Atomically Precise Pd_n Nanoclusters with Bidentate Phosphine Ligands for the Selective Hydrogenation of 5-Hydroxymethylfurfural

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Experimental section

Synthesis of Pd_n nanoclusters and Pd_n/C catalysts

$(NH_4)_2PdCl_4$ (28.4 mg, 0.100 mmol) was dissolved in 5 mL H_2O and 10 mL CH_2Cl_2, and the aqueous phase turns yellow. TOAB (68.3 mg, 0.125 mml) was added to transfer Pd^{2+} from aqueous to organic phase and the water was removed after 10 minutes. And then, bis(2-(diphenylphosphino)phenyl) ether (53.8 mg, 0.100 mmol) was added and the red solution turns yellow, indicating the combination of Pd and ligands. After 1 hour, 3 mL water with $NaBH_4$ (38.0 mg, 1.000 mmol) was poured into the bottles and the solution turns crimson immediately. The reaction should proceed about 48 h at room temperature. The mixture was dried by vacuum rotary evaporator and washed with large amounts of methanol and toluene. And the final products were obtained by dichloromethane extracting. Finally, 9.1 mg Pd_n nanoclusters were dissolved in 30 mL dichloromethane and mixed up with 600.0 mg AC with 3 h stirring. The catalysts dried at 80 °C for 12 h.

Synthesis of Pd-PPh$_3$ catalysts

All the details are the same as Pd_n nanoclusters except the ligands was triphenylphosphine (52.4 mg, 0.200 mmol).

Synthesis of Pd/C, Pd/C-TOAB, Pd/C-DPEphos and Pd-TOAB-DPEphos catalysts

Pd/C was prepared by wet impregnation process followed by H_2 reduction. 6.9 mg $(NH_4)_2PdCl_4$ was dissolved in 10 mL H_2O and 500 mg AC was added with 6 h stirring. The catalyst was dried at 343 K in air overnight, reduced under a flowing hydrogen at 533 K for 6 h (with a heating rate of 2 K/min). The other catalysts were obtained by **Pd/C** treated with different reagents.[1]

Pd/C-TOAB: 500 mg **Pd/C** dispersed in 20 mL ethanol and 5 mL dichloromethane and mixed up with 65.0 mg TOAB. After string for 5 h, the mixture was centrifuged and dried at 80 °C for 12 h.

Pd/C-DPEphos: 500 mg **Pd/C** dispersed in 20 mL ethanol and 5 mL dichloromethane and mixed up with 62.7 mg Bis(2-(diphenylphosphino)phenyl) Ether. After string for 5 h, the mixture was centrifuged and dried at 80 °C for 12 h.

Pd-TOAB-DPEphos: 500 mg **Pd/C** dispersed in 20 mL ethanol and 5 mL dichloromethane and mixed up with 65.0 mg TOAB and 62.7 mg Bis(2-(diphenylphosphino)phenyl) Ether. After string for 5 h, the mixture was centrifuged and dried at 80 °C for 12 h.

Catalytical test

The catalyst test was conducted in the autoclave, and the conversion and yield were obtained by internal standard method. The dodecane was chosen as internal standard substance. Approximately 20.0 mg catalyst and 10 mL mixture (1000.0 mg 5-HMF dissolved in a 100 mL volumetric flask with solvents) were placed into a 25 mL autoclave. The system was purged with H_2 flow to remove air, and then pressurized by 2.0 MPa H_2. After reaction, the product mixture was analyzed by gas chromatography. The products were further confirmed by gas chromatography-mass spectrometry.

$$Conversion\ of\ HMF(\%) = \frac{moles\ of\ converted\ HMF}{initial\ moles\ of\ HMF} * 100\%$$

$$Selectivity\ of\ products(\%) = \frac{moles\ of\ products}{moles\ of\ converted\ HMF} * 100\%$$

In the recycle experiments, the catalyst was separated from solution by filtrate through a Nylon membrane (Φ50mm×0.2 μm). The catalyst was washed by ethanol for several times, and then dried at 353 K overnight. The recovered catalyst was used for the next cycle.

Characterization

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

The concentration of palladium was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) on a PerkinElmer ICP-OES 7300DV.

Electrospray ionization mass spectrometry (ESI-MS)

The ESI-MS spectrum of the Pd_n nanocluster was tested by Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (SolariX XR-15T) and, the nanocluster was dissolved in dichloromethane. A drop of solvents was added in a mixture of CH_2Cl_2 and methanol (v: v= 1:1).

Transmission Electron Microscope (TEM) and HAADF-STEM

The TEM was performed on a JSM 7800F transmission electron microscope and the HAADF-STEM was performed on an ARM 200F high-solution transmission electron

microscope under low temperature by the liquid nitrogen. The samples were prepared by dropping an ethanol dispersion of samples onto carbon-coated copper grids and immediately evaporating the solvent.

X-ray photoelectron spectroscopy (XPS)

XPS data were recorded on a Thermofisher Escalab 250 Xi+ spectrometer using a standard Al Kα mono-chromated flood source (150 W, pass energy = 200 eV, spot size = 500 μm). All binding energies were referenced to C1s peak at 284.8 eV.

Attenuated Total Refraction (ATR)

The ATR data were collected at Bruker's Platinum ATR.

Thermogravimetric Analysis (TGA)

TGA data were collected on Mettler Toledo TGA 2 (SF) thermal analyzers heated from room temperature to 600 °C at a rate of 10 K min−1 in N_2.

Gas chromatograph- mass spectrometer (GC-MS)

The hydrogenation products are analyzed by the Agilent GC-MS and GC (7890B) equipped with DB-35MS capillary column.

