Revealing the Size Effect of P-Coated Carbon-Supported Palladium Nanoparticles in Complete Hydrodeoxygenation of Biobased Aromatic Alcohols

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Text S*. EXPERIMENTAL SECTION

Text S1. Catalysts preparation

Text S1.1. Controllable preparation of 2-7 nm Pd nanoparticles

Preparation of AC-P matrix. A controlled phosphoric acid activation process was performed by reflux-assisted polycondensation in 85 wt% H_3PO_4 aqueous solution at 343±1 K for 4 h under N_2 atmosphere (flow rate: 50 mL/min), during which phosphoric acid polymerizes on the surface of the carbon matrix. The viscous product was then transferred to a centrifuge (8000 rpm) for precisely 5 min, yielding a activated carbon precursor with homogeneous acid distribution, and named AC-P matrix.

Controllable preparation of 2-7 nm Pd nanoparticles. Pd nanoparticles with precisely controlled diameters (2.2-7.2 nm) were synthesized via a polyol reduction method with polyvinylpyrrolidone (PVP) as the stabilizing agent. In a standard procedure (4.7 nm), 40 mg of PVP (K29-32, average molecular weight 58000) was dissolved in 2 mL of ethylene glycol under vigorous stirring (800 rpm) in an oil bath preheated to 160 °C. After 10 min of thermal equilibration, 1 mL of Na_2PdCl_4 ethylene glycol solution (16 mg/mL) was rapidly injected into the reaction mixture. The system was maintained at 160 °C for 1 h to ensure complete reduction of Pd^{2+} ions. The reaction was quenched by immediate immersion in an ice bath, followed by repeated washing with acetone and deionized water (5×20 ml each) until PVP residues were undetectable by TEM analysis. The purified Pd nanoparticles were redispersed in 10 mL of ethanol via 30 min ultrasonication (40 kHz, 100 W) to form a homogeneous colloidal suspension.

Particle size modulation was achieved by varying the PVP/Pd molar ratio and precursor concentration: 2.2 nm NPs: 1600 mg PVP (PVP/Pd = 120:1 molar ratio), 3.2 nm NPs: 200 mg PVP (PVP/Pd = 15:1) + 16 mg Na_2PdCl_4, 7.2 nm NPs: 200 mg PVP (PVP/Pd = 15:1) + 80 mg Na_2PdCl_4 (5×precursor concentration).

Text S2.2. Characterization Methods

Powder X-ray diffraction (XRD) was performed using a Netherlands PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.54050 Å).

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted on a JEOL JEM-2100F microscope operated at an accelerating voltage of 200 kV. The Pd content was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). Nitrogen physisorption measurements were carried out at 77 K using a Micromeritics ASAP 2020 PLUS analyzer to determine the Brunauer-Emmett-Teller (BET) surface area and pore volume. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi system, with the C 1s peak of adventitious carbon (284.8 eV) serving as the reference for binding energy calibration. Fourier transform infrared (FTIR) spectroscopy analyse were conducted on a Nicolet Nexus 110W (±5V/±12V) spectrometer. Prior to analysis, all samples were pretreated at 80 °C for 8 h, and measurements were taken using identical amounts of KBr and sample for consistency. For temperature-programmed reduction (TPR), 50 mg of the sample was pretreated at 100 °C under an Ar flow (27 mL·min^{-1}) for 1 h, followed by heating to 900 °C at a ramp rate of 10 °C·min^{-1} in a 10 vol% H_2/Ar mixture (30 mL·min^{-1}, H_2:Ar = 1:9). In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted on a Thermo Scientific IS50 spectrometer equipped with a CRCP-7070 in situ reaction cell. Approximately 10 mg of the catalyst was finely ground and diluted with KBr at a weight ratio of 1:100. The sample was pretreated under a He flow (30 mL min^{-1}) at 80 °C for 1 h to remove adsorbed contaminants. After cooling to room temperature, a background spectrum was collected. The reactant was introduced via a micro-syringe injection of 20 μL into a vaporizer maintained at 200 °C, carried by the He flow (30 mL min^{-1}) over the catalyst bed. Spectra were recorded thereafter to monitor the surface species.

