Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

Efficient Selective Hydrogenation of 2-Butyne-1,4-Diol to 2-Butene-1,4-Diol by Silicon Carbide Supported Platinum Catalyst

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1. Experimental Section

1.1. Raw Materials

All used agents in this work were analytical grade and without modification and purified anymore. The tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$, 99.99%) was purchased from Alfa Aesar Chemical Reagent Co., Ltd. The silicon carbide (SiC, 99.9%, 30 nm) and silicon nitride (SiN, 99.9%, 50 nm) was purchased from Shanghai Yaotian New Material Technology Co., Ltd. The silicon dioxide (SiO_2, AERISIL 380) was purchased from Nippon Aerosil Co. Ltd. The active carbon (AC, analytical reagent) and the cerium nitrate hexahydrate ($Ce(NO_3)_3·6H_2O$, 99%) was purchased from the Sinopharm Chemical Reagent Co., Ltd.

1.2. Preparation of Ceria Nanorods

The ceria nanorods synthesized by hydrothermal method.[1] In details, firstly, $Ce(NO_3)_3·6H_2O$ (0.05 mol/L) solution was added into NaOH (6 mol/L) solution with fierce stirring about 15 minute. After that, moved the turbid liquid into Teflon bottle and then tightly seal in stainless-steel autoclave. Hydrothermal treatment operated in electric temperature-controlled oven at 100 °C for 24 h and naturally cooled to room temperature. Then, the precipitates were washed by deionized water (1000 mL) four times and ethanol (250 mL) once. Finally, the ceria nanorods were acquired by drying in vacuum under 70 °C overnight.

1.3. Preparation of Catalysts

Deposition of platinum onto the silicon carbide adopted by incipient wetness impregnation (IMP) approach in this work. In details, first, the saturation of water absorption of SiC tested by deionized H_2O is 860 μL/g. Secondly, the certain amount of $Pt(NH_3)_4(NO_3)_2$ dissolved in 860 μL deionized H_2O and were added dropwise into the 1.0 g SiC powders (30.1 m^2/g, 0.071 cm^3/g) under manually stirring. And the SiC supports had calcined in air at 400 °C for 4 h (ramping rate: 2 °C /min) before application. The mass rate of platinum was designed as 0.1, 0.5, 1, 5 wt.%, which denoted as **0.1Pt/SiC**, **0.5Pt/SiC**, **1Pt/SiC**, **5Pt/SiC**, respectively. Other catalysts (**0.5Pt/SiO$_2$**, **0.5Pt/SiN**, **0.5Pt/AC**, **0.5Pt/CeO$_2$**) prepared by the same method, only the active carbon had calcined in air at 200 °C for 2 h (ramping rate: 2 °C /min) before application. Then, the as-prepared catalysts were placed in ambient condition for 2 h and then dried at 65 °C overnight, following grinded and calcined at 300 °C for 4 h (ramping rate: 2 °C /min).

1.4. Characterization

The bulk concentrations of copper were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) with the Optima 5300DV (PerkinElmer Co., USA). 0.1 g powder sample was dissolved by 8 mL aqua regia around 4 h, and then filtered and extracted the stock solution for ICP-AES test.

The adsorption-desorption isotherm and pore size distribution were resulted from the nitrogen adsorption–desorption measurements handled on the ASAP2020-HD88 analyzer (Micromeritics Co., Ltd., Atlanta, USA) at -196 °C. The as-calcined catalytic powders were pre-activated at 250 °C for 4 h under vacuum condition (< 100 μm Hg) before the introduction of N$_2$. The BET specific surface areas (S_{BET}) of catalysts were counted from analytic data between 0.05 and 0.20 in the relative pressure. The pore size (r_{p}) distribution was calculated with the BJH method on the basis of desorption branch of the tested isotherms.

The powder X-ray diffraction (XRD) patterns were operated on the Bruker D2 (Bruker Co., USA) (40 kV, 40 mA) using Cu Kα_1 radiation (λ= 1.5406 Å), with a scanning rate of 4°/min. The 2θ angles of powders were detected from 10 to 80° with 0.02°/step. The ground samples' powders were flattened on a quartz holder before test.

The thermal decomposition of catalysts was studied by thermogravimetric analysis (TGA) method by using TGA2 (METTLER TOLEDO Co., Switzerland). The around 8 mg catalysts placed into the 70 μL alumina crucible and heated in argon atmosphere from 30 to 800 °C at the heating rate of 10 °C /min.