Density functional theory (DFT) calculations

All electronic calculations were performed using the Gaussian 16 program package.[2] The geometric optimization, frequency, energies calculations of all structures were carried out using B3LYP function[3-5] with Grimme's dispersion correction[6] and def2-SVP basis set[7]. All minima exhibited no imaginary vibrational frequencies, and the energies were corrected by the zero-point energy (ZPE).
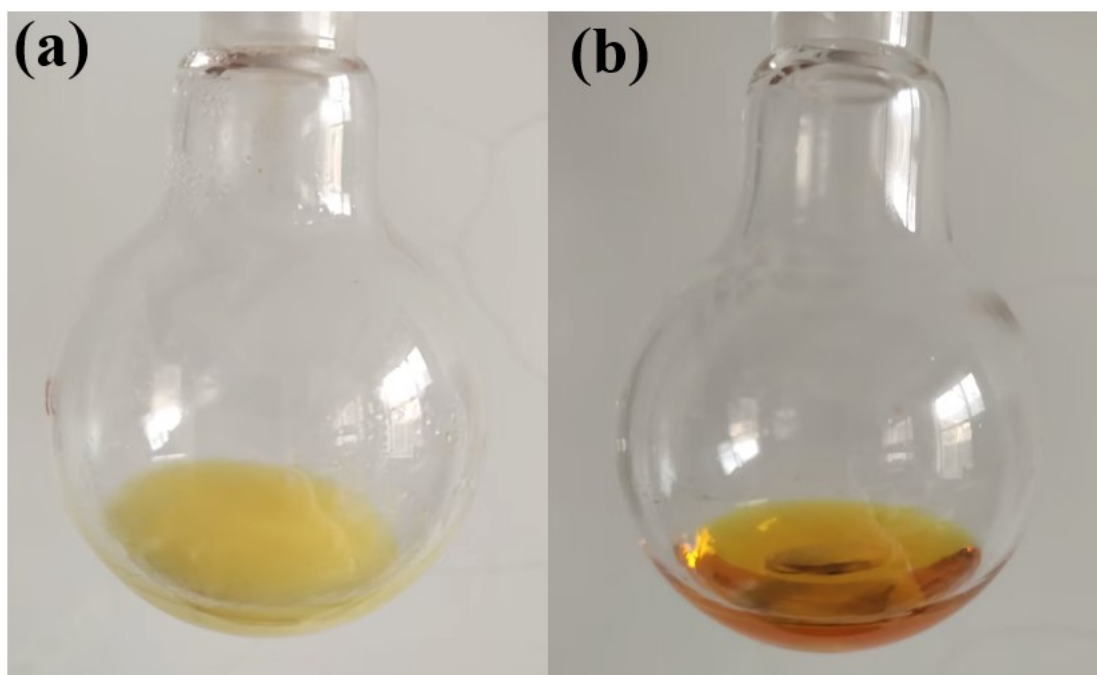
Figure S1. The state of intermediate in the synthesis of (a) Pd-PPh$_3$ and (b) Pd$_n$-DPEphos.