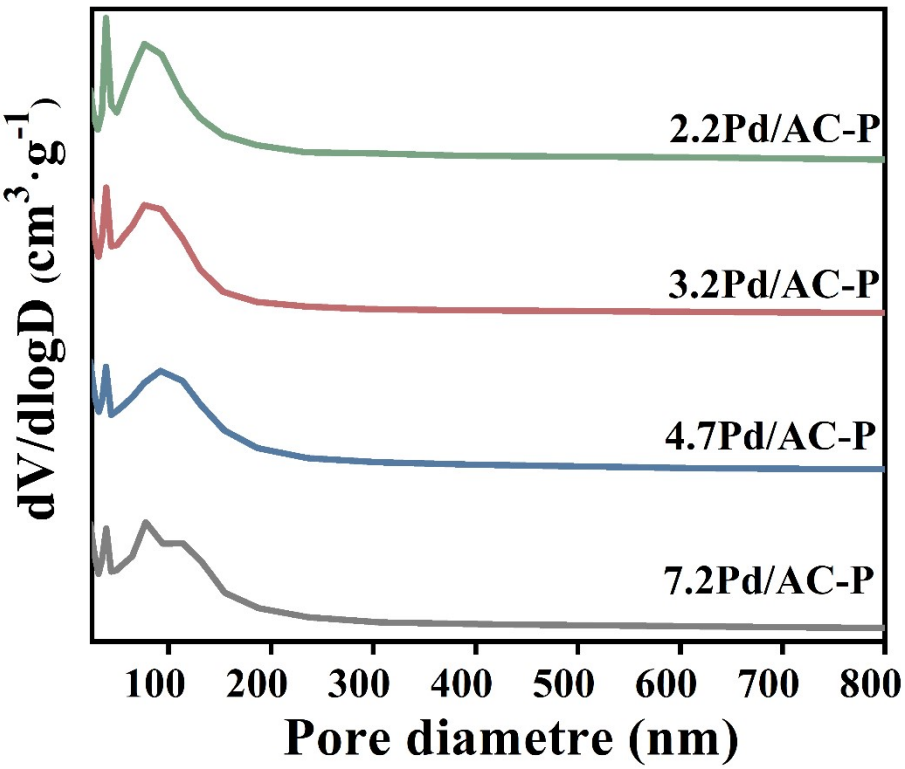

Figure S1 Brunauer-Emmett-Teller (BET) nitrogen sorption isotherms of *x*Pd/AC-P catalysts at 77 K.

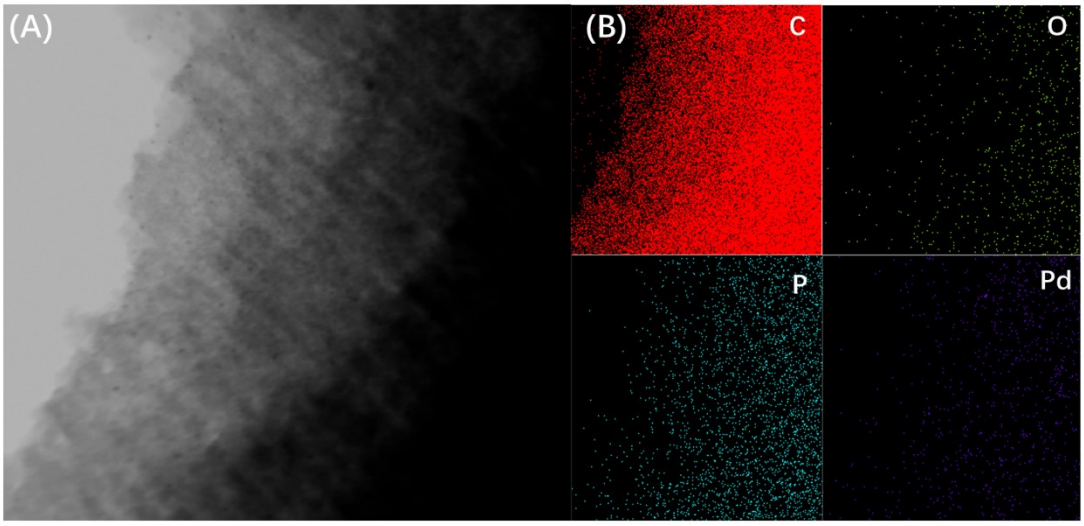

Figure S2 (A) TEM and (B) Mapping images of the C, O, P and Pd elements of 2.2Pd/AC-P catalyst.