The morphology of silicon carbide and distribution of platinum nanoparticles observed by the high-resolution transmission electron microscopy (HRTEM) images obtained from a FEI Tecnai G2 F20 microscope (FEI Co., USA) working at 200 kV. Samples were dispersed in anhydrous alcohol under sonication about 3 min, and then drip a blob of suspension on a Cu grid coated by the ultra-thin (3-5 nm) carbon film. Finally, the sample grid was dried under infrared radiation conditions before inserted into the sample holder.

1.5. X-Ray Absorption Fine Structure

The X-ray absorption fine structure (XAFS) spectroscopy at the Pt L_{III} edge (E_0 = 11564 eV) edge was conducted at 3.5 GeV in “top-up” mode with a constant current of 240 mA at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The XAFS data were collected with a Lytle ion chamber in fluorescence mode. The X-ray energy was calibrated by the absorption edge of pure Pt foil. Before the XAFS measurement, we ground the investigated Pt/SiC samples and lithium fluoride (weight rate about 2:1) into fine powders, and then pressed the mixed powders to a thin piece with 13 cm in diameter. The collected profiles of XAFS were pretreated with Athena software. The “normalized absorption” was defined as experimental absorption coefficients as a function of energies μ(E) were processed by background subtraction and normalization procedures. The chemical valence of Pt was determined with the linear combination fit[2] by comparison to the corresponding references of Pt foil and PtO_2 based on the normalized profiles of X-ray absorption fine structure (XANES) in Athena software. The corresponding Fourier transform of k^3-weighted extended X-ray adsorption fine structure (EXAFS) spectra in R space were fitted by the Artemis software. The fitting modes for the R space applied with Pt foil and PtO_2 to contribute the Pt-Pt and Pt-O/Pt-O-Pt shells, respectively, and the fitting range to 1.2–4.1 and 1.8–4.3 Å in R space for fresh and used **0.5Pt/SiC** catalyst, respectively.

1.6. Hydrogenation Reaction

The catalytic properties of silicon carbide supported platinum catalysts were tested in the hydrogenation of 2-butyne-1,4-diol (BYD) in aqueous phase. Before the reaction testing, the catalysts were activated at 300 °C for 2 h under the atmosphere of pure H_2 with flow rate of 30 sccm. The freshly reduced catalyst (0.05 g) was mixed with the reactants of BYD (1.0 g) and the internal standard of 1,2-propylene glycol (1.0 g) in 18 mL H_2O. The mixture was charged in a 50 mL batch reactor. After the reactor was flushed with H_2 for 3 times, catalytic hydrogenation was conducted under 1 MPa H_2 pressure and 100 °C. The reaction product was analyzed by off-line gas chromatography (Agilent 7890B) equipped with an FFAP capillary column (30 m × 0.32 mm × 0.5 μm) and a flame ionization detector.

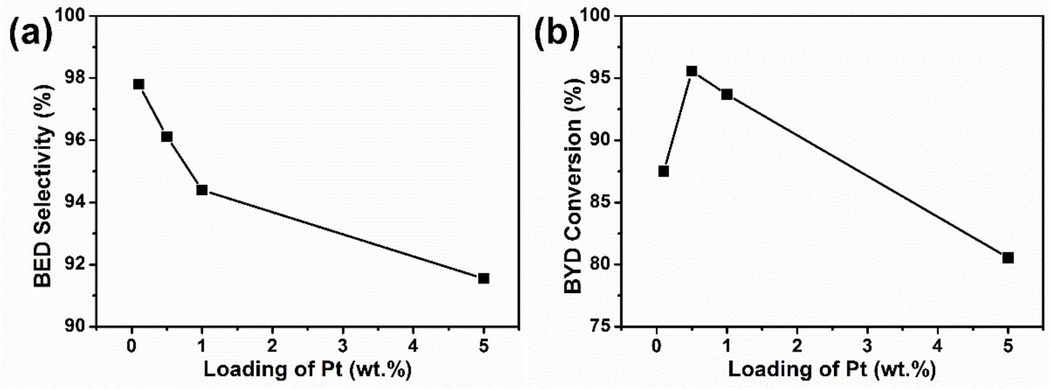

Figure S1 Effect of Pt loading for silicon carbide-supported platinum catalysts on: **(a)** selectivity of BED and **(b)** conversion of BYD (reaction time: 10 h).