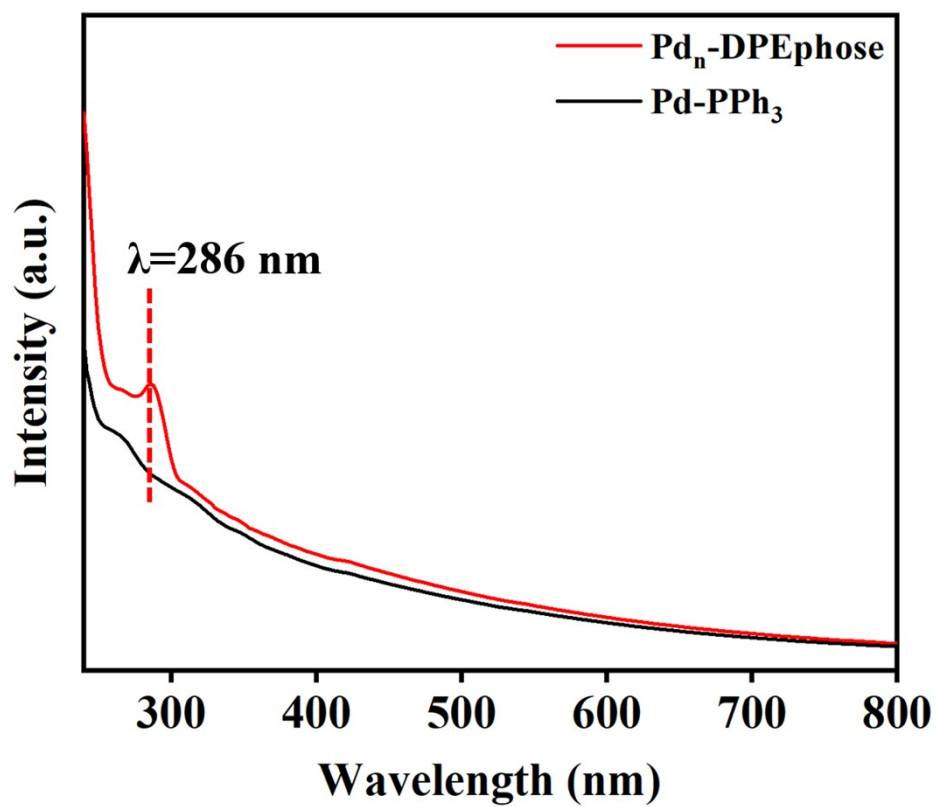
Figure S2. The Uv-vis of Pd-DPEphos (red line) and Pd-PPh$_3$ (black line).
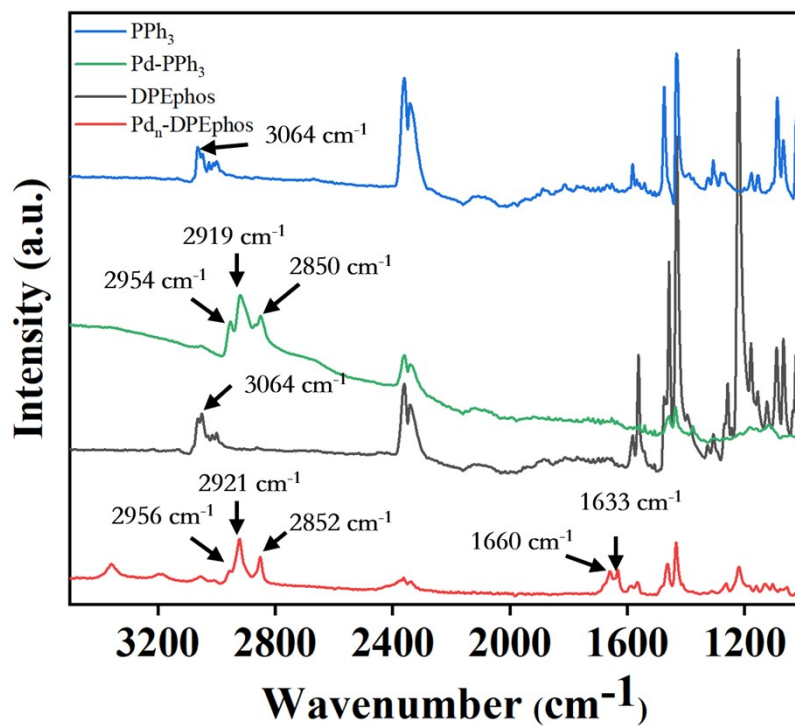
Figure S3. The ATR-IR analysis of triphenylphosphine (PPh$_3$), bis(2-(diphenylphosphino)phenyl) ether (DPEphos), different nanoclusters dissolved in dichloromethane.
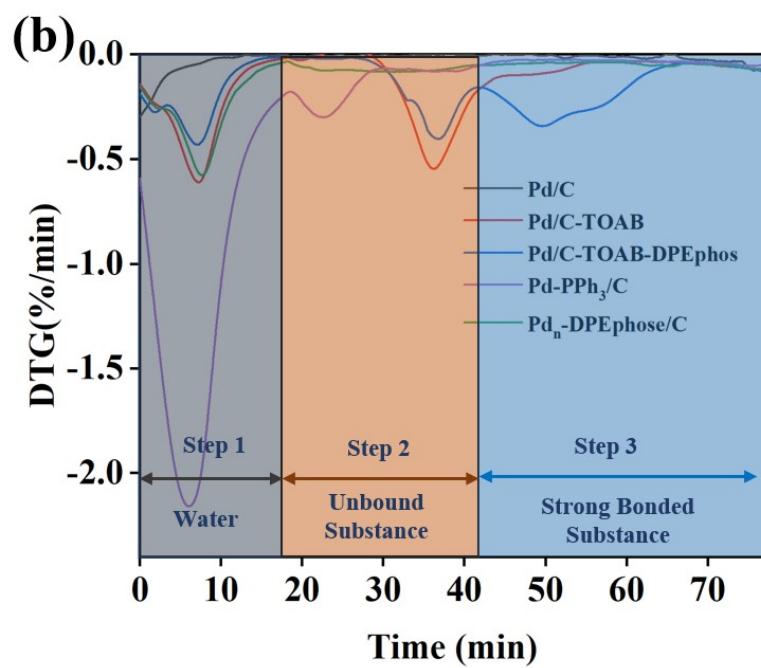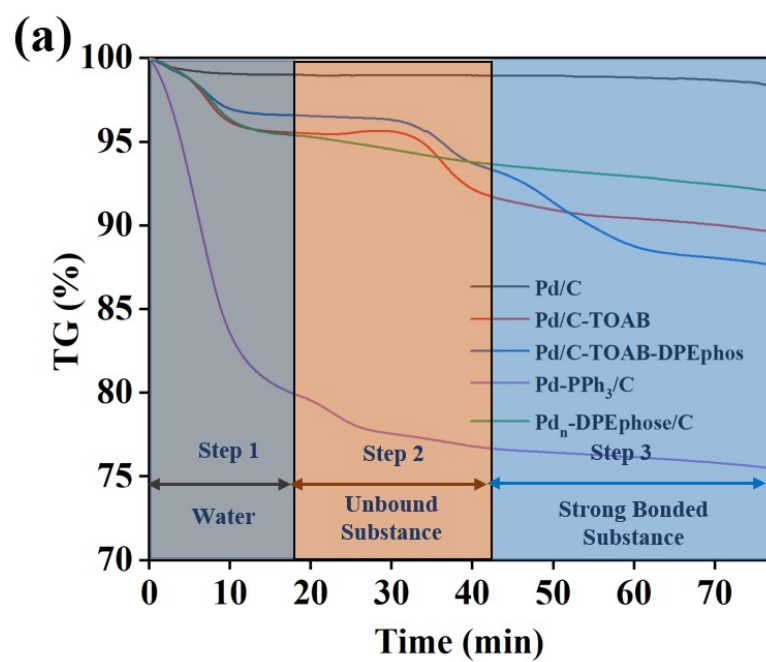
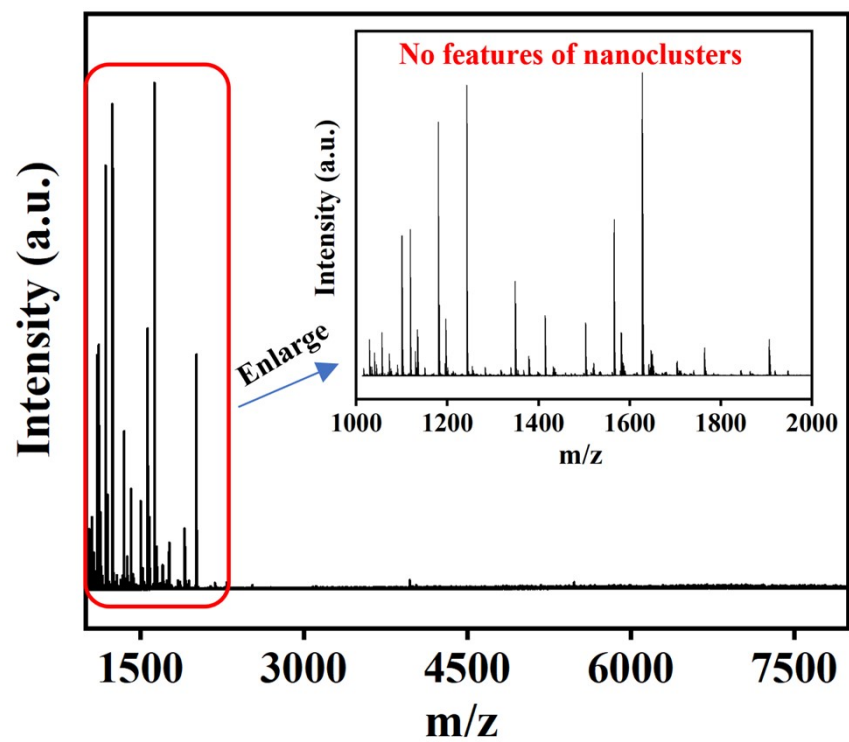**Figure S4.** Thermogravimetric analysis of different catalysts. (a) TG curve. (b) DTG curve.

