ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Selectivity Boost in Partial Hydrogenation of Acetylene via Atomic Dispersion of Platinum over Ceria

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Synthesis of the catalysts

The flame spray pyrolysis (FSP) samples were produced employing a commercial NPS10 FSP system (Tethis), which is currently available as NPS-20 FSP system (ParteQ GmbH). The NPS10 is a bench top FSP system that allow the production of nanopowders with laboratory mass scale for R&D purposes. Briefly, a liquid solution containing the metal organometallic precursors is injected, by a syringe pump through a stainless-steel capillary, in a nozzle where is dispersed by an oxygen flow. A concentric flameless ring was fed with a premixed mixture of methane/oxygen (CH_4 1.5 L min^{-1}, O_2 3.2 L min^{-1}) for generating the supporting flame. The liquid precursor was fed by a syringe pump with a rate of 3 mL min^{-1}, and was dispersed by 5 mL min^{-1} of oxygen (pressure drop = 1.5 bar). Additional oxygen (5 L min^{-1}) was supplied by an outer sheath flow to assure enough oxidant for complete conversion of the reactants. The powder was collected on a glass fiber filter (GF/A Whatman, Kent), 150 mm in diameter. The filter was placed in a water-cooled holder 400 mm above the nozzle.

The liquid precursor was prepared by dissolving Pt(II)-acetylacetonate (Strem Chem. Inc., 78-1400) in acetonitrile (Sigma Aldrich, 271004) and then put a suitable quantity of the obtained solution into a premixed solution of Ce(III)-2-ethylhexanoate (abcr GmbH, AB110472) in xylene (Carlo Erba Reagents, 492301) forming solutions with wanted Pt and Ce concentration to obtain 0 (**CeO_2**), 0.23 (**0.23%Pt/CeO_2**), 0.5 (**0.5%Pt/CeO_2**)and 5 (**5%Pt/CeO_2**) wt.% loading of Pt onto CeO_2 (Fig. S1).

Catalytic tests

The activities of the catalysts were measured in a downward continuous gas flow reactor connected to online gas chromatograph (GC, Schimadzu GC-2010 plus) for real time activity measurement as we previously reported.[1] The GC injection was set to 20 min intervals. In a typical reaction, certain predetermined amount of catalyst was pressed, crushed, and sieved to obtain particle size range between 180 and 350 μm. The catalyst was mixed with SiC (1 : 100), supported on quartz wool in the glass tube reactor and fitted into the reactor compartment in the furnace.

Helium (He) gas, used as the carrier gas at a flowrate of 50 mL min^{-1}, was passed through the catalyst in the reactor as the reactor temperature reached the catalyst reduction temperatures of 385 and 180 °C for **0.23%Pt/CeO_2** and **5%Pt/CeO_2** catalysts, respectively. The catalysts were kept at that temperature for 20 min to remove strongly bonded moistures and maintain thermal equilibrium. During catalyst activation, a mixture of H_2 (50 mL min^{-1}) and He (20 mL min^{-1}) gases was introduced for 1 h to reduce the PtO to metallic Pt. Prior to the catalytic test, He gas was passed for 20 min at a flow of 50 mL min^{-1} to purge the reaction line. To avoid inadvertent presence of H_2 that may interfere with the accuracy of the baseline, after setting the H_2 flowrate value to 0.0 mL min^{-1} on the digital mass flow controller (MFC), the valve was closed and H_2 line was depressurized to completely drain all the residual H_2 from the line, as monitored on the MFC software. This was followed by passing a mixture of the feed gas (1, 20 and 59 mL min^{-1} of C_2H_2, C_2H_4, and He, respectively) without H_2 for 1 h and the initial GC peaks areas of C_2H_2, C_2H_4, and C_2H_6 were obtained after every 20 min. The peak average areas were recorded as the baseline for evaluation of the amount of C_2H_2

conversion, and C_2H_4 and C_2H_6 for selectivity (Eqs. 1–2). The other products' selectivity and yields were calculated from Eqs. 3–4. Acetylene hydrogenation was conducted under atmospheric pressure with feed gas composition of 1, 20, 20 and 59 mL min^{-1} of C_2H_2, C_2H_4, H_2 and He, respectively.