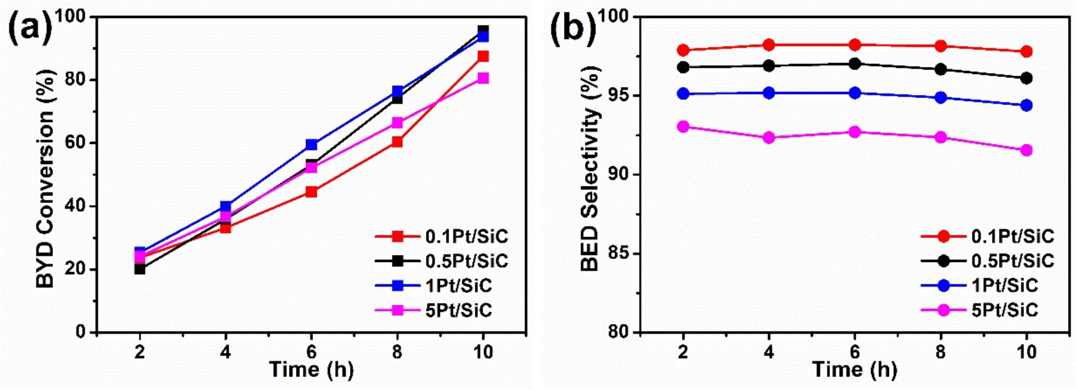

Figure S2 Effect of Pt loading for silicon carbide-supported platinum catalysts on: **(a)** conversion of BYD and **(b)** selectivity of BED as the function of reaction time at 100 ˚C and $p(H_2)$ = 1 MPa.

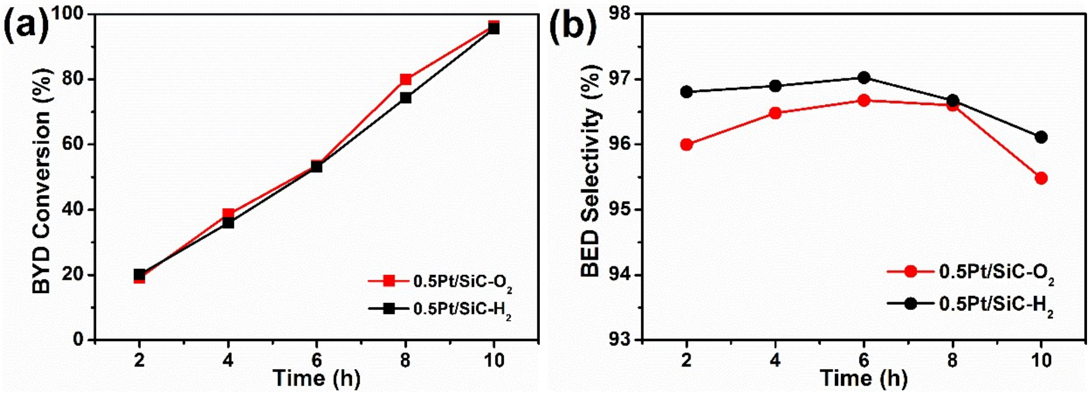

Figure S3 Effect of pretreatment on 0.5Pt/SiC for: **(a)** Conversion of BYD; **(b)** Selectivity of BED.

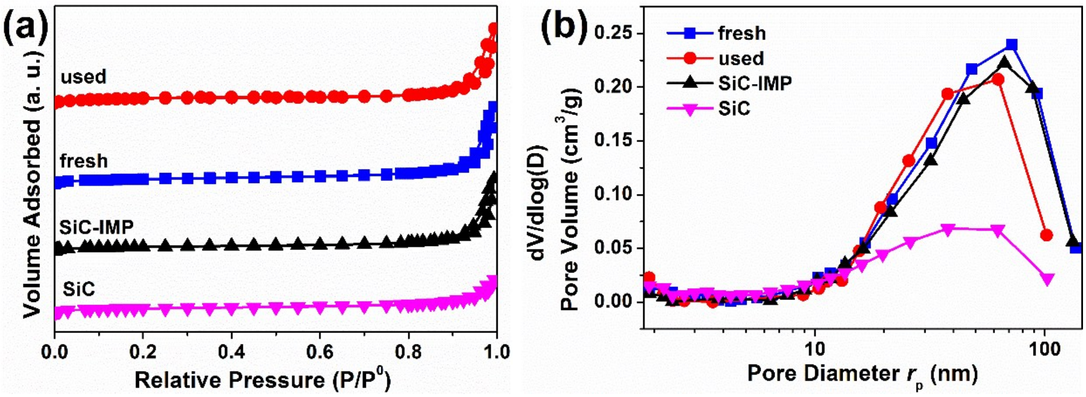

Figure S4 **(a)** Adsorption-desorption isotherm; **(b)** BJH pore-size distribution of fresh and used 0.5Pt/SiC after the 3rd run reaction.