Figure S5. Positive-ion ESI-MS spectrum of Pd-PPh$_3$ dissolved in a mixture of dichloromethane, methanol and toluene.
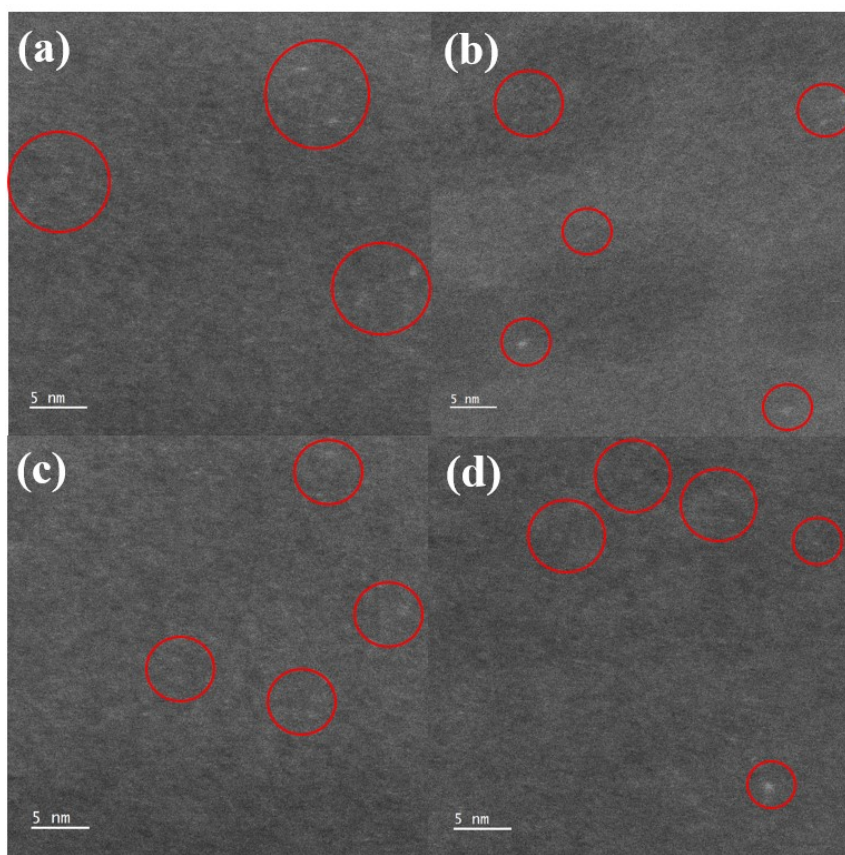
Figure S6. HAADF-STEM images of the unsupported Pd_n nanoclusters dispersed in a mixture of ethanol and dichloromethane.
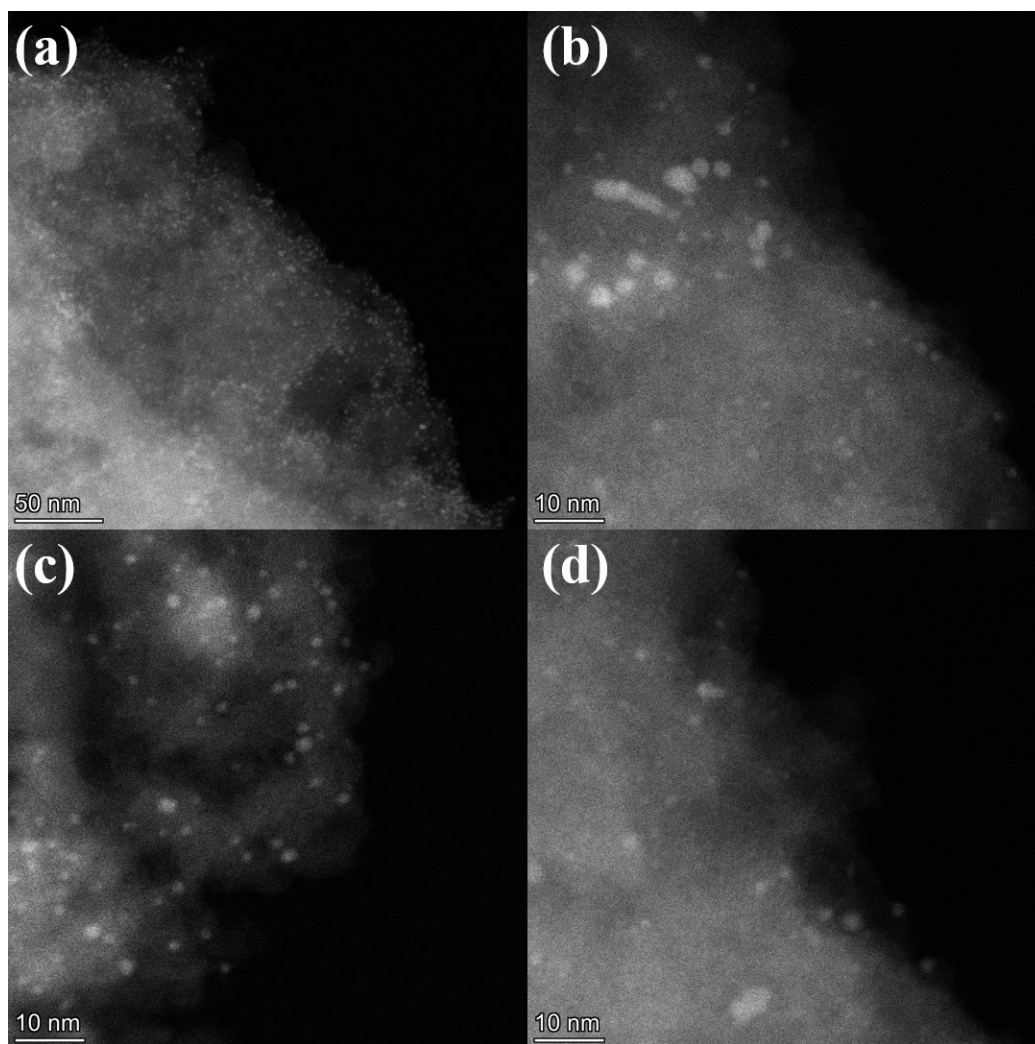
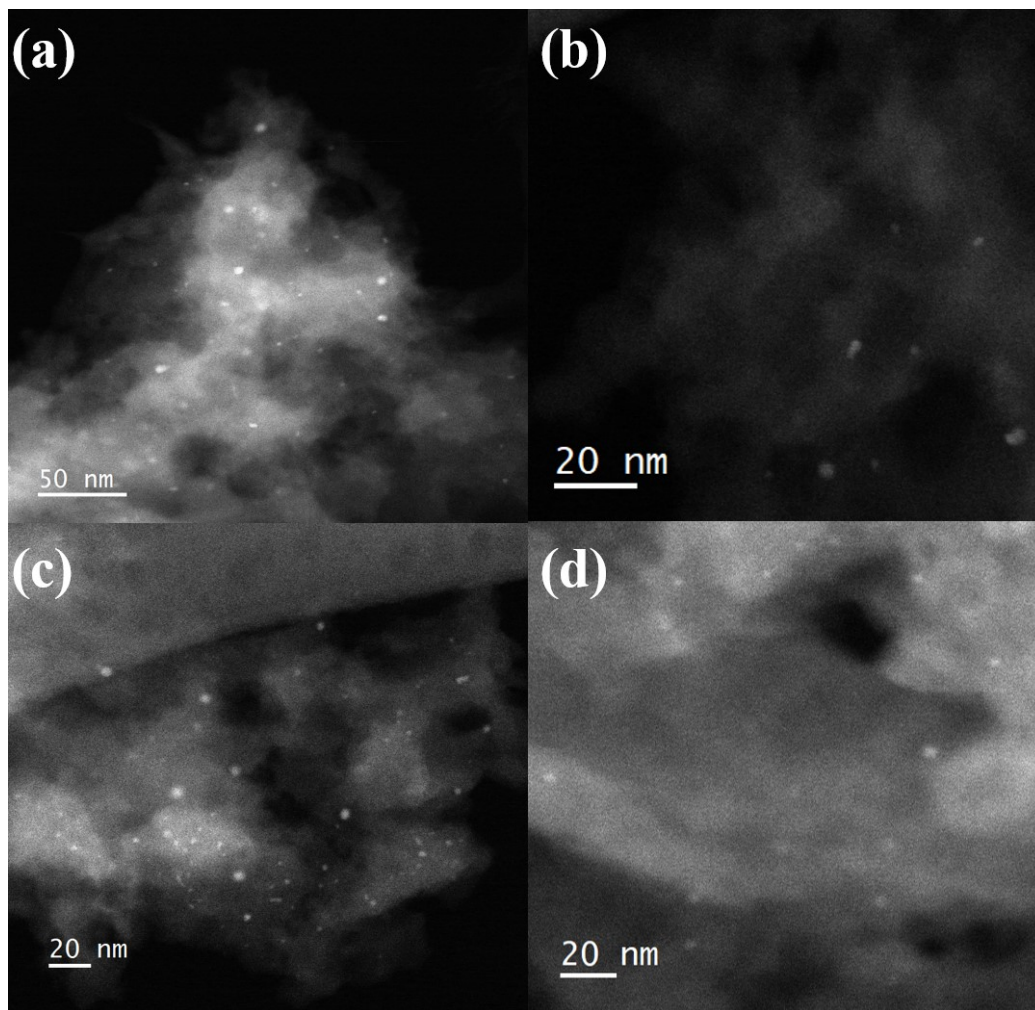**Figure S7.** HAADF-STEM image of Pd-PPh$_3$/C in different scale.