$$X_{C_2H_2} = \frac{C_2H_2(feed) - C_2H_2}{C_2H_2(feed)} * 100\% \qquad (1)$$

$$S_{C_2H_4} = \left(1 - \frac{\sum P_i}{C_2H_2(feed) - C_2H_2}\right) * 100\% \qquad (2)$$

$$S_i = \left(\frac{P_i}{C_2H_2(feed) - C_2H_2}\right) * 100\% \qquad (3)$$

$$Y_i = S_i * \frac{C_2H_2(feed) - C_2H_2}{C_2H_2(feed)} \qquad (4)$$

P_i refers to other products such as ethane, butane, and butadiene. S_i and Y_i refer to respective product selectivity and yield. Since our electron microscopy results (Figs. 2 and 3) have demonstrated that the Pt nanoclusters agglomerates as temperature rises, after loading the catalyst into the reactor a reverse temperature ramping was employed during activity measurement. That is, the reactor temperature was first increased to the highest reaction temperature of study (after H_2 reduction) and the reaction products were measured as the temperature ramped down at a predetermined programmed rate. In this way, any nefarious effect of Pt nanocluster size variation (i.e., sintering, coalescence) with temperature change was cancelled out.

Characterization

ICP-OES

Chemical analysis was performed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP–OES) methods on an ICPE-9000 spectrometer (Shimadzu). All values are the average of at least three replicates.

XRD

Powder X-ray diffraction (XRD) data were collected on a X'Pert PRO diffractometer (PANalytical) set at 45 kV and 40 mA, and equipped with Cu $K\alpha$ radiation (λ = 1.541874 Å) and a PIXcel detector. Data were collected using Bragg-Brentano geometry in the 20 to 80° 2θ range with a scan speed of 0.01° s^{-1}. The XRD patterns were matched to International Centre for Diffraction Data (ICDD) PDF-4 database using HighScore software package (PANalytical). The XRD results are presented in Fig. S2.

N_2 physisorption

The surface area, pore size, and pore volume of the samples were estimated using the N_2 physisorption at 77 K. The characterization was performed on a Quantachrome Autosorb IQ2 multi-station apparatus. Approximately 300 mg of the sample were placed in the sample holder and outgassed under vacuum at 120 °C for 4 hours before analysis. The specific surface area of the samples was determined according to the Brunauer–Emmett–Teller (BET) method in the range of $0.05 < P/P_0 < 0.3$, the pore size was determined by the Barrett–Joyner–Halenda (BJH) method, and the total pore volume was determined using the amount of N_2 adsorbed at relative pressure $P/P_0 = 0.97$. The estimated textural properties of the catalysts are summarized in Fig. S4 and Table S1.

Electron microscopy

The transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM), energy-dispersive X-ray spectroscopy (EDX) in STEM mode (STEM–EDX) and electron energy-loss spectroscopy (EELS) studies were performed using probe-corrected Titan ChemiSTEM microscope (FEI, Super-X EDX System, Gatan Energy Filter), as well as double-corrected Titan G3 Cubed Themis microscope (FEI, Super-X EDX System, Fast Dual EELS spectrometer), both operated at 200 kV. *In situ* heating TEM experiments were performed using MEMS microheater chip (FEI), while the temperature was controlled by a dual channel source-measure unit Model 2604B (Keithley).

H_2–TPR

The catalysts reduction behavior was performed on an AMIe200 Catalyst Characterization apparatus (Altamira) with a thermal conductivity detector. Typically, 20 mg catalyst was placed in the U-shaped quartz tube. Catalyst samples were degassed under argon flow at 120 °C to remove traces of water and impurities from the catalyst pores. H_2 temperature program reduction (TPR) was performed using 5%H_2/N_2 gas mixture with a flow rate of 20 ml min^{-1} while heating from 40 °C to 990 °C at 5°C min^{-1}.

XPS

The chemical composition of the catalysts surface and metal oxidation states were analyzed by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 Xi system (Thermo Scientific). The samples were scraped onto Al foil and measured using a non-monochromatic Al K_α X-ray source (operating at 400 W) to minimize charging artifacts. Peak fitting was performed in Avantage instrument software (Thermo Scientific), choosing a minimal number of components that produced random residuals consistently for all the samples. A convolution of Gaussian and Lorentzian line shapes was used for most of the spectral components. The binding energy (BE) scale is based on a BE shift (uniformly applied for all the samples) that placed the aliphatic C 1s peak associated with the supported catalyst material to 285.0 ± 0.2 eV.