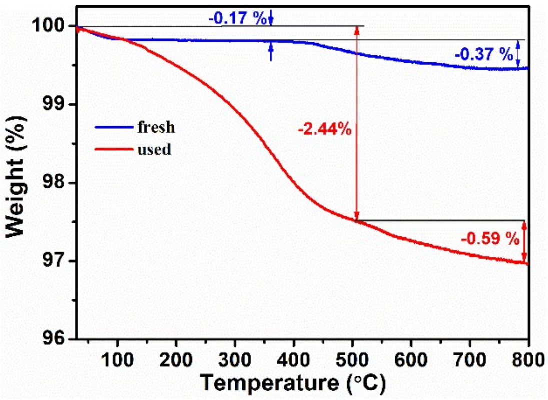

Figure S5. TGA curves of 0.5Pt/SiC before and after reaction.

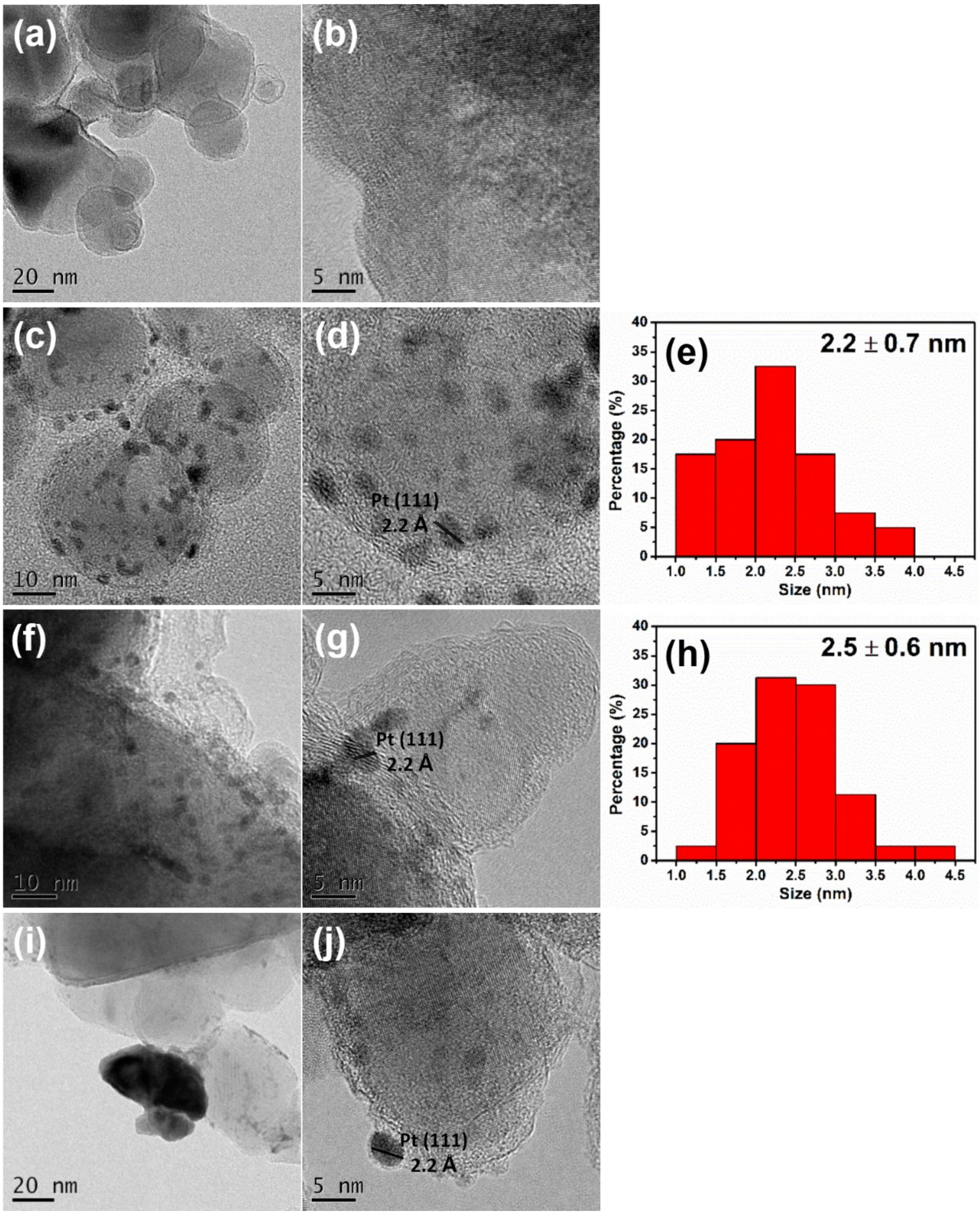

Figure S6 TEM **(a, c, f, i)**, HRTEM images **(b, d, g, j)** and Pt particle size-distribution histograms **(e, h)** for: **(a, b)** 0.1Pt/SiC; **(c, d, e)** 0.5Pt/SiC; **(f, g, h)** 1Pt/SiC; **(I, j)** 5Pt/SiC.