Figure   S8.   HAADF-STEM   image   of   Pd/C   in   different   scale.
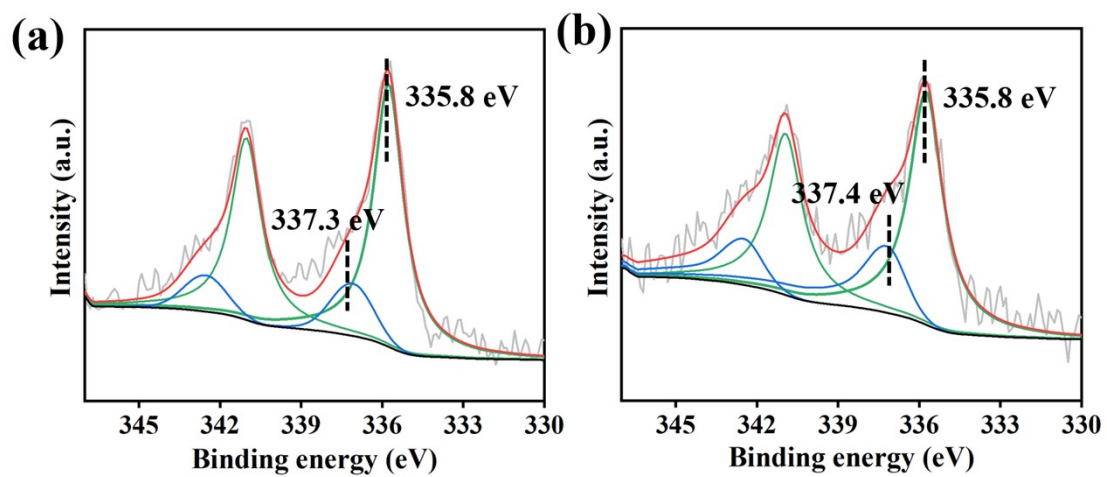
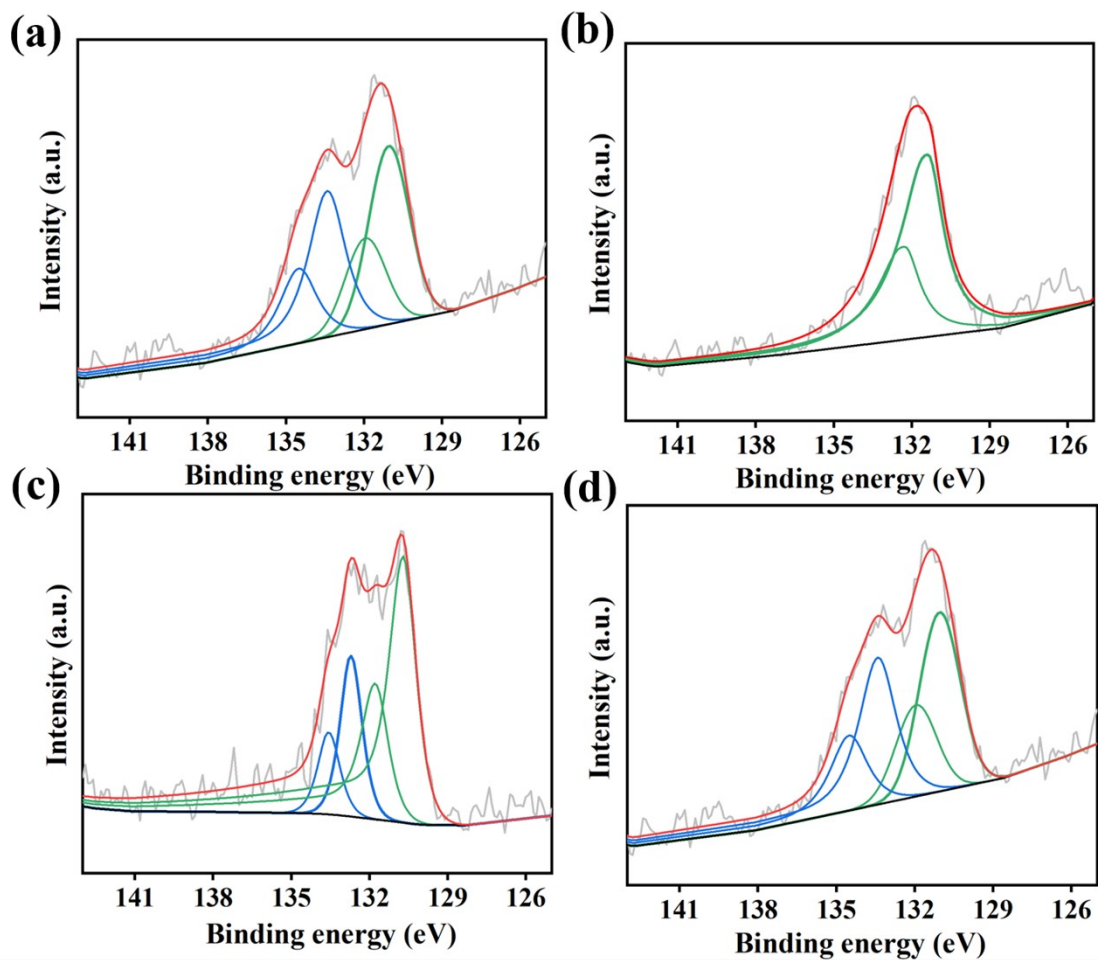**Figure S9.** The XPS of (a) Pd/C-TOAB-PPh$_3$ and (b) Pd/C-TOAB-DPEphos.