DRIFT

The DRIFT spectroscopy experiments were carried out using a Cary 680 FTIR spectrometer (Agilent) equipped with a liquid-nitrogen cooled MCT detector at a spectral resolution of 2 cm^{-1} and accumulation of 512 scans using a Praying Mantis™ Low Temperature Reaction Chamber. The samples were activated in flowing H_2 (71% in Ar, 35 ml min^{-1}) at 453 K with a heating rate of 10 K min^{-1} followed by evacuation at 313 K. CO was adsorbed at 77 K increasing the equilibrium pressure up to 60 hPa. After reaching 40 hPa, the gas phase was desorbed under dynamic vacuum at 77 K. All CO adsorption spectra were recorded at 77 K with a background spectrum of the sample after treatment without adsorbed CO.

Figures

Fig. S1 Image showing color change as a function of Pt loading for the catalysts as-synthesized by FSP.

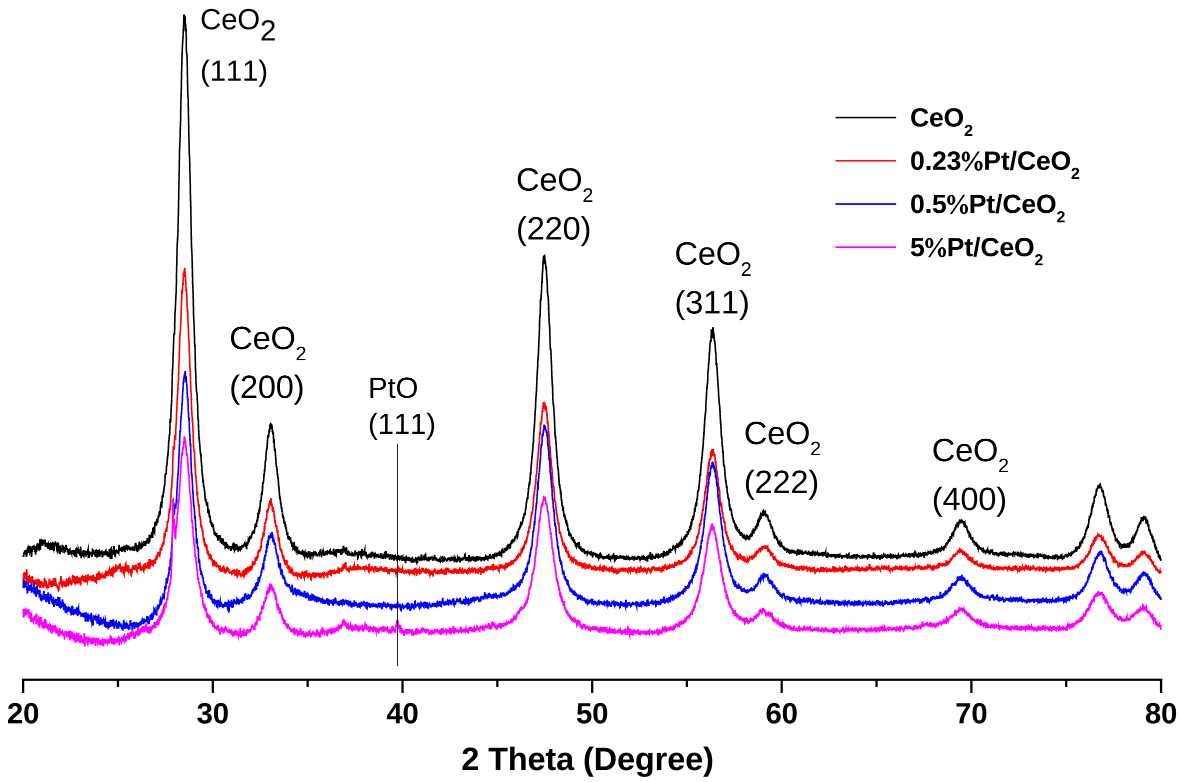

Fig. S2 Comparison of XRD patterns for **CeO_2**, **0.23%Pt/CeO_2**, **0.5%Pt/CeO_2** and **5%Pt/CeO_2** as-synthesized by FSP.

