Supporting Information

Interaction between Pt nanoparticles and bamboo charcoal support regulates hydrodeoxygenation of 5-hydroxymethylfurfural under mild conditions

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Experimental Section

Material

$H_2PtCl_6 \cdot 6H_2O$,$NaBH_4$,5-Hydroxymethylfurfural, (5-Methyl-2-furyl)Methanol, 5-Methyl furfural, purchased from Adamas Reagents Co., Ltd. Sulfuric acid (98%), hydrogen peroxide (30%), acetic acid, methanol purchased from Sinopharm Chemical Reagent Co., Ltd. Bamboo was sourced from Southwest Forestry University.

Catalyst preparation

Place 60.0 g of bamboo chips in a conical flask. Add 250 mL acetic acid, 250 mL hydrogen peroxide (30%), and 1 mL sulfuric acid (98%). Subsequently, place the conical flask in an oil bath at 65°C and heat for 48 h. Remove the delignified bamboo chips and rinse with deionized water until neutral pH is achieved. Dry in a 60°C oven for 12 h to obtain bamboo cellulose. Weigh 3.0 g of bamboo cellulose and calcine at 900°C for 4 h using a biomass pyrolysis furnace. Cool to room temperature and grind into powder to obtain the BC support.

Weigh 0.3 g of BC-900 into a 50 mL beaker, add 30 mL of deionized water, and stir for 30 min to uniformly disperse the bamboo charcoal, yielding Solution A. Separately weigh $H_2PtCl_6 \cdot 6H_2O$ corresponding to 0.5 wt%, 1 wt%, and 2 wt% (Pt content) into 25 mL beakers, add 15 mL deionized water to obtain Solution B. Slowly add Solution B to Solution A while stirring for 4 h. Then slowly add 20 mL of 0.5 mol/L $NaBH_4$ solution to the mixture while stirring for 4 h. After stirring, filter using a sand core filtration apparatus. Place the resulting solid in a vacuum drying oven and dry at 60°C for 12 h to obtain $Pt_{0.5}$/BC-900, Pt_1/BC-900, and Pt_2/BC-900.

Evaluation method of catalytic performance

HDO of HMF was conducted in a high-pressure reactor equipped with a magnetic stirrer and temperature controller. The catalyst (25 mg), HMF (1 mmol), and methanol (8 mL) were placed into the high-pressure reactor. The reactor was purged five times with H_2 before pressurizing to 2 MPa. Reaction parameters (reaction time and temperature) were set, with a stirring speed of 800 rpm.

After the reaction, the catalyst was filtered and recovered for reuse in subsequent experiments. The reaction mixture was analyzed by gas chromatography-mass spectrometry (GC-MS) for substance identification, employing an Agilent GC-7890A gas chromatograph (USA) with FID detection. The conversion rate of reactants and the selectivity of products were calculated using the internal standard method. The formulas for conversion (%) and selectivity (%) are as follows:

$$\text{Conversion}_{\text{HMF}}\,(\%) = \frac{\text{Mole of HMF converted}}{\text{Mole of HMF loaded}} \times 100\%$$

$$\text{Selectivity}_{\text{DMF}}\,(\%) = \frac{\text{Mole of DMF produced}}{\text{Mole of product produced}} \times 100\%$$

n_{HMF} denotes the initial molar quantity of HMF, C_{HMF} represents the conversionof HMF, S_{DMF} indicates the selectivity for 2,5-dimethylfuran, and n_{Pt} signifies the molar quantity of Pt in the catalyst.

Characterization method

Transmission electron microscopy (TEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and EDS mapping were performed on a FEI Talos F200X (USA) instrument.

Powder X-ray diffraction (XRD) spectra of the catalyst were collected using Cu-Kα radiation (40 kV and 40 mA) on a Rigaku Ultima X-ray diffractometer (Japan). X-ray photoelectron spectroscopy (XPS) of the catalyst was measured using an XPS instrument (Japan) equipped with a PHI 5000 Versaprobe II X-ray source. Raman spectra in the range of 100–3000 cm^{-1} were recorded using a Renishaw inVia spectrometer (UK) with a 532 nm laser. EPR spectra were acquired using a Bruker EMXplus-6/1 spectrometer (Germany). Nitrogen adsorption-desorption tests were conducted at 77 K liquid nitrogen using a Micromeritics ASAP 2460 fully automated specific surface area and pore size analyzer (USA) to record the specific surface area, pore volume, and pore size distribution of the catalyst and support. Pt content in the catalyst was determined using an Agilent 5110 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Changes in adsorption models on the catalyst were observed via in situ CO-FTIR on a Bruker VERTEX 80v infrared spectrometer (Germany).