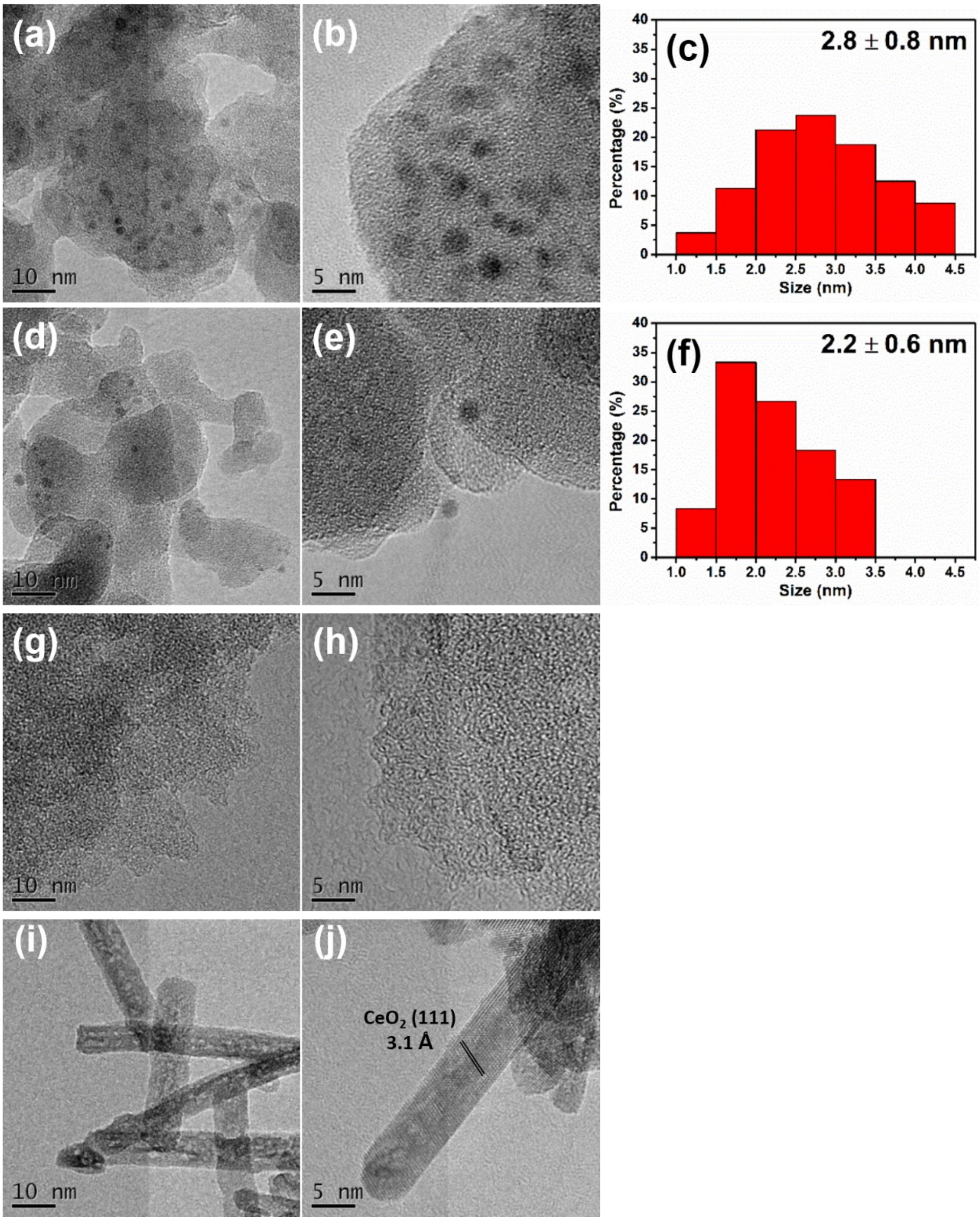

Figure S7 TEM **(a, d, g, i)**, HRTEM images **(b, e, h, j)** and Pt particle size-distribution histograms **(c, f)** for: **(a, b, c)** 0.5Pt/SiO_2; **(d, e, f)** 0.5Pt/SiN; **(g, h)** 0.5Pt/AC; **(i, j)** 0.5Pt/CeO_2.

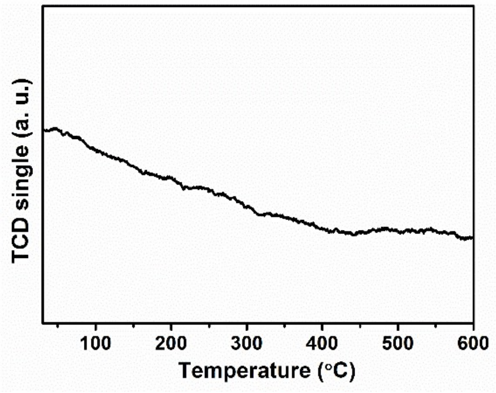

Figure S8 H_2-TPR profile for fresh 0.5Pt/SiC.

Table S1. Comparison of the activity over the various Pt-based catalysts for hydrogenation of BYD to BED in this work (100 °C; *p*(H_2) = 1 MPa; 10 h).

Support	**Pt Loading (wt%)**	**BYD Conversion (%)**	**BED Selectivity (%)**
SiC	0.1	87.4	97.8
SiC	0.5	95.6	96.1
SiC	1	93.7	94.4
SiC	5	80.5	91.5
SiC (O_2-pretreated)	0.5	96.4	95.5
SiO_2	0.5	85.3	86.8
SiN	0.5	99.2	78.3
AC	0.5	92.3	85.2
CeO_2	0.5	95.5	90.6

Table S2 Concentrations and average sizes (*D*) of Pt, BET specific surface areas (S_{BET}) and BJH pore volumes (V_p) for SiC-supported Pt catalysts.

Sample	Pt (wt.%)[a]	S_{BET} (m^2/g)[b]	V_p (cm^3/g)[b]	*D* (nm)[c]
SiC	––	30	0.071	––
SiC-IMP	––	29	0.162	––
0.5Pt/SiC (fresh)	0.39	32	0.172	2.2±0.7