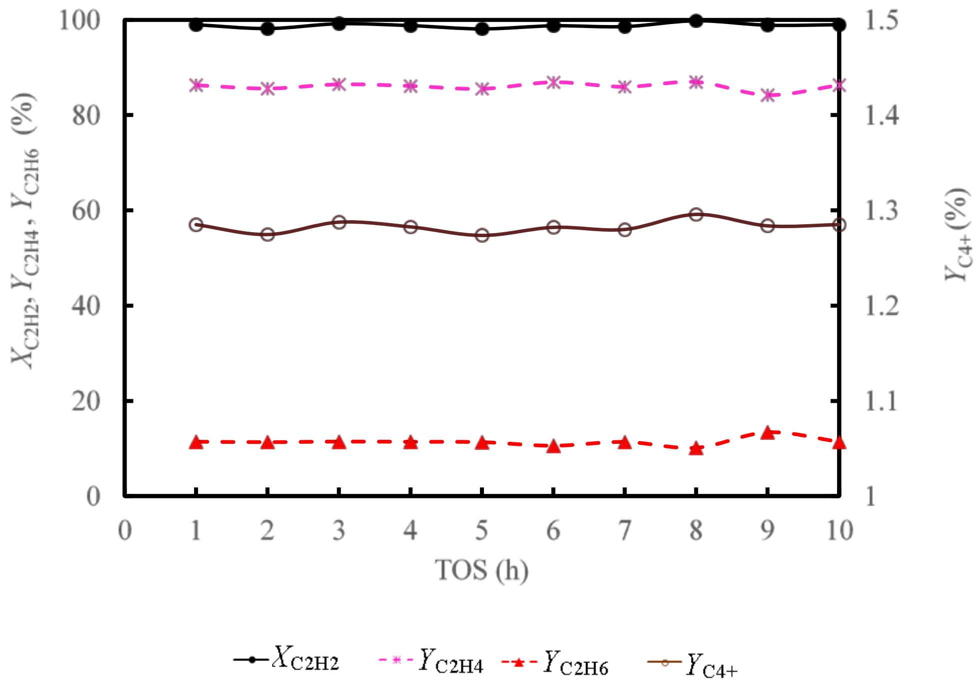

Fig. S3 TOS results for **0.23%Pt/CeO2** at 180 °C. Feed stream: 1, 20, 20 and 59 mL min^{-1} of C_2H_2, C_2H_4, H_2 and He, respectively.

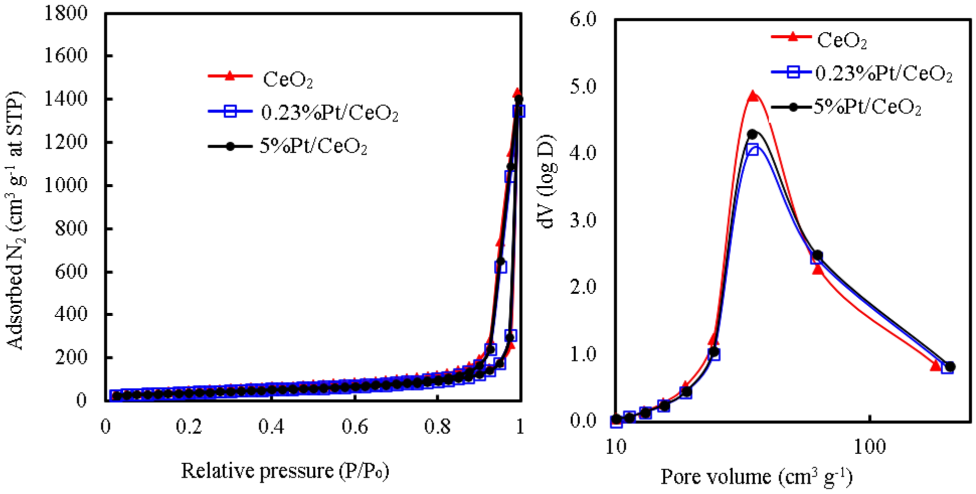

Fig. S4 Comparison of textural properties for **CeO_2, 0.23%Pt/CeO_2** and **5%Pt/CeO_2** as-synthesized by FSP.