Calculation method

All density functional theory (DFT) calculations were performed using the Vienna Aerosimulation Package (VASP) tool . The exchange-correlation functional uses the Perdew-Burke-Ernsthof (PBE) functional within the generalized gradient approximation (GGA) framework. In the calculations, the cutoff energy for the plane-wave basis set was set to 400 eV. To assure computational accuracy and efficiency, the K-point sampling in the Brillouin zone (BZ) uses a Gamma-centered 3×3×1 grid with a convergence threshold below -0.03 eV·Å-1. A 15 Å vacuum layer was employed to limit interactions between thin layers. The adsorption energy (Eads) was defined by the following formula:

$$E_{ads} = E_{total} - (E_{slab} + E_g)$$

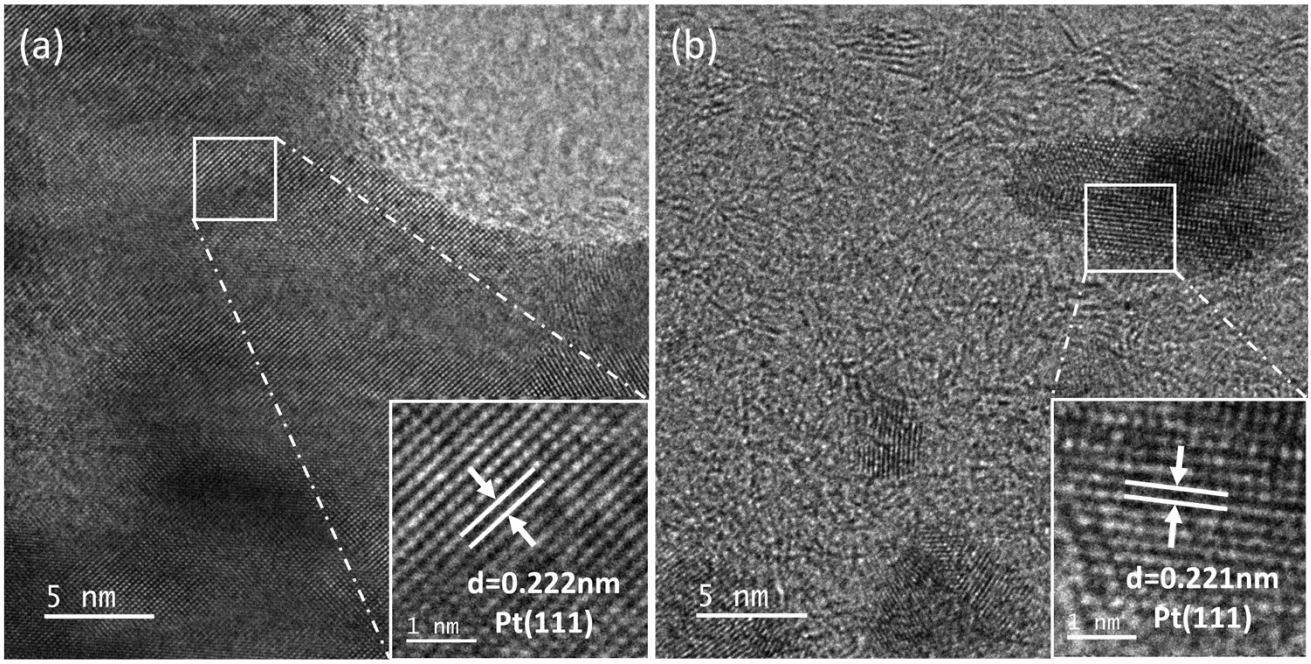

Fig. S1 (a-b) HR-TEM image of Pt_x/BC.(a: $Pt_{0.5}$/BC, b: Pt_2/BC)