0.5Pt/SiC (used)	0.39	28	0.166	2.5±0.8

[a] Determined by ICP-AES; [b] From N_2 adsorption/desorption measurements; [c] From TEM.

Table S3. Linear combination fitting and EXAFS fitting results of Pt L$_{III}$-edge (δ: fitting valence state; ***R***: distance; ***CN***: coordination number; σ^2: Debye–Waller factor; ΔE_0: inner potential correction) of SiC-supported Pt samples.

Catalyst	δ	**Pt-O**		**Pt-Pt**		**Pt-O-Pt**		σ^2 (Å^2)	ΔE_0 (eV)
		***R* (Å)**	***CN***	***R* (Å)**	***CN***	***R* (Å)**	***CN***		
Pt foil	0	—	—	2.766±0.002	12	—	—	0.0044±0.0002	8.4±0.5
PtO$_2$	4	2.009±0.006	6	—	—	—	—	0.004±0.001	15.1±1.1
0.5Pt/SiC -fresh	1.7	2.01±0.01	2.9±0.2	2.79±0.04 3.95±0.04	2.4±0.4 1.2±0.9	3.10±0.04	0.9 ±0.5	0.003(O) 0.0045(Pt)	12.4±1.6
0.5Pt/SiC -used	0.1	—	—	2.76±0.01 3.93±0.02	7.7±0.3 2.4±0.8	—	—		5.6±1.2

References

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2 A. I. Frenkel, Q. Wang, N. Marinkovic, J. G. Chen, L. Barrio, R. Si, A. L. Camara, A. M. Estrella, J. A. Rodriguez and J. C. Hanson, *J. Phys. Chem. C*, 2011, **115**, 17884-17890.