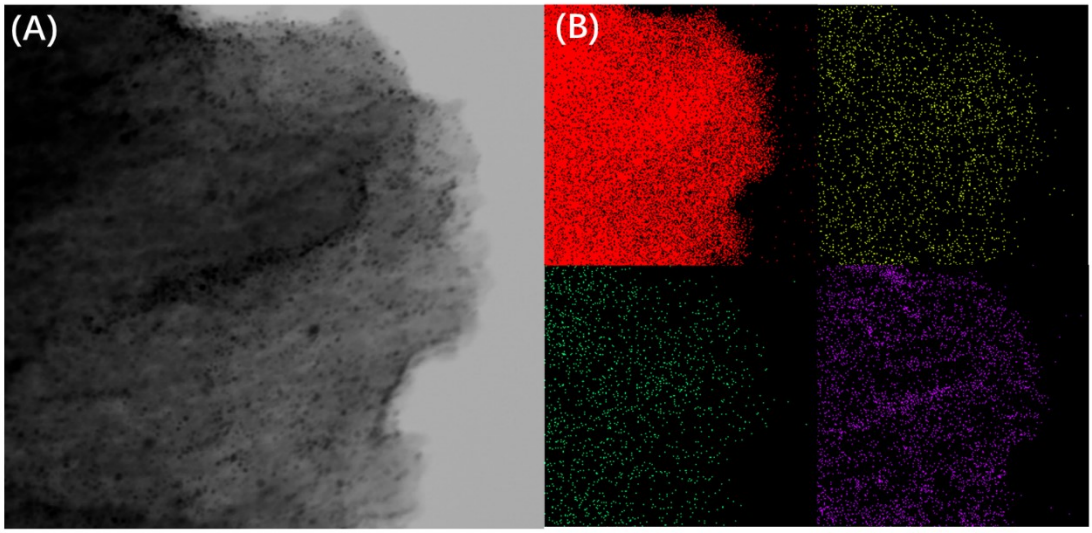

Figure S3 (A) TEM and (B) Mapping images of the C, O, P and Pd elements of 3.2Pd/AC-P catalyst.

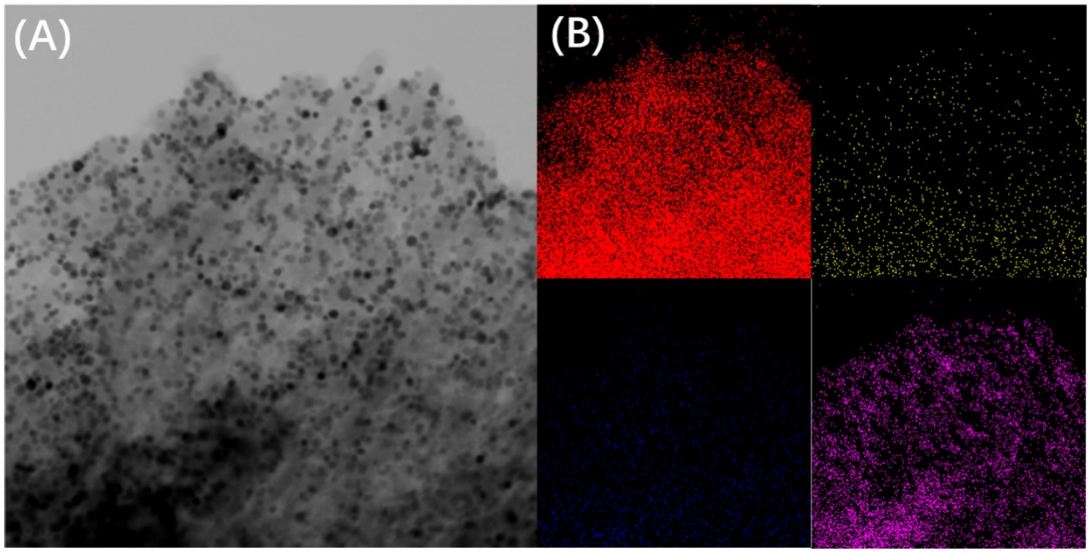

Figure S4 (A) TEM and (B) Mapping images of the C, O, P and Pd elements of 4.7Pd/AC-P catalyst.