Figure S10. High resolution XPS analysis of Pd 2p. (a) Pd-PPh$_3$/C; (b) Pd$_n$-DPEphos/C; (c) Pd/C-TOAB-DPEphos; (d) Pd/C-PPh$_3$.
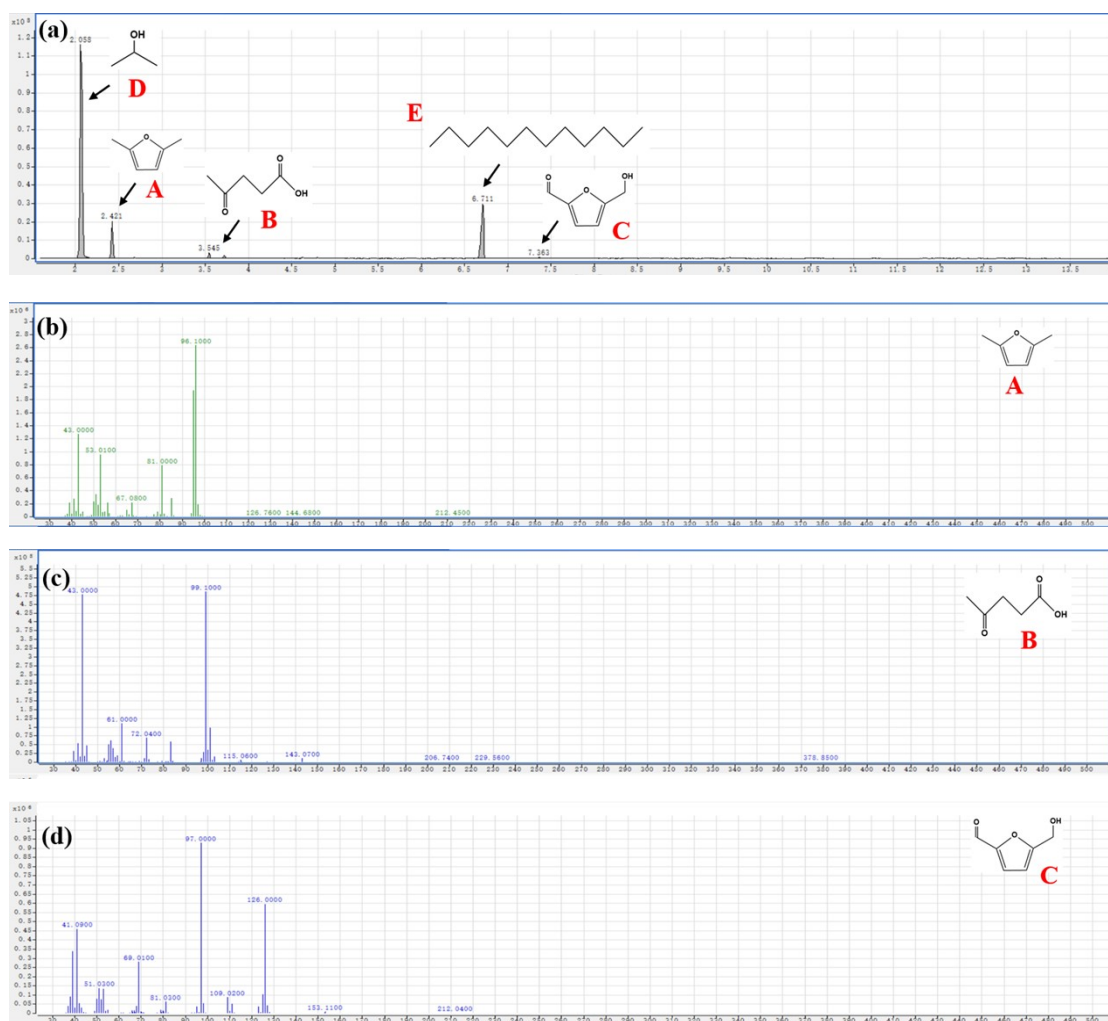
Figure S11. (a) Gas chromatography of the solution after catalytic reaction and the mass spectra of corresponding products. (b) 2,5-dimethylfuran, (c) levulinic acid and (d) 5-hydroxymethylfurfural. The D (isopropanol) is the solvent and E (dodecane) is the internal standard substance.
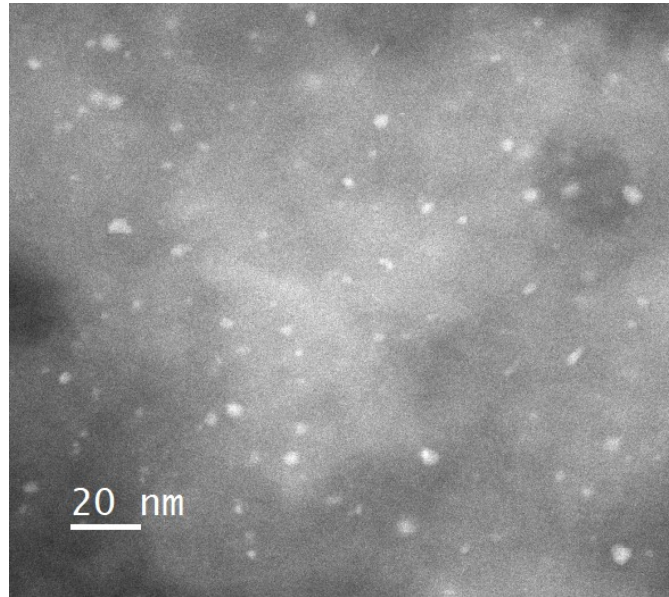
Figure S12. HAADF-STEM of Pd/C prepared by wet impregnation.
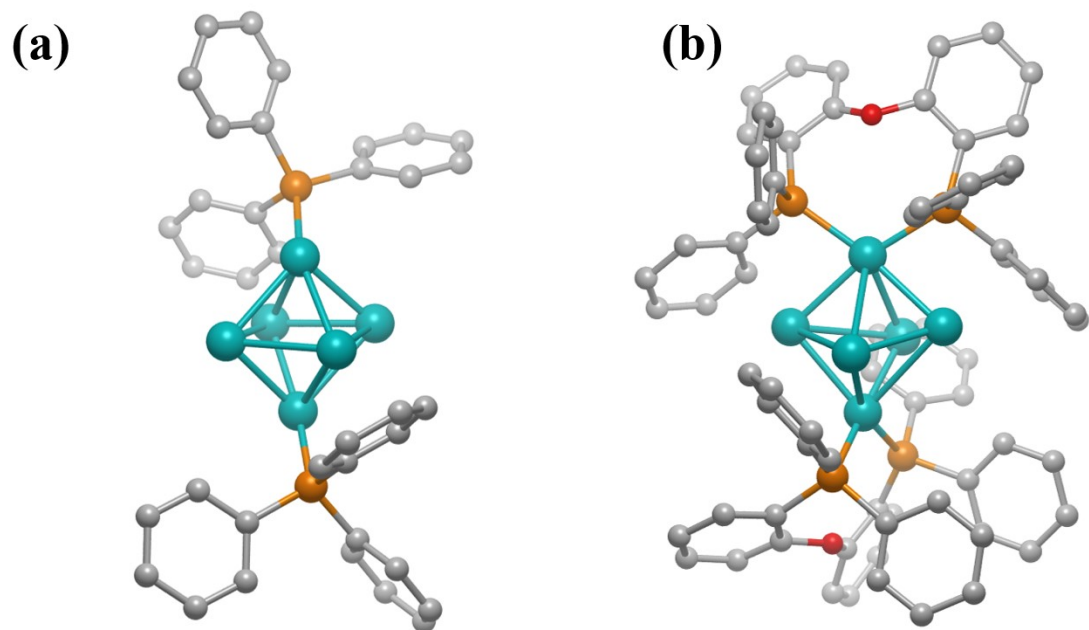
