	Conversion	CTL	Sel. (C% in liquid products)					V:-14 (0/)
(K)	(%)	(%)	1,3-PDO	1,2-PDO	1-PrOH	2-PrOH	Others	$Y = 1010_{1,3-PDO} (\%)$
403	60.5	60.3	74.5	1.4	15.3	8.7	0.1	44.9
423	88.0	86.8	70.8	1.2	19.8	6.6	1.6	61.5
443	97.2	83.1	61.8	0.9	29.4	5.8	2.1	50.4

Table S3 The temperature-dependent catalytic performances of the Pt/W–SBA-15(1/640) catalyst in glycerol hydrogenolysis^a

^a Other reaction conditions: 200 mg of catalyst, 2.0 g of 30 wt% glycerol aqueous solution, H₂ pressure of 4.0 MPa, stirring rate of 500 rpm, and

30 h.

Pressure Convers	Conversion	on CTL	Sel. (C% in liquid products)					
(MPa)	(%)	(%)	1,3-PDO	1,2-PDO	1-PrOH	2-PrOH	Others	$1 \text{ let} \mathbf{a}_{1,3-\text{PDO}}$ (%)
4.0	88.0	86.8	70.8	1.2	19.8	6.6	1.6	61.5
2.0	57.6	57.2	66.5	1.0	25.8	6.2	0.5	38.0
1.0	49.5	49.3	63.1	0.7	30.4	5.8	trace	31.2

Table S4 The pressure-dependent catalytic performances of the Pt/W–SBA-15(1/640) catalyst in glycerol hydrogenolysis^a

^a Other reaction conditions: 200 mg of catalyst, 2.0 g of 30 wt% glycerol aqueous solution, temperature of 423 K, stirring rate of 500 rpm, and

30 h.



Fig. S1 (A) N_2 adsorption–desorption isotherms and (B) BJH pore size distribution of the Pt/W–SBA-15 catalysts with the W/Si atomic ratios of (a) 0, (b) 1/1280, (c) 1/960, (d) 1/640, (e) 1/320, (f) 1/160, and (g) 1/80.



Fig. S2 Raman spectra of the Pt/W–SBA-15 catalysts with the W/Si atomic ratios of (a) 0, (b) 1/1280, (c) 1/960, (d) 1/640, (e) 1/320, (f) 1/160, and (g) 1/80.



Fig. S3 TEM images and PSD histograms with Gaussian analysis fittings of the Pt/W–SBA-15 catalysts with the W/Si atomic ratios of (a) 0, (b) 1/1280, (c) 1/960, (d) 1/640, (e) 1/320, (f) 1/160, and (g) 1/80.



Fig. S4 NH₃-TPD profiles of the Pt/W–SBA-15 catalysts with the W/Si atomic ratios of (a) 0, (b) 1/1280, (c) 1/960, (d) 1/640, (e) 1/320, (f) 1/160, and (g) 1/80.

Fig. S5 Experimental $k^3\chi(k)$ data (\circ) and fitted curves (—) of the Pt/W–SBA-15 catalysts with the W/Si atomic ratios of (a) 0, (b) 1/1280, (c) 1/640, and (d) 1/160.

Fig. S6 Py-IR spectra acquired by co-feeding H_2 with Py at 373 K on the Pt/W–SBA-15 catalysts with the W/Si atomic ratios of (a) 0, (b) 1/1280, (c) 1/960, (d) 1/640, (e) 1/320, (f) 1/160, and (g) 1/80.

Fig. S7 Catalytic activities of the Pt/W–SBA-15(1/640) (\square) and Pt/SBA-15 catalysts (\bigcirc) in cumene cracking at 523 K in H₂ stream (filled symbols) or in He stream (open symbols).

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