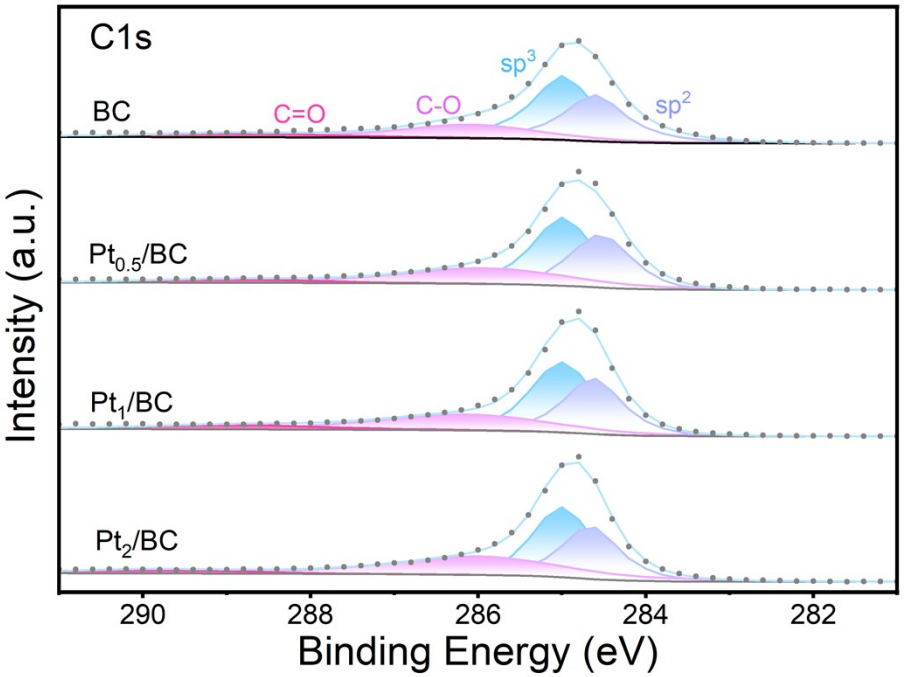

Fig. S2 C1s XPS spectra of Pt_x/BC.

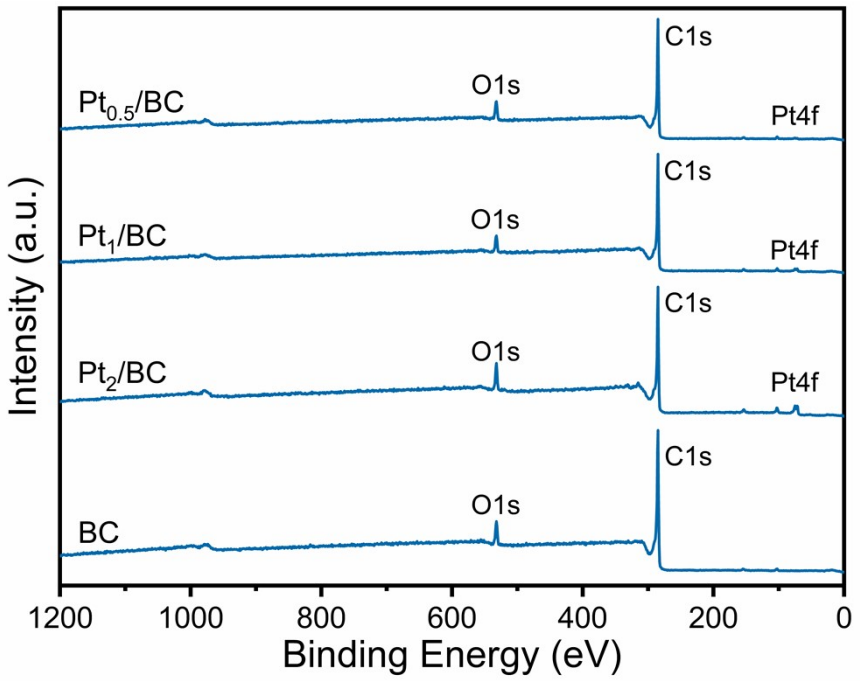

Fig. S3 XPS survey spectra of Pt_x/BC.