Figure S13. The optimized geometric structures of (a) monodentate phosphine catalyst and (b) bidentate phosphine catalyst. Green, orange, gray, red balls represent Pd, P, C and O atoms, respectively. For clearer visualization, all C-H keys are hidden.
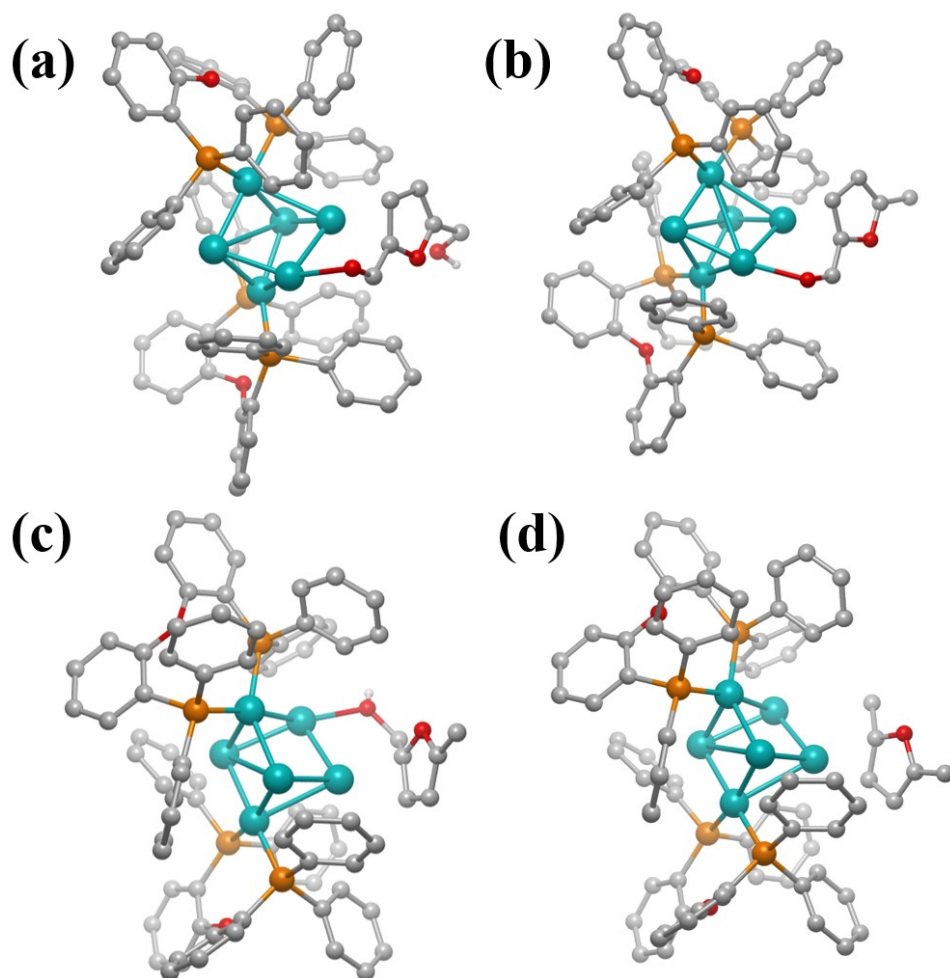
Figure S14. The optimized geometric structures of (a) *HMF, (b) *5MF, (c)*MFA and (d) *DMF. * represents bidentate phosphine catalyst.
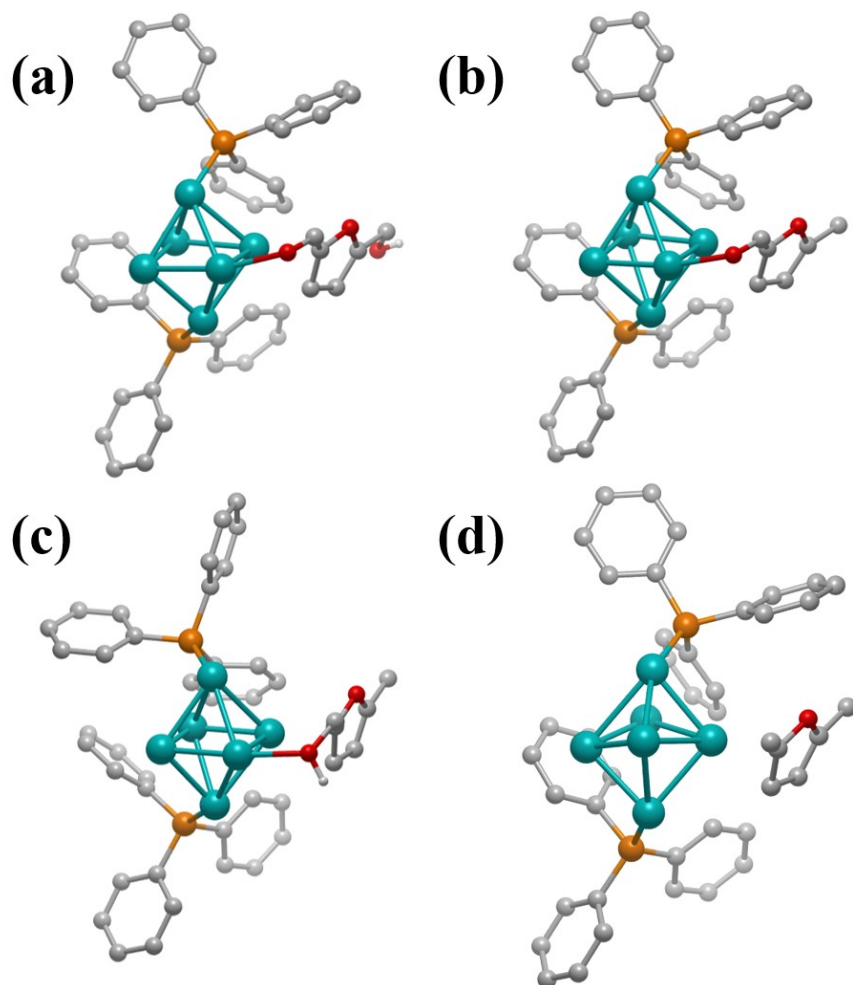
Figure S15. The optimized geometric structures of (a) *HMF, (b) *5MF, (c)*MFA and (d) *DMF. * represents monodentate phosphine catalyst.