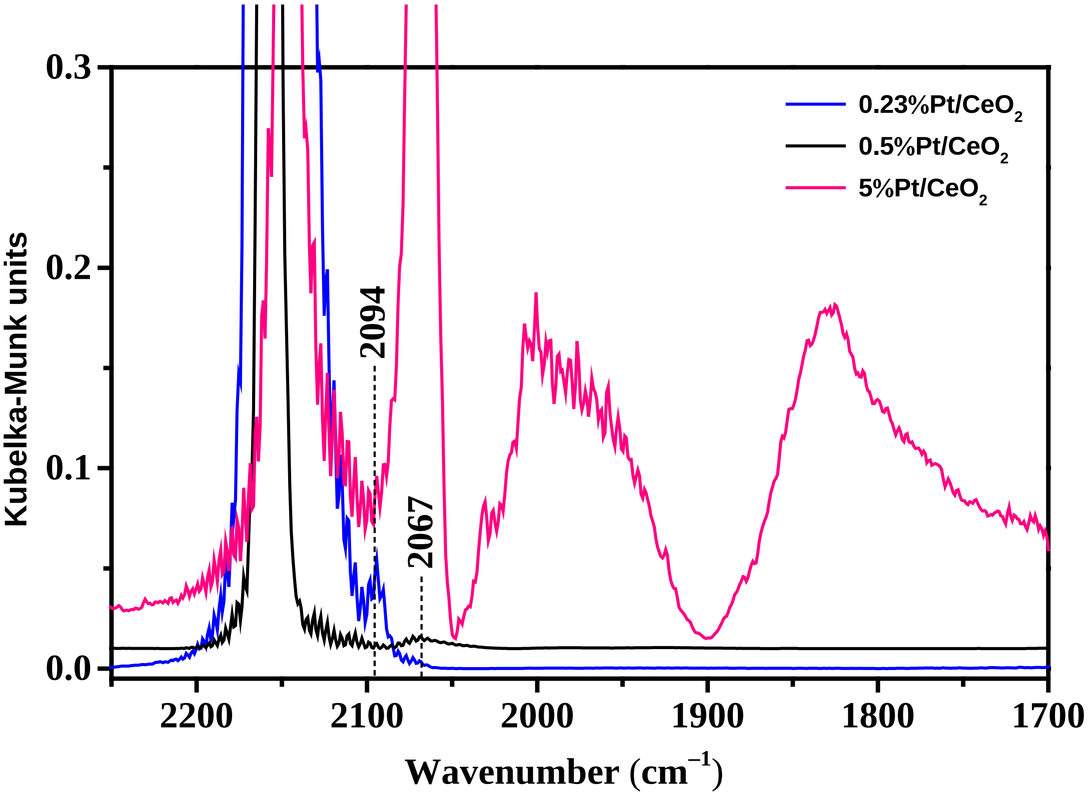

Fig. S5 Comparison of DRIFT spectra of CO adsorption over **0.23%Pt/CeO_2**, **0.5%Pt/CeO_2** and **5%Pt/CeO_2** catalysts.