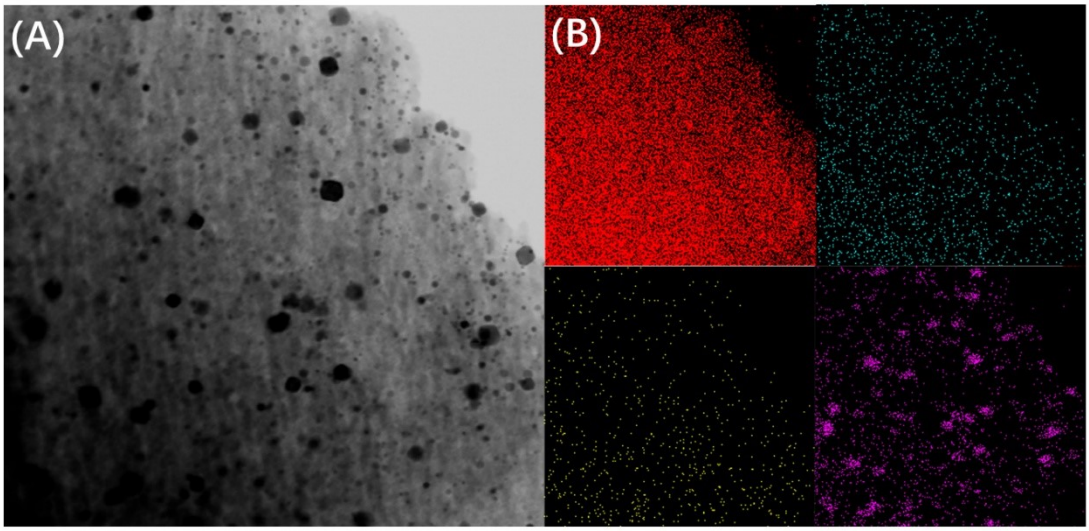

Figure S5 (A) TEM and (B) Mapping images of the C, O, P and Pd elements of 7.2Pd/AC-P catalyst.