Table S1. The XPS element analysis of catalysts.

Catalysts	Pd^0 ~335.8 eV	$Pd^{\delta+}$ ~336.2 eV	Pd^{2+} ~337.4 eV	P^{a+} ~131.0 eV	P^{b+} ~133.4 eV
Pd/C	87.0%	--	13.0%	--	--
Pd/C-TOAB	57.1%	--	42.9%	--	--
Pd/C-TOAB-DPEphos	72.4%	--	27.6%	41.5%	58.5%
Pd/C-TOAB-PPh$_3$	58.8%	--	41.2%	64.5%	35.5%
Pd-PPh$_3$/C	--	71.9%	28.1%	49.5%	49.5%
Pd$_n$-DPEphos/C	--	54.9%	45.1%	100%	--

Table S2. The catalytic performance of different catalysts for the hydrogenation of 5-HMF.

Entry	Catalyst	Conv. (%)	yeild (%)				
			5-MF	BHMF	MFA	DMF	others
1	Blank	27.2	0	0	0	0	27.2
2	DPEphos	25.5	0	0	0	0	25.5
3	Activated Carbon	44.3	0	0	0	0	44.3

Conditions: 20 mg catalysts, 100 mg 5-HMF, 10 mL isopropanol, 120 $^\circ$C, 4 h, 2 MPa H_2, 1000 rpm.

Table S3. The catalytic performance of different catalysts for the hydrogenation of 5-HMF in previous report.

Catalysts	Pressure/MPa	Temperature/K	Time/h	Yield/%	Reference
Pd-DPEphos	2.0	393	4.0	94.1	This Work
Pd-Co$_9$S$_8$/S-CNT	0.3	393	13.0	83.7	8
Pd/C	0.2	393	15.0	85.0	9
PdAu$_4$/GC800	1.0	423	4.0	94.4	10
Pd/Fe$_2$O$_3$	2.5	453	0.4	72.0	11
Pd-GVL/C	2.0	353	24.0	95.6	12
Cu–Pd/RGO	3.0	473	3.0	95.0	13
Pd/MOF-808	1.0	373	3.0	99.0	14
Pd@UiO–CH$_2$SO$_3$H	2.0	423	2.0	86.0	15

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