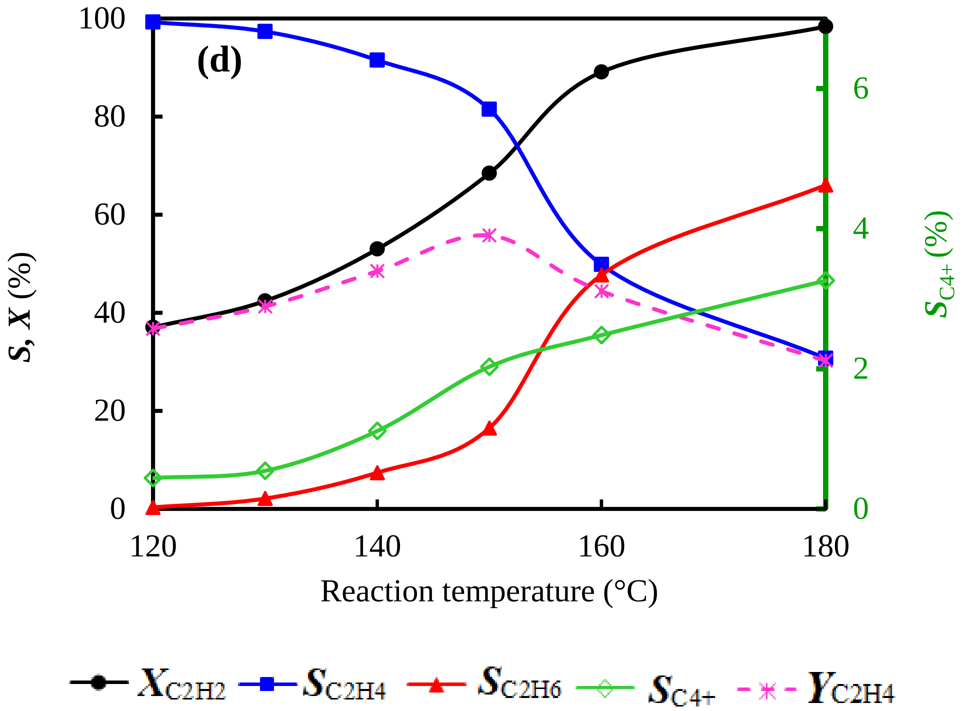

Fig. S6. Catalytic properties of **0.5%Pt/CeO$_2$** as a function of reaction temperature. Feed stream: 1, 20, 20 and 59 mL min^{-1} of C_2H_2, C_2H_4, H_2 and He, respectively. Space velocity: 630 000 mL g^{-1} h^{-1}.

Tables

Table S1. Ethylene selectivity at best acetylene conversions over various state-of-the-art catalysts.

Catalyst	***T*** **(°C)**	**Feed composition (vol.%)**			***X*** $_{C2H2}$ **%**	***S*** $_{C2H4}$ **%**	**Space velocity of (mL g^{-1} h^{-1})**	**Ref.**
		C_2H_2	**H_2**	**C_2H_4**				
Pd_2Ga	200	0.5	5	50	95	75	180,000	[2]
$AgPd_{0.01}/SiO_2$	160	1.0	20	20	67	87	240,000	[3]
$AgPd_{0.01}/SiO_2$	320	1.0	20	20	>90	>80	240,000	[3]
1%Pd/ZnO	60	2.0	20	40	54	88	180,000	[4]
1%Pd/ZnO	80	2.0	20	40	92	89	180,000	[4]
1%Pd/ZnO	150	2.0	20	40	100	91	180,000	[4]
1%Pd/ZnO	150	2.0	20	40	97	97	540,000	[4]
$PtCu/Al_2O_3$	260	1.0	12	20	98	74	540,000	[1]
$PtCu/Al_2O_3$	150	1.0	10	20	67	85	540,000	[1]
$AuPd–P/TiO_2$	200	1.0	3	96	60	88	63,000	[5]
$1\%Pd_4S/CNF$	250	0.6	3	5.4	100	74	480,000	[6]
$1\%Pd_4S/CNF$	250	0.6	2	5.4	100	82	480,000	[6]
$Ni_{10}In/SiO_2$	180	1.0	5.0	–	100	61	36,000	[7]
nPdAg/$Mg_{0.5}Ti_{0.5}O_y$	65	0.33	0.66–2.64	32.8	93	>85	10,050	[8]
$CuPd_{0.006}/SiO_2$	160	1.0	20	20	100	85	60,000	[9]
1.42%PdAg/NiTi–LDH	90	0.967	0.6	34.33	90	82	10,050	[10]
$1.44\%PdAg/TiO_2$	90	0.967	0.6	34.33	90	75	10,050	[10]
$0.23\%Pt/CeO_2$	180	1.0	20	20	≈99	87.17	630,000	This work

Table S2. Pt loading and textural properties of the synthesized materials.

Sample	**Pt loading (wt.%)**		**BET surface area (m^2 g^{-1})**	**Average pore size (nm)**	**Pore volume (cm^3 g^{-1})**
	Nominal	**Actual***			
Pure CeO_2	0.00	0.00	142	34.498	2.20
$0.23\%Pt/CeO_2$	0.23	0.27	144	34.490	2.11
$5.0\%Pt/CeO_2$	5.00	4.83	159	34.594	2.24

* Estimated by ICP–OES measurements.

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