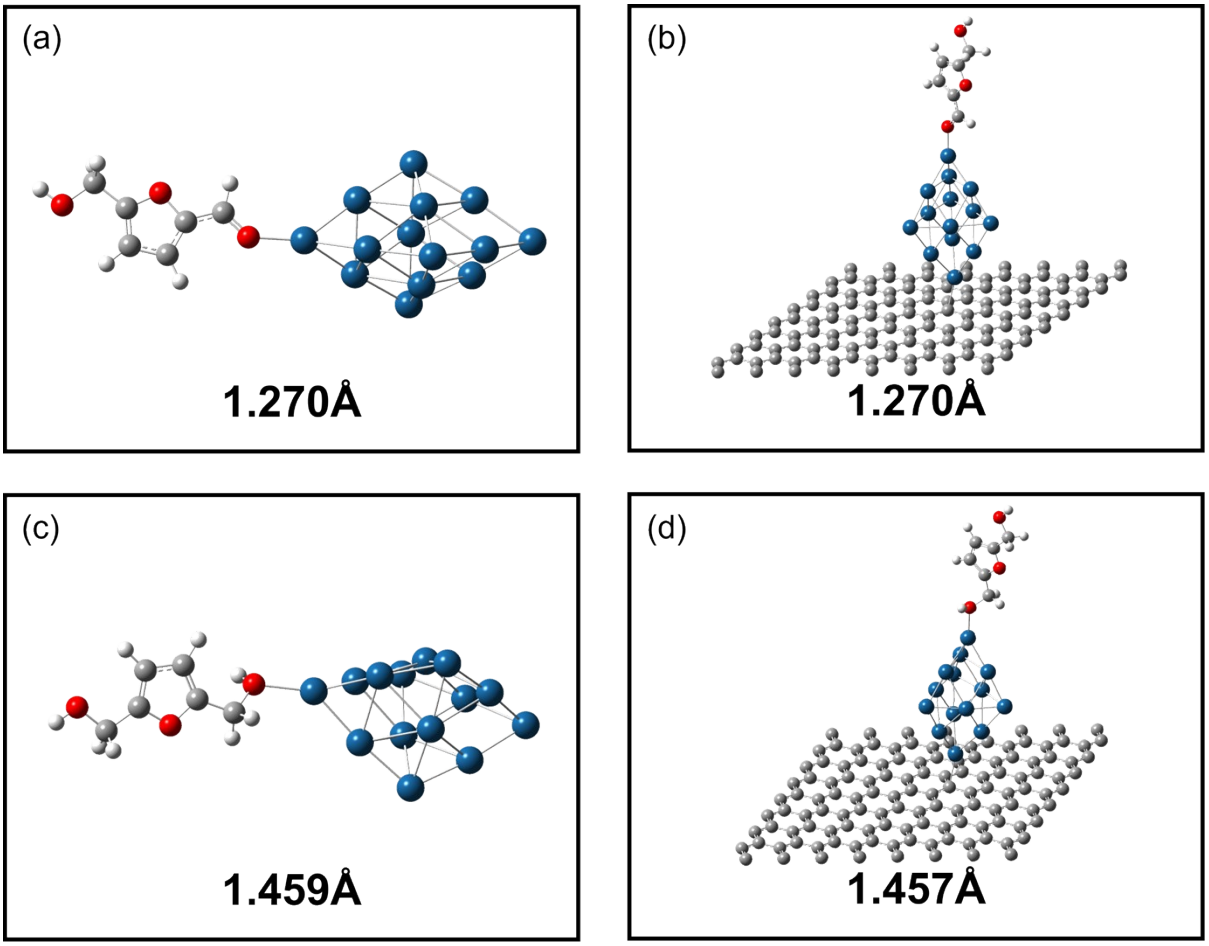

Fig. S4 (a-d) Adsorption of HMF and BHMF on Pt sites of Pt and Pt_1/BC (white: H, gray: C, red: O, blue: Pt).

Table S1 N_2 adsorption/desorption pore size data and metal loading of Pt_x/BC

Sample	S_{BET} (m^2 g^{-1})	Pore Size (nm)	Pore Volume (cm^3 g^{-1})	Ave. Size (nm)	Pt (wt%)	Pt^0 (%)
BC	1782.64	4.044	0.85	-	-	-
$Pt_{0.5}$/BC	1726.72	3.92	0.77	2.50	0.40	72.01
Pt_1/BC	1726.13	3.93	0.80	2.83	0.72	76.41
Pt_2/BC	1490.82	4.08	0.68	3.74	1.50	81.88