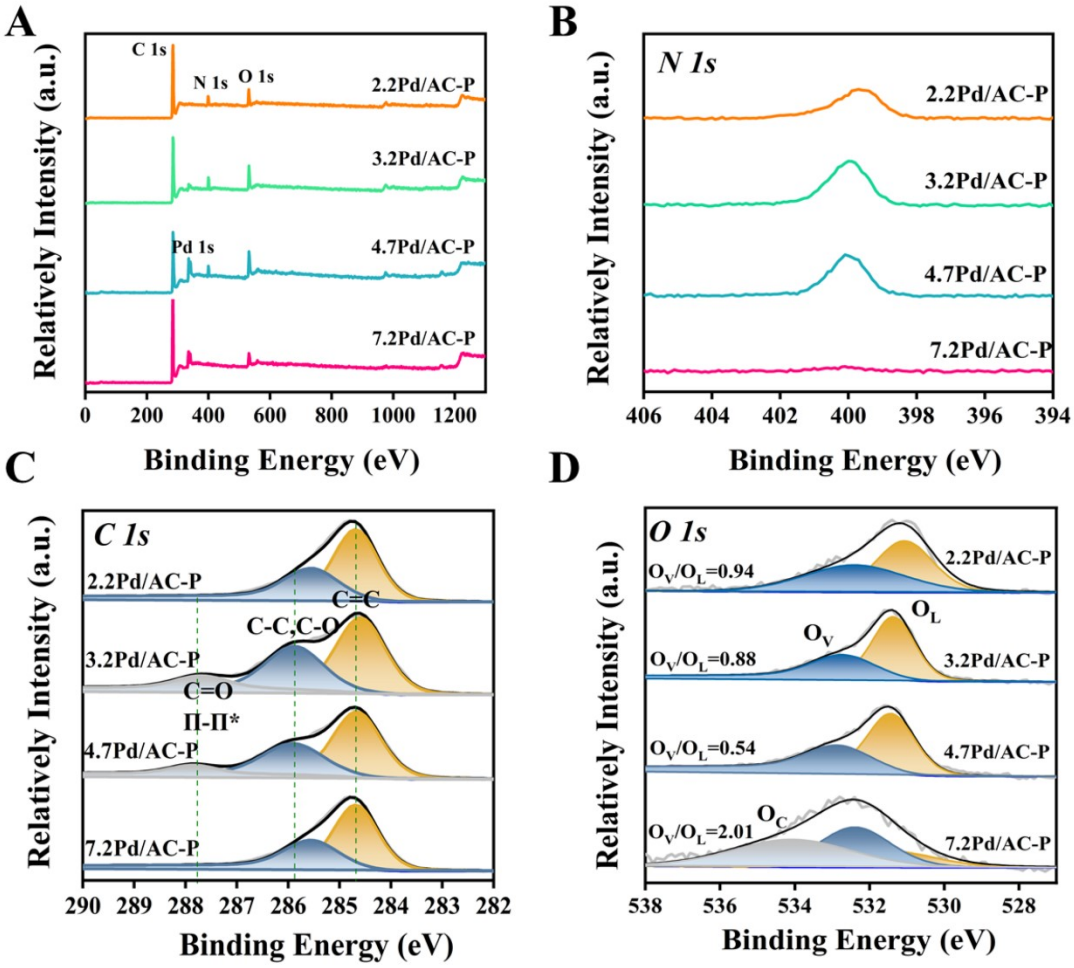

Figure S6 The full (a) and high resolution XPS spectra: (b) N 1s, (c) C 1s and (d) O 1s of the *x*Pd/AC-P catalysts.

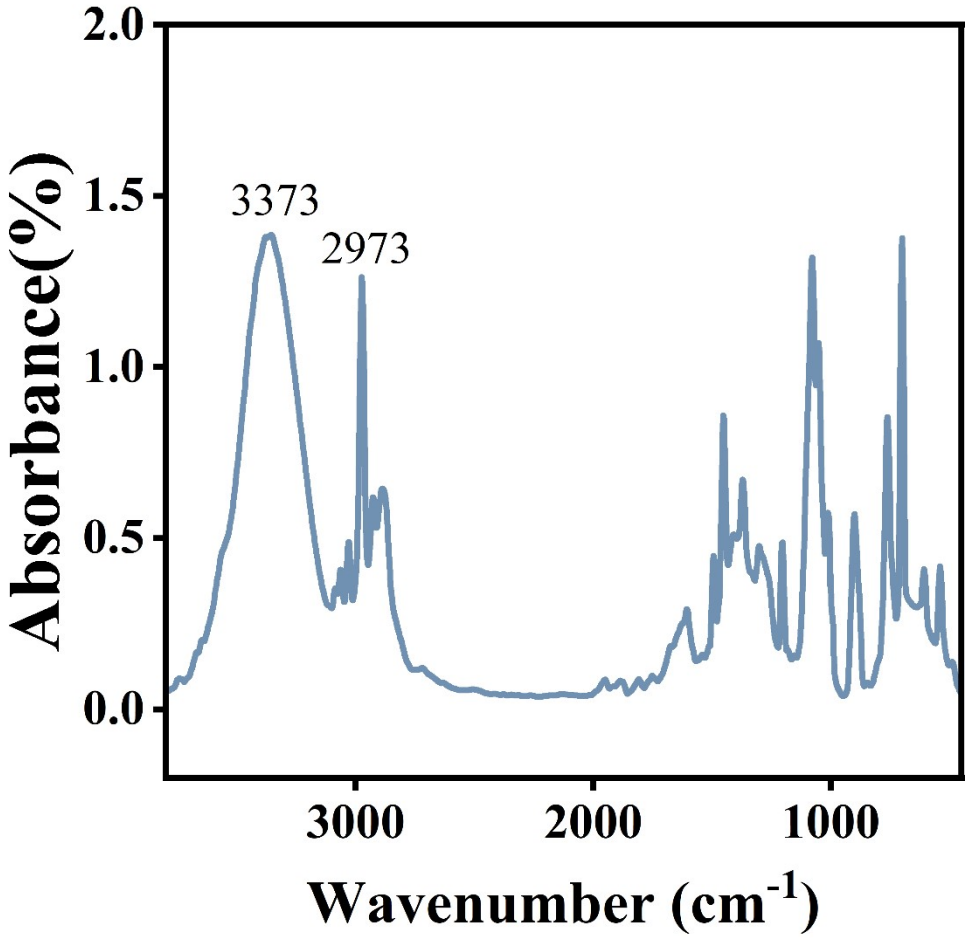

Figure S7 The IR spectra of PE.

1/T (*10^{-3})	2.2Pd/AC-P	3.2Pd/AC-P	4.7Pd/AC-P	7.2Pd/AC-P
3.36				8.0%, 120 min
3.19	20.93%, 40 min, -5.10	7.89%, 20 min -5.49	27.47%, 90 min -5.63	
3.00	25.01%, 10 min, -3.55	4%, 10 min -5.50	11.17%, 10 min -2.18	13.42%, 10 min
2.83		30.78%, 10 min, -1.93	23.11%, 10 min -3.63	42.67%, 20 min
2.68			46.83%, 5 min 35.92%, 20 min	